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Bioavailability and bioremediation of perchlorate salts

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Abstract

Perchlorate anion (ClO_4^-) has been detected in drinking water, plants, and animals in multiple locations throughout North America. Perchlorate poses a human health concern because this contaminant is the same ionic size as iodide, and can compete with iodide for uptake into the thyroid gland, causing changes in thyroid hormone levels and possibly thyroid disorders. Although the long-term effects on humans are currently being debated, concerns by scientists and the public have generated considerable legislation designed to minimize potential damage. Current remediation efforts primarily focus

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on ion exchange technology, but the future of alternative remediation strategies is promising. The environmental impacts of perchlorate have been less well studied, but the pollutant is clearly being transferred between abiotic and biotic ecosystem components, causing significant developmental problems for some species. Suggestions for future research on perchlorate are proposed.

Introduction

This review is intended to provide an overview of the occurrence and consequences of environmental contamination with perchlorate. Throughout this document the reader will be directed to more complete sources for further information on individual topics. Although the problem with perchlorate contamination is almost certainly worldwide, the preponderance of the available information has been collected from the U.S., and this review necessarily focuses mostly on information from North America.

Description of perchlorate

The perchlorate anion (ClO_4^-) consists of a central chlorine atom surrounded by four oxygen atoms. Although perchlorate thermodynamically should be a reactive oxidizing agent, its kinetic properties make it quite stable. The negative charge is highly dispersed and protects the central chlorine atom from reduction. For more information on the chemical properties and reactions of perchlorate, see Urbansky (1) and Espenson (2). Most perchlorate salts are soluble. Once in water, the perchlorate anion is mobile and also extremely stable, with the potential to persist for many decades (1). Dissolved perchlorate does not sorb appreciably to soil (3), though the movement of dissolved perchlorate through soil can be affected by biodegradation (4). Perchlorate salts used commercially include ammonium perchlorate, sodium perchlorate, and potassium perchlorate. The toxicity of these chemicals is due to the perchlorate ion since the salts readily dissociate in water (1).

Sources of perchlorate contamination

In solid form and at high concentrations, perchlorate salts are extremely effective oxidizing agents, and are known for their explosive properties. Starting in the 1940s, rockets were manufactured with solid rocket fuel consisting of perchlorate as an oxidizing agent, aluminum for combustible material, and a carboxyl terminated polybutadiene binder (5). Rockets with solid fuel, such as the Minuteman rocket could be readied for launch much more quickly than those rockets requiring liquid fuel. Perchlorate was also a key ingredient of the disposable rocket engines that allowed relatively heavy planes to take off from ships. Perchlorate is currently used for fuel in both the aerospace industry and the military. Collectively, these industries represent

about 90% of the perchlorate consumption in the U.S.A. The other 10% of perchlorate consumption includes use in roadside flares, airbag inflation systems, and fireworks; as components of nuclear reactors and electronic tubes; as additives in lubricating oils; in electroplating and aluminum refining; in tanning and finishing leather; and in the production of paints and enamels (6, 5, 1). Perchlorate use has been recorded in 49 of the 50 states in the U.S. It seems likely that virtually every country throughout the world has been using perchlorate if they have military or civilian rocketry programs.

Demand for perchlorate has been further increased by the need to periodically replace supplies (7). If perchlorate-fueled rockets remain unused for extended periods, the perchlorate oxidizes and the fuel becomes compromised, requiring replacement. For many years, the standard procedure for disposing of expired fuel was to burn the old fuel directly on the ground, or dissolve the material in water and either pour the now non-combustible residue onto the ground, or flush the residue into waste ponds. All disposal methods resulted in contamination that ultimately entered into groundwater (8).

Perhaps the most egregious known example of a pollution source for perchlorate can be found in Henderson, Nevada, where manufacturing plants produced and disposed of this chemical since the early 1950s. The Kerr-McGee plant, though now defunct, is still leaching up to 230 kg/day into a nearby drainage known as the Las Vegas Wash, where concentrations can reach 600-800 $\mu\text{g}/\text{L}$. Water from the Las Vegas Wash flows into Lake Mead and contaminates the Colorado River, where the perchlorate level has been steady at about 5-7 $\mu\text{g}/\text{L}$. About 15 million people in the U.S. utilize the Colorado River as a source for drinking water and irrigation. The Colorado River is diverted in aquifers that travel hundreds of miles away from the river itself, reaching communities in San Diego, CA, and Tucson and Phoenix, AZ. Furthermore, Colorado River water is used to irrigate crops, particularly lettuce and other vegetables, that are shipped throughout the entire United States. For an overview of the Kerr-McGee and Colorado River situation, see Hogue (9).

A second, but minor source of perchlorate contamination is certain fertilizer products (10, 11). In northern Chile there are rich sources of naturally occurring sodium nitrate (Chile saltpeter, NaNO_3) that are mined for fertilizer. The sodium nitrate deposits also contain perchlorate. Urbansky et al. (11) found 15,000 to 18,000 $\mu\text{g}/\text{kg}$ perchlorate in commercial fertilizer products containing Chilean sodium nitrate. Modern processing now removes most of the perchlorate from commercial Chilean fertilizer, but past use of these products was unrecorded, and may explain some findings of perchlorate in water far away from any manufacturing, defense, or aerospace activity. Ultimately, use of contaminated fertilizer has not led to environmental contamination on a large scale (12). Natural saltpeters now constitute only 0.14% of annual U.S. fertilizer consumption (10).

Though most of the available data on the occurrence of perchlorate is from the United States, perchlorate is likely to be a problem in many countries. As previously mentioned, perchlorate has long been known to exist in naturally occurring deposits in some parts of Chile. In a recent study in China, Liu et al. (13) discovered that drinking water supplies in Beijing are contaminated with levels up to 6.3 $\mu\text{g/L}$. The perchlorate was determined to be present in groundwater, but the actual source was not identified. Unfortunately, perchlorate contamination in many countries has not yet been thoroughly investigated, or has not been reported by scientists or authorities.

Analysis and detection

Perchlorate detection methods include ion-selective electrodes, ion chromatography, capillary electrophoresis, HPLC, and spectrophotometry (1). However, before 1997, the detection limit for perchlorate anion in water was 400 $\mu\text{g/L}$. Even with this relatively poor detection capability, concern was raised in 1957 when perchlorate was found in groundwater 14 miles east of Sacramento, CA at levels of 3.5-5 million $\mu\text{g/L}$ (14). In 1985, an alarm was raised again when water in the San Gabriel Valley was found to have 50 to 2600 $\mu\text{g/L}$ perchlorate. However, the San Gabriel Valley study was never considered finalized because control samples were also found to have perchlorate (15). In 1997, a new ion chromatography detection method was developed that could quantify perchlorate in water at levels of 4 $\mu\text{g/L}$ and above (16). With this new testing method, agencies detected perchlorate in water throughout Southern California, Nevada, Utah, and the rest of the Southwest. Today, perchlorate contamination has been found in at least 20 states (17). Some communities have chosen to utilize bottled water to avoid perchlorate exposure. Urbansky et al. (18) found no perchlorate (detection limit 6 $\mu\text{g/L}$) in sixteen kinds of bottled water.

Improved detection of perchlorate in various substrates other than water continues to be an important goal. Ellington and Evans (19) published an extraction and ion chromatography method for detecting perchlorate in plant tissues at levels to 5 $\mu\text{g/L}$. In 2002, Anderson and Wu (20) published a cleanup method for samples of animal tissue. The procedure reduces background conductivity of samples, allowing perchlorate detection by ion chromatography. Perchlorate in tissue can be detected at levels down to 180 $\mu\text{g/kg}$. Using this technique, Anderson and Wu (20) found perchlorate in bird and rodent tissue at a contaminated site in Texas. Smith et al. (21) used the detection methodology to quantify perchlorate in rodents collected from Las Vegas Wash, Nevada. The discovery of perchlorate in plant and animal tissues as well as water generated a surge of interest in determining the toxicological importance of these newly reported concentrations of perchlorate.

General physiological effects in humans

It has been known since 1952 that perchlorate interferes with iodide uptake (22). The perchlorate anion is approximately the same ionic size as iodine. In the mammalian body, perchlorate has shown to competitively inhibit iodine uptake by the sodium iodide symporter (NIS), which is responsible for concentrating iodide in the thyroid gland (23). Though the most attention has been focused on thyroid effects, it is important to note that an NIS also exists in the mammary tissue of mammals to concentrate iodine in milk (24).

The thyroid gland produces thyroid hormones T3 and T4. If blood levels of T3 and T4 drop, the pituitary gland releases thyroid stimulating hormone, TSH, which stimulates the growth and activity of the thyroid, and can cause the thyroid to become enlarged (forming a goiter). Thus, people who are iodine deficient can end up with enlarged thyroid glands. Thyroid hormones T3 and T4 regulate growth, cell differentiation, and metabolism of lipids, proteins, and carbohydrates. The hormone T4 is necessary for the normal function of the central nervous system (CNS) and for the normal development of the CNS in the fetus. When perchlorate competitively inhibits iodide uptake by the sodium iodide symporter, levels of T3 and T4 in the blood decrease, and levels of TSH increase. The effects of acute perchlorate toxicity can be substantial. Clark (25) and Soldin et al. (26) provide further information on the health effects of perchlorate. Clewell et al. (27) have modeled the path of perchlorate in the body, proposing that the perchlorate ion is actively transported, instead of iodine, into thyroid follicles and into the thyroid lumen, then diffuses back into the blood and is excreted in the urine.

The potential for mammalian effects has led to a fierce, ongoing debate over what is a safe level of perchlorate in drinking water. The NOAEL (no observable adverse effect level) is one of the metrics used for determining drinking water safety. The NOAEL will probably be much different for healthy adult males than for pregnant women and young children. Additionally, those with an abundance of iodine in their diet may be less at risk from perchlorate exposure than those with low iodine intake. When establishing drinking water guidelines, high-risk subpopulations must be evaluated.

Much of the data available regarding human perchlorate exposure comes from records of medical use of perchlorate to treat thyroid issues. Since the 1950s perchlorate has been used medicinally to treat overactive thyroid (hyperthyroidism) and for iodine poisoning resulting from the use of the anti-arrhythmic agent amiodarone. Medicinal doses were as high as 600-1000 mg/day, and in one case perchlorate usage continued at 200 mg/day for 22 years. Perchlorate is still used medically today for single-dose iodide discharge tests. Wolff (23) provides an overview of clinical uses of perchlorate.

Physiological studies on humans have elucidated some details of short-term perchlorate exposure. Greer et al. (28) gave perchlorate in drinking water

to humans for fourteen days, recording iodine uptake at various intervals. Though important for understanding the physiological action of perchlorate, short-term studies do not provide enough information to establish the safety of chronic exposure through drinking water.

Some researchers have turned to epidemiological studies, comparing communities with and without perchlorate in drinking water, to attempt to determine the human health effects of perchlorate. These studies largely have shown no adverse health effects of perchlorate ingestion at low concentrations. Li et al. (29) compared Medicaid medical records from Clark County (Las Vegas) Nevada (4 to 24 $\mu\text{g}/\text{L}$ perchlorate in drinking water) with those from Washoe County, Nevada (no detectable perchlorate), and with records from the rest of the state (no detectable perchlorate). The authors found no evidence of increased thyroid disease. Kelsh et al. (30) used hospital records from 1983-1997 to compare TSH levels in Redlands, CA, where perchlorate has been detected, to certain communities in San Bernardino and Riverside where perchlorate has never been detected. No differences were observed in TSH levels in newborns from these populations. Crump et al. (31) compared three cities in Chile with historically high (110-120 $\mu\text{g}/\text{L}$), low (7 $\mu\text{g}/\text{L}$), and undetectable levels of perchlorate in drinking water. In these cities, perchlorate contamination is from naturally occurring deposits. The authors took blood samples from school children and surveyed parents to determine family history. They concluded that there was no difference in blood levels of thyroid hormones in the three cities, but parents from Taltal, the city with the highest levels of perchlorate, were significantly more likely to report a family history of thyroid problems than parents from the cities with low and non-detectable perchlorate levels. In a controversial study, Brechner et al. (32) used computerized city records to compare the TSH levels of newborns in Yuma, Arizona (6 $\mu\text{g}/\text{L}$ perchlorate) with newborns in Flagstaff, Arizona (non-detectable perchlorate). Newborns from Yuma were found to have significantly higher levels of TSH. Some authors have objected to this study because of methodological and statistical concerns (33).

Rats are used most often to model possible perchlorate effects on humans. Siglin et al. (34) found that rats had increased blood levels of TSH and decreased levels of T3 and T4 when ingesting 0.1 mg/kg/day perchlorate in drinking water, the lowest dose examined in the study, for only 14 days. Doses of 10 mg/kg/day increased thyroid size after 14 days. Despite these results, the authors suggest that the NOAEL should be 1.0 mg/kg/day because the changes in thyroid hormones did not influence the health of the rats, and they argue that histological changes in the thyroid should be used to determine safe dosage rather than hormone levels in the blood. York et al. (35) exposed pregnant female mice to perchlorate in drinking water. In the pups, the authors found no difference in brain measurements and behavior, but did find histological

changes in the thyroid tissue and differences in thyroid hormone levels. Their reported NOAEL for the pups was 0.1 mg/kg/day, the lowest level examined in their study. Rats are known to be more sensitive to perturbations of the thyroid than humans, because rat T3 and T4 hormones have shorter half-lives than their human analogues (36). Nevertheless, these studies are an essential route to understanding human exposure.

Environmental effects

Though human health effects of perchlorate get most of the attention from the press, environmental effects are generating serious concerns in the scientific community. We have at least some understanding of the action of perchlorate in mammals, but we are surprisingly ignorant of the physiological effects of perchlorate on plants and non-mammalian animals.

At high levels, perchlorate can be toxic to plants. Miller et al. (14) stated that perchlorate at levels of 1000-2000 $\mu\text{g/L}$ is herbicidal, and had actually been used as a weedicide in the past. Susarla et al. (37) noted that at 5000 $\mu\text{g/L}$ perchlorate some leaf damage to lettuce seedlings was observed. Many studies have documented the capacity of plants to accumulate and to degrade perchlorate. This capacity varies by plant species, root mass, rhizosphere bacteria present, nitrate concentration, nitrogen source, nitrogen concentration, and carbon concentration (38). Perchlorate accumulation and degradation in some plant species are desirable because they provide attractive remediation options, but accumulation in crop plants also represents a potential exposure route for humans and animals.

Agricultural crops that accumulate perchlorate may end up reaching consumers directly through food plants or indirectly through feed for livestock. For example, the Imperial Valley, California, is a huge agricultural area that is irrigated almost entirely by water from the Colorado River (5-7 $\mu\text{g/L}$ perchlorate). This area produces lettuce that is shipped and eaten throughout the U.S. In April 2003, the Environmental Working Group (39) and the Press Enterprise newspaper (40) independently released analyses finding perchlorate present in lettuce at levels up to 121 $\mu\text{g/kg}$ wet weight. Laboratory studies have shown that lettuce (37, 41), cucumber, soybean (41), and tobacco (42) accumulate perchlorate in leaf tissue. The amount of perchlorate accumulated varies by plant species and growing conditions, but can be quite high. Susarla et al. (37) found up to 1.5 million $\mu\text{g/kg}$ in lettuce, while Yu et al. (41) found up to 750,000 $\mu\text{g/kg}$ in lettuce. Yu et al. (41) also observed that perchlorate levels increased to plateau, suggesting there may be a threshold for accumulation. The potential for accumulation thresholds must be evaluated in future studies. The Imperial Valley is also a major producer of alfalfa that is fed to cattle that are subsequently eaten by consumers. To the best of our

knowledge, this potential route of exposure in humans has not been investigated in detail.

Relatively few studies have examined health effects of perchlorate on animals other than mammals. Patiño et al. (43) found that zebrafish were relatively resistant to perchlorate effects. In contrast, research on frogs (*Xenopus laevis*) has shown these organisms to be quite sensitive to perchlorate at low concentrations (1-1000 $\mu\text{g/L}$), exhibiting abnormal thyroid function and altered sex ratio (44) and inhibited development and metamorphosis (45). Anderson et al (20) found perchlorate concentrations ranging from 900-7190 $\mu\text{g/kg}$ in bird (and rodent tissue) from an ammonium perchlorate contaminated site in east Texas.

Clearly, one of the best approaches to determining ecosystem-level effects of perchlorate has been to survey perchlorate in water, soil, vegetation, and/or animal tissue collected from a contaminated site. Urbansky et al. (46) analyzed salt cedar (*Tamarix ramosissima*) growing in contaminated water in the Las Vegas Wash, Nevada. The salt cedar was found to have 5000-6000 $\mu\text{g/kg}$ perchlorate in twigs. Although this tree is an invasive species and the target of removal efforts, salt cedar has become established throughout much of the southwest (47). Salt cedar grows in riparian ecosystems and accumulates salts, which are secreted from the leaves. Because of these properties, salt cedar likely plays a significant role in the fate and movement of perchlorate in riparian ecosystems. In a more extensive study, a survey of an army ammunition plant in Karnack, Texas by Smith et al. (21) found perchlorate in vegetation (555-5,557,000 $\mu\text{g/L}$), aquatic insects (811-2038 $\mu\text{g/L}$), fish (below detection to 207 $\mu\text{g/L}$), frogs (below detection to 580 $\mu\text{g/L}$), and mammals (2,328 $\mu\text{g/L}$). The authors concluded that scientists need to approach the assessment of potential perchlorate-related effects "at the individual (thyroid function, growth, reproduction), population (population dynamics, demography), and community (community structure, predator-prey dynamics) levels of biological organization." In a third study, Smith et al. (48) surveyed the Las Vegas Wash in Nevada. The objective of the study was to correlate levels of perchlorate in rodent tissue with levels found in soil, water, and vegetation. Of the 58 total rodents captured, 21 had detectable levels of perchlorate (maximum 33000 $\mu\text{g/kg}$). The correlation was significant between soil (maximum 512,000 $\mu\text{g/kg}$) and rodent perchlorate concentration. Perchlorate was detected in plants at levels ranging from below the detection limit to 4,460,000 $\mu\text{g/L}$; water levels ranged from 150 $\mu\text{g/L}$ to 1,040 $\mu\text{g/L}$. For a review of studies on perchlorate effects in aquatic systems, see Dean et al. (49). Thus, regardless of the system evaluated, all studies to date have shown that perchlorate can be transferred throughout the food web. Thus, research

should be initiated to determine the movement and potential biomagnification of perchlorate in both natural and agricultural ecosystems.

Legislation

Perchlorate contamination continues to be found in new areas. Testing at first centered on water contamination, but as analytical techniques have developed, perchlorate has been found in lettuce (39; 40), in milk (50), beef cattle (51), and fish (52). Official guidelines outlining how much perchlorate intake is safe have yet to be determined. In 1998, the US Environmental Protection Agency (53) added perchlorate to a contaminant candidate list, indicating that the health effects of perchlorate would be evaluated and potentially added to the National Primary Drinking Water Regulations. In 1999, the EPA recommended a 4-8 $\mu\text{g/L}$ "interim" range for exposure, and in 2002 that recommendation was dropped to 1 $\mu\text{g/L}$. The EPA draft assessment is currently being reviewed by the National Academy of Sciences for further recommendation. This process requires considerable time, and several years may pass before a U.S. federal standard for perchlorate in drinking water is established.

However, individual states are seeking to deal with the perchlorate issue more quickly. Some states such as Nevada (18 $\mu\text{g/L}$) and Maryland (1 $\mu\text{g/L}$) have set their own provisional action levels. In March of 2004, California became the first state to set a drinking water standard for perchlorate when the California EPA named a "public health goal" of 6 $\mu\text{g/L}$ (54).

Remediation options

Phytoremediation

Phytoremediation is a desirable option for remediation of contaminated soil and water because this technique is potentially cost effective both initially and long term, and because plants have the potential to transform contaminants into substances that are not hazardous to human health (55). Some other remediation options can remove perchlorate from water, but the perchlorate waste product still must be disposed of properly.

Several recent studies have examined phytoremediation strategies for perchlorate. Nzengung et al. (56) investigated woody plant species for phytoremediation, and found that willow trees (*Salix* species) were the most effective species tested. These authors also discovered that rhizosphere microorganisms were responsible for much of the degradation of perchlorate to chloride, and that high nitrate concentrations interfered with this process. Results of later studies have been consistent with rhizodegradation as the perchlorate removal mechanism and with the inhibition of rhizodegradation by nitrate (41, 57). Bacchus et al. (55) evaluated nine herbaceous plants for their

phytoremediation potential. Blue hyssop and perennial glasswort were documented as the most promising species. The authors emphasized that ecological knowledge of the range and properties of plant species is absolutely essential for successful phytoremediation.

A review by Nzengung and Wang (56) states that while phytodegradation does occur, it occurs at a rate proportional to the rate of water uptake by the plant. Crude extracts of green leaves were shown to degrade perchlorate, suggesting that leaves possess an enzyme capable of catalyzing perchlorate degradation. However, when the roots of plants harbor bacteria suitable for degrading perchlorate, rhizodegradation may cut remediation time from days to hours. Many bacteria use perchlorate only when no NO_3^- is available to act as a terminal electron acceptor, and others only thrive in an anaerobic environment. Therefore, one potential remediation strategy is injection of perchlorate utilizing bacteria into the root zone of local plants for in-situ remediation of contaminated sites (57). An elevated level of carbon also speeds up the bacterial degradation process. Using this approach, Nzengung et al. (57) found that in willow trees with favorable root-zone conditions (low nitrate, biostimulated perchlorate degraders), perchlorate can be rapidly rhizodegraded to chloride. Approximate times for complete perchlorate elimination from water were 15-30 days under anaerobic conditions, and much longer under aerobic conditions. Under aerobic conditions more of the perchlorate was concentrated in plant tissues rather than being rhizodegraded. Generally, the plants accumulated less than 5% of the perchlorate present in the water (initial water concentration 75,000-20,0000 $\mu\text{g/L}$). Although low accumulations in plants used for phytoremediation may appear counterintuitive, minimal concentrations in plants are desirable to decrease phytotoxicity and reduce the potential for transfer into the food web.

Physical removal

Because of the chemical properties and stability of perchlorate dissolved in water, prospects for chemical reduction as a remediation technique are not promising (2). Potential remediation methods have been reviewed in Urbansky (1), Urbansky and Schock (58), Logan (59), Motzer (5), and Urbansky (12), and include membrane separation, ion exchange, and biological reduction. The membrane filtration category includes both reverse osmosis and nanofiltration. Water is forced through a semiporous polymer membrane, and dissolved salts are unable to penetrate. The end product is relatively deionized water. Membrane filtration is not considered a promising method because deionized water is generally thought to have an unpleasant taste and because the membrane is easily fouled by dissolved materials and microbiota (58). Moore et al. (60) found that that iron metal added to perchlorate solution was able to sorb perchlorate anion to the surface of the metal and reduce it to chloride. The

authors concluded that the reaction rate is too slow for immediate use, but may provide a basis for future remediation strategies.

Ion exchange technology is the most commonly used method for water treatment, with facilities currently in use in California, Nevada, Massachusetts, and other states. In the anion exchange treatment, water flows through a resin matrix (usually small beads the size of sand grains) containing a high concentration of a relatively harmless anion such as chloride. Due to the concentration difference, the perchlorate anion exchanges positions with the chloride, such that the chloride ends up in the water and the perchlorate ends up bound to the resin. When the resin can take up no more perchlorate, it must either be disposed of, or the resin may be regenerated, resulting in perchlorate waste that must be safely discarded. For anion exchange to be feasible on a large scale, resins must be selective and inexpensive (58). In January 2003 the first full-scale ion exchange facility began treating the perchlorate plume from the Lockheed Propulsion Company in Mentone, CA. A separate ion exchange facility at the Kerr-McGee site in Nevada has reduced the amount of perchlorate leached daily from 400 kgs to 230 kgs (9).

Jackson et al. (61) proposed electrokinetic extraction and electrokinetic injection of substrates as another alternative for perchlorate remediation. In electrokinetic extraction, a pair of electrodes is implanted into the ground on either side of the soil area to be treated. A low voltage current is applied across the electrodes and the contaminants migrate to one electrode or the other depending on their charge. This system has been used in the oil recovery industry but has not been applied for remediation. This method has maximum potential for use in areas where soil has low permeability. Jackson et al. (61) were able to remove perchlorate from sand, clay and soil in a laboratory setting to below their detection limit of 5 ppb. They also used electrokinetics to inject lactic acid and glycine, organics that promote microbial degradation of perchlorate. Though more research is necessary, electrokinetics ultimately may be a useful remediation option for severely contaminated sites.

One problem that all physical removal methods share is the creation of a contaminated waste product. The waste is sometimes disposed of by incineration (62), but the waste also may be treated with perchlorate reducing microbes.

Microbial remediation

Many microbes have been discovered that are capable of reducing perchlorate (63, 64). These microbes are potentially useful in remediation processes, including water treatment, in-situ remediation of contaminated sites, and bioreactors where contaminated soil is removed from the ground for treatment. Microbes may also be used to treat the waste products produced by other removal methods, such as ion exchange. The waste produced by ion

exchange treatment contains high levels of salts or ammonium, requiring microbes that can tolerate harsh condition (65; 62, 66). Many researchers have participated in the search for perchlorate-reducing microbes that can be used for biodegradation. Extensive reviews of microbial perchlorate reduction can be found in Xu et al. (63) and in Coates and Achenbach (64), and the details will not be repeated here. Interestingly, perchlorate reducing soil microbes are nearly ubiquitous, but they are not all equally useful. Many microbes only reduce perchlorate in anaerobic conditions, some preferentially utilize nitrate instead of perchlorate, and still other microbes are pathogenic to humans. Most require some form of organic material to provide electrons. Microbes also vary in how quickly and to what concentration they can eliminate perchlorate. Nonetheless, the outlook for microbial remediation is promising. Our understanding of the biochemistry of microbial perchlorate reduction is rapidly evolving and some of the genes involved have been cloned. Genetic knowledge may allow molecular identification of the useful microbes (64) and, though there is much well founded concern about bioengineering of bacteria, genetic knowledge may eventually allow bioengineering of improved microbes.

Conclusions

The global perchlorate contamination problem is likely to get worse before beginning to improve. Although perchlorate is no longer dumped freely into the environment in the U.S.A., old sites such as the Kerr-McGee factory in Nevada are still releasing the anion and new sites are being found. We are still discovering the full extent of past contamination in the United States, and scientists have not yet begun to investigate the extent of perchlorate release in other countries. News reports from war zones such as Iraq suggest munitions are being burned, buried or otherwise disabled in ways that will allow percolation of perchlorate into the groundwater. Not surprisingly, in such situations possible future contamination is considered secondary to immediate objectives. In addition, production, storage and disposal of military munitions and fireworks in many countries are essentially unregulated. Since 1997, a substantial body of knowledge has been amassed regarding perchlorate, including evidence of toxicity, environmental transport, and microbial degradation. However, much more remains to be understood about perchlorate, especially regarding ecosystem effects. Evidence indicates that some plants can accumulate perchlorate, and that this contaminant is present in both wild and domesticated animals, but the biotransfer processes have not been adequately quantified. Insects, among the most important and abundant organisms on the planet, have yet to be studied for perchlorate effects. Another significant concern is the interaction of perchlorate with other compounds. There is a critical shortage of information on effects of multiple toxicants: over 95% of all toxicological studies only examine the impact of individual

chemicals (67). Thus, there exists a substantial need for additional study of perchlorate contamination and remediation. However, without the recognition by world governments that funding for research on perchlorate is a priority, problems regarding this contaminant will likely exceed solutions for the foreseeable future.

References

1. Urbansky, E. T. 1998, *Biorem.* J., 2, 81.
2. Espenson, J. H. 2000, In: Urbansky, E.T. (Editor), *Perchlorate in the Environment*, Page 1, Kluwer Academic/Plenum Publishers, New York.
3. Urbansky, E. T. and Brown, S. K. 2003, *J. Environ. Monit.*, 5, 455.
4. Tipton, D. K., Rolston, D. E. and Scow, K. M. 2003, *J. Environ. Qual.*, 32, 40.
5. Motzer, W. E. 2000, *Environ. Forensics*, 2, 301.
6. Fisher, J., Todd, P., Mattie, D., Godfrey, D., Narayanan, L. and Yu, K. 2000, *Drug Chem. Toxicol.*, 23, 243.
7. Damian, P. and Pontius, F. W. 1999, *Environmental Protection*, 10, 24.
8. Waldman, P. 2002, *Wall Street Journal*, December 16, 2002.
9. Hogue, C. 2003, *Chemical and Engineering News*, August 18, 2003. Page 37.
10. Urbansky, E. T., Magnuson, M.L., Kelty, C.A., Gu, B. and Brown, G. M. 2000, *Environ. Sci. Technol.*, 34, 4452.
11. Urbansky, E. T., Brown, S.K., Magnuson, M.L., Kelty, C.A. 2001, *Environ. Pollut.*, 112, 299.
12. Urbansky, E. T. 2002, *Environ. Sci. & Pollut. Res.*, 9, 187.
13. Liu, Y-J., Mou, S-F., Lin, A., Du, B. 2004, *Huanjing Kexue/Environmental Science*, 25, 51.
14. Miller, L. M., Ferris, J. G., Fiedler, A. G., Glover, G. E., Schaefer, E. J. and Wells, S. W. 1957, *J. Amer. Water Works Assoc.*, 49, 1334.
15. Lee, J. 2004, *The New York Times*, March 2, 2004.
16. CDHS (California Department of Health Services) 1999, *Chemical Detection Limits for Purposes of Reporting*, (<http://www.dhs.ca.gov/ps/ddem/chemicals/dlr/dlrindex.htm>).
17. U.S. EPA 2004. Known Perchlorate Releases in the U.S. (http://www.epa.gov/swerffrr/documents/perchlorate_map/nationalmap.htm).
18. Urbansky, E. T., Gu, B., Magnuson, M. L., Brown, G. M. and Kelty, C. A. 2000, *J. Sci. Food Agric.*, 80, 1798.
19. Ellington, J. J. and Evans, J. J. 2000, *J. Chromatogr. A*, 898, 193.
20. Anderson, T. A. and Wu, T. H. 2002, *Bull. Environ. Contamin. Toxicol.*, 68, 684.
21. Smith, P. N., Theodorakis, C. W., Anderson, T. A. and Kendall, R. J. 2001, *Ecotoxicology*, 10, 305.
22. Stanbury, J. B. and Wyngaarden, J. B. 1952, *Metab. Clin. Exp.*, 1, 533.
23. Wolff, J. 1998, *Pharmacol. Rev.*, 50, 89.
24. Perron, B., Rodriguez, A. M., Leblanc, G. and Pourcher, T. 2001, *J. Endocrinol.*, 170, 185.
25. Clark, J. J. J. 2000, *Toxicology of Perchlorate*, Kluwer Academic/Plenum Publishers, New York.
26. Soldin, O. P., Braverman, L. E. and Lamm, S. H. 2001, *Ther. Drug Monit.*, 23, 316.

27. Clewell, R. A., Merrill, E. A., Narayanan, L., Gearhart, J. M. and Robinson, P. J. 2004, *Int. J. Toxicol.*, 23, 17.
28. Greer, A., Goodman, G., Pleus, R. C. and Greer, S. E. 2002, *Environ. Health Perspect.*, 110, 927.
29. Li, X., Squartsoff, L., Lamm, S.H. 2001, *J. Occup. Environ. Med.*, 43, 630.
30. Kelsh, M.A., Buffler, P.A., Daaboul, J.J., Rutherford, G.W., Lau, E.C., Barnard, J.C., Exuzides, A.K., Madl, A.D., Palmer, L.G., Lorey, F.W. 2003, *J. Occup. Environ. Med.*, 45, 1116.
31. Crump, C., Michaud, P., Tellez, R., Reyes, C., Gonzales, G., Montgomery, E. L., Crump, K. S., Lobo, G., Beccerra, C. and Gibbs, J. P. 2000, *J. Occup. Environ. Med.*, 42, 603.
32. Brechner, R. J., Parkhurst, G. D., Humble, W. O., Brown, M. B. and Herman, W.H. 2000, *J. Occup. Environ. Med.*, 42, 777.
33. Lamm, S.H. 2003, *J. Occup. Environ. Med.*, 45, 1131.
34. Siglin, J. C., Mattie, D. R., Dodd, D. E., Hildebrandt, P. K. and Baker, W. H. 2000, *Toxicol. Sci.*, 57, 61.
35. York, R. G., Barnett, J., Jr., Brown, W. R., Garman, R. H., Mattie, D. R. and Dodd, D. E. 2004, *Int. J. Toxicol.*, 23, 191.
36. Capen, C. C. 1997, *Toxicol. Pathol.*, 25, 39.
37. Susarla, S., Wolfe, N. L. and McCutcheon, S. C. 1999, In: Urbansky, E.T. and Schock, M.R. (Editors) *Perchlorate in the Environment, Symposia Papers Presented Before the Division of Environmental Chemistry, American Chemical Society, New Orleans, August 1999*, Page 66.
38. Nzengung, V. A. and Wang, C. 2000, In: Urbansky, E.T. (Editor) *Perchlorate in the Environment*, Kluwer Academic/Plenum Publishers, New York.
39. Sharp, R. and Lunder, S. 2003. Environmental Working Group Report: Suspect Salads, (<http://www.ewg.org/reports/suspectsalads/es.php>).
40. Danelski, D. and Beeman, D. E. 2003, *The Press Enterprise*, April 27, 2003. Page 1.
41. Yu, L., Canas, J. E., Cobb, G. P., Jackson, W. A. and Anderson, T. A. 2003, *Ecotox. Environ. Safety*, 58, 44.
42. Ellington, J. J., Wolfe, L., Garrison, A. W., Evans, J. J., Avants, J. K. and Teng, Q. 2001, *Environ. Sci. Tech.*, 35, 3213.
43. Patino, R., Wainscott, M. R., Cruz-Li, E. I., Balakrishnan, S., McMurry, C., Blazer, V. S. and Anderson, T. A. 2003, *Environ. Toxicol. Chem.*, 22, 1115.
44. Goleman, W. L., Carr, J. A. and Anderson, T. A. 2002, *Environ. Toxicol. Chem.*, 21, 590.
45. Goleman, W. L., Urquidi, L. J., Anderson, T. A., Smith, E. E., Kendall, R. J. and Carr, J. A. 2002, *Environ. Toxicol. Chem.*, 21, 424.
46. Urbansky, E. T., Magnuson, M. L., Kelty, C. A. and Brown, S. K. 2000, *Sci. Total Environ.*, 256, 227.
47. DeLoach, J. C., Lewis, P. A., Herr, J. C., Carruthers, R. I., Tracy, J. L. and Johnson, J. 2003, *Biol. Control*, 27, 117.
48. Smith, P. N., Yu, L., McMurry, S. T. and Anderson, T. A. 2004, *Environ. Pollut.*, 132, 121.
49. Dean, K. E., Palacheck, R. M., Noel, J. M., Warbritton, R., Aufderheide, J. and Wireman, J. 2004, *Environ. Toxicol. Chem.*, 23, 1441.

50. Kirk, A. B., Smith, E. E., Tian, K., Anderson, T. A. and Dasgupta, P. K. 2003, *Environ. Sci. Tech.*, 37, 4979.
51. Cheng, Q., Perlmutter, L., Smith, P. N., McMurry, S. T., Jackson, W. A. and Anderson, T. A. 2004, *J. Ag. Food Chem.*, 52, 3456.
52. Dodds, E. D., Kennish, J. M., von Hippel, F. A., Bernhardt, R. and Hines, M. E. 2004, *Anal. Bioanal. Chem.*, 379, 881.
53. U.S. EPA 1998, Announcement of the Drinking Water Contaminant Candidate List, (http://www.epa.gov/OGWDW/ccl/ccl_fr.html).
54. Fan, A.M., Howd, R., Ting, D. 2004, Public Health Goal for Perchlorate in Drinking Water, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, (<http://www.oehha.ca.gov/water/phg/index.html>)
55. Bacchus, S. T., Susarla, S., Wolfe, L., Harvey, G. and McCutcheon, S. C. 1999, In: Urbansky, E.T. and Schock, M.R. (Editors) Perchlorate in the Environment, Symposia Papers Presented Before the Division of Environmental Chemistry, American Chemical Society, New Orleans, August 1999, Page 98.
56. Nzengung, V. A., Wang, C. and Harvey, G. 1999, *Environ. Sci. Tech.*, 33, 1470.
57. Nzengung, V. A., Penning, H. and O'Neill, W. 2004, *Int. J. Phytoremediation*, 6, 63.
58. Urbansky, E. T. and Schock, M.R. 1999, *Environ. Management*, 56, 79.
59. Logan, B. E. 2001, *Environ. Sci. Tech.*, 35, 482A.
60. Moore, A. M., DeLeon, C. H. and Young, T. M. 2003, *Environ. Sci. Tech.*, 37, 3189.
61. Jackson, A. W., Anderson, T. A. and Pardue, J. H. 2004, *Biorem. J.*, 8, 65.
62. Gingras, T. M. and Batista, J. R. 2002, *J. Environ. Monit.*, 4, 96.
63. Xu, J., Song, Y., Min, B., Steinberg, L. and Logan, B. 2003, *Environ. Eng. Sci.*, 20, 405.
64. Coates, J. D. and Achenbach, L. A. 2004, *Nat. Rev. Microbiol.*, 2, 569.
65. Okeke, B. C., Giblin, T. and Frankenberger, W. T., Jr. 2002, *Environ. Pollut.*, 118, 357.
66. Cang, Y., Roberts, D. J. and Clifford, D. A. 2004, *Water Res.*, 38, 3322.
67. Yang, R. S. H. 1994, *Toxicology of chemical mixtures*, Academic Press, New York.