Chapter 4

Alternative Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater

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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.

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.

While natural sources or formation mechanisms for perchlorate may explain its presence in some cases,[1,2] 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.

The potential impacts of these non-military perchlorate products and processes on the environment are discussed in the following sections.

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.[3,4] Historical agronomic literature indicates that Chilean nitrate fertilizers were widely used in specific agricultural practices in the early to mid 1900s.[5,6,7] Past import statistics for Chilean nitrate and historical agronomic guidelines for sodium nitrate application for various crops (discussed below) 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,[8] respectively. Since 2002, it is estimated that some 75,000 tons of Chilean nitrate fertilizer have been used annually in the U.S.

This section 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.

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,[5,6] respectively, for a total of approximately 13,000,000 tons of Chilean nitrate. If we assume (based on these estimates) 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.

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%.[9] 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[3] 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[3]. 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.[3,10] 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%,[4] 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.

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."[11] Similarly, the USDA Fertilizer Consumption and Trends in Usage report[7] 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.[12] 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.[12] This application rate is equivalent to 110 to 190 pounds per acre of nitrate of soda, which is approximately 16% nitrogen,[13] 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.[12] 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.[12] For example, during this time period, Georgia, Alabama, South Carolina and North Carolina typically fertilized 91 to 97% of the total cotton acreage.[12] While the contribution of Chilean nitrate to fertilization of the cotton acreage is not clearly defined, in 1928, Chilean nitrate accounted for approximately 35% of total nitrogen fertilizer used that year on a nitrogen basis.[6]

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.[7] 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.[14] 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.[15]

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.[16] 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 yd^2 or 195-325 lb/acre[17]). 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[18] 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.

Potential to Impact Groundwater

While 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*[19] determined that water produced from 59 of 176 public water supply wells in the Los Angeles Basin was in excess of 50 years old. Bohlke[20] presents data for four representative surficial aquifers in the eastern U.S. with mean ages of 27-50 years, with some fraction of the groundwater being older. Fogg *et al*[21] and Weissman *et al*[22] 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 chapter 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.

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 discuss the potential for perchlorate to impact the environment.

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.[23] Potassium perchlorate can be used to produce colored flames, noise, and light as summarized in Table 1. Ammonium perchlorate is also used in some fireworks formulations. 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.

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 1. 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.[24]

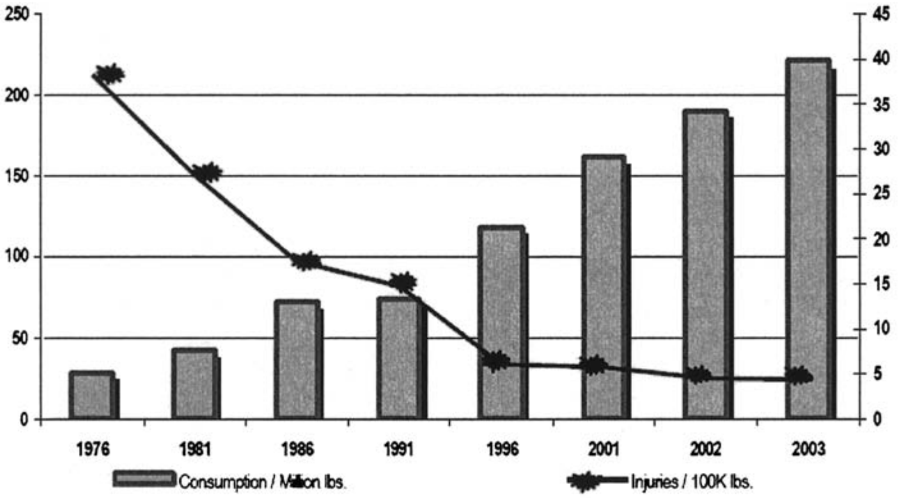

Figure 1: Fireworks Consumption in the United States from 1976-2003[26]

Table 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 percholrate	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
Whistle	Potassium Perchlorate	70
	Potassium Bensoate	30

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

Most of the fireworks consumed in the U.S. are imported from China, with only approximately 3% of the total mass of fireworks produced in the U.S.[24] 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.[25]

Potential to Impact Groundwater

Raw perchlorate from fireworks manufacturing facilities and perchlorate residue from detonated fireworks both have the potential to contaminate surface water 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.[27] However, statistics on dud rates (fireworks that are launched but not burned) do not exist.[28] 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.

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.

Perchlorate contamination linked to fireworks displays was examined by the Massachusetts Department of Environmental Protection (MADEP) at the

University of Massachusetts at Dartmouth. Eight monitoring wells were installed at a site where fireworks were launched/displayed over the Labor Day weekend of 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 <1 to 62 ug/L.[29] Soil samples were collected the day following the display, while groundwater samples were collected periodically throughout the fall. Results of soil sampling immediately after the display indicted a maximum perchlorate concentration of 560 ug/kg. Groundwater concentrations were not substantially different than they were before the display.[29]

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.[30] 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.[31]

SAFETY FLARES

Safety flares (or fusees) are used in emergency situations for road-side accidents and rail and marine emergencies. The following sections describe the main components of commercial safety flares and assess the potential for perchlorate to impact the environment.

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.[32]

Through experiments conducted by the Santa Clara Valley Water District in California, Silva[33] 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).

Production/Use Statistics

In 1997, approximately $101.5 million dollars worth of pyrotechnics (NAICS product code of 325998H107) were produced in the U.S.[34] 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,[25] with 92% from China. 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 U.S. manufacturer, then at least 20 to 40 million flares may be sold annually.

Potential to Impact Groundwater

Preliminary research by Silva[32,33] 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,[33] this amount of perchlorate can potentially contaminate 2.2 acre-feet of drinking water above 4 ug/L (the standard EPA Method 314.0 quantitation limit). Interestingly, even fully burned flares leached 1.9 mg perchlorate/flare.[33] More than 40 metric tons of flares were reported to be used/burned in 2002 in Santa Clara County, California alone.[33] 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.[35] From 1956 to 1996, highway flares were manufactured at this location.[35] 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.[36] 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 earlier.

BLASTING AGENTS

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 2). 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.

Common Blasting Agents and Their Perchlorate Content

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) [37] and is available in bulk form for on-site mixing or in premixed bags.

As shown in Table 2, some water gels, emulsions, and non-electric detonators can contain substantial amounts of perchlorate (e.g., up to 30%). Furthermore, MSDS sheets for some ANFO products list other “inorganic oxidizers”, which may include perchlorate, in their contents. The inclusion of sodium nitrate of Chilean origin, which is known to contain perchlorate, may also have potential to impact groundwater. Further testing is required to determine if these products contain perchlorate.

Consumption/Market

In 2003, the U.S. production of explosives, reported by 23 commercial explosive manufacturers, was 2,520,000 tons.[38] This amount of explosives is typical of the annual U.S. production in the last decade. Of the total U.S commercial production, 2,475,000 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[38]. 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.[38]

Table 2: Blasting Agents and Explosives Containing Perchlorate (% Composition)

Type Product	Blasting Agent (1.5) or Explosive (1.1)	NH_4NO_3	$NaNO_3$	$NaClO_4$	other energetic fuel
gel bulk or packaged	blasting agent	55-85	--	0-4	--
packaged gel	blasting agent	33-40	10-15	--	25 - 51
package emulsion	explosive	60-70	0-5	0-15	--
package emulsion	explosive	60-80	0-12	--	--
packaged gel	explosive	<65	<20	<7	--
ANFO	blasting agent	94.5	--	--	--
water gel	blasting agent	<80	--	<5	
water gel	blasting agent	< 75	<5	<5	
water gel	explosive	<65	<20	<7	
water gel	explosive	<65	<20	<7	
water gel, presplit	explosive	<65	<20	<7	
water gel	blasting agent	10-20	10-20	20-30*	

* ammonium perchlorate

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 un-detonated 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.[37]

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 perchlorate in groundwater and surface water, particularly in Massachusetts.[39,40,41] Perchlorate concentrations as high as several hundred parts per billion have been measured in close proximity to blasting sites.

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.[42,43] 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.

Manufacture of Chlorate

Sodium chlorate is produced electrochemically by the electrolysis of aqueous sodium chloride, and its production is governed by the following equation:[43]

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$$

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.[42] 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.[42,43] The formation of perchlorate stems from anodic oxidation of chlorate during the electrochemical reaction in accordance with the following reaction:[43]

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$

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 3 lists the total domestic production and consumption rates of sodium chlorate. The total annual consumption of sodium chlorate is approximately 1.2 million tons.[44]

Table 3: U.S. Production and Consumption of Sodium Chlorate

	Production (tons)	**Exports (tons)**	**Imports for Consumption**	**Apparent Consumption (tons)**
1991[45]	448,908	n/a	n/a	n/a
1992[45]	554,564	n/a	n/a	n/a
1993[45]	539,259	n/a	n/a	n/a
1994[45]	559,015	n/a	n/a	n/a
1995[45]	614,536	n/a	n/a	n/a
1996[46]	600,890	54,375	395,199	941,714
1997[46]	567,797	65,680	411,687	913,804
1998[47]	706,909	49,425	430,384	1,087,868
1999[47]	742,476	57,543	439,567	1,124,500
2000[48]	852,756	48,983	440,461	1,244,234
2001[44]	792,167	32,834	495,379	1,254,712
2002[44]	721,086	39,828	528,239	1,209,497

Chlorate Use

Historic and current uses for chlorate include pulp and paper bleaching, non-selective contact herbicide application, and plant defoliation.[49] 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.[49] 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.

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.[49] As a defoliant, approximately 99% of sodium chlorate application is used on cotton plants.[50] 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.

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. 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.[51]

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.,[44] 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.[52] 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 sewered. 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.

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. Furthermore, evidence exists that perchlorate can be formed naturally in evaporate deposits and through atmospheric mechanisms.

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.

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