MONTANA STATE UNIVERSITY

Photochemical oxidation of arsenic(III) in ferrioxalate solutions and elk exposure to arsenic in Yellowstone's geothermal environments
by Benjamin David Kocar

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Resources and Environmental Sciences '
Montana State University
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Abstract:

Photochemical reactions generate products, such as OH', that are responsible for the chemical transformation of many natural water constituents. However, little work has been performed studying the mechanisms of arsenite (As(III)) photochemical oxidation, and no work has been performed which directly links the oxidation of As(III) to OH.. Ferrioxalate, a compound found in atmospheric and surface waters, produces OH. upon irradiation and has been used to study the mechanisms of photochemically-induced oxidation for a variety of environmentally relevant compounds. Consequently, ferrioxalate solutions with varying concentrations of As(III), Fe(III) and 2-propanol were irradiated with a quartz tungsten halogen lamp to determine rates and mechanisms of As(III) oxidation. Results indicate that rates of oxidation in the ferrioxalate system are rapid (0.5-254.0 µM hr"1). Furthermore, experiments using 2-propanol to scavenge OH. demonstrate that As(III) is directly oxidized by OH. Finally, significant rates of As(III) oxidation (3.7 and 5.6 µM hr-1) were observed in a solution containing natural DOC, indicating that photochemical oxidation of As(H) may significantly influence arsenic (As) cycling in natural waters.

Elk (Cervus elaphus) residing in the MF watershed, YNP are exposed to elevated levels of As, primarily through ingestion of high- As aquatic and terrestrial plants, sediments, and algae. Plants and soils collected from dry, terrestrial environments contained low As concentrations, and Madison, Firehole, and Gibbon River water contained low As relative to aquatic and terrestrial plants and sediment samples. Consequences of exposure via these routes include elevated levels of As in elk tissues, rumen content and feces compared to a control population; some of these levels approach or exceed levels found in dosing studies where ruminants exhibited signs of chronic arsenic toxicosis. Analysis of As species in selected plant and elk samples indicate that the ingested forms of As are predominately inorganic, and that M-F elk may be detoxifying As via methylation. Increasing As:creatinine in elk urine over the course of high total snow water equivalence (SWE) winters indicate seasonally driven As exposure, with As: creatinine reaching peak levels between the months of February and March. Finally, average As:creatinine values are positively correlated with total winter SWE for several years, implying that snow depth is an important variable governing overall elk exposure to As.

PHOTOCHEMICAL OXIDATION OF ARSENIC(III) IN FERRIOXALATE SOLUTIONS AND ELK EXPOSURE TO ARSENIC IN YELLOWSTONE'S GEOTHERMAL ENVIRONMENTS

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Benjamin David Kocar

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of a thesis submitted by

Benjamin David Kocar

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

William P. Inskeep, Ph. D. William Inskeep 8/22/02
(Signature) (Date)

Approved for the Department of Land Resources and Environmental Sciences

Jeffrey S. Jacobsen, Ph. D. Jeffrey S. Jacobsen 8/23/02
(Signature) (Date)

Approved for the College of Graduate Studies

Bruce R. McLeod, Ph. D. Bruce R. McLeod 8-26-02
(Signature) (Date)

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ABSTRACT

Photochemical reactions generate products, such as $OH^{\bullet}$, that are responsible for the chemical transformation of many natural water constituents. However, little work has been performed studying the mechanisms of arsenite (As(III)) photochemical oxidation, and no work has been performed which directly links the oxidation of As(III) to $OH^{\bullet}$. Ferrioxalate, a compound found in atmospheric and surface waters, produces $OH^{\bullet}$ upon irradiation and has been used to study the mechanisms of photochemically-induced oxidation for a variety of environmentally relevant compounds. Consequently, ferrioxalate solutions with varying concentrations of As(III), Fe(III) and 2-propanol were irradiated with a quartz tungsten halogen lamp to determine rates and mechanisms of As(III) oxidation. Results indicate that rates of oxidation in the ferrioxalate system are rapid (0.5-254.0 $\mu M\ hr^{-1}$). Furthermore, experiments using 2-propanol to scavenge $OH^{\bullet}$ demonstrate that As(III) is directly oxidized by $OH^{\bullet}$. Finally, significant rates of As(III) oxidation (3.7 and 5.6 $\mu M\ hr^{-1}$) were observed in a solution containing natural DOC, indicating that photochemical oxidation of As(III) may significantly influence arsenic (As) cycling in natural waters.

Elk (*Cervus elaphus*) residing in the MF watershed, YNP are exposed to elevated levels of As, primarily through ingestion of high-As aquatic and terrestrial plants, sediments, and algae. Plants and soils collected from dry, terrestrial environments contained low As concentrations, and Madison, Firehole, and Gibbon River water contained low As relative to aquatic and terrestrial plants and sediment samples. Consequences of exposure via these routes include elevated levels of As in elk tissues, rumen content and feces compared to a control population; some of these levels approach or exceed levels found in dosing studies where ruminants exhibited signs of chronic arsenic toxicosis. Analysis of As species in selected plant and elk samples indicate that the ingested forms of As are predominately inorganic, and that M-F elk may be detoxifying As via methylation. Increasing As:creatinine in elk urine over the course of high total snow water equivalence (SWE) winters indicate seasonally driven As exposure, with As:creatinine reaching peak levels between the months of February and March. Finally, average As:creatinine values are positively correlated with total winter SWE for several years, implying that snow depth is an important variable governing overall elk exposure to As.

CHAPTER 1

INTRODUCTION

Arsenic (As), the 20th most abundant element in the earth's crust (*1*), is a known toxin and human carcinogen (*2*). A major health crisis has arisen in a multitude of countries around the world where As in drinking water supplies exceed 10 μg L^{-1}, the current minimum contaminant level suggested by the World Health Organization (*3*). In Bangladesh alone, the estimated potential As-exposed population is 30 million, and drinking water concentrations may surpass 2 mg L^{-1} (*4*). Consequently, thousands living in these regions are afflicted with a variety of As-associated maladies, including hyperpigmentation, keratosis, skin lesions, and a variety of cancers (*5*). Although information regarding As poisoning is circulating in stricken locations, millions of inhabitants consume tainted well-water irregardless of the associated health risks due to severe shortages of sanitary drinking water. Unfortunately, water treatment processes and facilities designed to remove high levels of As are costly, so As poisoning is especially prominent in the impoverished. Most people living in As-impacted locations struggle to simply meet daily nutritional requirements (*5*), let alone pay for water treatment technology; thus a dire need exists for cheap, simple and effective treatment processes that may be implemented on a large scale.

Well-waters in Bangladesh and other countries that contain high levels of As often contain high levels of ferrous iron (Fe(II)), which is rapidly oxidized (on a time scale of minutes) to ferric iron (Fe(III)) and amorphous Fe(III) oxyhydroxides upon exposure to air (*6*). This process is beneficial, since arsenate (As(V)) adsorbs strongly to amorphous Fe(III)-oxyhydroxide (*7*), resulting in a decrease of As_{ts} in well-water that is allowed to oxygenate and settle over a period of hours. Unfortunately, arsenite (As(III)) is the dominant species of As pumped from groundwater, which adsorbs only weakly to Fe(III)-oxyhydroxides (*7*), and may persist without being oxidized (by dissolved O_2) to As(V) for many days (*6,8*). Consequently, an initial As(III) oxidation step is needed to facilitate As adsorption to amorphous Fe(III)-oxyhydroxides. Photooxidation is a process which has recently been used to oxidize As(III) in simulated Bangladesh well-water and in acid mine drainage containing high concentrations of Fe(III) (milligrams L^{-1}) (*9*). However, few studies have been performed directly linking photochemical reaction mechanisms to As(III) oxidation (*9,10*), and very little data exists to date which accurately describe mechanisms of photochemical oxidation of As(III) in environmentally relevant systems (i.e. surface and atmospheric waters). Furthermore, no studies have been performed that describe the potential influence of photochemistry on biogeochemical cycling of As(III) in the environment.

Photochemical processes generate important reaction products that are responsible for the chemical transformation of elements and carbon compounds found in atmospheric and surface waters. During a cloudless, summer noon hour, surface waters receive approximately 1 kW m^{-2} of sunlight; equivalent to about 2 moles of photons per square meter within wavelengths 300-500 nm (*11*). A large portion of these photons are absorbed by dissolved organic carbon (DOC), such as oxalate, to form excited DOC intermediates, which may further react with other dissolved constituents such as Fe(III) and dissolved O_2 to produce oxidative products (*13*). Some of these products include superoxide anion ($O_2^{\bullet-}$), singlet oxygen ($^1O_2$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($OH^\bullet$) (*11*). Of these, $OH^\bullet$ has been found to oxidize a variety of environmentally relevant compounds, such as herbicides (*14*), and has also been shown to strongly influence the oxidation state and resulting biogeochemistry of several elements such as Fe (*11,12*). Although As(III) is oxidized by $OH^\bullet$ generated via pulse irradiation (*15*), no studies have been performed directly linking oxidation of As(III) by $OH^\bullet$ generated via irradiation of DOC. Hence, the objectives of the study in Chapter 2 were to (1) evaluate oxidation rates of As(III) in irradiated ferrioxalate (Fe(III) + oxalate) solutions as a function of pH, (2) identify probable mechanisms of photochemical As(III) oxidation, and (3) evaluate the oxidation of As(III) in a representative natural water containing dissolved organic carbon.

In addition to using As laden well-water for drinking and cooking, inhabitants of Southeast Asia and other As-afflicted regions often use it to water livestock and irrigate crops (*16*). This may result in widespread transfer of As into soils, surface waters, and food chains existing in these locations. Unfortunately, there is a paucity of data regarding the distribution of As in biota inhabiting As-impacted ecosystems, and there is no data describing the concentration of As in large mammals that frequent such areas. Since many human inhabitants of these locations depend on ruminants as a source of food (*17*), it is important to determine the biological endpoints of As in ruminants which frequent As-impacted locations.

One environment that contains naturally elevated levels of As and a large population of free-ranging ruminants is the Madison-Firehole (M-F) watershed in Yellowstone National Park (YNP), Wyoming, USA. Concentrations of As in M-F surface waters may exceed 3 mg L^{-1} (*18*), providing a unique opportunity to elucidate the ecotoxicity of As across different trophic levels in a model system. Specifically, the biological endpoints of As may be observed in elk (*Cervus elaphus*) with permanent home-ranges (*19*) located in the M-F watershed, providing insight regarding ingestion routes and seasonal exposure of As. Hence, the objectives of my study in Chapter 3 were to: (1) determine concentrations of As in the tissues, excretia, and rumen contents of elk residing in the upper Madison River basin (2) evaluate potential exposure pathways responsible for elevated levels of As in elk and (3) correlate As exposure to elk with frequency of habitation in high-As thermal locations.

REFERENCES CITED

(1) Cullen, W.R.; Riemer, K.J. 1989. Arsenic speciation in the environment. *Chem Rev* 89: 713-764.

(2) Abernathy, C. 2001. In *United Nations Synthesis Report on Arsenic in Drinking Water*; Morgan, A. Ed.; World Health Organization: Geneva, Switzerland.

(3) World Health Organization. 2002. Guidelines for drinking-water quality, 2nd ed. Vol. 2. Available at http://www.who.int/water_sanitation_health/GDWQ/

(4) Nordstrom, D.K. 2002. Worldwide Occurrences of Arsenic in Ground Water. *Science* 296: 2143.

(5) Mandal, B.K.; Chowdhury, T.R.; Samanta, G.; Mukherjee, D.P.; Chanda, C.R.; Saha, K.C.; Chakraborti, D. 1998. Impact of safe water for drinking and cooking on ive arsenic-affected families for 2 years in West Bengal, India. *Sci Tot Environ* 218: 185-201.

(6) Nickson, R.; McArthur, J.; Burgess, W.; Ahmed, K.M.; Ravenscroft, P.; Rahman, M. 1998. Arsenic poisoning of Bangladesh groundwater. *Nature* 395: 338.

(7) Pierce, M.L.; Moore, C.B.1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res* 16: 1247-1253.

(8) Cherry, J.A.; Shaikh, A.U.; Tallman, D. E.; Nicholson, R. V. 1979. Arsenic species as an indicator of redox conditions in groundwater. *J Hydrol* 43: 373-392.

(9) Hug, S.J.; Canonica, L.; Wegelin, M.; Gechter, D.; Von Gunten, U. 2001. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environ Sci Technol* 35: 2114-2121.

(10) Emett, M.T.; Khoe, G.H. 2001. Photochemical oxidation of arsenic by oxygen and iron in acidic solutions. *Wat Res* 35: 649-656.

(11) Stumm, W.; Morgan, J.J. 1996. Aquatic Chemistry, 3rd Edition; John Wiley and Sons; New York.

(12) McKnight, D. 1988. Iron photoreduction and oxidation in an acidic mountain stream. *Science* 240: 637-640.

(13) Cooper, W.J.; Shao, C.; Lean, D.R.S.; Gordon, A. S.; Scully, F. E., Jr. 1994. In *Environmental Chemistry of Lakes and Reservoirs*; Baker, L.A., Ed.; ACS Symposium Series 237; American Chemical Society: Washington, DC; pp 391-422.

(14) Sun, Y.; Pignatello, J.J. 1993. Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$. *Environ Sci Technol* 27: 304-310.

(15) Klaning, U.K.; Bielski, B.H.J.; Sehested, K. As(IV). 1989. A pulse-radiolysis study. *Inorg Chem* 28, 2717-2724.

(16) Abedin, J.; Cotter-Howells, J.; Meharg, A.A. 2002. Arsenic uptake and accumulation in rice (*Oryza sativa* L.) irrigated with contaminated water. *Plant and Soil* 240, 311-319.

(17) Biswas, U.; Sarkar, S.; Bhowmik, M.K.; Samanta, A.K.; Biswas, S. 2000. Chronic toxicity of arsenic in goats: clinicobiochemical changes, pathomorphology and tissue residues. *Small Rum Res* 38: 229-235.

(18) Stauffer, R.E.; Thompson, J.M. 1984. Arsenic and antimony in geothermal waters of Yellowstone-National-Park, Wyoming, USA. *Geochim Cosmochim Ac* 48: 2547-2561.

(19) Craighead, J.J.; Craighead, F.C.; Ruff, R.L.; O'Gara, B.W. 1973. Home ranges and activity patterns of nonmigratory elk of the Madison Drainage herd as determined by biotelemetry. *Wildlife Monographs* 33: 5-50.

CHAPTER 2

PHOTOCHEMICAL OXIDATION OF AS(III) IN FERRIOXALATE SOLUTIONS

Introduction

The speciation of arsenic (As) in soils and natural waters is an important factor controlling the environmental fate and subsequent toxicology of this metalloid (*1,2*). The two common inorganic forms of As present in surface waters are arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$) and arsenite ($H_3AsO_3^0$), and transformation rates between these two valence states may be mediated by both chemical and microbiological processes (*3*). The reduction of As(V) can occur chemically by dissolved sulfide at low pH (*4*), and via microbial processes including dissimilatory reduction (*5,6*) and detoxification via As-induced *ars* genes (*7*). Likewise, the oxidation of As(III) can be due to microbiological (*8,9*) and chemical processes. Chemical species common in natural waters that may contribute to the oxidation of As(III) include $Mn^{IV}O_2(s)$, Fe(III), and H_2O_2 (*10-14*). Of these, δ-MnO_2 is capable of rapid rates of As(III) oxidation under conditions typical of natural water systems (e.g. pH values ranging from 4-9). Oxidation rates of As(III) by Fe(III) are only significant at low pH (<3) and at high concentrations of Fe(III) (*13*).

Although the production of H_2O_2 in natural water has been well documented (*15-20*), significant rates of As(III) oxidation via H_2O_2 require pH values greater than the pKa for $H_3AsO_3^0$ (e.g. pH > 9.3), and high concentrations of H_2O_2 relative to As(III) (*13,14*). However, H_2O_2 is an important reactant involved in the production of free radical species (e.g. $OH^•$, $HO_2^•$), which have been reported to oxidize As(III) (*21,22*). Specifically, the oxidation of As(III) has been reported in low pH (<2.5) irradiated ferric perchlorate solutions (*21*), and attributed to the production of free radical species, $OH^•$ and $Cl_2^{•-}$. In Fe(III)-citrate solutions, $O_2^{•-}$ was hypothesized to be the important free radical species responsible for the photochemical oxidation of As(III) (*22*). Although different mechanisms of As(III) oxidation were suggested in these studies, it is clear that free radical species such as $O_2^{•-}$ and $OH^•$ generated from photochemical reaction products, such as H_2O_2, are responsible for As(III) oxidation in these systems.

The photochemical formation of H_2O_2 in natural waters is thought to occur as a result of disproportionation of hydroperoxyl ($HO_2^•$; pKa =4.8) and superoxide ($O_2^{•-}$) radicals, formed from the capture of light energy by dissolved organic carbon (DOC) and subsequent reduction of $O_{2(g)}$ (*17,26,27*):

$$DOC + h\nu + O_2 \rightarrow DOC^{•+} + O_2^{•-} \qquad (1)$$

$$2HO_2^• \rightarrow H_2O_2 + O_2 \qquad (2)$$

The absorption of light by appropriate chromophore(s) of DOC results in an excited state intermediate $DOC^•$, which transfers electrons to O_2 to form the superoxide radical $O_2^{•-}$ followed by disproportionation of $HO_2^•$ to form H_2O_2 (*28*). Alternatively, H_2O_2 may be produced via the reaction of superoxide with reduced metals such as Fe(II):

$$O_2^{•-}\ (HO_2^•) + 2H^+ + Fe(II) \rightarrow H_2O_2 + Fe(III) \qquad (3)$$

Once H_2O_2 is formed, it can react further with Fe(II) (Fenton's Reaction) in the dark to yield the hydroxyl radical ($OH^{\bullet}$), a strong oxidant capable of oxidizing many organic compounds and other environmentally relevant species (*23,29,30*):

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + OH^{\bullet} + OH^{-} \tag{4}$$

The formation of H_2O_2 and $OH^{\bullet}$ has also been studied extensively in irradiated ferrioxalate solutions (*18,31-33*). Not only is the ferrioxalate system a classic model for the study of photochemical formation of H_2O_2 and $OH^{\bullet}$ (*33,34*), oxalate is also a common natural and anthropogenic compound found in nearly all natural waters including soil pore waters, surface waters, and atmospheric water (*18,35*). Oxalate has a high affinity for ferric iron, and even at molar oxalate:Fe ratios as low as 1:1, the Fe(III)-oxalato complexes are the dominant solution species of Fe(III) at pH values < 7 . It is thought that photolysis of the tri-oxalato ferrioxalate species yields the free radical $CO_2^{\bullet-}$ via the spontaneous decarboxylation of the oxalyl radical anion, $C_2O_4^{\bullet-}$ (*36*):

$$Fe^{III}(C_2O_4)_3^{3-} + h\nu \rightarrow Fe(II) + 2C_2O_4^{2-} + C_2O_4^{\bullet-} \tag{5}$$

$$C_2O_4^{\bullet-} \rightarrow CO_2^{\bullet-} + CO_2 \tag{6}$$

The oxalyl radical has a short lifetime before decarboxylation to form $CO_2^{\bullet-}$, thus preventing its participation in other reactions (*36*). Under aerobic conditions, $CO_2^{\bullet-}$ reacts quickly with O_2 (*24*):

$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \tag{7}$$

which, depending on pH, results in the formation of either the superoxide radical, $O_2^{\bullet-}$ or the hydroperoxyl radical, $HO_2^{\bullet}$ (Table 1.2). Once the superoxide radical is formed, the formation of H_2O_2 and $OH^{\bullet}$ in the ferrioxalate system proceeds as described in eqs 2-4. Importantly, the exclusion of O_2 via bubbling with N_2 (g) has been shown to effectively curb the production of $O_2^{\bullet-}$ and the subsequent formation of H_2O_2 (*18*).

The photochemical production of $OH^{\bullet}$ free radicals in natural waters either via DOC or oxalate pathways may contribute to As(III) oxidation occurring in surface waters of lakes, oceans and rivers. Consequently, my objectives were to (1) evaluate oxidation rates of As(III) in irradiated ferrioxalate solutions as a function of pH, (2) identify probable mechanisms of photochemical As(III) oxidation, and (3) evaluate the oxidation of As(III) in a representative natural water containing dissolved organic C (DOC). Our results indicate that the photochemical oxidation of As(III) in ferrioxalate solutions can be rapid (half-lives ranging from 0.01 to 1 h), and that photochemical oxidation of As(III) may also be important in natural waters containing Fe(III) and DOC.

Materials and Methods

Reacting Solutions

Reaction mixtures (total volume = 0.2 or 0.4 L) were prepared under a red safelight in a 1.0 L glass vessel via the sequential addition of analytical grade KCl, $FeCl_3$, $K_2C_2O_4$, and NaH_2AsO_3 stock solutions (fresh NaH_2AsO_3 stock solutions prepared every 3 days). All solutions were prepared in a background of 0.01 M KCl or $KClO_4$ and the concentration of initial oxalate in the reaction vessels was kept constant at 1 mM. With the exception of experiments designed to determine the influence of Fe(III) concentration, experiments were conducted at 18.0 μM Fe(III). At these ratios of oxalate:Fe(III), over 99% of the total soluble Fe(III) existed as oxalate complexes, of which the tri-oxalato species was dominant (Figure 1.1; See [*18*] for log K values). The distribution of aqueous species was estimated with GEOCHEM (*48*), using equilibrium constants for soluble Fe(III)-complexes as presented by Zuo and Hoigne (*18*). In one set of experiments at pH 5.0, initial As(III) concentrations were varied from 1.3 μM to 13.5 mM As(III) to determine the rate dependence of As(III) photooxidation on initial As(III) concentration. The influence of pH on As(III) photooxidation was evaluated at pH values ranging from 3 to 7 at initial As(III) concentrations of 17.4 μM. In addition, one set of experiments was conducted at 133 μM As, but at variable Fe(III) concentrations ranging from 0.02 to 18 μM.

Experimental Apparatus and Irradiation Source

Ferrioxalate reaction mixtures were exposed to light emitted from a 250 W Quartz Tungsten Halogen lamp (QTH, Oriel Instruments). The effective photon flux of the lamp between wavelengths 300-500 nm was determined to be approximately 97 μE cm^{-2} h^{-1} using ferrioxalate actinometry (*37*). The temperature of all reaction mixtures was held constant at 25 ±2°C with a circulating water bath connected to a jacketed reaction vessel. The pH of the reacting solutions was held constant during irradiation

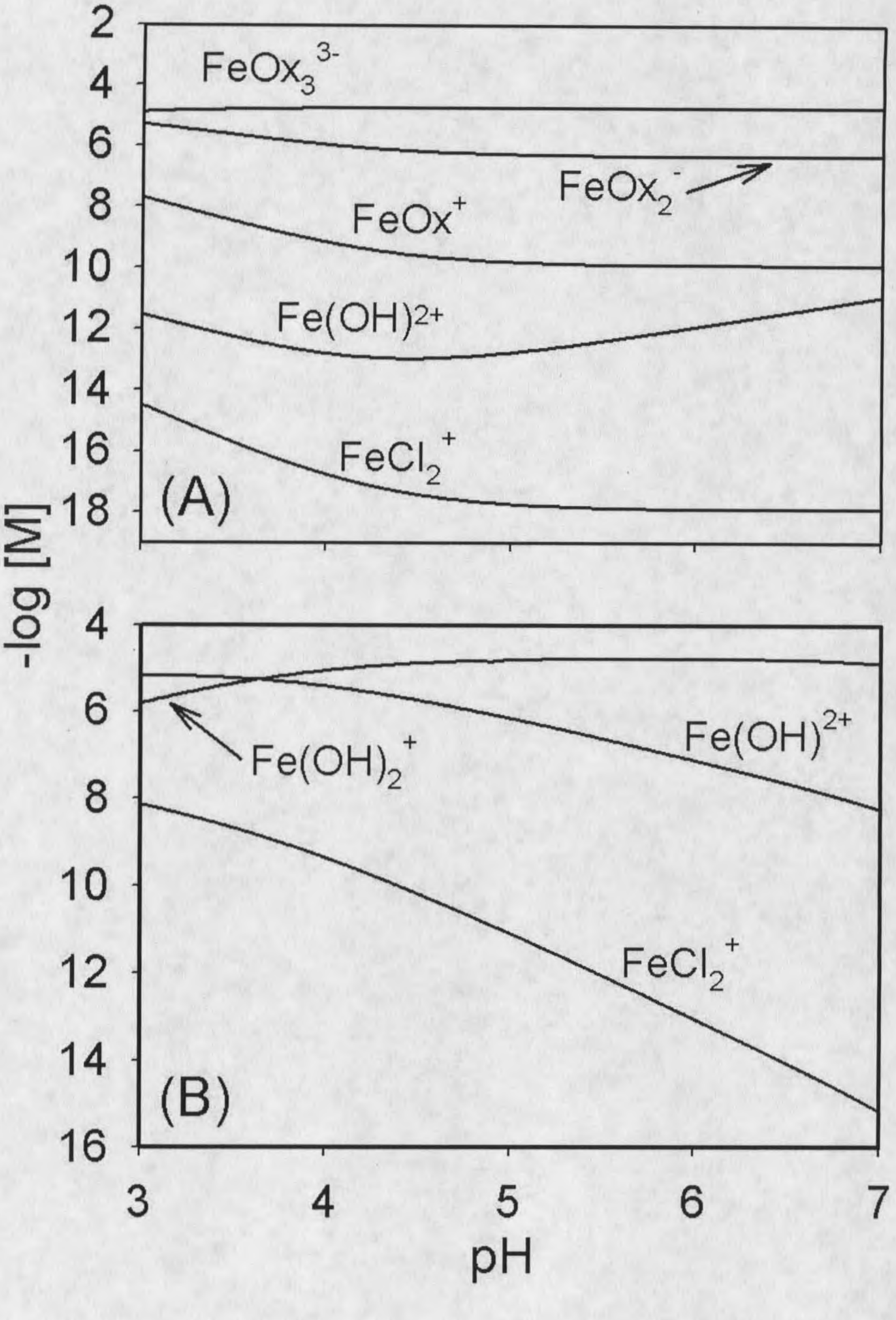

FIGURE 1.1. Calculated (GEOCHEM) distribution of aqueous Fe(III) species as a function of pH in the presence (A) and absence (B) of 1 mM oxalate (0.01 M KCl, 18 μM Fe(III), 18 μM As(III) and 10 mM KCl).

using an autotitrator (Radiometer, Copenhagen) operating in pH-stat mode while being constantly stirred with a Teflon bar and vigorously bubbled with compressed air. Reaction mixtures were sampled as a function of time (generally for periods up to 30 min) and analyzed for total soluble As(III), As(V), Fe(II), Fe(III), and H_2O_2 (methods discussed below). The majority of irradiation experiments discussed in the current study were performed in triplicate.

Analytical Methods

Determination of As(V) was performed by adding 5 mL of reaction mixture to a 15 mL HDPE bottle containing 1 mL of 2.0 M TRIS buffer ((hydroxymethyl) aminomethane). While sparging the mixture with N_2, 1 mL of 0.025 M NaOH and 1.59 M $NaBH_4$ was added in 0.5 mL increments over 7 min to reduce As(III) to arsine gas. The sample was then sparged for an additional 7 min to purge arsine. Concentrations of As(III) were determined by difference between As(ts) and As(V) (*5,38*) measured using continuous flow hydride generation atomic adsorption spectrometry (HG-AAS)(*5*). Samples were acidified with 3M HCl, pre-reduced with 1% potassium iodide (KI), and mixed with 0.6% $NaBH_4$ in 0.5% NaOH. Subsequent emission of arsine gas was quantified at 193.4 nm in a quartz cuvet immersed in an air-acetylene flame (Perkin Elmer model 3100 atomic adsorption spectrophotometer). The detection limit for As using this method was 3.4 nM. Concentrations of H_2O_2 were determined using the N,Ndiethyl-1,4-phenylenediamine method developed by Bader et al (*39*), and concentrations of Fe(II) and Fe(III) were determined using the o-phenanthroline method (*40*).

Effect of 2-Propanol on Initial As(III) Oxidation Rate

Reaction mixtures of 0.01 M KCl, 18 μM Fe(III), 1 mM oxalate, 13.5 mM 2-propanol, and varying amounts of As(III) (0-13.5 mM) were irradiated to determine the initial rate of $OH^{\bullet}$ formation (when [As(III)] = 0) and to determine the effect of an $OH^{\bullet}$ scavenger on initial As(III) oxidation rates. These reaction mixtures were sampled as a function of time for a total of 30 min, and analyzed for 2-propanone using gas chromatography (Varian Gas Chromatograph, Model 3400, Walnut Creek CA, operating under flame ionization mode). In the presence of excess 2-propanol relative to other potential $OH^{\bullet}$ scavengers, the production of 2-propanone can be used to estimate the formation rate of $OH^{\bullet}$ (*33*):

$$R_o\ (OH^{\bullet}\ \text{formation}) = R_o\ (\text{2-propanone formation})/0.87 \qquad (8)$$

where R_o is initial rate (μM h^{-1}) and 0.87 represents the fraction of 2-propanol molecules attacked by $OH^{\bullet}$ that ultimately result in the formation of 2-propanone (*33*). In experiments designed to determine the affect of an $OH^{\bullet}$ scavenger on initial As(III) oxidation, ferrioxalate solutions containing three concentrations of As(III) (0.135, 1.35, and 13.5 mM) were irradiated in the presence of 13.5 mM 2-propanol. Reaction mixtures were sampled as a function of time for a total of 30 min, after which samples were analyzed for 2-propanone and As(III)/As(V) as described above.

Oxidation of As(III): H_2O_2 and Fe(II) Dark Controls

Solutions of 2.66 μM As(III) and 20 mM H_2O_2 were prepared under a red safelight and sampled as a function of time for 10 min. An equal volume solution containing either 3.6, 7.2, 17.8 or 35.8 μM Fe(II) was then added, and the reaction mixture sampled as a function of time for an additional 20 min for a total of 30 min per experiment. Samples were analyzed for Fe(II)/Fe(III), As(III)/As(V), and H_2O_2 as described above. Both solutions were prepared at pH 2.7, had a background ionic strength of 0.01 mM KCl and were constantly bubbled with air. Care was taken not to exceed the amount of Fe(II) in solution which upon oxidation to Fe(III), would result in the precipitation of amorphous Fe(III) hydroxide. The solubility limit of Fe(III) was estimated using a log $K = 3.54$ for the reaction $Fe(OH)_{3\,(s)} + H^+ = Fe^{3+} + 3H_2O$ (*41*). The maximum estimated solubility of Fe(III) at pH 2.7 was 70.5 μM, significantly greater than the concentration of Fe(II) used in our solutions. In one experiment, As(III) oxidation was measured in the presence of 13.5 mM 2-propanol to confirm the affect of an $OH^{\bullet}$ scavenger on the oxidation of As(III).

Apparent Quantum Yield

Apparent quantum yields of As(V) and H_2O_2 were determined from the rates of formation of As(V) and H_2O_2. The apparent quantum yield (Φ_a) was defined as the number of moles of As(V) or H_2O_2 formed per mole of photon absorbed by the solution:

$$\Phi_a = \frac{d[X]/dt}{I_o' (1-10^{-Abs})/l} \qquad (9)$$

where $d[X]/dt$ represents the rate of formation of As(V) or H_2O_2 ($\mu M\ h^{-1}$) at the wavelengths of irradiation, I_o' is the photon flux through the irradiated cell (97 $\mu E\ cm^{-2}\ h^{-1}$), $1\text{-}10^{-Abs}$ is the average fraction of light absorbed over wavelengths 300-500 nm, and l is 3.46 cm, the average path length of the jacketed reaction vessel.

Photochemical Oxidation of As(III) in a Natural Water

To determine whether photochemical oxidation of As(III) may occur under sunlight conditions in natural waters containing dissolved organic C (DOC), a water sample was collected from a pristine wetland (pH = 6.5) at an elevation of 2000 m in Hyalite Canyon located 25 km south of Bozeman MT. The natural water sample was filter-sterilized (0.22 μM) following collection, then refrigerated in an autoclaved vessel until use. The amount of DOC was determined using a DC-80 carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH) and found to equal 0.86 mM C. Total and non-carbonate alkalinity were determined by titration with standardized 0.025 M HCl, using unpurged and purged ($N_{2(g)}$) samples. Since the Hyalite water sample was found to contain below detectable Fe(III) or Fe(II) (<0.45 μM), it was spiked to a concentration of 18 μM Fe(III) one hour prior to irradiation under natural sunlight at 12 p.m., August 22, 2000. Natural sunlight intensity was measured in the photosynthetically relevant wavelengths using a quantum sensor (LiCOR, Model 190, Lincoln, NE) and total solar irradiance was measured with a solarimeter (Kipp and Zonen Model CM5, Delfft, Netherlands). Experiments involving the Hyalite natural water sample were performed in duplicate, and concentrations of As(III), As(V) and H_2O_2 were determined as described previously.

Results and Discussion

Photochemical Oxidation of As(III)

At pH 3.0, the oxidation of 17.4 μM As(III) in irradiated ferrioxalate solutions was complete within 10 min (Figure 1.2A), corresponding to an initial oxidation rate of 255 ± 16 μM h^{-1} (Table 1.1). The rate of As(III) oxidation in irradiated solutions decreased with increasing pH, falling to 14 μM h^{-1} at pH 7.0 (Figure 1.2A, Table 1.1). To verify that the measured oxidation of As(III) occurred as a direct result of photochemical processes resulting from the irradiation of Fe(III)-oxalate solutions, irradiated experiments were compared to appropriate dark controls (Figure 1.2B). The dark control containing identical concentrations of Fe(III), oxalate and As(III) showed no oxidation of As(III) (Figure 1.2B) during a 30 min incubation. Further insights regarding the mechanism of As(III) oxidation were obtained from controls in the presence of H_2O_2 or Fe(III) at pH 3.0 (Figure 1.2B). Insignificant oxidation of As(III) was observed in dark or irradiated controls containing 300 μM H_2O_2. An additional control was performed at a

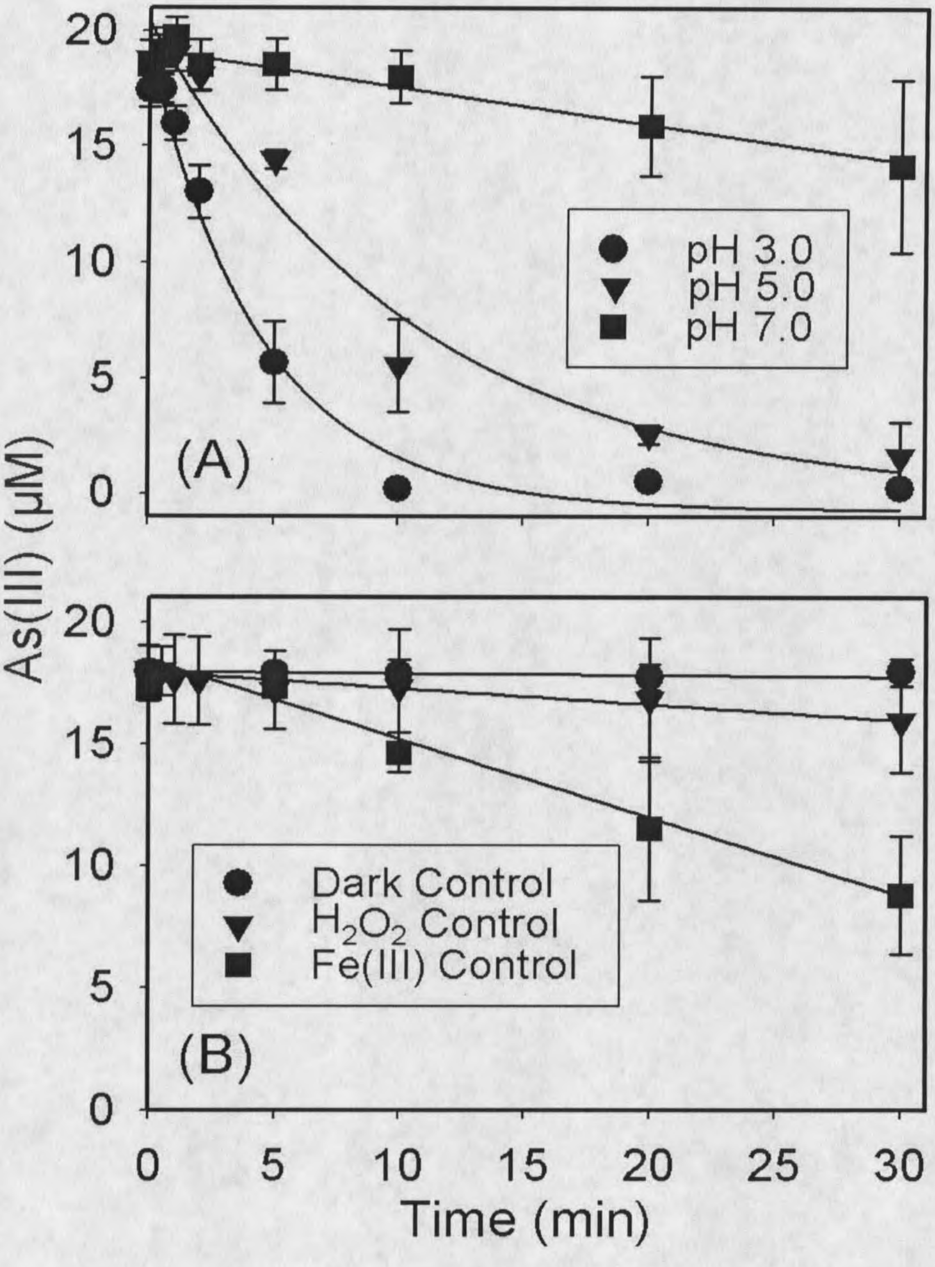

FIGURE 1.2. Disappearance of As(III) in (A) irradiated ferrioxalate solutions and in (B) dark or irradiated controls. Irradiated ferrioxalate solutions and the dark control contained 18 μM As(III), 18 μM Fe(III), and 1 mM oxalate. The H_2O_2 control contained 18 μM As(III) and 300 μM H_2O_2, while the Fe(III) control contained 18 μM As(III) and 18 μM Fe(III). Background ionic strength of all solutions = 0.01 M KCl.