

ANDREW JACKSON, PH.D. is part of a team that focuses on perchlorate and its implications, putting the university in the forefront of research about the subject.

A PERCHLORATE PUZZLE

[THE PERCHLORATE PROBLEM]

A routine analysis of water samples during the summer of 2002 detected trace levels of perchlorate in drinking water supplies in Midland, Texas, and 100 miles away in Levelland, Texas. The Texas Commission on Environmental Quality (TCEQ) could not readily determine the origin of the perchlorate and turned to researchers at Texas Tech University for help in investigating this contamination. Andrew Jackson, Ph.D., associate professor in the Department of Civil Engineering, had been doing research on perchlorate for a number of years, and readily agreed to assist the TCEQ. Jackson's research team continued collecting samples, ultimately revealing the presence of perchlorate in more than 80 percent of the wells over a 60,000 square mile area that includes 54 counties in Texas and two counties in New Mexico. Although the levels of perchlorate varied, some of the wells contained amounts that surpassed those generally considered safe.

The project involved contributions from civil, environmental and chemical engineering, chemistry and biochemistry, and the Institute for Environmental and Human Health (TIEHH). The team collected groundwater samples and began to investigate potential sources of perchlorate. Researchers at TIEHH were measuring perchlorate in West Texas groundwater samples, but they soon found that, due to the high salinity of the water, the methods recommended by the U.S. Environmental Protection Agency were not sensitive enough to detect perchlorate. Purnendu Dasgupta, Ph.D., former Horn Professor in the Department of Chemistry and Biochemistry, was called upon to help develop a more sensitive measure.

He had been working with ion chromatography, which allows for the separation of ions and polar molecules based on the charge properties of the molecules. His work in this field has earned him the distinguished Ion Chromatography Outstanding Achievement Award not once, but twice. His particular technique proved to be a highly selective and sensitive measure of perchlorate. >

by Mónica Muñoz
photos by Artie Limmer



The

[THE COMMON SOURCES]

ORIGINS OF PERCHLORATE ARE BOTH NATURAL and anthropogenic in origin. Natural perchlorate first was identified in Chilean nitrates, a common ingredient in some fertilizers, more than 100 years ago.

For a long time, people believed that significant amounts of natural perchlorate were confined to these nitrate deposits in the Atacama Desert in Chile. Over the years, however, researchers have discovered other deposits of naturally occurring perchlorate in New Mexico, California, Canada, and Bolivia. The anthropogenic origin of perchlorate lies in the manufacture of ammonium perchlorate. Ammonium perchlorate has been produced in the United States since the 1900s; in the 1940s and 1950s, perchlorate was used in the production of explosives and propellants. Military sources of ammonium perchlorate include solid rocket fuels, signal flares, smoke generators, numerous types of munitions, artillery tracers, and railway torpedoes. Non-military sources include match manufacturing, tanneries, signal and road flares, seismic explosives, fireworks, paint and enamel production, magnesium batteries, air bag inflators, and even methamphetamine laboratories. Perchlorate contamination in groundwater often can be attributed to runoff from irrigated crops that were treated with fertilizers containing Chilean nitrates, or to waste at the hands of industries from the manufacture of or the improper disposal of chemicals that contain perchlorate.

[THE PUZZLE]

JACKSON'S RESEARCH TEAM CAME TO THE CONCLUSION that, although fertilizer containing Chilean nitrates had been used in the area of interest, the levels of perchlorate that were detected in groundwater samples exceeded those that would be expected if the contamination was due to the sole use of fertilizers. When they examined the production of ammonium perchlorate in the area, they found that manufacturing sites could not account for the widespread contamination they were encountering. Therefore, the research team ruled out fertilizers and man-made perchlorate as sources of the perchlorate contamination in West Texas and New Mexico. The scholars determined that the perchlorate had to be of natural origin. Now, the researchers had to determine how the sources formed in the area, and the search for a solution to this puzzle began.

Texas Tech University researchers became aware that this was not the first time the origins of perchlorate had presented a mystery. For many years, the origins of the perchlorate deposits in the Atacama Desert had baffled scientists, but recent research suggested that atmospheric processes played a role in the production of naturally occurring perchlorate, and that millions of years of deposition accounted for this large perchlorate reservoir in Chile. With the development of sensitive analytical methods for detecting the presence of naturally occurring perchlorate, scientists had been able to propose that perchlorate can form naturally in the atmosphere or by surface oxidation. Jackson's research team decided to test these hypotheses with the groundwater samples from West Texas and New Mexico.

[THE PIECES]

"FOR A LONG TIME, perchlorate was your classic contaminant, where everybody pointed the finger at industry or at the U.S. Department of Defense. As it turns out, a lot of natural perchlorate exists out there. We are exploring the following questions: How much is out there? Where is it? Why is it in these places and not in other places? How did it form? What are the implications? Does it really have an impact on cleanup or not?" Jackson explains. The research team focused first on providing evidence that perchlorate forms in the atmosphere by collecting rain and snow samples from Lubbock, Texas, and analyzing them for perchlorate, which was detected in 70 percent of the samples. This initially supported the idea that atmospheric processes play a role in the production of natural perchlorate. To supplement these findings, researchers correlated perchlorate levels in rain and snow samples with several compounds and found that the highest correlations occurred with iodate, a compound that is known to have atmospheric origins.

Researchers decided to simulate in the laboratory several of the processes that occur in the lower atmosphere or on surfaces such as sand. They theorized that natural perchlorate forms through ozone or ultraviolet (UV) reactions with chloride in aerosols and sands, and possibly, through electrical discharge or lightning. Experiments involving high energy electrical pulses were carried out in the Texas Tech Pulsed Power.

[THE RESEARCH LABORATORY]

AFTER SONICATION, A PROCESS OF DISRUPTING biological materials through the use of sound waves, produced no perchlorate in water samples, researchers began investigating surface oxidation in the form of ozone and UV reactions with sodium chloride. Glass dishes containing a single layer of sand and sodium chloride dissolved in water were exposed to four UV lights and various concentrations of ozone. Although no significant amounts of perchlorate were produced during the UV exposure experiments, researchers found that perchlorate is formed at exposure to high concentrations of ozone. These processes simulated desert conditions, such as those in New Mexico and West Texas.

The experiments with electrical discharges also proved to be fruitful. Researchers submerged two stainless steel electrodes in water samples to discharge high energy electrical pulses, and they found that with 10 successive discharges, perchlorate levels above that found in control samples were produced. Electrical discharge also can produce perchlorate from sodium chloride aerosol. When an electrical discharge was passed through sodium chloride aerosol that had been oxidized, significant amounts of perchlorate were detected in nine out of nine samples. This experiment simulated the effects of lightning, a process that routinely occurs in the atmosphere.

These findings were reported in "The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes," a paper that was named the Best Science Paper of 2005 by Environmental Science & Technology, one of the American Chemical Society's premier peer-reviewed journals. A follow-up paper, "Widespread Presence of Naturally Occurring Perchlorate in High Plains of Texas and New Mexico," was published in the same journal in 2006. Researchers reported evidence that supports atmospheric deposition as the origin of perchlorate in the region. Groundwater samples were collected from more than 1,000 public water systems and wells, and researchers determined that perchlorate is most likely distributed over the surface and is not attributed to anthropogenic sources. They first determined that perchlorate distribution is not related to well type and aquifer, nor is it related to land use. The researchers went on to look at the vertical distribution of perchlorate in five well clusters, and they found that as they went deeper into the water source, perchlorate levels decreased. They also found that samples from sources of lower saturated thickness contained higher levels of perchlorate. Their conclusion was that the perchlorate contamination is most likely due to atmospheric deposition and that it has been driven into groundwater by irrigation.

[THE IMPLICATIONS]

THE EVIDENCE FOR NATURALLY OCCURRING PERCHLORATE HAS LED to concerns about health issues. "Out of these questions comes health questions you could ask," Jackson says. "Is it possible that people have been exposed to perchlorate in some degree for a long time because it is natural? It is important to keep in mind that being natural does not make perchlorate good for you. Arsenic is natural too, but you don't want to drink it."

Perchlorate is known to interfere with the functioning of the thyroid gland by inhibiting the uptake of iodide. "Perchlorate has a very similar size and charge to iodine," Dasgupta explains. "The sodium/iodine symporter, called NIS, cannot really distinguish between iodine and perchlorate. In fact, it has 30 times the affinity for perchlorate that it has for iodine. So, basically perchlorate is not intrinsically toxic, but it inhibits the transport of iodine in the thyroid." Iodine deficiency, Dasgupta suggests, should be the main concern when talking about perchlorate contamination of drinking water and food supplies. The thyroid hormone is critical in neural development, and iodine deficiency is the leading cause of mental retardation, so exposure to perchlorate poses a serious problem for developing fetuses and infants. For adults, perchlorate may not be such a big concern, unless individuals have diets that are very low in iodine or they have compromised thyroid function. However, Dasgupta warns that when he has spoken with doctors in West Texas, most report that thyroid problems in adults are common in this area, so the presence of perchlorate may be worrisome for people of all ages.

[THE IMPACTS]

THE RESEARCH ON perchlorate has managed to put Texas Tech University at the forefront of a great deal of interest in the topic because perchlorate currently is a highly charged political issue.

Research on perchlorate at Texas Tech University has helped inform many of the questions that surround current water issues. Certainly, the findings from the research will have far-reaching implications unconfined to water problems in West Texas and New Mexico. Texas Tech researchers have carried out ecological risk assessments, investigations of toxicity, work on treatment of perchlorate-contaminated water, analyses of the natural distribution of perchlorate, studies on plant uptake of perchlorate and the exposure for people from plants, and examinations of food sources, like milk and lettuce. "The findings and research have been really great for Texas Tech," Jackson says. "If someone mentions perchlorate, everybody knows that Texas Tech has a hand in the research." ■