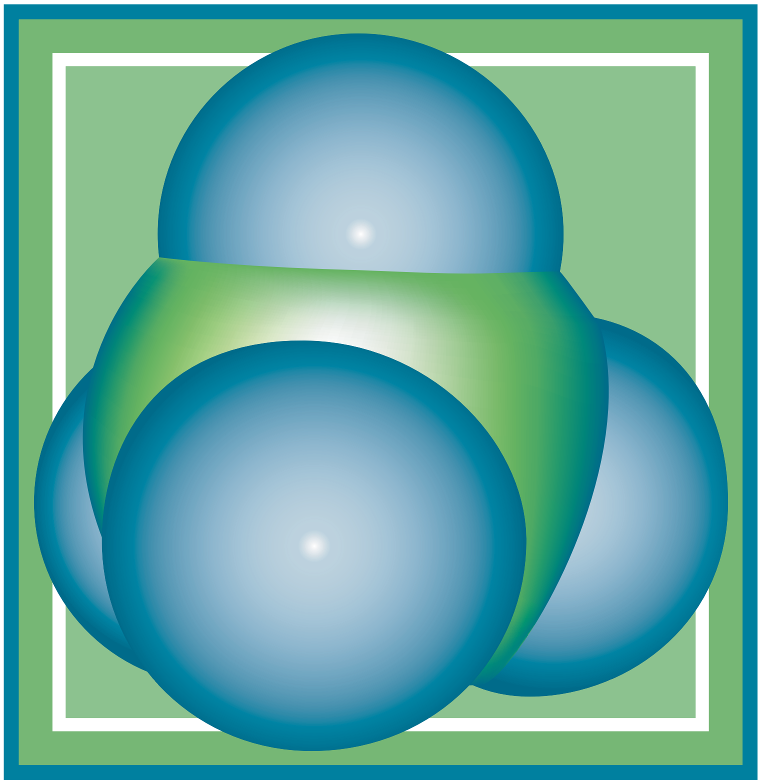
Technology Overview

Perchlorate: Overview of Issues, Status, and Remedial Options



September 2005

Prepared by
The Interstate Technology & Regulatory Council
Perchlorate Team

ABOUT ITRC

Established in 1995, the Interstate Technology & Regulatory Council (ITRC) is a state-led, national coalition of personnel from the environmental regulatory agencies of some 40 states and the District of Columbia, three federal agencies, tribes, and public and industry stakeholders. The organization is devoted to reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers. More information about ITRC and its available products and services can be found on the Internet at **www.itrcweb.org.**

DISCLAIMER

This document is designed to help regulators and others develop a consistent approach to their evaluation, regulatory approval, and deployment of specific technologies at specific sites. Although the information in this document is believed to be reliable and accurate, this document and all material set forth herein are provided without warranties of any kind, either express or implied, including but not limited to warranties of the accuracy or completeness of information contained in the document. The technical implications of any information or guidance contained in this document may vary widely based on the specific facts involved and should not be used as a substitute for consultation with professional and competent advisors. Although this document attempts to address what the authors believe to be all relevant points, it is not intended to be an exhaustive treatise on the subject. Interested readers should do their own research, and a list of references may be provided as a starting point. This document does not necessarily address all applicable heath and safety risks and precautions with respect to particular materials, conditions, or procedures in specific applications of any technology. Consequently, ITRC recommends also consulting applicable standards, laws, regulations, suppliers of materials, and material safety data sheets for information concerning safety and health risks and precautions and compliance with then-applicable laws and regulations. The use of this document and the materials set forth herein is at the user's own risk. ECOS, ERIS, and ITRC shall not be liable for any direct, indirect, incidental, special, consequential, or punitive damages arising out of the use of any information, apparatus, method, or process discussed in this document. This document may be revised or withdrawn at any time without prior notice.

ECOS, ERIS, and ITRC do not endorse the use of, nor do they attempt to determine the merits of, any specific technology or technology provider through publication of this guidance document or any other ITRC document. The type of work described in this document should be performed by trained professionals, and federal, state, and municipal laws should be consulted. ECOS, ERIS, and ITRC shall not be liable in the event of any conflict between this guidance document and such laws, regulations, and/or ordinances. Mention of trade names or commercial products does not constitute endorsement or recommendation of use by ECOS, ERIS, or ITRC.

Perchlorate: Overview of Issues, Status, and Remedial Options

September 2005

Prepared by
The Interstate Technology & Regulatory Council
Perchlorate Team

50 F Street NW, Suite 350, Washington, DC 20001

Permission is granted to refer to or quote from this publication with the customary acknowledgment of the source. The suggested citation for this document is as follows:

ITRC (Interstate Technology & Regulatory Council). 2005. *Perchlorate: Overview of Issues, Status, and Remedial Options*. PERCHLORATE-1. Washington, D.C.: Interstate Technology & Regulatory Council, Perchlorate Team. Available on the Internet at http://www.itrcweb.org.

ACKNOWLEDGEMENTS

The members of the Interstate Technology & Regulatory Council (ITRC) Perchlorate Team wish to acknowledge the individuals, organizations, and agencies that contributed to this overview document.

As part of the broader ITRC effort, the Perchlorate Team is funded primarily by the U.S. Department of Energy. Additional funding and support have been provided by the U.S. Department of Defense and the U.S. Environmental Protection Agency. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers.

The team recognizes the following states' support of team leadership and guidance document preparation:

- Sara Piper, Nevada Division of Environmental Protection, Team Co-Leader
- Laurie Racca, California Department of Toxic Substances Control, Team Co-Leader
- Mark Malinowski, California Department of Toxic Substances Control, former Team Co-Leader
- Richard Albright, District of Columbia Department of Health
- Bob Barnwell, Alabama Department of Environmental Management
- Annette Cusher, Arkansas Department of Environmental Quality
- T. R. Hathaway, California Department of Toxic Substances Control
- Rosemary Knox, Massachusetts Department of Environmental Protection
- Kurt Limesand, Kansas Department of Health and Environment
- Lee Lippincott, New Jersey Department of Environmental Protection
- Alexander MacDonald, California Regional Water Quality Control Board
- Christopher Maurer, State of Washington Department of Ecology
- Brian Rakvica, Nevada Division of Environmental Protection
- Supalak (Sue) Rogers, Texas Council on Environmental Quality
- Clayton Trumpolt, Colorado Department of Public Health and Environment
- Allen Wolfenden, Department of Toxic Substances Control

The Perchlorate Team would also like to thank all of the federal, military, industry, and consulting personnel who provided significant contributions to this document. This document could not have been published without your participation, expertise, and guidance. Thanks also to Stacey Kingsbury, ITRC Program Advisor, for her guidance and assistance in helping the team to complete this document.

EXECUTIVE SUMMARY

Perchlorate is both a naturally occurring and manmade anion consisting of chlorine bonded to four oxygen atoms (ClO_4^-). It is typically found in the form of perchloric acid and salts such as ammonium perchlorate, potassium perchlorate, and sodium perchlorate. This introduction provides basic information regarding perchlorate and perchlorate contamination. It is important to understand that information on perchlorate is continually being updated and that this document provides a snapshot in time of the current perchlorate situation.

While perchlorate was once thought to occur naturally only in one location in Chile, ongoing study has found naturally occurring perchlorate in other locations as well. As a manmade compound, it has been manufactured since before the turn of the last century, primarily for use in defense activities and the aerospace industry.

Highly soluble and mobile in water, perchlorate is also very stable. Most of the attention focused on perchlorate contamination concerns groundwater and surface water contamination. However, perchlorate can also contaminate soil and vegetation. The potential for perchlorate contamination in drinking water and food supplies is a human health concern because it can interfere with iodide uptake by the thyroid gland and, through this mode of action, result in decreased thyroid hormone production.

In general, past management practices did not prevent the release of perchlorate to the environment because it was not recognized or regarded as a contaminant of concern. Widespread perchlorate contamination in the United States was observed after the spring of 1997, when an analytical method with a reporting limit of 4 ppb was developed. Additional sampling and analysis techniques have since been developed that can detect perchlorate at concentrations of 1 ppb and lower.

A variety of remediation technologies are currently commercially available and being used for perchlorate remediation. These remediation technologies fall into two broad categories—ion exchange and biological processes. The majority of these treatment technologies have been applied to remediation of groundwater; however, biological processes are also being applied to the remediation of soils. This document provides an overview of the commercially available technologies (and summaries of emerging technologies) still at the bench or pilot-scale stage.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

PERCHLORATE: OVERVIEW OF ISSUES, STATUS, AND REMEDIAL OPTIONS

1. INTRODUCTION

This overview document is designed primarily for state[1] regulators and stakeholders who may not be familiar with issues related to perchlorate. This introduction provides basic information regarding perchlorate and perchlorate contamination. Subsequent chapters of this document provide more detailed information regarding sources of perchlorate (Section 2), sampling and analysis techniques (Section 3), a discussion of the risk-related issues concerning perchlorate contamination (Section 4), risk management strategies and regulatory status (Section 5), and a summary of current remediation technologies (Section 6). It is important to understand that information on perchlorate is continually being updated and that this document provides a snapshot in time of the current perchlorate situation.

1.1 What Is Perchlorate?

Perchlorate is an anion consisting of a chlorine atom bonded to four oxygen atoms (ClO_4^-) (Figure 1-1). It is typically found in the form of perchloric acid and salts such as ammonium perchlorate, potassium perchlorate, and sodium perchlorate. Perchlorate is usually found as the anion component of a salt most often associated with one of the following common cations: ammonium (NH_4^+), sodium (Na^+), or potassium (K^+). The resulting salts are ammonium perchlorate (NH_4ClO_4), potassium perchlorate ($KClO_4$), and sodium perchlorate ($NaClO_4$).

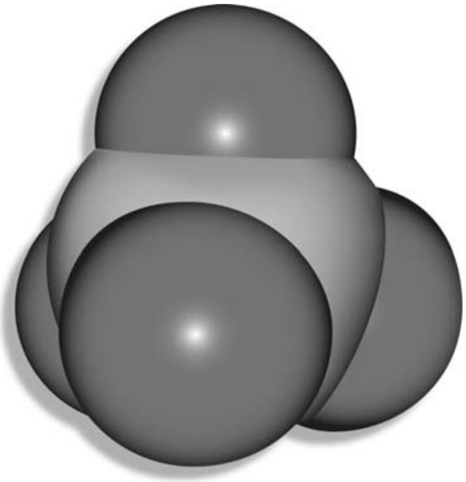


Figure 1-1. Perchlorate anion.

Table 1-1 lists the physical properties of the common perchlorate compounds. Perchlorate exhibits the characteristics of high solubility and mobility in water, as well as being very stable. These characteristics lead to the formation of long and persistent contaminant plumes when it is released into either groundwater or surface water. Like the water contaminant nitrate, perchlorate is not attenuated to any great degree by soil surface chemistry. However, it can be broken down by naturally occurring bacteria in the environment.

1.2 Sources of Perchlorate

Perchlorate occurs both naturally and as a manmade compound. While it was once thought to occur naturally only in one location in Chile, ongoing study has found naturally occurring perchlorate in other locations as well. The United States Geological Survey (USGS) is currently conducting studies on natural occurring sources of perchlorate (Section 2.1).

---

[1] Throughout this document, the term “state” is used to refer to all regulatory entities having the general regulatory responsibilities of the states, including U.S. territories and commonwealths.

Table 1-1. Properties of perchlorate compounds

Properties*	Ammonium perchlorate (NH_4ClO_4)	Potassium perchlorate ($KClO_4$)	Sodium perchlorate ($NaClO_4$)	Perchloric acid ($HClO_4$)
CAS#	7790-98-9	7778-74-7	7601-89-0	7601-90-3
Molecular weight	117.49	138.55	122.44	100.47
Color/form	White orthorhombic crystal	Colorless orthorhombic crystal or white crystalline powder	White orthorhombic deliquescent crystal	Colorless oily liquid
Taste/odor	Odorless	Slightly salty	Odorless	Strong odor
Density/specific gravity	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.77 g/cm^3
Solubility	200 g/L water at 25ºC	15 g/L water at 25ºC	2096 g/L water at 25ºC	Miscible in cold water
Sorption capacity	Very low	Very low	Very low	Very low
Volatility	Nonvolatile	Nonvolatile	Nonvolatile	Volatile
Octanol/H_2O partition coefficient (log K_{ow})	–5.84	–7.18	–7.18	–4.63
Vapor density (air = 1)	No information	4.8	No information	3.5
pH	5.5–6.5	6.0–8.5	7.0	Highly acidic

**Vapor pressure and evaporation rate are insignificant and therefore not included in this table.*

Although perchlorate was first manufactured commercially around the turn of the last century, its widespread manufacture in the United States began only in the mid-1940s. Since then, it has found widespread use in industry. Approximately 90% of perchlorate compounds, primarily ammonium perchlorate, are manufactured for use in defense activities and the aerospace industry. For example, ammonium perchlorate is used in a variety of commercially available products and industrial processes (Section 2.2). Besides salts of perchlorate, other forms of perchlorate exist, such as perchloric acid ($HClO_4$), reagents for experimental use, and some fertilizers. Perchlorate has been used medically to control hyperthyroid conditions and Graves disease in the human thyroid (Wolf 1998).

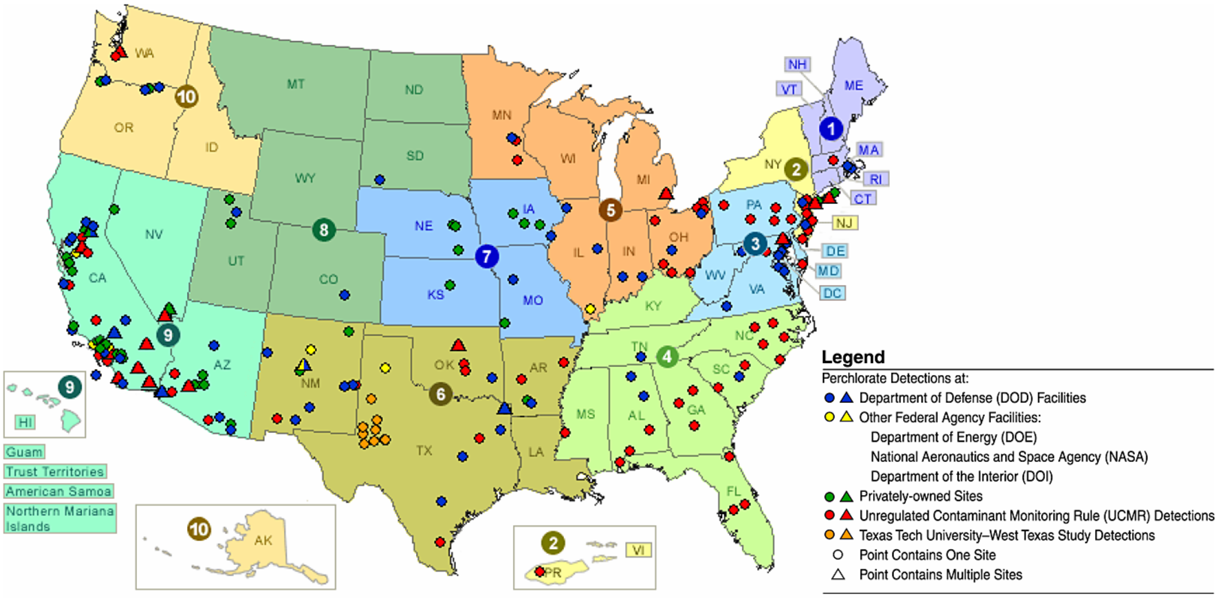
1.3 Perchlorate Occurrences

Advances in analytical chemistry have allowed for the detection of perchlorate at gradually lower levels since 1997. More sensitive analytical detections have increasingly proven perchlorate to be more widespread in the environment than previously thought. In addition, recent investigations indicate that natural sources of perchlorate exist in the environment. As a result, contamination of soil, vegetation, groundwater, and surface water has been detected in a number of states.

In general, past management practices did not prevent the release of perchlorate to the environment because it was not recognized or regarded as a contaminant of concern. Widespread perchlorate contamination in the United States was observed after the spring of 1997 when an analytical method with a reporting limit of 4 ppb was developed. Additional sampling and analysis techniques have since been developed that can detect perchlorate at concentrations of 1 ppb and lower (Section 3.2).

USEPA has monitored for perchlorate in public drinking water systems through the Unregulated Contaminant Monitoring Rule (UCMR) program. Under UCMR 1, detections of perchlorate were analyzed using USEPA Method 314.0 at approximately 2,800 large public water systems and a representative sample of 800 (out of 66,000) small public water systems. As of January 2005, perchlorate had been detected in 153 public water systems and 25 states across the United States (USEPA, n.d.). Geographically, the highest density of perchlorate detection is in southern California, west central Texas, along the east coast between New Jersey and Long Island, and in Massachusetts. The apparent absence of perchlorate occurrence in some regions may merely be because relatively few sources have been sampled. More intensive sampling, particularly of small systems, may detect perchlorate-contaminated drinking water sources in these regions (Brandhuber and Clark 2005). Monitoring under UCMR 1 has been completed. The proposed rule for monitoring of perchlorate and other contaminants under UCMR 2 was published in August 2005. The proposed rule includes the list of proposed contaminants and methods for monitoring (Federal Register 2005). Monitoring for perchlorate and other contaminants under UCMR 2 is proposed for 2007–2011.

Additional sampling efforts have been undertaken by the Department of Defense, other federal agencies, site owners, and universities. The majority of detections in drinking water have not been associated with USEPA-identified perchlorate releases, and most detections have been below 12 ppb (Figure 1-2).



Map source: EPA

Figure 1-2. National perchlorate detections as of September 2004 (USEPA 2004a).

The greatest amount of attention to perchlorate contamination concerns drinking water; however, recent studies have also found perchlorate in the food supply. In December 2004, the U.S. Food and Drug Administration (FDA) released an initial set of exploratory data on perchlorate levels in individual samples of lettuce, milk, spring water, and bottled water (USFDA 2004a). Information on the full extent of perchlorate occurrences in the United States has yet to be determined.

1.4 Perchlorate Risk

Perchlorate is of concern because it can interfere with iodide uptake by the thyroid gland. Because iodide is an essential component of thyroid hormones, perchlorate exposure may result in decreased thyroid hormone production. Section 4 of this document discusses toxicity, exposure, and risk in detail.

1.5 Perchlorate Regulation

The U.S. Environmental Protection Agency (USEPA) established a human reference dose (RfD) for perchlorate at 0.0007 milligrams/kilogram/day (mg/kg/D) in February 2005. A reference dose is a scientific estimate of a daily exposure level that is not expected to cause adverse health effects in humans. The 0.0007 mg/kg/D RfD equates to a drinking water equivalent level (DWEL) of 24.5 parts per billion (ppb) (Section 4.4.2). A DWEL, which assumes that all of a contaminant comes from drinking water, is the concentration of a contaminant in drinking water that will have no adverse effect with a margin of safety. Because margins of safety are built into the RfD and the DWEL, exposures above the DWEL are not necessarily considered unsafe. However, DWELs are not an enforceable standard. In most cases, the standard is a maximum contaminant level (MCL), the maximum permissible level of a contaminant in water delivered to any user of a public water system.

USEPA is in the process of establishing an MCL for perchlorate. Some states have adopted advisory levels for perchlorate in drinking water, and a few are considering or are in the process of promulgating state levels. Section 5 of this document discusses the regulatory status of perchlorate in greater detail.

1.6 Perchlorate Remediation

The majority of remediation technologies associated with perchlorate contamination address perchlorate in groundwater and drinking water. This document provides an overview of proven and commercially available technologies, specifically ion exchange and bioremediation. Emerging technologies with tested bench-scale and/or pilot-scale studies, as well as those in the development stage, are also briefly discussed (Section 6). A more detailed review and discussion of perchlorate treatment technologies, including a number of case studies and associated costs, will be provided in a subsequent technical and regulatory guidance document planned by the ITRC Perchlorate Team for publication in 2006.

2. SOURCES, USES, AND OCCURRENCES

Perchlorate occurs both naturally and as a manufactured compound. Knowing the sources of perchlorate and the variety of uses it has served will help to guide perchlorate investigations. While a variety of sites where perchlorate contamination is known to occur have already been identified, it can be assumed that additional sites will be discovered as more geographical areas are tested and additional information becomes available.

2.1 Sources of Perchlorate

At this time, most naturally occurring sources of perchlorate appear to be geographically limited to arid environments. These deposits tend to be low in concentration, except for the relatively high natural perchlorate concentrations found in Chilean caliche[2] and some potash ores. In contrast, manmade perchlorate sources can be many times more concentrated than most natural sources. In environments where both types exist, research to discriminate between the two types is ongoing.

Sites that been identified with high concentrations of perchlorate contamination (in the thousands of part per billion or more) have involved manufacturing, testing or disposal of solid rocket propellant; manufacturing of perchlorate compounds; and industrial manufacturing operations where perchlorate compounds were used as reagents. In addition to covering these kinds of sources of contamination, this section will also address potential sources of manmade perchlorate that are likely to have created lower concentration perchlorate contamination. In these cases, it is assumed that the quantities of perchlorate causing the contamination are smaller or that the sources are disseminated. It should be noted that in some cases the source of perchlorate contamination has not been determined.

2.1.1 Natural Sources of Perchlorate

2.1.1.1 Theory of the Origin of Natural Sources of Perchlorate

A current theory regarding the origin of naturally occurring perchlorate in the environment centers on natural atmospheric processes. While the exact mechanism for the creation of perchlorate is unknown, the theory suggests that chloride, possibly in the form of sodium chloride from the sea or land-based chloride compounds blown in from the atmosphere, reacts with atmospheric ozone to create perchlorate. This process probably occurs over much of the earth and is analogous to nitrate formation in the atmosphere (Walvoord et al. 2003). In addition, there is the possibility that lightening may play a role in the creation of some atmospherically produced perchlorate (Dasgupta et al. 2005 and Jackson et al. 2003a), but this theory has not been confirmed. The rate of perchlorate creation in the atmosphere has not been determined, although it is thought to be a relatively slow process.

---

[2] "Caliche" is generally defined as a desert soil formed by the near-surface crystallization of calcite and/or other soluble minerals by upward-moving solutions. Commonly referred to as "hardpan" in the United States, caliche also results when precipitation dissolves salts in the soil, percolates downward, and then precipitates these cementing salts at some generally shallow depth, where the evaporation rate exceeds the rate of precipitation.

Following atmospheric creation, perchlorate returns to the earth's surface dissolved in precipitation. In arid environments, where the rate of deposition exceeds the rate of dissolution by ongoing precipitation, perchlorate can be incorporated into certain geologic formations (Orris 2004). Sampling and analysis of geologic materials from both existing collections and new field additions is ongoing by USGS. Initially, samples were taken in the southwestern United States, but now this sampling effort includes other geographical areas, more diverse terrains, and areas outside the United States. Samples terrains include playas, caliche-containing soils, dry lakebeds, and evaporite deposits (see Appendix B). USGS is also studying perchlorate in groundwater around the United States to help determine the geographical extent and concentration of perchlorate in the environment; determine which geologic materials contain perchlorate; and confirm the rate, concentration, and pervasiveness of perchlorate in precipitation and groundwater. Although USGS studies are ongoing, preliminary analytical results show that perchlorate appears to be naturally present in arid environments and appears to concentrate in a manner similar to that of nitrate (Walvoord et al. 2003).

In addition to these USGS studies, analysis of precipitation samples collected from weather station evaporation pans is being conducted by the National Weather Service in cooperation with USGS. Sampling of the atmosphere at altitude for perchlorate and precursor chemicals may be an additional area for investigation (Orris 2004).

2.1.1.2 Chilean Nitrate

Until recently, naturally occurring perchlorate was known to exist in the environment at only one location—the Atacama Desert in Chile. Similar but less extensive deposits have also recently been found in Peru and Bolivia. The perchlorate in Chile exists in mineralogical association with nitrate of soda caliche deposits that may have been derived in part from past local volcanic activity (Ericksen 1983 and Schumacher 1960). Chilean nitrate deposits have been mined to produce fertilizer and saltpeter for gunpowder for export since the 1830s. Chilean nitrate ore has been imported into the United States since at least the late 1800s for use as fertilizer, for saltpeter used in gunpowder, and as a feedstock to making nitric acid, explosives, fireworks, and additional end products.

2.1.1.3 Evaporite Deposits

Evaporite deposits are those formed by evaporation concentration in arid environments. These marine and nonmarine deposits include salts of bromine, boron and borates, gypsum and anhydrite, nitrogen compounds, potash, iodine, sodium sulfate, and sedimentary phosphate (Lefond 1975). Evaporites tend to be deposited in a specific chemical sequence as the concentration increases, such that potassium or other salts that precipitate after halite (rock salt or sodium chloride) are those most likely to contain perchlorate, based on current sample analysis.

In an initial round of USGS testing, more than 90% of the natural materials samples had detectable perchlorate, some at low concentrations and others involving potash (sylvite) deposits with perchlorate values up to 489 parts per million (ppm) (Orris et al. 2003, Orris 2004; see Appendix B). Potash is mined and milled in the United States, Canada, and elsewhere. Potash ore has also been recovered via solution mining and exists in solution in the Great Salt Lake in

Utah. Economic ore minerals of potash include sylvite, sylvinite, langebinite, kiainite, and carnallite. Most potash production is dedicated to feedstock for making fertilizers. The remaining commercial and industrial uses include potassium-bearing chemicals and reagents, flux in the aluminum industry, as an alternative to deicing salt, water conditioning, detergents, ceramics, and pharmaceuticals (Downey 2002). Samples of processed potash products have not tested positive for perchlorate to date.

Other evaporite deposits besides potash may also have the potential of associated perchlorate. Some examples include trona, borax, gypsum, Epsom salts, and others. Borates have been used for boric acid production, as a pesticide/lumber preservative, and as an ointment. Borax is also used as part of an abrasive hand cleaner. Colemanite is used as a component for some fertilizers for alfalfa and clover (Lefond 1975).

2.1.1.4 Other Potentially Naturally Occurring Perchlorate Sources

Perchlorate has been detected in seaweed at a concentration of 885 ppm in a sample of kelp collected and analyzed by the USGS (Orris et al. 2003). Whether other types of seaweed or marine algae contain perchlorate has not yet been determined.

2.1.2 Manmade Perchlorate

Perchlorate was first manufactured in commercial quantities in Masebo, Sweden in the 1890s by Stockholms Superfostfat Fabrisk AB. Commercial production elsewhere in Europe and the United States followed shortly thereafter. The earliest production in the United States appears to have been by Oldbury Electro-Chemical in Niagara Falls, New York, in 1910. Several perchlorate production plants are known to have operated in the United States since that time (Table 2.1). In 1960, Schumacher documented over 40 different perchlorate compounds that had been produced in laboratory and industrial settings (Schumacher 1960). One chemical manufacturer lists 80 perchlorate chemicals in its product line. However, the vast majority (>99%) of manufactured perchlorate compounds consist of the following four: ammonium perchlorate, sodium perchlorate, potassium perchlorate, and perchloric acid. See Appendix C for a compilation of other, less-common manufactured specialty perchlorate compounds.

A number of processes have been patented for the production of perchlorates. In general, sodium perchlorate is manufactured electrolytically using sodium chlorate as the feedstock. Potassium perchlorate and ammonium perchlorate are produced in a second step by reacting sodium chlorate as a water solution with other chemicals to create concentrated solutions of either potassium perchlorate or ammonium perchlorate, depending on the added chemical(s). Perchlorate crystals are precipitated from the solution and are then dried to produce a homogeneous, dry, granular product that is shipped in sacks and drums for sale to manufacturers of various perchlorate-containing end products.

Table 2-1. U.S. perchlorate manufacturers[3]

Company	Location	Years of operation or production	Comments
Oldbury Electro-Chemical (later became Hooker Electrochemical)	Niagara Falls, New York	1910–1940	Hooker Electrochemical was acquired by Occidental Chemical Company in 1968
Western Electrochemical Company	Los Angeles, California	1943–1945	Manufactured potassium perchlorate
Western Electrochemical Company	Henderson, Nevada	1945–2002	Merged with American Potash and Chemical Company in 1955; acquired by Kerr-McGee in 1967; manufactured ammonium perchlorate, sodium perchlorate, and potassium perchlorate
Hooker Chemical and Foote Mineral (joint venture H.E.F., Inc.)	Columbus, Mississippi	1958–1965	Currently Eka Nobel
Pennsalt Chemicals Corp.	Portland, Oregon	1958–1965	Currently Arkema, Inc.
Pacific Engineering and Production Company of Nevada	Henderson, Nevada	1958–1988	Ammonium perchlorate plant destroyed by explosion in 1988; never reopened
American Pacific Corporation	Cedar City, Utah	1989–present	Sole remaining North American producer of ammonium perchlorate for solid propellant

USEPA has compiled information on known or suspected users or manufacturers who have shipped more than 500 pounds of perchlorate in any one year (USEPA 2003a). American Pacific Corporation manufactures ammonium perchlorate in Cedar City, Utah, and is currently the sole domestic manufacturer of commercial quantities of propellant-grade ammonium perchlorate.

2.1.3 Differentiating Between Natural and Manmade Perchlorate

Some locations may have a mixture of manmade and naturally occurring perchlorate (Duncan, Morrison, and Varicka 2005). The western half of the United States appears to represent the most likely area for mixed plumes to occur due to favorable geological and precipitation conditions. The continued evolution of analytical forensic techniques may permit the fingerprinting of detected perchlorate plumes to ascertain whether the source is natural or manmade and to what extent each source type is represented (see Section 3.4).

---

[3] The information in this table is derived from many sources and is not comprehensive. Western Electrochemical Company, Pacific Engineering and Production Company of Nevada, and American Pacific Corporation are linked through successive corporate acquisitions. Other plants are believed to have operated and continue to operate, especially for the production of perchloric acid and specialty reagent compounds.

2.2 Uses for Perchlorate and Associated Releases

Indications are that perchlorate use was limited prior to World War II, with the most prevalent applications being fireworks and railroad signal flares. In 1939, *Uses and Applications of Chemicals and Related Materials* lists uses only for perchloric acid (Gregory 1939). Volume II of the same document, published in 1944, added uses of potassium perchlorate (Gregory 1944). Potassium perchlorate was placed on the list of strategic chemicals in 1940. See Appendixes C–E for more information.

Because it is an exceptional oxidizer with additional useful properties, perchlorate is widely used today by industry, the U.S. Department of Defense (DoD), and National Aeronautics and Space Administration (NASA) and in a few specific medicinal applications. Perchlorate usage appears to be ubiquitous across the United States, with new information on applications and locations of usage increasing as time passes (see Appendixes D and E). In the United States, approximately 90% by weight of industrial perchlorate production is dedicated to making ammonium perchlorate for use as an oxidizing agent for solid propellant rockets and missiles. The majority of the remaining U.S. production capacity consists of perchloric acid, sodium and potassium perchlorate, and a variety of other perchlorate salts.

2.2.1 Solid Propellants

Of the four main manufactured perchlorate compounds, ammonium perchlorate as used for solid propellant rockets and missiles makes up the largest proportion by volume of U.S. production. However, the earliest use of perchlorate as a solid propellant was in the form of potassium perchlorate. The Guggenheim Aeronautical Laboratory at the California Institute of Technology developed a formulation that combined asphalt as a binder and fuel with the oxidizer potassium perchlorate for use in jet-assisted take-off units (Hunley 1999). In the middle to late 1940s and early 1950s, perchlorate-based rocket motors that used potassium perchlorate were developed for smaller tactical missiles.

In the early to middle 1950s, ammonium perchlorate began replacing potassium perchlorate as the preferred oxidizer for solid propellants in large rocket motors. By 1958, the NIKE Hercules missile, which replaced the NIKE Ajax missile, used a solid propellant motor of polysulfide–ammonium perchlorate. In the 1960s, solid propellant mixtures of ammonium perchlorate and powdered aluminum replaced liquid propellant systems in intercontinental ballistic missile systems. Other examples of solid rocket motors that use ammonium perchlorate include the space shuttle and commercial satellite vehicles. Each of NASA's space shuttle booster rockets contains solid propellant made up of fine aluminum powder fuel and ammonium perchlorate oxidizer. Many commercial satellite launch vehicles also use solid rocket motors with ammonium perchlorate propellant as strap-on boosters to increase payload capacity.

Small rockets attached to ejector seats for pilots, explosive bolts for separating missile stages or other components, and oxygen generators for both civilian and defense aircraft also use perchlorate. Due to degradation issues, many of these devices are replaced as the shelf life expires.

2.2.1.1 Disposal of Solid Propellants

Perchlorate-containing debris, scraps of solid propellant and explosives, and rejected rocket motors have been disposed of by burning in open burn/open detonation (OB/OD) areas. However, in the past, solid propellant or explosives not burned to completion could permit perchlorate to be dissolved and cause contamination in soils and waters. Current practice is to use burn pas for the destruction of propellants. After the initial burn, a clean up is performed and any unconsumed material is treate again. At many DoD sites, even the ash is reburned, collected in drums and tested to ensure complete combustion of all energetic material.

Other processes have been used to dispose of solid propellants. For example, hydro-mining or a hog-out process is used to wash out solid propellant with high-pressure water jets to enable reuse of rocket motor hardware. Unfortunately, in the original system configuration, the liquid waste from the hog-out process was discharged untreated to the ground surface or into leaky lagoons and contaminated surface and groundwaters. This practice of untreated discharge is no longer employed due to the discovery of associated groundwater plumes. Current practice is to capture and treat the waste stream prior to discharge.

2.2.1.2 Replacement of Ammonium Perchlorate in Solid Rocket Propellants

DoD has development programs under way to replace ammonium perchlorate in solid rocket propellants. While alternative energetic oxidizers exist, significant cost, availability, environmental, and performance issues remain that have so far prevented their use in fielded weapon systems and launch vehicles. Each rocket or missile systems has unique performance demands that require consideration when attempting to replace ammonium perchlorate. The Green Missile Program is a development program to demonstrate the viability of replacing ammonium perchlorate in large rocket or missile systems with an environmentally friendly alternative oxidizer.

NASA recently announced a new paraffin-based solid propellant being developed and tested to replace perchlorate-based fuels for spacecraft use (NASA 2003). In testing since 2001, the fuel’s advertised advantages include nontoxicity, carbon dioxide and water combustion products, increased safety due to high stability, and the ability to be shut down and restarted quickly. However, the applicability of this paraffin-based fuel to meet DoD requirements for solid propellants is unknown.

2.2.1.3 Missile Recycling

Within DoD, a backlog of perchlorate-based solid propellant rockets and missiles that have exceeded their perchlorate shelf life are currently in storage. These will eventually require treatment or perhaps recycling of the perchlorate. If not treated or recycled, corrosion of these weapon systems will eventually become a concern.

The Army Aviation and Missile Command’s Research Development and Engineering Center has developed and demonstrated a missile-recycling capability. In this process, the energetic materials processing module uses supercritical anyhydrous ammonia in a closed-loop system to recover HMX (high-melting-point explosive), RDX (royal demolition explosive), and ammonium perchlorate for recycling. In 2003 and 2004, 14,600 tactical optical wire-guided missiles were processed in this way. Up to 15,000 missiles are projected for recycling in 2005.

2.2.1.4 Perchlorate Contamination Associated with Solid Fuel Launch Vehicles

Perchlorate releases to groundwater associated with the space shuttle and other solid-fuel launch vehicles at various locations within the NASA sphere of operations have been documented at Jet Propulsion Laboratory, Cape Canaveral, and elsewhere. At least one study assessing the potential for perchlorate release from launching operations has been published (Lang et al. 2002).

2.2.2 Munitions

All of the services within DoD have current and/or past weapon systems that contain perchlorate in varying amounts. A 2001 DoD survey of weapons systems containing perchlorate listed 259 different munitions and related items such as fuzes, flares, illumination rounds, simulators, grenades, etc., as well as 41 missile systems in the DoD Munitions Items Disposition Action System (MIDAS) database. For example, current families of munitions containing perchlorate in use by the Army include training simulators, insensitive munitions, smokes or obscurants, pyrotechnics, grenades, signals and flares, and fuzes. Some types of simulators contain relatively high perchlorate concentrations, as do most of those with solid rocket motors.

The Army, Navy, and Air Force are all looking more thoroughly at historical records related to research and development, manufacture, use, storage and disposal to develop a timeline for perchlorate-containing munitions to better understand the residues that may be on various training and testing ranges.

2.2.2.1 Munitions Manufacturing

In the past, munitions manufacturing facilities and operators conducted hydraulic wash out (often referred to as hog-out) of equipment used in solid propellant and munitions production. These operations present another opportunity for potential releases of perchlorate into the environment.

2.2.2.2 Munitions Disposal

Prior to 1970, unused munitions were buried on ranges. Over long periods of time, corrosion degrades the munitions casing, resulting in the potential release of incorporated perchlorate into the environment. However, the potential for perchlorate release to the environment can vary greatly, depending on the length of use and the types and amounts of munitions disposed. For example, not all of the munitions contained any appreciable amount of perchlorate. In addition, the larger munitions that contained ammonium perchlorate would have been subject to OB/OD (See Section 2.2.1.1). These factors would reduce the probability of the burial sites contributing perchlorate.

2.2.2.3 Perchlorate Replacement Programs

Efforts are under way to replace perchlorate in at least some munitions. For example, the Army has a preliminary perchlorate replacement program focused on two specific munitions that constitute a large percentage of perchlorate usage. Edgewood Chemical Biological Center (ECBC) has proposed replacing the photoflash power (the explosive charge inside the pyrotechnic device that contains perchlorates and provide the "bang") with an organic compound to eliminate the use of perchlorate in the two simulators—the M115A2 Artillery Simulator and the M116A1 Hand Grenade Simulator. Alternatively, Picatinny Arsenal has proposed replacing the photoflash powder with a metallic base material. One compound from ECBC and one compound from Picatinny Arsenal will be selected and compared to determine the better one for replacement of these two simulators; however, these two compounds have yet to be chosen. These alternatives will undergo selective testing and comparison to determine better replacement. Other services are also exploring perchlorate replacement.

In addition to service specific programs, DoD's Strategic Environmental Research and Development Program (SERDP) has a new project investigating perchlorate alternatives. This project is designed to develop propellants that have a modifiable burn rate, meet or exceed current performance specifications, and are environmentally benign (SERDP 2005).

2.2.2.4 Perchlorate Contamination at Current and Former Military Facilities

A number of military facilities have documented perchlorate groundwater and surface water contamination (selected examples, Table 2.2 and GAO 2005). Some defense-related facilities, such as some ammunition and missile/rocket manufacturing facilities, also have known releases (Table 2.2). However, it is generally difficult to ascertain which military bases, depots, formerly used defense sites, weapons manufacturing installations, and other defense-related facilities might have perchlorate releases associated with them because site specific documentation may not be available. It is also important to note that the storage, processing and/or use of perchlorate-containing weapons systems does not necessarily correlate to a probable release of perchlorate release to the environment.

Expended munitions and simulators found in the impact areas can contribute to perchlorate contamination in two ways: (a) munitions containing perchlorate or rocket motors do not function as intended through low-order detonation or (b) function as intended by completely detonating but do not completely consume the propellant or main change and subsequent precipitation leaches perchlorate into the environment. These release mechanisms may contribute a relatively low but long-term mass loading of perchlorate to the environment. The current perchlorate groundwater contamination at the impact areas of the Massachusetts Military Reservation in Cape Cod, Massachusetts, reflects this condition. As more ranges are tested for perchlorate contamination, it seems likely that more contamination will be discovered over time. In addition to impact areas, burial areas, OB/OD areas, launching points for rockets and missiles, and missile test stands could also be areas of contamination potential (see Section 2.2.2.2 for discussion of burial areas and OB/OD areas).

Table 2-2. Example DoD facilities with known perchlorate contamination*

Installation	Military service	State	Perchlorate concentration initially detected or reported (ppb)	Perchlorate cleanup demonstration projects under way?
Edwards Air Force Base	Air Force	California	160,000 groundwater (detected 1997)	Yes
Holloman Air Force Base	Air Force	New Mexico	16,000 surface water (detected 1999)	
Aberdeen Proving Ground	Army	Maryland	5 drinking water, 24 groundwater (reported 1998)	
Redstone Arsenal	Army	Alabama	160,000 groundwater (as of 2003)	Yes
White Sands Missile Range	Army	New Mexico	21,000 groundwater (reported in 1998)	
Naval Air Weapons Station, China Lake	Navy	California	560 groundwater (detected in 2001)	
Naval Surface Warfare Center, Indian Head	Navy	Maryland	1,000 surface water (reported in 1998)	Yes

** Not a comprehensive list of DoD facilities with perchlorate contamination.*

2.2.3 Commercial Explosives

2.2.3.1 Black Powder

Black powder is made of a blended mix of saltpeter (potassium or sodium nitrate), charcoal, and sulfur in a 75:15:10 ratio by weight. Nitrate from Chile was used as a source of sodium nitrate in black powder. Chilean nitrate ore, containing naturally occurring perchlorate, was first imported in the United States in 1857. The sodium nitrate content of the ore made it particularly suitable for use in manufacturing explosives, specifically black powder, and replaced the more expensive potassium nitrate. Black powder consumption for commercial blasting peaked in 1917 at nearly 300 million pounds, but by 1970 had decreased to 83,000 pounds, used primarily for safety fuses and fireworks (*Blaster's Handbook* 1980).

2.2.3.2 Black Powder Substitutes

There are several black powder substitutes on the market that contain perchlorate. The addition of perchlorate is intended to increase velocity and range. These substitutes are mainly ascorbic acid (vitamin C). The use of substitute black powders is becoming increasingly popular, especially with hunters. It is believed that the substitute black powder operations in general are small in terms of overall production, but past practices may have resulted in perchlorate releases and contamination.

2.2.3.3 Nitric Acid

An explosives manufacturing site in Arizona uses Chilean nitrate to manufacture nitric acid as an intermediate for explosives manufacture, including the production of dynamite and other explosive compounds. This process resulted in an otherwise unexpected perchlorate groundwater plume (Arizona Department of Environmental Quality n.d.). Although most nitric acid today is made using other chemical processes, Chilean nitrate has been used in the past for its production. Consequently, historical locations of nitric acid manufacturing using Chilean nitrate are potential areas of perchlorate contamination.

2.2.3.4 Modern Commercial Explosives

A number of modern commercial explosives products may contain sodium perchlorate, ammonium perchlorate, or potassium perchlorate as a chemical sensitizing agent. These products may include emulsions,[4] water gels,[5] delay elements in detonators, and some seismic explosives.

Under some circumstances, an explosives manufacturer may use a chemical sensitizer such as perchlorate to increase the shock initiation sensitivity of an emulsion or water gel product. This type of product sensitized using perchlorates is generally designed for specialized applications such as wet/hard/dense rock blasting, in applications to expand drilling patterns or to address excessive rock burdens, in tight underground cuts and tight trenching situations, high-precompression conditions, and deep wet trenches and boreholes. In these applications, including certain trenching and utility work, some mining blasting, and specific construction-related blasting activities, perchlorates may be used to preserve product sensitivity where normal sensitizing agents may be conditionally compromised. In these applications, perchlorates have been found particularly effective in maintaining the sensitivity of the explosive.

The amount of perchlorate present in typical perchlorate-containing explosives is quite variable. Some illustrating examples of perchlorate-containing explosives by weight as derived from material safety data sheets (MSDSs) include some seismic products: 66%–72% sodium perchlorate; bulk and packaged water gel products: 0%–4% sodium perchlorate; packaged continuous water gel explosives: 0%–7% sodium perchlorate; emulsion explosives: 0%–30% perchlorate; electric detonators: 0%–0.5% potassium perchlorate; and nonelectric detonators: 0%–0.89% potassium perchlorate. Some emulsion and water gel explosives may exceed even these concentration ranges.

2.2.3.5 Perchlorate Contamination Associated with Explosives Manufacture, Storage, and Use

Manufacture. At some explosives manufacturing locations, the past practice of using unlined ponds to collect production-derived wastewater may have resulted in releases of perchlorate to groundwater. Explosive solids containing perchlorate also may have accumulated in ponds as sludge. In other instances, wastewaters may have been discharged to surface waters.

---

[4] The Institute of Makers of Explosives (IME) defines an “emulsion” as an explosive material containing substantial amounts of oxidizer dissolved in water droplets, surrounded by an immiscible fuel, or droplets of an immiscible fuel surrounded by water containing substantial amount of oxidizer (IME 2002).

[5] IME defines a “water gel” as an explosive material containing substantial portions of water, oxidizers and fuel, plus a cross-linking agent (IME 2002).

Explosives manufacturing has resulted in significant groundwater perchlorate contamination at some locations. In Kansas, for example, a former manufacturer of slurry explosives has contaminated the groundwater as well as surface water ponds. Plants surrounding the ponds have tested positive for perchlorate, as have largemouth bass and channel catfish from the ponds, and local cattle have significant perchlorate plasma as a result of drinking from the ponds (Kansas Department of Health and Environment n.d.). Plumes associated with these situations may contain perchlorate as well as explosives and nitrates, the presence of which make it more difficult to bioremediate the perchlorate due to selective chemical uptake preferences, depending upon the bioremediation technology (see Section 6.1). Therefore, these situations may pose remediation challenges.

At other explosives manufacturing facilities, wastes containing perchlorates may have been disposed of at OB/OD units with the potential for perchlorate residue generation and subsequent groundwater contamination. Past practices at manufacturing facilities may represent the largest environmental release potential in the commercial explosives industry. Certainly, older explosives manufacturing facilities that utilized Chilean nitrate as feedstock should be carefully examined due to the presence of perchlorate in historically higher concentrations as well as past management practices.

Soil, surface water, and an associated groundwater plume have also been found at the site of a black powder substitute manufacturer in Kansas. At an adjacent property, sampling conducted by the Kansas Department of Health and Environment has detected perchlorate in agricultural products associated with use of this contaminated water in chicken meat, eggs, milk, beets, and cucumber pickles.

Storage. Historical releases of perchlorate from storage areas used for perchlorate-containing raw materials may be a concern at some locations. Potential historical releases could be due to leakage of perchlorate from bags and containers, such as dust from sacks of perchlorate salts. Other concerns related to the storage of perchlorate include the disposal of bags and containers of perchlorate in landfills. However, contemporary raw material storage areas are designed and constructed to prevent or minimize any releases of product. Therefore, there is little contemporary risk of release from complete and packaged explosives unless carelessness results in packaging puncture with subsequent leakage.

Explosives Use. Contamination at blasting sites may occur if detonation is incomplete; for example, some rock formations may contain cracks and fissures angling off the main borehole into which explosives may migrate during the loading process (not all explosives are packaged). The explosives contained in such fissures may then fail to detonate in the blast. In addition, the potential for residual contamination is increased in the event of a misfire, in which a loaded hole or group of holes in a blasting pattern fails to detonate. Undetonated explosive products remaining after a misfire or incomplete detonation will have more residence time to contact and contaminate groundwater. This scenario is of particular concern where the explosives contain highly soluble perchlorates. Blasting misfires do occur with some variable frequency. Significant effort is made to avoid misfires, primarily because they represent a serious safety hazard. Blast efficiency and cost considerations are secondary concerns. If possible, attempts are usually made to detonate the misfired hole or holes. In some cases, perchlorate contamination associated with blasting may be attributable to preblast loss of explosives due to poor housekeeping practices and/or improper spill cleanup.

Groundwater contamination associated with explosives use is suspected at a construction site in Westford, Massachusetts. In a water sample from a pond near the site, Massachusetts Department of Environmental Protection (MADEP) officials detected a perchlorate concentration of 819 ppb and detected a perchlorate concentration of 12 ppb in an on-site retention pond. One town water supply well with a detection of 3.3 ppb has been shut down, while a privately owned water well several hundred feet from the site also has a perchlorate concentration of 425 ppb. MADEP officials believe the perchlorate contamination is related to explosives used in rock blasting. An examination of the MSDSs by MADEP officials for the emulsion and water gel type explosives used by the sole contractor at these sites showed the explosives contained 20%–30% by weight of perchlorate. According to MADEP, the cause (blasting explosives) and effect (water contamination) relationship at this time appears clear (MADEP 2005a). Mandated testing of the public water supplies by MADEP led to this discovery and others related to perchlorate impacts.

2.2.4 Fireworks

In general, fireworks manufacturers encase their chemical compounds in cardboard cylinders or spheres called "shells." The lofting charge or propellant usually consists of black powder, which may also be a component of the explosive charge. When fireworks have a loud, concussive bang and a flash of white light, they are termed a "photoflash" or a "flash and sound" effect. This effect is produced using a mixture of potassium perchlorate and fine aluminum or magnesium powder. Common applications include special effects for rock concerts, firecrackers, illumination for night photography, and of course fireworks.

Perchlorate or chlorate oxidizers are also typically used because they decompose at high temperatures and release free chlorine. The chlorine is then available to combine with barium, strontium, or copper incorporated as compounds that produce the characteristic green, red, and blue hues respectively (Conkling 1990). In some fireworks shells, an oversupply of potassium perchlorate beyond the stoichiometric need is used to suppress the effects of certain chemical elements during reactions.

2.2.4.1 Perchlorate Contamination Associated with Fireworks Manufacture and Use

Manufacture. Whether fireworks-making facilities have had perchlorate releases during manufacture or storage of perchlorate in the United States is unknown and deserves some scrutiny due to the stability of perchlorate in water. It is likely that some of the older sites probably used perchlorate containing Chilean nitrate. Currently, according to the American Pyrotechnics Association, close to 100% of fireworks are imported, and in 2003 approximately 221 million pounds of fireworks were sold in the United States. However, some current domestic fireworks production still exists, with several facilities having accidentally exploded over the past 30 years.

Fireworks display designers have been building custom made shells in the United States for their shows since before the turn of the last century. Some of these may constitute potential sources, at least for those that were using perchlorate in their formulations and some older production that was based on Chilean nitrate.

Fireworks Use. In Massachusetts MADEP is investigating perchlorate contamination that appears to be from the residue of fireworks displays conducted over time. Fireworks-based perchlorate residue is suspected to have contributed to perchlorate groundwater contamination located in the Northwest Corner at Massachusetts Military Reservation (MMR). This area has perchlorate groundwater plumes that emanate from both off and on base with perchlorate concentrations as high as 19 ppb along with associated explosives such as RDX at up to 7 ppb. The groundwater contamination appears to be the result of annual fireworks displays that occurred 1996–2003, as well as military pyrotechnics such as smoke pots, smoke grenades, and various perchlorate-containing simulators. Further, perchlorate contamination potentially related to the use of fireworks has been found following water supply well sampling and testing in several other locations around the state (MADEP 2005a).

MADEP is conducting a fireworks residue field test at the University of Massachusetts Dartmouth Campus. Predisplay analytical results show perchlorate concentrations in various types of fireworks from nondetect to 36 ppb. The site has hosted displays for about 10 years. The amount of perchlorate available for groundwater contamination from fireworks depends upon how many displays, the types of fireworks involved, amount of misfiring, and the length of time over which displays were conducted in a specified area. Misfires may contribute significant perchlorate to the environmental loading as well, and their frequency, although relatively low, does vary. Disposal of these misfires may also be of concern (MADEP 2005a).

2.2.5 Safety or Hazard Flares

Perchlorate is one of the primary components found in emergency and signal flares. Flare use is believed to be widespread across the United States. In Santa Clara County, California, more than 40 metric tons of flares was used/burned in 2002 alone (Silva 2003). Flares containing perchlorate have also been used in aircraft seeding operations in some locations.

In safety or hazard flares, strontium nitrate is combined in a mixture with an oxidizer and a chlorine source (potassium perchlorate), along with various fuels. The available chlorine from the perchlorate and the strontium combine to color the emitted light bright red (Conkling 1990). Tests indicate that the residue from fully burned flares may still contain a significant leachable amount of perchlorate, up to almost 2000 µg of perchlorate per flare, and that partially burned flares leach even greater concentrations of perchlorate when placed in contact with water (Silva 2003).

The manufacturing sites of flares are known to have precipitated perchlorate releases into groundwater in California, and releases are also possible in other locations where similar facilities are or were situated.

2.2.6 Matches

Potassium perchlorate is used in the production of common stick matches, which use a blend of potassium chlorate and sulfur to act as a fuel and binder (Conkling 1990). If an environmental concern exists associated with matches, it is likely to be at the production facilities. As of 1997, only four American companies produced matches: Lion Corp., Superior Match Co., Atlantis Match Co., and D. D. Bean & Sons Co. (Retskin 1997).

2.2.7 Industrial Uses

Industrial uses of perchlorate vary widely in scope, as perchlorate is incorporated into or used to make many common products (Appendix E). Laboratories also make use of the strong oxidizing and other properties particular to perchlorate. Perchloric acid, for example, is used in some industrial processes, such as in processing rare-earth element ores. In Tewksbury, Massachusetts, discharges of perchlorate to a river were found to be associated with a medical device manufacturer's use of perchloric acid). It is expected that the number of industrial uses will continue to expand as our understanding and awareness of its usage matures. Also, some previous list of perchlorate uses contained erroneous information. Efforts were made in this document to correct these errors, but work to verify all of the reported uses through reliable documentation is still under way.

The applications of the various perchlorate compounds are so varied that it is difficult to characterize the practices or mechanisms that may lead to releases to the environment. This problem is further complicated by the fact that perchlorate compounds may be used in solid or liquid form. The practices at each facility producing, handling, or using perchlorate will have to be examined individually to determine what possibilities exist for releases to the environment to occur.

2.2.8 Laboratories

Some laboratories in industry, academia, DoD, Department of Energy (DOE), or other settings are using or may have used perchlorate compounds or perchloric acid in research or analytical work. Several examples follow where perchlorate compounds or perchloric acid have been released, or are suspected to have been released, from a laboratory setting. At Los Alamos National Laboratory (LANL), perchlorate found in groundwater has been associated with past actinide research and high-explosives synthesis and testing (Hjeresen et al. 2003). There has also been at least one case of a university chemistry building being temporarily closed due to an accumulation of perchlorate in the ventilation system. As a result, special fume hoods specific to perchloric acid use are now available.

Some detergents may contain perchlorate. For example, detergent-based laboratory glassware cleaning agents such as Alconox, Alcotabs, Liquinox, and NeuTrad have been tested and shown to contain up to 2.5 mg/kg perchlorate. (Some types of laundry detergent could also potentially contain perchlorate.)

2.2.9 Agricultural Uses

Some naturally occurring perchlorate is present in products used to enhance agricultural output, e.g., fertilizers. Commonly, nitrates are added to phosphates and potash to produce fertilizers, the ratios of which can be varied to provide for specific plant needs. Potash, a source of soluble potassium essential for plant growth, is mined to produce a fertilizer for agricultural use. USEPA tested various fertilizers used in the United States and determined that these fertilizers do not generally contain perchlorate. This conclusion appears to contradict the USGS findings of perchlorate in some potash samples. Domestic production of potash occurs in Michigan, Utah, and New Mexico. Canada also produces potash, as do some foreign sources. Potash is also used as feedstock in the production of other chemicals (Milford 1999, USEPA 1999a). Other evaporate-derived minerals such as borate are components of certain fertilizers used for plants that need them as trace elements, e.g., alfalfa and clover (Lefond 1975).

Bulldog Soda, marketed by Sociedad Quimica Y Minera De Chile S.A. (SQM) and derived from Chilean nitrate deposits (containing 0.03% perchlorate on average, as mined), is used as approximately 0.14% of the total fertilizer currently applied in the United States. On a historical basis prior to the 1960s, Chilean nitrate–derived fertilizer was the principal fertilizer used in the United States. The USEPA fertilizer study completed in 2001 found that fertilizer derived from Chilean nitrate contained accessory perchlorate in significant concentrations. Subsequently, SQM, the sole mining and processing company of caliche-type deposits, has changed the process for refining the ore, going from 0.5–2 mg/g to 0.1 mg/g, or 0.01% perchlorate. This fertilizer is still applied to a small percentage of cropland in the United States. SQM promotes the use of its products in agriculture for the cotton, tobacco, and citrus sectors. The historical application of higher concentration perchlorate-containing fertilizer may present a legacy of unknown contamination potential to groundwater, as may the lower concentration product applied currently (Urbansky et al. 2001, UC SAREP 2002).

2.2.10 Medical/Pharmaceutical

Historically, potassium perchlorate has been used in medical practice for the treatment of thyroid disorders to suppress the overproduction of hormones due to an overactive thyroid gland (see Section 4.1 for more on the effect of perchlorate on thyroid hormones). Potassium perchlorate is employed in current medical procedures in three different ways. First, it is used in the treatment of induced hypothyroidism or thyrotoxicosis resulting from the primary treatment of tachyarrhythmia or ischemic heart disease by the iodine-containing drug amiodarone. Potassium perchlorate is also used to limit the uptake of sodium pertechnetate in the thyroid when pertechnetate is administered in the course of brain and blood-pool imaging and placenta localization. Third, potassium perchlorate has been used as a diagnostic agent in the treatment of certain thyroid disorders. The potassium form of perchlorate appears to be used exclusively for medicinal purposes over other salts of perchlorate probably due to lessened physiological impacts of the potassium over other possible cations (California Department of Toxic Substances Control n.d.).

The likelihood of medical perchlorate source release to the environment appears to be slight given that amounts stored for medical purposes are small, storage occurs in containers and structures, and hospitals have waste disposal programs.

2.2.11 Water and Wastewater Treatment

Sodium hypochlorite (NaOCl) is one commonly used method to disinfect water supplies. It is also used to treat pool water, to disinfect groundwater production wells, to treat wastewater in publicly owned treatment works, and other instances where an effective disinfectant is required. Sodium hypochlorite in solution normally produces some perchlorate ions during the dissociation reactions. This effect is evidenced by the formation of highly unstable and shock-sensitive perchlorate crystals that can form around the rim and cap of long-stored sodium chlorite solutions in laboratories. Thus, the use of sodium hypochlorite has the potential in these applications to introduce detectable perchlorate into the environment. MADEP has measured perchlorate levels of 0.20–0.28 μg/L in samples of finished drinking water from three drinking water plants where perchlorate levels in raw water coming into the plants were below the 0.20 μg/L detection limit. MADEP has attributed the perchlorate detections at all three plants to the sodium hypochlorite used for water disinfection (MADEP 2005b).

Household bleach may also contain perchlorate. According to MADEP, some preliminary testing of household bleach from store shelves shows the presence of perchlorate up to 390 μg/L (equivalent to ppb). Chemical age appears to be a factor for perchlorate concentration strength in bleach, as another sampled bottle of bleach on the shelf for two years tested for perchlorate at 8000 ppb. Other applications for sodium hypochlorite include its use as a bleaching agent in laundry cleaning; for brightening, oxidizing, deodorizing, and sterilizing in general industry; for decolorizing in textile manufacturing; and for bleaching in the paper and pulp industry. It is also used for skinning of vegetables in the food processing industry.

MADEP has also sampled and tested for perchlorate in the effluent from two separate septic tanks where the influent source water contained approximately 1000 and 500 μg/L perchlorate. Both effluents were nondetect for perchlorate using liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) analytical technology (see also Section 3.2.2 for more information on analytical methods). It is possible that perchlorate degraded in the anaerobic environment of the septic effluent, although this proposed relationship remains to be proven.

2.2.12 Landfills

Historically, landfills have received waste perchlorate and perchlorate-contaminated wastes and debris as a matter of course. Some of these landfills were or are located on site near a facility using perchlorate, while other landfills were or are located some distance off site from the facility. It is believed these perchlorate wastes were primarily in the solid form, although whether any perchlorate-containing liquids were also disposed is unknown. Users of perchlorate products who discarded the packaging are also a potential source of perchlorate to landfills due to the perchlorate residue adhering to that packaging. How many landfills may be impacted by perchlorate is unknown.

2.2.13 Sodium Chlorate Manufacture

In the electrolytic cell process for manufacturing sodium chlorate, the perchlorate ion is produced as an unintended by-product. In 1999, total U.S. sodium chlorate production capacity was 946,000 short tons per year, produced at 10 manufacturing sites (Tables 2-3 and 2-4).

Table 2-3. Sodium chlorate production capacity and locations in 1999 in the United States

Facility	Location	Capacity (short tons/year)
CXY Chemicals, USA	Hahnville, La.	134,000
Eka Chemicals (Eka-Columbus)	Columbus, Miss.	219,000
Eka Chemicals (Eka-Washington)	Moses Lake, Wash.	63,000
Elf Atochem North America, Inc.	Portland, Oreg.	58,000
Georgia Gulf Corp.	Plaquemine, La.	27,000
Huron Tech-442 Corp. (Huron Tech 442)	Perdue Hill, Ala.	40,000
Huron Tech (Huron Tech-Augusta)	Augusta, Ga.	145,000
Kerr-McGee Chemical LLC	Hamilton, Miss.	143,000
Sterling Pulp Chemicals	Valdosta, Ga.	110,000
Western Electrochemical	Cedar City, Utah	7,000
Total		946,000

Source: USEPA 2000b.

Table 2-4. Former sodium chlorate production facilities in the United States and changes as of 1999

Facility	Location	Capacity (short tons/year)	Comments
Elf Atochem	Tacoma, Wash.	25,000	Closed 9/97
Georgia-Pacific	Brunswick, Ga.	27,000	Closed 4/97
Huron Tech Corp.	Eastover, S.C.	90,000	Came on line 3/99
Huron Tech 442 Corp.	Perdue Hill, Ala.	40,000	Scheduled closure mid-2000

Source: USEPA 2000b.

Sodium chlorate is used in agriculture as a nonselective herbicide, mainly on noncropland for spot treatment of weeds and as a defoliant and for desiccant purposes for crops (PMEP 1995, Pesticide Action Network North America n.d.). Nonagricultural uses of sodium chlorate include household and industrial bleaching, pulp and paper bleaching, and food processing. Sodium chlorate is also used in numerous applications as well as a feedstock to make other chemical products (PMEP 1995).

It is possible that some current and former sodium chlorate production facilities could also be potential perchlorate sources, as could locations where sodium chlorate is being used for intended purposes.

2.2.14 Uncertain Sources

The problem when investigating an emerging environmental contaminant is that new information continues to come to light regarding past management practices, current uses, locations of use, or newly suspected but uncertain sources. In the case of the latter, there is a small but apparently growing list of suspected perchlorate sources. Confirmation and verification testing has not necessarily been done in all cases, and research in these areas is ongoing. A short list of these sources would include cloud-seeding operations, clandestine methamphetamine laboratory wastes, and certain anticorrosion cathodic protections systems.

Cloud-seeding operations have used potassium perchlorate as a component of some flare designs to produce nuclei for water-drop formation leading to precipitation. Whether this formulation is still in use is unknown.

There is also the possibility that in some clandestine methamphetamine laboratories the process of obtaining red phosphorus from matches and also road flares containing perchlorate may produce a waste stream containing concentrated perchlorates as a by-product.

A Texas Tech University study showed perchlorate being produced at measured rates of 71–77 µg/L by a cathodic protection system in a steel chlorinated water supply storage tank in Levelland, Texas (Jackson et al. 2003, 2004). The Texas Tech University Water Resources Center is also investigating the potential for the generation of perchlorate by pipelines, buried tanks, and water and oil wells protected by anticorrosion cathodic protection systems in the presence of natural chlorides in soil and groundwater (Jackson et al. 2003, 2004).

2.3 Environmental Fate and Transport

As previously discussed, perchlorate may be released into the environment in the form of a number of different salts, including ammonium perchlorate, potassium perchlorate, sodium perchlorate, and others. All are highly soluble in water, though the solubility of the various salts varies (Table 1-1). Perchlorate may also be released into the environment in the form of a liquid, such as in solution with water as a concentrated brine or as perchloric acid. This liquid form of perchlorate increases the potential as well as the speed of a spill reaching groundwater or surface water.

Very little is known about the distribution of perchlorate in soil. What is known is that the perchlorate does not bind to soil particles appreciably and that the movement of perchlorate in soil is largely a function of the amount of water present. Perchlorate salts that are released to the soil in solid form will readily dissolve in whatever moisture is available. If sufficient infiltration occurs, the perchlorate will be completely leached from the soil. Soil moisture containing perchlorate in solution can be taken up by plants through the roots, and several ecological studies have demonstrated the tendency of some plants to concentrate the perchlorate in plant tissues (Urbansky et al. 2000; Ellington et al. 2001). Some perchlorate may be held in solution in the vadose zone by capillary forces. In arid regions, crystallized perchlorate salts may accumulate at various horizons in the soil due to evaporation of infiltrating rainfall that leached perchlorate from shallower depths.

In dilute concentrations typically found in groundwater, perchlorate behaves conservatively, with the center of mass of the plume moving at the same average velocity as the water. Dispersion will cause the contaminant front actually to move faster than the average groundwater velocity. Perchlorate is kinetically very stable under environmental conditions and will not react or degrade in solution under ambient conditions. Biodegradation of perchlorate in groundwater will not occur unless significant levels of organic carbon are present, oxygen and nitrate are depleted, and perchlorate-degrading anaerobic bacteria are present. The combination of high solubility, low sorption, and lack of degradation tends to create plumes that are large and persistent.

If perchlorate is released as a high-concentration brine solution, the movement of the brine in a groundwater system may be controlled by density effects (Flowers and Hunt 2000). The density contrast between the brine and groundwater may cause the brine to move vertically with minimal influence by groundwater movement and little or no dilution. Brine pools may form on top of confining layers, and significant perchlorate mass may move into low-permeability confining layers by diffusion. The brine pools and perchlorate mass absorbed by the confining layers may serve as a long-term source of dissolved contaminant as perchlorate is released to the groundwater by diffusion. This type of release may occur where perchlorates have been manufactured, at rocket motor washout facilities, or other locations where perchlorate has been slurried or handled in concentrated brines.

2.4 Environmental Management

2.4.1 Past Practices

In general, some past management practices were inadequate to contain or prevent the release of perchlorate to soils and surface/groundwater because perchlorate was not recognized or regarded as a contaminant of concern. Efforts to contain perchlorate releases were primarily directed at product retention or recovery to maximize production output. Even though the historical practices should no longer occur or are being corrected when recognized, they have left a legacy of known and unknown sites.

2.4.2 Current Practices

Due to the properties of perchlorate, namely high solubility, little attenuation, stability, persistence, and the fact that a relatively small amount of perchlorate can contaminate a large amount of water, the management of perchlorate requires that users exercise the utmost in prevention techniques to prevent release to the environment. Also, since perchlorate compounds and the perchlorate ions in water are not volatile, there is no risk of perchlorate air emissions.

It is apparent that for some applications, there may be no adequate or cost-effective substitute for perchlorate, at least for some time. Banning the use of perchlorate is not necessarily a solution, but effective management practices certainly can be. Therefore, best management practices (BMPs) should be developed and rigorously followed where perchlorate is used. Some of these BMPs are general and apply to the use of any chemical, and others are industry and use specific.

Examples of these would include spill contingency plans, secondary containment, waterproof storage, and treatment of waste streams, where necessary. Some facilities also practice zero discharge. These efforts are doubly important when liquid forms of perchlorate such as concentrated solutions and perchloric acid are stored, used, and transported. Generally, these general techniques are familiar to practitioners in industry and DoD and have been known to environmental professionals for a considerable time, especially those with experience with the requirements of the Resource Conservation and Recovery Act (RCRA) and other environmental laws. It should be kept in mind that even though perchlorate is not currently regulated, it is likely to be in the future.

2.5 Site Characterization Approaches

Sampling for possible perchlorate contamination on a site requires some knowledge of the perchlorate usage at the site. This knowledge can be acquired through a historical review and interviews with on-site or former personnel. Knowing the quantity of perchlorate released at any one time, the number of occurrences, and the time period over which the releases occurred can provide some guidance for testing. In addition, knowledge of the environment and geology can help guide sampling approaches. For example, in dry or desert environments with a deep groundwater table, there can be a precipitation front of perchlorate below the surface but above the groundwater as a caliche layer. If the area has significant precipitation, diffuse source(s), or dispersed source(s), then groundwater and/or adjacent surface water should be tested, as the soil is likely flushed.

Perched aquifers, windows in confining layers, seasonal water-level changes, and potential density currents point to the importance of understanding the groundwater flow regime. Existing groundwater monitoring wells can be taken advantage of, and temporary push-point wells permit investigators to scope the nature and extent of a source rapidly. Since perchlorate acts like nitrate when dissolved in water, perchlorate contamination tends to move with groundwater flow unless stagnant conditions exist. Depending on specific uses, perchlorate may be associated with other contaminants, such as nitrates, explosives, solvents, or metals, and more associations may become apparent over time. The association is site specific but may provide important clues.

Releases of perchlorate, either continuous or intermittent, should lead to soil testing as well as testing of groundwater/surface water at any point sources, especially in dry or desert environments. Because deeper soil samples may indicate the presence of perchlorate even if surface soil samples do not, both surface and at depth samples should be taken if soil testing is indicated.

3. SAMPLING AND ANALYSIS

In the spring of 1997, an analytical method for perchlorate detection with a reporting limit of 4 ppb was developed. Since then, additional sampling and analysis techniques have been developed that can detect perchlorate at concentrations of 1 ppb and lower. It is important to note that perchlorate sampling and analytical techniques require special considerations due to potential interferences, laboratory contamination, and potential false positives. This section will address sampling protocols, analytical methodologies, and forensics techniques for perchlorate.

3.1 Sampling Protocols

A brief discussion of sampling requirements specific to perchlorate for water and for soil is provided below. General information regarding surface water, sediment, soil, and groundwater sampling can be found in many documents including, but not limited to, the following:

- *Contract Laboratory Program Guidance for Field Samplers*, EPA/540/R-00-003 (USEPA 2004b)
- *Requirements for the Preparation of Sampling and Analysis Plans*, EM 200-1-3 (USACE 2001b)
- *Model Field Sampling Plan*, Vers. 1.1 (AFCEE 1997)
- *Interim Guidance on Sampling and Testing of Perchlorate at DOD Installations (*U.S. Navy 2004)
- *U.S. Geological Survey Techniques of Water-Resources Investigations* (USGS variously dated)

The primary concern regarding perchlorate detection is the potential for false positives and false negatives. The secondary concern regarding perchlorate detections is the potential for bias in the analytical results due to field or laboratory activities. To address these concerns in the field, one or more equipment rinseate blanks should be collected during each sampling event when sampling equipment is reused, because analysis of solutions containing some of the commercial detergents commonly used during field decontamination (such as Alconox, Alcotabs, Liqui-Nox and Neutrad) have been shown to have detectable levels of perchlorate. To address these concerns in the laboratory, method blanks should be routinely analyzed and evaluated by the laboratory. Also, if reusable equipment is used for sampling, decontamination must be documented as effective through the use of quality control (QC) samples to ensure contributions from laboratory and field equipment are not causing high bias in analytical results.

3.1.1 Water

For groundwater and surface water, sampling for perchlorate can be performed with typical techniques discussed in the referenced sources. The holding time for perchlorate in water is currently established at 28 days, when the sample is held at 4º ± 2ºC. Although Method 314.0 (USEPA 1999b) does not require chemical preservation, there is anecdotal evidence of microbial degradation (see Section 3.2.1 for more information on Method 314.0). According to USEPA, two new sampling requirements will be added to updated or new perchlorate methods (USEPA 2005a, b, c). The first requirement is preservation in the form of field ultrafiltration through a sterile 0.2-micron filter into a presterilized nalgene bottle. The second requirement is that the sample be collected with significant headspace.

3.2.1 Soil

For soil and sediment, sampling for perchlorate can be performed with typical techniques discussed in the referenced sources. One anticipated issue specific to perchlorate is sample representativeness due to anticipated heterogeneity (Gerlach and Nocerino 2003). Very little is known about distribution of perchlorate in soil.

Perchlorate salts are solids at ambient temperature. The distribution almost certainly depends on the form of the source (i.e., contaminated groundwater or other dissolved source vs. distribution in solid phase). If the perchlorate is distributed in a dissolved source, it should be expected to be very mobile in the soil. If the perchlorate is distributed in the solid phase (such as via a detonation), it could be expected to be distributed due to the physical transport of the detonation and it should be expected to initially be distributed similarly to secondary explosives.

Cold Regions Research Engineering Laboratory (CRREL) has conducted numerous studies led by Dr. Thomas Jenkins regarding the distribution of secondary explosives on active ranges. Secondary explosives are often dispersed as variously sized and shaped particles that slowly dissolve in precipitation because they are sparingly soluble and are wetted on only a periodic basis. They also possess low vapor pressures and hence do not volatilize to any extent. Their distribution is typically very heterogeneous, and they are transported through soil only after they are dissolved in water. The primary difference between secondary explosives and perchlorate is the solubility. Given perchlorate's greater solubility, it should be expected to migrate through the soil more readily even if it is initially distributed in particles. Until more data have been gathered, it would be prudent to conduct perchlorate sampling in soil based on the type of anticipated source. If the anticipated source is a detonation, composite sampling is recommended (Walsh et al. 1993; Crockett et al. 1996; Jenkins et al. 1996, 1997a, 1997b, 1997c, 2004; Thiboutot et al. 1997; Thiboutot, Ampleman, and Hewitt 2002.)

Concerns regarding sample heterogeneity do not end when the samples are collected. It is critical that laboratory subsampling also be conducted appropriately, regardless of what analytical methodology is used, particularly if a particulate source is anticipated. For additional information on laboratory subsampling, see *Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples* (Gerlach and Nocerino 2003). The holding time for perchlorate in soil has not been established. In lieu of an established holding time for soil, the water holding time (28 days) has been used on an advisory basis when the sample is held at 4º ± 2ºC.

3.2 Analytical Methodologies

Analytical methodologies for perchlorate are discussed briefly below. Tables 3-1 and 3-2 (in Section 3.2.2) provide a comparison of the primary analytical methodologies in use. Key factors for choice of analytical methodology include the following:

- regulatory acceptance of method,
- state/USEPA certification of laboratory (if required by the state or the program),
- sensitivity, and
- selectivity.

Table 3-1. Perchlorate analytical laboratory methods comparison

Method (technique)	Applicability	Analytical limitations	Aqueous reporting limits (µg/L)
EPA 314.0 (ion chromatography [IC])	• Mandatory for drinking water samples reported under UCMR 1 • Aqueous samples with low dissolved solids (conductivity <1 mS/cm total dissolved solids [TDS]) and chloride, sulfate, and carbonate concentrations <100 mg/L each • Conductivity of samples must be below the laboratory's established matrix conductivity threshold	• Analysis is subject to false positives due the unspecific nature of the conductivity detector • Method has been validated in drinking water only; no guidance provided for use with soils, biota, etc. • The lower reporting limit of 0.5 ppb is achievable only in samples with very low TDS • Inappropriate for use in samples with high TDS	4
EPA 314.1 (IC)	• Method has been used on aqueous samples, including those with high TDS • Published EPA method (EPA 2005a) • Planned option for UCMR 2	• Analysis may be subject to occasional false positives due to the unspecific nature of the conductivity detector • Uses second dissimilar chromatographic column to aid in qualitative identification • Requires the use of anion reduction cartridges if used to analyze samples with high TDS	0.5–1
EPA 9058 (IC)	• Aqueous samples w/ <1 mS/cm TDS • Soil samples • EPA method published (EPA 2000a)	• Analysis may be subject to false positives due to lack of confirmation requirements or conformational chromatographic column • EPA method currently under revision	0.5–1
EPA 6850 (LC/MS)	• Aqueous samples to include those with high TDS • Soil samples • Biota samples • Determinative method for perchlorate • Published EPA method undergoing validation studies	• None reported	0.2 for water and soil; 0.6 for biota
EPA 331.0 (LC/MS or LC/MS/MS)	• Method limited to aqueous samples to include those with high TDS • Planned option for UCMR II • Determinative method for perchlorate • Published EPA method available (EPA 2005b) • Planned option for UCMR 2	• Pretreatment recommended in Winkler, Minteer, and Willey (2004) method • May be subject to false positives unless ion ratio monitored • Under MS/MS, method is highly selective, but may be subject to false negatives unless adequate separation from common anions is achieved	0.02
EPA 332.0 (IC/MS or IC/MS/MS)	• Method has been used on aqueous samples, including those with high TDS, and on milk and biota samples • Determinative method for perchlorate • Published EPA method (EPA 2005c) • Planned option for UCMR 2	• May be subject to false positives unless ion ratio monitored • Under MS/MS, method is highly selective but may be subject to false negatives unless adequate separation from common anions is achieved	0.1
FDA Method (IC/MS/MS)	• Fruits and vegetables, bottled water, and milk	• None noted in literature	0.5 (limit of quantitation)

To detect perchlorate in the environment, analytical chemists use several techniques. As of the writing of this document, the only method that has been approved for compliance monitoring (UCMR 1) is USEPA Method 314.0. Method 314.0 is a presumptive method, and when perchlorate is detected for the first time in an environmental medium and this method is used, the presence of perchlorate should be confirmed using a determinative method. To confirm the presence of perchlorate in an environmental sample, it is preferable to use the analytical technique MS, which confirms the chemical composition of unknown ions by their molecular weight (mass-to-charge ratio).

As noted previously, some supplies of the laboratory detergents contain detectable levels of perchlorate. Considering the potential bias from these detergents, laboratories using these products either directly or indirectly during perchlorate analysis should consider analyzing a diluted sample of the detergent to eliminate the potential for this bias. Use of disposable equipment for any sample manipulation is recommended to limit the potential for cross-contamination.

3.2.1 Laboratory Methods

Published USEPA methods include Method 314.0 (promulgated) and Method 9058 (draft, Method 846, Revision IVB), Method 331.0, and Method 332.0. Methods 331.0 (LC/MS and LC/MS/MS) and 332.0 (IC/MS and IC/MS/MS) have extensive discussion of interferents. USEPA's Office of Solid Waste is currently performing method validation studies on a determinative method—Method 6850.

QC requirements are similar for most of the determinative laboratory methods. Some of the QC evaluations that are unique to emerging laboratory methods include the analysis of a suppression standard (500 mg/L bicarbonate, carbonate, chloride, and sulfate) spiked at the reporting limit, comparison of the isotopic ratio for chlorine in the perchlorate to natural isotopic abundance ratio, and the use of an $18O_4$-labeled perchlorate internal standard. Analysis using the determinative methods is more sophisticated than for the ion chromatography (IC) methods, requiring more education/training for both the analysts and the data reviewer. However, IC/MS/MS, LC/MS, and LC/MS/MS are more expensive than IC methods alone.

A description of the published and emerging methods, and their limitations, are discussed in the following subsections.

3.2.1.1 Method 314.0—Ion Chromatography

Method 314.0, the only method for perchlorate promulgated by the USEPA to date, was developed for drinking water. Aqueous samples are introduced into an ion chromatograph. The perchlorate ion is separated from other ions in the sample based on its affinity for the material in the chromatographic column and is detected using a conductivity detector. The conductivity detector cannot specify the ion producing the analytical response; ions are differentiated based solely on retention times.

Sample matrices with high TDS and high concentrations of common anions such as chloride, sulfate, and carbonate can destabilize the baseline in the retention time window for perchlorate and also add or suppress the response of the detector to perchlorate. These can be indirectly assessed by monitoring the conductivity of the matrix. Therefore, the laboratory must determine its instrument-specific matrix conductivity threshold (MCT), and all sample matrices must be monitored for conductivity prior to analysis. When the MCT is exceeded, sample dilution and/or pretreatment must be performed. However, sample dilution leads to elevated reporting limits and pretreatment to remove potential interfering ions has the potential to reduce the actual perchlorate content of the sample at low concentrations.

There is evidence of cases where Method 314.0 has resulted in the reporting of false positives, falsely elevated results, and false negatives. Additionally, the method has been used as the basis for laboratories reporting to sub-ppb levels despite the method's documented capability of 4.0 µg/L. MADEP set a "demonstration of capability" involving very rigid QC requirements and proficiency evaluation samples rounds to allow laboratories to report sub-ppb levels (see www.mass.gov/dep/brp/dws/files/perchlor.doc).

3.2.1.2 Method 314.1—Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection

Several options have been explored to improve Method 314.0, including sample enrichment/ isolation techniques intended to improve sensitivity, such as increased sample size and preconcentration/preelution, and resolution and analysis improvement strategies, such as heart cutting/column switching, noise suppression, and the use of dual channels. Samples are collected using a sterile filtration technique and stored with headspace to reduce the potential for degradation by any remaining anaerobic organisms. Laboratories employing these improvements/ alterations report their results as Method 314.0 analyses as the changes are not considered to be outside the method.

This method is intended to add increased sensitivity, better tolerance of TDS, and better selectivity through use of a confirmation column and in-line concentration. Method 314.1 was published in 2005 (USEPA 2005a).

3.2.1.3 Method 9058—Ion Chromatography with Chemical Suppression Conductivity Detection

Method 9058 is the USEPA's Office of Solid Waste (OSW) method for IC. The method is substantially the same as Method 314.0, although the MCT requirement is not included. The method is stated to perform adequately on water samples with conductivities up to 1000 µS/cm and is potentially applicable to surface water, mixed domestic water, and industrial wastewaters. The limitations described above for Method 314.0 apply similarly to Method 9058.

OSW is in the process of revising the November 2000 version of Method 9058 given the known interferences and the high probability of false positive and false negative results. The areas being considered for the optimization of the method are to include an extraction procedure for solids, to broaden the scope so that the method is applicable for aqueous samples having high TDS, to lower the level of detection for perchlorate at sub-ppb level, to have better separation, and to minimize false positive and negative results. After the revised method is drafted, an interlaboratory validation study will be conducted.

3.2.1.4 Method 6850—Liquid Chromatography/Mass Spectrometry

The LC/MS method uses a liquid chromatograph with a peptide-impregnated reverse-phase column to perform the separation followed by an MS for detection. Minimal sample pretreatment is required. Perchlorate parent ions (mass-to-charge [m/z] 99 and 101) are used for peak identification. This method has been evaluated with drinking water, soil, biota, synthetic groundwater (7700 µS/cm^2), and Great Salt Lake water (10× dilution, 21,000 µS) (Di Rienzo et al. 2004). The advantages of LC/MS are the increased sensitivity, increased specificity, the lack of sample pretreatment, and the lack of additional instrumentation. An interlaboratory validation study of Method 6850 is taking place in 2005. The reporting limit in water is reported to be 0.1 µg/L. This method will address environmental matrices other than drinking water.

3.2.1.5 Method 331.0— Liquid Chromatography Electospray Ionization Mass Spectrometry

This method, published in 2005 (USEPA 2005b) is a liquid chromatography/electrospray ionization/mass spectrometry (LC/ESI/MS) method for the determination of perchlorate in raw and finished drinking waters. This method can be used to acquire data using either selected ion monitoring or multiple reaction monitoring detection.

In this method, water samples are collected in the field using a sterile filtration technique. Prior to analysis, isotopically enriched perchlorate is added to the sample as an internal standard. The sample is injected without cleanup or concentration onto a chromatographic column, which separates perchlorate from other anions and background interferences. Perchlorate is subsequently detected by negative electrospray ionization mass spectrometry. A remote-controlled valve is used to divert early-eluting cations and anions to waste. Prior to the elution of perchlorate, the valve is switched sending the chromatographic eluent to the mass spectrometer. This diversion helps prevent unnecessary fouling of the electrospray source. Perchlorate is quantified using the internal standard technique. The reporting limit in water is reported to be 0.02 µg/L.

3.2.1.6 Method 332.0—Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry

This IC/MS method, also published in 2005 (USEPA 2005c), is essentially the same as the IC method; however, an MS with an electrospray interface is added. This method requires the use of a suppressor to avoid inorganic salt buildup and uses a conductivity meter to check its efficiency. It uses m/z 99 and 101 ions for peak identification of perchlorate, and monitors the ion ratio of the naturally occurring abundance of Cl-35 and Cl-37, which should be 3.08.

The advantages of IC/MS are the increased sensitivity and increased specificity; however, high hydrogen sulfate (HSO_4^-) content will elevate the baseline at m/z 99 because it elutes prior to perchlorate. High concentrations (~1000 ppm) will tail into the perchlorate peak retention time. However, even with a sulfate concentration of 1000 ppm, 0.1 ppb perchlorate can still be detected. If the baseline is elevated, there is a mandatory cleanup step to remove the sulfate prior to sample injection. Quantitation is done on the m/z 101, which is not affected by sulfate. The quantitation limit in water is reported to be 0.1 µg/L.

3.2.1.7 FDA Method—IC/MS/MS

IC/MS methodology can be enhanced by coupling the IC with a conductivity detector and a tandem MS, thereby increasing the sensitivity and specificity over that of IC/MS. The second MS allows further fragmentation of the perchlorate ions into the daughter ions (m/z) 83 and 85, eliminating false positives or negatives that can be caused by interferences. The quantitation limit in water is reported to be 0.01 µg/L (Penfold 2004 and personal communication).

The method has been used on water, soil, milk, lettuce, and other biota samples.

3.2.1.8 Availability of Emerging Methods

At this time, more and more commercial laboratories are adding these methods to their capabilities. With the publication of new methods in 2005, availability is expected to increase dramatically as regulatory agencies approve and require their use.

3.2.1.9 Other Laboratory Methods

Capillary electrophoresis (CE) has been used to analyze perchlorate for certain applications (primarily forensics). CE is not currently viable for analysis of perchlorate in environmental media at low concentrations. The best limit of detection available with most widely available equipment and reagents for CE is 100 µg/L (Urbansky 2000).

3.2.2 Field Methods

Two field methods have been employed to varying degrees of success for perchlorate (see Table 3-2 for comparison). The use of ion-selective electrodes and colorimetry is described below.

Table 3-2. Perchlorate field methods comparison

Method (technique)	Applicability	Analytical limitations	Reporting limits
Ion-selective electrode	• Can potentially detect perchlorate in the low-ppb range • Potential for in situ sampling for groundwater monitoring wells • Commercially available models suitable for both field and laboratory applications	• Commercial availability of low-ppb electrodes unknown • Presence of ions can interfere with the perchlorate electrode	• Low ppb (as tested); 200 µg/L (commercially available) • Detection limit may be too high to be useful
Colorimetry	• Used for surface water, well water, bioreactor effluent, and soil extracts. • Method published: USACE ERDC/CRREL TR-04-8 (Thorne 2004)	• Humic and fulvic acids from soil surface or root zone may cause false positives, requiring cleanup • Presence of chlorophyll or machine oils causes false positives	• 1.0 µg/L

3.2.2.1 Ion-selective electrode

A project sponsored by the USEPA and the U.S. Army Corps of Engineers (USACE) in 2001 created an ion-specific electrode to sample for perchlorate in groundwater monitoring wells. The electrode can detect perchlorate in the low-ppb range, but it is not evident whether this particular electrode is commercially available.

However, there are commercially available electrodes, such as the Perchlorate Ion-Selective Electrode by NICO2000 Ltd, which has a solid-state polyvinyl chloride polymer matrix membrane. The electrode is designed for the detection of perchlorate ions in aqueous solutions and is suitable for use in both field and laboratory applications. The detection limit for this electrode is 200 µg/L for perchlorate. The time for a stable reading after immersion is 2–3 minutes. The following ions can interfere with the perchlorate electrode: thiocyanate, iodide, nitrate, chloride, phosphate, and acetate. Nitrate can be tolerated up to the same concentration as perchlorate, and chloride can be tolerated up to 100 times the concentration of perchlorate without significant interference.

3.2.3.2 Colorimetry

A reliable and inexpensive colorimetric method for perchlorate in water and soil extracts has been developed and tested with surface water, well water, bioreactor effluent, and soil extracts. The detection limit for water is 1 µg/L and 0.3 µg/g for spiked soils. This method uses a solid-phase extraction cartridge conditioned with a perchlorate-specific ion pair reagent. The perchlorate that has been isolated from water or a soil extract by the resin cartridge is eluted into a dye, forming an ion pair that is extracted with xylene and measured with a field-portable spectrophotometer. Certain humic materials, colored biological materials (like chlorophyll), and machine oils cause false positives. Cleanup procedures can solve most of these problems but not that caused by chlorophyll. In such a case filtering may solve the problem (Thorne 2004).

3.3 Analytical Strategies

The strategy employed to choose analytical methodologies depends upon data quality objectives (DQOs), site information, and the agency conducting the investigation or oversight.

3.3.1 Data Quality Objectives

The uncertainty of results obtained using the IC method increases as the reporting level necessary to achieve project objectives approaches the lower performance limitations of the instrumentation. Therefore, depending upon the required reporting level, use of determinative methods exclusively could be appropriate. Until USEPA determinative methods are promulgated for perchlorate, some use of Method 314.0 will almost certainly be required by regulatory agencies, particularly for compliance monitoring.

3.3.2 Site Information

Site history and background information (e.g., production or use of explosives, possible releases of perchlorate) provides good information about the possible presence of perchlorate in groundwater or soil. However, the analytical strategy selected for the analysis of perchlorate depends upon the decision to be made and the DQOs needed to make that decision.

If the site has documented perchlorate releases, minimal use of determinative methods would probably be appropriate. However, if only the use of perchlorate on the site is documented or a known release was very small, the use of determinative methods would be advisable. Additionally, if the site has known interferences with Method 314.0, use of determinative methods would be appropriate. If determinative analyses have already been conducted at a site and have confirmed the quantitative value of Method 314.0 analysis, additional use of determinative analytical techniques may be unnecessary.

Figure 3-1 illustrates one example of a drinking water sampling strategy implemented in California for low TDS. Please note that this is only one example strategy; strategies should be determined based on different needs.

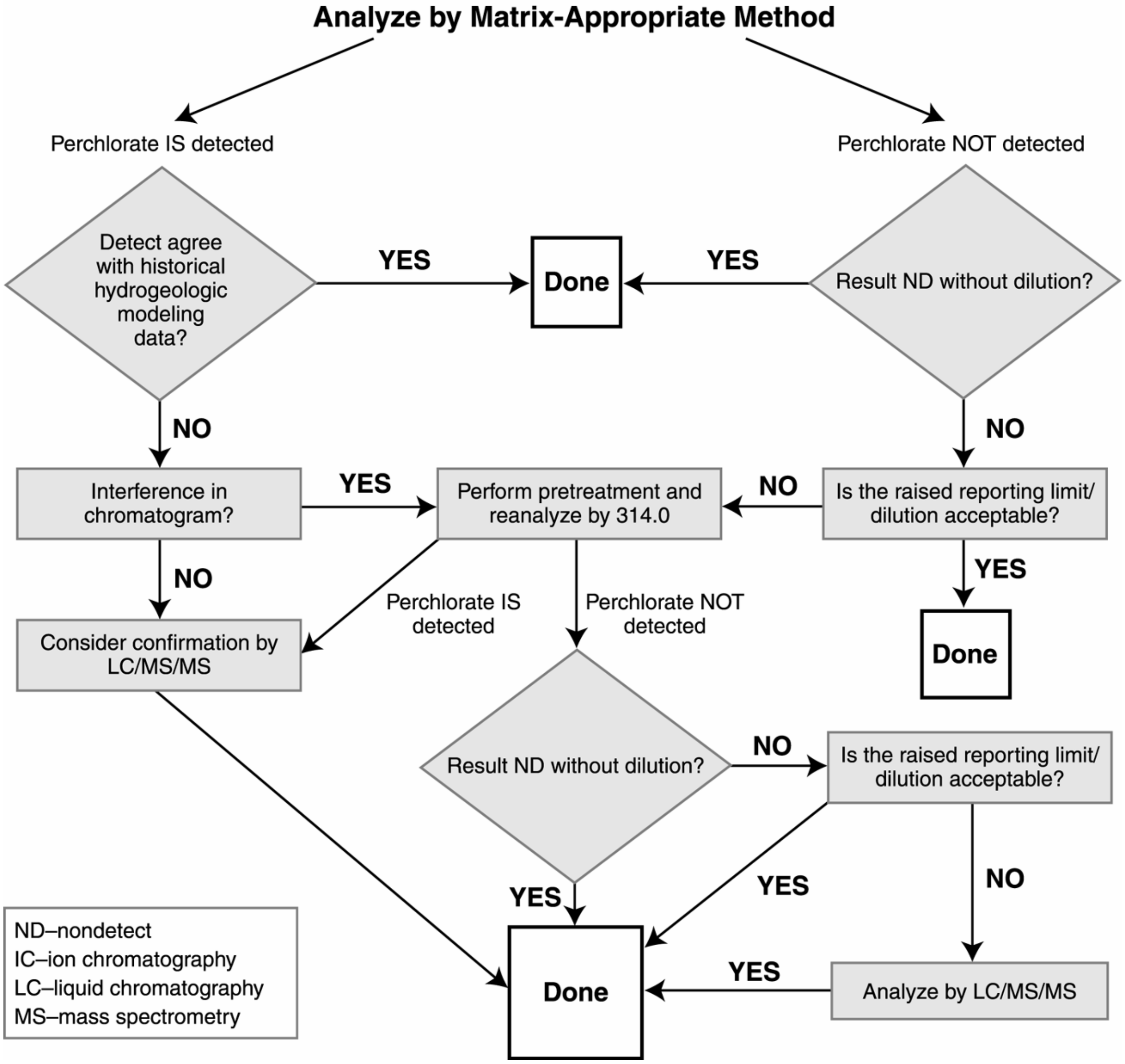


Figure 3-1. Perchlorate decision tree.

3.3.3 Agency Conducting the Investigation

FDA laboratories are anticipating use of the FDA method (USFDA 2004b). DoD agencies are required to follow the "Interim Guidance on Sampling and Testing for Perchlorate" (DoD EDQW 2004), which requires the confirmation of any detections above action levels with determinative methods. State agencies differ in their approaches.

3.4 Forensics Techniques/Chemometrics

Environmental forensics is the systematic investigation of a contaminated site or event focused on defensibly allocating liability for the contamination. Forensic investigative approaches available to identify the source(s) of perchlorate contamination in soil or groundwater include traditional source identification and concentration profiling, association with affiliated chemicals, and isotopic analysis.

Most perchlorate salts have high water solubilities; concentrated solutions have densities greater than water. Once dissolved, perchlorate is extremely mobile and persistent, requiring decades to degrade. Perchlorate is not significantly retarded by organic materials in groundwater; advection is the primary mechanism of dispersal. Therefore, it may be used as a tracer for hydrocarbon and metal contaminants that are significantly more retarded. Possible forensic techniques include chlorine isotopes for defining multiple or commingled perchlorate plumes (Motzer 2001).

As with other forensic investigations, the detection and use of associated chemicals is often of more forensic value in identifying and allocating sources than for the contaminant of concern. For identifying perchlorate associated with highway road flares, for example, identifying the distribution of strontium nitrate, which often composes up to 70% of a road flare, may provide insight as to the source of the perchlorate (see Section 6.1 for more information on cocontaminants.).

Research is being conducted to develop methods for differentiating between naturally occurring and manmade perchlorate in the environment. One approach is to use stable isotope ratio analysis of the perchlorate molecule. Stable isotope ratio analysis relies on the fact that the major elements composing the inorganic molecules occur as isotopes that can be quantified using isotope ratio mass-spectrometry. The ratio of the specific isotopes in the perchlorate molecule, chlorine and oxygen, can be used to track the source of the perchlorate in the environment (Bao and Gu 2004). Limited data collected to date reveal that the chlorine isotope ratio in a naturally occurring perchlorate source is considerably lower than that in manmade perchlorate. Conversely, the oxygen isotope ratio for the natural perchlorate is appreciably higher than in manmade sources. Researchers at Louisiana State University and Oak Ridge National Laboratory (ORNL) have been on the developmental forefront in this technique (Erickson 2004). Some locations may have a mixture of manmade and naturally occurring perchlorate. The western half of the United States would appear to represent the most likely area for mixed plumes to occur due to favorable geological and precipitation conditions.

The ability to use stable isotope ratio analysis depends highly upon the matrix and concentration of perchlorate present. Solid samples typically require multistep cleanup procedures to eliminate the presence of other nonperchlorate oxygen sources and the concentration of perchlorate in trace-level aqueous samples may be too low initially for isotopic analysis and require concentration on an ion exchange resin. The distinction that can be identified through stable isotope ratio analysis is between perchlorate that forms by natural environmental processes and perchlorate that is manufactured through an industrial electrolytic process. Anthropogenic perchlorate that was released to the environment through the use of products manufactured from material containing naturally occurring perchlorate (such as Chilean nitrate) will likely have the same stable isotope ratio as other natural environmental occurrences of perchlorate. The continued evolution of analytical forensic techniques may permit the fingerprinting of detected perchlorate plumes to ascertain whether the source is natural or manmade and to what extent each source type is represented.

4. TOXICITY, EXPOSURE, AND RISK

Perchlorate has been detected in surface and groundwater, drinking water, food, and soil. Therefore, it is important to evaluate the effects of perchlorate exposure in humans and in wildlife and to communicate that information to a broad audience. The types of information presented in this overview are used by federal and state regulatory agencies as the basis for the promulgated standards, guidelines, policies, and procedures that direct the assessment and remediation of perchlorate-contaminated sites. Because of the uncertainty involved in evaluating toxicological data, the states and the federal government evaluating this information may use and evaluate this information somewhat differently to promulgate different standards and advisory levels (see Section 5.3.2). It is also important to note that the status of our knowledge of perchlorate exposure and risks is evolving; it will be important to periodically reevaluate what is known about this chemical.

Perchlorate is one of several compounds that can interfere with the thyroid's uptake of iodide, an essential component of thyroid hormones. Consequently, perchlorate exposure may result in a dose-dependent decrease in thyroid hormone production. Therefore, this chapter begins with an overview of thyroid hormone physiology; continues with a discussion of the potential effects (toxicity) of perchlorate, including a review of studies that examine the potential effects of decreases in thyroid hormone production; examines perchlorate exposure pathways; reviews the current status of perchlorate risk assessment; and explores the remaining data gaps and uncertainties of these topics.

4.1 Importance of Thyroid Hormone

The thyroid is a small gland located at the base of the throat. It synthesizes hormones that play a crucial role in the body's metabolism, reproduction, growth, and function of the cardiovascular and central nervous systems. The thyroid uses iodide (I^-), converted from ingested iodine (I_2), to synthesize the two key thyroid hormones, tetraiodothyronine (also known as thyroxine, T_4) and triiodothyronine (T_3).

Because of the importance of thyroid hormones in human physiological function, thyroid hormone synthesis is tightly regulated by a feedback control loop involving the anterior pituitary gland and the hypothalamus, two regions of the brain. Thyroid hormones are synthesized in response to the secretion of thyroid-stimulating hormone (TSH) from the anterior pituitary. TSH production in the anterior pituitary is regulated by levels of TSH-releasing hormone (TRH) secreted by the hypothalamus. For instance, the anterior pituitary increases the production of TSH in response to decreased circulating thyroid hormone levels. In addition, there are compensatory responses that can include increased thyroidal blood flow, volume, iodide clearance, and preferential synthesis of the more biologically active T_3, which helps regulate the availability of appropriate thyroid hormone levels (Morreale de Escobar, Obregon, and Escobar del Ray 2000). The human thyroid maintains a reserve of thyroid hormones to compensate for fluctuations in iodide content in the diet. Additionally, humans have circulating levels of inactive T_4 attached to thyroid-binding globulin, which also provides reserve thyroid hormones.

Hypothyroidism is the most common type of thyroid disorder and occurs when the thyroid makes too little of the thyroid hormone that the body needs to function properly. Significant and/or sustained decreases in thyroid hormone levels in the bloodstream have been found to result in effects ranging from a decrease in metabolism, dry skin, cold intolerance, and tiredness to impairment in behavior, movement, speech, hearing, vision and intelligence (Felz and Forren 2004). Hypothyroidism is a common disorder that is more likely to affect women than men (Surks et al. 2004). According to Hollowell et al. (2002), 4.6% of Americans have elevated TSH levels, 0.3% of whom could be classified as having overt hypothyroidism and 4.3% of whom could be classified as having mild or subclinical hypothyroidism. For individuals 65 years and older, 1.7% have overt hypothyroidism, and 13.7% have mild hypothyroidism. Surks et al. (2004) estimate the number of individuals with subclinical hypothyroidism to be between 4% and 8.5%, with women over age 60, approaching 20% incidence.

During pregnancy, extra stress is placed on many maternal biological functions, including thyroid activity (Glinoer et al. 1992). Significant and/or sustained decreases in thyroid hormone levels could affect development of the fetus. If the maternal thyroid is not able to maintain adequate levels of thyroid hormones, especially during the first trimester, irreversible alterations in fetal neurological development could occur. Sufficient thyroid hormone (especially T_4) is required during fetal development of the central nervous system. T_4 is solely supplied by the mother before the fetal thyroid gland becomes functional at the end of the first trimester (approximately 12 weeks) (Tillotson et al. 1994). After the first trimester, the fetal thyroid is functional and can maintain its own hormone levels. However, some studies suggest that T_4 supplied by the mother throughout pregnancy has an overall protective effect from fetal neurological impairment (Morreale de Escobar, Obregon, and Escobar del Ray 2000). Unfortunately, the impact of maternal versus fetal hormone production during brain development is not well understood. The American Thyroid Association (2003) recommends that women of childbearing age consult their physician for guidance concerning their proper thyroid hormone levels.

4.2 Perchlorate Toxicity

Perchlorate is one of several compounds that competitively interfere with iodide uptake in the thyroid. Other compounds such as nitrates, thiocyonate in cigarette smoke, and others are more prevalent in the environment than perchlorate. Iodide uptake inhibition is considered the mode of action (MOA) for perchlorate (Figure 4-1). The MOA also identifies that perchlorate has a threshold for effects and that the degree of effects are dependent on the dosage.

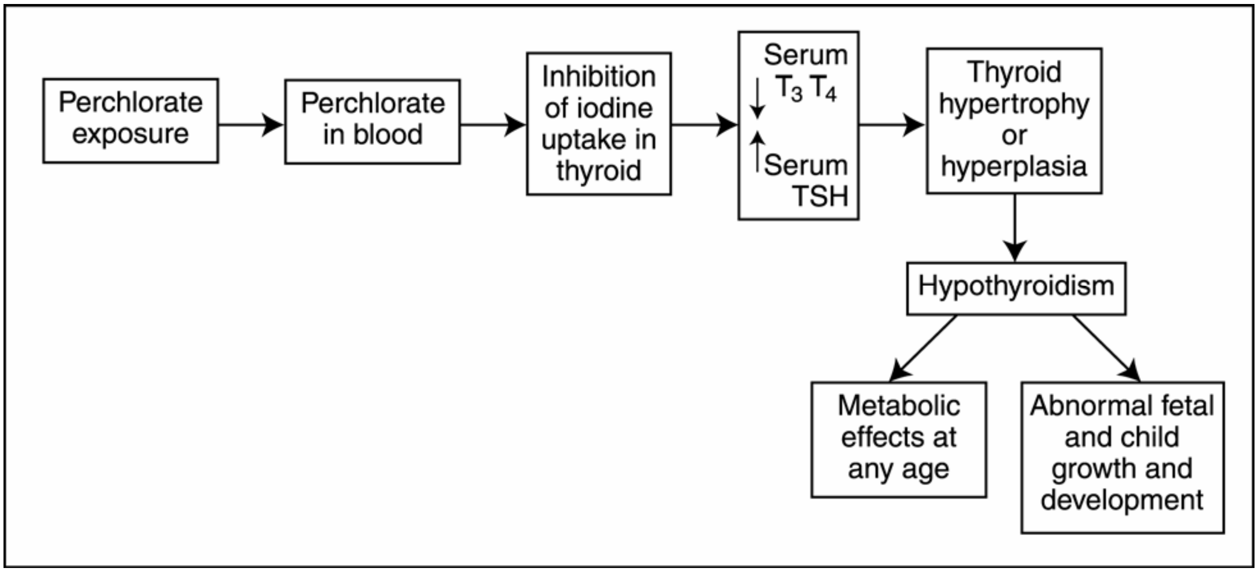


Figure 4-1. Mode of action model for perchlorate toxicity (Adapted from NRC 2005a)**.**

Animal and clinical studies conducted since 1997 were all designed based on this MOA for perchlorate. This MOA has been a point of agreement between toxicologists and risk assessors throughout the process to develop the perchlorate risk assessment; however, there is still some disagreement on defining the adverse or critical effect following perchlorate exposure and iodide inhibition.

4.2.1 Animal Toxicity Studies

To determine the health effects of perchlorate in humans, a fairly extensive database of animal toxicity studies was built in keeping with risk assessment guidelines and the MOA of perchlorate. This database includes a 90-day MOA study in rats (Siglin et al. 2000), immunological effects in mice (Keil et al. 1999), developmental effects in rats and rabbits (York et al. 2001a, 2003), two-generation reproductive studies in rats (York et al. 2001b), and developmental neurobehavioral studies in rats (Bekkedal et al. 2000; Bekkedal et al. 2004; York et al. 2004). It is not in the scope of this chapter to review these studies individually; the reader is referred to the studies listed in the references. The animal study database collectively supports the accepted MOA for perchlorate, competitive iodide uptake inhibition, and does not produce evidence of effects outside of that MOA.

Because rat and human thyroids work similarly, rat toxicity studies are valuable tools for qualitative information regarding the human thyroid; however, there are physiological differences between the human and rat pituitary-thyroid axis, which make rats inappropriate for quantifying predicted changes in humans for risk assessment purposes (NRC 2005a).

4.2.2 Epidemiological Studies

Perchlorate exposure of individuals is difficult to measure and has not been assessed directly in any of the studies conducted outside the occupational setting. Nearly all the studies were ecologic, including those in newborns and children, the groups potentially most vulnerable to the effects of perchlorate exposure. Ecologic studies, epidemiological studies without individual exposure characterization, can provide supporting evidence of a possible association but cannot themselves provide definitive evidence regarding cause. Epidemiologic studies have examined the associations of environmental exposure to perchlorate in drinking water at about 4–120 ppb (4–120 μg/L) and abnormalities of thyroid hormone and TSH production in newborns and thyroid diseases in infants and adults (Lamm and Doemland 1999, Brechner et al. 2000, Crump et al. 2000, F. X. Li et al. 2000, Z. Li et al. 2000, Schwartz 2001, Morgan and Cassady 2002, Kelsh et al. 2003, Lamm 2003, Buffler et al. 2004). Occupational studies of respiratory exposures up to 0.5 mg/kg perchlorate per day and abnormalities of thyroid hormone and TSH production in adult workers have been conducted (Gibbs et al. 1998, Lamm et al. 1999, Braverman et al. 2004). Only one study (Chang et al. 2003) has examined a possible relation between perchlorate exposure and adverse neurodevelopmental outcomes in children (attention-deficit/hyperactivity disorder and autism). A number of the studies have samples that are too small to detect differences in frequency of outcomes between exposure groups, and adjustment for potentially confounding factors was limited. The only study with measures of perchlorate made directly from drinking-water samples taken from faucets potentially used by people was a study in Chile (Crump et al. 2000).

4.2.3 Pharmacological Use and Clinical Studies

In the 1950s and 1960s, potassium perchlorate was given in doses of 400–2000 mg daily to more than 1000 patients for the treatment of hyperthyroid disease for many weeks or months with beneficial results. In general, treatment resulted in few side effects; however, the development of aplastic anemia in six patients raised concerns that resulted in decreased use of potassium perchlorate as a pharmacological agent, despite the fact that a direct cause-effect relationship between perchlorate and aplastic anemia was never established (Wolff 1998).

A number of studies collected clinical data from adult human volunteers in a controlled setting after exposure to known amounts of perchlorate in drinking water ranging from 0.007 to 12 mg/kg per day (Brabant et al. 1992; Lawrence et al. 2000; Lawrence, Lamm, and Braverman 2001; Greer et al. 2002; Braverman et al. 2004). Except for the Brabant study, the clinical studies measured inhibition of iodide uptake into the thyroid glands as well as TSH and thyroid hormones. The Brabant study was conducted for four weeks, the Lawrence and Greer studies for two weeks, and the Braverman study for six months. Serum TSH levels did not increase, and thyroid hormones did not decrease in any group.

4.2.4 Perchlorate Ecological Toxicity

While most of the available research on perchlorate has focused on determining effects of human exposure, perchlorate may have deleterious effects on other species throughout the environment. Field and laboratory studies assist in our understanding of the fate of perchlorate contamination in the environment.

Current field studies have demonstrated an overall lack of bioconcentration. Detectable concentrations of perchlorate were found only in a limited number of terrestrial mammals, birds, fish, amphibians, and insects exposed to elevated levels perchlorate in the environment (Parsons 2001). Similarly, rodent tissue sampled along the Las Vegas Wash had surprisingly low concentrations of perchlorate compared to and correlating with high concentrations in soil and surface water (Smith et al. 2004). Field studies of biota potentially impacted by releases of perchlorate associated with the former Naval Weapons Industrial Reserve Plant in McGregor, Texas, indicated detectable concentrations of perchlorate in periphyton (below detection to 0.376 mg/kg), tree leaves (below detection to 48 mg/kg), aquatic plants (below detection to 61.6 mg/kg) and small bird and mammals (kidney and liver tissue, below detection to 64 mg/kg in mammals and 86 mg/kg in birds). Perchlorate was also detected in native fish, but not detected in the blood plasma of opossums and raccoons collected near impacted streams (Tan et al 2005).

Perchlorate effects have also been assessed in both aquatic and terrestrial species of ecological relevance in laboratory studies. In aquatic environments, perchlorate concentrations under 1000 mg/L did not significantly affect aquatic microbial photosynthesis, aquatic bacterial production, sediment bacterial decomposition (i.e., respiration), or bog peat bacterial carbon dioxide and methane production in freshwater or marine systems (Hines et al. 2002). Aquatic invertebrates, including the water flea (*Ceriodaphnia dubia*), tolerated 9.3 mg/L perchlorate under chronic conditions and up to 20 mg/L under acute (i.e., short-term) conditions (Dean et al. 2004). An *in vitro* study of larval lamprey thyroids demonstrated that perchlorate's MOA is the same in fish as in humans (i.e., decreased iodide uptake and production of T_4) (Manzon and Youson 2002). At concentrations greater than 10 mg/L, perchlorate had no demonstrated effects on mortality, mating or offspring of adult threespine stickleback fish (*Gasterosteus* sp.) (Hines et al. 2002). Fathead minnow (*Pimephales promelas*) embryos reared for 28 days in 1–100 mg/L perchlorate exhibited decreased whole-body T_4 levels, delayed development, decreased scale production, and altered thyroid histopathology (Crane et al. 2005). Toxicity studies in amphibians indicate that they may be sensitive to high concentrations of perchlorate in the environment during metamorphosis (Dean et al. 2004, Goleman et al. 2002, Miranda et al. 1995). Studies of terrestrial species include a few bird studies (McNabb, Jang, and Larsen 2004; McNabb 2003) and multiple laboratory animal studies (York et al. 2001a, 2001b, 2003) performed to assess potential human health effects. Ecologically relevant studies in laboratory animals have shown that perchlorate does not affect reproduction end points in rats and rabbits. Decreases in T_4 and increases in TSH demonstrated in maternal laboratory rats at doses as low as 0.0085 mg/kg/day perchlorate (York et al. 2003) would be expected to occur among wild rodent populations at similar exposures. Whether these changes would result in an ecologically relevant population end point is not clear.

Ecological toxicity of perchlorate will be important on a site-by-site risk assessment basis. At some sites, ecological interests instead of human health concerns may drive remediation efforts. Ecological risk will not be addressed further in this document.

4.3 Perchlorate Exposure

Recent developments in analytical chemistry have allowed perchlorate to be measured at low concentrations in water, soil, food, and vegetation (Section 3). These advances in chemistry allow researchers to test for perchlorate in various media to levels as low as a few parts per trillion.

To determine how humans and ecosystems may be exposed, routes of exposure must be identified. Routes of exposure to perchlorate in ecosystems are complex and not well defined in available literature; therefore, only human exposure is discussed in the remainder of this section (Section 4.3).

4.3.1 Primary Routes of Exposure

Chemicals may enter the human body in several ways, known as "routes of exposure," including ingestion, dermal (skin) absorption, and inhalation. The primary route of human exposure to perchlorate is via ingestion of perchlorate-contaminated water and/or food. Human studies have indicated that ingested perchlorate is readily and completely absorbed from the gastrointestinal tract and excreted rapidly primarily via the urine (Eichler 1929 as cited in Stanbury and Wyngaarden 1952, Durand 1938). Based on available literature, ingestion of perchlorate-contaminated drinking water is one of the major exposure routes of concern, although ingestion of contaminated food and human milk are other potential sources of exposure.

When compared to ingestion, skin absorption and inhalation of perchlorate can be considered negligible exposure pathways. The compounds most readily absorbed through the skin are primarily organic chemicals. Because perchlorate is an inorganic compound and completely ionized in water, the potential for dermal absorption of perchlorate while bathing and washing is minimal.

Perchlorate particles can be suspended in the air and can be inhaled by individuals working in areas where perchlorate is manufactured (Lamm et al. 1999). Although release of perchlorate to the atmosphere is possible during the launching of solid propellant rockets, setting off fireworks, and as a result of the open detonation of old propellant, no published data were found on levels of perchlorate in the ambient air. Since perchlorate is not volatile, inhalation exposure from domestic use of contaminated water should not pose a problem (USEPA 2002).

4.3.1.1 Drinking Water

Public water systems, monitored under the UCMR, have detected perchlorate concentrations in several drinking water sources across the United States. In California, perchlorate has been found in more than 350 of the approximately 6,700 public drinking water sources (California Department of Health Services 2005). The lower Colorado River, a major source of irrigation and drinking water for southern California, also contain levels of perchlorate. Data collected by the Nevada Division of Environmental Protection and the Metropolitan Water District of Southern California reflect perchlorate concentrations in the lower Colorado River, downstream of Hoover Dam, at less than 4 µg/L since June of 2004 (USEPA 2004c). The Texas Commission on Environmental Quality has detected perchlorate concentrations in an area exceeding 30,000 square miles in western Texas (Jackson et al. 2003). Extensive testing of Massachusetts' public water supplies has shown several drinking water sources to have perchlorate.

4.3.1.2 Food and Agriculture

In some agricultural settings, perchlorate-contaminated groundwater or surface water is used to irrigate foodstuff crops and animal feed crops. Recent studies have investigated the presence of perchlorate in these crops.

Studies conducted by Sanchez and Krieger (2004) revealed accumulation of perchlorate takes place in some plants and is accumulated mostly in leafy greens. Studies on lettuce have shown that accumulation occurs mostly in outer leaves and not consumable portions, such as the head (Susarla et al. 1999c, Sanchez and Krieger 2004). Susarla, Wolfe, and McCutcheon (1999) reported that when lettuce was irrigated with perchlorate-contaminated water (0.2–5 mg/L), total perchlorate concentrations within the leaves, stems, and roots ranged 248–1559 mg/kg. FDA collected lettuce samples from fields or packing sheds and various lettuce types (e.g., romaine, red leaf, green leaf, iceberg) that were found to contain average perchlorate concentrations from 7.76 to 11.9 ppb. (See Table 4-1 for preliminary results from data collected in five states). Tomatoes, carrots, cantaloupe, and spinach were also sampled, but results are not available at this writing (USFDA 2004a, 2004b).

Besides foodstuff crops, perchlorate has been detected in some animal feed crops, dairy, and meat. Alfalfa, a beef cattle and milk cow feed, tested at 109–555 µg/kg for samples from the Imperial Valley and 146–668 µg/kg from Yuma (Sanchez and Krieger 2004). Perchlorate has been detected in milk. The California Department of Food and Agriculture measured perchlorate at 1.5–10.6 ppb in milk samples. Milk samples (whole, 1% fat, fat-free, and organic) collected at grocery stores in 14 states were found to contain an average perchlorate level of 5.76 ppb (USFDA 2004a, 2004b) (see Table 4-1 for preliminary results from data). In addition to these studies, information obtained by the Environmental Working Group (a private nonprofit environmental group) indicated that perchlorate in eight samples of lettuce from a California grower ranged 0.110–6.9 mg/kg (EWG 2004b), and researchers from Texas Tech University measured perchlorate concentration up to 6.4 ppb in samples of supermarket milk (Kirk et al. 2005).

Other food sources where perchlorate has been detected include those detected by the Kansas Department of Health and the Environment. Unpublished data on perchlorate contamination in meat, chicken, eggs, produce, and fish indicate the following: chicken (8 and 14.6 ng/g wet weight), eggs (<4 and 102 ng/g wet weight), and milk (4 ng/g wet weight) collected in the vicinity of a site that has contaminated groundwater ranging from <0.3 to 118 µg/L. Last, kelp analyzed by Orris et al. (2003) contained 885,000 ppb perchlorate. Since kelp is used in many different food products, these high concentrations may be of concern.

Table 4-1. Summary of FDA preliminary data from samples collected through August 2004

Item	Number of samples	LOQ* (ppb)	Mean value (ppb)	Lowest value (#) (ppb)	Highest value (#) (ppb)
Green leaf lettuce	25	1.0	10.7	1.0 (1)	27.4 (1)
Iceberg lettuce	38	1.0	7.76	NQ** (8)	71.6 (1)
Red leaf lettuce	25	1.0	11.6	NQ (2)	52.0 (1)
Romaine lettuce	40	1.0	11.9	NQ (2)	129 (1)
Milk (all varieties)	104	3.0	5.76	NQ (3)	11.3 (1)

*LOQ = limit of quantitation, **NQ = not quantifiable, ½ LOQ used in averaging.

Even though perchlorate has been found in multiple food sources at varying concentrations, FDA continues to recommend that consumers eat a balanced diet, choosing a variety of foods that are low in trans fat and saturated fat, and rich in high-fiber grains, fruits, and vegetables.

4.3.2 Secondary Routes of Exposure: Fetal and Neonatal and Infant Exposure Pathways

Secondary routes of exposure are also of significant concern because they can impact sensitive receptors. Perchlorate can pass through the placenta and enter the fetal bloodstream; the lower the dose, the greater the percentage of maternal perchlorate that passes through the placenta to reach the fetus (Clewell et al. 2003a).

Infants, which have been identified as a potentially sensitive receptor population, may also be exposed to perchlorate in human milk. In laboratory studies, perchlorate was found in higher concentrations in the milk of treated animals than was present in the serum of the treated animals (Clewell et al. 2003b). Recently, Kirk et al. (2005) measured perchlorate concentrations in 36 samples of human milk from 18 states. This exposure pathway is of concern because perchlorate may inhibit the active transport of iodide into the mammary gland (Tazebay et al. 2000). During early development, infants depend on maternal iodide present in the milk.

4.4 Perchlorate Human Health Risk Assessment

An oral RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime. A high-confidence RfD is based on data that address all potentially critical life stages.

Although there is a standard process for risk assessment, its application on a site-specific basis can be complex. The difficulty of site characterization, the likelihood of exposure under different scenarios, the ongoing scientific debate over toxicity, and the weighting of uncertainty result in a range of different outcomes and risk evaluations. These difficulties are evident in the site-specific risk assessments for most chemicals, including perchlorate.

4.4.1 Sensitive Subpopulations

Concern for perchlorate toxicity is rooted in our common understanding of thyroid hormone imbalance as described in Section 4.1. While there is general agreement that fetal and neonatal neurodevelopment is the main end point of concern, the disagreement has occurred over what biological change constitutes a key event on which to base toxicity values. Potential key events for setting perchlorate toxicity values include inhibition of iodide uptake, alterations in thyroid hormone synthesis, or some other measurable end point.

Based on the review of available studies, the sensitive receptor of concern for perchlorate exposure is the developing fetus in a mother who is hypothyroid. It is postulated that hypothyroid pregnant women would not have sufficient compensatory mechanisms to manage reduced iodide uptake due to perchlorate competitive inhibition, although the dose-response relationship is still uncertain. Thyroid hormones are critical for both the fetus and neonate. Although the periods of development that are most sensitive to thyroid perturbations are known, our understanding is limited by lack of data on perchlorate dose-response, making it difficult to predict the potential effects of perchlorate (Howdeshell 2002).

Fetal effects associated with severe iodide deficiencies (e.g., cretinism and mental retardation) are rare in the United States. Therefore, the primary concerns regarding iodide deficiency are decreased IQ and alterations in psychomotor development. A recent study by Auso et al. (2003) indicates that in rats even short-term iodide deficiency during fetal development results in altered neuronal migration, along with aberrant response to acoustic stimuli, including seizures. However, no studies of perchlorate conducted to date have documented these types of outcomes in humans. Uncertainties in the identification of the threshold for maternal and fetal thyroid effects and their relationship to fetal brain development (Morreale de Escobar, Obregon, and Escobar del Ray 2000) complicate deriving allowable perchlorate concentrations. While fetuses of hypothyroid pregnant women are considered to be the most sensitive subpopulation, other populations of concern may include nursing infants, children, postmenopausal women, and hypothyroid individuals (Table 4-2).

Adequate dietary iodine intake may reduce the susceptibility of individuals to the effects of perchlorate exposure; however because iodine overdose can have serious adverse impacts on thyroid function, it must be emphasized that individuals should not use iodine supplements, unless specifically directed to do so by their doctor.

4.4.2 Reference Dose

To calculate an RfD, risk assessors must first select a study that demonstrates a dose-response relationship between the chemical of interest and some critical effect. The critical effect is usually an adverse effect resulting from the chemical exposure. An analysis of the study is performed to determine the dose where there is no observed adverse effect (the no observed adverse effect level [NOAEL]). In some cases, the NOAEL cannot be determined, so the lowest dose corresponding to the adverse effect is used (low observed adverse effect level [LOAEL]). The NOAEL or LOAEL is then used as the point of departure for the calculation of the RfD.

Table 4-2. Subpopulations of potential concern

Potential receptor of concern	Rationale	References
Developing fetus	Thyroid hormones necessary for normal brain development	Haddow et al. 1999, Howdeshell 2002, Heindel and Zoeller 2003, Lavado-Autric et al. 2003, Auso et al. 2003
Nursing infants	Exposure to perchlorate via human milk; brain still developing, thyroid hormones necessary for brain development	Clewell et al. 2003b, Tazebay et al. 2000
Children	Brain still developing; thyroid hormones necessary for brain development, as well as growth and metabolism	Giedd et al. 1999, Sowell et al. 1999, Thompson et al. 2000, Webster et al. 2003
Postmenopausal women	High rates of hypothyroidism	Hollowell et al. 2002, Surks et al. 2004

To calculate the RfD, uncertainty factors are used to ensure that the RfD will be adequately protective of public health. Uncertainty factors (traditionally 10 or 3) can be applied to compensate for studies that are based on subchronic (short-term) exposure, rather than chronic (long-term) exposure, studies conducted using laboratory animals, calculations based on the LOAEL, rather than the NOAEL, or database insufficiencies. The uncertainty factors are combined via multiplication, and the NOAEL (or LOAEL) is divided by the uncertainty factors to derive the RfD. Table 4-3 illustrates how the reference dose for perchlorate has changed over time, as data have accumulated. The DWEL is a nonregulatory value that is based on the assumption that 100% of perchlorate ingestion is from drinking water.

To address these differences, the National Academy of Sciences, the National Research Council (NRC) established a committee to assess the health implications of perchlorate ingestion. At the request of DoD, DOE, NASA and USEPA, the NRC committee has recently addressed a number of charge questions covering key scientific issues associated with perchlorate risk and recommended an RfD of 0.0007 mg/kg/day (NRC 2005a). The NRC findings were summarized in the "Report in Brief: Health Implications of Perchlorate Ingestion," which is available online (NRC 2005b).

The NRC report determined that the inhibition of iodide uptake is the key biochemical event, is not an adverse effect, and should be used as the basis of the risk assessment (NRC 2005a). The NRC committee considered rats to provide only qualitative information on potential adverse effects of perchlorate exposure. The committee found that human data provided a more reliable point of departure than the animal data. They used iodide inhibition as the point of departure for developing the RfD. Inhibition of iodide uptake is a more reliable and valid measure, has been unequivocally demonstrated in humans exposed to perchlorate, and is the key biochemical event that precedes all other thyroid-mediated effects of perchlorate. Using a nonadverse effect that is a precursor to any adverse effects is an especially health-protective approach to the perchlorate risk assessment (NRC 2005a).

Table 4-3. Review of proposed RfDs

	USEPA 1992	**USEPA 1995**	**USEPA 1999**	**USEPA 2002**	**NRC 2005 USEPA IRIS**
Critical study	Stanbury & Wyngaarden (1952)	Stanbury & Wyngaarden (1952)	Argus 1998 Developmental Neurotoxicity Study	Argus 2001 Effects Study	Greer 2002
Species	Human	Human	Rat	Rat	Human
Critical effect or biochemical event	Release of iodide in the thyroid due to competitive inhibition by perchlorate	Release of iodide in the thyroid due to competitive inhibition by perchlorate	Altered brain morphometry (size and shape) in rat pups	Decrease T4 levels in dams and altered brain morphometry in rat pups	Inhibition of iodide uptake in humans (key biochemical event)
NOAEL/ LOAEL, mg/kg/day	0.14	0.14	0.1	0.01	0.007*
Uncertainty factors	1000	300	100	300	10
Calculated reference dose, mg/kg/day	0.00014	0.00046	0.001	0.00003	0.0007
DWEL, ppb	4	18	32	1	24.5

*This value is a No Observed Effect Level (NOEL). It differs from the NOAEL in that it is the highest dose at which there are no statistically or biologically significant increases in the frequency or severity of any effect between the exposed populations and its appropriate control.

The committee applied a total uncertainty factor of 10 (variability among humans) to the point of departure, which was the NOEL of 0.007 mg/kg/day in humans from the Greer et al. (2002) study. One committee member felt that an additional uncertainty factor of 3 should be used for database adequacy. However, the other 14 committee members concluded that the database—which includes five human clinical studies, occupational and environmental epidemiologic studies, studies of long-term perchlorate administration to patients with hyperthyroidism, and animal toxicology studies—is sufficient. The NRC committee concluded that a reference dose of 0.0007 mg/kg body weight per day would protect the health of even the most sensitive groups of people over a lifetime of exposure (NRC 2005a).

Based on the NRC report, USEPA posted the RfD for perchlorate on the Integrated Risk Information System (IRIS) as 0.0007 mg/kg/day in February 2005. The USEPA has not yet set an MCL for perchlorate in drinking water. In lieu of this regulatory value, various entities may calculate DWELs. As described previously, the DWEL is a nonregulatory value calculated on the assumption that 100% of perchlorate ingestion is from drinking water. Its sole utility is in making rough comparisons among different reference doses. Since other sources, such as milk and food, contribute to the total perchlorate ingestion, a risk-based regulatory value should include an estimate of the relative source contribution of water. To accomplish this goal, exposure from all sources must be accounted for, as well as exposure factors, such as water consumption, and intake of (potentially contaminated) foods. As noted by NRC, such an assessment requires policy decisions, which are beyond the scope of their document and this chapter.

4.5 Perchlorate Uncertainties and Data Gaps

There are currently many unanswered questions surrounding the prevalence of perchlorate in the environment, the possible exposures and effects, and the risk management strategies available to manage perchlorate contamination. Further information must be obtained in each of these areas to develop successful and appropriate strategies for handing perchlorate contamination now and in the future.

4.5.1 Toxicity Uncertainties and Data Gaps

While animals are useful models because scientists can conduct multigenerational exposures (which cannot be conducted in humans), it is difficult to extrapolate effects in laboratory animals to effects in humans. This is particularly true for neurological effects, since animal models may not adequately capture the complexity of the human brain.

Since iodide uptake fluctuates every day as a result of diet and other factors and the body's natural adaptive processes compensate for these fluctuations, it would be helpful to gain a better understanding of when iodide uptake inhibition by perchlorate reaches the threshold of iodide deficiency. We still need to elucidate the relationship between reduced iodide uptake with compensatory changes in thyroid regulation and an irreversible developmental effect (hormone dysregulation).

There are several confounding factors that limit the value of epidemiological studies, including gaps in our understanding of these data. Comprehensive human epidemiologic studies may help quantify effects of perchlorate in sensitive subpopulations, assuming that researchers can develop adequate controls for potentially confounding factors.

Although very high concentrations of perchlorate can cause cancer in laboratory animals (Capen 1997; York et al. 2001a), exposure to perchlorate in the environment has not been shown to cause cancer in humans, and USEPA has concluded that perchlorate is unlikely to cause thyroid cancer in humans. The laboratory animal studies are somewhat controversial. Perchlorate does not produce tumors through alteration of genetic material in animals (USEPA 2002). Tumor production in laboratory animals is thought to be dependent on dose and the physiological perturbation of the thyroid hormone feedback system (USEPA 1998). The concentrations of perchlorate required to produce tumors are far greater than the amounts encountered by human populations, even in highly contaminated industrial settings (Gibbs et al. 1998, Lamm et al. 1999).

Finally, there are numerous other compounds that can modulate thyroid hormone homeostasis (for example, see list of chemicals compiled by Howdeshell [2002]). We lack data to evaluate potential interactions with these additional compounds.

4.5.2 Exposure Uncertainties and Data Gaps

The prevalence of perchlorate in public and private drinking water supplies and in foodstuffs must be further evaluated. The results of recent sampling efforts in water and food indicate that perchlorate may be more widely prevalent than originally recognized. Additional sampling of these exposure media is ongoing. The results of such testing should be compiled and evaluated.

Since nursing infants are considered to be a potentially sensitive subpopulation, further research on measuring possible exposure to perchlorate in human milk would be a significant addition to the database. In particular, further research should focus on understanding the effects of perchlorate exposure on lactation and the iodide and perchlorate concentrations in human milk, and in particular, the concentrations of perchlorate in human milk over time.

In quantifying the scope of existing contamination, research efforts can be aimed at understanding effects of environmentally relevant concentrations and the development of appropriate risk management strategies.

4.5.3 Risk Assessment Uncertainties and Data Gaps

Uncertainties, such as dose-response extrapolation and exposure estimation, confound the risk assessment process. In general, chemical concentrations of contaminants in food and water are much lower than those used in experimental settings (using rats as models, for example). Therefore, it is always difficult to estimate the potential effects of exposure to concentrations that are much lower than those used in experiments.

The primary sources of uncertainty in estimating an RfD for perchlorate in drinking water arise from the absence of data on possible effects of exposure among populations at greatest risk of adverse effects of iodide deficiency (pregnant women and their fetuses and newborns). Therefore, to reduce the uncertainty in the understanding of human health effects associated with perchlorate exposures, NRC has recommended additional research in several areas. Some of the major research areas include studies to determine the effects in humans of chronic low-dose exposure to perchlorate and studies to determine the effects of perchlorate on sensitive subpopulations (fetuses, infants, and pregnant women). The NRC committee also recommended a clinical study to provide information on the potential chronic effects of perchlorate exposure on thyroid function. Finally, to ensure that all pregnant women have adequate iodide intake, the committee recommends that consideration be given to adding iodide to all prenatal vitamins (NRC 2005a).

4.6 Summary

There are several significant and unique challenges in identifying and managing risks associated with perchlorate. In summary:

- Perchlorate competes with iodide uptake in the thyroid; this is the only known mode of action.

- The fetus of a hypothyroid woman is considered to be the most sensitive receptor. Other sensitive receptors may include nursing infants, children, postmenopausal women, and hypothyroid individuals.
- Toxicological uncertainty exists around the question, "What perchlorate exposure level leads to an adverse effect?" or conversely, "What perchlorate exposure level shows no effect in the most sensitive population?"
- Humans can be exposed to perchlorate primarily through ingestion of contaminated water and foods. Exposure of infants to perchlorate in human milk is of concern as well.
- Currently more is known about perchlorate exposure via drinking water than via other media since water supplies have recently begun testing for perchlorate. Less is known about exposure through food, although this data gap is receiving more attention.
- Potential for impacts to other species—plants, animals, and fish—is another area for further evaluation; primary interest will be in accumulation and transmittal to humans through the food chain, but the potential for direct effects on other species should also be investigated.
- NRC recently concluded that a reference dose of 0.0007 mg/kg body weight per day would protect the health of even the most sensitive groups of people over a lifetime of exposure. USEPA adopted NRC's recommended reference dose.

5. RISK MANAGEMENT AND REGULATORY STATUS

This section briefly discusses the role of risk management strategies, presents some possible risk management actions, and discusses the current regulatory status of perchlorate. Risk management involves the evaluation of strategies to eliminate or minimize risks due to contaminants at a site.

Because of the potential risks to human health associated with perchlorate exposure, the regulatory status of perchlorate has received increasing attention in recent years. At this point, the federal government and state governments have not yet set regulatory standards for perchlorate. However, some states have adopted advisory levels for perchlorate in drinking water, and a few states are considering or are in the process of promulgating state levels. It is important to note that although the federal government may set an MCL based upon the RfD recently established by USEPA, states retain the right to set stricter state standards.

5.1 Risk Management

Risk management involves evaluation of several different factors to decide how best to eliminate or minimize risks due to contaminants at a site. Risk management typically involves either implementing remedial activities that reduce contaminant concentrations to acceptable risk-based levels (established during the risk assessment), taking other measures to prevent completion of exposure pathways, or combining these approaches. Because of site- and location-specific factors, risk management strategies may not be consistently applied across site and programmatic boundaries.

The foundation for risk management strategies is information provided in the risk assessment. Other factors evaluated as part of risk management include regulatory requirements, technical feasibility, cost, effectiveness, and public acceptance.

Risk management begins with initial evaluation of the potential and actual occurrence of a perchlorate source. Short-term response actions generally evaluate sources relative to potential or completed exposure pathways. Initial efforts by regulatory entities may include identifying likely key source areas and sampling nearby water wells to help determine the need for immediate response actions to mitigate ongoing exposures. Environmental impacts that do not pose an immediate threat still require response actions, but using the more traditional, systematic approach common to all regulatory programs.

5.1.1 Risk Management Strategies

5.1.1.1 Pollution Prevention

The best risk management approach is to prevent a chemical release before it occurs. Therefore, the regulatory agencies and the regulated community have taken steps to eliminate or minimize perchlorate releases and improve management practices. In addition, some states have initiated reporting requirements for facilities that store or manage perchlorate materials.

In some cases, it is possible to manufacture products without perchlorate. For example, some manufacturers are now marketing alternatives to perchlorate-based road flares in the form of high-visibility lighting. However, replacing perchlorate is not always possible or practical.

Proper management and storage of perchlorate can also prevent perchlorate release to the environment. Solid perchlorate may be delivered in “super-sacks” or bags and typically stored on pallets within buildings constructed with concrete floors. Perchlorate may also be supplied in drums. Steel drums containing perchlorate are stored separately from potential fuels such as wood, oil, grease, etc. and provide isolation from the environment. Perchlorate salts and solutions are very corrosive to steel and degrade fiberglass and concrete. For example, corrosion impacts to concrete and steel, at least in part, have resulted in the release of perchlorate to groundwater at the former manufacturing facility at Henderson, Nevada. Unless the storage vessels, piping, and secondary containment are corrosion resistant and monitored, leakage to the environment and groundwater contamination can occur. Storage of bags and super-sacks and pouring/transfer operations may release perchlorate in the form of dust with similar results.

Some commercial explosives manufacturing facilities in operation today are equipped to ensure zero discharge of perchlorate waste. At these facilities, all wash water is captured and used in production, and affected containers are rinsed to remove all perchlorate before being disposed. Some facilities capture and recycle all residual perchlorate into new product. Incineration at a RCRA Treatment Storage or Disposal Facility, though very expensive, is also a disposal option for any perchlorate wastes. Explosives ready for use are typically stored in magazines for safety purposes. There is little risk of release from complete and packaged explosives unless carelessness results in packaging puncture with subsequent leakage.

California requires that perchlorate facilities have an unsaturated zone monitoring program and that all existing groundwater monitoring wells in the state be available for use as early warning or sentinel wells to warn of impending threat to drinking water resources. By the end of 2005, the California Department of Toxic Substances Control will adopt regulations specifying BMPs for managing perchlorate materials and prohibiting the management of perchlorate materials after the effective date of those regulations except in compliance with the specified BMPs. The California Environmental Protection Agency will also be required to establish a statewide data base for the electronic collection of perchlorate data.

5.1.1.2 Recycling

Since the early 1990s, the armed services have been developing methods of recycling solid rocket propellant, primarily because of concerns over air emissions from open burning. See Section 2.2.1.3 for more information on recycling of solid rocket propellants.

5.1.1.3 Risk Reduction

Assuming that "no action" has been eliminated as a potential response action, potential response actions fall into two broad categories: (a) the use of engineering or institutional actions to interrupt exposure media and ingestion pathways and (b) treatment solutions to address contaminant sources that pose an ongoing threat of release and environmental degradation.

Alternative Water Supply. When perchlorate has contaminated a drinking water source, one option is to provide an alternative drinking water supply (e.g., providing bottled water or switching to different source waters). Due to the volume of water supplied to most communities, this strategy may greatly affect the infrastructure and incur some costs. In some cases other sources may not be available, or the alternative supply may have other contaminants of concern not yet identified. In some cases states have issued warnings to the public without or before ensuring an alternative water supply. This approach allows the public to decide for themselves—based on age, condition, etc.—whether there is enough risk to identify an alternative water source. However, finding an alternative water supply does not lessen the need to clean up the source and impacted groundwater areas.

Blending. Some water purveyors have traditionally blended water from different sources and with different characteristics to produce a suitable, deliverable water supply. Blending is typically conducted to ensure that water supplied to the public is below an MCL or other regulatory standard and is a strategy that has been previously used in some cases of inorganic and organic contamination. Blending may be the only available option for a water purveyor with perchlorate contamination because of significant water demands, insufficient water treatment facilities, and insufficient resources.

As a long-term strategy, blending essentially allows lower-level exposure to a larger population instead of higher exposure to a smaller population. This strategy imposes exposure to concentrations below regulatory thresholds on populations who were not originally exposed to a contaminant. From a cost standpoint, blending may require additional services or construction of a new distribution infrastructure. It is also likely that the source areas and highly impacted groundwater require cleanup.

Treatment Prior to Use. Based on the extensive volume of drinking water supplied to most areas, surface water or groundwater treatment for perchlorate contamination would be costly. Available technologies for treating perchlorate include filtration through resins or other media that remove the compound and biological treatment of perchlorate that destroys the perchlorate ion. Section 6 presents several different treatment technologies and factors and limitations for the treatment technologies.

Plume/Source Remediation. Groundwater contaminants that have moved away from the source are typically characterized as "plumes." In the event that a contaminant plume has not yet affected a drinking water supply system, treatment of the plume and its source may be one alternative for preventing exposure in the future. In the event that a contaminant plume has already affected a drinking water supply well, treating the plume and/or the source may be components of a remedy that could eventually restore the quality of the drinking water supply. Groundwater remediation technologies are addressed in Section 6.

5.2 Regulatory Status

5.2.1 Federal Status

USEPA has not yet set an MCL for perchlorate in drinking water; however, the 1999 *Interim Assessment Guidance for Perchlorate* is still in effect (USEPA 1999a). In 2003, the USEPA reaffirmed the guidance with the added suggestion to carefully consider the low end of the provisional 4–18 ppb range (USEPA 2003b). In February 2005, based on the National Academy of Science's January 2005 report (NRC 2005a), USEPA established an official RfD of 0.0007 mg/kg/day of perchlorate.

In lieu of a regulatory value, various entities may calculate DWELs. As described previously, the DWEL is a nonregulatory value calculated on the assumption that 100% of perchlorate ingestion is from drinking water. Its sole utility is in making rough comparisons among different reference doses.

5.2.2 State Status

Some states have adopted advisory levels for perchlorate in drinking water, while a few are considering or are in the process of promulgating state levels. Massachusetts and California are currently in the process of promulgating state levels. Massachusetts has recently reaffirmed its proposed level of 1 ppb, while California has proposed a level of 6 ppb. These two states, and others that are considering promulgating state levels, evaluate the same toxicological data as presented in Section 4 to determine a proposed level. It is this interpretation and evaluation of data (such as applying a different uncertainty factor or considering food sources in addition to drinking water sources of perchlorate) that results that results in different proposed numbers at the state and federal levels.

The ITRC Perchlorate Team conducted a survey in 2004 to assess the most recent and current status of state regulatory, advisory, health-based, and/or other levels for perchlorate. The results of the survey represent a snapshot in time and will be outdated by the ongoing assessment of perchlorate toxicity data and any resulting federal standard and/or state standards.

The survey focused on perchlorate health-based goals, cleanup goals, and action levels in groundwater, soil, surface water, and drinking water and consisted of the following five questions:

- Does your state have a health-based goal for perchlorate?
- Does your state have a state-promulgated drinking water standard for perchlorate?
- Does your state have a regulatory cleanup standard or level for perchlorate in groundwater?
- Does your state have a cleanup standard or level for perchlorate in surface water?
- Does your state have cleanup levels of standards for perchlorate in soil?

Fourteen states responded to the survey directly, and additional information was obtained via telephone call (New Mexico), via e-mail (Alabama) from the Texas Interoffice Memo (November 14, 2001) discussing an interim standard for perchlorate, and the USEPA Web site (MD) (Table 5-1).

Based on the survey results, states have not yet established official promulgated perchlorate standards or cleanup levels. The results also indicate that only a few states are evaluating official drinking water standards and that at least two states, Massachusetts and California, appear to be near completion of officially establishing state standards. California has proposed an MCL of 6 ppb and Massachusetts has established a health-based goal of 1 ppb for sensitive populations.

Currently, some states are using interim action levels based on the USEPA *Interim Assessment Guidance of Perchlorate* or site-specific risk-based cleanup standards to conduct remediation activities. For example, the Superfund Record of Decision for the Aerojet facility in Rancho Cordova, California, established a discharge and cleanup standard of 4.0 ppb for perchlorate. In July 2001, USEPA Region I established a perchlorate groundwater cleanup level of 1.5 ppb for Camp Edwards at MMR in Massachusetts. At least one state has adopted usage of the reference dose in the IRIS database. This state, Texas, has modified their risk reduction rules to adopt the RfD for use in their risk based exposure limit equations.

Table 5-1. Results of perchlorate levels survey (quantities are in parts per billion)

	Health-based goal	Health-based goal under consideration	Cleanup standard for groundwater	Cleanup standard for groundwater under consideration	Cleanup standard for surface water	Cleanup standard for surface water under consideration	Drinking water standard	Drinking water standard under consideration	Soil standard
AZ	14		No		No		No		No
AL[a]	No		No		No		No		No
AR	No		No	<4[b]	No	<4[b]	No		No
CA	6		No	Under evaluation	No	Under evaluation	No	Under evaluation	No
CO	No		No		No		No		No
KS	No	4	No	4	No		No		No
MA	1[c]		No	Under development	No	Under development	No	Under development	No
MD	1								
MO	No		No		No		No		No
NM	1[h]		No		No				No
NV	No		18[d]		18[d]		No		No
NH	No		No		No		No		No
NJ	No		No		No		No		No
NY	No		No	Under development	No		No		No
OR	No		No		No		No		No
TX	No		17[e]		17[e]		No		14[g]
UT	No		No		No		No		No
VA	No		No		No		No		No

[a] Alabama is currently developing a program to set site-specific risk-based standards for some chemicals of concern, including perchlorate.

[b] Arkansas currently uses this number for plume definition.

[c] Massachusetts: health-based goal for sensitive populations.

[d] Nevada has adopted a provisional action level of 18 ppb in groundwater and surface water until a new national standard is set by USEPA.

[e] Texas has established an action level, based on residential land use, for drinking water (Class 1 groundwater) at 17 ppb and 1700 ppb for nondrinking water (Class 3 groundwater). Where impacted groundwater is released to surface water used/designated as drinking water sources, the 17 ppb would apply as a surrogate standard.

[g] This level is the protective level for leachate of perchlorate from soil to drinking water; human health protective level in soil (combination of inhalation, ingestion, dermal contact, and vegetable consumption pathways) is 51,000 ppb.

[h] Drinking water screening level.

The following are additional responses and information provided by a number of respondents that could not be incorporated into Table 5-1:

- California, New Hampshire, and New Mexico indicated that current cleanup standards would be health risk based and site specific.
- Oregon indicated that no guidance or rulemaking on perchlorate is anticipated in the near future, but the state continues to track developments at a national and regional level.
- MADEP is currently conducting occurrence monitoring of public water supplies to support the development of a drinking water MCL and is also developing soil and groundwater standards.
- Arkansas will adopt a national standard as soon as one is set and use the soil number that USEPA Region VI will produce.
- Nevada has adopted a provisional action level of 18 ppb in groundwater and surface water for managing characterization and remediation at the Kerr-McGee and AMPAC facilities. When a national standard is set, Nevada will adopt this new standard.
- New York indicated that a drinking water standard is being developed by New York State Department of Health.

6. REMEDIATION TECHNOLOGIES

This section surveys the current state of perchlorate remediation technologies, with a focus on proven and commercially available technologies. Emerging technologies with tested bench-scale and/or pilot-scale studies, as well as those perchlorate treatment technologies in developmental stages, are also briefly discussed. The majority of the technologies discussed have primarily been applied to groundwater contamination. However, this section includes a brief review of perchlorate remediation technologies that are applicable for remediation of perchlorate in soil. A summary of different technologies, including each technology's applied scale (i.e., bench, pilot, or full), throughput (amount by volume treated), effectiveness, and current applicability towards a specific media is provided in Appendix F. A more detailed review and discussion of perchlorate treatment technologies, including a number of case studies and associated costs, will be provided in the ITRC Perchlorate Team's technical and regulatory guidance document, currently under development.

The success of any perchlorate treatment technology depends on several factors, including perchlorate concentration, the presence and concentrations of cocontaminants, and groundwater geochemistry. In general, ion exchange is more cost-effective when perchlorate concentrations are low (<50 μg/L). In addition, common anions in groundwater, including nitrate, sulfate, and bicarbonate, compete with perchlorate for binding sites on ion exchange resins. As the concentrations of these anions increase, the cost of ion exchange for perchlorate removal tends to also increase. Alternatively, microbial perchlorate reduction is negatively impacted by specific geochemical parameters, including low pH and high TDS. High levels of cocontaminants, such as heavy metals and organic solvents, could also be anticipated to negatively impact perchlorate degradation. It is important to consider these site-specific factors when selecting treatment technologies.

6.1 Cocontaminants

Cocontaminants can have an impact on the successful remediation of perchlorate. The most common cocontaminants found at perchlorate-contaminated sites are nitrate and sulfate (Table 6-1). Nitrate concentrations in contaminated media are generally far greater than those of perchlorate, and the presence of nitrate typically interferes with efficient reduction of the perchlorate anion. However, nitrate is commonly removed along with perchlorate because most perchlorate-reducing bacteria are denitrifiers as well (Logan 2001). The presence of sulfate should not adversely impact perchlorate removal, as perchlorate is generally reduced before sulfate. However, if the redox potential is too low, sulfate may become the electron acceptor (ITRC 2002). Additionally, cocontaminants such as sulfate, nitrate, bicarbonate, carbonate, and bromide can also compete with perchlorate during the ion exchange process.

Table 6-1. A partial list of characterized perchlorate-contaminated sites with identified cocontaminants

Site	Contaminated media	Other identified contaminants
Aerojet Facility, Rancho Cordova, California	Groundwater	TCE, N-nitrosodimethylamine (NDMA), nitrate, sulfate
Aerojet Facility, San Gabriel, California[a]	Groundwater	Nitrate, TCE
Big Dalton Well Site, Los Angeles, California[a]	Groundwater	Nitrate, sulfate
La Puente, California[a]	Groundwater	NDMA, 1,4-dioxane, sulfate, VOCs
Confidential site	Groundwater	Nitrate, chlorate[b]
DoD site, West Virginia	Groundwater	Nitrate, sulfate
Edwards Air Force Base, California	Groundwater	Nitrate, sulfate
Henderson, Nevada	Groundwater	Sulfate, sodium, calcium, magnesium, nitrate, boron, hexavalent chromium, chlorate
Lawrence Livermore National Laboratory, Site 300, Livermore, California	Groundwater	VOCs, nitrate, explosive compounds
Pueblo Chemical Depot, Colorado	Soil, groundwater	HMX, RDX, nitrate

[a] These are three different plumes from the same site, San Gabriel Valley Area 2 Superfund Site, also known as the Baldwin Park Operable Unit.

[b] Chlorate may be present as a cocontaminant as well as a potential degradation product. Isotopic analyses of these surrogate chemicals associated with perchlorate may similarly provide a means of source identification and cost apportionment.

Source: Hjeresen et al. 2003.

The presence of cocontaminants at perchlorate sites also depends on facility-specific operations and historical practices. For example, the majority of major weapons system with solid propulsion, explosive devices, or pyrotechnic devices contain perchlorate compounds. At such sites, typical cocontaminants also include volatile organic compounds (VOCs), halogenated VOCs such as trichloroethylene (TCE), solvents, and explosive compounds such as trinitrotoluene (TNT), RDX, and HMX (ITRC 2002). The presence of these compounds makes perchlorate treatment systems more difficult to design.

Because of these concerns regarding cocontaminants, all cocontaminants should be well characterized before selecting a perchlorate treatment technology. This document does not review the effects of cocontaminants in any further detail for individual treatment systems. A more detailed discussion of the impact of cocontaminants on perchlorate treatment technologies will be addressed in the ITRC Perchlorate Team's next document.

6.2 Remediation Technology Applicability Matrix

There are a variety of remediation technologies for perchlorate remediation. Some technologies are proven and commercially available, while others are still in the research and development phase. This document provides an overview of the commercially available technologies (Section 6.3) and summaries of emerging technologies still at the bench- or pilot-scale stage (Section 6.4).

To summarize the state of technology development at this point in time, a detailed list of the various remediation technologies being used for 120 different projects has been compiled and provided in Appendix F. Of these 120 projects, 51 are full-scale systems. Thirty-nine treatment units were operational at the time of the completion of this report.

6.3 Proven/Commercially Available Technologies

A variety of remediation technologies are currently commercially available and being used for perchlorate remediation. These remediation technologies fall into two broad categories, ion exchange and biological processes. The majority of these treatment technologies have been applied to remediation of groundwater; however, biological processes are also being applied to the remediation of soils.

6.3.1 Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion from solution is exchanged for a similarly charged ion attached to an immobile solid. Similar to adsorption or chemical reactions, ion exchange depends on several variables, including the presence and concentrations of competing ions.

Ion exchange is the most commonly used physical treatment process for the treatment of perchlorate-impacted groundwater. During ion exchange, perchlorate, which is a negatively charged ion (anion), is exchanged with another anion, typically chloride (Cl^-). The ion exchange medium consists of a polymer (ion exchange resin) containing a positively charged functional group (e.g., a quaternary amine, R_4N^+) with a strong preferential affinity to the perchlorate ion. The following is the primary ion exchange equilibrium reaction of perchlorate with a strong base ion exchange resin in the chloride form:

$$R_4N^+Cl^- + ClO_4^- \Leftrightarrow R_4N^+ClO_4^- + Cl^- \ .$$

Ion exchange is an equilibrium process, and exposing the contaminant-laden ion exchange resin to a concentrated (sodium) chloride brine can reverse the equilibrium of the reaction to the left, thus displacing the perchlorate from the resin. This equilibrium reversal is used in the regeneration of spent resin and creates a brine with relatively high perchlorate concentrations that needs to be managed further. Once the resin is reloaded with chloride, it is placed back in service, and the ion exchange cycle is repeated. Another spent-resin management option that is widely used for resins based on styrene-divinylbenzene copolymers involves removal of the ion exchange resin when loaded with perchlorate for thermal destruction by blending the resin with boiler fuel. Figure 6-1 presents a conceptual schematic of the ion exchange process showing the two main management options for perchlorate-impacted ion exchange resins.

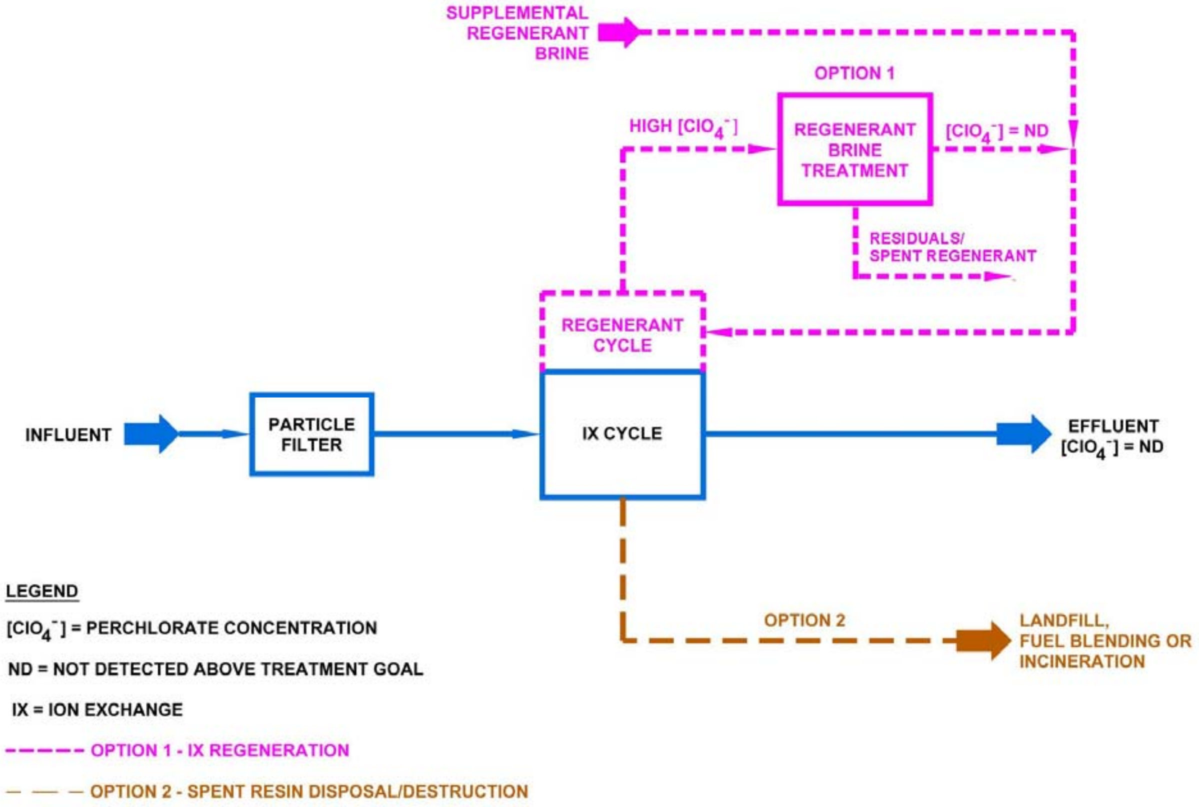


Figure 6-1. General schematic of ion exchange.

Many other anions commonly present in groundwater will compete with the perchlorate ion for this reaction. These include sulfate (SO_4^{2-}), nitrate (NO_3^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and bromide (Br^-). Trace ions can also compete with the perchlorate ion for the resin surface (e.g., chlorate, bromate [BrO_3^-], arsenate, etc.). Water that contains high TDS values can significantly hinder ion exchange effectiveness and can become cost-prohibitive to treat. Interference from other anion species on the perchlorate loading of an ion exchange resin can be minimized by selecting a resin with functional groups that favor the exchange of perchlorate over other anions.

Several ion exchange equipment designs are currently employed, including fixed-bed downflow or upflow contactor systems that can be operated in either concurrent or countercurrent (service flow in the direction opposite to the regeneration), continuous moving-bed systems, and continuous multiport rotating distributor systems (e.g., Calgon Carbon's Ion SEParator [ISEP®] system). Some newer resin designs, however, take advantage of a greater selectivity for perchlorate, making it possible to operate the ion exchange unit for a protracted period of time while removing mainly perchlorate and not all of the other ions in the influent stream. Depending on the method of ion exchange system operation, the volume of the regenerant waste stream can range 2%–8% of the volume of water treated by ion exchange.

ORNL and the University of Tennessee have developed bifunctional resins that have the highest selectivity for perchlorate (CalEPA, 2004). These resins can be regenerated or removed for off-site disposal; several ompanies now market commercially available ion exchange resins. The quaternary ammonium groups combined with small alkyl groups afford these bifunctional resins high perchlorate selectivity and highly favorable exchange kinetics.

6.3.1.1 Concentrated Brine Treatment

Although regeneration of ion exchange resins is widely practiced in general, the management of the regenerant brine containing high levels of perchlorate in the presence of high chlorides and other anions poses significant challenges. The following summarizes three regenerant brine treatment alternatives: catalytic chemical reduction, ferrous chloride reduction, and biological reduction. Aside from the destruction of the perchlorate in the brine, the catalytic and ferrous iron reduction options aim to recycle the treated brine and reuse it for the regeneration of perchlorate laden resin.

Catalytic Chemical Reduction. In 1999, Calgon Carbon pilot-tested catalytic chemical reduction using ammonia as the reductant on the concentrated brine of their ion exchange system. The process was conducted under high pressure and temperature. The test results demonstrated effective destruction of perchlorate to levels below the (elevated) detection limit of 125 µg/L (Calgon, 1999). Calgon Carbon has coupled this technology with the ISEP® system to treat the concentrated ion exchange regenerant solution. The combined system is referred to as the ISEP®+ system.

Ferrous Chloride Reduction. ORNL has developed a new technology to regenerate selective ion exchange resins using a ferric chloride solution acidified with hydrochloric acid, creating a tetrachloroferrate ion ($FeCl_4^-$). The tetrachloroferrate ion displaces the perchlorate from the ion exchange resin. Desorption of the tetrachloroferrate ion from the resin takes place with water or a dilute acidic solution, so the resin becomes available again for perchlorate removal. The perchlorate-rich regenerant solution is subsequently reduced using ferrous chloride under elevated temperatures (<200°C) and/or pressures (~20 atmospheres) (Gu et al. 2001). Although this regeneration technology could be used either on or off site, it is likely that off-site regeneration will be appropriate for most low resin usage applications.

Biological Reduction. A membrane bioreactor system (MBR) is undergoing testing by Applied Research Associates for the treatment of perchlorate in the brine produced by regenerable ion exchange systems. The MBR has been successful at treating perchlorate-laden brine with TDS levels as high as 7% in the laboratory and underwent field testing in late 2004. (Section 6.3.2.1).

6.3.1.2 Spent Resin Disposal/Destruction

The vast majority of full-scale ion exchange applications for perchlorate treatment employ a once-through treatment where the perchlorate-laden (spent) resin is disposed of at an off-site location. Although landfill disposal could be considered, it is not widely used and does not eliminate the generator's ongoing liability. Instead, most spent resin management options center around thermal destruction, either via fuel blending or hazardous waste incineration.

6.3.2 Biological Processes

Perchlorate-reducing bacteria appear to be widespread in the environment, even though the presence of perchlorate is localized. This conclusion is supported by both microbial isolations and a multitude of microcosm studies showing that the addition of an appropriate electron donor (i.e., energy source) to a site sample causes perchlorate degradation without the addition of exogenous bacteria (Coates et al. 1999; Hatzinger et al. 2002; Waller, Cox, and Edwards 2004; Tan, Anderson, and Jackson 2004). That biological perchlorate reduction is occurring so widely in nature in the absence of perchlorate may reflect the similarity of the enzymatic reduction to biological denitrification and the conservation of this metabolism by microorganisms.

The biological degradation of chlorate was first observed in the 1920s and is the basis of an assay for biochemical oxygen demand (BOD) in wastewater (Bryan 1966, Logan 1998). A limited amount of research was also performed in the degradation of perchlorate as early as the 1960s (Hackenthal et al. 1964), but significant studies in this area began in only the mid-1990s concurrent with the first reports of widespread perchlorate contamination in the United States. Despite the rather short period of study, appreciable knowledge has been gained concerning the types of perchlorate-reducing bacteria, their ecology, and the pathway and kinetics of the biological reduction process.

A variety of perchlorate-reducing bacteria have been isolated, many of which are members of the newly identified genera *Dechloromonas*, *Dechlorospirillum,* and *Azospira* (formerly *Dechlorosoma*) (Achenbach et al. 2001, Xu et al. 2003). All of the bacteria isolated to date are facultative anaerobes, i.e., organisms that can grow in either the presence or the absence of oxygen, provided proper nutrients are available in the medium. Using this metabolic versatility, these organisms are capable of degrading perchlorate, chlorate, and in most cases, nitrate. For perchlorate, these bacteria use an organic substrate or, in some cases, hydrogen gas as an electron donor and use the perchlorate molecule as a terminal electron acceptor. As shown in Figure 6-2, the bacteria oxidize the organic substrate to carbon dioxide (or sometimes an intermediate) and reduce perchlorate initially to chlorate and then chlorite and finally to chloride and oxygen (Van Ginkel et al. 1996, Kengen et al. 1999). The enzyme (per)chlorate reductase is known to carry out this initial two-step reaction. A second enzyme, chlorite dismutase, subsequently disproportionates chlorite to chloride (Cl^-) and oxygen (O_2) (Coates et al. 1999).

An immunoprobe for the chlorite dismutase gene has been developed to detect perchlorate-reducing bacteria in environmental samples (O'Conner and Coates 2002).

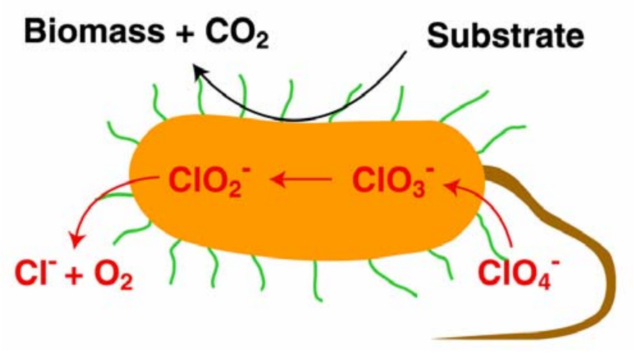


Figure 6-2. Schematic of biological reduction of perchlorate.

A variety of different electron donors have been shown to promote the biological reduction of perchlorate by individual strains and/or in environmental microcosms. These substrates include fatty acids (e.g., acetate, citrate, lactate), mixed and pure sugars (e.g., molasses, glucose), protein-rich substrates (whey, casamino acids), alcohols (e.g., ethanol), vegetable oils (Borden, Lindow, and Rodriguez 2004; Henry et al. 2003), and hydrogen gas (Logan 1998; Hunter 2002; Waller, Cox, and Edwards 2004; Zhang, Bruns, and Logan 2002; Hatzinger 2002). However, the specific substrates utilized as energy sources are strain- and site-specific.

The irony of perchlorate remediation is that despite the large numbers of microorganisms shown to be capable of reducing perchlorate and the breadth of metabolic capabilities that these microorganisms possess, perchlorate continues to persist in the environment. Thus, it remains important to develop approaches to address the large volumes of perchlorate-contaminated groundwater and soil. Biological processes offer many powerful and manageable solutions to this problem and are discussed in the following sections.

6.3.2.1 Ex Situ Bioremediation

A variety of different biological reactors, including continuous-flow stirred tank reactors (CSTRs), packed-bed reactors (PBRs), and fluidized-bed reactors (FBRs), have been tested for the ex situ bioremediation of perchlorate in water and wastewater. A recent review summarizing pilot- and full-scale bioreactor systems for perchlorate is provided by Hatzinger (2005). Figure 6-3 presents a diagram of a generalized ex situ bioremediation system. In addition, brief descriptions of these reactor designs are provided in the subsequent sections, and information concerning current status for perchlorate treatment can be found in Table 6-2.

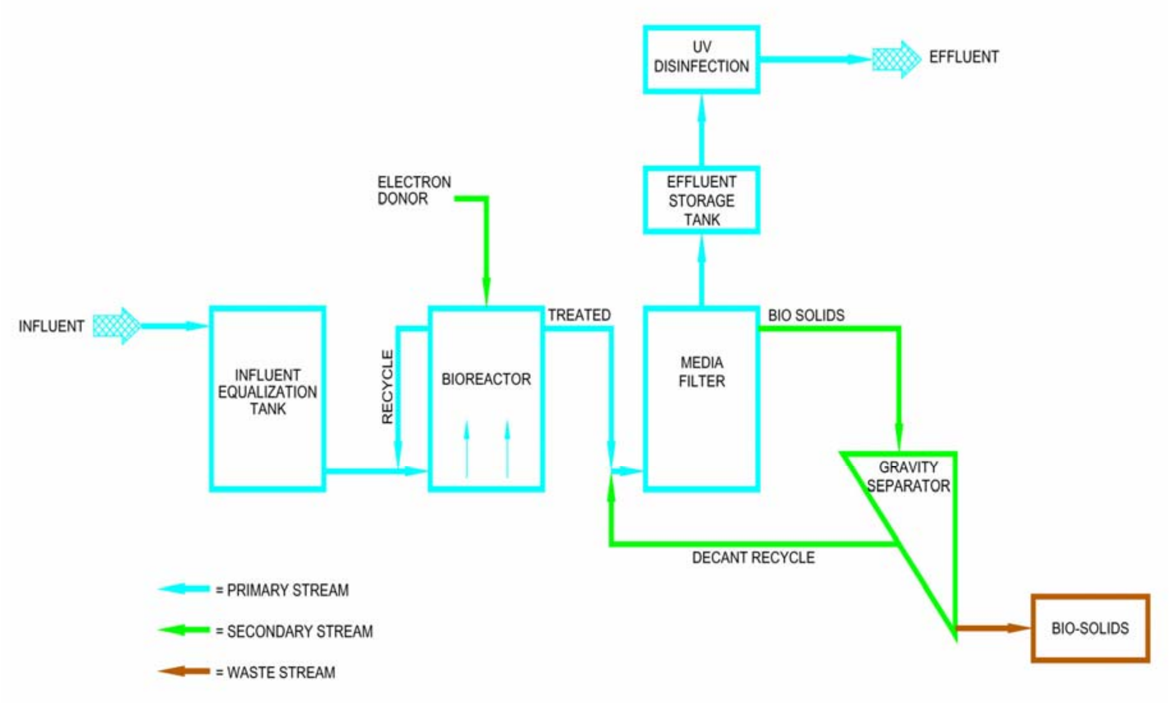


Figure 6-3. General schematic of ex situ bioremediation.

Table 6-2. Bioreactor system information

Reactor type	Description/location	Scale	Status	Perchlorate levels treated
Continuous-flow stirred tank reactors, Applied Research Associates	For treatment of hog-out[a] wastewater, Thiokol, Brigham City, Utah, using *Wolinella succinogenes* HAP-1 and desugared molasses	Originally: 1,600 and 720 gal, 2 × 1,000 gal added	Prototype 1997, expanded in 2002, currently operational	Capable of treating ~100,000 pounds per year
	For treatment of wastes from gunpowder manufacture, Hodgdon Powder Co., Kansas	2,500–5,000 gpd	Currently operational	Influent of 3,000 ppm to less than ~20 ppb (minimum reporting level [MRL])
Fluidized bed reactor, Shaw Environmental (formerly Envirogen) and U.S. Filter/Envirex Products	Treatment of both nitrate and perchlorate in groundwater, AeroJet General Corp., Rancho Cordova, California,[b] using granular activated charcoal (GAC), with ethanol	Required flow 4,000 gpm, currently 5,300 gpm	Operational since 1998	Designed to treat 8 ppm perchlorate and 1.5 ppm nitrate, currently, influent of 1,700 ppb to less than 4 ppb (MRL)
	Treatment of groundwater, Longhorn Army Ammunition Plant, Karnak, Texas,[c] using GAC, with acetic acid	50 gpm	Operational since 2001	Influent averaging 25 ppm to effluent less than 4 ppb
	Treatment of groundwater, McGregor Naval Weapons facility, McGregor, Texas,[d] using GAC, with carbon source not specified	Up to 400 gpm	Operational since 2002	Influent average of 2.3 ppm (range 0.5–5 ppm), effluent less than 4 ppb

Reactor type	Description/location	Scale	Status	Perchlorate levels treated
	Treatment of groundwater at Henderson, NV[e] (Kerr-McGee plant) using sand and GAC, with ethanol and mixed microbial population	~1000 gpm	Operational since 2004	Effluent nondetect levels <18 ppb
Packed bed reactor laboratory studies	This type of system has been pilot-tested for drinking water treatment at Castaic Lake	Up to 20 gpm	No operational units	See references
Other bioreactor designs	Treatment of drinking water at laboratory scale using a hollow-fiber membrane[f]	1.5 gpm	Pilot-scale testing	Influent initially 60 ppb, effluent going to <6 ppb
	Treatment of brine from ion exchange systems, Applied Research Associates, using membrane bioreactor technology	1 gpm	Pilot-scale testing	Influent initially 3–4 ppm, effluent going to <50 ppb reporting limit

[a] Hog-out wastewater is generated when high-pressure water is used to remove solid propellants from rockets and missiles (a process often termed “hog-out”). Initial laboratory and pilot-scale studies were performed at Tyndall Air Force Base (Pensacola, Fla.) in the early 1990s.

[b] System consists of four FBRs, 14 inches in diameter by 22 feet high. First commercial installation of FBR. System discharges overland toward the American River and has treated more than 8 billion gallons since 1998.

[c] System consists of one FBR, 5 feet in diameter by 22 feet high.

[d] Single 7.5-foot-diameter FBR. The groundwater feeding the reactor at McGregor emanates from a series of cut-off trenches installed at the site, a subset of which are also designed to promote in situ perchlorate treatment.

[e] Largest system to date, consists of eight FBRs, four sand and four GAC media. Sand and GAC reactors configured in series. Influent water initially flows through sand FBRs (removes chlorate, nitrate, and most perchlorate), then through GAC units for additional perchlorate removal. Influent concentrations were initially 2122 pounds/day, full-scale system will be ~2400 pounds/day.

[f] System is a suspended-growth reactor, using hollow-fiber membranes to supply/distribute hydrogen as substrate for microbial growth.

Continuous-Flow Stirred-Tank Reactors. The CSTR is a suspended-growth reactor (i.e., maintains biodegradative organisms in suspension) that has continuous influent and effluent flow (Figure 6-4). The use of a flow-through system differentiates these reactors from batch reactor systems, which treat specific volumes of water under static conditions. CSTRs have been applied most commonly for the treatment of commercial and domestic wastewaters. These systems are generally best suited for low-flow, high-strength waste streams.

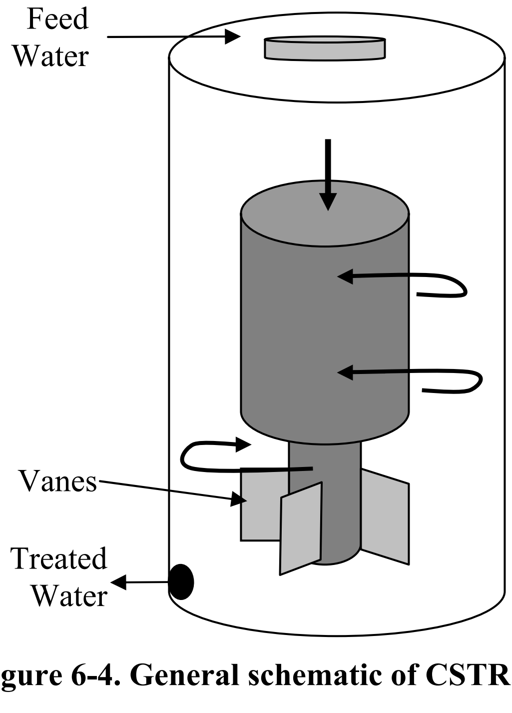


Figure 6-4. General schematic of CSTR.

Fluidized-Bed Reactors. The FBR is a fixed-film bioreactor that uses a solid media, often sand or GAC, to support microbial biofilms. FBR media is suspended or “fluidized” by the flow of water through the reactor (Figure 6-5). The up-flow velocity of water is sufficient to overcome the gravitational force on the particles and to achieve a significant expansion (20%–30%) of the particles composing the FBR bed. The high surface area of the media within the expanded reactor bed (essentially the entire surface of the GAC or sand particles is exposed) allows high biomass densities to be achieved and maintained and subsequently reduces reactor size compared to more conventional designs. Moreover, most commercial-scale FBRs are designed with efficient biomass control devices that prevent the reactor fouling. As such, some commercial FBRs have been in operation for more than 15 years (Hatzinger 2005; Sutton and Mishra 1991; USEPA 1993; Hatzinger et al. 2000; Polk et al. 2002; Beisel, Craig, and Perlmutter 2004).

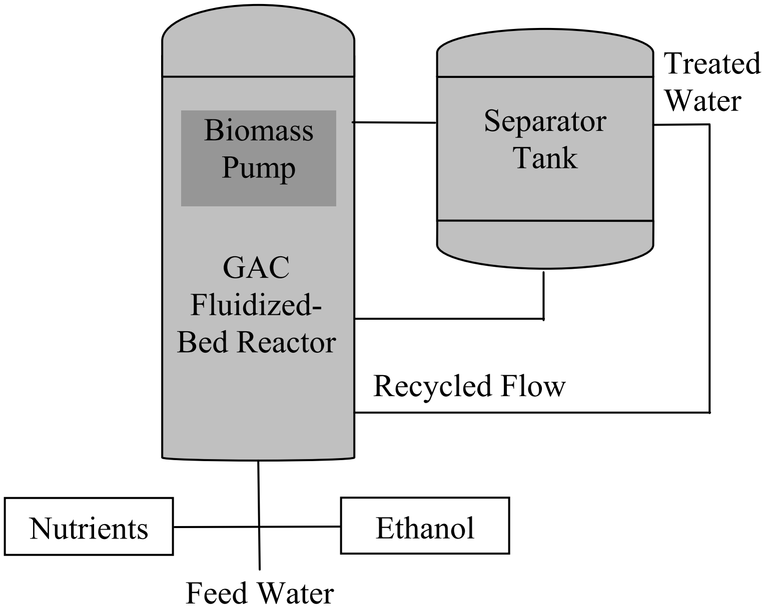


Figure 6-5. General schematic of a fluidized bed reactor.

Packed Bed Reactors. The PBR is a fixed-film bioreactor that uses a solid media to support biodegradative organisms. These organisms grow as a biofilm on or within the packing material and degrade aqueous contaminants as water moves through the reactor in either an up-flow or down-flow manner. The basic reactor consists of a vessel filled with sheet packing, coarse sand, plastic rings, or other support media, and all associated pumps and controls to set water flow and to supply necessary amendments to the water being treated. The key advantage of fixed-film systems compared to suspended-growth reactors is the ability to achieve high concentrations of biomass within the reactor, even in the presence of rapidly flowing water.

At present, there are no full-scale PBR systems treating perchlorate in groundwater or wastewater that are fully operational. However, several different researchers have evaluated PBRs for this purpose at the laboratory and the pilot scales with flow rates as high as 20 gpm. Overall, the testing has shown that this reactor design can effectively remove perchlorate and nitrate in groundwater to below the respective MRLs for these contaminants for short periods of time. However, the absence of an effective technique to control biomass within these reactors has caused questions concerning their long-term operability in the field. With time, biomass overgrowth within the PBR can cause channeling through the reactor and a subsequent loss of performance due to a subsequent shortening of the hydraulic residence time. Techniques such as periodic backwashing have been effective for controlling this problem in pilot-scale units and this technique may also be effective at full scale (Hatzinger 2005; Min et al. 2004, Xu et al. 2003, Losi et al. 2002, Hatzinger et al. 2002).

Other Bioreactor Designs. In addition to the aforementioned reactors, other biological reactor designs have been tested for specific perchlorate treatment applications, including the treatment of perchlorate in drinking water and in ion exchange brine. These include a specialized hollow-fiber membrane reactor and a membrane bioreactor system, which is a suspended-growth reactor that uses a membrane to separate biomass from effluent water (letting effluent pass through but not bacterial solids). These systems are very different in that the hollow-fiber reactor uses a membrane to regulate hydrogen supply, while the MBR uses a membrane to retain biomass within the reactor vessel. MBRs have previously been applied at large scale for treatment of chemical manufacturing wastes and other concentrated streams, but their application for perchlorate treatment has been limited at this point. It is likely that the technology will find a niche for low-flow, high-concentration streams, such as that produced during resin regeneration (see Section 6.4).

6.3.2.2 In Situ Bioremediation

As previously noted, laboratory microcosm studies have shown that perchlorate-reducing bacteria are indigenous to many soils, sediments, surface waters, and groundwaters. Moreover, these organisms can often be stimulated to degrade perchlorate to below detection by adding a microbial growth substrate to these environments (Wu et al. 2001; Hatzinger et al. 2002; Waller, Cox, and Edwards 2004; Tan, Anderson, and Jackson 2004). There are two general strategies for delivering amendments to the contaminated groundwater—fixed biobarriers and mobile soluble amendments.

Fixed Biobarriers. Fixed biobarriers (Figure 6-6) are solid or viscous amendments emplaced across the flow path of the contaminated groundwater and allowing the contaminated groundwater to flow to, through, and past the fixed amendment. This fixed biobarrier approach can use engineered trenches or barriers containing solid-phase, slow-release substrates (Perlmutter et al. 2001) or viscous substrates emplaced cross gradient via direct-push injections (Zawtocki, Lieberman, and Birk 2004). A number of fixed biobarrier electron donors, including vegetable oil, pecan shells, chitin, Hydrogen-Release Compound (HRC™), and compost materials have been observed to support microbial reduction of perchlorate. The following are three examples of fixed biobarriers:

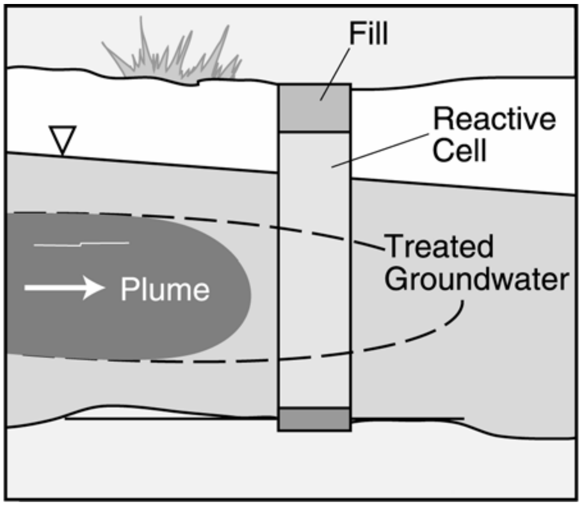


Figure 6-6. General schematic of a biobarrier.

- A barrier at the Naval Weapons Industrial Reserve Plant (NWIRP), McGregor, Texas, is the largest installation to date. It consists of a series of trenches (several thousand feet in combined length) that contain a mixture of mushroom compost, soybean oil, and wood chips as slow-release electron substrates. The shallow trenches (10–25 feet in depth) are cut into limestone and designed to capture groundwater and runoff water at the site. Influent perchlorate levels as high as 13,000 ppb have been reduced to below detection in this barrier.

- The second barrier system, installed in Mortandad Canyon at LANL, consists of the mineral apatite, a phosphate mineral, to remove various radionuclides from groundwater and a mixture of pecan shells and cottonseed as slow-release substrates for the reduction of perchlorate and nitrate.
- The third barrier example is an emulsified vegetable oil injected into a shallow, perchlorate-contaminated aquifer in Maryland to create a passive barrier (Zawtocki, Lieberman, and Birk 2004). Within 35 days of injection, perchlorate levels had declined from 9,000 μg/L to <10 μg/L within 20 feet of the barrier.

Mobile Amendments. Mobile amendment systems are characterized by injecting water-soluble amendments with low viscosity into the upgradient portion of the plume or source area and allowing that amendment to move downgradient, treating the groundwater as it moves. This technology can be implemented by direct-push injections or injection wells. Injection strategies dictate the need for passive or active treatment. Passive treatment (Figure 6-7) requires no extraction or recirculation. Active treatment (Figure 6-8) can use groundwater extraction and reinjection systems to distribute substrates in the subsurface (Hatzinger 2005; Cramer et al. 2004; Cox, McMaster, and Neville 2001) or horizontal-flow treatment wells to mix and distribute electron donor in groundwater. A variety of soluble amendments can be used, including but not limited to lactate, ethanol, citric acid, acetate, molasses, and corn syrup. Following are examples of mobile amendments.

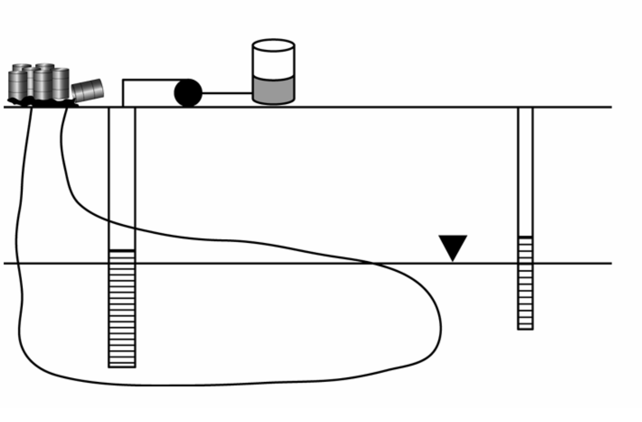


Figure 6-7. Schematic of passive in situ bioremediation.

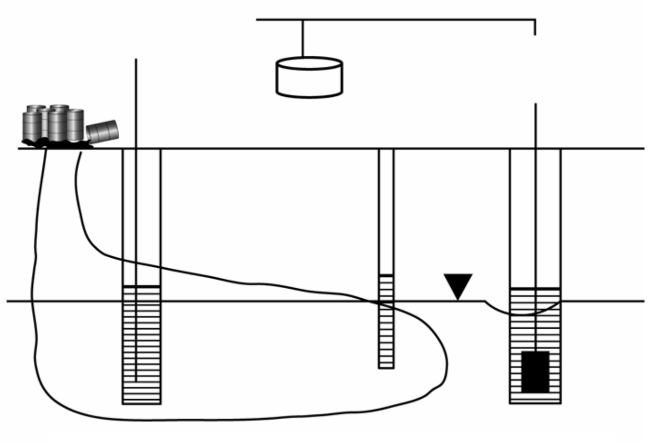


Figure 6-8. Schematic of active in situ bioremediation recirculation system.

- At Indian Head Division Naval Surface Warfare Center in Maryland, lactate was injected via injection well using the passive approach. A buffer was also added to the aquifer to increase groundwater pH and enhance the kinetics of perchlorate reduction. Over a 20-week demonstration, during which lactate was added as an electron donor, the perchlorate concentration in groundwater declined by >95% in eight of the nine monitoring wells in the field plot from an initial average of 170 mg/L, with five wells reaching <1 mg/L during the demonstration and two wells declining to below the MRL for the study (5 μg/L) during this period (Cramer et al. 2004).

- At Aerojet-General Corp. in Rancho Cordova, California, groundwater was extracted, amended with an electron donor (ethanol, lactate, and citric acid were tested), and then reinjected to the subsurface. Several active mobile amendment studies have also been conducted at Aerojet-General, the most extensive of which consisted of a groundwater extraction/reinjection system designed to capture a perchlorate plume that is approximately 600 feet wide (Cox, McMaster, and Neville 2001). During this demonstration, ethanol was used as the electron donor. Perchlorate was reduced from 8 mg/L to <4 µg/L within 35 feet of the groundwater reinjection well. In addition, a pilot study is ongoing at Aerojet-General in which horizontal flow treatment wells have been installed to mix to distribute electron donors within a perchlorate-contaminated groundwater plume without bringing water to the surface. Citric acid is being used as the electron donor for this pilot project. This demonstration and several others have been funded by the Environmental Security Technology Certification Program (ESTCP, www.ESTCP.org).

- At the former Pacific Engineering and Production Company in Henderson, Nevada, GeoSyntech Consulting, Inc. conducted a recirculating in situ pilot study in November 2002 though May 2003. The pilot study initially included ethanol amendments, which result in mineral precipitation and well fouling. This problem was resolved by replacing ethanol with citric acid. Perchlorate concentrations were reduced from a range of 510–780 mg/L to a range of 0.6–28 mg/L.

6.3.2.3 Soil Remediation

Remediation processes for perchlorate in soil, both ex situ and in situ, have focused mainly on the application of bioremediation. Laboratory studies suggest that perchlorate-reducing bacteria are present in most surface soils and that perchlorate bioreduction can be stimulated through the addition of appropriate organic substrates to these soils (e.g., Wu et al. 2001, Hatzinger 2002). Field-scale treatment of perchlorate-contaminated soils has been performed using in situ and ex situ techniques. Insufficient food and moisture appear to be the limiting factors in stimulating bacterial reduction of perchlorate in soils.

In Situ Soil Bioremediation. In situ treatment has been tested at several sites with near-surface perchlorate contamination, including the Longhorn Army Ammunition Plant (LHAAP) in Karnack, Texas, and Aerojet-General Corporation in Sacramento, California. A variety of different carbon sources, including various types of manure, ethanol, molasses, and calcium magnesium acetate, have been tested as biological substrates. These amendments were either placed on the surface (followed by soil wetting) or dissolved directly into water prior to application. At LHAAP, for example, horse manure, chicken manure, and ethanol were tested as soil amendments in small field plots (O'Niell and Nzengung 2003). Up to 99.7% of the perchlorate in the upper 3 feet of the soil column was remediated in 10 months. Similar results were seen at Aerojet's Area 41 site, where cow manure and acetate were used as carbon sources for food.

Ex Situ Soil Bioremediation. Ex situ treatment methods have focused on treatment cells using anaerobic composting or lined treatment cells containing excavated soils. These methods have been evaluated in pilot- and/or full-scale applications. For composting applications, carbon sources, water and, in some cases, bulking agents, are blended with the contaminated soil. In a study conducted at Aerojet, perchlorate-contaminated soils were prepared in a 7-foot-diameter by 5-foot-high compost pile on an impermeable liner. The soil was mixed with carbon amendments, wetted, then covered with a plastic tarp to prevent moisture loss and oxygen intrusion. Perchlorate levels within the compost pile were observed to decline from 23 mg/kg to less than the reporting limit for the study (0.1 mg/kg) within 7 days (Cox et al. 2000). A large-scale soil demonstration was performed at the NWIRP McGregor Area M. Approximately 1500 cubic yards of perchlorate-contaminated soil was excavated and transported to a biotreatment cell. The soil was mixed with amendments (citric acid, nitrogen, phosphorus, and soda ash as a buffer) and saturated with water. Perchlorate was reduced from an estimated average of 500 mg/kg to below the reporting limit (0.1 mg/kg).

Thermal Processes. Thermal remediation is another process investigated for the remediation of perchlorate in soils. Thermal remediation systems generally rely on volatilization or evaporation mechanisms as an integral part of the destruction process. In general, these processes can be applied to soil contaminated with perchlorate; however, because of cost, many of these should probably be considered only when perchlorate-impacted soils are mixed with other hazardous and toxic substances, such as explosives, radionuclides, or various metals (Gangopadhyay et al. 2005). Thermal destruction of perchlorate was tested at MMR and at a Thiokol facility in Utah. At both of those sites, the goal was to destroy not only perchlorate but other explosive materials as well. The MMR test was performed on soils contaminated with perchlorate at up to 100 mg/kg using a thermal desorption process operating at temperatures ranging 725°–900°F. Perchlorate was reduced to <0.001 mg/kg. Higher temperatures would be need for concentrations of perchlorate >100 mg/kg.

6.4 Emerging Processes

Previous sections of this document have given some insight into various processes and technologies that have been used effectively to remove or degrade perchlorate from natural resources. The emerging processes described in this section are all in the developmental stages. To date, the work on the emerging technologies shows great promise for implementation in areas where more traditional technologies are not readily implementable. The new approaches and processes described in this section are being investigated and tested but have yet to be applied or accepted as viable treatment approaches. The successful development and documentation of these approaches will provide remediation practitioners and regulators with additional resources for treating perchlorate contamination that will be both innovative and protective of human and environmental health.

6.4.1 Vapor-Phase Electron Donor Injection

The treatment of contaminated soil using vapor-phase electron donor injection is an emerging technology that has been applied in various ways to a number of contaminants that are amenable to reductive biodegradation processes. So far the process has been shown to be feasible for some types of high explosives (e.g., RDX), some chlorinated VOCs (e.g., perchloroethylene, TCE, and dichloroethylene), and inorganic compounds such as nitrate and perchlorate. This process involves injection of an inert gas (e.g., nitrogen) and volatile, carbon-based substrate (electron donor) to enhance in situ growth of bacteria that use the contaminant as an electron acceptor under reducing conditions in vadose zone soils. After oxygen and residual nitrate have been depleted by aerobic and denitrifying microorganisms, reduction of perchlorate mediated by naturally occurring perchlorate-reducing bacteria usually occurs.

Vapor-phase nutrient injection confers important advantages over processes relaying on infiltration of liquids. Solutions used for infiltration tend to follow preferential pathways as they migrate downward. Use of vapor-phase amendments can result in more uniform distribution of amendments within the vadose zone relative to infiltration. Infiltration can result in leaching of perchlorate to groundwater, whereas vapor-phase injection does not use enough water to cause leaching and favors in situ destruction.

This process will be especially applicable to contaminated areas of the vadose zone that are not easily accessible. Near-surface soils that are easily accessible could be excavated and treated via an ex situ process (see Section 6.3.5). Vapor-phase injection could be applicable under buildings and paved surfaces, around active utility corridors where excavation is not practical, and at depths beyond the practical limit of excavation. This type of nutrient injection would generally not be practical for near-surface soils without the use of an impermeable cover to prevent exchange of oxygen between the atmosphere and the pore space of the soil.

Several projects have tested this type of technology. A field demonstration for treatment of RDX-contaminated soils was conducted at the DOE Pantex site (Rainwater et al. 2001). A commercially available version of a similar process was developed at Savannah River (Jackson, Tan, and Anderson 2003) and patented by the DOE and is being adapted for use in treating perchlorate-contaminated vadose zone soil at a depth of ~100 feet. Treatability studies are in process, to be followed by a pilot-scale installation. Another version of the technology is being developed by Camp, Dresser & McKee, Inc.; a funded ESTCP proposal to test this process is titled "In Situ Bioremediation of Perchlorate in Vadose Zone Soil using Gaseous Electron Donors."

6.4.2 Phytoremediation

Perchlorate remediation by plants has been investigated at a research level. This work has considered the possibility that natural plant processes, with or without the participation of soil microorganisms, may be able to remove perchlorate from the environment. Plant root system processes involving water and nutrient uptake may remove, sequester, or degrade perchlorate dissolved in soil moisture or flowing groundwater. This technology is anticipated to be most applicable to surface soil contamination, shallow groundwater contamination, or surface runoff. However, with the possibility for perchlorate accumulation in plant tissues, it is unclear whether phytoremediation technologies will provide any significant advantages compared to more traditional bioremediation approaches using substrate amendments. The rate at which the plants become established and phytoremediation treatment occurs may also be a consideration (www.hqafcee.brooks.af.mil/products/techtrans/phytorem.asp).

6.4.3 Constructed Wetlands

Constructed wetlands have been used for decades for the management and treatment of many wastewaters, including municipal wastewaters, acid mine drainage, agriculture, petrochemical and textile industries, and storm water (Kadlec and Knight 1996, Moshiri 1994, Hammer 1990). However, constructed wetlands are increasingly being used for the remediation of groundwater or surface water impacted by industrial chemicals and wastes such as landfill leachate (Mulamoottil, McBean, and Rovers 1998) and explosives such as TNT or RDX (Best et al. 1998).

Treatment of perchlorate by constructed wetlands is a potentially effective remediation method due to the following conditions: the reducing conditions of wetland soil/sediment, the high biological activity of wetland soil/sediment in terms of microbial diversity and numbers, the availability of a variety of dissolved carbon sources, the ability of plants to uptake and transform perchlorate, and the ubiquity of bacteria which degrade perchlorate. Biological methods such as constructed wetlands treatment are particularly attractive since they cost-effectively destroy many contaminants, perchlorate included, rather than merely transferring them to another media (e.g., impacted resin or brine).

6.4.4 Nanoscale Bimetallic Particles

With diameters on the order of 100–200 nm, nanoscale bimetallic (iron [Fe]/palladium [Pd]) particles (nanoparticles) have large surface areas and surface reactivity to rapidly degrade redox-amenable contaminants such as chlorinated solvents and perchlorate. In addition, these particles can be effectively delivered to the subsurface. Laboratory research has reportedly shown that nanoscale iron particles are effective reductants and catalysts for a wide variety of contaminants, including perchlorate (Zhang 2003).

6.4.5 Titanium^{3+} Chemical Reduction

Georgetown University has developed a technique using titanous ions (3+) to chemically reduce perchlorate. Several new organic ligands have been developed that have been shown to catalyze reduction of perchlorate by titanous ions (3+) to titanium dioxide and chloride in acidic aqueous media. A preliminary patent application has been filed for this process.

6.4.6 Zero-Valent Iron Reduction under Ultraviolet Light

Gurol and Kim (2000) investigated chemical reduction of perchlorate using iron and iron oxide under various conditions. The main result of their investigation was that the addition of metallic iron (100 g/L) combined with exposing the solutions to ultraviolet light at wavelengths <185 nm achieved 77% reduction in perchlorate and an intensity of 0–9 W/cm^2. A patent (#6,531,065) was issued for this technology in 2003, and a field demonstration program is currently being planned to develop a commercial prototype. The large concentrations of iron needed to make this reaction effective, however, may cause this method to become impracticable due to the potential for fouling, which will in turn inhibit effective ultraviolet exposure.

6.4.7 Electrochemical Reduction

A bench-scale study of electrochemical reduction of perchlorate was conducted using two-chambered batch reactor systems. An ion exchange membrane separated cathodic and anodic compartments, and electrodes consisted of titanium coated with a thin film of titanium dioxide particles. Initial perchlorate concentration ranged 50–500 mg/L. Perchlorate reduction was limited due to the competition among anions for active sites on the electrode surface, with perchlorate being less strongly adsorbed than both sulfate and chloride. The time required for ions in the water to travel to the electrode surface is a design concern in developing a practical full-scale system.

6.4.8 Capacitive Deionization

This technology, patented in 1995 by Lawrence Livermore National Laboratory, relies on the separation of ions from solution by applying an electric field between carbon-aerogel electrodes. The cations and anions are electrosorbed onto the carbon aerogel of the cathode and anode, respectively. Regeneration is accomplished by electrically discharging the electrodes and yields a stream of purified water and a concentrated reject stream similar to membrane and ion exchange processes. In the case of perchlorate removal, the concentrate solution will require further treatment (e.g., via catalytic or biological reduction) before it can be discharged. A limitation of capacitive deionization is that the sorption capacity of the carbon-aerogel anodes decreases with the size of the ion. In the case of perchlorate, a relatively large monovalent anion, the electrosorption capacity is less than the capacity for chloride (Farmer et al. 1996).

6.4.9 Reverse Osmosis

In the reverse osmosis process, the influent stream is driven, under pressure, through a semipermeable membrane that does not allow the contaminants to pass. In this case, the perchlorate is removed from the process in a concentrate or brine, which requires further treatment or destruction. The lack of ionic selectivity in the semipermeable membrane can alter the pH of the effluent stream and make it corrosive. Membrane resilience may also be a performance issue in treating perchlorate.

6.4.10 Electrodialysis

Within the electrodialysis process, water is passed through flow channels of alternating semipermeable and permeable membranes (for either anions or cations) while a direct current voltage potential field is applied across the membranes. As the influent feed flows through the flow channels between the membranes, the direct current voltage potential induces the cations to migrate towards the negatively charged anode through the cation-transfer membrane. Simultaneously, the anions migrate toward the positively charged cathode through the anion-transfer membrane. Electrodialysis also produces a contaminated brine waste by-product, the treatment or destruction of which is an important design consideration.

6.4.11 Monitored Natural Attenuation

There is extensive documentation that perchlorate is biodegradable under anaerobic conditions and can be expected to naturally attenuate in some aquifers. Currently, there is no conclusive evidence for natural attenuation of perchlorate, but studies are under way to document the rate and extent of natural attenuation at selected sites (Lieberman, Knox, and Borden 2005). Without clear, convincing evidence for the natural attenuation of perchlorate, there may be a tendency to push for aggressive remediation approaches whenever perchlorate is detected. While aggressive remediation is warranted at some sites, there may be other sites where monitored natural attenuation is an appropriate approach.

6.4.12 Nanofiltration/Ultrafiltration

Nanofiltration and ultrafiltration are membrane treatment technologies like reverse osmosis. In these technologies, the synthetic porous material of membranes acts like a shield, preventing particles of a defined size or larger from passing through. A water pressure higher than that used with other methods of filtration then pumps water through the membrane. Membranes are classified by the size of particle that the membrane removes (AWWA 2001). These membrane filtration technologies have high energy requirements and produce brines equal to 20% of the volume of groundwater treated. The brine contains high TDS and perchlorate concentrations that require treatment or further disposal. The American Water Works Association is currently funding ongoing research to investigate the feasibility of membrane filtration technology for perchlorate removal in water sources of different quality.

6.4.13 Catalytic Gas Membrane

This emerging technology, which is in the early stages of development, is based on the fact that reduction of perchlorate by hydrogen is thermodynamically favorable. However, the reaction is kinetically very slow in dilute solutions at relevant groundwater temperatures due to the high activation energy required to initiate the reaction. Use of a proper catalyst is thus necessary to facilitate perchlorate reduction in a time frame that would be potentially useful in a water or waste stream treatment scenario. Catalytic gas membrane techniques may eventually be useful for the removal of perchlorate from water; however, convincing data are currently lacking. Work is ongoing to find and coat an effective catalyst onto the outer surface of an inorganic membrane such as stainless steel or carbon materials. The membrane system is envisioned as a tubular configuration in which hydrogen gas would be purged into system. The action exhibited by the catalyst on the membrane surface would bring about the reduction of perchlorate by hydrogen.

6.5 Technology Summary

This section briefly touched upon the current state of perchlorate remediation technologies. To date, perchlorate remediation has focused primarily on groundwater cleanup with ion exchange technology and ex situ bioremediation and on a pilot-scale in situ bioremediation. Full scale in situ bioremediation systems are likely to be implemented at specific sites by the time this document is published. A number of remediation technologies for both soil and water have been implemented at only bench and pilot scale and have yet to be used as full-scale remediation systems.

The technology and regulatory guidance document to be completed by the ITRC Perchlorate Team will discuss in detail the remediation technologies touched upon in this review and include various case studies as well as any new information since the finalization of this document.

7. REFERENCES

Achenbach, L. A., U. Michaelidou, R. A. Bruce, J. Fryman, and J. D. Coates. 2001. "*Dechloromonas agitata* gen. nov., sp. nov. and *Dechlorosoma suillum* gen. nov., sp. nov., Two Novel Environmentally Dominant (Per)chlorate-Reducing Bacteria and Their Phylogenetic Position," *International Journal of Systematic and Evolutionary Microbiology* **51**: 527–33.

AFCEE (Air Force Center for Environmental Excellence). 1997. *Model Field Sampling Plan*, Vers. 1.1.

"Air Force Unveils New Cleanup System at AFRL." 2001. Edwards Air Force Base, Calif. Available at www.edwards.af.mil/penvmng/Documents/RTS/2001/JUL01/Jul01pg1.htm.

American Thyroid Association. 2003. "Thyroid Disease and Pregnancy." Available at www.thyroid.org/patients/brochures/Thyroid_Dis_Pregnancy_broch.pdf.

Arizona Department of Environmental Quality. n.d. "Apache Powder." Available at http://www.azdeq.gov/environ/waste/sps/download/state/apache.pdf.

Auso, E., R. Lavado-Autric, E. Cuevas, F. Escobar del Rey, G. Morreale de Escobar, and P. Berbel. 2003. "A Moderate and Transient Deficiency of Maternal Thyroid Function at the Beginning of Fetal Neocorticogenesis Alters Neuronal Migration," *Endocrinology* **145**: 4037–47.

AWWA (American Water Works Association). 2001. "Membrane Technology Comes into Its Own in Last Few Years," *AWWA MainStream*. Available at www.awwa.org/Communications/mainstream/Archives/2001/November/ms1101membrane.cfm.

Bao, H., and B. Gu. 2004. "Natural Perchlorate Has a Unique Oxygen Isotope Signature," *Environmental Science and Technology* **38**(19): 5073–77.

Bates, R. L. 1969. *Geology of the Industrial Rocks and Minerals*. New York: Dover Publications.

Beisel, T. H., M. Craig, and M. Perlmutter. 2004. "Ex Situ Treatment of Perchlorate-Contaminated Groundwater," presented at the National Ground Water Association Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy, Costa Mesa, Calif., June 3–4.

Bekkedal, M. Y. V., D. Arffsten, and D. Mattie. 2004. "An Evaluation of Neurobehavioral Tests Used to Assess the Neurodevelopmental Effects of Early Ammonium Perchlorate Exposure," *Journal of Toxicology and Environmental Health A* **67**: 835–44.

Bekkedal, M. Y. V., T. Carpenter, J. Smith, C. Ademujohn, D. Maken, and D. R. Mattie. 2000. *A Neurodevelopmental Study of the Effects of Oral Ammonium Perchlorate Exposure on the Motor Activity of Pre-Weanling Rat Pups*. TOXDET-00-03. Wright-Patterson AFB, Ohio: Naval Health Research Center Detachment (Toxicology).

Bellinger, D. C. 2004. What Is an Adverse Effect? A Possible Resolution of Clinical and Epidemiological Perspectives on Neurobehavioral Toxicity," *Environmental Research* **95**: 394–405.

Best, E. P. H., S. L. Sprecher, S. L. Larson, and H. L. Fredrickson. 1998. *Environmental Behavior and Fate of Explosives from Groundwater from the Milan Army Ammunition Plant in Aquatic and Wetland Plants: Fate of TNT and RDX*. SFIM-AEC-ET-CR-97060. Prepared for the U.S. Army Environmental Center by the U.S. Army Engineer Waterways Experiment Station, Environmental Laboratory, Vicksburg, Miss.

Blaster's Handbook. 16th ed. 1980. Wilmington, Del.: E. I. duPont de Nemours.

Borden, R. C., N. L. Lindow, and B. X. Rodriguez. 2004. "Treatment of Nitrate, Perchlorate, Chromate, and ARID Using Edible Oils," in *Proceedings, 4th International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, Calif. Columbus, Ohio: Battelle Press.

Brabant, G., P. Bergmann, C. M. Kirsch, J. Kohrle, R. D. Hesch, and A. von zur Muhlen. 1992. "Early Adaptation of Thyrotropin and Thyroglobulin Secretion to Experimentally Decreased Iodine Supply in Man," *Metabolism* **41**: 1093–96.

Brandhuber, P., and S. Clark. 2005. "Perchlorate Occurrence Mapping." American Water Works Association. Available at www.awwa.org/advocacy/perchlorateoccurrencereportfinalb02092005.pdf.

Braverman, L. E., X. He, S. Pino, M. Cross, B. Magnani, S. H. Lamm, M. B. Kruse, A. Engel, K. S. Crump, and J. P. Gibbs. 2005. "The Effect of Perchlorate, Thiocyanate, and Nitrate on Thyroid Function in Workers Exposed to Perchlorate Long Term," *Journal of Clinical Endocrinology and Metabolism* **90**: 700–06.

Braverman, L. E., X. He, S. Pino, B. Magnani, and A. Firek. 2004. "The Effect of Low-Dose Perchlorate on Thyroid Function in Normal Volunteers," (abstract) *Thyroid* **14**(9): 691.

Brechner, R. J., G. D. Parkhurst, W. O. Humble, M. B. Brown, and W. H. Herman. 2000. "Ammonium Perchlorate Contamination of Colorado River Drinking Water Is Associated with Abnormal Thyroid Function in Newborns in Arizona," *Journal of Occupational and Environmental Medicine* **42**: 777–82.

Bryan, E. H. 1966. "Application of the Chlorate BOD Procedure to Routine Measurement of Wastewater Strength," *Journal of the Water Pollution Control Federation* **38**: 1350–62.

Buffler, P. A., M. A. Kelsh, E. C. Lau, C. H. Edinboro, and J. C. Barnard. 2004. *Epidemiologic Studies of Primary Congenital Hypothyroidism and Newborn Thyroid Function Among California Residents*. Final Report. Berkeley, Calif.: University of California.

CalEPA (California Environmental Protection Agency). 2002. *Public Health Goal for Perchlorate in Drinking Water*. Office of Environmental Health Hazard Assessment, Pesticide Environmental Toxicology Section.

CalEPA. 2004. *Perchlorate Contamination Treatment Alternatives*, Draft. Office of Pollution Prevention and Technology Development, Department of Toxic Substances Control.

Calgon Carbon Corporation. n.d. "Perchlorate Info Web Site." Available at www.perchlorateinfo.com.

Calgon Carbon Corporation, 1999. Executive Summary, Pilot Study conducted by Calgon Carbon Corporation at JPL, 1998-1999.

California Department of Health Services. 2005. "Perchlorate in California Drinking Water: Monitoring Update." Available at www.dhs.ca.gov/ps/ddwem/chemicals/perchl/monitoringupdate.htm.

California Department of Toxic Substances Control. n.d. "List of Perchlorate Materials." Available at www.dtsc.ca.gov/HazardousWaste/Perchlorate/HWMP_List_Perchlorate.pdf.

California Department of Toxic Substances Control. n.d. "Perchlorate Use Descriptions," provided by T. R. Hathaway via e-mail.

Canadian Centre for Occupational Health and Safety. 2003. "Perchloric Acid Solutions Greater than 72.5%," CHEMINFO Chemical Profile. Available at http://intox.org/databank/documents/chemical/perchac/cie108.htm.

Capen, C. C. 1997. "Mechanistic Data and Risk Assessment of Selected Toxic End Points of the Thyroid Gland," *Toxicologic Pathology* **25**: 39–48.

Carr, J. A., W. L. Goleman, T. Anderson, R. Bounds, and R. Kendall. 2002. *The Effects of Contaminated and Reference Surface Waters on Metamorphosis in* Xenopus laevis *Using a Modified USEPA Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC, USEPA, 1998) Tier 1 Tail Resorption Assay*. Final report submitted to the Strategic Environmental Research and Development Program, Project No. T9700.2. Lubbock, Tex.: Texas Tech University, Institute of Environmental and Human Health.

Chang, S., C. Crother, S. Lai, and S. Lamm. 2003. "Pediatric Neurobehavioral Diseases in Nevada Counties with Respect to Perchlorate in Drinking Water: An Ecological Inquiry," *Birth Defects Research A* **67**: 886–92.

Chaudhuri, S. K., S. M. O'Connor, R. L. Gustavson, L. A. Achenbach, and J. D. Coates. 2002. "Environmental Factors that Control Microbial Perchlorate Reduction," *Applied and Environmental Microbiology* **68**(9): 4425–30.

Cheng, Q., L. Perlmutter, P. N. Smith, S. T. McMurry, W. A. Jackson, and T. A. Anderson. 2004. "A Study on Perchlorate Exposure and Absorption in Beef Cattle." *Journal of Agricultural and Food Chemistry* **52**: 3456–61.

Clewell, R. A., E. A. Merrill, K. O. Yu, D. A. Mahle, T. R. Sterner, D. R. Mattie, P. J. Robinson, J. W. Fisher, and J. M. Gearhart. 2003a. "Predicting Fetal Perchlorate Dose and Inhibition of Iodide Kinetics During Gestation: A Physiologically Based Pharmacokinetic Analysis of Perchlorate and Iodide Kinetics in the Rat," *Toxicological Sciences* **73**: 235–55.

Clewell, R. A., E. A. Merrill, K. O. Yu, D. A. Mahle, T. R. Sterner, J. W. Fisher, and J. M. Gearhart. 2003b. "Predicting Neonatal Perchlorate Dose and Inhibition of Iodide Uptake in the Rat During Lactation Using Physiologically Based Pharmacokinetic Modeling," *Toxicological Sciences* **74**: 416–36.

Coates, J. D., U. Michaelidou, R. A. Bruce, S. M. O'Connor, J. N. Crespi, and L. A. Achenbach. 1999. "Ubiquity and Diversity of Dissimilatory (Per)chlorate-Reducing Bacteria," *Applied and Environmental Microbiology* **65**(12): 5234–41.

Coates, J. D., U. Michaelidou, S. M. O'Connor, R. A. Bruce, and L. A. Achenbach. 2000. "The Diverse Microbiology of (Per)chlorate Reduction," pp. 257–70 in *Perchlorate in the Environment*, E. T. Urbansky, ed. New York: Kluwer/Plenum.

Coates, J. D., and J. Pollock. 2003. "Potential for In Situ Bioremediation of Perchlorate in Contaminated Environments," presented at the 7th International In Situ and On-Site Bioremediation Symposium, Orlando, Fla.

Conkling, J. A. 1990. "Pyrotechnics," *Scientific American* **263**(1): 96–102.

Corwin, D. 1998. "Rotary Kilns in the Hazardous Waste Industry," in *Standard Handbook of Hazardous Waste Treatment and Disposal*, 2nd ed., H. M. Freeman, ed. New York: McGraw Hill.

Cox, E. E., E. Edwards, S. Neville, and M. Girard. 2000. "Cost-Effective Bioremediation of Perchlorate in Soil and Groundwater," presented at Perchlorate Treatment Technology Workshop, 5th Annual Joint Services Pollution Prevention and Hazardous Waste Management Conference and Exhibition, San Antonio, Tex., August 21–24.

Cox, E. E., M. McMaster, and S. L. Neville. 2001. "Perchlorate in Groundwater: Scope of the Problem and Emerging Remedial Solutions," pp. 27–32 in *Proceedings, 36th Annual Engineering Geology and Geotechnical Engineering Symposium*, Las Vegas.

Cramer, R. J., C. A Yates, P. B. Hatzinger, and J. Diebold. 2004. *Naval Ordnance Safety and Security Activity*. Naval Sea Systems Command Technical Report NOSSA-TR-2004-001.

Crane H. M., D. B. Pickford, T. H. Hutchinson, and J. A. Brown. 2005. "Effects of Ammonium Perchlorate on Thyroid Function in Developing Fathead Minnows, *Pimephales promelas*," *Environmental Health Perspectives* **113**(4): 396–401.

Crockett, A. B., H. D. Craig, T. F. Jenkins, and W. E. Sisk. 1996. *Field Sampling and Selecting On-Site Analytical Methods for Explosives in Soil*. EPA/540/R-97/501, Federal Facilities Forum Issue. U. S. Environmental Protection Agency, Office of Sold Waste and Emergency Response.

Crump, C., P. Michaud, R. Tellez, C. Reyes, G. Gonzalez, E. L. Montgomery, K. S. Crump, G. Lobo, C. Becerra, and J. P. Gibbs. 2000. "Does Perchlorate in Drinking Water Affect Thyroid Function in Newborns or School-Age Children?" *Journal of Occupational and Environmental Medicine* **42**: 603–12.

Dasgupta, P. K., P. J. Nartubekabgim, W. A. Jackson, T. A. Anderson, K. Tian, R. W. Tock, and S. Rajagopalan. 2005. "The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes," *Environmental Science and Technology* **39**(6): 1569–75.

Dean, K. E., R. M. Palachek, J. M. Noel, R. Warbritton, J. Aufderheide, and J. Wireman. 2004. "Development of Fresh Water-Quality Criteria for Perchlorate," *Environmental Toxicology and Chemistry* **23**: 1441–51.

Dickerson, D. 2003. *Update on Perchlorate Groundwater Pollution Within the Los Angeles Region*. Memorandum. Los Angeles: California Regional Water Quality Control Board. Available at www.swrcb.ca.gov/~rwqcb4/html/perchlorate/03_0428_PerchlorateUpdate.pdf.

Dionex Corporation. 2004. "Determination of Perchlorate in Environmental Waters by Ion Chromatography Coupled with Electrospray Mass-Spectrometry (IC-MS)," Application Note 151. Available at www1.dionex.com/en-us/webdocs/application/industry/environmental/ic/AN151_V19.pdf.

Di Rienzo, R. P., K. Lin, T. T. McKay, and R. W. Wade. 2004. "Analysis of Perchlorate in Drinking Water, Groundwater, Saline Water, Soil, and Biota by LC/MS," submitted for publication to *Analytical Chemistry*.

DoD EDQW (U.S. Department of Defense Environmental Data Quality Workgroup). 2002. *Department of Defense Quality Systems Manual for Environmental Laboratories*, Vers. 2. Available at www.navylabs.navy.mil/Archive/DoDV2_Jun02_Final.pdf.

DoD EDQW. 2003. "State of the Art in Analysis of Perchlorate in Environmental Samples." Meeting summary, Joint IDQTF/DoD EDQW Roundtable. Available at www.navylabs.navy.mil/Archive/RoundtableMinutes.pdf.

DoD EDQW. 2004. "Interim Guidance on Sampling and Testing for Perchlorate." Memorandum from Principal Assistant Deputy Under Secretary of Defense (Installations and Environment) to Components, dated 29 September. Available at www.navylabs.navy.mil/Archive/PerchlorateInterim.pdf.

Dondero, A. C. 2001. *Phytoremediation of Perchlorate under Greenhouse and Natural Conditions*. Masters thesis, University of Georgia, Athens.

Downey, R. 2002. "Global Changes in Potash Capacity and Use: Implications for Trade," presented at the International Fertilizer Association Production and International Trade Conference, Quebec City, Canada. Available at www.fertilizer.org/ifa/form/pub_det.asp?id=1080.

Duncan, P. B., Morrison, R. D. and E. Varicka. 2005. "Forensic Identification of Anthropogenic and Naturally Occurring Sources of Perchlorate," *Environmental Forensics* **6**(2): 205–11.

DuPont. n.d. "DuPont Methylamines, Uses." Available at www.dupont.com/methylamines/uses.html.

Durand, J. 1938. "Recherches sur l'elimination des perchlorates, sur leur repartition dans les organs et sur leur toxicite [Research on the Elimination of Perchlorate, Its Distribution in Organs and Its Toxicity]," *Bulletin de la Societe de Chimie Biologique* **20**: 423–33 (cited in Stanbury and Wyngarrden 1952).

Eichler, O. 1929. "Our pharmakologie der perchloratwirkung [The Pharmacology of the Perchlorate Effect]," Naunyn-Schmiedebergs *Arch. Exp. Path. Pharmakol.* **144**: 251–60 (cited in Stanbury and Wyngaarden 1952)

Ellington, J. J., N. L. Wolfe, A. G. Garrison, J. J. Evans, J. K. Avants, and Q. Teng. 2001. "Accumulation of Perchlorate in Tobacco Plants and Tobacco Products," *Environmental Science and Technology* **35**: 3213–18.

Ericksen, G. E. 1981. *Geology and Origin of the Chilean Nitrate Deposits*. USGS Professional Paper 1188.

Ericksen, G. E. 1983. "The Chilean Nitrate Deposits," *American Scientist* **71**: 366–74.

Erickson, Britt A. 2004. "Tracing the Origin of Perchlorate," *Analytical Chemistry* **76**: 388A–89A.

EWG (Environmental Working Group). 2004a "Rocket Fuel Contamination in California Milk." Available at www.ewg.org/reports/rocketmilk.

EWG. 2004b. "Rocket Fuel in Lettuce." Available at www.ewg.org/reports/rocketlettuce.

EWG. 2004c. "Suspect Salads." Available at www.ewg.org/reports/suspectsalads.

Farmer, J. C., D. V. Fix, G. V. Mack, R. W. Pehala, and J. F. Poco. 1996. "Capacitive Deionization of NH4CLO4 Solutions with Carbon Aerogel Electrodes," *Journal of Applied Electrochemistry* **26**: 1007–18.

Federal Register. 2005. Proposed Rules, Vol. 70, No. 161, August 22, 2005. Available at www.epa.gov/safewater/ucmr/ucmr2/regulations.html.

Felz, M. W., and A. C. Forren. 2004. “Profound Hypothyroidism—A Clinical Review with Eight Recent Cases: Is It Right before Our Eyes?” *Southern Medical Journal* **97**: 490–98.

Fertilizer Institute. n.d. “Perchlorate.” Available at www.tfi.org/Issues/perchloratepage.asp.

Flowers, T. C., and J. R. Hunt. 2000. “Long-Term Release of Perchlorate as a Potential Source of Groundwater Contamination,” Chap. 14 in *Perchlorate in the Environment*, E. T. Urbansky, ed. New York: Kluwer/Plenum.

Frisch, M. A. 1998. “Supercritical Water Oxidation,” in *Standard Handbook of Hazardous Waste Treatment and Disposal*, 2nd ed., H. M. Freeman, ed. New York: McGraw Hill.

Gangopadhyay, S., G. Meyers, I. T. Osgerby, and P. Nixon. 2005. “Thermal Treatment of Explosives and Perchlorate in Soil Media,” Incineration and Thermal Treatment Technologies Conference, May 2005.

GAO (U.S. Government Accounting Office). 2005. “Perchlorate: A System to Track Sampling and Cleanup Results Is Needed.” GAO-05-462. Available at http://www.gao.gov/new.items/d05462.pdf.

Gerlach, R. W., and J. M. Nocerino. 2003. *Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples*. EPA/600/R-03/027. Available at www.clu-in.org/download/char/epa_subsampling_guidance.pdf.

GFS Chemicals, Inc. n.d. “Perchlorate Compounds.” Available at http://gfschemicals.com/productcatalog/Perchlorate_Compounds.asp.

Gibbs, J. P., R. Ahmad, K. S. Crump, D. P. Houck, T. S. Leveille, J. E. Findley, and M. Francis. 1998. “Evaluation of a Population with Occupational Exposure to Airborne Ammonium Perchlorate for Possible Acute or Chronic Effects on Thyroid Function,” *Journal of Occupational and Environmental Medicine* **40**: 1072–82.

Giedd, J. N., J. Blumenthal, N. O. Jeffries, F. X. Castellanos, H. Liu, A. Zijdenbos, T. Paus, A. C. Evans, and J. L. Rapoport. 1999. “Brain Development during Childhood and Adolescence: A Longitudinal MRI Study,” *Nature Neuroscience* **2**(10): 861–63.

Glinoer, D., F. Delange, I. Laboureur, P. De Nayer, B. Lejeune, J. Kinthaert, and P. Bourdoux. 1992. “Maternal and Neonatal Thyroid Function at Birth in an Area of Marginally Low Iodine Intake,” *Journal of Clinical Endocrinology and Metabolism* **75**(3): 800–05.

Goleman W. L., L. J. Urquidi, T. A. Anderson, E. E. Smith, R. J. Kendall, and J. A. Carr. 2002. “Environmentally Relevant Concentrations of Ammonium Perchlorate Inhibit Development and Metamorphosis in *Xenopus laevis*,” *Environmental Toxicology and Chemistry* **21**: 424–30.

Greer, M. A., G. Goodman, R. C. Pleus, and S. E. Greer. 2002. “Health Effects Assessment for Environmental Perchlorate Contamination: The Dose Response for Inhibition of Thyroidal Radioiodine Uptake in Humans,” *Environmental Health Perspectives* **110**: 927–37.

Gregory, T. C. 1939. *Uses and Applications of Chemicals and Related Materials*, Vol. I. New York: Reinhold.

Gregory, T. C. 1944. *Uses and Applications of Chemicals and Related Materials*, Vol. II. New York: Reinhold.

Gu, B., G. M. Brown, L. Maya, M. J. Lance, and B. A. Moyer, 2001, “Regeneration of Perchlorate (ClO_4^-) Loaded Anion Exchange Resins by a Novel Tetrachloroferrate ($FeCl_4^-$) Displacement Technique,” *Environmental Science and Technology* **35**: 3363–68.

Gunston, B. 1979. *The Illustrated Encyclopedia of the World's Rockets and Missiles*. New York: Crescent.

Gurol, M. D., and K. Kim, 2000. "Investigation of Perchlorate Removal in Drinking Water Sources by Chemical Methods," Chap. 10 in *Perchlorate in the Environment*, E. T. Urbansky, ed. New York: Kluwer/Plenum.

GWRTAC (Ground Water Remediation Technologies Analysis Center). 2001. *Perchlorate Treatment Technologies*, 1st ed. Technology status report.

Hackenthal, E., R. Mannheim, R. Hackenthal, and R. Becher. 1964. "Die reduktion von perchlorat durch bacterien. I. Untersuchungen an intakten zellen," *Biochem. Pharm.* **13**: 195–206.

Haddow J. E., G. E. Palomaki, W. C. Allan, J. R. Williams, G. J. Knight, J. Gagnon, C. E. O'Heir, M. L. Mitchell, R. J. Hermos, S. E. Waisbren, J. D. Faix, and R. Z. Klein. 1999. "Maternal Thyroid Deficiency during Pregnancy and Subsequent Neuropsychological Development of the Child," *New England Journal of Medicine* **341**: 549–55.

Hammer, D. A., ed. 1990. *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial, and Agricultural*. Boca Raton, Fla.: CRC Press.

Hatzinger, P. B. 2002. *In Situ Bioremediation of Perchlorate*. Final Report to the Strategic Environmental Research and Development Program, Project CU-1163.

Hatzinger, P. B. 2005. "Perchlorate Biodegradation for Water Treatment," *Environmental Science and Technology* **39**: 239A–47A).

Hatzinger, P. B., M. R. Greene, S. Frisch, A. P. Togna, J. Manning, and W. J. Guarini. 2000. "Biological Treatment of Perchlorate-Contaminated Groundwater Using Fluidized-Bed Reactors," pp. 115–22 in *Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds*, G. B. Wickramanayake, A. R. Gavaskar, and N. Gupta, eds. Columbus, Ohio: Battelle Press.

Hatzinger, P. B., M. C. Whittier, M. D. Arkins, C. W. Bryan, and W J Guarini. 2002. "In Situ and Ex Situ Bioremediation Options for Treating Perchlorate in Groundwater," *Remediation* **12**: 69–86.

Hautman, D. P., D. J. Munch, A. D. Eaton, and A. W. Haghani. 1999. *Method 314.0, Determination of Perchlorate in Drinking Water Using Ion Chromatography*, Rev. 1.0. Cincinnati: U.S. Environmental Protection Agency, National Risk Management Research Laboratory. Available at www.epa.gov/OGWDW/methods/met314.pdf.

Heindel, J. J., and R. T. Zoeller. 2003. "Thyroid Hormone and Brain Development: Translating Molecular Mechanisms to Population Risk," *Thyroid* **13**(11): 1001–04.

Henry, B. M., D. R. Griffiths, J. R. Gonzales, and P. E. Haas, 2003. "Strategies Using Vegetable Oil for Enhanced Bioremediation of Chlorinated Solvents," presented at the 7th International In Situ and On-Site Bioremediation Symposium, Orlando, Fla.

Herman, D. C., and W. T. Frankenberger, Jr. 1998. "Microbial-Mediated Reduction of Perchlorate in Groundwater," *Journal of Environmental Quality* **27**: 750–54.

Heyerdahl, S. 2001. "Long-Term Outcome in Children with Congenital Hypothyroidism," *Acta Paediatrica* **90**: 1220–22.

Hines, M. E., F. von Hippel, J. Kennish, M. Mach, and D. Pilson. 2002. *Biological Effects of Inadvertent Perchlorate Releases During Launch Operations*. Prepared under contract with

TRW Space & Electronics for U.S. Air Forced Space and Missile Systems Center, Environmental Branch.

Hjeresen, D., S. Rae, B. Beers, M. Saladen, C. L. Nylander, A. Barr, A. Pope, J. Dziewinski, J. Scott, R. Holcomb, D. Hollis, L. Dale, L. Williams, B. Strietelmeier, B. Carlson, R. Alexander, P. Worland, S. Hanson, J. Stine, M. Hiskey, J. Archuleta, S. Kinkead, A. Sherrard, P. Longmire, M. Witkowski, and M. Gard. 2003. *Los Alamos National Laboratory Perchlorate Issues Update*. LA-CP-03-0441. Los Alamos, N.M.: Los Alamos National Laboratory.

Hollowell, J. G., N. W. Staehling, W. D. Flanders, W. H. Hannon, E. W. Gunter, C. A. Spencer, L. E. Braverman. 2002. "Serum TSH, T4, and Thyroid Antibodies in the United States Population (1988 to 1994): National Health and Nutrition Examination Survey (NHANES III)," *Journal of Clinical Endocrinology and Metabolism* **87**: 489–99.

Howdeshell, K. L. 2002. "A Model of the Development of the Brain as a Construct of the Thyroid System," *Environmental Health Perspectives* **110**: 337–47.

Hummel Croton, Inc. 2004. "Pyrotechnics." Available at www.hummelcroton.com/pyro.html.

Hunley, J. D. 1999. "The History of Solid-Propellant Rocketry: What We Do and Do Not Know," presented at the 35th AIAA, ASME, SAE, ASEE Joint Propulsion Conference and Exhibit, Los Angeles, Calif., June 20–23. American Institute of Aeronautics and Astronautics, Inc.

Hunter, W. J. 2002. "Bioremediation of Chlorate or Perchlorate Contaminated Water Using Permeable Barriers Containing Vegetable Oil," *Current Microbiology* **45**: 287–92.

IME (Institute of Makers of Explosives). 2002. *Glossary of Commercial Explosives Industry Terms*. Safety Library Publications (SLP) No. 12. Washington, D.C.

ISEE (International Society of Explosives Engineers). 2003. *Blasters' Handbook*, 17th ed., p. 82.

ITRC (Interstate Technology & Regulatory Council). 2002. *A Systematic Approach to In Situ Bioremediation in Groundwater*. ISB-8. Washington, D.C.: ITRC In Situ Bioremediation Team. Available on the Internet at www.itrcweb.org.

Jackson, W. A., J. Preethi, P. Laxman, K. Tan, P. N. Smith, L. Yu, and T. A. Anderson. 2005. "Perchlorate Accumulation in Forage and Edible Vegetation," *Journal of Agricultural Food Chemistry* **53**: 369–73.

Jackson, W. A., K. A. Rainwater, T. Anderson, T. M. Lehman, Tock, R. Mollhagen, and M. Ridley. 2003. "Distribution and Potential Sources of Perchlorate in the High Plains Region of Texas: Final Report Phase 1." Water Resources Center, Texas Tech University.

Jackson, W. A., K. A. Rainwater, T. Anderson, T. M. Lehman, M. Ridley, S. Walden, and W. R. Tock. 2004. "Occurrence and Source of Perchlorate in the High Plains Aquifer System of Texas," presented at the 11th Symposium in GRA's Series on Groundwater Contaminants, Glendale, Calif.

Jackson, W. A., K. Tan, and T. Anderson. 2003. "Distribution, Degradation, and Uptake of Perchlorate (PC) in Contaminated Stream Sediments," presented at the 7th International In Situ and On-Site Bioremediation Symposium, Orlando, Fla.

Jasinski, S. M., D. A. Kramer, J. A. Ober, and J. P. Searls. 1999. "Fertilizers—Sustaining Global Food Supplies." USGS Fact Sheet 155-99. Available at http://pubs.usgs.gov/fs/fs155-99/fs155-99.html.

Jenkins, T. F., C. L. Grant, G. S. Brar, P. G. Thorne, T. A. Ranney, and P. W. Schumacher. 1996. *Assessment of Sampling Error Associated with the Collection and Analysis of Soil Samples at Explosives Contaminated Sites*. Special Report 96-15. Hanover, N.H.: U.S. Cold Regions Research and Engineering Laboratory. Available at www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR96_15.pdf.

Jenkins, T. F., C. L. Grant, G. S. Brar, P. G. Thorne, P. W. Schumacher, and T. A. Ranney. 1997a. *Assessment of Sampling Error Associated with the Collection and Analysis of Soil Samples at Explosives Contaminated Site*s*: Field Analytical Chemistry and Technology*, Vol. 1, pp. 151–63.

Jenkins, T. F., T. A. Ranney, A. D. Hewitt, M. E. Walsh, and K. L. Bjella. 2004. *Representative Sampling for Energetic Compounds at an Antitank Firing Range*. ERDC/CRREL TR-04-7. Hanover, N.H.: U.S. Army Cold Regions Research and Engineering Laboratory. Available at www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR04-7.pdf.

Jenkins, T. F., P. G. Thorne, M. E. Walsh, C. L. Grant, S. Thiboutot, G. Ampleman, T. A. Ranney, and M. H. Stutz. 1997b. "Sampling Strategy for Site Characterization at Explosives-Contaminated Sites," in *Proceedings, 2nd Tri-service Environmental Technology Workshop*, St. Louis.

Jenkins, T. F., M. E. Walsh, P. G. Thorne, S. Thiboutot, G. Ampleman, T. A. Ranney, and C. L Grant. 1997c. *Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at a Firing Range Contaminated with HMX*. Special Report 97-22. Hanover, N.H.: U.S. Army Cold Regions Research and Engineering Laboratory. Available at www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR97_22.pdf.

Kansas Department of Health and Environment. n.d. Bureau of Environmental Remediation Identified Sites List Information. Available at http://kensas.kdhe.state.ks.us/pls/certop/Iop?id=C506471298.

Kadlec, R. H., and R. L. Knight. 1996. *Treatment Wetlands*. Boca Raton, Fla.: Lewis.

Keil, D., D. A. Warren, M. Jenny, J. EuDaly, and R. Dillard. 1999. *Effects of Ammonium Perchlorate on Immunotoxicological, Hematological, and Thyroid Parameters in B6C3F1 Female Mice*. DSWA01-97-0008. Charleston, S.C.: Medical University of South Carolina.

Kelsh, M. A., P. A. Buffler, J. J. Daaboul, G. W. Rutherford, E. C. Lau, J. C. Barnard, A. K. Exuzides, A. K. Madl, L. G. Palmer, and F. W. Lorey. 2003. "Primary Congenital Hypothyroidism, Newborn Thyroid Function and Environmental Perchlorate Exposure Among Residents of a Southern California Community," *Journal of Occupational and Environmental Medicine* **45**: 1116–27.

Kengen, S. W. M., G. B. Rikken, W. R. Hagen, C. G. Van Ginkeland, and A. J. M. Stams. 1999. "Purification and Characterization of (Per)chlorate Reductase from the Chlorate-Respiring Strain GR-1," *Journal of Bacteriology* **181**: 6706–11.

Kirk, A. B., P. K. Martinelango, K. Tian, A. Dutta, E. E. Smith, and P. Dasgupta. 2005 "Perchlorate and Iodide in Dairy and Breast Milk," *Environmental Science and Technology*. **35:** 2011–17.

Krauter, P. W. 2001. "Using a Wetland Bioreactor to Remediate Ground Water Contaminated with Nitrate (mg/L) and Perchlorate (μg/L)," *International Journal of Phytoremediation* **3**(4): 415–33.

Kuhlman, M., and I. T. Osgerby. 2003. "Modeling Hot Air Vapor Extraction of Trichlorobenzene at the Corinna, Maine Superfund Site," presented at the Environmental and Natural Resource Conference, Fort Worth, Tex.

Lamm, S. H. 2003. "Perchlorate Exposure Does Not Explain Differences in Neonatal Thyroid Function Between Yuma and Flagstaff," (letter) *Journal of Occupational and Environmental Medicine* **45**(11): 1131–32.

Lamm, S. H., L. E. Braverman, F. X. Li, K. Richman, S. Pinoand, and G. Howearth. 1999. "Thyroid Health Status of Ammonium Perchlorate Workers: A Cross-Sectional Occupational Health Study," *Journal of Occupational and Environmental Medicine* **41**: 248–60.

Lamm, S. H., and M. Doemland. 1999. Has Perchlorate in Drinking Water Increased the Rate Of Congenital Hypothyroidism?" *Journal of Occupational and Environmental Medicine* **41**: 409–11.

Lang, V. I., K. R. Bohman, J. Tooley, S. A. Frolik, E. W. Fournier, B. B. Brady, and D. C. Nealy. 2002. *Assessment of Perchlorate Releases in Launch Operations II*. SMC-TR-03-13, Aerospace Report No. TR-2003(1306)-1. The Aerospace Corporation, prepared for Space and Missile Systems Center Air Force Command, Los Angeles Air Force Base, Calif. Available at http://ax.losangeles.af.mil/axf/studies/docs/tr200313051.pdf.

Langan, B. S., and R. J. Borrego. 2004. "Overview of Available Treatment Options for Perchlorate Removal and Destruction in Drinking Water," p. 31 in *Proceedings, NGWA Conference on MTBE and Perchlorate: Assessment, Remediation and Public Policy*.

Lavado-Autric, R., E. Auso, J. V. Garcia-Velasco, M. del Carmen Arufe, F. Escobar del Rey, P. Berbel, and G. Morreale de Escobar. 2003. "Early Maternal Hypothyroxinemia Alters Histogenesis and Cerebral Cortex Cytoarchitecture of the Progeny," *Journal of Clinical Investigation* **111**(7): 1073–82.

Lawrence, J. E., S. H. Lamm, S. Pino, K. Richman, and L. E. Braverman. 2000. "The Effect of Short-Term Low-Dose Perchlorate on Various Aspects of Thyroid Function," *Thyroid* **10**: 659–63.

Lawrence, J. E., S. H. Lamm, and L. E. Braverman, 2001. "Low-Dose Perchlorate (3 mg Daily) and Thyroid Function," *Thyroid* **11**: 295.

Lee, C. C., and G. L. Huffman. 1998. "Plasma Systems," in *Standard Handbook of Hazardous Waste Treatment and Disposal*, 2nd ed., H. M. Freeman, ed. New York: McGraw Hill.

Lee, K. C., and B. E. Rittmann. 2002. "Applying a Novel Autohydrogenotrophic Hollow-Fiber Membrane Biofilm Reactor for Denitrification of Drinking Water," Water Research **36**: 2040–52.

Lefond, S. J., ed. 1975. *Industrial Rocks and Minerals*, 4th ed. American Institute of Mining, Metallurgical, and Petroleum Engineers.

"Lessons Learned; Knowledge Gained." n.d. Edwards Air Force Base, Calif. Available at www.edwards.af.mil/penvmng/documents/rts/2003/sep03/sep03pg1.htm.

Li, F. X., D. M. Byrd, G. M. Deyhle, D. E. Sesser, M. R. Skeels, S. R. Katkowsky, and S. H. Lamm. 2000. "Neonatal Thyroid-Stimulating Hormone Level and Perchlorate in Drinking Water," *Teratology* **62**: 429–31.

Li, Z., F. X. Li, D. M. Byrd, G. M. Deyhle, D. E. Sesser, M. R. Skeels, and S. H. Lamm. 2000. "Neonatal Thyroxine Level and Perchlorate in Drinking Water," *Journal of Occupational and Environmental Medicine* **42**: 200–05.

Lieberman, M. T., S. Knox, and R. C. Borden. 2005. "Monitored Natural Attenuation of Perchlorate in Groundwater," presented at the 2005 NGWA Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy, San Francisco.

Logan, B. E. 1998. "A Review of Chlorate- and Perchlorate-Respiring Microorganisms," *Bioremediation Journal* **2**: 69–79.

Logan, B. E. 2001. "Assessing the Outlook for Perchlorate Remediation," *Environmental Science and Technology* **35**(23): 482A–87A.

Losi, M. E., T. Giblin, V. Hosangadi, and W. T. Frankenberger, Jr. 2002. "Bioremediation of Perchlorate-Contaminated Groundwater Using a Packed-Bed Biological Reactor," *Bioremediation Journal* **6**: 97–103.

Noria Corporation. 2001. "Q & A" in Lube-Tips, Nov. 6. Available at www.lube-tips.com/BackIssues/2001-11-06.htm.

MADEP (Massachusetts Department of Environmental Protection). 2005a. The Occurrences and Sources of Perchlorate in Massachusetts (Draft). Available at www.mass.gov/dep/files/clo4/perchlorate-sources-0805.pdf.

MADEP. 2005b. "Progress Report: Merrimack River Perchlorate Sampling Summer 2005." Available at www.mass.gov/dep/files/clo4/merrimack-sampling-summer2005.htm.

Manzon, R. G., and J. H. Youson. 2002. "$KClO_4$ Inhibits Thyroidal Activity in the Larval Lamprey Endostyle In Vitro," *General and Comparative Endocrinology* **128**(10): 214–23.

Mathew, J., J. Gandhi, and J. Hedrick. 2004. *The Analysis of Perchlorate by Ion Chromatography/Mass Spectrometry (Application)*. 5989-0816EN. Agilent Technologies. Available at www.chem.agilent.com/scripts/LiteraturePDF.asp?iPubNo=5989-0816EN.

McNabb, F. M. A. 2003. *The Effects of Perchlorate on Developing and Adult Birds*. Final Report for Strategic Environmental Research and Development Program.

McNabb, F. M. A., D. A Jang, and C. T. Larsen. 2004. "Does Thyroid Function in Developing Birds Adapt to Sustained Ammonium Perchlorate Exposure?" *Toxicology Science* **82**:106–13.

Milford, H. 1999. "Extractive Non-Fuel Resources: A Look Back at Mining in New Mexico," Chap. 3 in *New Mexico's Natural Resources 1999*. New Mexico Energy, Minerals and Natural Resources Department. Available at www.emnrd.state.nm.us/Mining/resrpt/99/3NonFuel.pdf.

Miller, D. J. 1998. "Pyrolysis Processes," in *Standard Handbook of Hazardous Waste Treatment and Disposal*, 2nd ed., H. M. Freeman, ed. New York: McGraw Hill.

Min, B., P. J. Evans, A. Chu, and B. E Logan. 2004. "Perchlorate Removal in Sand and Plastic Media Bioreactors," *Water Research* **38**: 47–60.

Miranda, L. A., D. A. Paz, R. E. Dezi, and A. Pisano. 1995. "Immunocyto-Chemical and Morphometric Study of TSH, PRL, GH, and ACTH Cells in *Bufo arenarum* Larvae with Inhibited Thyroid Functions," *General and Comparative Endocrinology* **98**: 166–76.

Morgan, J. W., and R. E. Cassady. 2002. "Community Cancer Assessment in Response to Long-Time Exposure to Perchlorate and Trichloroethylene in Drinking Water," *Journal of Occupational and Environmental Medicine* **44**: 616–21.

Morreale de Escobar, G., M. J. Obregon, and F. Escobar del Rey. 2000. "Is Neuropsychological Development Related to Maternal Hypothyroidism or to Maternal Hypothyroxinemia?" *Journal of Clinical Endocrinology and Metabolism* **85**: 3975–87.

Morss, C. G. 2003. "Perchlorate Groundwater Treatment," *Pollution Engineering* **35**(9): 18–23. Available at www.pollutionengineering.com/CDA/ArticleInformation/features/BNP__Features__Item/0,6649,110403,00.html.

Moshiri, G. A., ed. 1994. *Constructed Wetlands for Water Quality Improvement*. Boca Raton, Fla.: Lewis.

Motzer, W. E. 2001. "Perchlorate: Problems, Detection, and Solutions," *Environmental Forensics* **2**(4): 301–11.

Mulamoottil, G., E. A. McBean, F. Rovers. 1998. *Constructed Wetlands for the Treatment of Landfill Leachates*. Boca Raton, Fla.: Lewis.

NASA (National Aeronautics and Space Administration). 2003. "NASA Tests Environmentally Friendly Rocket Fuel." News Release 03-03AR. Available on the Internet at www.nasa.gov/centers/ames/news/releases/2003/03_04AR.html.

Nerenberg, R., B. E. Rittmann, and I. Najm. 2002. "Perchlorate Reduction in a Hydrogen-Based Membrane-Biofilm Reactor," *Journal of the American Water Works Association* **94**: 103–14.

Neumayer, A., W. Ball, E. Bouwer, C. O'Melia, and A. Stone. 2004. *Perchlorate Chemistry, Occurrence, and Remediation: Literature Review*. The John Hopkins University Department of Geography and Environmental Engineering, submitted to U.S. Department of Army.

NRC (National Research Council). 2005a. *Health Implications of Perchlorate Ingestion*. Washington, D.C.: National Academies Press.

NRC. 2005b. "Report in Brief: Health Implications of Perchlorate Ingestion." Available at www.nap.edu/html/perchlorate/perchlorate-brief.pdf.

Nzengung, V. A. 2002. *Phytoremediation of Perchlorate Contaminated Soils and Water*. Report for the U. S. Air Force, Air Force Material Command and the University of Georgia Research Foundation, Inc.

Nzengung, V. A., and C. Wang. 2000. "Influences on Phytoremediation of Perchlorate Contaminated Water," pp. 219–29 in *Perchlorate in the Environment*, E. T. Urbansky, ed. New York: Kluwer/Plenum.

Nzengung, V. A., C. Wang, and G. Harvey. 1999. "Plant-Mediated Transformation of Perchlorate into Chloride," *Environmental Science and Technology* **33**: 1470–78.

Nzengung, V. A., C. Wang, G. Harvey, S. C. McCutcheon, and N. L. Wolfe. 1999. "Phytoremediation of Perchlorate Contaminated Water: Laboratory Studies," pp. 239–44 in *Proceedings, 5th International Symposium on In Situ and On-Site Bioremediation: Phytoremediation*, A. Leeson and B. C. Alleman, eds. Columbus, Ohio: Battelle Press.

O'Conner, S. M., and J. D. Coates. 2002. A Universal Immunoprobe for (Per)chlorate-Reducing Bacteria," *Applied Environmental Microbiology* **68**: 3108–13.

O'Niell, W. L., and V. A. Nzengung. 2003. "In Situ Bioremediation of Perchlorate," *Hazardous Waste Consultant* **21**(6): 1.10–1.12.

O'Niell, W. L., V. A. Nzengung, and A. Adebola. 2000. "Treatment of Perchlorate-Contaminated Water in Microbial Mat, Algae, and Ebb-and-Flow Hydroponic Bioreactors," pp. 101–06 in *Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds*, G. B. Wickramanayake, A. R. Gavaskar, N. Gupta, J. T. Gibbs, and J. L. Means, eds. Columbus, Ohio: Battelle Press.

Orris, G. J. 2004. "Perchlorate in Natural Minerals and Materials," *USGS Quarterly Report* (April).

Orris, G. J., G. J. Harvey, D. T. Tsui, and J. E. Eldrige. 2003. *Preliminary Analyses for Perchlorate in Selected Natural Materials and their Derivative Products*. USGS Open-File Report 03-314.

Parsons. 2001. *Scientific and Technical Report for Perchlorate Bio-Transport Investigation: A Study of Perchlorate Occurrence in Selected Ecosystems*. Interim Final Report. Brooks Air Force Base, Tex.: Air Force Institute for Environment, Safety and Occupational Health Risk Analysis.

Penfold, L. 2004. "Critical Issues for Definitive Analysis of Low Concentrations of Perchlorate in the Environment" (briefing).

Perlmutter, M. W., R. Britto, J. D. Cowan, and A. K. Jacobs. 2001. "In Situ Biotreatment of Perchlorate and Chromium in Groundwater," pp. 315–22 in *Bioremediation of Inorganic Compounds*, *Proceedings, 6th International In Situ and On-Site Bioremediation Symposium*, Vol. 6, No. 9, A. Leeson et al., eds., Columbus, Ohio: Battelle Press.

Perlmutter, M., T. H. Beisel, and M. Craig. 2004. "In Situ Treatment of Perchlorate in Groundwater Using Permeable Reactive Barriers," presented at the National Ground Water Association Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy, Costa Mesa, Calif.

Pesticide Action Network North America. n.d. "Sodium Chlorate," PAN Database entry. Available at http://pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34361.

PMEP (Pesticide Management Education Program). 1995 "Sodium Chlorate," Extension Toxicology Network (EXTONET) pesticide information profile. Ithaca, N.Y.: Cornell University. Available at http://pmep.cce.cornell.edu/profiles/extoxnet/pyrethrins-ziram/sodium-chlorate-ext.html.

Polk, J., C. Onewokae, W. J. Guarini, C. Murray, D. E. Tolbert, and A. P Togna. 2002. "Army Success Story: Ex Situ Biological Treatment of Perchlorate-Contaminated Groundwater," *Federal Facilities Environmental Journal* **13**(2): 85–94.

Praskins, W. 2002. *Treatment of Perchlorate in Water*. Presentation. San Francisco: EPA Region 9. Available on the Internet at www.clu-in.org/studio/perchlorate_060402/prez/ppframe2.cfm?res=800x600&id=17.

Rainwater, K, C. Heintz, T. Mollagen, and L. Hansen. 2001. "In Situ Biodegradation of High Explosives in Soils: Field Demonstration," *Bioremediation Journal* **6**(4): 351–71.

Retskin, B. 1997. "Striking It Rich: Match Collecting," *Cigar Aficianado*, July/August.

Rikken, G. B., A. G. M. Kroon, and C. G. van Ginkel. 1996. “Transformation of (Per)chlorate into Chloride by a Newly Isolated Bacterium: Reduction and Dismutation,” *Applied Microbiology and Biotechnology* **45**: 420–26.

Sanchez, C., and R. I. Krieger. 2004. “Occurrence of Perchlorate in Vegetable Crops Produced in the Lower Colorado River Region,” Risk Forum presentation, U.S. Department of Agriculture, Office of Risk Assessment and Cost-Benefit Analysis. Available at www.usda.gov/agency/oce/oracba/forum.htm.

Schnoor, J. L., G. F. Parkin, C. L. Just, B. van Aken, J. D. Shrout. 2001. *Phytoremediation and Bioremediation of Perchlorate at the Longhorn Army Ammunition Plant*, Progress Report Number 3. Iowa City, Iowa: University of Iowa, Department of Civil and Environmental Engineering.

Schumacher, J. C., ed. 1960. *Perchlorates: Their Properties, Manufacture and Uses*. American Chemical Society Monograph Series. New York: Reinhold.

Schumacher, J. C. 1999. “History of Establishing a Source of Potassium and Ammonium Perchlorates for Use in Solid Propellant Rockets.” Paper 99-2926. American Institute of Aeronautics and Astronautics, Inc.

Schwartz, J. 2001. *Gestational Exposure to Perchlorate Is Associated with Measures of Decreased Thyroid Function in a Population of California Neonates*. Thesis. Berkeley, Calif.: University of California.

SERDP (Strategic Environmental Research and Development Program). 2005. “Synthesis, Evaluation, and Formulation Studies in New Oxidizers as Alternatives to Ammonium Perchlorate in DoD Missile Propulsion Applications.” Fact Sheet PP-1403. Available at www.serdp.org/research/PP/PP-1403.pdf.

Siglin, J. C., D. R. Mattie, D. E. Dodd, P. K. Hildebrandt, and W. H. Baker. 2000. “A 90-Day Drinking Water Toxicity Study in Rats of the Environmental Contaminant Ammonium Perchlorate,” *Toxicological Sciences* **57**: 61–74.

Silva, M. A. 2003. “Safety Flares Threaten Water Quality with Perchlorate.” Santa Clara Valley Water District.

Smith, P. N., C. W. Theodorakis, T. A. Anderson, and R. J. Kendall. 2001. “Preliminary Assessment of Perchlorate in Ecological Receptors at the Longhorn Army Ammunition Plant (LHAAP), Karnack, Texas,” *Ecotoxicology* **10**: 305–13.

Smith, P. N., L. Yu, S. T. McMurray, and T. A Anderson. 2004. “Perchlorate in Water, Soil, Vegetation, and Rodents Collected from the Las Vegas Wash, Nevada, USA,” *Environmental Pollution* **132**: 121–27.

Soldin, O. P., L. E. Braverman, and S. H. Lamm. 2001. “Perchlorate Clinical Pharmacology and Human Health: A Review” *Therapeutic Drug Monitoring* **23**(4): 316–21.

Sowell, E. R., P. M. Thompson, C. J. Holmes, T. L. Jernigan, and A. W. Toga. 1999. “In Vivo Evidence for Post-Adolescent Brain Maturation in Frontal and Striatal Regions,” *Nature Neuroscience* **2**(10): 859–61.

Spritzer, M. H., D. A. Hazlebeck, and K. W. Downey. 1995. *Supercritical Water Oxidation of Chemical Agents. Solid Propellants, and Other DoD Hazardous Wastes*. Prepared for the U.S. Army Program manager for Chemical Demilitarization. San Diego: General Atomics.

Stanbury, J. B., and J. B. Wyngaarden. 1952. "Effect of Perchlorate on the Human Thyroid Gland," *Metabolism* **1**: 533–39.

Streitelmeier, B. A., M. L. Espinosa, J. D. Adams, P. A. Leonard, and E. M. Hodge. 2001. "Use of a Unique Biobarrier to Remediate Nitrate and Perchlorate in Groundwater," presented at the International Containment and Remediation Technology Conference, Orlando, Fla.

Surks M. I., E. Ortix, G. H. Daniels, C. T. Sawin, N. F. Col, R. H. Cobin, J. A. Franklyn, J. M. Hershman, K. D. Burman, M. A. Denke, C. Gorman, R. S. Cooper, and N. J. Weissman. 2004. "Subclinical Thyroid Disease: Scientific Review and Guidelines for Diagnosis and Management," *Journal of the American Medical Association* **291**: 228–38.

Susarla, S., S. T. Bacchus, S. C McCutcheon, and N. L. Wolfe. 1999a. "Phytotransformation of Perchlorate and Identification of Metabolic Products in *Myriophyllumaquaticum*," *International Journal of Phytoremediation* **1**: 97–107.

Susarla, S., S. T. Bacchus, S. C McCutcheon, and N. L. Wolfe. 1999b. "Phytotransformation of Perchlorate Using Parrot-Feather," *Soil and Groundwater Cleanup* February/March: 20.

Susarla, S., S. T. Bacchus, S. C McCutcheon, and N. L. Wolfe. 1999c. *Potential Species for Phytoremediation of Perchlorate*. EPA/600/R-99/069. Athens, Ga.: U.S. Environmental Protection Agency.

Susarla, A., N. L. Wolfe, and S. C. McCutcheon. 1999. "Perchlorate Uptake in Lettuce Seedlings," presented at the American Chemical Society meeting, New Orleans.

Sutton, P. M., and P. N. Mishra. 1991. "Biological Fluidized Beds for Water and Wastewater Treatment," *Water Environment and Technology* **8**: 52–56.

Tan, K., T. A. Anderson, and W. A. Jackson. 2004. "Degradation Kinetics of Perchlorate in Sediments and Soils," *Water, Air, and Soil Pollution* **151**: 245–59.

Tan, K., T. A. Anderson, M. W. Jones, P. vN. Smith, and W. A. Jackson. 2005. "Accumulation of Perchlorate in Aquatic and Terrestrial Plants at a Field Scale," Journal of Environmental Quality **33**: 1638–46.

Tazebay, U. H., I. L. Wapnir, O. Levy, O. Dohan, L. S. Zuckier, Q. H. Zhao, H. F. Deng, P. S. Amenta, S. Fineberg, R. G. Pestell, and N. Carrasco. 2000. "The Mammary Gland Iodide Transporter Is Expressed during Lactation and in Breast Cancer," *Nature Medicine* **6**: 871–78.

Thiboutot, S., G. Ampleman, and A. D. Hewitt. 2002. *Guide for Characterization of Sites Contaminated with Energetic Materials*. ERDC/CRREL TR-02-1. Hanover, N.H.: U.S. Cold Regions Research and Engineering Laboratory. Available at www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR02-1(ERDC-CRL).pdf.

Thiboutot, S., G. Ampleman, T. F. Jenkins, M. E. Walsh, P. G. Thorne, T. A. Ranney, and G. L. Grant. 1997. "Assessment of Sampling Strategy for Explosives-Contaminated Soils," Paper 94-WP 101.08 in *Proceedings, 90th Annual Air and Waste Management Meeting*, Toronto.

Thompson, P. M., J. N. Giedd, R. P. Woods, D. MacDonald, A. C. Evans, and A. W. Toga. 2000. "Growth Patterns in the Developing Brain Detected by Using Continuum Mechanical Tensor Maps," *Nature* **404**: 190–93.

Thorne, P. G. 2004. *Field Screening Method for Perchlorate in Water and Soil*. ERDC/CRREL TR-04-8. Hanover, N.H.: U.S. Cold Regions Research and Engineering Laboratory. Available at www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR04-8.pdf.

Tillotson, S. L., P. W. Fuggle, I. Smith, A. E. Ades, D. B. Grant. 1994. "Relation between Biochemical Severity and Intelligence in Early Treated Congenital Hypothyroidism: A Threshold Effect," *British Medical Journal* **309**: 440–45.

Turbosystems Engineering. n.d. "Overview of Supercritical Water Oxidation." Available at www.turbosynthesis.com/summitresearch/sumscw1.htm.

UC SAREP (University of California Sustainable Agriculture Research and Education Program). 2002. "Chilean Nitrate for General Use as an Adjuvant in Crop Production." National Organic Standards Board Technical Advisory Panel Review, compiled for the USDA National Organic Program. Available at www.sarep.ucdavis.edu/Organic/tap/Chileannitrate-GeneralUse.pdf.

Urbansky, E. T. 2000. "Quantitation of Perchlorate Ion: Practices and Advances Applied to the Analysis of Common Matrices," *Critical Reviews in Analytical Chemistry* **30**(4): 311–43. Available at www.clu-in.org/download/contaminantfocus/perchlorate/critrevClO4.pdf.

Urbansky, E. T., T. W. Collette, W. P. Robarge, W. L. Hall, J. M. Skillen, and P. F. Kane. 2001. *Survey of Fertilizers and Related Materials for Perchlorate* (ClO_4^-). EPA/600/R-01/047. Cincinnati: U.S. Environmental Protection Agency, National Risk Management Research Laboratory. Available at www.epa.gov/ORD/NRMRL/Pubs/600/R01/047.pdf.

USACE (U.S. Army Corps of Engineers). 2001a. *Perchlorate Screening Study: Low Concentration Method For the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes*. Letter Report of Findings for the Method Development Studies, Interference Studies, and Split Sample Studies, Including Standard Operating Procedure. Prepared for the U.S. Environmental Protection Agency, Region IX by Department of the Army, U.S. Army Engineering District, Sacramento.

USACE. 2001b. *Requirements for the Preparation of Sampling and Analysis Plans*. EM 200-1-3. Available at www.usace.army.mil/publications/eng-manuals/em200-1-3/toc.htm.

USEPA (U. S. Environmental Protection Agency). 1993. *Process Design Manual for Nitrogen Removal*. EPA/625/R-93/010. Cincinnati.

USEPA. 1998. *Assessment of thyroid follicular cell tumors*. Risk Assessment Forum, U.S. Environmental Protection Agency, Washington, D.C. EPA/630/R-97/002.

USEPA. 1999a. *Interim Assessment Guidance for Perchlorate*.

USEPA. 1999b. *Method 314.0, Determination of Perchlorate in Drinking Water Using Ion Chromatography*, Rev. 1.0. Available at www.epa.gov/safewater/methods/sourcalt.html.

USEPA. 2000a. *Method 9058, Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection*, Rev. 0. Available at www.epa.gov/epaoswer/hazwaste/test/pdfs/9058.pdf.

USEPA. 2000b. *Sodium Chlorate Listing Background Document for the Inorganic Chemical Listing Determination.* Available at www.epa.gov/epaoswer/hazwaste/id/inorchem/docs/sodchlor.pdf.

USEPA. 2002. *Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization*. NCEA-1-0503 (External Review Draft). Washington, D.C.: U.S. Environmental Protection Agency, Office of Research and Development.

USEPA. 2003a. "List of Known Perchlorate Manufacturers/Users." Available at www.epa.gov/swerffrr/documents/knwn_perch_mftrs_usrs_04_03.xls.

USEPA. 2003b. "Status of EPA's Interim Assessment Guidance for Perchlorate." January 22 Memorandum from Marianne Lamont Horinko, Assistant Administrator. Available at www.epa.gov/swerffrr/documents/perchlorate_memo.htm.

USEPA. 2004a. "National Perchlorate Detections as of September 23, 2004." Federal Facilities Restoration and Reuse Office. Available at www.epa.gov/swerffrr/documents/perchlorate_map/nationalmap.htm.

USEPA. 2004b. *Contract Laboratory Program Guidance for Field Samplers*. EPA/540/R-00/003. Office of Superfund Remediation and Technology Innovation. Available at www.epa.gov/superfund/programs/clp/guidance.htm.

USEPA. 2004c. *Perchlorate Monitoring Results Henderson, Nevada to the Lower Colorado River June 2004 Report*. Available at www.epa.gov/fedfac/pdf/PerchlorateFifthMonRpt_062004.pdf.

USEPA. 2005a. *Method 314.1, Determination of Perchlorate in Drinking Water Using Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection*, Rev 1.0. Available at www.epa.gov/safewater/methods/sourcalt.html.

USEPA. 2005b. *Method 331.0, Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry*, Rev. 1.0 Available at www.epa.gov/safewater/methods/sourcalt.html.

USEPA. 2005c. *Method 332.0, Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry*. Available at www.epa.gov/nerlcwww/ordmeth.htm.

USEPA. n.d. "Accessing Unregulated Contaminant Monitoring Data." Available at www.epa.gov/ogwdw000/data/ucmrgetdata.html#desc.

USEPA. n.d. "Contaminant Focus: Perchlorate—Overview." Technology Innovation Program. Available at www.clu-in.org/contaminantfocus/default.focus/sec/perchlorate/cat/Overview/.

USEPA. n.d. "Perchlorate." Federal Facilities Restoration and Reuse Office. Available at www.epa.gov/swerffrr/documents/perchlorate.htm.

USFDA (U.S. Food and Drug Administration). 2004a. "Exploratory Data on Perchlorate in Food." Center for Food Safety and Applied Nutrition, Office of Plant and Dairy Foods. Available at www.cfsan.fda.gov/~dms/clo4data.html.

USFDA. 2004b. "Rapid Determination of Perchlorate Anion in Foods by Ion Chromatography–Tandem Mass Spectrometry," Rev. 1. Center for Food Safety and Applied Nutrition, Office of Plant and Dairy Foods. Available at www.cfsan.fda.gov/~dms/clo4meth.html.

USGS (U.S. Geological Survey). Variously dated. *National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations*, Book 9, Chaps. A1–A9. Available at http://pubs.water.usgs.gov/twri9A.

U.S. Navy. 2004. *Interim Guidance on Sampling and Testing for Perchlorate*. Available at http://www.navylabs.navy.mil/Archive/PerchlorateInterim.pdf.

U.S. Navy. n.d. *Navy Environmental Compliance Sampling and Field Testing Procedures Manual*. NAVSEAT0300-AZ-PRO-010. Available at www.navylabs.navy.mil/Archive/smanual.pdf.

Van Den Berg, H., and K. Baugh. 2004. "Selection of Remedial Technologies for Perchlorate-Impacted Sites," presented at the National Ground Water Association Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy, Costa Mesa, Calif.

Van Ginkel, C. G., G. B. Rikken, A. G. M. Kroon, and S. W. M. Kengen. 1996. "Purification and Characterization of Chlorite Dismutase: A Novel Oxygen-Generating Enzyme," *Archives of Microbiology* **166**: 321–26.

Waller, A. S., E. E. Cox, and E. A. Edwards. 2004. "Perchlorate-Reducing Microorganisms Isolated from Contaminated Sites," *Environmental Microbiology* **6**: 517–27.

Walsh, M. E., T. F. Jenkins, P. S. Schnitker, J. W. Elwell, and M. H. Stutz. 1993. *Evaluation of Analytical Requirements Associated with Sites Potentially Contaminated with Residues of High Explosives*. CRREL Report 93-5. Hanover, N.H.: U.S. Cold Regions Research and Engineering Laboratory.

Walvoord, M. A., F. M. Phillips, D. A Stonestrom, R. D. Evans, P. C Hartsough, B. D. Newman, and R. G. Striegl. 2003. "A Reservoir of Nitrate beneath Desert Soils," *Science* **302**: 1021–24.

Webster, G., M. C. Vigone, L. Stroppa, and G. Chiumello. 2003. "Thyroid Function and Puberty," *Journal of Pediatric Endocrinology* **16**(Supp. 2): 253–57.

Western Electrochemical Company. 1994. "Material Safety Data Sheet—Ammonium Perchlorate."

Winkler, P., M. Minteer, and J. Willey. 2004. "Analysis of Perchlorate in Water and Soil by Electrospray LC/MS/MS," *Analytical Chemistry* **76**(2): 469–73.

Wolff, J. 1998. "Perchlorate and the Thyroid Gland," *Pharmacological Reviews* **50**(1): 89–105. Available at http://pharmrev.aspetjournals.org/cgi/reprint/50/1/89.

Wu, J., R. F. Unz, H. Zhang, and B. E. Logan. 2001. "Persistence of Perchlorate and the Relative Numbers of Perchlorate- and Chlorate-Respiring Microorganisms in Natural Waters, Soils and Wastewater," *Bioremediation Journal* **5**(2): 119–30.

Xu, J. Y., Y. Song, B. Min, L. Steinberg, and B. E. Logan. 2003. "Microbial Degradation of Perchlorate: Principles and Applications," *Environmental Engineering Science* **20**(5): 405–22.

York, R. G., J. Barnett, W. R. Brown, R. H. Garman, D. R. Mattie., and D. Dodd. 2004. "A Rat Neurodevelopmental Evaluation of Offspring, Including Evaluation of Adult and Neonatal Thyroid, from Mothers Treated with Ammonium Perchlorate in Drinking Water," *International Journal of Toxicology* **23**: 191–214.

York, R. G., W. R. Brown, M. F. Girard, and J. S. Dollarhide. 2001a. "Oral (Drinking Water) Developmental Toxicity Study of Ammonium Perchlorate in New Zealand White Rabbits," *International Journal of Toxicology* **20**: 199–205.

York, R. G., W. R. Brown, M. F. Girard, and J. S. Dollarhide. 2001b. "Two-Generation Reproduction Study of Ammonium Perchlorate in Drinking Water in Rats Evaluates Thyroid Toxicity," *International Journal of Toxicology* **20**: 183–97.

York, R. G., K. A. Funk, M. F. Girard, D. Mattie, and J. E. Strawson. 2003. "Oral (Drinking Water) Developmental Toxicity Study of Ammonium Perchlorate in Sprague-Dawley Rats," *International Journal of Toxicology* **22**: 453–64.

Yu, L., J. E. Canas, G. P. Cobb, W. A. Jackson, and T. A. Anderson. 2004. “Uptake of Perchlorate in Terrestrial Plants,” *Ecotoxicology and Environmental Safety* **58**(1): 44–49.

Zawtocki, C., T. M. Lieberman, and G. Birk. 2004. “A Dash of Oil and Let Marinate,” *Pollution Engineering* **36**(5): 30–34.

Zhang W. X. 2003. “Nanoscale Iron Particles for Environmental Remediation: An Overview,” *Journal of Nanoparticle Research* **5**: 323–32.

Zhang, H., M. A. Bruns, and B. E. Logan. 2002. “Perchlorate Reduction by a Novel Chemolithoautotrophic, Hydrogen-Oxidizing Bacterium,” *Environmental Microbiology* **4**: 570–76.

APPENDIX A

Acronyms

ACRONYMS

BMP	best management practice
BOD	biochemical oxygen demand
CE	capillary electrophoresis
CRREL	Cold Regions Research Engineering Laboratory
CSTR	continuous-flow stirred tank reactors
DoD	(U.S.) Department of Defense
DOE	(U.S.) Department of Energy
DQO	data quality objective
DWEL	drinking water equivalent level
ECBC	Edgewood Chemical Biological Center
ESI	electrospray ionization
ESTCP	Environmental Security Technology Certification Program
FBR	fluidized-bed reactor
FDA	(U.S.) Food and Drug Administration
GAC	granular activated carbon
HMX	high-melting-point explosive
IC	ion chromatograph(y)
IME	Institute of Makers of Explosives
IRIS	Integrated Risk Information System
ITRC	Interstate Technology & Regulatory Council
LANL	Los Alamos National Laboratory
LC	liquid chromatography
LHAAP	Longhorn Army Ammunition Plant
LOAEL	low observed adverse effect level
LOQ	limit of quantitation
m/z	mass-to-charge
MADEP	Massachusetts Department of Environmental Protection
MBR	membrane bioreactor
MCL	maximum contaminant level
MCT	matrix conductivity threshold
MIDAS	Munitions Items Disposition Action System
MMR	Massachusetts Military Reservation
MOA	mode of action
MRL	minimum reporting level
MS	mass spectrometry
MSDS	material safety data sheet
NASA	National Aeronautics and Space Administration
ND	nondetect
NDMA	N-nitrosodimethylamine
NOAEL	no observed adverse effect level
NOEL	no observed effect level
NRC	National Research Council
NWIRP	Naval Weapons Industrial Reserve Plant
OB/OD	open burn/open detonation

O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
OSW	Office of Solid Waste
PBR	packed-bed reactors
ppb	parts per billion
ppm	parts per million
QC	quality control
RCRA	Resource Conservation and Recovery Act
RDX	royal demolition explosive
RfD	reference dose
SERDP	Strategic Environmental Research and Development Program
SQM	Sociedad Quimica Y Minera De Chile S.A.
TCE	trichloroethylene
TCEQ	Texas Council on Environmental Quality
TDS	total dissolved solids
TNT	trinitrotoluene
TRH	TSH-releasing hormone
TSH	thyroid-stimulating hormone
UCMR	Unregulated Contaminant Monitoring Rule
USACE	U.S. Army Corps of Engineers
USDA	U.S. Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
UXO	unexploded ordnance
VOC	volatile organic compound

APPENDIX B

Naturally Occurring Perchlorate

NATURALLY OCCURRING PERCHLORATE

Table B-1. Perchlorate in natural minerals and materials

Samples	Measured concentration		Final conc. in extract (ppb)	MDL (ppb)	Spike recov. (%)	Sample weight (kg)	Extrac-tion volume (L)	Conc. (g/Kg)
	(ppb)	Dilution factor						
Muriate potash	ND	1	ND	1		0.001	0.03	ND
Mission Chem	ND	1	ND	1		0.001	0.03	ND
Miracle Grow	ND	1	ND	1		0.001	0.03	ND
Bonemeal, Brand 1	ND	1	ND	1		0.001	0.03	ND
Bloodmeal, Brand 1	5.4	1	5.4	1		0.001	0.03	0.161
Bloodmeal, Brand 1, DUP	4.8	1	4.8	1	111%	0.001	0.03	NA
Fishmeal	9.2	1	9.2	1		0.001	0.03	0.276
Fishmeal, DUP	11.0	1	11	1	84%	0.001	0.03	NA
Miracid	ND	1	ND	1		0.001	0.03	ND
Joebesi fertilizer spikes	ND	1	ND	1		0.001	0.03	ND
Peters Pro plant food	ND	1	ND	1		0.001	0.03	ND
Potash fertilizer, Brand 1	ND	1	ND	1		0.001	0.03	ND
Potash fertilizer, Brand 1, DUP	ND	1	ND	1		0.001	0.03	ND
Great Salt Lake ppt	ND	1	ND	1		0.001	0.03	ND
Salt substitute, Brand 1	ND	1	ND	1		0.001	0.03	ND
Salt substitute, Brand 1, DUP	ND	1	ND	1		0.001	0.03	ND
Salt substitute, Brand 2	ND	1	ND	1		0.001	0.03	ND
Salt substitute, Brand 3	ND	1	ND	1		0.001	0.03	ND
Lite salt, Brand 1	ND	1	ND	1		0.001	0.03	ND
Lite salt, Brand 1	48.8	1	48.8	1	98%	0.001	0.03	NA
Triple superphosphate	ND	1	ND	1		0.001	0.03	ND
Soft rock phosphate ore	ND	1	ND	1		0.001	0.03	ND
10-10-10 fertilizer	ND	1	ND	1		0.001	0.03	ND
Urea	ND	1	ND	1		0.001	0.03	ND
10-4-10 fertilizer	ND	1	ND	1		0.001	0.03	ND
Phosphate ore 1	ND	1	ND	1		0.001	0.03	ND
Phosphate ore 2	ND	1	ND	1		0.001	0.03	ND
Phosphate ore 3	ND	1	ND	1		0.001	0.03	ND
Phosphate ore 4	ND	1	ND	1		0.001	0.03	ND
Limestone	ND	1	ND	1		0.001	0.03	ND
Potash ore 1 (Sylvite 1a)	25,000		-			0.00114	0.03	0.025
Potash ore 2 (Sylvite 1b)	3,741,000		-			0.00105	0.03	3.741
Potash ore 3 (Sylvite 2)	42,000		-			0.0114	0.03	0.042
Playa crust 1 (B43)	1,745,000		-			0.00101	0.03	1.745
Playa crust 2 (B29)	560,000		-			0.00101	0.03	0.560
Playa crust 2 (B29), DUP	489,000		-			0.00101	0.03	0.489
Hanksite 1	280,000		-			0.00116	0.03	0.280
Hanksite 1, DUP	285,000		-			0.00116	0.03	0.285
Kelp	885,000		-			0.00116	0.03	0.885

Source: Preliminary Analyses for Perchlorate in Selected Natural Materials and Their Derivative Products, USGS Open File Report 03-314 (Orris et al. 2003).

Table B-2. Perchlorate in natural minerals and materials

Sample type	Number of locations	Number of samples	Percent with CLO_4	Pending	Number with NO_3
Playas	28	57	86[a] (96)	>11	>11^{++}
Soils	7	15		>12	
Soil-caliche	4	10	100	>3	All
Soil-nitrate				>9	All
Older lakebeds	3	3	100[b]	>1	2
Nitrate deposits	3	5	100	>6	All
Evaporites	19	26	27[a]	>5	Unknown
Nonhalite[c]	9	16	44[a]	>3	Unknown[d]
Halite	10	10	0	>2	NA
Related H_2O	2	3	100	1	Unknown

[a] High detection limit for some samples.

[b] All values <2 ppb.

[c] Samples other than “pure” halite, commonly mixed salts.

[d] Early samples not tested for NO_3.

Source: “Perchlorate in Natural Minerals and Materials,” *USGS Quarterly Report*, April 2004 (Orris 2004).

APPENDIX C

Manufactured Perchlorate Compounds

MANUFACTURED PERCHLORATE COMPOUNDS

The vast majority of manufactured perchlorate compounds (>99% of production) consist of the following four chemical species:

- ammonium perchlorate
- sodium perchlorate
- potassium perchlorate
- perchloric acid

Other much less common, even rare, manufactured specialty perchlorate compounds (list not comprehensive) include the following:

2, 2′, 2″-terpyrine perchlorate
acetylcholine perchlorate
aluminum perchlorate, hydrated
barium perchlorate, anhydrous
barium perchlorate, hydrated
bismuthyl perchlorate monohydrate
cadmium perchlorate
ceric perchlorate, solution (perchlorato-ceric acid)
cerous perchlorate, hydrated
cesium perchlorate
chromium perchlorate, hydrated
cobalt perchlorate, hydrated
cupric perchlorate, hydrated
dysprosium perchlorate, hydrated
erbium perchlorate, hydrated
europium perchlorate, hydrated
ferric perchlorate, hydrated, yellow
ferric perchlorate, non-yellow
ferrous perchlorate
gadolinium perchlorate, hydrated
gallium perchlorate, hydrated
holmium perchlorate, hydrated
indium perchlorate, hydrated
lanthanum perchlorate, hydrated
lead perchlorate solution
lead perchlorate, trihydrate
lithium perchlorate, anhydrous
lithium perchlorate, hydrated
magnesium perchlorate, anhydrous
magnesium perchlorate, hydrated
mercuric perchlorate, trihydrate
mercurous perchlorate, hydrated
neodymium perchlorate, hydrated
nickel perchlorate, hydrated
praseodymium perchlorate, hydrated
rubidium perchlorate
samarium perchlorate, hydrated
scandium perchlorate, hydrated
silver perchlorate, anhydrous
silver perchlorate, hydrated
strontium perchlorate, hydrated
terbium perchlorate, hydrated
tetrabutylammonium perchlorate
tetraethylammonium perchlorate
tetrahexylammonium perchlorate
tetramethylammonium perchlorate
thulium perchlorate, hydrated
trimethylammonium perchlorate
ytterbium perchlorate, hydrated
yttrium perchlorate, hydrated
zinc perchlorate, hydrated
zirconyl perchlorate, hydrated

Source: GFS Chemicals, Inc. Web site. Available at
www.gfschemicals.com/productcatalog/Perchlorate_Compounds.asp

APPENDIX D

Historical and Current Sources and Uses of Perchlorate

HISTORICAL AND CURRENT SOURCES AND USES OF PERCHLORATE

Table D-1. Uses of perchloric acid in 1939

Analysis	Reagent in • assaying various alkaloids, such as morphine, codeine, and cocaine; • carrying out Kjeldahl digestions for the determination of the nitrogen content of various products; • determining potash in various products by the formation of an insoluble potassium perchlorate; and • effecting electroanalysis (used for the purpose of destroying the organic matter contained in the product that is to be analyzed).
Chemical	• Oxidizing agent in making inorganic chemicals, intermediates, organic chemicals, pharmaceuticals, synthetic aromatics • Starting point in making various salts
Explosives	• Manufacture of matches • Reagent in making explosive compounds, such as the perchlorated esthers of monochlorohydrin
Metallurgical	• Ingredient of lead-plating baths (used for the purpose of facilitating the deposition of lead from baths containing lead perchlorate)
Pharmaceutical	• In compounding and dispensing practice

Source: Uses and Applications of Chemicals and Related Materials, Vol. I (Gregory 1939).

Table D-2. Uses of potassium perchlorate in 1944

Analytical	• Oxidizing agent in analytical processes • Reagent in analytical processes
Chemical	• Ingredient of catalytic mixtures used in making ammonia • Oxidizing agent in chemical processes • Starting point in making perchlorates
Explosives and matches	• Constituent of detonating compositions and flare compositions • Matchhead compositions • Perchlorate explosives—primer compositions; pyrotechnic compositions; railroad signal (fuse) compositions; and smoke-producing compounds
Fuel	• Constituent of briquetted fuel binder compositions based on such materials as coal, coke • Charcoal, lignite, bituminous dust, breeze, tar, pitch, and the like
Metallurgical	• Constituent of brazing fluxes, welding fluxes
Miscellaneous	• Constituent of chemical heating compositions
Pharmaceutical	• In compounding and dispensing practice
Photographic	• Oxidizing agent in photographic processes

Source: Uses and Applications of Chemicals and Related Materials, Vol. II (Gregory 1944).

Table D-3. Current perchlorate commercial and industrial uses

Production of matches
Air bag initiators for vehicles
Nuclear laboratories in actinide research
Chemical laboratories in analytical testing, desiccant, oxidizing agent, and digestion (perchloric acid)
Engine oil testing to determine base number (BN) ASTM D2896
Some electroplating operations
Electromachining, sodium perchlorate solution
Electropolishing operations with perchloric acid
Lithium-magnesium dioxide batteries as part of electrolyte
Rare-earth extractive metallurgy using perchloric acid
Etching brass and copper with perchloric acid
Paints and enamels
Bleaching agent to destroy dyes
Photography as flash powder
Incidental by-product in some sodium chlorate, which itself has many uses, including weed killer or herbicide and defoliant in agriculture and as chemical building block
Oxygen generators
Road flares
Ejection seats
Propellant in model rocket engines
Propellant in rockets used for research, satellite launches, and space shuttle
Some explosives in construction, mining and other uses
Fireworks
Perchloric acid production and its many uses

Table D-4. Application of perchloric acid in analytical chemistry

As a solvent for metals and alloys
As a dehydrating agent, particularly in the determination of silica in iron and steel and in cement and other silicate materials
As an oxidizing agent, especially in the determination of chromium in steel, ferrochrome, chromite, leather, and chromatized catgut
In combination with nitric acid for the destruction of organic matter, especially in preparation for the determination of calcium, arsenic, iron, copper, and other metals in such materials; also in the determination of sulfur in coal and rubber
As a solvent for sulfide ores for the determination of copper and other metals
In the separation and determination of the alkali metals, sodium, and potassium
In combination with hydrochloric acid in the separation of chromium from other metals by distillation of chromyl chloride
In the isolation of fluoride prior to its determination, by distillation as hydrofluosilicic acid
As an adjunct to increase the reduction potential of cerate salts in volumetric analysis
As a primary standard acid—perchloric acid, when distilled in a vacuum at a carefully regulated pressure of 7 mm, has exactly the composition of the dihydrate, 73.6% $HClO_4$
Indirectly in the manufacture of anhydrous magnesium perchlorate, the best of the absorbents for water in analytical work
As a strong, standard acid for the titration of bases
As the strongest of the strong acids when dissolved in anhydrous acetic acid for the titration of bases in nonaqueous solvents
Mixtures of perchloric acid dihydrate with nitric acid or sulfuric acid, or of these three acids together, are employed extensively in analytical procedures for the destruction of organic matter preparatory to the determination of metallic and nonmetallic ingredients. Such procedures include • determination of sulfur in coal, coke, and oils; • determination of iron in wine, beer, and whiskey; • determination of chromium and of iron in leather and tanning liquors; • determination of phosphorus, alkali metals, lead, and other ingredients; and • analysis of blood for calcium and of urine for lead.
Mixtures of perchloric and phosphoric acids or perchloric and sulfuric acids are superior solvents for refractory oxides, stainless steel, and other high-melting ferrous alloys, as well as ores and minerals
A solution containing perchloric acid dihydrate dissolved in acetic acid is commonly used as a standard solution for the titration of organic bases in nonaqueous solvents.

Source: GFS Chemicals, Inc. Web site. Available at www.gfschemicals.com/productcatalog/Perchlorate_Compounds.asp

Table D-5. Commercial applications of perchloric acid and perchlorates

Perchloric acid as catalyst in broad range of diverse reactions: acetylations, acylations, alkylations, chlorinations, polymerizations, esterifications, and hydrolyses
Esterifications of cellulose to produce cellulose acetate
Polymerizations of phenols with formaldehyde
Polymerization of styrene
Electrolytic solutions for the purpose of electropolishing, electromachining, and electrothining of metal parts, films, and alloys
Perchloric acid employed as electrolyte in anodization of metals to produce noncorroding surfaces
Pickling and passivation of iron and steels
Dissolving refractory substances such as titanium slags, copper-yttrium oxide, and metal fluorides
Lithium perchlorate as an electrolyte in voltaic cells and batteries involving lithium or lithiated anodes, nonaqueous solvents or polymeric films, and manganese dioxide or other transition metal oxides
In nonaqueous systems, zinc perchlorate and magnesium perchlorate serve as electrolyte for zinc and magnesium batteries, respectively
Perchlorate salts serve as electrolytes in electropolymerization reactions involving monomers such as aniline, benzidine, azulene, biphenyl, divinylbenzene, and indole
As aqueous electrolytes perchlorates are found in electrochromic devices and employed for anodic dissolution of difficultly oxidizable metals, such as lead and palladium
Perchlorate salts as dopants in plastics and polymers to impart antistatic and conductive properties
Perchlorate salts as dopants in polyvinyl chloride to improve heat stability and fire retardation characteristics
Lithium perchlorate as dopant in thin films of polymers such as polyethylene oxide, polyethylene glycol, or poly (vinylpyridine) to impart conductive properties in various electrochemical devices
Anhydrous magnesium perchlorate as a desiccant or drying agent for industrial gases and other similar applications

Source: GFS Chemicals, Inc. Web site. Available at www.gfschemicals.com/productcatalog/Perchlorate_Compounds.asp

Table D-6. Perchloric acid uses

In determining the trace metals present in oxidizable substances
As a laboratory reagent
As an oxidizing agent
For the destruction of organic matter
As a dehydrating agent
As starting material for the manufacture of pure ammonium perchlorate and in the production of high-purity metal perchlorates
As a stable reaction medium in the thermocatalytic production of chlorine dioxide
As an acetylation catalyst for cellulose and glucose
In the preparation of cellulose fibers
For fluoride determination
As an ingredient of electrolytic bath in deposition of lead
In the electropolishing of metals

Source: CHEMINFO Web site (Canadian Centre for Occupational Health and Safety 2003).

APPENDIX E

Perchlorate-Containing Materials and Activities or Industries that Use Perchlorate

PERCHLORATE-CONTAINING MATERIALS AND ACTIVITIES OR INDUSTRIES THAT USE PERCHLORATE

Note: As part of developing best management practices for perchlorate materials, which are required by AB 826 the Perchlorate Contamination Act, California Department of Toxic Substances Control compiled the following list of materials that contain perchlorate and activities or industries that use perchlorate:

- Adhesive—Steel plate bonding may contain perchlorate
- Batteries—Li-Ion[6]
- Cathodic protection systems—May contain perchlorate
- Chemistry—Analysis, desiccants, feedstock, oxidizing agent
- Chemistry—Brine separation may contain perchlorate
- Chlorate/chlorite manufacturing—May contain perchlorate
- Clandestine methamphetamine labs—May be contaminated by perchlorate from dissolving flare striker caps to obtain red phosphorus
- Cloud seeding
- Coatings—Enamel paint may contain perchlorate
- Dielectric for transformers—May contain perchlorate
- Electroplating—May contain perchlorate
- Electropolishing
- Explosives—Military
- Explosives—Geoseismic, nitrate-based may contain perchlorate
- Evaporites—May contain perchlorate
- Fertilizer—Some contain perchlorate (Bulldog Soda from Chile)
- Flares/fuses
- Gas generator—Airbag, ejection seat
- Gas generator—Aircraft oxygen
- Laboratory—Rocket motor, ordnance testing
- Laundry bleach—May contain perchlorate
- Nitric acid manufacturing—May contain perchlorate
- Pharmaceutical—Diagnosis, treatment
- Photography—Flash powder and possibly other uses, potassium
- Pool sanitizer
- Pool shock—May contain perchlorate
- Propellant—Chemical cutter
- Propellant—Ordnance (gunpowder), tracer bullets (red phosphorus) may contain perchlorate
- Propellant—Solid rocket motor, ammonium perchlorate
- Pyrotechnics (fireworks)

---

[6] Lithium battery types include lithium-manganese dioxide, lithium-sulfur dioxide, and lithium-thionyl chloride. The anode is composed of lithium and the cathode is composed of manganese dioxide (or sulfur dioxide, or thionyl chloride). The electrolyte of the lithium-magnesium dioxide battery is composed of an organic solvent (propylene carbonate and 1,2 dimethoxyethane) solution of lithium perchlorate. In the case of the lithium-sulfur dioxide, the electrolyte is also an organic solvent (acetonitrile) solution with lithium-bromide. Lithium-thionyl chloride batteries have a nonaqueous thionyl chloride solution containing lithium aluminum chloride. Lithium-sulfur dioxide batteries contain pressurized sulfur dioxide gas and lithium-thionyl chloride batteries contain lithium thionyl chloride which vaporizes upon exposure too air, both of which are highly toxic.

- Regenerable drying agent for gases—Magnesium
- Safety matches—May contain perchlorate
- Well drilling—Permeability aid, may contain perchlorate

Previously reported to contain perchlorate but recent research shows does not contain perchlorate:

- Aluminum refining—Aluminum electropolishing only
- Animal-fattening agent—Ice cream butterfat analysis. Feedlot contamination
- Electronic tubes—Electron tube with contaminant found on it at military base
- Leather tanning—$HClO_4$ used to digest leather samples for chromium content
- Lubricating oil additive—Antioxidants added; fluorocarbon lubricating oils compatible with perchlorate pumping
- Nuclear reactor—Nuclear warheads on rockets; uranium analytical chemistry
- Synthetic rubber—Rubber as binder in rocket motors

Source: California Department of Substances Control Web site: www.dtsc.ca.gov.

APPENDIX F

Remediation Technology Applicability Matrix

REMEDIATION TECHNOLOGY APPLICABILITY MATRIX

The Remediation Technology Applicability Matrix provides a summary of the technologies available as of December 2004. The matrix thus represents a “snapshot in time” of what technologies were being employed for the removal and treatment of perchlorate. The matrix contains information on the type of process, scale, throughput, treatment effectiveness, media, residuals, location and the vendor implementing the project. The information in this section was developed from reports, presentations, and state and federal summaries of technology developments.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
BIOLOGICAL PROCESSES				
Ex Situ Bioremediation				
Applied Research Associates, Inc.—Custom-designed biological treatment systems.				
Thiokol, Brigham City, Utah—Full scale, operational: Continuously stirred tank reactor (CSTR) biological system has operated continuously since 12/97 to treat industrial wastewater prior to discharge to sewer to treat waste stream high in salts (>2%) and nitrate. Initial pilot-scale work was performed by the Air Force Research Laboratory at Tyndall AFB, Florida. Cost: $0.02/gal	3 gpm, ~8000 lb/month of ammonium and potassium perchlorate	>5,000 mg/L to 4–400 µg/L	Wastewater	Biological oxygen demand (BOD), total suspended solids (TSS), nitrogen, phosphorous, total organic carbon (TOC), pH, turbidity, and dissolved oxygen (DO) may need to be monitored at effluent. Requires treatment of high salt effluent.
Hodgdon Powder Company, Kansas—Full scale, operational: Wastewater containing 1,000–5,000 mg/L perchlorate and 200–4,000 mg/L nitrate/nitrite is being treated down to a method reporting limit for perchlorate of 20 µg/L. Cost: $0.02/gal	3 gpm	1,000–5,000 mg/L to <20 µg/L reporting limit (RL)	Wastewater	
American Water Works Association Research Foundation (AWWARF)–sponsored project, La Puente, California—Pilot scale, completed: Mobile system treats up to 1 gpm diluted (2%–3% salt) waste ion exchange brine containing 3–4 mg/L perchlorate and 2–3000 mg/L of nitrate.	1 gpm	3–4 mg/L to 50 µg/L RL	Wastewater (drinking water plant brine)	Sulfate builds up in brine and eventually must be disposed.
Water utility–sponsored project, La Puente, California—Pilot scale, under way: Mobile system treats up to 1 gpm concentrated (6%–7% salt) brine containing 3–4 mg/L perchlorate and 2–3000 mg/L nitrate.	0.1 gpm	3–4 mg/L to 50 µg/L RL	Wastewater (drinking water plant brine)	Sulfate builds up in brine and eventually must be disposed.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Bench-scale testing at ARA—Bench scale: Reactor operated as both a fixed-film process and a suspended-growth CSTR process for a patented full-scale process on 5× and 10× reverse osmosis (RO) rejectate containing high total dissolved solids (TDS) and up to 10 mg/L of perchlorate.		To <20 µg/L	Wastewater (RO rejectate)	
Kerr-McGee, Henderson, Nevada—Designed: Based on treatability studies, ARA with Biothane Corporation designed an 825 gpm suspended-growth, CSTR biological treatment plant to treat 400 mg/L (~4000 lb/day) of perchlorate to below 4 µg/L. (Not selected due to higher capital costs.)	825 gpm	400 mg/L to <4 µg/L	Groundwater	
Biologically Active Carbon (BAC)/University of Illinois at Urbana–Champaign and the Metropolitan Water District of Southern California (MWDSC)—AWWARF-funded bench- and pilot-scale tests indicate that BAC filtration can effectively remove low levels of nitrate and perchlorate under anaerobic conditions with the addition of an electron donor. Nitrate reduction can also enhance perchlorate reduction kinetics, making BAC filtration particularly attractive for combined nitrate-perchlorate remediation. Carrollo Engineers conducted additional pilot testing based upon the work of the University of Illinois.				
Pilot scale			Drinking water	Biosolids
Castaic Lake Water Agency, Santa Clarita, California—Pilot scale, complete: Packed-bed bioreactor used acetic acid as electron donor. Submitted for conditional approval for use on drinking water system. Perchlorate was spiked into the influent water at a concentration of 50 ppb. Granular activated carbon (GAC) was found to be the most effective media because it allowed best growth of microorganisms and it has the potential for low-level perchlorate removal.	1.75–5.2 gpm/cubic ft	50 to <6 ppb	Drinking water	Biosolids
EcoMat Hall Reactor—This patented reactor provides an efficient circulation pattern and uses a floating porous media, Ecolink, which has a very high surface area–to–volume ratio. Ecolink is a polyurethane-based sponge that is cut into 1 cm cubes. The dense biological growth supported with this system reported to provide high efficiencies with lower reactor volumes.				
Department of Defense (DOD) facility, southern California—Commercial, completed: A 200 L capacity, two-stage biological system consisting of the Hall reactor and a deaeration chamber mounted on a 4 ft × 4 ft skid was used treat perchlorate-contaminated groundwater stored in two 20,000 gal Baker tanks. Methanol was used as the electron donor. Cost: $0.50/1000 gal.	~2 gpm	300–410 µg/L to <4 µg/L	Groundwater	Biosolids

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Pilot test—Pilot scale, planned: Funded by the California State University, San Bernadino, Office of Technology Transfer and Commercialization Initiative to be conducted in the Rialto Area.			Groundwater	
Foster Wheeler				
NASA Jet Propulsion Laboratory (JPL), Pasadena, California—Pilot-scale packed-bed bioreactor (PBR), completed: Assisted by Naval Facilities Engineering Service Center, NASA managed pilot tests conducted on several different reactors. Results as of 05/01 on the PBR indicate reactors can successfully treat low concentrations of perchlorate.	2 gpm	0.42 mg/L to <4 µg/L	Groundwater	Biosolids
NASA JPL, Pasadena, California—Pilot-scale dynamic suspended bed bioreactor (DSBR): Assisted by Naval Facilities Engineering Service Center, NASA managed pilot tests conducted on the DSBR in 2002. The DSBR was designed to provide improved flow characteristics (by using different media for bacterial attachment with less surface area and greater pore volume and allowing for limited bed flux and expansion in the reactors) than those used in the PBR above.	1 gpm	6 mg/L to <4 µg/L	Groundwater	Biosolids
Hollow-Fiber Membrane Biofilm Reactors—Patented hollow-fiber membrane biofilm reactor uses hydrogen as the electron donor to biologically degrade perchlorate. Hydrogen gas is fed to the inside of the membrane fibers, and the hydrogen diffuses through the membrane walls into the contaminated water that flows past the fibers. A biofilm on the exterior surface of hollow-fiber membranes houses microbes that act as catalysts by transferring electrons from supplied hydrogen gas to an oxidized contaminant.				
La Puente, California—Pilot scale: Northwestern University, the technology developer, teamed with Montgomery-Watson-Harza Engineers, Inc. to conduct a pilot study treating groundwater with perchlorate and nitrate initiated in 2002 and continuing through 2003. Results indicate the biofilm reactor can effectively treat 1.5 gpm to remove both perchlorate and nitrate.	1.5 gpm	60 µg/L to <6 µg/L	Drinking water	Biosolids

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
ICBM System Program Office—Demonstration of anaerobic percolating biofilters funded by Environmental Security Technology Certification Program (ESTCP).				
Hill AFB, Utah—Pilot scale, planned: Applying the principle of anaerobic perchlorate reduction in a reactor configured as a hybrid between a multimedia filter and a conventional leach-bed reactor. The system includes a contact chamber where the electron donor is added to the wastewater and a fixed-film biofilter that serves as the reactor where perchlorate biodegrades. The reactor packing consists of gravels, sand, and peat in grading sizes over the filter depth. Limestone gravel can be used to buffer the system against pH changes in low alkalinity soils. The biofilter is designed to prevent filter desiccation and oxygenation between loadings so that the anaerobic organisms remain viable.			Wastewater	
Pennsylvania State University—Anaerobic PBR filled with sand and plastic media fed with acetate and nutrients; hydrogen reactors.				
Crafton-Redlands Plume, Redlands, California—Pilot and lab scale: Funded by AWWARF, PSU is conducting anaerobic PBR tests, one with sand and one with plastic media. Initial results show both reactors with acetate and trace nutrient additions capable of reducing concentrations of 70 µg/L perchlorate to less than 4 µg/L. Prior to the pilot-scale tests, PSU conducted perchlorate degradation studies in laboratory-scale reactors evaluating both acetate-fed PBRs and hydrogen reactors.		70 µg/L reduced to <4 µg/L	Drinking water	
Shaw (Envirogen)/U.S. Filter–Envirex fluidized-bed reactors (FBR) with GAC media—Typically, ethanol or acetic acid is used as the electron donor.				
Aerojet, Rancho Cordova, California—Full scale, operational: Four FBRs with GAC media and ethanol feed as the food source have been in operation since 1998. The system was designed to treat 8 mg/L of perchlorate with a perchlorate loading of 44 lb/day per 1000 cubic ft of reactor volume. Total throughput design capacity of 4000 gpm, but processing 5300 gpm as of 10/03. The Aerojet System is based on pilot-scale laboratory testing using a 30-gpm FBR developed by U.S. Filter and Envirogen. The pilot-scale FBR also successfully reduced high concentrations of chlorate (480 mg/L) and nitrate (20 mg/L).	5300 gpm	Can reliably treat relatively high or low concentrations to below the 4 µg/L detection limit (DL)	Groundwater, wastewater, surface water, drinking water	Biosolids that slough off the FBR are trapped in the sand filters, which are periodically backwashed. Biosolids from filters and backwash are discharged to the sanitary sewer.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Longhorn Army Ammunition Plant (LHAAP), Texas—Full scale, operational: FBR with carbon media and acetic acid/nutrient additions treats groundwater with perchlorate concentrations up to 35 mg/L to below 5 µg/L. Acetic acid and nutrient additions. $650K capital cost, $25K operation and maintenance (O&M) cost.	35 gpm	35 µg/L to <5 µg/L	Groundwater	
NASA, JPL, Pasadena, California—Pilot scale, completed: Pilot test completed with FBR using native "JPL bacteria" and ethanol as the food source.	5 gpm	350–770 µg/L to <4 µg/L	Groundwater	Elevated natural chloride levels required a variance for reinjection.
NASA, JPL, Pasadena, California—Full scale, under way: In the source zone of Operating Unit 1. Influent perchlorate concentration is 7–15 ppm.	250 gpm		Groundwater	
Kerr McGee facility, Nevada—Full scale: FBR system with four sand-media primary reactors and four carbon-media secondary reactors will replace the single-pass ion exchange resin systems. The primary reactors biodegrade the high chlorate and nitrate concentrations to allow the secondary reactors to treat the perchlorate. Denatured alcohol will be used as the electron donor. The system is currently in start-up mode and is expected to treat a blended influent from the three well fields averaging 350 ppm perchlorate.	900 gpm	350 ppm to <18 ppb permit limit for discharge; limit may be >18 ppb due to high concentrations of TDS and sulfate concentrations that result in higher RLs.	Groundwater, surface water	
Massachusetts Military Reservation, Massachusetts (MMR)—Laboratory/pilot scale, completed: FBR to treat perchlorate and RDX with different electron donors. Influent concentrations were perchlorate 100 µg/L, RDX 200 µg/L, HMX 20 µg/L, and nitrate 8 mg/L.		100 µg/L perchlorate to <4 µg/L with acetic acid as electron donor	Groundwater	
Naval Weapons Industrial Reserve Plant (NWIRP), McGregor, Texas—Full scale, operational: FBR system using acetate as electron donor, treating blended influent from collection/biobarrier trenches averaging 1–2 ppm perchlorate.	400 gpm	2000 µg/L to <4 ppb RL	Groundwater, surface water (seeps)	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
In Situ Bioremediation				
Arcadis—Injection of corn syrup or other carbon source as the electron donor to promote biodegradation of perchlorate.				
NASA, JPL, Pasadena, California—Pilot test, completed: Conducted in 2003 to evaluate use of in situ bioremediation to reduce perchlorate concentrations in the source area. Instead of molasses, corn syrup was used as the electron donor because it does not contain significant amounts of sulfur and nitrogen (sulfur creates potential for hydrogen sulfide formation; bacteria preferentially degrade the added nitrogen before perchlorate contamination.		Up to 90% reduction	Groundwater	Conversion to a reducing environment can potentially mobilize some metals such as Mn and Fe.
GET B, Aerojet, California—Pilot test, completed: Corn syrup was injected into two aquifers upgradient of existing extraction wells in an effort to remove perchlorate through biodegradation prior to the extraction wells. Significant reduction of perchlorate occurred near the extraction wells. However, mechanical difficulties in delivering the corn syrup in an efficient and consistent manner helped lead to less of a reduction than anticipated. Perchlorate was not reduced to concentrations (<4 µg/L) that would eliminate the need for aboveground perchlorate removal.			Groundwater	
Ensafe, Inc.—Groundwater collection trench constructed with composting materials, cotton seed meal, and cotton seed.				
Area M, NWIRP, McGregor, Texas—Full scale, operational: Industrial area using 25 ft deep, 30 inch wide trench. Water is run through ex-situ bioreactor for polishing.		100–13,000 µg/L to <4 µg/L	Groundwater, surface water (seeps)	
Area F, NWIRP, McGregor, Texas—Pilot scale, operational: Industrial areas using 12 ft deep, 30 inch wide trenches with composting materials, wood chips, acetic acid, and vegetable oil.		From 100s of ppb to very low ppb levels	Groundwater, surface water (seeps)	
Area S, NWIRP, McGregor, Texas—Full scale, operational: Industrial area using 30 inch wide trench with composting materials, wood chips and vegetable oil.	3500 ft of trenching	From the 100s of ppb to very low ppb levels	Groundwater, surface water (seeps)	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
GeoSyntec Consultants—Delivery of soluble electron donors via groundwater recirculation systems and active biobarriers. Typically groundwater is extracted, amended with an electron donor, and reinjected to the aquifer to promote in situ treatment.				
Area 20, Aerojet, Sacramento, California—Pilot scale, completed: Conducted to accelerate in situ bioremediation of perchlorate in a deep contaminated aquifer ~70 ft thick and extending to 100 ft below ground surface. Groundwater was extracted, amended with electron donor (acetate, lactate), and reinjected upgradient to promote biodegradation of perchlorate (12,000 µg/L) and trichloroethene (TCE, 2 mg/L). Included a donor delivery well, an extraction well, and two monitoring wells. One-time bioaugmentation of the test cell with a TCE-degrading microbial consortia (KB-1) was required to achieve TCE dechlorination to ethene.		12,000 µg/L perchlorate reduced to <4 µg/L within 15 ft of donor delivery well in ~50 days; remained below detection through end of study (~250 days). TCE reduced to <5 µg/L through reductive dechlorination to ethene.	Groundwater	
Area 20, Aerojet, Sacramento, California—Pilot scale, completed: A follow-on test was conducted to demonstrate a single-pass active biobarrier. The project created a 600 ft wide biologically active zone across the groundwater plume using two groundwater extraction wells and a single centralized electron donor delivery/recharge well. Ethanol was used as the electron donor. Chlorine dioxide was used to control biofouling of the injection well. Funded by DOD's Strategic Environmental Research and Development Program (SERDP).	20 gpm	8,000 µg/L perchlorate reduced to <4 µg/L in downgradient monitoring wells within ~20 days; remained below detection through end of study (120 days). TCE reduced to <5 µg/L through reductive dechlorination to ethene.	Groundwater	Dissolved Mn and Fe concentrations exceeded secondary maximum contaminant levels (MCLs) due to creation of reducing conditions. This issue is expected with all in situ bioremediation projects, but most projects do not measure these constituents.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
GET D, Aerojet, Sacramento, California—Pilot scale, completed: An existing groundwater extraction and treatment system for volatile organic compounds (VOCs) required retrofit to treat perchlorate (250 µg/L). Ethanol was added to the effluent from the treatment system, and the effluent was recharged to the aquifer to promote in situ bioremediation of the perchlorate. Perchlorate was effectively removed to less than 4 µg/L a short distance (25–75 ft) downgradient from the extraction well. Chlorine dioxide was used to control biofouling of the injection well.	150 gpm	250 µg/L perchlorate reduced to <4 µg/L in downgradient monitoring wells within 30 days, and remained below detection through end of the study.	Groundwater	When concentration of electron donor addition was balanced with stoichiometric demand posed by oxygen, nitrate, and perchlorate in recharge water, perchlorate reduction occurred without mobilization of dissolved Mn and Fe above secondary MCLs.
AMPAC (formerly Pepcon) facility, Nevada—Pilot scale, completed: A 6-month in situ biological treatment pilot project in the hot spot area of the plum was completed in 5/03. Groundwater was recirculated at rate of 10 gpm between an injection and extraction well located 100 ft apart in line with groundwater flow. A number of electron donors were tested. The electron donor was switched from ethanol to citrate after 3 months to correct mineral precipitation problems. The groundwater has high TDS (3000–5000 ppm) with high concentrations of nitrates and chlorates that are preferentially biodegraded over perchlorate.	10 gpm	After 160 days, perchlorate concentrations of 600,000 µg/L were reduced to <2 µg/L at the downgradient performance monitoring well 50 ft from injection well.	Groundwater	
Former rocket testing facility, Nevada—Pilot scale, completed: Groundwater recirculation system was implemented to treat a source of perchlorate to groundwater. Groundwater was extracted, amended with citric acid, and reinjected to subsurface to treat the remaining source. No biofouling control was required for this application.	5 gpm	540 µg/L to <4 µg/L within 4 months. Concentrations have not rebounded in 6 months following bioremediation.	Groundwater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
WNN, Aerojet, Sacramento, California—Pilot scale, completed: A large-scale test of in situ bioremediation using a 900 ft wide active biobarrier was conducted to generate site-specific data in support of a Feasibility Study. The biobarrier employed two groundwater extraction wells and a single centralized electron donor delivery/recharge well. Ethanol was used as the electron donor. Chlorine dioxide was used to control biofouling of the injection well.	60 gpm	3000 μg/L) to <4 μg/L in downgradient monitoring wells within 14 days; remained below detection through end of study (~200 days).	Groundwater	Production of dissolved Mn and Fe controlled by balancing electron donor addition versus demand.
LHAAP, Karnack, Texas—Pilot scale, in progress: A demonstration of in situ bioremediation of perchlorate impacted groundwater using a semipassive approach to electron donor (sodium lactate) addition. The biobarrier uses periodic (e.g., semiannual) bulk additions of electron donors to create a biologically active zone across the perchlorate plume to prevent migration. Funded by DOD's ESTCP.		1000 μg/L concentrations significantly reduced, in most downgradient wells down to <4 μg/L. Additional electron donor injections planned to improve biobarrier effectiveness in very heterogeneous aquifer.	Groundwater	
NIROP, Magna, Utah—Interim remedial measure: An active in situ biobarrier where groundwater is captured, amended with an optimized concentration (based on stoichiometric needs) of electron donors, and recharged to the aquifer to promote in situ perchlorate reduction (and hence perchlorate migration control). This approach allows for addition of a controlled and optimized amount of electron donor and therefore has minimal adverse impact on secondary groundwater quality. Funded by DOD's ESTCP.	100 gpm		Groundwater	

Technology & Vendor Name/Projects	**Throughput**	**Treatment Effectiveness**	**Media**	**Residuals**
Groundwater Barrier Trench—Joint DOD/ESTCP–funded project.				
Pilot scale, planned: The objective is to evaluate the efficiency and design criteria of a permeable mulch biowall to degrade perchlorate in groundwater. The demonstration will evaluate critical design parameters such as biowall composition and contaminant residence time that are required to successfully implement this technology on a broader scale.			Groundwater	
Los Alamos National Laboratory (LANL)—A multilayered permeable reactive barrier (PRB) incorporates a sequence of four reactive media layers to immobilize or destroy a suite of contaminants present in alluvial groundwater, including Sr-90; Pu-238, -239, -240; Am-241; perchlorate; and nitrate. The four sequential media cells consist of gravel-sized scoria, apatite, pecan shells and cottonseed with an admixture of gravel (biobarrier), and limestone.				
LANL, Mortandad Canyon, New Mexico—Full scale, operational: PRB was installed in 02/03 to demonstrate in situ treatment of contaminants within alluvial and deeper perched groundwater. The 27 ft deep by 20 ft wide by 20 ft long PRB was designed with a 10-year lifetime and 1-day residence time within the biobarrier. Preliminary results indicate that both nitrate and perchlorate are being reduced by microbial activity. After the PRB was installed, drought conditions lowered the groundwater table to below the bedrock-alluvium interface and hence below the bottom of the PRB. A meaningful evaluation of PRB effectiveness has thus been delayed until groundwater levels recover to normal levels. Cost to install: $900K.		Field data indicate nondetectable levels (2 ppb) in wells within biobarrier, but this is residual water in bedrock under alluvium; 20 ppb was detected in residual groundwater in upgradient monitor well.	Groundwater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Shaw—Injection of lactate and carbonate/bicarbonate amended water into aquifer.				
Naval Surface Warfare Center, Indian Head, Maryland—Pilot scale, completed: Site required the addition of the carbonate/bicarbonate buffer due to low pH. After 20 weeks, eight of nine wells had >95% reduction, with two wells down to the RL. Funded by DOD's SERDP and Navy.		170,000 µg/L to <4 µg/L	Groundwater	
Aerojet, California—Pilot scale, under way: An innovative, recirculating well technology developed at Stanford University will be evaluated for electron donor addition and mixing. This horizontal-flow treatment well technology was chosen for this application because it is anticipated to be the most effective and inexpensive method for applying electron donor to deep aquifers contaminated with perchlorate. Funded by DOD's ESTCP.			Groundwater	
Whittaker Bermite Facility, Santa Clarita, California—Pilot scale, planned: A groundwater recirculation system will be installed to distribute and mix electron donor with perchlorate-contaminated groundwater in a shallow, alluvial aquifer. This system will create a wide capture zone for the contaminated water, provide hydraulic control within the test region, and facilitate modification of the aquifer geochemistry to promote perchlorate biodegradation. Funded by Army Corps of Engineers.			Groundwater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Solutions-IES—Biologically active permeable barrier: injection of emulsified soybean oil product (EOS®) as the electron donor to promote biodegradation of perchlorate. The emulsion is prepared using soybean oil, food-grade surfactants, and vitamins (commercially available as EOS) and then distributed throughout the treatment zone using temporary injection wells to create a permeable reactive biologically active barrier.				
Northern Maryland—Pilot scale, under way: This ESTCP-funded project is investigating an innovative, low-cost approach for distributing and immobilizing a water-miscible emulsion with a controlled droplet size as the biodegradable organic substrate in a perchlorate- and 1,1,1-trichloroethane (TCA)-contaminated aquifer. The aquifer contains elevated concentrations of perchlorate (~10,000 mg/L) and TCA (~23,000 mg/L) released from a closed lagoon. The test barrier is 60 ft long and 10 ft deep in the contaminated, saturated, shallow aquifer. A portion of the oil becomes trapped within the soil pores, leaving a residual oil phase to support long-term anaerobic biodegradation of the perchlorate. This approach provides good contact between the slowly biodegradable organic substrate (oil), the perchlorate, and TCA and substantially reduces initial capital costs with virtually no long-term (O&M) costs.		Within 1 month, rapid, complete, and sustained removal of perchlorate (<0.004 mg/L) traversing the treatment barrier and no rebound downgradient of the contact zone. Within 68 days of contact with the substrate, TCA concentrations decreased by 95% in monitor wells up to 20 ft downgradient with increasing concentrations of biological daughter products.	Groundwater	
Phytoremediation				
GeoSyntec Consultants				
Rocket manufacturing facility, California—Pilot scale, completed: An engineered planting of Sudan grass was constructed to prevent perchlorate in VOC treatment system effluent from reentering groundwater. Sudan grass has a high water-uptake capability. Perchlorate concentrations in infiltrating water declined during the test as a result of biodegradation in the rhizosphere and possibly reduction within plant tissues.	7 acres		Wastewater (from VOC treatment plant)	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Salt cedar trees—These trees are known to mine salt from the water. Stalks of the plant in the Las Vegas Wash picked up significant concentrations of perchlorate per gram of tissue.				
Research			Groundwater	
University of Georgia and Iowa—Performed in conjunction with the Air Force Research Laboratory and LHAAP.				
California—Pilot scale, completed: Rhizodegradation and enzymatic degradation in leaves has been observed in different plant species. Species tested include French tarragon and cottonwood. Current research focuses on enhancing rhizodegradation over slower enzymatic degradation pathway, which can allow for accumulation of perchlorate in plant tissues.			Groundwater	
Willow trees—In bench-scale tests, willows successfully treated water contaminated with both perchlorate and TCE. Rhizodegradation accounted for most of the removal of perchlorate with little uptake into the plant. Plant uptake might be significant with high-nitrate environments (a competing terminal-electron acceptor).				
Bench scale			Groundwater	
Constructed Wetlands				
Containerized Wetlands, Lawrence Livermore National Laboratory (LLNL)—Engineered use of plants to assimilate or degrade nitrate and perchlorate in water via the interaction of the contaminant with plant roots and their associated rhizosphere microorganisms. System consists of fiberglass tanks in series, containing coarse, aquarium-grade gravel and native wetland plants, such as bulrushes (*Scripus*), cattails (*Typha*), and sedges (*Carex*).				
Pilot study, completed: A containerized wetland system designed to remove nitrate and perchlorate from groundwater was tested over a 7-month period.		Removal of nitrate (as NO_3 to <4 mg/L) and perchlorate (to <4 µg/L)	Groundwater, surface water	BOD, TSS, nitrogen, phosphorous, TOC, pH, turbidity, DO may need to be monitored at effluent.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Simulated Wetland Drum—Work performed by the University of Georgia in conjunction with the Air Force Research Laboratory.				
Laboratory study, completed: The system consists of a 55 gal drum filled with sand and potting mix. One drum was planted with native wetland plants, such as cattails (*Typha*), duckweed (*Spirodela*), and parrot feather (*Myriophyllum*). The media quickly developed reducing conditions, and drums containing wetland plants showed the highest removal rates for perchlorate (half-lives ~1.5–4 days).		250 mg/L perchlorate to ? µg/L	Groundwater, surface water	BOD, TSS, nitrogen, phosphorous, TOC, pH, turbidity, DO may need to be monitored at effluent.
Soil Bioremediation				
CDM—In situ bioremediation of vadose zone soil. Funded by DOD's ESTCP.				
Gaseous Electron Donor Injection Technology (GEDIT)—Pilot scale, planned in location to be determined: Patent-pending technology for treatment of perchlorate injects gaseous electron donors into soil using injection wells in combination with optional soil vapor extraction wells. These electron donors can include hydrogen/carbon dioxide or VOCs such as methanol, ethanol, butanol, acetic acid, ethyl acetate, and butyl acetate.			Soil	
Earth Tech/Geosyntec—Ex situ anaerobic composting				
Edwards AFB, California—Feasibility study, completed: A pilot study of anaerobic composting of perchlorate soils was conducted in 55 gal drums. Objectives were to reduce the perchlorate concentrations in soil below the residential primary remediation goal (PRG) of 7.8 mg/kg by using horse stable compost as the electron donor.	130 cubic yd	Up to 57 mg/kg to <7.8 mg/kg	Soil	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Ensafe, Inc.—Anaerobic landfarming in lined, flooded cell.				
NWIRP, McGregor, Texas—Full scale, completed: Perchlorate-contaminated soil was excavated; transported to a biotreatment cell; mixed with amendments (citric acid, nitrogen, phosphorus, and soda ash as a buffer) in a 40 cubic yd roll-off container; and placed in the treatment cell lined with 30 mil high-density polyethylene (HDPE). The soil was saturated as it was placed in the cell, and more water was added to maintain at least 2 inches of water above the soil to foster anaerobic conditions.	1500 cubic yd	500,000 µg/kg average to <100 µg/kg RL	Soil	
Environmental Alliance/Geosyntec—Ex situ anaerobic composting.				
Rocket manufacturing facility, Arkansas—Full scale, completed: Ex situ anaerobic composting was employed to treat 1500 cubic yd of soil containing perchlorate. Mulch and hay were used as electron donors.	1500 cubic yd	100 mg/kg average to <0.01 mg/kg in 12 months	Soil	
ENSR/Geosyntec—Ex situ anaerobic composting.				
Rocket manufacturing facility, San Jose, California—Full scale, completed: Pilot test to confirm the ability to reduce perchlorate concentrations to below a site-specific cleanup level of 0.02 mg/kg. Methyl soyate and acetate used as electron donors.	500 cubic yd	No data yet	Soil	
GeoSyntec Consultants—Ex situ and in situ anaerobic degradation.				
Ex situ anaerobic composting Area 41, Aerojet, Sacramento, California—Pilot scale, complete: Composting of soils from former perchlorate burn area. Two ~10 cubic yd piles treated. Degradation half-life was 1–2 days. Cost: $65/cubic yd.	20 cubic yd	23 mg/kg average to <0.1 mg/kg in 14 days	Soil	
Ex situ anaerobic composting Rocket manufacturing facility, San Jose, California—Full scale, completed: Treated soil adjacent to a grinder station. Horse stable compost used as electron donor. Cost: $45/cubic yd.	200 cubic yd	175 mg/kg to <1 mg/kg within 90 days	Soil	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Ex situ anaerobic composting Former road flare manufacturing facility, Santa Clara County, California—Full scale, completed: Acetate and citric acid used as electron donors. Cost: $50/cubic yd.	1000 cubic yd	7 mg/kg to <0.1 mg/kg within 90 days	Soil	
In situ anaerobic composting Area 41, Aerojet, Sacramento, California—Pilot-/full-scale, completed: Based on pilot test above, project was modified to perform the same function without excavating the soils. Cow manure and calcium magnesium acetate was applied directly over the hot spots of perchlorate with the addition of moisture. Pilot was successful and turned into full scale. Unique site characteristics allowed penetration of the electron donor to the full depth of the soil column (2–3 ft soil overlying bedrock). Cost: $25/cubic yd.	65 hot spots over 550 acres	450 mg/kg average to 1.4 mg/kg average; 96.4% average perchlorate reduction	Soil	
In situ soil and groundwater treatment Former road flare manufacturing facility, Santa Clara County, California—Full scale, under way: Through infiltration of electron donors (acetate and citric acid) to a depth of 16 ft (average water table elevation).	40,000 cubic yd	No data yet	Soil	
In situ soil and groundwater treatment Hogout Facility, Aerojet, Sacramento, California—Pilot scale, under way: The goal is to bioremediate perchlorate in a 35 ft vadose zone sequence using a combination of technologies—a radial biobarrier for groundwater extraction and infiltration flushing of vadose zone. Using oleate and calcium magnesium acetate as electron donors to treat perchlorate being flushed from vadose zone at a major source of perchlorate in soil and groundwater.		No data yet	Soil, groundwater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
GeoTrans—In situ soil washing.				
Inactive Rancho Cordova Test Site, Aerojet, Sacramento, California—Pilot scale, under way: Soil washing using ethanol-blended water injected into a recharge well was attempted to bioremediate a 120 ft thick vadose zone. Results to date have not been successful.		Variable	Soil	
MWH/Geosyntec—Combined in situ and ex situ bioremediation.				
Boeing, Santa Susana Field Laboratory, Ventura Co., California—Full scale, under way: A combined in situ/ex situ bioremediation remedy is treating soils to a depth of 3 ft in three production areas by mixing with an electron donor (acetate) to promote in situ bioremediation of perchlorate in surface soils. Soils excavated from other areas have been subsequently mixed with electron donor (methyl soyate) and placed over top of the amended in situ soils to combine in situ and ex situ treatment.	20,000 cubic yd in situ, 8000 cubic yd ex situ	No data yet	Soil	
Naval Surface Warfare Center/Shaw—In situ bioremediation of vadose zone soil. Funded by DOD's ESTCP.				
Pilot scale, planned: Objective is to demonstrate and validate treatment of perchlorate in vadose zone soils through two approaches aimed at bioremediation and flushing via the infiltration of liquid electron donor. First, an engineered infiltration gallery will be designed to deliver and distribute the electron donor to perchlorate-impacted vadose zone soils. In conjunction with the infiltration gallery, an injection well may be used to supply donor to deeper vadose zone soils. The second approach will use a simple soil-mixing and watering approach, wherein donor agents are mixed with the upper 2–3 feet of the soil column and then watered regularly to deliver donor agents to contaminated vadose zone soils. Both liquid and solid donor amendments will be evaluated in the second approach. For both approaches, the most effective electron donor will be determined using site-specific column studies.			Soil	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Planteco and University of Georgia—In situ biological treatment of perchlorate-contaminated soil.				
LHAAP, Texas—Pilot scale, completed: Laboratory testing indicated that soils containing 300 mg/kg could be treated to nondetectable levels in less than 9 days using chicken manure, horse manure, and ethanol as carbon sources. Perchlorate reduced to below RL after 10 months to 30 inches, with varied levels of reduction in the deeper layers. Perchlorate concentrations in the wettest cells had decreased to nondetectable levels. Estimated cost: $25–50/cubic yd.	110 square ft	6700 µg/kg to <40 µg/kg RL in first 30 inches	Soil	
LHAAP, Texas—Pilot scale, completed: The site was subdivided into three sections. Approximately 2/3 of the southern section of the 1-acre plot was treated with 600 cubic yd of mushroom compost. The northeast 1/6 was treated with 125 cubic yd of cow manure compost only. The northwest 1/6 was treated with 125 cubic yd of cow manure compost and then with perchlorate-degrading bacteria. An irrigation system was used to mobilize the nutrient amendments into the vadose and saturated zones, and tensiometers were installed to monitor moisture content in the site soils.	1 acre	80% reduction in mass	Soil	
Soil Composting				
Pueblo Army Depot, Colorado—Full scale: Performed to remediate soils contaminated with explosives (HMX and RDX) and now known to also be contaminated with perchlorate. Analyses are under way to assess the effectiveness of the process in reducing perchlorate concentrations.			Soil	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
PHYSICAL PROCESSES				
Conventional Ion Exchange Resins				
Calgon ISEP® (Ion SEParator), Continuous Anion Exchange and Regeneration—System includes multiple (20–30) anion exchange columns mounted on a turntable attached to a rotating multiport valve. During a rotation, each resin cell is subjected to a cycle of adsorption, regeneration (with an NaCl solution) or elution, and one or two rinse steps.				
La Puente Valley County Water District, California—Full scale, operational: Designed to treat 2500 gpm with 600 µg/L perchlorate; began operating 02/00. Uses Purolite A 850, strong base anion, acrylic, Type 1 gel resin and operates 19 hours/day to control the perchlorate plume in the San Gabriel Groundwater Basin. Capital cost = $2 million; operating cost = $145/acre-ft.	2500 gpm	~200 µg/L to <4 µg/L	Drinking water	Concentrated brine potentially containing nitrate, sulfate, and perchlorate requires treatment or disposal.
Kerr-McGee, Henderson, Nevada—Full scale, operational: Perchlorate destruction module started in 03/02 and operated for about 6 months to treat extracted groundwater from Athens Road Well Field and Las Vegas Wash seep area. Actual flow rates varied 200–560 gpm. Maintenance problems were caused by high TDS, hardness, and sulfate. Operation discontinued due to corrosion in heat exchangers.	450 gpm	80–100 mg/L to <2 mg/L (DL, ion-specific electrode)	Groundwater	
Big Dalton Well, Baldwin Park, California—Pilot scale, completed: Study initiated in 5/98; brine produced was 0.75% of the inflow.	4.3 gpm	18–76 µg/L to <4 µg/L.	Drinking water	
San Gabriel Valley Water Company, El Monte, California—Full scale, planned: B6 well site; system built, first phase of start-up under way; expected operational by 02/04.	7800 gpm		Drinking water	
Valley County Water District, Baldwin Park, California—Full scale, planned: Under construction, start-up 01/04.	7800 gpm		Drinking water	
City of Pasadena, California—Full scale, proposed: 3500–5000 gpm system proposed at existing wells next to JPL site; planning stage.	7000 gpm		Drinking water	

Technology & Vendor Name/Projects	**Throughput**	**Treatment Effectiveness**	**Media**	**Residuals**
Calgon Anion Exchange—Fixed-bed nonregenerable anion exchange resin treatment.				
California Domestic Water Company, Whittier, California—Full scale, operational: Start-up 7/02. Cost: $125/acre ft.	5000 gpm	<14 µg/L to <4 µg/L	Drinking water	Perchlorate-laden resin requires disposal.
Tippecanoe Treatment Facility, City of Riverside, California—Full scale, operational: Start-up 12/02.	5000 gpm	Distribution system 6.4 ppb average in 2001 to 4.6 ppb average in 2002	Drinking water	
Gage 51-1 Treatment Facility, City of Riverside, California—Full scale, operational: Start-up 05/03.	2000 gpm	<60 µg/L to <? µg/L	Drinking water	
West San Bernadino Water District, Rialto, California—Full scale, operational: Start-up 05/03.	2000 gpm		Drinking water	
City of Monterey Park, Delta Treatment Plant, Well 12 (San Gabriel GW basin—Full scale, planned: System constructed and tested, awaiting permit, expected operational 01/04.	4050 gpm		Drinking water	Perchlorate-laden resin requires disposal.
B5 Site, San Gabriel Valley Water Company, El Monte, California—Full scale, planned: Under construction, start-up 04/04.	7800 gpm		Drinking water	
Kerr-McGee facility, Nevada. Full scale, operational: Once-through ion exchange system to treat captured surface water in the seep area has been ongoing since 11/99. Groundwater in seep area has been pumped and treated since 10/01. The initial four-well extraction system was expanded to nine wells in 03/03. Pumping rates varied 300–600 gpm 10/02–03/03.	>300 gpm	Influent averages ~30 ppm. Combined with effluent from ion exchange system, effluent varies <0.5–2 ppm and averages 1.3 ppm.	Surface water, groundwater	
NWIRP, McGregor, Texas—Full scale, completed: Modular system was brought in to treat a blended influent from the collection/biobarrier trenches averaging 1–2 ppm perchlorate. System was replaced by a biological FBR.	200 gpm?	2000 µg/L to < 4 ppb RL	Groundwater, surface water (seeps)	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Loma Linda, California—Full scale, planned: Single-pass ion exchange treatment; start-up planned spring 2004.	2000 gpm		Drinking water	
Kerr McGee facility, Nevada—Full scale, operational: A single-pass ion exchange system was installed to replace the Calgon ISEP system and to allow continuous treatment of the extracted groundwater from the Athens Road wells. Continuous operation since 10/03.	850 gpm	Influent varies 200–300 ppm. Combined with effluent from ion exchange system, effluent varies <0.5–2 ppm and averages 1.3 ppm.	Groundwater	
Ion Exchange—Originally designed for nitrate removal, anion exchange system achieves perchlorate removal.				
City of Pomona, California—Full scale, operational.	10,000 gpm		Drinking water	Concentrated brine potentially containing nitrate, sulfate, and perchlorate requires treatment or disposal?
U.S. Filter Anion Exchange—Fixed-bed nonregenerable anion exchange resin treatment.				
Aerojet, California—Full scale, operational: Sacramento GET D facility.	1000 gpm	200 ppb to <4 ppb	Groundwater	Perchlorate-laden resin requires disposal.
Aerojet, California—Full scale, operational: Sacramento GET B facility.	2000 gpm	50 ppb to <4 ppb	Groundwater	
Aerojet and Boeing (formerly McDonald Douglas), Sacramento, California—Full scale, operational.	800 gpm	250 ppb to <4 ppb	Groundwater	
City of Morgan Hill, California—Full scale, operational: Two wells: Nordstrom well operating; Tennant well installed. Perchlorate plume due to Olin Corp. manufacture of road flares.	800 gpm	<10 ppb to <4 ppb	Drinking water	
West Valley Water Co., West San Bernadino, California—Full scale, operational: Start-up 05/03.	2000 gpm	<10 ppb to <4 ppb	Drinking water	
City of Rialto, California—Full scale, operational: Start-up 08/03.	2000 gpm	<10 ppb to <4 ppb	Drinking water	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
City of Colton, California—Full scale, operational: Start-up 08/03.	3500 gpm	<10 ppb to <4 ppb	Drinking water	
Fontana Union Water Co., Fontana, California—Full scale, operational: System being loaded with resin as of 12/19/03; operational by 01/04.	5000 gpm	15 ppb to <4 ppb	Drinking water	Perchlorate-laden resin requires disposal.
West San Martin Water Co., California—Full scale, operational.	800 gpm	17 ppb to <4 ppb	Drinking water	
Selective Ion Exchange Resins				
Applied Research Associates, Inc.—ESTCP-funded selective resin demonstration.				
Redstone AAP—Pilot scale, planned: A perchlorate-selective ion exchange resin and ferrate ion displacement regeneration technique will be demonstrated with a skid-mounted, field demonstration unit. Multiple, ion-exchange-column regenerations will be performed using this resin and regeneration technique that can reduce effluent volume to 0.1%–0.2% of state-of-the-art ion exchange processes. Biological and thermal effluent treatment techniques will be demonstrated that enable discharge or reuse of the spent regeneration solution. A low-cost, prototype field monitor capable of online, real-time, perchlorate analysis to <1 ppb will also be demonstrated.			Groundwater	Perchlorate-laden resin requires disposal.
Carrollo Engineers, Inc.				
Castaic Lake Water Agency, Santa Clarita, California—Pilot scale, completed: Study on three single-use resins: USF 9708, USF 9710, and CalResin #2. Influent feed water concentration was spiked to approximately 50 ppb perchlorate. All the resins removed perchlorate, with breakthrough occurring at 25,000 bed volumes for USF 9708; 72,000 bed volumes for USF 9710; and 76,000 bed volumes for CalResin #2.		50 ppb to <1 ppb		
SYBRON IONAC SR-7 Anion Exchange Resin, LLNL—Commercially available regenerable nitrate selective anion exchange resin manufactured by Sybron; resin is effective for perchlorate, whose ion exchange properties are similar to nitrate's. In these systems, anion exchange is part of a treatment train, preceded with biological treatment to remove nitrate and followed with GAC to remove TCE.				
LLNL, Building 815 SR-7—Full scale, operational: Start-up 07/00; regenerant flow rate 0.25–0.5 gpm/cubic ft.	1400 gpd	10 µg/L to <4 µg/L	Groundwater?	Perchlorate-laden resin requires disposal.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
LLNL, Building 830-DISS—Full scale, operational: Start-up 11/00; regenerant flow rate 0.25–0.5 gpm/cubic ft.	5000 gpd	10 µg/L to <4 µg/L	Groundwater?	
LLNL, Building 854-PRX—Full scale, operational: Start-up 09/00; regenerant flow rate 0.25–0.5 gpm/cubic ft.	1000 gpd	7.2 µg/L to <4 µg/L	Groundwater?	
Oak Ridge National Laboratory (ORNL) and University of Tennessee Purolite A-530E Bifunctional Resin—Bifunctional anion exchange resins highly selective for perchlorate consist of quaternary ammonium groups with large (C6) and small (C2) alkyl groups resulting in high selectivity and good exchange kinetics. The technology has been licensed to Purolite to develop a commercial version of the resin. Difficulty with regeneration of bifunctional resins has limited their use. ORNL has patented a process using a ferric chloride-hydrochloric acid displacement technique to regenerate bifunctional and other selective anion-exchange resins. Lab studies indicate a high recovery of ion-exchange sites can be achieved with the regenerant solution without affecting the resin's performance after repeated cycles.				
ORNL lab studies demonstrating D3696 resin (aka Purolite A-530E) to remove perchlorate.			Groundwater	Perchlorate-laden resin requires disposal.
Stringfellow Site, Riverside Co., California—Full scale, planned: A system to treat the downgradient "toe" of the perchlorate plume (~30 µg/L) began continuous operation in 12/03. The system consists of two 10-cubic-ft beds in series and can treat perchlorate to below the 4-ppb DL. The highly selective resin is expected to last several months before change-out is required. On-site regeneration was not an option because of location in a residential area which required a low profile and minimal operational requirements. High TDS, including sulfates (~200 mg/L) and nitrates (~70 mg/L) makes use of nonselective anion exchange resins problematic for this application due to frequent regeneration or change-outs and no brine disposal options. Significant concentrations of tetrahydrafuran and methyl ethyl ketone were detected during system start-up but not in subsequent sampling. The source of these contaminants is unclear (may be from the resin system) as these compounds are not normally found in groundwater plume at this location.	25 gpm	30 ppb to <4 ppb	Groundwater	Perchlorate-laden resin requires disposal.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Site 285, Edwards AFB, California—Full scale, under way: The system, including a chemical regeneration process and destruction module, became operational in the spring of 2003 and has removed 32 lb of perchlorate from approximately 9 million gal of water processed through 06/04. Destruction module is expected to become operational in summer 2004.	35 gpm	300 µg/L to <4 µg/L	Groundwater	
Castaic Lake—Pilot scale, completed: Five-month pilot plant study (Kennedy-Jenks), three wells	300 gpm	to <4 µg/L	Groundwater?	
Purolite A-520E Anion Exchange Resin—Commercially available nitrate selective anion exchange resin manufactured by Purolite; effective for perchlorate, whose ion exchange properties are similar to nitrate's. Reported by ORNL as one of the best nitrate-selective resins; higher affinity for nitrates over sulfates.				
Paducah Gaseous Diffusion Plant—Lab study to treat pertechnetate.			Groundwater?	Perchlorate-laden resin requires disposal.
ORNL comparison study for bifunctional resins—Lab study.			Groundwater	
Rohm and Haas Corporation Amberlite PWA2 Perchlorate Selective Resin—A proprietary perchlorate-selective resin that is NSF 61–certified for potable use. Amberlite PWA2 is a nonregenerable resin for "load and toss" applications.				
Aerojet, Sacramento, California—Full scale, operational.	2000 gpm	50 ppb to <4 ppb	Drinking water	Perchlorate-laden resin requires disposal.
Lincoln Avenue, Altadena, California—Full scale, operational.	2000 gpm	20 ppb to <6 ppb	Drinking water	
Rohm and Haas Corporation Amberlite PWA 555 Nitrate Selective Resin—Commercially available nitrate selective anion exchange resin is effective for perchlorate, whose ion exchange properties are similar to nitrate's.				
W. San Martin Colony and County wells, California—Full scale, operational.	1000 gpm	15 ppb to <4 ppb	Drinking water	Perchlorate-laden resin requires disposal.
Selective strong-base anion exchange resin				
Site 9, Vandenberg AFB, California—Pilot scale, operational: System consists of two 560 gal tanks, each containing ~42 cubic ft of a selective strong-base anion resin; associated interconnection and process piping, and instruments and controls. Columns are arranged in series (lead-lag configuration) and installed inside a double-contained treatment pad. Cost: $81K/year for O&M.		204 µg/L to <4 µg/L	Groundwater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Tailored Granular Activated Carbon/GAC				
Granular Activated Carbon				
Crafton-Redlands Plume, City of Redlands, California—Full scale, operational: System installed to treat VOC contamination for drinking water supply later found effective to treat low concentrations of perchlorate. In 09/01, the Department of Health Services issued a domestic water supply permit amendment to the City of Redlands Municipal Utilities Department to operate the Texas Street GAC facility to remove perchlorate in the domestic water supply system. Penn State University is using 4 of the 24 GAC vessels at the same facility for additional studies, looking at enhancing GAC performance by preloading with iron organic complex and regenerating with reducing solution.		Influent concentration of 60–138 µg/L perchlorate; GAC bed regenerated every 6 weeks for perchlorate treatment vs. the 8 months required for treatment of VOCs.	Drinking water	GAC loaded with perchlorate and potentially other compounds requires treatment or disposal.
Site 133, Edwards AFB, California—Full scale, operational: Liquid-phase GAC system. Three 2000 lb carbon canisters in series, constructed in 05/01 to remove VOCs, are now treating 92 µg/L perchlorate as a cocontaminant; U.S. Filter has conducted bench-scale testing of modified carbon to treat perchlorate at the treatment system effluent.	100 gpm	Influent concentration of 92 µg/L perchlorate; 09/03 report indicates system not effective for perchlorate.	Drinking water	
City of Monterey Park, Well 5, California—Full-scale, planned. Coconut carbon to treat low levels.			Drinking water	
Penn State University, Tailored GAC—Preloaded with quaternary ammonium compounds				
Crafton-Redlands Plume, City of Redlands, California—Pilot scale, completed: A number of different quaternary ammonium compounds have been pilot tested using rapid, small-scale columns. Results concluded that for Redlands water, commercially available GAC can be tailored to extend the service life for perchlorate from 1 month to 2.5 years.	2.65 mL bed volume	60–140 µg/L to <6 µg/L	Drinking water	Tailored GAC loaded with perchlorate and potentially other compounds requires treatment or disposal.

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Crafton-Redlands Plume, City of Redlands, California—Full scale, under way: Testing began in the spring 2004 to last 6–9 months. Results after 6 weeks of operation have treated 7100 bed volumes of water with no breakthrough of perchlorate, which averaged 49 ppb at the influent.		49 µg/L average to 6 µg/L	Drinking water	
MMR, Cape Cod, Massachusetts—Pilot scale testing of tailored GAC				
Reverse Osmosis				
Reverse Osmosis (RO)—Water is forced through a semipermeable membrane. RO has been used to treat various water sources to remove high concentrations of total dissolved salts. Although performance data is not available, RO would also be expected to effectively remove perchlorate ions. Unselective removal of dissolved ions results in a more corrosive, lower pH effluent. Degradation of the membrane in treating perchlorate may be a concern.				
NASA, JPL, Pasadena, California—Bench scale: A laboratory treatability study was performed to assess the effectiveness of RO to remove perchlorate from groundwater. A thin film composite and a cellulose acetate membrane were tested. In both tests, 80% of influent stream was recovered as permeate and 20% as rejectate. High energy requirements due to operating pressures required.		Influent 800 µg/L, thin film permeate 12–16 µg/L, thin film rejectate 3600 µg/L, cellulose acetate permeate 680 µg/L, cellulose acetate rejectate 1600 µg/L	Groundwater	Effluent (rejectate) brine production (TDS, perchlorate) can be equal to 20% of influent flow rate and require further treatment or disposal.
Electrodialysis				
Electrodialysis—Water is passed through channels of alternating semipermeable and permeable membranes (to either anions or cations), while being exposed to an electrical field.				
Magna Water Co., Utah—Pilot scale, completed: An electrodialysis reversal pilot unit (Ionics Aquamite III) was installed at an uncontaminated well with high TDS (1300 mg/L) and silica (80 mg/L) and operated continuously for 4 days to evaluate perchlorate removal effectiveness. Extracted groundwater feed to the pilot unit was dosed to 130 µg/L perchlorate. Cost: $1.10–1.50/1000 gal	7.4 gpm	Stabilized in the low 70% range; higher rates (94%) possible with a four-stage system	Drinking water?	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
CHEMICAL PROCESSES				
Concentrated Brine Treatment				
Calgon Carbon ISEP™ System Perchlorate and Nitrate Destruction Module (PNDM)—A catalytic chemical reduction process for treating perchlorate and nitrate ions in the waste regeneration brine. A hydrogen source (ammonium) is added as a reductant, and perchlorate is reduced to chloride ($ClO_4^- + 8e^- + 8H^+ \rightarrow Cl^- + 4H_2O$). The system operates at 250ºC and is relatively energy intensive.				
NASA, JPL Pasadena, California—Pilot scale, completed: Seven-month study conducted 1998–99 on groundwater with 1200-µg/L perchlorate and high concentrations of nitrate and sulfate. PNDM effectively reduced the perchlorate and nitrate present in regeneration brine waste, while >96% of sulfate was removed. Treated regenerant stream was recycled to effectively regenerate the resin. Overall process waste from the system was about 0.16% of the feed volume. O&M costs are estimated at about two times the cost of a comparable biological treatment unit.	<2 gpm	1200 µg/L to <4 µg/L; nitrates and sulfates removed to acceptably low levels	Wastewater (brine from water treatment plant)	A small concentrated brine (sulfate buildup) waste stream requires treatment or disposal.
Kerr-McGee, Henderson, Nevada—Full scale, operational: System started up in 03/02 and operated for about 6 months to treat extracted groundwater from the Athens Road Well Field and the Las Vegas Wash seep area. Actual flow rates varied 200–560 gpm. Maintenance problems were caused by high TDS, hardness, and sulfate. Operation was discontinued due to corrosion in the heat exchangers.	450 gpm	80–100 mg/L to <2 mg/L (DL, ion-specific electrode)	Wastewater (brine from water treatment plant)	
ORNL Chemical Reduction of Perchlorate $FeCl_3$-HCl Regenerant Solutions—Perchlorate in $FeCl_3$-HCl regenerant solutions is degraded using ferrous iron and/or nontoxic organic reducing agents (patent pending). While perchlorate is reduced, ferrous (Fe^{2+}) ions are oxidized to ferric (Fe^{3+}) ions, which replenish or “regenerate” the $FeCl_3$-HCl solution.				
Site 285, Edwards AFB, California—Full scale, under way: Bifunctional resin treatment system including a chemical regeneration process and destruction module, is under way. Destruction module became operational in fall 2004. Destruction of perchlorate to chloride and water required up to 1-hour residence time in pilot testing.	35 gpm	50 µg/L to <5 µg/L	Wastewater (brine from water treatment plant)	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Nanoscale Bimetallic Particles				
Lehigh University—Nanoscale bimetallic particles (Fe/Pd, 99.9% Fe) are being investigated for their possible use as remediation technology. Nanoparticles feature large surface area and extremely high surface reactivity.				
In lab research, nanoscale zero-valent iron particles degraded perchlorate to chloride after a lag period at an estimated rate of 1.2 mg/L-day.			Groundwater?	
Ozone Peroxide				
AWWARF-Funded Study				
In "Removal of Perchlorate and Bromate in Conventional Ozone/GAC Systems," investigators explored water quality conditions under which ozone/GAC and other advanced oxidation processes (AOPs) may result in by-products that donate electrons sufficiently to facilitate destruction of perchlorate. Results indicated that perchlorate ions exchanged to some extent onto the GAC, but that abiotic reduction of perchlorate did not occur under these conditions. Since perchlorate solutions in water cannot be reduced by strong common reductants, it is unlikely that AOPs would be successful unless the kinetic barrier to reduction can be overcome.			Drinking water	
Titanium				
Titanium +3 Chemical Reduction, Georgetown University				
A technique using titanous ions (3+) to chemically reduce perchlorate. Several new organic ligands have been developed that have been shown to catalyze reduction of perchlorate by titanous ions (3+) ions to titanium dioxide and chloride in acidic aqueous media. A preliminary patent application has been filed.			Wastewater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
UV/Zero-Valent Iron				
UV Light/Zero-Valent Iron Reduction—Lab studies (Gurol and Kim 2000) indicate that perchlorate can be reduced by iron (FeO) under anoxic conditions and that UV light can accelerate the reaction rate to levels for practical application. Patent #6,531,065 was issued March 11, 2003. The patent also covers use of the iron metal with a catalyst and with phosphoric acid.				
Pilot test, planned: Funded by the California State University, San Bernadino, Office of Technology Transfer and Commercialization Initiative to be conducted in the Rialto Area.		77% reduction in perchlorate concentration in laboratory study	Drinking water	
Electrochemical				
Capacitive Deionization, Carbon Aerogel, LLNL—Influent water containing salts enters space between two carbon-aerogel electrodes; electrostatic field forces ions into aerogel, where they are held, and purified water leaves the space between the electrodes. CDI systems potentially use 10–20 times less energy per gallon and achieve the same results as a convention electrodialysis or RO system.				
LLNL patented the carbon aerogel capacitive deionization technology in 1995 and has licensed the technology for commercialization to CDT Systems, Inc. (formerly FarWest Group, Inc.), based in Tucson, Arizona. CDT Systems, Inc. has a proposal to install a system to clean up brackish water at the municipal water treatment plant in Carlsbad, California.			Wastewater? Drinking water?	
Capacitive Deionization, Flow-Through Capacitor, Biosource, Inc.—Made up of alternating electrodes of porous activated carbon. With small-voltage applications, dissolved salts in the water moving through the capacitor are attracted to the high surface area carbon and removed. Once the capacitor is fully charged, the electrodes are shorted to regenerate the capacitor, causing absorbed contaminants to be released as a small volume of concentrated liquid waste.				
Research and development: Covered by a number of U.S. patents. Biosource, Inc. indicated in May 2004 that it had recently been awarded a contract to develop water purification technology for military use and that it will be used in Iraq.			Drinking water?	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Electrochemical Reduction—Clarkson University, City of Redlands and City of Riverside, California (AWWARF-funded).				
Bench-scale study of electrochemical reduction of perchlorate used two-chambered batch reactor systems. Cathodic and anodic compartments were separated by an ion exchange membrane, and electrodes consisted of titanium coated with a thin film of titanium dioxide particles. Initial perchlorate concentration ranged 50–500 mg/L. Perchlorate reduction was limited due to the competition among anions for active sites on the electrode surface, with perchlorate less strongly adsorbed than both sulfate and chloride. The time required for ions in the water to travel to the electrode surface is a design problem in developing a practical full-scale system.			Drinking water	
THERMAL PROCESSES				
Applied Research Associates, Integrated Thermal Treatment Process—Perchlorate in regenerant brine is thermally decomposed at elevated temperature and pressure with the addition of reducing agents and promoters. Concentration of the brine with reverse osmosis would be necessary to make the process cost-effective. A patent application is pending.				
Laboratory research, completed.			Wastewater (brine from water treatment plant)	
Environmental Chemical Corp., Burlingame, California, Thermal Treatment Unit—Dry, perchlorate-contaminated soils were thermally destroyed in bench tests in 10 minutes at 775ºF in a laboratory-scale rotary kiln. Temperatures required in the full-scale unit were higher (up to 950ºF) depending on moisture evaporation requirements at a fixed total residence time of 10 minutes.				
MMR, Cape Cod, Massachusetts—Bench and full scale, under way: In full production mode, summer 2004.	40 tons/hour	To <4 ppb (µg/kg)	Soil	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
General Atomics, Super Critical Water Oxidation—Supercritical water sustains combustion and oxidation reactions because it mixes well with oxygen and with nonpolar organic compounds. Reductions, such as those necessary to destroy the perchlorate ion, also take place.				
Thiokol, Brigham City, Utah—Bench scale, completed: The concentration of ammonium perchlorate in CYH is 10.8%. During optimization testing, destruction removal efficiencies of 99.9% were achieved. The critical point of water is 374.2ºC and 22.1 Mpa. Costs are expected to be high due to high temperature and pressure.	Up to 800 lb of CYH propellant	99.9% DRE	Wastewater	
EMERGING PROCESSES				
Monitored Natural Attenuation (MNA)				
Solutions IES—A long-term process using groundwater monitoring to evaluate and track the natural degradation of perchlorate. Preliminary evidence suggests that conditions similar to those promoting denitrification may be appropriate for perchlorate MNA. These include anaerobic conditions along with depleted concentrations of oxygen and nitrate. However, at this time there is a little or no evidence of perchlorate natural attenuation at field sites as few studies have investigated this process.				
Pilot-scale, under way: ESTCP-funded project to identify perchlorate sites, monitor site conditions over an extended period, and seek commonality in conditions from sites where perchlorate appears to be controlled compared to locales where is it continuing to migrate unabated. This effort will help develop a protocol that will be useful to regulators and the public, providing the needed assurances that this approach is protective of human and environmental health.			Groundwater	

Technology & Vendor Name/Projects	Throughput	Treatment Effectiveness	Media	Residuals
Iodide Addition				
U.S. Air Force and U.S. Geological Survey—The remediation of perchlorate-contaminated wetlands using potassium iodide or elemental iodine addition to the water.				
Laboratory: Results indicate this maybe a promising method, requiring only a small amount of iodide to counteract significantly higher concentrations of perchlorate (as little as 10 ppb iodide can offset the effects of up to 50 ppm perchlorate). Additional testing at the pilot and field scale needs to be performed, as well as determining logistics and physical form of iodide application, effects on other wetland species, and stability and potential side effects of iodide addition.			Surface water	
Nanofiltration/Microfiltration				
Nanofiltration/Ultrafiltration—A partially permeable membrane is used to preferentially separate different fluids or ions. Nanofiltration generally works for particle sizes over 10 angstroms (10^{-10} m), rejecting selected salts (typically divalent). Ultrafiltration is a selective fractionation process using pressures up to 145 psi. It concentrates suspended solids and solutes with high molecular weights. Ultrafiltration process typically removes particles in the 0.002–0.1 micron range.				
AWWARF-funded studies: Nanofiltration passes more water at lower operating pressure than RO systems and thus requires less energy to perform the separation. Based on the size of the perchlorate ion, about 3.5 angstroms, nanofiltration may not prove to be effective for perchlorate removal. Ultrafiltration targets compounds that are larger than those removed by nanofiltration; thus, ultrafiltration is not expected to effectively remove perchlorate. High energy requirements due to operating pressures.			Drinking water	Effluent brine production (TDS, perchlorate) can equal 20% of influent flow rate and require further treatment or disposal.
Catalytic Gas Membrane				
University of Delaware				
Catalytic hydrogen membrane—Research				

APPENDIX G

Perchlorate Team Contacts, Fact Sheet, and Product List

PERCHLORATE TEAM CONTACTS

Sara Arav-Piper, Co-Team Leader
NV Division of Environmental Protection
702-486-2868
spiper@ndep.nv.gov

Laurie Racca, Co-Team Leader
CA Dept. of Toxic Substances Control
916-255-3668
lracca@dtsc.ca.gov

Stacey Kingsbury, ITRC Program Advisor
Sky Research
540-961-9132
Stacey.kingsbury@skyresearch.com

Richard Albright
DC Department of Health
202-535-2283
richard.albright@dc.gov

Brian Ambrose
DuPont Corp. Remediation Group
302-992-5869
brian.ambrose@usa.dupont.com

Caroline (Cal) Baier-Anderson
University of Maryland
410-706-1767
cbaie001@umaryland.edu

Keith Bailey
Kerr-McGee Shared Services
405-270-3651
kbailey@kmg.com

Jean Balent
Technology Innovation Program
EPA
703-603-9924
balent.jean@epa.gov

Joshua Barber
EPA
703-603-0265
barber.joshua@epa.gov

Bob Barnwell
ADEM
334-271-7746
bbarnwell@adem.state.al.us

Erica Becvar
HQ AFCEE / TDE
210-536-4314
erica.becvar@brooks.af.mil

Bradley Call
US Army Corps of Engineers
916-557-6649
bradley.a.call@usace.army.mil

Sandip Chattopadhyay
Battelle
614-424-3661
chattopadhyays@battelle.org

Jay Clausen
ERDC / CRREL
603-646-4597
jay.l.clausen@erdc.usace.army.mil

David O. Cook
Kleinfelder, Inc.
916-366-1701
dcook@kleinfelder.com

Charles G. Coyle
US Army Corps of Engineers
402-697-2578
charles.g.coyle@usace.army.mil

Michael Crain
US Army Corps of Engineers
402-697-2657
michael.e.crain@usace.army.mil

Geoffrey D. Cullison
Operational Environmental Readiness &
Planning Branch
Chief of Naval Operations
703-602-5329
geoffrey.cullison@navy.mil

Annette Cusher
Arkansas Dept. of Environmental Quality
501-682-0841
cusher@adeq.state.ar.us

Shana R. Dalton
US Army Corps of Engineers, ERDC
402-444-4317
shana.r.dalton@nwo02.usace.army.mil

Susan Flanagan
Institute of Makers of Explosives (IME)
202-429-9280
sjflanagan@ime.org

Kimberly Gates
US Navy NFESC
805-982-1656
kimberly.gates@navy.mil

Bill Guarini
Shaw Environmental
609-895-5384
william.guarini@shawgrp.com

Paul Hadley
CA Dept. of Toxic Substances Control
916-324-3823
phadley@dtsc.ca.gov

Mark Hampton
US Army Environmental Center
410-436-6852
mark.hampton2@us.army.mil

Bryan Harre
NFESC
805-982-1795
bryan.harre@navy.mil

Lornette D. Harvey
GA Environmental Protection Division
404-656-2833
lornette_harvey@dnr.state.ga.us

T.R. Hathaway
Human & Ecological Risk Division
California EPA
916-255-6636
lazytr1@aol.com

Paul Hatzinger
Shaw Environmental
609-895-5356
paul.hatzinger@shawgrp.com

Keith Hoddinott
USACHPPM
410-436-5209
keith.hoddinott@amedd.army.mil

Rose Knox
MA Dept. of Environmental Protection
617-556-1026
rosemary.knox@state.ma.us

Limesand Kurt
KS Dept. of Health & Environment
785-296-1671
klimesan@kdhe.state.ks.us

Katharine Kurtz
Navy Environmental Health Center
757-953-0944
kurtzk@nehc.med.navy.mil

M. Tony Lieberman
Solutions-IES
919-873-1060
tlieberman@solutions-ies.com

R. Lee Lippincott
NJ Dept. of Environmental Protection
609-984-4899
lee.lippincott@dep.state.nj.us

Paul Locke
MA Dept. of Environmental Protection
617-556-1160
Paul.Locke@state.ma.us

Mark E. Losi
Center for Environmental Microbiology
949-756-7516
mlosi@biocem.com

Alexander MacDonald
CA Water Resources Control Board
California - Region 5
916-464-4625
amacdonald@waterboards.ca.gov

Malinowski Mark
Dept. of Toxic Substances Control
California EPA
916-255-3717
mmalinow@dtsc.ca.gov

Heidi Maupin
Navy Environmental Health Center
757-953-0947
maupinh@nehc.med.navy.mil

Christopher Maurer
State of Washington Dept. Of Ecology
360-407-7223
cmau461@ecy.wa.gov

Richard Newill
BEM Systems, Inc.
602-266-2011
rnewill@bemsys.com

Eric Nuttall
University of New Mexico
505-277-6112
nuttall@unm.edu

Dee O'Neill
Columbia Analytical Services, Inc.
360-577-7222
doneill@caslab.com

Ian T. Osgerby
US Army Corps of Engineers
978-318-8631
ian.t.osgerby@usace.army.mil

Gail L. Pringle
Naval Facilities Engineering Service Center
805-982-1411
gail.pringle@navy.mil

Matt Rhoades
Golder Associates
303-980-0540
matt_rhoades@golder.com

Rey Rodriguez
H2O-R1 Consulting Engineers, Inc.
626-852-1235
reyrh2or2@aol.com

Supalak (Sue) Rogers
TCEQ
512-239-6213
srogers@tceq.state.tx.us

Blaine Rowley
Office of Cleanup Technologies
US Department of Energy
301-903-2777
blaine.rowley@em.doe.gov

Lenny Siegel
Center for Public Environmental Oversight
650-961-8918
lsiegel@cpeo.org

David R. Smith
Shieldalloy Metallurgical Corporation
856-692-4201
dsmith@shieldalloy.com

Betty A. Strietelmeier
Los Alamos National Laboratory
505-665-9986
bastriet@lanl.gov

Clayton Trumpolt
CO Dept. of Public Health and Environment
303-692-3460
clayton.trumpolt@state.co.us

Harry Van Den Berg
ARCADIS
714-278-0992
hvandenberg@arcadis-us.com

Deborah Dixon Walker
US Army Corps of Engineers
256-895-1796
deborah.d.walker@hnd01.usace.army.mil

Allen Wolfenden
CA Dept. of Toxics Substances Control
916-255-6540
awolfend@dtsc.ca.gov