Tracing the origin of perchlorate

A main ingredient in rocket fuel is showing up almost everywhere researchers look, but where is it all coming from?

A survey of drinking-water wells in western Texas, which began in the summer of 2002, turned up some surprising results. Perchlorate, a main ingredient in rocket fuel, was found in >80% of the wells tested over an area of ~60,000 square miles. The levels of perchlorate varied—most were quite low, but ~25% were ≥4 ppb, the level many consider to be of concern. The Texas Commission on Environmental Quality (TCEQ) couldn't figure out where the perchlorate was coming from.

TCEQ turned to researchers at Texas Tech University (TTU) for help. Environmental engineer Andrew Jackson, analytical chemist Purnendu "Sandy" Dasgupta, and their colleagues have been trying to solve the mystery ever since.

It has been, and still is, a huge effort. "We looked at vertical distribution in the aquifer and at unsaturated soils. We looked at land use in the area to see if there was any correlation with a certain industry or practice. We looked at a number of other constituents to see if we could find correlations with the occurrence of perchlorate. We did some modeling and determined in which geologic features it occurred," says Jackson. "What it comes down to in our best guess is that what we are dealing with is natural perchlorate," he says.

Most of the media attention surrounding perchlorate has focused on rocket-fuel contamination. The Texas panhandle wells, however, are nowhere near any source of munitions, says Dasgupta. Other sources, such as roadside flares, fireworks, and explosives, have also been ruled out. Analytical methods for detecting perchlorate have become so sensitive that the chemical is turning up just about everywhere people look, says Dasgupta. The question now is: How much of it is manmade?

Stable-isotope analysis

Although scientists are fairly certain that the perchlorate in the Texas wells is of natural origin, they still need more evidence to prove it. Researchers at Louisiana State University (LSU) and Oak Ridge National Laboratory (ORNL) have developed a new stable-isotope ratio technique that could provide the missing piece of information. "We can tell easily whether it is a natural source or not by looking at both the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios," says geochemist Huiming Bao of LSU.

In the new approach, all three stable oxygen isotopes are measured after a thermal decomposition method generates O_2 from perchlorate crystals. Measuring just $^{18}O/^{16}O$ won't give you the answer, because $^{18}O/^{16}O$ values for anthropogenic and atmospheric perchlorate overlap, says Bao. But if you measure $^{17}O/^{16}O$ at the same time and compare the two ratios, you will be able to tell, he says. Most oxygen-containing compounds on earth have a correlation between $^{18}O/^{16}O$ and $^{17}O/^{16}O$. Any deviation from this relationship is referred to as the ^{17}O anomaly, or $\Delta^{17}O$.

In photochemical reactions, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ often do not follow this mass-dependent isotope fractionation relationship; there is a large deviation and a positive $\Delta^{17}O$. Atmospheric ozone (O_3) is known to have a highly positive $\Delta^{17}O$. If atmospheric O_3 is involved in the creation of perchlorate, then natural perchlorate would also have a highly positive $\Delta^{17}O$. Although the researchers only have a limited data set, "So far all natural perchlorate has shown this ^{17}O anomaly," says Bao.

With the help of environmental chemist Baohua Gu of ORNL, Bao and colleagues measured the three stable oxygen isotopes in perchlorate extracted from a handful of Chilean salt deposits, which are known to contain trace levels of perchlorate. In all the samples tested, they found that the perchlorate had a unique oxygen isotope signature. Gu is now collaborating with Neil Sturchio of the University of Illinois at Chicago to analyze $^{37}Cl/^{35}Cl$ in the samples. So far, natural perchlorate also appears to have a unique chlorine isotope signature, says Gu.

To perform the isotopic analyses, the researchers need a minimum of 0.1 mg of pure crystallized perchlorate. One of the biggest challenges was extracting and analyzing trace levels of perchlorate from the deposits, which also contain large amounts of nitrate and other impurities, says Bao. And that is where Gu's expertise came in handy.

Several years ago, Gu and colleagues at ORNL developed an ion-exchange resin to remove parts-per-trillion levels of radioactive pertechnetate from groundwater. They later demonstrated that the resin also worked well for removing perchlorate. "The resin is so selective that it picks up perchlorate even in the presence of high concentrations of nitrate, sulfate, or chloride in water," says Gu. The researchers eventually developed a procedure for removing the perchlorate from the resin so that they could reuse it. "Perchlorate is so strongly [ad]sorbed you cannot remove it with a sodium chloride brine solution," says Gu. Instead, the researchers used a ferric chloride/hydrochloric acid mixture, which resulted in ~99% recovery of the perchlorate. That same procedure turned out to be useful for concentrating perchlorate for isotopic analysis.

Jackson and colleagues at TTU are currently pumping perchlorate-contaminated groundwater from western Texas through columns containing the special resin so that they can obtain stable-oxygen-isotope signatures. "It'll say whether the perchlorate is anthropogenic, but it won't be the nail in the coffin," says Jackson. We cannot positively rule out Chilean fertilizer, which is known to contain ~0.1% perchlorate, as the source, he says. However, it is highly unlikely because perchlorate has been detected in several areas where there has never been any agricultural activity, he adds. All the evidence points to perchlorate being generated in the atmosphere or by surface oxidation, he says.

The Texas researchers are also trying to produce perchlorate in the laboratory by processes that mimic those in the lower atmosphere or on surfaces such as sand. "We are looking at ozone reactions and UV reactions with chloride in aerosols and in sands," says Jackson. Dasgupta's group is investigating mechanisms that involve electrical discharge or lightning. Although the researchers have been able to produce significant quantities of perchlorate using various techniques, exactly how perchlorate forms in nature is still elusive. "It is all speculation," says Bao. "What we can provide is a stable isotope constraint. If you propose a model, our data provide two constraints. One is the $^{18}O/^{16}O$ ratio. The other is $\Delta^{17}O$," he says.

The next step is to obtain more stable-oxygen-isotope data on samples that are likely to contain natural perchlorate, says Bao. He and his colleagues intend to analyze more soils, including soil from southern California, the Nevada desert, and possibly other deserts. "As long as we have enough of those data, we can go ahead and put a very good constraint in terms of the formation pathway," says Bao.

COURTESY OF HUMING BAO, LOUISIANA STATE UNIVERSITY

Mystery in the desert. Nitrate salt deposits from the Atacama Desert in Chile are known to contain trace levels of naturally occurring perchlorate. Researchers are still trying to determine how the perchlorate got there.

The regulatory side

If some of the perchlorate found in drinking water really is of natural origin, it could affect how the U.S. Environmental Protection Agency (EPA) decides to regulate the compound in drinking water. Although EPA recommended a limit of 1 ppb in 2002, it is waiting for the National Academies' Institute of Medicine to finish reviewing the issue before it actually sets a perchlorate limit for drinking water. Experts predict that the level will be >1 ppb.

Meanwhile, the U.S. Food and Drug Administration (FDA) has become concerned about perchlorate in the food supply. It all started when a nonprofit environmental group released a report in the spring of 2003 showing that lettuce irrigated with contaminated water in California and Arizona contained detectable levels of perchlorate. "We found that 4 out of 18 lettuce samples contained perchlorate," recalls Dasgupta, who performed the analyses for the environmental group. "It was really not a scientifically large enough sample," he says. Nonetheless, the report received a lot of attention from the press.

Perchlorate was once thought to be safe because it is not very reactive. Now, however, many consider it to be a cumulative toxin because it interferes with the transport of iodide in the body. Without iodide, the thyroid gland will not function properly. Thyroid hormones are particularly important for infants and young children, who rely on them for proper development.

Because kids don't typically eat lettuce, Dasgupta and his graduate student Andrea Kirk decided to investigate the occurrence of perchlorate in milk. In the summer of 2003, they analyzed seven milk samples purchased randomly from Lubbock, Texas, supermarkets. All of them contained perchlorate, at levels ranging from 1.7 to 6.4 ppb.

The results prompted FDA to take a closer look at perchlorate in the U.S. food supply. In December 2003, the agency announced its plans to analyze lettuce, bottled drinking water, and many other foods, as appropriate sample preparation methods become available.

Although the final report from FDA is not expected until next year, some of the early results were published in the September 15 issue of *Analytical Chemistry* (**2004**, *76*, 5518–5522). In that paper, Alexander Krynitsky and colleagues describe a new ion chromatography (IC)/MS/MS method for analyzing perchlorate in lettuce, cantaloupe, bottled water, and milk. The method incorporates an $^{18}O_4$-labeled perchlorate internal standard, which corrects for matrix effects that can enhance or suppress the MS signal. According to the researchers, the labeled internal standard greatly simplified the extraction procedure and cleanup prior to IC/MS/MS analysis.

The analysis of perchlorate in foods is still in its infancy, and some technical hurdles need to be overcome before the results are meaningful. Only time will tell how widespread perchlorate has become in our food chain.

—Britt E. Erickson