ARSENIC GEOCHEMISTRY IN SOURCE WATERS OF THE LOS ANGELES AQUEDUCT

by

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ABSTRACT

Arsenic is a widely distributed constituent of geologic materials, with an average crustal abundance of 1.8 ppm. The natural processes of weathering of arsenic-containing minerals and volcanism contribute arsenic to groundwaters, surface freshwaters, and seawater. Recently, increased attention has focused on arsenic geochemistry in natural waters. This attention has been motivated by concern over the human health effects of arsenic exposure; consumption of drinking water can be a significant, if not the primary, route for ingestion of inorganic arsenic. Since the concentrations of inorganic arsenic in various foods and source waters can vary widely, the exposure of any individual or group depends strongly on both diet and the quality of locally-supplied drinking water.

Two field studies were conducted to examine arsenic occurrence and redox speciation in natural waters in California with elevated arsenic concentrations. In Hot Creek, located in the Owens Valley, elevated arsenic concentrations are the result of geothermal inputs. Hot Creek flows into the Owens River, a source of drinking water to the City of Los Angeles. In Hanford, located in the San Joaquin Valley, elevated arsenic concentrations occur in groundwater wells emplaced in Quaternary alluvial sediments. These municipal supply wells serve the City of Hanford (population ca. 39,000).

At Hot Creek, concentrations of total arsenic, arsenic(III) and chloride (as a conservative tracer of geothermal inputs) were measured above, within, and downstream of the major geothermal inputs of arsenic in Hot Creek Gorge. Consistent with previous studies, extremely elevated arsenic concentrations were found in waters collected from geothermal pools. Lower concentrations were found in Hot Creek as a result of dilution by meteoric surface waters. Total arsenic behaved conservatively in Hot Creek. Rapid in situ arsenic(III) oxidation was observed. Comparison with batch oxidation studies conducted in the field demonstrated that the in situ arsenic(III) oxidation is microbially mediated.

At Hanford, total arsenic concentrations were found to vary considerably in the 16 municipal supply wells and 4 storage tanks tested. Higher arsenic concentrations (up to 75 μg/L) were found in the shallower wells; deeper wells contained lower arsenic concentrations. Arsenic was found to occur predominantly in the +III oxidation state. Occurrence of arsenic(V) in one of the storage tanks tested indicated that As(III) is oxidized within the distribution system.

keywords: Biogeochemical Cycling, Environment-Organism Interactions, Geochemistry, Ground Water Quality, Oxidation, Streams and Stream Dynamics, Trace Elements, Water Chemistry, Water Quality

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PROBLEM AND RESEARCH OBJECTIVES

Thermal springs in Long Valley, Mono County, CA are the sources of significant inputs of arsenic to Lake Crowley and thus to the Los Angeles Aqueduct. Water delivered to the Los Angeles Aqueduct Filtration Plant contains approximately of 20 μg/L arsenic (ACWA 1994). The Filtration Plant supplies, on average, 450 million gallons of water per day to the City of Los Angeles. Under current operating conditions, minimal arsenic removal is accomplished during water treatment (Ramberg et al. 1995). Municipalities relying on groundwater in arid regions, such as Hanford, CA and Albuquerque, NM, must also address the problem of reducing arsenic concentrations in source waters (Reid 1994). Although the current drinking water standard for arsenic (50 μg/L) is not exceeded in the Los Angeles water supply, a downward revision of the standard to between 2 and 20 μg/L is under consideration by the USEPA (Pontius 1994, 1995; Pontius et al. 1994; AWWA 1996).

The feasibility of treating source waters containing elevated arsenic will depend, in part, on the chemical speciation of arsenic in source waters, particularly on its oxidation state (Hering and Elimelech 1996; Hering et al. 1997). The chemical speciation of arsenic in source waters is a critical question in evaluating the mobility of arsenic in natural systems and in designing treatment systems for its removal (Ferguson and Gavis 1972; Cullen and Reimer 1989).

The goals of this project were to investigate the redox chemistry of arsenic in hydrothermally-influenced surface waters in the Eastern Sierra and in groundwater, specifically to identify the ambient redox speciation and to estimate rates of arsenic(III) oxidation under natural conditions. The specific objectives of the study included:

1. Validation of analytical methods for arsenic determination and speciation

2. Development of protocol for collection, handling, and storage of field samples
3. Field-study of arsenic redox speciation in hydrothermally-influenced surface waters using conservative tracers (e.g., chloride) as markers for inputs of geothermal waters
4. Investigation of arsenic(III) oxidation kinetics in surface waters through comparative laboratory and field studies
5. Field study of arsenic redox speciation in groundwaters from arid regions
6. Study of comparative oxidation kinetics of arsenic(III) in natural waters

REVIEW OF METHODOLOGY

Field studies were conducted at Hot Creek in the Owens Valley, California and in the City of Hanford in the San Joaquin Valley, California. Field studies consisted of the collection of water samples, which were analyzed for total arsenic and arsenic(III) as well as for a range of other analytes. Incubation studies were performed in the field to assess the rates of arsenic(III) oxidation as determined by measurement of arsenic(III) concentrations over time. Details of the experimental procedures are provided in Wilkie (1997), Hering and Chiu (1997), and Wilkie and Hering (submitted). A summary of the experimental methods is given here.

Analytical Methods

Arsenic concentrations were determined by hydride generation-flame atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS). Chloride samples were analyzed by ion-chromatography. Concentrations of boron and other major and trace elements were determined by ICP-MS.

Arsenic samples were acidified in the field with either 1% (v/v) trace metal grade hydrochloric acid (AAS analysis) or 1% (v/v) trace metal grade nitric acid (ICP-MS analysis). Samples for chloride determination were collected and stored without preservatives (i.e. without acidification). Samples were stored at 4 °C and analyzed within 1 week.

In the field, pH was measured with an Orion Model 230A portable pH meter. A Fisher Model 15 pH meter was used in the laboratory. The pH electrodes were calibrated with 2 or 3 buffers (pH 4.0, 7.0 and 10.0). Temperature was measured with a type K thermo-couple thermometer.

Determination of Arsenic Speciation. An anion exchange method (Ficklin 1983) was adapted for separation of As(III) and As(V) in the field. Columns were prepared in the laboratory prior to each field trip. The anion exchange resin was obtained in the chloride form and converted to the acetate form prior to column packing. Chloride counterions were removed by three batch resin washings in 1 M NaOH followed by a DI water rinse. The OH^- counterions were then replaced with CH_3COO^- by four batch resin washings in 1 M acetic acid (Wilkie 1997). Each column was slurry packed with approximately 2 mL resin and excess DI water to keep the resin moist. Columns were capped and refrigerated until transported to the field.

On-site separation of inorganic arsenic species was accomplished by acidifying the source water to approximately pH 3.5 then passing it through an anion-exchange column allowing anionic As(V) species to be retained by the column resin and neutral As(III) species to pass through the column. Sub-samples of the acidified source water were obtained before (inlet) and after (effluent) column separation for determination of total arsenic and As(III) concentrations, respectively. As(V) concentrations were determined by difference (i.e. inlet $[As]_T$ - effluent

[As(III)]). Each column was used only once. The method was validated in a standard addition test conducted in the field with both geothermal and creek water (Wilkie 1997).

Field Studies at Hot Creek

Spatial Variability in Arsenic Concentration and Oxidation State. Ambient arsenic concentration and redox speciation as a function of distance were determined along a reach of slightly less than 1 mile (ca. 1200 meters) of Hot Creek in January 1996. At selected points along the reach, creek water samples were collected for determination of chloride, total arsenic and arsenic redox speciation.

Cross-sectional and depth variations in arsenic concentration and speciation were determined at several sites both within Hot Creek Gorge and downstream of the approximate hydrothermal boundary. Gorge and downstream samples were collected in February 1996 and July 1996, respectively. A cross-stream sampler was used to collect samples at 1 m intervals across the creek and a depth sampler to collect samples at 0.3 m intervals. Water samples were collected simultaneously by drawing water into 1 L bottles through tubing attached to a rigid support. The bottles and associated tubing were connected in parallel to a vacuum hand pump and samples were collected over a period of approximately 4 minutes.

Incubation Studies. Arsenite oxidation rates were determined in batch studies by determining arsenic(III) concentrations in sub-samples collected over time. Batch studies were conducted under both ambient conditions and after the addition of a 2 μM As(III) spike. Arsenic(III) oxidation was examined in the presence of aquatic macrophytes and/or macrophyte surface matter; "sterile" filtered and antibiotic controls were performed.

Field Studies at Hanford

Sample Collection. Samples were collected at 16 municipal water supply wells and 4 storage tanks on July 11-12, 1996 with the assistance of personnel from the City of Hanford Dept. of Public Works. On July 11, 1996, water samples were collected from wells 33 and 8, tanks 4, 1 and 2, wells 34, 32, 3, 35 and 2, tank 2, wells 11, 22, 38, 25, 31, 18, and 36 (in the order listed). Collection was begun at 0820 h and continued throughout the day; sample processing at each station required approximately 15 min. On July 12, 1996, water samples were collected from wells 39 and 16 beginning at 0815 h. In some cases (for wells 22, 18, and 16), pumping was started manually at the wells at least 20 min before sample collection. All other wells were already pumping at the time of sample collection. On December 17-18, 1996, 3 wells and 1 storage tank were re-sampled and aeration experiments were conducted with collected water samples. On December 17, 1996, samples were collected from wells 33 and 16 and tank 4 beginning at 0840 h. Well 33 was started manually 30 minutes before sample collection; well 16 was already pumping. Both wells were pumped continuously throughout the sampling period. Sampling and sample processing was conducted at these sites throughout the day (in the order listed). On December 18, 1996 pumping at well 8 was started and this well was added to the site rotation. Sampling on December 18, 1996 was begun at 0835 h at well 33. Sampling at well 8 was begun at 1000 h. Samples were collected at sampling taps and at least 6 to 10 L of water was wasted before the sample was taken.

Samples were collected into 2-L high density polyethylene bottles. Plastic syringes were used to transfer water sub-samples into storage bottles or beakers. The original sample bottle was kept capped except during transfers. Sub-samples for trace element analysis were withdrawn first, then sub-samples for chloride analysis, and finally sub-samples were transferred to 150 mL beakers to be acidified for the speciation procedure.

Aeration Studies. For the aeration experiments, approximately 1.4 L sub-samples were transferred into 2 L polycarbonate mason jars with caps fitted with fritted gas bubbling tubes. Aeration was initiated at 1017 h on December 17, 1996 for samples from wells 33 and 16 and tank 4 and at 1020 h on December 18, 1996 for the sample from well 8. The aeration experiment was set up at the pump house for well 33. Samples were aerated by bubbling with air from a pressurized cylinder. Aliquots were removed from the aeration experiment vessels for determination of total As and As(III) each time well 33 was sampled.

DISCUSSION OF RESULTS AND THEIR SIGNIFICANCE

Field Studies at Hot Creek

Field studies were conducted within, upstream, and downstream of Hot Creek Gorge; Hot Creek, a tributary to the Owens River, is located in the eastern Sierra Nevada (Figure 1). Within the gorge area, an approximately 370 meter reach of Hot Creek (Eccles 1976), there are numerous hot springs, seeps, and fumaroles, some at boiling temperatures, located both along the banks of the creek and in the streambed. Geothermal waters containing high concentrations of reduced inorganic arsenic, chloride, boron, and other dissolved minerals, mix with dilute, oxic surface waters before traveling downstream (Eccles 1976; DWR 1967; Sorey and Clark 1980; Sorey et al. 1994). This mixing dominates seasonal temperature variations and results in a relatively constant downstream temperature profile. During the low flow, winter months, downstream temperature measurements ranged from 24 to 28 °C. July measurements were slightly lower, 23 to 25 °C, as a result of spring runoff. Temperature decreases of 1 to 3 °C were generally observed over a one mile reach downstream of the Gorge.

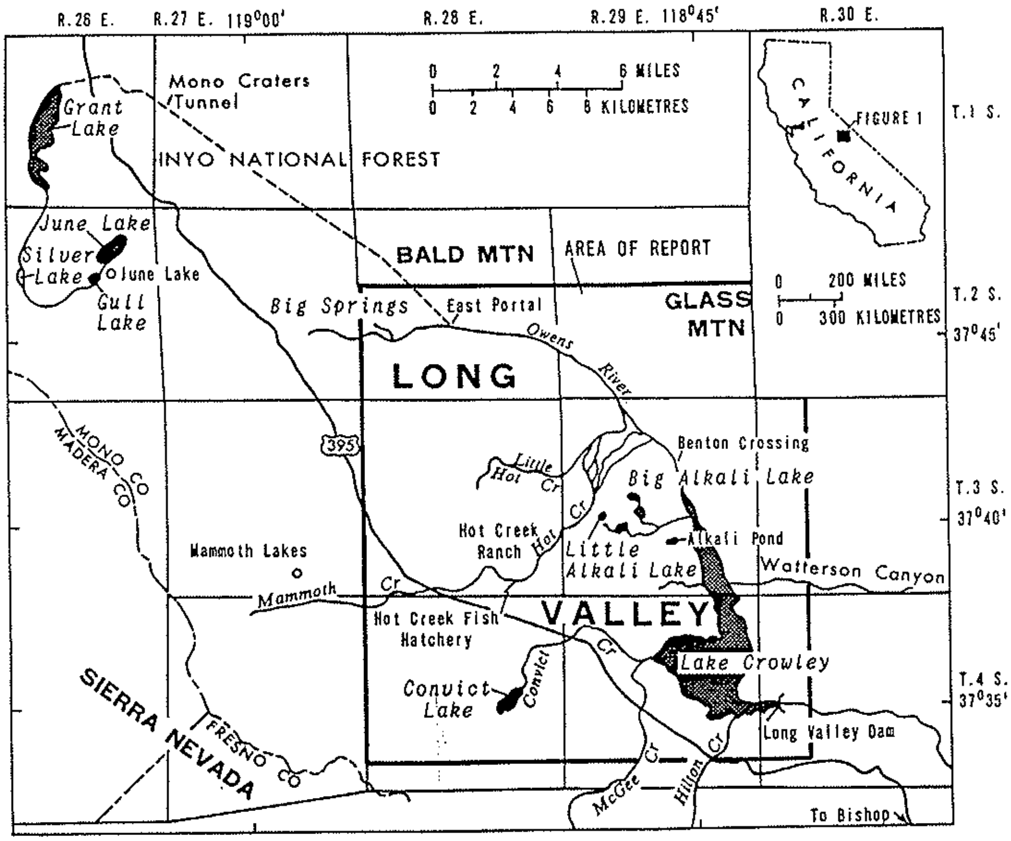


Figure 1. Map of Hot Creek field study area (from Eccles 1976).

Arsenic Concentrations and Speciation in Hot Creek. Above Hot Creek Gorge, total arsenic concentrations were approximately 0.5 μM (37 μg/L). Arsenic occurred entirely in the oxidized form as As(V). It should be noted that some geothermal activity does occur upstream of this sampling site (Eccles 1976) and thus these values, although low compared to those measured downstream, do not represent the background for meteoric surface waters in this region.

Total arsenic concentrations in thermal pools along the banks of Hot Creek ranged from 10.0 to 18.1 μM (750 to 1360 μg/L) as shown in Figure 2; temperatures in the pools ranged from 93 to 27 °C. These temperature decreases can, in general, be attributed to cooling during contact with the atmosphere rather than to dilution with meteoric surface water. Only two pools exhibited decreased total arsenic concentrations indicative of dilution. Decreasing fractions of As(III) were observed in the pools at lower temperatures; values for %As(III) ranged from 73% in an 85 °C pool to 0% in a 61 °C pool (Figure 2). These results suggest that the extent of oxidation is related to residence time within the hot spring pools with lower pool temperatures associated with longer residence time and an increased fraction of oxidized arsenic.

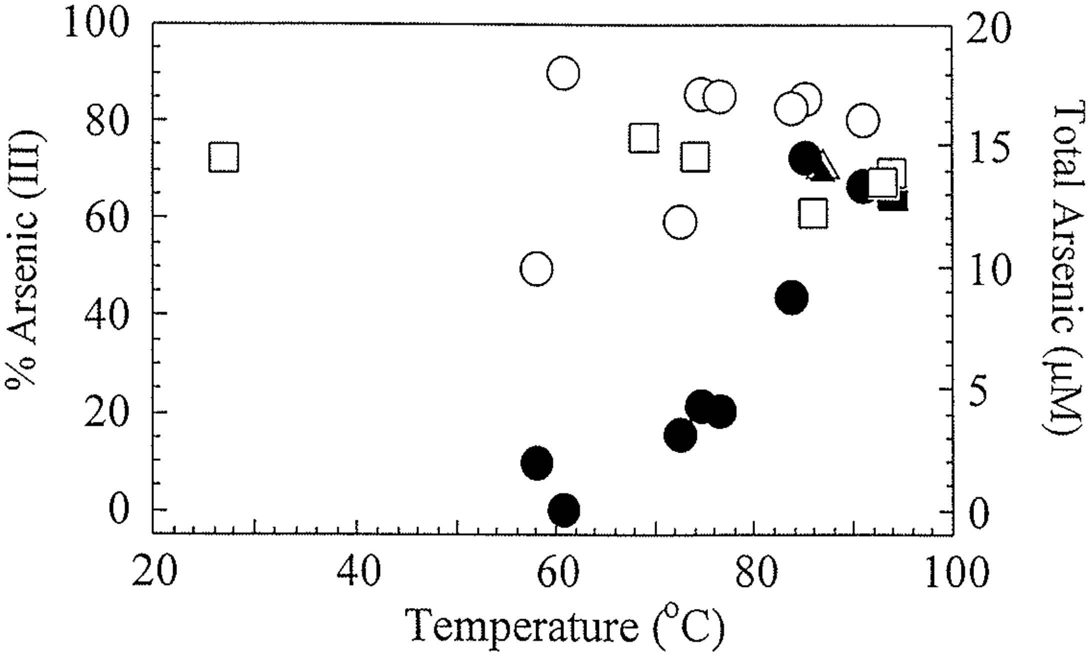


Figure 2. Total arsenic concentrations (open symbols) and %As(III) (closed symbols) as a function of hot spring pool temperature. Samples collected in November 1995 (■,□), January 1996 (▲,△), and July 1996 (●,○). Samples above 25 °C cooled on ice for 5-10 minutes before on-site sample processing through anion-exchange columns.

In the gorge area of Hot Creek, total arsenic concentrations varied considerably, consistent with the spatial distribution of arsenic inputs in this reach of the stream. Total arsenic concentrations ranged from 1.14 to 2.04 μM (85.4 to 153 μg/L). The values for %As(III) ranged from 39 to 50%. At a single location, the cross-sectional variability in %As(III) was less pronounced (varying from 39 to 44%).

Although the boundary of the geothermal inputs is difficult to define precisely, the concentrations of total arsenic and of other conservative tracers of geothermal inputs, such as chloride and boron, were relatively constant below the gorge area (Figure 3). Conservative behavior of total arsenic in the Hot Creek system has been reported previously (Sorey and Clark 1980; Sorey et al. 1994). The redox speciation of arsenic, however, changes dramatically. Within an approximately one mile reach downstream of Hot Creek Gorge, As(III) is almost entirely oxidized to As(V). An exponential decrease in %As(III) was observed with distance downstream (Figure 3). Based on an estimated flow velocity of 0.4 m/s, this corresponds to a pseudo first-order half-life for As(III) (with respect to oxidation) of about 0.3 h.

Microbial Mediation of As(III) Oxidation. In oxic waters, As(III) is thermodynamically unstable with respect to oxidation by oxygen. The kinetics of the oxygenation reaction, however, are too slow to account for the rapid As(III) oxidation observed in Hot Creek (Eary and Schramke 1990). Based on a series of batch studies (presented in detail in Wilkie 1997), this rapid oxidation was attributed to microbial mediation. Aquatic macrophytes, which are present in abundance in Hot Creek below the gorge area, appear to serve as a solid substrate for As(III)-oxidizing bacteria. Rapid As(III) oxidation was observed in batch studies in the presence of material obtained from the surface of aquatic macrophytes (Figure 4); As(III) oxidation rates were the same at ambient As(III) concentrations and with a 2 µM (150 µg/L) spike of As(III). Similar oxidation rates were observed in the presence of the plant material (data not shown). Pre-incubation of the samples with antibiotics for 3 or 72 h completely eliminated As(III)-oxidizing activity (Figure 4). Consistent with the mechanism of antibiotic action, a pre-incubation period was required for the effects of antibiotics to be observed. As(III) oxidizing activity could also be eliminated by "sterile" filtration (using 0.22 µm filters) (Wilkie 1997; Wilkie and Hering, submitted).

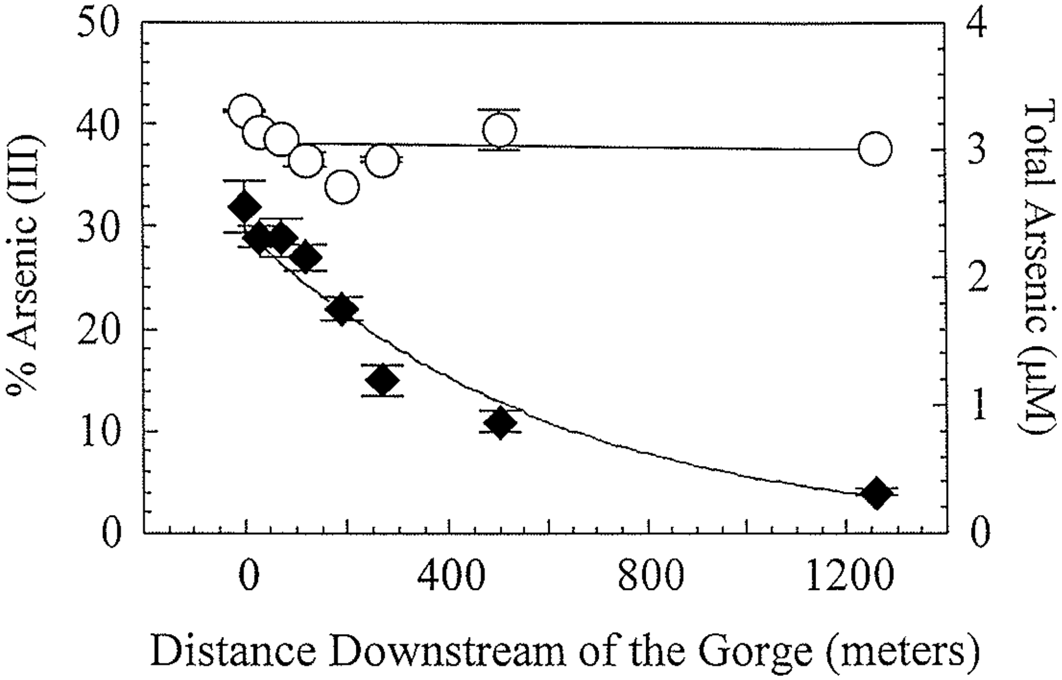


Figure 3. Variations in ambient % As(III) (◆) and total arsenic concentration (○) as a function of distance downstream of Hot Creek Gorge. Samples collected in January 1996. Symbols represent the mean of samples run through duplicate columns and error bars indicate ±1 SD.

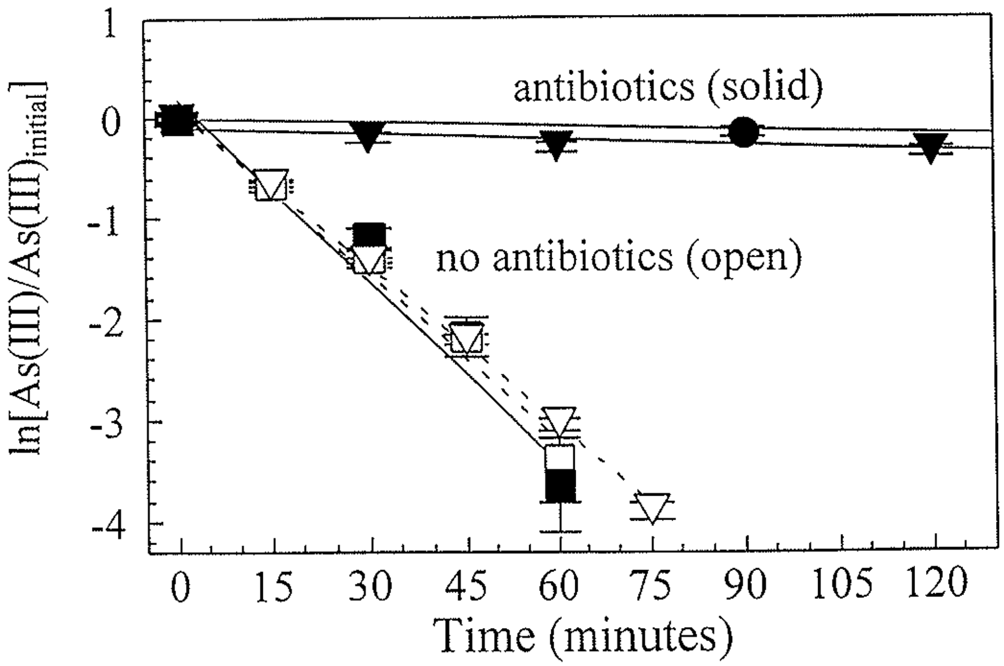
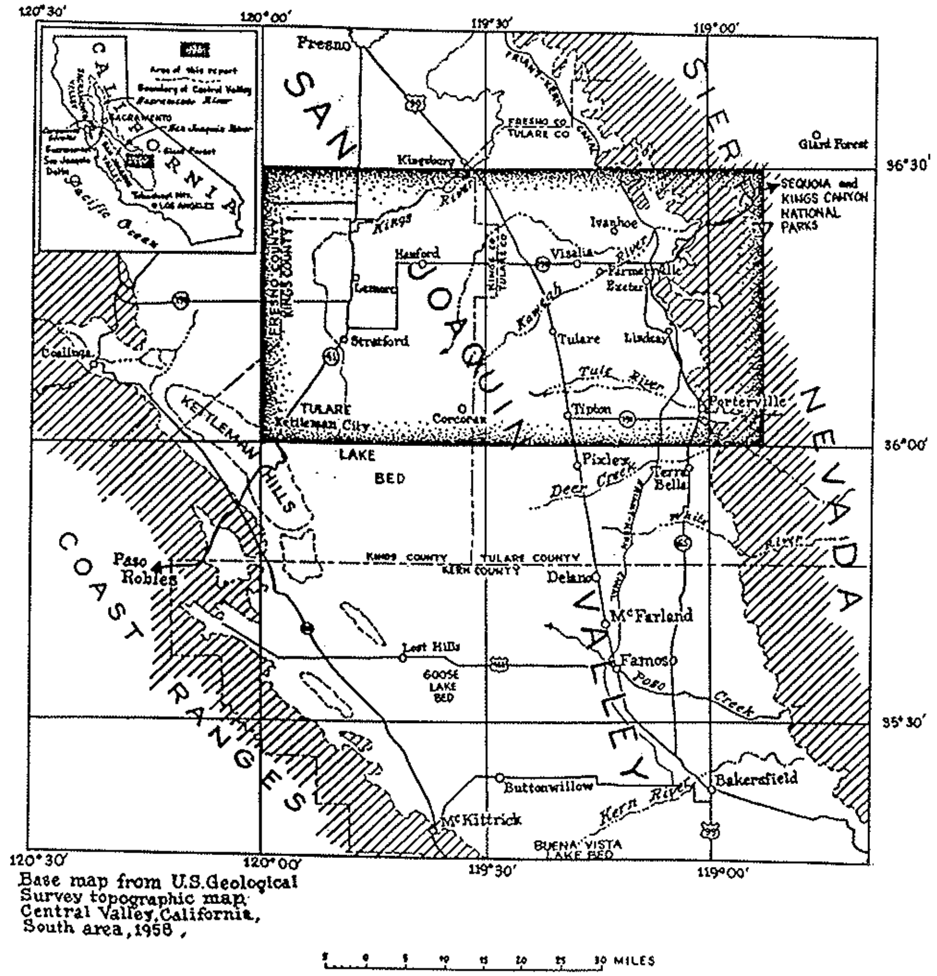


Figure 4. Logarithmic plots of normalized As(III) concentrations as a function of time in the presence (solid symbols) and absence (open symbols) of antibiotics with samples collected in April 1997. Samples containing water from Hot Creek and macrophyte surface matter were pre-incubated with antibiotics for 0 h (■), 3 h (▼), and 72 h (●) before addition of a 2 μM As(III) spike. Experiments without antibiotics were conducted under ambient conditions (□) and with a 2 μM As(III) spike (▽). Symbols represent the mean of samples run through duplicate columns and error bars indicate ±1 SD.

Field Studies at Hanford

A second field study was conducted in the City of Hanford, CA located in the San Joaquin Valley (Figure 5). In Hanford, elevated concentrations of arsenic occur in groundwater wells emplaced in Quaternary alluvial sediments (Norris and Webb 1990). Arsenic concentrations in municipal supply wells frequently exceed the current drinking water standard

(50 ppb) although some dilution is achieved within the distribution system. Water samples were collected on July 11-12, 1996 from 16 municipal water supply wells and 4 storage tanks. On December 17-18, 1996, 3 wells and 1 storage tank were repeatedly re-sampled over the two day period and aeration experiments were conducted.



Base map from U.S. Geological Survey topographic map Central Valley, California, South area, 1958.

Figure 5. Map of Hanford field study area (from Croft and Gordon 1968).

Total Arsenic Concentrations in Hanford Well Water. Total As concentrations measured in July 1996 ranged from a low of 9 μg/L (well 32) to a high of 75 μg/L (well 11). Measured values of total As concentrations were generally consistent with monitoring records provided by the City of Hanford Dept. Public Works as illustrated for wells 25 and 36 in Figure 6. This figure also illustrates that total As concentrations are relatively constant over time in some wells but not in others; well 25 appears to show a trend of increasing total As concentrations over the last year. Previous studies have indicated that total As concentrations in Hanford wells vary with hydrologic conditions (as indicated by static water levels) (Johnson, 1990).

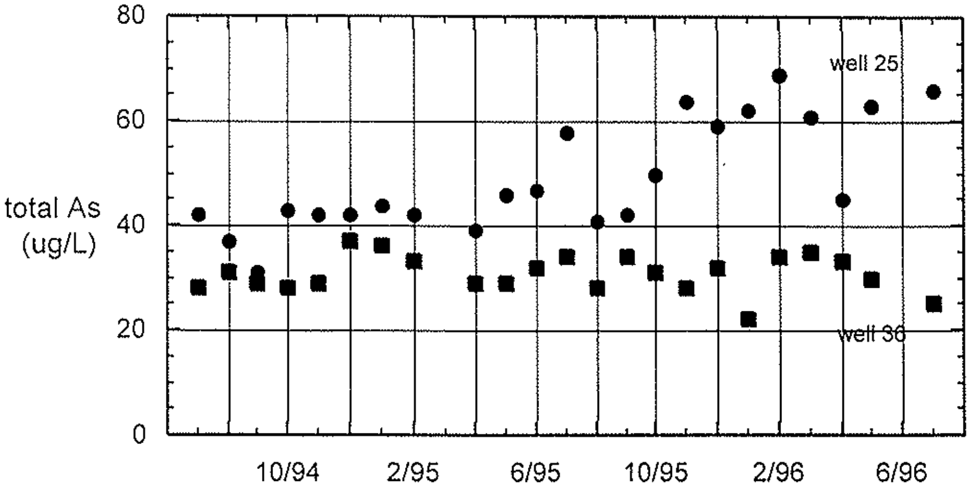


Figure 6. Total arsenic concentrations (μg/L) in samples from wells 25 and 36. Data from July 1994 through May 1996 provided by the City of Hanford Dept. of Public Works. Data from July 1996 obtained in this study.

Total arsenic concentrations showed no consistent spatial distributions. However, higher arsenic concentrations (>35 μg/L) were generally found in shallower wells (approx. 500 ft. maximum depth) drilled before 1981 and lower concentrations (<35 μg/L) in more recently-drilled, deeper wells (approx. 1500 ft. maximum depth) (Johnson pers. comm.).

Examination of correlations between concentrations of total As and other groundwater constituents suggest that the groundwaters sampled cluster into two types, high chloride (Cl > 100 mg/L) and low chloride (Cl < 30 mg/L) as shown in Figure 7. Concentrations measured in one storage tank (tank 4) indicate mixing between these water types. The composition of waters sampled at the wells located nearest to tank 4 (wells 8 and 33) are consistent with this hypothesis; observed Cl concentrations were 22 mg/L at well 8 and 141 mg/L at well 33. In general, the high Cl water samples were found to have lower total As concentrations (22 ± 6 μg/L) and the low Cl water samples to have higher total As concentrations (55 ± 11 μg/L). Within these two clusters, however, there appears to be no correlation between total As and Cl.

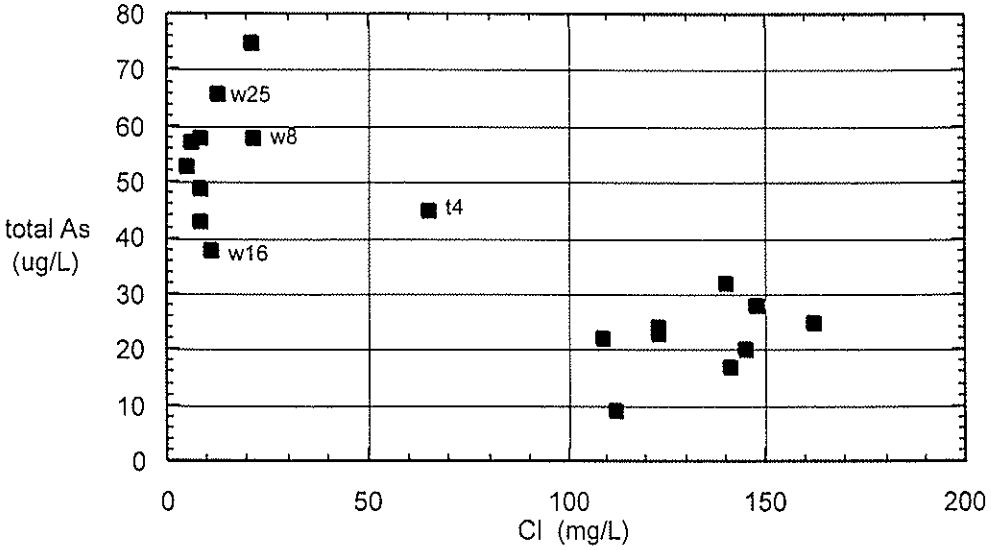


Figure 7. Total arsenic concentrations (μg/L) as a function of chloride concentrations (mg/L) in wells and storage tanks sampled in July 1996. Note that the data appears to cluster into two types distinguished as low and high Cl with tank 4 showing possible mixing effects. Samples from wells 8, 16, and 25 contained < 70% As(III).

Arsenic Redox Speciation and Evidence for As(III) Oxidation. In most of the samples collected, arsenic was found to occur in the +III oxidation state (Figure 8) consistent with previous observations made in the course of testing treatment options (Clifford 1990). In July 1996, lower contributions of As(III) to total arsenic concentrations were found in 3 wells and 1 storage tank; As(III) as a percent of total arsenic was 25% in well 8, 45% in well 16, 67% in well 25 and 1% in tank 4. For all other samples collected, the percent As(III) was 89 ± 6%. In December 1996, wells 8, 16, and 33 and tank 4 were repeatedly re-sampled over a 2-day period. Average values are shown in Figure 8 (open symbols). Some differences were observed between the total As concentrations measured in July and December 1996 and also in the Cl concentrations. The %As(III) values were consistent for both sampling times. Based on the July 1996 data, all three wells with lower %As(III) values fell into the high Cl water type but no other obvious similarities in the composition of these three water samples could be identified.

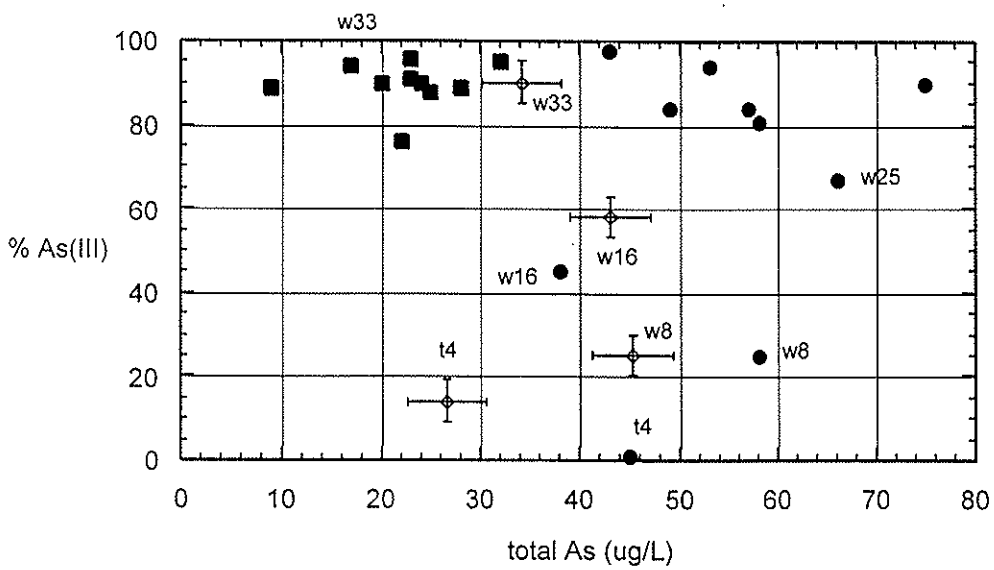


Figure 8. Contribution of As(III) to total arsenic concentrations (percent) shown as a function of total arsenic (μg/L). As(III) predominates in most samples. Closed symbols July 1996 for low Cl (●) and high Cl (■) water samples. Open symbols December 1996. Note that the bars indicate the range in measured values; standard deviation of total As measurements is ± 1 μg/L.

The low values of %As(III) in tank 4 indicates that the As(III) oxidation process is occurring within the distribution system and/or during storage. Tank 4 is located on the outskirts of the distribution system; the closest wells are wells 8 and 33. The estimated residence time of water in tank 4 is approximately 1 day (T. Carr, pers. comm). The lower %As(III) values measured in wells 8, 16, and 25 may also be due to As(III) oxidation, perhaps by contact with minerals in the groundwater flowpath.

Aeration experiments were conducted in December 1996 with water samples from wells 8, 16, and 33 and tank 4. Minimal As(III) oxidation was observed even after 15 h of constant aeration (for detail see Hering and Chiu 1997). The lack of appreciable As(III) oxidation in the aeration experiments is consistent with the known inertness of As(III) with respect to reaction with oxygen (Eary and Schramke 1990). The apparent rapid As(III) oxidation within the distribution system (i.e., based on the low %As(III) measured in tank 4) must thus be due to reaction with an alternate oxidant or catalysis of oxygenation.

PRINCIPAL FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

Two field studies were conducted in areas with naturally-elevated arsenic concentrations, the first study at Hot Creek in the Owens Valley. Concentrations of total arsenic, arsenic(III) and chloride (as a conservative tracer of geothermal inputs) were measured in Hot Creek, above, within, and downstream of the major geothermal inputs of arsenic in Hot Creek Gorge. Consistent with previous studies, extremely elevated arsenic concentrations were found in waters collected from geothermal pools. Lower concentrations were found in Hot Creek as a result of dilution by meteoric surface waters. Total arsenic behaved conservatively in Hot Creek. Rapid in situ arsenic(III) oxidation was observed. Comparison with batch oxidation studies conducted in the field demonstrated that the in situ arsenic(III) oxidation is microbially mediated.

The second study was conducted in the City of Hanford in the San Joaquin Valley. Total arsenic concentrations were found to vary considerably in the 16 municipal supply wells tested. Arsenic was found to occur predominantly in the +III oxidation state. Occurrence of arsenic(V) in one of the storage tanks tested indicated that As(III) is oxidized within the distribution system.

These observations have important practical implications, particularly for water treatment. Many treatment technologies are more effective with As(V) than with As(III). Thus, if arsenic occurs in the +III oxidation state, an oxidation unit operation must be included in the treatment system for maximum efficiency. In the case of Hot Creek, As(III) oxidation occurs naturally in the stream channel. A treatment facility sited even a mile downstream of the geothermal arsenic inputs could rely on these natural processes thus eliminating the need for conventional oxidants, such as chlorine, permanganate, etc. At Hanford, groundwaters collected at the wellheads contained predominantly As(III). Thus an oxidation step would need to be included in wellhead treatment for maximum efficiency. The As(III) oxidation which was observed to occur within the distribution system might eliminate the need for this unit operation in point-of-use treatment but the extent of in situ As(III) oxidation throughout the system remains to be quantified.

SUMMARY

Arsenic biogeochemistry was studied in two very different regimes. At the Hot Creek study site, elevated arsenic concentrations occur in surface streamwaters as a result of geothermal inputs. At the Hanford study site, elevated arsenic concentrations are found in groundwater wells emplaced in Quaternary alluvial sediments.

At both Hot Creek and Hanford, arsenic is derived from reducing environments and is initially present predominantly in the +III oxidation state. The redox speciation of arsenic affects its toxicity, its mobility in natural systems, and the efficiency with which it can be removed from potable water in treatment systems. In oxygenated waters, As(III) is thermodynamically unstable with respect to oxidation to As(V). The reaction of As(III) with oxygen, however, is sufficiently slow that As(III) can occur in oxic waters as a metastable species.

In both the Hot Creek and Hanford systems, evidence for in situ As(III) oxidation was observed. In Hot Creek, rapid oxidation was observed; the pseudo first-order half-life for As(III) with respect to oxidation was approximately 0.3 h. Batch kinetics studies, including antibiotic and "sterile" filtered controls, indicated that this rapid oxidation was microbially mediated. In the Hanford system, the predominance of As(V) in water samples collected from a storage tank on the outskirts of the distribution system indicated that As(III) oxidation was also occurring in this system. The proximate oxidant for As(III) in this system has not yet been determined.

Ph.D. Dissertation: Jennifer A. Wilkie, Processes Controlling Arsenic Mobility in Natural and Engineered Systems, Civil and Environmental Engineering Department, University of California, Los Angeles, June 1997.

SOURCES CONSULTED

ACWA 1994. Survey of Low Level Arsenic Concentrations in Surface and Ground Water in California, Association of California Water Agencies, Sacramento, CA.

AWWA 1996. "Bill Signed to Overhaul SDWA", *AWWA Mainstream*, 40(9): 1, Amer. Water Works Assoc., Denver, CO.

Clifford, D.A. 1990. Ion exchange and inorganic adsorption. In *Water Quality and Treatment*, 4th ed., Ed. F.W. Pontius, AWWA, Mc-Graw-Hill, New York, pp. 561-639.

Croft, M.G. and Gordon, G.V. 1968. Geology, hydrology, and quality of water in the Hanford-Visalia area, San Joaquin Valley, California. U.S. Geological Survey, Open-File Report. Water Resources Division, Menlo Park, CA, April 10, 1968.

Cullen, W.R. and Reimer, K.J. 1989. Arsenic Speciation in the Environment. *Chem. Rev.* 89, 713-764.

DWR 1967. Investigation of Geothermal Waters in the Long Valley Area, Mono County, California Dept. of Water Resources.

Eary, L.E. and Schramke, J.A. 1990. Rates of Inorganic Oxidation Reactions Involving Dissolved Oxygen, in *Chemical Modelling of Aqueous Systems*, II, ed. D.C. Melchior and R.L. Bassett, ACS Symp. Ser. 416, pp. 379-396.

Eccles, L.A. 1976. Sources of arsenic in streams tributary to Lake Crowley, CA., U.S. Geological Survey Water-Resources Investigations 76-36.

Ferguson, J.F. and Gavis, J. 1972. A review of the arsenic cycle in natural waters, Wat. Res. 6, 1259-1274.

Ficklin, W.H. 1983. Separation of arsenic(III) and arsenic(V) in ground waters by ion-exchange. Talanta, 30, 371-373.

Hering, J.G. and Elimelech, M. 1996. Arsenic removal by enhanced coagulation and membrane processes. Final Report (No. 90706), Amer. Water Works Assoc. Res. Fdn., Denver, CO.

Hering, J.G., Chen, P.Y., Wilkie, J.A., and Elimelech, M. 1997. Arsenic removal from drinking water during coagulation. *J. Environ. Eng. ASCE*, 123: 800-807.

Hering, J.G. and Chiu, V.Q. 1997. Arsenic occurrence and speciation in groundwater, Hanford CA: Implications for health effects and treatment options. Proceedings CSCE-ASCE Environmental Engineering Conference, July 23-25, Edmonton, Alberta, Canada.

Johnson, C.S. 1990. The Occurrence of Arsenic in Ground Water, Hanford, CA: Possible Geologic and Geochemical Explanations. M.S. Thesis, School of Natural Sciences, California State University, Fresno, CA.

Norris, R.M. and Webb, R.W. 1990. *Geology of California*, 2d ed. John Wiley, NY.

Pontius, F.W. 1994. Crafting a new arsenic rule. *J. Am. Water Works Assoc.*, 86(9), 6-10.

Pontius, F.W. 1995. Uncertainties drive arsenic rule delay. J. Amer. Water Works Assoc., 87(4), 12.

Pontius, F.W., Brown, K.G., Chen, C.-J. 1994. Health implications of arsenic in drinking water. *J. Amer. Water Works Assoc.*, 86(9), 52-63.

Ramberg, S.H., Pintar, G.M. and Stolarik, G.F. 1995. "Arsenic removal in a direct filtration plant." *Proc. AWWA Annual Conf.*, Anaheim, CA.

Reid, J. 1994. Arsenic occurrence: USEPA seeks a clearer picture. *J. Amer. Water Works Assoc.*, 86(9), 44-51.

Sorey, M.L. and Clark, M.D. 1980. Changes in the discharge characteristics of thermal springs and fumaroles in the Long Valley caldera, California, resulting from earthquakes on May 2-5, 1980. Open-File Report 81-203, U.S. Geolog. Survey.

Sorey, M.L., Colvard, E.M., and Ingebritsen, S.E. 1994. Measurment of thermal water discharge outside Lassen Volcanic National Park, CA 1983-1994. Water Resources Investigations Report 94-4180B, U.S. Geolog. Survey.

Wilkie, J.A. 1997. Processes Controlling Arsenic Mobility in Natural and Engineered Systems Ph.D. Dissertation, Civil and Environmental Engineering Dept., University of California, Los Angeles, CA.

Wilkie, J.A. and Hering J.G., "Rapid Oxidation of Geothermal Arsenic(III) in Streamwaters of the Eastern Sierra Nevada", submitted to *Environmental Science and Technology.*