Article originally appeared in the July/August 2007 issue of *Southwest Hydrology* magazine.

Assessing Perchlorate Origins
Using Stable Isotopes

NAS7.10486
NASA-JPL
SSIC No. 9661

Thomas K.G. Mohr *– Santa Clara Valley Water District*

Readers of *Southwest Hydrology* are by now familiar with the perchlorate problem afflicting groundwater basins in the West and elsewhere. Perchlorate is a simple molecule comprised of one chlorine and four oxygen atoms. It is used as a propellant for missiles and the space shuttle, as well as in automotive air bags, highway safety flares, fireworks, and many smaller quantity applications. Perchlorate also occurs naturally and has been detected in mineral deposits and at low levels in rain. It will soon be regulated in California due to concerns over health effects to the thyroid.

Perchlorate has contaminated numerous municipal supply wells and hundreds of private wells. It is a particularly challenging contaminant because it migrates at rates approximating the velocity of groundwater. Long plumes of perchlorate contamination—measured in miles—make remediation difficult and costly.

The "Perchlorate" Isotopes

As investigators delineate large perchlorate plumes, the proven or potential existence of multiple sources of perchlorate inevitably leads to disputes about which source contaminated a given well. Naturally occurring stable isotopes can be used to distinguish sources of water and probable sources of contaminants such as nitrate, perchlorate, and chlorinated solvents, using $^{18}O/^{16}O$ ($\delta^{18}O$) and $^{37}Cl/^{35}Cl$ ($\delta^{37}Cl$) ratios. "Isotopomers," that is, different configurations of the perchlorate molecule that include heavier isotopes of oxygen and chlorine, are shown below right.

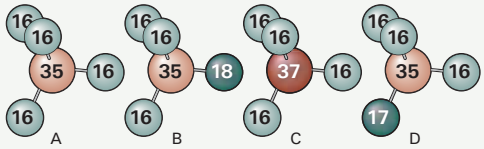
The process of sampling and analyzing for perchlorate isotopes is more involved and costly than routine water analyses. Samples of at least 10 mg of perchlorate are collected using a highly selective bifunctional anion-exchange resin (Purolite A530E). The resin cartridges are typically operated at a flow rate of about 1/8 of a gallon per minute, and thousands of gallons may be required to accumulate sufficient perchlorate mass for isotope analysis of low concentrations of perchlorate. A single sample therefore may take as much as a week to collect and cost $2,000 or more to analyze.

> *Isotope data ... led NASA to conclude that the perchlorate found in the Sunset Well was of a different origin than perchlorate at JPL.*

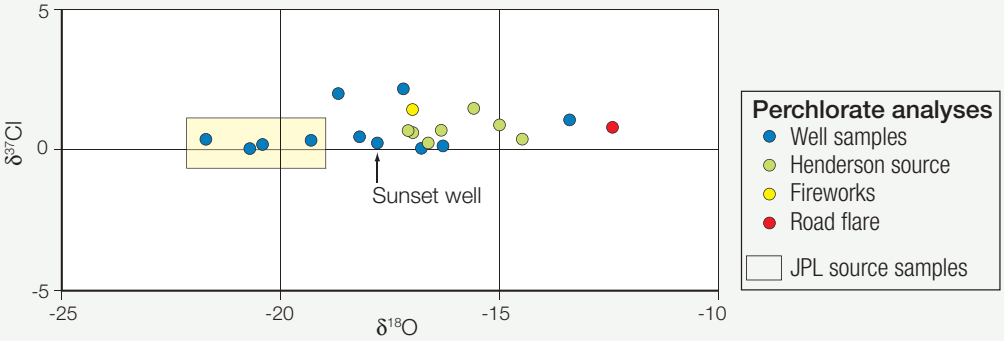
Perchlorate isotope analytical methods are highly specialized and the domain of research laboratories. Currently, most samples are analyzed at the Environmental Isotope Geochemistry Laboratory of the University of Illinois, Chicago (Sturchio and others, 2007). Researchers at Louisiana State University have also developed methods for perchlorate isotope analysis. Results are interpreted by plotting the $\delta^{18}O$ and $\delta^{37}Cl$ ratios against each other, and by contrasting the values obtained from different sources of perchlorate, different locations within the study area, and literature values.

The JPL Example

A recent study by NASA's Jet Propulsion Laboratories (JPL) in Pasadena, California, illustrates the application of perchlorate isotope data in conjunction with other forensic techniques. JPL used perchlorate in propellant research and production. A well located several miles from the JPL site (the "Sunset Well") was found to have 10 to 15 parts per billion perchlorate, and JPL, the nearest active perchlorate cleanup site, was assumed by some to be the source. However, the Raymond Basin, where the Sunset Well is located, has received about 1 million acre-feet of imported Colorado River



Perchlorate isotopomers: The perchlorate molecule (A) usually incorporates the most abundant stable isotopes of chlorine and oxygen, ^{16}O and ^{35}Cl. A small percentage will include one or more ^{18}O isotopes (B), some will have ^{37}Cl instead of ^{35}Cl (C), and perchlorate of atmospheric origin is more likely to incorporate the rare ^{17}O atom (D).



Perchlorate isotope plot, modified from NASA (2007). JPL site samples appear in the box; samples representative of Henderson, Nevada perchlorate plants are used to represent the probable range of past perchlorate values from the Colorado River (no actual river samples appear in this plot). Full context and locations of features in this plot are available in the JPL study at jplwater.nasa.gov/.

water that contains perchlorate due to past large-scale releases from two former perchlorate production facilities in Henderson, Nevada (NASA, 2007).

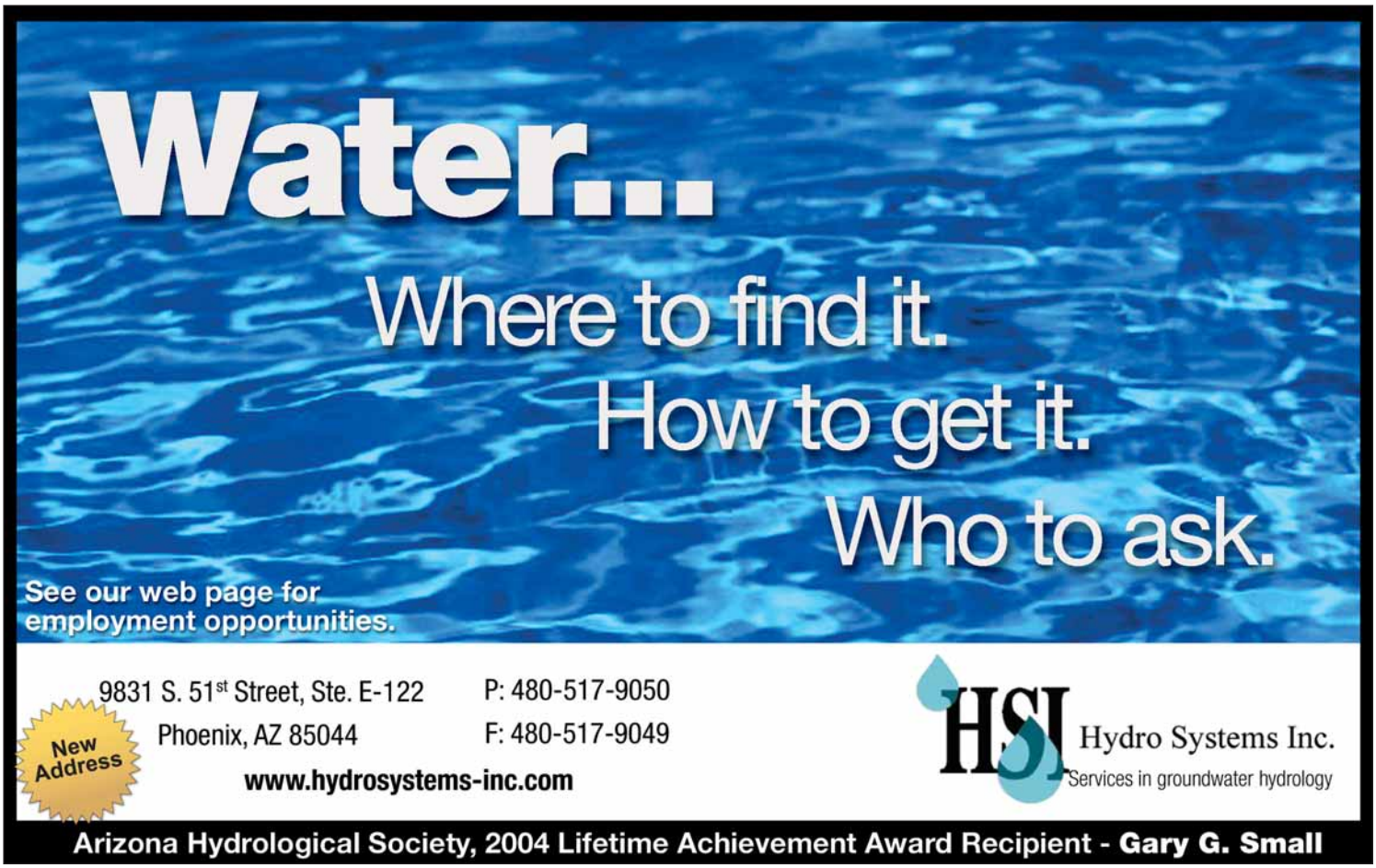
NASA's study employed conventional groundwater geochemical analysis, hydrogeologic data and groundwater modeling, stable isotopes of water, marker chemicals, tritium-helium and other groundwater age-dating methods, and isotopes of strontium and perchlorate. Perchlorate isotope data, supported by the other lines of evidence, led NASA to conclude that the perchlorate found in the Sunset Well was of a different origin than perchlorate at JPL. NASA's perchlorate isotope plot for this study is shown in the chart above.

NASA derived the main evidence that perchlorate in the Sunset Well has a different source than the JPL site from the $\delta^{18}O$ data for perchlorate from the JPL site, the Colorado River sources, and the Sunset Well. Perchlorate at the JPL site has more negative $\delta^{18}O$ values than were found in other wells sampled in the Raymond Basin or from Colorado River sources associated with perchlorate plants in Henderson, Nevada, and the Las Vegas Wash. In addition, groundwater modeling indicated that flow originating from the JPL site is captured by a production wellfield upgradient of the Sunset Well. This was corroborated by the absence of carbon tetrachloride, the primary volatile organic compound associated with the JPL site and with known JPL perchlorate, outside the production well capture zones.

Not All Are Convinced

Because the perchlorate isotope data can reflect a mixture of different perchlorate sources, the data have not initially convinced all stakeholders that the origin of perchlorate has been definitively determined by the isotope method. Controversy abides where economic conflict persists, but in the author's view, the JPL study provides a robust demonstration of the technical

see Perchlorate, page 34



Perchlorate, continued from page 23

utility of perchlorate isotope data together with other forensic techniques to distinguish sources. Nevertheless, deliberations continue; it remains to be seen whether regulators will find the isotope data persuasive.

Several factors can complicate the interpretation of perchlorate isotope data. Perchlorate is biodegradable by naturally occurring soil microbes under anoxic conditions where a carbon substrate is present. When biodegradation of perchlorate occurs, the remaining perchlorate may become enriched in the heavier isotope of oxygen through fractionation. It is therefore important to distinguish fractionation from other processes that may affect bulk isotopic signatures, such as mixing of waters bearing two or more different sources of perchlorate (Sturchio and others, 2007).

To confirm that isotopic fractionation from biodegradation is not affecting the isotopic signature, analysis for presence and activity of perchlorate respiring bacteria is recommended (Coates). Through such analyses, the JPL study confirmed that biodegradation did not affect perchlorate isotope signatures.

An Ongoing Study

Another perchlorate isotope study is underway in southern Santa Clara County. The Santa Clara Valley Water District is conducting a large-scale study of background levels and sources of perchlorate affecting the Llagas groundwater subbasin, where perchlorate from a former highway safety flare production facility was released to groundwater, affecting hundreds of wells. It remains to be seen whether possible additional sources in the Llagas study provide sufficiently distinct isotopic signatures to allow reliable interpretations of different origins of perchlorate at different locations, or whether only a single source is present.

Perchlorate isotopes provide a strong line of evidence, but must be interpreted within the basic hydrogeologic framework of the problem. The perchlorate isotope method is an effective tool that can add clarity where the right conditions and circumstances permit unambiguous interpretation. That interpretation is strengthened where multiple conventional indicators also point toward the same conclusion.

Thomas Mohr is a hydrogeologist with the Santa Clara Valley Water District and President of the Groundwater Resources Association of California. The views presented are the author's alone and do not reflect policy or positions of the Santa Clara Valley Water District or the Groundwater Resources Association of California. Contact him at tmohr@valleywater.org.

References

Coates, J.D. BioInsite Laboratories, Carbondale, Ill., personal communication.

NASA, 2007. Technical memorandum: Additional investigation results, National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, CA. Memorandum from Steven Slaten, NASA Remedial Project Manager, to Mark Ripperda, US EPA Region IX, Jan. 31, 2007. jplwater.nasa.gov/

Sturchio, N.C., J.K. Böhlke, A.D. Beloso, Jr., S.H. Streger, L.J.Heraty and P.B. Hatzinger, 2007. Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: Laboratory results and implications for forensics and natural attenuation studies, Environ.Sci. and. Tech., 41(8): 2796-2802.

AWRA

Upcoming Conferences

43rd AWRA Annual Water Resources Conference
Embassy Suites Hotel * Albuquerque, NM
November 12-15, 2007
For the best rate register by Oct. 22, 2007

2008 Spring Specialty Conference
GIS & Water Resources V
San Mateo Marriott * San Mateo, CA
March 17-19, 2008
Submit abstracts by Oct. 29, 2007

2008 Summer Specialty Conference
Riparian Ecosystems & Buffers: Working at the Water's Edge
Founder's Inn & Spa * Virginia Beach, VA
June 30 – July 2, 2008
Mark Your Calendar

Program, Registration, Exhibit & Sponsor Info
www.awra.org

American Water Resources Association
4 West Federal St., P.O. Box 1626
Middleburg, VA 20118-1626
Ph: 540.687.8390 FAX: 540.687.8395
Questions? info@awra.org

Courting, continued from page 25

The Move Toward Standards?

Some professional organizations have begun to consider whether rules and standards should be set for their members' involvement in litigation. For example, the State of Arizona's Board of Technical Registration recently promulgated a rule prohibiting registered professionals from providing expert witness services if compensation is based all or in part on a contingency fee related to the outcome of the dispute. And recently, the American Society of Testing and Materials convened a subcommittee within its Environmental Assessment, Risk Management and Corrective Action Committee. The subcommittee, now ASTM E50-05, is exploring the need to develop standards in the field of environmental forensics, including qualifications for experts, and anticipates producing a document, *Standard Guide for Environmental Forensic Expertise*.

Whether or not there is a need to regulate or standardize the conduct of scientists in the courtroom could be a matter of continuing debate. Indeed, if all were to practice within the bounds of good science and ethics, it would not be so much a matter of discussion. In any case, it is good advice for any technical professional to: understand something about how the legal process works; keep good records on project work; always conduct work in a systematic manner using good scientific principles; be consistently professional, prudent, and patient; and above all maintain strict ethical standards. If called upon to present your technical opinions, remember the advice of the 19th century journalist, Charles Anderson Dana, who said, "Fight for your opinions, but do not believe they contain the whole truth or the only truth."

References

Arizona Revised Statutes §32-101 et seq., specifically Article 3, R4-30-301, Rules of Professional Conduct, no.21.

American Society of Testing and Materials (ASTM) WK13999, www.astm.org.

International Society of Environmental Forensics website, www.environmentalforensics.org/journal.htm