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Perchlorate: Not Only Rocket Science

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It's Not Only Rocket Science

The perchlorate story follows the arc of other major controversial chemical management challenges, such as dioxin, where the initial focus on end-of-pipe controls missed key sources in the environment

By Andrew Rak



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The ongoing debate over the potential health effects from exposure to low levels of perchlorate is overshadowing an equally important dialogue on the sources of contamination. Perchlorate first became a headline concern when it was discovered that it entered the environment from rocket fuel and munitions at Department of Defense sites — seemingly just another legacy of the Cold War — but it can also be found in fertilizer, bleach, fireworks, road flares, and blasting compounds. It can be present as an ingredient or impurity in lubricating oils, matches, and automotive airbag deployment initiators. It is associated with aluminum, rubber, dye, and paint manufacturing, leather tanning, and pulp processing. Solutions used in water and wastewater treatment plants for disinfection have also been identified as a potential problem.

While some research has addressed the relative importance of multiple sources, the perception that military activities are the overwhelming contributor to the environment may be hindering appropriate and effective regulation. While perfect knowledge about the sources of perchlorate is unobtainable, continuing to focus solely on a few point sources will not adequately spur effective public health regulation.

Extensive toxicological studies have been undertaken related to the potential health risks from exposure to perchlorate, including a National Research Council review of the Environmental Protection Agency's toxicity assessment. The chemical may pose a health risk if taken up by the thyroid, where it disrupts the production of hormones and affects metabolism and neurodevelopment. But toxicity is only part of a risk-based approach to public health. As the NRC famously declared in 1983 in the Red Book — more properly "Risk Assessment in the Federal Government: Managing the Process" — only by combining toxicity data with information about the sources of exposure to a contaminant can a thorough risk-based approach be constructed. In other words, the same scientific rigor and expertise applied to the investigation of a chemical's toxicity should be applied to the identification of sources that lead to significant exposures.

A thorough examination of the sources of exposure to perchlorate has not been completed, and this lack of knowledge hinders attempts by regulatory agencies to provide an effective risk-based approach for protecting public health. Through an

understanding of sources in the environment and releases to the environment, regulatory agencies can take appropriate steps to directly reduce exposure and control public health risk.

While defense activities have often been assumed to be the dominant fraction of perchlorate's environmental presence, military contributions alone cannot be the explanation for the geographically dispersed detection of the compound. Nor can military sources be responsible for the perchlorate detected in a wide variety of food stuffs, including dairy items and produce. Sampling of dairy products from Maryland and organic lettuce from Wisconsin have found trace amounts of perchlorate; however, any direct connection to military point sources at these locations is lacking, thereby suggesting the importance of other contributors.

Early impressions about perchlorate sources helped federal and state regulators develop preliminary plans for addressing contamination. However, more complete evaluations may increase the focus on newly identified sources. In a 2005 letter to the federal Environmental Protection Agency, state regulatory officials wrote that "none of the nine water supplies that have tested positive for perchlorate in Massachusetts appear to have any connection to military bases or activities." The use of perchlorate-containing explosives in construction activities, and even in bleach, were among the new sources identified by the state. Earlier this year, Maine Drilling and Blasting agreed to contribute \$1 million to the city of Westford, Massachusetts, for remediating perchlorate associated with construction explosives. Grappling with the risk from other sources is just a matter of time.

The advent of new scientific fingerprinting methods that distinguish natural from man-made sources will allow regulatory managers to tackle this multi-faceted source challenge with targeted risk reduction measures. As new sources are identified and quantified, lingering misperceptions about the

role of point and non-point sources of perchlorate should be displaced.

The perchlorate story follows the arc of other major controversial chemical management challenges, such as dioxin, where the initial focus on end-of-pipe controls from incinerators and chlorine, and pesticide production proved to miss key sources in the environment. During the multi-decade interagency and public debate over the appropriate



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health risk estimates for dioxin, EPA issued a pivotal emissions report. In 2000, the emissions inventory analysis for dioxin found that backyard burning of plastics and other waste in rural areas was a major remaining non-point source of deposition to soil. This surprising finding shifted the regulatory debate and highlighted areas where the traditional focus on point sources and end-of-pipe enforcement approaches could not be applied. Any new reduction strategy for dioxin emissions would likely have to include multiple non-point sources in order to be effective. The

same dynamic appears to be developing for perchlorate.

While early data helped regulatory agencies focus on perchlorate as an emerging problem, to holistically address its risks a more comprehensive assessment of the sources contributing to environmental exposures is necessary. With improved sampling technology and the additional data that are being generated relating to dietary and other exposure routes, food safety regulators, environmental agencies, and local governments will be able to more effectively regulate the use, disposal, and cleanup of perchlorate, and reduce public exposure. Information on unusual suspects will increase the government's grasp of the problem and enhance risk mitigation as our understanding advances.

At the federal level, EPA has elected to address

exposure to perchlorate in groundwater and drinking water using authorities under Superfund and the Safe Drinking Water Act. Although the agency has yet to make a final regulatory determination for perchlorate in drinking water, some state regulatory agencies have already promulgated regulations, with California and Massachusetts setting enforceable limits of 6 parts per billion and 2 parts per billion, respectively. However, it is not clear if these regulations will result in a meaningful public health benefit because we do not know what role drinking water plays in overall exposure to perchlorate. Addressing the need for appropriate regulation requires a more complete understanding of the sources (and relative amounts) of synthetic and natural perchlorate in the environment.

While EPA has elected to address perchlorate in groundwater and drinking water, other regulatory agencies and researchers have paid attention to potentially more widespread exposures in the diet. Ongoing food monitoring surveys have found perchlorate in mothers' milk and cows' milk, as well as in infant-formula. Perchlorate has also been found in lettuce, spinach, cantaloupe, cabbages, and beets. The Food and Drug Administration has completed studies of the occurrence of perchlorate in food items, but has yet to issue any health advisories. Likewise the Department of Agriculture conducts monitoring through its National Residue Program. But an analysis of the relative sources of perchlorate and how these sources may influence entry into the food chain has not been conducted. In the future, the NRP may generate key opportunities for risk reductions should trends related to perchlorate in food warrant mitigation.

A continued focus on military sources will not provide a complete analysis of the sources of perchlorate. The defense establishment uses perchlorate in numerous items as an oxidizer. While the military continues to purchase large amounts of perchlorate for solid rocket motors and other items (6.2–8.1 million pounds per year from 2004–2006), solid perchlorate inside a rocket motor casing is unavailable for release to the environment. Industrial recycling of rocket motors, which previously released wash water into the environment, is now a closed loop system. Annual military training uses of perchlorate in detonators, initiators, and ground burst simulators, which are confined to certain ranges, is approximately 1.6 million pounds, and substitutes are now being employed for some of these uses. As a result of remediation activities, substitution efforts, best management practices, and compliance with Clean Water Act permits, defense-related releases of perchlorate should be diminishing.

In California, one of the states thought to be most contaminated with perchlorate, the military collaborated with state officials to investigate reports of widespread contamination. In 2003, the Defense Department and state regulators established a partnership to investigate the presence of perchlorate throughout California to locate previously unidentified threats to public water supplies. More than 900 military sites were screened using a consensus-based protocol; 870 of these sites were deemed to be not of concern. State regulators agreed that military installations and formerly used defense sites did not appear to be significantly impacting California public drinking water wells. As a result of the collaboration, California also adopted many of the department's best management practices for perchlorate.

The department began an extensive perchlorate monitoring program and, by 2008, had collected more than 47,500 samples at 309 locations nationwide to define the scope of its perchlorate contamination problem. The results of this monitoring program — posted and annually updated on the Defense Environmental Network Information Exchange website — show that the vast majority of perchlorate samples from military locations were below 4 parts per billion, and large groundwater plumes of perchlorate exist at only a limited number of military sites.

While the military appears to be defining and controlling many of its potential sources of perchlorate, it is unclear what controls are being put in place elsewhere. Recent research announced in the Fourth National Report on Human Exposure to Environmental Chemicals by the Centers for Disease Control and Prevention together with a number of academic findings suggest that exposure to perchlorate is widespread, indicating there may be many undocumented sources. These sources should be thoroughly evaluated in order to better understand total human exposure.

The contribution of perchlorate from the use of sodium hypochlorite for various household, drinking water, and commercial disinfection purposes may be an important non-point source contributor to total perchlorate exposure. Sodium hypochlorite, a bleach, generates perchlorate in storage and when it is exposed to sunlight. The compound is used in a variety of household applications (household bleach is a 3–6 percent solution) and industrial applications (water and waste water disinfection solutions are 12–15 percent solutions) related to disin-

Perchlorate Will Accumulate

fection. Nearly \$3 billion of sodium hypochlorite bleach is sold globally each year. In a 2008 study, perchlorate contamination was found to occur in more than 90 percent of sodium hypochlorite samples.

The most recent part of the perchlorate source picture to come to light is the volume of the compound entering the United States in fireworks. Recent data from the Department of Commerce indicate a large increase in firework imports over a five-year span, from 174.7 million pounds in 2002 to 271.2 million pounds in 2006. Potassium perchlorate constitutes up to 70 percent of the chemical fraction in fireworks. Based on these data, the American Pyrotechnics Association estimates that 14.2 million pounds of perchlorate entered the country in fireworks in 2002, and 21.8 million pounds in 2006. Imports represent about 90 percent of fireworks used in the United States. For 2006, the amount of perchlorate imported in fireworks represents nearly three times the amount purchased by the military. While importation does not necessarily equate with amounts released into the environment, these data highlight an important potential non-point source.

Recent field studies also support focusing on perchlorate discharges from fireworks. EPA analyzed water in an Oklahoma lake before and after fireworks displays. Testing performed 14 hours after an event showed that perchlorate levels rose 24 to 1,028 times above the pre-display baseline. The agency found that concentrations of perchlorate peak about 24 hours after a display and then decrease to the baseline within 20 to 80 days. Thus, Fourth of July activities and sporting events may be important in future efforts to define sources and routes of exposure. Efforts to restrict and manage releases at the local level may be able to control exposure.

The millions of emergency road

In 2008 NASA's Phoenix Lander found perchlorate in three different Martian soil samples. That discovery prompted a re-analysis of the soil samples we had brought back from an expedition a year earlier to Antarctica's Dry Valleys, a site used as a Mars analogue for training because of the subzero temperatures and extreme aridity. For both Earth and Mars, the evidence implies that given the right conditions and a source of chlorine, perchlorate will accumulate.

Free of anthropogenic influences, the Dry Valleys provide an ideal location for such studies. The Antarctic soil samples had been collected from pits dug in three types of Dry Valley microclimate zones: coastal (wet), inland (arid), and highland (hyperarid). Samples were collected from every identifiable soil horizon (boundaries between different kinds of soil) down to the ice-cemented soil. All the samples were reanalyzed for perchlorate.

To our amazement, perchlorate was found in all the highland soils, in all the horizons from the surface to the ice-cemented soil. Its concentration ranged up to 630 parts per billion and in a continuous vertical profile. In contrast, for the inland valley soil horizons, it was found to vary with a more heterogeneous distribution, while in the coastal valleys it appeared very randomly distributed, approaching 1,100 ppb in one isolated soil horizon, and totally absent in others, with no regular or discernible pattern.

How the perchlorate is deposited in these valley soils is clearly evident from its correlation to nitrate and chloride, both of which have been shown to be atmospherically formed and deposited. Thus, the

best explanation for its changing distribution in the soil when moving from the upper to lower valleys is the difference in the amount of liquid water present and its effect, leading to depletion or concentration of the perchlorate. In the highlands the atmospheric deposition of perchlorate is left undisturbed, while in the lower wet valleys its distribution becomes chaotic.

Combining our findings with those for the Arctic, North America, and other regions provides an emerging picture for the global presence of natural perchlorate. In addition, our results from Antarctica clearly point to the conclusion that even though natural perchlorate is atmospherically and homogeneously deposited, over time it will accumulate at high levels at some locations while it will be non-existent at others.

Our results support the hypothesis that perchlorate must also have a variety of long-term, widely, and irregularly distributed sinks. Since aqueous perchlorate is chemically stable in the natural environment, its lack of accumulation in the ocean or aquifers may also be attributable to microbial utilization in anaerobic or low nitrate media.

To help us understand the full impact of perchlorate, we need to more accurately determine its global distribution and accumulation patterns, its interactions with terrestrial ecology, and its atmospheric formation mechanisms.

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flares sold annually contain significant concentrations of perchlorate, which is often released into the environment. A study in Santa Clara, California, found that 88,184 pounds of road flares are used in the county annually with a corresponding perchlorate content of 5,732 pounds. Field testing has shown maximum concentrations of perchlorate in runoff leaving highways of 314,000 parts per billion after road flare use. Considering the volume nationwide, discarded or partially used emergency flares may be another important non-point source of exposure. Communities could take steps to consider the use of alternative safety-lighting systems such as those adopted by Seattle and other local police organizations to reduce the contribution from flares.

Natural sources of perchlorate from geological materials, such as potash ore, playa crust, and hanksite, also contribute to environmental perchlorate. Natural deposits have been found in the Texas panhandle and north-central New Mexico. Other research suggests that perchlorate may be produced via atmospheric processes, then enters the food chain through rainfall. Atmospheric formation may explain the discovery of perchlorate in soil and ice from the Antarctic [See ANOTHER VIEW, page 41] where concentrations reach up to 1100 micrograms per kilogram. Finally, there is a possible connection between tropospheric ozone and the formation of perchlorate in plants, a factor that could in part explain the presence of perchlorate in agricultural products.

One source of perchlorate in the environment that is receiving some additional attention is the over 100 million pounds of Chilean nitrate fertilizer — which contains perchlorate at levels of 100,000 parts per billion — that have been applied in the United States. There are over 400,000 pounds still being applied annually to commercial agricultural land and homeowner gardens. In 2006, Texas Tech University scientists reported in the journal *Environmental Science & Technology* that perchlorate-containing Chilean nitrate fertilizer likely accounts for more low-level contamination in the United States than all military and industrial sources put together.

Perhaps the most important development driving the understanding of sources of perchlorate in the environment is new forensic fingerprinting technology that can help differentiate man-made and natural types of perchlorate. Isotopic methods are powerful tools when applied to the intractable problems of

source attribution for groundwater contaminants. Elements in compounds can have widely different isotopic ratios based on their mode of formation. Stable ratios have a fingerprint, allowing scientists to distinguish sources from one another. The isotopic method for perchlorate is available for use through some university and Department of Energy laboratories. Scientific validation of the new method is underway.

The new clarity made available through forensic inquiries into sources may provide a much better understanding about the proportion of contributions of perchlorate in the environment from commercial, consumer, agricultural, and military sources. Forensic methods distinguished synthetic from natural sources of perchlorate at contaminated sites in southern California and elsewhere, and proved helpful in disentangling possible sources. A 2009 study by the U.S. Geological Survey used forensic isotopic methods to identify historic use of fertilizer as the most likely cause of groundwater contamination in areas of Long Island and concludes that these findings may have national implications.

The growing concern over the possible health effects of exposure to low levels of perchlorate should not overshadow the investigation of perchlorate sources. There appears to be a growing body of evidence that perchlorate sources should be reappraised, particularly in light of findings that perchlorate in fireworks, bleach, safety flares, and Chilean fertilizer may outweigh military-industrial uses. The new data on sources in the environment and releases to the environment should be used to better inform regulatory decisions on controlling exposure. More importantly, the application of fingerprinting methods that distinguish natural from man-made sources will empower regulatory managers to tackle this multi-faceted source challenge with tailored risk reduction measures. As consumer, natural, military, and agricultural sources continue to be identified and quantified, misperceptions about the role of point and non-point sources should be displaced.

While early data allowed regulatory agencies to focus initially on perchlorate as an emerging problem, to holistically address the risks from exposure a more comprehensive assessment of sources is necessary. More information about the unusual suspects among perchlorate sources will enhance risk mitigation and protect public health. With improved sampling technology, food safety regulators, environmental agencies, and local governments will be able to control the use, disposal, and cleanup of perchlorate to reduce public exposure. •