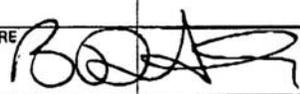


**ALTERNATIVE CAUSES OF WIDE-
SPREAD, LOW CONCENTRATION
PERCHLORATE IMPACTS TO
GROUNDWATER**

FINAL

**Prepared by:
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for the
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Arlington, Virginia**

May 5, 2005

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EXECUTIVE SUMMARY

The frequency of detection of perchlorate in groundwater and drinking water supplies has been steadily increasing since its initial identification as a chemical of concern in 1997. It is currently estimated that perchlorate is present in groundwater in at least 30 states and affects the drinking water supplies of more than 20 million people in the southwestern United States (U.S.). The source of perchlorate in water supplies has typically been attributed to U.S. Department of Defense (DOD), National Aeronautics & Space Administration (NASA) and/or defense contractor facilities that have used ammonium perchlorate (AP) in rocket and missile propellants. Perchlorate impacts to groundwater and surface waters in southern Nevada and southern California have also been attributed to the historic production and release of perchlorate from a former chemical manufacturing facility in the Las Vegas, Nevada area (Hogue, 2003), which has impacted the surface waters of Lake Mead and the Colorado River.

As a result of its high profile and its addition to the Unregulated Contaminant Monitoring Rule (UCMR List 1), which requires perchlorate analysis by large public water suppliers and selected small water utilities, most public water supplies are now being routinely analyzed for perchlorate. Through monitoring activities, perchlorate has been detected at low levels (typically less than 50 µg/L) in a significant number of areas without apparent military sources. Investigation activities have linked these perchlorate impacts to various non-military sources, including use of perchlorate-containing blasting agents for quarrying and construction, manufacture of road flares, manufacture and use of fireworks and pyrotechnics, use of perchloric acid in industrial manufacturing, and use of Chilean nitrate fertilizers.

Perchlorate is known to be present in a significant number of products and processes. Unfortunately, it has proven exceedingly difficult to obtain records of perchlorate handling related to production and use of many of these products and processes. As such, this review focuses on five major perchlorate-containing products for which significant quantity and use information is available: Chilean nitrate fertilizers; fireworks; safety flares; blasting explosives; and electrochemically-prepared (ECP) chlorine products. The key findings of this review for each of these major perchlorate-containing products can be summarized as follows:

Chilean Nitrate Fertilizer: Between 1909 and 1929 (the period for which detailed information could be obtained), the U.S. imported an estimated 19 million tons of Chilean nitrate (Goldenwieser, 1919; Howard, 1931), of which an average of 65% was used as fertilizer (Brand, 1930). Assuming an average perchlorate content of about 0.2% in Chilean nitrate (based on U.S. Environmental Protection Agency research results), approximately 49 million pounds of perchlorate may have been unknowingly applied to

agricultural soils during this time period, for fertilization of crops such as cotton, tobacco, fruits and vegetables. While the use of Chilean nitrate fertilizers has steadily declined since about the 1930s, there is evidence of continued use through the present day. Additional evaluation of soils and groundwater in agricultural areas that have used (and may still be using) Chilean nitrate fertilizers seems warranted to evaluate whether past and/or present fertilizer practices can be expected to be the cause of long-term, low concentration perchlorate impacts to groundwater in some agricultural areas and watersheds.

Fireworks: In 2003, 221 million pounds of fireworks were consumed in the U.S., with an estimated 3% produced domestically and the remainder imported from China (APA, 2004a). Although perchlorate is widely used as an oxidizer in firework formulations, there is little information related to the amount of perchlorate residue remaining after burning of fireworks and/or statistics on dud rates and blind stars that occur during fireworks displays. As such, it is difficult to estimate potential perchlorate inputs from fireworks to the environment. Recent studies have detected perchlorate in soils, groundwater and/or surface water following fireworks displays, and therefore, the potential environmental impact of perchlorate from fireworks displays warrants further scientific study.

Safety Flares: Preliminary research by Silva (2003a, 2003b) of the Santa Clara Valley Water District in California indicates that 3.6 grams of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. While numbers are not available for total domestic flare production, assuming an average cost per flare of \$0.50 to \$1.00 per flare and annual sales of \$20 million by the largest domestic manufacturer, some 20 to 40 million flares may be sold annually. Given this estimate, up to 237,600 pounds of perchlorate could leach from road flares annually. Surface runoff from highways and roads represents a potentially significant and largely uninvestigated impact to surface water and groundwater quality. Additional evaluation of the potential for perchlorate impacts to surface waters and groundwater from safety flare use appears warranted.

Blasting Explosives: Some water gels, emulsions, and non-electric detonators can contain substantial amounts of perchlorate (e.g., up to 30% by weight). While, most of the perchlorate in the explosives is expected to be consumed in the detonation, poor housekeeping practices (i.e., spillage), improper use, or misfires can potentially result in perchlorate contamination of surface and ground waters, as has been reported for multiple sites in Massachusetts. Given that the U.S produces approximately 2.5 million tons of explosives annually, perchlorate could potentially be released into the environment nationwide in substantial amounts. Currently, no publicly-available data exist to quantify

potential perchlorate impacts from blasting. More studies are required to assess and quantify the potential impact of blasting explosives on perchlorate contamination of surface and ground waters.

ECP Chlorine Chemicals: During the electrochemical manufacture of chlorine products, such as chlorate, from chloride brine feedstocks, perchlorate may be formed as an impurity at concentrations of 50 to 500 mg/kg. The estimated North American annual chlorate manufacturing capacity is 2.4 million tons, whereas the total annual consumption of sodium chlorate in the U.S. is approximately 1.2 million tons. The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the U.S. for on-site production of chlorine dioxide to bleach cellulose fibers. Effluents from pulp mills have been reported to contain chlorate (1 to 70 mg/L) but there is little information available as to the potential for perchlorate release from these facilities. Sodium chlorate is also used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers. The use of sodium chlorate in the pulp and paper industry and as a defoliant has the potential to contribute perchlorate to the environment and needs to be better understood.

The United States DoD, NASA and related defense contractors are likely to be the most significant domestic users of perchlorate, and as such, a significant percentage of identified groundwater perchlorate impacts are likely to be attributable to DoD, NASA, and related defense contractor facilities. However, cases exist, and many more are likely to surface, where perchlorate impacts result from combinations of military, non-military, and/or natural inputs. The ability of DoD, NASA, and defense contractors to accurately apportion the relative contributions from these varying sources, and hence to properly determine liability and control cleanup cost, lies in having a good understanding of the wide variety of products and processes that may contribute perchlorate to the environment and through the development and validation of appropriate forensic tools. This review is intended to assist DOD, NASA, and defense contractors in identifying the significant number of industrial and commercial processes and products that contain perchlorate and to estimate the potential contribution of perchlorate to the environment (past and/or present) from non-military products or processes.

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1. INTRODUCTION

The frequency of detection of perchlorate in groundwater and drinking water supplies has been steadily increasing since its initial identification as a chemical of concern in 1997. It is currently estimated that perchlorate is present in groundwater in at least 30 states and affects the drinking water supplies of more than 20 million people in the southwestern United States (U.S.). The source of perchlorate in water supplies has typically been attributed to U.S. Department of Defense (DOD), National Aeronautics & Space Administration (NASA) and/or defense contractor facilities that have used ammonium perchlorate (AP) in rocket and missile propellants. Perchlorate impacts to groundwater and surface waters in southern Nevada and southern California have also been attributed to the historic production and release of perchlorate from a former chemical manufacturing facility in the Las Vegas, Nevada area (Hogue, 2003), which has impacted the surface waters of Lake Mead and the Colorado River.

As a result of its high profile and its addition to the Unregulated Contaminant Monitoring Rule (UCMR List 1), which requires perchlorate analysis by large public water suppliers and selected small water utilities, most public water supplies are now being routinely analyzed for perchlorate. Through monitoring activities, perchlorate has been detected at low levels (typically less than 50 µg/L) in a significant number of areas without apparent military sources. As examples:

- Researchers at Texas Tech University have detected perchlorate in groundwater over a contiguous area of some 30,000 square miles in the High Plains region of West Texas (Cristen, 2003). Of 217 public drinking wells tested in the study area, 73% contained detectable perchlorate concentrations of more than 0.5 µg/L, while 35% had perchlorate concentrations equal to or greater than 4 µg/L. Potential sources for perchlorate in groundwater over this large area were speculated to include leaching from evaporite deposits and/or in situ generation of perchlorate by an electrochemical reaction, possibly related to cathodic protection of water systems and/or oil wells.
- Perchlorate has been detected in more than 400 private water supply wells (domestic, industrial, agricultural) in the Santa Clara Valley in California near the cities of Morgan Hill and Gilroy (Ruby, 2004). The distribution of perchlorate, generally ranging between 4 and 10 µg/L, extends for approximately 9 miles. Perchlorate impacts have been attributed to a former road flare manufacturing facility.

- Perchlorate has been detected in more than 148 wells in the small town of Hills, Iowa (Bello, 2004) at concentrations in the range of 4 to 52 µg/L. According to the U.S. Environmental Protection Agency (EPA), the source of these impacts is unknown, although Chilean nitrate is suspected.
- Perchlorate has been detected in water supply wells in at least four towns in Massachusetts (Westford, Millbury, Boxborough, and Dracut). These impacts are suspected to be related to the use of explosives for rock blasting for development and/or quarrying.
- Perchlorate (related to the use of perchloric acid) was detected at elevated concentrations (2,000 mg/L) in the effluent (sewer discharge) from a medical device manufacturer in Billerica, Massachusetts. The discharge was processed through the Billerica wastewater treatment facility and was subsequently discharged to the Concord and Merrimack Rivers, causing impacts to downgradient water suppliers in Tewksbury, Massachusetts (Hughes & Murphy, 2004).

While natural sources or formation mechanisms for perchlorate may explain its presence in several of the aforementioned cases (Jackson et al., 2004; Dasgupta et al., 2005), widespread, low concentration perchlorate impacts in groundwater can apparently also result from a variety of non-military-based inputs as well, potentially including:

- i) storage, handling and use of Chilean nitrate-based fertilizers containing perchlorate;
- ii) manufacturing, storage, handling, use and/or disposal of fireworks containing perchlorate;
- iii) manufacturing, storage, handling, use and/or disposal of road flares containing perchlorate;
- iv) manufacturing, storage, handling, use and/or disposal of explosives or pyrotechnics containing perchlorate; and/or
- v) manufacture, storage, handling and use of electrochemically-prepared (ECP) chlorine products, primarily those that contain chlorate or were manufactured from chlorate feedstocks.

While various research organizations are evaluating potential natural sources of perchlorate (e.g., Orris et al. 2003; Jackson et al., 2004), few organizations are generating quantitative evidence of the potential impacts of perchlorate-containing products on wide-spread, low-level perchlorate detections in groundwater. Releases of perchlorate from these products/processes may be responsible for causing a raised baseline perchlorate concentration in some areas or watersheds.

The objective of this review is to identify the significant number of industrial and commercial processes and products that contain perchlorate, so as to understand the potential prevalence of perchlorate in the environment. Where sufficient information exists, this review attempts to estimate the potential contribution of perchlorate to the environment (past and/or present) from industrial, agricultural, commercial and/or consumer use of perchlorate-containing products or processes.

1.1 Perchlorate Properties and Uses

Perchlorate is an inorganic anion and oxidant consisting of chlorine bonded to four oxygen atoms (ClO_4^-). It is typically found in association with ammonium, sodium, or potassium cations as a salt. Hydrogen perchlorate (or perchloric acid) is another commonly used form of perchlorate. Perchlorate exhibits high solubility and mobility in water and is very stable, being degraded only under anaerobic conditions (Coates et al., 1999). Consequently, perchlorate releases can result in long, persistent contaminant plumes in groundwater, as has been observed at many sites.

Perchlorate is known to be present in a significant number of products and processes, as listed in Table 1-1. While it is anticipated that DOD and NASA propulsion products represent the most significant percentage of domestic perchlorate use, the consumption of perchlorate-containing industrial, agricultural, commercial and consumer products is likely to be significant. Unfortunately, it is exceedingly difficult to obtain records of perchlorate handling related to production and use of many of the products and processes listed in Table 1-1, and therefore this review will focus on five major perchlorate-containing products for which significant quantity and use information is available: Chilean nitrate fertilizers (Section 2); fireworks (Section 3); safety flares (Section 4); blasting explosives (Section 5); and ECP chlorine products (Section 6).

Table 1-1: Current and Historical Uses of Perchlorate

Raw Product	Product/Process	Role of Perchlorate in the Product/Process
Perchlorate Salts	Ammonia production	Ingredient of catalytic mixtures used in making ammonia
	Detonating compositions	Oxidizing agent
	Matches	Oxidizing agent
	Pyrotechnic compositions	Oxidizing agent
	Railroad signal (fuse) compositions	Oxidizing agent
	Smoke-producing compounds	Oxidizing agent
	Metallurgical	Constituent of brazing fluxes, welding fluxes
	Pharmaceutical	Used in compounding and dispensing practice
	Air bag for vehicles	Initiators
	Paints and enamels	Curing/Drying Agent
	Photography	Flash powder/ oxidizing agent
	Oxygen generators	Burn Rate Modifier
	Road flares	Oxidizing agent
	Ejection seats	Propellant
	Model rocket engines	Propellant
	Rockets used for research, satellite launches, and Space Shuttle	Propellant
	Some explosives in construction, mining and other uses	Oxidizing agent
	Fireworks	Oxidizing agent
	Voltaic cells and batteries involving lithium or lithiated anodes, non-aqueous solvents or polymeric films, and manganese dioxide or other transition metal oxides	Electrolyte (Lithium perchlorate)
	Zinc and magnesium batteries	Electrolytes (zinc perchlorate and magnesium perchlorate)
	Electropolymerization reactions involving monomers such as aniline, benzidine, biphenyl, divinylbenzene, and indole	Electrolyte
	Polyvinyl chloride (PVC)	Dopants to improve heat stability and fire retardation characteristics
	Thin film polymers such as polyethylene oxide (PEO), polyethylene glycol, or poly(vinylpyridine)	Dopant to impart conductive properties in various electrochemical devices
	Drying agent for industrial gases and other similar applications	Desiccant (Anhydrous magnesium perchlorate)
	Plastics and polymers	Dopants to impart antistatic and conductive properties

Table 1-1: Current and Historical Uses of Perchlorate (continued)

Perchloric Acid	Nitrogen measurement	Used for Kjeldahl digestions
	Leather tanning	Extraction of chromium
	Potash measurement	Used to form insoluble potassium perchlorate
	Manufacture of inorganic chemicals, intermediates, organic chemicals, pharmaceuticals, synthetic aromatics	Oxidizing agent
	Manufacture of explosive compounds, such as the perchlorated esters of monochlorohydrin.	Reagent
	Ingredient of lead-plating baths	Facilitates the deposition of lead from baths containing lead perchlorate
	Electropolishing operations	Electrolyte in anodization of metals to produce non-corroding surfaces
	Metallurgy	Extraction of rare earth metals
	Etching brass and copper	Acid
	Acetylations, alkylations, chlorinations, polymerizations, esterifications, and hydrolyses	Catalyst
	Cellulose acetate production	Esterification of cellulose
	Destruction of organic matter, especially in preparation for the determination of calcium, arsenic, iron, copper, and other metals	Acid digestion, in combination with nitric acid
	Determination of copper and other metals in sulfide ores	Acid digestion
	Dissolving refractory substances such as titanium slags	Acid digestion
	Ammonium perchlorate, high purity metal perchlorates	Starting material for the manufacture of pure ammonium perchlorate and in the production of high purity metal perchlorates
	Pickling and passivation of iron and steels	Oxidant
	Determination of silica in iron and steel and in cement and other silicate materials	Dehydrating agent
	Determination of chromium in steel, ferrochrome, chromite, leather, and chromatized catgut	Oxidizing agent
	Separation of chromium from other metals by distillation of chromyl chloride	Used in combination with hydrochloric acid
	As a primary standard acid	Perchloric acid, when distilled in a vacuum at a carefully regulated pressure, has exactly the composition of the dihydrate, 73.6% HClO ₄

Table 1-1: Current and Historical Uses of Perchlorate (continued)

Perchloric Acid (Cont'd)	Indirectly in the manufacture of anhydrous magnesium perchlorate	Dehydrating agent
	Titration of bases in non-aqueous solvents	As the strongest of the strong acids dissolved in anhydrous acetic acid
	Analytical procedures for the destruction of organic matter prior to the determination of metallic and non-metallic ingredients such as: 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.	Destruction of organic matter (mixtures of perchloric acid dihydrate with nitric acid or sulfuric acid, or of these three acids together)
Chilean Sodium Nitrate	Fertilizers	Incidental ingredient in fertilizers (largely historical, but soils previously treated may still contain perchlorate)
	Charcoal briquettes	Naturally occurring by-product
	Meat tenderizers	Naturally occurring by-product

2. CHILEAN NITRATE FERTILIZERS

Research by the U.S. Environmental Protection Agency (EPA) has confirmed that perchlorate is present in nitrate-based fertilizers manufactured from naturally-occurring caliche deposits mined from the Atacama Desert region of Chile (Urbansky et al., 2001a; Urbansky et al., 2001b). Historical agronomic literature indicates that Chilean nitrate fertilizers were widely used in specific agricultural practices in the early to mid 1900s, (Howard, 1931; Goldenwieser, 1919; Mehring, 1943). Past import statistics for Chilean nitrate (see Section 2.2) and historical agronomic guidelines for sodium nitrate application for various crops (see Section 2.3) indicate that significant quantities of perchlorate may have been unknowingly applied to agricultural soils over many decades from the early to mid 1900s. While the use of Chilean nitrate fertilizers steadily declined since about the 1930s, there is evidence of continued use through to the present day. For example, imports of fertilizer grade sodium nitrate supplied 27% and 6% of the total nitrogen used as fertilizer in 1939 and 1954, respectively. Since 2002, it is estimated that some 75,000 tons of Chilean nitrate fertilizer have been used annually in the U.S.

The application of these perchlorate-containing fertilizers over many decades through to the present day (albeit in much lower amounts) may explain the continued presence of low concentrations of perchlorate in soil and groundwater in some agricultural areas and watersheds. The continuing impacts of nitrate to groundwater in former agricultural areas urbanized since the 1940s is clear evidence of the potential for long lasting impacts of past fertilization practices on some regional watersheds (Fogg et al., 1998).

This chapter summarizes pertinent information related to the import and use of Chilean nitrate fertilizers and explores the potential for present-day perchlorate impacts to groundwater from historical and on-going Chilean nitrate fertilizer uses for specific agricultural practices.

2.1 Perchlorate Concentrations in Chilean Nitrate Fertilizer

Chilean nitrate fertilizers are derived from naturally-occurring caliche deposits that are mined from the Atacama Desert region of Chile (Urbansky et al., 2001a). The raw product used in the production of nitrate fertilizers was commonly called Chilean nitrate, nitrate of soda, sodium nitrate, Chilean saltpeter, and/or soda nitre. Chilean nitrate fertilizers are still sold commercially as “Bulldog Soda” in the U.S. The presence of perchlorate in the caliche deposits mined for Chilean nitrate fertilizer has been documented for over 100 years. Schilt (1979) briefly summarizes the early history of the

discovery of naturally-occurring perchlorate in Chilean caliche and Chilean nitrate fertilizer. He records that perchlorate was first discovered in the caliche deposits in 1886. This discovery was followed in 1896 by the confirmation of perchlorate in “Chile saltpeter” (sodium nitrate) over the widely varying concentration range of 0 to 6.79%. Schilt (1979) reports that a 1914 study determined that the maximum perchlorate concentration in refined sodium nitrate was about 1%. More recently, Ericksen (1983) provided production chemical data for caliche ores from 1932 to 1967 for the two largest production plants in Chile. Over this 35-year period, the ores contained about 30% soluble salts and averaged 6.3% nitrate and 0.03% perchlorate. The refining process for the caliche ore takes advantage of the high solubility of nitrate relative to the other anions, but perchlorate, which is even more soluble than nitrate, was not substantially separated from the nitrate. Assuming that the ratio of nitrate to perchlorate in the ore is preserved in the refined product, then the average perchlorate concentration in Chilean nitrate fertilizer would have been approximately 3,500 mg perchlorate/kg sodium nitrate or 0.35%.

Little attention was subsequently paid to the natural occurrence of perchlorate in Chilean nitrate, except as a geological curiosity, until the emergence of perchlorate as a chemical of concern at military sites. The U.S. Air Force Research Laboratories (AFRL) conducted a study in which multiple laboratories analyzed samples of a variety of lawn and garden fertilizers for perchlorate (Eldridge et al., 2000). The data from this inter-laboratory comparison study suggested the widespread presence of perchlorate in consumer fertilizers. The current definitive study of perchlorate in agricultural fertilizers was conducted in 2000 by a separate U.S. EPA laboratory (EPA-ORD-NRML-WSWRD) and is summarized in Urbansky et al. (2001a; 2001b). This study concluded that the occurrence of perchlorate in fertilizer was restricted to fertilizer products derived from Chilean nitrate produced by SQM Corporation and that all fertilizers derived partially or completely from Chilean nitrates contain appreciable perchlorate.

Today, SQM Corporation produces several nitrate products. The mined product consists predominantly of sodium nitrate (approximately 98%), with a minor component of other types of soluble salts, including perchlorate. Other current SQM products include potassium nitrate, which is produced by a chemical reaction between sodium nitrate and potassium chloride, and mixtures of sodium and potassium nitrate. Accordingly, potassium nitrate products may also contain appreciable levels of perchlorate according to the EPA-ORD-NRML-WSWRD and AFRL studies.

Data for two samples of Chilean sodium nitrate were analyzed in the EPA-ORD-NRML-WSWRD study. The inter-laboratory average of these two samples was 1,917 mg/kg and 1,590 mg/kg, for an average of 1,750 mg/kg. The AFRL study analyzed one sample consisting entirely of sodium nitrate, as indicated by the lack of P (phosphorous)

and K (potassium) in the manufacturer's information (sodium nitrate fertilizer is listed as 16-0-0). This sample had an inter-laboratory average perchlorate concentration of 7,687 mg/kg when analyzed by ion chromatography (IC) using the AS 16 column, the preferred IC method for analyzing perchlorate. These two studies yielded a range of perchlorate concentrations in Chilean sodium nitrate fertilizer of approximately 1,750 to 7,700 mg/kg, spanning the 3,500 mg/kg average (derived from the ratio of nitrate to perchlorate) in the original caliche ore. The average perchlorate concentration obtained by the EPA-ORD-NRML-WSWRD of 1,750 mg/kg or approximately 0.2% is a reasonably conservative estimate of the average perchlorate concentration of Chilean nitrate fertilizer and will be used in the subsequent calculations in this section.

2.2 Chilean Nitrate Imports

Between 1909 to 1918 and 1925 to 1929, the U.S. imported approximately 7,500,000 and 5,300,000 tons of Chilean nitrate (Goldenwieser, 1919; Howard, 1931), respectively, for a total of approximately 13,000,000 tons of Chilean nitrate (Table 2-1). If we assume that approximately 1 million tons of Chilean nitrate were imported annually during 1919 through 1924, then approximately 19 millions tons of Chilean nitrate fertilizer were likely imported into the U.S. between 1909 and 1929.

Table 2-1: Chilean Nitrate Imports

Year	Chilean Nitrate import to US (tons)
1909	329,124
1910	538,119
1911	528,435
1912	475,560
1913	573,773
1914	561,209
1915	577,120
1916	1,067,005
1917	1,264,659
1918	1,606,498
1925	1,245,693
1926	1,024,010
1927	838,635
1928	1,156,860
1929	1,042,113

During this period, it is estimated that between 49 and 70% of the imported Chilean nitrate was used as fertilizer, with an average of approximately 65% (Brand, 1930). The percentage of Chilean nitrate used for fertilizer reportedly fluctuated based on its demand for use in explosives manufacturing. Assuming an average perchlorate concentration of about 0.2% in the Chilean nitrate and that 65% of the imported Chilean nitrate (about 12 million tons) was used as fertilizer, then approximately 49 million pounds of perchlorate is likely to have been applied to agricultural soils during this time period.

Chilean nitrate fertilizer is still produced by SQM Corporation and makes up 0.14% of the total annual U.S. fertilizer application (Urbansky et al., 2001a). It is sold commercially as Bulldog soda and is primarily used in a few niche markets and specialty products. Currently, world production is 900,000 tons/year of which 75,000 tons are sold to U.S. farmers for use on cotton, tobacco, and fruit crops (Urbansky et al, 2001a; Renner, 1999). SQM reports that the perchlorate concentration in Chilean nitrate fertilizer has been reduced through changes in the refinement processes since 2002. The current perchlorate concentration is reported as 0.01% (Urbansky et al., 2001b), which is more than an order of magnitude improvement compared to historic perchlorate contents. However, this amount still represents the potential introduction of more than 15,000 pounds of perchlorate annually to agricultural soils, the fate of which is not well understood.

2.3 Use of Chilean Nitrate Fertilizers

A wide variety of agricultural publications document that Chilean nitrate was a common nitrate fertilizer in the U.S. during the first half of the 20th century. For example, in its 1938 Yearbook, the U.S. Department of Agriculture (USDA) stated that “sodium nitrate and ammonium sulfate are undoubtedly the most widely used nitrogen fertilizers at the present time”. Similarly, the USDA Fertilizer Consumption and Trends in Usage report (Mehring, 1943) identified Nitrate of Soda as the second most consumed fertilizer during its reporting period. While the use of Chilean nitrate fertilizers steadily declined since about the 1930s, there is evidence of continued use through to the present day. The following section discusses the use of Chilean nitrate fertilizer specifically related to the production of cotton, tobacco, and fruit, three crops for which Chilean nitrate use has been documented.

Cotton

Chilean nitrate fertilizer was often used to fertilize cotton and provided the necessary nitrogen for high yield crops (Skinner, 1932). It was typically used in delayed

applications (side dressings). The application of nitrate of soda to cotton is dependant on soil quality and the corresponding amount of nitrogen available for plant uptake. Typical delayed application rates of nitrogen for cotton were 18 to 30 pounds per acre (Skinner, 1932). This application rate is equivalent to 110 to 190 pounds per acre of nitrate of soda, which is approximately 16% nitrogen (Nelson et al, 1925), or approximately 0.2-0.3 lb of perchlorate per acre.

Between 1909 and 1929, Texas was the largest cotton producing state, harvesting approximately 283 million acres of cotton over a twenty year period. However, only 7% of the acreage in Texas required fertilizer application (Skinner, 1932). By comparison, southeastern states such as North Carolina, South Carolina, Georgia, and Alabama harvested lower quantities of cotton, but the fertilizer requirement for these soils was much greater (Skinner, 1932). For example, during this time period, Georgia, Alabama, South Carolina and North Carolina typically fertilized 91 to 97% of the total cotton acreage (Table 2-2). While the contribution of Chilean nitrate to fertilization of the cotton acreage is not clearly defined, data available in Howard (1931) suggest that in 1928 Chilean nitrate accounted for approximately 35% of total nitrogen fertilizer used that year on a nitrogen basis.

Table 2-2: Acres Fertilized for Cotton Production from 1909 to 1929, Top 4 States

State	Acres Harvested (1909-1929)¹	% of Acres Fertilized¹	Total Acres Fertilized
Georgia	87,242,000	95.9	83,665,078
Alabama	65,957,000	91.9	60,614,483
South Carolina	48,926,000	90.9	44,473,734
North Carolina	31,224,000	97.0	30,287,280
			219,040,575

References:

1 - Skinner, 1932

Mehring (1943) indicated that Georgia, Alabama, South Carolina, and North Carolina were heavily dependent on the use of Chilean Nitrate fertilizer, consuming between 63% to 75% of the total Chilean nitrate used domestically. Based on the 1909 to 1929 import statistics (about 12 million tons of Chilean nitrate as fertilizer), a consumption rate of 63% to 75% for these states would represent the use of 7.6 to 9.0 million tons of Chilean nitrate, which in turn would represent the potential application of 30 to 36 million pounds of perchlorate to agricultural soils (all crops) in these states over the 1909 to 1929 time frame.

Tobacco

Chilean nitrate fertilizer was commonly used in the U.S. as a source of nitrogen for tobacco plants. In a 1927 test of fertilizers on flue-cured tobacco, “nitrate of soda showed average yields and values which were considerably better than were obtained with ammonium sulphate” (Moss, 1927). From 1909 to 1929, Kentucky was the largest producer of tobacco and harvested 10,000,000 acres. North Carolina was the second highest producer of tobacco, harvesting over 9,000,000 acres (www.nass.usda.gov:81/ipedb/tobacco.htm).

Fertilizer application rates for tobacco vary with the season and soil quality; however, application rates of 30 to 40 pounds of nitrogen per acre were typically recommended (Bennett et al, 1953). To obtain this amount of nitrogen from nitrate of soda (16% nitrogen), approximately 185 to 250 pounds of nitrate of soda would have been applied per acre of tobacco. This range of application rates is similar to the application rates of nitrate of soda used today for certain tobacco crops (i.e., 3-5 lb/100 yd² or 195-325 lb/acre, www.ncagr.com/agronomi/stnote2.htm). Prior to 2002, this Chilean nitrate fertilizer application rate would correspond to a perchlorate application rate of approximately 0.4 to 0.5 lb per acre.

Fruit

The historic use of Chilean nitrate fertilizers has been reported for fruit trees in California, with an accepted fertilization rate between 100 and 200 pounds per acre as nitrogen. This translates to application rates ranging between 625 and 1250 pounds per acre of sodium nitrate (16% nitrogen). For simplicity, if the average application rate is assumed to be 1000 pounds per acre per year of Chilean nitrate as suggested by Collings (1949) in the textbook *Commercial Fertilizers*, then 2 pounds of perchlorate per acre per year may have potentially been applied to fruit orchard soils in some parts of California. Furthermore, between 1923 and 1960, 305,614 tons of Chilean Sodium Nitrate fertilizer were reported to have been used in California, according to data compiled by the California Department of Food and Agriculture. Assuming a perchlorate concentration of 0.2%, application of this mass of Chilean nitrate fertilizer would have resulted in the application of over 1.2 million pounds of perchlorate to agricultural soils/crops in California during this timeframe.

2.4 Potential to Impact Groundwater

While data summarized in the previous sections suggest that significant quantities of Chilean nitrate have historically been used to fertilize various crops, it is difficult to predict the fate and persistence of the applied perchlorate. The behavior of perchlorate in agricultural settings has not been investigated in detail, and several crucial aspects of perchlorate behavior in such settings (e.g., plant uptake, biodegradation, mobility in relation to soil factors, etc) are not well documented. However, nitrate (the principal component of the Chilean nitrate fertilizer) and perchlorate share important chemical features, and many aspects of the large body of literature concerning nitrate contamination of groundwater due to fertilizer use can be applied directly to understanding the potential for perchlorate contamination of groundwater through the same mechanism. The important aspects of the relationship between nitrate and perchlorate are summarized as follows:

- Nitrate and perchlorate are present in the potential source material, Chilean nitrate fertilizer.
- Nitrate (NO_3^-) and perchlorate (ClO_4^-) are both negatively charged ions and, as such, are highly mobile in soils. Soil particles are predominately negatively charged, and, therefore, electrostatic repulsion prevents adsorption.
- Sodium nitrate and sodium perchlorate, the predominant forms of these constituents in Chilean nitrate fertilizer, are both highly soluble in water (1.8 and 4.4 pounds per gallon, respectively), and thus there are no solubility constraints on the flushing of these compounds from soil into groundwater.
- Once in the vadose zone and groundwater, both nitrate and perchlorate are environmentally persistent and are not subject to chemical or biological breakdown under common groundwater conditions. The biological reduction of both nitrate and perchlorate requires the presence of organic matter, which can serve as electron donors, and anoxic conditions.

While the use of Chilean nitrate fertilizers containing perchlorate was most intense prior to 1950, the potential exists that impacts from these practices are only now being discovered in public water supplies. For example, Hudson *et al.* (2002) determined that water produced from 59 of 176 public water supply wells in the Los Angeles Basin was in excess of 50 years old. Of the remaining wells, only a small number of wells situated adjacent to large scale artificial recharge projects produce recent water, while the remainder produce mixed aged water of which at least 50% was recharged more than 50

years ago. Bohlke (2001) presents data for four representative surficial aquifers in the eastern U.S. with mean ages of 27-50 years. Note that these are mean ages and that some component of the groundwater must be older. Similarly, Crandall (2000) presents age data for a surficial aquifer in Florida where wells produce water with a spread in ages of from 3-50 years. Fogg *et al.* (1998) and Weissman *et al.* (2002) discuss the significance of the dispersion of groundwater ages with regard to breakthrough time and persistence of agricultural pollutants, noting that in areas with deep alluvial aquifers the observed nitrate pollution may be the result of agricultural practices more than 50 years previously. Given that perchlorate was a component of Chilean nitrate-based fertilizers, the hypothesis may be true for perchlorate.

The available nitrate literature reviewed for this paper indicates that it is possible that low level perchlorate impacts to groundwater in some areas may be the result of historic use of Chilean nitrate fertilizers. Additional evaluation of soils and groundwater in common crop areas discussed in this section seems warranted to evaluate whether historical fertilizer practices can be expected to be the cause of low concentration perchlorate impacts to groundwater in some agricultural areas and watersheds.

2.5 Summary

Between 1909 and 1929, the U.S. imported approximately 19 million tons of Chilean nitrate (Goldenwieser, 1919; Howard, 1931), of which an average of 65% was used as fertilizer (Brand, 1930). Assuming an average perchlorate content of about 0.2% in Chilean nitrate, approximately 49 million pounds of perchlorate may have been unknowingly applied to agricultural soils/crops during this time period for fertilization of crops such as cotton, tobacco and fruits. Since 2002, it is estimated that some 75,000 tons of Chilean nitrate fertilizer containing 0.01% perchlorate have been used annually in the U.S, suggesting that 15,000 pounds of perchlorate continue to be applied to agricultural soils on an annual basis. While the behavior of perchlorate in agricultural settings has not been investigated in detail, nitrate (the main component of Chilean nitrate fertilizer) and perchlorate share important chemical and transport characteristics, and many aspects of the large body of literature concerning nitrate contamination of groundwater due to historical fertilizer use may be applied directly to understanding the potential for perchlorate contamination of groundwater through the same mechanism. Clearly, additional evaluation of soils and groundwater in agricultural areas that used Chilean nitrate fertilizers seems warranted to evaluate whether historical fertilizer practices can be expected to be the cause of long-term, low concentration perchlorate impacts to groundwater.

3. FIREWORKS

Fireworks are widely used by both pyrotechnic professionals and individual consumers for celebratory displays. Perchlorate is known to be a component of many pyrotechnics, and as such, the manufacturing, storage, handling, use and disposal of these products have the potential for introduction of perchlorate into the environment. Many pyrotechnic displays are launched near or over surface waters, presumably for visual impact and safety reasons, increasing the potential for perchlorate impacts to water sources. The following sections describe the main components of commercial pyrotechnics and assess the potential for perchlorate to impact the environment.

3.1 Components of Fireworks

A display firework consists of multiple components, including one or several “breaks”, a time-delay fuse, stars, black powder, a launch tube, main fuse and a lift charge, as shown in Figure 3-1. The break or breaks house the stars in cardboard compartments within the shell. Each compartment has its own bursting charge, which ignites and throws out the stars. The breaks in a firework may also contain sound charges. To make these loud explosions, which are often accompanied by a bright white flash, perchlorate is often used.

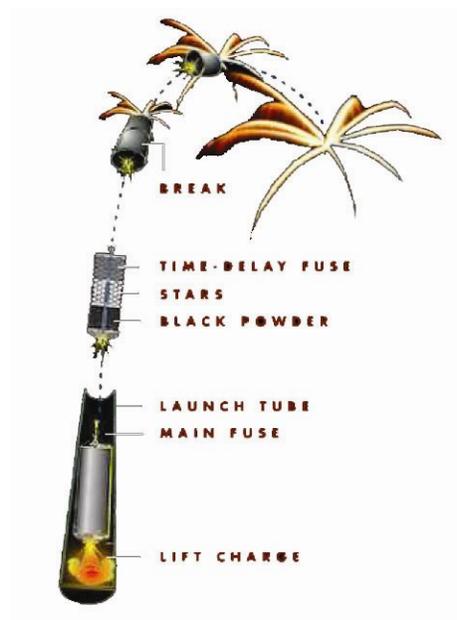


Figure 3-1: Display Firework Schematic
(from www.pbs.org/wgbh/nova/fireworks/anat_flash.html)

The stars, contained in the breaks, produce the bright colored firework displays. To produce different colors, perchlorate and black powder are typically blended with binding and coloring agents such as: magnesium or aluminum for white; sodium salts for yellow; strontium nitrate or carbonate for red; barium nitrate for green; copper salts for blue; and charcoal/carbon for orange (www.pbs.org/wgbh/nova/fireworks/anat_flash.html). Black powder is composed of 75% saltpeter (potassium nitrate), 15% charcoal, and 10 percent sulfur. The particle size of the black powder controls the burn rate, with finer particles burning faster than coarser ones. The lift charge consists of black powder in a pouch at the bottom of the firework cylinder. As the black powder burns, the heat and gas push at the inside of the launch tube until an explosion results, which propels the firework shell as high as 1,000 feet in the air.

3.2 Perchlorate in Fireworks

Perchlorate is a major component of fireworks and is used primarily as an oxidizing agent. It decomposes at moderate-to-high temperatures, liberating oxygen gas. Because oxidizers must be low in hygroscopicity, potassium salts are preferred over sodium salts. Potassium perchlorate has gradually replaced potassium chlorate as the principal oxidizer in civilian pyrotechnics because of its superior safety record. Potassium perchlorate produces mixtures that are less sensitive to heat, friction, and impact than those made with potassium chlorate, because of its higher melting point and less-exothermic decomposition (Conkling, 1985). Potassium perchlorate can be used to produce colored flames, noise, and light as summarized in Table 3-1. Ammonium perchlorate is also used in some fireworks formulations.

Table 3-1: Perchlorate Content and Effects in Fireworks

Purpose/Effect	Composition (% by Wt)	
White Light	Potassium Perchlorate	64
	Antimony, Sb	13
	Gum	10
	Potassium Nitrate	13
White Sparks	Potassium Perchlorate	42.1
	Titanium	42.1
	Dextrine	15.8
White Sparks "water fall"	Potassium Perchlorate	50
	"Bright" Aluminum Powder	25
	"Flitter" Aluminum, 30-80 mesh	12.5
	"Flitter" Aluminum, 5-30 mesh	12.5
Red Torch	Ammonium Perchlorate	70
	Strontium Carbonate	10
	Wood Meal (slow fuel)	20
Red Fireworks	Potassium perchlorate	67
	Strontium Carbonate	13.5
	Pine Root Pitch	13.5
	Rice Starch	6
Green Fireworks	Potassium Perchlorate	46
	Barium Nitrate	32
	Pine Root Pitch	16
	Rice Starch	6
Purple Flame	Potassium Perchlorate	70
	Polyvinyl Chloride	10
	Red Gum	5
	Copper Oxide	6
	Strontium Carbonate	9
	Rice Starch	5 (additional %)
Blue Flame	Ammonium Perchlorate	70
	Red Gum	10
	Copper Carbonate	10
	Charcol	10
	Dextrine	5 (additional %)
Yellow Flame	Potassium Perchlorate	70
	Sodium Oxalate	14
	Red Gum	6
	Shellac	6
	Dextrine	4
Black Smoke	Potassium Perchlorate	56
	Sulfur	11
	Anthracene	33
Flash and Sound	Potassium Chlorate	43
	Sulfur	26
	Aluminum	31
Whistle	Potassium Perchlorate	70
	Potassium Bensoate	30

Reference: J.A. Conkling. 1985 Chemistry of Pyrotechnics. Basic Principles and Theory. Marcel Dekker, Inc. New York.

Another potential source of perchlorate is from the potassium nitrate in the black powder used in the lift charge. Potassium nitrate made from Chilean nitrate can contain perchlorate, as has been well documented for sodium nitrate fertilizers.

3.3 Fireworks Consumption/Market

In 2003, 221 million pounds of fireworks were consumed in the U.S. This represents almost a 10-fold increase in consumption since 1976, as shown in Figure 3-2. The demand for fireworks is expected to increase, due to an upsurge of patriotism and an increase in the number of states permitting consumer fireworks. It is now legal to sell consumer fireworks in 43 states plus the District of Columbia (APA, 2004a.). Although the consumer fireworks industry is having record-breaking sales and profits, the public display industry has suffered as a result of the additional regulations following the events of 9/11. Additional security concerns have resulted in increased insurance costs, increased transportation and fuel fees, and criminal background checks for pyrotechnic professionals and large quantity users (APA, 2004b).

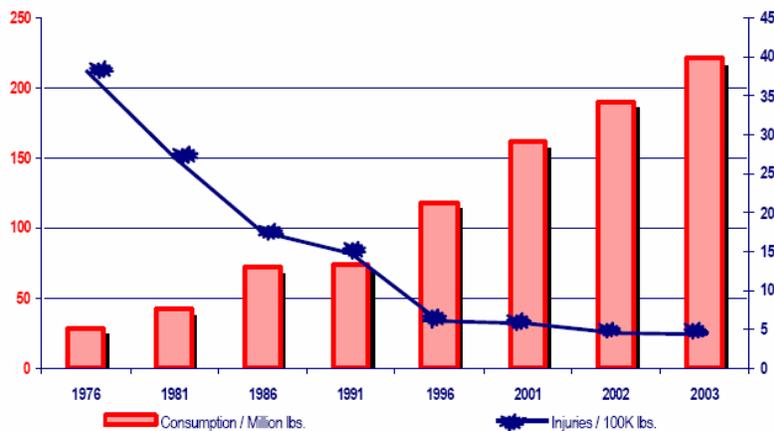


Figure 3-2: Fireworks Consumption in the United States from 1976-2003
(from www.americanpyro.com)

Import and export data for consumer and display fireworks in 2003 (the most recent census with data in all categories) is summarized in Table 3-2. Production statistics were estimated by taking the fireworks consumption data in Figure 3-2 and subtracting the imports and adding the exports. Import and export statistics categorized the type of firework to some degree. Import statistics were obtained for consumer, display, and other

fireworks, while export statistics were only collected for consumer and other firework category types, with the other category capturing display fireworks.

From Table 3-2, it is clear that most of the fireworks consumed in the U.S. are imported. Only approximately 3% of the total mass of fireworks is produced in the U.S. Most of the consumer fireworks are made in China (APA, 2004a). In 2003, 87.5 million kilograms (192 million lbs) of the 89.2 million kilograms (196 million lbs) of imported consumer fireworks or 98% and 7.5 million kilograms (16.5 million lbs) of the 8.1 million kilograms (17.8 million lbs) or 93% of imported display fireworks were from China (www.ita.doc.gov/td/industry/otea/Trade-Detail/Latest-December/Imports/36/360410).

Table 3-2: Production, Import, and Export Data For Fireworks - 2003

	Display Fireworks (Class 1.3G)		Consumer Fireworks (Class 1.4G)		Other Classes (NESOI) ¹		All Classes	
	<i>Mass (kg)</i>	<i>Value (\$)</i>	<i>Mass (kg)</i>	<i>Value (\$)</i>	<i>Mass (kg)</i>	<i>Value (\$)</i>	<i>Mass (kg)</i>	<i>Value (\$)</i>
Production²	--	--	--	--	--	--	3,486,384	--
Import³	8,101,763	27,273,000	89,153,821	135,561,000	90,989	233,000	97,346,573	163,067,000
Export⁴	167,796	5,728,000	--	--	210,616	8,032,000	378,412	13,760,000
Net Consumption							100,454,545	--

Notes:

1. NESOI = Not elsewhere specified or included; for Imports this classes includes fireworks not in Class 1.3G and 1.4G. For Exports Other Classes includes fireworks not in Class 1.3G
2. Production Statistics were obtained by subtracting Import data and adding export data from the net consumption of fireworks reported by the APA in Figure 3-2
3. U.S. Census Bureau, Foreign Trade Division, "U.S. Imports of Merchandise, December 2003"
4. U.S. Census Bureau, "U.S. Exports of Merchandise, December 2003"

3.4 Potential to Impact Groundwater

Raw perchlorate from fireworks manufacturing facilities and perchlorate residue from detonated fireworks both have the potential to contaminate surface and groundwater. Although fireworks contain high percentages of perchlorate, it is not currently known how much of the perchlorate finds its way into the environment. If we assume that most of the perchlorate present in the firework is ultimately decomposed with the burning of the firework, it seems necessary to consider only the perchlorate from blind stars, un-ignited display shells, and residues from the fireworks or lift charges (Schneider et al., 2001). However, statistics on dud rates (fireworks that are launched but not burned) do not exist (R. Schneider, personal communication). To date, housekeeping (i.e., post-event cleanup) related to fireworks displays has been done for safety purposes with the main aim being removal of unexploded fireworks. Typically, dud display shells are removed, but blind stars (which contain perchlorate) are typically not collected. Blind stars are often released at high altitudes and can therefore travel great distances from the launch site. Blind stars can also be released as a result of the breakage of dud shells.

As previously indicated, many fireworks displays occur at the water's edge or on barges, presumably for safety reasons and/or to enhance visual impact. Post-display clean-up becomes more difficult as duds and blind stars can be submerged. The advantage is that there is likely to be less dud breakage. However, perchlorate may leach out of the shell either through the fuse or as the result of de-lamination of the shell casing. The latter is more likely to result in perchlorate releases when the shell casing is comprised of paper/cardboard, as is often the case with fireworks produced in China.

3.5 Past and Current Environmental Studies

The number of case studies in the literature discussing extent of soil and water contamination at firework discharge sites is limited. More controlled studies are currently being conducted, which should shed more light on the extent of perchlorate contamination associated with fireworks.

A limited test to determine whether perchlorate contamination resulted as a consequence of fireworks displays was conducted at Harbor Island, in Milwaukee, Wisconsin. The island had been used since 1991 by the Bartolotta Fireworks Company to conduct public fireworks displays, using both domestic and imported fireworks (Schneider et al., 2001). Ten soil samples were collected for perchlorate analysis, 5 before a fireworks display and 5 after the display. The soil samples were extracted and the aqueous extract was analyzed using a rapid, field colorimetric method. No perchlorate

was detected above the 1 ug/mL detection limit in the extract of any of the samples. However, this detection limit corresponds to a detection limit in soil of 1 ppm (Phil Thorpe, personal communication), which is relatively high.

A study was conducted to evaluate the impact of more than 2000 fireworks displays over a small lake located at EPCOT Center in Lake Buena Vista, Florida (DeBusk, et al, 1992). Water chemistry data were collected from 1982 to 1992 and sediment data were collected in 1992. As this study pre-dated interest in perchlorate, perchlorate analysis was not conducted. However, detectable amounts of barium, strontium, and antimony were detected in the water and sediments. Gradual increases in water column concentrations of antimony paralleled the cumulative number of fireworks displays at the site, indicating that antimony may prove to be a good “marker” for detecting fireworks activity (DeBusk, et al, 1992). Antimony has a very low crustal abundance and, therefore, is not expected to be present in uncontaminated sediments (Riley and Chester, 1981).

Perchlorate contamination linked to fireworks displays is currently being examined by the Massachusetts Department of Environmental Protection (MADEP) at the University of Massachusetts at Dartmouth. Eight monitoring wells have been installed at a site where fireworks were launched/displayed over the Labor Day weekend of 2004 (Berckshire Eagle Online, Sept. 2, 2004). The campus has been the site of summertime fireworks for more than 10 years. Prior to the 2004 display, soil samples had no detectable levels of perchlorate, while groundwater samples had perchlorate concentrations ranging from 0 to 36 µg/L (Cape Cod Times, Sept. 4, 2004). Soil samples were collected the day following the display, while groundwater samples were collected periodically throughout the fall. Modeling will be conducted by MADEP to estimate the fate and transport of any perchlorate released by the fireworks display (R. Knox, Mass. DEP, personal communication, Sept., 7, 2004). The results of this study are not yet publicly available.

There is speculation that some of the perchlorate detected in groundwater at Camp Edwards on Cape Cod may be due to fireworks displays conducted at the Upper Cape Cod Regional Technical School. Soil samples taken by the Army after the 2003 Independence Day fireworks display contained 7500 µg/kg perchlorate. Regulators are not yet convinced that fireworks are the only cause of perchlorate in groundwater at this site, given the proximity of the site to the Massachusetts Military Reservation (Cape Cod Times, Sept. 4, 2004).

Perchlorate contamination may also originate from fireworks manufacturing facilities, given that perchlorate is handled on site. For example, perchlorate was detected at a concentration of 270 µg/L in an inactive well near a defunct fireworks site in Rialto,

California (<http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/earlyfindings.htm>). Perchlorate has also been detected at a concentration of 24 µg/L in groundwater from a well near a fireworks manufacturing facility in Mead, NE (<https://www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/releases.html>).

3.6 Summary

In 2003, 221 million pounds of fireworks were consumed in the U.S., with an estimated 3% produced domestically and the remainder imported from China (APA, 2004a). Although perchlorate is widely used as an oxidizer in firework formulations, there is currently little information related to the amount of perchlorate residue remaining after burning of fireworks and/or statistics on dud rates and the fraction of blind stars that occur during fireworks displays. As such, it is difficult to estimate potential perchlorate inputs from fireworks to the environment. Several recent studies have detected perchlorate in soils, groundwater and/or surface water following fireworks displays, and therefore, the potential environmental impact of perchlorate from fireworks displays warrants further scientific study.

4. SAFETY FLARES

Safety flares (or fusees) are used in emergency situations for road-side accidents and rail and marine emergencies. Road flares typically come in 15 minute, 20 minute, and 30 minute burn times. The average burn time for an automotive emergency flare is a function of its length and, to some degree, minor variations in flare composition. The use of 2 road flares per event is recommended by most flare manufacturers for most automotive emergencies. The following sections describe the main components of commercial safety flares and assess the potential for perchlorate to impact the environment.

4.1 Perchlorate Content in Safety Flares

A flare generally consists of a waxed cardboard tube casing filled with a burn mixture and a cap at the end to ignite the flare. Based on Material Safety Data Sheets (MSDS), the burn mixture contains primarily strontium nitrate (75% by weight), potassium perchlorate (<10% by weight), sulfur (<10% by weight) and sawdust/soil (<10% by weight). Other ingredients present in lesser amounts can include: synthetic rubber, aromatic polycarboxylic anhydride fuel, benzene tetracarboxylic acid (dianhydride and metallic dianhydride), sodium nitrate, polyvinyl chloride case binder, dextrin, magnesium, cellulose nitrate, black powder, wax, and red phosphorus (Silva, 2003b). The ignition mix is liquid and is heated and dried into a black button on the end of the flare and is used for igniting the flare by using the striking pad on the cap.

Through experiments conducted by the Santa Clara Valley Water District in California, Silva (2003a) analyzed the contents of an unburned road flare and detected 50,000 mg/kg of perchlorate and 450,000 mg/kg nitrate in a single flare. Comparison of perchlorate leaching from unburned flares that had been damaged (i.e., sliced open) to completely burned flares indicated that the unburned damaged flares leached 2000 times more perchlorate than damaged road flares that were completely burned (3,645 mg versus 1.95 mg).

4.2 Production/Use Statistics

In 1997, approximately \$101.5 million dollars worth of pyrotechnics (NAICS product code of 325998H107) were produced in the U.S. (U.S. Census Bureau, 2001). This classification includes road flares, jet fuel igniters, railroad torpedoes, and toy pistol

caps, but not fireworks. Production and trade statistics for road flares alone are not available. In 2003, 7.0 million lbs or \$10.6 million dollars worth of pyrotechnics were imported (www.ita.doc.gov/td/industry/otea/trade-detail/latest-december/imports), with 92% from China. Only 0.57 million pounds of pyrotechnics were exported in 2003 (www.ita.doc.gov/td/industry/otea/trade-detail/latest-december/exports). The world's largest manufacturer of emergency flares is located in the U.S. and has annual sales of \$20,000,000, based on available data.

Annual flare consumption data are not available; however, annual purchase records by state and federal agencies provide some insight into the volume of flares that may be purchased annually across the nation. Table 4-1 provides a summary of the number of flares procured by some large urban centers in the U.S.

Table 4-1: Summary of Flares Procured in Selected Urban Centers

Purchasing Entity	Total Number of Flares Procured	Comments
New York, NY	93,816	2 contracts (initiated in 2004, assumed to be annual), both through the NY statewide procurement. Total contract cost and per dozen unit price given - total number of flares based on these numbers.
Los Angeles, CA	576,000	Documentation for contract initiated in 2003 (assumed to be annual) for 4000 gross.
Chicago, IL	3,600	Documentation for single purchase (in 4/2002) for 50 cases of flares from local all-purpose supplier. A request for detailed flare procurement information submitted on 10/21/04.
Houston, TX	115,000	Bid tabulation for two year contract (FY2001-2003) for two types of flares. Total is for combined flare purchase.
San Antonio, TX	216,000	FY2003 bid tabulation for 1500 gross.
Milwaukee, WI	25,200	Contract initiated in 2004 (assumed to be annual).
Miami, FL	204,000	A 2-year contract beginning 5/04. Only the total price is given - total number of flares based on estimated cost per-flare of \$0.85.
Florida Hwy Dept	293,760	FY2005 award. Total contract cost and per gross unit price given - total number of flares based on these numbers.
Pennsylvania Turnpike	500,000	FY2005 RFQ. Total number of flares requested.
Michigan State Police	298,080	A 3-yr contract beginning 7/04. Total contract cost and per gross price given - total number of flares based on these numbers.
Illinois Toll way	10,588	FY2004 contract list (assumed to be annual). Only total price is given - total number of flares based on estimated cost per-flare of \$0.85.

While numbers are not available for total flare production, assuming an average cost per flare of \$0.50 to \$1.00 per flare and annual sales of \$20 million by the largest manufacturer, then between 20 to 40 million flares may be sold annually. The fate of these flares is largely unknown. For example, it is unlikely that all flares procured on an annual or contract basis are burned through the course of the contract, and it's therefore assumed that disposal or controlled burn of some portion of the unused flares may periodically occur.

4.3 Potential to Impact Groundwater

Preliminary research by Silva (2003a, 2003b) of the Santa Clara Valley Water District (SCVWD) indicates that 3.6 g of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. According to Silva (2003a), this amount of perchlorate can potentially contaminate 2.2 acre-feet of drinking water above 4 µg/L (the standard EPA Method 314.0 quantitation limit). Interestingly, even fully burned flares leached 1.9 mg perchlorate/flare (Silva, 2003a). More than 40 metric tons of flares were reported to be used/burned in 2002 in Santa Clara County, California alone (Silva, 2003a). Given this estimate, the potential for perchlorate leaching from road flares and subsequent surface runoff from highways and roads represents a potentially significant and largely uninvestigated impact to surface water and groundwater quality.

Road flare manufacturing has also been implicated in perchlorate contamination at a site in Morgan Hill, California (www.valleywater.org). From 1956 to 1996, highway flares were manufactured at this location (www.valleywater.org). Perchlorate was detected at one on-site monitoring well in 2001 and was detected in a municipal well in March 2002. The perchlorate plume is estimated to be 9 miles long (The Mercury News, Sept. 10, 2003). It is important to note that this site is located in an area that was historically used for fruit and nut production, and perchlorate impacts to soil and groundwater in some areas may also be the result of past fertilizer practices, as discussed in Section 2).

4.4 Summary

Preliminary research by Silva (2003a, 2003b) of the Santa Clara Valley Water District (SCVWD) indicates that 3.6 g of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. Even fully burned flares leached 1.9 mg perchlorate per flare (Silva, 2003a). While numbers are not

available for total domestic flare production, assuming an average cost per flare of \$0.50 to \$1.00 per flare and annual sales of \$20 million by the largest manufacturer, then at least 20 to 40 million flares may be sold annually. Given this estimate, up to 237,600 pounds of perchlorate could leach from road flares annually. Surface runoff from highways and roads represents a potentially significant and largely uninvestigated impact to surface water and groundwater quality. Additional evaluation of the potential for perchlorate impacts to surface waters and groundwater from safety flare use appears warranted.

5. BLASTING EXPLOSIVES

Blasting agents are non-cap sensitive explosives. Generally, they are intimate mixtures of inorganic oxidizers and fuels, rather than the organic explosives commonly used in military applications (e.g., RDX, TNT, HMX). While the main oxidizer employed is usually ammonium nitrate (AN), ammonium perchlorate and other perchlorates (sodium or potassium perchlorate) are compatible with the AN mixtures and can be employed for special applications and to take advantage of perchlorate available from DOD demilitarization activities. Furthermore, sodium nitrate (Chilean origin) historically used in commercial explosives may contain perchlorate as an impurity. Review of MSDS information identifies perchlorate as a common component of many slurry gel explosives (Table 5-1). The following sections discuss the composition of various commercial blasting agents based on review of MSDS information and examine the potential for perchlorate impacts to soil and groundwater from blasting operations.

5.1 Common Blasting Agents, Explosives & Detonators

Blasting agents, as opposed to explosives, require a booster, in addition to a detonator, to initiate. This is a significant advantage in terms of less stringent and more economical storage and transport considerations. The most common and simplest blasting agent is ammonium nitrate fuel oil (ANFO), which consists of ammonium nitrate prills soaked with fuel oil (about 5 to 6 wt%). ANFO accounts for a large share of the domestic commercial explosives market (about 80% in 1998) (ISEE, 1998) and is available in bulk form for on-site mixing or in premixed bags. The hydrophilicity of AN precludes its use in wet conditions without special precautions (ISEE, 1998), and a number of products have been developed to address this issue.

AN remains the key oxidizer in commercial explosives. The problem of its high hydrophilicity is addressed by gelling the AN in an aqueous matrix (slurries or water gels) or encapsulating it in a water-in-oil emulsion. Both types of products are sold in bulk or prepackaged chubbs. Slurries, also referred to as water gels, contain AN in aqueous solution. To aid water resistance and handling, they are thickened and gelled with a gum, such as guar gum. Depending on the remainder of the ingredients, slurries can be classified as either blasting agents (not cap-sensitive) or explosives. Slurry blasting agents contain non-explosive sensitizers or fuels such as carbon, sulfur, or aluminum; whereas slurry explosives contain cap-sensitive ingredients such as PETN. As shown in Table 5-1, several water gels contain sodium perchlorate.

As emulsion technology advanced over the years, AN in emulsion, rather than in slurries, became popular. Emulsions generally contain AN dissolved in water, but it is

possible to prepare waterless emulsions where an AN/salt eutectic serves alone as the discontinuous phase. Emulsions have made it possible to shoot small diameter and wet boreholes. A typical formulation would be 80-90% AN, 4-6% hydrocarbon, 10-15% water, and 1-2% emulsifier (Oxley, 1989, 1992). Unlike slurries, emulsions are generally sensitized with a gassing agent or micro-balloons rather than a sensitizing chemical.

Another popular blasting product consists of a blend of prilled ANFO or AN with AN emulsion in various ratios. Blends containing less than 50% emulsion are sometimes referred to as “heavy ANFO.” Their benefits include reduced mining costs, increased water resistance and increased density/strength (ISEE, 1998). MSDS sheets for some heavy ANFOs list “inorganic oxidizers”. Further testing is required to determine if these products contain perchlorate.

A number of AN products include sodium perchlorate to increase shock initiation sensitivity (Table 5-1). Furthermore, some list sodium nitrate as a constituent. Since sodium nitrate of Chilean origin is known to contain perchlorate, these blasting agents are likely to contain perchlorate.

**Table 5-1: Blasting Agents and Explosives Containing Perchlorate
(% Composition)**

Type Product	Blasting Agent (1.5) or Explosive (1.1)	NH ₄ NO ₃	NaNO ₃	NaClO ₄	Al	hexamine dinitrate	PETN	other energetic fuel	fuel oil	stabilizer
gel bulk or packaged	blasting agent	55-85	--	0-4	0-10	0-15	--	--	0-5	--
packaged gel	blasting agent	33-40	10-15	--	0-9	--	--	25 - 51	--	1-3
package emulsion	explosive	60-70	0-5	0-15	0-5	--	0.5 - 3	--	--	--
package emulsion	explosive	60-80	0-12	--	0-10	--	--	--	0-12	--
packaged gel	explosive	<65	<20	<7	<7	<20	--	--	--	--
ANFO	blasting agent	94.5	--	--	--	--	--	--	5.5	--
water gel	blasting agent	<80	--	<5	--	<15	--	--	--	--
water gel	blasting agent	< 75	<5	<5	<3	< 23	--	--	--	--
water gel	explosive	<65	<20	<7	<7	<20	--	--	--	--
water gel	explosive	<65	<20	<7	<7	<20	--	--	--	--
water gel, presplit	explosive	<65	<20	<7	<7	< 20	< 2	--	--	--
water gel	blasting agent	10-20	10-20	20-30*	--	10-15	--	--	--	--

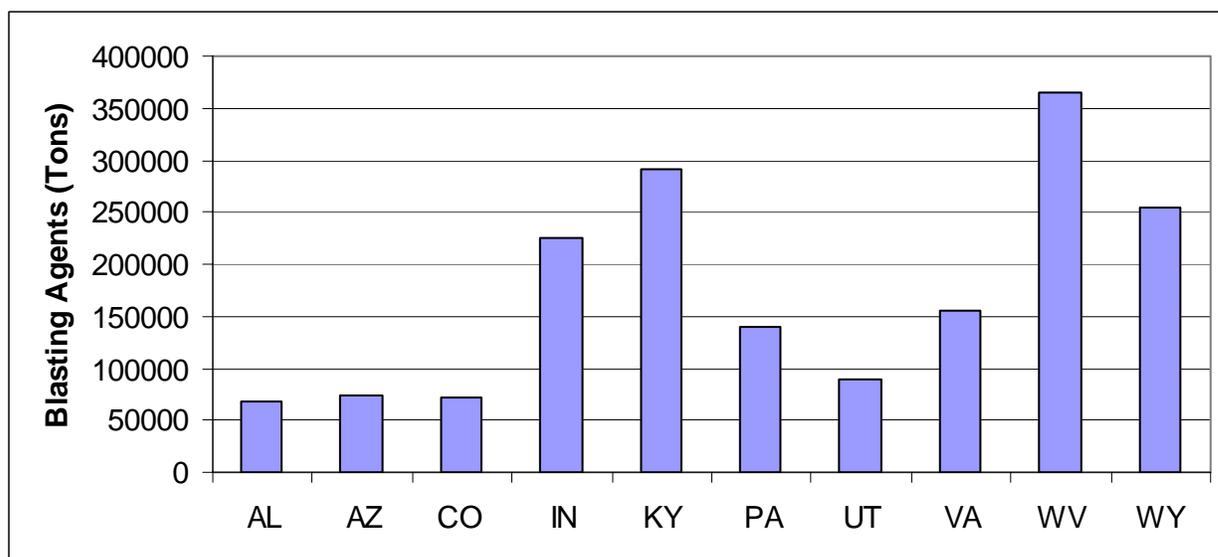
* ammonium perchlorate

Detonators initiate a shock wave in a primary explosive and amplify it to a secondary explosive. Detonators may be electric or non-electric. Some non-electric detonators can contain up to 10% potassium perchlorate.

5.2 Consumption/Market

In 2003, the U.S. production of explosives, reported by 23 commercial explosive manufacturers, was 2,525,000 tons (Kramer, 2003). This amount of explosives is typical of the annual U.S. production in the last decade. Of the total U.S. commercial production, 2,723,000 tons were classed as blasting agents. Sales of blasting agents were reported in all states with West Virginia, Kentucky, Wyoming and Indiana consuming the highest quantities (Figure 5-1). Sixty seven percent of the blasting agents were used in coal mining. Quarrying and nonmetal mining, the second-largest consuming industry, accounted for 14% of total explosives sales. Construction, metal mining and miscellaneous uses accounted for 8%, 8%, and 3% of explosives sales, respectively (Kramer, 2003).

Figure 5-1: Blasting Agents and Oxidizers – Usage by Top Ten States (2003)



5.3 Potential to Impact Groundwater

Although most perchlorate should be consumed during detonation of blasting agents, there are instances where groundwater contamination related to perchlorate in blasting agents may occur. The following are examples of practices that could lead to perchlorate contamination:

- Poor housekeeping of perchlorate-containing explosives (i.e., spillage on-site);
- Exceeding the sleep time of the explosive. Sleep time is the length of time that an explosive can remain in the ground after charging and still detonate with full energy. Blast hole conditions have a large impact on the sleep time of explosives in wet conditions;
- Poorly designed initiation of the charge, permitting small pockets of undetonated material after the blast; and
- Blasting misfires, where a loaded hole(s) fails to detonate or partially explodes. If the blaster follows proper methods of priming, loading, stemming, hooking up the shot and firing it, the likelihood of a misfire is small (ISEE, 1998).

To our knowledge, no detailed studies are publicly available that quantify the amount of perchlorate originating from blasting agents and explosives. There have been several newspaper and internet reports that attempt to link blasting operations to high perchlorate concentrations in groundwater and surface water, particularly in Massachusetts (Ward, 2004; Wims, 2004; Town of Tewksbury, 2004). Perchlorate concentrations as high as several hundred parts per billion have been measured in close proximity to blasting sites. In response to perchlorate contamination in the Boxborough, Massachusetts area, the Fire Chief has issued a ban on the use of perchlorate-based agents for all blasting activities in Boxborough (town.boxborough.ma.us). In addition, the State of Massachusetts is prohibiting its own contractors from using blasting agents that contain perchlorate (Hughes, 2004).

5.4 Summary

Some water gels, emulsions, and non-electric detonators can contain substantial amounts of perchlorate (e.g., up to 30%). While, most of the perchlorate is expected to be consumed in the detonation, poor housekeeping practices (i.e., spillage), improper use, or misfires can potentially result in perchlorate contamination of surface and ground waters. Given that the U.S produces approximately 2.5 million tons of explosives annually, perchlorate could potentially be released into the environment in relevant amounts. Currently, no publicly-available data exist that indicate what amount of perchlorate might impact the environment from blasting. More studies are required to assess and quantify the potential impact of blasting explosives on perchlorate contamination of surface and ground waters.

6. ELECTROCHEMICALLY-PRODUCED CHLORINE PRODUCTS

During the electrochemical manufacture of chlorine products, such as chlorate, from chloride brine feedstocks, small amounts of perchlorate may be formed as an impurity (Wanngard, 1991; Betts et al., 1997). Because perchlorate was not known to be a chemical of environmental concern until quite recently (1997), and because the impurity level was considered small relative to the primary chemical being produced (e.g., chlorate), little attention has been paid to its presence. Therefore, little publicly-available information regarding perchlorate contamination in ECP chlorine products exists. Recent analysis of several sodium chlorate feedstocks being used for large-scale commercial perchlorate manufacturing suggest that perchlorate is present in the chlorate products at concentrations ranging from 50 to 230 mg/kg chlorate, and therefore, potential exists for release of perchlorate to the environment through chlorate manufacture, storage, handling, and use. The following sections provide information related to chlorate manufacturing and use and discuss the potential for impacts to soil and groundwater.

6.1 Manufacture of Chlorate

Sodium chlorate is produced electrochemically by the electrolysis of aqueous sodium chloride, and its production is governed by the following equation (Betts, 1997):



During the production of sodium chlorate, sodium perchlorate is often produced as an impurity in the electrolytic cell. Concentrations of up to 500 mg of sodium perchlorate per kg sodium chlorate are not uncommon (Wanngard, 1991). Accumulation of sodium perchlorate decreases the solubility of sodium chlorate and is actually undesirable to the manufacturer of the chlorate product. As such, several processes have been developed and patented to improve the efficiency of the electrolytic cell, prevent perchlorate formation, and/or remove the perchlorate from the chlorate (Wanngard, 1991; Betts et al., 1997). The formation of perchlorate stems from anodic oxidation of chlorate during the electrochemical reaction in accordance with the following reaction (Betts, 1997):



Significant amounts of ECP chlorine chemicals such as sodium chlorate are produced in the U.S. on an annual basis. The majority of sodium chlorate produced in the U.S. is used domestically, with only 3% of the annual domestic production exported. To satisfy demand for use, it is estimated that an additional 40% is imported for domestic

consumption. Table 6-1 lists the total domestic production and consumption rates of sodium chlorate. The total annual consumption of sodium chlorate is approximately 1.2 million tons (U.S. Department of Commerce, 2003).

Table 6-1: U.S. Production and Consumption of Sodium Chlorate

	Production (tons)	Exports (tons)	Imports for Consumption	Apparent Consumption (tons)
1991 ^a	448,908	n/a	n/a	n/a
1992 ^a	554,564	n/a	n/a	n/a
1993 ^a	539,259	n/a	n/a	n/a
1994 ^a	559,015	n/a	n/a	n/a
1995 ^a	614,536	n/a	n/a	n/a
1996 ^b	600,890	54,375	395,199	941,714
1997 ^b	567,797	65,680	411,687	913,804
1998 ^c	706,909	49,425	430,384	1,087,868
1999 ^c	742,476	57,543	439,567	1,124,500
2000 ^d	852,756	48,983	440,461	1,244,234
2001 ^e	792,167	32,834	495,379	1,254,712
2002 ^e	721,086	39,828	528,239	1,209,497

Notes:

- a - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: Fourth Quarter 1996, February 27, 1997
- b - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 1997, September 29, 1998
- c - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 1999, September 28, 2000
- d - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 2001, August 2002
- e - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 2002, August 2003

In North America, chlorate production is dominated by a relatively small number of companies. Due to anticipated differences in the manufacturing process/technology employed by these various companies, significant differences in perchlorate levels in chlorate may exist. Table 6-2 provides a summary of estimated North American annual chlorate manufacturing capacity for the five major chlorate producers.

Table 6-2: Summary of North American Annual Chlorate Manufacturing Capacity

Chlorate Producer	State/Province	Capacity (tons)
Company 1	MS	225,000
	WA	65,000
	QB	165,000
Company 2	QB	125,000
	GA	150,000
	SC	90,000
Company 3	MS	150,000
Company 4	GA	115,000
	AB	83,000
	MAN	44,000
	QB	132,000
	AB	55,000
	BC	101,000
	SK	55,000
	ON	55,000
Company 5	ON	55,000
	QB	48,000
	MAN	190,000
	AB	75,000
	BC	20,000
Total Capacity - USA		1,022,000
Total Capacity - Canada		1,323,000
Total Capacity - North America		2,460,000

6.2 Chlorate Use

Historic and current uses for chlorate include pulp and paper bleaching, non-selective contact herbicide application, and plant defoliation (OMRI, 2000). Sodium chlorate is also used in limited capacities for water treatment, mining, and in the production of other chemicals such as sodium perchlorate and other metallic perchlorates.

The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the U.S. (OMRI, 2000). In this industry, it is primarily used for the on-site production of chlorine dioxide to bleach cellulose fibers. In 1998, the U.S. EPA ruled that, by April 2001, pulp and paper mills in the U.S. would have to use elemental chlorine free (ECF) bleaching instead of the traditional chlorine bleaching, which has the potential to produce organic halides. Chlorine dioxide produced from sodium chlorate meets this requirement. As a result, the sodium chlorate industry has grown annually at about 3%, similar to that of the paper industry (TIG, 2004). If perchlorate is indeed a chemical of concern in chlorate materials, then the potential for perchlorate impacts from chlorate use are likely to increase with increased demand for paper products.

In addition to pulp and paper bleaching, sodium chlorate is used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers (Table 6-3; OMRI, 2000). As a defoliant, approximately 99% of sodium chlorate application is used on cotton plants (PAN Pesticide Database, 2002). By removing the foliage, a better yield is obtained during harvest and the cotton does not become stained. The application of chlorate defoliants is generally unique to Arizona and California because of their warm climates. Elsewhere, early frost causes foliage to drop from cotton plants naturally. In California and Arizona, the frost typically occurs too late, if at all, and the leaves remain on the plants during harvesting, requiring the use of defoliants. Depending on the yearly weather conditions, other states including Mississippi, Texas, Alabama, Arkansas, Georgia, Louisiana, Tennessee and North Carolina may use sodium chlorate as a defoliant for cotton.

Table 6-3: National Totals for Sodium Chlorate Use for Defoliation

Crop	Pounds Active Ingredient	Acres Treated
Cotton	4,581,793	1,507,850
Sunflower	10,091	1,771
Safflower	29,856	5,043
Rice	19,606	4,005

Source : <http://ca.water.usgs.gov/pnsp/crop/index.html>

In terms of quantity of use, California used more than 24 million pounds of sodium chlorate on cotton between 1991 and 2003, with an average application rate of 4.6 lbs/acre (Table 6-4). By comparison, Arizona, Mississippi, and Texas had total application rates of 6.3, 4.5, and 1.7 million pounds, respectively, between 1991 and 2003 (Table 6-4).

**Table 6-4: Sodium Chlorate Application to Cotton Crops by State,
1991-2003**

State	1991		1992		1993		1994	
	Total Applied (lbs)	Application Rate (lbs/acre)						
Alabama	-	-	-	-	-	-	-	-
Arizona	1,231,000	6.29	709,000	4.56	644,000	4.31	773,000	5.73
Arkansas	-	-	-	-	337,000	2.77	152,000	2.08
California	2,448,000	4.98	3,326,000	5.13	3,072,000	5.47	1,924,000	2.86
Georgia	-	-	-	-	-	-	-	-
Louisiana	-	-	138,000	1.17	-	-	70,000	0.84
Mississippi	696,000	2.16	256,000	2.08	-	-	489,000	3.32
North Carolina	-	-	-	-	-	-	-	-
Tennessee	-	-	-	-	-	-	-	-
Texas	185,000	1.10	-	-	116,000	1.03	330,000	2.12

State	1995		1996		1997		1998	
	Total Applied (lbs)	Application Rate (lbs/acre)						
Alabama	-	-	-	-	42,000	0.88	36,000	0.6
Arizona	769,000	5.77	456,000	4.43	450,000	4.29	550,000	5.24
Arkansas	251,000	2.55	-	-	-	-	208,000	2.53
California	4,624,000	5.79	2,317,000	4.93	1,123,000	3.79	499,000	4.13
Georgia	-	-	-	-	113,000	1.21	150,000	1.03
Louisiana	321,000	1.25	-	-	181,000	2.89	106,000	2.28
Mississippi	305,000	2.10	973,000	2.64	262,000	1.29	-	-
North Carolina	-	-	-	-	-	-	-	-
Tennessee	-	-	-	-	19,000	0.8	-	-
Texas	343,000	1.66	-	-	482,000	1.35	-	-

State	1999		2000		2001		2002	
	Total Applied (lbs)	Application Rate (lbs/acre)						
Alabama	-	-	-	-	-	-	-	-
Arizona	372,000	4.81	155,000	2.98	-	-	-	-
Arkansas	429,000	4.25	62,000	1.01	-	-	-	-
California	1,106,000	4.89	815,000	4.82	-	-	2,379,994	6.05
Georgia	72,000	0.95	-	-	-	-	-	-
Louisiana	70,000	2.57	16,000	1.13	-	-	-	-
Mississippi	324,000	3.53	199,000	1.29	819,000	3.73	-	-
North Carolina	14,000	0.57	21,000	0.57	-	-	-	-
Tennessee	-	-	-	-	-	-	-	-
Texas	-	-	141,000	0.66	76,000	0.71	-	-

State	2003		1991 to 2003			
	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Average Application Rate (lbs/acre)	Total Potential Perchlorate Applied (lbs)	Average Potential Perchlorate Application Rate *
Alabama	15,000	0.62	93,000	0.70	47	0.00035
Arizona	172,000	4.98	6,281,000	4.85	3,141	0.00243
Arkansas	24,000	0.86	1,463,000	2.29	732	0.00115
California	680,000	2.73	24,313,994	4.63	12,157	0.00232
Georgia	-	-	335,000	1.06	168	0.00053
Louisiana	-	-	902,000	1.73	451	0.00087
Mississippi	192,000	1.85	4,515,000	2.40	2,258	0.00120
North Carolina	-	-	35,000	0.57	18	0.00029
Tennessee	11,000	0.35	30,000	0.58	15	0.00029
Texas	-	-	1,673,000	1.23	837	0.00062

Note: "-" usage data are not published.

* These values assume that the sodium chlorate is contaminated with 0.05% sodium perchlorate

Source: Agricultural Statistics Board, NASS, USDA Agricultural Chemical Usage Field Crop Summary.(1991 to 2003)

Sodium hypochlorite has also been used as an herbicide and may contain trace amounts of perchlorate. However, application quantities for sodium hypochlorite are substantially lower than sodium chlorate (35,414 lbs applied to crops in California in 2002; PAN Pesticide Database, Sodium Hypochlorite, 2002), and therefore sodium hypochlorite is unlikely to represent a major source of perchlorate contamination relative to defoliant use.

6.3 Potential to Impact Surface Water and Groundwater

Based on the documented occurrence of perchlorate in sodium chlorate and available use statistics, it appears that chlorate use by the pulp and paper industry and as a defoliant has the potential to introduce perchlorate to the environment. For example, assuming 1.2 million tons of sodium chlorate are consumed annually in the U.S. (U.S. Department of Commerce, 2003), and that sodium chlorate may contain perchlorate at concentrations ranging from 50 to 500 mg/kg, this represents the potential handling of 120,000 to 1,200,000 lbs of perchlorate annually, the fate of which is largely unknown.

Chlorine dioxide production for pulp and paper bleaching involves the addition of a sodium chlorate solution and a reducing agent to produce chlorine dioxide. Reducing agents include sulfur dioxide, methanol, chloride ion, and hydrogen peroxide (Dence and Reeve, 1996). Chlorine dioxide is produced as a gas and later absorbed into water prior to being used as a bleaching agent. As such, perchlorate originating in the sodium chlorate would not be expected to be present in the gas stream because of its non-volatility. However, perchlorate is likely to end up in the by-product salt-cake from the chlorine dioxide generator, which is generally added back to the kraft liquor cycle, where it may undergo reduction. On occasion, excess salt-cake is sewerred. The fate of perchlorate in this process is unknown, but low ppb levels of perchlorate in mill effluents are possible if the perchlorate is not significantly treated by the plant's effluent treatment system. Further study of the fate of perchlorate in pulp and paper mills is warranted.

With respect to sodium chlorate use as a defoliant, the average yearly application of sodium chlorate in California is nearly 2 million pounds, applied directly to agricultural lands. Assuming a perchlorate impurity level of between 0.05 to 0.5% sodium perchlorate, the use of sodium chlorate as a defoliant may result in the application of 1,000 to 10,000 pounds of sodium perchlorate to agricultural lands in California per year. While this annual application appears to be relatively small, repeated application over many years to decades may result in an accumulation of perchlorate in soils because of its recalcitrance in most soil environments. Over time, perchlorate in soils could impact

surface waters due to overland flow during rainfall events or groundwater through longer term infiltration.

6.4 Summary

During the electrochemical manufacture of chlorine products, such as chlorate, from chloride brine feedstocks, perchlorate may be formed as an impurity at concentrations of 50 to 500 mg/kg. The estimated North American annual chlorate manufacturing capacity is 2.4 million tons, whereas the total annual consumption of sodium chlorate in the U.S. is approximately 1.2 million tons. The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the U.S. for on-site production of chlorine dioxide to bleach cellulose fibers. Effluents from pulp mills have been reported to contain chlorate (1 to 70 mg/L; Warrington, 2002), but there is little information available as to the potential for perchlorate release from these facilities. Sodium chlorate is also used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers. The use of sodium chlorate in the pulp and paper industry and as a defoliant has the potential to contribute perchlorate to the environment.

7. CONCLUSIONS

The frequency of detection of perchlorate impacts to soil, groundwater and surface water, unrelated to military activities, is likely to increase as water utilities analyze for this constituent as part of their UCMR monitoring programs. Based on emerging product and process information, perchlorate is present (intentionally or not) in many more products and processes than initially understood.

The U.S. DOD, NASA and related defense contractors are likely to be the most significant domestic users of perchlorate in North America, and as such, a significant percentage of identified groundwater perchlorate impacts are attributable to DOD, NASA, and related defense contractor facilities. However, cases exist, and many more are likely to surface, where perchlorate impacts result from combinations of military, non-military, and/or natural inputs. The ability of DoD, NASA, and defense contractors to accurately apportion the relative contributions from these varying sources, and hence to properly determine liability and control cleanup cost, lies in having a good understanding of the wide variety of products and processes that may contribute perchlorate to the environment, and through the development and validation of forensic tools, such as chlorine isotope analyses.

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