Automated System Measures Flow Direction, Velocity in Wells

The Cold Regions Research and Engineering Laboratory at the U.S. Army Corps of Engineers' Engineer Research and Development Center has developed an automated system to measure in-situ seepage direction and velocity in monitoring wells, as well as water levels. The system was designed to address data needs for contaminant fate and transport analyses. Site-specific, in-situ seepage direction and velocity are critical parameters necessary for modeling contaminant migration, but they cannot be accurately predicted. Site-specific flow data are particularly important at sites where remediation will be accomplished by monitored natural attenuation. Because many sites are remote and lack power, a device that permits unattended operation is essential.

The sensor utilizes a thermal "tag-and-trace" technique to measure flows at velocities ranging from 0.5 to 10 ft/day. Each system consists of a flow sensor, data logger, data storage module, 12-volt battery, and solar panel. The system can take measurements up to four times per day, with data storage capabilities requiring downloading to a computer every three months or longer. Laboratory calibration results in flow sensors with an accuracy of within 0.5 ft/day for seepage and within 5 degrees for direction of flow.

Prototype systems are now installed in more than 100 monitoring wells at Superfund sites in Alaska. Field and lab tests are being used to guide further development and improvement of system operation, reliability, and accuracy.

More information is available at www.crrel.usace.army.mil/erd/ground_water.html.

USGS Study Detects Toxic Rainfall in San Joaquin Valley

The toxic pesticides diazinon and chlorpyrifos were found in all rainfall samples collected by the U.S. Geological Survey (USGS) in the area of Modesto, Calif., during January and February 2001 storms. The concentrations of these two insecticides in the rainfall samples exceeded proposed state guidelines for the protection of aquatic life in most samples, by up to a factor of 10 for diazinon, and up to a factor of 7.4 for chlorpyrifos.

Rainfall samples collected during the no-spray season in Modesto and surrounding agricultural areas also exceeded the state's concentration guidelines by an average factor of 5.7 for diazinon and 3.1 for chlorpyrifos. Simultaneously, storm runoff samples were collected from an urban storm drain where diazinon concentration exceeded the proposed state aquatic life guidelines by an average factor of 9.5. Sixty-eight percent of the diazinon concentration found in the storm drain runoff could be accounted for by the concentration in the rainfall.

Samples were also collected from the San Joaquin, Merced, Stanislaus, and Tuolumne rivers and Orestimba Creek during this study. Forty percent of the 240 samples exceeded the proposed state guideline for diazinon and seven percent exceeded the proposed chlorpyrifos guideline.

The study will continue through 2004 at six sites in the San Joaquin River Basin and two additional sites in the Sacramento River Basin. Complete results of the study are forthcoming. The study was funded by the California Department of Pesticide Regulation. The data provide additional information to the Central Valley Regional Water Quality Control Board for their development of Total Maximum Daily Load regulation for diazinon and chlorpyrifos in the San Joaquin Basin.

The USGS report, "Diazinon and Chlorpyrifos Loads in Precipitation and Urban and Agricultural Storm Runoff During January and February 2001 in the San Joaquin River Basin, California," by C. Zamora, C.R. Kratzer, M. S. Majewski, and D.L. Knifong, is available at water.usgs.gov/pubs/wri/wri034091.

OCWD Part of NSF Water Purification Center

Orange County Water District (OCWD) is part of a new team selected by the National Science Foundation (NSF) to perform water purification research. The team also includes researchers at Stanford University, University of Illinois, and Clark Atlanta University. The research conducted by these institutions will focus on developing advanced materials and systems to increase and improve the world's potable water supplies. The institutions were brought together under the umbrella of the new NSF Center for Advanced Materials for Purification of Water with Systems.

The goal of the center is to bring together top education and research centers around the United States to address pressing problems in water purification. OCWD's Research and Development Department will work together with researchers at Stanford University's Terman School of Engineering and will use its reverse osmosis membrane testing facilities to evaluate the performance of new

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membrane materials. Reverse osmosis membranes are of increasing importance for seawater desalination and water recycling and are commonly used by commercial water companies to make bottled water from tap water.

OCWD will receive $99,000 per year, renewable for five years, to test reverse osmosis membranes for susceptibility to fouling by biological processes, resistance to chemical reactions, and removal of contaminants in drinking water.

This NSF research will help to reduce energy requirements for future reverse osmosis water purification, provide ways to slow the processes that clog membranes, produce membranes that last longer, improve the membranes' effectiveness in removing trace amounts of low molecular weight organic compounds, and develop advanced reverse osmosis membrane materials that may have short-term practical industrial applications. Other benefits could include the development of more efficient membranes that will lower operation and maintenance costs and increase the volume of pure water produced.

OCWD has been using and testing reverse osmosis membranes since the mid-1970s when the technology was first applied to water purification at its Water Factory 21 advanced treatment plant in Fountain Valley, Calif. A new, improved generation of reverse osmosis membranes will be used in the Groundwater Replenishment System, OCWD's new wastewater purification plant, which will begin production in 2007 and be the largest of its kind in the nation.

Visit www.OCWD.com

Perchlorate: 20th Century Contaminant–21st Century Solutions

William E. Motzer, Ph.D., R.G., *Senior Geochemist and* **Phyllis Stanin, R.G., CEG, CHG,** *Vice President – Todd Engineers*

Over the past decade, a very simple molecule has attracted considerable scrutiny by the public, the environmental community, and federal and state regulators. This molecule, known as perchlorate (ClO_4^-), is a negatively charged ion, or anion, containing a central chlorine atom, surrounded by four oxygen atoms. The perchlorate anion is produced when highly soluble solid salts of ammonium, potassium, and sodium perchlorate, and perchloric acid dissolve in water.

Perchlorate Characteristics

Most perchlorate salts have high water solubilities (ranging from 217,000 ppm to 220,000 ppm for ammonium perchlorate, for example), and concentrated solutions have densities greater than water. Therefore, a concentrated solution may sink through the groundwater column, similar to the behavior of concentrated chlorinated solvents, which are also denser than water. Once dissolved, the perchlorate anion is extremely mobile and very stable, requiring decades to naturally degrade.

Space Shuttle Endeavor lifts off from the Kennedy Space Center, June 5, 2002. The large clouds produced upon launch result from the "burning" of approximately 385 tons of the oxidizer, ammonium perchlorate, in each of the two solid rocket boosters. Photo by NASA.

Perchlorate anion movement in groundwater through porous, unconsolidated sandy and silty alluvium is relatively unretarded and will travel at groundwater flow rates, a process known as advection.

Since the late 1950s, ammonium perchlorate has been used in solid rocket engines, where it is the oxidizer for the fuel. Perchlorate salts are also used in munitions, fireworks, road flares, air bags, and electroplating, and naturally occurring sodium perchlorate has been found in imported Chilean nitrate fertilizer. Because most perchlorate salts have limited shelf lives, they require periodic replacement, particularly in solid rocket fuel. In the past, such replacement was done by high pressure steam washing of the rocket casings. Discharged wastewater containing dissolved perchlorate was often washed into unlined waste pits and ponds, where it percolated downward to the local groundwater.

Contaminant Locations

Before 1997, perchlorate could not be readily detected in groundwater at concentrations below about 100 parts per billion (ppb). At that time, the California Department of Health Services developed a U.S. Environmental Protection Agency (EPA)-accepted ion chromatographyanalytical method, which had detection limits of about 4 ppb. As a result, groundwater perchlorate plumes began to be detected in California and several other western states, particularly in areas downgradient from solid rocket engine manufacturing and testing facilities, defense munitions plants, and military bases. As of April 2003, the EPA listed 95 separate locations in 25 different states with known perchlorate soil and groundwater contamination.

As of July 2003, California reported 32 confirmed contaminant sites were regulated by the State Water Resources Control Board or the Department of Toxic Substances Control. In Southern California, extensive perchlorate plumes have been found in the Rialto-Colton area, the San Gabriel Valley, and at the Stringfellow Superfund site in Glen Avon. In Arizona, perchlorate has been detected in groundwater at the Atlantic Research plant in East Camden, at Apache Nitrogen products in Benson, and at the Phoenix Goodyear Airport in Goodyear. Perchlorate-contaminated groundwater occurs in New Mexico at the White Sands Missile Range, at Los Alamos National Laboratory, and at the Fort Wingate Depot in Gallup.

Surface water contamination by perchlorates also occurs in the Southwest, particularly in Lake Mead and in the Colorado River. This contamination was traced back to a seep in Las Vegas Wash; it was caused by contamination from a nearby perchlorate manufacturing facility at Henderson, Nevada, where a large explosion occurred in 1988. In the winter of 2000, perchlorate concentrations at the drinking water intakes of Lake Mead averaged 24 ppb.

Potential Heath Effects

Health effects from ingesting water contaminated with low dosages of perchlorate are not well known, but at relatively high doses perchlorate interferes with the body's iodine intake, inhibiting human thyroid production. In the past, perchlorate salts were used to treat Graves' disease, a condition in which an individual's thyroid produces too much thyroxin. Perchlorate-contaminated irrigation water may also be absorbed by leafy vegetables such as lettuce. Recent findings by the EPA and the Environmental Working Group suggest that lettuce grown in Southern California and Arizona may be absorbing perchlorate from Colorado River-derived irrigation water. Controlled scientific studies have not been performed and the toxicological effects of ingesting perchlorate-contaminated vegetables are not known. Such potential health effects worry federal and state regulators, because perchlorate may affect the undeveloped thyroid of fetuses and children.

Regulatory Actions

Because of these concerns, at least eight states have established some actionable drinking water levels for perchlorate. California instituted a draft public health goal of between 2 and 6 ppb and an action level of 4 ppb. A recently enacted state law requires

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California to establish a maximum contaminant level (MCL) by Jan. 1, 2004, but this MCL may be challenged in the courts. Nevada established a public notice standard of 18 ppb, New Mexico has an interim groundwater screening level of 1 ppb, Arizona has an action level of 14 ppb, and Texas has a drinking water action level of 4 ppb. Establishment of a perchlorate MCL by the EPA is not anticipated for several years.

Remediation

Pilot programs are currently underway at many sites for remediating perchlorate-contaminated groundwater; these include ion exchange technologies, which tend to be expensive, and fluidized bed reactors that employ biological techniques. However, contaminated surface and groundwater treatment may require newer bio- and/or phyto-remediation technologies.

Environmental Forensics

Because perchlorate moves at groundwater flow rates, it has been used as a tracer for hydrocarbon and metal contaminants that are significantly more retarded. However, methods for determining perchlorate sources have been lacking. New forensic techniques are being developed, including defining the anion's chlorine and oxygen isotope ratios to fingerprint perchlorate plumes and potentially trace them back to their original source.

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Additional Information

California Department of Health Services, 2003, Perchlorate in California Drinking Water: Status of Regulations and Monitoring Results, www.dhs.ca.gov/ps/ddwem/chemicals/perchl/perchlindex.htm.

Environmental Working Group (EWG), 2003, Suspect Salads. EWG, Washington, D.C. www.ewg.org/reports/suspectsalads/.

Giannopoulous, J., and K. Baker, 2003, Perchlorate Contamination of California's Groundwater Supplies, California State Water Resources Control Board, www.swrcb.ca.gov/rwqcb4/html/perchlorate.html.

Hogue, C., 2003, Rocket-Fueled River, Chemical & Engineering News, 81(33): 37-46.

Mayer, K. P., 2003, Occurrence and Potential Sources of Perchlorate Releases to the Environment as of April 2003, EPA, San Francisco, CA, www.clu-in.org/download/contaminantfocus/perchlorate/perchlorateoccurrenceapril03a.pdf

Motzer, W.E., 2001, Perchlorate: Problems, Detection, Solutions, Environmental Forensics, 2(4): 301-311.

Schilt, A.A., 1979, Perchloric Acid and Perchlorates, The G. Frederick Smith Chemical Company, Columbus, OH, 189 p.

Schumaker, J.C. (ed.), 1960, Perchlorates: Their Properties, Manufacture and Uses, Reinhold Publishing Company, NY, 257 p.

Urbansky, E.T. (ed.), 2000, Perchlorate in the Environment, Kluwer Academic Press, New York, NY, 299 p.

Urbansky, E.T., T.W. Collette, W.P. Robarge, W.L. Hall, J.M. Skillen, and P.F. Kane, 2001, Survey of Fertilizers and Related Materials for Perchlorate (ClO_4^-): Final Report: EPA/600/R-01/047, EPA, Office of Research and Development, Cincinnati, OH, 26 p.