

Review Articles

Perchlorate as an Environmental Contaminant

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Abstract. Perchlorate anion (ClO_4^-) has been found in drinking water supplies throughout the southwestern United States. It is primarily associated with releases of ammonium perchlorate by defense contractors, military operations, and aerospace programs. Ammonium perchlorate is used as a solid oxidant in missile and rocket propulsion systems. Traces of perchlorate are found in Chile saltpeter, but the use of such fertilizer has not been associated with large scale contamination. Although it is a strong oxidant, perchlorate anion is very persistent in the environment due to the high activation energy associated with its reduction. At high enough concentrations, perchlorate can affect thyroid gland functions, where it is mistakenly taken up in place of iodide. A safe daily exposure has not yet been set, but is expected to be released in 2002. Perchlorate is measured in environmental samples primarily by ion chromatography. It can be removed by anion exchange or membrane filtration. It is destroyed by some biological and chemical processes. The environmental occurrence, toxicity, analytical chemistry, and remediative approaches are discussed.

Keywords: Anion exchange; bioremediation; drinking water; ion chromatography; perchlorate; potable water; rocket propellant; solid oxidant; thyroid; thyrotoxicity

Introduction

The objective of this review is to provide an overview of the general chemistry, occurrence, toxicology/pharmacology, analytical chemistry applicable to environmental samples, drinking water treatment technologies, and land or sourcewater remediative technologies available. It is not intended to provide exhaustive coverage, but to serve as an introduction to the topic for readers who are generally unfamiliar with it. The interested reader is directed to more comprehensive reviews within the individual sections, or to the primary literature when advancements have occurred since the time of those original reviews. At present, perchlorate contamination is known to be a problem only within the United States. As a result, the discussion is focused on experience within the U.S., and a description of monitoring and regulatory frameworks in other nations is beyond the scope of this report. While it appears that drinking water can be satisfactorily treated, current analytical methods cannot reach the detection limits suggested by toxicology studies. In addition, it is not possible to accurately estimate the costs associated with treatment since nearly all work has been conducted on laboratory or pilot scales. Accordingly, issues associated with mass production, implementation, capitalization, and economies of scale are unresolved and preclude a satisfactory cost analysis at this time.

1 General Chemistry

The perchlorate anion (ClO_4^-) consists of a tetrahedral array of oxygen atoms around a central chlorine atom (Fig. 1).

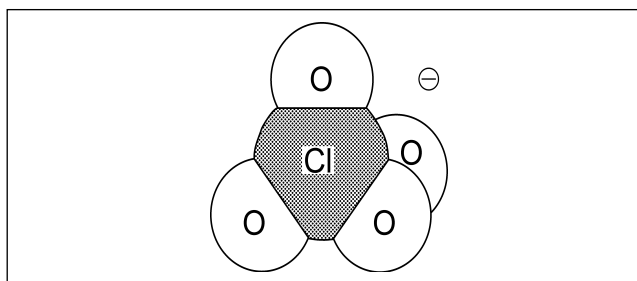
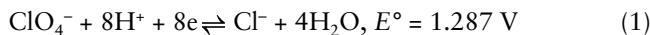


Fig. 1: The perchlorate anion

As the oxidation state of the chlorine is +7, the species is a strong oxidizing agent (eqn 1). In this respect, perchlorate is slightly weaker than dichromate or permanganate. However, perchlorate reduction is extremely nonlabile (slow) and can usually be observed only in concentrated strong acid. In fact, the redox behavior of perchlorate is so rarely observed in chemical systems that sodium perchlorate is used to adjust the ionic strength of solutions prior to electrochemical or other laboratory studies. In 0.1–4.0 M acid, perchlorate is not reduced by common reagents such as thiosulfate, sulfite, or iron(II).



Perchlorate can be reduced by air-sensitive metal cations, such as titanium(III) or ruthenium(II). Such behavior has been summarized elsewhere [1,2]. Since then, several investigators have concentrated on catalytic rhenium species [3] or titanium(III) [4]. Other than some bacterial systems (*vide infra*), perchlorate reduction is generally not observable except when hot, concentrated (>70%) perchloric acid meets a reducing agent, such as organic matter, in which case it is explosive. For this reason, perchloric acid wet-ashing is always preceded by nitric acid wet-ashing. Some transition metal perchlorate salts and most organic perchlorates (esters) decompose violently or explosively; some detonate at just a touch.

In addition to its resistance to reduction, perchlorate has a relatively low charge density. Consequently, it does not generally form complexes with metals the way other anions do. Perchlorate is routinely employed as a counterion in the synthesis of metal compounds when a noncomplexing anion is

required. Complexes of perchlorate are rare and usually noteworthy when they are encountered [5]. Perchlorate does not sorb well to most surfaces and most perchlorate salts are quite soluble. Notable exceptions include tetraphenylarsonium perchlorate and some quaternary ammonium perchlorate salts, which form stable ion pairs. Sometimes these ion pairs remain soluble and are used as phase-transfer catalysts/agents.

2 Occurrence

The EPA added perchlorate to its Contaminant Candidate List (CCL) for drinking water in 1998 following discoveries of its presence in drinking water supplies throughout the southwestern United States [6]. Most of the perchlorate contamination that has been found environmentally has been associated with military activities or defense contractors [7]. Ammonium perchlorate is used as a solid oxidant in rocket propulsion. It also turns up in fireworks. Considerable attention has been focused on Lake Mead and the Colorado River because of the ammonium perchlorate production facilities formerly located in Henderson, Nevada (near Las Vegas). Perchlorate salts have been found along the Las Vegas Wash and are working their way into Lake Mead. So far, perchlorate concentrations measured by the Las Vegas Valley Water District or Southern Nevada Water Authority have not reached 18 ng mL^{-1} at the water intake. This concentration represents a provisional action level. Authorities in northern California have closed or abandoned a number of wells that exceeded the action level. Other states have set alternative concentrations, such as Arizona (14 ng mL^{-1}) and Texas (22 ng mL^{-1}). EPA's Regional offices have also set different limits for clean-up of contaminated sites.

Low concentrations of perchlorate have been detected sporadically around the U.S., for example, in New York and Iowa. These sites are not associated with any known defense activities, and the source of this perchlorate is not known. It has been speculated that historical use of Chile saltpeter from decades ago may be responsible for some. It is well-known that caliche ore deposits in Chile (which are refined to make sodium nitrate fertilizer) contain natural perchlorate that persists in the final product as a small residue [8–10]. Manufacturing changes have further reduced this concentration (currently $\approx 100 \text{ } \mu\text{g g}^{-1}$) to 5–10% or less of what it was just a year ago [11]. At present, natural saltpeter fertilizers and products derived from them make up less than 0.1% of the fertilizer applied in the U.S. Data on the historical use of saltpeters is almost nonexistent. Although some fertilizers were implicated as a source of perchlorate in two studies [12,13], later studies demonstrated that products on the market are perchlorate-free and suggested that the original phenomena were anomalous [14,15].

3 Toxicology/Pharmacology

The perchlorate ion is similar in size to the iodide ion and can therefore be taken up in place of it by the mammalian thyroid gland. In this way, perchlorate can disrupt the production of thyroid hormones and thus disrupt metabolism. Additionally, other physiologic systems may be indirectly affected. The toxicologic mechanisms through which perchlorate ex-

erts its effects have been reviewed in some detail [16,17]. In occupational and environmental settings, most of the available epidemiological data suggest that exposure to various levels of perchlorate has had no adverse effect on the thyroid or indirectly on other physiologic systems [18–21].

The ability to disrupt thyroid hormone production has resulted in medicinal use of perchlorate. The cardiac drug amiodarone, when administered for arrhythmia, is degraded in the body to give free iodide anion in the blood. Amiodarone-induced thyrotoxicosis has been treated with the pharmaceutical use of perchlorate [22–24].

Epidemiological data alone have generally not been considered adequate for development of drinking water regulations to protect human health. A variety of animal model toxicological studies have been undertaken to determine the possible risk to vulnerable subpopulations, such as developing fetuses. The EPA's National Center for Environmental Assessment is responsible for establishing a reference dose (RfD, in $\text{mg kg}^{-1} \text{ day}^{-1}$ or similar units) that is safe. Such a dose is then converted to a drinking water equivalent level (DWEL) using a relative source contribution (RSC). The RSC sets how much of a contaminant is provided by drinking water rather than diet or other means of exposure, and usually varies from 20% to 80%. Finally, a no observable adverse effects level (NOAEL) is calculated based on some assumptions about how much water people drink and how much they weigh.

The NCEA's first risk assessment draft was released in 1999 and proposed an RfD of $900 \text{ ng kg}^{-1} \text{ day}^{-1}$, which equated to an NOAEL of 32 ng mL^{-1} if an RSC of 100% is assumed. Following an external peer review process, the NCEA undertook a series of additional studies to address issues raised. In its most recent draft report, the NCEA revised its RfD downward to $0.03 \text{ } \mu\text{g kg}^{-1} \text{ day}^{-1}$ ($30 \text{ ng kg}^{-1} \text{ day}^{-1}$). The NCEA emphasizes that this RfD, like all others, has an associated uncertainty, so that it should not be used as a rigid cutoff. However, a DWEL based on an RSC of 100% and a 3.0-L daily water intake for a 70-kg human would be 0.7 ng mL^{-1} for this RfD. Present ion chromatographic methods are incapable of reliably measuring such a concentration in most drinking water matrixes. It is important to realize that an NOAEL is intended to ensure safety and represents the highest concentration at which no adverse health effects are anticipated. It is not the same as the lowest observable adverse effects level (LOAEL) or lowest observable effects level (LOEL); the LOEL includes those physiological changes which are not viewed as adverse. There is always a gap between the NOAEL and the LOAEL as a result of the uncertainties associated with all toxicological studies or risk assessments based on toxicological studies. The NCEA plans on releasing a final RfD in mid-2002.

None of these parameters (RfD, NOAEL, or DWEL) has any regulatory force at the federal level; however, the states (or other governmental units, e.g., counties or cities) may use these values to set their own regulatory levels. For example, California has now lowered the upper concentration to 4 ng mL^{-1} . The Office of Ground Water and Drinking Water has the authority to promulgate regulations for drink-

ing water and may propose one at some future point. Such a regulation may be put forth as a maximum contaminant level (MCL), which represents an upper limit for the concentration based on a set monitoring and averaging strategy (e.g., an unweighted average of quarterly test results). Alternatively, OGWDW may require that utilities use the best available technologies (BAT). BAT regulations may be promulgated in situations where meeting an MCL would place an excessive economic burden on a utility (or its customers) or where no technology is capable of achieving the MCL. The European Union has set a maximum admissible guide level of $20 \mu\text{g mL}^{-1} \text{NaClO}_4$ (which corresponds to $16 \mu\text{g mL}^{-1}$ as ClO_4^-) in water intended for human consumption [25]. Otherwise, the EPA is unaware of regulatory actions in other nations. The basis for this limit is unclear, but it appears to be based on professional judgment about the concentration of any one ionic species within potable water supplies.

4 Analytical Chemistry

Attention was drawn to perchlorate ion largely by advances in ion chromatography at the California Department of Health Services [26]. The primary means of analyzing drinking water and environmental samples for perchlorate has been and will continue to be ion chromatography. The selectivity combined with the low detection limit make this the optimal technique. EPA's Office of Ground Water and Drinking Water released Method 314 for the analysis of drinking water [27]. A similar method 9058 has been issued by the EPA's Office of Solid Waste and Emergency Response [28]. A variety of papers have been published on the ion chromatographic determination of perchlorate in potable water [29–31].

A thorough and recent review of the analytical chemistry of perchlorate has been done elsewhere, and the reader is directed there for more detailed information and guidance to the primary literature [32]. Nonetheless, some recent developments bear mention. Additional work has taken place on more complicated matrixes, including plant products and fertilizers. Sample clean-up procedures were developed to remove many of the interferents found in fruit and vegetable samples [33,34]. Validation of an IC method [35] for fertilizers was completed recently using both Dionex IonPac AG16/AS16 and Metrohm Metrosep Supp 5 columns [36,37].

Although IC is the principal technique used for perchlorate, confirmatory techniques can be useful for refractory samples, instances of unexpected occurrence, or complex matrixes. Several spectroscopic techniques have been applied to a variety of matrixes. Complexation electrospray mass spectrometry (cESI-MS) has been applied to raw and treated drinking water [38–42] supplies as well as fertilizer [14]. Tandem electrospray MS-MS has been applied to groundwater analysis [43]. High-field asymmetric waveform ion mobility spectrometry (FAIMS) has been used to test both water and urine [44,45]. Raman spectroscopy has been applied to fertilizers and plant tissues [12,46,47]. A method for determining isotopic distribution of chlorine in perchlorate has been developed [48]; however, it is unlikely to prove useful for forensic applications in the U.S. except possibly to rule out an occa-

sional source since there are no archived samples of perchlorate salts available for comparison.

5 Water Treatment and Site Remediation

In the U.S., there are contaminated water supplies (aquifers and surface waterways) and contaminated land sites. Some of these are commingled. These can be viewed in terms of remediating sites to make them usable again or in terms of making a water supply drinkable. The same technologies may not be applicable to both for a variety of reasons ranging from public perception to cost to ease of operation. Various approaches have been examined recently in some detail in a special review paper, and the reader is directed there for current information and more comprehensive comparison and contrast of the available strategies [49]. A number of options for treatment and the issues affecting their viability were discussed previously [50]. Although there have been some advances, which are described below, many of the considerations raised previously are still applicable today. These options are briefly summarized below, but the reader is warned that their implementation is not always a straightforward matter.

5.1 Biological degradation

Biological remediation appears to have the most promise in dealing with contaminated sites. A number of bacteria possess perchlorate reductases, enzymes that facilitate the otherwise sluggish reduction of perchlorate [51–53]. A number of fluidized and fixed bed biological reactors have been constructed in the laboratory [54–56]. Unfortunately, many of the organisms prefer oxygen. They also tend to selectively reduce nitrate and chlorate. That notwithstanding, some are able to reduce perchlorate in the presence of nitrate. Many land sites suffering from perchlorate pollution are also tainted with nitrate. The combination of oxidants (electron acceptors) simply raises the time required for complete treatment. Early on, high levels of dissolved salts presented a problem, but hardier strains have been found or developed of late [57,58]. There is some question about the public's acceptance of using bacteria to treat drinking water, but bioremediation is already being used for contaminated soil. Aerojet has set up a pilot scale biological reactor in combination with other treatment processes to produce a finished water that appears to meet drinking water standards (as seen by the author during a tour of the facility), but the technology has not been approved for treating water for human consumption. At present, such systems have not been commercialized and are not used by any U.S. waterworks.

Phytoremediation (degradation by plants) is probably a special case of bacterial remediation. Current thinking is that the plants serve as a safe environment for the bacteria that actually do the work. Some trees, such as willows, will reduce perchlorate [59,60]. In addition, *Myriophyllum aquaticum* (a feathery, bright green plant commonly called parrot feather) has been shown to degrade perchlorate [61–63]. The time and space requirements for phytoremediation prohibit its use for treating drinking water, but it could have some applicability for contaminated soils or even *in situ* land remediation.

5.2 Anion exchange

Several new resins and engineering processes have been developed for removing perchlorate by anion exchange. In this process, chloride ions are substituted for perchlorate ions one for one. One of the problems initially plaguing anion exchange was the unselective removal of all anions, but more selective resins have been developed that preferentially replace the perchlorate, but leave behind bicarbonate, sulfate, silicate, and other native background anions. A new resin developed by Oak Ridge National Laboratory relies on a mixture of triethyl and trihexyl quaternary ammonium functionalities to achieve rapid and selective removal [64]. These investigators have developed a novel regeneration scheme that produces a modest amount of waste [65]. Other investigators have also been working on finding selective anion exchange resins [66], and one product has even been commercialized at the drinking water plant scale [67]. The plant uses a revolving system of anion exchange columns so that some are being regenerated while others are being used or are ready for use. It may be that a hybrid system where anion exchange is used to remove perchlorate and then the spent regenerant is subjected to biodegradation is a superior approach.

Commercial anion exchange systems are widely accepted by and familiar to utilities and regulatory agencies and are likely to be the first choice. Dealing with the spent regenerant (brine) solution represents an obstacle to their implementation. On the other hand, ion exchange systems are readily worked into existing waterworks, and the level of expertise required for their operation is commensurate with other duties in treatment plants.

5.3 Membrane processes

Reverse osmosis and nanofiltration can remove simple salts, including perchlorate salts [68]. However, such processes result in demineralization of the water because the removal of salts is unselective. This precludes their use in water treatment plants because of potential for corrosion to metal piping in the distribution system. In addition, membrane systems are subject to fouling, scaling, and other problems that require maintenance or replacement. On the other hand, membrane filtration point-of-use devices can be practical options for homeowners, small businesses, or isolated users. In those cases, the concentrate (waste) can often be discarded via the sanitary sewer system, while the diluate (also called the filtrate or retentate) is used for drinking and other purposes.

6 Outlook

Based on current information, perchlorate may be a problem for water supplies in some regions of the U.S., but there does not appear to be widespread occurrence of significant levels. At present, the EPA is unaware of any contaminated sites in Europe, Asia, or Africa, but there are some sites in South America. On the down side, some of the affected U.S. water supplies serve substantial populations. Moreover, some of these water supplies are used to irrigate crops consumed

throughout the U.S. as fresh produce (e.g., lettuce). Consuming such produce is probably of no risk at all for those whose drinking water is perchlorate-free as the ion is rapidly eliminated from healthy humans (mostly in the urine). Most contamination is highly localized. Drinking water problems and ecological impacts are likely to be restricted to those regions. Local ecological impacts are only beginning to be studied. So far, only one paper has been published on the detection of perchlorate in the tissues and fluids of animals living in regions where perchlorate can be found in soil or water [68]. Although there has been some research on fish and some wildlife, the impacts on secondary consumers (e.g., skunks, badgers, wolves, foxes) are not necessarily clear. In addition, some omnivores may eat not only fish or macroinvertebrates (e.g., mussels, crayfish, insects), but also fruits, seeds, nuts, or other vegetable tissues that may contain perchlorate. Whether the exposure is high enough to induce pathological or physiological changes remains to be seen. Ecological data are too scarce to make any meaningful statements at this time. While fertilizers are not generally a source of perchlorate in the U.S., Chile saltpeter (NaNO_3) and KNO_3 derived from it may contain perchlorate at low levels ($\leq 100 \mu\text{g g}^{-1}$, as set by the manufacturer for U.S. products). These products are used on citrus fruits (root and foliar application) in California. It is not known whether those plants can absorb or accumulate perchlorate in the leaves or in the fruits. While such products are used minimally in the U.S., worldwide use is altogether unknown; therefore, it is not possible to assess if exposure is possible via produce, which has a significant seasonal variation in country of origin. In addition, the sources of fertilizers and their composition may vary dramatically, including for natural saltpeters. Because historical usage of Chile saltpeter is not documented in the U.S. (and probably not in other nations either), it remains to be seen whether isolated unexpected locations will be found. The prevalence of perchlorate in European fertilizers is essentially unknown.

In the U.S., potable water data gathered under the EPA's Unregulated Contaminant Monitoring Regulation should provide the information relative to the contamination of drinking water supplies. The EPA has not made any determinations on regulating perchlorate and appears unlikely to do so soon; therefore, the decision to restrict the use of some water supplies or to require treatment is left up to states, local authorities, and utilities. For those waterworks that decide to treat their water or are compelled to do so, it appears that anion exchange will be the most feasible technology for the near future, although biological treatment is promising for the distant future. Costs associated with treatment of drinking water cannot be effectively estimated at this time. In part, this is because the anion exchange resins, for instance, have not been mass produced (which results in a lower cost); on the other hand, there have been some difficulties associated with the manufacturing process. Should it eventually appear that a federal regulation is desirable, the EPA's Office of Ground Water and Drinking Water normally would perform an economic feasibility study to determine what financial burdens would be placed on utilities and their customers for various treatment technologies as a part of the regulatory process.

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