

# Helping Water Managers Ensure Clean

*Livermore experts are developing advanced models and new methods to help protect California's*

**M**OST Americans take cheap and plentiful supplies of pure drinking water for granted. Some even consider it to be an inalienable right. However, clean water sources, especially pristine underground aquifers, are being consumed at an increasing rate, and contaminants and changing patterns in rain and snowfall are threatening the adequacy of supplies.

Ensuring plentiful water supplies is becoming a critical issue in California,

which uses 10 percent of the nation's freshwater. State water managers are closing many contaminated or impaired drinking wells; Sierra snowpacks have diminished in recent years; and the state's farmers, fishermen, environmentalists, and city dwellers cannot always agree on the best uses for a limited supply.

California is not alone with respect to these issues. They are relevant throughout the western U.S. and are becoming more so in other parts of the country. They also are critically important in highly populated and developing nations such as China, India, and Mexico as well as in many parts of Africa and the Middle East.

# and Reliable Supplies

*precious water sources.*

To consider possible methods to address these challenges, a team of Lawrence Livermore scientists is working on a three-year Water Initiative that is managed by Livermore's Energy and Environment (E&E) Directorate. The initiative, now in its second year, marshals Livermore's expertise in chemistry, materials science, environmental science, microbiology, and computer modeling. The team's goal is to develop innovative tools that water resource managers can use to make informed decisions about the state's water-supply infrastructure, protection and purification efforts, and flood control. In so doing, the scientists are helping to position the Laboratory as a leader in the science and management of water resources.

## Three Projects Tap Lab Expertise

"We are creating tools and methods that will serve the water management

community," says Robin Newmark, who leads the E&E Water and Environment Program as well as the Water Initiative. When Newmark and her colleagues studied the problems facing California water managers, they found three areas where Livermore's expertise could make the greatest contributions: providing better predictive models, improving the scientific understanding of water contamination, and developing more cost-effective technologies for purifying water.

The three resulting scientific projects that form the Water Initiative are funded by Livermore's Laboratory Directed Research and Development Program. Additional institutional funding supports planning and outreach activities aimed at establishing relationships with water managers at the local and state level.

The first project links climate and surface hydrology models run on

Livermore's supercomputers to predict how climate variability can affect the supply of freshwater in the coming decades. The second project studies ways to better understand and manage nitrate, the leading contaminant of California groundwater. The third project focuses on treating contaminated water with new, cost-effective membranes for electro dialysis.

The Department of Energy (DOE) might not seem a logical choice to be leading a water effort, but energy and water are inextricably linked. "Energy security depends on water security," says Newmark. The production of energy is the second largest consumer of freshwater in the nation, after agriculture. At the same time, the processes involved in treating and distributing an abundant supply of clean water depend on having low-cost energy readily available. Nationally, about

The Del Valle Reservoir in California.

4 percent of electricity is used to pump, process, and treat water.

The demands for both energy and water are expected to grow substantially in the next 25 years. “As a result,” says Newmark, “a strong federal role is needed to provide scientific research, technology development, and analysis capabilities so

the nation can achieve energy and water security and sustainability.”

**Simulations Guide Decision Makers**

In California, the availability of sufficient freshwater to meet agricultural, urban, fishing, recreational, and other needs depends on properly managing a complex

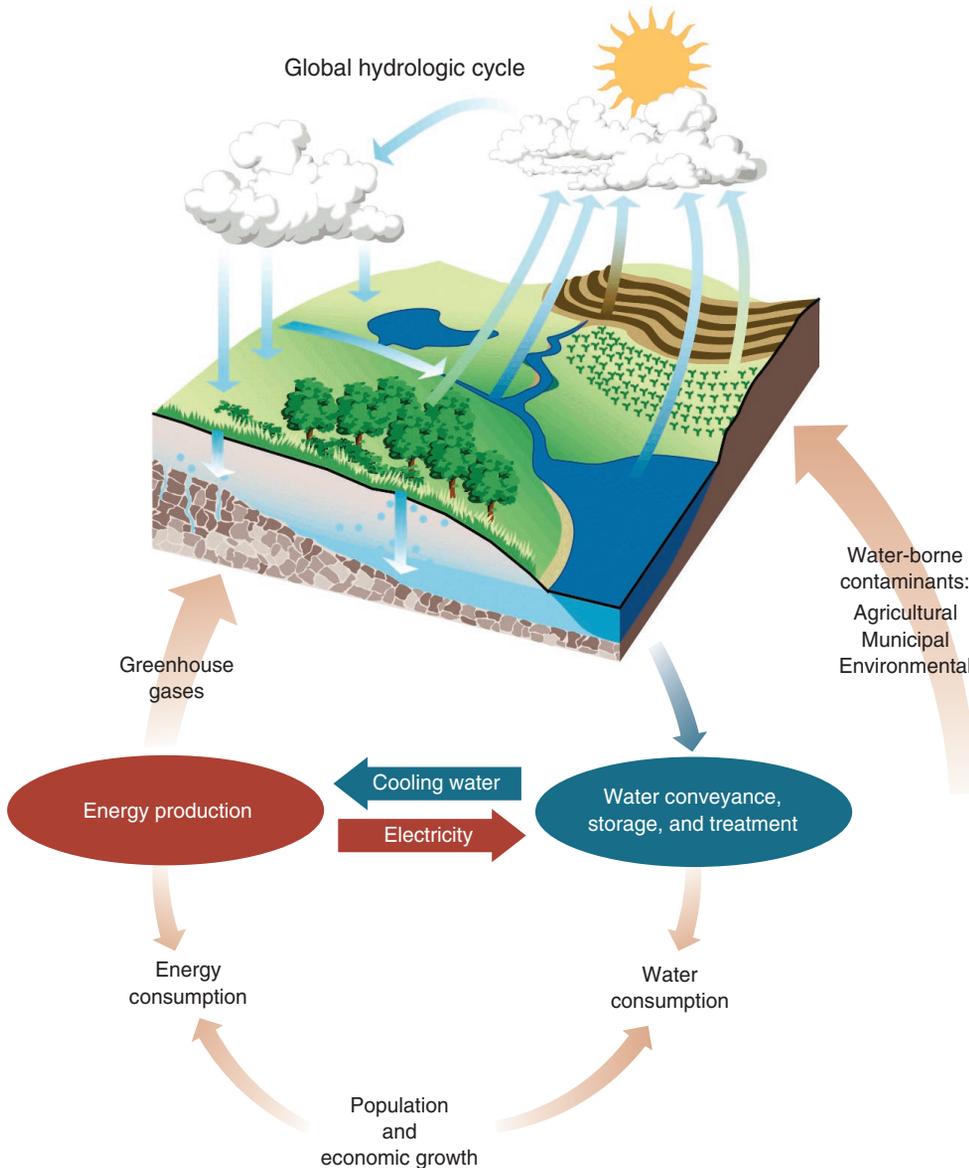
system of water storage and delivery. In making decisions, water managers are guided by past observations of the natural hydrologic cycle, including such factors as rainfall, the water content of snow, and river flow rates.

These observations are useful only if the future behavior of California’s hydrologic system is similar to its past behavior. Yet, such an assumption may no longer be correct. If the natural hydrologic cycle continues to change significantly, water management practices must adapt to the new patterns. These changes require building new reservoirs, pipelines, aqueducts, flood-control projects, and treatment plants and in many cases, operating existing facilities differently.

“There’s a compelling need for improved water management based on the best models,” says Livermore physicist Philip Duffy, who leads the initiative’s modeling project and is director of the University of California’s (UC’s) Institute for Research on Climate Change and Its Societal Impacts. The goal of the modeling effort is to project future changes in the hydrologic cycle in California and determine how those changes will affect the availability of freshwater. Water managers and policy makers would benefit if such projections were available for assessing proposed changes in water management practices.

“We’re looking at how water supplies are likely to change during the next several decades,” says Duffy. The team’s simulations of future water supplies are done on Livermore’s massively parallel supercomputers. Fortunately, California’s water system is well suited for modeling because most of its supply comes from precipitation or groundwater within the state. Only 5 percent is drawn from out of state (from the Colorado River).

California’s water system is dependent on storage of water in reservoirs and in the snowpack. However, few new reservoirs are being built, and increasing



Water and energy are inextricably linked. Energy production is the second largest consumer of the nation’s freshwater, after agriculture. The treatment, storage, and distribution of water are dependent on readily available energy. The needs for both resources are expected to grow substantially for the next 25 years.

amounts of precipitation are falling as rain, not as snow.

“The only source that feeds reservoirs and rivers in the summer is melting snowpack,” says Duffy. Measurements show that snowpack water levels are dropping as California’s climate continues to warm. If that decrease continues, it could reduce late spring and summer stream flows into reservoirs. And unless the state increases its reservoir capacity, additional water supplies cannot be stored during the winter even if river flow rates increase because of the changing precipitation pattern. Ironically, to protect against flooding, water managers may need to lower water levels in reservoirs, effectively reducing the total volume of water in storage. As a result, less water would be available in summer to support agriculture, hydropower production, fisheries, and recreation, thus compounding the state’s need for increased storage capacity.

### Linking More Detailed Models

To better understand how these changes will affect California’s water supply, Duffy’s team is using a sequence of models, starting with global climate models and ending with surface hydrology models. Each successive model increases the simulation’s spatial resolution, which improves how closely the results agree with observations. “High spatial resolution is even more important for simulating the hydrologic cycle than it is for simulating climate,” says Duffy.

A model with fine resolution can more realistically represent the topographic features of an area and, thus, its surface temperature, which determines whether precipitation is rain or snow. The spatial pattern of precipitation within California is strongly influenced by topographic variations such as coastal hills, inland valleys, and the Sierra Nevada, so surface hydrology models must map topography at a fine resolution to show accurate routes for surface runoff into rivers.

Duffy’s team generates the initial predictions of the sequence using a global climate model run at a spatial resolution of about 75 kilometers. Although this resolution is much finer than typical for global models, it does not provide enough detail for the project. Data from the global climate models are then used to drive two regional climate models, one with a grid size of 9 kilometers and the other with a grid of 36 kilometers. Having results from two models helps the team estimate uncertainties in the model predictions.

Next, the researchers feed surface temperatures and precipitation data from the regional climate model into a surface hydrology model run with a lumped-mode grid—that is, each watershed is treated as one irregularly shaped grid cell. This simulation is designed to predict snow depth, soil moisture, surface runoff, and

most importantly, selected stream and river flow rates. The spatial resolution is fine enough to provide the detailed information needed by water managers who oversee different watersheds.

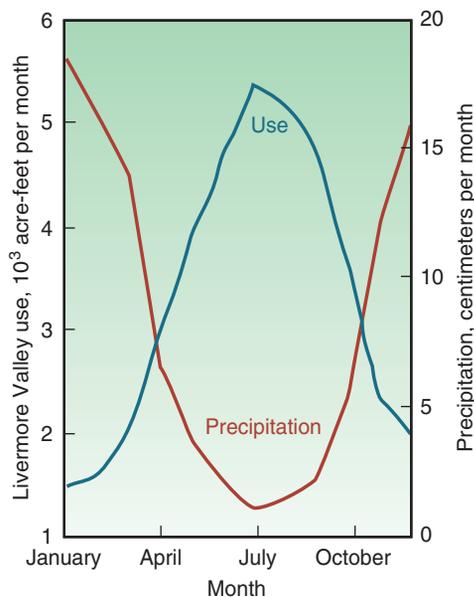
The data generated by the hydrologic model will also be useful for flood control. Because California’s water system is used for both flood control and water storage, water managers need accurate predictions of the maximum values for precipitation, runoff, and river flows as well as the averages over time. That way, they can make informed decisions about how much reservoir capacity is needed to absorb surges in river flow and runoff.

A key component of this project is making the research results useful to water managers and policy makers. “Our approach is to predict exactly the same quantities at the same observation points that water managers use to guide their decisions,” says Duffy. “For example, when we simulate future climate patterns, we’ll predict river flows at locations above major reservoirs. With data from these important reference points, water managers can use the predictions to understand how to operate the water system in an altered climate regime.”

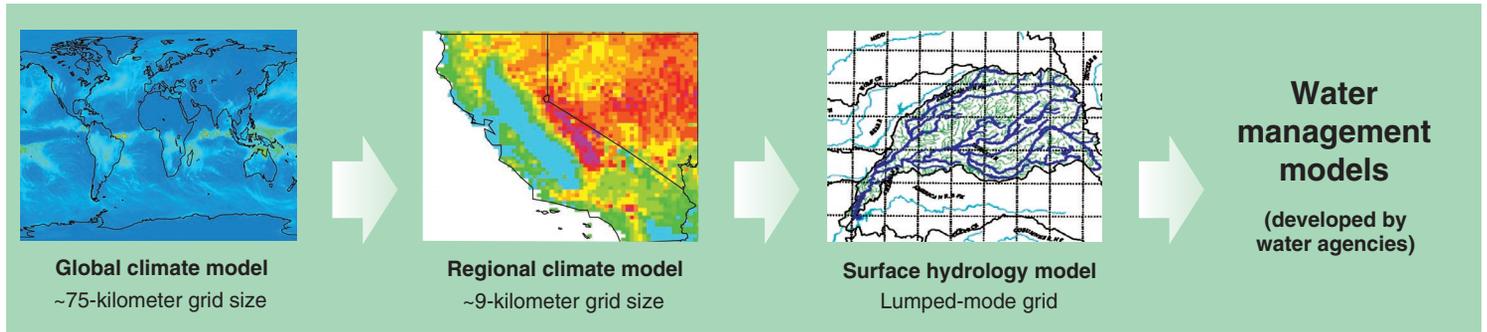
### Estimating Uncertainty

Another emphasis of the project is to estimate the uncertainty in the predictions. “We’re emphasizing the uncertainties both from a research perspective and in response to discussions with water managers,” says Duffy. “They gave us a clear message: ‘Tell us the uncertainties associated with your models.’ One approach is to compare results from a range of accepted models.”

The project team has compared the simulations of present and future climates in California provided by 15 global climate models. These models predict surface temperature, precipitation rate, solid moisture content, water-equivalent snow depth, and other meteorological quantities. Because each model was developed at



Melting snowpack is the only water source for California reservoirs and rivers in summer, when water usage increases. For example, as the chart shows, residents of California’s Livermore Valley (blue line) use the most water during summer—the time of lowest precipitation in the Sierra (red line), where much of the valley’s water originates. (1 acre-foot equals 1,214 cubic meters of water.)



Livermore simulations are being used to project future changes in California’s hydrologic cycle and determine how these changes will affect the availability of freshwater. Researchers use a sequence of models, and each successive model increases the simulation’s spatial resolution. The surface hydrology models are run with a lumped-mode grid—that is, each watershed is treated as one irregularly shaped grid cell.

a different research institution, each one treats climate physics slightly differently. Thus, the models give a range of predictions for both the present and future climates of the western U.S., which provides a measure of uncertainty.

Initial results from this project have led to endorsements by federal, state, and local agencies for a center to address long-term water-supply predictions for California. Such a center would provide projections of regional climate hydrology to water managers, much as the Program for Climate Model Diagnosis and Intercomparison, established at Livermore in 1989, develops methods to validate and compare global climate models. The proposed center would include participants from the major research groups working to improve the science of predicting future water-supply patterns and problems.

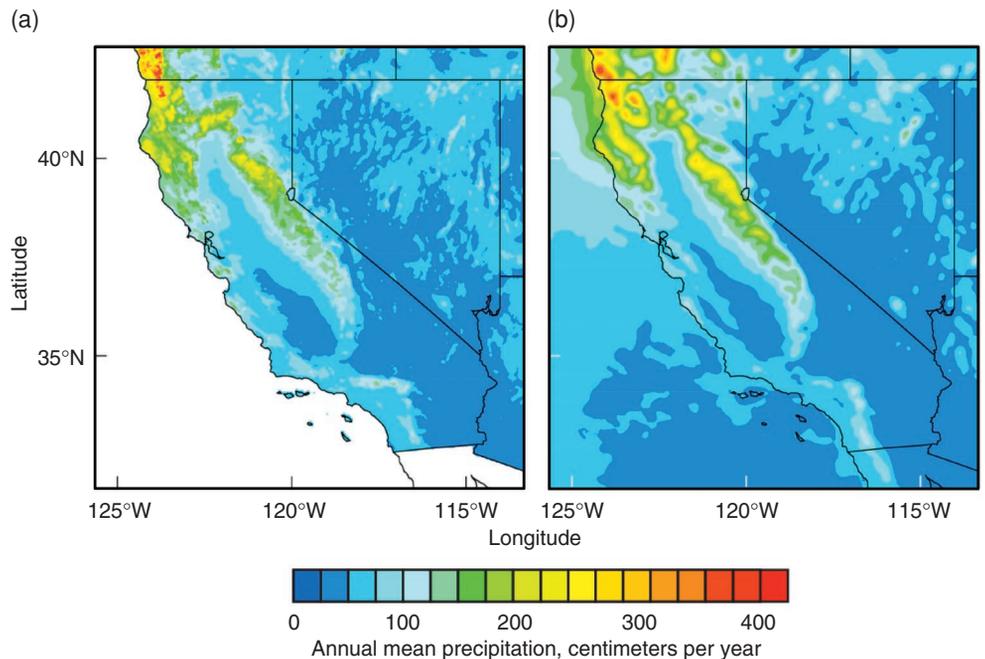
**The Threat of Nitrate Contamination**

One of the most important tasks for California water managers is to protect the purity of groundwater, which supplies about half of the state’s drinking water. However, since 1988, about one-third of the state wells that supply public drinking water have been abandoned, destroyed, or inactivated, frequently because they have been contaminated with nitrate from fertilized farmland, dairies, feedlots, and septic tanks.

Nitrate, a nitrogen–oxygen compound, is a significant source of nitrogen, an essential nutrient. However, high levels of nitrate in drinking water can cause serious illness and sometimes death. Nitrate poses a special risk for infants. It can diminish the oxygen-carrying

capacity of an infant’s blood (called blue baby syndrome), which can lead to death. High nitrate levels can also harm the ecosystems of lakes, streams, and the coastal ocean.

Ten percent of active California public supply wells have nitrate contamination



To validate the accuracy of a computer model, scientists compare the model’s results with observations. In this example comparison, the Livermore team used (a) the observed mean annual precipitation in the western U.S. from 1971 to 2000 and (b) results from a regional climate model of annual precipitation for that same period. The model’s resolution is 9 kilometers.

exceeding the drinking water standard of 45 parts per million, and another 20 percent contain nitrate levels that are significantly above background levels. In agricultural counties, up to 80 percent of groundwater tapped for drinking water is affected or polluted by nitrate. Alternatives such as drilling a new well or treating contaminated water to remove nitrate are costly.

With a better understanding of how nitrate levels in these wells will evolve over time, water managers can decide which approach to use. In addition, their efforts to protect drinking water will be improved if they have more accurate information on how land-use and farming practices affect nitrate levels in groundwater.

The second project of the Water Initiative, which is led by Livermore chemist Brad Esser, is designed to address the nitrate contamination problem. Esser's team is studying the natural processes that control groundwater nitrate movement and degradation. In this effort, the researchers are applying new diagnostic tools and computer models and drawing on Livermore expertise in isotope hydrology, groundwater modeling, and molecular biology. They are studying the problem at the laboratory, farm, and water-basin scales.

### Solubility, Stability Are a Problem

Because of its mobility, nitrate readily contaminates groundwater. Nitrate is mobile because it is soluble and stable in oxygen-rich water and does not bind readily to soils. In oxygen-deficient waters, certain bacteria convert nitrate to molecular nitrogen—a harmless component of the atmosphere—in a process called denitrification. Esser and his colleagues are studying microbial denitrification under laboratory and field conditions, so they can determine a groundwater basin's capacity to assimilate nitrate and understand how nitrate distributions will evolve over time.

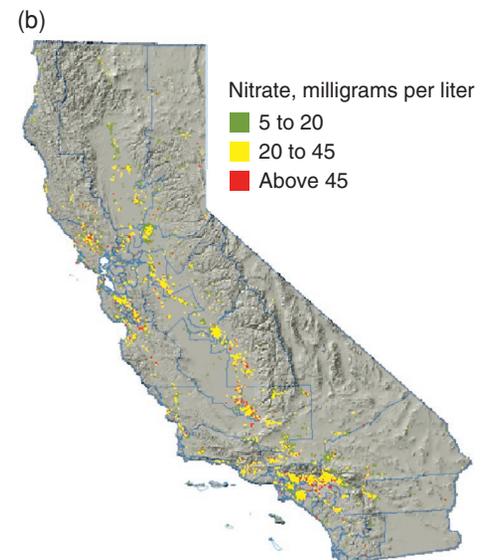
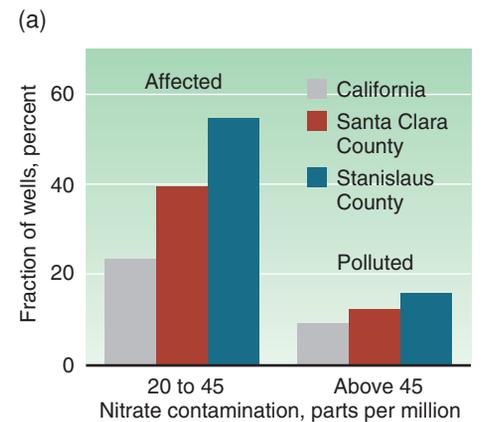
“We are developing better tools to detect and understand denitrification,” says Esser. For example, one test is designed to determine whether bacteria capable of denitrification are present and if they are removing groundwater nitrates. The test detects a gene in the bacteria that indicates the presence of enzymes responsible for the process. In addition, Livermore scientists have developed a mass-spectrometry method to quantify the amount of nitrogen that has dissolved in groundwater as a result of denitrification. The two tests allow researchers to study what factors control the rate of denitrification in groundwater.

Water managers also need to know the source or sources of nitrate contamination. For example, if the source is septic discharge, then converting septic tanks to sewer lines will be more effective than implementing a farm fertilizer management program. Esser notes that many water contaminants, such as trichloroethylene, are found in high-concentration plumes with easily identified sources. Groundwater nitrate contamination, however, is often low-level and pervasive, reflecting multiple sources such as septic systems or synthetic fertilizer or manure used on crops, so identifying nitrate sources is more difficult.

To understand groundwater flow paths and trace contaminants such as nitrate back to their source, the Livermore team is combining an isotopic technique to determine groundwater age (see *S&TR*, November 1997, pp. 12–17) with groundwater flow models that take advantage of the Laboratory's supercomputing capability (see *S&TR*, June 2001, pp. 13–21).

For this project, the team is working with colleagues from the UC Cooperative Extension and UC Davis in a study of a dairy farm in California's Central Valley. The scientists are installing multilevel monitoring wells to determine groundwater flow paths and to understand nitrate transport and denitrification.

The team is also working with the Santa Clara Valley Water District to characterize nitrate transport in the Llagas basin, a primary source of the groundwater needed to meet future demands in southern Santa Clara County. The basin has pervasive nitrate contamination in shallow aquifers but little contamination in deep aquifers.



(a) About 10 percent of active California public water-supply wells have nitrate contamination exceeding the drinking water standard of 45 parts per million. In agricultural areas, such as Stanislaus County, up to 80 percent of groundwater is affected or polluted by nitrate. (b) The map shows the extent of nitrate contamination throughout the state.

“Deep wells in the basin do not contain nitrate either because denitrification is occurring or because the deep water is old and uncontaminated,” says Esser. “We’d like to determine which process is at work here. We also want to identify the source of nitrate in the basin’s shallow wells.”

For this project, the Livermore scientists are using geochemical models to identify input of nitrate from synthetic fertilizer and developing analytical methods to distinguish septic discharge from manure as sources of groundwater nitrate. So far, they are finding that shallow wells contain young water, whereas the deeper water is older and oxygen deficient. However, they have found no evidence of denitrification under current conditions, indicating that nitrate contamination has not yet penetrated deeper parts of the basin.

The researchers are incorporating these data into a highly resolved three-dimensional (3D) model of Llagas basin groundwater flow and transport. The flow field is based on a 3D geostatistical model of sediment distribution that is derived from drilling logs of more than 300 wells. Results from these simulations will be used to develop groundwater resources in the basin and protect the basin from future nitrate contamination.

### Creating “New” Water

Many wells closed by nitrate contamination could be reopened if a cost-effective treatment were found. One significant cost of the water treatment technologies developed in the 1960s and 1970s is their high energy use. For example, one-half the overall cost of seawater desalination using reverse

osmosis is the cost of energy. Another treatment technology, electro dialysis, is more energy efficient at removing salt from less saline, or brackish, waters. However, even electro dialysis is not a cost-effective treatment method for the growing volumes of marginally impaired waters—those that contain small concentrations of one or more contaminants but are otherwise adequate for domestic use. A better approach would be selective technologies designed to extract only a few problem species, which would reduce both the volume of the waste stream and the overall energy cost for treatment.

The third project of the Water Initiative is focused on providing a cost-effective option for treating these marginally impaired waters. If successful, the new technology would undoubtedly help increase water supplies everywhere. In this project, lead investigators geochemist Bill Bourcier and engineer Kevin O’Brien are creating energy-efficient membranes to replace the solid polymer membranes used in electro dialysis. This approach taps Livermore’s capabilities in computational chemistry and nanomaterials synthesis. Says Bourcier, “We want to use it to treat brackish water in a way that sharply lowers operating costs.”

In electro dialysis, transport of either positively charged ions (cations) or negatively charged ions (anions) through copolymer membranes is driven by a voltage applied by a pair of flat electrodes. The ions are driven toward the electrode with the opposite charge. Water flows between alternate cation-permeable and anion-permeable copolymer membrane sheets sandwiched between the electrodes and separated by spacers. As water flows between the membranes, salt is removed from one compartment and concentrated in adjacent compartments, with up to a hundred or more membrane pairs per stack. A manifold separates the exiting fluid into a relatively salt-free permeate product and a salt-enriched brine for disposal.



Livermore researchers are installing a network of multilevel monitoring wells near a dairy farm in California’s Central Valley so they can study the groundwater flow paths, nitrate transport, and denitrification. The arrow shows the direction of groundwater from an irrigation canal toward the monitoring wells. Manure used on crops is one possible source of nitrate found in groundwater.

The current electro dialysis technology is inefficient because it forces all dissolved ions, including those that are considered benign or healthy, through the solid membranes. The Livermore team is replacing these membranes with “smart” membranes of polycarbonate—the material used to make compact disks—which are then coated with a thin layer of gold. (See the **top left figure** on p. 12.) These smart membranes can be designed to selectively remove only one contaminant of interest by specifying the pore size, voltage, and electric field to attract the target contaminant. For nitrate cleanup, a small fraction of a volt will be applied to each membrane, and the overall electric field will measure 1 to 2 volts per membrane pair.

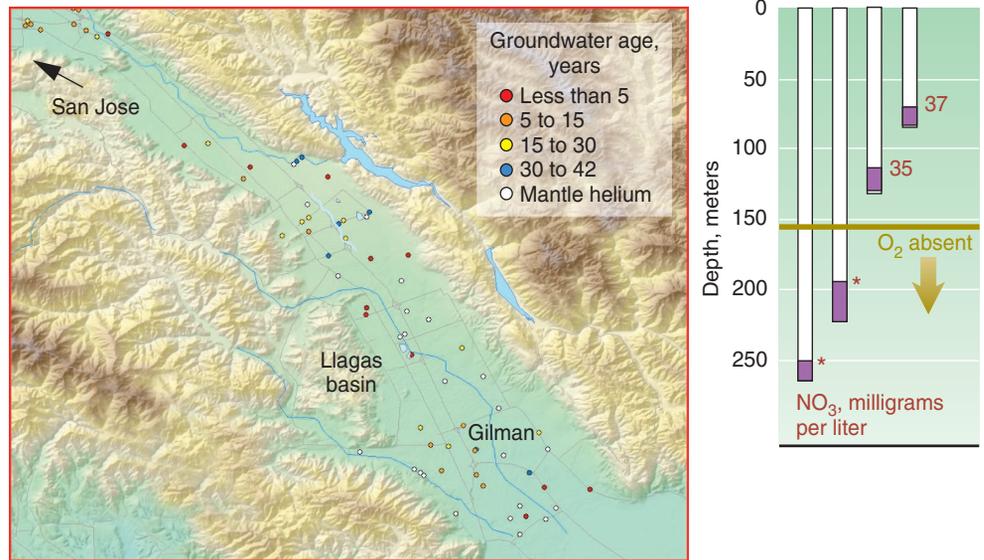
“With current electro dialysis design, every ion is pushed through a solid plastic membrane that has high electrical resistivity and no selectivity,” Bourcier says. “The smart membrane is designed to have low resistivity to ion transport and, therefore, high energy efficiency—up to 50 percent greater than standard electro dialysis.”

**Pores Drilled in Smart Membranes**

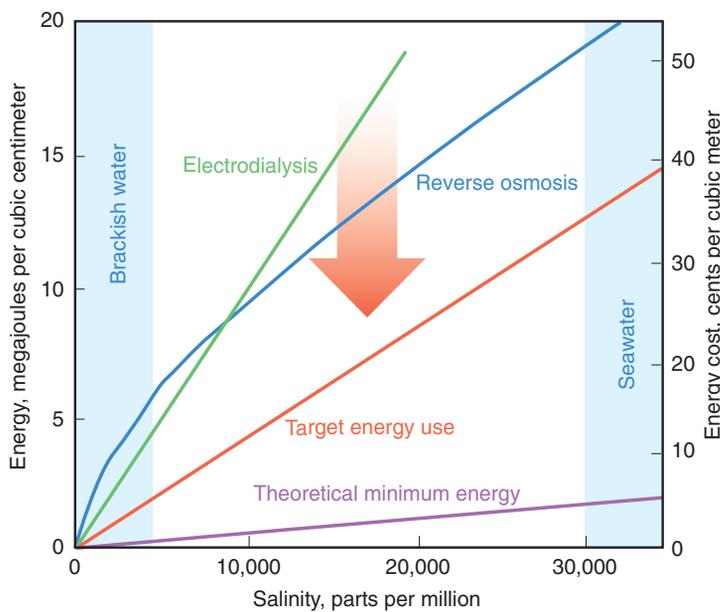
The membranes have pores drilled to an optimal size for selective removal of the ions of interest. If the system is optimized for nitrate ions, for example, those ions will preferentially pass through the pores, while others remain with the stream of water. The nitrates can then be collected in the waste stream.

The pores are created with an etching process using Livermore’s ion-beam technology. For nitrate treatment, the membrane pores are about 10 nanometers in diameter. (See the **bottom left figure** on p. 12.) Current polycarbonate membrane samples contain about 1 billion holes per square centimeter.

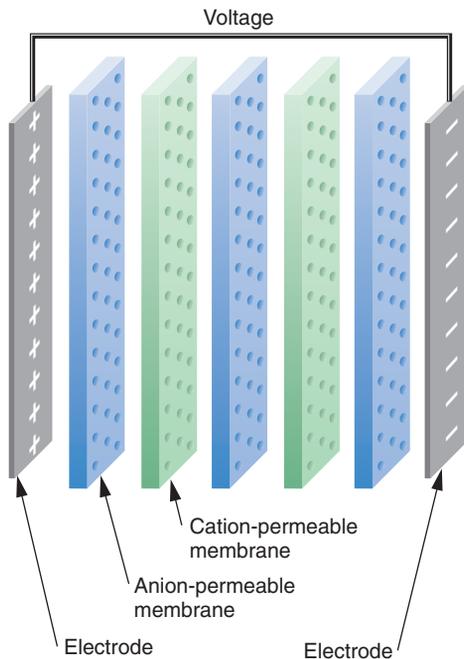
Membranes are being designed using quantum mechanical modeling, which simulates the ions of interest in electrolyte solutions in varying concentrations. The modeling work, which is done on



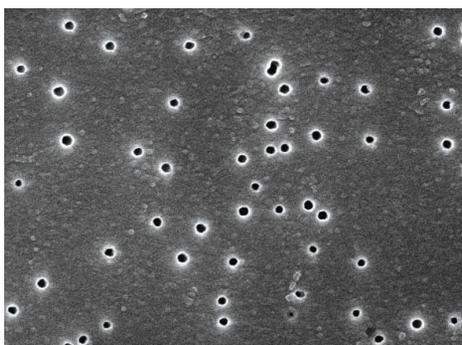
Livermore is characterizing the Llagas groundwater basin, which is managed by the Santa Clara Valley Water District. As shown in data from wells at one location (Gilman), the basin has pervasive nitrate (NO<sub>3</sub>) contamination in shallow aquifers but little contamination in deep aquifers, where oxygen (O<sub>2</sub>) is absent. (\* = less than 1 milligram per liter.)



Livermore researchers are evaluating a modified electro dialysis setup to lower the energy costs for this process by 50 percent. If the goal is met, electro dialysis would become a much more important technology in treating brackish water.



Livermore's modified electrodialysis technology replaces the solid polystyrene membranes with "smart" membranes of gold-coated polycarbonate. By specifying the pore size, voltage, and electric field that will best attract and isolate a target contaminant, researchers can design each membrane to selectively remove only one contaminant of interest.



This image shows a smart membrane with pores drilled to 10 nanometers in diameter—the size needed for nitrate ions to pass through.

supercomputers and led by physicist Bill Wilson, uses a numerical method for calculating the electrostatic field in the vicinity of the charged membrane pore surfaces. The modeling takes into account an ion's unique 3D geometry and electronic charge distribution. Its motion through the membrane is determined by potentials applied to the membrane elements. The modeling results determine the pore size and the optimum voltage to be applied to the membrane. "Water purification research has always been an empirical field," says Bourcier. "We're modeling the membranes before they are manufactured to avoid a lot of trial and error."

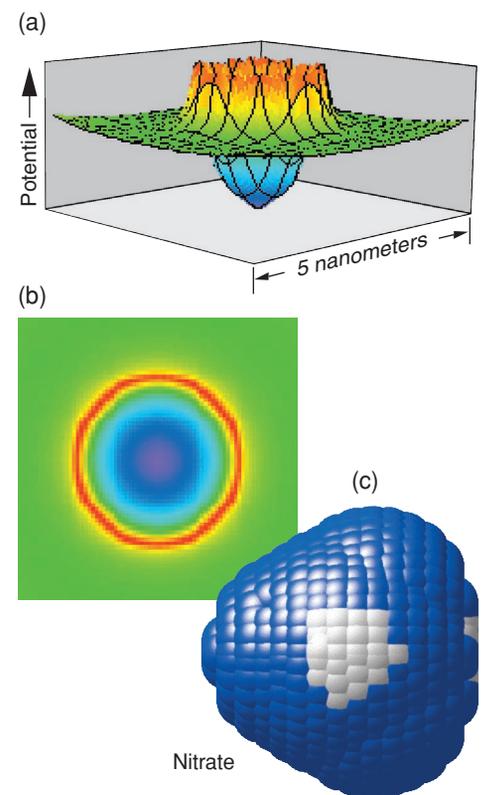
The project team also wants to research contaminants besides nitrate. Many community wells do not meet the new lower limits for arsenic, but treating them with reverse osmosis would cost millions of dollars. Electrodialysis with smart membranes could be a viable alternative. Other contaminants of interest include perchlorate, a by-product of rocket fuel that is found in Santa Clara County groundwater, and selenium, a natural element found in Central Valley groundwater and elsewhere.

Within a year, the researchers plan to test a prototype unit in the field, and they are evaluating potential demonstration sites. Bourcier believes that the technology will be capable of purifying a metric ton of water for 20 cents in energy costs, half of current costs. In addition, large-scale smart membrane manufacturing would cost less than a dollar per square meter.

The team is confident the pores also could be used to trap minor contaminants, such as perchlorate molecules, which typically are present in parts-per-billion concentrations. For those applications, the voltage applied to the membranes would be turned up to electrochemically destroy the perchlorate molecules and, thus, eliminate any waste stream.

In a similar manner, a membrane could be designed to selectively remove

viruses and then deactivate them. Bourcier foresees specialized membranes for the military, such as a unit mounted on a Humvee to purify brackish water for troops in the field, or membranes designed to remove chemical and biological warfare agents from water. The technology could also be used to purify the wastewater from the production of oil, gas, and coal and to recover metals in industrial wastewater and in silicon chip manufacturing. "There are



Quantum mechanical modeling is being used to design the smart membranes. (a) A simulation of a smart membrane pore shows the strong electric field gradients near the pore surface, where blue is the lowest voltage and red is the highest. The electrostatic forces will induce a nitrate molecule to pass through the pore where the molecule can be collected in a waste stream. (b) The same gradient is shown from the top, looking down on the pore. (c) This model shows the charge distribution of a nitrate ion, where the white area denotes an area of negative charge.

many tricks we can try,” says Bourcier. “If we’re successful, we’ll see much greater use of electro dialysis.”

### California Again Leads the Nation

Newmark says she is seeing results from early progress of the Water Initiative. For example, Livermore researchers have received letters of endorsement from many water districts and agencies. “Successful development of these tools and methods may revolutionize the options water managers have to address the challenges facing them.”

Although the immediate focus is California, the Livermore tools and methods can be applied anywhere in the nation. The state, Newmark says, is akin to “a canary in a coal mine” because looking at California’s water picture is like looking at America’s water future.

—Arnie Heller

**Key Words:** denitrification, electro dialysis, global climate change, hydrologic cycle, Laboratory Directed Research and Development, nitrate contamination, water purification.

**For further information contact**

**Robin Newmark (925) 423-3644**

**([newmark1@llnl.gov](mailto:newmark1@llnl.gov)).**