

Toxic Substances in Surface Waters and Sediments—A Study to Assess the Effects of Arsenic-Contaminated Alluvial Sediment in Whitewood Creek, South Dakota

Edited by James S. Kuwabara and Christopher C. Fuller

Section I

Effects of Benthic Flora on Arsenic Transport in Whitewood Creek, South Dakota

By James S. Kuwabara, Cecily C.Y. Chang, and Sofie P. Pasilis

Section II

Evaluation of the Processes Controlling Dissolved Arsenic in Whitewood Creek, South Dakota

By Christopher C. Fuller and James A. Davis

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Conversion Factors, Datum, and Abbreviated Water-Quality Units

Multiply	By	To obtain
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
cubic centimeter (cm ³)		cubic inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square kilometer (km ²)	0.3861	square mile
cubic meter per second (m ³ /s)	35.3107	cubic foot per second
cubic meter per second per meter (m ³ /s/m)		cubic foot per second per foot
liter per second (L/s)	15.85	gallon per minute
megagram (Mg)	10 ⁶ grams	2,204.6 pounds
microgram (μg)	10 ⁻⁶ gram	2.2046×10 ⁻⁹ pound
gram (g)		0.0022046 pound
micrometer (μm)	10 ⁻⁶ meter	3.937×10 ⁻⁵ inch
nanometer (nm)	10 ⁻⁹ meter	3.937×10 ⁻⁸ inch
milligram (mg)	10 ⁻³ gram	2.2046×10 ⁻⁶ pound
liter (L)		0.3785 gallon
milliliter (mL)		0.03785 gallon
cubic meter per second (m ³ /s)		35.3198 cubic feet per second
square meter (m ²)		10.7650 square feet
square centimeter (cm ²)		0.1550 square inch
gravitational constant (G)		
parts per million (ppm)		
micromoles per square meter per day (μmol/m ² /d)		
square centimeter per second (cm ² /s)		
micromoles per liter per day (μmol/L/d)		
milligrams per liter (mg/L)		
micromoles per gram (μmol/g)		
milliequivalents per liter (meq/L) and (μmol/L) micromoles per liter		
liter per day (L/d)		
microeinsteins		
microsiemens per centimeter at 25 degrees Celsius (μS/cm)		

Air temperatures are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$^{\circ}\text{F} = 1.8(^{\circ}\text{C}) + 32$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Chemical concentration and water temperature are given only in metric units. Chemical concentration in water is given in millimoles per liter (mmol/L) or micromoles per liter (μmol/L). Millimoles per liter is a unit expressing the solute per unit volume (liter) of water. One thousand micromoles per liter is equivalent to 1 millimole per liter. Molar concentrations can be converted to mass concentration by multiplying the molar concentration (moles per liter) by the molecular weight of the solute (grams per mole). For example, 1 micromole per liter (μmol/L) dissolved arsenic is equivalent to 7.49×10⁻⁵ grams per liter or 74.92 μg/L. Total alkalinity is given in units of milliequivalents per liter (meq/L). Chemical concentration of solid-phase samples is given in moles per gram (mol/g).

SECTION I. Effects of Benthic Flora on Arsenic Transport in Whitewood Creek, South Dakota

By James S. Kuwabara, Cecily C.Y. Chang, and Sofie P. Pasilis

Abstract

Field measurements and bioassay experiments were done to investigate the effects of arsenic and phosphorus interactions on sorption of these solutes by the benthic flora (periphyton and submerged macrophytes) in Whitewood Creek, a stream in western South Dakota. Short-term (24-hour) sorption experiments were used to determine arsenic transport characteristics for algae (first-order rate constants for solute sorption, biomass, and accumulation factors) collected in the creek along a transect beginning upstream from a mine discharge point and down-gradient through a 57-kilometer reach. Temporal changes in biomass differed significantly between and within sampling sites. Arsenic concentrations in plant tissue increased with distance downstream, but temporal changes in concentrations in tissues differed considerably from site to site. Cultures of *Achnanthes minutissima* (Bacillariophyceae) and *Stichococcus* sp. (Chlorophyceae) were isolated from four sites along a longitudinal concentration gradient of dissolved arsenic within the study reach and were maintained at ambient solute concentrations. Arsenic accumulation factors and sorption-rate constants for these isolates were determined as a function of dissolved arsenate and orthophosphate. Cell surfaces of algal isolates exhibited preferential orthophosphate sorption over arsenate. Initial sorption of both arsenate and orthophosphate followed first-order mass transfer for each culturing condition. Although sorption-rate constants increased slightly with increased dissolved-arsenate concentration, algae, isolated from a site with elevated dissolved arsenic in the stream channel, had a significantly slower rate of arsenic sorption compared with the same species isolated from an uncontaminated site upstream.

In diel studies, amplitudes of the pH cycles increased with measured biomass except at a site immediately downstream from water-treatment-plant discharge. Inorganic pentavalent arsenic dominated arsenic speciation at all sites—not a surprising result for the well-oxygenated water column along this reach. Concentration fluctuations in dissolved-arsenic species lagged pH fluctuations by approximately 3 hours at the most downstream site, but no discernible lag was observed at an artificially pooled area with an order of magnitude higher biomass. Furthermore, the amplitudes of diel fluctuations in

arsenic species were greater at the pooled area than at the most downstream site. Lack of correspondence between changes in dissolved-orthophosphate concentrations and arsenic species may have resulted from preferential sorption of orthophosphate over arsenate by the biomass. Based on carbon-fixation estimates, the phosphorus demand from photosynthetic activity required water-column concentrations to be supplemented by another source such as phosphate regeneration within the benthic community or desorption of particle-bound phosphate.

Introduction

Biological uptake and chemical transformations can affect transport of reactive solutes in streams and, consequently, the complexity of water-quality modeling and monitoring (Kuwabara and others, 1984; Cain and others, 1988; Kuwabara and others, 1988; Kuwabara and Helliker, 1988). For example, solute uptake by organisms may retard downstream transport, whereas metabolic reactions might change chemical speciation (Andreae, 1977; Sanders, 1985) and thereby effect changes in surface activity and transport characteristics. The effects of biological processes can be difficult to quantify because characteristics of the benthic and planktonic communities (for example, species composition and biomass) can change temporally and spatially. These changing characteristics can influence, and be affected by, interacting chemical and hydrologic processes.

Although biological processes have long been considered in water-quality and nutrient-cycling models for macronutrients, the importance of integrating biological models into trace-contaminant transport models has only recently been acknowledged (Zison and others, 1978; Jorgensen, 1983; Kuwabara and others, 1984). This can be due, in part, to the complexity of quantifying or even identifying the pertinent mechanisms that affect transport and distribution of a given solute. Biological processes that need to be considered in solute-transport models include solute uptake and release, toxicity and adaptation, metabolism and storage, community structure, and species interactions. In particular, attempts to model the influence of the benthic flora on arsenic transport within an aquatic environment have been hampered by a number of factors: (1) arsenate

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inhibits the growth of certain algal species at submicromolar concentrations, presumably because of interference with phosphate metabolism (Button and others, 1973; Sanders, 1979); (2) the effects of arsenic speciation on uptake rates and solute accumulation by periphyton are not well known; (3) possible changes in metabolic reaction rates as a consequence of prolonged exposure at elevated arsenic concentrations (and further uptake of arsenic) are poorly understood; and (4) data to quantify the effects of physical and chemical factors (for example, light intensity and surface reactions with inorganic particles) on arsenic uptake are sparse.

Purpose and Scope

The dependence of arsenic transport and speciation in Whitewood Creek on algal growth was investigated. This report presents results of a field and laboratory study of arsenic transport characteristics of periphyton and submerged macrophytes along a 57-km reach of Whitewood Creek in South Dakota, where both dissolved-arsenate and orthophosphate concentrations varied substantially. A first-order mass transfer equation was tested as a model to describe solute sorption on cell surfaces of the benthic flora. The variables in the equation (for example, algal biomass, sorption and release rates, and accumulation factors) may be used as a biological term in a comprehensive transport model consisting of hydrologic, chemical, and biological terms.

Results of a subsequent study done between August 30 and September 2, 1988, also are presented that examine diel relationships among benthic flora and pH, specific conductance, water temperature, and photosynthetically active radiation. The effects of these relations on concentration trends for dissolved-orthophosphate and arsenic species are discussed.

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Study Site

Whitewood Creek, a perennial, snow-fed stream in the Black Hills of South Dakota, has received effluents from gold mining since 1876 and from municipal activities such as sewage treatment and power-generator cooling. Four sites along the creek were selected for this study, beginning upstream from the mining activities and continuing approximately 1 km upstream from the confluence of Whitewood Creek and the Belle Fourche River (fig. I-1). Although direct discharge of mine tailings into the creek ended in 1977, residual mine tailings still form most of the bank and bed sediment over the 57-km study reach. These accumulated tailings contribute to a dissolved-arsenic concentration gradient that increases in the downstream direction from less than 0.1 micromolar ($\mu\text{mol/L}$) upstream from the mining activities to 1.5 $\mu\text{mol/L}$ at the most downstream site (Goddard, 1988). Conversely, inputs of phosphorus and other macronutrients from a municipal wastewater-treatment facility at Deadwood, downstream from major mining activities, provides a dissolved-orthophosphate gradient that decreases in the downstream direction from 20 $\mu\text{mol/L}$ immediately downstream from the wastewater facility to less than 1 $\mu\text{mol/L}$ at 57 km downstream (Goddard, 1988). A dense community of attached algae and submerged macrophytes quickly forms in Whitewood Creek after snowmelt and remains throughout the summer months. Dissolved arsenic (primarily as arsenate) in the streamwater also reaches maximal concentrations during the summer downstream from mining activities, possibly because of (1) elevated water-column pH during the summer that causes desorption of arsenic and (2) summer inputs of arsenic-laden ground water influenced by both percolation of irrigation water and lower summer surface-water flow after snowmelt (Goddard and others, 1988; Christopher C. Fuller, section II of this report). The study reach, therefore, represents ideal field conditions for the examination and quantification of potentially important contributions of the benthic flora to arsenic mobilization and attenuated transport.

Methods of Study

Arsenic transport characteristics were determined for algae and macrophytes collected at four sampling sites (fig. I-1): (1) 7 km upstream from the mining activities (1,700-m elevation); (2) 15 km downstream from the first site and within the town of Deadwood (0.25 km downstream from the municipal wastewater-treatment plant, 1,390-m elevation); (3) 39 km farther downstream at a U.S. Geological Survey gaging station (870-m elevation); and (4) approximately 1 km upstream from the confluence of Whitewood Creek and the Belle Fourche River (850-m elevation). These sites are hereinafter referred to as the Headwater (HW) site, the Sewage-Treatment-Plant (STP) site, the Above Vale (AV) site, and the Sheeler Seep (SS) site, respectively (Kuwabara and others, 1988). Abundant ground-water seepage occurs as springs along the banks of the creek at the farthest downstream site.

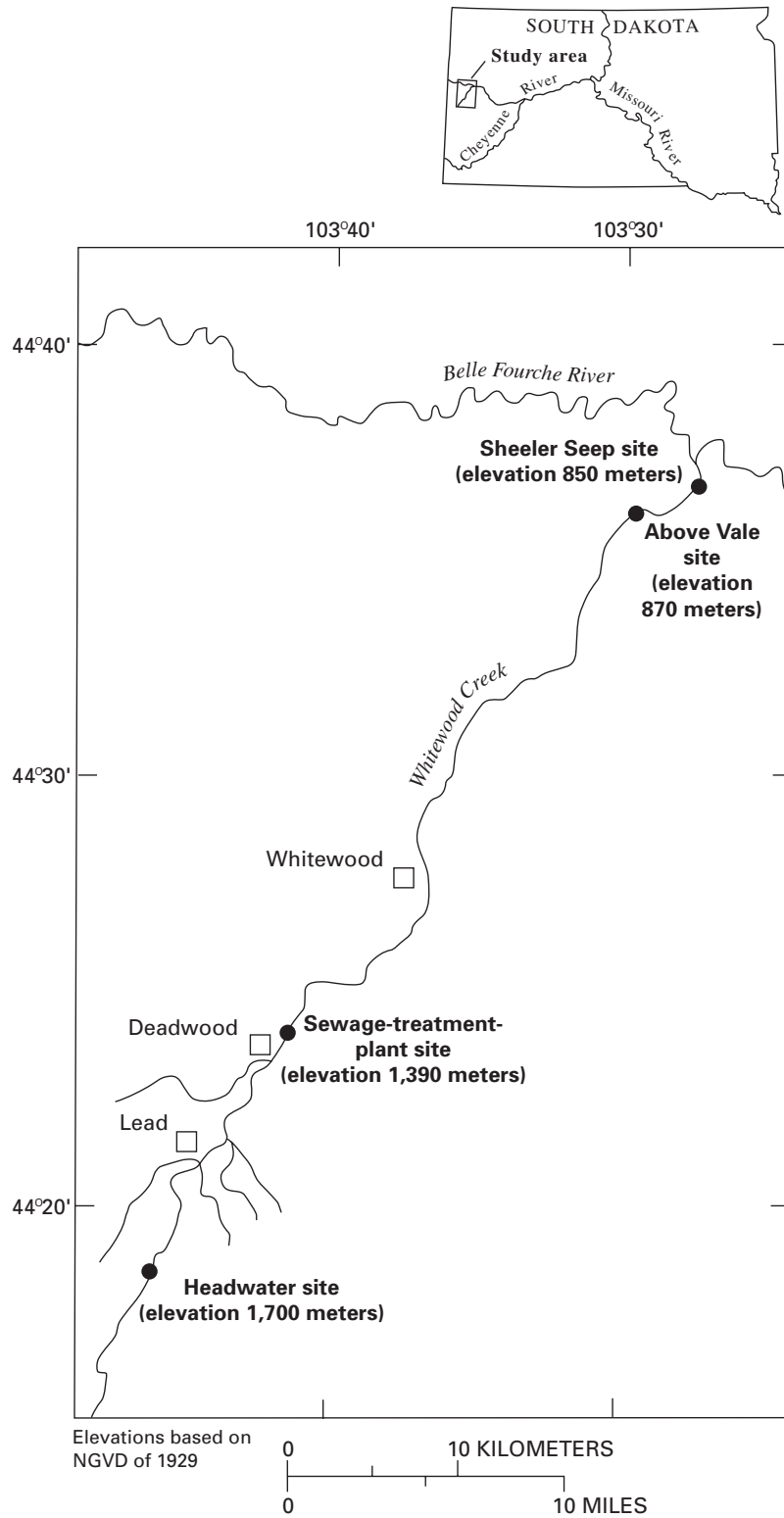


Figure I-1. Map of the study area along Whitewood Creek, South Dakota.

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Estimated transport characteristics included biomass (ρ_b) or the accessible biomass per unit streambed area, net sorption-rate constant (λ_b), and accumulation factor (that is, biological partitioning coefficient, K_b). The estimates were used to describe a biological component of a comprehensive transport model describing hydrologic, chemical, and biological processes. Assuming a first-order process, the rate of change of dissolved arsenic resulting from plant tissue accumulation would take the form

$$\begin{aligned} (\rho_{bj}/D_j)R_{bj} &= -(\rho_{bj}/D_j)(\delta C_{bj}/\delta t) \\ &= -\lambda_{bj}(\rho_{bj}/D_j)(C_{bj} - K_{bj}C_j) \end{aligned}$$

where

(ρ_{bj}/D_j) = biomass factor that scales changes in solute concentrations in plant communities to changes in water-column solute concentration, in units of biotic mass per cubic length;

R_b = temporal change in C_b , in units of solute mass per biotic mass per unit time;

j = finite interval of the stream reach (dimensionless);

C_b = concentration associated with the benthic plant material, in units of solute mass per biotic mass;

D = mean interval channel depth, in units of length;

t = time;

and

C = solute concentration in the stream as a function of time, in units of solute mass per cubic length.

Field Studies

During an initial reconnaissance of Whitewood Creek, August 4–9, 1986, algal biomass (periphyton and macrophyte abundance in grams ash-free dry weight per square meter) was estimated from cobble scrapings (number of sample replicates, $n=6$) taken from the four sites illustrated in figure I-1 (table I-1). Acetone (99.5 percent) extractions of chlorophyll-*a* were analyzed fluorometrically (Franson, 1985). Ash-free dry weights from the scrapings also were taken in order to calculate an autotrophic index (mass ratio of plant biomass to chlorophyll-*a*) for each site as a potential indicator of environmental stress.

Table I-1. Estimated biomass for four sampling sites along Whitewood Creek, August 4–9, 1986.

[Headwater site, HW; Sewage-Treatment-Plant site, STP; Above Vale site, AV; and Sheeler Seep site, SS; Biomass, ρ_b , in grams per square meter; and temperature in degrees Celsius. The mass ratio of periphyton and macrophytes to chlorophyll-*a*, the autotrophic index, has been used as an indicator of environmental stress with increasing values indicating greater abundance of senescent algal cells or increased heterotrophic growth (Weber, 1973)]

Site	Temperature	Autotrophic index	Biomass
HW	13.2	120	21+14
STP	17.5	210	34±13
AV	19.0	140	77±27
SS	24.2	190	25±11

Subsequent field studies during the summer of 1987 examined temporal fluctuations in characteristics of the benthic flora. Benthic plant abundance (ρ_b) at each of the four sites was estimated monthly from late May to September 1987 by using ash-free dry weight and chlorophyll-*a* measurements ($n=9$) of streambed areas (Franson, 1985). Measurements of channel width (W , in meters, $n=3$), depth (D , in meters, $n=9$), and channel velocity (V , in meters per second, $n=9$) were made at all sites, as were temperature (TEMP, in degrees Celsius), specific conductance (COND, in microsiemens per centimeter at 25 degrees Celsius), dissolved oxygen, and pH (table I-2). Periphyton and submerged macrophytes were collected for arsenic analyses. Tissues were rinsed four times in stream-water and then four times in deionized water (18 megohms). Macrophyte root tissue was excluded from the samples in order to minimize arsenic contamination by attached inorganic particles that could not efficiently be removed by rinsing (that is, to improve precision in measurements of plant-tissue arsenic concentrations). The macrophyte sampling procedure did not exclude epiphytic algal cells. Lyophilized plant tissue was prepared and analyzed using a dry-ash procedure (Johns and Luoma, 1988). Reconstituted samples also were analyzed for total iron by flame atomic absorption spectroscopy to check for contamination by attached inorganic particles. Error bars presented in tables represent 95-percent confidence intervals for the specified replicate measurements.

Diel variations in biologically significant characteristics were examined using data loggers (Campbell, Model CR-10) at the four sampling sites. Data loggers were used with various probes to monitor the following variables: photosynthetically active radiation between 400 and 700 nm (LICOR probe, Model LI-192SA), water temperature (Campbell Scientific Probe, Model 107), air temperature (copper constantan thermocouple), specific conductance (4-lead probe fabricated by the Hydrologic Instrumentation Facility, U.S. Geological Survey), and pH (Innovative Sensors probe, Model M-12 with 9-volt preamplifier). Parameters monitored by data loggers and presented in tables I-3 to I-6 represent 15-minute averages of measurements taken at 10-second intervals. Data from the irradiance probe were verified against an irradiance meter (LICOR, Model LI185B) before the sampling study. Water and air temperature, and temperature corrected specific-conductance measurements (Cole Parmer, Model 1500-20) were taken manually every 3 hours during the sampling period. Measurements from the pH probe, designed for long-term data-logging applications, also were calibrated every 3 hours against temperature-compensated pH determinations (Orion Research, Model SA250). Therefore, with the exception of the irradiance measurements, the plotted data-logger values are identical to the manually determined measurements taken at 3-hour intervals (fit to manually determined measurements is imposed). Analysis of time-series data was performed using a statistical computer program (Minitab; Ryan and others, 1985) to produce correlograms for a range of lag times.

During the diel study, periphyton and macrophytes were sampled at noon at each site ($n=9$) for ash-free dry mass and spectrophotometric determination of chlorophyll-*a* corrected

Table I-2. Field data collected monthly during the summer of 1987 from four sites along Whitewood Creek.

[Headwater site, HW; Sewage-Treatment-Plant site, STP; Above Vale site, AV; and Sheeler Seep site, SS. Measured characteristics include: specific conductance, COND, in microsiemens per centimeter at 25 degrees Celsius; water temperature, TEMP, in degrees Celsius; pH; stream-channel width, W, in meters with 95-percent confidence intervals ($n=6$); mean channel depth, D, in meters with 95-percent confidence intervals ($n=9$); mean velocity, V, in meters per second with 95-percent confidence intervals ($n=9$); biomass, ρ_b , in grams per square meter with 95-percent confidence intervals ($n=9$); and autotrophic index, AI, in grams ash-free dry mass per gram chlorophyll-*a*. Sampling times are given in military format. The symbol “–” in the ρ_b or AI column indicates that the benthic-plant community at that time was not present in sufficient mass for analysis]

Date	Time	Site	COND	TEMP	pH	W	D	V	ρ_b	AI
05/27	0930	HW	420	8.2	8.3	2.6±0.1	0.12±0.05	0.82±0.02	37±15	120
05/27	1430	STP	545	15.2	8.1	7.7±0.5	0.38±0.09	0.94±0.12	34±17	110
05/28	1300	AV	890	18.4	8.2	21.6±1.6	0.35±0.12	0.30±0.11	–	–
05/28	1550	SS	980	20.0	8.2	3.9±0.4	0.38±0.15	0.77±0.20	–	–
07/07	1255	HW	450	16.0	8.3	2.4±0.3	0.10±0.02	0.58±0.10	52±19	110
07/08	1040	STP	760	17.0	8.4	7.3±0.5	0.24±0.04	0.74±0.11	71±51	120
07/09	1300	AV	1,180	21.5	8.6	17.9±0.7	0.05±0.02	0.39±0.14	469±65	90
07/10	1610	SS	1,310	28.0	8.6	3.4±0.5	0.24±0.11	0.86±0.16	28±5	80
08/19	0940	HW	429	9.0	8.7	2.5±0.3	0.15±0.03	0.51±0.16	51±27	140
08/19	1300	STP	899	17.6	8.3	7.1±0.3	0.23±0.06	0.65±0.19	54±19	100
08/26	1400	AV	1,108	17.0	8.0	18.0±0.5	0.21±0.18	0.13±0.03	280±30	180
08/26	1015	SS	1,245	14.5	8.1	3.6±0.3	0.27±0.04	0.72±0.20	29±14	160
09/16	1315	HW	563	11.1	8.3	1.7±0.2	0.10±0.02	0.25±0.05	60±34	170
09/16	1730	STP	930	16.8	7.9	6.5±0.7	0.19±0.04	0.53±0.07	82±60	120
09/28	1745	AV	1,167	18.3	8.1	17.8±0.8	0.33±0.06	0.07±0.01	237±25	310
09/28	1435	SS	1,222	19.5	8.3	3.7±0.4	0.24±0.05	0.46±0.09	7±4	20

for pheophytin-*a* (Franson 1985; Kuwabara and others, 1990). Streamwater sampled ($n=5$) at 3-hour intervals was filtered (Nuclepore, 0.2- μm polycarbonate membranes) for dissolved-arsenic and orthophosphate analyses. Water samples were simultaneously taken at 6-hour intervals for alkalinity determination by titration (Franson, 1985). Filtered orthophosphate samples ($n=2$ per sampling time) were preserved with mercuric chloride (1-mL mercury-saturated solution per 250-mL sample), and filtered arsenic samples were acidified to pH 2 with 6 normal, quartz-distilled hydrochloric acid. All processed water samples were refrigerated (approximately 5°C) in darkness.

Arsenic speciation was determined in the laboratory by the following steps. The acidified sample was buffered to pH 5 by using an acetate buffer (Tallman and Shaikh, 1980) and analyzed directly for trivalent arsenic [As(III)] by hydride generation, atomic absorption spectrometry (AAS). The sample was then reduced with potassium iodide in 40-percent hydrochloric acid for 1.5 hours and analyzed again to determine the total of inorganic As(III) and pentavalent arsenic [As(V)] (Tallman and Shaikh, 1980; Glaubig and Goldberg, 1988). The reduced sample then was analyzed by graphite furnace AAS to provide a measure of total dissolved arsenic. Dissolved orthophosphate was determined colorimetrically by the molybdate method using an autoanalyzer (Technicon, Model II) with an extended cell-path length (50 mm) for greater sensitivity (Murphy and Riley, 1962; Merle Shockey, oral commun., September 6, 1988).

Laboratory Studies

Algal species common to each of the four sampling sites were isolated for use in arsenate and orthophosphate sorption studies. Algal suspensions generated from periphyton scrapings were streaked on 1-percent agar plates containing an algal growth medium (Kuwabara and others, 1985) enriched with silica. Algal clusters that formed on the plates were transferred to liquid media for one week to increase algal density. This agar plate streaking and resuspension procedure was repeated until unialgal cultures were achieved. *Stichococcus* spp. and *Scenedesmus* spp. (Chlorophyceae), common to the four sampling sites, were initially isolated. It is not clear why common diatoms were not obtained from this isolation procedure because an abundance of diatoms was observed in the initial scrapings. One possibility is that chlorophyte growth was more rapid than diatoms on these agar plates. Another possibility is that the agar color obscured diatom clusters on the plates while chlorophyte clusters were readily visible. *Stichococcus* isolates were selected for use in subsequent sorption experiments over *Scenedesmus* because in agitated cultures, *Stichococcus* typically remained unicellular and therefore could be quickly and precisely enumerated with a particle counter. Algal isolates were maintained in a chemically defined growth medium with added solute concentrations similar to ambient levels at their respective collection sites (0.0 $\mu\text{mol/L}$ for HW, 0.5 $\mu\text{mol/L}$ for STP, and 1.0 $\mu\text{mol/L}$ for AV and SS isolates).

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Table I-3. Physical and chemical characteristics in Whitewood Creek at the Headwater site, monitored between August 29 and 30, 1988, to examine diel fluctuations in these characteristics.

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/29/88	1645	0	16.9	8.77	216	160.5
	1700	15	16.8	8.76	222	184.5
	1715	30	16.8	8.75	228	160.7
	1730	45	16.8	8.73	232	139.8
	1745	60	16.7	8.73	236	151.9
	1800	75	16.6	8.72	236	150.8
	1815	90	16.6	8.71	242	123.6
	1830	105	16.6	8.69	248	66.8
	1845	120	16.3	8.66	252	42.1
	1900	135	16.1	8.63	255	31.6
	1915	150	15.8	8.60	252	22.4
	1930	165	15.5	8.57	255	9.7
	1945	180	15.4	8.53	248	3.4
	2000	195	15.0	8.50	255	1.5
	2015	210	14.7	8.47	255	1.5
	2030	225	14.4	8.44	265	1.6
	2045	240	14.2	8.41	261	1.7
	2100	255	14.0	8.39	268	1.5
	2115	270	13.6	8.37	268	1.6
	2130	285	13.4	8.36	271	1.5
	2145	300	13.2	8.34	268	1.6
	2200	315	12.8	8.33	274	1.4
	2215	330	12.6	8.33	271	1.4
	2230	345	12.4	8.32	284	1.4
	2245	360	12.2	8.31	278	1.4
	2300	375	12.0	8.31	274	1.4
	2315	390	11.7	8.31	281	1.4
2330	405	11.5	8.30	278	1.4	
2345	420	11.3	8.31	281	1.4	
08/30/88	0	435	11.1	8.31	281	1.4
	15	450	10.9	8.31	287	1.4
	30	465	10.8	8.31	287	1.4
	45	480	10.7	8.31	281	1.4
	100	495	10.6	8.31	284	1.4
	115	510	10.4	8.31	290	1.4
	130	525	10.3	8.31	281	1.4
	145	540	10.0	8.31	287	1.4
	200	555	9.9	8.31	300	1.4
	215	570	9.8	8.32	300	1.4
	230	585	9.8	8.32	284	1.4
	245	600	9.7	8.32	294	1.4
	300	615	9.4	8.32	303	1.4
	315	630	9.4	8.32	300	1.4
	330	645	9.3	8.32	290	1.4

Table I-3. Physical and chemical characteristics in Whitewood Creek at the Headwater site, monitored between August 29 and 30, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/30/88—Continued	345	660	9.2	8.32	294	1.4
	400	675	9.0	8.32	310	1.4
	415	690	9.0	8.33	307	1.4
	430	705	9.1	8.33	294	1.4
	445	720	9.0	8.33	313	1.4
	500	735	8.9	8.33	297	1.4
	515	750	8.9	8.33	300	1.4
	530	765	8.8	8.33	307	1.4
	545	780	8.7	8.33	316	1.4
	600	795	8.7	8.33	316	1.4
	615	810	8.6	8.33	313	1.7
	630	825	8.5	8.34	303	3.3
	645	840	8.5	8.34	303	6.5
	700	855	8.5	8.34	307	9.7
	715	870	8.3	8.35	310	14.1
	730	885	8.3	8.36	313	19.4
	745	900	8.3	8.36	317	25.4
	800	915	8.3	8.37	318	34.5
	815	930	8.4	8.39	320	55.3
	830	945	8.5	8.41	307	76.5
	845	960	8.5	8.44	317	107.9
	900	975	8.8	8.47	307	111.3
	915	990	9.0	8.49	314	112.6
	930	1,005	9.1	8.52	317	136.8
	945	1,020	9.4	8.55	317	146.4
	1000	1,035	9.7	8.57	304	159.5
	1015	1,050	10.0	8.60	310	173.9
	1030	1,065	10.5	8.63	301	189.0
	1045	1,080	10.9	8.65	310	210.2
	1100	1,095	11.5	8.67	294	240.7
	1115	1,110	12.0	8.69	290	318.0
	1130	1,125	12.5	8.70	291	348.6
	1145	1,140	13.1	8.71	278	465.3
	1200	1,155	13.6	8.72	271	641.8
	1215	1,170	14.2	8.73	261	421.8
	1230	1,185	14.8	8.74	261	327.3
	1245	1,200	15.4	8.74	252	594.7
	1300	1,215	15.9	8.75	248	762.3
	1315	1,230	16.4	8.75	236	831.7
	1330	1,245	16.7	8.76	232	535.4
	1345	1,260	17.1	8.77	232	626.4
	1400	1,275	17.5	8.78	232	925.9
	1415	1,290	17.8	8.77	229	1,026.6
	1430	1,305	18.2	8.77	229	987.1

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Table I-3. Physical and chemical characteristics in Whitewood Creek at the Headwater site, monitored between August 29 and 30, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/30/88—Continued	1445	1,320	18.4	8.78	226	402.5
	1500	1,335	18.5	8.78	223	451.6
	1515	1,350	18.6	8.78	223	212.4
	1530	1,365	18.8	8.78	223	198.8
	1545	1,380	18.8	8.78	226	91.7
	1600	1,395	18.6	8.78	223	113.3
	1615	1,410	18.5	8.78	232	138.9
	1630	1,425	18.5	8.78	232	156.0
	1645	1,440	18.3	8.77	226	166.3
	1700	1,455	18.2	8.77	232	153.3

Table I-4. Physical and chemical characteristics in Whitewood Creek at the Sewage-Treatment-Plant site, monitored between August 30 and 31, 1988, to examine diel fluctuations in these characteristics.

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second. Symbol “—” indicates the malfunction of the water-temperature probe]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/30/88	845	0	12.4	8.26	820	152.5
	900	15	12.6	8.26	817	172.3
	915	30	12.6	8.27	817	195.9
	930	45	12.7	8.28	814	210.6
	945	60	12.9	8.29	812	241.0
	1000	75	13.0	8.31	813	255.9
	1015	90	13.3	8.32	807	338.3
	1030	105	13.3	8.33	811	384.8
	1045	120	13.6	8.34	806	412.9
	1100	135	13.6	8.36	802	393.9
	1115	150	13.8	8.38	794	443.8
	1130	165	14.2	8.41	787	478.0
	1145	180	14.4	8.42	777	454.0
	1200	195	14.6	8.44	776	419.4
	1215	210	14.9	8.45	771	393.9
	1230	225	14.9	8.45	763	422.4
	1245	240	15.3	8.46	758	429.4
	1300	255	15.3	8.46	761	387.9
	1315	270	15.5	8.47	761	301.4
	1330	285	15.7	8.49	762	260.4
	1345	300	16.0	8.50	757	258.1
1400	315	16.0	8.51	751	248.3	
1415	330	16.2	8.52	745	243.3	
1430	345	16.3	8.53	744	239.7	

Table I-4. Physical and chemical characteristics in Whitewood Creek at the Sewage-Treatment-Plant site, monitored between August 30 and 31, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second. Symbol “—” indicates the malfunction of the water-temperature probe]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/30/88—Continued	1445	360	16.4	8.53	739	229.9
	1500	375	16.6	8.54	733	229.0
	1515	390	17.1	8.55	722	225.5
	1530	405	17.1	8.56	723	224.9
	1545	420	17.1	8.56	723	188.4
	1600	435	17.1	8.55	726	209.0
	1615	450	17.1	8.54	720	164.0
	1630	465	17.0	8.54	724	146.3
	1645	480	16.7	8.53	730	143.8
	1700	495	16.7	8.53	732	128.3
	1715	510	16.6	8.52	734	131.2
	1730	525	16.5	8.51	733	95.0
	1745	540	16.7	8.50	728	93.6
	1800	555	16.4	8.49	734	103.3
	1815	570	16.7	8.47	729	101.2
	1830	585	16.5	8.46	735	60.4
	1845	600	16.4	8.45	734	37.7
	1900	615	16.3	8.43	730	21.8
	1915	630	16.3	8.41	722	17.0
	1930	645	16.1	8.40	724	7.4
	1945	660	16.0	8.39	728	1.1
	2000	675	16.0	8.38	734	0.1
	2015	690	15.8	8.37	736	0.1
	2030	705	15.6	8.36	740	0.1
	2045	720	15.6	8.34	738	0.1
	2100	735	15.3	8.33	745	0.1
	2115	750	15.3	8.32	748	0.1
	2130	765	15.2	8.32	752	0.1
	2145	780	15.0	8.31	757	0.1
	2200	795	14.9	8.31	762	0.1
	2215	810	14.9	8.30	754	0.1
	2230	825	14.6	8.29	755	0.1
	2245	841	14.6	8.28	752	0.1
2300	856	14.6	8.28	753	0.1	
2315	871	14.4	8.27	753	0.1	
2330	886	14.2	8.26	756	0.1	
2345	901	14.2	8.25	757	0.1	
08/31/88	0	916	14.0	8.25	762	0.1
	15	931	13.8	8.24	766	0.1
	30	946	13.6	8.23	774	0.1
	45	961	13.6	8.23	775	0.1
	100	976	13.6	8.23	775	0.1
	115	991	13.5	8.22	766	0.1
	130	1,006	13.2	8.21	761	0.1
	145	1,021	13.2	8.20	755	0.1
	200	1,036	13.2	8.20	759	0.1

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Table I-4. Physical and chemical characteristics in Whitewood Creek at the Sewage-Treatment-Plant site, monitored between August 30 and 31, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second. Symbol “—” indicates the malfunction of the water-temperature probe]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/31/88—Continued	215	1,051	13.0	8.19	762	0.1
	230	1,066	12.9	8.19	771	0.1
	245	1,081	12.8	8.18	775	0.0
	300	1,096	12.6	8.18	783	0.1
	315	1,111	12.6	8.17	784	0.0
	330	1,126	12.6	8.17	784	0.0
	345	1,141	12.4	8.16	783	0.2
	400	1,156	12.3	8.15	793	0.2
	415	1,171	12.3	8.14	792	0.3
	430	1,186	12.3	8.14	789	0.4
	445	1,201	12.1	8.15	783	0.3
	500	1,216	12.0	8.15	786	0.3
	515	1,231	12.0	8.15	786	0.5
	530	1,246	12.0	8.15	789	0.5
	545	1,261	12.0	8.16	789	0.6
	600	1,276	12.0	8.16	791	0.6
	615	1,291	12.0	8.16	791	1.3
	630	1,306	12.0	8.17	795	1.7
	645	1,321	12.0	8.17	796	4.4
	700	1,336	12.0	8.18	805	7.9
	715	1,351	—	8.19	804	10.8
	730	1,366	—	8.19	799	15.7
	745	1,381	—	8.20	794	20.7
	800	1,396	—	8.21	791	24.7
	815	1,411	—	8.22	787	35.1
	830	1,426	—	8.23	791	55.4
	845	1,441	—	8.23	789	80.9
	900	1,456	—	8.25	792	75.9
	915	1,471	—	8.26	795	116.2
	930	1,486	—	8.27	802	144.2
	945	1,501	—	8.28	817	153.6
	1000	1,516	—	8.29	830	166.2
	1015	1,531	—	8.31	830	308.9
	1030	1,546	—	8.32	819	474.6
	1045	1,561	—	8.33	814	517.8
	1100	1,576	—	8.35	810	529.0
	1115	1,591	—	8.37	812	552.3
	1130	1,606	—	8.39	814	631.6
	1145	1,621	—	8.41	821	686.0
	1200	1,636	—	8.43	816	816.9
1215	1,651	—	8.45	808	941.1	
1230	1,666	—	8.47	803	931.4	
1245	1,681	—	8.50	804	808.8	
1300	1,696	—	8.53	800	711.9	
1315	1,711	—	8.55	780	388.2	

Table I-4. Physical and chemical characteristics in Whitewood Creek at the Sewage-Treatment-Plant site, monitored between August 30 and 31, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second. Symbol “—” indicates the malfunction of the water-temperature probe]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/31/88—Continued	1330	1,726	—	8.56	762	134.9
	1345	1,741	—	8.56	748	90.8
	1400	1,756	—	8.57	741	91.5
	1415	1,771	—	8.57	737	102.2
	1430	1,786	—	8.56	736	102.4
	1445	1,801	—	8.54	730	91.4
	1500	1,816	—	8.51	730	79.7
	1515	1,831	—	8.49	727	92.0
	1530	1,846	—	8.46	728	121.2
	1545	1,861	—	8.43	729	130.2
	1600	1,876	—	8.41	735	127.9
	1615	1,891	—	8.39	731	123.8
	1630	1,906	—	8.36	726	120.8

Table I-5. Physical and chemical characteristics in Whitewood Creek at the Above Vale site, monitored between August 31 and September 1, 1988, to examine diel fluctuations in these characteristics.

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/31/88	700	0	15.1	8.37	1,177	9.7
	715	15	15.1	8.38	1,177	19.8
	730	30	15.1	8.40	1,177	32.3
	745	45	15.1	8.41	1,178	43.4
	800	60	14.9	8.43	1,179	53.5
	815	75	14.8	8.44	1,180	69.7
	830	90	14.9	8.47	1,180	75.9
	845	105	14.8	8.49	1,180	92.2
	900	120	14.9	8.52	1,179	129.8
	915	135	15.0	8.55	1,179	175.3
	930	150	15.1	8.58	1,178	286.2
	945	165	15.1	8.62	1,177	376.3
	1000	180	15.3	8.66	1,176	423.6
	1015	195	15.4	8.70	1,174	486.0
	1030	210	15.7	8.74	1,172	531.5
	1045	225	16.0	8.77	1,170	580.1
	1100	240	16.2	8.80	1,168	599.6
	1115	255	16.4	8.84	1,166	646.8
	1130	230	16.7	8.88	1,163	675.1
1145	285	17.1	8.90	1,160	685.3	
1200	300	17.3	8.92	1,158	698.3	

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Table I-5. Physical and chemical characteristics in Whitewood Creek at the Above Vale site, monitored between August 31 and September 1, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
08/31/88—Continued	1215	315	17.6	8.93	1,155	723.2
	1230	330	18.0	8.95	1,152	732.5
	1300	360	18.7	9.00	1,147	831.51
	1315	375	19.0	9.01	1,145	450.1
	1330	390	19.4	9.03	1,141	354.4
	1345	405	19.8	9.03	1,139	252.1
	1400	420	20.1	9.03	1,136	281.9
	1415	435	20.5	9.03	1,134	799.8
	1430	450	20.9	9.04	1,131	813.5
	1445	465	21.1	9.04	1,130	655.1
	1500	480	21.4	9.05	1,128	429.7
	1515	495	21.7	9.03	1,126	361.5
	1530	510	22.1	9.02	1,124	348.9
	1545	525	22.2	8.98	1,123	211.6
	1600	540	22.5	8.94	1,122	172.8
	1615	555	22.6	8.93	1,121	179.1
	1630	570	22.8	8.92	1,120	182.4
	1645	585	22.9	8.91	1,120	204.4
	1700	600	23.0	8.89	1,120	254.8
	1715	615	23.2	8.85	1,120	232.4
	1730	630	23.1	8.80	1,120	157.7
	1745	645	23.0	8.77	1,121	127.1
	1800	660	22.9	8.76	1,122	117.6
	1815	675	22.8	8.75	1,122	80.9
	1830	690	22.6	8.74	1,123	45.8
	1845	705	22.5	8.73	1,124	37.6
	1900	720	22.3	8.72	1,125	27.9
	1915	735	22.1	8.71	1,126	22.7
	1930	750	22.1	8.71	1,126	11.2
	1945	765	21.9	8.70	1,128	3.3
	2000	780	21.5	8.69	1,130	1.4
	2015	795	21.4	8.69	1,130	1.3
	2030	810	21.1	8.67	1,132	1.4
	2045	826	21.1	8.67	1,132	1.4
	2100	841	20.8	8.66	1,134	1.6
	2115	856	20.6	8.66	1,135	1.9
	2130	871	20.4	8.65	1,136	1.6
	2145	886	20.2	8.64	1,137	1.7
	2200	901	10.0	8.63	1,138	2.0
	2215	916	19.7	8.62	1,140	1.9
	2230	931	19.7	8.60	1,140	1.8
	2245	946	19.4	8.59	1,141	1.8
	2300	961	19.4	8.57	1,142	1.7
	2315	976	19.1	8.56	1,144	1.5
	2330	991	18.8	8.54	1,145	1.7
	2345	1,006	18.7	8.54	1,146	1.4

Table I-5. Physical and chemical characteristics in Whitewood Creek at the Above Vale site, monitored between August 31 and September 1, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
09/01/88	0	1,021	18.5	8.54	1,147	1.5
	15	1,036	18.5	8.51	1,147	1.4
	30	1,051	18.3	8.51	1,149	1.4
	45	1,066	18.2	8.50	1,150	1.5
	100	1,081	18.0	8.49	1,152	1.4
	115	1,096	17.9	8.49	1,152	1.4
	130	1,111	17.7	8.49	1,153	1.4
	145	1,126	17.4	8.49	1,155	1.4
	200	1,141	17.4	8.49	1,156	1.3
	215	1,156	17.2	8.48	1,157	1.3
	230	1,171	17.2	8.48	1,158	1.3
	245	1,186	17.1	8.48	1,158	1.3
	300	1,201	16.9	8.48	1,160	1.3
	315	1,216	16.6	8.47	1,161	1.6
	330	1,231	16.6	8.46	1,162	1.6
	345	1,246	16.5	8.45	1,164	1.7

Table I-6. Physical and chemical characteristics in Whitewood Creek at the Sheeler Seep site, monitored between September 1 and 2, 1988, to examine diel fluctuations in these characteristics.

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
09/01/88	645	0	15.3	7.98	1,367	34.3
	700	15	15.3	7.98	1,369	45.8
	715	30	15.2	7.99	1,370	62.4
	730	45	15.2	8.00	1,374	78.9
	745	60	15.2	8.00	1,377	97.5
	800	75	15.2	8.01	1,378	135.2
	815	90	15.2	8.03	1,380	186.9
	830	105	15.2	8.04	1,383	133.3
	845	120	15.3	8.05	1,383	366.0
	900	135	15.3	8.07	1,386	485.9
	915	150	15.5	8.08	1,385	549.7
	930	165	15.6	8.09	1,390	624.8
	945	180	15.9	8.10	1,388	696.7
	1000	195	16.2	8.12	1,387	771.1
	1015	210	16.5	8.14	1,385	850.5
	1030	225	16.8	8.16	1,385	935.1
	1045	240	17.3	8.17	1,383	980.9
1100	255	17.7	8.19	1,381	1,018.7	
1115	270	18.1	8.20	1,378	1,091.0	
1130	285	18.6	8.22	1,370	1,122.9	
1145	300	19.3	8.23	1,370	1,146.0	

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Table I-6. Physical and chemical characteristics in Whitewood Creek at the Sheeler Seep site, monitored between September 1 and 2, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
09/01/88—Continued	1200	315	19.8	8.24	1,368	1,177.4
	1215	330	20.3	8.26	1,365	490.7
	1230	345	21.0	8.27	1,364	663.8
	1245	360	21.5	8.28	1,359	1,152.1
	1300	375	22.1	8.29	1,355	1,218.8
	1315	390	22.6	8.30	1,354	1,237.5
	1330	405	23.0	8.31	1,349	1,256.4
	1345	420	23.5	8.32	1,346	1,246.7
	1400	435	24.0	8.32	1,344	1,214.4
	1415	450	24.6	8.33	1,342	1,189.8
	1430	465	24.9	8.34	1,341	1,167.1
	1445	480	25.1	8.34	1,338	1,128.1
	1500	495	25.4	8.34	1,338	1,071.4
	1515	510	25.7	8.34	1,333	1,045.5
	1530	525	25.8	8.34	1,325	986.5
	1545	540	25.8	8.34	1,323	907.8
	1600	555	26.1	8.33	1,325	838.3
	1615	570	26.2	8.32	1,325	781.0
	1630	585	26.2	8.32	1,325	717.5
	1645	600	26.0	8.31	1,326	619.2
	1700	615	25.8	8.31	1,325	545.4
	1715	630	25.8	8.29	1,326	483.7
	1730	645	25.5	8.28	1,326	279.4
	1745	660	25.3	8.27	1,329	137.4
	1800	675	25.0	8.25	1,326	82.6
	1815	690	24.9	8.23	1,329	73.9
	1830	705	24.6	8.21	1,331	60.5
	1845	720	24.2	8.19	1,332	38.5
	1900	735	23.9	8.18	1,334	33.9
	1915	750	23.7	8.16	1,332	26.1
	1930	765	23.5	8.15	1,334	10.8
	1945	780	23.4	8.13	1,335	2.7
	2000	795	23.0	8.11	1,336	1.7
	2015	810	22.8	8.09	1,337	1.5
	2030	825	22.5	8.08	1,337	1.4
	2045	840	22.3	8.07	1,338	1.3
	2100	855	22.0	8.05	1,339	1.3
	2115	870	21.8	8.04	1,342	1.4
	2130	885	21.4	8.03	1,344	1.3
	2145	900	21.2	8.02	1,344	1.3
	2200	915	20.9	8.01	1,344	1.3
	2215	930	20.7	8.00	1,347	1.3
	2230	945	20.3	8.00	1,351	1.3
	2245	960	20.1	7.99	1,351	1.3
	2300	975	19.8	7.99	1,349	1.3
	2315	990	19.7	7.98	1,351	1.3
	2330	1,005	19.4	7.97	1,349	1.3
	2345	1,020	19.2	7.96	1,349	1.3

Table I-6. Physical and chemical characteristics in Whitewood Creek at the Sheeler Seep site, monitored between September 1 and 2, 1988, to examine diel fluctuations in these characteristics.—Continued

[Elapsed time in minutes; water temperature in degrees Celsius; COND, specific conductance in microsiemens per centimeter at 25 degrees Celsius; photosynthetically active radiation, IRRADIANCE, between 400 and 700 nanometers in microeinsteins per square meter per second]

Date	Time	Elapsed time	Water temperature	pH	COND	IRRADIANCE
09/01/88—Continued	0	1,035	19.0	7.96	1,354	1.3
	15	1,050	18.7	7.96	1,351	1.3
	30	1,065	18.5	7.95	1,354	1.3
	45	1,080	18.2	7.95	1,357	1.3
	100	1,095	18.2	7.95	1,357	1.3
	115	1,110	18.0	7.95	1,360	1.3
	130	1,125	17.7	7.94	1,359	1.3
	145	1,140	17.6	7.94	1,360	1.3
	200	1,155	17.4	7.94	1,360	1.3
	215	1,170	17.4	7.94	1,360	1.3
	230	1,185	17.2	7.93	1,362	1.2
	245	1,200	17.1	7.93	1,355	1.3
	300	1,215	16.9	7.93	1,360	1.3
	315	1,230	16.7	7.93	1,354	1.3

In initial experiments, sorption of arsenate and phosphate was observed in living and heat-killed cells from three collection sites (HW, STP, and AV). The SS isolate was not initially used because of the similarity in media formulations for the AV and SS isolates. Algal suspensions (105 cells per milliliter) in 40-mL fluoroethylene polymer Oakridge tubes were spiked with arsenic-73 and phosphorus-32-labeled stock solutions yielding a 0.5- $\mu\text{mol/L}$ concentration for both total dissolved arsenate and orthophosphate. Suspensions then were placed on a mechanical shaker and agitated. After 24 and 48 hours of exposure, suspensions were centrifuged at 10,000 revolutions per minute for 10 minutes to remove the algal cells from suspension. Five-milliliter volumes of the resulting supernatant, the algal suspension before centrifugation, and an internal arsenic-73 and phosphorus-32 standard were counted by liquid scintillation to determine the extent of arsenic and orthophosphate sorption by these cultures (table I-7).

In subsequent experiments, arsenic sorption by algal cells was studied in laboratory experiments as a function of dissolved-arsenate and orthophosphate concentrations in media formulations. Unialgal cultures of the diatom *Achnanthes minutissima* (isolated by micropipetting from all four sampling sites) were used to determine sorption-rate constants. *A. minutissima* was selected for this series of experiments over the initially isolated chlorophytes (*Stichococcus* spp. and *Scenedesmus* spp.) because *A. minutissima* were present in greater abundance in periphyton samples and also were easily enumerated with a particle counter. Sorption-rate constants for arsenate and phosphate were determined from arsenic-73 and phosphorus-32-labeled experiments using heat-killed cells as described by Fisher and others (1984). Previous experiments (Kuwabara and others, 1988) indicated that use of heat-killed cells for short-term arsenate and orthophosphate sorption experiments yielded results comparable to living cell cultures and avoided the need for biomass corrections. A 3² full-factorial experimental design ($n=3$) was used to examine the

interactive effects of arsenic and phosphorus on sorption rates and accumulation in *A. minutissima*. Isolates from the HW and AV sites were used because of contrasting ambient dissolved-arsenic concentrations. Arsenic-73 and phosphorus-32-labeled stock solutions were used to achieve 0.0-, 0.5-, and 1.0- $\mu\text{mol/L}$ initial concentrations of dissolved arsenate and orthophosphate in the nine chemically defined formulations (representative of ambient concentration ranges observed at these two sites). An inoculum of heat-killed cells was then added (10^6 cells per milliliter). After periods of 0.5, 1, 2, 4, 8, and 24 hours, supernatant from centrifuged cell suspensions were counted by liquid scintillation to determine solute removal from solution by the cells.

Table I-7. Algal cell sorption of arsenate and orthophosphate at 24 and 48 hours by living and heat-killed cells using three *Stichococcus* isolates from three sites along Whitewood Creek.

[Headwater site, HW; Sewage-Treatment-Plant site, STP; and the Above Vale site, AV. Calculated 95-percent confidence intervals are given for three replicate cultures. Culture media additions of dissolved arsenate and dissolved orthophosphate at 0.5 micromole per liter were used]

Sample	Elapsed time (hours)	Percent arsenate sorbed		Percent orthophosphate sorbed	
		Living	Heat-killed	Living	Heat-killed
HW	24	25 \pm 12	29 \pm 11	93 \pm 2	94 \pm 2
	48	23 \pm 8	20 \pm 6	96 \pm 2	95 \pm 2
STP	24	19 \pm 3	27 \pm 10	93 \pm 2	90 \pm 4
	48	20 \pm 4	18 \pm 6	96 \pm 2	92 \pm 2
AV	24	24 \pm 6	21 \pm 10	88 \pm 2	84 \pm 2
	48	16 \pm 5	19 \pm 3	94 \pm 2	84 \pm 2

Results and Discussion

Field Experiments

Biomass in August 1986 increased downstream from the Headwater site (HW) to the Above Vale (AV) site and then decreased at the Sheeler Seep site (SS). Estimates for benthic plant biomass abundance (table I-1) represent the ash-free dry weights per unit area of scrapings multiplied by the percent coverage of algal growth at the sampling site. Autotrophic indices (AI) ranged from 120 at the HW site to 210 downstream from the municipal water-treatment plant (STP). This index has been used as an indicator of environmental stress, whereby increasing values indicate increasing abundance of senescent or stressed cells or an increasing proportion of heterotrophic growth (Leland and Carter, 1985; Weber, 1973). The HW and AV sites displayed AI values typical of unstressed communities (about 100 ± 50), but elevated values at the STP and SS sites were observed.

Temporal changes in biomass observed in 1987 monthly samples differed among sites. Measured plant mass per unit streambed area was similar at the HW and STP sites, highest at the AV site once the mat was established, and lowest at the most downstream (SS) site (table I-2). At the HW site, which was dominated throughout the summer by a submerged macrophyte (*Ranunculus longirostris*), biomass increased from an average of 37 grams per square meter in late May to 60 grams per square meter in September. However, differences between monthly biomass measurements at the HW site were not significant at the 95-percent confidence level (table I-2). The large confidence intervals relative to average ρ_b values, even with nine replicates per site, is indicative of a patchy distribution of the benthic plant communities. At the STP site, a community dominated by *Ranunculus* during June and July changed during August and September to a dense growth of the pondweed *Zannichellia galustris* and the chlorophytes *Cladophora* spp. and *Ulothrix* spp. Monthly biomass at the STP site did not differ significantly (table I-2). Because of streambed scouring, dense plant growth was not established at the AV site in June. However, by July, a thick (approximately 20 cm) mat of *Ranunculus* and epiphytic diatoms blanketed more than half the stream channel. Similar to the STP site, August and September samples showed a shift toward *Zannichellia* and filamentous chlorophyte species at the AV site. Once a dense periphyton and macrophyte assemblage was established, biomass was most abundant at the AV site, where estimated biomass was an order of magnitude higher than at other sites. Elevated stream discharge in late May also inhibited the establishment of a dense assemblage at the SS site, but *Zannichellia* was observed in abundance by July under much lower flow conditions (table I-2). Epiphytic diatoms and filamentous chlorophytes dominated benthic plant communities in August and September samples. Biomass was consistently lower at the SS site than at the three upstream sites.

AI ranged from 80 at the SS site in July to 310 at the AV site in September (table I-2). All four sites in late May and July displayed AI values typical of unstressed or nonsenescent benthic plant communities, whereas elevated values were measured at the AV and SS sites in August and at the HW, AV, and SS sites in September. Dissolved oxygen was consistently at or above saturation in water-column samples.

Arsenic concentrations in algal tissues consistently increased between the late May and August sampling dates at the HW and STP sites and between July and August at the AV and SS sites except for the macroalgae at the SS site, which showed not significant concentration difference between July and August samples (table I-8). Concentrations measured in August and September samples were similar or showed a decrease in September. There also was a discernible increase in tissue arsenic concentration with distance downstream. However, the range of concentrations observed during the sampling period at the upstream (HW) site was greater than that observed at the downstream sites (table I-8). Arsenic in submerged macrophyte tissue was slightly higher than in macroalgae, although general concentration trends at each site were similar between plant groups. As noted in the "Methods of Study" section, arsenic concentrations for macrophyte tissue include contributions from epiphytic algal cells that are not excluded in the sampling procedure. Iron concentrations in digested samples indicate minimal effects on arsenic concentrations due to residual inorganic particles attached to plant tissues (table I-8).

Data from the diel study done between August 30 and September 2, 1988, at the four sampling sites are shown in tables I-3 to I-6 for the HW to SS sites, respectively, and in figures I-2 to I-5 plotted with dissolved-arsenic and orthophosphate concentrations. A comparison of measured parameters in this late summer sampling (data summarized in table I-9) shows trends in biomass and autotrophic indices (ratio of ash-free dry mass to chlorophyll-*a*) that were typical of the study sites for this period of the algal growth season (table I-2). Algal abundance increased from the HW to the AV site and decreased at the SS site. The highest estimated autotrophic index (210) at the AV site (the artificially pooled area) coincided with observed senescence of the benthic plant community at that site (for example, degraded macrophyte fronds and algal filaments, and visually observed organic detrital material within the mat).

The ranges for irradiance (table I-9) and the irradiance time course for the four sites (fig. I-2) were indicative of intermittent cloud cover, especially during the afternoons at the HW, STP, and AV sites, but indicated a consistently clear sampling day at the SS site. The water-temperature cycle typically lagged by 2 to 3 hours behind the irradiance (table I-10), and mean water temperature increased downgradient (that is, with decreased altitudes).

With the exception of the STP site, the amplitude of the pH cycle increased with increasing biomass, as one would expect of sites with metabolically active flora (the highest and lowest values for both pH amplitudes and biomass at the AV and SS sites,

respectively). The pH cycle at each of the four sites lagged the irradiance cycle by 1 to 2 hours, which is similar to observed fluctuations in water temperature (table I-10).

An increase in total dissolved arsenic was observed between the HW and AV sites; a decrease occurred at the SS site (table I-9)—results are consistent with water years 1985 and 1986 (Goddard, 1988). The predominant arsenic species at all four sites were inorganic. Our analytical protocol for arsenic

Table I-8. Total arsenic concentrations in dominant benthic plant species collected from four sites along Whitewood Creek.

[Arsenic concentrations in plant tissues in micrograms solute per gram dry tissue with 95-percent confidence intervals ($n=4$ replicates). Iron concentrations in plant tissues in micrograms solute per gram dry tissue also were checked ($n=1$ replicate) for possible effects of residual inorganic particles (that is, particles remaining on plant tissue samples after the rinsing procedure) on reported arsenic concentrations. The Headwater and most upstream site, HW; Sewage-Treatment-Plant site, STP; Above Vale site, AV; and Sheeler Seep site (and most downstream sampling site for this study, SS). Symbol “—” indicates that the benthic plant community had not yet been established at that site and therefore tissues could not be sampled in adequate quantities for analysis]

Sampling site		Arsenic	Iron
Tissues sampled 05/27–28/87			
HW	Macroalgae ¹	1,465±38	2,180
	Macrophyte ²	1,552±16	2,070
STP	Macroalgae	1,709±22	1,960
	Macrophyte	1,757±14	1,850
AV	Macroalgae	—	—
	Macrophyte	—	—
SS	Macroalgae	—	—
	Macrophyte	—	—
Tissues sampled 07/07–10/87			
HW	Macroalgae	1,633±33	2,470
	Macrophyte	1,866±9	2,140
STP	Macroalgae	1,819±31	2,090
	Macrophyte	1,971±8	1,690
AV	Macroalgae	2,051±45	4,040
	Macrophyte	2,390±8	5,170
SS	Macroalgae	2,358±91	3,570
	Macrophyte	2,480±16	3,150
Tissues sampled 08/19–26/87			
HW	Macroalgae	1,884±43	2,630
	Macrophyte	2,180±52	2,860
STP	Macroalgae	1,903±18	1,970
	Macrophyte	2,030±49	2,210
AV	Macroalgae	2,151±15	5,370
	Macrophyte	2,479±39	4,830
SS	Macroalgae	2,418±24	3,340
	Macrophyte	2,572±42	3,020

Table I-8. Total arsenic concentrations in dominant benthic plant species collected from four sites along Whitewood Creek. —Continued

Sampling site		Arsenic	Iron
Tissues sampled 09/16–28/87			
HW	Macroalgae	1,931±50	2,960
	Macrophyte	1,991±83	2,340
STP	Macroalgae	1,933±50	2,550
	Macrophyte	2,099±112	2,070
AV	Macroalgae	2,117±94	5,460
	Macrophyte	2,184±95	5,160
SS	Macroalgae	2,317±189	4,120
	Macrophyte	2,352±23	4,760

¹Samples dominated by filamentous chlorophytes and epiphytic diatoms. Specific changes in community structure are described in the text.

²Early summer samples typically dominated by the submerged macrophyte, *Ranunculus longirostris* and associated algal epiphytes, whereas later samples commonly dominated by the pondweed, *Zannichellia palustris*. Specific changes in dominant macrophyte species are discussed in the text.

species indicated that inorganic trivalent arsenic represented less than 30 percent of the total dissolved arsenic at all sites, and significant dissolved organic arsenic was not detected as the difference between total dissolved arsenic and dissolved inorganic trivalent and pentavalent arsenic. There is a controversy as to whether the preservation technique prescribed by Glaubig and Goldberg (1988) does in fact prevent significant oxidation of trivalent arsenic to pentavalent arsenic. Therefore, the presence of reduced arsenic species may be even more significant than indicated by the analytical protocol used here. As expected, dissolved-orthophosphate concentrations were highest at the STP site and decreased downstream (table I-9). Concentration cycles in dissolved-arsenic species and dissolved orthophosphate lagged approximately 3 hours and 6 hours, respectively, behind pH cycles at the SS site, but no lag was resolved at the AV site for the major arsenic species (table I-10). Specific conductance at these sites cycled out of phase with fluctuations in arsenic species (fig. I-3). Diel cycles for dissolved arsenic and orthophosphate were not evident at the HW site upstream from mining activities because of low total dissolved-arsenic concentrations (less than 0.05 $\mu\text{mol/L}$) nor at the STP site downstream from water-treatment-plant discharge (table I-9).

Laboratory Experiments

In experiments using the chlorophyte *Stichococcus*, arsenate and orthophosphate sorption was similar for living and dead cells over the first 24 hours of exposure (table I-7). Concentrations accumulated (for both arsenic and phosphorus) were similar for algae collected from different sites and maintained at ambient solute concentrations. A preference of orthophosphate sorption over arsenate was observed for all species isolates.

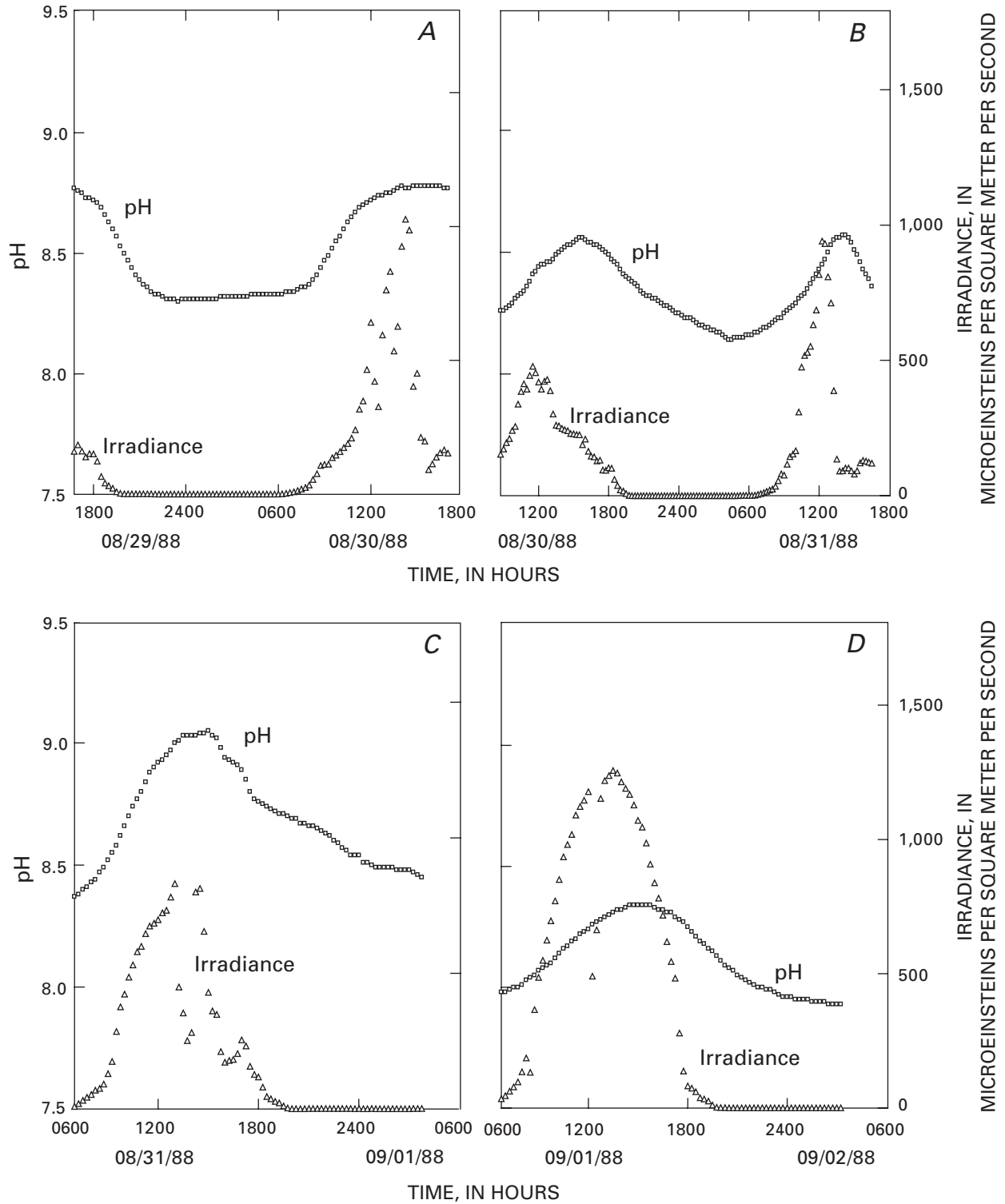


Figure I-2. Diel trends in pH and irradiance along Whitewood Creek at (A) the Headwater site, (B) the Sewage-Treatment-Plant site, (C) the Above Vale site, and (D) the Sheeler Seep site.

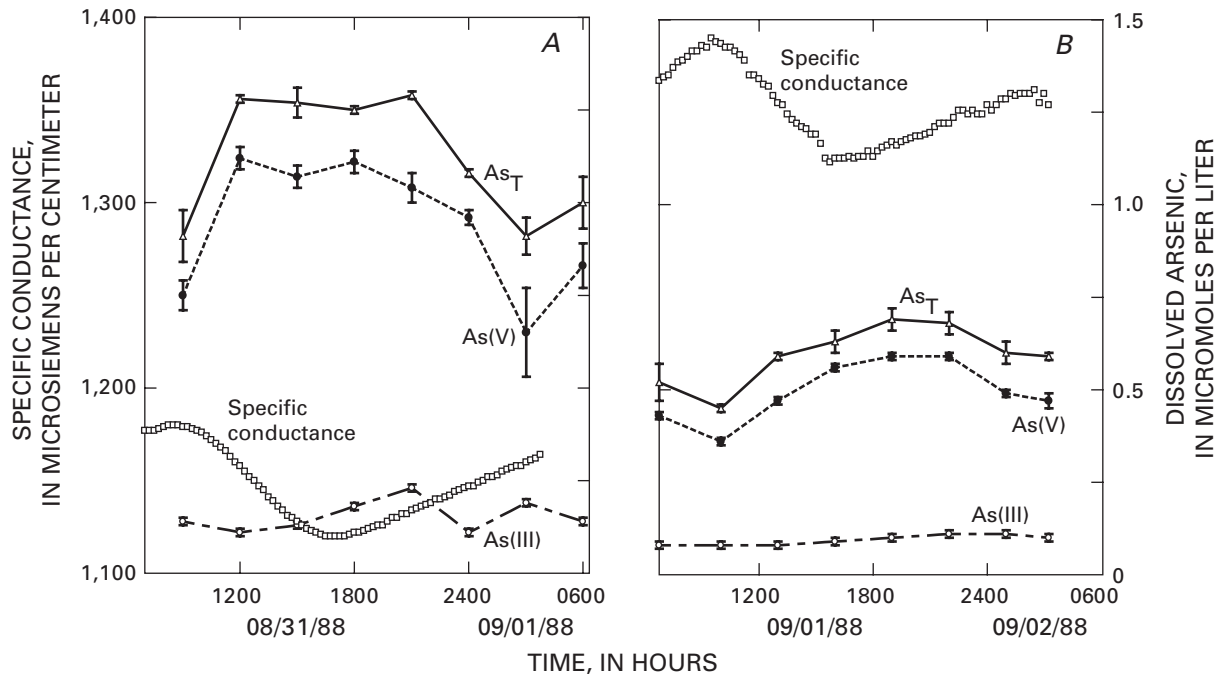


Figure I-3. Diel trends in specific conductance and laboratory determinations for dissolved-arsenic species for (A) the Above Vale site and (B) the Sheeler Seep site.

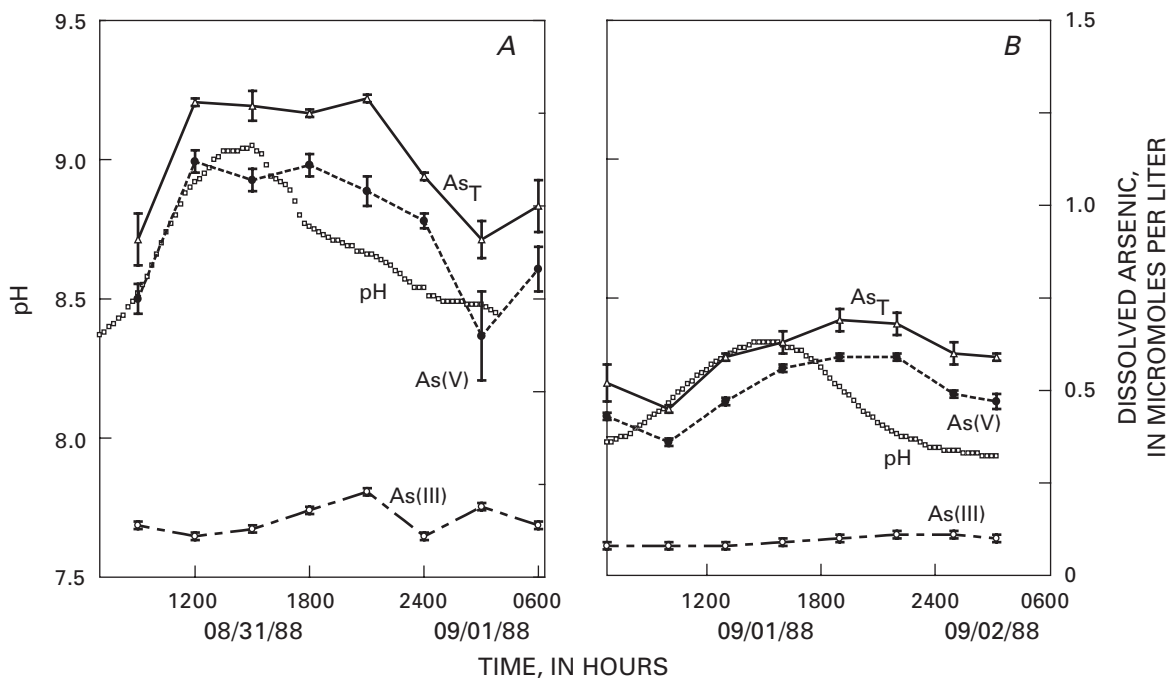


Figure I-4. Diel trends in pH and concentrations of arsenic species for (A) the Above Vale site and (B) the Sheeler Seep site.

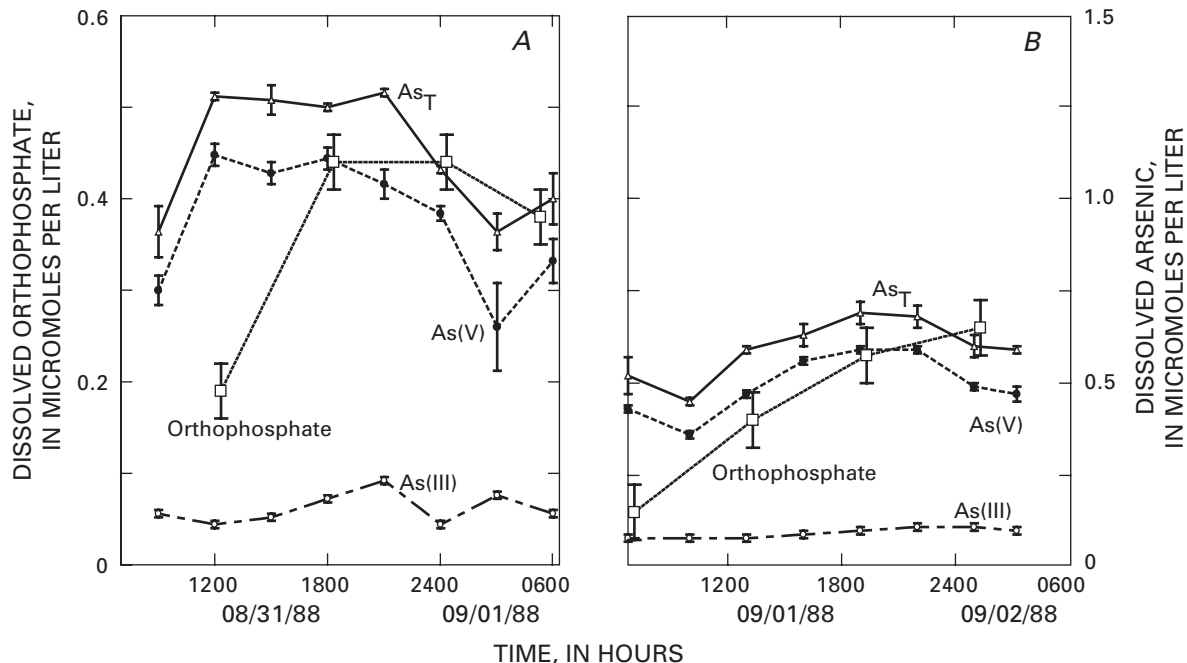


Figure I-5. Diel trends in concentrations of dissolved orthophosphate and arsenic species at (A) the Above Vale site and (B) the Sheeler Seep site.

Table I-9. Site comparison for parameters monitored along Whitewood Creek.

[Headwater site, HW; Sewage-Treatment-Plant site, STP; Above Vale site, AV; and Sheeler Seep site, SS. Mass concentrations of benthic flora, biomass, in grams per square meter are tabulated with 95-percent confidence intervals ($n=9$). Autotrophic indices reflect the ratio of mean ash-free dry mass to chlorophyll-*a*. Photosynthetically active radiation, irradiance, represents solar radiation between 400 and 700 nanometers in microeinsteins per square meter per second. Water and air temperatures are tabulated in degrees Celsius. Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius. Concentrations for total dissolved arsenic, pentavalent arsenic, As(V), trivalent arsenic, As(III), and orthophosphate are given in micromoles per liter. Alkalinity measurements are given in milliequivalents per liter. Values tabulated for data-logger parameters represent 15-minute averages of measurements taken at 10-second intervals. Brackets denote inclusive ranges for monitored parameters. Abbreviation "N.D." indicates that parameter values were not determined]

Parameter description	HW	STP	AV	SS
Biomass	48±19	57±26	316±53	32±17
Autotrophic index	120	110	210	190
Data-logger parameter ranges				
Irradiance	[0, 1030]	[0, 940]	[0, 830]	[0, 1240]
Air temperature	[3.1, 28.1]	[7.7, 25.5]	[10.1, 37.3]	[6.3, 37.9]
Water temperature	[8.5, 18.8]	[12.0, 17.1]	[14.8, 23.2]	[15.2, 26.3]
pH	[8.30, 8.78]	[8.14, 8.57]	[8.37, 9.02]	[7.93, 8.34]
Specific conductance	[220, 320]	[720, 830]	[1120, 1180]	[1320, 1390]
Ranges for laboratory analysis ¹				
Total dissolved arsenic	<0.05	[0.23, 0.28]	[0.91, 1.28]	[0.45, 0.69]
Dissolved As(V)	<0.05	[0.14, 0.18]	[0.65, 1.12]	[0.36, 0.59]
Dissolved As(III)	<0.05	[0.06, 0.07]	[0.11, 0.23]	[0.08, 0.11]
Dissolved orthophosphate	[0.04, 0.41]	[13.1, 15.5]	[0.19, 0.44]	[0.06, 0.25]
Alkalinity	N.D.	N.D.	[2.84, 3.24]	[2.89, 3.40]

³Tabulated ranges indicate the minimum and maximum 15-minute average values for the site monitoring period (1 day for the Headwater, Above Vale, and Sheeler Seep sites; 2 days for the Sewage-Treatment-Plant site).

⁴Arsenic, orthophosphate, and alkalinity determinations by S.P. Pasilis, M.W. Shockey, and C.C. Fuller, respectively.

Table I-10. Lag times, in hours, between selected water-quality variables monitored along Whitewood Creek.

[Total dissolved arsenic, As_T; dissolved pentavalent arsenic, As(V); and dissolved trivalent arsenic, As(III). Lag times in hours; cross correlation coefficient, r , is dimensionless, as is the number of time-corresponding measurements, n . Abbreviation "N.D." indicates that values were not determined because diel fluctuations in dissolved-arsenic species and orthophosphate were not evident at the Headwater and Sewage-Treatment-Plant sites as described in the "Results" section]

Water-quality characteristic	Lag time	Maximal r value	n
Headwater site			
pH lags irradiance	1.5	0.75	98
Water temperature lags irradiance	2.0	0.77	98
As _T lags pH ¹	N.D.		
As(V) lags pH	N.D.		
As(III) lags pH	N.D.		
Orthophosphate lags pH	N.D.		
Sewage-Treatment-Plant site			
pH lags irradiance	2.0	0.80	126
Water temperature lags irradiance	2.0	0.77	98
As _T lags pH	N.D.		
As(V) lags pH	N.D.		
As(III) lags pH	N.D.		
Orthophosphate lags pH	N.D.		
Above Vale site			
pH lags irradiance	1.0	0.82	82
Water temperature lags irradiance	3.0	0.71	82
As _T lags pH	0	0.80	8
As(V) lags pH	0	0.77	8
As(III) lags pH	6	0.55	8
Orthophosphate lags pH	6	0.55	4
Sheeler Seep site			
pH lags irradiance	1.5	0.88	83
Water temperature lags irradiance	3.2	0.70	83
As _T lags pH	3	0.58	8
As(V) lags pH	3	0.69	8
As(III) lags pH	6	0.55	8
Orthophosphate lags pH	6	0.42	4

¹Lower significant figures in lag estimates involving arsenic and orthophosphate data reflect the lower sampling frequency for laboratory-analyzed concentrations relative to data-logged parameters.

Short-term sorption-kinetics experiments using the diatom *Achnanthes minutissima* indicated that a first-order rate equation closely describes the observed algal sorption of arsenate. Fit of the kinetic data for HW and AV isolates at the nine treatment combinations to a first-order model (Dixon, 1985) yielded consistently high coefficients of determination ($r^2 \geq 0.84$, table I-11). Sorption-rate constants were significantly increased by elevating dissolved-arsenate concentrations. A comparison of rate constants for HW and AV isolates shows significantly lower constants for the apparently arsenic-tolerant

AV isolate. The accumulation of arsenic by both isolates was inhibited by increasing orthophosphate concentrations. The AV isolate had slightly lower K_b values than did the HW isolate. Increasing dissolved-arsenate concentrations in the media did not result in a corresponding increase in biologically sorbed arsenic (note in table I-11 that the K_b values significantly decreased at higher dissolved-arsenic concentrations).

As with arsenic sorption, orthophosphate sorption also was well described by first-order mass transfer (table I-12). Sorption-rate constants for orthophosphate were consistently lower than for arsenate, and unlike arsenate, sorption did not vary significantly between isolate or with variations in dissolved arsenate or orthophosphate (table I-12). Accumulation of phosphorus decreased with increase in dissolved arsenate. As observed in initial chlorophyte experiments, orthophosphate was preferentially accumulated over arsenate by *A. minutissima*, as clearly indicated by the orders of magnitude larger K_b scale for phosphorus relative to arsenic. Large K_b error bars for orthophosphate reflect low solution concentrations at equilibrium in these batch experiments.

Table I-11. Results from experiments examining arsenate sorption by heat-killed *Achnanthes minutissima* cells isolated from the Headwater site and the Above Vale site.

[Headwater (HW) site with low (less than 0.1 micromole per liter) dissolved arsenic; Above Vale (AV) site with elevated (approximately 1 micromole per liter) dissolved arsenic. Sorption-rate constants, λ_b , in reciprocal hours; accumulation factors, K_b , ratio of micromoles solute per gram algae to micromoles solute per gram media. Confidence intervals (95 percent) reflect the multivariate regression from a 3² full factorial design ($n=3$) sampled at elapsed times of 0.5, 1.0, 2.0, 4.0, 8.0, and 24.0 hours after inoculation. The coefficients of determination (r^2) are given for a fit of the kinetic data to a first-order model (Dixon, 1985). Details of the experimental design are provided in the text]

Treatments (micromolar solute added)		Arsenate transport characteristics		
Arsenate	Orthophosphate	λ_b	K_b	r^2
HW isolate				
0.5	0.0	0.73±0.08	1,790±70	0.96
0.5	0.5	0.56±0.08	1,340±90	0.92
0.5	1.0	0.94±0.13	990±50	0.92
1.0	0.0	1.08±0.11	990±20	0.96
1.0	0.5	1.37±0.22	800±30	0.90
1.0	1.0	1.77±0.17	500±30	0.84
AV isolate				
0.5	0.0	0.39±0.02	1,750±30	0.99
0.5	0.5	0.48±0.06	1,240±30	0.98
0.5	1.0	0.57±0.07	960±30	0.99
1.0	0.0	0.74±0.08	870±30	0.98
1.0	0.5	0.81±0.11	630±30	0.94
1.0	1.0	1.09±0.19	500±20	0.97

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Table I-12. Results from experiments examining orthophosphate sorption by cell surfaces of *Achnanthes minutissima* isolated from the Headwater site and the Above Vale site.

[Headwater (HW) site with low (less than 0.1 micromole per liter) dissolved arsenic; Above Vale (AV) site with elevated (approximately 1 micromole per liter) dissolved arsenic. Sorption-rate constants, λ_b , in reciprocal hours; accumulation factors, K_b , ratio of micromoles solute per gram algae to micromoles solute per gram media. Confidence intervals (95 percent) reflect the multivariate regression from a 3^2 full factorial design ($n=3$) sampled at elapsed times of 0.5, 1.0, 2.0, 4.0, 8.0, and 24.0 hours after inoculation. The coefficients of determination (r^2) are given for a fit of the kinetic data to a first-order model (Dixon, 1985). Details of the experimental design are provided in the text]

Treatments (micromolar solute added)		Orthophosphate transport characteristics		
Ortho- phosphate	Arsenate	λ_b	$K_b(\times 1,000)$	r^2
HW isolate				
0.5	0.0	0.43±0.02	28±10	0.97
0.5	0.5	0.36±0.02	28±7	0.98
0.5	1.0	0.35±0.02	11±4	0.96
1.0	0.0	0.41±0.02	58±13	0.99
1.0	0.5	0.32±0.03	38±9	0.97
1.0	1.0	0.30±0.17	7.9±2.1	0.98
AV isolate				
0.5	0.0	0.44±0.03	58±17	0.97
0.5	0.5	0.33±0.02	7.2±1.1	0.99
0.5	1.0	0.41±0.01	1.8±0.3	0.98
1.0	0.0	0.35±0.03	120±48	0.95
1.0	0.5	0.38±0.03	28±10	0.97
1.0	1.0	0.44±0.03	18±7	0.97

Effects of Benthic Flora on Physico-Chemical Processes

Our observation that arsenic accumulation (K_b values in table I-11) in *A. minutissima* decreased with increasing dissolved-orthophosphate concentrations is interesting but not surprising. Preferential sorption of orthophosphate over arsenate was observed in initial chlorophyte experiments (table I-7) and for marine diatoms (Morris and McCartney, 1984). Sanders (1985) suggested that the arsenic reactivity and toxicity to estuarine phytoplankton species could be altered by algal transformation of arsenic and subsequent release of methylated forms of arsenic. The mechanism of cell-surface preference for orthophosphate sorption in Whitewood Creek algal isolates has not been identified. However, the fact that preference was observed in experiments using cells from the HW site, not previously exposed to elevated dissolved-arsenate concentrations, suggests that the mechanism is not acquired by previous arsenic exposure.

Differences between algal isolates in arsenic sorption suggest that *A. minutissima* from the AV site exhibited arsenic tolerance in two ways. First, this isolate accumulated significantly less

arsenic than did controls (the HW isolate) when initial dissolved-arsenate concentrations were high (1.0 $\mu\text{mol/L}$) and dissolved-orthophosphate concentrations were low (0.0 and 0.5 $\mu\text{mol/L}$) (table I-11). Second, the AV isolate consistently demonstrated slower arsenic sorption kinetics than did the HW isolate. Both observations represent distinctive advantages for cells exposed to elevated and fluctuating dissolved-arsenic concentrations. Conway (1978) observed that arsenic sorption by *Asterionella formosa* in continuous culture was linearly dependent on ambient dissolved-arsenate concentrations less than 1.8 $\mu\text{mol/L}$ but reached a plateau at higher ambient concentrations. He hypothesized that this "leveling off" of cellular arsenic was due to saturation of arsenic sorption sites on cell surfaces. Our results using heat-killed cells support this hypothesis. However, K_b values for Whitewood Creek isolates suggest saturation above 0.5 $\mu\text{mol/L}$ dissolved arsenate (table I-11). Arsenic saturation by *A. minutissima* at lower ambient concentrations relative to *Asterionella formosa* suggests a contributory factor toward the survival of *A. minutissima* over the arsenic concentration range of the four sampling sites (less than 0.1 to approximately 1 $\mu\text{mol/L}$). Algal accumulation factors measured here (table I-11) are within the range of values observed in other laboratory studies (Conway, 1978; Giddings and Eddlemon, 1977).

Increasing algal abundance with distance downstream may be attributed to inputs of macronutrients from the water-treatment-plant effluent, ground-water inputs, and irrigation runoff from fertilized land. In addition, increased algal growth rates (Jorgensen, 1983) as a result of increasing water temperature in the downstream direction may contribute to the downstream increase in algal abundance (tables I-1 and I-2). At the SS site, decreased abundance may be caused by scarcity of firm substrate needed to establish a dense algal community. Visibly high turbidity also may have hindered photosynthetic activity at this site. Although periphyton and macrophyte growth was patchy, especially at the SS site, replicate ash-free, dry-weight measurements indicated similar biomass concentrations within the patches.

Elevated AI values, particularly at the AV and SS sites in August and September 1987, suggest a change in the condition of the submerged plant community. Senescence was visibly evident in these samples and probably represents typical growth progression and recession within these mats. It is interesting to note that the elevated AI observed in August 1986 at the STP site (Kuwabara and others, 1988) was not observed in 1987, probably because of a shift in community structure of benthic plants at the STP site in 1987 to include new growth of *Z. palustris* and various filamentous chlorophytes.

Without development of models describing physical and chemical transport of arsenic in this reach, it is difficult to directly apply the results of this modeling study to accurately determine the effects of the benthic flora on arsenic transport. However, episodic significance of the plant community can be demonstrated. In the spring, the most discernible change in plant abundance occurs with the establishment of the periphyton and macrophyte mat. Once the mat is formed, changes in the community structure principally observed at the STP and SS sites, and continued

periphyton growth to maintain relatively constant ρ_b values as observed at the HW and STP sites, contribute to dynamics of the mat. In the fall, senescent tissues are scoured off and transported downstream or are decomposed and buried beneath settling sediment. These fluxes in the biomass parallel corresponding arsenic fluxes into and out of the mat as indicated by the temporal changes in biomass (ρ_b) and arsenic concentrations in the plant tissues (C_b) (tables I-2 and I-8). For example, at the SS site between May 28 and July 10, a 28 gram-per-square-meter change in ρ_b was observed. This corresponds to an average doubling time of 8.9 days. Using that 8.9-day doubling time and a 28 gram-per-square-meter final biomass value in July, the greatest daily increase in biomass for this 43-day period would be 2.1 g/m²/d. Given an average channel depth of 0.24 m (table I-2) and an algal tissue concentration of about 2,300 µg/g dry weight (table I-8), this daily mass flux during the establishment of the mat corresponds to a 0.3-µmol/L arsenic per day water-column flux. This is similar to the diurnal arsenic fluctuations observed by Fuller and others (1988) at the SS site. However, those measured fluctuations were made in August after the mat had been established. A similar calculation for the AV site results in a maximum daily mass flux and corresponding water-column arsenic flux of 62.5 g/m²/d and 7.8 µmol/L arsenic per day, respectively. This arsenic flux is an order of magnitude greater than the diurnal arsenic fluctuation observed at the AV site by Fuller and others (1988). The SS site was consistently dominated by epiphytic and filamentous algae that sorb solutes over the entire thallus (that is, water-column uptake). In contrast, at the AV site, 50 to 80 percent of the plant biomass is composed of submerged macrophytes that take up solutes from pore water through root systems in addition to water-column uptake. The effect on water-column solute concentrations for the AV site may therefore be overestimated by a factor of 2 to 5 but nevertheless is environmentally significant.

An inconsistency should be noted between the laboratory and field-measured values for arsenic accumulation by algal cells. Given the K_b values for the AV-site isolate (630 at 1 µmol/L dissolved arsenate and 0.5 µmol/L orthophosphate, table I-11), algal concentrations at that site should be approximately 400 µg arsenic per gram dry weight. Yet algal tissue concentrations of greater than 2,000 µg/g were measured. This discrepancy initially was believed to be due to arsenic associated with inorganic particles attached to plant tissues that remained after plants were washed. However, low iron concentrations in leachate used to measure algal arsenic concentrations do not support this hypothesis (table I-8). On the basis of arsenic-to-iron ratios reported for Whitewood Creek sediment (approximately 1 to 70, Goddard and others, 1988), attached particles made up less than 10 percent of the total dry weight of the plant samples. Conway (1978) found that arsenic taken up by the diatom *Asterionella formosa* was concentrated in an organic layer surrounding the frustule. Enhanced accumulation by algae at the field sites could have been due to sorption and retention of particulate arsenic in this organic surface layer that was not effectively removed during washing. Results from laboratory algal cultures in the absence of particles would consequently underestimate measured algal accumulation.

Maintaining data-logger monitoring at the STP site for more than 24 hours allowed a comparison of pH trends during days when the site was exposed to different time courses in light intensity. Table I-4 indicates that the gradual irradiance fluctuations during the first day of monitoring relative to the second resulted in a corresponding gradual pH fluctuation on the first day relative to observed pH changes during the second. That is, pH lagged irradiance (table I-10) and showed similar trends in their time course over the two sampling days.

The STP site, unlike the other three sites, exhibited a low pH amplitude relative to the biomass estimate (less than the HW site; 0.43 pH unit). This inconsistency may result at least in part from effects of the effluent from the municipal water-treatment plant on rates of photosynthesis or the buffering capacity at the STP site. This effluent represents a significant portion (approximately 10 percent) of the creek discharge at the STP site during the summer.

Diel fluctuations in specific conductance were examined as an indicator of ground-water effects on observed changes in solute concentrations. The observation that specific conductance was out of phase with irradiance is explained by the fact that the creek flows over a perched aquifer with high sulfate concentrations that contribute to high specific conductance of ground water (approximately 5,000 µS/cm with no diel fluctuations at the SS site, K.E. Goddard, oral commun.). Hem (1948) reported diel fluctuations in chloride concentration in the Gila River as a result of changes in the hydraulic gradient.

Diel variations in specific conductance have been reported (Kuwabara, 1992) as an indicator of trends in ground-water inflow. These trends are typical of streams where evapotranspiration in the riparian zone causes diel fluctuations in the hydraulic gradient (Rantz and Eakin, 1971; Wood, 1975; Winter and others, 1988). Changes in the hydraulic gradient also were evident in the increase in specific conductance with decrease in elevation between the HW and SS sites (table I-9). Maximal specific conductance, corresponding to maximal ground-water inflow into the creek, was not in phase with maximal dissolved-arsenic concentrations (figs. I-4 and I-5), thus supporting the hypothesis that the ground water was not the direct source driving observed fluctuations in dissolved arsenic, as observed by Fuller and others (1989), or dissolved orthophosphate. However, As(III), present at elevated concentrations in the ground water, oxidizes upon atmospheric or surface-water exposure (maximal channel inflow of ground water at night) then coprecipitates or adsorbs onto mineral surfaces. The ground water thereby may serve as an important source of particle-bound arsenic that desorbs in response to photosynthetically driven increases in pH (Cherry and others, 1986; Goddard, 1988; Fuller and Davis, 1989).

The observed lag in the arsenic species relative to the pH cycle observed at the SS site has been previously observed for total arsenic at the SS site and at another site 7 km upstream from the AV site (Fuller and others, 1988). A discussion of the significance of these lags was previously presented and involves shifts in sorption equilibria in response to pH shifts (Fuller and Davis, 1989; Kuwabara, 1992). The

lag of dissolved-arsenic species behind the observed pH cycle at the SS site was more pronounced than at the AV site, which had a greater biomass and a higher pH range than the SS site. In fact, the statistical analysis (table I-10) indicates that at a 3-hour sampling interval, a lag at the AV site cannot even be resolved for the dominant arsenic species. The amplitude of the cycles for dissolved-arsenic species at the AV site also were greater than at the SS site. In spite of lower cumulative irradiance at the AV site relative to the SS site on the respective sampling days for each site, the pH fluctuation was greater at the AV site, the artificially pooled area with higher biomass, than at the SS site.

Kuwabara (1992) discussed possible abiotic and biotic explanations for the lack of correspondence between temporal changes in dissolved orthophosphate and arsenic species observed at the AV and SS sites. Based on carbon-fixation estimates, Kuwabara (1992) determined that the demand for phosphorus by photosynthetic activity far exceeded the solution phase pool. Possible sources of supplementary phosphorus included solute regeneration within the mat or particle-bound phosphorus. Preferential sorption of orthophosphate over arsenate and the demand for orthophosphate imposed by photosynthetic activity provided a reasonable explanation for the dissolved orthophosphate lag behind changes in arsenic species. These observations for orthophosphate were contrasted by Fuller and Davis (1989) who concluded that periphyton uptake in Whitewood Creek was not a major process affecting arsenic diel cycles. These contrasting dissolved-orthophosphate and dissolved-arsenic observations might be expected based upon preferential phosphorus sorption by the benthic flora and consistently greater dissolved arsenic than dissolved orthophosphate at the AV and SS sites (table I-9), making the effects of the benthic flora on arsenic retention more difficult to resolve.

It is clear from these studies that algal isolates from Whitewood Creek have the ability to sorb orthophosphate over arsenate preferentially. Given the arsenic-transport characteristics reported here for *A. minutissima*, the rapid growth of biomass between late May and July at the AV and SS sites represents both a rapid and significant accumulation of arsenic (table I-8) within this single biological component. Furthermore, *A. minutissima*, which was exposed to elevated concentrations of dissolved arsenic, seems to be able to slow down the kinetics of cellular arsenic sorption. The results presented here suggest a number of extensions to this work that address complex questions related to the modeling of the effects of the benthic flora on stream transport of arsenic: What causes large annual variations in community structure of the type seen between 1986 and 1987 samples? How do solute sorption processes differ between the algae and submerged macrophytes seen in abundance in 1987? How does the state of the periphyton and macrophyte communities affect arsenic sorption and accumulation (that is, what other physical and chemical perturbations that account for changes in observed autotrophic indices, in addition to elevated orthophosphate concentrations, affect arsenic sorption)? How long does it take for plant species to adapt to ambient arsenic concentrations by way of changing sorption characteristics, and

how does this vary among benthic plant species? Given the apparent importance of effects of cell sorption on solute transport, it is believed that a quantitative response to the above questions may be critical for incorporation into more sophisticated and ultimately predictive transport models for reactive solutes.

Summary and Conclusions

Effects of the benthic flora on arsenic transport in a mining-affected stream have been examined by estimating parameters for a kinetic sorption model. Using a first-order mass transfer equation, the effects of dissolved arsenate, orthophosphate, and previous solute exposure on transport parameters were determined for an algal species present at all four sampling sites along the 57-km study reach. Test algae took up orthophosphate preferentially over arsenate. Algae isolated from an area of elevated dissolved arsenate concentrated less arsenic than did the same species isolated upstream from mining activities when dissolved arsenate was high (1.0 $\mu\text{mol/L}$) and dissolved orthophosphate was low (0.0 and 0.5 $\mu\text{mol/L}$). Lower arsenic sorption-rate constants also were determined for the apparently arsenic-tolerant isolate. These factors represent obvious advantages for species exposed to elevated and fluctuating dissolved-arsenic concentrations. Field and laboratory results reported here suggest that increases in plant biomass during mat development represent both a rapid and significant accumulation of arsenic within this single biological component and therefore may have significant effects on water-column concentrations.

In diel studies, characteristic shapes for diel pH fluctuations followed irradiance, while pH and water temperature lagged behind irradiance by 1 to 3 hours. Amplitudes of the pH cycles increased with biomass except at the STP site immediately downstream from water-treatment-plant discharge. Inorganic pentavalent arsenic dominated arsenic speciation at all sites. Concentration fluctuations in dissolved-arsenic species lagged pH fluctuations by approximately 3 hours at the Sheeler Seep site, but no discernible lag was observed at the Above Vale site, which has an order of magnitude higher biomass. Furthermore, the amplitudes of diel fluctuations in arsenic species were greater at the Above Vale site than at the Sheeler Seep site. The lack of phase correspondence between dissolved-orthophosphate concentrations and arsenic species may have resulted from preferential sorption of orthophosphate over arsenate by the biomass. The phosphorus demand from photosynthetic activity, based on carbon-fixation estimates, suggests a supplemental source, such as phosphate regeneration within the mat or desorption of particle-bound phosphate. The observed relationships provide further evidence for the need for a process-interactive approach to describe stream systems and for consideration of diel variations in water-quality monitoring programs.

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SECTION II. Evaluation of the Processes Controlling Dissolved Arsenic in Whitewood Creek, South Dakota

By Christopher C. Fuller and James A. Davis

Abstract

Coupled physical, chemical, and biological processes affect the concentration of dissolved arsenic in Whitewood Creek, South Dakota. In the lower reaches of the stream, dissolved-arsenic concentrations were controlled primarily by adsorption and coprecipitation with iron oxyhydroxides (ferrihydrite) as ground water enriched in arsenic entered the stream. Periphyton photosynthesis induced a diurnal pH fluctuation of 0.25 to 0.5 in surface water that had a pH of 8.1 to 8.7 and a concomitant diurnal cycle in arsenate (30- to 40-percent variation). The fluctuation in arsenate reflects the dynamic equilibrium of adsorption-desorption processes occurring in response to the pH cycle. Kinetics of the sorption processes are slow, which results in a cycle of dissolved arsenic that lags 2 to 4 hours behind the pH cycle. A mass balance for dissolved arsenate indicates that adsorption-desorption of arsenate on ferrihydrite surfaces in and on streambed sediments was the primary control of dissolved arsenic. Uptake of arsenate by algae and input from reducing sediments were of secondary importance to the dissolved-arsenic budget. The results demonstrate the importance of adsorption-desorption processes in controlling trace-element concentrations in aquatic systems and the need to incorporate sorption kinetics into transport models. The effect of diurnal pH cycles on trace-element and nutrient cycling and availability may be of significance in other surface-water systems.

Introduction

Development of transport models to adequately describe and predict the fate of reactive solutes requires knowledge of the time dependence of chemical processes, such as adsorption, ion exchange, and precipitation, that control the partitioning between solution and solid phases (Rubin, 1983; Jaanasch and others, 1988). Incorporation of kinetic terms for such reactions is of particular importance in systems where the equilibrium that controls dissolved constituents fluctuates on time scales similar to or shorter than the partitioning process (reaction). For example, adsorption commonly is treated as an equilibrium process in partition-and-transport models, although kinetic studies of adsorption have shown a slow approach to equilibrium, particularly for the oxyanions (Hingston, 1981).

Adsorption processes commonly are invoked as a control on the concentrations of dissolved inorganic trace elements and contaminants in natural waters at concentrations below their solubilities (Morel, 1983; Drever, 1982). Recognition of the importance of this process of trace-element partitioning is the result of many laboratory studies on the uptake of metals and oxyanions by synthetic oxides (Davis and Leckie, 1980; Pierce and Moore, 1982; Anderson and others, 1976), natural solids (Lions and others, 1982; Frost and Griffin, 1977), and from partial extractions of sediments from natural waters (Belzile and Tessier, 1990; Aggett and Roberts, 1986; Tessier and others, 1985).

Interest in the geochemical behavior of arsenic has developed because of growing concerns about contamination of surface water and ground water from agricultural and mining activities and as a consequence of power generation from fossil-fuel combustion (Cullen and Reimer, 1989). The cycling of dissolved arsenic in surface-water systems is influenced by processes of absorption and desorption by chemical, physical, and biological constituents (Holm and others, 1980; Ferguson and Gavis, 1972; Aggett and O'Brien, 1985). Recent studies have suggested that iron is effective in the deposition, removal, and control of arsenic concentrations (Aggett and O'Brien, 1985; Belzile and Tessier, 1990; DeVitre and others, 1991). The arsenate anion is strongly sorbed by iron oxyhydroxides and, as in adsorption of other oxyanions by oxides, increases with decreasing values of pH (Leckie and others, 1980; Pierce and Moore, 1982; Goldberg, 1986; Fuller and others, 1993).

pH is a determining factor in sorption equilibrium, and diurnal cycles of pH in surface water of upward of ± 1 unit have been reported by Dunn (1967) and Turk (1988). Trace-element concentrations are controlled by sorption reactions. The effect of fluctuations of pH on trace-element cycles, however, has received little attention.

Purpose and Scope

The purpose of this report is to describe a mass balance for dissolved arsenic in order to evaluate the importance of sorption and other instream processes that control concentrations of dissolved arsenic. A field study was conducted to investigate the effect of adsorption processes on concentrations of dissolved arsenic in a small, perennial stream that was heavily contaminated by gold-mine tailings. A diurnal cycle in pH in surface water was observed that results from algal photosynthesis

(Fuller and Davis, 1989). The concentration of dissolved arsenic also fluctuates diurnally in response to changes in the adsorption-desorption equilibrium with changing pH. A lag in the diurnal-arsenic cycle was attributed to the time dependence of the adsorption-desorption process. Kuwabara (1992) also observed diurnal cycles in pH, dissolved phosphate, and arsenic in this stream; the magnitude of the pH cycle was correlated to the standing crop of periphyton.

Description of Study Area

Between 1876 and 1977, about 100 million Mg of finely ground mill tailings were discharged into Whitewood Creek in South Dakota. These tailings contain 0.25 to 0.75 percent arsenopyrite and other metallic-sulfide minerals (Goddard, 1987). This discharge has resulted in the deposition of contaminated flood-plain sediments that contain as much as 11,000 μg of arsenic per gram of sediment (Goddard, 1987). Field and mineralogic data indicate that a substantial fraction of the arsenic now is associated with iron oxyhydroxides and oxides. Transfer of arsenic from tailings to adjacent alluvial deposits has occurred when sulfide oxidation and flood-plain erosion and deposition were more active processes (Cherry and others, 1986). As of 1987, most of the arsenic in fine-grained (<63 μm in diameter) suspended and bed sediments and in oxidized flood-plain deposits is associated with light mineral fractions in which density is less than 2.89 g/cm^3 . In contrast, the arsenic in reduced flood-plain sediments is mainly in the heavy mineral fraction in which density is <2.89 g/cm^3 , perhaps as unoxidized arsenopyrite (McKallip and others, 1988). Oxidized flood-plain deposits mainly are coarse grained (>63 μm in diameter), and the bulk of the arsenic is in iron-oxide coatings on sand grains (Horowitz and others, 1988). Horowitz and others (1988) found arsenopyrite grains both in suspended- and bed-sediment samples that were not fractionated by density. However, attempts were not made to quantify the abundance of the unoxidized mineral. Iron-oxide rinds were on the surfaces of arsenopyrite and other sulfide mineral grains and may provide shielding from further oxidation (Horowitz and others, 1988).

Release of arsenic from the flood-plain deposits into ground water and surface water occurs by dissolution of, or desorption from, arsenic-rich ferrihydrite in alluvium (Cherry and others, 1986). Oxidation of arsenopyrite in tailings deposits is of minor importance because the abundance of carbonate minerals in flood-plain deposits (Marron, 1988) acts to buffer the acidity generated during oxidation of sulfides within the contaminated sediments. As a result, ground water in the flood-plain aquifers generally is of neutral pH (Cherry and others, 1986; Fuller and others, 1987). In the lower 35 km of the stream, input of arsenic to the stream results from seepage of arsenic-bearing and ferrous-iron-bearing ground water from the flood-plain aquifers after periods of high stream discharge (Cherry and others, 1986; Goddard, 1987). Dissolved arsenic in the ground water is present in the more reduced +3 oxidation state, arsenic(III); and in surface water, dissolved arsenic is

essentially all in the +5 oxidation state, arsenic(V) (Fuller and others, 1987). Oxidation and precipitation of ferrous iron in the ground water occurs rapidly on contact with the atmosphere and the stream remove most of the dissolved arsenic through coprecipitation with iron or subsequent adsorption onto the ferrihydrite (Fuller and Davis, 1989). The buildup of arsenic-rich iron oxides in the streambed and a general downstream increase in dissolved arsenic result from the continuous discharge of contaminated ground water (Goddard, 1987). In addition, an increase in dissolved arsenic at a given site is observed at low stream stages during summer and fall because of the buildup of arsenic-bearing iron oxides in the streambed (Goddard and others, 1988). The abundance of iron oxides in the bed sediments and flood-plain sediments of this stream and the strong affinity of arsenate for iron oxyhydroxides (Pierce and Moore, 1982; Goldberg, 1986) suggest that control of dissolved arsenic is from reactions with the ferrihydrite surfaces. The small range in the molar ratio of arsenic to iron in iron precipitates, in coarse- and fine-grained bed sediments (average arsenic/iron: 0.022 ± 0.006), and in oxidized and unoxidized flood-plain deposits suggests that arsenic largely remains associated with iron throughout this system (Fuller and others, 1987).

Acknowledgments

G.W. Zellweger contributed his expertise and efforts in conducting the conservative-tracer injection. J.S. Kuwabara provided suspended-sediment samples and data on concentrations of arsenic in algae.

Methods of Sample Collection and Analysis

Diurnal Sampling

In order to define the role of sorption processes in arsenic partitioning, hourly samples were collected in a 3-day period at the Sheeler Seep site (site A) in August 1987 (fig. II-1). This site is in the lower gradient reach of the stream about 2 km upstream from the confluence with the Belle Fourche River and 1 km upstream from the Sheeler site studied by Cherry and others (1986). Site A is 100 m downstream from a large, abandoned meander that contains unoxidized tailings and oxidized, coarser grained alluvium into which the stream was cutting as of 1987. Many seeps discharge ground water from this cutbank, and iron oxyhydroxide precipitates form as the ground water discharges into the stream. In this part of the stream, the flood plains are extensively contaminated with arsenic, and many visible ground-water seeps issue from the streambank during low flow.

At sites B and C (fig. II-1), hourly sampling also was conducted during the second and third days. Site B (Custer Camp) is 11.8 km upstream from site A in an area of extensive flood-plain contamination and visible ground-water discharge. Site C (Whitewood Creek above Whitewood) is in the higher gradient

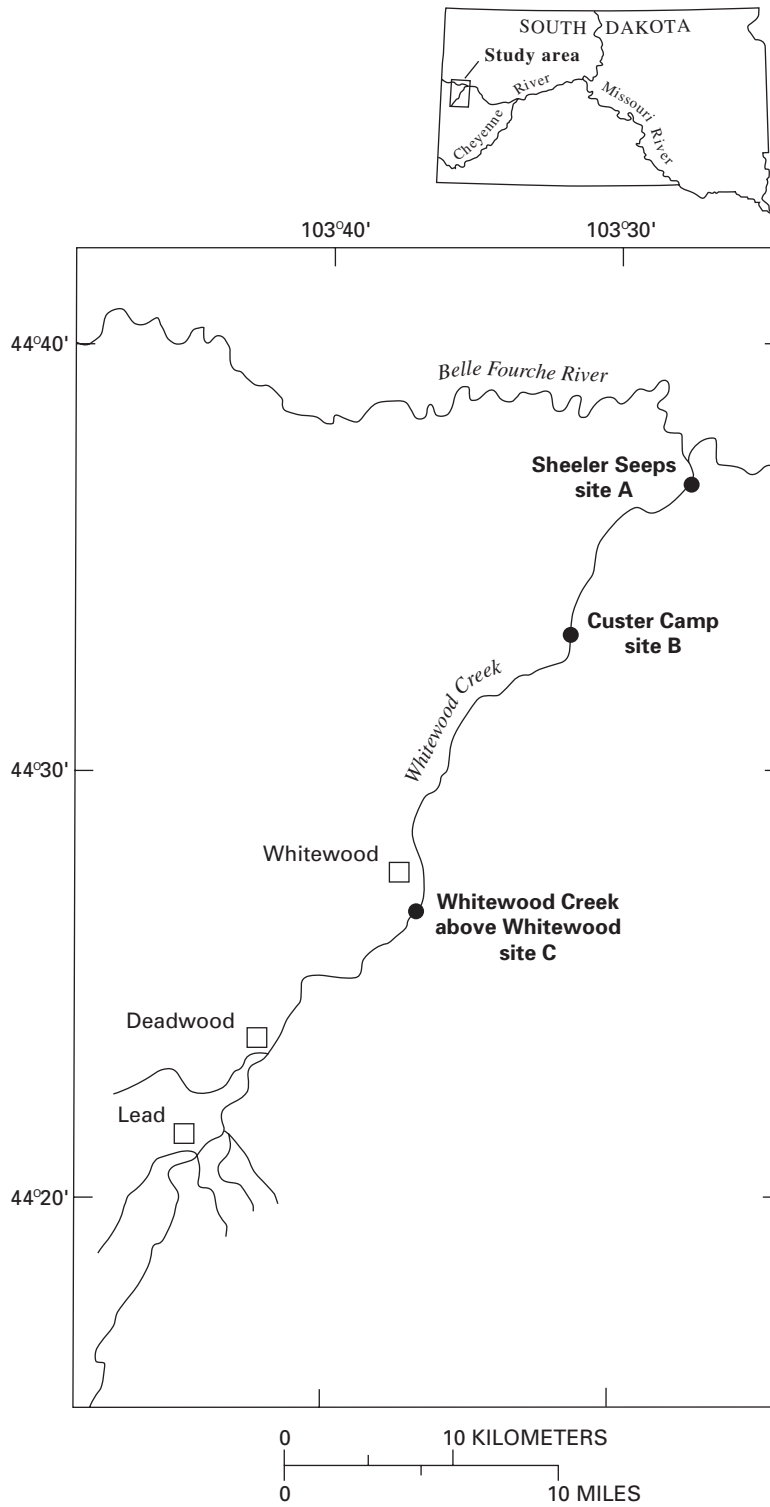


Figure II-1. Map showing location of study area and location of sampling sites in Whitewood Creek.

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part of the stream and had no apparent inflow of arsenic-bearing or iron-bearing ground water. At sites B and C, hourly water samples for determination of dissolved inorganic arsenic and other dissolved constituents were collected in a single container from the center of flow. At site A, samples were composited from four subsamples collected across the channel. Samples were filtered through 0.1- μm membrane filters and preserved by acidification with trace-metal grade hydrochloric acid to a pH of 1. A threefold greater iron concentration was measured in <0.45- μm filtrates than in <0.1- and <0.01- μm filtrates, which indicates a large component of colloidal iron (Fuller and others, 1988a). The pH electrodes were calibrated at hourly intervals with buffers at surface-water temperature. Concurrent measurements of pH and water temperature also were made at one-half-hour intervals. At site A, integrated incident-light intensity (400- to 700-nm wavelength) was measured at the water surface at one-half-hour intervals. Alkalinity samples were collected at 3-hour intervals during the first 36 hours at site A. Total alkalinity was determined by Gran titration (Franson, 1985). Dissolved calcium was determined by flame atomic-absorption spectroscopy. Dissolved sulfate was determined by ion chromatography. Partial pressure of carbon dioxide of surface water was calculated with the chemical-equilibrium program MINEQL (Westall and others, 1976) from the measured pH and alkalinity during the first 24 hours at site A. Temperature-corrected stability constants from Plummer and Busenberg (1982) were used.

Total dissolved inorganic arsenic was determined by hydride-generation atomic-absorption spectroscopy after reduction of arsenic(V) to arsenic(III) in strong acid by the addition of an excess of potassium iodide. The average uncertainty in analyses was $\pm 0.03 \mu\text{mol/L}$. Preliminary sampling indicated that dissolved arsenic in surface water is greater than 98 percent in the +5 oxidation state as the arsenate oxyanion (Fuller and others, 1987). Arsenic speciation was determined by graphite-furnace atomic-absorption spectroscopy after separation by anion exchange in the field immediately after filtration and acidification (Ficklin, 1983). The agreement between hydride generation and graphite-furnace analyses indicates that the concentrations of organic arsenic species are negligible. For the purpose of this report, dissolved-arsenic concentrations reported here are assumed to be entirely arsenic(V) as arsenate oxyanion species and will be referred to as C_{As} .

Statistical Analysis of Diurnal Surface-Water Chemistry Data

A cross-correlation analysis was conducted on the diurnal time-series data to determine if observed variations in one constituent were in phase or lagging behind another constituent. The statistical computer program, Minitab (Ryan and others, 1985), was used to generate correlograms of a range of lag times and their associated correlation coefficients (r). The correlation interval with the maximum r value was accepted as the lag time provided that the correlation was significant ($P < 0.05$). The program required data sets with fixed time intervals. Missing

intervals in time-series data were filled in by linear interpolation of adjacent time intervals. The resolution of the correlogram is equal to the sampling-time interval (± 0.5 or ± 1 hour).

Conservative-Tracer Injection

In small streams, conservative-tracer injections are used to accurately determine stream discharge, fluctuations in discharge, and ground-water inflows (Bencala and others, 1987; Jackman and others, 1984/1985; Zellweger and others, 1989; Bencala and others, 1990). Traditional methods of stream gaging are inappropriate in streams that have a significant component of the total discharge flowing through streambed deposits (Zellweger and others, 1989). These subsurface zones have been described as transient-storage zones (Bencala and others, 1990). The stream discharge determined by conservative-tracer injection includes flow through the transient-storage zones, assuming that sufficient time is allowed for the tracer to equilibrate between the surface flow and the transient-storage zones. In this study, a conservative tracer was injected 2.8 km upstream from site A on the second and third days of diurnal sampling. Results from this conservative-tracer injection provided estimates of the magnitude of concentrations of dissolved arsenic in ground-water inflow to the stream along this reach.

A concentrated solution of bromide ($4.02 \pm 0.14 \times 10^5 \text{ mg/L}$) was prepared by dissolving technical-grade lithium bromide into 100 L of streamwater and injecting the solution into the stream for 28 hours at a flow rate of $69 \pm 1 \text{ mL/min}$ from a constant-flow-rate metering pump. At this concentration and flow rate, about 1 mg/L of bromide in surface water was expected on dilution. This amount is above the background level for bromide concentration in surface water and ground water ($< 0.02 \text{ mg/L}$). During the first 3 hours of injection, samples were collected at 5- to 10-minute intervals at four sites along the reach to determine the mean traveltime of the stream through the reach. Sampling times at these points were determined from a traveltime of about 170 minutes for the reach on the basis of a dye test conducted before the injection. After the injected bromide had reached a plateau in concentration, stream discharge at any point downstream from the injection can be calculated from the bromide concentration at that point by the following relation (Zellweger and others, 1989):

$$Q_s = \frac{Q_i(C_i - C_b)}{(C_a - C_b)} \quad (1)$$

where

Q_s = stream discharge below injection point in liters per second;

Q_i = tracer-injection flow rate in liters per second;

C_a = bromide concentration in surface water, in milligrams per liter;

C_i = bromide concentration in injectate, in milligrams per liter;

and

C_b = bromide concentration above injection point, in milligrams per liter.

Synoptic samples were collected 24 hours after the start of the injection at 20 points along this reach to determine the stream discharge as a function of distance. In addition, surface-water samples were collected at 10 of these sites for dissolved-arsenic analysis concurrent with the synoptic samples for bromide analysis. At the downstream end of the reach (the diurnal C_{As} sampling site), hourly samples for bromide analysis were collected throughout the duration of the injection to identify diurnal fluctuations in stream discharge. All surface-water samples for bromide analysis were filtered through 0.45- μm membrane filters. Concentrations of dissolved bromide, chloride, and sulfate were determined by ion chromatography. This method had a detection limit of 0.02 mg/L and a precision of ± 0.01 mg/L.

Sampling of Ground-Water Inflows

Samples were collected at four seeps from the cutbank of the abandoned meander upstream from site A. A wide-mouth bottle was used to sample directly from the seep outflow, and the samples were filtered and acidified for determination of dissolved arsenic and iron. Separate samples were collected for anions and alkalinity. The other seeps along the 2.8-km reach were not suitable for sampling. In June 1987, at one of the four seeps, a 30-cm section of perforated 1.3-cm-diameter PVC tubing covered with 60- μm nylon screen was inserted horizontally into the streambank at the seep outlet, at the contact between the overlying flood-plain alluvium and the Pierre Shale. The outlet of the pipe was fitted with 0.64-mm (inside diameter) nylon tubing. Water was allowed to flow for 24 hours before sample collection. The seep was sampled in June and July 1987 as well as during the diurnal sampling. Ground water from this seep was filtered through a nitrogen-purged filtration tower and acidified before exposure to the atmosphere (Fuller and others, 1988a). Arsenic speciation after separation by anion exchange (Ficklin, 1983) and iron speciation (Stookey, 1970) were determined for this sample. pH was measured in a flow-through cell that was fitted to the outlet of the horizontal well.

Solid-Phase Characterization and Adsorption Properties

To characterize the iron precipitate that forms as a result of oxygenation of ground water, a 20-L sample was collected in a glass carboy from the horizontal well seep. This sample was purged with air to oxidize and precipitate dissolved iron. The resulting precipitate was concentrated by settling and centrifugation. The iron oxyhydroxide precipitate was aged for 1 week at a pH of 8.0. An aliquot was dried and ground for X-ray diffraction characterization and for total arsenic and iron analyses following acid dissolution. The time dependence of arsenate adsorption onto this iron oxyhydroxide precipitate was studied by transferring 1.0-mL aliquots of the precipitate suspension into centrifuge tubes containing 30 mL of surface water collected at a pH of 8.4 and filtered through a 0.1- μm filter. These tubes then were mixed on an end-over-end mixer at 12 revolutions per minute.

At various time intervals through 120 hours, the solution phase from pairs of tubes was sampled for dissolved arsenic after pH measurement and centrifugation at 16,000 gravitational constant (G).

To determine the amount of arsenic associated with the solid that is available for desorption, arsenic isotopic exchange was measured on an additional set of tubes of the surface-water precipitate. The isotopic-exchange technique is based on the attainment of isotopic equilibrium between the solution phase (dissolved arsenic) and the fraction of adsorbate (arsenic) available for desorption (Davis and others, 1987). The radioisotope arsenic-73 in the +5 oxidation state was added to an aliquot of supernatant from one tube and mixed for 24 hours to ensure isotopic equilibrium in the solution phase. A 1.00-mL aliquot of the labeled solution then was added to each of 10 tubes that were equilibrated for 120 hours before the addition of the isotope. During the next 4 days, pairs of tubes were sampled, and the arsenic-73 activity that remained in solution was determined by gamma spectroscopy of the supernatant. The amount of exchangeable sorbed arsenic was calculated by mass balance from the amount of arsenic-73 removed from solution (Davis and others, 1987). This calculation assumes the total dissolved-arsenic concentration did not change significantly during isotopic exchange.

Results and Discussion

Diurnal Fluctuations in Surface-Water Chemistry

A diurnal fluctuation in the pH cycle of surface water varied as much as 0.5 unit at all three sites (figs. II-2, II-3, and II-4). The pH cycle results from algal photosynthesis that lowers the partial pressure of carbon dioxide during the day (Dunn, 1967; Turk, 1988). The diurnal cycle of pH is attributed to photosynthesis because of the correlation of pH maxima with light-intensity maxima at site A (fig. II-2A, table II-1) and because of the diurnal variations of dissolved oxygen (Fuller and Davis, 1989) and calculated partial pressure of carbon dioxide. At all three sites, the cycle of pH either preceded change in water temperature by as much as 2.5 hours or was in phase with the measured diurnal variation in water temperature (table II-1). The amplitude of the pH fluctuation generally was constant during the two or three cycles measured at each site, and the amplitude of the temperature cycle varied as much as 50 percent between cycles at each site. These differences between pH and water-temperature cycles suggest that increases in pH did not result from a decrease in carbon dioxide solubility as surface-water temperature increased. Partial pressure of carbon dioxide in surface water ranged from 680 ppm at high pH to 1,200 ppm at low pH and always was supersaturated with respect to equilibrium with the atmosphere. Stream reaeration probably is insufficient for equilibrium with the atmosphere. This disequilibrium results in the fluctuations of pH in response to changes in partial pressure of carbon dioxide as the rate of photosynthesis varies diurnally. Diurnal pH fluctuations observed in other surface-water systems have been attributed to photosynthetic activity (Dunn, 1967; Turk, 1988).

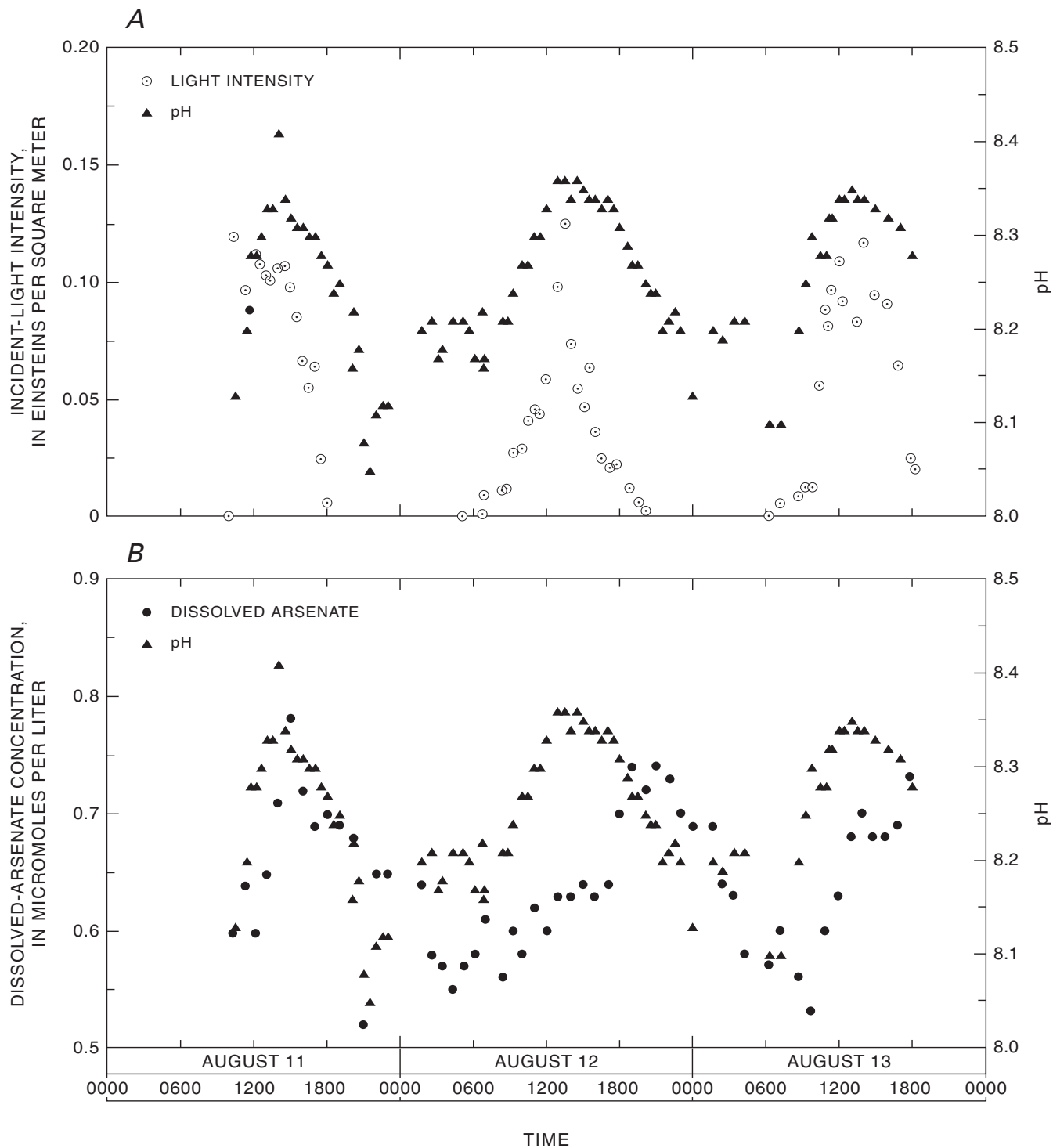


Figure II-2. Incident-light intensity, dissolved-arsenate concentration, and pH compared to time of day at site A, August 11–13, 1987.

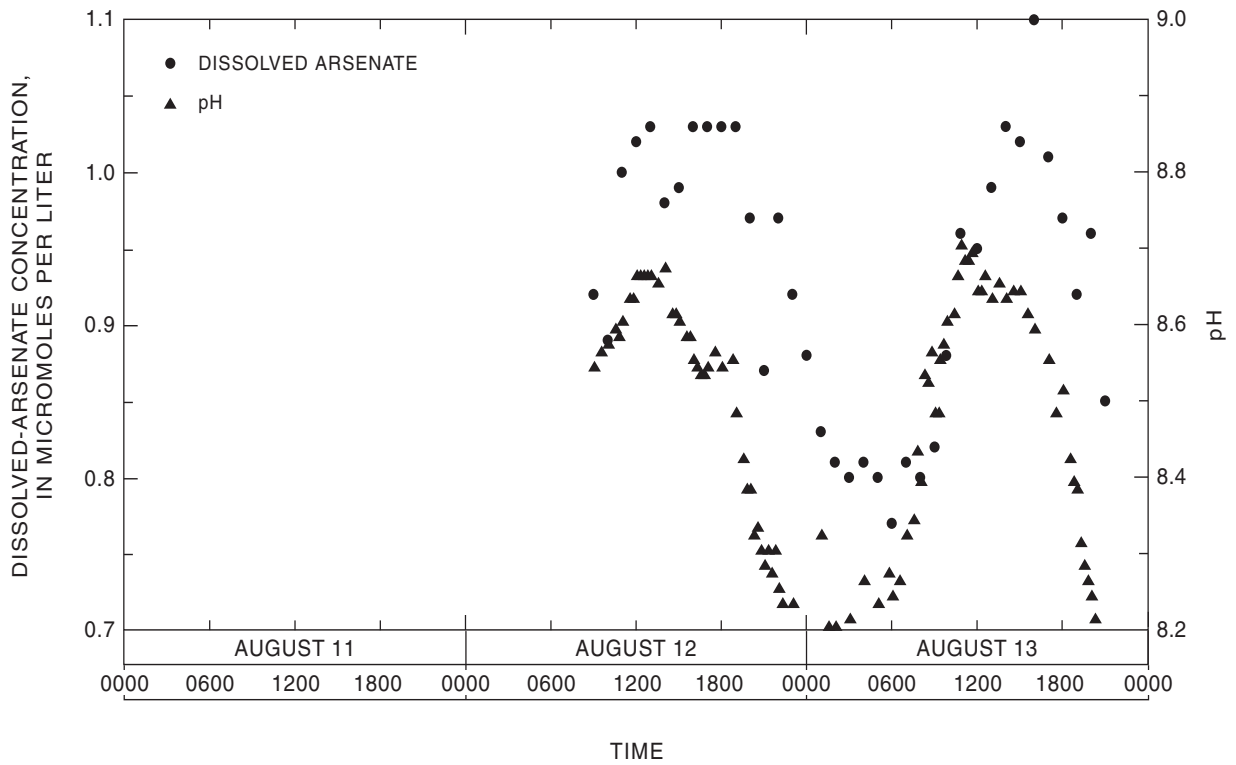


Figure II-3. Dissolved-arsenate concentration and pH compared to time of day at site B, August 12-13, 1987.

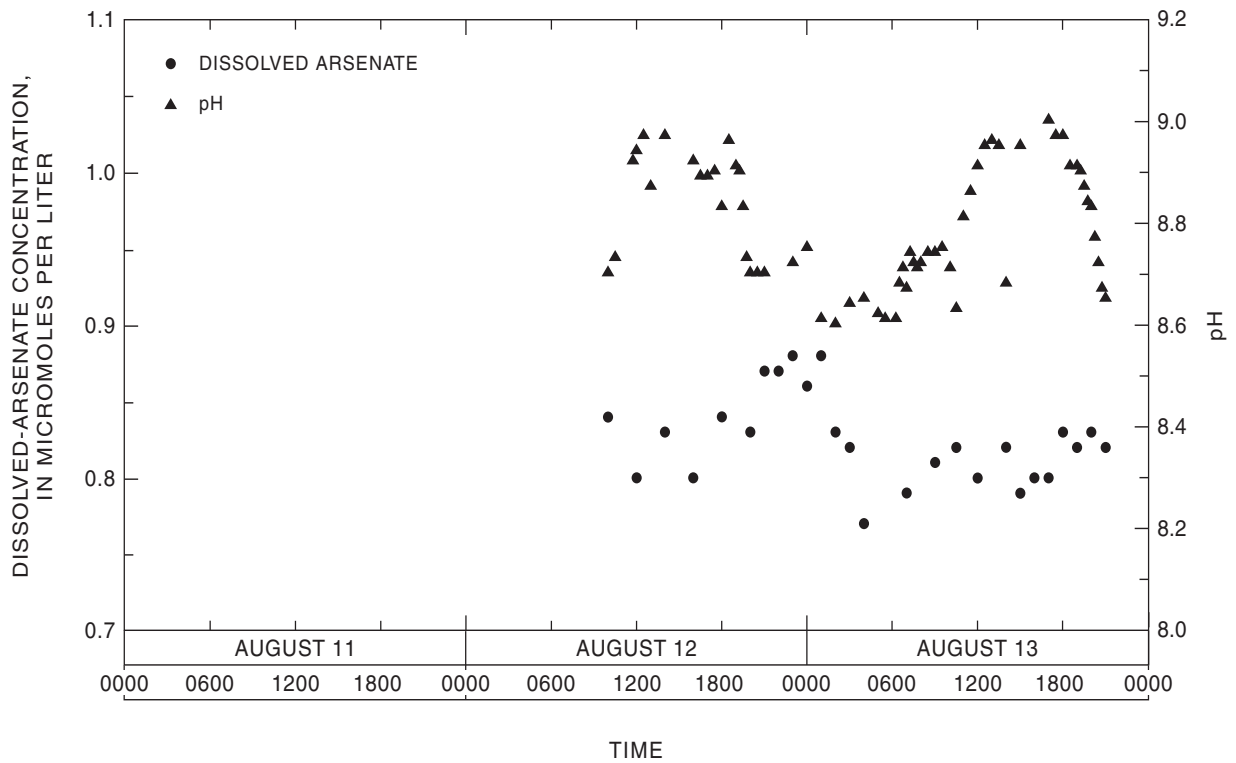


Figure II-4. Dissolved-arsenate concentration and pH compared to time of day at site C, August 12-13, 1987.

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Table II-1. Cross-correlation analysis of diurnal time-series data.

Cross correlation of first component time series to second component time series	Time interval, in hours	Lag of first component time series behind second component ¹ (hours)	Maximum correlation coefficient used to define lag time ² (<i>r</i>)	Number of pairs of data used in cross-correlation analysis
I. Site A				
Arsenic, dissolved to pH	1	4	0.62	55
pH to light	0.5	0.5	0.79	110
Water temperature to light.....	0.5	3.0	0.86	110
Water temperature to pH	0.5	1.5	0.66	110
Sulfate to pH.....	1	10	0.76	52
Bromide to sulfate	1	-1	0.77	23
II. Site B				
Arsenic, dissolved to pH	1	2	0.83	37
Water temperature to pH	0.5	2.5	0.83	73
III. Site C				
Arsenic, dissolved to pH	2	(3)	(4)	18
Water temperature to pH	0.5	0.5	0.80	71
IV. Intersite Comparison				
1. Sites A and B				
Arsenic, dissolved, site B to arsenic, dissolved, site A	1	-2	0.67	33
pH, site B to pH, site A	0.5	-1.5	0.92	67
pH, site B to light, site A	0.5	-0.5	0.83	67
Temperature, site B to temperature, site A	0.5	0	0.93	67
2. Sites A and C				
pH, site C to pH, site A	0.5	0	0.73	67
pH, site C to light, site A.....	0.5	-1.0	0.79	67
Temperature, site C to temperature, site A	0.5	0	0.96	67

¹Negative lag indicates second component proceeds first.

²Resolution equals length of data-time intervals.

³No correlation observed.

⁴Maximum *r* value insignificant ($P < 0.05$).

A diurnal cycle in dissolved arsenate was observed at sites A and B (figs. II-2B and II-3). The fluctuation in C_{As} of as much as 40 percent lagged behind the cycle of pH by 2 to 4 hours (table II-1). Fluctuations in both pH and C_{As} were greater at site B than at site A. Additionally, a shorter lag time of C_{As} behind pH also was observed at site B. The general trend of C_{As} fluctuation with pH at these sites is consistent with the pH dependence of arsenate adsorption by iron oxyhydroxides (Pierce and Moore, 1982; Goldberg, 1986). The higher C_{As} at site B was because of higher pH range and a slightly higher arsenic to iron molar ratio in bed sediments in this reach. The shorter lag time of the C_{As} cycle for pH cycles of greater amplitude also was observed by Kuwabara (1992). Although a diurnal fluctuation in

pH of 0.5 unit also was observed at site C, no significant variation in C_{As} was observed (fig. II-4). C_{As} , pH, and water-temperature data for the three sites are given in Fuller and others (1989).

Total alkalinity ranged from a minimum of 2.93 meq/L to a maximum of 3.42 meq/L and appeared to fluctuate in phase with pH (fig. II-5). A significant cross correlation of alkalinity with pH was not possible because of the small number of alkalinity samples. Sulfate fluctuated diurnally by 0.35 mmol/L but was out of phase with pH cycle by about 10 hours (fig. II-5 and table II-1). Dissolved calcium also fluctuated diurnally and ranged from 3.05 to 3.38 mmol/L and was in phase with sulfate (data not shown). Dissolved ferrous and total iron both were below the detection limit of 0.1 $\mu\text{mol/L}$ in all samples.

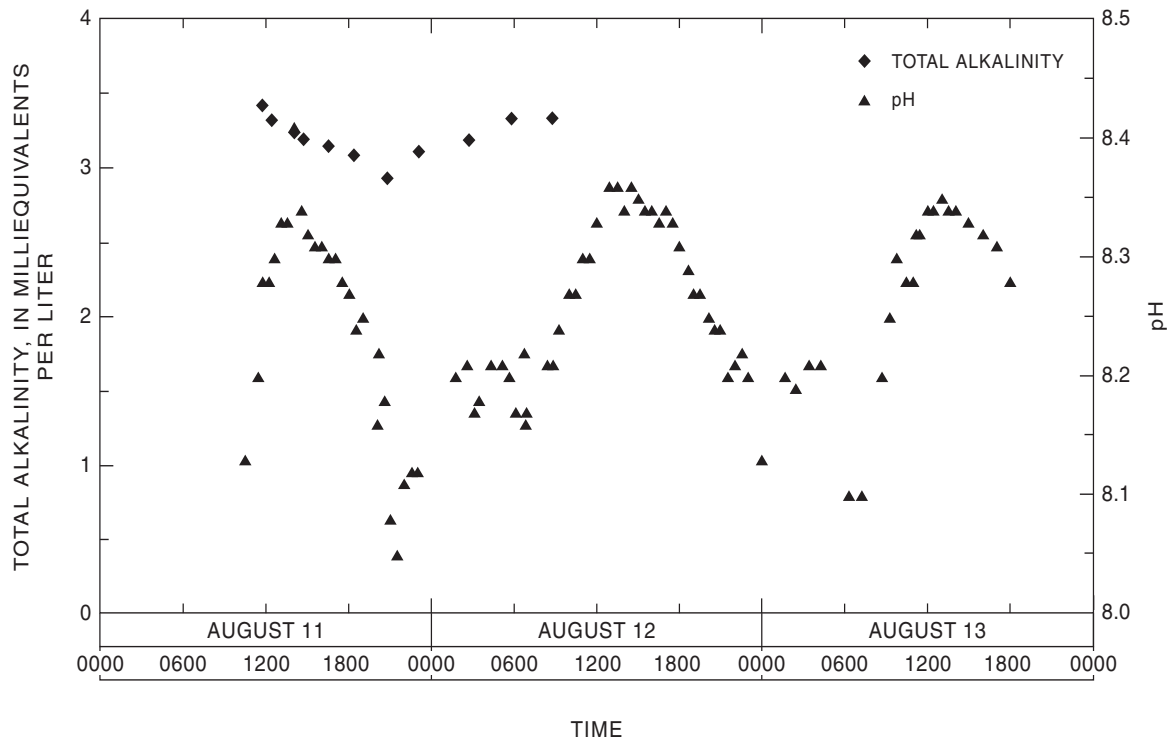


Figure II-5. Total alkalinity concentration and pH compared to time of day at site A, August 11–13, 1987.

Ground-Water Chemistry

The results of analyses of ground-water data collected from seeps in the abandoned meander upstream from site A (table II-2) are similar to results of analysis of ground-water data collected by piezometer in tailings and oxidized alluvium at several sites along Whitewood Creek (Cherry and others, 1986; Fuller and others, 1988a). The concentration of dissolved arsenic was five to eight times higher in the ground-water seeps than in surface water and, in contrast to surface water, was predominantly in the +3 oxidation state. The predominance of +5 oxidation state in surface water suggests that oxidation of arsenic is rapid. Belzile and Tessier (1990) have argued that only arsenic in the +5 oxidation state should be associated with iron oxyhydroxides. Concentrations of dissolved iron—essentially all as ferrous iron—in ground water were more than three orders of magnitude greater than concentrations of dissolved iron in surface water. Sulfate and alkalinity also were elevated in ground water. Data for each constituent from the various sampling dates were averaged for use in modeling ground-water inflow to the stream (table II-2).

Variations in Stream Discharge

The increase in dissolved bromide from background level (<0.02 mg/L) to the plateau concentration (1.1 mg/L) at site A yielded a mean traveltime of 147 minutes through the 2.8-km injection reach (fig. II-6). Mean traveltime is defined as the time between the start of the bromide injection and the point at which

bromide reaches 50 percent of plateau concentration. Triska and others (1989) have defined this as the nominal traveltime. An overall velocity of water in the reach of 0.32 m/s is calculated by dividing the length of the reach by the mean traveltime (Jackman and others, 1984/1985). Velocities within each subreach between adjacent sampling points were 0.34 m/s for the subreach 0 to 1,518 m downstream from the injection point; 0.36 m/s for the subreach between 1,518 to 2,267 m, 0.22 m/s for the subreach between 2,267 to 2,543 m, and 0.32 m/s for the subreach between 2,543 and 2,842 m. The lowest velocity was in a 276-m reach that included a ponded section of lower gradient stream reach that had thick, fine-grained bed sediments. The ponded section is not characteristic of the rest of the study reach. The overall traveltime and velocity for the 2.8-km reach are used in modeling ground-water inflows and rates of instream processes.

A linear decrease ($r=0.91$) in bromide concentration of 7 percent through the 2.8-km injection reach (fig. II-7A) was measured in the synoptic samples. An increase in the stream discharge from 0.453 m³/s at the injection point to 0.484 m³/s at the downstream end of the reach was calculated from equation II-1 and the bromide concentrations from the linear regression for the upstream and downstream ends of the reach. The increase in stream discharge of 0.031 m³/s is attributed to ground-water discharge from perched aquifers in the flood plain to the stream along the reach. This increase also is evident from a linear ($r=0.98$) downstream increase in dissolved sulfate (fig. II-7B) because ground water that discharges from flood-plain aquifers and the underlying shale is enriched in sulfate. The linear downstream decrease in bromide and the increase in sulfate indicate that

Table II-2. Ground-water chemistry data for Whitewood Creek near site A.

Date	pH	Sulfate, in millimoles per liter	Alkalinity, in millimoles per liter	Arsenic, total, in micromoles per liter	Arsenic(III), in micromoles per liter	Arsenic(V), in micromoles per liter	Iron, total, in micromoles per liter	Iron(II), in micromoles per liter
August 1986	6.6	12.0	(1)	3.63	3.39	0.24	151	125
June 1987	7.1	12.3	(1)	² 4.48±0.05	3.71±0.12	0.79±0.06	147	142
June 1987	7.1	12.9	5.3	4.06±0.07	(1)	(1)	142	143
July 1987	7.0	12.7	(1)	3.57±0.13	3.50±0.05	0.26±0.11	191	190
July 1987	7.0	12.3	(1)	3.93±0.03	3.76±0.09	0.48±0.13	202	200
August 1987	(1)	13.7	(1)	2.42±0.11	(1)	(1)	(1)	(1)
August 1987	(1)	12.8	(1)	4.11±0.11	(1)	(1)	(1)	(1)
August 1987	(1)	12.1	(1)	4.22±0.24	(1)	(1)	(1)	(1)
August 1987	(1)	12.9	(1)	3.73±0.18	(1)	(1)	(1)	(1)
Average concentrations	7.0±0.1	12.7±0.8	5.3	3.8±0.6	3.6±0.2	0.4±0.3	167±28	160±33

⁵Not analyzed.

⁶Plus minus sign represents standard error of mean of replicate analyses.

ground-water inflow to the stream is distributed evenly along the length of the reach. The fractional increase in stream discharge also can be calculated from the increase in sulfate throughout the reach by assuming a value of sulfate in ground water that is equal to the average concentration of sulfate determined in the seeps near site A (12.7 millimoles per liter [mmol/L], table II-2) as follows:

$$Q_d = Q_{gw} + Q_j \quad (\text{II-2})$$

and

$$[\text{SO}_4]_d Q_d = [\text{SO}_4]_{gw} Q_{gw} + [\text{SO}_4]_j Q_j \quad (\text{II-3})$$

where

Q_d = discharge at the diurnal sampling site A, in cubic meters per second;

Q_{gw} = discharge from ground-water inflow, in cubic meters per second;

Q_j = discharge at the injection point, in cubic meters per second;

SO_{4d} = sulfate concentration at diurnal sampling site A, in millimoles per liter;

SO_{4gw} = sulfate concentration in ground water, in millimoles per liter;

and

SO_{4j} = sulfate concentration at injection point, in millimoles per liter.

If Q_d is set to 1 and equation II-2 is substituted into equation II-3, solving for Q_{gw} yields the fraction of discharge at site A because of ground-water inflow along the injection reach. This inflow results in a fractional increase in stream discharge of 0.11 in the 2.8-km reach that is significantly greater than discharge determined from the bromide data (0.07). Based on the range of sulfate—7 to 200 mmol/L— in ground water from piezometer measurements in the flood-plain aquifers of

this stream (Cherry and others, 1986), the disparity probably results from ground water that contains higher sulfate concentrations than values of sulfate measured near site A. If values of stream discharge from bromide are used, an average value of sulfate in ground water of 18.7 mmol/L is required for the observed downstream increase in sulfate in surface water. Because of the uncertainty in concentration of sulfate in ground-water inflows, the fractional increase in stream discharge calculated from the injected bromide will be used for estimating the ground-water contribution to C_{As} .

Coincident diurnal fluctuations in bromide and sulfate were observed. Maximum concentrations for both constituents occurred at night, and minimal concentrations for sulfate occurred in early afternoon (fig. II-6). Cross-correlation analysis of diurnal bromide with sulfate time series yielded a 1-hour lag of sulfate behind bromide (table II-1). Because this diurnal fluctuation was observed both for the injected bromide and for sulfate, which is increased by ground-water inflow, the diurnal fluctuation in both constituents must be the result of an increase in stream discharge from sources upstream from the lithium-bromide injection site. The increase in stream discharge dilutes both constituents during the day. An increase in ground-water inflow only within the reach at night would result in the observed increase in sulfate but would cause a decrease in bromide from greater dilution. Concentrations of sulfate ranged from 5.93 to 6.33 mmol/L, and concentrations of bromide ranged from 0.93 to 1.18 mg/L. The greater relative fluctuation in bromide compared to sulfate may be attributed to a variation in sulfate in water entering the reach that dampens out the observed diurnal fluctuation in sulfate at the downstream end of the reach. On the basis of the concentrations of bromide in surface water, stream discharge at site A ranged from a minimum 0.391 m³/s at night to a maximum of 0.497 m³/s at midday. The diurnal cycles of sulfate and bromide and, therefore, the stream-discharge minima, lag behind the pH cycle by 9 to 10 hours (table II-1).

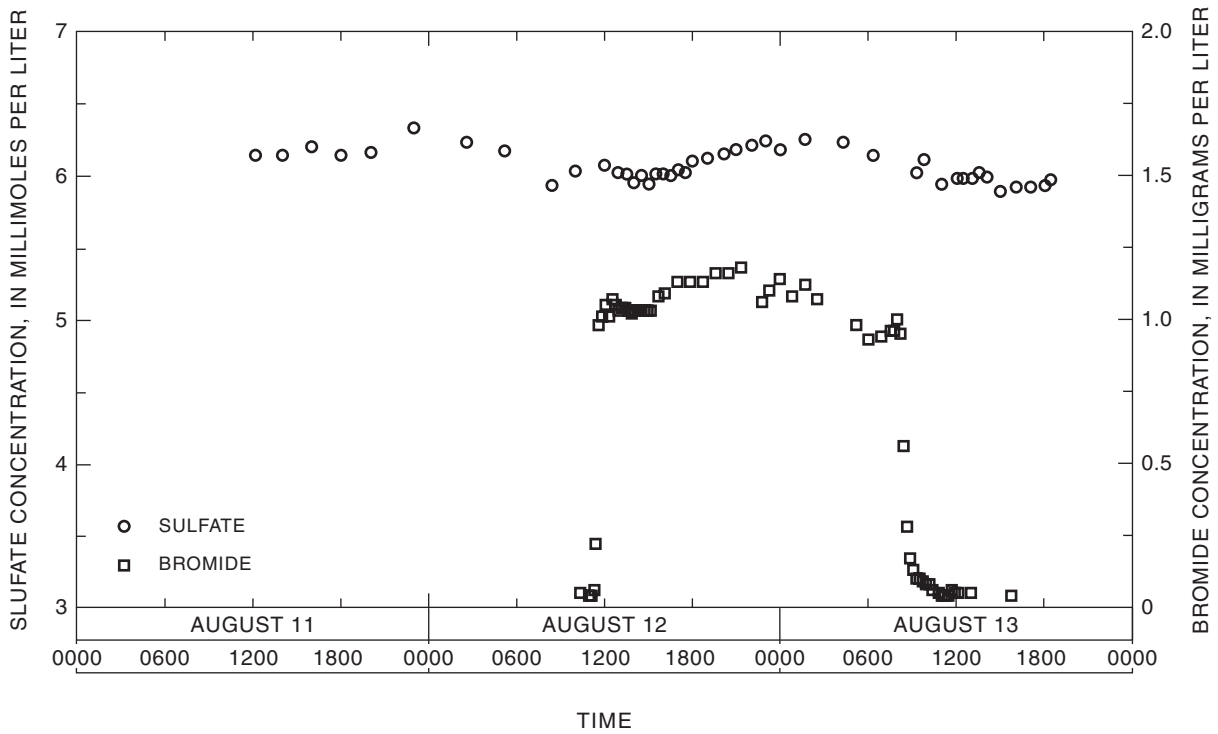


Figure II-6. Sulfate and bromide concentrations compared to time of day at site A, August 11-13, 1987.

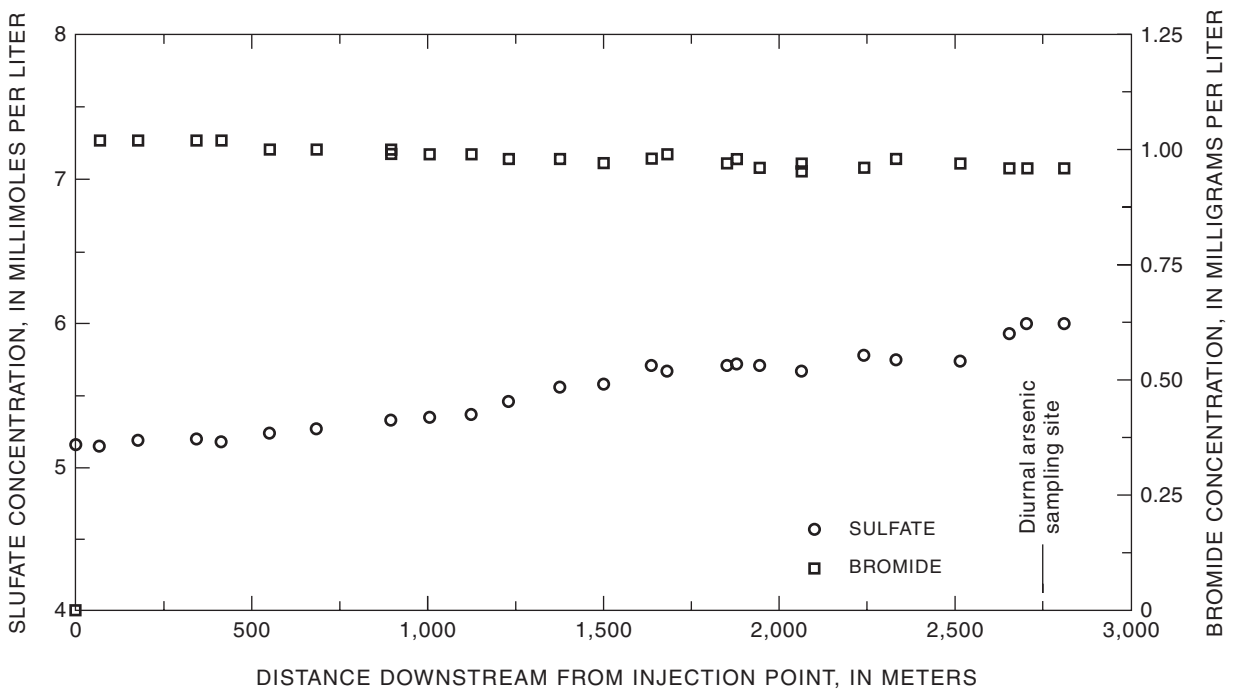


Figure II-7. Bromide and sulfate concentrations compared to distance downstream for lithium-bromide injection site, August 13, 1987, 9 a.m. to 1 p.m.

Diurnal fluctuations in stream discharge have previously been observed in tracer studies by Kennedy and others (1984/1985) and Bencala and others (1987), although no driving mechanism was proposed. Others have attributed these fluctuations to diurnal effects of evapotranspiration on ground-water discharge (Rantz and Eakin, 1972). Many large cottonwood trees growing in the flood plains of the stream may account for the observed fluctuation in ground-water inflow.

Dissolved Arsenic in Synoptic Samples

Concentrations of dissolved arsenic in samples collected during synoptic sampling along the injection reach were variable but fell within the range of dissolved arsenic measured at site A (fig. II-8). If the synoptic sample C_{As} and the C_{As} measured at site A during the synoptic sampling period are plotted in relation to time instead of distance, the synoptic samples follow the trend of increasing C_{As} that was measured at site A. The measured variation then can be explained by the diurnal fluctuation in C_{As} . The results indicate that the processes that control the diurnal arsenic cycle occur throughout the reach and are present because of instream processes rather than variable point-source inflows and downstream transport. This hypothesis also is indicated by the concurrent cycles of C_{As} occurring at sites A and B (table II-1), which are 11.8 km apart. If the cycle was a result of transport from an upstream point source, the cycle of C_{As} at site A should lag behind the cycle at site B by 9.5 hours, assuming the travel-time per kilometer is the same as measured in the 2.8-km reach. Instead, the C_{As} cycle at site A lagged the C_{As} cycle at site B by 1 hour (table II-1).

Arsenate Adsorption and Isotopic Exchange on Iron Oxyhydroxides

The reddish-orange iron oxyhydroxide precipitate that was formed and was isolated from ground water yielded an X-ray diffraction pattern characteristic of 2-line ferrihydrite (Carlson and Schwertmann, 1981). This least crystallized form of ferrihydrite results from the hydrolysis of ferric iron solutions at neutral pH and consists of primary crystallites of 0.8 to 1.5 nm in length (Waychunas and others, 1993). The ferrihydrite crystallites aggregate and coalesce rapidly under favorable conditions to form large, porous gelatinous floccules of 100 nm or greater length (Bottero and others, 1991). Ferrihydrite has a high reactive surface area for the adsorption of cations and anions (Dzombak and Morel, 1990). The field samples had a total iron concentration of 1.77×10^{-3} mol/g and total arsenic concentration of 2.36×10^{-5} mol/g that was determined by acid dissolution of the precipitate. Inductively coupled plasma-emission spectroscopic analysis of the acid leachate yielded, in addition to arsenic and iron, significant concentrations for manganese (4.9×10^{-5} mol/g) and cobalt (5.5×10^{-6} mol/g).

In laboratory studies of arsenate sorption by synthesized 2-line ferrihydrite designed to simulate ground-water inflow to the stream, arsenic uptake during coprecipitation of arsenic with iron was rapid and was followed by constant C_{As} concentration during the next 24 hours (Fuller and Davis, 1989). The magnitude of uptake by coprecipitation decreased with increasing pH and resulted in a linear increase in C_{As} from a pH of 8.0 to a pH of 9.0. This pH dependence was similar to pH dependence in the sorption of oxyanions on oxides (Davis and Leckie, 1980;

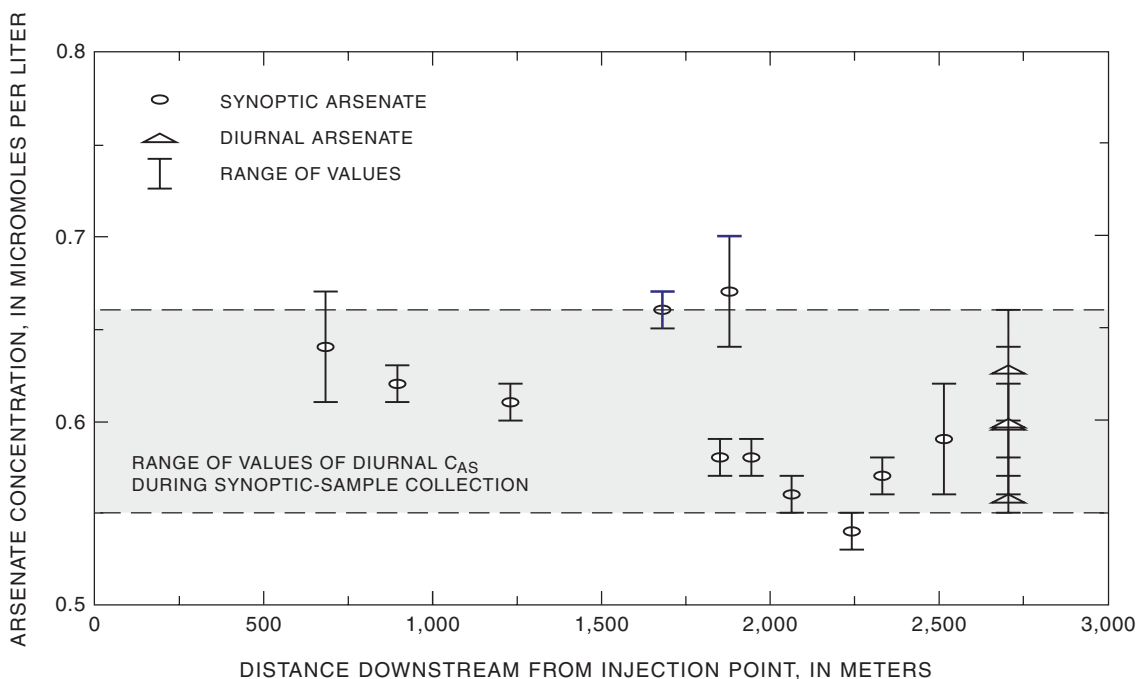


Figure II-8. Synoptic dissolved-arsenate concentration related to distance from lithium-bromide injection site, August 13, 1987, 9 a.m. to 1 p.m.

Belzile and Tessier, 1990). In contrast, lower uptake and a slow approach to equilibrium were observed for the adsorption of arsenic when it was added subsequent to precipitation and aging of ferrihydrite (adsorption). Adsorption was characterized by a rapid (<5 minutes) uptake in arsenic that continued for 8 days as the arsenic diffused to adsorption sites on ferrihydrite surfaces within aggregates of colloidal particles (Fuller and others, 1993). Desorption of arsenic from both adsorbed and coprecipitated systems with an increase in pH also exhibited this slow approach to equilibrium. Arsenate adsorbs to ferrihydrite primarily as an inner-sphere bidentate-surface complex in both coprecipitation and adsorption systems (Waychunas and others, 1993). Adsorption is rapid in coprecipitation systems because arsenate adsorbs to ferrihydrite crystallite surfaces before aggregation. The rate of adsorption or desorption is limited by diffusion to or from sorption sites buried within ferrihydrite aggregates (Fuller and others, 1993). A slow approach to adsorption equilibrium often is observed for phosphate uptake onto ferrihydrite and soils (Barrow, 1983; Bolan and others, 1985; Crosby and others, 1984). The rate-controlling process is attributed to the diffusion of phosphate into ferrihydrite aggregates (Willett and others, 1988).

A slow approach to equilibrium was measured for the uptake of arsenic at a pH of 8.0 from filtered surface water (<0.1- μm filter, collected at a pH of 8.4) onto the ferrihydrite precipitate formed from ground water (fig. II-9). This slow approach to equilibrium also was observed for arsenic adsorption and desorption by synthesized ferrihydrite (Fuller and others, 1993). After 5 days of uptake, the reversible fraction of sorbed arsenic was determined by arsenic-isotopic exchange.

The exchange of arsenic-73 with particle-bound arsenic also exhibited a slow approach to equilibrium following an initial rapid exchange (fig. II-10). After 96 hours of arsenic-73 uptake by the ferrihydrite, the calculated fraction of exchangeable arsenic was small (about 5 percent) compared with the total arsenic associated with the solid phase. The exchangeable fraction of sorbed arsenic would result in a solution concentration of 0.8 $\mu\text{mol/L}$ if all the arsenic was desorbed. This amount is equivalent to about two times the uptake measured from pH 8.4 to pH 8.0. These experiments indicate that the arsenate-sorption behavior of iron precipitates from the field is similar to arsenate-sorption behavior in laboratory-synthesized 2-line ferrihydrite (Fuller and others, 1993). Although the ferrihydrite precipitates and coatings on streambed sediments have high arsenic concentrations, the isotopic-exchange study indicates that, at most, only about 5 percent of the total arsenic is available for desorption.

Processes that Contribute to the Diurnal Cycle of Dissolved Arsenic in Surface Water

Diurnal cycles of C_{As} resulted from adsorption-desorption of arsenic from iron oxyhydroxides in the streambed (Fuller and Davis, 1989). A mass balance for dissolved arsenic at site A is presented to demonstrate the importance of adsorption processes in the streambed in controlling C_{As} in surface water. Processes contributing to the C_{As} cycle are estimated in units of micromoles per liter per day for comparison with the measured

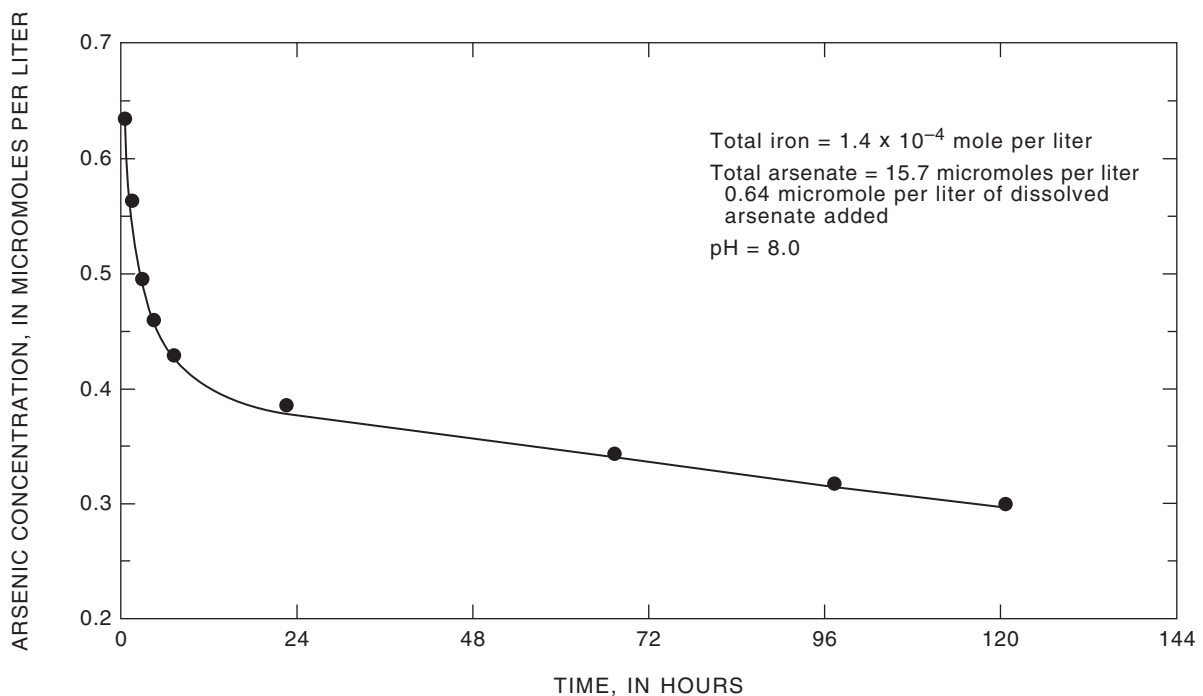


Figure II-9. Uptake of arsenate at pH 8.0 from surface water by ferrihydrite formed from ground-water seep, as a function of time.

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fluctuation in C_{As} of $0.21 \mu\text{mol/L/d}$. A schematic representation of the dissolved-arsenic cycle illustrates the processes that may contribute to the diurnal cycle of C_{As} (fig. II-11). The fluctuation in concentrations of dissolved arsenate in surface water can be described by a one-dimensional advection-dispersion equation that includes the contribution to C_{As} from ground-water inflows. The equation was modified from Bencala (1983) to include other sources and sinks for C_{As} (fig. II-11) as follows:

$$\begin{aligned} \frac{\partial C_{As}}{\partial t} = & \frac{-Q}{A} \frac{\partial C_{As}}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left(AD \frac{\partial C_{As}}{\partial x} \right) \\ & + \frac{q_{gw}}{A} \frac{\partial [C_{gw}(1-f_c)]}{\partial pH} \frac{\partial pH}{\partial t} \\ & + J_{sed} A_c - F_c R + P_s + B_s \end{aligned} \quad (\text{II-4})$$

where

- C_{As} = concentrations of dissolved arsenate in surface water, in micromoles per liter;
- t = time, in seconds;
- Q = volumetric streamflow, in cubic meters per second;
- x = distance, in meters;
- A = cross sectional area of streamflow, in square meters;
- D = dispersion coefficient, in square meters per second;
- q_{gw} = inflow of ground water per length of streamflow, in cubic meters per second per meter;

- C_{gw} = C_{As} of ground-water inflow, in micromoles per liter;
- f_c = fraction of arsenic adsorbed during coprecipitation with iron from ground-water inflow;
- J_{sed} = molecular diffusive flux of arsenic out of reducing fine-grained sediments, in micromoles per square meter per second;
- A_c = contact area of streamflow with streambed, in liters per square meter;
- F_c = net carbon fixation by algae, in moles of carbon per liter per second;
- and
- R = ratio of arsenic uptake by algae to carbon fixed, in micromoles of arsenic per moles of carbon.

The last two terms of equation II-4— P_s and B_s —describe the time-dependent adsorption and desorption of arsenate on ferrihydrite in suspended sediments and in bed sediments in contact with streamflow, respectively, as a function of pH and time as follows:

$$P_s = S_s \frac{\partial \lambda_a (S_{As} - K_s C_{As}^{1/n})}{\partial pH} \frac{\partial pH}{\partial t} \quad (\text{II-5})$$

and

$$B_s = A_c Z_b (1 - \phi) \rho_b B_{As} \frac{\partial \lambda_a (B_{As} - K_s C_{As}^{1/n})}{\partial pH} \frac{\partial pH}{\partial t} \quad (\text{II-6})$$

where

- S_s = suspended-sediment concentrations, in grams per cubic meter;
- λ_a = adsorption-desorption rate constant (s^{-1}), in reciprocal seconds;

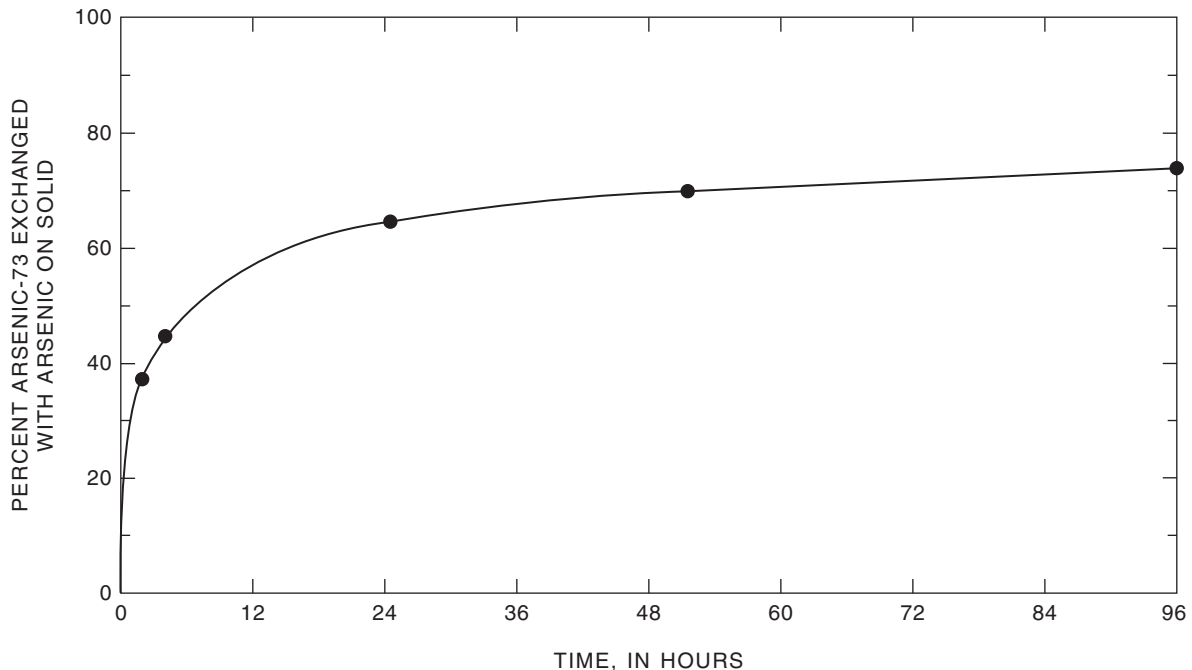


Figure II-10. Arsenic-isotope exchange as a function of time on ferrihydrite following 96 hours of uptake.

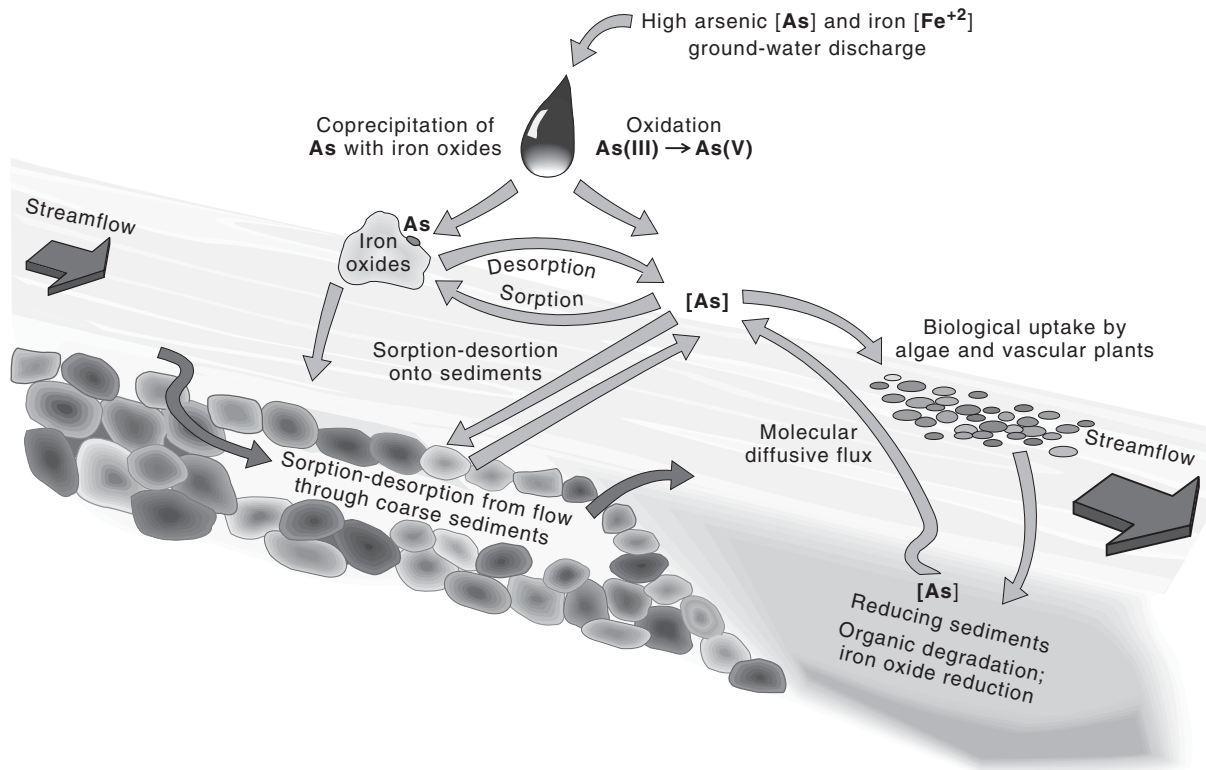


Figure II-11. Generalized diagram showing dissolved-arsenate cycle.

S_{As} = concentration of arsenic in suspended sediments, in micromoles per gram;

n, K_s = Freundlich isotherm adsorption coefficients;

Z_b = depth of bed sediment in contact with streamflow, in centimeters;

ϕ = porosity of bed sediments;

ρ_b = dry sediment density, in grams per cubic centimeter;

and

B_{As} = total arsenic concentration of bed sediment, in micromoles per gram.

Arsenate adsorption and desorption by ferrihydrite are described by a nonlinear Freundlich adsorption isotherm (Fuller and others, 1993). The rate of adsorption and desorption is limited by diffusion within aggregates of ferrihydrite (Fuller and others, 1993). For simplicity, a first-order rate constant is used to approximate the adsorption-desorption kinetics.

Instead of solving the complex transport equation (II-4), the individual input, reaction, and loss terms are evaluated over one diurnal cycle to illustrate the contribution of each process to the cycle in C_{As} . The source and loss terms are determined from the data collected in the 2.8-km study reach (2.4-hour travel-time) and are used to represent conditions along a reach with a 24-hour traveltime.

The various components contributing to the C_{As} cycle are estimated in units of micromoles per liter per day for comparison with the observed fluctuation in C_{As} of 0.21 $\mu\text{mol/L}$ in 1 day. The coincidence of pH and C_{As} cycles between sites

(table II-1) indicates that the cycles are the result of processes that occur throughout the stream rather than the result of transport from upstream point sources. The measured variation in C_{As} with time in the 2.8-km reach also provides evidence that instream processes control the C_{As} cycle. Because the inflow of ground water is uniform throughout the 2.8-km reach as indicated by the linear decrease in bromide and increase in sulfate (fig. II-7), inflow of ground water per length of streamflow is assumed to be constant and equals ground-water discharge divided by reach length.

The following mass balance is limited to arsenic(V) species that comprises more than 98 percent of the total dissolved inorganic arsenic. In contrast, Kuwabara (1992) observed concentrations of arsenic(III) of 0.08 to 0.11 $\mu\text{mol/L}$ at this site in the late summer of 1988; a slight fluctuation of arsenic(III) appears out of phase with arsenic(V). Possible reduction of arsenic(V) in acidified samples that occurs between sampling and analysis may account for the greater concentrations of arsenic(III) (Kuwabara, 1992). In this study, arsenic(III) and arsenic(V) were separated immediately upon filtration by anion exchange (Ficklin, 1983) to eliminate reduction at low pH during sample storage.

Ground-Water Sources of Streamflows

Results of the bromide injection indicate that a 7-percent increase in stream discharge in the length of reach was attributed to ground-water inflow. The average concentration of dissolved arsenic in ground water at this site (3.8 $\mu\text{mol/L}$,

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table II-2) and the results of arsenic and iron coprecipitation experiments (Fuller and Davis, 1989) were used to estimate dissolved arsenic in ground-water inflow to the stream. By assuming that ground-water inflow to the surface water is uniform and constant in a distance equivalent to a 24-hour travel-time, the change in ground-water contribution to C_{As} is estimated by evaluating the third term in equation II-4 over one 24-hour pH cycle as follows:

$$\Delta C_{As}^{gw} = \frac{q_{gw} \Delta t}{A} C_{gw} (1 - f_c) \Big|_{pH8.15}^{pH8.35} \quad (\text{II-7})$$

where

ΔC_{As}^{gw} = change in C_{As} from ground-water inflow, in micromoles per liter per day;

Δt = change in time, in seconds;

and

f_c = fraction of arsenic adsorbed with iron during coprecipitation from ground-water inflow.

Assuming that arsenic was not removed during precipitation of iron from ground water entering the stream ($f_c=0$), a ground-water inflow of 2.37 $\mu\text{mol/L/d}$ was calculated. Values of f_c are determined from laboratory data for coprecipitation of arsenic under conditions simulating ground-water inflow to the stream as a function of pH (Fuller and Davis, 1989). Inputs of dissolved arsenic of 0.17 and 0.22 $\mu\text{mol/L/d}$ are calculated when arsenic uptake is accounted for during coprecipitation with iron at a pH of 8.10 ($f_c=0.93$) and 8.35 ($f_c=0.91$), respectively. The difference in uptake of arsenic at a pH of 8.15 and 8.35 results in a net change in C_{As} of 0.05 $\mu\text{mol/L/d}$ (ΔC_{As}^{gw}) because of input from ground water during a pH cycle. Because diurnal samples for arsenic and anion analyses were not collected at the upstream end of the injection reach, the effect of the measured diurnal fluctuations (fig. II-6) on ground-water inflows and on C_{As} cannot be determined. If inflow of ground water per length of streamflow increases by an amount equivalent to the observed day-to-night increase in sulfate of 7 percent, however, a ΔC_{As}^{gw} of 0.04 $\mu\text{mol/L/d}$ in a pH cycle is estimated by equation II-7.

Molecular Diffusive Flux from Bed Sediments

Release of arsenic to sediment interstitial water during the reductive dissolution of iron oxides and degradation of organic matter (Aggett and O'Brien, 1985; Peterson and Carpenter, 1986; Cullen and Reimer, 1989) results in a diffusive flux to the overlying water column that contributes to C_{As} . A concentration of dissolved arsenic in pore water of 4.7 $\mu\text{mol/L}$ was determined at a depth of 4 cm in a deposit of fine-grained reducing sediment (U.S. Geological Survey, unpub. data, 1987). Molecular-diffusive flux of arsenic from reducing fine-grained sediments (J_{sed}) was calculated from the gradient between C_{As} in pore water at 4 cm and the overlying surface water by using Fick's first law (Berner, 1980) and evaluating the following equation over 4 cm:

$$J_{sed} = \frac{\theta D}{\phi^2} \frac{\partial C_{As}^{pw}}{\partial Z} \quad (\text{II-8})$$

where

D = self-diffusion coefficient, in square centimeters per second;

θ = sediment tortuosity, unitless;

ϕ = porosity, unitless;

C_{As}^{pw} = concentrations of dissolved arsenic in pore water, in micromoles per liter;

and

Z = depth in sediment, in centimeters.

A J_{sed} of 1.65 $\mu\text{mol/m}^2/\text{d}$ is calculated using D for arsenate of $9.05 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C (Li and Gregory, 1974) and fine-grained sediment values for ϕ and θ of 0.8 and 2.0, respectively. This flux of arsenic is an upper limit because removal of arsenic by adsorption near the sediment/water interface is not accounted for (Aggett and O'Brien, 1985; Peterson and Carpenter, 1986).

Because the areal distribution of reducing sediments is unknown, quantifying the molecular-diffusive flux of arsenic in the length of the stream reach in the mass balance is difficult. An upper limit of the flux, however, can be calculated by converting the J_{sed} to micromoles per liter per day by multiplying by the effective contact area of surface water with the streambed, A_c . A_c is estimated from the overall mean-flow velocity for the 2.8-km reach of 0.32 m/s. First, a cross-sectional area of flow (A) of 1.51 m^2 is calculated by dividing the discharge (0.48 m^3/s) by the velocity (Jackman and others, 1984/1985). In 1 second, therefore, a volume of 0.48 m^3 of water overlies 0.32 m of streambed. A vertically well-mixed stream that has a rectangular stream-channel geometry of 0.3 m in depth and 5.0 m in width for a cross-sectional area (A) of 1.5 m^2 is assumed. For these cross-sectional dimensions and a 0.32-m length traversed in 1 second, a 0.48-cubic meter volume is in contact with 1.8 m^2 of streambed for a contact area (A_c) of 270 L/m^2 . Multiplying J_{sed} by A_c (equation II-4) results in a volumetric input of 0.006 $\mu\text{mol/L/d}$. This value is an upper limit because the assumption is made that the streambed along the reach is fine-grained reducing sediments. The streambed, however, typically consists of sand, gravel, cobbles, and limited areas of fine-grained (<63 μm) sediments that would reduce the magnitude of this input of C_{As} from the sediments by an unknown amount. The sediment-diffusive flux is assumed to be constant during the diurnal period and accounts for, at most, 3 percent of the measured diurnal fluctuation in C_{As} of 0.21 $\mu\text{mol/L/d}$.

Algal Uptake of Arsenate from Surface Water

The similarity between the arsenate and phosphate molecules results in the uptake of arsenate by algae during photosynthesis (Apte and others, 1986; Andreae, 1978). Kuwabara and others (1990) observed preferential uptake of phosphate over arsenate by several orders of magnitude for algal cultures that were isolated from contaminated reaches of Whitewood Creek and that included site A. Despite this preferential uptake of phosphate, elevated arsenic content in algae at site A has been

measured in the algal species, *Cladophora* and *Ulothrix*, that dominated the plant biomass. The rate of algal arsenic uptake from surface water ($F_c R$ in eq. II-4) is calculated by assuming that arsenic is incorporated during carbon fixation at the arsenic-to-carbon molar ratio, R , observed in algae collected at this site 1 week before the diurnal sampling ($R=1.8 \times 10^{-5}$; J.S. Kuwabara, hydrologist, U.S. Geological Survey, oral commun., 1987). Because nitrate uptake, which is light dependent (Triska and others, 1989), results in a concomitant increase in alkalinity (Stumm and Morgan, 1981), the observed diurnal fluctuation in alkalinity is attributed to algal productivity. The carbon-fixation rate, F_c , was estimated from the change in alkalinity (Stumm and Morgan, 1981) and the Redfield nitrogen-to-carbon-molar ratio. Multiplying the resulting F_c of 1.8×10^{-3} moles of carbon per liter per day by R yields an arsenic uptake rate by algae of $0.033 \mu\text{mol/L/d}$. This estimate may be low because alkalinity, like sulfate, is about two times greater in ground water than in surface water (table II-2). Because ground-water inflow may fluctuate diurnally, the surface-water alkalinity should increase at night and diminish the measured surface-water alkalinity fluctuation. An increase in alkalinity on the order of the 7-percent increase in sulfate measured from day to night, however, would not change the magnitude of algal arsenic uptake significantly. If the uptake of arsenic is directly correlated with phosphate uptake, which may be light enhanced (Wetzel, 1975; Stewart, 1974), the phase of algal arsenic uptake would diminish the measured diurnal fluctuation in C_{As} by $0.033 \mu\text{mol/L/d}$.

Potential for Desorption of Arsenic from Suspended Sediments and Bed Sediments

The contribution to C_{As} by adsorption and desorption on suspended sediments in a cycle of pH could not be evaluated from equation II-5 because the pH dependence on nonlinear-adsorption coefficients and the appropriate adsorption-rate constant are not well known. Instead, equation II-5 is simplified as follows to estimate the potential desorption of arsenate from suspended sediments by assuming that the fraction of S_{As} available to desorb is equivalent to the fraction of exchangeable arsenic associated with the seep precipitate as defined by isotopic exchange (5 percent). Desorption of arsenic is assumed to reach equilibrium rapidly.

$$\Delta C_{As}^{ss} = S_s f_d S_{As} \tag{II-9}$$

where

ΔC_{As}^{ss} = change in C_{As} due to desorption from suspended sediments, in micromoles per liter per day;

and

f_d = fraction of adsorbed arsenic available for desorption.

Suspended sediments ($S_s=22 \text{ mg/L}$) collected at this site in July 1987 had a concentration of arsenic of $5.2 \times 10^{-6} \text{ mol/g}$ (S_{As}) and a concentration of iron of $5.1 \times 10^{-4} \text{ mol/g}$. These values were determined after digestion of suspended-sediment samples in concentrated nitric acid (U.S. Geological Survey,

unpub. data, 1987). Assuming these values for S_s and S_{As} were the same in August 1987 and that a maximum of 5 percent of the arsenic can desorb ($f_d=0.05$), a maximum ΔC_{As}^{ss} of $0.006 \mu\text{mol/L/d}$ would result from desorption from suspended sediments, P_s , during a pH cycle. This estimate does not account for desorption of arsenic in or on streambed sediments.

The contribution to the diurnal fluctuation of C_{As} by adsorption and desorption from bed sediments in contact with streamflow, B_s , cannot be estimated independently because the depth of sediment, Z_b , in equation II-6 is not known. The difference in the measured diurnal fluctuation in C_{As} of $0.21 \mu\text{mol/L/d}$ and the sum of the other sources and sinks, however, indicate that by mass balance, B_s must account for 85 percent of the diurnal C_{As} cycle (table II-3).

Sand-size and coarser grained bed sediments have visible iron-oxide coatings and contain high arsenic content (2.1 to $20 \mu\text{mol/g}$; Fuller and others, 1987). The arsenic-to-iron molar ratios both of fine- and coarse-grained sediments are similar to the arsenic-to-iron ratio of ferrihydrite precipitates collected at seep outflows. The continuous inflow of ground water to the stream results in a large reservoir of sorbed arsenic in the bed sediments because more than 90 percent of the dissolved-arsenic load is adsorbed to ferrihydrite that is formed during precipitation of iron in ground-water inflows. The ferrihydrite precipitates form coatings on the grains of the bed sediments. An additional source of adsorbed arsenic to the streambed occurs during high stream stages by the erosion of oxidized flood-plain deposits in which most of the arsenic is associated with iron-oxide coatings (Horowitz and others, 1988).

In order to estimate the contribution of the bed sediments to the diurnal cycle of C_{As} , the mass of sediment in contact with the streamflow must be determined. Bencala and others (1990) observed that a significant flow of streamflow moves through the streambeds of high-gradient gravel-bed and cobble-bed streams and that an exchange of water occurs between the surface flow and the flow within the streambed. The areas of flow through the streambed that exchange water with streamflow are transient-storage zones. The cross-sectional area of flow through the transient-storage zones can be estimated by modeling the increase of conservative-tracer concentration with time

Table II-3. Estimated sources and sinks of dissolved arsenic (C_{As}) in Whitewood Creek, South Dakota.

	Dissolved arsenic, in micromoles per liter per day
Ground-water inflow, ΔC_{As}^{gw}	0.05
Sediment diffusive flux, $J_{sed} A_c$	0.006
Algal uptake of As, $F_c R$	-0.033
Desorption from suspended sediments, P_s	0.006
Sum of inputs and loss	0.03
Observed diurnal fluctuation in C_{As}	0.21
Desorption from bed sediment, B_s , by difference.....	0.18

after start of an injection and the decrease to background levels at the end of the injection period (Bencala and others, 1990). This flow includes a zone in which surface water exchanges rapidly with streambed flow.

Whitewood Creek is primarily a gravel-bed stream (Cherry and others, 1986), although significant amounts of sand and fines were measured within the streambed sediments. Quantifying the cross-sectional area of transient-storage zones was not possible with the present data set because bromide was not increased sufficiently above background levels to provide adequate resolution of the slow decrease to background levels following the rapid decrease in bromide after the injection ended. The absence of a resolvable slow decrease in the post-injection bromide and the rapid initial decrease in bromide (fig. II-6) suggest that the cross-sectional area of the transient-storage zones is limited. Triska and others (1989) used the ratio of time for a conservative tracer to reach 50 percent of the plateau to the first arrival time of the tracer above background concentration as an indicator of the hydrologic retention of solutes in transient-storage zones within the streambed. A ratio of 1.06 for the 2.8-km injection reach indicates that these zones make up a small but significant fraction of the cross-sectional area of flow in Whitewood Creek.

Because the injection data do not allow determination of the cross-sectional area of the transient-storage zones or the mass of sediment in contact with this component of streamflow, desorption from a 1-cm-thick zone of bed sediment is calculated to illustrate the potential contribution of the bed sediments to the diurnal cycle in C_{As} . The assumption was made that a 1-cm-thick zone is in chemical equilibrium with streamflow and that water in this zone exchanges rapidly with streamflow. The amount of arsenic that can desorb from a 1-cm-thick zone of streambed sediments during an increase in pH is calculated by simplifying equation II-6 to

$$\Delta C_{As}^{bs} = f_d B_{As} (1 - \phi) \rho_b Z_{bs} A_c \quad (\text{II-10})$$

where

$$\Delta C_{As}^{bs} = \text{change in } C_{As} \text{ due to desorption from bed sediments, in micromoles per liter per day;}$$

and

$$f_d = \text{fraction of } B_{As} \text{ that desorbs because of increases in pH.}$$

For a pH increase from 8.15 to 8.35, f_d is about 0.015 based on the arsenic adsorption and isotopic-exchange experiments (figs. II-9 and II-10). The arsenic concentration ($6.4 \pm 1.0 \mu\text{mol/g}$) of fine sand (63 to 210 μm ; U.S. Geological Survey, unpub. data, 1987) was used to represent arsenate sorbed onto ferrihydrite coatings of sediments, B_{As} . Using a value of 0.5 for fine-sand bed-sediment porosity, ϕ , and a density, ρ_b , of 2.5 g/cm^3 , a ΔC_{As}^{bs} of $4 \mu\text{mol/L}$ was calculated from equation II-10. Although this estimate is much greater than the measured fluctuation in C_{As} of $0.21 \mu\text{mol/L/d}$, the result suggests that the abundant sorbed arsenate in the bed sediments accounts for the cycle in C_{As} .

Additional Controlling Processes

Other physical and chemical processes, such as variation in stream discharge and ground-water inflow, also may contribute to fluctuation of C_{As} . The coincident diurnal variations in sulfate and the injected bromide measured at site A suggest an increase in stream discharge from upstream sources that dilutes both constituents during the day rather than an increase in ground-water inflow along the reach at night. The magnitude of the fluctuation in discharge (7 to 25 percent on the basis of sulfate and bromide, respectively), however, is insufficient to result in the magnitude of the measured diurnal variation in C_{As} and is out of phase with the C_{As} cycle.

Reductive dissolution of ferrihydrite by photoreduction of iron (McKnight and others, 1988) would result in a release of adsorbed arsenic. The magnitude of this process was not evaluated because low ferrous-iron concentrations in surface water suggest that either photoreduced iron undergoes rapid reoxidation and precipitation (most arsenic sorbed during coprecipitation) or that iron photoreduction is negligible.

Solubility controls of C_{As} are unlikely because few arsenic compounds are stable in well-oxygenated water (Crecelius and others, 1986; Cullen and Reimer, 1989). For example at site A, the log degree of saturation with respect to calcium arsenate [$\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$] ranged from -8.8 to -9.4 in the range of measured C_{As} , pH, and concentrations of dissolved calcium. These saturation indices were calculated using MINEQL (Westall and others, 1976) and a solubility product of 1.26×10^{-19} (Naumov and others, 1974). Evaluation of aluminum arsenate (AlAsO_4) was not possible because concentrations of dissolved aluminum were not determined. If the concentration of dissolved aluminum, however, is assumed to be in equilibrium with amorphous $\text{Al}(\text{OH})_3$ using the solubility and complexation constants of Lindsay and Walthall (1989), a log degree of saturation for AlAsO_4 on the order of -9 is estimated. These calculated saturation indices, which are many orders of magnitude below saturation, agree with calculations by Belzile and Tessier (1990) and indicate a lack of solubility control on C_{As} . In contrast to Belzile and Tessier (1990), no solubility calculation for ferric arsenate was made because ferric arsenates are unstable with respect to ferrihydrite at a pH greater than 2 (Robins, 1987). Ferric arsenates do not form during coprecipitation at the pH of 8.0 to 8.5 in Whitewood Creek (Waychunas and others, 1993).

The absence of other instream processes of sufficient magnitude to generate the measured fluctuation of C_{As} is evidence that the diurnal cycle in C_{As} at sites A and B are the result of arsenic adsorption and desorption processes on the surfaces of ferrihydrite on and in streambed sediments. The results of the laboratory experiments on the time and pH dependence of arsenate adsorption on synthetic 2-line ferrihydrite are consistent with the measured diurnal fluctuations of C_{As} .

Summary

At the time of this study, dissolved arsenic (C_{As}) in the lower reaches of Whitewood Creek was controlled primarily by adsorption and coprecipitation with ferrihydrite as reducing ground water that contained dissolved arsenic contacted the atmosphere and surface water. Subsequent diurnal variations in C_{As} resulted from shifts in the adsorption and desorption equilibrium in response to a biologically induced diurnal pH cycle. The primary source and sink of dissolved C_{As} in the diurnal cycling was arsenic adsorption and desorption by the abundant ferrihydrite in bed sediments. The rate of adsorption and desorption process caused the C_{As} cycle to lag behind the pH cycle. Thus, the dynamic equilibrium of the chemical processes that control C_{As} are coupled to biological processes in the stream. This cycle of pH determines the importance of adsorption and desorption in controlling C_{As} . Development of an adequate model for arsenic transport in Whitewood Creek will require incorporation of adsorption kinetic terms into an advection-dispersion reaction model (for example, see eq. II-4). The adsorption control of C_{As} by ferrihydrite and the large "reservoir" of adsorbed arsenic in the streambed should act to support C_{As} even during high stream discharge.

Despite the cycle in pH at site C, the absence of a diurnal cycle and the lower levels of C_{As} are difficult to resolve with the present data set. In this higher gradient reach of the stream, contaminated flood-plain deposits and bed sediments with arsenic concentrations and molar ratios of arsenic to iron exist that are similar to the lower reaches. Ground-water seeps that supply dissolved arsenic and fresh ferrihydrite precipitates to the stream are not visible. Either the aging of the ferrihydrite or the adsorption of organics on ferrihydrite surfaces may diminish the role of sorption on ferrihydrite in the cycle of C_{As} by decreasing the availability of sorbed arsenate for desorption and decreasing the number of available sorption sites.

Evaluation of the diurnal pH cycles in other surface waters and their effect on the partitioning, cycling, and availability of trace elements and nutrients need to be made in order to adequately apply geochemical and biological models. For example, diurnal pH cycles generated by algal photosynthesis may increase availability of nutrients such as phosphate as well as toxic elements such as arsenate, selenium, and trace metals through the shifting of sorption equilibria. Diurnal cycles in orthophosphate concentration observed in Whitewood Creek appeared to lag the pH cycle by about 6 hours. The phase of the fluctuation of dissolved phosphate suggested the light dependence of phosphate uptake. In this study, a phosphate fluctuation of similar magnitude and phase also was measured; however, the data are not reported here because the measured concentrations of phosphate (0.05 to 0.15 $\mu\text{mol/L}$) had an uncertainty of 20 percent or greater. In both studies, the net change in phosphate was more than an order of magnitude lower than the phosphate-uptake rate predicted by the carbon-fixation rate and Redfield ratios. This difference argues that

an additional source of dissolved phosphate exists such as phosphate adsorbed on ferrihydrite. The competition of arsenate and phosphate for adsorption sites on ferrihydrite, greater uptake rates for phosphate by algae, and the factor of 4 or more higher C_{As} than phosphate all act to mask the cycle of phosphate that would result from pH fluctuations alone.

Diurnal pH fluctuations should have a greater effect on the bioavailability of metals in more acidic systems in which metals are not as strongly adsorbed. The continual disturbance of the sorption equilibria may result in an increase in the residence time of metals in surface water and a decrease in the effective rate of the processes that remove reactive elements from a surface-water system.

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