

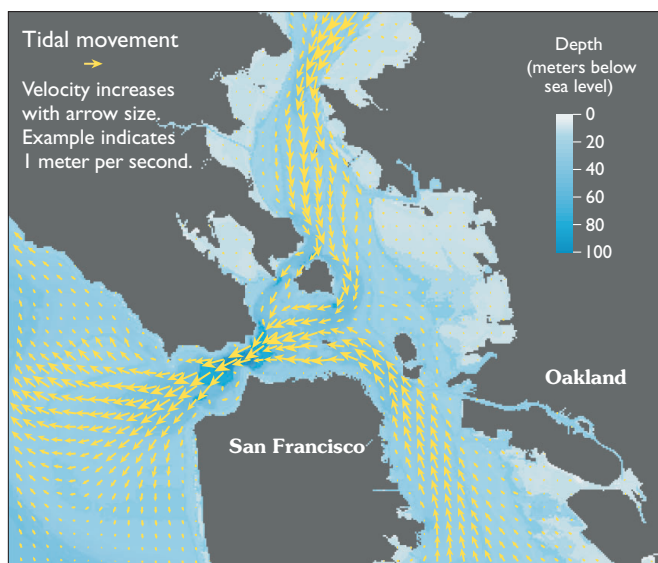
# Sustained Progress in Estuarine Studies—San Francisco Bay

Many economically and ecologically important estuaries in the United States have been influenced by intense human activity. The problem of distinguishing changes that are natural from those caused by humans is critical in these coastal regions where dense populations and diverse human activities alter ecosystems. The San Francisco Bay has served as an estuarine laboratory for the USGS since 1968. Sustained, multi-disciplinary studies are being used to examine the effects of climate; wind; tides; river flow; water-mixing processes; urban, industrial, and agricultural area runoff; waste disposal; and the invasion of exotic (non-native) species on the water quality and ecosystem functioning of this estuarine system. USGS research, which is conducted in cooperation with other scientists, is used to examine processes in time scales that range from seconds to decades.

## Flow and Circulation

Hydrodynamic data have been used to develop models that describe tidal- and river-in-flow driven estuarine circulation patterns. For example, in collaboration with the National Oceanic and Atmospheric Administration (NOAA), real-time data, such as wind and currents, are being used in a numerical model, TRIM (Tidal, Residual, Intertidal, Mudflat), that provides a means to track the effect of tides and currents in the Bay. This model is particularly suitable to coastal plain estuaries and tidal embayments in which tidal currents are dominant. A useful application

of the model was to predict the trajectory of oil from the 200-barrel tanker spill of October 1996. This collaborative program represents a critical integration of emerging technologies and includes the California Office of Oil Spill Prevention and Response; the San Francisco Bar Pilots Association; the Ports of Oakland, Richmond, and San Francisco; the Marine Exchange of the San Francisco Bay Region; and the U.S. Coast Guard.



*In collaboration with NOAA, wind and tidal observations in San Francisco Bay are entered into a computer model and used to predict current velocity, which is shown here along with water depth. Observations from the past 24 hours are used to predict conditions for the next 24 hours, providing information needed by maritime pilots and for emergency oil-spill response.*

Real-time data and the interactive model are on the Internet at <http://sfports.wr.usgs.gov/sfports.html>

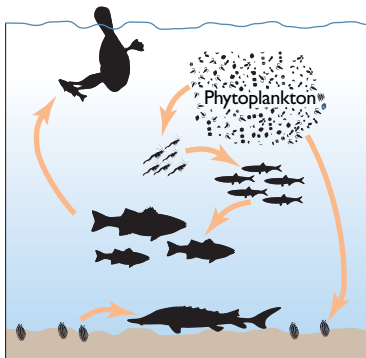


## Exotic Species

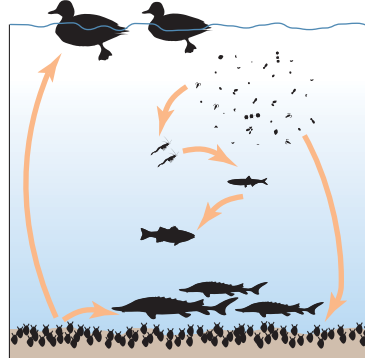
The introduction of exotic species is a particular problem in coastal environments where organisms are redistributed through ballast water from commercial shipping. Within months of its first detection in October 1986, the Asian clam, *Potamocorbula amurensis*, became the most abundant benthic organism in the northern part of the

Bay. An efficient filter feeder, it has caused a decrease in abundance of small planktonic species upon which it feeds and in other species that compete with it for planktonic food. The clam has survived a wide range of conditions, including salinity changes caused by a severe 6-year drought and a record flood, and has become a permanent resident of the Bay. The result has been a major change in the food web of the upper estuary with reduction of phytoplankton abundance and possible detrimental effects on important native species such as shrimp and fish. A key finding is that *P. amurensis* concentrates contaminants in its tissues and represents a major vector for the transfer of contaminants to the fish and bird species that feed upon it. This case study demonstrates how, on a local scale, the functioning of large ecosystems can be greatly altered by species invasions and how, on a worldwide scale, modern coastal and estuarine faunas are becoming homogeneous and how native communities are being threatened.

Food web before *Potamocorbula* invasion



Food web after *Potamocorbula* invasion



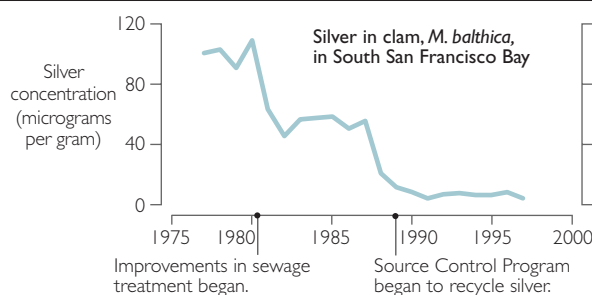
Aquatic systems like San Francisco Bay can be dramatically affected by the proliferation of exotic species. *Potamocorbula amurensis*, a clam believed to have been introduced in the ballast water of a cargo ship from China, has changed the composition and distribution of the biota in the Bay. Its invasion has caused a decline of species that compete with it for phytoplankton as a food source, whereas species that feed on *P. amurensis* are benefiting from an increased food source.

## Water Quality

The collection and use of comprehensive, long-term data sets have made it possible to progressively attack difficult problems related to changes in water quality in the Bay. One example is the use of data collected by sampling sediments and organisms near the South San Francisco Bay outfall of the Palo Alto Wastewater Treatment Plant. In the late 1970s, scientists demonstrated that there was substantial contamination in the aquatic biota (clams, mussels, snails) from potential toxins. Copper and silver were at concentrations that had a measurable effect on the sur-

vival and reproduction of a resident invertebrate species and probably represented a threat to other aquatic organisms in the Bay, and to mammals and birds in a nearby marsh refuge. Improvements in the treatment plant (equipment and operations), begun in 1980, resulted in a consistent decrease in contamination of both sediment and aquatic organisms.

Water-quality data is on the Internet at <http://sfbay.wr.usgs.gov/access/wqdata/>  
It is the longest continuous dataset for an estuary in the United States



In 1976, samples collected near the Palo Alto sewage treatment plant in South San Francisco Bay indicated elevated concentrations of silver. Improvements in treatment processes and a Source-Control Program—to encourage the electronics industry to recycle silver—decreased concentrations of silver. By 1995, silver concentrations in clams 1 kilometer from the plant discharge had decreased a hundred-fold compared to the originally observed concentrations.

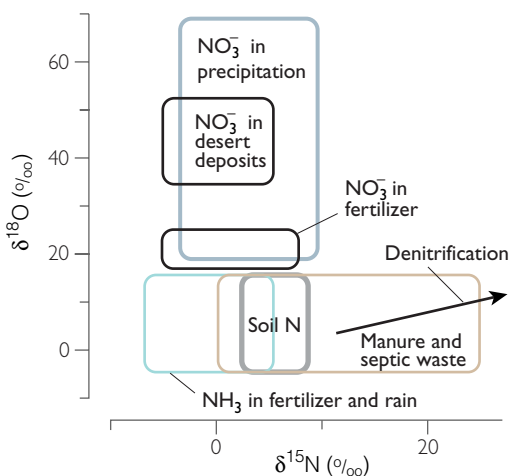
# Use of Environmental Tracers to Track Nitrogen Contamination

Environmental tracers are useful to determine sources of specific constituents, such as nitrate in an aquifer, and to understand how processes affect the distribution, transformation, and removal of constituents. Common environmental tracers are specific compounds introduced into the atmosphere and hydrosphere, such as chlorofluorocarbons (CFCs), and isotopes of certain elements. The stable isotopes of nitrogen are particularly useful to investigate the effect of human activities, such as the use of nitrogen fertilizers. Investigating the sources of nitrogen-containing species, such as ammonia, nitrite, and nitrate, using isotopic tracers can provide information that affects decisions about stream and ground-water quality. Biologically mediated reactions (assimilation, nitrification, and denitrification) are known to strongly affect the isotopic ratios of nitrogen. On a global scale, nitrate is one of the most prevalent contaminants in ground-water systems, and thus it is essential to understand the processes that generate nitrate and the mechanisms that affect its transport, dispersion, and transformation or removal within surface-water/ground-water systems.

## Stable Isotopes

A major activity in recent years has been to develop analytical methods and conduct field tests for the combined use of nitrogen (N) and oxygen (O) isotopes to distinguish sources of nitrate. For example, N and O isotopic data may be used in some circumstances to determine if nitrate in ground water is derived predominantly from precipitation, manure spreading, or artificial fertilizer applications. Also, correlations between nitrate concentrations and isotopic compositions may be used to delineate regions of mixing or denitrification (natural remediation by microbial reduction of nitrate to nitrogen gas). Another isotopic approach used in studies of nitrogen transport and reaction is to add small amounts of  $^{15}\text{N}$ -enriched ammonium or nitrate to streams, aquifers, or soils and to monitor the distribution of the  $^{15}\text{N}$ -enriched tracer and its reaction products. By using these techniques it is possible to measure rates of nitrification and denitrification reactions that are too slow to be detected by chemical methods. Rates of reaction determined by these field (*in situ*) tracer methods, which are designed to cause relatively little disturbance to the aquifer conditions, often differ significantly from rates determined from some types of laboratory experiments. A site with a 4-kilometer plume of contaminated ground water on Cape Cod, Massachusetts, has been used to compare *in situ* rates of microbial denitrification with rates from laboratory experiments. A comparison of results indicated that the laboratory rates of denitrification are 1.2

to 13 times higher than *in situ* rates. Realistic estimates of reaction rates and how they change with time are essential for accurate assessment of natural remediation processes.



This schematic shows typical ranges of  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  values of nitrate from various sources. It appears possible, for example, to distinguish atmospheric nitrate (in rain or snow) from most other sources because it has an unusually high  $\delta^{18}\text{O}$  value. Likewise, variations in  $\delta^{15}\text{N}$  values are particularly useful for distinguishing fertilizer nitrate sources from animal waste sources, such as manure and wastewater disposal.  $\delta$  notation is an expression of the abundances of two isotopes for a given element relative to a standard; given in parts per thousand (‰).

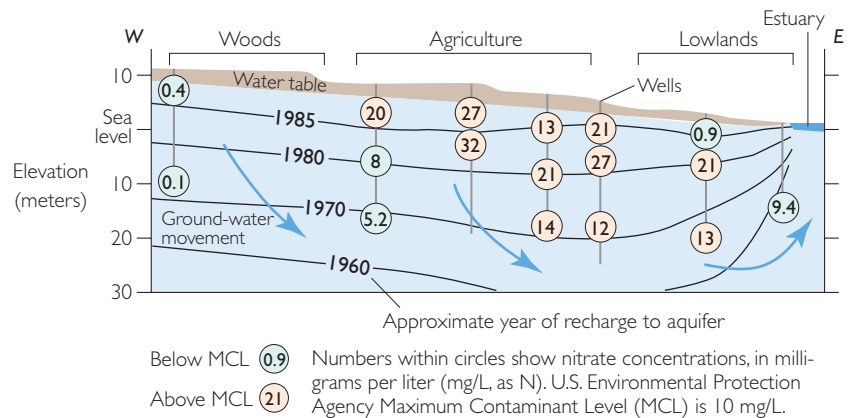
This stable isotope ratio mass spectrometer is used to analyze solid materials for carbon, nitrogen, and sulfur isotopes. Powdered samples are loaded and are automatically analyzed for isotopic composition.



## Agricultural Contamination

The combined use of isotopic measurements and dating of ground water using CFCs (described below) was applied to agricultural areas in eastern Maryland to determine the sources of nitrate and examine its removal by denitrification. Most of the nitrate in the streams is from agricultural runoff and ground-water discharge. The history of nitrate contamination of ground water was derived from records of fertilizer use and analyses of water samples that were dated using CFCs. The nitrate concentrations in streams were then related to both the age distribution of the discharging ground water and to geologic settings of the local drainage systems. Although forested riparian zones (areas adjacent to and impacted by streams) commonly are thought to remove nitrate from ground water approaching streams, recent studies involving environmental tracers and isotopes indicate that nitrate-rich ground water can bypass riparian interactions, in some cases by following relatively deep flow paths (tens of meters). The study in eastern Maryland indicated that the riparian zones may not be effective in removing nitrate from ground water that follows relatively deep flow paths before converging and

discharging upward to streams. Results from applying these techniques to small agricultural watersheds in the Delmarva Peninsula in Maryland and Delaware indicate that many years may be needed to flush the high-nitrate water in ground water that discharges to streams and drains into the Chesapeake Bay and the Atlantic Ocean.



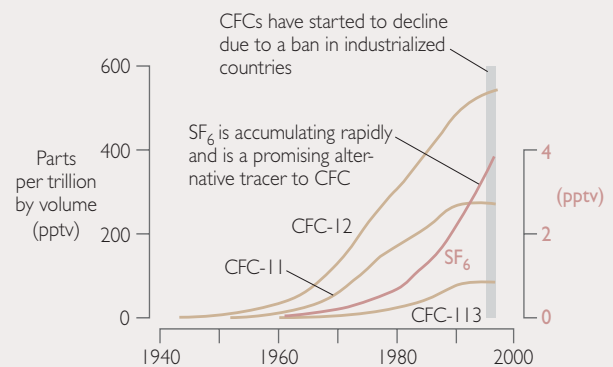
The cross section on the Delmarva Peninsula, Maryland, is about 6 kilometers from the wooded uplands to the lowlands and ground-water discharge area. The history of nitrate contamination was derived from isotopic measurements and dating of water using chlorofluorocarbons.

### Use of Chlorofluorocarbon (CFC) Concentrations to Date Ground Water

The dating of ground water can be used to help define the direction and velocity of ground-water flow and residence times. CFCs (known as Freon™) are useful compounds to date ground water because they were released to the atmosphere in increasing amounts from about 1930 to 1990. Three CFC compounds were used to determine recharge ages.

The presence of CFCs in ground water indicates that the water was recharged during the past 50 years or is a mixture of old and young water. The use of CFCs to date ground water is possible because (1) the amount of CFCs in the atmosphere over the past 50 years has been reconstructed, (2) their solubilities in water are known, and (3) concentrations in air and young water are high enough to measure. Today the USGS procedure is used in many areas throughout the Nation as well as in other countries to provide a sensitive tracer of recent recharge. In general, CFC dating is most successful in rural settings, with shallow water tables, where the ground water is aerobic and is not impacted by local contaminant sources. Where CFC dates agree with another method, such as tritium/helium-3, or where all three CFCs (CFC-11, CFC-12, and CFC-113) indicate similar ages, considerable confidence can be placed in the apparent age. Because

atmospheric concentrations of CFCs have begun to decrease, USGS scientists are exploring alternative methods for dating young ground water, such as dating with sulfur hexafluoride (SF<sub>6</sub>), a compound that began to be used in the 1960s in high-voltage electrical switches.



CFCs and sulfur hexafluoride (SF<sub>6</sub>) concentrations (mixing ratios) for air over North America during the last 50 years

Information about dating of young ground waters is on the Internet at <http://water.usgs.gov/lab/cfc/>

# Ground-Water Movement in Fractured Rock

In parts of the United States and other countries, water from fractured rock is a primary source of drinking water. Once contaminants enter fractured-rock systems, they are very difficult to find and remove because most of the ground-water movement occurs in complex networks of fractures. To better understand how water and dissolved substances move in fractured rock, studies were started in 1990 near Mirror Lake, New Hampshire. The Mirror Lake research site has been used by USGS and university scientists to conduct one of the most comprehensive studies of flow and transport for environmental assessments in a fractured crystalline rock terrain, and to develop the tools needed to understand complexities of ground-water flow and chemical migration.

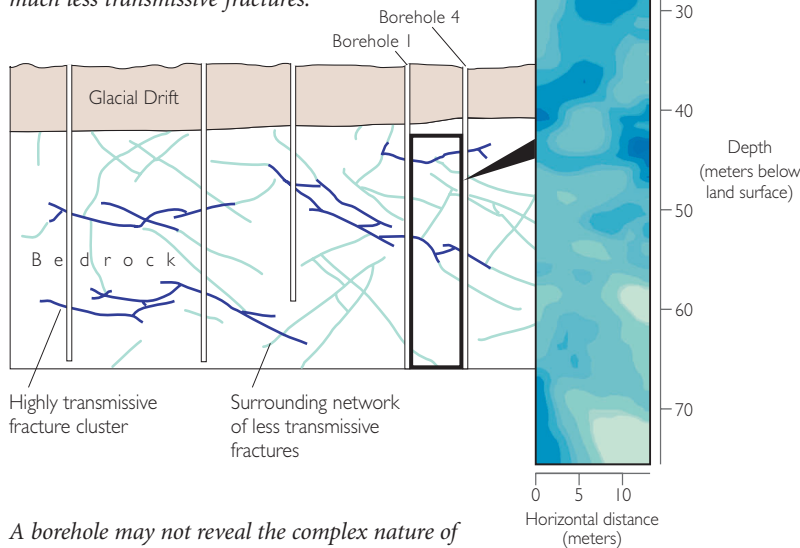
## Flow and Transport

At the Mirror Lake site, boreholes were drilled at two intensely studied portions of the area, and about 20 other boreholes were drilled throughout the larger Mirror Lake Basin. The wellfields in the intensely studied areas were used to characterize fracture flow on scales of 100 meters and smaller, whereas boreholes scattered across the basin provided insights into kilometer-scale properties and characteristics. This dual approach was adopted to address one of the fundamental questions hydrogeologists ask about fractured-rock terrains: how does one apply small-scale measurements from borehole tests to solve large-scale flow and transport problems?

Wellfields in the intensely studied areas were characterized by single and multiple well hydraulic tests integrated with surface and borehole geophysics, such as seismic and electromagnetic tomography, borehole television, and ground-penetrating radar. These techniques are used to determine the spatial distribution of highly transmissive fractures and the hydraulic conductivity of these fractures. Hydraulic conductivity is a measure of the ease with which water moves through the rock, where larger hydraulic conductivity implies the potential for larger volumes of ground-water flow. Investigations at the wellfields yielded an unanticipated result—flow takes place in clusters of highly transmissive fractures that are themselves interconnected by networks of much less transmissive fractures. The clusters have hydraulic conductivities of  $10^{-5}$  to  $10^{-4}$  meters per second, whereas that of the connecting fracture network is about  $10^{-7}$  meters per second. It was discovered that cross-borehole geophysical techniques, such as electro-

magnetic tomography, may help locate the more transmissive fractures between boreholes. Results from a numerical simulation of ground-water flow over the entire Mirror Lake Basin yielded an estimated hydraulic conductivity of  $10^{-7}$  meters per second, similar to that of the less transmissive fractures in the wellfield studies. This indicates the network of less transmissive fractures controls the volume of ground-water flow at the kilometer-scale.

*The bedrock at the Mirror Lake site is characterized by clusters of interconnected highly transmissive fractures forming horizontal permeable regions that are themselves connected by networks of smaller, much less transmissive fractures.*



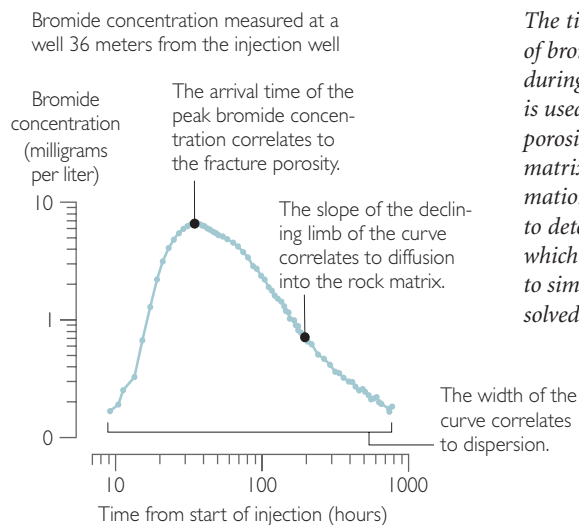
*A borehole may not reveal the complex nature of the ground-water flow through the horizontal clusters, but seismic tomography reveals the presence of the highly transmissive fractures (darkest colors) between boreholes 1 and 4. Tomography is done using a movable energy source in one borehole and multiple receivers in the other borehole, mimicking the technique used in medical CAT scans.*



## Flow Velocities

Hydraulic conductivity indicates the volume of water that the rock can transmit but does not reveal the ground-water velocity, a quantity that controls the movement of contaminants. It is the porosity of the fractures (fracture volume per total volume of the rock) that controls the ground-water velocity. For a given volume of water moving through the rock, a smaller porosity implies a smaller fracture volume, and the potential for a larger ground-water velocity. At the Mirror Lake site, fracture porosity is estimated by conducting controlled tracer tests in the wellfields, where a known mass of a dissolved constituent is injected into the rock and its arrival is monitored at other locations. Tracer tests can also be used to estimate diffusion into the rock matrix and dispersion (spreading due to variations in the water velocity). By using estimates of fracture porosity from the wellfield tests, the ground-water velocity at the kilometer-scale is estimated to be about 50 meters per year, which would imply significant travel distances for naturally occurring constituents in precipitation, such as CFCs (described in the box on p. 7) and tritium ( $^3\text{H}$ ). Concentrations of CFCs and  $^3\text{H}$  in water samples collected from wells in the Mirror Lake Basin, however, are significantly

reduced in relation to their initial concentration in precipitation, indicating the important role that diffusion into the rock matrix and dispersion will play in characterizing contaminant migration at fractured rock sites. The application of these results and field techniques will help us understand how to manage and apply remediation technology at contaminated fractured-rock sites.



*The time-varying concentration of bromide in a collection well during a controlled tracer test is used to estimate fracture porosity, diffusion into the rock matrix, and dispersion. Information from tracer tests is used to determine these parameters, which are then used in models to simulate the transport of dissolved constituents.*

### Computer Simulation

The USGS has been a leader in the development of hydrologic and geochemical simulation models since the 1960s. USGS models are widely used to predict responses of hydrologic systems to changing stresses, such as changes in precipitation or ground-water pumping rates, as well as to predict the fate and movement of solutes and contaminants in water.

Some recent major advances in computer models include:

BIOMOC — a multi-species solute-transport model with biodegradation

MOC3D — a three-dimensional Method-of-Characteristics solute-transport model

MODFLOW-GUI — a graphical user-interface for the USGS modular three-dimensional finite-difference ground-water flow model (MODFLOW)

MMS — set of modular modeling tools that provide a framework to incorporate a variety of models and thus create an “optimal” model that can be used, for example, in watershed management

PHREEQCI — graphical user-interface for PHREEQC, a program for speciation, reaction-path, advective transport, and inverse geochemical calculation

SUTRA-GUI — a graphical user-interface for the USGS code, SUTRA, a saturated-unsaturated zone model with energy or reactive species transport

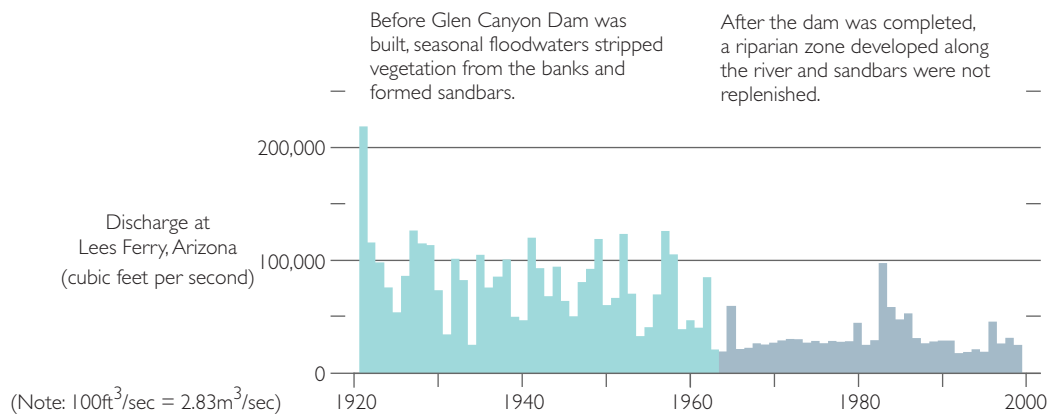
UCODE — a universal parameter estimator designed for use with any model

VS2DH — a program to simulate energy transport in variably saturated porous media—a modification of the USGS computer program VS2DT for solute transport

USGS models are available for free on the Internet at  
<http://water.usgs.gov/nrp/models.html>

# Modeling and Experimental Flooding in the Grand Canyon

The USGS has a strong commitment to understand and predict flow and sediment transport in rivers, including the impacts of dams, the processes responsible for building and eroding sand bars, and the manner in which sediment is supplied to the river systems. The knowledge gained from these studies is being applied to a problem on the Colorado River in Grand Canyon National Park. In 1963, Glen Canyon Dam was constructed about 24 kilometers upstream from the Park boundary at Lees Ferry, which is the launch point for boating trips through the Grand Canyon. Prior to the dam, the river's floodwaters prevented growth of vegetation on the channel banks, deposited sand bars, and eroded boulder deposits in the main channel left by flash floods in tributaries. After the dam was completed and most large floods were controlled, a riparian zone developed along the river, marshes were formed, sand bars eroded, and boulders were left in the main channel. By the mid-1970s, river runners expressed concern about eroding sand bars that were used as campsites. In 1978, the U.S. Fish and Wildlife Service concluded that Glen Canyon Dam and its operation were jeopardizing an endangered fish, the humpback chub (*Gila cypha*). These findings led the U.S. Bureau of Reclamation to establish the Glen Canyon Environmental Studies, which organized and supported research in Grand Canyon starting in 1983.



View upstream of the Colorado River at Carbon Creek (mile 64) in Grand Canyon. Sediment deposition in the eddy formed by the Carbon Creek debris fan was studied intensively during and after the 1996 controlled flood.



## Modeling

The first step in understanding the impacts of Glen Canyon Dam on the Colorado River was to develop a conceptual model linking flow, sediment movement, and river channel morphology. Sediment sources also were investigated to understand how sediment particles are redistributed with change in flow. All upstream sediment supply was cut off by the dam. However, the two major tributaries downstream from the dam, the Paria River and Little Colorado River, supply nearly 20 million tons of sediment in an average year. Once the rudiments of the post-dam sediment budget were understood, it was realized that in most years there would be enough sediment in the channel downstream from these tributaries to redeposit eroded sand bars. However, to move the sediment, the river discharge (stage) had to increase

enough to entrain sediments from the river channel and deposit the sands at higher elevations along the channel margins. Relatively low regulated flows are insufficient to deposit sediment bars. Periodic flooding is required to manage sediment deposits and achieve some resemblance to the pre-dam condition. Models were refined to incorporate additional information as the channel geometry of the river became better known, and experiments were performed in laboratory flumes. Hydrologic modeling and the observation of channel morphology over a number of years led scientists to predict that flood flows greater than 33,000 cubic feet per second would have sufficient energy to suspend the sand in the river bottom and deposit bars higher up the river banks.

## The Experimental Flood

The result of the predictions led to the first managed flood for environmental purposes. The flood began on March 26, 1996, when Glen Canyon Dam released 45,000 cubic feet of water per second for 7 days. Because the models that were used to simulate erosion, transport, and deposition of sediment in the Grand Canyon had been developed on the basis of data collected, for the most part, at much lower flows, there was a fair amount of uncertainty as to what would happen. When the flood water receded, large new sand bars had been deposited at many locations. Following the success of the experimental flood, the operating rules at Glen Canyon Dam have been revised to provide for future flow releases whenever the volume of water stored in Lake Powell and accumulated in snowpacks are such that the reservoir is likely to fill and overflow. It is expected that these conditions will occur on average about once in 6 years. This significant advance in river management was possible through a partnership of the USGS and the U.S. Bureau of Reclamation, the National Park Service, the U.S. Fish and Wildlife Service, and the Arizona Game and Fish Department.

*These downstream views of a sandbar are located at mile 122 in the Grand Canyon.*



### PRE-FLOOD

Before the flood, there is a large open sand bar about 70 centimeters above the low-flow water surface.



### FLOOD

During the "experimental flood," the sand bar is under water.



### POST-FLOOD

Immediately after the experimental flood, a larger and thicker sand bar has formed. Although some of the new sand bar eroded after the flood, part of it remains.



# Devils Hole—A Paleoclimate Treasure Chest

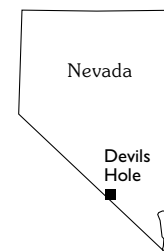
To understand whether climate variations are caused by natural processes or are caused by human activities is one of the challenging science topics of our time. One way to understand natural variability in the climate record is to study past records of glacial/interglacial cycles from the last half million years. During several scuba-diving expeditions, USGS scientists sampled calcite lining the walls of Devils Hole, which is a nearly vertical cavern extending over 122 meters below the water table in southern Nevada. The calcite was deposited by ground water that has moved through the cavern for millions of years. Analysis of the oxygen isotopes in the calcite has revealed a 560,000-year-long paleotemperature record. The Devils Hole climate record is unusual in the length of the record, in the absence of discontinuities, and in the quality of its dating. Other than Devils Hole, there are only two long continuous paleoclimate records of the last half million years—the oxygen-isotope record from deep-sea sediments (SPECMAP) and the Vostok, Antarctica ice core; both are indirectly dated using models. The Devils Hole calcite samples are directly dated by radiometric techniques (mass-spectrometric uranium-series dating) for which they are ideal material. The SPECMAP, Vostok, and Devils Hole records all show alternations of glacial and interglacial climates. However, there are significant differences in the timing and duration of events.

## Timing and Duration of the Ice Ages

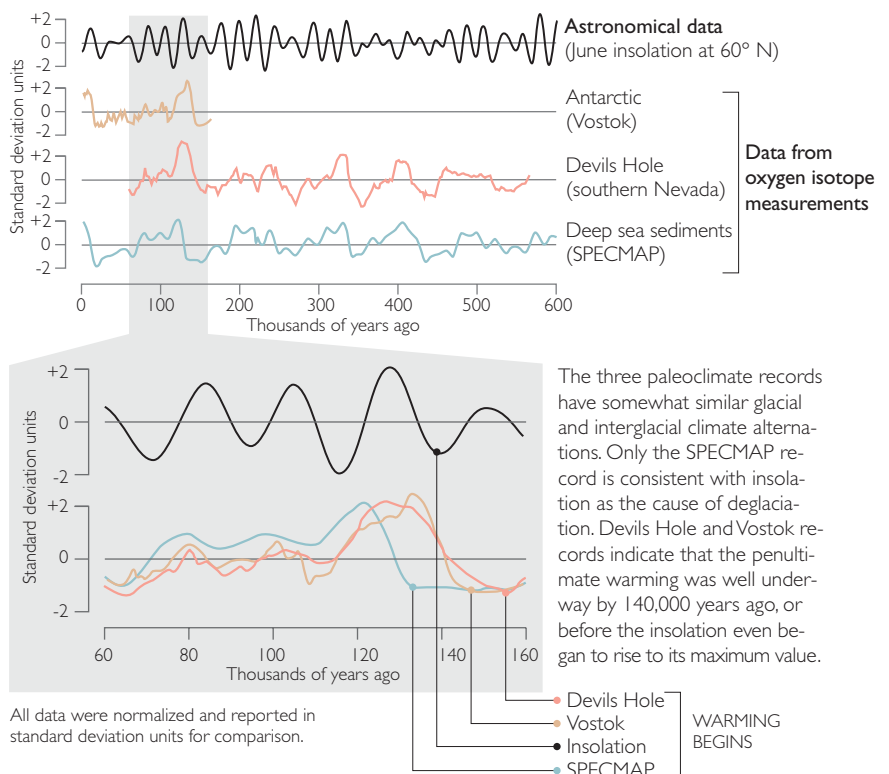
The marine record shows that warming at the end of the penultimate glaciation (next to last large glacial period) started about 130,000 years ago, a time consistent with the Milankovitch\* hypothesis. By contrast, the radiometrically dated Devils Hole record indicates that warming was well underway as early as 140,000 years ago. This difference has been the subject of an intensive ongoing scientific debate.

Additionally, until now there has been a general consensus that interglacial climates lasted about 10,000 years. We are about 10,000 years into the Holocene and hence we can reasonably expect the climate to start a slow cooling as we head into the next glacial cycle. However, the Devils Hole record clearly shows that two of the last four interglaciations were marked by periods of maximum warmth lasting 15,000 years. Thus, unraveling our impact on normal climate may not be as straightforward as thought. The stakes in these issues are high—paleoclimate records are a primary key in our efforts

\* The Milankovitch hypothesis attributes glacial/interglacial climatic cycling to changes in the distribution of solar energy arriving at the Earth's surface due to cyclical variations in the Earth/sun configurations. Specifically, the sharp increase in high latitude summer insolation between 140,000 to 128,000 years ago is widely held to have terminated the penultimate glaciation.



The three paleoclimate records, which depict glacial periods represented by troughs and interglacial periods by peaks, show some similarities but also distinct differences in timing of climate changes. The top record is the June insolation record (solar radiation received by the earth at 60° N).



All data were normalized and reported in standard deviation units for comparison.

The three paleoclimate records have somewhat similar glacial and interglacial climate alternations. Only the SPECMAP record is consistent with insolation as the cause of deglaciation. Devils Hole and Vostok records indicate that the penultimate warming was well underway by 140,000 years ago, or before the insolation even began to rise to its maximum value.

These data indicate that factors other than the position of the earth relative to the sun (insolation records) need to be considered when determining the cause of glacial and interglacial periods.

to untangle the determinants of climate and climate change, as we must if we are to successfully address contemporary issues such as predicted global warming due to anthropogenic greenhouse gas emissions.

## Other Records in Devils Hole

A different kind of paleoclimate record has been preserved in Brown's Room, an air-filled chamber in Devils Hole that is accessible only through submerged passages. The walls of Browns Room are encrusted with alternating layers of calcite that were deposited at the water table as it fluctuated. By dating such deposits from measured heights above the present water level, a water table history was reconstructed that extends back 116,000 years.

In the course of scuba mapping and exploration of Devils Hole, it became apparent that Devils Hole is an atypical cave. Instead of being formed by the dissolution of limestone by slightly acidic waters like most caves, Devils Hole is a tectonic fissure—a crack being continuously opened by extension that has been pulling apart the Great Basin of the intermountain West for the last 15 million years. Thus, ground water is restricted to flowing through a few large fissures in otherwise nearly impermeable rock rather than passing through the multitudes of small-to-microscopic interconnected flow paths found in more typical aquifers. As a consequence, non-reactive chemical constituents, such as

the oxygen isotopes that record paleotemperature, can be transmitted quickly over distances of tens of kilometers with little modification of their initial concentration. This effect gives the Devils Hole paleotemperature record its unexpectedly high resolution. Other records (carbon-13, aerosols, and rare-earth elements) are also preserved in the calcite lining the walls of Devils Hole and are just beginning to be studied. The isotope records, combined with newer records, are expected to continue to provide important information about past climates.



*Calcite deposits on the wall in Browns Room of Devils Hole. As the water table moved up and down, CO<sub>2</sub> outgassed from the ground water, and horizontal layers of calcite formed (and are forming today) at the water surface. The water-table history, which was reconstructed by dating the layers, reflects the amount of rainfall that fell on the southern Great Basin. Deposits are found at heights up to 9 meters above the modern water table, suggesting that past precipitation in the Great Basin was much greater than it is today. (Top to bottom of photo is about 1 meter.)*

## Climate Variability and Climate Change

Long-term trends in local, regional, or global climate can cause significant trends in hydrologic conditions. Often, the identification of climatic controls helps to decipher the role of other driving forces, including human influences. Listed below are findings of studies that are helping to identify the causes and effects of climate variability and change.

- Natural climatic fluctuations are a major control on the chemistry and ecology of San Francisco Bay.
- The risks of extreme hydrologic events in the western United States vary over time according to the state of the El Niño/Southern Oscillation, or ENSO.
- The analysis of vegetation preserved in packrat middens has led to insights on climate variability and ecological response, particularly in arid regions, over the last tens of thousands of years.
- The amount of carbon that has accumulated in sediments deposited in lakes, reservoirs, wetlands, flood plains, rice paddies, and other terrestrial environments is comparable in magnitude to the “missing sink” of carbon arising in estimates of human effects on the global carbon budget.
- Improved representations of continental hydrology in a climate model are providing a basis for improved assessments of water-resource implications of “greenhouse” climate change.
- Field studies at five small watershed (Water, Energy, and Biogeochemical Budgets Program) sites, ranging from tropical to alpine environments, are leading to a better understanding of carbon cycling in small watersheds.

# Microbial Activity and Transport in Ground Water

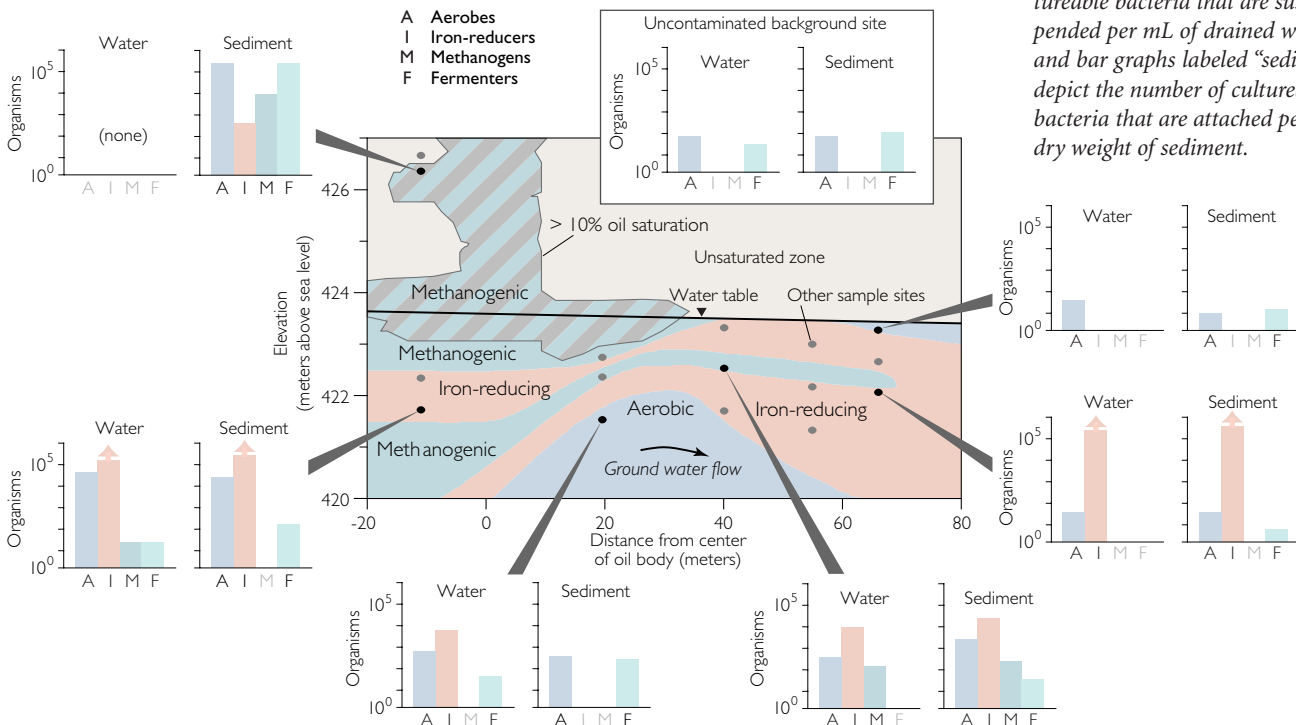
Examining microbial activity and the transport of microbes in the subsurface is important to understand the transmission of waterborne diseases, microbially-enhanced oil recovery, the mobility of ground-water contaminants, the clogging of aquifers near wells, and the bioremediation of some organically contaminated aquifers. Current USGS investigations seek to develop a better understanding of the various controls that affect the activity and movement of microorganisms in both contaminated and potable aquifers by using an iterative approach that combines field and laboratory investigations.

## Investigations of Microbial Activity

As part of the Toxic Substances Hydrology Program of the USGS, several field sites are being investigated to determine the extent and type of microbial activity in aquifers. Investigations of an aquifer that is contaminated by crude oil at a site near Bemidji, Minnesota resulted in the characterization and spatial delineation of four types of microbes: aerobes, iron-reducers, heterotrophic fermenters, and methanogens. The microorganisms derive the energy to grow by coupling the breakdown of organic compounds in crude oil (an oxidative process) to the reduction of other chemical species. For example, aerobes use oxygen, iron-reducers use ferric iron, heterotrophic fermenters break large organic compounds into smaller compounds, and

methanogens break small organic compounds into products, one of which is methane. Microbes that use nitrate (denitrifiers) and sulfate (sulfate-reducers) were low in abundance at this site. The results indicate major differences in the microbial activity throughout the plume. The number of microbes below the water table is lower than the number in the unsaturated zone location. This suggests that nutrient limitations may be important in limiting growth and, therefore, limiting natural remediation of the crude oil in the saturated zone. This type of characterization of aquifers is useful to evaluate the potential for natural remediation and to determine the best approach for enhanced remediation.

A cross-section of an aquifer contaminated with crude oil demonstrates physiological zones inferred from the water chemistry and complex distribution of microorganisms in water and sediment. The four physiological types of microorganisms shown are: aerobes, iron-reducers, methanogens, and heterotrophic fermenters. For selected sampling points, bar graphs labeled "water" show the number of culturable bacteria that are suspended per mL of drained water, and bar graphs labeled "sediment" depict the number of culturable bacteria that are attached per gram dry weight of sediment.



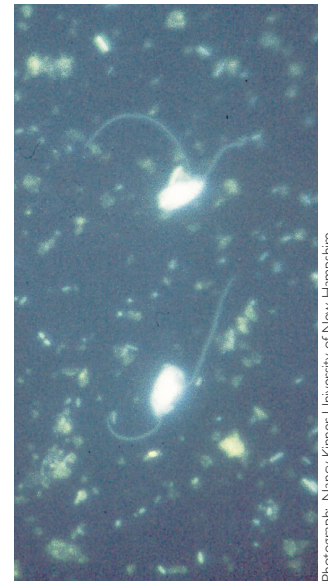
## Protozoa and Virus Transport

Protozoa are common inhabitants in aquifers and use bacteria as a food source. A decline in the number of bacteria will affect remediation methods that depend on bacterial growth to degrade contaminants. For example, at the aquifer study site in Cape Cod, Massachusetts, it was determined that protozoa removed bacteria from contaminated aquifer sediments. Through collaboration of research scientists in the United States and England, the protozoa in aquifer sediments at the site were characterized, and information about their ecology and transport characteristics was obtained. New enumerating and culturing procedures were developed to work with these delicate organisms. Results from column experiments indicate that protozoa in ground water immediately down-gradient from the source of contamination can completely remove the unattached bacteria within a few days.

Viruses in ground water account for over half of the disease outbreaks that result from consumption of contaminated ground water. Currently, models predicting virus transport through the subsurface consider only temperature as a mechanism of virus inactivation. However, experiments at the Cape Cod site, in collaboration with university scientists, suggest that virus particles are

attached to metal oxides (particularly iron) on sand grains. This is responsible for much of the natural disinfection that occurs when viruses move through aquifer sediments at ground-water temperatures less than 15° Celsius. Also, it was determined that virus transport within the aquifer was significantly enhanced by the presence of certain organic contaminants, particularly surfactants (commonly detected in sewage water), that sorbed to iron-oxide surfaces, thereby protecting the sites and prohibiting the removal of viruses. The significance of these findings is that these organic contaminants are often released from the same sources of contamination (for example, septic tanks, landfills, on-land sewage disposal facilities) that contribute viral pathogens to ground water.

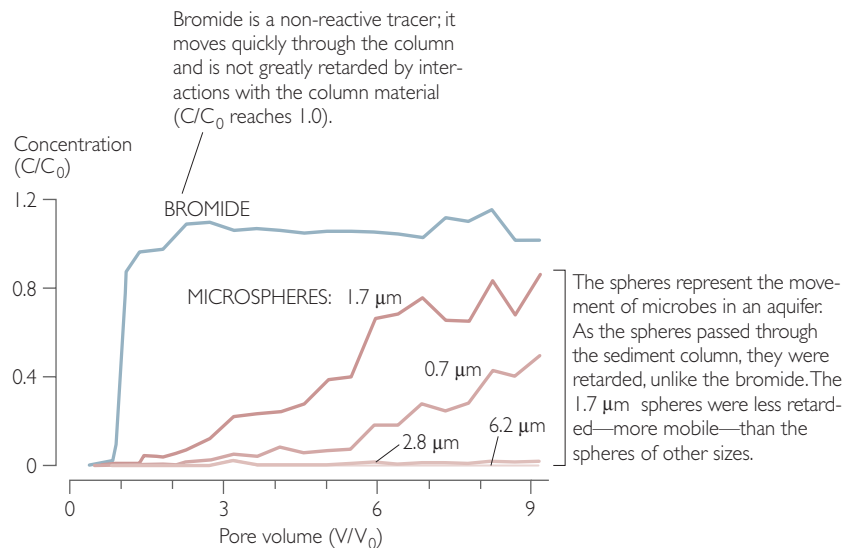
Valuable information also has been gained by examining the transport of microspheres to provide data on the optimal size for transport of protozoa in the Cape Cod aquifer. Microspheres that are 1.7  $\mu\text{m}$  in diameter and protozoa at the Cape Cod site exhibit similar transport properties. This suggests that microspheres may be useful in future investigations of the transport of protozoa.



Photograph: Nancy Kinner, University of New Hampshire

*Protozoa (2–3 micrometers in diameter) from the Cape Cod aquifer—USGS Toxics Study site, Falmouth, Massachusetts. (USGS/University of New Hampshire collaborative study on ground-water protozoa.) Protozoa in aquifers use bacteria as a food source thereby affecting the number of bacteria that degrade contaminants.*

*Modeling the movement of microbes in the subsurface will lead to better interpretations and predictions of reactions that degrade contaminants. Solutions containing bromide and different sizes of microspheres were passed through a column packed with Cape Cod aquifer sediment (0.5 to 1.0 mm grain size). The results are expressed as the concentration (C) in the effluent from the column relative to the initial concentration (C<sub>0</sub>) in the solution being added as a function of the volume of the solution added to the column (V) relative to the initial volume of water (V<sub>0</sub>) in the column at the start of the experiment. The results suggest that microbes that are 1.7  $\mu\text{m}$  in diameter will be transported in aquifers farther than smaller or larger particles.*



# Lake Ecosystem Studies

The characteristics of lake ecosystems are determined by the interaction of hydrological, chemical, geological, biological, and atmospheric processes. An integrated, interdisciplinary understanding of the effects and interactions of processes is needed to determine how lakes respond to environmental change and how such change may affect lake- and land-management practices at multiple scales. An Interdisciplinary Research Initiative was started in 1989 to bring together scientists from diverse disciplinary backgrounds so that they can share their collective knowledge and conduct collaborative research on a watershed scale. Lakes were selected as a focal point of the Initiative because they integrate the effects of many environmental processes, while preserving a sediment record of past environmental change. The lakes being studied are in the Shingobee River Headwaters Area (SRHA), located in north-central Minnesota.

## Water and Chemistry Budgets

The investigations have focused on two lakes having similar major ion chemistry, but different hydrologic characteristics. Williams Lake is a closed-basin lake (that is, it has no streams flowing to or from it), has sandy near-shore sediments, and has high water clarity. Shingobee Lake, about 5 kilometers from Williams Lake, is an open-basin lake that has the Shingobee River flowing through it. The water in Shingobee Lake is not as clear as that in Williams Lake, and it has soft organic-rich sediments near the shore. Investigations of the SRHA by USGS and university scientists include studies of ground-water and surface-water hydrology; lake and stream chemistry; and lake, stream, and wetland biology and biogeochemistry.

Lake and watershed managers commonly need to determine water and chemical budgets, and much of the work at the SRHA study site has focused on development and comparison of new methods for determining these budgets. Chemical mass balances for sodium, magnesium, chloride, dissolved organic carbon and oxygen-18 were used to estimate ground-water seepage to and from Williams Lake. The results indicate that different seepage rates are obtained by using isotopic, solute-budget, and flow-net approaches, and that a combination of hydrogeological and chemical approaches is

required to define seepage and to identify uncertainties in chemical fluxes. Environmental isotopes proved to be a reliable method for determining hydrological budgets for closed lakes, such as Williams Lake, which receives no streamflow. The method is now being evaluated for Shingobee Lake, which has a river flowing through it and is flushed rapidly.

## Carbon Balances

Carbon balances of the lakes are also a topic of research. Williams Lake has greater concentrations of dissolved organic carbon (DOC) (about 7 mg carbon/liter) than Shingobee Lake (about 4.5mg carbon/liter). Examination of the composition of the DOC indicates that DOC from Williams Lake is dominated by photosynthetic processes occurring within lake, and that the Shingobee Lake DOC is dominated by the influx of organic material in the Shingobee River. Measurements of carbon dioxide and methane exchange between lakes and the atmosphere indicate net annual loss of carbon from lakes to the atmosphere. The magnitude of the annual loss depends largely on lake hydrologic characteristics. For example, Shingobee Lake loses carbon dioxide to the atmosphere for most of the open-water season because dissolved inorganic carbon inputs from ground water and the



*A stable tower anchored to the bottom of Williams Lake is one of the few sites where water evaporation and carbon dioxide flux have been directly measured over a lake.*

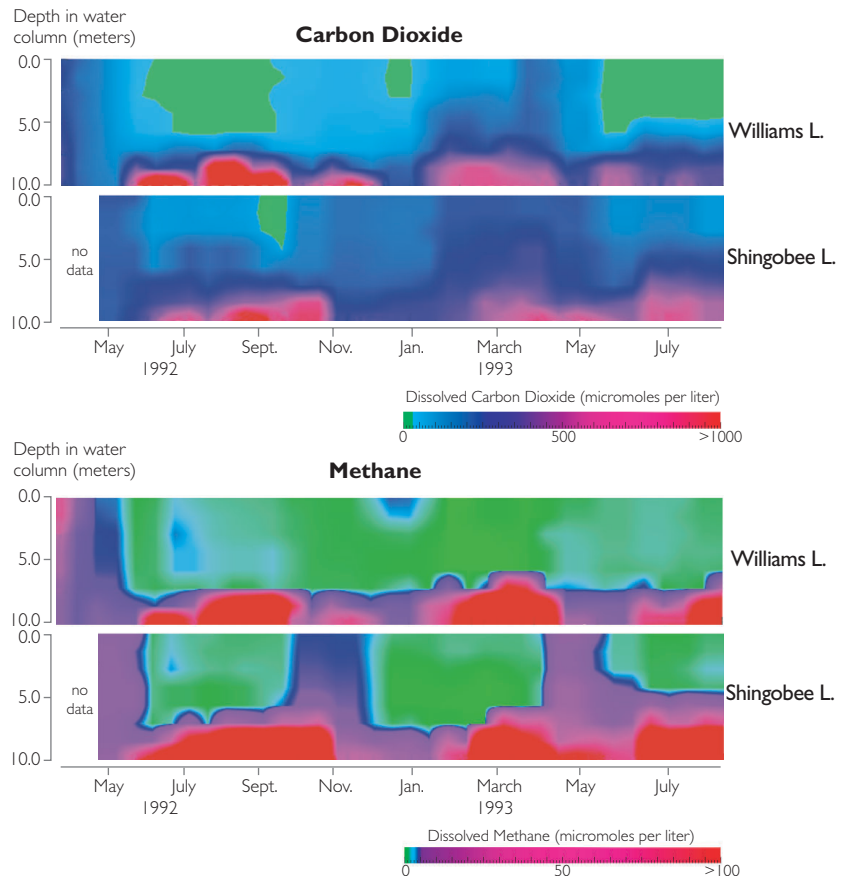
More information is on the Internet at  
<http://wwwbrr.cr.usgs.gov/projects/IRI/>

Shingobee River exceed photosynthetic uptake of carbon dioxide in the lake plus outputs from the lake via the river.

Other interdisciplinary investigations continue to advance the understanding of lake and watershed processes. These studies involve the storage of carbon in sediments, the use of hydrological, chemical, and biological tools to determine the source of ground-water

ter discharge to fens; the development of new flux chambers to measure focused ground-water discharge in streams; determination of the role of focused ground-water discharge on nitrification and denitrification processes in streams; and the use of distinctive aquatic plants as indicators of areas of ground-water discharge to lakes.

*Carbon dioxide (CO<sub>2</sub>) and methane concentrations show cyclic patterns in Williams and Shingobee Lakes. The largest concentrations of gases are below 7.5 meters in the water columns of both lakes. The largest releases of the gases to the atmosphere occur in spring after ice melt and in fall when the lakes mix before freezing. Shingobee Lake loses CO<sub>2</sub> to the atmosphere throughout most of summer, while Williams Lake utilizes atmospheric CO<sub>2</sub> for photosynthesis. More methane is released from Shingobee Lake than from Williams Lake. Amounts in green are slightly greater than atmospheric levels for methane and are less than atmospheric for carbon dioxide.*



### Natural Organic Material

Non-living naturally occurring organic material (NOM) originates from the decomposition and leaching of organic detritus in soils, sediments, and water bodies. It is transported in streams and shallow ground water and is difficult to characterize because of its solubility in water and complex molecular structure. Over many years, techniques were developed by USGS scientists to isolate and characterize NOM in surface and ground waters. Characterization of NOM is important because its composition is a key factor in determining how it reacts with other substances in water and soils.

In northern Minnesota, where the Shingobee River flows into Shingobee Lake, NOM samples were collected and isolated from water during melting of the winter snowpack. The concentrations of NOM were high (up to 10 mil-

ligrams of carbon per liter) and the NOM contained more aromatic structures than were found in NOM collected from the river during base-flow conditions. The difference in structures is related to the source material and the residence time of the NOM in soils before it is transported to the lake. Other current investigations are focused on the interactions of NOM with trace metals, radionuclides, and organic contaminants; the relationship of NOM and mercury cycling in ecosystems; and the formation of disinfection by-products (DBPs). DBPs are formed by the treatment of potable water with chlorine that reacts with NOM in water to produce trihalomethanes and other chlorinated organic substances. The structure and reactivity of the NOM is a factor that determines how DBPs form during chlorination.

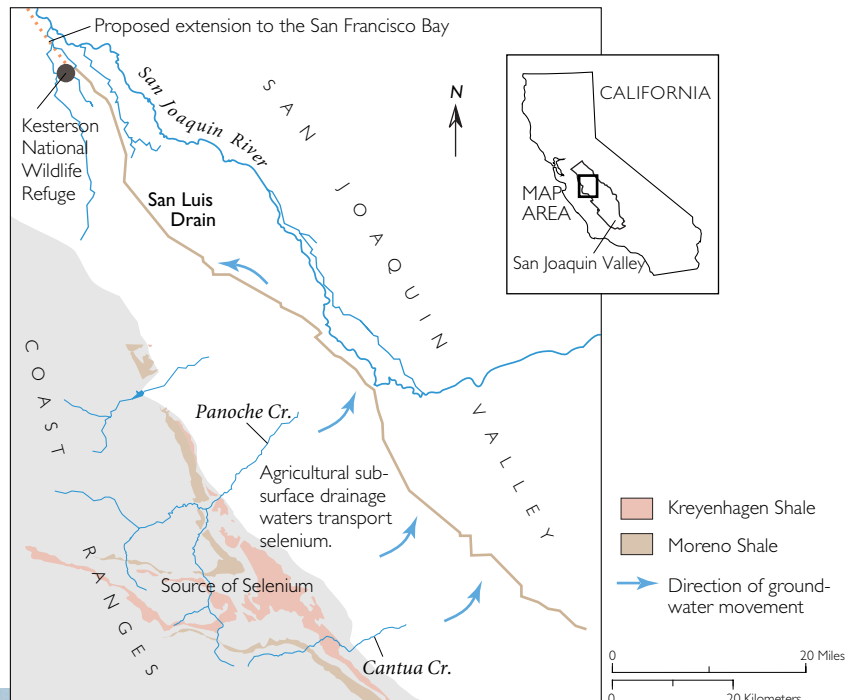
# Selenium: Rocks, Ducks, Microbes, and Membranes

The increasing salinization of soils and the elevated selenium (Se) and salt concentrations in irrigation water that drains from those soils are recognized as problems throughout the arid West. In the San Joaquin Valley, drainage of low-quality irrigation wastewater from more than 180,000 hectares (444,000 acres) has been the subject of debate and litigation. Changes in drainage conveyance, water management, and Se treatment in California may affect future Se loads from the San Joaquin Valley. Predicting the effects of these changing Se loads on the San Joaquin River and the San Francisco Bay/Delta ecosystems is the focus of on-going studies.

## Selenium and its Source

During the summer of 1983, the U.S. Fish and Wildlife Service contacted USGS scientists because of unusually high numbers of deformities and deaths of waterfowl embryos and hatchlings at the Kesterson National Wildlife Refuge and high levels of selenium (Se) in mosquito fish. The ultimate source of the Se was shown to be the marine sedimentary rocks of the California Coast Ranges. Using techniques to quantitatively measure the isotopic signatures of source waters entering the refuge and the chemical species of selenium, scientists determined that the Se was transported to the refuge in agricultural drainage water. Selenium concentrations in drainage waters in contact with Se enriched soils were 10 to 100 times that considered safe for the protection of wildlife. Additional work has demonstrated the link between Se and reproductive effects, elucidated key pathways in the biogeochemical cycling of Se in natural and disturbed ecosystems, and aided in designing remediation strategies for Se-laden water. In 1986, farmland subsurface drains were plugged and the 137-kilometer San Luis Drain canal that collected and discharged the agricultural drainage water to the refuge was closed. The most contaminated parts of the refuge were buried in 1988 as part of on-site remediation for Se.

Marine sedimentary rocks of the Moreno and Kreyenhagen Shales contribute selenium to soil, surface water, and ground water of the San Joaquin Valley. Irrigation funnels selenium into agricultural drains and eventually into surface water, including wetlands. Because of disposal of seleniferous subsurface drainage into the San Luis Drain from 1981 to 1986, levels of selenium toxic to aquatic wildlife occurred at the Kesterson National Wildlife Refuge. Current drainwater management efforts include recycling, storage, and discharge to the San Joaquin River.

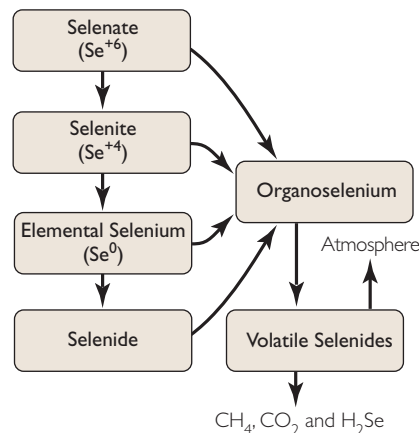


In 1996, a 45-kilometer section of the San Luis Drain was re-opened to transport agricultural drainage to the San Joaquin River and ultimately to the San Francisco Bay/Delta Estuary. The drain is posted with a state health advisory because of selenium.

## A Bioremediation Process

With the source of the problem identified, scientists began work on the biogeochemical cycling of Se in aquatic systems. In the arid climate of the San Joaquin Valley, Se in source shales and soils is rapidly weathered to highly mobile selenate in the alkaline oxidizing waters of the Valley. The presence of selenate accounts for the extensive dispersal of Se in the surface and ground waters of the region. Studies showed that selenate-respiring bacteria present in the anoxic sediments of the irrigation water collection system could reduce the soluble selenate to insoluble elemental Se ( $\text{Se}^0$ ) and immobilize it as a precipitate in the sediments. This suggested that the process identified in natural systems might be incorporated into engineered treatment systems for the remediation of the approximately 400 million cubic meters of potentially contaminated irrigation return water produced annually in the San Joaquin Valley.

A treatment process was developed that uses indigenous microorganisms and a two-zone system. The first zone removes nitrate, which inhibits the reduction of selenate



while the second zone converts the selenate to  $\text{Se}^0$ . In the first zone, aerobic conditions facilitate the removal of nitrate by assimilation into biomass. In the second zone, anoxic conditions enable selenate-respiring microorganisms to perform the conversion of selenate to elemental selenium. Nutrients required by the microorganisms are produced through the wastewater treatment, so no additional external materials are needed.

The biogeochemical cycle of selenium shows that bacteria reduce selenate to selenite after which chemical or microbiological reactions may reduce the selenite to immobile, elemental selenium. It may be possible to treat irrigation return water with bacteria, such as *Sulfurospirillum barnesii*, which have been found in anoxic sediments and which can reduce soluble selenate so that it precipitates as elemental selenium. Further reduction to selenide is also possible. Metallic selenides are insoluble in water.

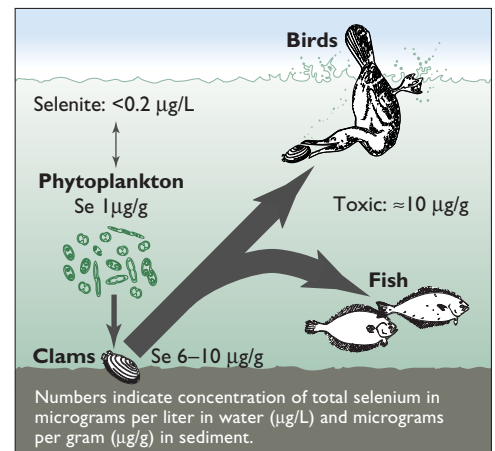
Selenate, selenite, elemental selenium, and selenide can be assimilated into organic matter by living microorganisms and plants. Organoselenium compounds can be degraded to volatiles (for example, dimethyl selenide [DMSe]) and released to the atmosphere. DMSe can also be attacked by microbes and broken down.

## Selenite Toxicity and Removal

The immobilization of  $\text{Se}^0$  in anoxic sediments of evaporation ponds constructed in a drainage-collection system might appear to be a permanent sink for Se. However, the ecosystems are complex, and opportunities exist for remobilization and food-chain magnification of Se. USGS and university scientists raised clams in mud containing microbially produced  $\text{Se}^0$ . They found that about a quarter of the  $\text{Se}^0$  was incorporated into the clams' soft tissues, demonstrating the need to isolate treatment systems from other segments of the ecosystem in order to ensure Se containment. They also found that there is nearly 100 percent assimilation by clams if Se enters ecosystems as selenite and is taken up and transformed by phytoplankton. Thus, ecosystems exposed to selenite (for example, in fly-ash ponds or refinery wastes) are even more vulnerable to Se toxicity than those exposed to selenate.

Another method of removal of Se was investigated using synthetic, nanofiltration membranes. Studies done in collaboration with scientists from the filtration industry demon-

strated the potential for membranes to selectively remove more than 95 percent of the Se from agricultural drainage water. The membranes also remove other toxic solutes from the drainage water, including uranium, molybdenum, arsenic, and organic contaminants. This new technology may have additional applications in Se removal from other problem effluents, such as petroleum refinery wastewater and mine-drainage waters. These studies on the geochemistry, microbiology, and selective filtration of Se species have led to a better understanding of processes and possible remediation strategies to remove Se from agricultural drainage water.



In an estuarine environment, selenite is taken up by phytoplankton. Phytoplankton transform the selenite into a form readily assimilated by clams, with the result that virtually all of the selenium is passed on to clams that eat the phytoplankton. Bioconcentrated selenium may reach levels that are toxic to birds and other wildlife that feed on the clams.