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ABSTRACT

Ammonium and potassium perchlorate are strong oxidants widely employed in the pyrotechnic compositions in fireworks. Although its reduction is thermodynamically highly favorable, the perchlorate anion's reactivity is kinetically inhibited, primarily attributable to steric hindrance of access to the central chlorine atom within the tetrahedral ClO_4^- structure. This relative inactivity has historically made perchlorate a spectator anion in aqueous solution chemistry and explains its classification as a persistent environmental contaminant. The perchlorate anion is a potent competitive inhibitor of iodide (I^-) transport by the sodium iodide symporter (NIS) expressed in the basolateral membranes of human thyroid follicular cells. This inhibition can result in the reduction of thyroid hormone production critical for the normal growth and development of fetuses, infants and young children. Perchlorate has no other adverse physiological effects and is normally excreted quantitatively. However, public concern over the suppression of thyroid function has engendered government regulation and the research, development and use of technologies for the detection, measurement and removal of perchlorate contamination in drinking water supplies. In 2005, the U.S. Environmental Protection Agency adopted a Reference Dose (RfD) for ClO_4^- of 0.7 μg/kg/day and recently established an Interim Drinking Water Health Advisory level of 15 μg/l. In the last ten years, researchers have investigated the transformation of perchlorate to chloride (Cl^-), called mineralization, in which plants and plant-microbe systems serve as the mediators. This plant-assisted degradation of perchlorate is an example of phytoremediation. Perchlorate can be decomposed in the plant's leaves (phytodegradation) and in the root environment or rhizosphere (rhizodegradation). Phytodegradation is a slow process and is normally accompanied by phytoaccumulation, in which perchlorate is stored inside plant tissues. This accumulated perchlorate will likely either return to the plant's local environment or enter the food chain. Rhizodegradation is a much faster process involving bacteria in anaerobic conditions in which perchlorate is sequentially converted to chlorate (ClO_3^-), chlorite (ClO_2^-) and chloride by reaction with many organic compounds (e.g., acetate). This rhizodegradation is hampered by the presence of nitrate, which is preferentially reduced by the bacteria in the root zone. Many species of terrestrial and aquatic plants are capable of remediating perchlorate, provided adequate levels of oxidizable (electron donating) organic compounds are available. A recently reported study of the contamination of

lake waters with perchlorate from fireworks display fallout has shown that perchlorate concentrations rise immediately following the display, then decrease to background levels within days. It is likely aquatic microbial fauna phytoremediation is playing a principal role in the perchlorate mineralization. Towards minimizing long term environmental contamination with fireworks associated perchlorate, fireworks displays should be conducted whenever possible at sites rich in terrestrial and/or aquatic vegetation.

INTRODUCTION

Potassium perchlorate (KP) and ammonium perchlorate (AP) are strong oxidants, which are now used extensively worldwide in pyrotechnic compositions and are certainly important compounds to the fireworks industry. While other perchlorates of pyrotechnic interest are known and available, their use is restricted to special, low volume usage. From the pyrotechnics standpoint, KP and AP have chemical and physical properties, which are nearly ideal. Pyrotechnic compositions containing these perchlorates produce the visual, acoustical, propulsive and explosive effects desired with relatively low ignition sensitivities and good storage and handling characteristics.

The perchlorate anion, ClO_4^-, has become the subject during the last twelve years of intense environmental interest, as it is considered a significant threat to drinking water supplies. The perchlorate anion is a potent competitive inhibitor of iodide (I^-) transport into human thyroid cells (thyrocytes). This inhibition can result in the reduction of thyroid hormone production critical for the normal growth and development of fetuses, infants and young children. Because of this inhibitory effect, low-dose exposure to ClO_4^- is expected to produce adverse health effects similar to those caused by dietary iodide deficiency. Perchlorate has no other adverse physiological effects and is normally excreted quantitatively. However, public concern over the suppression of thyroid function has engendered government regulation and the research, development, and use of technologies for the detection, measurement and removal of perchlorate contamination in drinking water supplies.

In the last decade, researchers have investigated the transformation of perchlorate to chloride (Cl^-), called mineralization, in which plants and plant-microbe systems serve as the mediators. This plant-assisted degradation of perchlorate is an example of phytoremediation. Phytoremediation may serve to mitigate any contamination of the environment with perchlorate, associated with the discharge of fireworks.

REGULATING PERCHLORATE

With authority under the Safe Drinking Water Act (SDWA), in March 1998, the U.S. Environmental Protection Agency's (USEPA) Office of Water formally added perchlorate to the drinking water contaminant candidate list (CCL)[1-3]. In December 2008, an Interim Drinking Water Health Advisory for Perchlorate [4] was promulgated establishing the advisory level of 15 μg/l (15 ppb) and an oral Reference Dose (RfD) of 0.7 μg/kg/day. The RfD corresponds to a "no observable adverse effects level" (NOAEL), and is an exposure level considered to be without significant risk to humans, including sensitive or vulnerable subgroups (e.g., very young and very old), when perchlorate is ingested daily over protracted periods. This RfD for ClO_4^- is the equivalent of a 24.5 μg/l (24.5 ppb, 250 nM) maximal concentration limit in drinking water for a 70 kg individual consuming 2 liters of water per day as the only dietary source of perchlorate. Several states have adopted the 15 μg/l concentration as an action level. Three states have action levels well below the USEPA advisory level: Massachusetts (2 μg/l), Texas (4 μg/l), and California (6 μg/l)[4].

TOXICOLOGY

Upon ingestion, perchlorate is readily absorbed through the gastrointestinal tract. Absorption through the skin is minimal, and because perchlorates have extremely low vapor pressures at normal ambient temperatures, an inhalation hazard could only exist where perchlorates are present as suspended dusts. Perchlorate is excreted rapidly and quantitatively in the urine, and no evidence exist suggesting perchlorate is metabolized[5]. According to the USEPA, perchlorate is "not likely to pose a risk of thyroid cancer in humans, at least at doses below those necessary to alter hormone homeostasis," and " the epidemiological evidence is insufficient to determine whether or not there is a causal association between exposure to perchlorate and thyroid cancer."[4]

The thyroid gland uses iodide (I^-) from the bloodstream to biosynthesize the two metabolic hormones, L-tetraiodothyronine (T_4) and L-triiodothyronine (T_3). T_4 is also known as thyroxine. T_3 and T_4 regulate growth, cell differentiation, and the metabolisms of lipids, proteins, and carbohydrates[6]. Iodide is transported by the sodium iodide symporter (NIS), a glycoprotein expressed in the basolateral membranes of human thyroid follicular cells (thyrocytes)[7]. Each thyrocyte is serviced by many NISs. The transport process, called the cellular iodide pump, preferentially selects anions on the basis of ionic volume: iodide (I^-) ≈ thiocyanate (SCN^-) $<ClO_4^-$, pertechnetate (TcO_4^-)[2]. The NIS prefers to transport perchlorate over iodide[7]. Thus, the presence of ClO_4^- in the bloodstream inhibits the uptake of iodide by the thyroid and can stimulate excessive release of stored iodide from the gland. The inhibition can result in the reduction of thyroid hormone production critical for the normal growth and development, especially in the central nervous system, of fetuses, infants and young children.

Within the healthy adult population, perchlorate ingestion manifests a considerably lower risk of adverse effects. A study at an ammonium perchlorate plant in 1999 found that workers who daily inhaled NH_4ClO_4 dust suffered no thyroid effects and the bloodstream perchlorate was readily egested through urination[6]. Because ClO_4^- merely competes with I^- for transport through the NIS, maintaining adequate dietary levels of iodine will minimize the risk of adverse health effects associated with chronic perchlorate ingestion.

PECULIAR PERCHLORATE

The conversion of ClO_4^- to chlorate, ClO_3^-, is thermodynamically favored ($\Delta E<0$). Based upon this and other thermodynamic data, perchlorate salts should be very highly reactive substances. They should be unstable in the solid state, and in solution, the perchlorate anion should be a strong and readily reactive oxidant, able to oxidize water to oxygen[2]. In reality, most inorganic perchlorates are stable solids, and when in solution at low concentration (<10%w/w) or in weakly acidic to basic (pH>1) conditions, the perchlorate anion is with most reducing agents essentially unreactive[3].

Perchlorate's non-lability is well known and exploited in synthetic and analytical chemistry. This relative inactivity has historically made perchlorate a spectator anion in aqueous solution chemistry and explains its classification as a persistent environmental contaminant. The stability of the perchlorate anion is attributable to the strength of the chlorine-oxygen bonds and the requirement that reduction must initially proceed through the abstraction of an oxygen atom rather than through direct attack of the central chlorine atom. The tetrahedral structure of $ClO_4^-$and the delocalization of the negative charge over all four oxygens provide a steric control on reductive vulnerability. The reduction of the perchlorate anion is strongly kinetically controlled, with the abstraction of the first oxygen having a high activation energy.

QUANTITATIVE ANALYTICAL CHEMISTRY

Urbansky[2,3] has reviewed the several perchlorate determination methods, which were employed in analytical laboratories prior to the year 2000. In February 2000, USEPA announced[4,8] their selection of the standard analytical method, 314.0, for perchlorate which is based upon ion chromatography with conductivity detection. It was approved for the monitoring of perchlorate in the years 2001-2003. The method detection limit (MDL) is 0.53 μg/l (0.5 ppb). USEPA Methods 314.1, 314.2, 331.0, and 332.0 were published in 2005 through 2008 and reflected improvements in the MDL[4]. Method 331.0 employs liquid chromatography with electrospray ionization mass spectrometry (LC/ESI-MS). The MDL for perchlorate using this method is 0.008 μg/l (8 ppt, parts per trillion) with single stage mass spectrometry and 0.005 μg/l (5 ppt) with tandem mass spectrometry (LC/ESI-MS-MS)[4]. The MDLs of the state-of-the-art analytical methods is now at least three orders of magnitude below the action levels for perchlorate in drinking water supplies.

PERCHLORATE USES AND ENVIRONMENTAL OCCURRENCE

Environmental perchlorate can have both natural and anthropogenic (man-made) origins. Reports dating to the late 1800s document findings of perchlorates in natural deposits of Chilean saltpeter (sodium nitrate). Analyses of Chile saltpeter by USEPA and the Department of Energy have found concentrations of approximately 1 g ClO_4^-per kg $NaNO_3$ [3]. Chili saltpeter is used as a fertilizer, particularly favored by tobacco farmers. Questions as to how perchlorate is or was produced naturally remain the subject of speculation[9], but lightning and reactions with ozone are frequently cited. Perchlorate has been detected in rain and snow samples indicating an atmospheric origin[10]. Very recently, NASA reported and confirmed that the Phoenix Mars Lander discovered perchlorate in Martian soil[11]. Perchlorate is not found in significant levels in seawater, and high levels of fresh water contamination can usually be attributed to one or more steps in the life cycle of perchlorate containing fertilizers, energetic materials (propellants, explosives and pyrotechnics), and other products. Perchlorates are used in nuclear reactors, electronic tubes, as additives in lubricating oils, in tanning and finishing of leather, as mordants for dyed fabrics, in electroplating and electropolishing, aluminum refining, rubber manufacture, and in the production of paints and enamels.

Commercial quantities of sodium perchlorate are usually prepared by electrolysis of aqueous solutions of sodium chloride, in which the chloride ion is successively oxidized through hypochlorite (ClO^-), chlorite (ClO_2^-), chlorate (ClO_3^-), and finally to perchlorate. Large commercial quantities of ammonium perchlorate are used in 1.3 solid rocket propellants and to a limited extent in pyrotechnic and explosive compositions. Potassium perchlorate is used extensively in pyrotechnic compositions and in black powder-substitute gun propellants. Both the ammonium and potassium perchlorates are prepared from the sodium salt by metathesis (double decomposition) reactions. The much higher aqueous solubility of sodium perchlorate allows the facile fractional crystallization of the ammonium and potassium salts.

The manufacture, transportation and disposal (recycling and/or demilitarization) of ammonium perchlorate based rocket propellants and potassium perchlorate based pyrotechnics can result in soil and ground water contamination. However, the normal burning of rocket propellants and pyrotechnic compositions containing a perchlorate as the oxidizer, results in the decomposition of the perchlorate anion, with little, if any, unreacted. The potassium perchlorate in black powder substitutes, such as Pyrodex, is also decomposed, with little unreacted, in the normal functioning of the propellants. The use by sportsmen of black powder substitutes in their muzzle-loading rifles, pistols and cannons would not be expected to be a significant source of perchlorate contamination in the environment. Many pyrotechnic compositions found in signal devices, such as highway flares, railroad fusees, and marine flares and meteors contain potassium perchlorate. Some marine smoke signal compositions also contain perchlorates. If these compositions burn normally, they too would not be expected to be significant sources of environmental perchlorate[12].

Railroad fusees, which contain potassium perchlorate at levels typically below 10% by weight are often burned incompletely. Users will intentionally extinguish the flame if the burn time of the fusee exceeds the time needed for signaling. The railroad workers will often drop and leave the unburned portion of the fusee on the ground near the rails. Although relatively small quantities of potassium perchlorate are involved, this source of perchlorate could be environmentally significant, depending upon the regulatory action levels for soil and water contamination. In years past, railroads used sodium chlorate, contaminated with perchlorate, as an ingredient in herbicides to suppress the growth of foliage along rail corridors. Soils around rail beds may be contaminated with perchlorate, but subject to phytoremediation.

Potential contamination attributable to fireworks

Many of the pyrotechnic compositions employed in display fireworks (US Department of Transportation hazard class 1.3G Fireworks, UN0335) and in consumer fireworks (USDoT 1.4G Fireworks, UN0336) contain potassium perchlorate and to a lessor extent ammonium perchlorate. Ammonium perchlorate's use in firework compositions is relatively new. It can be found in mixtures, which burn steady, producing bright, rich colored flames, or burn stroboscopically with bright white or colored flames.

The aerial display shells seen at public displays of fireworks are propelled ballistically from mortars, using black powder as the propellant. These shells (projectiles) "break" or "burst" (explode) in the sky, to produce the colorful burst patterns (visual effects) or bright flash / deafening booms so often seen and heard. The colorful burst patterns are created by burning "stars" ejected radially from the breaking shells. Stars are chunks of pyrotechnic compositions in the form of spheres, cubes, cylinders and irregular shapes. Many of these star compositions contain perchlorates as oxidizers. Sometimes stars within a breaking shell, fail to be ignited. Such stars, called "blind stars," or "blown black stars," fall back to the ground, and can be dispersed over a large area of the display site. Other components of aerial display shells, which contain potassium perchlorate, such as pyrotechnic whistles, can also fail to be ignited and be dispersed over the display site. Potassium perchlorate is commonly employed as the oxidizer in "salute compositions", also known as flash powders. Some manufacturers produce salute compositions containing ammonium perchlorate. These explosive mixtures are used in devices, called salutes, reports, shots or siatenes, which produce the bright white flash and deafening booms. When a salute functions, it is not uncommon for some unreacted perchlorate to be present in the flash powder decomposition products. With a reasonable assumption that most of the perchlorate present in the pyrotechnic compositions is ultimately decomposed in the burning of fireworks, it would only be necessary to consider perchlorate which survives the normal discharge of product, such as that in blind stars, unignited display shell inserts, and residues[12].

While research has been reported concerning the environmental effects of fireworks on bodies of water, it did not address perchlorate[11].

PHYTOREMEDIATION OF PERCHLORATE

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Phytodegradation of perchlorate in poplar tree leaves was demonstrated by Van Aken and Schnoor[14] in a study in which small cuttings grown in hydroponic conditions were incubated in the presence of ^{36}Cl radioisotopically labeled ClO_4^-at an initial concentration of 25 mg/l [25,000 μg/l (ppb)]. The isotopic label provided the means of unambiguously determining the amount and location within the plant tissues of unreacted ClO_4^-, and it's degradation products, ClO_3^-, ClO_2^-, and Cl^-. About a 50% reduction in the initial ClO_4^- concentration was realized after 30 days of incubation. Because the experiments were performed under sterile conditions, the results show that poplar tree tissues are able to mineralize ClO_4^-, and that the reduction proceeds through a sequential pathway similar to the microbial metabolism of ClO_4^- involving perchlorate reductases and chlorite dismutases. Unlike microbial perchlorate-reducing enzymes, the plant biocatalysts tolerate oxygen (aerobic conditions).

Yifru and Nzengung[15], investigated the uptake and phytoaccumulation of perchlorate by natural terrestrial and aquatic vegetation growing within perchlorate-contaminated sites in arid [Las Vegas Wash (LVW), Nevada] and subhumid [Longhorn Army Ammunition Plant (LHAAP), Karnack, Texas] climates, during multiple seasons. All vegetation species collected from the two sites contained measurable levels of perchlorate. Plants sampled at LHAAP included willow, pine, sweet gum, oak, goldenrod, crabgrass, Bermuda grass, and bullrush. At the LVW site, samples of salt cedar, black willow, cattail, algae, and sedge were collected. In general, higher concentrations of phytoaccumulated perchlorate were observed in the leaf tissue of plants growing in the arid than in the subhumid climate. The high concentrations of phytoaccumulated perchlorate, observed at both sites, suggests that the inadequate levels of organic compounds, serving as electron donors, were available to the plants to promote or sustain rhizodegradation. The amount of perchlorate uptaken and accumulated by terrestrial and aquatic plants is influenced by the local perchlorate concentration, the plant species, and the season. Grasses and salt cedar trees phytoaccumulated significantly higher amounts of perchlorate than woody plants, and leaves harvested in late summer contained higher perchlorate concentrations than leaves harvested in spring and early summer. Senescent leaves and litter fall, containing phytoaccumulated perchlorate, evidences a potential for perchlorate recycling in an ecosystem. If a perchlorate-contaminated site is to be phytoremediated, it is important that senesced vegetation, including leaves and cuttings, be collected and composted and rhizodegradation be enhanced.

Rhizodegradation of perchlorate by willow trees was investigated by Yifru and Nzengung[10] in which hydroponically prerooted cuttings in bioreactors, under greenhouse conditions, were dosed with ClO_4^- and one of four organic carbon sources. The organic carbon sources were acetate (CH_3COO^-), ethanol (CH_3CH_2OH), 100% organic mushroom compost, and chicken litter extracts; the later two being agricultural waste derivatives. In the bioreactors dosed with dissolved organic carbon at 500 mg/l and an initial perchlorate concentration of 25 to 40 mg/l (25,000 to 40,000 ppb), rhizodegradation produced a reduction in the perchlorate to below the ion chromatography method detection limit of 2 μg/l in approximately 9 days. The results of these experiments clearly show that supplying electron donors derived from organic carbon sources to the root zone of plants biostimulates rapid rhizodegradtion of perchlorate. Similar results in rhizodegradation efficacy were achieved by Yifru and Nzengung[16] in which aqueous perchlorate was a co-contaminant with the potent carcinogen, N-Nitrosodimethylamine (NDMA).

Wilkin, et al[17], investigated the perchlorate contamination of the surface waters of Wintersmith Lake, near Ada, Oklahoma from the fallout of public displays of fireworks in July of 2004, 2005, 2006 and November 2005. Water samples taken from locations adjacent to the launch site, preceding the displays, had perchlorate concentrations in the range of 0.005 to 0.081 μg/l , with a mean of 0.043 μg/l. Measurements taken within 14 hours after the displays showed increases in the perchlorate concentrations ranging from 24 to 1028 times the mean baseline value. The wide range in concentrations immediately after the displays could be attributed to variations in the quantities of fireworks discharged, the amounts of unreacted potassium and ammonium perchlorates, and wind speed and direction. A maximum perchlorate concentration of 44.2 μg/l was measured following the July 4th 2006 display. Although the ClO_4^- concentration returned to the background value in about 24 days, it is important to note that the concentration decreased by nearly 80% within the first two days. The rate of attenuation correlated to surface water temperature and could be modeled as pseudo-first order. As lake sediments showed low adsorption capacity (< 100 nmol/g), the researchers suspected the lake's microbial fauna were responsible for the perchlorate degradation. Experiments confirmed a rapid microbial-based degradation in the absence of nitrate (NO_3^-). [Rhizodegradation is also hampered by the presence of nitrate, which is preferentially reduced by the bacteria in the root zone.] The results of the study suggests that at display sites with appropriate biogeochemical conditions, natural aquatic systems have the ability to remediate perchlorate released by the discharge of fireworks.

RECOMMENDATIONS

Towards minimizing long term environmental contamination with fireworks associated perchlorate, fireworks displays should be conducted whenever possible at sites rich in terrestrial and/or aquatic vegetation.

The normal paper and plastic fallout from the display including shell casing fragments, spent inserts, and, of course, unreacted pyrotechnics should be harvested where practicable and either processed by composting, incineration, or sent to an appropriate industrial landfill.

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