

Rapid Oxidation of Geothermal Arsenic(III) in Streamwaters of the Eastern Sierra Nevada

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Arsenic redox cycling was examined in source waters of the Los Angeles Aqueduct, specifically at Hot Creek, a tributary of the Owens River. Elevated arsenic concentrations in Hot Creek result from geothermal inputs. Total arsenic and As(III) concentrations were determined in the creek and in hot spring pools along its banks. Samples were processed in the field using anion-exchange columns to separate inorganic As(III) and As(V) species. Downstream of the geothermal inputs, decreasing contributions of As(III) to total arsenic concentrations indicated rapid in-stream oxidation of As(III) to As(V) with almost complete oxidation occurring within 1200 m. Based on assumed plug flow transport and a flow velocity of about 0.4 m/s, the pseudo-first-order half-life calculated for this reaction was approximately 0.3 h. Conservative transport of total dissolved arsenic was observed over the reach. Pseudo-first-order reaction rates determined for As(III) oxidation in batch studies conducted in the field with aquatic macrophytes and/or macrophyte surface matter were comparable to the in-stream oxidation rate observed along Hot Creek. In batch kinetic studies, oxidation was not observed after sterile filtration or after the addition of antibiotics, which indicates that bacteria attached to submerged macrophytes are mediating the rapid As(III) oxidation reaction.

Introduction

Geothermal activity in the Long Valley area of Mono County, CA, is responsible for a significant discharge of arsenic (As) to tributaries of Lake Crowley and thus to the Los Angeles Aqueduct (1–3). Because of these inputs, water supplied to the City of Los Angeles through the Los Angeles Aqueduct contains an average As concentration of 20 µg/L, which is significantly higher than in typical U.S. source waters (4, 5). On the basis of recent epidemiological studies, the U.S. Environmental Protection Agency is reevaluating the current maximum contaminant level (MCL) for As of 50 µg/L; the range under consideration is from 20 to 2 µg/L (6, 7).

The concentration and speciation of As in the aquatic environment are governed by numerous biogeochemical

processes, which may be abiotic or biologically mediated (8–16). Inorganic As species usually predominate in surface waters, although methylated species may become dominant in epilimnetic waters overlying a suboxic hypolimnion (12, 14, 16). Of the inorganic species, As(V) is thermodynamically stable under oxic conditions, and As(III) predominates under reducing conditions (8, 9). As(III), however, may be present as a metastable species in oxic environments as a result of slow oxidation kinetics and biologically mediated reactions.

Site Characteristics. Arsenic in Hot Creek is primarily of magmatic origin with source reservoir temperatures estimated at 200–240 °C (3, 17). The primary manifestation of geothermal activity occurs along Hot Creek Gorge, an approximately 370 m reach of Hot Creek (1). Constant concentrations of Cl, a natural tracer, confirm the absence of detectable geothermal activity downstream of the gorge. The gorge encompasses numerous hot springs and seeps located both along the banks of the creek and within the streambed. Here, geothermal waters containing high concentrations of inorganic As(III), Cl, B, and other dissolved minerals mix with dilute, oxic surface waters. The geothermal waters also contribute significant alkalinity (1); the average pH measured in Hot Creek was 8.3. Seasonal temperature variations are muted by the geothermal inputs. During the low flow, winter months, downstream temperatures ranged from 24 to 28 °C. July temperatures were slightly lower, 23–25 °C, as a result of spring runoff. Temperature decreases of 1–3 °C were generally observed over a 1200-m reach downstream of the gorge.

Submerged macrophytes are located both upstream and downstream of the gorge but are sparse within the gorge area. The relatively constant water temperatures downstream of Hot Creek Gorge allow year-round plant growth. Similar species are found in both locations with the most abundant species growing throughout the water column and forming mats at the surface of the creek. One type of plant has slender stems with branched, grass-like leaves; average stem lengths are approximately 3 m. Another has 60–120-cm branches with thick foliage of 1-cm leaves completely covering the perimeter of the stem; the leaves were covered with a silty material. Although the macrophytes have not been positively identified, the predominant species resemble *Hydrilla verticillata* and *Egeria densa* (18). *Egeria densa* is one of three major plant species growing in the geothermally influenced Waikato River system, New Zealand (19).

In this work, field studies were conducted to gain insight into the factors controlling As concentration, mobility, and redox speciation in Hot Creek. Spatial variations in ambient As concentration and speciation were determined along Hot Creek and its adjacent hot spring pools. This information was complemented by batch kinetic studies conducted in the field to estimate the rate of As(III) oxidation within Hot Creek and to identify the proximate oxidants for oxidation of As(III) to As(V) in this system.

Materials and Methods

Standards and Reagents. All chemicals were reagent grade or better and were used without further purification. Solutions were prepared with water purified by reverse osmosis and deionized (DI) using a Barnstead Nanopure system or a Millipore Milli-Q 18 MΩ system. Preparation of As(III) stock solutions from arsenic trioxide, As₂O₃(s), (Aldrich, ACS primary standard) and As(V) stock solutions from sodium arsenate heptahydrate, Na₂HAsO₄·7H₂O (Sigma) and of reagents for As analytics are described elsewhere (20, 21).

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Analytical Methods. Arsenic concentrations were determined as total As by hydride generation-flame atomic absorption spectrometry (AAS) or inductively coupled plasma-mass spectrometry (ICP-MS) (20, 21). Samples collected prior to July 1996 were analyzed by AAS. All of these samples were prereduced with KI before analysis using a Perkin-Elmer Model 3300 atomic absorption spectrometer equipped with an electrodeless discharge lamp (EDL) and coupled to a Perkin-Elmer MHS-10 hydride generation system. Samples collected on or after July 1996 were analyzed by ICP-MS using a Perkin-Elmer/Sciex Elan 5000A system.

Cl samples were analyzed by ion chromatography (IC) using a Dionex DX500 ion chromatograph with an IonPac AG11, 4 mm guard column (Dionex), and IonPac AS11, 4 mm analytical column (Dionex). B concentrations were determined by ICP-MS.

Samples for As analysis were acidified in the field with either 1% (v/v) trace metal grade HCl (AAS analysis) or 1% (v/v) trace metal grade HNO₃ (ICP-MS analysis). Samples for Cl determination were collected and stored without acidification. Samples were stored at 4 °C and analyzed within 1 week.

Measurements of pH were made with an Orion Model 230A portable pHmeter in the field and with a Fisher Model 15 pHmeter in the laboratory calibrated with two or three buffers (pH 4.0, 7.0, and 10.0). Temperature was measured with a type K thermocouple thermometer.

Separation of As Species. An anion-exchange method (22) was adapted for separation of As(III) and As(V) in the field. Columns were prepared in the laboratory prior to each field trip. Dowex 1 × 8 anion-exchange resin, 50–100 mesh (Bio-Rad), was obtained in the chloride form. The resin was converted to the acetate form by equilibration in batch with 1 M NaOH (trace metal grade, VWR) repeated three times and followed by a DI water rinse, then equilibration in batch with 1 M acetic acid (trace metal grade, Fisher), repeated four times, and followed by a DI water rinse; resin and solutions were separated by filtration (20). Poly-Prep 0.8 × 4 cm chromatography columns (Bio-Rad) were slurry packed with approximately 2 mL of resin and excess DI water to keep the resin moist. Columns were capped and refrigerated until transported to the field.

Separation of inorganic As species was accomplished in the field by acidifying the source water to approximately pH 3.5 and then passing it through an anion-exchange column; neutral As(III) species pass through the column, and anionic As(V) species are retained. Subsamples of the acidified source water were obtained before (inlet) and after (effluent) column separation for determination of total As and As(III) concentrations, respectively. As(V) concentrations were determined by difference. 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 (20).

Field Studies. *Spatial Variations in As Speciation.* Downstream of Hot Creek Gorge, water samples were collected at selected locations along a 1200-m reach in January 1996 for determination of Cl, total As, and As(III) concentrations and processed in the field for separation of As species. Ambient water temperature and time were recorded at each location.

Cross-sectional and depth variations in As concentration and speciation were determined at sites within Hot Creek Gorge (in February 1996) and downstream of the geothermal boundary (in July 1996). Samples were collected at 1-m intervals with a cross-stream sampler and at 0.3-m intervals with a depth sampler. Water samples were collected simultaneously by drawing water into 1-L bottles through tubing attached to a rigid support. Bottles and tubing were connected in parallel to a vacuum hand pump, and samples were collected over a period of approximately 4 min and processed in the field.

Batch Kinetic Studies. As(III) oxidation in the presence of aquatic macrophytes was examined using macrophytes collected from within the stream bed, ca. 10 m downstream of the geothermal boundary. The macrophytes were obtained by submerging a 4-L polyethylene bottle approximately 10 cm below the surface and, while submerged, cutting 15-cm lengths of plant (1.2–2 g dry wt/L) from vines trapped in the bottle. The sampling was conducted with as little disturbance to the macrophytes as possible.

All batch studies with macrophytes and/or macrophyte surface matter were conducted in the field at both ambient As concentrations and with the addition of a 2.0 μM As(III) spike. The extent of As(III) oxidation was followed by withdrawing 25-mL subsamples (by syringe) over a 3-h period. Each subsample was immediately filtered through a 0.45-μm cellulose nitrate membrane filter (Sartorius), acidified, and then processed through duplicate anion-exchange columns. The filter apparatus consisted of a 25-mm, polycarbonate, filter holder (Nuclepore) attached to a 30-mL Lur-lock disposable syringe (Becton-Dickinson).

Oxidation in batch studies with macrophyte surface matter (i.e., with material collected from the macrophyte surface but without the plants) was examined by collecting approximately 9 L of creek water containing aquatic macrophytes in a 10-L HDPE carboy. The carboy was immediately capped and vigorously mixed by shaking for 1 min. Approximately 4 L of this mixture was carefully decanted into a 4-L wide-mouth bottle without the transfer of plant material. Oxidation of As(III) was followed over a 3-h period.

The macrophyte/water mixture remaining in the 10-L carboy was used in two additional experiments run concurrently with the untreated experiment described above. One portion of the sample was sterile filtered, and a second portion was treated with antibiotics. In the former case, a three-stage filtration was performed in which samples were prefiltered by transferring the sample, by hand vacuum pump, through a two-stage (0.8-μm prefilter followed by a 0.45-μm final filter) filter cartridge (Gelman). The prefiltered water was then filtered through a 0.22-μm cellulose nitrate membrane, sterile filtration system (Corning). In the latter case, Guillard's antibiotic solution (Sigma) was added to the batch reactors at a ratio of 40 mL of antibiotic solution per 1 L of sample. This solution contained a mixture of 16 250 units of penicillin G, 2 mg of chloramphenicol, and 5 mg of streptomycin sulfate per 100 mL.

Results and Discussion

In-stream Oxidation of As(III). Rapid in-stream oxidation of As(III) upon mixing of high-temperature, geothermal waters with Hot Creek surface waters was demonstrated by the decreasing contribution of As(III) to the total As concentration downstream of the geothermal inputs. The gorge boundary was defined by the plateau in the concentration of natural tracers of geothermal inputs, such as Cl. The fraction of As(III) decreased exponentially from 32% near the boundary of the geothermal (gorge) region to 4% approximately 1200 m downstream (Figure 1). A flow velocity of 0.4 m s⁻¹ was measured at two locations in Hot Creek in November 1995; the corresponding discharge of 1.7 m³ s⁻¹ was in agreement with the discharge of 1.6 m³ s⁻¹ reported by the U.S. Geological Survey (23). Discharge at the flume during the January sampling period was comparable (1.5 m³ s⁻¹), and the same flow velocity (0.4 m s⁻¹) was therefore assumed. On the basis of this flow velocity, the observed gradient in As(III) concentrations corresponds to As(III) oxidation over a period of approximately 1 h. Total As concentrations measured in these samples averaged 3.0 ± 0.3 μM with no systematic change observed over the reach. Scatter in the data may be attributed to cross-sectional variations observed in ancillary experiments (discussed later).

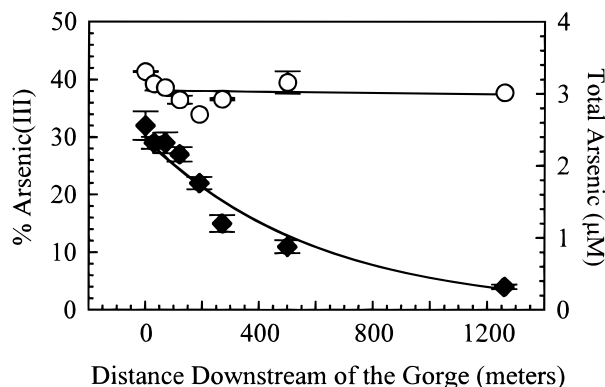


FIGURE 1. Variations in ambient % As(III) (◆) and total As concentration (○) as a function of distance downstream of the boundary of Hot Creek Gorge. Samples were collected in January 1996. Symbols represent the mean of samples run through duplicate columns, and error bars indicate ± 1 SD.

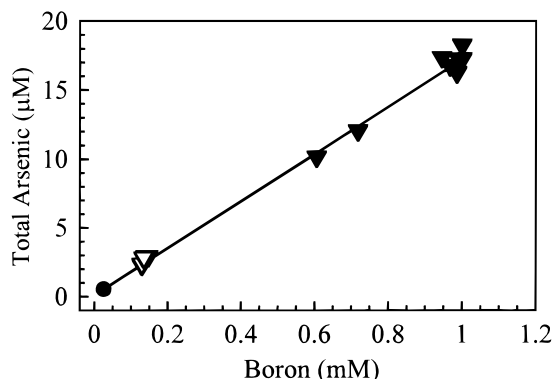


FIGURE 2. Total As versus B concentrations for samples collected upstream (●) and downstream (▽) of the Gorge and from hot pools on the north bank of the Gorge (▼). Samples were collected July 1996.

Upstream total As concentrations (average $0.5 \mu\text{M}$) are negligible compared to concentrations measured in hot spring pools within the gorge ($10\text{--}18 \mu\text{M}$).

The conservative behavior of geothermally derived As during concurrent dilution and cooling by meteoric waters is illustrated by the linear correlation between total As and B in samples collected both upstream and downstream of the gorge and from hot spring pools along the bank (Figure 2). This conservative behavior of (total) As is consistent with previous studies of the area (1, 24) but contrasts with other studies of geothermal systems in which loss of As has been attributed to sorption/coprecipitation with iron and aluminum oxides (25–27) or to uptake by sediments and aquatic macrophytes (19). Oxidation of As(III) to As(V) is often followed by adsorption to the sediments since As(V) is more strongly adsorbed to metal oxides than As(III) (20, 28). Therefore, distinguishing between oxidation and adsorption can be difficult in nonconservative systems. The conservative behavior of total As in Hot Creek permits the direct examination of natural oxidative processes.

The in-stream As(III) oxidation rate observed along Hot Creek is substantially greater than those reported for other nongeothermal systems. On the basis of the estimated flow velocity of 0.4 ms^{-1} , a pseudo-first-order half-life of 0.3 h was calculated for As(III) oxidation. Oxidation observed in sediment and water samples collected from nongeothermal systems has been attributed to both biological (29) and abiotic (30) processes. In general, calculated pseudo-first-order half-lives for As(III) oxidation ranged from 6 to 13 h, however, a value on the order of 0.5 h was observed for one soil isolate

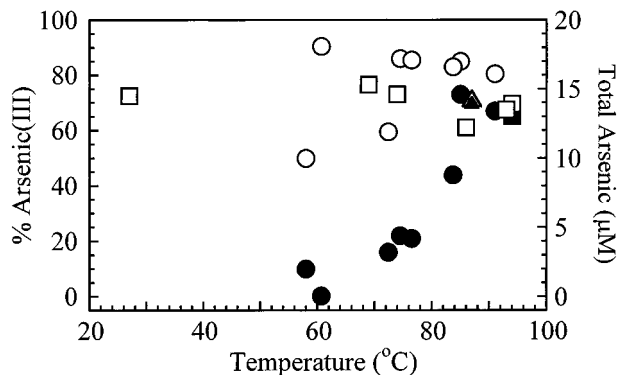


FIGURE 3. Total As concentrations (open symbols) and %As(III) (closed symbols) as a function of hot spring pool temperature. Samples were collected in November 1995 (■, □), January 1996 (▲, △), and July 1996 (●, ○). Samples above 25°C were cooled on ice for 5–10 min before on-site sample processing through anion-exchange columns.

of bacteria (31). Abiotic oxidation has been attributed to manganese oxides in several natural systems (32–34). Rates reported for As(III) oxidation by synthetic manganese oxides varied widely with half-lives between 0.15 and 203 h (32, 35–37). Rapid oxidation of As(III) has previously been reported in the Azure Spring drainage in Yellowstone National Park (25) and in pipelines at geothermal power stations (38) but these rates were not quantified.

Hot Spring Pool Study. Arsenic redox speciation was determined in several hot spring pools located on the north bank of Hot Creek Gorge; temperatures in the pools ranged from 93 to 27°C (Figure 3). 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 As concentrations indicative of dilution (as demonstrated by the linear correlation between total As and B in Figure 2). 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 undetectable in a 61°C pool (Figure 3). Variable As(III)/As(V) ratios have been observed in other geothermal systems and attributed to processes including cooling, mixing with surficial water, and water–rock interactions; however, no clear correlation could be made between %As(III) and temperature (39). Our data are consistent with the extent of oxidation being related to residence time within the hot spring pool with lower pool temperatures associated with longer residence time and an increased fraction of oxidized As. Alternatively, the microbial processes (discussed later) may not be operative at elevated temperature.

Cross-Sectional and Depth Variations. Spatial variations in simultaneously collected samples were examined at several locations along Hot Creek (Table 1). Within the gorge, significant cross-sectional variations were observed for total As concentrations, which ranged from 1.14 to $2.04 \mu\text{M}$. This result is consistent with geothermal inputs in the stream bed. Variability in Cl concentration paralleled total As with values between 0.50 and 0.76 mM . The fraction of As(III), however, was relatively constant among the samples at 41%.

The degree of cross-sectional heterogeneity downstream of the gorge was investigated at three locations to determine the extent of mixing between geothermal and surface waters. The first site was located immediately downstream of the gorge boundary, and the other two sites were approximately 200 and 400 m downstream. Constant total As concentrations (2.74 ± 0.12 , 2.73 ± 0.05 , and $2.67 \pm 0.06 \mu\text{M}$) were found at all three locations. Concentrations of Cl were also constant, but slight variations in %As(III) were observed for the two locations closest to the gorge boundary (Table 1).

TABLE 1. Depth and Cross-Sectional Characterization along Hot Creek

cross-sectional variations	As total (μM)	As(III) (μM)	% As(III)	chloride (mM)
within Hot Creek Gorge ^a	1.49 ± 0.40	0.61 ± 0.20	40.8 ± 1.0	0.61 ± 0.12
~ 10 m downstream ^b	2.74 ± 0.12	0.53 ± 0.11	19.3 ± 4.0	0.82 ± 0.04
~ 200 m downstream ^b	2.73 ± 0.05	0.41 ± 0.09	14.9 ± 3.3	0.80 ± 0.04
~ 400 m downstream ^b	2.67 ± 0.06	0.25 ± 0.04	9.4 ± 1.7	0.80 ± 0.03
depth variations ^c	As total (μM)	As (III) (μM)	% As(III)	chloride (mM)
4.6 m from south bank				
surface	2.34	0.51	21.7	0.69
-0.3 m	2.24	0.56	25.1	0.69
-0.6 m	2.35	0.60	25.7	0.70
9.1 m from south bank				
surface	2.48	0.74	29.9	0.79
-0.3 m	2.48	0.77	30.9	0.78
-0.6 m	2.44	0.77	31.6	0.77
13.7 m from south bank				
surface	2.44	0.70	28.7	0.78
-0.3 m	2.44	0.75	30.9	0.76
-0.6 m	2.40	0.70	29.1	0.74

^a Samples collected February 1996 at a single location within Hot Creek Gorge; additional discharge of geothermal occurred downstream of this sampling location. ^b Samples collected July 1996 at sites downstream of the gorge boundary. ^c Samples collected in July 1996 at a site ~ 50 m downstream of the gorge boundary at three locations across the width of the creek (4.6 m \approx 1/4 creek width, 9.1 m \approx 1/2 creek width, and 13.7 m \approx 3/4 creek width) and at 3 depths (surface, 0.3 m, and 0.6 m below surface).

Vertical profiles were obtained at three locations across the width of the creek immediately downstream of the gorge boundary. The average depth at this location and the downstream locations chosen for cross-sectional characterization was 1 m. Minimal variations in total As, %As(III), Cl, temperature, and conductivity indicate that the reach is vertically well mixed (Table 1).

As(III) Oxidation Kinetics. A preliminary batch study was conducted in the field with water collected within Hot Creek Gorge. Unfiltered samples were transferred into a capped polyethylene bottle. Over 3 h, subsamples were removed and processed (without filtration) for determination of As speciation. Total As and As(III) concentrations remain constant over the 3-h period (Figure 4a) demonstrating the absence of As(III) oxidation. This contrasted markedly to the rapid, in-stream oxidation of As(III).

The absence of As(III) oxidation in the batch study suggested that removal of water from Hot Creek effectively isolated As(III) from its proximate oxidant. Experiments were conducted to examine the effects of sunlight, sediments, and aquatic macrophytes and/or their attached microbial community on As(III) oxidation. Neither (indirect) photochemical reactions nor reactions with creek sediments could account for the rapid, in-stream oxidation of As(III) (20). However, a batch study conducted in the presence of aquatic macrophytes collected from Hot Creek showed extremely rapid oxidation of As(III) both at ambient concentrations and after the addition of $2.0 \mu\text{M}$ As(III) with almost complete oxidation occurring within 45 min (Figure 4b).

These results suggest that the aquatic macrophytes or some component associated with the plants are responsible for the rapid As(III) oxidation occurring within Hot Creek. The rapid oxidation rate observed in the batch studies with the macrophytes compares well with the oxidation rate calculated from the As(III) concentrations observed in Hot Creek as a function of distance. In both cases, the pseudo-first-order half-life calculated for As(III) was 0.3 h.

Evidence for Microbially Mediated As(III) Oxidation. Further studies were conducted to determine whether the observed As(III) oxidation required the presence of the aquatic macrophytes or whether the plants serve merely as a solid support for As(III)-oxidizing bacteria.

To distinguish the role of the aquatic macrophytes from that of their attached microbial communities, As(III) oxidation

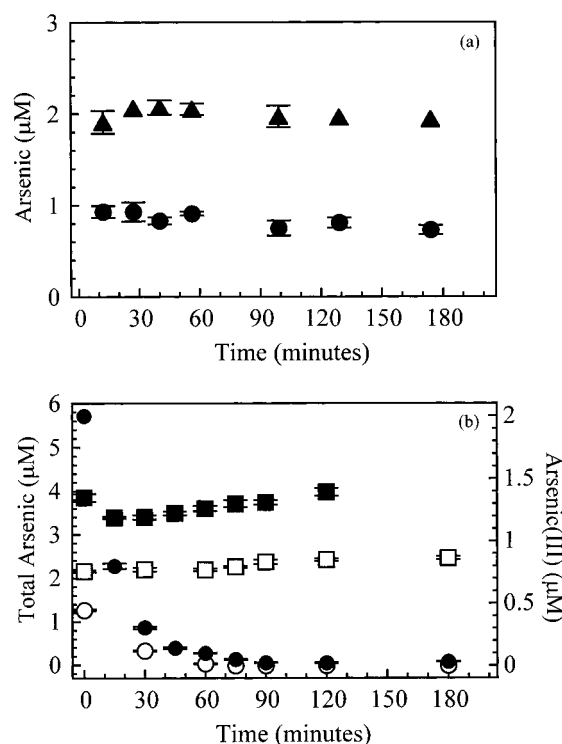


FIGURE 4. As(III) and total As concentrations over time in batch studies of (a) unfiltered water samples collected from Hot Creek Gorge in January 1996: total As (\blacktriangle) and As(III) (\bullet); (b) samples containing water from Hot Creek and aquatic macrophytes collected in April 1997 under ambient conditions (open symbols; $[\text{As}]_T = 2.2 \mu\text{M}$, $[\text{As(III)}]_{\text{init}} = 0.45 \mu\text{M}$) and with a $2.0 \mu\text{M}$ As(III) spike (closed symbols; $[\text{As}]_T = 3.9 \mu\text{M}$, $[\text{As(III)}]_{\text{init}} = 2.0 \mu\text{M}$). Symbols: total As (\square , \blacksquare); As(III) (\circ , \bullet).

rates were determined in batch studies conducted in the field under four conditions: (a) with the aquatic macrophytes, (b) with material collected from the macrophyte surface but without the plants (referred to as macrophyte surface matter), (c) after sterile filtration, and (d) with macrophyte surface matter and antibiotic treatment. These experiments were conducted in the field in April 1997 with aquatic macrophytes

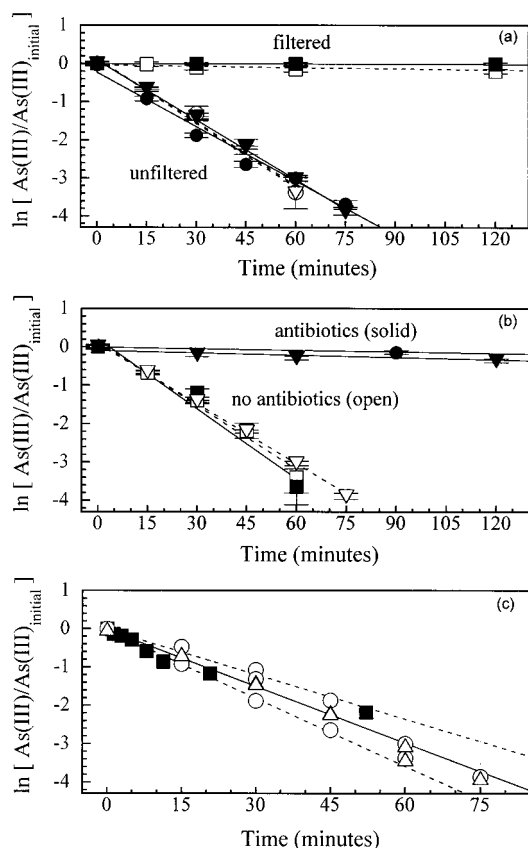


FIGURE 5. Logarithmic plots of normalized As(III) concentrations as a function of time showing (a) the effects of sterile filtration and (b) antibiotic treatment and (c) comparison of batch and in-stream studies. Batch studies were conducted in April 1997 and in-stream studies in January 1996. (a) Experiments with sterile-filtered (\square , \blacksquare) and unfiltered creek water samples, which contained aquatic macrophytes (\circ , \bullet) or macrophyte surface matter (∇ , \blacktriangledown), conducted at ambient As concentrations (open symbols) and with a $2.0 \mu\text{M}$ As(III) spike (closed symbols). Symbols represent the mean of samples run through duplicate columns and error bars indicate ± 1 SD. (b) Samples containing water from Hot Creek and macrophyte surface matter were preincubated with antibiotics for 0 (\blacksquare), 3 (\blacktriangledown), and 72 h (\bullet) before addition of a $2.0 \mu\text{M}$ As(III) spike. Experiments without antibiotics were conducted under ambient conditions (\square) and with a $2.0 \mu\text{M}$ As(III) spike (\triangle). Symbols represent the mean of samples run through duplicate columns and error bars indicate ± 1 SD. (c) As(III) concentrations measured in Hot Creek (\blacksquare) as a function of time calculated from travel distance and flow velocity shown with data from batch studies with aquatic macrophytes (\circ) and with macrophyte surface matter (\triangle). Linear regression for all samples is shown as the solid line with ± 1 SD shown as dashed lines.

and creek water collected from a location approximately 10 m downstream of the geothermal boundary.

With either the aquatic macrophytes or the macrophyte surface matter, an exponential decrease in As(III) concentration was observed (Figure 5). This loss in As(III) was accompanied by an increase in As(V) as demonstrated by a constant total As concentration (cf. Figure 4b). In all cases, almost complete oxidation of As(III) was observed within 60 min. The oxidation rate was independent of the initial As(III) concentration. Pseudo-first-order rate constants ranged from 2.5 to 3.4 h^{-1} for reactions conducted with the macrophytes and from 3.1 to 3.3 h^{-1} for experiments conducted with the macrophyte surface matter. These findings imply that a component that can be removed from the macrophyte surface is mediating the rapid oxidation of As(III).

Effects of Sterile Filtration on As(III) Oxidation. Samples containing macrophyte surface matter were subjected to a three-stage filtration; in the final step, samples were filtered through a $0.22\text{-}\mu\text{m}$ sterile filtration unit. Subsequent batch studies were performed both with ambient As(III) concentrations and with a spike of $2.0 \mu\text{M}$ As(III). In both cases, the oxidizing capacity of the system was completely lost upon sterile filtration. Constant concentrations of As(III) and total As were observed over a 3-h period (Figure 5a).

Effects of Antibiotics on As(III) Oxidation. Scanning electron micrographs of surfaces of aquatic macrophytes collected from Hot Creek show an abundant attached microbial community (20). Batch studies were conducted in which antibiotics were added to samples containing macrophyte surface matter to suppress bacterial activity.

The addition of antibiotics strongly inhibited As(III) oxidation but the effect of the antibiotic treatment was not immediate. With preincubation periods of either 3 or 72 h (during which the samples were exposed to the antibiotics) before being spiked with As(III), negligible As(III) oxidation was observed (Figure 5b). Without any preincubation, the As(III) oxidation rate was unaffected by the addition of the antibiotics. These observations are consistent with the mechanism of antibiotic action.

Comparison of Reaction Rates. As(III) oxidation rates observed in batch studies conducted with aquatic macrophytes and/or with macrophyte surface matter were remarkably similar to the in-stream rate determined for As(III) oxidation along Hot Creek. Logarithmic plots of As(III) concentration as a function of time (Figure 5c) illustrate that, in both in-stream and batch studies, pseudo-first-order oxidation of As(III) was observed with comparable rates. The half-life calculated for in-stream oxidation of As(III) was 0.3 h. The half-lives obtained with aquatic macrophytes and/or with macrophyte surface matter ranged from 0.20 to 0.28 h. The lack of oxidation found in batch studies conducted after sterile filtration of the sample or after the addition of antibiotics to the reactor strongly suggests that bacteria attached to submerged macrophytes are mediating As(III) oxidation in Hot Creek below the gorge boundary where the plants are abundant. It remains to be determined whether microbial processes are also responsible for the As(III) oxidation in the hot spring pools and within the gorge area where the plants are sparse.

Acknowledgments

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