SECTION 4
PERCHLORATE CONTAINING PRODUCTS

I. INTRODUCTION

Perchlorates are used in a number of applications including as an oxidizer in solid rocket fuel and as a component of fireworks, pyrotechnics, flares and explosives. Other uses include as a pharmaceutical for hyperthyroid, as a gas generator, as an electrolyte for lithium cells, and as a chemistry reagent. The occurrence of perchlorate in the environment is principally anthropogenic in nature.

Military operations, defense contracting, or manufacturing facilities are among the many industrial makers and users of perchlorate. The use of perchlorate is referenced in documents such as textbooks, scientific journals, military specification sheets, and material safety data sheets supplied by manufacturers. Perchlorate concentrations used in various applications are difficult to find due either to the sensitive nature of defense munitions or the proprietary nature of commercial products. Classified information and trade secretes are simply not available. Other sources of information may vary in the reliability of the information provided.

The list of perchlorate chemicals reportable under the Toxic Substances Control Act is almost 100, and some specialty chemical distributors make available over 500 perchlorate compounds for sale. Chemical reference books include the properties of only a few of these salts. The perchlorate compounds that have been produced in the greatest quantities historically are ammonium perchlorate, sodium perchlorate, potassium perchlorate, and perchloric acid. These four compounds account for the majority of perchlorate manufactured. Ammonium perchlorate alone accounts for about 90% of all perchlorate manufactured in the United States and is used as a solid propellant for missiles and the space shuttle program. Other principal uses of perchlorate include military ordnance, fireworks, flares, gas generators, and chemical reagents.

Perchlorate materials are comprised of products containing perchlorate, products that contain perchlorate as an impurity or by-product, waste or residuals with detectable levels of perchlorate, hazardous waste perchlorate, and environmental media contaminated with trace perchlorate. A release of these perchlorate materials onto or into soil or water may cause groundwater contamination due to the mobility of perchlorate in the environment. Perchlorate is assumed to migrate at about the same rate as groundwater because it does not interact readily with soil, is highly soluble in water, and does not transform or degrade in the presence of oxygen.

In addition to the identification of perchlorate materials, an understanding of handling, storage and disposal activities associate with perchlorate use is needed to detect other possible routes of releases. A principal source of perchlorate contamination is the discharge of concentrated perchlorate process waste water to the ground. This was a common practice for removing ammonium perchlorate from rocket engines is washing out to remove the solid fuel once it had exceeded its shelf life.

II. PRODUCTS WITH PERCHLORATE AS AN INGREDIENT

Propellants

Propellants are energetic materials which provide for the controlled propulsion of a projectile or a rocket in flight. Propellants are segregated into subcategories based on their energetic composition. Propellants include both rocket and gun propellants.

It is difficult or impossible to build a large rocket vehicle that uses black powder or double-base explosives as a propellant. Such materials are both difficult and dangerous to handle in large quantities. These materials burn very rapidly and provide high thrust for short period of time. This works well for simple, short range rocket projectiles, but not for putting huge payloads into space.

After the war, more sophisticated solid propellants were developed, using synthetic polymers, particularly synthetic rubbers such as butadiene tire rubbers, mixed with ammonium perchlorate oxidizer (which provides higher performance than potassium perchlorate and burns cleaner) and large proportions of powdered aluminum. The powdered aluminum burned at a high temperature, helping improve thrust. This propellant mix based on rubberlike polymers allowed the fuel to be cast in large blocks that resisted shrinkage or cracking, which would have affected the continuity of their burn at the very least and caused catastrophic failure at worst.

Modern solid-fuel rocket engines are ideal for military applications. They can be stored almost indefinitely and can be used and launched at any time with little preparation. Solid fuels are also denser than liquid fuels, allowing missiles to be more compact. This compactness was a particular plus for the development of solid-fuel long-range strategic nuclear missiles, since it allowed them to be stored in a smaller and cheaper missile silo or be carried on a submarine.

Other high-performance solid fuels include proportions of nitroglycerine and a particulate form of nitrocellulose, and in some cases a high explosive known as HMX as well. These high-performance mixes are less stable than conventional mixes, and so they are used for small final stages that are handled more easily.

Ammonium perchlorate is used in space shuttles, expendable launch vehicles, and virtually ever solid-fueled tactical and strategic missiles in the U.S. inventory.

Air Force	Army	Navy	NASA
Peacekeeper	Multiple Launch Rock System	Trident	Shuttle solid rocket motors
Minuteman	Chapparral	Tamahawk Cruise Missile	
Maverick	Army Tactical Missile System	Sparrow	
Advanced Medium Range Air to Air Missile	Hawk	Harpoon	
Titan	Patriot	Sidewinder	
Delta II	Stinger	Phoenix	
Inertial Upper Stage		Harm	
		Standard Missile	

The amount of ammonium perchlorate required in a given motor varies by the type of solid rocket or missile propellant. For example, approximately 70 percent of the weight of the space shuttle solid rocket motor propellant consists of ammonium perchlorate. Each set of shuttle motors uses about 1.7 million pounds of ammonium perchlorate; thus, the space shuttle is the largest user of ammonium perchlorate. The estimated demand for ammonium perchlorate was reported as:

Millions of pounds	Allocated	Estimated					
	1988	1989	1990	1991	1992	1993	1994
Air Force	8.2	14.0	16.1	12.9	10.0	10.0	10.0
Army	5.7	16.5	11.7	9.1	9.1	9.4	10.3
Navy	3.1	4.2	5.4	5.1	5.1	5.1	5.1
NASA	8.5	17.6	22.1	24.2	28.0	31.3	29.7
Commercial	3.0	3.7	5.2	0.4	1.0	0.6	0.6
European Multiple Launch Rocket System		4.4	5.3	5.3	7.0	5.3	5.3
Other		2.0	2.0	2.0	2.0	2.0	2.0

Explosives:
In 2002 approximately 2.51 million metric tons of explosives of all types were produced in the U.S. Coal mining consumed the greatest quantity of explosives at 68% of production, followed by quarrying and non-metal mining at 13%, metal mining at 8%, construction at 8%, and miscellaneous (pyrotechnics, demolition, avalanche control, etc) at 3% (Kramer, 2003).

These figures represent overall U.S. explosives production. The percentage of explosives products included in this total figure contains perchlorate is unknown. The quantity of perchlorate-containing explosives imported into the U.S. also is unknown. (IME, white paper)

Propellants and pyrotechnics are a subset of low explosives. In an effort to improve munitions survivability and safety, DOD established a policy requiring all new munitions be capable of withstanding accidents, fires, or enemy attack. In response to these new requirements, a new class of Insensitive Munition explosives was developed to meet MIL-STD-2105, Hazard Assessment Tests, Non-Nuclear Munitions standard for propellants and explosives. The melt pour explosives include ammonium perchlorate in the formulations. Some advantages provided over pressed explosives are increased Insensitive Munition characteristics, the ease of loading of melt pour explosives into various munitions items and reduced cost to manufacture. Performance and shock sensitivity can be tailored for a given system based on particle size and the percentage of ingredients. (globalsecurity.org/military/systems/munitions/im.htm)

Blasting

Perchlorates are present in a relatively small percentage of some blasting agents and explosives; primarily water gel and emulsion formulations. These products are used in difficult blasting applications, and contain sodium perchlorate, ammonium perchlorate, and/or potassium perchlorate as a sensitizing agent. Perchlorate-containing explosives typically have a high density and high explosive energy, making them suitable in wet/hard/dense rock blasting applications, or in general blasting applications to expand drilling patterns or to address excessive rock burdens. These types of explosives can be used in wet-hole conditions or below the water table and retain their explosive characteristics after being submerged for weeks or even months. (ISEE Blaster's Handbook)

Additional situations where perchlorate-containing products are sometimes used include tight underground cuts, tight trenching applications, deep wet trenches, deep wet boreholes, and locations with high pre-compression conditions. The content of perchlorate in these products is variable, depending on the manufacturer, but can be 20% to 30% or more by weight. (MA 2005)

These products are manufactured and used specifically as an alternative to nitroglycerin (NG) based explosives products. Accordingly, given that NG-based explosives make up approximately 0.4% of the total commercial explosives market in the U.S., the perchlorate-based commercial explosives market can reasonably be projected to be even smaller. (IME 2005, white paper)

Oil Drilling

High Energy Gas Fracturing is name used by the oil and gas industry for the technology of stimulating wells with propellant gas generators. Western Technologies has developed a high energy exothermic fracturing method using a

special blend of ammonium perchlorate to create a high energy pressure fracture. Initial testing of this product have resulted in positive field results with costs which are typically less than half that of conventional hydraulic fracturing methods.

The amount of perchlorate present in typical perchlorate-containing explosives is quite variable. Some illustrating examples of perchlorate containing explosives 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 up to 30% perchlorate, electric detonators: 0 – 0.50% potassium perchlorate, and non-electric detonators: 0 – 0.89% potassium perchlorate (IME, 2004). Some emulsion and water gel explosives may exceed even these concentration ranges.

Ordnance/Munitions
The types of ordnance commonly use by the military include small arms ammunition, large caliber gun ammunition, projectiles and warheads, high explosive cartridges, bulk explosives, grenades, submunitions, rockets, mines, torpedoes, and propellant charges.

Pyrotechnics
Pyrotechnics are energetic materials used to produce light, smoke, heat, or sound effects. Pyrotechnics include illuminating flares, signaling flares, colored and white smoke generators, tracers, incendiary delays, fuses, and photo-flash compounds. Pyrotechnics usually are composed of an inorganic oxidizer and metal powder in a binder. Illuminating flares contain sodium nitrate, magnesium, and a binder. Signaling flares contain barium, strontium, or other metal nitrates.

All pyrotechnic chemical compositions contain an oxidizer component and a fuel component. Additional ingredients that are present in most pyrotechnic compositions include binding agents, retardants and waterproofing agents. Smoke dyes and color intensifiers are present as required.
A delay element uses a contained pyrotechnic delay composition in an ignition train to provide a delayed ignition. Examples of uses for the delay compositions are fuze explosive trains and cartridge actuated devices. (KP, IPI website)

Flares
Perchlorate is one of the primary components found in emergency and signal flares. Flares are designed for use to illuminate, identify, signal or warn. Their use is believed to be widespread across the U.S. In Santa Clara County, California, more than 40 metric tons of flares were used/burned in 2002 alone (Silva, 2003). Flares containing perchlorate have also been used in some aircraft cloud seeding operations in some locations.

One study has been performed to attempt to measure the amount of perchlorate that may be released from road safety flares under various conditions. Tests

indicate that the residue from fully burned flares may still contain a significant leachable amount of perchlorate and that partially burned flares leached even greater concentrations of perchlorate when placed in contact with water (Silva, 2003). Silva points out that fully burned flares can still leach up to almost 2000 ppb of perchlorate per flare.

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

Fuse/Fuze
Fuse and fuze are sometimes considered to be different spellings of the same word. Fuse refers to a cord-like igniting device consisting of cotton yarns impregnated with fine black powder which burns with an external flame and is used in ignition of fireworks, etc. When ignited, it burns at a predetermined rate without any external explosive effect.

Fuze refers to a device designed to start a detonation in ammunition. They incorporate mechanical, electrical, chemical or hydrostatic components and generally protective features.

Airbag Initiators
Automotive safety airbags have to be inflated almost instantly, which requires a pyrotechnic that generates a large amount of gas quickly, but does not cause fire or any more blast than necessary. This requirement led to the development in the 1970s of small, cheap, solid-propellant inflators, based on the combustion of sodium azide with an oxidizer, rapidly producing a great quantity of nitrogen gas that can inflate an airbag in a little over 50 milliseconds. Approximately 110 to 1000 milligrams of pyrotechnic material is used which is comprised of potassium perchlorate mixed with zirconium, titanium, or boron. (US Patent 5639986, Airbag Initiator and Method of Manufacture).

NASA Standard Initiator
NSI is a two-pin electrically activated, hot wire, electroexplosive that was designed for use on the Space Shuttle. The NSI's function is to translate an electrical stimulus into a pyrotechnic action, this is known as a first fire. It primarily produces a flame and hot particles that ignite or initiate other powders, but it can be used for pressure impulse in some applications. Over 100,000 NSIs have been manufactured to date. NSI uses as its propellant finely powdered zirconium metal mixed with finely powdered potassium perchlorate held together by a Viton-B rubber binder.

Oxygen Gas Generators
Oxygen generators contain chemicals that upon activation release oxygen as a product of chemical reaction. Chemical oxygen generators are used for the generation of oxygen for respiratory support, e.g. in aircraft, submarines,

spacecraft, bomb shelters and breathing apparatus. Oxidizing salts such as chlorates and perchlorates of lithium, sodium and potassium evolve oxygen when heated. These salts are mixed with a fuel, usually iron powder, to form a chlorate candle, which produces oxygen by continuous reaction. The fuel is used to generate heat by oxidation. Once the reaction begins, oxygen is released from the hot salt by thermal decomposition. A portion of the oxygen reacts with the fuel to produce more heat which produces more oxygen, and so on. Initiation of the reaction can be achieved by a percussion device, friction device or electric wire.

Sodium Chlorate is used as the primary source of aircraft oxygen generators, but small amounts of potassium perchlorate are also incorporated.

Fire Extinguishing Cartridge
Some specialized aircraft fire extinguisher designs include the use of pyrotechnic cartridges that are able to discharge at a very high rate. This is needed when it is more important to get the agent into the protected area as quickly as possible, than to distribute a greater dispersion volume at a slower rate.

Aircraft Ejector Seats
Some systems have been reported to contain perchlorate compounds. Ejector seats need the ability to clear the aircraft's vertical tail at a high speed. This problem was addressed by a pyrotechnic sequence combining a rocket motor with the catapult to form a propulsion system for the seat. The catapult provides the initial removal for the seat from the aircraft. Once clear of the cockpit, the rocket motor comes on line to act in a sustainer mode. Most propellants used are double-base, but some are composite. (www.upco.goodrich.com)

Metallurgical Uses – Electro-polishing
Electropolishing with perchloric acid (historical): The O'Connor Electroplating Company located south of downtown Los Angeles was studying the polishing of aluminum using perchloric acid on an industrial scale on February 20, 1947 when an explosion occurred. The ensuing blast destroyed the factory, damaged 116 houses in the vicinity, injured 150 people and cost the lives of 15. Perchloric acid has not been used in a commercial electroplating setting since the incident occurred (“The Safe Use of Perchloric Acetic Electroplating Baths”, Dr. Pierre A Jaquet, Metal Finishing November 1949). This process is not commercially significant today, but may have relevance to historical releases.

Metallurgical Uses – Electro-Machining
Perchlorate salts are also used in electrolytic solutions for the purpose of electropolishing, electro-machining and electro-thinning of metal parts, films, and alloys. In a closely related application, perchloric acid is employed as electrolyte in anodization of metals to produce non-corroding surfaces. Other applications include use in pickling and passivation of iron and steels and dissolving refractory

substances such as titanium slags, copper-yttrium oxide and metal fluorides. (GFS site)

Batteries – Lithium Cells
Extensive use is made of lithium perchlorate as an electrolyte in voltaic cells and batteries involving lithium or lithiated anodes, non-aqueous solvents or polymeric films, and manganese dioxide or other transition metal oxides. These so-called lithium batteries, because of their long life and electrochemical efficiency, find use in implantable pacemakers and other special applications.

Batteries – Zinc-Magnesium
In non-aqueous systems, zinc perchlorate and magnesium perchlorate serve as electrolyte for zinc and magnesium batteries, respectively. For example, zinc perchlorate has found use as an electrolyte in dry cells comprised of zinc anodes and manganese dioxide cathodes.

Reagent Chemicals for Laboratory Applications – Perchloric Acid
Perchloric acid has usual properties as an effective precipitant, dehydrating agent and oxidant. Perchloric acid is frequently used to dissolve or digest substances prior to analysis for trace elements. Due to these properties, perchloric acid has many uses in analytical testing and is routinely used in industrial and testing laboratories (GSF site):

- As a deproteinization reagent in food analysis; for example, in the determination of butterfat in dairy products.
- As a dehydrating agent, particularly in the determination of silica in iron and steel and in cement and other silicate materials.
- In chromatography as eluents and spray reagents,
- 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 an oxidizing agent, especially in the determination of chromium in steel, ferrochrome, chromite, leather, and chromatized catgut.
- 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.
- As a solvent for metals and alloys.
- 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 7mm., has exactly the composition of the dihydrate, 73.6% HClO4.
- 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 non-aqueous solvents.
- As an engine oil testing (ASTM D2896) method to determine the base number.
- As a reagent for nuclear laboratories in actinide research. The research includes process chemistry, metallurgy, separation sciences, characterization and analysis, and manufacturing technologies for uranium and plutonium.
- Leather tanning extraction of chromium.

Reagent Chemicals for Laboratory Applications – Perchlorate Salts
Anhydrous magnesium perchlorate is the best of the absorbents for water in analytical work. As a desiccant it has been marketed under the trade names Dehydrite and Anhydrone.

Catalyst
The strongly acidic nature of perchloric acid and the ease by which its oxidation power can be controlled by concentration and temperature make it an ideal choice for use in a variety of important commercial processes. Numerous applications are made of perchloric acid as catalyst in a broad range of diverse reactions: acetylations, acylations, alkylations, chlorinations, polymerizations, esterifications, and hydrolyses. Important industrial examples include esterifications of cellulose to produce cellulose acetate, polymerizations of phenols with formaldehyde and polymerization of styrene. (GFS site)

Dopant
A dopant is an element introduced into semiconductor to establish either acceptor or donor conductivity. Their solubility and conductivity in plastics and polymers have led to extensive use of perchlorate salts as dopants in such materials to impart antistatic and conductive properties. As dopants in polyvinylchloride (PVC) and other chlorine containing polymers they lead to improved heat stability and fire retardation characteristics. Various electrochemical devices incorporate thin films of polymers such as polyethylene oxide (PEO), polyethylene glycol, or poly(vinylpyridine) doped with lithium perchlorate to impart conductive properties necessary for the devices to function.

Drying Agent: Anhydrous magnesium perchlorate has long been used as an efficient drying agent, especially for industrial gases. It affords a special advantage over most desiccants in that it does not deliquesce but remains porous for easy passage of gas through a column containing it.

Electrolytes
As aqueous electrolytes perchlorates are found in electrochromic devices and employed for anodic dissolution of difficultly oxidizable metals, such as lead and palladium.

Laser Dyes
Laser Dyes are complex fluorescent organic compounds. In solution with organic solvents, these dyes form a lasing medium. There are a few active dyes containing perchlorate currently available for experimental purposes. (www.exciton.com/laserdyerefs.htm)

Pharmaceuticals
Until the 1950's, potassium perchlorate was used to treat hyperthyroidism associated with Grave's disease. This disease causes the thyroid gland to operate at a dangerously fast rate. The extent of its use was rather limited, and its use was curtailed when aplastic anemia and other hematological side effects were reported and better anti-thyroid drugs became available. Although the practice of treating hyperthyroidism with perchlorate stopped decades ago, it is still used diagnostically in small amounts to detect defects in the synthesis of thyroid hormones in some clinical settings.

Photography Flash Powder
Flash powers are a pyrotechnic substance which, when ignited, produces an intense light. Flash powders contained perchlorate salts. Photographers were still using flash powder into the 1950s and 1960s and possibly later, although most sources state it became obsolete with the invention of flash bulbs around 1930.

Flash powder cartridges used in the military consist of a casing, a primer and flash powder, all assembled in one piece ready for firing. They are designed to produce a single bright flash of intense light for lighting up an area.

III. Products with Perchlorate By-Products or Impurities

Small concentrations of perchlorate have been found as impurities or by-products in products that contain chlorite or chlorate ingredients. Although the concentration of perchlorate in these chloroxy chemicals is low, the widespread use may make these compounds an environmental concern.

Fertilizer
Mineral deposits of caliche ores in northern Chile are a natural source of sodium nitrate and until recently, the only known natural source of perchlorate. The caliche deposits may have been derived from past local volcanic activity (Erickson, 1960 and 1983). Chilean nitrate deposits have been mined and refined to produce fertilizer and saltpeter for gunpowder for export. In the past, Chilean

nitrate ore has been imported into the U.S. since at least the late 1800s for use as fertilizer and later for additional end products.

Sociedad Quimica y Minera S.A. (SQM) produces this fertilizer in Chile and markets its products in the U.S. under the name Bulldog Soda. Chilean nitrate is used primarily for cotton, tobacco, citrus fruit and some vegetables, and accounts for only 0.14% of US fertilizer application. Current analyses put perchlorate anion concentrations at approximately 0.5-2.0 mg g^{-1} (500-2000 ppb) of this Chilean sodium nitrate fertilizer (Urbansky, 2000). However, recently the refining process to produce fertilizer has been modified to reduce the perchlorate to .01 mg g^{-1} (100 ppb). Although use of this fertilizer may be highly localized, it is not considered a significant source of perchlorate nationally. (National Organic Standards Board Technical Advisory Panel Review, April 2002)

This unique source of nitrate has been used extensively and is approved for organic crop production. Detectable levels of perchlorate have been found in food crops and milk. Fertilizer application is assumed to be one of the potential pathways for food plants to take up perchlorate.

A fertilizer manufacturing site in Arizona used the Chilean sodium nitrate with perchlorate impurities as feedstock for fertilizer production until 1995. This resulted in an unexpected perchlorate groundwater contamination plume.

Manufacturing and Use of Chlorate

Commercial production of chlorate used for herbicides and beaching agents is by the incomplete electrolysis of sodium chloride. Analysis of laboratory grade chlorate found nearly percent levels of perchlorate (Burns 1989). It is reasonable to assume the industrial-grade chlorate may contain several percent of perchlorate as a result of slight variations in process conditions. This may result in the detectable levels of perchlorate being released to surface waters when chlorates are discharged.

Currently 10 plants in the United States produce 1,024,000 short tons per year, both solution and crystal material of sodium chlorate. Commercial production is by electrolysis of a sodium chloride solution using diaphragm cells. About 96 percent of this sodium chlorate is used for paper and pulp bleaching. The sodium chlorate is used as a raw material for the on-site production of chlorine dioxide, the bleaching agent. The other 4 percent of sodium chlorate is used as herbicides and for uranium mining. (TiG, 2004) Chlorates may also used in the manufacture of matches and explosives, dyeing and printing of fabrics and tanning and finishing of leather (McGee, J.E. and Wolf, H.W. 1963. Water Quality Criteria. Pub. No. 3-A, State Water Resources Control Board, California).

Herbicide

A nonselective herbicide used extensively for the last 50 years is sodium chlorate. It had been known for centuries that salts kill plants if applied at heavy

rates. If used at rates of 200 lbs/acre, sodium chlorate acts as a soil sterilant leaving the soil unusable for a period of time. This salt was used extensively on railroad and highway rights of way. It can be used as a foliar spray at 5 lbs/acre as a cotton defoliant. Although inorganics are still useful in weed and brush control, but are rapidly being replaced by organic materials. EPA has placed heavy restrictions on some inorganics because of their persistence in soils. (http://ipmworld.umn.edu/chapters/wareherb.htm). The California Department of Pesticide Regulation maintains a database of pesticide and herbicide use. About 96 percent of all the sodium chlorate used in 2003 was on cotton crops. The counties that applied the most pounds of this herbicide were Kings, Fresno, and Kern. The following two tables summarize the 2003 use of sodium chlorate.

SUMMARY OF USE OF SODIUM CHLORATE AS A PESTICIDE OR HERBICIDE IN CALIFORNIA FOR THE YEAR 2003 BY COUNTY

COUNTY NAME	POUNDS PRODUCT APPLIED	POUNDS OF SODIUM CHLORATE APPLIED	PERCENT of NaClO3 TOTAL	AMOUNT TREATED
KINGS	2702888	646898	36%	139924
FRESNO	1903406	558742	31%	130008
KERN	1446693	262410	15%	59502
TULARE	535977	112631	6%	23308
MERCED	453028	90688	5%	19355
MADERA	137216	33717	2%	7672
RIVERSIDE	91304	17362	1%	3808
SAN JOAQUIN	26008	12276	1%	2204
SUTTER	24090	11370	1%	2011
ALL OTHER COUNTIES	9463	34785	2%	5735
Grand Total	7415240	1780879	100%	393527

SUMMARY OF USE OF SODIUM CHLORATE AS A PESTICIDE OR HERBICIDE IN CALIFORNIA FOR THE YEAR 2003 BY CROP

CROP	POUNDS PRODUCT APPLIED	POUNDS SODIUM CHLORATE APPLIED	PERCENT OF NaClO3 TOTAL	ACRES TREATED
COTTON	7256508	1714379	96%	382872
RICE	25413	11995	1%	2087
SAFFLOWER	20364	9612	1%	1835
SUNFLOWER	45114	21294	1%	3698
ALL OTHER CROPS AND USES	67841	23599	1%	3035
Grand Total	7415240	1780879	100%	393527

The California Department of Pesticide Regulation's CalPIP data (July 2005)

Manufacturing and Use of Hypochlorite and Chlorite - Bleach
Sodium hypochlorite 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 (POTWs), and other instances where an effective disinfectant is required. Sodium hypochlorite in solution normally produces some perchlorate ions during the dissociation reactions. This 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.

High concentrations of perchlorate were found in discharge water from a wastewater treatment plant in Massachusetts. Test results showed a high of 158 ppb of perchlorate in water exiting the wastewater treatment. Consequently, testing of the sodium hypochlorite bleach at the water treatment plant showed perchlorate concentrations of 4300 to 5000 ppb in the disinfectant. Although detectable levels of perchlorate were also found in treated drinking water, the plant discharge has not been linked to the perchlorate contamination. An ion-exchange treatment system has been installed to ensure that future discharges will not cause problems.

Manufacturing and Use of Hypochlorite and Chlorite – Household Bleach
According to Massachusetts DEP, some preliminary testing of household bleach from store shelves shows the presence of perchlorate up to 390 micrograms/liter (390 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.

Manufacturing and Use of Hypochlorite and Chlorite - Pool Sanitizers
Swimming pools are can be treated with sodium hypochlorite (liquid bleach), calcium hypochlorite (granular or tablet), or lithium hypochlorite. When any of these compounds contact water, they release hypochlorous acid (HOCl), the active sanitizing agent. Shock treatment is the practice of adding significant amounts of an oxidizing chemical to water to destroy ammonia, nitrogen-containing and organic contaminants.

Perchlorate has been detected in swimming pools at levels over 300 ppb. Some of the contamination has been attributed to using contaminated water to fill the pools. A second source of this perchlorate has been attributed to the impurities in the chlorine chemicals used to maintain pool.

Manufacturing and Use of Nitrate - Sodium Nitrate
Chilean Nitrate (sodium nitrate, Bulldog Soda, Chilean saltpeter) is a mined source of highly soluble nitrogen. This naturally occurring form is derived from caliche deposits that are sporadically located in a band 30 kilometers wide by

700 kilometers long. The ore is a crude composite of salts formed from nitrogen fixation by microorganisms in playa lakes and associated soils about 10-15 million years ago (Erickson, 1983).

Manufacturing and Use of Nitric Acid
Although most nitric acid today is made using other chemical processes, Chilean nitrate has been used in the past to produce this acid. Consequently, historical locations of the manufacture and those of usage of Chilean nitrate-derived nitric acid may be areas subject to perchlorate contamination.

Manufacturing of Matches
Most matches are produced in Asia. There are many chemicals used to make a match. The head of a match may contain as many as thirty-two substances, including potassium chlorate, zinc oxide, sulfur, glue, starch, resin, ground glass, clay, plaster of Paris, paraffin, formaldehyde, dyes, and pigments. Potassium chlorate provides oxygen to make the match burn strongly under many conditions, and the main fuel is sulfur. Dilutants are used to modify the burning rate so that the oxidizer and fuel do not react too violently. Perchlorate may occur as an impurity of the potassium chlorate. It would likely to be an environmental issue at the manufacturing facility where greater quantities are used.

Clandestine Labs
Large quantities of unburned highway flares and unburned matches have been found abandoned during raids on clandestine methamphetamine labs. Makeshift labs set up at rental homes, apartments, motel rooms, garages, and various outbuildings are used to illegally make methamphetamine. Red phosphorus is used as a catalyst in the production of this drug. The fuses on highway road flares or the strike pads on matches are a typical household source used for the phosphorus. Every pound of methamphetamine produced generates five or more pounds of hazardous waste. Much of this waste is dumped down drains and toilets or on the ground, creating many additional contaminated sites. Such dumping has created septic tanks full of dangerous waste and chemically-contaminated drain fields, soils and surface waters. (www.streetdrugs.org/methlabs2.htm, www.noodor.net/id60.htm)

Evaporite
Evaporite minerals are those formed by evaporation concentration in arid environments. Evaporites tend to be deposited in a specific chemical sequence as the concentration of salt increases. 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) (USGS Reports, 2003, 2004). Potash is mined and milled in the U.S., Canada, and elsewhere. Potash ore has also been recovered via solution

mining and exists in solution in the Great Salt Lake in Utah. 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 de-icing salt, water condition, detergents, ceramics, and pharmaceuticals (International Fertilizer Association, 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).

Colorado River
The perchlorate originated in an ammonium perchlorate production facility outside of Las Vegas. Large amounts of process wastewater containing perchlorate were discharged into unlined evaporation ponds at the facility. Over time the aquifer beneath the facility and the ponds became contaminated with high levels of ammonium perchlorate. The groundwater seeped into the Las Vegas Wash which drains into Lake Mead and then down into the Colorado River. The Colorado River is an important source of drinking water and irrigation. Perchlorate decreases in concentration from 6 ppb at Lake Mead to 2.4 ppb further down river.

The perchlorate contamination of the lower Colorado River is unusual because of the sheer number of people exposed in their drinking water to a chemical that came from a single source of pollution. Roughly 15 to 20 million people are exposed to perchlorate through drinking water. The Colorado River Basin is used in the general irrigation of approximately 15% of all U.S. crops. (Colorado River Profile, Colorado River Water Users Association, http://crwua.mwd.dst.ca.us/tcr/crwuaptc.htm, 2000, p. 1–4)

IV. UNCONFIRMED OR EXPERIMENTAL USES

Adhesives
Ferrous perchlorate has been tested as a dental adhesive primer.

Animal Fattening Agent
Potassium perchlorate was identified as an animal fattening agent. It was added to cattle feed to slow the animal's thyroid function and thus cause fattening.

Cathodic Protection Systems and Lightning
Texas Tech University has studied perchlorate occurrences in Texas. Researchers found perchlorate contamination in a municipal water storage tank

with cast-iron anodes. They have concluded that the perchlorate was generated in situ by the cathodic protection system after ruling out other sources of possible contamination. In a laboratory study, 64 to 113 ppb of perchlorate was formed by reproducing effects of lightening and the conditions found in the storage tank. These findings are preliminary. Perchlorate contaminated water in storage tanks would not be considered a major source of perchlorate contamination. If it can be shown that lightening under certain conditions can create perchlorate, it may offer an explanation for low levels of perchlorate that can not be attributed to another source.

Cloud Seeding
Experiments have been preformed using pyrotechnic flares to seed clouds for the formation of rain. Salts that are more hygroscopic are more effective in forming water droplets, so perchlorates may be a preferred salt for seeding.

Coatings
There is literature that indicates perchlorate salts have been used in propriety blend of paints and enamels, but there is little evidence of extensive use.

Transformer Dielectrics
Dielectric materials are characterized by their high insulating value or poor electrical conductance. Most perchlorate salts would be unsuitable as dielectrics. There is little to substantiate widespread commercial use as a dielectric material.

V. PRODUCTS OR USES THAT ARE UNLIKELY

The following are included as unlikely but have been included as perchlorate sources in other references. No independent confirmation of these uses was found:

Aluminum Refining
Electric Tubes
Lubricating Oil Additive
Rubber Manufacturing

VI. DTSC'S LIST OF MATERIALS CONTAINING PERCHLORATE

As part of its undertaking to develop regulations establishing best management practices for materials containing perchlorate, DTSC has compiled a list of products and industrial activities that utilize perchlorate. The listing below is not exhaustive and was prepared for the purpose of assessing those products and processes that may come within the scope of DTSC's Best Management Practices regulations.

Since the publication of this list, additional research indicates that this list should be revised.

Products and industrial activities that contain/generate perchlorate:

Adhesive - Steel plate bonding: may contain perchlorate.
Batteries - Li-Ion.
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 - Paint, Enamel - 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" brand, from Chile)
Flares, fuses
Gas generator - Airbag, Ejection seat
Gas generator - Aircraft oxygen.
Laboratory - Rocket motor, Ordnance (gunpowder) testing
Laundry bleach - may contain perchlorate.
Nitrate 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)

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 do not contain perchlorate:

Aluminum refining – Aluminum electro-polishing 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-Anti-oxidants added. Fluorocarbon lubricating oil compatible with perchlorate pumping.
Nuclear reactor – Nuclear warheads on rockets. Uranium analytical chemistry.
Synthetic rubber – Rubber as binder in rocket motors.