



Across the United States and around the world, scientists are studying the migration of radioactive elements through the ground under former nuclear weapons sites. At the Hanford Site in Washington State, uranium and other radionuclides are moving toward the Columbia River, a major waterway in the Pacific Northwest. (Photo by Scott Butner)

Six Science Secrets of THE SUBSURFACE

Today, former nuclear weapons sites in the United States contain 1.7 trillion gallons of contaminated groundwater, an amount equal to about four times the daily U.S. water consumption. In addition, the sites hold an estimated 40 million cubic meters of contaminated soil and debris.

By Kristin Manke and Julie Wiley

Many of the subsurface contamination problems at former nuclear weapons sites have no practical remedy. The work at these sites, where ore milling, nuclear fuel fabrication, and other activities were performed, created radioactive wastes. In the early years, recovering slightly more than a pound of plutonium created 2000 to 25 000 gallons of radioactive liquid waste. These wastes were stored in underground tanks and other systems. In some cases, wastes were released directly to the ground.

Today, such sites in the United States contain 1.7 trillion gal of contaminated groundwater, an amount equal to about four times the daily U.S. water consumption. In addition, the sites hold an estimated 40 million cubic meters of contaminated soil and debris, which would fill about 17 professional athletic stadiums. Federal and state regulations call for reducing contaminant levels in the subsurface to protect nearby populations and ecosystems.



Underground tanks were constructed to hold radioactive and chemical wastes from nuclear weapons activities. At the Hanford Site, 177 underground tanks were built, and more than 60 of these have leaked or are suspected of leaking waste to the surrounding soil.

Removing or immobilizing the waste in the subsurface is complicated for three reasons. First, the radionuclide and chemical contamination is present at low concentrations. Second, the radionuclides are dispersed over a wide volume in the subsurface. Finally, the pollutants are present in extremely complex matrices. For example, subsurface areas often contain microenvironments and transition zones that can significantly impact contaminant migration. Microenvironments are small areas that exert a disproportionate amount of influence on the larger area. This influence is the result of microbial, geochemical, and physical processes working together. Transition zones are larger features where chemical, physical, or microbiologic properties change dramatically over relatively short distances, usually less than a meter.

Because of these challenges, conventional excavation or pump-and-treat technologies are costly and inefficient. For example, six years of pump-and-treat work at one site recovered 1.1 curies of strontium and cost \$18 million. In the same time frame, 12 Ci of strontium decayed naturally. Innovative, effective, and affordable methods are needed to remediate these contaminants.

To that end, national laboratories, universities, and others are discovering how to remove, immobilize, or stabilize subsurface contaminants. These discoveries begin with fundamental science focused on understanding how chemical, physical, and biological processes function in an integrated manner to influence contaminant transport in the subsurface. With this understanding, scientists can predict the fate and transport of radionuclides. "An important aspect of the science is prediction, understanding where and when remediation is needed to protect the environment and when natural attenuation will do the job and all that is required is monitoring," said Jim Fredrickson, an expert in geomicrobiology at Pacific Northwest National Laboratory (PNNL).



The Six Science "Secrets"

By integrating research done in the laboratory and the field, interdisciplinary teams of scientists have gained new insights into what happens to radionuclides in the subsurface. Here are six recent discoveries.

Uranium moves more slowly as it gets near the river. How fast and how much uranium reaches the nearby Columbia River is a major issue at the Hanford Site, in southeastern Washington State. One area of keen interest is the shoreline, where groundwater mixes with river water. An accurate determination of the uranium that arrives at the shoreline allows scientists and engineers to design and implement technologies that capture or stabilize the uranium before it enters the river, which supplies water for agriculture and drinking water for downstream communities as well as being a major route for migrating salmon.

In a recent study, scientists wanted to know how the chemistry of the shoreline influences uranium's movement.

The Hanford Site, Washington State

The 586-square-mile Hanford Site was created in 1943 to produce weapons-grade plutonium for national defense. Located in the dry, shrub steppe of southeastern Washington State, the site contained nine nuclear reactors, four major reprocessing complexes, 177 underground tanks, and waste disposal facilities. The operation of the reactors and the associated facilities created overlapping technical, political, regulatory, financial, and cultural issues.

During the two-plus decades of plutonium production, liquid waste entered the ground. The waste led to more than 15 contaminated groundwater plumes. Groundwater contaminant levels exceed drinking water standards beneath about 70 square miles of the site. Uranium and technetium in the plumes are of concern



The Columbia River, which runs past the old reactors on the northern tip of the Hanford Site, provides water for agriculture and drinking water for downstream populations. It is also a major route for migrating fish, including Chinook salmon.



Construction on the Hanford Site began in the early 1940s. The site would eventually contain nine reactors and produce 74 tons of plutonium.

because of their environmental mobility and persistence. Plutonium is of concern because of its toxicity. The inventory of the three contaminants is significant: 202 703 kilograms of uranium, 1709 curies of technetium-99, and 400 kg of plutonium.

Groundwater from beneath the site is not a source of public drinking water; however, the U.S. Department of Energy, which manages the site, must predict where and when uranium and other contaminants will arrive along the Columbia River shoreline to implement efficient, cost-effective technologies to capture or stabilize the uranium before it enters the river, a major waterway in the Pacific Northwest that supplies water for agriculture and drinking water for nearby communities as well as being an important route for migrating salmon.



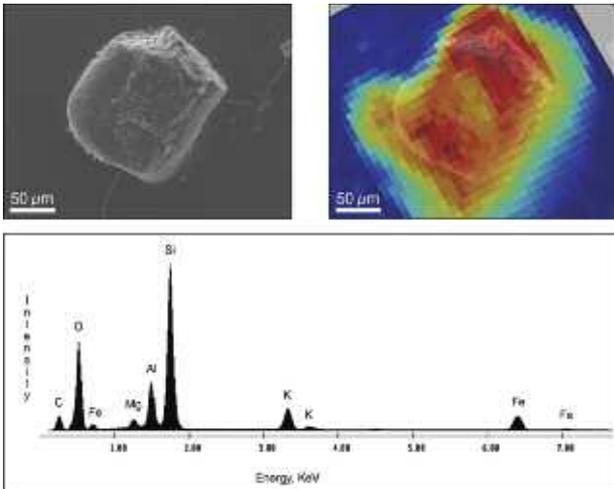
To control uranium's fate and transport, scientists must understand how fast uranium attaches to and releases from soil particles along riverbanks at contaminated sites. These studies rely on carefully collected real-world samples of soil, groundwater, and river water.

To find out, they began with uranium-contaminated sediment. In the laboratory, they exposed the sediment to solutions with different pH, calcium, and carbonate levels.

They found uranium's detachment from the sediment slowed when the groundwater was at neutral pH and had low levels of dissolved carbon dioxide or carbonate. Similar conditions exist along the shoreline. Inland, the conditions are different. The uranium detaches from the soil and migrates with the groundwater much more quickly.

2 Unusual state of uranium forms during simulation of subsurface reactions. Work done by Eugene S. Ilton at PNNL has shown that what was believed to be a rare form of uranium, known as uranium(V) or uranium with five electrons missing, can form during electron-swapping reactions with uranium(VI) at the surface of iron-based minerals.

More recently, Ilton collaborated with an international team led by John Bargar at the SLAC National Accelerator Laboratory and discovered that uranium(V) also formed on the surface of tiny particles of another form of uranium suspended in water. In this case, uranium(IV), in the form of uranium dioxide particles, lost electrons to form uranium(V). This study shows that the transformation of uranium from a relatively immobile state, uranium(IV), to a relatively mobile state, uranium(VI), is not the single-step process previously thought.



Left: By using different scientific techniques, scientists can provide new information about the behavior of technetium and other radionuclides that migrate through the subsurface.

Below: By integrating the microscopic and the spectroscopic at the Environmental Molecular Sciences Laboratory, scientists obtained extremely detailed views of the framboidal (from the French for “raspberry”) pyrites in the soil. The top image is of a sphere-like structure, and the bottom image is an irregular framboidal structure. Framboidal pyrites in certain sediments may initially sequester subsurface uranium and then serve as a long-term source under conditions of slow oxidation. Thus, microbially altered, loose sediment may contribute to the persistence of uranium in the groundwater at former uranium mill sites.

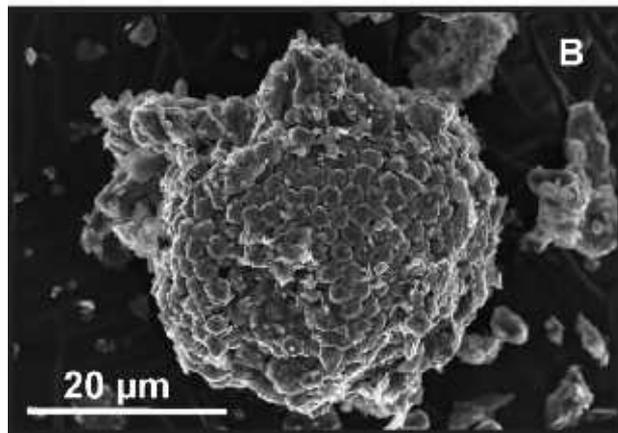
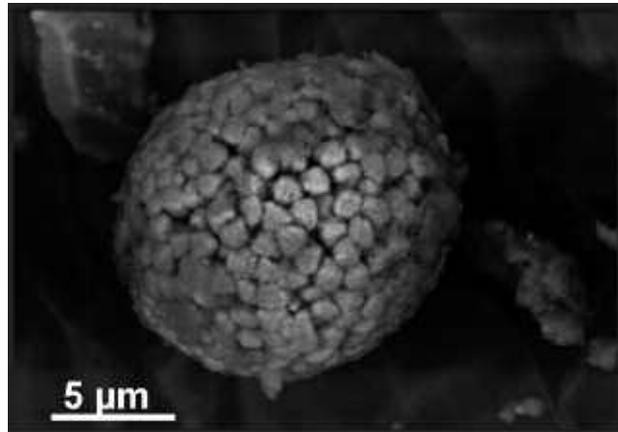
“Laboratory experiments indicate that under certain conditions the intermediate state of uranium(V) is longer lived than previously thought,” said Ilton. “This may have implications in the environment and remediation schemes that manipulate the state of the uranium.”

3 Diet matters for microbes turning radionuclides into less mobile forms. Many diverse species of bacteria thrive in the subsurface beneath places such as the Hanford Site. Under certain conditions, some of these microbes can, as a result of their metabolism, transform uranium, technetium, and other mobile radionuclides into less mobile forms. One such microorganism is *Anaeromyxobacter dehalogenans*. It converts technetium and uranium to solid, less mobile forms, but the distribution of such organisms in the Hanford subsurface and their in-situ activities is not well understood.

Consequently, scientists conducted a study in 2009 to determine if the type of food provided to the microbe changed the reaction rates. Some of the microbes were fed hydrogen (H₂). Others were fed acetate, a simple organic compound that is the major component of vinegar. While the microbe produced immobile uranium and technetium on either diet, the radionuclide transformation was far faster with hydrogen. The acetate-fed microbes, however, produced larger aggregates of particles that could ultimately influence the migration of the particles in the subsurface.

4 Iron in the soil can help technetium stay put. The minerals present in the sediment influence when technetium is turned into its less mobile form, according to a study by scientists at PNNL and Argonne National Laboratory. Soils with high levels of sheet-like minerals consisting of iron, silicon, and oxygen, such as those found at the Oak Ridge site in Tennessee, allow the less mobile technetium to combine with iron-containing clay particles. The resulting iron-technetium complex in the clay is exceedingly resistant to remobilization.

5 Fool’s gold may grasp and then slowly release uranium. A form of pyrite, or fool’s gold, may initially serve as a trap for uranium, sequestering the radionuclide under certain conditions of naturally occurring subsurface microbial activity (see item #6 following). However, this type of pyrite, known as framboidal pyrite, may also serve as a long-term source of uranium, slowly leaking it to the



surrounding subsurface as the uranium changes and becomes more mobile.

More studies are planned to better understand the processes that occur in this sediment. Clearly not all pyrites, framboidal or otherwise, contain high levels of uranium, so understanding what controls uranium uptake in pyrite is a crucial next step.

6 Electricity can be used to see through the subsurface. Tracking biogeochemical reactions in the field is hampered by the need for expensive, invasive monitoring wells. A new approach, called surface spectral-induced polarization (SSIP), allows monitoring without wells. Using this method, scientists send variable frequency currents into the ground and measure the results with electrodes embedded in the ground surface. The electrical response depends on the predominant metabolic processes active in the subsurface at the time.

“Similar to how noninvasive medical imaging has reduced the need for invasive, exploratory surgeries,



Understanding the structure, chemistry, and nanoscale geometry of subsurface components, water, and radionuclides is key to learning how radioactive pollutants from former nuclear sites move in the subsurface. At the Environmental Molecular Sciences Laboratory, scientists unravel the molecular, atomic, and subatomic phenomena of geochemical and biogeochemical reactors. (Photo of the EMLS by Andrew Rakowski)

Inside and Out: The Facilities That Make the Science Possible

Understanding microenvironments and other subsurface complexities requires facilities capable of characterizing properties and materials at the molecular



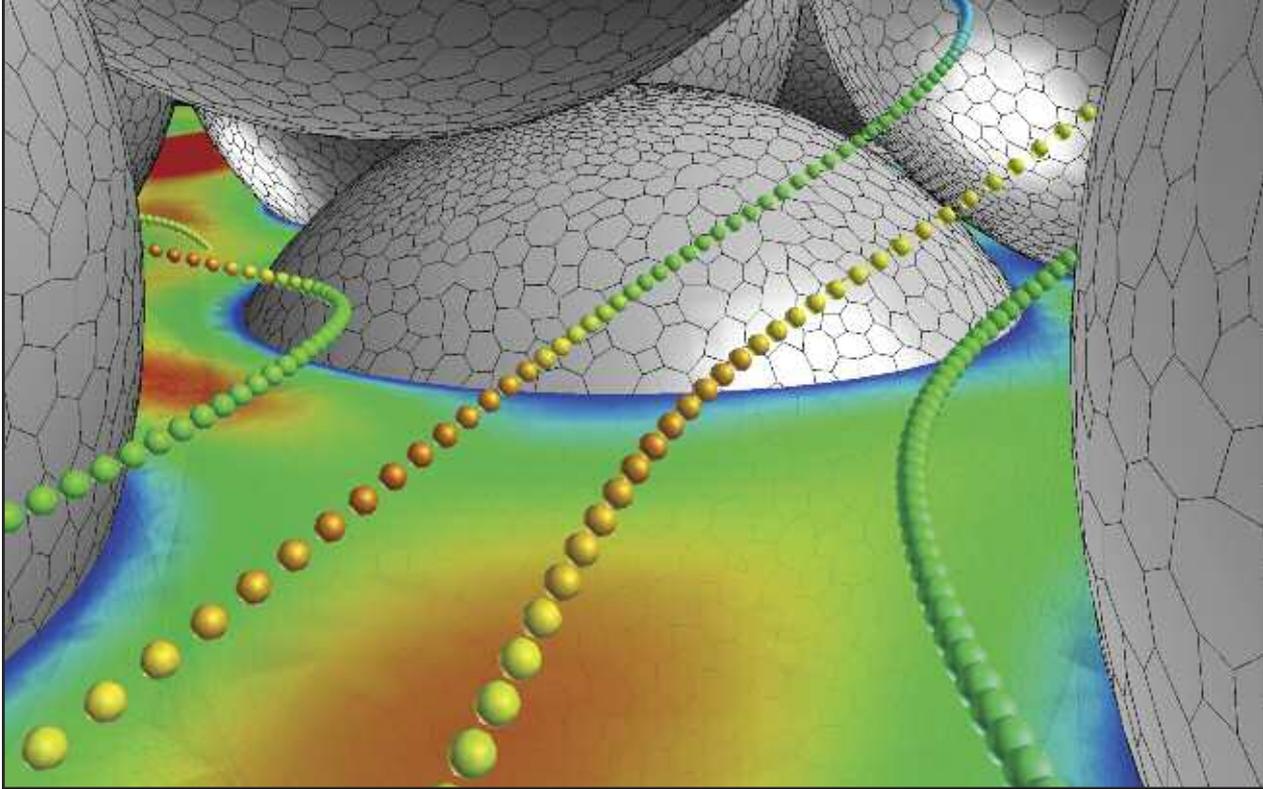
Located on Hanford's Integrated Field Research Challenge Site, this subsurface experimental system contains nearly three dozen monitoring wells equipped with sophisticated instrumentation. The research being done here is bringing scientists closer to determining why groundwater contamination persists on the southern tip of the Hanford Site. The subsurface area surrounding the wells is being comprehensively characterized to determine the subsurface processes that contribute to the persistent groundwater contamination.

scale. This work is being done in facilities such as the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory, the Advanced Photon Source at Argonne National Laboratory, and the Stanford Synchrotron Radiation Laboratory.

For example, the U.S. Department of Energy's Environmental Molecular Sciences Laboratory provides scientists from around the world with integrated experimental and computational resources. These resources include laser-induced fluorescence spectroscopy, Mössbauer spectroscopy, electron microscopy, and micro X-ray diffraction. In addition, the facility offers supercomputing capabilities. This scientific user facility is on the PNNL campus in Richland, Wash.

Because of the vast area subsurface contamination covers at some sites, field research sites are needed. The creation of three Integrated Field Research Challenge Sites allows investigation of coupled hydrologic, microbiologic, and geochemical processes in complex field settings. The sites are at the Hanford Site in Washington State, the Oak Ridge site in Tennessee, and a former uranium and vanadium milling site (see <http://ifcrifl.pnl.gov/about/>) near Rifle, Col. (www.congressional.energy.gov/documents/9-10-09_Final_Testimony_Palmisano.pdf).

Both the Environmental Molecular Sciences Laboratory and the Integrated Field Research Challenge Sites are overseen by the DOE's Office of Biological and Environmental Research.



With powerful computers, scientists can model how groundwater and its contaminants move through sand. For example, scientists recently did a simulation showing how particles (shown here as trails of dots colored by speed) in the groundwater move around large grains of sand (gray spheres). They found that the particles take complex paths and pass through faster and slower regions. These types of models can further the understanding of contaminant transport in groundwater. (Simulations were done by Cindy Rakowski and visualizations were created by John Serkowski, both of PNNL.)



Left: Kenneth Williams, of Berkeley Lab, and graduate student Adrian Flores Orozco, of the University of Bonn, collect surface spectral-induced polarization at the Rifle Integrated Field Research Challenge Site. This work is helping to detect and delineate regions of naturally elevated subsurface microbial activity that could aid in halting the progress of radionuclides and other contaminants.

geophysical monitoring techniques such as SSIP allow us to monitor large volumes of aquifer sediments without having to drill groundwater wells, which saves money and disturbs less land,” said Kenneth Williams, of Lawrence Berkeley National Laboratory.

Need for Continued Understanding

The biological, chemical, and physical complexities of the subsurface, coupled with the sheer volume impacted, present scientific challenges to providing reliable, cost-effective remediation approaches for the nation’s contaminated sites. Research such as discussed herein will help advance our understanding of the fundamental processes that control contaminant behavior in the environment in ways that help solve the DOE’s intractable problems in environmental remediation and stewardship. ■

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