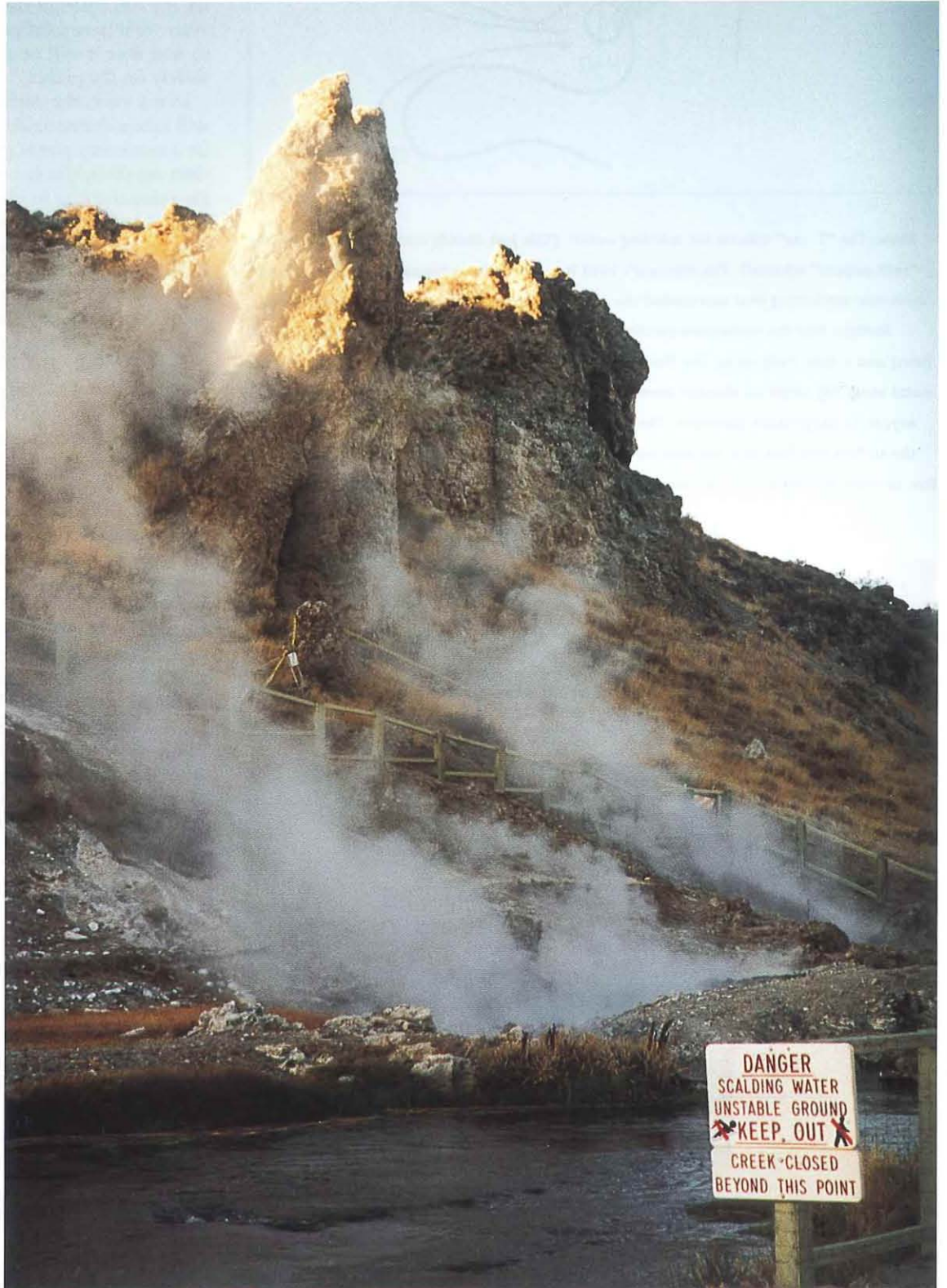To find the source of the arsenic in this water supply, we have to go back up to the Owens Valley. . . . The focus of our studies has been the geothermal inputs of arsenic at Hot Creek Gorge.

DANGER
SCALDING WATER
UNSTABLE GROUND
KEEP OUT
CREEK CLOSED
BEYOND THIS POINT

Chinatown Revisited:
Arsenic and the Los Angeles Water Supply

by Janet G. Hering

Above: L. A. Aqueduct workers set a record for hard-rock drilling at the Elizabeth Tunnel, just north of the San Fernando Valley.
Left: Steam rises off the bubbling hot springs of Hot Creek Gorge; geothermal activity loads relatively high concentrations of arsenic into the creek, which flows into the Owens River and eventually to Los Angeles.

In his 1974 film *Chinatown*, Roman Polanski created an enduring modern myth based loosely on the fascinating history of the Los Angeles Aqueduct. Although separating all the details of historical fact from fiction is beyond the scope of this presentation, it is worth examining some of this history, particularly from an engineering perspective. We will also see how this development of water resources set the stage for environmental problems that persist to the present day.

Even though massive hydraulic works characterize water supply throughout the western United States, it's still hard to realize just how dramatically the patterns of development in Los Angeles have been shaped by water resource management. Los Angeles originally obtained its water from three sources—rainfall, groundwater, and the Los Angeles River—all of which supported a population of about 100,000 people in 1900. This number had almost doubled by 1904, and there was widespread concern at the time that development would soon be limited by insufficient water. Indeed, at the dedication of the Los Angeles Aqueduct in November 1913, William Mulholland, chief engineer of the Los Angeles Department of Water and Power (DWP) and architect of the Big Ditch, declared of the city: "We have the fertile lands and the climate. Only water was needed to make this region a rich and productive empire, and now we have it."

Certainly, the existing level of growth in Los Angeles would have been impossible without many water projects, of which the Los Angeles Aqueduct was only the first. A number of other aqueducts, including the California Aqueduct (from the Sacramento Delta down through the Central Valley) and the Colorado River Aqueduct, followed, making possible the population of 9 million that Los Angeles supports today, as well as extensive agriculture throughout Central and Southern California.

The development made possible by the L.A.

Aqueduct, however, came at the price of the prosperity of Owens Valley, a thriving agricultural area at the turn of the century. The problem was exacerbated when, beginning in 1919, Owens Valley groundwater was pumped into the Los Angeles Aqueduct to supplement the drought-depleted surface waters of the Owens River. Within a decade the Owens Valley was transformed, in the words of Will Rogers, into a "valley of desolation."

Despite the political machinations surrounding the L.A. Aqueduct and its economic impacts on the Owens Valley, its engineering accomplishments still must provoke admiration. Although the entire aqueduct is gravity-fed, some impressive mountain ranges stand between the Owens Valley and Los Angeles. The drilling of the tunnels through these mountains was one of the most technically challenging aspects of the entire project. Recognizing this, Chief Mulholland ordered the tunneling begun before the rest of the aqueduct construction. The Elizabeth Tunnel through the Sierra Madre Mountains was drilled from both the north and south ends simultaneously to meet in the center, an engineering feat that would be considered challenging even today. A world's record for hard-rock drilling was set there—567 feet in a single 24-hour period with crews working around the clock. In the entire drilling period of 1,239 days, they drilled 26,860 feet.

Another remarkable engineering task was the construction of the giant siphons that were built as an alternative to tunnels in some areas. When this project was started, there was no motorized transport powerful enough to move the huge siphon pieces (8 to 12 feet in diameter), so they were transported by mule trains. The siphons were the most vulnerable links in the aqueduct; the Jawbone Siphon, one of the longest, failed the first time the aqueduct was opened, delaying the actual opening for repairs. The siphons were also

The Los Angeles Aqueduct
carries water about 250
miles—from Lake Crowley
to the Fairmont Reservoir
in the San Fernando Valley.
Over part of its length,
giant siphons, such as the
Jawbone Siphon below,
pipe the water over
mountains. The enormous
siphon sections had to be
lugged to their positions
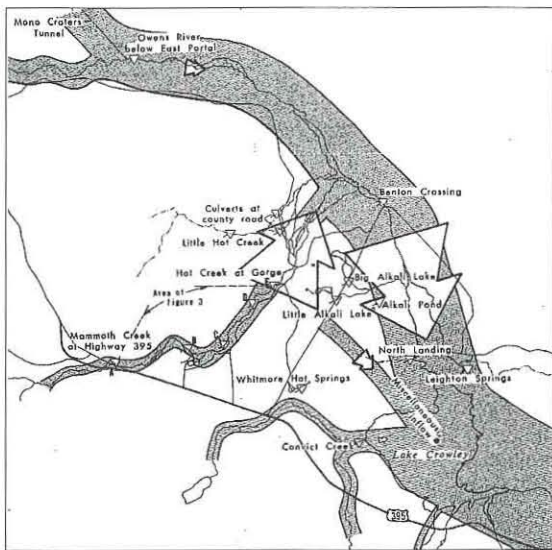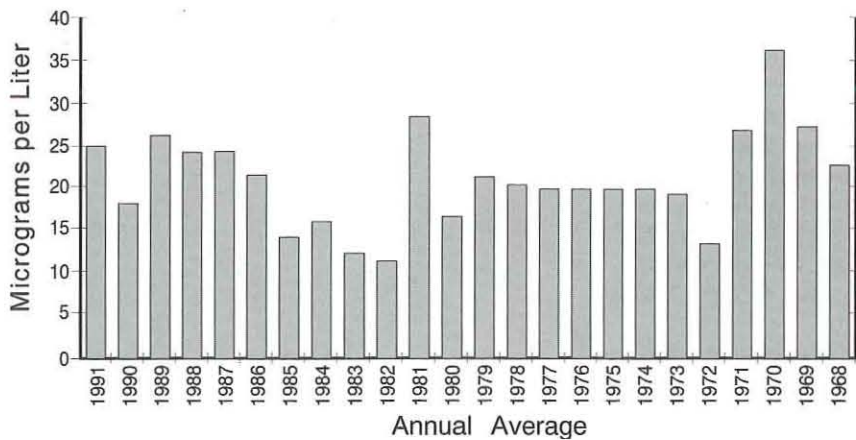by mule train (above,
right).
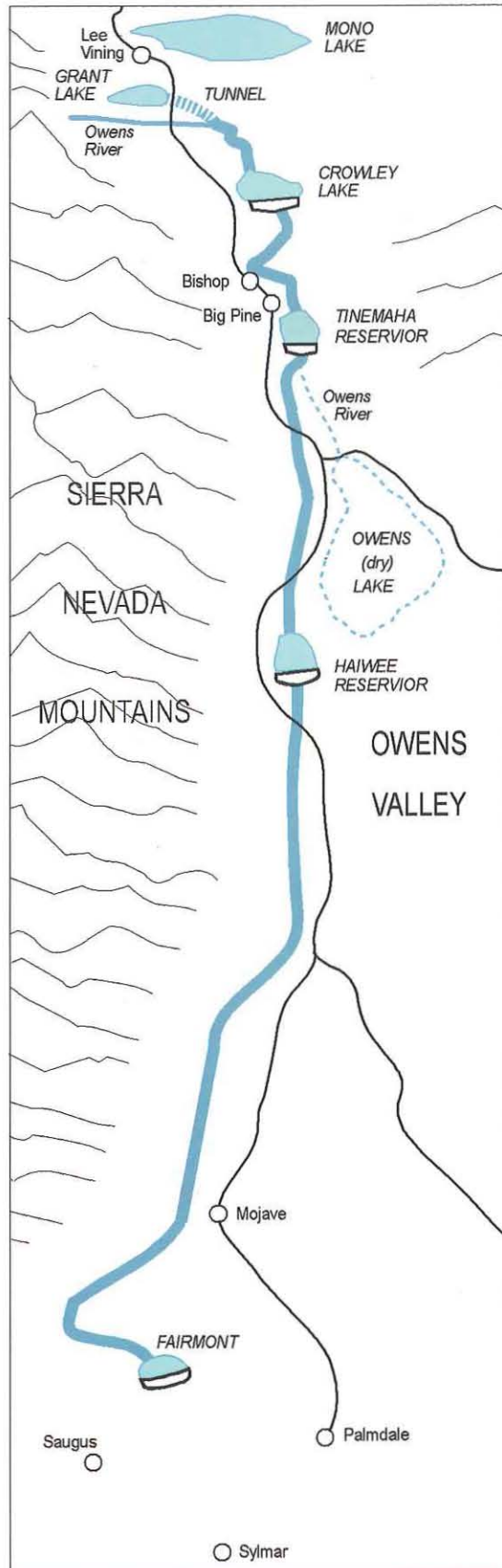
vulnerable to sabotage. After exhausting all other possibilities to forestall the export of Owens Valley water through the aqueduct, Valley residents resorted to dynamiting the siphons.

Nonetheless, the aqueduct, begun in 1907, was opened on schedule and within budget on November 5, 1913. About one in five Los Angeles inhabitants, who were obviously much happier about the project than the people of Owens Valley, joined the party for the San Fernando opening. In the view of the people of Los Angeles, the aqueduct would enable the city to achieve its true potential as a world-class city. They were right.

As we will see, it may be that present-day Owens Valley residents may recover through the courts at least some of what their ancestors could not, even with dynamite, retain. But for the meantime, the L.A. Aqueduct system provides a sizeable percentage of the city's water supply by transporting water from the Owens Valley. Snowmelt runoff from the Sierra Nevada drains into the Owens River, a tributary of Lake Crowley, the terminal reservoir in the aqueduct system. From Lake Crowley, the water is transported approximately 250 miles through the aqueduct to the Fairmont Reservoir in the San Fernando Valley and treated at the filtration plant in Sylmar.

In general, the quality of this water is excellent. The DWP has done a very good job in protecting the watershed and preventing any contamination of the water. But one of the water's natural constituents—arsenic—does pose a potential problem. The plot at the top of the next page shows data from 1968 to 1991 collected by the DWP at their Sylmar filtration plant. As the bars show, the concentration of arsenic over this roughly 25-year period averages approximately 20 micrograms (millionths of a gram) per liter. Since the current drinking-water standard, or maximum contaminant level (MCL), is 50 micrograms per liter, the DWP values are well below it. The U. S. Environmental Protection Agency is, however, reevaluat-

Above: Concentrations of arsenic at the DWP's Sylmar filtration plant from 1968 to 1991 lie well below the current drinking-water standard of 50 micrograms per liter. If that standard drops to 2–20 µg/l, however, there will be trouble meeting it.

The schematic view of the region north of Lake Crowley (above) shows that most of the water flowing into the aqueduct system, indicated by the width of the gray bands, comes from the Owens River. The flux of arsenic, however, shown by the size of the white arrows, comes predominantly from Hot Creek Gorge (above right), which is contributing relatively little water. (Diagram from Eccles, USGS Water Resources Investigations, 1976.)

ing the standard, and the range under consideration is between 20 and 2 micrograms per liter. It's clear that the DWP is going to have a problem meeting a standard in that range. In 1993, the World Health Organization recommended a value of 10 micrograms per liter, based both on health effects and other considerations. Epidemiological studies in Taiwan and in the West Bengal region of India have shown that chronic exposure to arsenic in drinking water causes health effects that range from skin diseases to cancer.

To find the source of the arsenic in this water supply, we have to go back up to the Owens Valley. Studies conducted by the U.S. Geological Survey in the 1970s quantified the fluxes of water and arsenic to Lake Crowley. In the illustration above, the width of the shaded lines shows that the water flux to Lake Crowley comes predominantly from the Owens River; very little flow, in comparison, comes from Hot Creek Gorge. The size of the arrows indicates the flux of arsenic, and here you can see the opposite: the arsenic comes mostly from Hot Creek Gorge, with very little of it coming down from the Owens River.

As its name indicates, Hot Creek is a geothermal area. It's in an active volcanic region, where a massive volcanic explosion occurred about 750,000 years ago, with lesser eruptions more recently. The area, which is at an altitude of 7,000 feet, is characterized by geothermally altered rocks and by the hot springs that provide most of the local place names. Arsenic occurs at extremely elevated concentrations in the geothermal waters and is derived from degassing of arsenic (a volatile element) from the magma. The focus of our studies has been the geothermal inputs of arsenic at Hot Creek Gorge.

The gorge itself is about half a mile long with very steep sides. Geothermal pools lie along both sides of the creek, and a large number of springs occur within the streambed itself. This gives the water a comfortable constant temperature in the low- to mid-70s (22-24 degrees C) year-round, making it a popular place for swimmers. Many of the pools along the bank, however, are close to boiling.

We studied the arsenic concentrations in these pools and in the creek as well as the oxidation state of the arsenic. In natural waters, arsenic commonly occurs in two oxidation states, the more oxidized +V state and the less oxidized (or more reduced) +III state. As(V), or arsenate, is the thermodynamically stable form in water exposed to the atmosphere; As(III), or arsenite, is stable under more reducing conditions.

The oxidation state in which arsenic occurs in water is important because it affects the toxicity of arsenic, its mobility in aquatic systems, and the efficiency with which it can be removed in treatment processes. As(III) has been shown to be more acutely toxic than As(V). This distinction may be less consequential for chronic exposure and carcinogenesis since As(III) and As(V) can be interconverted within the body. The mobility of arsenic in natural waters is often governed by the sorption of arsenic onto mineral surfaces—these interactions are generally stronger with As(V) than with As(III). Many treatment processes similarly rely on sorption and are thus more effective for As(V).

At Hot Creek, we found that, in the hot bubbling pools, As(III) was roughly 60 to 70 percent of the total arsenic concentration. At depth, the contribution of As(III) might be even higher, but we were unable to sample geothermal water that had not already been exposed to the atmosphere. In the gorge area of the creek, we found less of the arsenic as As(III)—only 40 to 50 percent, the remainder being As(V). Interpreting this information, however, is complicated by the variable total arsenic concentrations in the creek water, which result from the numerous and scattered sources of arsenic within the gorge.
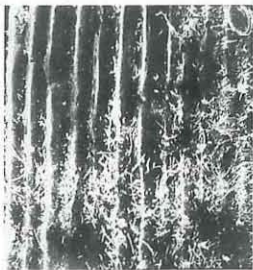
This finding led us to the boundary of the hydrothermal area and to look downstream from

it. We found that the concentration of total arsenic was quite constant, indicating that we were, in fact, downstream of the source of any significant arsenic inputs to the creek water. The percentage of As(III) dropped from about 30 percent at that boundary down to nearly 0 about a mile downstream. What's interesting here is the contrast between total arsenic, which is conserved, and As(III), which is being lost; the total arsenic concentration is not changing, but As(III) is being oxidized to As(V).

We could estimate the rate of oxidation based on the time of travel for this one-mile stretch of the river by assuming that the water is simply traveling in a plug-flow manner and by measuring its velocity, which is about 0.4 meters per second. This gives a half-life for this oxidation process of about a third of an hour, which is very fast. As(III) is thermodynamically unstable with respect to As(V) in the presence of oxygen, but that reaction is very slow, with a half-life on the order of 100 days. So we cannot account for this fast reaction simply by the reaction of As(III) with oxygen. What, then, is the oxidizing agent?

In trying to discover this agent we looked at a number of possibilities, including indirect photochemical reactions and reactions with constituents

from sediments (manganese oxide, for example). But both of these were too slow to provide the explanation. The last possibility that we looked at was a biologically mediated reaction. Right around the boundary of Hot Creek's hydrothermal area, particularly just downstream of the hydrothermal inputs, we observed very lush vegetation of various species of aquatic plants (or macrophytes). One of these has slender stems and grass-like leaves and another a thick foliage of small leaves that form dense mats on the water. Since the water temperature in this stream remains constant throughout the year, this plant life is also present year-round. These macrophytes haven't yet been positively identified, but the predominant species resemble plants growing in the geothermally influenced Waikato River system in New Zealand.

We then designed an experiment to compare our field observations of rapid As(III) oxidation with a number of different controlled cases. In the first case, we took a sample of the macrophytes along with anything that happened to be attached to their surface, and simply enclosed the sample in a container of some of the surrounding water. In the second case, we shook off anything attached to the plants' surface and, removing the plants, left only the surface material, which has a large component of bacteria, in the container of stream water. We also had two abiotic controls. In the first of these, we took the sample with the surface material from the macrophytes and put it through a sterile filtration system—a 0.2 micrometer filter that removes most bacteria fairly effectively. And in the second case, we added antibiotics to the subsample containing surface material from the plants to eliminate any bacterial activity. To make a long story short, in the first two cases, with the plants plus surface material and the surface bacteria alone, we saw rapid arsenic oxidation. When we eliminated the biological activity, either by the sterile filtration or the antibiotic treatment, the arsenic oxidation did not occur.
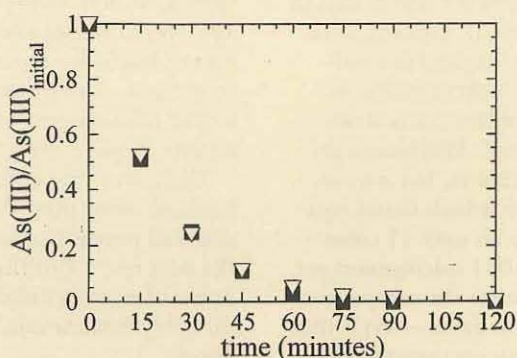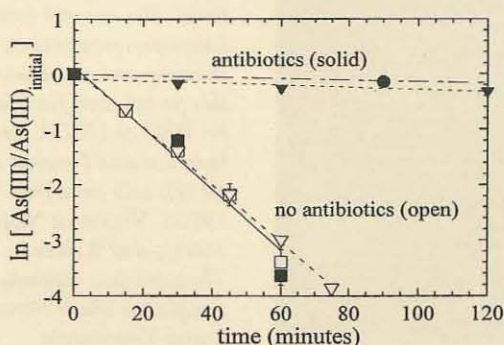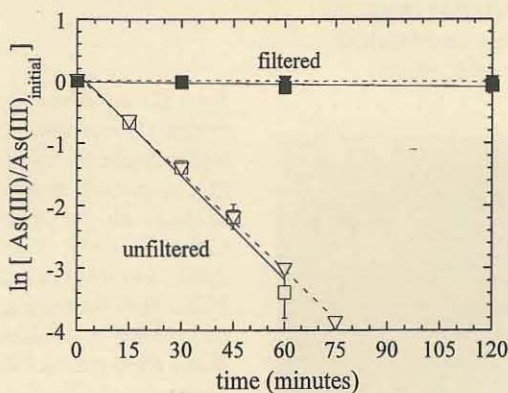
Some of our data appear opposite. The top graph shows the loss of As(III) with distance from the geothermal inputs; total arsenic is conservative. The lower three graphs show the results of the incubation studies. In the upper panel, As(III) is seen to be rapidly oxidized in the presence of surface material from the macrophytes. This same data (marked "unfiltered") is shown in logarithmic form in the middle panel. In contrast, the abiotic, sterile-filtered sample shows no As(III) oxidation—the As(III) concentration remains constant over the course of the incubation. The antibiotic treatment in the bottom plot looks a little more complicated, because antibiotic activity is not instantaneous. Antibiotics are not a poison. They don't kill the organism immediately, but rather they interfere with its metabolic processes, and it

The plot at right shows As(III) as a percentage of the total concentration of arsenic, measured downstream of Hot Creek Gorge. Total arsenic remains constant, but As(III) decreases dramatically.
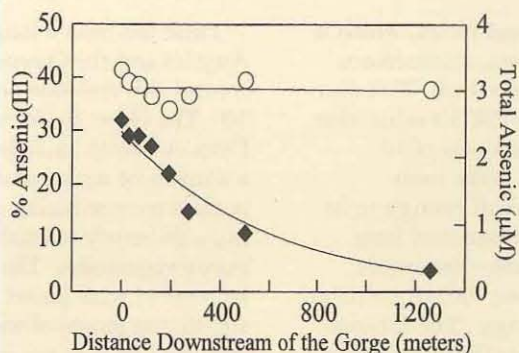
All of the lower three plots show the ratio of As(III) concentrations to their initial value over time. The top one represents two experiments done with water containing the surface material from the macrophytes (the squares are ambient As(III) and the triangles represent an additional spike of As(III)). The concentration under both conditions drops to zero in just under an hour. In the next plot, this data is shown in logarithmic form. First-order loss of As(III) is observed in the unfiltered system, but when the water is run through a sterile filter to remove the bacteria, the As(III) concentration does not decline. The bottom plot shows what happens to As(III) in the presence of antibiotics added at the beginning of the experiment (solid squares), after three hours (solid triangles), and after 72 hours (solid circles).

To make a long story short, in the first two cases, with the plants plus surface material and the surface bacteria alone, we saw rapid arsenic oxidation.

takes a certain incubation time for that to happen. These observations indicate that the As(III) oxidation that we observed is due to the activity of microorganisms. When we compare all of our batch studies with the rates we measured in Hot Creek, we get a very good correspondence, indicating that the microbial oxidation of As(III) can indeed account for the oxidation that we see in the creek.

This is important, because the treatability of arsenic depends on its oxidation state. One of the possibilities that the DWP is considering, if they do need to meet a more stringent drinking-water standard for arsenic, is to site a treatment facility near the source of the arsenic, rather than waiting till the water arrives at the Sylmar filtration plant where they would have to deal with a much larger volume. The gauging station that already exists on Hot Creek is one of the possible sites that the DWP might consider for a treatment facility. Our studies show that such a facility could rely on the indigenous microorganisms in the stream to do the work of oxidizing As(III) to As(V). Then As(V) could be efficiently removed from the water by any one of a number of treatment technologies, such as sorption onto alumina or iron-coated sand.

Arsenic and the L.A. Aqueduct have also had environmental consequences for the Owens Valley. These are not part of my current research, but since they are the focus of intense current interest and some litigation, I'd like to mention them here. One of these problems is the airborne arsenic blowing off the Owens lake bed. Before the aqueduct was constructed, Owens Lake, at approximately 73,000 acres, was the third largest lake in California. It was a terminal alkaline lake, with very high salinity and most probably very high arsenic concentrations as well—similar to those in Mono Lake. With the construction of the aqueduct diverting water from the lower Owens River, Owens Lake just dried up. Thousands of acres of land that had formerly been covered with water
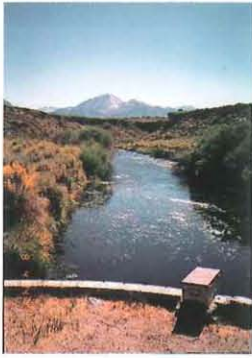
are now dry. And when the wind blows, which it does quite frequently in that area, an enormous amount of dust swirls off the lake bed. This dust poses two problems: one is the PM-10 value, that is, particulate matter with a diameter of 10 microns. This size of particles is the most troublesome, because they're small enough to be transported relatively long distances and large enough to cause health problems. You inhale them but you don't exhale them; PM-10 particles settle or are captured in the lungs. The national ambient air-quality standard for PM-10 particles is 150 micrograms per cubic meter in 24 hours. When the wind is blowing hard on Owens Lake, the PM-10 value has been measured at 3,000 micrograms per cubic meter, 20 times the national standard.

The other problem with the dust is its arsenic content. There is no national air-quality standard for arsenic concentration, but there's still reason to be concerned about it. The arsenic concentration in the dust is approximately 100 parts per million, so the particulate arsenic concentration in the air during one of these windstorms is about 0.3 micrograms per cubic meter. Unfortunately, there's not much to compare this to, but we can look at a 1994 Canadian study, which found that the mean concentration in the air over 11 cities and one rural area was only 0.001 micrograms per cubic meter. We could also make the comparison with occupational exposure standards—levels that are generally much higher than you would want in ambient air. The peak airborne arsenic concentrations near the Owens lake bed are within a factor of 10 of the suggested NIOSH (National Institute for Occupational Safety and Health) standard of 2 micrograms per cubic meter.

There has been a long-raging battle between Los Angeles and the Owens Valley over the need to control this airborne pollution, specifically PM-10. The Great Basin Air Quality Management District, which includes Owens Valley, has issued a number of recent administrative rulings that require reconstituting part of the lake by irrigating sufficiently to establish a salt-marsh kind of grassy vegetation. The rest of the lake bed would be covered with gravel. Even this would involve a significant return of water to the Owens Valley, a step the DWP is not eager to take.

The second issue is the loss of the riparian ecosystem on the lower Owens River, which, like Owens Lake, dried up when the water was diverted to Los Angeles. After a long court battle over the environmental impact of groundwater pumping in the valley, the DWP and various representatives of the Owens Valley signed a "memorandum of understanding" a few months ago, which would allow for the rehydration of the lower Owens River and re-establishment of its ecosystem. The measures agreed upon, however, would not solve the problem of the particulate arsenic blowing off the dry lake bed.

The historical conflicts involving water quantity have persisted from the turn of the last century and will probably continue through the turn of the next one. But the issues of water *quality*, in terms of ecosystem health and human health, will probably become equally important in the years ahead. ☐