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The Role of Photochemistry the Transport and Transformation of Arsenic

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### Authors

Sedlak, David L  
Bentley, Abra

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The Role of Photochemistry in the Transport and Transformation of Arsenic

By  
David L. Sedlak and Abra Bentley  
Department of Civil and Environmental Engineering  
University of California, Berkeley  
Berkeley, CA 94720

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## ABSTRACT

Arsenic, a toxic trace element, enters surface waters from abandoned mines and geothermal springs. Once arsenic is discharged to surface waters, photochemical reactions can alter the oxidation state of the metal or cause the dissolution of the mineral phases onto which it could adsorb. To assess the role of these photochemical reactions in arsenic fate and transport, we conducted laboratory studies and collected samples from arsenic-contaminated surface waters. Results of laboratory studies indicate that hydroxyl radical ( $\text{OH}^\bullet$ ) is the only photo-produced transient in sunlit surface waters that is capable of oxidizing As(III) at significant rates. A field study conducted at a geothermal spring (Hot Creek) indicated that As(III) is oxidized by photo-produced hydroxyl radical with a half-life of approximately 300 minutes. Photochemical oxidation of As(III) is likely to be faster in acid mine drainage streams, where hydroxyl radical concentrations are much higher. Results of laboratory studies also indicate that arsenic is released during the photoreductive dissolution of iron-containing sediments collected from an acid-mine drainage site (West Squaw Creek).

*keywords:* Watersheds and watershed management (2690), contaminant transport (0470), trace elements (2395), pollution and pollutants (1830), mines and mining (1505), water pollution (2590).

## PROBLEM AND RESEARCH OBJECTIVES

Arsenic, a toxic trace element, is present in many geologic formations (Mok and Wai, 1994). In California, elevated concentrations of arsenic have been detected in waters near abandoned mines and in geothermal springs. If new, more stringent drinking water standards are adopted (Reid, 1994), many surface waters in California will require additional treatment before they can be used as drinking water sources. To assess the sources of arsenic in surface waters and to develop new technologies for remediating arsenic-contaminated sites, a better understanding is needed of the chemical and biological process that affect arsenic mobility and toxicity.

One factor that affects the fate, transport and toxicity of arsenic is its oxidation state. In its trivalent form (As[III]), arsenic is very soluble and toxic, whereas in its pentavalent form (As[V]), arsenic has a high affinity for surfaces and is less toxic (NAS, 1977). Although the conversion of As(III) into As(V) is thermodynamically favored under aerobic conditions, As(III) oxidation is often extremely slow (Jekel, 1994). Any process that rapidly converts As(III) into As(V) is therefore important to the geochemistry of arsenic. Rapid As(III) oxidation reactions also could be useful in water treatment because As(V) is much easier to remove during water treatment than As(III) (Wilkie and Hering, 1996).

Available data suggest that, although arsenic does not absorb visible light (Daniels, 1962), its fate and transport could be affected by photochemical processes. For example, As(III) could be oxidized by photo-produced transients, such as hydroxyl radical ( $\text{OH}^\bullet$ ), superoxide radical ( $\text{O}_2^{\bullet-}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Photoprocesses also could result in the release of arsenic from sediments as iron-containing mineral surfaces undergo reductive dissolution. Photo-enhanced As(III) oxidation and/or release of arsenic from contaminated sediments could be particularly important in shallow streams near acid mines and geothermal springs.

The purpose of this project was to assess the role of photochemical reactions in the environmental fate of arsenic. Specific objectives included:

- (1) Evaluation of the rates of reactions between As(III) and photo-produced transients in sunlit surface waters.
- (2) Assessment of the rate of release of arsenic from sunlit iron oxide surfaces.
- (3) Measurement of the speciation of arsenic in samples collected from sunlit surface waters.

## METHODOLOGY

The role of photochemical reactions in the environmental fate of arsenic was evaluated in laboratory and field experiments. Laboratory experiments were conducted to assess the rate of oxidation of As(III) under conditions comparable to those encountered in sunlit surface waters. After identifying potential oxidants of As(III), samples were collected from streams near abandoned mines and a geothermal spring. Arsenic oxidation states were measured in field samples while water and sediments from the field sites were examined in the laboratory. Details of the analytical techniques and laboratory experiments are summarized below.

The concentration and oxidation state of arsenic was determined using hydride generation atomic adsorption spectrometry (AAS) (APHA, 1992; Driehaus and Jekel, 1992). In most experiments, As(III) was differentiated from As(V) by buffering the solution at pH 5 with acetate prior to analysis. Using deuterium background correction, the detection limit for this technique was approximately 1 nM. This analytical technique was inappropriate for measurements of arsenic oxidation states in the field because reactions could occur between the time of sample collection and analysis. For these samples, As(III) and As(V) were separated by measuring arsenic remaining in the solution after passing it through an anion exchange column (Ficklin, 1983). Total arsenic was measured by hydride generation AAS after acidification with hydrochloric acid.

Laboratory experiments were performed to assess the rate of oxidation of As(III) by  $\text{H}_2\text{O}_2$ ,  $\text{OH}^\circ$  and  $\text{HO}_2^\circ/\text{O}_2^{\cdot-}$ . Oxidation of As(III) by  $\text{H}_2\text{O}_2$  was evaluated by exposing

As(III) to H<sub>2</sub>O<sub>2</sub> concentrations (*i.e.*, 10 or 100 μM) that were several orders of magnitude higher than those encountered in sunlit surface waters (*i.e.*, typical H<sub>2</sub>O<sub>2</sub> concentrations in sunlit waters are < 1 μM [Cooper *et al.*, 1994]). Oxidation of As(III) by OH° was evaluated using Fenton's reagent (*i.e.*, Fe(II) and H<sub>2</sub>O<sub>2</sub>) as a well defined source of OH°. Fe(II) was monitored during the reaction with ferrozine (Stooky, 1974). In some experiments, oxygen was removed by sparging with nitrogen or OH° was scavenged with methanol.

Arsenic-contaminated water and sediments were collected from West Squaw Creek, California on September 12, 1996. Grab samples were placed in a cooler during their transport to the laboratory, where they were filtered and analyzed within 24 hours. Photochemical irradiations were conducted by exposing sample aliquots to light from a mercury lamp equipped with glass filters for removing ultraviolet light (Ace Glass). Samples were placed in stoppered 8-mL quartz tubes and exposed to light for suitable time intervals prior to analysis. The intensity of the lamp was approximately equal to twice the intensity of midsummer noon sunlight.

Field samples also were collected from Hot Creek, California on July 25, 1996. Samples collected before sunrise were placed in 8-mL quartz tubes and irradiated with sunlight for 60 minutes between 1100 and 1300. Potassium nitrate (final concentration 1 mM) was added to several samples as a source of additional OH° (Zepp *et al.*, 1987). Other aspects of arsenic geochemistry at Hot Creek are reported elsewhere (Wilkie and Hering, 1997).

## RESULTS AND SIGNIFICANCE

Our results indicate that, under certain conditions, photochemical reactions can affect the fate and transport of arsenic. The laboratory experiments demonstrate that As(III) is oxidized by  $\text{OH}^\bullet$  and that photoreductive dissolution of iron oxides can release arsenic from contaminated sediments. The field measurements suggest that, although photochemical reactions occur, other processes in surface waters can be more important to arsenic fate and transport. Details of the experiments and our assessment of the relative importance of photoprocesses to arsenic fate and transport are summarized below:

### 1. Oxidation of As(III)

The oxidation of As(III) by  $\text{H}_2\text{O}_2$  is slow under the conditions encountered in sunlit surface waters. Over a period of approximately 1 hour, no loss of As(III) was observed at  $\text{H}_2\text{O}_2$  concentrations of 10 or 100  $\mu\text{M}$  (Figure 1).

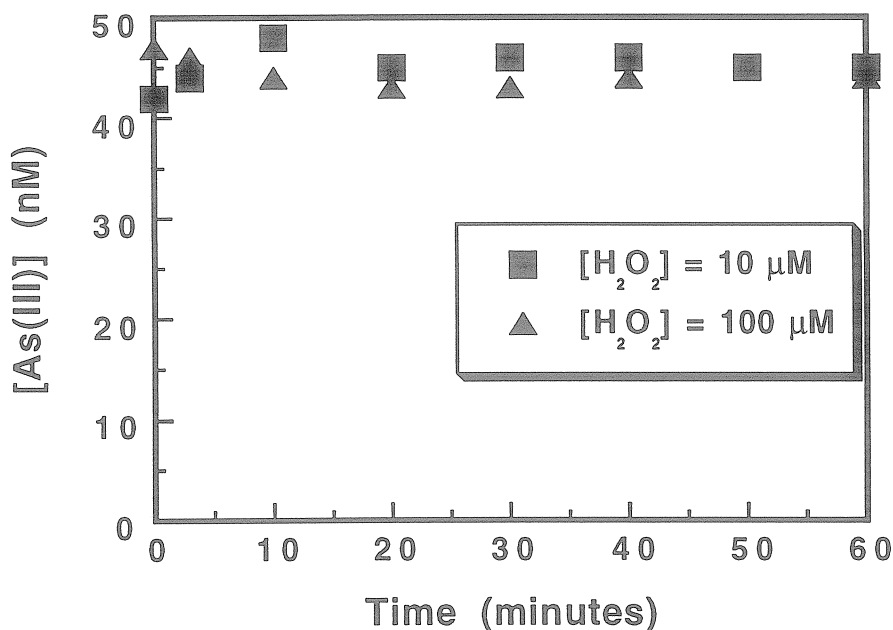


Figure 1. Stability of As(III) in the presence of  $\text{H}_2\text{O}_2$ .



The oxidation of As(III) by  $\text{OH}^\circ$  is relatively fast under conditions encountered in sunlit surface waters. When an As(III)-containing solutions were exposed to  $\text{OH}^\circ$ , most of the As(III) was oxidized within 15 minutes (figure 2). Using known rate constants for the formation and loss of  $\text{OH}^\circ$  and the reported rate of the initial reaction of As(III) with  $\text{OH}^\circ$  (Klänning *et al.*, 1989), the rate of oxidation of As(III) in the absence of oxygen agrees with predictions made by assuming that As(IV) is oxidized by Fe(III) (compare triangles and line in figure 2). The steady-state concentration of  $\text{OH}^\circ$  (*i.e.*,  $[\text{OH}^\circ]_{\text{ss}}$ ) under these conditions is approximately  $2.5 \times 10^{-12}$  M, which is approximately an order of magnitude higher than the concentration expected in sunlit mine drainage streams.

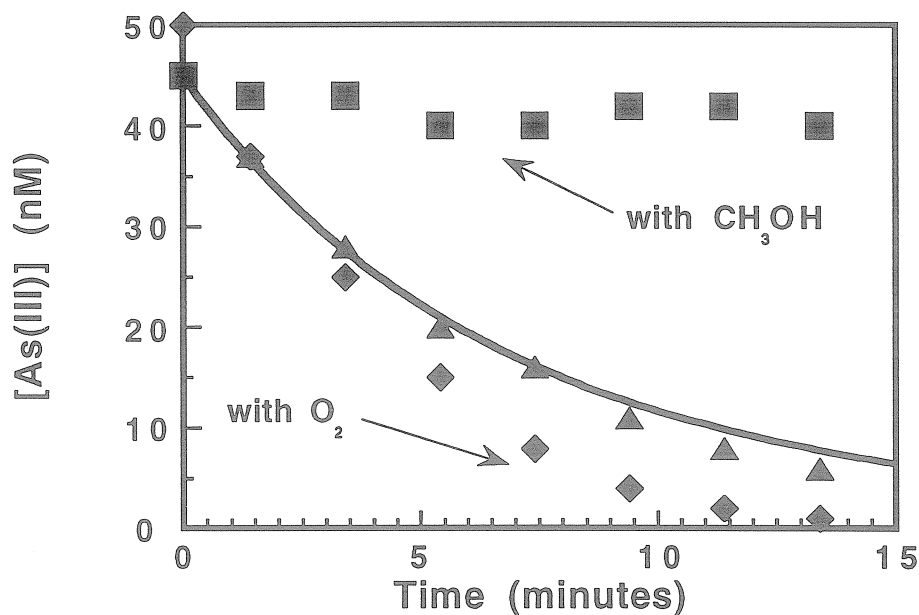


Figure 2. Oxidation of As(III) in the presence of  $\text{H}_2\text{O}_2$  and Fe(II). Conditions: pH= 4.8;  $[\text{H}_2\text{O}_2]_{\text{init}} = 5 \mu\text{M}$ ;  $[\text{Fe(II)}]_{\text{init}} = 1 \mu\text{M}$ . Line depicts kinetic simulation of reaction using Acuchem (Braun *et al.*, 1988)

As(III) oxidation is slightly faster in the presence of oxygen (diamonds in figure 2). The slightly faster rate of oxidation is attributable to the formation of additional  $\text{H}_2\text{O}_2$  during the redox cycling of iron (Voelker and Sulzberger, 1996).

The oxidation of As(III) by  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$  or other transient species is slow under the conditions encountered in surface waters. Experiments conducted using methanol ( $\text{CH}_3\text{OH}$ ) as a scavenger of  $\text{OH}^\bullet$  indicate insignificant oxidation of As(III) by other oxidants (squares in figure 2). In these experiments,  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$  concentrations are approximately equal to those observed in its absence (triangles in figure 2).

## 2. Release of arsenic during photodissolution of iron-containing minerals

The potential for release of arsenic from iron-containing minerals was evaluated by exposing sediment samples from West Squaw Creek to light in a photoreactor. In most experiments, photoreductive dissolution of the iron oxides was observed during the first twenty minutes of the experiment along with the release of small amounts of arsenic (figure 3). After approximately twenty minutes, the concentration of dissolved Fe(II) reached a relatively constant value. It is likely that larger releases of arsenic would have occurred if the iron-containing minerals had completely dissolved because arsenic released into solution could adsorb onto the remaining surfaces.

Analysis of the samples using infrared spectroscopy suggested the presence of amorphous iron hydroxides and other crystalline iron-containing mineral phases (data not shown). We hypothesize that the amorphous iron hydroxides underwent photoreductive dissolution, leaving behind a crystalline mineral phase (*e.g.*, jarosite) that was not affected by visible light. Arsenic released from the amorphous iron oxide phase could have adsorbed onto the more stable crystalline phase. An alternative explanation is that reactive transients produced during the photochemical reactions oxidized Fe(II), forming Fe(III) that precipitated from solution. Further experiments are needed to test these hypotheses and to better assess the rate of release of arsenic under the conditions encountered in sunlit

surface waters. Although relatively small concentrations of dissolved arsenic were observed in these experiments, releases could be more significant in an acid mine drainage stream where reaction products are washed away from the surface by the flowing water.

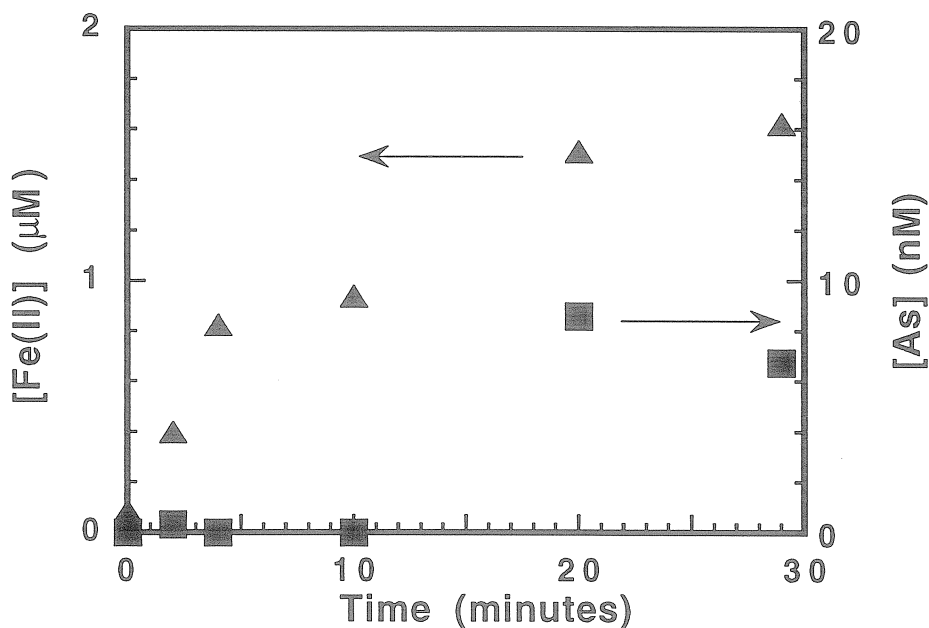


Figure 3. Representative results for the photoreductive dissolution of sediments from West Squaw Creek. Sediment concentration = 2,100 mg L<sup>-1</sup> (about 25 μM Fe); pH = 3.5.

### 3. Speciation of arsenic in surface waters

To assess the importance of photochemical processes in the fate and transport of arsenic, samples were collected from acid mine drainage streams and a geothermal spring. Arsenic speciation was measured in samples from the mine drainage while samples from the geothermal hot spring were used to study of the effects of sunlight on As(III) oxidation.

Samples were collected from six sites near abandoned mines in West Squaw Creek (table 1). The highest concentrations of arsenic were observed in seeps adjacent to two of

the mines. In these samples, As(III) accounted for approximately 20% of the dissolved arsenic. Concentrations of iron in these samples were at or above solubility limits for amorphous iron hydroxide, suggesting that colloidal forms of Fe(III) were present. These results suggest that iron-containing minerals coating the stream bed in West Squaw Creek contain significant amounts of arsenic. As demonstrated by the results depicted in figure 3, adsorbed or co-precipitated arsenic can be released during the photoreductive dissolution of these iron-containing coatings.

Table 1. Concentrations and speciation of arsenic and iron in West Squaw Creek.

<i>Location</i>	<i>pH</i>	<i>[Fe(II)]</i> ( <i>mM</i> )	<i>[Fe]<sub>tot</sub></i> ( <i>mM</i> )	<i>[As(III)]</i> ( $\mu$ <i>M</i> )	<i>[As]<sub>tot</sub></i> ( $\mu$ <i>M</i> )
Seep #1	2.8	0.13	0.24	<0.01	<0.10
Seep #2	2.9	0.88	0.90	<0.01	<0.01
Pool near Shasta King Mine	4.6	NA	NA	0.35	1.6
Shasta King Mine	2.4	1.0	13.4	0.33	1.8
Seep #3	2.1	0.53	14.1	0.40	1.9

The effect of photochemical processes on arsenic oxidation states was evaluated by using water collected from Hot Creek, located in Mono County, California. When samples collected before dawn at exposed to sunlight, approximately 10% of the As(III) was oxidized within one hour (squares in figure 4). Oxidation of arsenic did not occur in control samples stored in the dark. Assuming the photochemical reaction continues at the same rate, the half-life of As(III) is estimated to be approximately 300 minutes. When an additional source of OH<sup>•</sup> (*i.e.*, 1 mM KNO<sub>3</sub>) was added to the samples prior to irradiation, the rate of As(III) oxidation nearly doubled (triangles in figure 4). Based upon the results from the previously described laboratory experiments, we attribute the oxidation of As(III)

to  $\text{OH}^\bullet$ . Using those results, we calculate  $[\text{OH}^\bullet]_{\text{ss}}$  of approximately  $5 \times 10^{-14}$  M during the photolysis experiment without added nitrate and  $1 \times 10^{-13}$  M when nitrate was added.

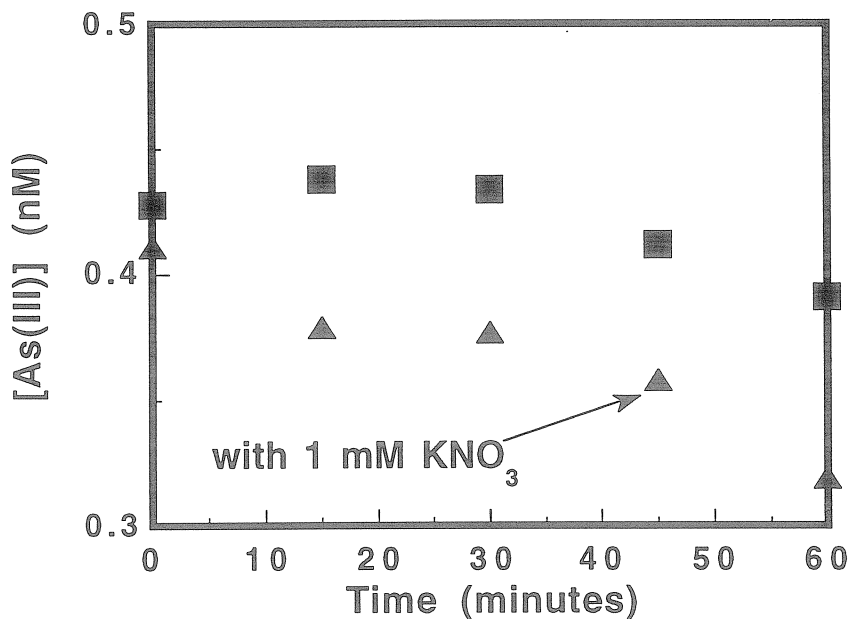


Figure 4. Oxidation of As(III) when pre-dawn samples from Hot Spring were exposed to noon sunlight on July 25, 1996. Total arsenic concentration =  $1.8 \mu\text{M}$ .

In Hot Creek, it has been observed (Wilkie and Hering, 1997) that most of the arsenic released from the geothermal source is oxidized within a kilometer of its source (*i.e.*, in less than 30 minutes). This relatively fast rate of oxidation suggests that some process other than photooxidation is responsible for most of the oxidation of As(III). Recent evidence (Wilkie and Hering, 1997) indicates that microbes attached to vegetation immediately downstream of the geothermal seep are responsible for oxidation of As(III). In acid mine drainage streams,  $[\text{OH}^\bullet]_{\text{ss}}$  is expected to be considerably higher than those observed in Hot Spring because the photolysis of iron would serve as an additional source

of  $\text{OH}^\circ$ . Under those conditions, photochemical reactions would be as fast or faster than any other oxidation process.

## CONCLUSIONS

In conclusion, results of laboratory experiments indicate that photochemical processes can affect the fate and transport of arsenic in the following ways:

- As(III) is rapidly oxidized by photo-produced  $\text{OH}^\circ$ . In surface waters near a geothermal spring, As(III) is oxidized by  $\text{OH}^\circ$  with a half-life of approximately five hours, under noon summer conditions. Although microbes are responsible for oxidation of much of the As(III) at the study site, photochemical oxidation of As(III) does occur. In the waters where conditions are not conducive to arsenic-oxidizing bacteria, photochemical reactions are probably more important to As(III) oxidation; however, more data are required to test this hypothesis.
- Arsenic is released from iron-containing sediments as they undergo photoreductive dissolution. Experiments indicate that the iron-rich materials coating surfaces in acid mine drainage streams readily undergo photoreductive dissolution and that arsenic is released during this process. Additional field measurements also are needed to determine the importance of this process.

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