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Environmental Bulletin

Emerging Chemical Concerns — Perchlorate

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Emergence of "New" Contaminants Raises Many Issues

by Rebecca L. Raftery

In this bulletin regarding emerging chemical concerns, we are discussing issues associated with perchlorate, a groundwater contaminant causing significant consternation among both the regulated community and the regulators. One of the more confounding environmental issues to emerge in the last several years is the emergence of "new" contaminants, particularly at sites already undergoing remediation or that in some cases have been completely remediated. Some of these contaminants were previously believed to pose little threat to human health and the environment, while others could not be detected in low concentrations. For environmental professionals, these issues pose troubling questions about the quality of past remediation, the use of risk analysis to judge whether and to what extent a site requires remediation, and how to determine when a site has truly been addressed.

Perchlorate is a classic example of such a contaminant. Ammonium perchlorate is a principal component of solid rocket and missile fuel and perchlorate salts like potassium perchlorate are widely used in pyrotechnics, road flares, explosives and ordnance. Perchlorate came into widespread use in the U.S. during the Second World War and continues to be widely used.

For decades, perchlorate was not considered to be a significant risk to human health or the environment, so its discharge was not restricted, and perchlorate containing materials were often rinsed into soils or settling ponds. Moreover, analytical tests could not readily detect perchlorate at concentration below 400 parts per billion ("ppb"), a relatively high amount. However, more recent research has raised health concerns by suggesting perchlorate may have a detrimental impact on thyroid function. In addition, new testing methodology now allows the detection of perchlorate at much lower levels, although there are questions regarding appropriate methods and reliability. A detailed discussion of some critical technical concerns is found in Dr. Tamara Sorrell's article, below.

Perchlorate is highly soluble and mobile in groundwater; plumes can extend in excess of ten miles. With the new detection limits, hundreds of water suppliers throughout the United States, but particularly in the West, realized that drinking water supplies contained previously undetected perchlorate. In California alone, perchlorate has been detected in over 300 water sources. Perchlorate contamination has become a top environmental priority for the state and its Regional Water Quality Control Boards. Indeed, the California Senate has empanelled a "select committee on perchlorate contamination."

But addressing perchlorate contamination is confounding on many levels. First, as discussed in Steve Siros' article below, there is no federal drinking water standard (MCL) for perchlorate, and there is a continuing dialogue over the development of a standard. EPA has suggested a standard in the 1 ppb range, but that has been sharply challenged by other interested parties who argue that there is no scientific basis for a standard that low. The National Academy of Sciences is currently reviewing the potential health risks and hopes to have a report available by the end of 2004; however, there will still need to be a rulemaking process after the report is issued.

Meanwhile, as the article below points out, the states are also grappling with this issue. The California legislature mandated that a state standard be established by January 1, 2004, but the state has been unable to do so, and the latest reports suggest that a standard may be more than a year away.

In addition to concerns over perchlorate in groundwater, perchlorate may also present an issue in surface water used for irrigation water. For example, Colorado River water has had measured perchlorate contamination averaging in the 7 ppb range, and there

BREAKING NEWS

On Friday, March 12, in a move that displeased industry and environmentalists alike, the state of California set a public health goal for perchlorate in drinking water of six parts per billion. This goal will form the basis of an enforceable drinking water standard. Industry and defense groups had argued California should wait for the results of National Academy of Science review before setting a standard, while environmental groups were advocating a goal of one part per billion. The public health goal, and any subsequent regulations, will very likely be the subject of legal challenges by the interested parties.

is growing concern that perchlorate may impact lettuce and other vegetables irrigated with surface water.

In addition, treatment technology for perchlorate contamination is still in the early stages. Traditional pump and treat technology, often used to contain and remediate VOC plumes, is ineffective for perchlorate. Various filtering and other technologies are still under development, but the usual treatment is to filter at the impacted well head.

Water suppliers, regulators, and current and former perchlorate users are left with a dilemma. In the absence of an accepted standard for perchlorate, should a supplier take all contaminated wells out of service, no matter how minimal the impact? Should the water be blended so non-detect levels are reached? What action can regulators take when the substance has no standard? And should the regulated community take proactive action or wait for clearer guidance?

In any event, the presence of perchlorate in a water supply is virtually certain to drive up costs for the suppliers, and prices to their customers. That, in turn, is likely to lead to claims against those who used or manufactured perchlorate. Although the question of what level of perchlorate is truly safe is not likely to be answered quickly, the issue of who should pay for perchlorate contamination will undoubtedly be contested, if not resolved, much sooner.

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Counseling Point

Environmental claims often involve activities engaged in by companies decades ago. In the case of perchlorate contamination, the focus can be on activity from as long ago as the 1940s or 1950s. Companies faced with such claims should immediately consider whether there might be insurance coverage available from older policies.

Although searching out old policies can be arduous, especially where corporate entities may have been bought, sold, merged or changed structures, the search also has the potential to lead to recovery of significant amounts for the company. It is critical that once a company becomes aware of a claim, that it:

- search out and preserve policies;
- provide prompt notice to all insurers;
- continue to provide information to insurers regularly and at important points; and
- seek defense costs and indemnification to the maximum extent possible under the policy.

Perchlorate: Analytical Detection Issues to Meet the Needs of Risk Management

by Tamara L. Sorell, PhD

Background

Within the past several years, perchlorate has emerged as a contaminant of increasing concern. Pursuant to the discovery in the late 1990s of perchlorate in groundwater and drinking water in a number of states, drinking water wells have been closed, and there has been growing regulatory scrutiny. The Department of Defense now requires that perchlorate be considered in environmental restoration projects and, in 1998, the United States Environmental Protection (USEPA) released for external review a draft of an extensive toxicological review that will serve as the basis for environmental regulation. An update of this draft was released in 2002 and is still undergoing public and peer review.

Perchlorate is an anion (ClO_4^-), a negatively charged molecular fragment that binds with positively charged cations to create salts (such as the chlorine in sodium chloride). A major source of perchlorate to the environment is the release of ammonium perchlorate, a primary component of propellants for rocket fuel. Concern has been raised about food contamination in the wake of findings that perchlorate accumulates in vegetables that have been irrigated with perchlorate-contaminated water.

A variety of studies have evaluated the toxicity of perchlorate in mammals. The toxicity endpoint in humans that serves as the basis for regulation is disruption of thyroid gland function. Although the USEPA has not established safe levels in food and water, based on existing information, the provisional drinking water equivalent level (DWEL) is 418 parts per billion (ppb). USEPA Regions 6 and 9 used risk-based screening levels of 3.7 and 3.6 ppb, respectively, and the California Department of Health Services (DHS) has proposed a public health goal (PHG) of 26 ppb. Therefore, it is certain that analytical laboratory methods are going to be needed that will accurately quantify perchlorate levels in soil, groundwater, and other media in the low-ppb range.

Analytical Issues

In 1999, the USEPA placed perchlorate on the unregulated contaminant monitoring rule (UCMR) list and the following year promulgated a laboratory approval and performance testing (PT) program that specified the use of Method 314.0 ("Determination of Perchlorate in Drinking Water Using Ion Chromatography"). The ion chromatography (IC) method was selected from among several possible analytical approaches that can be used for perchlorate, including gravimetry, spectrophotometry, electrochemistry, capillary electrophoresis, and mass spectrometry. The California DHS also specifies use of the IC method.

The principal advantages of ion chromatography are ease of use, selectivity for perchlorate, equipment availability in commercial laboratories, and low detection limits compared with other methods. Method 314.0 lists a method detection limit (MDL) of 0.53 µg/l (ppb) in clean laboratory water. However, the minimum reporting limit (MRL), which is the concentration that can be reliably quantitated, is in the range of 4 µg/l (the MRL is established at or above the lowest calibration standard; it is sometimes also referred to as the practical quantitation limit, or PQL). A variety of interferences exist that can confound detection, including other common anions (chloride, sulfate, carbonate), and particulates, creating false positives. Any dilution of the samples will further increase the reporting limit, with the potential for false negatives. Therefore, low-µg/l concentrations may not always be reliably quantified.

A modification proposed to address some of these concerns is the use of IC coupled with liquid chromatography and two mass spectrometers (LC/MS/MS). The estimated MRL using this approach is 0.2 µg/l, which would allow detections at levels below current criteria and below all currently proposed regulatory action levels. False positives are virtually eliminated by use of this method, and even if initial analytical costs are higher, eliminating false positives can be cost-effective in the long run. Whether regulators adopt this methodology remains to be seen.

EPA Method 314.0 is used only for drinking water. For other environmental media, the regulated community must look to alternate approaches. In addition to the standard environmental matrices (soil, sediment, surface water), media that may require analysis include agricultural runoff, plant and animal tissues, and foods (especially irrigated produce). Increasing complexity in the matrices to be analyzed creates additional challenges in accurate and sensitive quantitation. Field methods, such as *in situ* groundwater monitoring, with detection limits in the 23 µg/l range, are also under development.

Management Strategies

In view of the recognized analytical limitations, it is critical for parties with potential perchlorate liability to exercise caution and selection in site investigation methods. As concern over perchlorate grows, attention to the use of the appropriate investigative technologies will help to control costs and manage liabilities.

As concern over perchlorate grows, attention to the use of the appropriate investigative technologies will help to control costs and manage liabilities.

Consider all of the following:

The current regulatory situation: What is the acceptable limit that will be applied to the site? This will determine the reporting limit that then must be attained. Which methods will generate data that will be approved and be valid in the event of any litigation?

The future regulatory situation: Is the acceptable limit likely to drop in the future as new information and increasingly sensitive detection methods become available?

The media of interest: For media other than water, approved methods have not yet been published. Modifications or alternates to Method 314.0 are necessary.

Interferences: The presence of other contaminants can increase the potential for false positives.

Cost: Will the use of more expensive methods that increase sensitivity or decrease error be cost-effective in the long run?

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Regulatory Status Update: Perchlorate Summary of Federal and State Regulations

by Steven M. Siros

Although used for decades in the manufacture of solid rocket fuels, propellants and other explosive products, perchlorate has just recently begun to receive serious attention from federal and state regulators. This attention will likely increase in 2004 and beyond as federal and state agencies begin to focus on developing and implementing regulatory standards for perchlorate in soil and groundwater. However, as discussed below, there is no consistent state or federal standard for perchlorate in soil and groundwater. Because of the absence of a consistent state or federal standard, there is substantial uncertainty concerning the appropriate cleanup levels at perchlorate-contaminated sites. A brief overview of the current status of federal and state efforts to develop perchlorate standards follows.

Federal Regulation of Perchlorate

There are currently no federal regulatory standards which set acceptable concentration levels for perchlorate in soil or groundwater. However, this will likely change in the near future. Although perchlorate has been in common use since the mid-1940s, it was only in the early 1990s, following the discovery of high levels of perchlorate in drinking water wells in California, that the federal government began to focus on perchlorate from a regulatory standpoint. In 1992, the United States Environmental Protection Agency ("USEPA") set a provisional reference dose ("RfD") [1] for perchlorate of .0001 mg/kg-day, which corresponded to a groundwater cleanup standard of 4 parts per billion ("ppb"). The provisional RfD was deemed to be the best estimate of a "safe" level for perchlorate in the groundwater, and constituted the first step that USEPA needs to take in order to develop a primary drinking water standard ("MCL") under the authority of the Safe Drinking Water Act. In 1995, USEPA revised its provisional perchlorate RfD to provide for a range from .0001 to .0005 mg/kg/day, which corresponded to a groundwater cleanup level of between 4 to 18 ppb.

In March 1998, in response to subsequent information relating to the health impacts of perchlorate, USEPA proceeded to add perchlorate to its Contaminant Candidate List ("CCL"). The CCL is divided into two categories, with the first category being contaminants for which sufficient information existed for USEPA to begin making regulatory determinations in 2001, and the second category being contaminants for which additional research was required before a regulatory determination could be made. Perchlorate was added to the latter category, and therefore, USEPA recognized that additional research into the health impacts of perchlorate was needed before a regulatory determination could be made.

As a result of perchlorate's listing on the CCL, in March 1999, USEPA added perchlorate to the Unregulated Contaminant Rule ("UCMR"). This testing obligated large public water supply systems and a representative sample of small public water supply systems to monitor for perchlorate in drinking water beginning in January 2001.

In 1999, USEPA's Office of Research and Development issued an Interim Assessment Guidance for Perchlorate (the "1999 Interim Guidance") which recommended the use of USEPA's provisional RfD range of 0.0001 to 0.0005 mg/kg-day, which corresponded to a corresponding preliminary remediation goal ("PRG") of 4-18 ppb for perchlorate in groundwater. The PRG applied to remedial activities being performed under USEPA oversight, and was intended to be utilized by USEPA risk assessors and risk managers to assist in the evaluation of health risks at perchlorate-contaminated sites. The PRG set forth in the 1999 Interim Guidance did not constitute a legally-binding requirement, standard or procedure, but rather, was to be used as a departure point for risk characterization, in the absence of site specific risk assessments or applicable promulgated state standards.

> There are currently no federal regulatory standards which set acceptable levels for perchlorate in soil or groundwater. However, this will likely change in the near future.

The 1999 Interim Guidance was reaffirmed by USEPA in January 2003, when USEPA issued another memorandum (the "2003 Memorandum") to its risk assessors and risk managers which stated that in the continued absence of a final regulatory standard, the provisional RfD should continue to be used. However, the 2003 Memorandum went on to note that where the groundwater was not currently used as a source of drinking water, or there was no risk of human exposure to the groundwater, USEPA's risk assessors should consider values at or above the high end of the 4-18 ppb PRG range.

Meanwhile, a year earlier, in January 2002, following a number of studies on perchlorate's impact on human health and the environment, USEPA issued a draft toxicological report ("Draft Report") that proposed an RfD for perchlorate of .00003 mg/kg-day, which corresponded to a PRG of approximately 1 ppb for drinking water. USEPA noted that the proposed 1 ppb standard was just that, a proposed standard, and that USEPA was issuing the Draft Report so that interested parties could provide comments on the proposed standard.

Not surprisingly, the proposed 1 ppb standard generated numerous comments from regulated entities, including the Department of Defense ("DoD"). As a result of these comments, the National Academy of Science ("NAS") has been asked to review the science supporting USEPA's proposed RfD of 1 ppb. NAS' review is expected to be completed sometime in mid-2004, and a final version of the Draft Report is not expected to be issued by USEPA until sometime in early 2005. Once a final RfD is established, USEPA will then begin to evaluate whether an MCL should be established for perchlorate.

In light of the fact that USEPA's Draft Report is still in the process of being reviewed by the NAS, it appears that the only applicable federal guidance will continue to be USEPA's provisional perchlorate RfD of .0001 to .0005 (4 to 18 ppb), at least for the foreseeable future. In addition to this federal guidance, however, many individual states have implemented their own standards for perchlorate. These standards are discussed below.

State Regulatory Standards for Perchlorate

Although USEPA may still be a few years away from finalizing a perchlorate standard, several states have taken a more proactive approach. Not surprisingly, western states where historic perchlorate usage was more prevalent have taken the lead in this regard.

For example, California's Department of Health Services ("DHS") was under a statutory obligation develop an MCL for perchlorate by January 1, 2004. Although DHS did not meet this January 1, 2004 deadline, it is expected that DHS will promulgate an MCL for perchlorate later this year or early next year. Pending the adoption of an MCL, DHS has been using a 4 ppb advisory action level for perchlorate in drinking water systems. However, in March 2004, California's Office of Environmental Health Hazard Assessment issued a Public Health Goal ("PHG") of 6 ppb, which is expected to be the basis for DHS' establishment of an MCL for perchlorate. Both environmental and industry groups have indicated that they would challenge California's PHG of 6 ppb for percholorate.

Although the DoD submitted comments questioning the science behind USEPA's proposed RfD of .000003 (1 ppb), the DoD had agreed to accept California's 4 ppb advisory action level for remedial actions that are being conducted by DoD in California. Whether DoD will now seek to comply with higher PHG in cleanups occurring in California, as well as in cleanups occurring in other states, remains to be seen.

In addition to California, several other states also have developed perchlorate standards. The following chart provides an overview of various state perchlorate standards.

State	Regulatory Status
Arizona	14 ppb Action Level
California	6 ppb Public Health Goal
Maryland	1 ppb Advisory Action Level
Massachusetts	1 ppb Drinking Water Advice Level (pregnant women and children should not consume drinking water with more than 1 ppb)
New York	18 ppb Action Level
Nevada	18 ppb Recommended Action Level (for groundwater cleanup activities)
Texas	4 ppb Action Level

In the absence of a federal regulatory standard, there is a wide divergence of standards among the various states. In addition, many states have yet to develop perchlorate standards, although as more time passes without a federal standard, these states will likely develop their own perchlorate standards.

Conclusion

In the absence of a consistent regulatory standard, the appropriate or acceptable level of perchlorate in soil and groundwater will continue to be a function of site location, and whether the site is under state or federal jurisdiction. In any event, perchlorate will likely continue to be on regulators' radar screens, and the regulated community should remain cognizant of federal and state efforts to develop and implement standards for perchlorate in soil and groundwater.

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1 *USEPA defines RfD as "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime."*

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