ARSENIC GEOCHEMISTRY IN A GEOTHERMALLY IMPACTED SYSTEM: THE LOS ANGELES AQUEDUCT

THESIS BY

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Abstract

Elevated arsenic concentrations in the Los Angeles Aqueduct (LAA) derive from geothermal inputs in Hot Creek. This study examines arsenic geochemistry in three sections of the LAA system: Hot Creek, Crowley Lake and Haiwee Reservoir.

At Hot Creek, the accumulation of arsenic in the sediments is strongly influenced by hot springs and plants. Solid-phase arsenic is present as As(III) throughout the sediment column with an identifiable organic phase in the surface sediment and a sulfide phase in the deep sediment. Sediments carry only a small fraction of the arsenic load in Hot Creek. Concentration profiles obtained with a novel, high resolution pore water sampler reveal a net flux of arsenic out of the sediments. Sediment-water exchange of arsenic in Hot Creek depends on initial arsenic concentrations and the presence of other ions in solution; this latter effect may be partly due to colloid aggregation and peptization.

In Crowley Lake, water column profiles obtained during stratified and well-mixed conditions provide no evidence for sediment-water exchange of arsenic. Algal uptake and transformation of arsenic is not sufficient to perturb the distribution of arsenic species in the water column or to accumulate substantial arsenic concentrations in the sediment. Arsenic is associated, and immobilized, with sulfide in the sediments, which are permanently anoxic. Sediment arsenic concentrations are modestly elevated; release of arsenic from the sediments driven by decreased water column arsenic concentrations would be gradual and would not threaten the water quality of the LAA.

In Haiwee Reservoir, arsenic is deposited in the sediments as a result of the Los

Angeles Department of Water and Power's interim arsenic management plan. This solid-phase arsenic is unstable with respect to reductive dissolution of the iron oxyhydroxide with which it is associated. A strong redox gradient exists below the sediment water interface and solid-phase arsenic speciation evolves rapidly with depth from an As(V) to an As(III) phase. The potential for release of this arsenic to the overlying water poses a threat to the LAA water supply.

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Chapter 1

INTRODUCTION AND MOTIVATION

1.1 Arsenic in the Los Angeles Aqueduct Water Supply

The Los Angeles Aqueduct (LAA) delivers water from the Owens Valley to the City of Los Angeles (Fig. 1.1). The LAA provides up to 75% of the water supply for 3.7 million consumers. Arsenic concentrations in the LAA water supply are elevated due to geothermal inputs to tributaries in the Eastern Sierra Nevada mountains.

The historical annual average arsenic concentration delivered to the Los Angeles Aqueduct Filtration Plant in Sylmar is 20 μg/L (Stolarik and Christie 1999). Although this meets the current maximum contaminant level of 50 μg/L, this standard is under review. Compliance with the revised standard, which is anticipated to be 5 μg/L (USEPA 1999), will require treatment for arsenic removal.

Since March 1996, the Los Angeles Department of Water and Power (LADWP) has been operating an interim arsenic removal strategy so that the Hyperion Treatment Plant effluent can meet the National Pollutant Discharge Elimination System permit requirements for ocean discharge of less than 12 μg/L arsenic. This strategy involves the addition of ferric chloride and cationic polymer coagulants to the aqueduct at the Cottonwood Treatment Plant; the solids produced settle in Haiwee Reservoir, 27 km

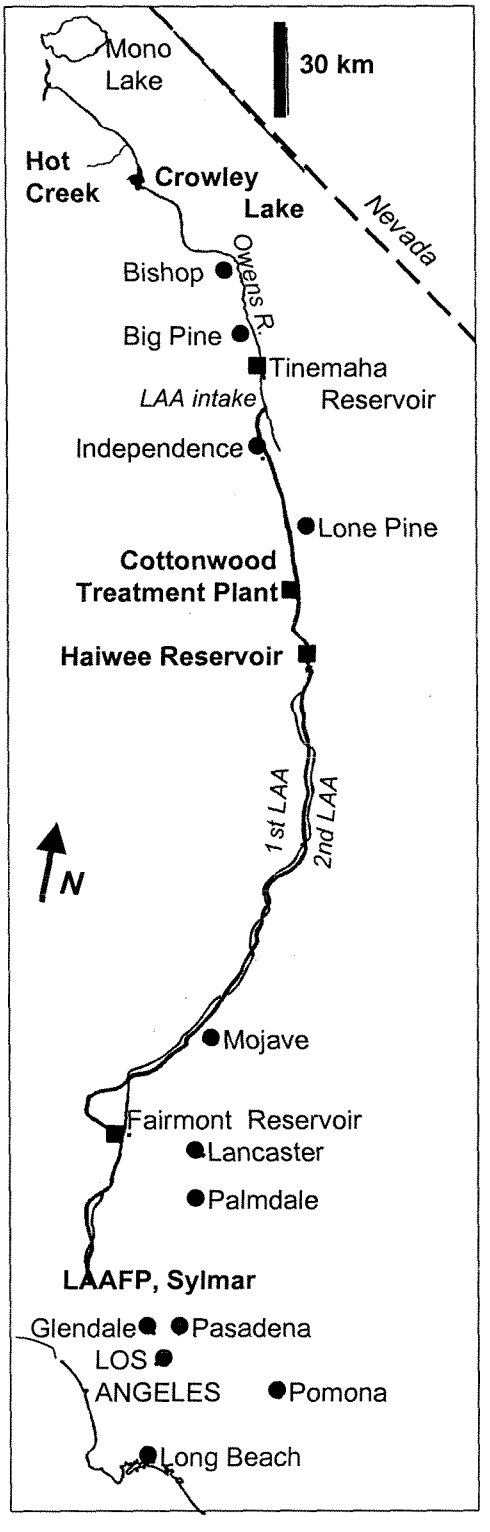

Figure 1.1: The Los Angeles Aqueduct (LAA) system, with points of interest to this study highlighted: Hot Creek, the Owens River, Crowley Lake, Cottonwood Treatment Plant, Haiwee Reservoir and the LAA Filtration Plant at Sylmar.

south of the application point (Stolarik and Christie 1999). Although this procedure is immediately successful in reducing the dissolved arsenic concentration in the LAA water supply, the accumulation of arsenic-bearing floc in Haiwee may prove problematic in the long-term.

The single largest contribution of arsenic to the LAA water supply is Hot Creek, specifically, the hot springs in the 0.4 km reach known as Hot Creek Gorge. Geothermal discharge, and hence arsenic flux, is relatively constant (Eccles 1976). Flow in the gorge typically ranges from 1 m^3/s (50 cfs) in winter to 6 m^3/s (200 cfs) following snowmelt (USGS 2000), while the total flow at Sylmar averages 18 m^3/s (650 cfs, LADWP 1989). The small volume and localized source of arsenic make Hot Creek an attractive site for a treatment facility for arsenic removal. Such treatment would have the added benefit of removing geothermal phosphorus which is responsible for eutrophication in Crowley Lake, the first and largest reservoir in the LAA system. If arsenic has accumulated in the sediments of Crowley Lake, its subsequent remobilization could compromise the effectiveness of arsenic removal at Hot Creek.

1.2 Scope and Objectives

Predicting arsenic release from the sediments in the LAA system following arsenic removal at Hot Creek is a complex problem. The objective of this research is to aid this prediction by examining the factors controlling the accumulation and mobility of arsenic in the sediments of three specific sections of the LAA system: Hot Creek, Crowley Lake and Haiwee Reservoir.

This thesis attempts to address the following questions:

(i) What is the extent of arsenic accumulation in the sediments of Hot Creek, Crowley Lake and Haiwee Reservoir?

(ii) What are the dominant mechanisms by which arsenic accumulates in the sediments of Hot Creek and Crowley Lake?

(iii) Which solid phases is arsenic associated with in the sediments of Hot Creek, Crowley Lake and Haiwee Reservoir, and does this give insight to the likelihood of release of arsenic from these sediments?

(iv) What controls the sediment-water exchange of arsenic in Hot Creek, and how might changes in water composition affect this?

(v) Are methylated arsenic species, of biological origin, important in the arsenic cycle in Crowley Lake and Haiwee Reservoir?

(vi) Is arsenic immobilized effectively in the sediments of Haiwee Reservoir, or is diagenesis compromising stability?

The accumulation and mobility of arsenic in sediments has been studied in many other rivers and lakes. An overview of the major findings of these studies is presented in Chapter 2. In Chapter 3, standard sediment analysis techniques are coupled with x-ray absorption fluorescence spectroscopy to examine the extent of, and mechanisms for, arsenic accumulation in Hot Creek and Crowley Lake sediment. The results of studies conducted in the laboratory on sediment-water exchange of arsenic in Hot Creek are reported in Chapter 4. In Chapter 5, water column profiles measured in Crowley Lake are analyzed to determine the potential for arsenic to be released from the sediments in this reservoir. The use of high resolution pore water sampling to determine the stability

of arsenic accumulated in Haiwee Reservoir sediment is reported in Chapter 6. Chapter 7 presents a review of works published regarding the uptake and transformation of arsenic by phytoplankton. The conclusions of this study are presented in Chapter 8.

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Chapter 2

GEOCHEMICAL ARSENIC CYCLING IN FRESHWATER-SEDIMENT SYSTEMS

2.1 Arsenic as a Sediment Contaminant

Instances of arsenic contamination of sediments are widespread. The average crustal abundance of arsenic is 1.8 μg/g (Lide 1994). In uncontaminated sites, arsenic concentrations have been reported in the range of 1 to 5 μg/g (Ferguson and Gavis 1972, Riedel et al. 1989). Enrichment factors of 10 to 10^3 have been reported in polluted sites (Riedel et al. 1989, Moore et al. 1988, Aggett and O'Brien 1985, Azcue et al. 1994) with maximum concentrations as high as 1000 μg/g in sediments and 6000 μg/L in interstitial waters (Azcue and Nriagu 1993, Aggett and Kriegman 1988).

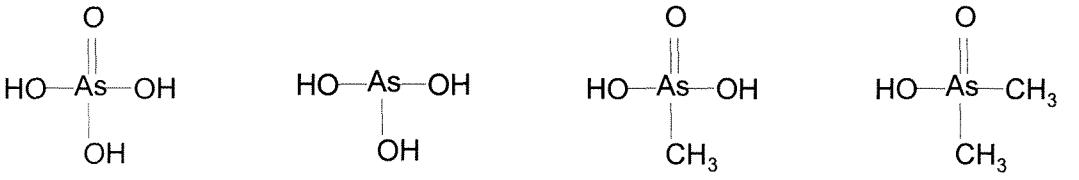
Arsenic enters waterways by both anthropogenic and natural pathways. The main anthropogenic sources are acidic leachate from mine tailings, smelting activity and run-off from agricultural land to which arsenical herbicides have been applied. It has been estimated that these sources constitute up to 70% of the total arsenic released to waterways annually. The remainder is attributed to natural sources including weathering and dissolution of arsenic-bearing minerals, such as magmatic sulfides and iron ores, volcanic activity and geothermal waters (Ferguson and Gavis 1972, Bhumbla and

Keefer 1994).

Sediments have long been viewed as an effective sink for heavy metals in aquatic systems. Adsorption onto sediment particles has been considered a permanent loss of heavy metals from the water column. It is now well documented that metals can be released from highly contaminated systems. In several systems receiving arsenic inputs, sediments have acted as a net sink for arsenic during the contamination period but a net source once the external loading was removed (Cornett et al. 1992, Bright et al. 1994, Azcue et al. 1994, Aurilio et al. 1994).

2.2 Arsenic Speciation in Natural Systems

Arsenic is ubiquitous in the environment. In natural water systems there are four major arsenic species, two inorganic and two organic (Fig. 2.1). Their different chemical and physical properties result in different mobility and toxicity. In most natural water systems the inorganic species are more abundant than the organic species (Spliethoff et al. 1995, Azcue et al. 1994).



Arsenic acid (arsenate)
pK_{a1} = 2.24
pK_{a2} = 6.96
pK_{a3} = 11.5

Arsenous acid (arsenite)
pK_{a1} = 9.26

Monomethylarsonic acid (MMA)
pK_{a1} = 4.19
pK_{a2} = 8.77

Dimethylarsinic acid (DMA)
pK_{a1} = 6.14

Figure 2.1: Arsenic species commonly encountered in natural waters. Acidity constants are for 25 °C, 0 ionic strength (Martel et al. 1993).

2.2.1 Inorganic Arsenic

The inorganic forms of arsenic, arsenite and arsenate, are more toxic than the organic forms. Arsenite, neutral at the pH of most natural waters, has the highest mammalian toxicity. It may bind to thiol groups, inhibiting enzyme activity. Arsenate may mimic phosphate and interfere with oxidative phosphorylation (Gorby 1994, ref. cit.). The lethal oral dose for 50% kill in rats is 20 μg/g for arsenite and 57 to 470 μg/g for arsenate (Richardson and Gangolli 1994). Chronic exposure to lower concentrations of arsenic can be carcinogenic (Smith et al. 1998).

In oxic systems, arsenate is thermodynamically stable, although frequently arsenite is also present as a metastable species. Similarly, in anoxic systems arsenite usually predominates but not always to the exclusion of arsenate (Aurilio et al. 1994, Azcue et al. 1994, Edenborn et al. 1986). These disequilibria are attributed to the disproportionate rates of oxidation and reduction of the species in natural, biotic systems (Freeman et al. 1986, Dowdle et al. 1996, McGheehan et al. 1996, Manning and Goldberg 1997 a). Bacterial reduction of arsenate can be very rapid while oxidation processes, which are usually abiotic, are frequently slower (Dowdle et al. 1996, McGheehan et al. 1996, Manning and Goldberg 1997 a). Bacterially mediated oxidation of arsenite in the Hot Creek system has been shown to be relatively rapid (Wilkie and Hering 1998).

It has long been recognized that arsenic mobility in sediment-water systems depends on its speciation (Kobayashi and Lee 1973). Arsenate, being anionic at the pH of many natural systems, is more strongly adsorbed by iron oxyhydroxides than arsenite. Since iron oxyhydroxides are an almost ubiquitous sediment component, arsenite is more mobile than arsenate in sediment-water systems when sulfide is not present

(Hermann and Neumann-Mahlkau 1985, Petersen et al. 1995, Manning and Goldberg 1997 b).

2.2.2 Organic Arsenic

There are many complex organic forms of arsenic, but the two most commonly found in natural waters are dimethylarsenate (DMA) and monomethylarsonate (MMA). These species have significantly lower mammalian toxicity than the inorganic species; the lethal oral dose for 50% kill in rats is 1800 μg/g for MMA and 640 to 1200 μg/g for DMA (Richardson and Gangolli 1994).

It is generally accepted that these species are of biological origin (Azcue et al. 1994, Sohrin et al. 1997, Millward et al. 1997). Methylated arsenic species have been observed in productive surface waters during periods of phosphorus limitation (Riedel 1993). Methylation by phytoplankton is possibly a detoxification mechanism following uptake of arsenate as a phosphate analog (Andreae and Klumpp 1979, Sanders and Windom 1980). Methylation was also observed in sediment microcosms to which arsenate was added under anaerobic conditions (Brannon and Patrick 1987).

There are arsenic contaminated sediment-water systems in which no organic arsenic species have been detected (Aggett and O'Brien 1985, Ficklin 1990) and others in which they dominate the speciation at certain times of the year (Anderson and Bruland 1991, Riedel 1993, Millward et al. 1997). Except for cases of direct anthropogenic input of these compounds (for example, Grabinski 1981), when organic arsenic species are present in interstitial water they usually constitute less than 10% of the total arsenic (Azcue et al. 1994, Bright et al. 1996, Millward et al. 1997). Larger proportions have

been reported in the surface waters of productive lakes (Anderson and Bruland 1991).

Adsorption studies with iron oxyhydroxides have shown that, at pH < 7, the sorption of the organic species is intermediary between arsenate (highest sorption) and arsenite (lowest sorption). At pH > 7, the sorption of the organic species is less than either of the inorganic species (Xu et al. 1991, Bowell 1994). Thus, in systems where iron oxyhydroxides are present, the organic arsenic species should be more mobile than arsenate at all pH values and more mobile than arsenite at low pH. Ferrous sulfide is a moderately effective adsorbent of organic arsenic species (Kuhlmeier and Sherwood 1996).

Analytical difficulties and insufficiently sensitive detection methods have hindered study of organic arsenic species. Detection methods based on ion chromatographic (IC) separation coupled with inductively coupled plasma mass spectrometry (ICPMS) detection have recently been developed for other matrices (Sheppard et al. 1992, Inoue et al. 1994, Yehl and Tyson 1997). These may be modified for the study of natural water and sediment systems.

2.3 Redox Cycling of Arsenic in Lakes

2.3.1 The Role of Manganese and Iron

The redox cycle of arsenic in lakes has been shown to be closely linked to that of iron and manganese. Iron and manganese are both redox active at the redox potentials encountered in many natural systems. The reduced forms, Fe(II) and Mn(II) are

very soluble while the oxidized forms, Fe(III) and Mn(IV), form insoluble oxyhydroxides at all but very low pH values. The amorphous precipitates are very soluble when conditions become reducing. The net surface charge of the oxyhydroxide phases varies with pH. Each phase has a characteristic pristine point of zero charge (PPZC). Electrostatic effects favor anion adsorption below the PPZC. However, even above the PPZC, cation adsorption may reverse the surface charge, thus favoring anion adsorption. A major pathway for inorganic arsenic flux from the dissolved to the particulate phase in oxic surface waters is adsorption onto, or co-precipitation with, these manganese and iron oxyhydroxides (Aggett and Roberts 1986, Azcue et al. 1994, Sullivan and Aller 1996). The consistency of As:P and P:Fe during sediment dissolution with ethylenediaminetetraacetic acid suggested that co-precipitation at the time of formation was more likely than adsorption to iron oxide surfaces in Lake Ohakuri (Aggett and Roberts 1986).

In a stratified lake with an oxic epilimnion and an anoxic hypolimnion, reduced iron and manganese dissolved in the hypolimnion will become oxidized upon diffusion into the epilimnion. The resulting oxyhydroxide particulates will be subject to gravitational settling and, upon descending to a sufficiently reducing environment in the hypolimnion, will undergo reductive dissolution. This redox cycling results in the maximum dissolved phase concentration occurring below the position of maximum particulate phase concentration (Fig. 2.2). If the settling oxyhydroxides reach the sediment, release of manganese and iron from the sediment may occur as stratification intensifies. Such release is inferred from water column concentrations increasing with depth and gradients intensifying with stratification. Arsenic scavenged by these oxyhy-

droxide phases in the oxic zone may, therefore, be either released in the anoxic zone of the water column, or transported to the sediment and released as anoxia intensifies (Fig. 2.3).

Manganese oxides formed upon lake turnover have been implicated in oxidizing arsenite; in the epilimnion, particulate manganese and dissolved arsenate concentrations increased while the arsenite concentration decreased (Kuhn and Sigg 1993).

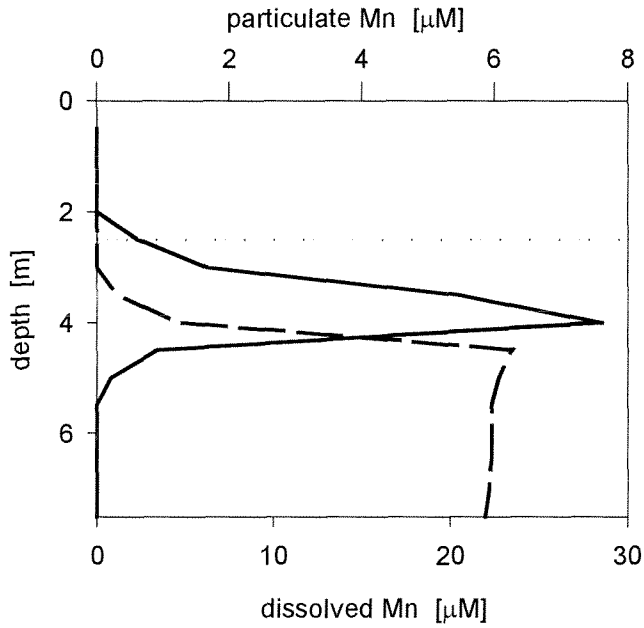


Figure 2.2: Particulate (—) and filterable (– –) manganese measured in Lake Fukami-ike. The dotted line (····) indicates the boundary between oxygenated surface water and deoxygenated bottom water (adapted from Yagi 1996).

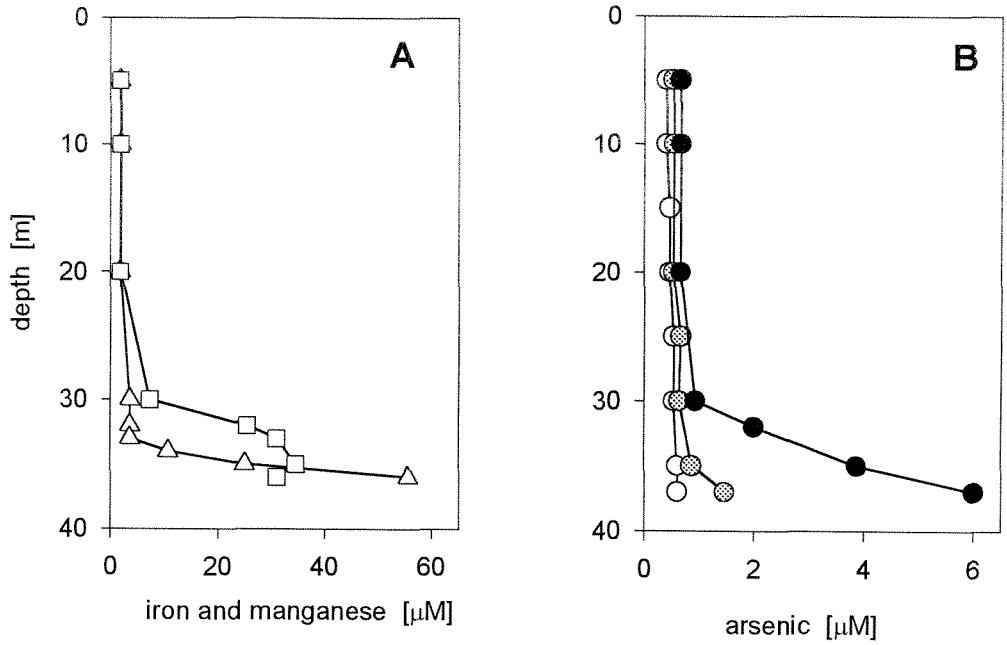


Figure 2.3: A: Iron (Δ) and manganese (□) measured at Lake Ohakuri in April 1986. The dotted line indicates the boundary between oxygenated surface water and de-oxygenated bottom water. B: Arsenic measured in Lake Ohakuri as stratification intensifies from well-mixed (○) to fully stratified (●). (Adapted from Aggett and Kriegman 1988).

2.3.2 The Role of Phytoplankton

Arsenic speciation in lakes often displays seasonal variation. The organic forms are sometimes more prevalent in summer (Fig. 2.4). The speciation of organic arsenic is controlled by biological processes such as phytoplankton metabolism and bacterial decomposition of organic matter (Riedel 1993, McLaren and Kim 1995, Millward et al. 1997, Sohrin et al. 1997). In stratified lakes, arsenate depletion has been observed together with the appearance of arsenite, DMA and MMA in the epilimnion (Kuhn and

Sigg 1993, Anderson and Bruland 1991).

Uptake of arsenic by phytoplankton would lead to deposition of arsenic with the dead algal matter and, ultimately, release of arsenic upon remineralization. Phytoplankton also constitute a source of particulate organic matter, but adsorption to this has been shown to be an unimportant sink for dissolved arsenic in lakes (Faye and Diamond 1996).

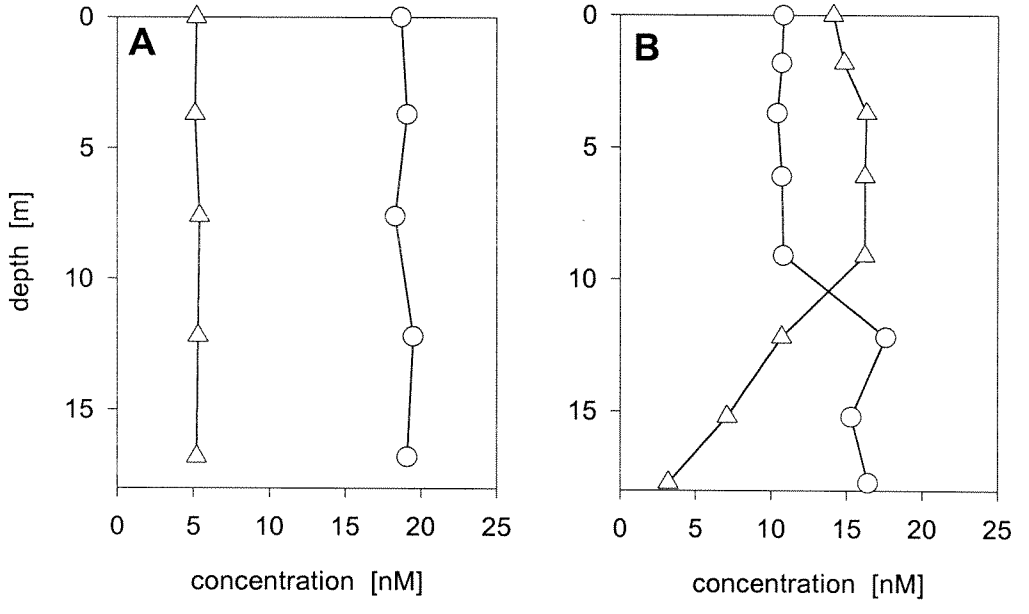


Figure 2.4: Inorganic (○) and organic (△) arsenic species in Davis Creek Reservoir, California, measured during well-mixed conditions (A) and stratified conditions (B). Under stratified conditions, only the upper 10 m is well oxygenated. Note that inorganic arsenic, As(V) + As(III), is dominant in well-mixed conditions, whereas organic arsenic, DMA + MMA, is dominant in the epilimnion under stratified conditions (adapted from Anderson and Bruland 1991).

2.4 Redox Cycling of Arsenic in Sediments

2.4.1 Transport of Arsenic to Sediments

Arsenic is transferred to sediments either by deposition of arsenic-bearing particulate matter in the water column or by adsorption onto or co-precipitation within the sediments themselves. The former route relies on advection of particulate matter, the latter on diffusion of dissolved species from overlying surface water or permeating ground water. Deposited particulate matter includes algal material and iron and manganese oxyhydroxides with which arsenic is associated.

Arsenic is sorbed to varying extents by different minerals (Xu et al. 1991, Bowell 1994) and soils (Manning and Goldberg 1997 b, Smith et al. 1999). Specifically, adsorption onto iron oxides has been shown to be more favorable for arsenate than arsenite while adsorption to quartz is minimal for both species (Xu et al. 1991). This is most likely an electrostatic effect. Iron oxides have a net positive surface charge while quartz has a net negative surface charge at most environmentally interesting pH values. Arsenate is deprotonated and arsenite neutral at these same pH values, favoring adsorption of arsenate on the iron oxide surfaces. Adsorption is subject to competition effects from other anions, especially isoelectronic phosphate (Darland and Inskeep 1997).

Arsenic can accumulate in very reducing, sulfur-rich sediments, by formation of sulfide phases (Moore et al. 1988). These are formed within the sediment itself, by diffusion of reduced arsenic through interstitial water. This process may be enhanced by sulfate reducing bacteria (Rittle et al. 1995). In most freshwater sediments, sulfate

concentrations are low and the sulfide produced by sulfate reduction is insufficient to bind reactive iron fully. Thus, there is no excess sulfide available to sequester arsenic in the solid phase. However, in geothermally impacted systems, large amounts of sulfide may be introduced directly in the geothermal waters.

2.4.2 Sediment-Water Exchange of Arsenic

The main mechanism for arsenic flux out of sediments is reductive dissolution of both arsenic-bearing minerals and oxyhydroxide species to which arsenic is adsorbed (Aggett and O'Brien 1985, Azcue et al. 1994, Petersen and Carpenter 1986). Such reductive dissolution may be biologically mediated either directly or indirectly, in response to reducing conditions generated by biota. As conditions become increasingly reducing, manganese oxyhydroxides dissolve before iron oxyhydroxides. Arsenic adsorbed to a manganese species and released upon its dissolution may be rapidly readsorbed to an iron oxyhydroxide which has not yet undergone reductive dissolution. Since manganese and iron oxyhydroxides often co-occur in natural systems, it is difficult to identify arsenic adsorbed to manganese oxides.

Dissolution of sulfide minerals may be a source of arsenic to overlying water in sulfide-rich, geothermal environments (Eary 1992, Webster 1990).

Microorganisms can enhance the flux of arsenic from sediments (Millward et al. 1997, Riedel et al. 1989, Riedel et al. 1997). This can occur by reduction of arsenate to the more mobile arsenite (Ahmann et al. 1997, Harrington et al. 1998).

The diffusive flux of arsenic from contaminated sediments is determined by pore water concentrations. Pore water concentrations are not necessarily determined by

the total arsenic present but by the phase with which it is associated, and the redox conditions persisting in the sediment (Brannon and Patrick 1987). In oxic systems, oxyhydroxide phases will control arsenic concentrations in interstitial water while in anoxic systems sulfides may be controlling (Moore et al. 1988).

The ability of sediment to sequester and/or release arsenic is dependent on several factors, including mineralogy, grain size, leachate composition, and redox conditions. In dredged sediments, the greatest arsenic release was observed in sediments with low iron and calcium carbonate content (Brannon and Patrick 1987). Extractions with oxygenated, deionized water leached 25% of total arsenic from calcerous sediments, whereas more than 60% was leached from organic rich sediments (Kobayashi and Lee 1978). Smaller grain size results in higher reactive surface area in a sediment, and this can significantly affect the extent of adsorption (Jain et al. 1999, Manning and Goldberg 1997 b). The presence of calcium in solution has been shown to enhance adsorption of arsenic on ferrihydrite (Wilkie and Hering 1996). This is most likely an electrostatic effect due to the more positive net surface charge induced by calcium adsorption.

Arsenic may be transported with sediments and subsequently remobilized by dissolution (Bright et al. 1994). In a dynamic stream system, a significant fraction of the total arsenic load could be transported in the solid phase with the sediment compared with the dissolved phase in the overlying water.

First order diffusive flux calculations have been applied to assess whether continuous release of arsenic from a contaminated sediment is likely (Azcue et al. 1994). These require linear concentration gradients at the sediment-water interface and assume

no readsorption of dissolved arsenic within the sediments, so are not widely applicable.

2.4.3 Determining the Route of Arsenic Delivery to Sediments

Information regarding the mechanisms for arsenic delivery and accumulation in sediments may be obtained by examining sediment and pore water concentration profiles.

In most situations, the source of arsenic to sediments is deposition of particulate matter from the overlying water or diffusion of dissolved arsenic from the overlying water. The concentration profiles expected under such a regime depend on the position of the interface between the oxic and anoxic regions and the presence or absence of sulfide at depth. Figure 2.5 A is a schematic of solid and dissolved arsenic concentration profiles if the oxic-anoxic boundary is below the sediment water interface, as is the case in most well-mixed, freshwater systems. Arsenic adsorbed to oxyhydroxides in the water column settles and the solid phase arsenic maximum exists where these oxyhydroxides reside. Below the redox interface, reductive dissolution of these species releases arsenic to the dissolved phase. A second maximum solid phase concentration is possible if precipitation with sulfide occurs at depth. The maximum dissolved phase concentration persists between the positions of maximum solid phase association. Arsenic is released from the dissolving oxide phase with which it was transported to the sediment, enters the dissolved phase and diffuses up or down following concentration gradients. Readsorption to oxic surface sediment and precipitation with sulfides at depth provide sinks for dissolved arsenic.

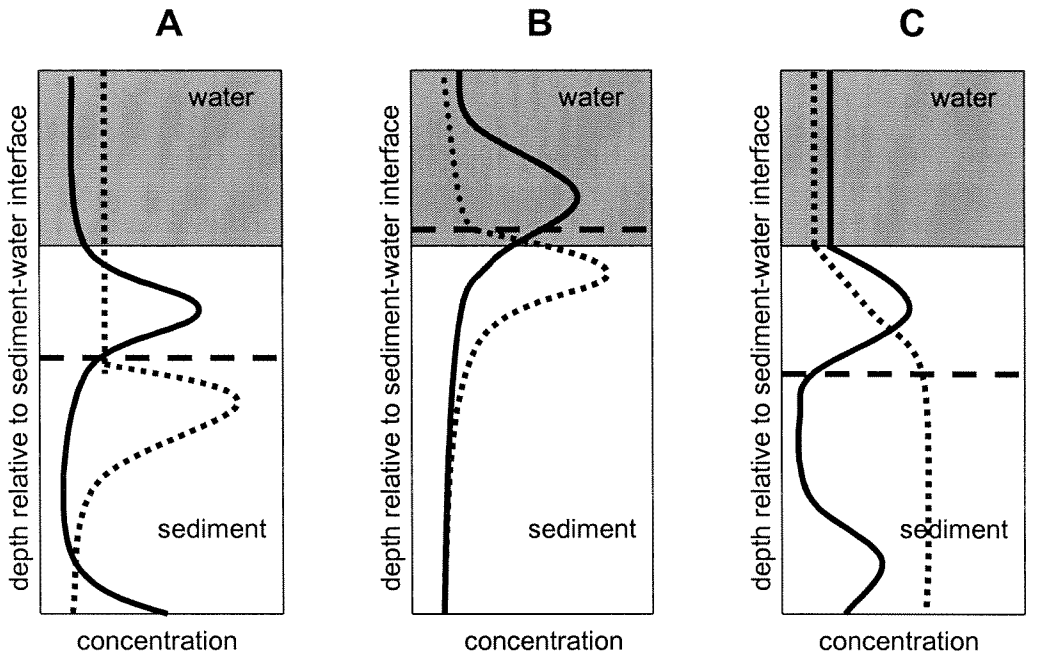


Figure 2.5: Schematic representation of solid phase (heavy solid line) and dissolved (dotted line) arsenic concentration profiles in a column of sediment (white) and overlying water (gray). The dashed line represents the redox interface. In A and B, the source of arsenic to the sediment is the water column, via advective transport of particulates or diffusion of dissolved species. In A, the redox interface lies within the sediment column, while in B it resides in the water column. In C, dissolved arsenic permeates the sediment from below, as in the case of geothermal input to a sediment bed.

If the redox interface occurs in the water column (Fig. 2.5 B), dissolved arsenic may be released to the overlying water. This has been observed in lake sediments under stratified conditions (Fig. 2.6). Indeed, a water column concentration profile in which an element's concentration increases with depth is a signature for release of that element from the sediment.

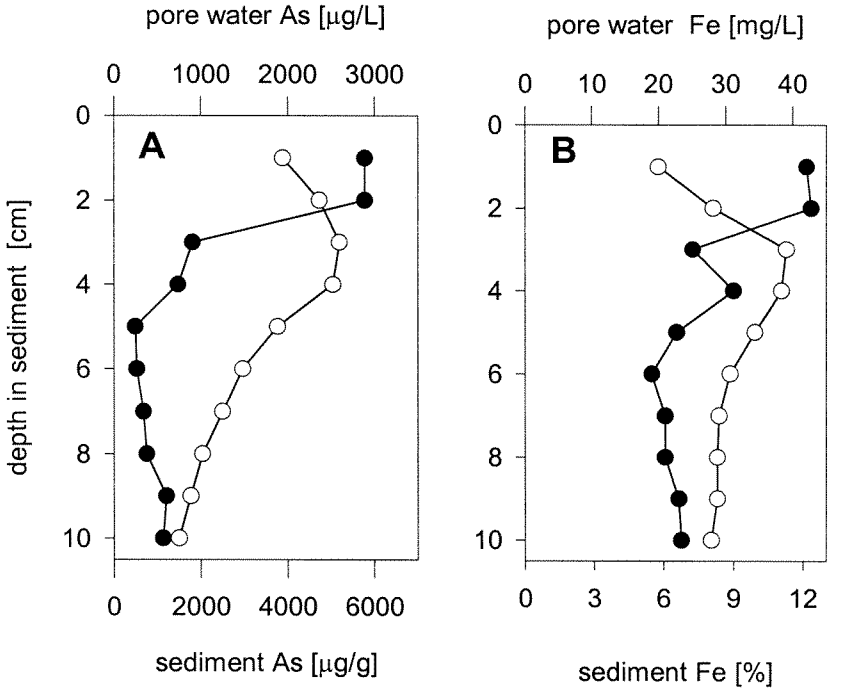


Figure 2.6: Solid phase (●) and dissolved phase (○) concentrations of arsenic and iron measured in Lake Ohakuri sediments during a period of release of arsenic from the sediment to the overlying water (adapted from Aggett and O'Brien 1985).

An alternate pathway for arsenic delivery to sediment may exist in geothermally impacted systems such as Hot Creek. Geothermal water permeating the sediment bed is reducing and enriched in arsenic and sulfide. This represents a very different source of arsenic to advection of particulate matter or diffusion of dissolved species from the overlying water column. If sufficient sulfide is present, the solid phase maximum arsenic concentration may be where precipitation with sulfides occurs at depth (Fig. 2.5 C). A second solid phase maximum may occur if the redox boundary resides within the sediment column and dissolved arsenic is adsorbed at the oxic surface layer. A constant source of buoyant, arsenic-rich fluid rising through the sediment column should result

in steady state concentration gradients. The dissolved phase will have a maximum at depth where the geothermal water first enters the sediment. The concentration gradient at the sediment-water interface should reflect the degree of mixing between the surface and interstitial water.

2.4.4 Early Diagenesis

Diagenetic processes are those which alter sediments following deposition. They include the reductive dissolution and microbial transformation processes discussed in Section 2.4.2, as well as physical processes such as compaction. The implication of diagenesis is that what has been deposited, and thereby immobilized, may be subject to alteration and remobilization. These processes can affect major changes in pore water chemistry very rapidly; in a 14 day experiment, sediment pore water profiles were established via diagenesis in previously homogeneous sediment cores (Petersen et al. 1995).

2.5 Concluding Remarks

The Los Angeles Aqueduct system is complex combination of surface water bodies. The Owens River, geothermally impacted by Hot Creek, flows into Crowley Lake, a large, eutrophic reservoir. The water is treated downstream of Crowley Lake, to accelerate deposition of arsenic-bearing particulates in North Haiwee, a smaller reservoir. The information presented in this literature review has been accumulated in laboratory, riverine and lacustrine studies. It provides a basis for understanding the

geochemical processes governing arsenic mobility in the complex Los Angeles Aqueduct system.

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Chapter 3

FORM AND ASSOCIATION OF ARSENIC IN THE SEDIMENTS OF HOT CREEK AND CROWLEY LAKE

3.1 Introduction

3.1.1 Motivation

Arsenic release from sediments is partially determined by the phase with which it is associated. Such association is determined initially by the mode of accumulation of arsenic in the sediment, but may be modified by diagenetic processes. Hot Creek and Crowley Lake are very different systems in terms of sedimentation and arsenic source. Hot Creek is subject to dramatic flow variations which affect sedimentation patterns, whereas sedimentation should be more gradual in the less dynamic Crowley Lake. Arsenic enters Hot Creek Gorge in hot, concentrated, reduced, geothermal fluid; it enters Crowley Lake in cold, less concentrated, well-oxygenated stream water.

In this study we examine the form and association of arsenic in the sediments of Hot Creek and Crowley Lake, attempting to elucidate the mechanisms by which arsenic has accumulated in these sediments.

3.1.2 Characteristics of Sediment Accumulation in Hot Creek and Crowley Lake

To understand the characteristics of sediment accumulation in Hot Creek and Crowley Lake, it is important to understand the flow regimes in these systems.

Flow in Hot Creek varies seasonally in response to snow melt. Minimum flows less than 1 m^3/s (30 cfs) are recorded in the winter months, while maximum flows are usually in the range of 3 to 6 m^3/s (100 to 200 cfs). A 1997 measurement of 12 m^3/s (433 cfs) reflects the extent of flow variability in the system (USGS 2000). The seasonal high flow in Hot Creek scours sediment from Hot Creek Gorge. Sediment deposition in Hot Creek is influenced by stream flow and plants. Sediment is deposited in regions protected by embayments and the thick plant beds growing in the creek.

Hot Creek sediment is very heterogeneous. It is sandy in the main channel, where fine sediment has been carried away by high flow. Fine-grained sediments accumulate near the hot pools on the banks of the creek. We might expect that the physical heterogeneity of Hot Creek sediment will result in chemical heterogeneity. The distribution of arsenic in the sediments in Hot Creek Gorge will most likely be very heterogeneous and strongly influenced by proximity to bank and bed hot springs.

Hot Creek Gorge lies at an elevation of 2120 m above sea level, about 8 km upstream of the confluence of Hot Creek with the Owens River. The Owens River enters Crowley Lake approximately 4 km downstream of this confluence. Crowley Lake is 2070 m above sea level.

The springs in Hot Creek Gorge contribute a relatively constant volume of arse-

nic-rich water; approximately 0.24 m^3/s (9 cfs, USGS 1987). Annual average arsenic concentrations in Hot Creek, after mixing with stream water, are around 200 μg/L (CSWRCB 1993). Further dilution in the Owens River reduces this concentration to below 100 μg/L entering Crowley Lake (CSWRCB 1993).

In contrast to Hot Creek, Crowley Lake is a much less dynamic system. The annual average residence time in Crowley Lake, calculated using month-end storage values and average outflow rates, is 0.6 years. The month-end storage over the averaging period ranged from 118 x 10^6 m^3 to 201 x 10^6 m^3 (CDEC 2000), and the daily average flow rate from 0 to 19 m^3/s (0 to 690 cfs; Bagaus 1999). Sediments collected from deep-water sites in Crowley Lake are black and very fine, almost gelatinous. Coarse sediments, which should settle in the shallower areas of the lake, were not examined in this study. Due to the high productivity of Crowley Lake in the summer months, we might expect a large component of the sediment to be decaying algal material. Thus, the form and association of arsenic in the sediments of Crowley Lake will be very different from those in Hot Creek.

3.1.3 Determining the Source of Arsenic to Sediments

There are three possible routes of arsenic transport to the sediment in Hot Creek: (i) deposition from the water column of particulates to which arsenic is adsorbed, (ii) diffusion of dissolved arsenic from the water column and (iii) upwelling of arsenic-rich geothermal water. The arsenic concentration profiles in the sediment and pore water and the form and association of arsenic in the sediments might indicate which is the

major source of arsenic.

In Hot Creek Gorge, the overlying water contains a mixture of arsenite and arsenate. Rapid, biologically mediated oxidation of the arsenite in the geothermal waters results in arsenate being the dominant species several hundred meters downstream of the hot pools (Wilkie and Hering 1998). If the major source of arsenic to the sediment is deposition of particulate matter from the overlying water, arsenic should be adsorbed to the surface sediments, associated with oxide phases. A solid phase arsenic concentration maximum would exist at, or near, the surface of the sediment. Freshwater plants are known to methylate (Nissen and Benson 1982) and accumulate arsenic, with up to 1200 μg/g measured in some lake weeds (Aggett and Aspell 1980, Robinson et al. 1995). *Potamogeton pectinatus*, a long-fronded plant, is abundant in Hot Creek Gorge. It is possible that arsenic may be associated with this plant, either by incorporation within its tissues or adsorption to its surfaces. If this is the case, we might see arsenic associated with organic phases in the sediments where decaying plant material resides.

The hot spring water contains about 1 mg/L arsenic, predominantly as arsenite. If the major source of arsenic to the sediment is permeation of this water through bed springs, we should see high arsenic concentrations in the deeper sediments. Arsenic may also be associated with sulfide phases, which might precipitate within the deep sediments.

There are three possible sources of arsenic to the sediment of Crowley Lake: (i) direct transport of sediment from the Owens River with arsenic accumulated in it, (ii) deposition of oxides or other particulates present in the water column to which arsenic is adsorbed or (iii) deposition of phytoplankton which has incorporated arsenic. During

sediment transport from Hot Creek to Crowley Lake, any As(III) solid phases present in the sediment will most likely be oxidized to As(V). Thus, it will be As(V) that is transported with sediments from the well-oxygenated Owens River. In the well-oxygenated surface waters of Crowley Lake arsenic is present as arsenate, so it is this species that will be adsorbed to oxides or particulates in the water column. In the lake surface water, algal incorporation might involve methylation of arsenic. Within the sediment, however, diagenetic processes may alter the form of arsenic from oxidized to more reduced. If sufficient sulfate is present and conditions are sufficiently reducing, solid arsenic-sulfide phases may form. In this more stable depositional system, diagenetic processes may transform the phases with which arsenic was initially transported to the sediments.

3.2 Experimental Methods

3.2.1 Sample Collection

Sediment samples were collected from Hot Creek Gorge on 5 March, 11 May, and 29 July 1999. Sediment samples collected in March and July were from the main channel of Hot Creek Gorge and near springs in the banks (Fig. 3.1). Sediment samples in May were collected in an array around the outlet of the largest hot pool in the gorge (Fig. 3.2).

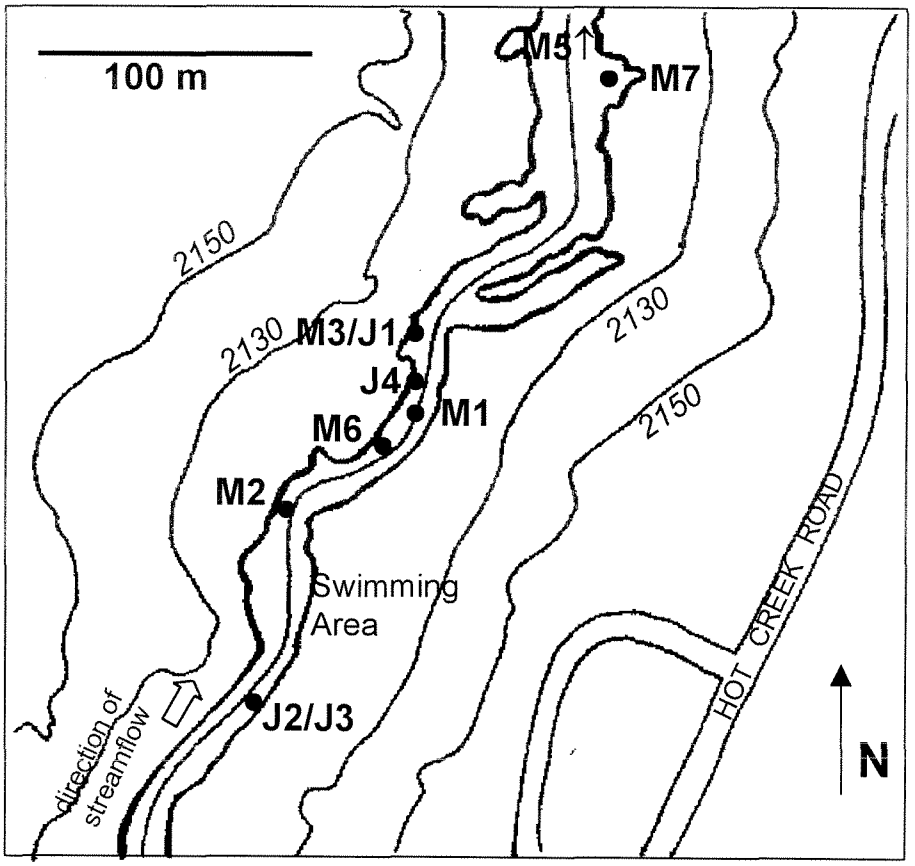

Figure 3.1: Sample collection sites in Hot Creek Gorge, March and July 1999. March sites are marked M1-M3, M5-M7, July sites J1-J4. Isoclines, marked in italics, represent meters above sea level.

Sediment cores were collected in polycarbonate tubes, 9 cm internal diameter, stoppered and sealed upon collection. In the moments prior to sealing the tubes, the bottommost sediment section is exposed to oxygen and it is possible that reduced manganese and iron species may be oxidized and precipitate out of the dissolved phase in the very deepest section of pore water collected. Sediment cores were transported, upright, on ice to the laboratory where they were frozen before further processing.

core	T [°C]	conductivity [µS/cm]
1	57 – 63	1400 – 1800
2	31 – 35	570 – 740
3	30 – 33	600 – 650
4	30 – 32	530 – 580
5	27.8	450
6	27.3	440
7	27.6	450

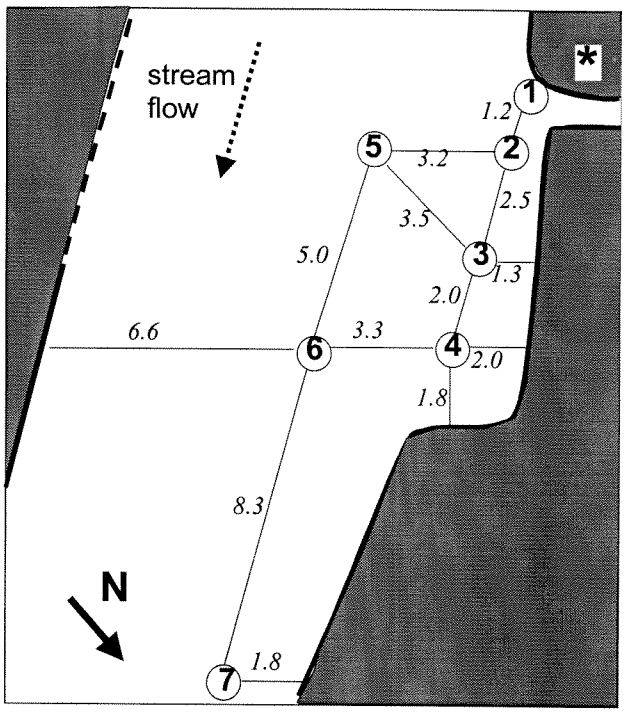

Figure 3.2: Sampling sites in Hot Creek Gorge, May 1999. Distance in meters is indicated in italics and core numbers are enclosed in circles. The position of the hot pool outlet is marked with an asterisk and the approximate stream bank marked with the heavy black line. The table at left shows temperature and conductivity measured at 0.2 m depth in stream water at each site.

Stream water samples were collected in July from approximately 0.2 m depth at each site. These were processed in the field for separation of arsenate from arsenite (Wilkie and Hering 1998). Aliquots of the whole sample were taken for total and filterable arsenic analyses. All water samples were transported to the laboratory on ice. Plant samples were collected in July 1999 from the main channel of Hot Creek Gorge.

Surface sediment samples were collected from Crowley Lake on 30 July 1999 from two sites (Fig. 3.3). Dissolved oxygen profiles of the water column were meas-

ured with a Hydrolab Data Sonde 4A equipped with Surveyor 4A display. Sediment samples were collected using an Ekman Bottom Grab sampler (Wildco) and sub-sampled into polycarbonate tubes, 3.5 cm inner diameter. The tubes were stoppered immediately and the headspace displaced with nitrogen. The sub-samples were stored on ice for transport to the laboratory where they were frozen, within 10 h of collection.

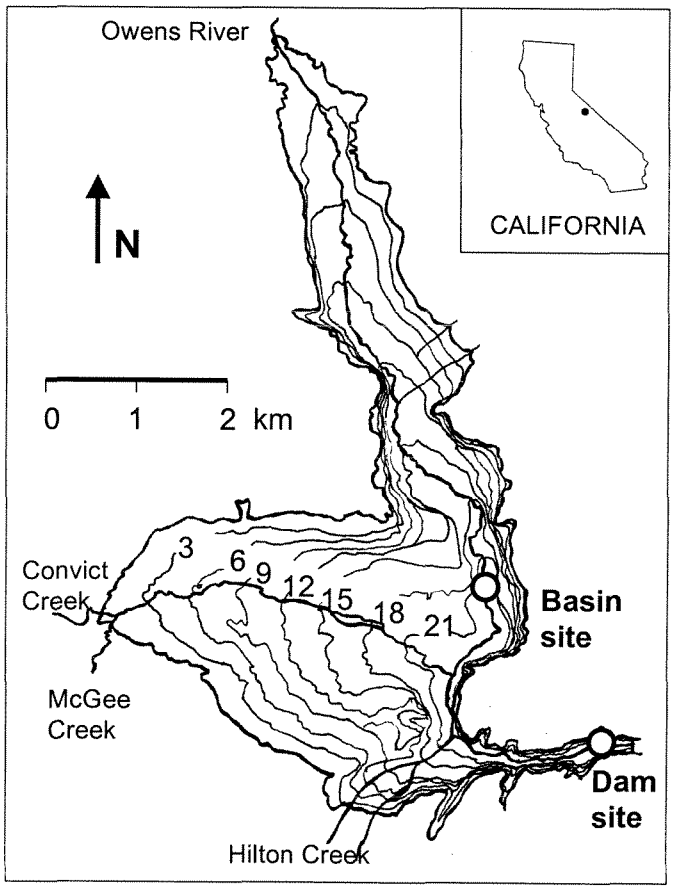

Figure 3.3: Sediment sample collection sites in Crowley Lake, July 1999. Basin and dam sites are marked with circles. Isoclines are in meters.

3.2.2 Sample Preparation

In the laboratory, frozen sediment cores were partially defrosted and extruded from the polycarbonate liners in a nitrogen atmosphere chamber. Sections were double-bagged in the chamber and returned to the freezer before defrosting.

The sections were defrosted and homogenized by kneading the bags. The bags were opened in the nitrogen chamber and sub-samples transferred to centrifuge tubes. Following 5 min centrifugation at 10,000 rpm, the supernatant was removed in a nitrogen atmosphere, filtered through a 0.45 μm cellulose nitrate membrane and diluted for metals analysis. The shear induced by centrifugation may generate colloidal material which would not be removed by the 0.45 μm filters used. Thus, the pore water concentrations obtained by this method are upper limits on the true, dissolved phase concentrations. Due to the disruptive nature of grab sampling, pore water samples were not extracted from Crowley Lake sediments.

Sediment sub-samples were taken for whole sediment digestion, and other analytical techniques outlined in Section 3.2.4. Samples for analysis by the x-ray techniques were ground to a fine paste in the nitrogen chamber.

3.2.3 Analytical Methods

The whole sediment digestion followed USEPA Method 6010, modified by omitting the final addition of HCl and using ICPMS for analysis. Sediment and plant samples were oven dried and refluxed with concentrated nitric acid, then 30% hydrogen peroxide was added. The digestate was filtered (0.45 μm, cellulose nitrate) and diluted

appropriately for metals analysis. This is not a complete sediment digestion; digestion of a reference soil (SRM 4711, NIST) and comparison with whole sediment concentrations obtained by x-ray fluorescence (XRF) suggest that it removes more than 75% of the arsenic in our samples. Sediment concentrations reported throughout as μg/g are on a dry sediment mass basis.

The total elemental concentrations in samples collected in March and July were determined by XRF. The samples were analyzed at EMMA Analytical Inc., a commercial laboratory, using the Energy-dispersive Miniprobe Multielement Analyzer developed by Drs. A. Cheburkin and W. Shotyk. Low detection limits are achieved using a monochromator to excite the sample with specific x-ray energies.

A selection of the July samples were subjected to total organic carbon (TOC), acid volatile sulfide analysis (AVS), sequential extraction and x-ray absorption spectroscopy (XAS).

TOC was measured by combustion using the thermal-optical instrumentation developed by Birch and Cary (1996). Pre-weighed samples are heated to 820 °C in a helium atmosphere. Volatilized carbon is first oxidized to carbon dioxide in a granular MnO_2 bed, then reduced to methane in a Ni/firebrick methanator, and the methane is quantified. The carbonate carbon peak was identified and subtracted from total carbon to obtain TOC.

AVS was determined using the method of Davison and Lishman (1983). The sample was heated with HCl in a sealed, borosilicate glass syringe and the sulfides released were stabilized with zinc acetate solution. Following filtration and addition of the reagents required for ethylene blue formation, the absorbance was measured at 670

nm (Shimadzu UV-2101 PC).

Sediment samples from the 0-3, 9-13 and 18-20 cm sections of core J1 collected from Hot Creek in July and from each of the two sites in Crowley Lake were subjected to a sequential extraction procedure. Extractions were run in duplicate on 1 g samples of dry sediment. Following each extraction step, the samples were centrifuged, the supernatant filtered (0.45 μm, cellulose nitrate) and the remaining sediment washed with 10 mL of 18.2 MΩcm water before the subsequent extraction. In the first extraction, sediments were shaken with 8 mL of 1 M $MgCl_2$ solution, at room temperature for 1 h. This step should extract the exchangeable fraction of arsenic in the sample (Tessier et al. 1979). In the second extraction, the samples were shaken with 8 mL of 1 M NaOAc (adjusted to pH 5 with HOAc) at room temperature for 5 h. This solution should extract carbonate phases from the sediment (Tessier et al. 1979). The third extraction was 20 mL of 0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAc, at 96 ± 3 °C, for 6 h with occasional agitation. This extraction solution should dissolve iron and manganese oxyhydroxide phases (Tessier et al. 1979). The fourth extraction was 10 mL 0.1 M sodium pyrophosphate (pH 10), at room temperature for 12 h. This solution should extract arsenic associated with organic phases (Moore et al. 1988). For the final extraction, the sediment was combined with 1 g of $KClO_3$ per gram of sample and 10 mL concentrated HCl and left to stand for 30 min. The solution was then diluted with 10 mL of 18.2 MΩcm water and mixed. This should remove arsenic associated with sulfide phases in the sediment (Chao and Sanzolone 1977). Arsenic, manganese and iron were measured in solution after each extraction.

The XAS was performed on beamline IV-3 at the Stanford Synchrotron Radiation Laboratory. In XAS, a sample is scanned with x-ray photons in the range of 200 to 35,000 eV. Core photoelectrons are ejected when the incoming photon energy exceeds the electron binding energy. The fluorescence emitted by the decaying excited state is detected. The energy at which absorption occurs is determined by the core electron binding energy, and is, therefore, characteristic of the oxidation state of the absorbing atom. Neighboring atoms backscatter the emitted photoelectron wave. Deconvolution of interference patterns calculated at the central absorbing atom provides information about the identity and distance of the neighboring atoms. XAS spectra were collected at ambient temperature with a Si(111) monochromator. Edge spectra were analyzed using WinXAS 1.3 (Ressler 1998). Critical points are very sensitive to changes in the oxidation state and association of the target arsenic atom. Linear combinations of differentiated (with respect to energy) reference spectra are attempted until critical points are well-matched with the differentiated sample spectra. To provide a range of arsenic oxidation states and chemical environments in the reference spectra set, spectra were collected from sodium salts and 10 mM solutions of arsenite, arsenate, MMA, DMA, arsenobetaine, and arsenocholine, and the solids jarosite, scorodite, orpiment, am-As_2S_3 (freshly precipitated), arsenopyrite, and As-pyrite. Spectra of all samples and model compounds are included in Appendix A.

3.3 Results and Discussion

3.3.1 Extent of Arsenic Accumulation in Sediments

A modest accumulation of arsenic was observed in samples collected from Hot Creek in March, May and July (Tables 3.1, 3.2, 3.3). All sediment concentrations are expressed on a dry weight basis. Surface sediment arsenic concentrations ranged from 20 to 100 μg/g. This is considerably above the background arsenic concentrations for the region; less than 2 μg/g was detected in surface sediment upstream of Hot Creek Gorge in a preliminary survey in 1996. However, concentrations an order of magnitude higher have been measured in sediments at other contaminated sites (Aggett and O'Brien 1985, Azcue et al. 1994). Arsenic concentrations in interstitial waters separated by centrifugation were high, sometimes higher than the 1 mg/L measured in hot spring water. This is most likely due to the inclusion of colloidal material generated during centrifugation.

Solid phase iron concentrations were low, ranging from 0.4 to 1.3%. Manganese concentrations in the solid phase were also low, ranging from 70 to 700 μg/g.

The variability of concentrations between sites and with depth reflect the high flow variability and uneven deposition patterns in the gorge. The modest arsenic accumulation may be due to the low iron content and sandiness of the sediment as both features disfavor arsenic adsorption (Xu et al. 1991). The high flow in Hot Creek may leach arsenic from the sediments and probably carries uncontaminated sediment into Hot Creek Gorge, diluting the sediment in the gorge.

Table 3.1: Characterization of Hot Creek Sediment Collected 5 March 1999

		SEDIMENT			PORE WATER		
core	depth cm	As µg/g	Mn µg/g	Fe %	As mg/L	Mn mg/L	Fe mg/L
M1	0 - 2	19	242	0.73	2.4	0.32	0.88
	2 – 4	32	323	0.91	2.3	0.29	0.73
	4 - 6	35	288	0.84	2.8	0.20	1.0
	8 - 11	32	286	0.86	2.7	0.19	0.79
	11 – 13				1.3	0.17	1.2
M2	0 – 2				0.50	0.48	2.3
	2 - 4				0.67	0.31	1.5
	4 - 7				0.66	0.21	0.86
	7 - 10				0.72	0.18	0.56
	10 - 13				1.1	0.28	0.58
	13 - 17				1.4	0.20	0.50
	17 - 20				0.65	1.0	1.6
M3	0 - 2	29	340	0.80	2.8	0.20	0.78
	2 - 6	39	348	0.83	3.4	0.17	0.62
	6 - 9	36	435	1.1	4.2	0.13	0.55
	9 - 13	31	301	0.76	3.5	0.23	0.48
	13 - 17	83	498	1.1	1.3	0.45	0.72
	17 - 19				1.1	0.28	0.87
M5	0 - 2				0.10	0.040	0.23
	2 - 6				0.36	0.54	1.3
	6 - 10				0.27	0.50	0.57
	10 - 15				0.47	0.90	0.80
	15 - 18				0.46	1.3	1.8
M6	0 - 2				0.55	0.23	1.3
	2 - 5				1.4	0.069	0.81
	5 - 8				1.0	0.039	0.40
	8 - 11				1.5	0.083	0.37
	11 - 14				2.6	0.34	0.72
	14 - 18				1.1	0.038	0.57
	18 - 22				2.3	0.18	0.79
M7	0 - 2				0.052	0.47	0.41
	2 - 6				0.43	0.90	0.96
	6 - 9				0.60	1.0	1.9
	9 - 11				0.78	1.1	1.6
	11 - 13				0.69	0.87	1.5
	13 - 17				0.60	0.58	1.5
M8	0 - 1				0.24	0.23	1.8
	1 - 3				0.036	0.032	0.31
	3 - 5				0.063	0.13	0.31
	5 - 7				0.075	0.11	0.49
	7 - 9				0.063	0.36	0.78
	9 - 11				0.068	0.55	3.1
	11 - 13				0.067	0.086	0.69

Sediment concentrations by x-ray fluorescence, expressed on a dry weight basis.
Pore water concentrations by centrifugation.

Table 3.2: Characterization of Sediment Collected at Hot Creek, 11 May 1999

		SEDIMENT			PORE WATER		
core	depth cm	As µg/g	Mn µg/g	Fe %	As mg/L	Mn mg/L	Fe mg/L
1	0 - 3.5	38	400	0.66	0.45	0.84	1.5
	3.5 - 8.5	43	350	0.56	1.1	0.31	0.80
2	0 - 5	48	430	0.60	1.0	0.35	0.48
	5 - 7	49	590	0.52	1.7	0.21	0.30
	7 - 11	63	620	0.71	1.3	0.44	0.40
	11 - 13	67	690	0.88	0.53	0.38	0.83
3	0 - 4	101	590	0.87	3.2	0.26	0.86
	4 - 7	103	440	1.0	2.2	0.27	0.87
	7 - 10	51	290	0.85	2.0	0.28	1.4
	10 - 13	48	180	0.59	2.3	0.20	1.4
	13 - 15	130	300	1.1	4.3	0.44	1.3
4	0 - 2	34	240	0.51	0.26	0.16	0.33
	2 - 4	36	166	0.47			
	4 - 6	64	210	0.65	2.6	0.12	0.31
	6 - 8	95	190	0.66	1.3	0.083	0.19
	8 - 10				2.2	0.038	0.17
	10 - 12	248	260	0.95	3.3	0.054	0.17
	12 - 14	180	210	0.89	3.3	0.011	0.21
	14 - 16	123	190	0.87	2.6	0.31	0.21
	16 - 18	118	250	1.1	3.6	0.30	0.63
	18 - 20	117	310	1.3	4.5	0.033	0.52
5	0 - 3	45	95	0.46	3.0	0.17	1.4
	3 - 6	24	59	0.37	2.6	0.045	1.1
	6 - 8.5	17	50	0.34	1.6	0.029	1.1
6	0 - 1.5	50	140	0.55	1.1	0.33	0.81
	1.5 - 6	124	160	0.57	2.1	0.30	0.52
	6 - 11	83	116	0.49	2.7	0.52	0.43
	11 - 14.5	23	88	0.42	1.7	0.26	1.0
	14.5 - 19	23	91	0.36	1.4	0.41	0.27
7	0 - 2	16	82	0.42	0.70	0.075	0.53
	2 - 5.5	17	77	0.38	2.5	0.052	0.64
	5.5 - 10	17	74	0.38	2.1	0.052	0.60
	10 - 11	18	76	0.40	0.69	0.039	0.56

Sediment concentrations by partial digestion, expressed on a dry weight basis. Pore water concentrations by centrifugation.

Table 3.3: Characterization of Sediment Collected at Hot Creek on 29 July 1999

		SEDIMENT			PORE WATER		
core	depth cm	As µg/g	Mn µg/g	Fe %	As mg/L	Mn mg/L	Fe mg/L
J1	0 - 3	20	300	0.73	0.24	0.50	1.2
	3 - 9	62	330	0.81	0.25	0.96	1.5
	9 - 13	22	240	0.67	1.5	0.52	0.47
	13 - 18	23	280	0.69	2.8	0.20	0.64
	18 - 20	27	240	0.68	3.6	0.15	0.46
J2	0 - 4				0.65	0.14	0.33
	4 - 8				0.69	0.90	0.62
J3	0 - 3	51	420	0.88	1.1	0.62	1.0
	3 - 8	83	510	0.98	0.95	0.92	1.8
J4	0 - 5				0.46	0.98	1.3
	5 - 9				0.48	0.81	0.41
	9 - 13				0.63	0.88	1.1
	13 - 16				1.2	0.28	0.71

Sediment concentrations by x-ray fluorescence, expressed on a dry weight basis. Pore water concentrations by centrifugation.

Arsenic concentrations, determined by partial digestion, in the five sediment samples collected from the two sites in Crowley Lake ranged from 62 to 105 µg/g. XRF analysis gave 137 µg/g at the basin site and 262 µg/g at the dam site. The discrepancy may be the result of the difficulty in homogenizing this watery, gelatinous sediment. The moderate accumulation of arsenic in Crowley Lake sediment is consistent with the absence of an efficient mechanism to transport arsenic to the sediment (see Chapter 5).

3.3.2 Source of Arsenic to Sediments in Hot Creek

Two sediment cores collected from the main channel of Hot Creek Gorge in March and July (M3 and J1, Fig. 3.1) were chosen for comparison because of their similar core length and collection site. Despite these similarities, the two cores have very different vertical concentration profiles for arsenic, manganese and iron (Fig. 3.4). The concentration ranges are similar in both cores, but the solid phase and dissolved phase maxima occur at different positions. The pore water arsenic profile in M3 has a mid-depth maximum in the 6-9 cm section, while the pore water manganese and iron profiles are at, or near, their minimum in this section. In contrast, in J1 the pore water arsenic concentration is similar to that in the overlying water in the first 9 cm and then increases with depth below 9 cm, while the pore water manganese and iron maxima occur in the 3-9 cm section. The variability between the two cores illustrates the heterogeneity of the system.

Interpretation of the profiles is severely constrained by the limited vertical resolution. However, with this caveat in mind, some speculations may be made regarding the mechanisms of arsenic accumulation in these sediments.

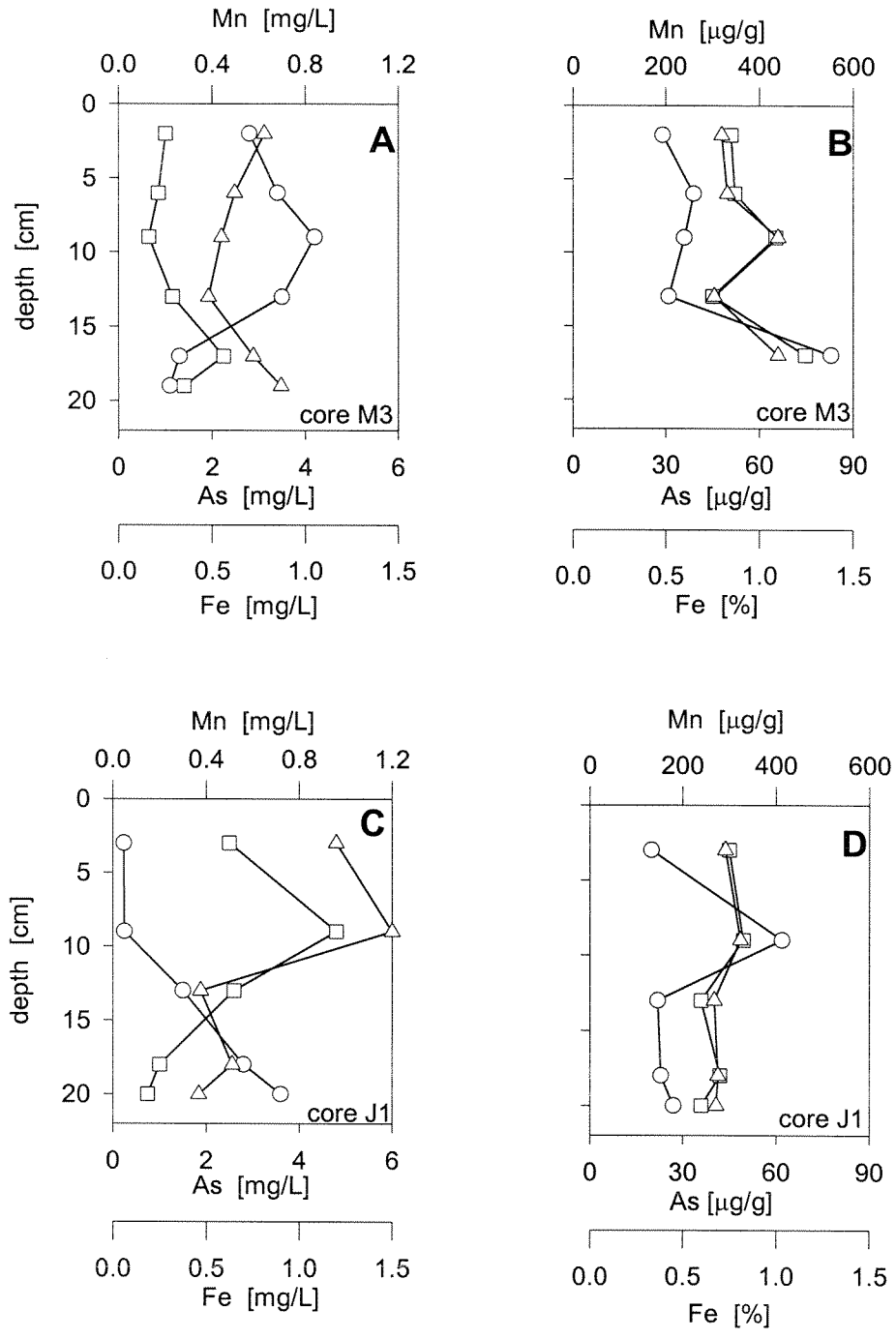

Figure 3.4: Pore water (A, C) and sediment (B, D) concentrations of arsenic (○), manganese (□) and iron (△) in sediment cores collected at Hot Creek Gorge in March (A, B, core M3) and July (C, D, core J1) 1999. Position of symbol denotes depth at bottom of section. Sediment concentrations are on a dry weight basis

3.3.2.1 Core J1: Direct Geothermal Input and Plant Material

The pore water profile of arsenic in J1 (Fig. 3.4 C) suggests that the dominant source of arsenic to the dissolved phase is a bed spring. Arsenic diffuses from the deep sediments, decreasing to a minimum in the 6-9 cm section. This pore water minimum coincides with a solid phase arsenic maximum (Fig. 3.4 D). Although the relative amounts of arsenic present in the dissolved and solid phase dictate that we should not expect the change in pore water arsenic concentration between the 9-13 and 3-9 cm sections to cause a noticeable change in the solid phase concentration, it is possible that the dissolved arsenic is sequestered by some solid phase in the 3-9 cm section.

In 1 g wet sediment in the 9-13 cm section of core J1, approximately 0.4 g is pore water and 0.6 g is dry sediment. We shall assume, for the sake of an order of magnitude calculation, that the pore water density is 1 g/mL. Thus, the distribution of total arsenic in the 9-13 cm section of core J1 is 0.6 mg in the pore water and 13 mg in the solid phase per 1 g of wet sediment. Therefore, we should not necessarily expect changes in dissolved phase concentration brought about by adsorption, desorption, precipitation or dissolution processes to be reflected in the solid phase profiles for these elements.

Arsenic concentrations in the solid phase are strongly correlated with total organic carbon in this core (Fig. 3.5). The sediment core J1 was collected from a region where sedimentation was protected from the stream flow by a plant bed. Two plant samples collected in the creek contained 260 and 1400 μg/g arsenic. Presumably, the

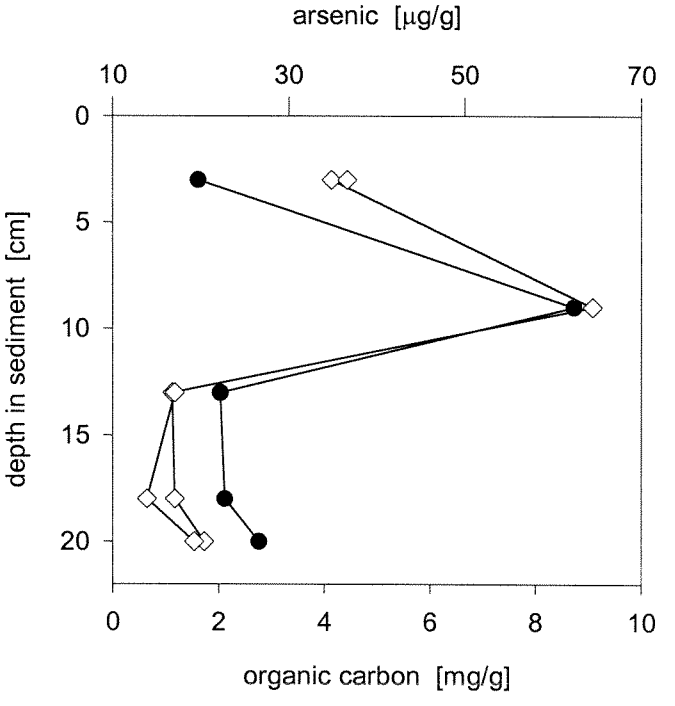

Figure 3.5: Arsenic by x-ray fluorescence (●) and total organic carbon by combustion (◇) in the sediments of core J1, collected from Hot Creek Gorge in July 1999. Position of symbol denotes depth at bottom of section.

plants are taking arsenic up from the stream water and accumulating it in their tissues. Buried, arsenic-enriched plant material may have contributed to the increased arsenic and organic carbon concentrations in the sediment in the 6-9 cm section of J1.

The plant samples contained 570 to 700 µg/g manganese and 0.15 to 0.2 % iron. The geothermal water permeating the sediment should have low concentrations of manganese and iron. In a 1985 study by the USGS, manganese and iron concentrations were measured in a hot spring and three geysers in Hot Creek Gorge. The hot spring

contained 12 μg/L manganese and < 3 μg/L iron, while the geysers contained 1, < 20 and 3 μg/L manganese and 3, < 10 and < 3 μg/L iron (Farrar et al. 1987).

3.3.2.2 Core M3: Decaying Plant Material?

The pore water profile in M3 (Fig. 3.4 D) suggests that the source of arsenic to the dissolved phase is not a bed spring. The maximum pore water arsenic concentration occurs in the 6-9 cm section. Diffusion up and down from this maximum could produce the observed pore water profile. Such diffusion requires a source of dissolved arsenic in the 6-9 cm section and sinks for dissolved arsenic above and below this section. Like J1, core M3 was collected from an area where sediment accumulation was protected by plant growth. The source of dissolved arsenic could, therefore, be decaying organic material at this depth, the presence of which was implicated in the J1 core. The solid phase concentrations of manganese and iron also have their maxima in the 6-9 cm section, suggesting the possibility that the source of dissolved arsenic may be dissolution of manganese and/or iron oxide phases with which arsenic is associated. However, the dissolved phase iron and manganese concentrations are at, or near, their minimum at this depth. This suggests that the source of dissolved arsenic in this section is not dissolution of manganese and/or iron oxide phases with which arsenic is associated. Such dissolution would be accompanied by an increase in the pore water concentrations of manganese and/or iron. The possible sinks for dissolved arsenic in the pore water are more easily identified than the source. The surface sink for dissolved arsenic in the pore water is most likely diffusion into the stream water, which has a much lower (0.19

mg/L) arsenic concentration. The deep sediment sink could be a solid phase, as solid phase arsenic concentrations increase between the 9-13 and 13-17 cm sections. This could be due to sequestration of arsenic from the dissolved phase by a sulfide phase in these deep sediments.

3.3.2.3 Effect of a Hot Pool Outlet

In May 1999, we attempted to investigate the effect on sediments of proximity to a hot pool outlet. Sediment cores were collected in an array around a hot pool outlet (Fig. 3.2) and sediment and pore water concentrations determined (Table 3.2).

The hot pool outlet has a significant impact on sediment composition. For the purposes of the correlation figures presented in Fig. 3.6, the cores were divided into two groups; those along the bank, near the hot pool outlet (cores 1 to 4) and those in the main channel (cores 5 to 7). Solid phase iron and manganese in the main channel cores were very strongly correlated. The corresponding correlation for the cores nearer the hot pool outlet was very weak (Fig. 3.6 A). This must be a direct effect of the proximity of these cores to the hot pool outlet.

Solid phase arsenic and solid phase iron were very weakly correlated in the cores near the outlet and slightly better correlated in the main channel cores (Fig. 3.6 B). For each element, pore water and solid phase concentrations were not correlated. There was no correlation between the pore water concentration of any two elements (Fig. 3.6 D-F).

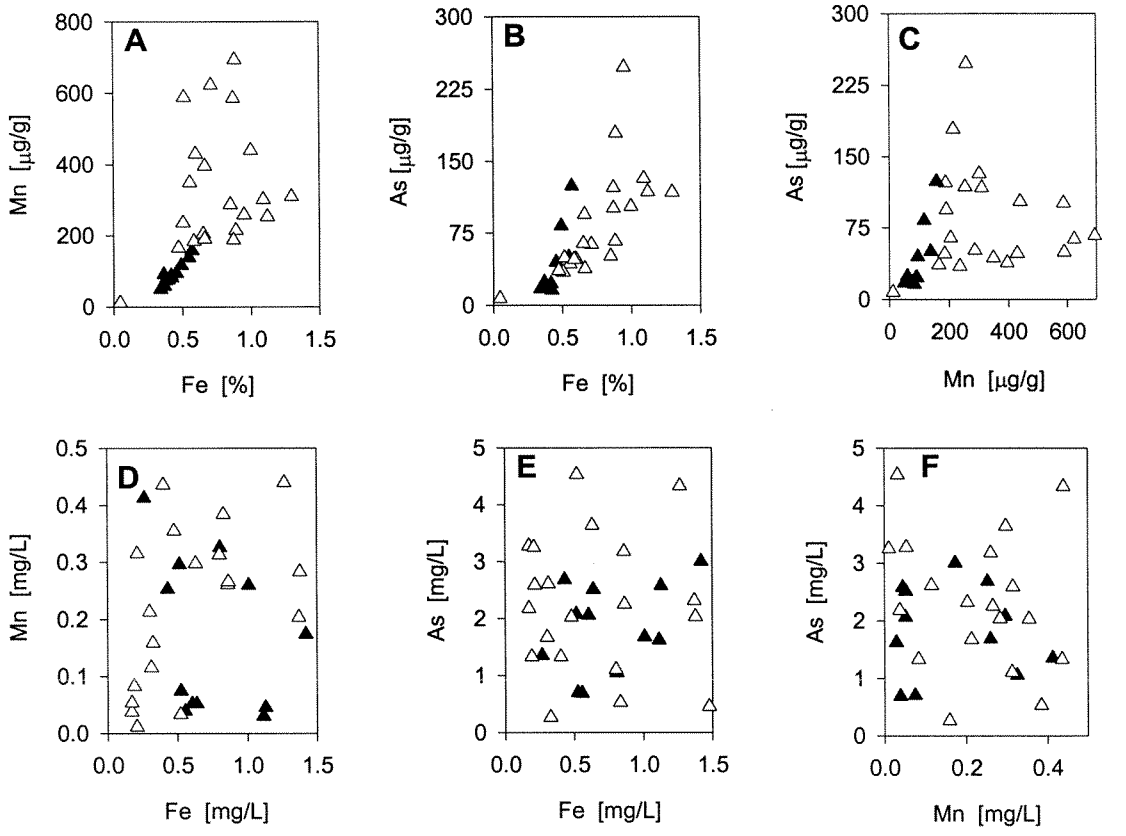

Figure 3.6: Sediment (A, B, C) and pore water (D, E, F) correlations between iron, manganese and arsenic in sediment samples collected May 1999. Cores 1 to 4 (△) were near a hot pool outlet and cores 5 to 7 (▲) were in mid-stream. Sediment concentrations are on a dry weight basis.

If the hot pool directly influences the dissolved and/or solid phase arsenic concentration in the sediments, we might expect arsenic concentrations to decrease with distance from the hot pool outlet, that is, decrease from core 1 to core 4. Solid phase and pore water arsenic concentrations in the surface sediment decrease between cores 3 and 4 but increase from core 1 to core 3 (Fig. 3.7). The maximum sediment and pore

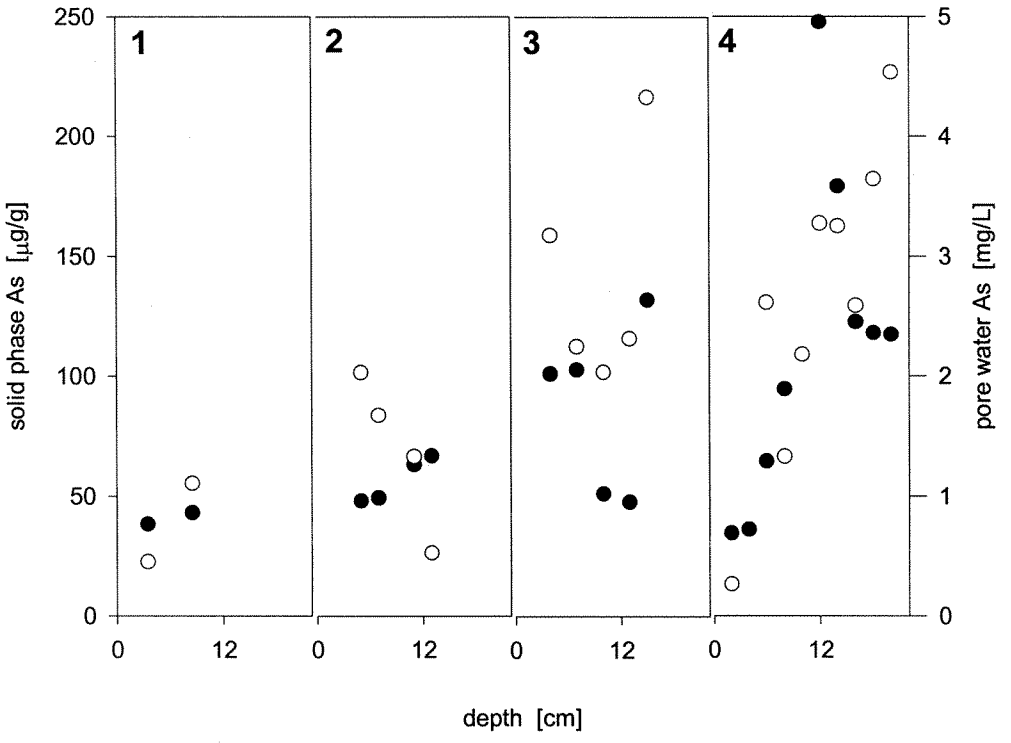

Figure 3.7: Arsenic concentrations in the solid phase (●) and pore water (○) in cores 1-4, collected in May 1999 from Hot Creek Gorge. Note that, in contrast to other figures throughout, depth in the sediment is shown on the abscissa, while concentrations are on the ordinate. Solid phase concentrations are on a dry weight basis. Cores were collected along the stream bank, with core 1 closest to a hot pool outlet and core 4 furthest from the outlet (see Fig. 3.2). Position of symbol denotes depth at bottom of section.

water arsenic concentrations in each core also increase with distance along the bank from the hot pool outlet. The maximum pore water arsenic concentrations in cores 3 and 4 occur in the deepest sediment, suggesting that these cores may be influenced by bed springs. This confounds our ability to detect a signal of the geothermal water from

the hot pool outlet in the sediments, as the bed spring arsenic concentration should be similar to the undiluted hot pool water, and therefore significantly higher than the diluted hot pool water in the overlying stream water.

In the main channel, far from the hot pool outlet (core 7), the solid phase vertical profiles are remarkably featureless (Table 3.2). The low solid-phase arsenic concentrations in the high flow area could be due to leaching of arsenic from the sediments by the stream water or dilution with uncontaminated upstream sediments carried into the gorge by the high flow.

3.3.2.4 May Core 4

As with the March and July data, the vertical resolution within each of the May cores makes it difficult to reach meaningful conclusions about correlation patterns in an individual core. However, core 4 was sectioned into 10 sections and therefore its profiles may bear closer scrutiny.

Unlike the M3 and J1 samples, core 4 was collected from an area free of plants. The pore water arsenic concentration in the uppermost section is comparable to the stream water concentration. The dissolved phase arsenic concentration increases with depth, suggesting that there is a bottom source of dissolved arsenic (Fig. 3.8 A). This may be a bed spring permeating the sediment bed. There is, perhaps, a secondary, local maximum in the pore water arsenic profile at 10-14 cm. Solid phase arsenic, iron and manganese and dissolved phase arsenic share a local maxima in the 10-12 cm section (Fig. 3.8). This suggests that the source of dissolved arsenic responsible for the secondary maximum could be dissolution of, or desorption from, iron- and manganese-

bearing solid phases. However, if this were true, the pore water manganese and iron concentrations should increase at the same depth, but this is not evident in the profiles. Pore water manganese concentrations only increase below 14 cm and iron below 16 cm. This suggests that the release of arsenic responsible for the secondary maximum is not due to reductive dissolution.

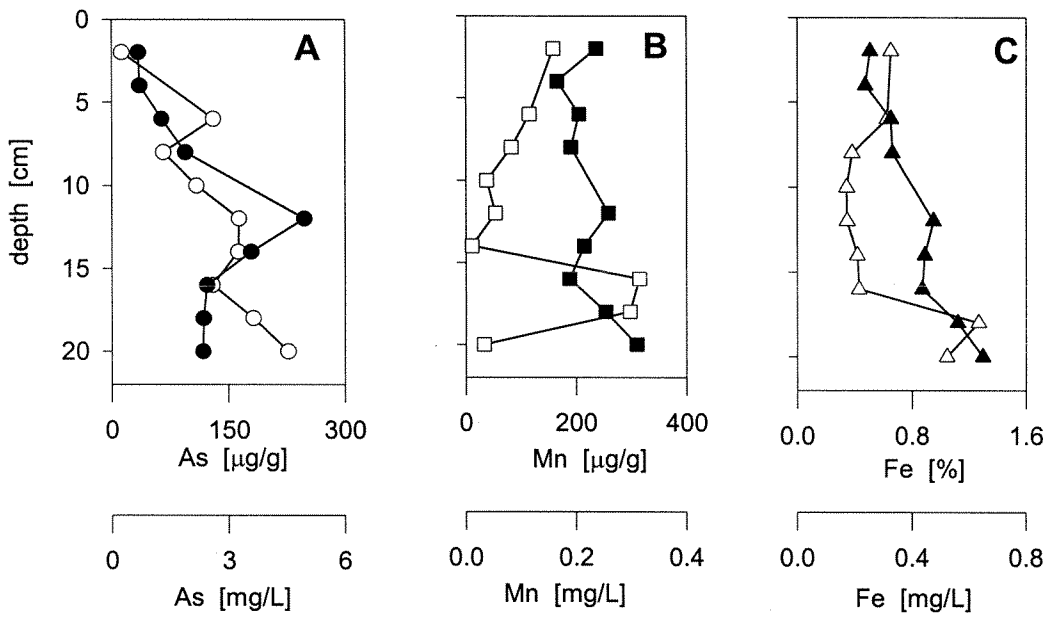

Figure 3.8: Solid phase (●, ■, ▲) and pore water (○, □, △) concentrations of arsenic (A), manganese (B) and iron (C) in sediment core 4 collected in Hot Creek Gorge, May 1999. Solid phase concentrations are on a dry weight basis. Position of symbol denotes depth at bottom of section.

The decrease in dissolved phase manganese and iron concentrations in the very deepest sediment section could be due to mixing with geothermal water, which has low concentrations of manganese and iron. It may also be an artifact of the sample collec-

tion technique; the bottommost sediment section is exposed to oxygen during collection and reduced manganese and iron species may be oxidized and precipitate out of the dissolved phase. However, a decrease in pore water concentrations in the deepest section is not evident in all cores.

3.3.2.5 Source of Arsenic to Sediments in Hot Creek: Concluding Remarks

Interpreting concentration profiles obtained in sediment cores collected in Hot Creek is difficult. It is clear that arsenic accumulation in Hot Creek sediments is strongly influenced by the presence of bed springs. The strong correlation of organic carbon with arsenic in the sediments of Hot Creek suggests that plants are likely to be influencing arsenic accumulation in these sediments. The main channel sediments have lower arsenic concentrations, suggesting that sequestration of arsenic from the stream water by adsorption onto sediment surfaces is not an important mechanism for arsenic accumulation in the sediments.

3.3.3 Transport of Arsenic from Hot Creek to Crowley Lake

An order of magnitude calculation comparing the export of arsenic from Hot Creek in the sediment with that in the dissolved phase suggests that less than 0.1% is carried with the sediment. This calculation assumes a sediment concentration of 20 μg/g arsenic, density 2.5 g/cm^3, an area of 300 m x 25 m, with 10% sediment coverage of 0.2 m depth, a streamwater average concentration of 200 μg/L (CSWRCB 1993) and yearly average flow rate of 1.7 m^3/s (60 cfs), based on an average of 79 cfs for 1998 and

57 cfs for 1990-1998 (USGS 2000). Under these assumptions, annual sediment export is $8f$ kg, where f is the fraction of sediment scoured, and the annual water export of arsenic is 1×10^4 kg.

Transport of arsenic out of Hot Creek occurs predominantly in the dissolved phase. Dissolved arsenic concentrations are diluted between Hot Creek and Crowley Lake. Therefore, there should not be significant adsorption of arsenic to sediments between Hot Creek and Crowley Lake. It is possible that some arsenic remains associated with the sediment, but we can reasonably expect that most transport of arsenic from Hot Creek to Crowley Lake is in the dissolved phase rather than associated with sediments.

3.3.4 Form of Arsenic in the Sediments of Hot Creek

3.3.4.1 X-Ray Absorption Spectroscopy

Core J1, collected in Hot Creek Gorge in July 1999, was analyzed by XAS. The XAS spectra revealed dramatic changes with depth in Hot Creek sediment (Fig. 3.9 A). Each section contained two distinct arsenic phases, as evidenced by the double maxima in each absorption edge spectrum.

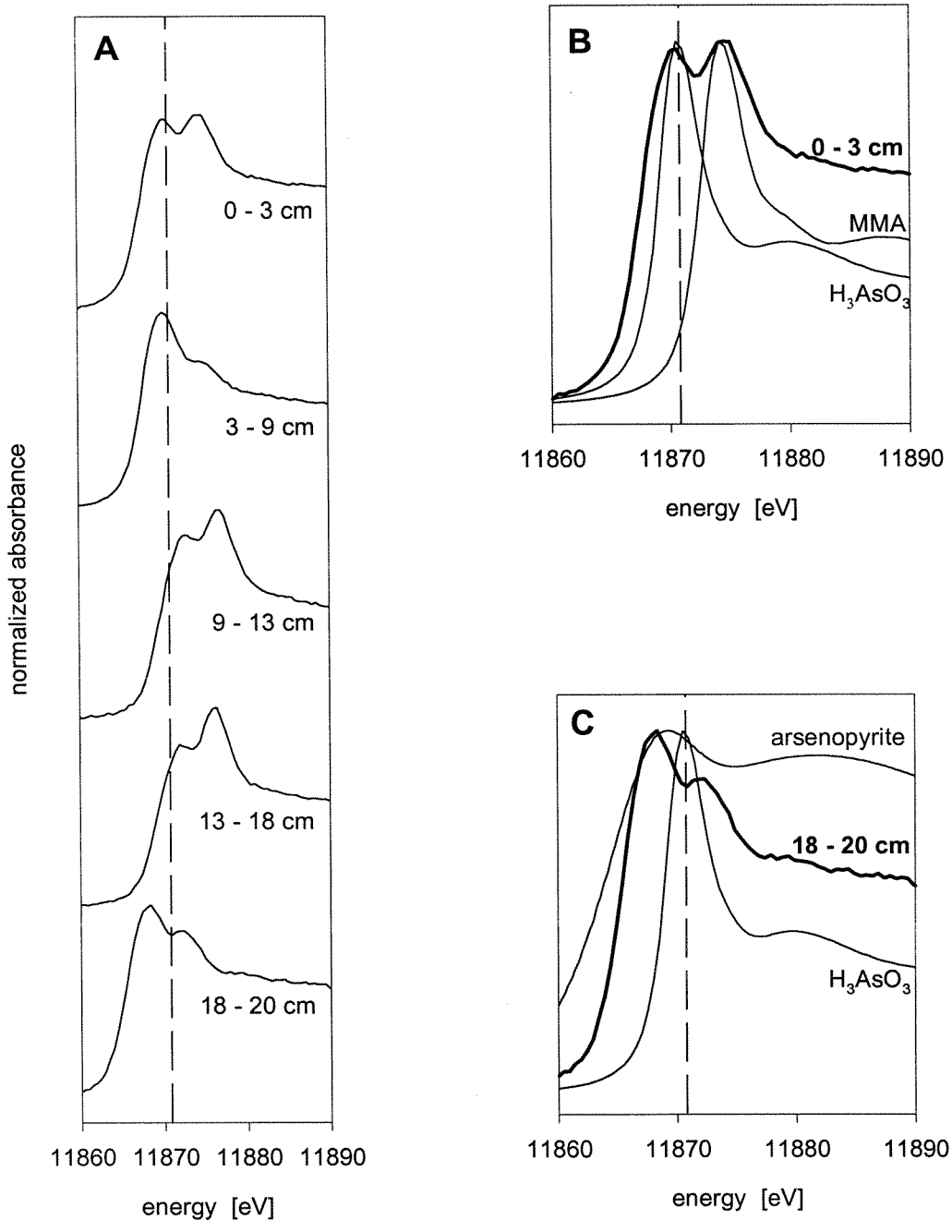

Figure 3.9: X-ray absorption edge spectra of Hot Creek sediment collected in July 1999, core J1. Normalized absorbtion spectra are shown for each of the five sediment sections, denoted by their depth below the sediment-water interface (A). The spectra from the surface (B) and deepest (C) sections (heavy lines) are overlaid with normalized spectra of reference compounds. Dashed vertical lines guide the eye.

An arsenic phase with absorption maximum at approximately 11871 eV was present in all sections. Comparison with reference compounds (sodium salts and 10 mM solutions of arsenite, arsenate, MMA, DMA, arsenobetaine, arsenocholine, and the solids am-As_2S_3, jarosite, arsenopyrite, and As-pyrite; see the spectra in Appendix A) showed that this was most similar to the arsenite solution and hence an As(III)-O phase The length of this core sample implies that sediment has accumulated at this site for some time. It is suspected that core J1 is impacted by a bed spring (§3.3.2.1). It is possible that diffusion of geothermal water from the bed spring has, over this accumulation period, distributed arsenite throughout the sediment column.

Fitting model compounds to the XAS spectra suggests that arsenic is associated with an organic phase in the first four sections (Fig. 3.9 B). The spectrum of a solution of MMA fit the inflection points in the sample spectra better than any of the available inorganic As(V) model compounds. The presence of an As-C association is supported by the strong correlation of arsenic with total organic carbon observed in this core (Fig. 3.5) and is possibly due to the incorporation of arsenic-bearing plant material in these sediments. Although the XAS spectrum of the plant sample (Appendix A) did not fit the As-C peak in the sediment spectra, decomposition occurring in the sediments may change the form of arsenic present. An extended x-ray absorption fine structure (EXAFS) spectrum was collected on the 0-3 cm sample. Analysis of this was confounded by the low signal-to-noise ratio resulting from the relatively low (for EXAFS) arsenic concentration in this sample. However, a slight deviation from the spectrum expected for an oxygen-only first coordination shell may have been due to the presence of a carbon atom in the first shell of arsenic. We were unable to collect EXAFS on the

3-9 cm section, which has a higher arsenic concentration and therefore may have provided more conclusive data.

In the 18-20 cm section of core J1, arsenic is associated with a sulfide phase (Fig. 3.9 C). The fit with arsenopyrite is not especially good and is not intended to imply that arsenopyrite is present in the sample. This fit is shown in Fig. 3.9 C to indicate that the position of the edge maximum is in the range of an As-S association. The precipitation of an arsenic-sulfide phase at depth corroborates our suggestion in §3.3.3 that the J1 sampling site is impacted by a bed spring. The AVS technique for sulfide determination was not sufficiently sensitive to measure sulfide in this sample. Sulfide was present, however. Although there was not enough sulfide generated to produce the blue color required for quantification of sulfide, sufficient sulfide was generated to change the color from the pink of the blank to colorless.

The XAS spectra provide evidence that the form of arsenic in the solid phase of Hot Creek sediment is different at different depths. It is suspected that the presence of bed springs and plant material strongly influences arsenic association.

3.3.4.2 Sequential Extraction of Hot Creek Sediments

The surface (0-3 cm), mid (9-13 cm) and deepest (18-20 cm) sections of core J1, collected in July 1999 from Hot Creek Gorge, were subjected to a sequential extraction procedure (Table 3.4). Extraction efficiencies were calculated for each element based on the total of each element extracted and the total concentration of each element determined by XRF analysis (Table 3.5).

Only 11 to 17% of the total manganese and 9 to 11% of the iron was extracted

Table 3.4: Sequential Extraction of Hot Creek Sediment, J1

section	TOTAL ARSENIC EXTRACTED WITH EACH EXTRACTION SOLUTION [μg/g][a] AND PERCENTAGE OF TOTAL ARSENIC EXTRACTED WITH EACH EXTRACTION SOLUTION [%]										resistant[b]
	$MgCl_2$		NaOAc		$NH_2OH.HCl$		pyrophosphate		ClO_4HCl		
	μg/g	%	μg/g	%	μg/g	%	μg/g	%	μg/g	%	μg/g
0-3	1.3	7	1.0	5	6.8	34	0.3	2	2.9	15	7.7
	1.6	8	0.9	5	6.7	34	0.2	1	3.1	16	7.5
9-13	1.5	7	1.9	9	8.5	39	0.4	2	3.2	15	6.5
	2.3	11	2.2	10	8.4	38	0.4	2	2.3	10	6.4
18-20	2.6	10	2.6	10	8.4	31	0.4	1	5.6	21	7.4
	2.5	9	2.5	9	8.6	32	0.3	1	4.6	17	8.5

[a] Total arsenic extracted in each fraction is expressed as μg/g dry sediment.
[b] Resistant fraction is the difference between the total extracted and the total concentration determined by x-ray fluorescence.
Iron and manganese released in each fraction is not shown due to the small percentage of total iron and manganese extracted from the samples.

Table 3.5: Extraction Efficiencies in Sequential Extraction Procedure

section [cm]	% OF TOTAL EXTRACTED OVER ALL EXTRACTIONS[a]		
	Arsenic	Iron	Manganese
0-3	74 80	9.1 10	12 13
3-9	76 92	12 11	17 15
18-20	74 63	13 11	15 11

[a] Calculated as: 100 x (total extracted in the five steps of the sequential extraction procedure) / (total of each element in the sample as determined by XRF)

from the sediment samples. Arsenic extraction was more complete, with 63 to 92% of the total arsenic extracted. In a similar sequential extraction (Moore et al. 1988), 90 to 100% of manganese, 40 to 80% of iron and 80 to 100% of arsenic was extracted. This study omitted the first two steps of the extraction and used a more concentrated $NH_2OH.HCl$ solution for the reductive extraction (which targets Mn/Fe oxyhydroxide dissolution).

Of the arsenic extracted from our three samples, most was extracted by the $NH_2OH.HCl$ solution. Slightly more arsenic was extracted by this solution from the surface and mid sections than from the bottom section.

More arsenic was extracted from the mid and deep sections by the $MgCl_2$ and NaOAc extractions (which target the exchangeable and carbonate fractions) than was extracted from the surface section.

A very small percentage of the total arsenic was extracted from the three samples in the pyrophosphate extractable, "organic" fraction. Unfortunately, the 3-9 cm section, which had the highest arsenic and organic carbon concentrations, was not subjected to the sequential extraction. Although only 1 to 2% of the total arsenic was released in the "organic" fraction, the XAS data and arsenic-TOC correlation are compelling evidence that arsenic is associated with an organic phase in these sediment samples.

The oxidizing, ClO_4HCl extraction solution is designed to extract arsenic associated with sulfide phases. Slightly more arsenic was extracted by this solution from the deep sediment sample (19%) than from the surface (16%) or mid (13%) sections. It appears that the increase of arsenic in this fraction occurs at the expense of arsenic in the Mn/Fe oxyhydroxide fraction in this deep sediment section.

3.3.5 Form of Arsenic in the Sediments of Crowley Lake

In Crowley Lake sediment, arsenic is associated with an orpiment-like sulfide phase (Fig. 3.10). Sulfide concentrations measured as AVS varied from 100 to 300 μg/g in different sub-samples of these sediments. This is likely the result of bacterial sulfate reduction in these anoxic sediments, and is thus indicative of diagenesis in the sediments. It is, therefore, not indicative of the initial phase with which arsenic was deposited to the sediment. Production of sulfide by bacteria and subsequent sequestration of arsenic by this sulfide (Rittle et al. 1995) may be responsible for formation of the orpiment-like phase observed. The correlation between arsenic and TOC observed in the

Hot Creek sediments extends to the Crowley Lake sediments (Fig. 3.11).

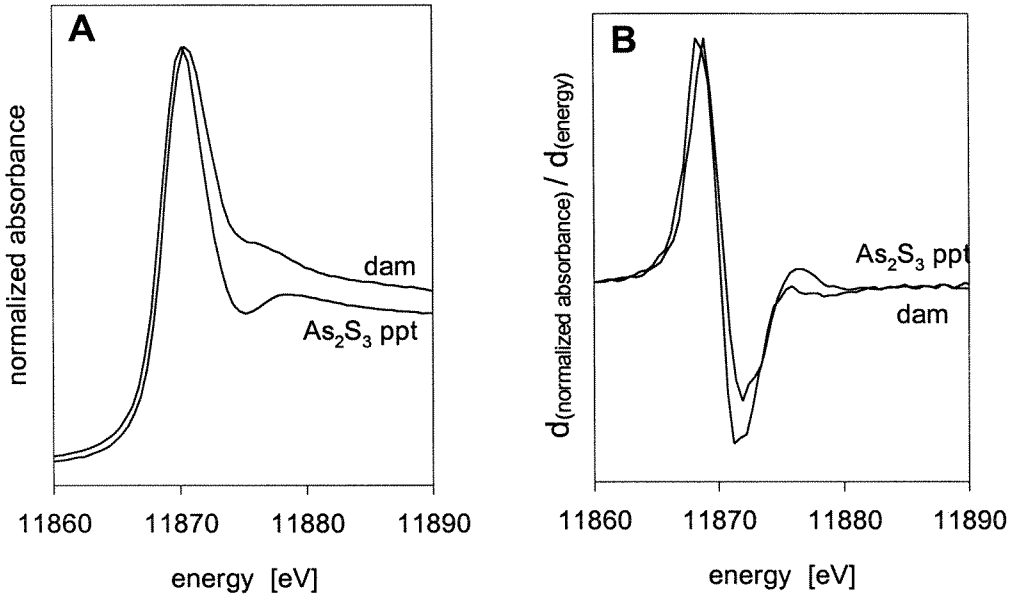

Figure 3.10: Normalized x-ray absorption edge spectra (A) and their first derivatives (B) of Crowley Lake sediment collected from the dam site (dam) and a freshly precipitated amorphous-As_2S_3 solid (As_2S_3 ppt).

Arsenic associated with sulfides in Crowley Lake sediment should be effectively immobilized as long as the sediment is anoxic. If the sediments are permanently anoxic there will be no release of arsenic to the overlying water and arsenic may slowly accumulate in these sediments. Dissolved oxygen measurements in the water column prior to sediment sample collection confirmed that the water was oxygen depleted below 12 m at both sites. Dissolved oxygen profiles measured in May, when the lake was not stratified, showed oxygen depletion near the sediment-water interface (Chapter 5).

Mineralization of deposited algal matter may maintain a high biological oxygen demand, keeping the sediments permanently reducing.

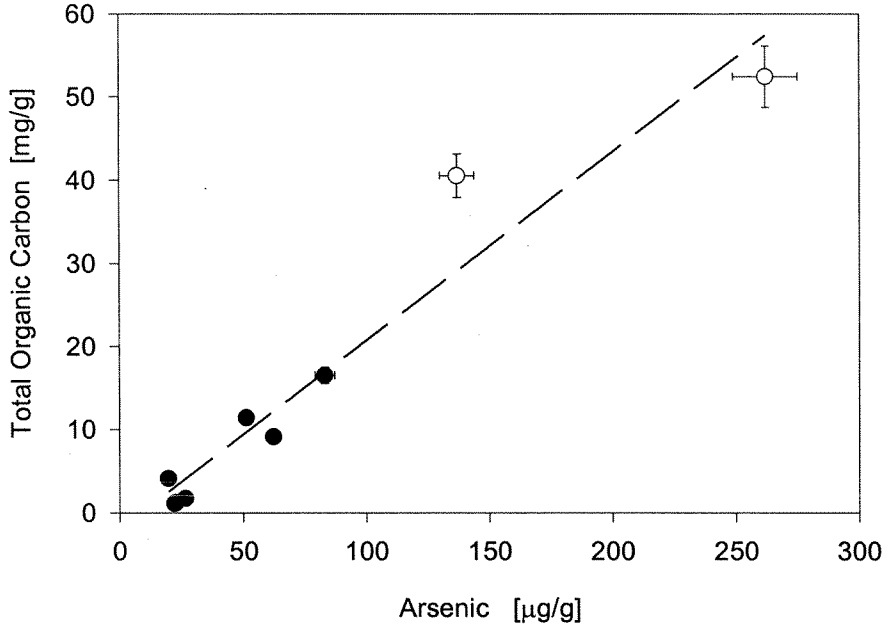

Figure 3.11: Total organic carbon by combustion against arsenic by x-ray fluorescence for Hot Creek (●) and Crowley Lake (○) sediment, collected in July 1999. Hot Creek data is for cores J1 and J3 are shown. Crowley Lake data is for the dam and basin sites. Concentrations are on a dry weight basis. The dashed line represents linear regression with r^2 =0.93.

3.4 Concluding Remarks

Examination of concentration profiles and XAS spectra in sediments collected in Hot Creek show that local arsenic accumulation is strongly influenced by hot springs and plants. Sediments in the main flow channel are leached or diluted by upstream

sediments to the point that the sediments carry an insignificant fraction of the arsenic load exported from Hot Creek.

The arsenic-sulfide phase identified in Crowley Lake sediments must be the product of diagenesis and, therefore, supplies no information regarding the mechanism for accumulation of arsenic in these sediments. It does, however, suggest that arsenic will remain associated with the sediments in the lake as long as the sediment-water interface remains anoxic.

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Chapter 4

MOBILITY OF ARSENIC IN HOT CREEK SEDIMENTS

4.1 Introduction

4.1.1 Motivation

Geothermal inputs in Hot Creek result in elevated sediment arsenic concentrations. Adsorption onto sediment phases and association with plant material buried in the sediment are the most probable mechanisms for arsenic accumulation in Hot Creek sediments. In this chapter, the sediment-water exchange of arsenic in Hot Creek is examined.

The capacity of Hot Creek sediments to release or to take up arsenic could influence arsenic transport in this system. Pore water profiles measured in the field can reveal whether the net flux of arsenic at the sediment-water interface is into or out of the sediment. Sediment-water exchange experiments conducted in the laboratory using natural sediments and synthetic solutions will determine the factors controlling sediment uptake and release of arsenic.

4.1.2 Factors Controlling Arsenic Uptake and Release by Sediments

Transport of arsenic may occur in the dissolved phase by advection or diffusion following dissolution or desorption. It may also occur in the solid phase by advection (Nimick et al. 1998). Adsorption/desorption and precipitation/dissolution reactions will control sediment uptake and release of arsenic.

Adsorption of arsenic on iron oxyhydroxides has been extensively studied (Xu et al. 1991, Bowell 1994, Manning and Goldberg 1997a, Smith et al. 1999). In oxic systems, arsenate (As(V)) is, in general, more readily sorbed to oxyhydroxide minerals than arsenite (As(III)) (Smith et al. 1999, Xu et al. 1991, Bowell 1994). Oxidation of As(III) to As(V) by manganese oxides has been shown to increase adsorption (Oscarson et al. 1983a, Manning and Goldberg 1997a). As(III) release from sediments was observed when As(V) amended sediments became anoxic (McGeehan 1996). Increasing ionic strength tends to decrease As(V) adsorption above pH 3 but has little effect on As(III) adsorption (Smith et al. 1999, Manning and Goldberg 1997b). Ions which compete for adsorption sites, especially phosphate, can inhibit As(V) adsorption (Darland and Inskeep 1997). Cation adsorption may indirectly enhance anion adsorption by creating a more positive surface charge on the adsorbing surface.

Sequestration of arsenic by sulfide phases has been observed in reducing environments (Moore et al.1988, Rittle et al. 1995). Precipitation of arsenic sulfides such as realgar, orpiment and am-As_2S_3 is observed in geothermal systems (Webster 1990, Eary 1992). These solid phases will be unstable to dissolution if conditions become sufficiently oxidizing.

4.1.3 High Resolution Pore Water Profiles

High resolution pore water sampling may aid determination of arsenic fluxes in interstitial water. Dialysis samplers have been used to measure pore water gradients (Urban et al. 1997). These devices consist of membrane cells containing deionized water, which are inserted into the sediment and left in place for several weeks to allow equilibration of the deionized water with the pore water. Polyacrylamide gel strips have been used to obtain higher resolution profiles with a shorter equilibration time (Krom et al. 1994). A continuous, thin sheet of polyacrylamide is mounted on a Plexiglas support, protected by a membrane and inserted into the sediment. Upon retrieval, the gel is either fixed with sodium hydroxide for iron and manganese determination or cut into slices which are back-equilibrated in deionized water for anion determination. The performance of the thin gel slabs in recovering pore water concentrations has been well characterized (Davison et al. 1994).

Due to lateral diffusion within the gel, the resolution in these devices is limited by the time between retrieval and fixing or slicing, but is generally better than 1 mm. For the purpose of determining the net transport of arsenic between sediments and water in the laterally heterogeneous Hot Creek, such high vertical resolution is not necessary. Using one-dimensional models to estimate the net transport of a chemical species between the sediments and overlying water requires at least one measured sediment pore water profile and the assumption that the sediment is laterally homogeneous. Very high resolution pore water sampling has revealed the presence of small, isolated regions in the sediment where the species of interest is highly concentrated (Harper et al. 1999). Including the concentrations of such micro-niches in a one-dimensional flux model in-

validates the assumption of lateral homogeneity. Therefore, very high resolution pore water profiles must be averaged before inclusion in a one-dimensional flux model. We report here a modification of the gel probe sampling device which has 6.7 mm vertical resolution, independent of the time between retrieval and processing.

4.2 Experimental Methods

4.2.1 Site Description and Sample Collection

Sediment samples were collected from above and within Hot Creek Gorge and from the Owens River at Benton Crossing (Fig. 4.1).

Sediment core samples were collected in November 1996 from Hot Creek below the State Fish Hatchery (HCH-96) and from Hot Creek Gorge (HCG-96). The surface sections of these core samples were used in this study. Although there are geothermal inputs above the hatchery, arsenic concentrations in the stream water at this site are low, with an annual average of approximately 10 μg/L (CSWRCB 1993). Therefore, HCH-96 should have the same mineralogy as the sediment in Hot Creek Gorge but has not had contact with arsenic-enriched water. HCG-96 was collected approximately 200 m downstream of the major hot spring inputs in Hot Creek Gorge.

The gel probe sampling device was deployed three times in Hot Creek Gorge: in September 1998 (GP1[1]), May 1999 (GP2) and July 1999 (GP3). Site GP1 is in an area which is seasonally flooded. The overlying water was 0.2 m deep at the time of

[1] GP1 was prepared and processed by F. Bohn.

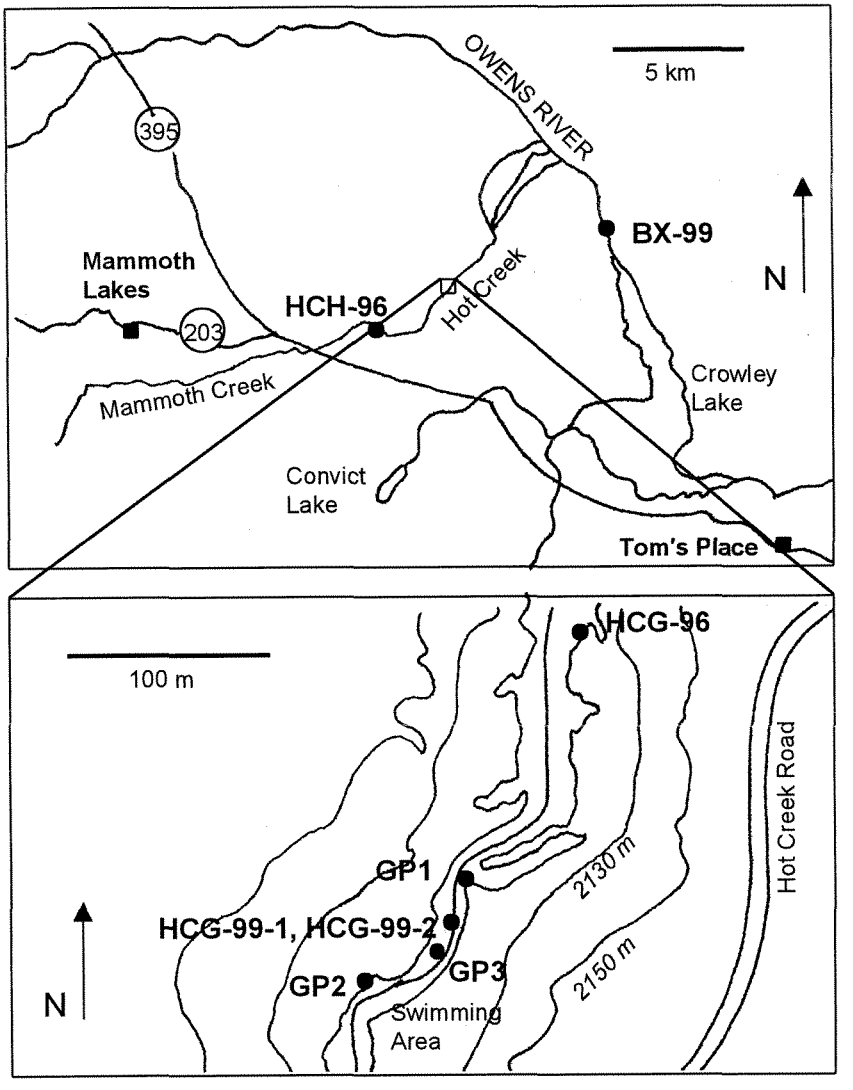

Figure 4.1: Sediment and gel probe sampling sites in Hot Creek and the Owens River. The direction of stream flow is SW to NE in Hot Creek and NE to SW in Owens River. HCH-96 and HCG-96 were collected in November 1996. HCH-96 was 100 m downstream of the State Fish Hatchery and HCG-96 was 200 m downstream of the major hot pools in Hot Creek Gorge. HCG-99-1, HCG-99-2 and BX-99 were collected in May 1999. HGC-99-1 and HCG-99-2 were from the main channel in Hot Creek Gorge; BX-99 was collected 50 m upstream of the bridge at Benton Crossing. Gel probe sites were in visually identified regions of maximal local deposition; GP1 was collected in September 1998, GP2 in May 1999, GP3 in July 1999.

collection. Site GP2 was 6 m downstream of a hot pool outlet. Site GP3 was in the main channel of Hot Creek. The gel probe was left in place for 4 hours on each occasion. We attempted to use a core squeezing device to collect pore water from cores collected 0.5 m from GP1 and GP2. This device was a 9 cm inner diameter polycarbonate tube with holes predrilled at 2 cm spacing along one side into which luer lock fittings could be screwed upon retrieval. Syringes were attached to the fittings and pressure applied to pistons at either end of the core to force pore water into the syringes. Samples were filtered (0.45 μm, cellulose nitrate, VWR Scientific) and stored on ice. Sediment core samples collected 0.5 m from the deployment sites were transported on ice to the laboratory, where they were frozen before further processing.

Bulk surface sediment samples were collected from two sites in Hot Creek Gorge, HCG-99-1 and HCG-99-2, and from the Owens River at Benton Crossing, BX, in May 1999. Sediments were scooped into 1 L, high density polyethylene screw-top jars, filled to minimize headspace. Bulk water samples were collected immediately prior to sediment collection. The Hot Creek samples were near mid-stream, approximately 50 m downstream of the visible hot springs on the bank of the creek. HCG-99-1 was warm to the touch upon collection, so it may have been impacted by a bed spring. Sample BX was collected 50 m upstream of the bridge at Benton Crossing. Samples were frozen in the laboratory until use.

4.2.2 Gel Probe Sampling Device

4.2.2.1 Probe Construction and Gel Preparation

The gel probe sampling device consists of 54 polyacrylamide gel pieces (0.5 x 2.5 x 0.2 cm) supported in a Plexiglas ladder, protected by a 0.45 μm cellulose nitrate membrane held in place by a Plexiglas face plate (Fig. 4.2). The gel pieces were made following the procedure of Krom et al. (1994). 7.5 g acrylamide (J. T. Baker) was dissolved in 50 mL water, 150 mg methylenebisacrylamide (Biorad) added and the solution deoxygenated. 0.30 mL of ammonium persulfate (J. T. Baker) solution (100 mg in 1 mL) was added with swirling and then 50 μL tetramethylethylenediamine (TEMED, E. M. Science) was added. Our method deviated from that of Krom in the casting step. The solution was cast between the lid and inverted base plate of a petri dish. Hot water was poured into the inverted base plate to aid polymerization. The solidified gel was hydrated in 18 MΩcm water, reaching 91% water by volume after 24 hours. The water was exchanged every 12 hours for at least 3 days before the gel was used. Gel pieces were cut to size using sharp edged plastic following a grid positioned under the petri dish and stored in 18 MΩcm water before use. The percent water by volume was determined for six gel pieces in each batch of gel pieces and the average of the six determinations used for the entire batch. The fully hydrated gel pieces were weighed before and after drying. Excess water on the surface of the hydrated gel pieces was removed with a tissue.

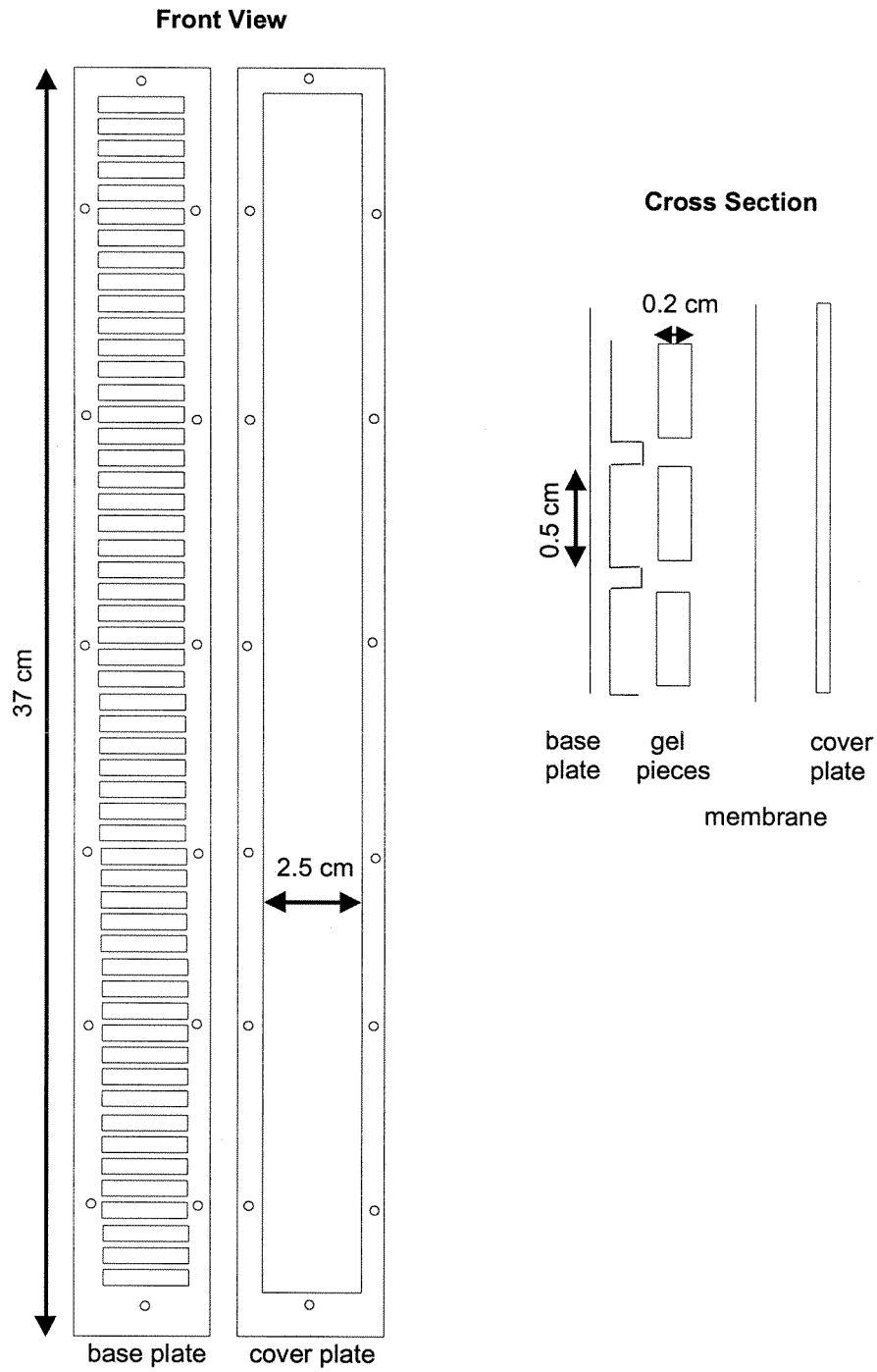

Figure 4.2: Front view and exploded cross section of gel probe sampling device. The base and cover plates are Plexiglas, the membrane is 0.45 μm cellulose nitrate, the gel pieces are polyacrylamide, and the assembly is held together with nylon screws.

4.2.2.2 Gel Performance Testing

The performance of the gel was determined in solutions of 18 MΩcm water and Hot Creek water spiked with arsenic. The recovery and equilibration time was assessed for free floating gel pieces and for gel pieces encased in the gel probe assembly. The experiments to determine equilibration time were conducted by F. Bohn (fluoride and phosphate) and N. Jones (arsenic). Phosphate and fluoride concentrations used in the equilibration time experiments were 10 mg/L. The arsenic concentrations in recovery and equilibration time experiments ranged from 10 to 2500 μg/L. Recovered concentrations are calculated following ICPMS analysis of the back-equilibrated solution using the equation

$$C = \frac{C_{measured}.(m_{gel}.\omega_{gel} + V_{1\%HNO3})}{m_{gel}.\omega_{gel}}$$

where C is the recovered concentration, $C_{measured}$ is the concentration measured in the back-equilibrated solution and m_{gel} is the mass of the gel piece. ω_{gel} is the fraction of gel mass which is water, determined by weight loss upon drying, and $V_{1\%HNO3}$ is the volume of 1% HNO_3 used for back-equilibration.

The gel probe was assembled 24 h prior to deployment and transported to the field in a tube filled with 18 MΩcm water. Upon retrieval of the device from the sediment, gel pieces were placed in pre-weighed test tubes containing 1.5 mL 1% (v/v) nitric acid. The solution was decanted upon return to the laboratory for analysis by inductively coupled plasma mass spectrometry (ICPMS).

4.2.3 Sediment Characterization

Surface samples from cores collected in November 1996 were homogenized in the zip-lock bags into which they had been sectioned. Bulk sediment samples collected in May 1999 were defrosted and homogenized by stirring in the sample collection jars. Sediment concentrations were determined using USEPA Method 6010, modified by omitting the final addition of HCl and using ICPMS for analysis. In this partial digestion, sediment samples were oven dried, refluxed with HNO_3, and 30% H_2O_2 added. The digestate was filtered (0.45 μm, cellulose nitrate, Sartorius) and diluted for analysis. More than 85% of the total arsenic was removed from a standard reference soil (SRM 4711, NIST). Arsenic concentrations in plants collected from Hot Creek Gorge were also determined using this method. All solid phase concentrations throughout are reported on a dry weight basis.

4.2.4 Sediment-Water Exchange Experiments

The conditions of the sediment-water exchange experiments are summarized in Table 4.1. The numbers in square brackets in the text below refer to the experiment numbers in the table. Wet sediment was used in all sediment-water exchange experiments. The sediment masses reported in the experimental procedures are wet sediment masses. Wherever they appear, sediment *concentrations* are reported on a dry weight basis.

Table 4.1: Conditions in Sediment-Water Exchange Experiments

No.	Sediment[a]	Solution[b]	s:w[c]	$As_{T,init}$ µg/L	As(III) init.%	Sampling Time	Parameters Measured[d]
1	HCH-96	18 MΩcm	1:10	0	0	30 min x 8	As_T, Fe, Mn
2	HCG-96	18 MΩcm	1:10	0	0	30 min x 8	As_T, Fe, Mn
3	HCG-96	18 MΩcm	1:50	0	0	series to 120h	As_T, Fe, Mn
4	HCH-96	18 MΩcm	1:50	300	0	series to 80 h	As_T
5	HCG-96	18 MΩcm	1:67	200	0	series to 46 h	As_T
6	HCH-96	18 MΩcm	1:50	0	0	24 h	As_T
7	HCH-96	18 MΩcm	1:50	30	0	24 h	As_T
8	HCH-96	18 MΩcm	1:50	100	0	24 h	As_T
9	HCH-96	18 MΩcm	1:50	500	0	24 h	As_T
10	HCH-96	18 MΩcm	1:50	1000	0	24 h	As_T
11	HCH-96	18 MΩcm	1:50	100	100	24 h	As_T
12	HCH-96	18 MΩcm	1:50	500	100	24 h	As_T
13	HCH-96	18 MΩcm	1:50	1000	100	24 h	As_T
14	HCG-99-1	18 MΩcm	1:10	0	0	30 min x 5	pH, *k*, As(III), As_T, P
15	HCG-99-1	SHC	1:10	0	0	30 min x 5	pH, *k*, As(III), As_T, P
16	HCG-99-1	18 MΩcm	1:10	348	40	series to 16 h	pH, *k*, As(III), As_T, P
17	HCG-99-1	SHC	1:10	367	40	series to 16 h	pH, *k*, As(III), As_T, P
18	HCG-99-1	SHC-Ca	1:10	365	40	series to 16 h	pH, *k*, As(III), As_T, P
19	HCG-99-1	6.3 mM	1:10	332	40	series to 16 h	pH, *k*, As(III), As_T, P
20	HCG-99-1	HCO_3^-	1:10	350	40	series to 16 h	pH, *k*, As(III), As_T, P
21	HCG-99-1	18 MΩcm	1:100	350	40	series to 16 h	pH, *k*, As(III), As_T, P
22	HCG-99-1	SHC	1:100	380	40	series to 16 h	pH, *k*, As(III), As_T, P

Table 4.1 (cont.): Conditions in Sediment-Water Exchange Experiments

No.	Sediment[a]	Solution[b]	s:w[c]	$As_{T,init}$ µg/L	As(III) init.%	Sampling Time	Parameters Measured[d]
23	HCG-99-2	18 MΩcm	1:10	360	40	series to 16 h	pH, *k*, As(III), As_T
24	HCG-99-2	SHC	1:10	380	40	series to 16 h	pH, *k*, As(III), As_T
25	HCG-99-1	0 mM	1:10	350	40	16 h	pH, *k*, As(III), As_T
26	HCG-99-1	3 mM	1:10	350	40	16 h	pH, *k*, As(III), As_T,
27	HCG-99-1	6 mM	1:10	350	40	16 h	pH, *k*, As(III), As_T
28	HCG-99-1	9 mM	1:10	350	40	16 h	pH, *k*, As(III), As_T
29	BX-99	BX	1:10	69	0	16 h	pH, As(III), As_T
30	BX-99	BX	1:10	124	0	16 h	pH, As(III), As_T
31	BX-99	BX	1:10	170	0	16 h	pH, As(III), As_T
32	BX-99	BX	1:10	262	0	16 h	pH, As(III), As_T
33	BX-99	BX	1:10	343	0	16 h	pH, As(III), As_T
34	BX-99	BX	1:10	69	0	series to 16 h	pH, As(III), As_T

[a] HCH-96 Hot Creek at hatchery November 1996. HCG-96: Hot Creek at Gorge November1996. HCG-99-1, HCG-99-2: Hot Creek at Gorge May 1999. BX-99: Owens River at Benton Crossing May 1999.

[b] 18 MΩcm nanopure water (note, may be amended with arsenic). SHC: synthetic Hot Creek water (see Table 4.2). SHC-Ca: calcium-free SHC. 0 - 9 mM: 18 MΩcm water with NaCl to stated concentration. HCO_3: 18 MΩcm water with HCO_3^- to pH 8.1. BX: water from Benton Crossing filtered through 0.45 µm membrane.

[c] s:w sediment-to-water ratio (mass wet sediment:mass solution).

[d] *k*: conductivity (µS/cm).

Initial sediment-water exchange experiments were conducted with HCH-96 and HCG-96. In the repeated extraction experiments [1, 2], 5 g wet sediment was shaken with 50 mL 18 MΩcm water for 30 minutes on a wrist action shaker then centrifuged at 10,000 rpm for 5 minutes. Total arsenic (As_T) was measured in the supernatant following filtration through a 0.45 μm cellulose nitrate membrane, and the procedure repeated 8 times. A 120 h time series of arsenic leaching from 40 g of HCG-96 sediment was determined in 2 L of 18 MΩcm water [3].

In large volume arsenic sequestration experiments [4, 5], 30-40 g of wet sediment was combined with 2 L of 18 MΩcm water spiked to 200-300 μg/L with a 1 g/L As(V) stock solution. Samples removed at various time intervals were analyzed for As_T. In small volume arsenic sequestration experiments [6-15], 5 g of HCH-96 was combined with 50 mL 18 MΩcm water spiked with either As(III) or As(V). After 24 h shaking, samples were centrifuged, filtered and analyzed for As_T.

Bulk surface sediment collected from Hot Creek Gorge in May 1999 (HCG-99-1) was used in a second series of sediment-water exchange experiments. The leaching experiments [14, 15] used 5 g wet sediment, 50 mL solution, and a 30 minute leach time. pH and conductivity were measured following centrifugation and filtration of the leachate. As(III) and As_T were determined in the leachate. 18 MΩcm water [14] and a synthetic Hot Creek water [15] were used as leaching solutions. The synthetic Hot Creek water contains the major ions suspected to influence arsenic adsorption to Hot Creek sediments, each at their annual average concentration as reported in CSWRCB (1993). The recipe for the synthetic Hot Creek water is given in Table 4.2.

Table 4.2: Recipe for Synthetic Hot Creek Water (SHC)[a]

Species	mg/L	mM
fluoride	2	0.1
boron	2	0.2
phosphate	0.2	0.002
chloride	45	1.3
sulfate	25	0.26
calcium	12	0.30
bicarbonate	180	2.9

[a] Synthetic Hot Creek water is SHC in Table 4.1. The pH of this solution is 8.1, the conductivity 510 μS/cm. Concentrations are annual average concentrations measured in Hot Creek, reported in the CSWRCB 1993.

In experiments with arsenic initially present in the solution [16-27], the As(III):As(V) ratio was initially 2:3 and the initial As_T was 332-380 μg/L. 5 g of wet sediment was combined with 50 mL solution in each of 12 centrifuge tubes. The tubes were shaken on a wrist action shaker and pairs removed for centrifugation and filtration at time intervals up to 16 h. The pH and conductivity were measured in the filtrate. An aliquot of the filtrate was acidified to pH 4 and run through anion exchange columns filled with an acetate form resin (after Wilkie and Hering 1998). The influent and eluent were analyzed by ICPMS for As_T and As(III), respectively. The solutions were 18 MΩcm water [16], synthetic Hot Creek water [17], synthetic Hot Creek water with calcium omitted [18], 18 MΩcm water with the ionic strength corrected with NaCl [19],

and pH corrected with bicarbonate [20] to that of the Hot Creek annual average. The effect of changing the sediment-to-water ratio [21, 22] and sediment heterogeneity [23, 24] were investigated. An apparent ionic strength effect was investigated using 0, 3, 6 and 9 mM NaCl solutions [25-28] with successive filtration through and 0.45, 0.1 and 0.025 μm membrane filters.

The Benton Crossing sediment (BX-99) was combined with water collected from Benton Crossing (BX), both unamended and spiked with different amounts of arsenic [29-34]. The water collected from Benton Crossing was filtered through a 0.45 μm cellulose nitrate filter prior to use. Because the Benton Crossing sediment was very gravelly, it was wet-sieved, using the Benton Crossing water, and the particles smaller than 2 mm were used in these experiments. 5 g wet sediment was shaken for 16 h with 50 mL arsenic-amended Benton Crossing water [29-33]. Initial arsenic concentrations in solution ranged from 69 μg/L (unamended) to 343 μg/L. After 16 h shaking, samples were centrifuged at 10,000 rpm for 5 min, and filtered through a 0.45 μm membrane. A 16 h time series of the sediment-water exchange of arsenic using the Benton Crossing sediment and unamended Benton Crossing water was also performed [34]. A series of samples containing 5 g wet sediment and 50 mL solution were shaken; the pairs were removed at various time intervals and centrifuged and filtered as above.

4.2.4 Analysis

Arsenic, iron, manganese and phosphorus were quantified by inductively coupled plasma mass spectrometry (ICPMS; Perkin-Elmer/Sciex Elan 5000A system). An

arsenic stock solution (1.00 g/L) was prepared from sodium arsenate, a phosphorus stock (0.0100 M) from monosodium phosphate. Iron and manganese stocks (1.00 g/L) were obtained commercially (VWR Scientific). Calibration standards were prepared immediately prior to each analysis by dilution of the stocks. All chemicals were reagent grade or better and used without further purification.

Fluoride and phosphate analyses for the polyacrylamide gel performance tests were performed by ion chromatography (IC; Dionex DX500 with an IonPac AG11 4 mm guard column and IonPac AS11 4 mm analytical column) with a sodium hydroxide gradient from 5 to 45 mM at 1 mL/min.

pH was measured using a Ross Model 81-02 combination electrode connected to the Orion Model 720A meter. Conductivity was measured with an Orion Model 013005A conductivity probe connected to an Orion Model 1230 Multimeter. Dissolved oxygen measurements were made with Orion Model 083005 dissolved oxygen probe connected to the Orion Model 1230 Multimeter.

4.3 Results and Discussion

In this study, we evaluate the mobility of arsenic in the sediments of Hot Creek. In order to determine the extent of, and the factors controlling, the exchange of arsenic between the sediment and stream water, we combine information obtained from high resolution pore water profiles measured in the gorge with sediment-water exchange studies conducted in the laboratory. High resolution pore water profiles allow us to estimate the diffusive flux of arsenic from the sediments to the overlying water. Sedi-

ment-water exchange experiments offer insight into the factors controlling the mobility of arsenic in the Hot Creek Gorge system.

Isolating the "dissolved" fraction by filtration through a 0.45 μm membrane is an operational definition. Colloidal material may pass a 0.45 μm membrane filter, so that the filterable fraction contains both dissolved and colloidal material. Both colloidal and dissolved arsenic are similarly available for transport in streamwater. Therefore, when considering the release of arsenic from the sediments, colloidal arsenic is as important as dissolved phase arsenic, so need not be excluded from the analysis.

Data ancillary to those presented in the following discussion are available in Appendix B.

4.3.1 Performance of Gel Probe Sampler

Arsenic recovery from gel pieces immersed in arsenic-bearing solutions is shown in Fig. 4.3. Recovery of arsenic from Hot Creek water, unamended and spiked with As(V), was excellent (better than 95%).

When gel pieces were immersed in solution, with all four sides exposed for diffusion, equilibration was complete in less than 1 h (Fig. 4.4 A). In the gel probe assembly, equilibration is complete after 2 h in a well-mixed solution (Fig. 4.4 B). The time for equilibration in a real sediment may be longer due to the reduced porosity. However, we note that this technique is not only rapid with high vertical resolution but also extremely efficient in terms of arsenic recovery.

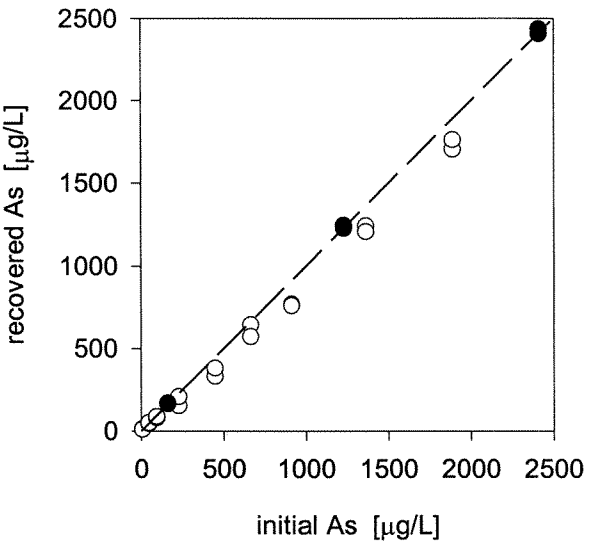

Figure 4.3: Recovery of arsenic from gel immersed in 18 MΩcm solutions with different arsenic concentrations (○) and from Hot Creek water, both untreated and spiked with arsenate solution (●). The dashed line represents 100% recovery.

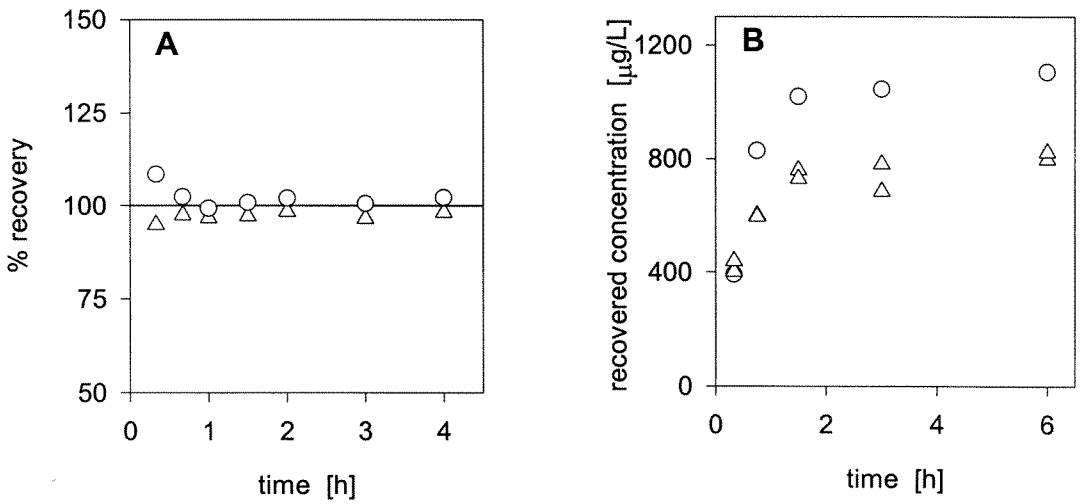

Figure 4.4: Equilibration time for polyacrylamide gel pieces free-floating in solution (A) and mounted in the gel probe sampler (B). A shows the recovery from 10 mg/L solutions of phosphate (○) and fluoride (△). B shows the recovery of total arsenic (○) and As(III) (△).

4.3.2 Diffusive Flux of Arsenic From Sediments in Hot Creek

Pore water profiles of arsenic were measured at three sites GP1, GP2 and GP3 (Fig. 4.1). The profiles all have concentration gradients at the sediment-water interface indicative of release of arsenic from the pore water to the overlying water (Fig. 4.5).

GP1 has relatively low pore water arsenic concentrations, perhaps because these sediments are not continuously flooded. The pore water concentrations obtained using the gel probe and core squeezer at this site agree within experimental error.

In contrast to GP1, profiles GP2 and GP3 have a stronger concentration gradient to 10 cm depth and reach higher, relatively constant concentrations below 10 cm. This is indicative of a bottom water source of arsenic at these sites. The arsenic concentration at depth in GP2 and GP3 is approximately 1000 μg/L, similar to the concentration measured in the hot spring pools. The dissolved arsenic concentration gradient in the upper 10 cm is similar at these two sites. This gradient may be the result of diffusion from the deep pore water to the overlying water. Alternatively, the gradient may be the result of advective mixing of the arsenic-rich pore water with the lower-arsenic surface water. If the gradient is dominated by advective mixing and dilution of geothermally derived pore water with surface water then a conservative, geothermal tracer should have the same profile. We attempted to measure boron as a tracer of geothermal fluid to confirm this theory. However, the sample had been almost exhausted by the arsenic analysis, and further dilution produced unreliable data.

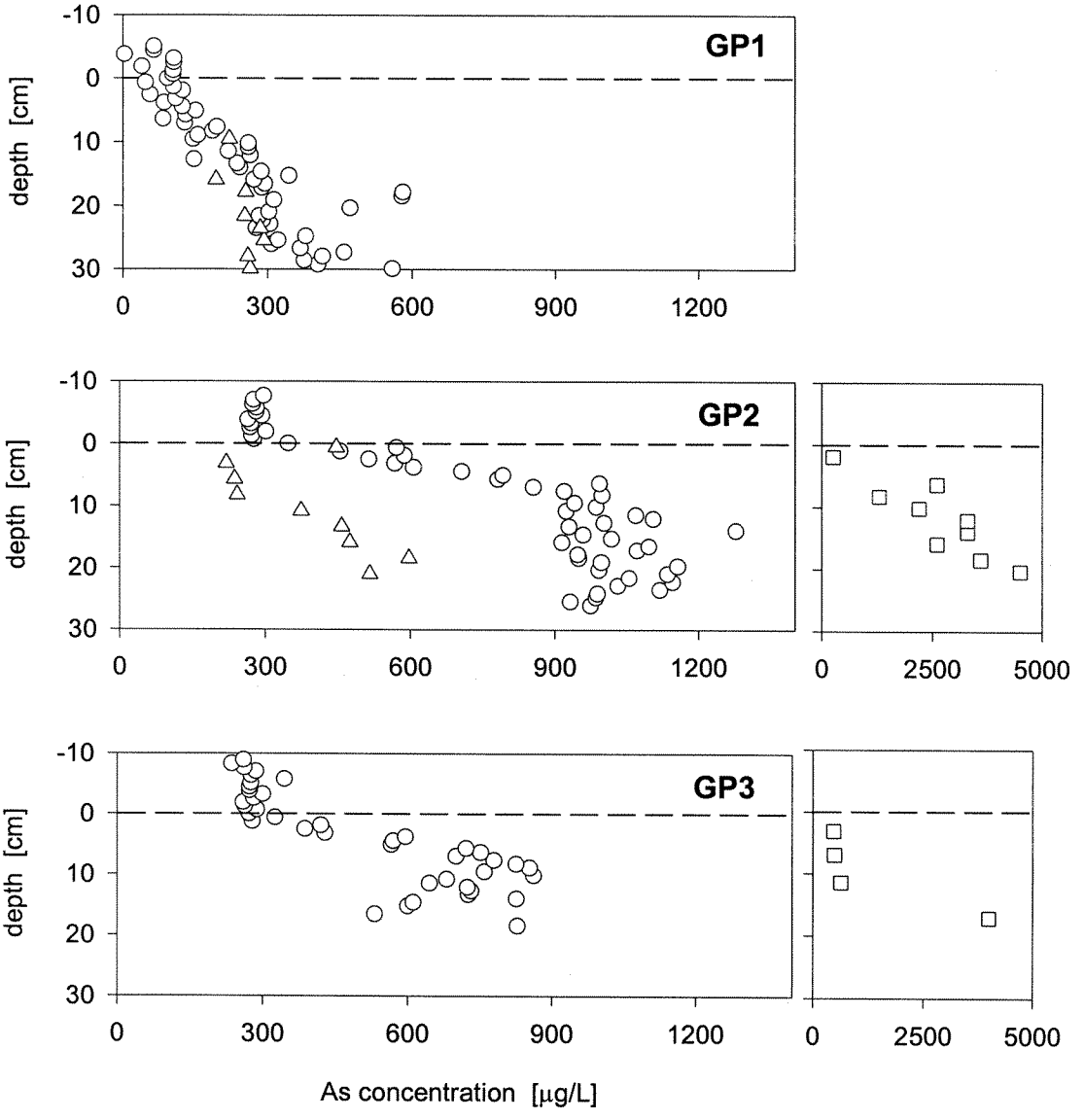

Figure 4.5: Arsenic concentration profiles measured in pore waters of Hot Creek Gorge sediments with the gel probe (○), by extraction using a core squeezer (△) and by extraction through centrifugation (□). Profiles were obtained in September 1998 (GP1), May 1999 (GP2) and July 1999 (GP3).

The concentration gradient measured in GP2 and GP3 is -62 ± 5 μg/L/cm. Assuming that the density, ρ_s, of the sandy sediment is 2.6 g/cm^3, the porosity, ϕ, can be calculated using $\phi = V_w/[V_w + (M_s/\rho_s)]$, where V_w is the volume of water in the sediment sample, and M_s is the dry mass of the sediment sample. For the surface sediments, $\phi = 0.61 \pm 0.03$.

Assuming a diffusion coefficient, D, for the arsenic anions of 5.3 x 10^{-6} cm^2/s, the one-dimensional diffusion equation, $F = \phi D_s(dC/dz)_{x,y}$, where $D_s = \phi^n D$, n = 2 (after Azcue et al. 1994), yields a flux of arsenic from the sediments to the overlying water of 2 μg/cm^2/year. A generous estimate of the gorge area in which this flux is occurring, 100 m x 10 m = 1000 m^2, yields a total flux of 24 g/year. This is insignificant compared with the total dissolved arsenic load in the stream water (10^4 kg/year, see §3.3.3).

The gel probe method for pore water profile determination has definite advantages over core squeezing and centrifugation. It not only provides better vertical resolution but also measures dissolved concentrations more accurately. The pore water arsenic concentrations determined using the core squeezer at site GP2 are lower than those obtained with the gel probe. This could be due to intrusion of surface water upon squeezing, preferential flow paths existing within the squeezed core, or adsorption of arsenic onto sediment when forced through the sediment core. In contrast, concentrations obtained by centrifugation were higher than the gel probe concentrations. Centrifugation may generate colloidal material which would not be removed by passage through a 0.45 μm membrane. Diffusion of colloidal material across the membrane of the gel probe sampler should be slow.

The results of the gel probe assembly equilibration experiment (Fig. 4.4 B) illustrate the potential for obtaining inorganic arsenic speciation using this technique. However, a small back-equilibration volume is required for gel pieces at the Hot Creek sites in order to remain above ICPMS detection limits. This would require that a coupled IC-ICPMS system be used for speciation studies, and hence the back-equilibration solution could not be preserved in the field. Thus, reduced species may oxidize, precipitate, and remove arsenic from solution, resulting in under-recovery. Therefore, determination of inorganic arsenic speciation in Hot Creek pore waters using the gel probe sampler was not attempted.

The high resolution pore water sampler provides a more accurate determination of dissolved concentrations than other conventional methods for determining pore water concentrations. The concentration gradients in the surface sediments obtained with the gel probe sampler show that the net flux of arsenic between the sediments and overlying water in Hot Creek is from the sediments to the overlying water. However, the annual flux of arsenic from the sediments in Hot Creek is small compared with the annual dissolved arsenic load carried by the stream water.

4.3.3 Capacity for Uptake and Release of Arsenic in Hot Creek Sediment

Concentrations of arsenic, iron and manganese in the sediments used in the sediment-water exchange experiments are reported in Table 4.3.

Sediment collected upstream from Hot Creek Gorge, HCH-96, and from within the gorge, HCG-96, released arsenic into 50 mL aliquots of 18 MΩcm water (Fig. 4.6). HCG-96 released more arsenic to solution, consistent with the higher arsenic concentration in this sample. Approximately 30% of the total arsenic in HCG-96 and 90% of the total arsenic in HCH-96 was released into solution. In this repeated extraction experiment, a fresh aliquot of 18 MΩcm water was used for each extraction step. However, in this and other experiments using 18 MΩcm water, ions are released from the sediment during extraction. Thus, the composition of the extraction solution evolves throughout the experiment.

Table 4.3: Concentrations[a] of Arsenic, Manganese and Iron in Sediment Samples

Sediment Sample[b]	Arsenic [µg/g]	Manganese [mg/g]	Iron [%]
HCH-96	1.8	0.30	0.64
HCG-96	29	0.6	0.6
HCG-99-1	45	0.12	0.40
HCG-99-2	17	0.074	0.35
BX-99	8	0.22	0.55

[a] Concentrations determined by partial extraction with concentrated HNO_3 and H_2O_2 (after EPA Method 6010). Numbers reported are the average of duplicate determinations.

[b] Sample HCH-96 collected at Hot Creek Hatchery, November 1996. HCG samples are collected from Hot Creek Gorge, HCG-96 in November 1996, HCG-99-1 and HCG-99-2 in May 1999. BX-99 is the < 2 mm size fraction of sediment collected from the Owens River at Benton Crossing, May 1999.

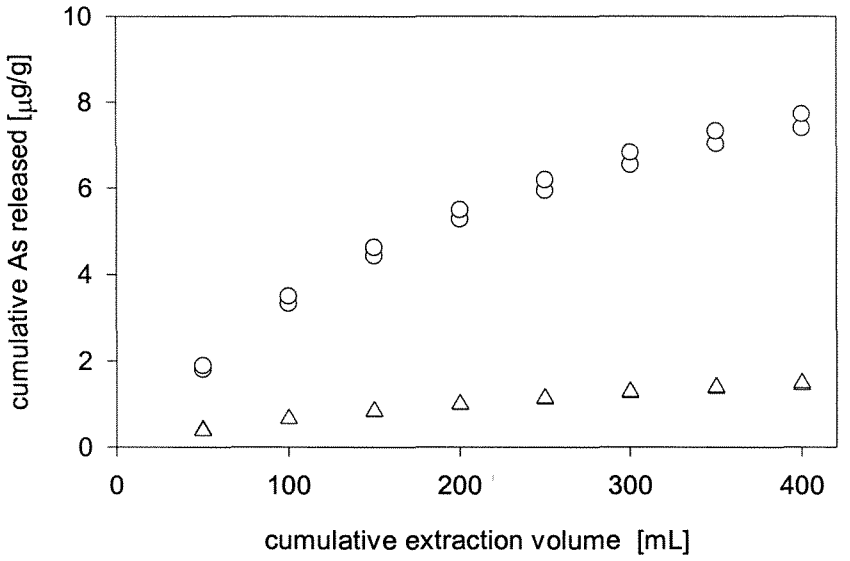

Figure 4.6: Release of arsenic from 5 g wet Hot Creek sediment collected upstream (△, HCH-96) and downstream (○, HCG-96) of Hot Creek Gorge, November 1996. Sediment arsenic concentrations were 29 µg/g for HCG-96 and 1.8 µg/g for HCH-96. All sediment concentrations are reported on a dry weight basis. 1 g wet sediment is equivalent to 0.7 g dry HCH sediment and 0.6 g HCG sediment.

HCH-96 sequestered arsenic from 18 MΩcm water amended with As(III) or As(V) (Fig. 4.7). The time-scale and concentrations in these experiments suggests that uptake of arsenic by the sediment is most likely adsorptive. The adsorption curves (Fig. 4.7 B) are almost linear for initial arsenic concentrations of 100 to 1000 µg/L; the percentage of initial arsenic in solution that was removed from solution by the sediment was 40 ± 10 % for As(V) and 31 ± 5 % for As(III). The initial arsenic concentration at which the sediment adsorption sites are saturated was not determined, since such high

arsenic concentrations are not relevant in the Hot Creek system. Removal of As(V) from solution was marginally greater than As(III) removal. As(III) oxidation was not monitored in these experiments. Thus, it is not clear whether As(III) is adsorbed directly or oxidized to As(V) before being adsorbed.

These preliminary experiments show that there is *potential* for arsenic from the overlying water in Hot Creek to accumulate in sediment.

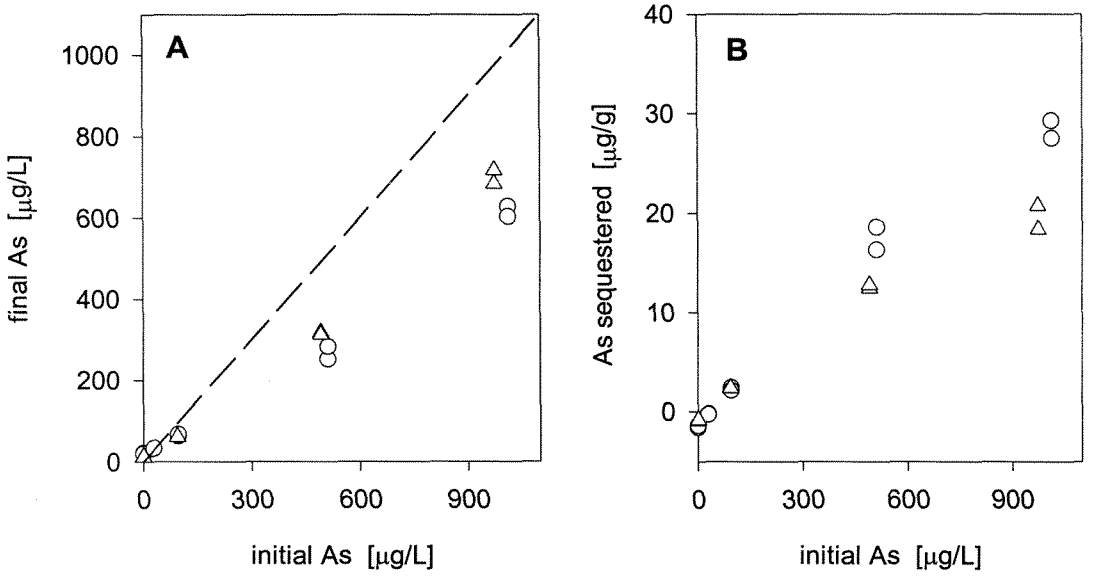

Figure 4.7: Uptake of arsenic by 1 g wet sediment collected from Hot Creek, below the State Fish Hatchery in November 1996, HCH-96. Initial solutions were 50 mL 18 MΩcm water spiked with As(V) (○) or As(III) (△). The initial sediment arsenic concentration is 1.8 µg/g. The arsenic concentration in solution after 24 h shaking with the sediment is shown in A. The dashed line represents no uptake of arsenic by the sediment. The same data is presented in B in terms of arsenic sequestered by the sediment per gram dry weight of sediment.

HCH-96 and HCG-96 both sequestered As(V) from solution (Fig. 4.8). Since both sediments were shown to release arsenic to arsenic-free solution (Fig. 4.6), the observed uptake of arsenic is a *net* process. Net uptake by HCG-96 was greater than HCH-96, despite the higher initial arsenic concentration in HCG-96 and its ability to

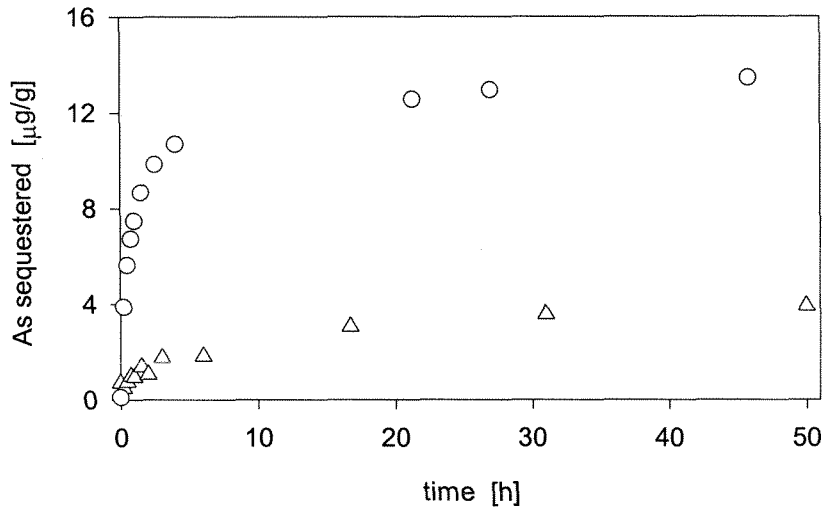

Figure 4.8: Arsenic sequestered by Hot Creek sediment from 2 L of 18 MΩcm water spiked with As(V). Sediment was collected upstream of Hot Creek Gorge (△, HCH-96) and downstream of the hot springs in Hot Creek Gorge (○, HCG-96). The initial wet sediment mass was 40 g HCH-96 and 30 g HCG-96. The equivalent dry mass of sediment is 28 g HCH-96 and 18 g HCG-96. The solid phase arsenic concentrations (dry weight basis) are 1.8 μg/g for HCH-96 and 29 μg/g for HCG-96. Initial arsenic concentration in solution, $[As]_0$, has been subtracted from the measured, dissolved concentration at each time interval and the result normalized to initial dry sediment mass. For the HCH-96 experiment, $[As]_0$ = 200 μg/L; for the HCG-96 experiment, $[As]_0$ = 300 μg/L.

release more arsenic to arsenic-free water. HCH-96 was coarser-grained than HCG-96; the more efficient uptake of arsenic by HCG-96 is probably due to the greater surface area available for adsorption in HCG-96 than in HCH-96. It should be noted that conductivity measurements confirmed the release of ions to solution, confirming that the major ion composition of the 18 MΩcm solution changes over the course of the experiment.

The surface sediments HCG-96 and HCH-96 release arsenic to arsenic-free water *and* sequester arsenic from water amended with arsenic. Exchange of arsenic between the sediment and water in the Hot Creek system is dynamic.

4.3.4 Factors Affecting Sediment-Water Exchange of Arsenic in Hot Creek

The arsenic concentrations used in these experiments dictate that precipitation of arsenic salts or mineral phases is unlikely. The observed uptake and release of arsenic is most likely due to adsorption and desorption processes. The ions present in Hot Creek water should affect the extent of these processes. In particular, adsorption of Ca^{2+} might aid arsenic adsorption by inducing a more positive surface charge (Wilkie and Hering 1996), while PO_4^{3-} and SO_4^{2-} may compete with arsenic oxyanions for adsorption sites. Thus, 18 MΩcm water is not representative of Hot Creek water in sediment-water exchange studies. Synthetic Hot Creek water (Table 4.2) was used in a series of sediment-water exchange experiments with surface sediment samples collected

in May 1999, HCG-99-1 and HCG-99-2. The solution composition, sediment and (wet) sediment-to-water ratio (s:w) were varied [14-24].

4.3.4.1 Extent of Release of Arsenic from Sediments to Arsenic-Free Solution

With no arsenic initially present in solution [14, 15], arsenic was released from HCG-99-1 to both 18 MΩcm water and synthetic Hot Creek water (Fig. 4.9). More arsenic was released to the 18 MΩcm solution. One possible reason for the inhibited desorption into SHC is the presence of calcium in solution; adsorption of calcium may aid arsenic adsorption. However, we would expect the presence of competing ions, especially phosphate, in the synthetic Hot Creek water to result in greater release of arsenic relative to the 18 MΩcm solution. Similarly, the dissolution of phases with which arsenic is associated should be favored in the solution with higher ionic strength. This result was investigated further in solutions in which arsenic was initially present.

We suspected that the increased release of arsenic with decreased ionic strength was a result of arsenic being associated with an organic phase in the sediment, the existence of which was suggested in Chapter 3. Certainly, plant material in Hot Creek Gorge accumulates arsenic: two plant samples collected in Hot Creek Gorge had arsenic concentrations of 260 and 1300 μg/g (dry weight basis). The abundance of plant material in the gorge may result in this organic material having a significant impact on sediment composition. However, when the sediment samples were collected in July 1999 for the sediment-water exchange experiments (HCG-99-1, HCG-99-2) a conscious effort was made to avoid collecting plant material with the sediment. The sam-

ples were collected from regions of shallow sedimentation in Hot Creek Gorge, free from plant growth. Therefore, we have minimized the effects of organic material on sediment-water exchange of arsenic in these experiments.

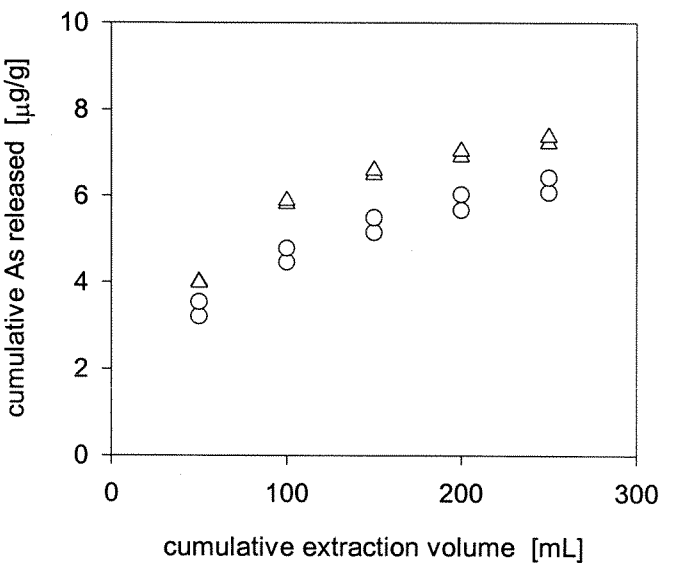

Figure 4.9: Cumulative arsenic released in duplicate repeated extractions of 5 g wet Hot Creek Gorge sediment collected May 1999 (HCG-99-1). 5 g wet sediment is equivalent to 3.5 g dry. Extraction solutions are 18 MΩcm water (△) and synthetic Hot Creek water (○), each with 0 µg/L initial arsenic concentration.

4.3.4.2 Oxidation of As(III) in Solution

A series of experiments began with solutions containing a mixture of As(III) and As(V), all with approximately the same total arsenic concentration [16-24]. The surface sediments were assumed to be well-oxygenated due to their interaction with the well-oxygenated stream water. This assumption was verified by measuring the sediment oxygen demand in the first series of experiments. Samples were prepared in a nitrogen atmosphere and the dissolved oxygen concentration measured in the solution before and after shaking with the sediment. The dissolved oxygen concentration in solution decreased by 0.1 mg/L. Disappearance of As(III) throughout the series of experiments was monitored. In the experiments in which total arsenic in solution remained relatively constant, that is, uptake or release of arsenic by sediments was minimal, it was assumed that the change in As(III) concentration was due to oxidation of As(III) to As(V). Biological oxidation of As(III) in Hot Creek Gorge has been shown to be rapid, with a pseudo-first-order half-life for As(III) of approximately 0.3 h (Wilkie and Hering 1998), whereas oxidation by oxygen is very slow. Pseudo-first order half-lives for As(III) in our sediment-water exchange experiments ranged from 2 to 10 h. This is within the range of half-lives reported for oxidation of As(III) by manganese oxides (Scott and Morgan 1995, Oscarson et al. 1983b), suggesting that the oxidation in our experiments may be promoted by manganese oxides in the sediment. Changing the (wet) sediment-to-water ratio from 1:10 to 1:100 reduced the oxidation rate (Fig. 4.10), consistent with the proximate oxidant being a sediment component.

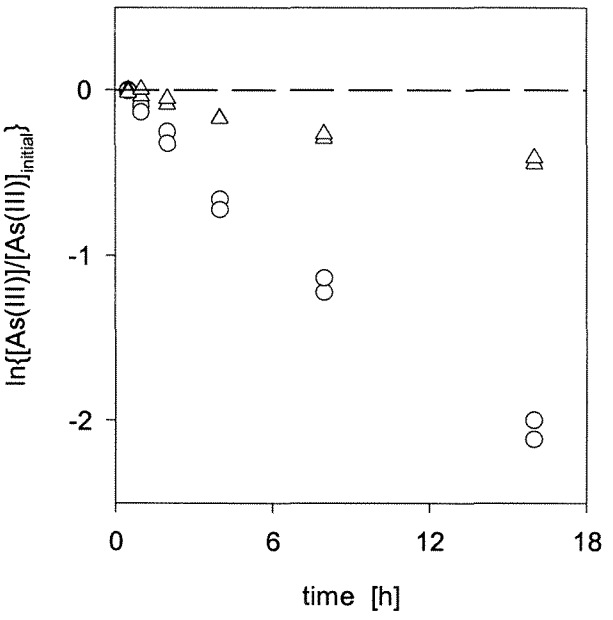

Figure 4.10: Logarithmic plot of normalized As(III) concentrations showing removal of As(III) from solution by Hot Creek sediment (HCG-99-1). Pairs of points are for duplicate samples at (wet) sediment-to-water ratios of 1:10 (○) and 1:100 (△) in synthetic Hot Creek water (SHC). Slopes are -0.13 h^{-1} for s:w = 1:10 and -0.03 h^{-1} for s:w = 1:100.

4.3.4.3 Effect of Solution Composition

When arsenic is initially present in solution, HCG-99-1 releases more arsenic into the 18 MΩcm solution than the synthetic Hot Creek solution (Fig. 4.11). Some component of the synthetic Hot Creek water is either enhancing arsenic adsorption, inhibiting arsenic desorption or inhibiting dissolution of a phase to which arsenic is adsorbed. Calcium adsorbed to oxyhydroxides in the sediment could create a more positive surface charge, enhancing arsenic adsorption. Indeed, significantly more arse-

nic was released from the sediment to the calcium-free synthetic Hot Creek water compared with the calcium-bearing solution. However, more arsenic is released to the arsenic-amended 18 MΩcm solution than to either of the solutions which initially contain other ions in addition to arsenic.

The average ionic strength in Hot Creek is 6.3 mM (CSWRCB 1993). Adjusting the ionic strength of the 18 MΩcm solution to 6.3 mM with NaCl appears to retard arsenic release (Fig. 4.11). Further investigation of the effect of ionic strength on the release of arsenic from the sediment reproduced this result (Fig. 4.12 A). However, filtration through successively smaller membranes suggested that this effect is due to the presence of colloidal material (Fig. 4.12 B). Colloidal material may have passed the 0.45 μm filters at low ionic strength, and thus have been included in the dissolved fraction. In the saltier solution, the colloidal material may have aggregated sufficiently that it would not pass the 0.45 μm filters. Similar filtration artifacts have been studied in more detail by others (Benoit and Rozan 1999, Horowitz et al. 1992, Horowitz et al. 1996).

This experiment suggests that the increased arsenic release from the sediment observed when calcium was omitted from the synthetic water may also be a colloidal effect. When calcium chloride was omitted from the synthetic water, the ionic strength deficit was made up with sodium chloride. Divalent calcium more efficiently aggregates colloidal material than monovalent sodium (Stumm and Morgan 1996). The colloidal material in the calcium-bearing solution may have been aggregated and held up by the 0.45 μm membrane while that in the calcium-free synthetic mixture may have

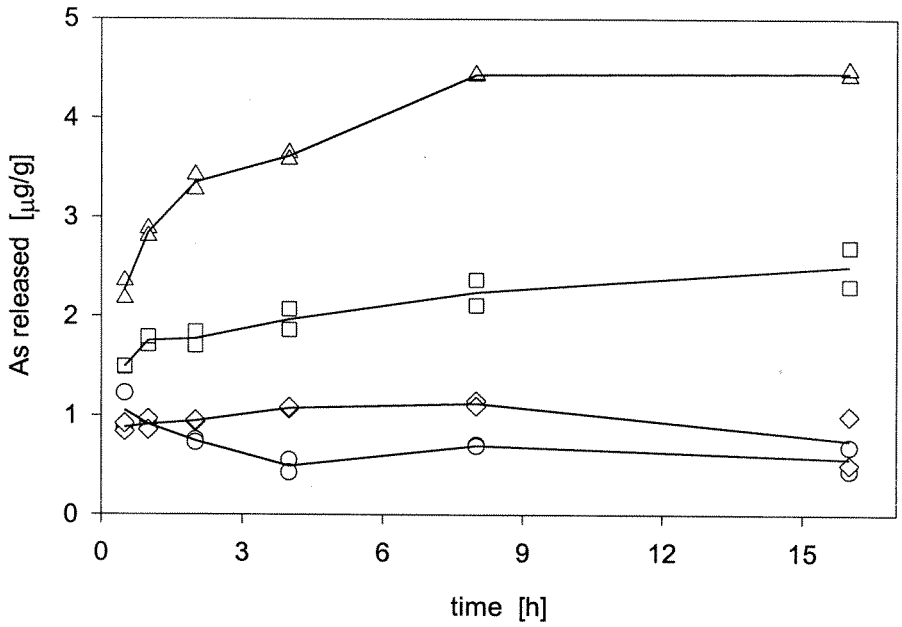

Figure 4.11: Arsenic released from 5 g wet Hot Creek sediment, collected May 1999 (HCG-99-1), into 50 mL solution. The initial arsenic concentration in each solution, $[As]_0$, has been subtracted from the concentration measured at each time and the result normalized to dry sediment mass. 5 g wet sediment = 3.5 g dry sediment. Solutions are 18 MΩcm water (△, $[As]_0$ = 348 µg/L), calcium-free synthetic Hot Creek water (□, $[As]_0$ = 365 µg/L), 6.3 mM NaCl (◇, $[As]_0$ = 332 µg/L), and synthetic Hot Creek water (○, $[As]_0$ = 367 µg/L).

passed through the membrane. The inclusion of colloidal material in the dissolved fraction overestimates the truly dissolved concentration. However, both colloidal and dissolved arsenic are similarly available for transport in streamwater. Therefore, in considering the leaching of arsenic from the sediments by the overlying streamwater or transport of arsenic with the streamwater, colloidal and dissolved phase arsenic are equally important.

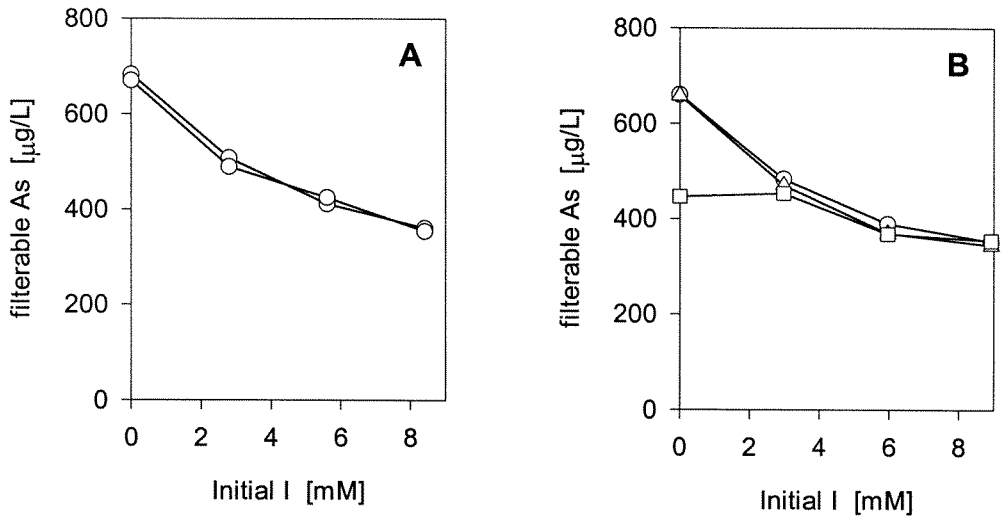

Figure 4.12: The effect of ionic strength (I) on the apparent release of arsenic from sediment to solution (A) and the effect of different sized filter membranes on the amount of arsenic measured as dissolved (B). 5 g wet Hot Creek surface sediment, HCG-99-1, was shaken for 16 h with 50 mL NaCl solutions of varying concentration then filtered. In A, 0.45 µm membrane filters were used. In B, 0.45 (○), 0.1 (△) and 0.025 (□) µm membrane filters were used in succession. Initial arsenic concentration in the solutions was 350 µg/L.

4.3.4.4 Effect of Sediment Heterogeneity

The ability of sediments to take up or release arsenic is strongly influenced by sediment heterogeneity. In the experiments with HCG-99-1 and arsenic-amended solutions, no net arsenic uptake of arsenic by the sediment was observed. However, in experiments with HCG-99-2, the sediment did sequester arsenic from the arsenic-amended synthetic Hot Creek water (Fig. 4.13). This is probably a direct result of the lower arsenic concentration in this sediment.

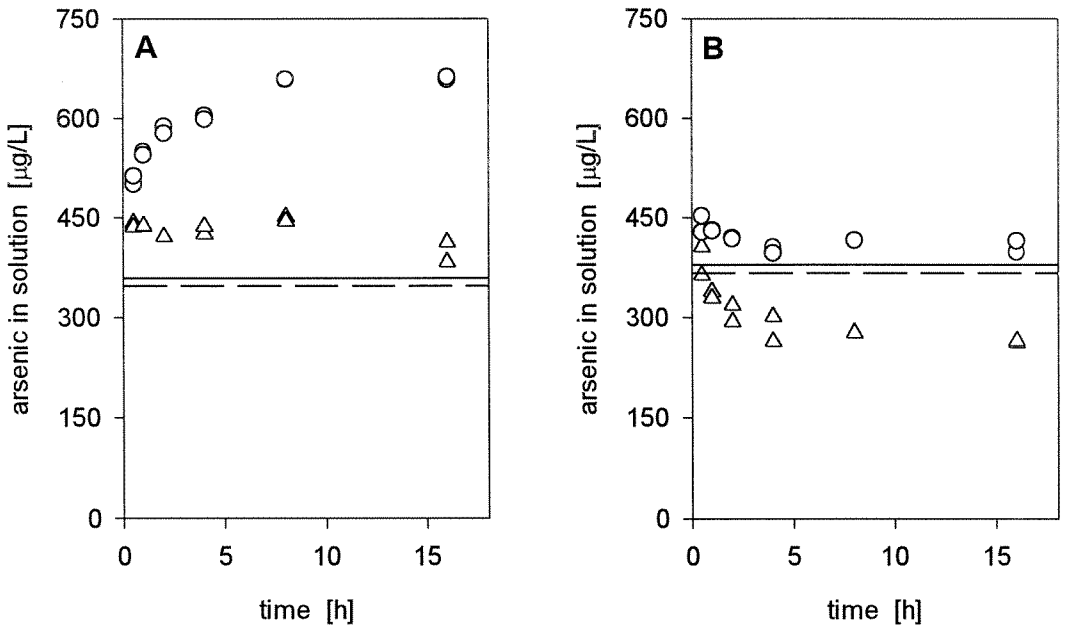

Figure 4.13: Effect of sediment heterogeneity on release of arsenic to solutions of 18 MΩcm water (A) and synthetic Hot Creek water (B). Sediments, HCG-99-1 (○) and HCG-99-2 (△), were collected in Hot Creek Gorge in May 1999. The solutions initially contained arsenic at concentrations indicated by (—) for the experiments with HCG-99-1 and (– –) for the experiments with HCG-99-2. HCG-99-1 initially contained 45 µg/g arsenic. HGC-99-2 contained 17 µg/g arsenic (concentrations on dry weight basis).

4.3.5 Capacity for Uptake and Release of Arsenic in Owens River Sediment

The sediment collected from the Owens River at Benton Crossing (BX-99) was very gravelly. The 0-2 mm size fraction was used in sediment-water exchange experiments. The arsenic concentration in this fraction was 8 µg/g. This is substantially

lower than the concentration measured in Hot Creek sediments. Sediment carried into the Owens River from Hot Creek will be diluted by arsenic-poor upstream sediments. Arsenic still associated with the sediment when it is carried from Hot Creek may be leached from the sediment by the streamwater.

The arsenic concentration in the water collected at the BX site was 69.7 μg/L. This water was used in the sediment-water exchange experiments after being filtered through a 0.45 μm membrane.

BX-99 sequestered arsenic from the water collected at Benton Crossing both when additional As(V) was added to the solution (Fig. 4.14 A) and when no additional As(V) was added (Fig. 4.14 B). In Fig. 4.7 B, we see that HCH-96 sequestered approximately 3 μg/g arsenic from 18 MΩcm water amended with 100 μg/L arsenic. In contrast, BX-99 sequestered less than 1 μg/g from Benton Crossing water with similar initial dissolved arsenic concentration. This may be due to the smaller amount of sediment in the HCH-96 experiment and the higher initial sediment arsenic concentration in BX-99. Also, other ions present in the BX water may compete for adsorption sites, reducing the ability of this sediment to sequester arsenic.

In the experiments with BX sediment and water, the sediment and water is shaken vigorously, and the smaller size fraction of the sediment is used. Hence, the average surface area is greater in the sediment fraction used in the experiment than it is in the natural composition of Benton Crossing sediments. In the Owens River, the surface sediment layer consists of large pieces of gravel, which may inhibit the movement of overlying water into the sediment bed. Therefore, there should be significantly less

contact between the water and the small size fraction of sediment in the river bed than is created in the experiments. Thus, the capacity of sediments in the Owens River to sequester arsenic from the overlying water may be further limited in their natural setting by the restricted mixing between the sediment and the water in the streambed.

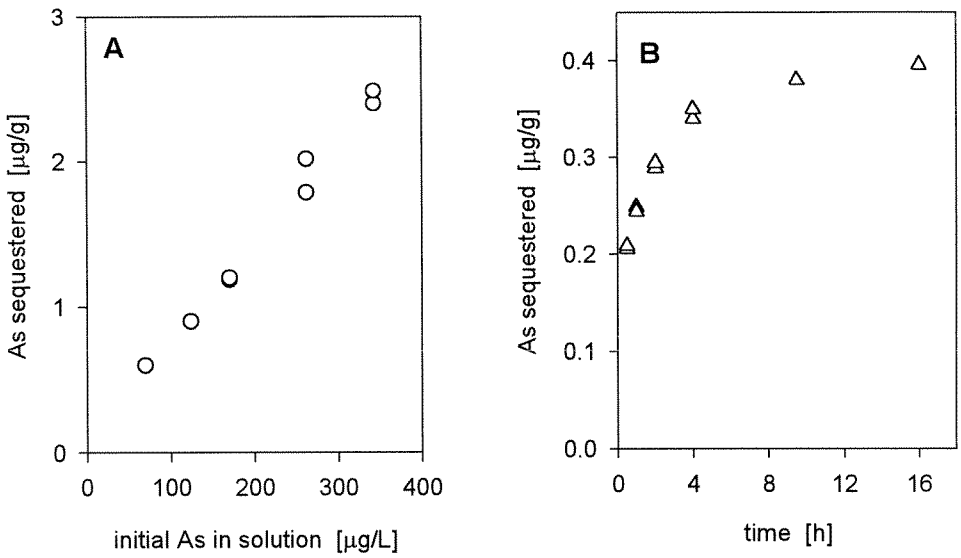

Figure 4.14: Uptake of arsenic by Owens River sediment collected at Benton Crossing (BX-99) from filtered Owens River water amended with arsenic (A) and from filtered Owens River water (B). The arsenic concentration in the Owens River water was 69.7 µg/L. The initial solid phase arsenic concentration in the sediment was 8 µg/g (on a dry weight basis). For A, 5 g wet sediment (equivalent to 3.5 g dry sediment) was shaken for 16 h with 50 mL solution. In B the same amounts of solid and solution were used and the sequestration of arsenic from solution by the sediments was monitored with time; no additional arsenic was added to the system in B.

To evaluate the possible arsenic release from the sediments of the Owens River, we can make a simple but illuminating calculation. The sediment bed in the Owens River at the sampling site was approximately 0.1 m deep. Assuming this is true for the entire river bed south of the confluence of the Owens River and Hot Creek, the total sediment is approximately 0.1 m x 4000 m x 20 m x 2500 kg/m^3 = 20 x 10^6 kg sediment. If we assume that all the Owens River sediment contains 8 μg/g arsenic, this is approximately 160 kg arsenic. If we assume all this arsenic is leached in 1 year, and that the stream flow in the Owens River is approximately 250 cfs (CSWRCB 1993), we get a stream concentration of 160 g / 220 x 10^6 m^3 = 0.7 $\mu g/m^3$ = 0.7 μg/L. Thus, if the arsenic concentration in the overlying streamwater of the Owens River is lowered, release of arsenic from the sediments of the Owens River should not significantly raise arsenic concentrations in the overlying water.

4.4 Concluding Remarks

Pore water profiles measured in the field near bed springs suggest that the net flux of arsenic between sediment and water is from sediments to the overlying water. This release occurs via diffusion of dissolved arsenic present in pore water and is small compared to the dissolved arsenic load carried by the stream water.

The laboratory experiments indicate that sediment-water exchange of arsenic in Hot Creek Gorge is controlled by several factors. The initial arsenic concentration of the sediment has a strong influence on the sediment-water exchange of arsenic; more

arsenic is released from sediments with higher arsenic concentration. The grain size of the sediment affects the extent to which arsenic is sequestered from solution, with less arsenic sequestered by coarser sediment. Hot Creek sediments are able to release arsenic to arsenic-free solution and sequester arsenic from arsenic-bearing solution. Thus, having arsenic present or not present in the initial extraction solution greatly affects the nature of sediment-water exchange of arsenic. For sediments collected upstream of the gorge, the relation between initial arsenic in solution and the amount of arsenic sequestered by sediments is almost linear for initial solution concentrations in the 100 to 1000 μg/L range. The presence of other ions in solution apparently retards the release of arsenic from sediments, although this may be due to aggregation of colloidal particles. Oxidation of As(III) added to the sediment-water solutions appears to be mediated by a sediment component, possibly a manganese oxide phase.

If arsenic concentrations in the stream water in Hot Creek were lowered, arsenic will be released from the sediment. However, the effect of this release on the arsenic concentration in the overlying water should be minimal due to the small reservoir of arsenic in these sediments.

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Chapter 5

BEHAVIOR OF ARSENIC AND OTHER REDOX-SENSITIVE ELEMENTS IN CROWLEY LAKE, CA: A RESERVOIR IN THE LOS ANGELES AQUEDUCT SYSTEM

* draft of submission to *Environmental Science and Technology,* 2000

5.1 Introduction

Elevated arsenic concentrations in Crowley Lake derive from geothermal springs in Hot Creek, an indirect tributary. These springs are the major source of arsenic to Crowley Lake, which is the first reservoir in the Los Angeles Aqueduct (LAA) system (Eccles 1976). The LAA provides up to 75% of the water supply for the City of Los Angeles, serving a population of approximately 3.2 million people. The historical annual average arsenic concentration in water delivered to the LAA Filtration Plant in Sylmar, CA, is 20 ppb (0.3 μM), which is below the current standard of 50 ppb (0.7 μM) but not below the anticipated range of 20 to 2 ppb (0.3 to 0.03 μM) for the new

standard required by the 1996 reauthorization of the Safe Drinking Water Act (Pontius 1995). The new standard, which will be proposed in June 2000 and finalized in January 2001, is expected to be 5 μg/L (USEPA 1999).

To meet the ocean water discharge standard for arsenic (12 ppb, 0.16 μM), the LAA water supply is currently being treated by addition of ferric chloride and polymer at the Cottonwood Treatment Plant, located 220 km south of Crowley Lake. The arsenic-bearing floc is subsequently deposited in Haiwee Reservoir, 27 km south of the treatment plant. Although this is a viable interim strategy, the long-term sequestration of arsenic in this sediment is uncertain (Stolarik and Christie 1999).

The springs in Hot Creek constitute a relatively localized source of arsenic and the total flow of Hot Creek is only 4-10% of the total flow at the LAA Filtration Plant. Thus, treatment for arsenic removal at Hot Creek could be a viable strategy for meeting the anticipated drinking water standard. The effectiveness of this treatment would be compromised if the resulting change in water conditions led to release of arsenic stored in the sediments of Crowley Lake.

Arsenic accumulates in lake sediments via processes that transfer arsenic from the water column to particulate material which is then deposited to the lake floor. These processes include sorption to manganese and/or iron oxyhydroxides and uptake by phytoplankton with incorporation into algal biomass (Seyler and Martin 1989, Anderson and Bruland 1991, Kuhn and Sigg 1993). Crowley Lake sediments have moderately elevated arsenic concentrations, ranging from 4 to 80 mg/kg with an average of 30 mg/kg (CA SWRCB 1993).

The surface waters of Crowley Lake are very productive because of large inputs of geothermally-derived phosphate (USEPA 1978, Melack and Lesack 1982, CA SWRCB 1993). Algal uptake of arsenate, which is chemically similar to phosphate, has been identified based on "nutrient-like" arsenic profiles (Seyler and Martin 1989, Kuhn and Sigg 1993). Occurrence of the methylated species monomethylarsonate (MMA) and dimethylarsenate (DMA) and of the reduced inorganic species arsenite in the oxygenated epilimnion is indicative of algal transformation of arsenic (Anderson and Bruland 1991, Kuhn and Sigg 1993, Aurilio et al. 1994, Sohrin et al. 1997). The methylated species are believed to be detoxification products (Andreae 1979, Sanders and Windom 1980).

Arsenic deposited to sediments can be either immobilized and buried or partially remobilized into the overlying water. Arsenic incorporated in algal biomass will be released upon remineralization of the biomass but may be subsequently immobilized, either by sorption onto metal oxyhydroxides in oxic sediments or by incorporation into sulfide solids in anoxic sediments (Aggett and O'Brien 1985, Aggett and Kriegman 1988). The concentration of dissolved arsenic in pore waters, and hence available for transport to the overlying water, can be controlled by the solubility of sulfide minerals in sulfidic environments (Moore et al. 1988). However, arsenic is usually more mobile under reducing conditions than under oxidizing conditions because of the strong tendency of arsenic to sorb to, and hence be immobilized by, iron and manganese oxyhydroxides, which persist only under oxidizing conditions.

Remineralization of organic matter and reductive dissolution of iron and manganese oxyhydroxides in anoxic sediments results in characteristic lake water column pro-

files for nutrient and redox-active elements under stratified conditions (Aggett and O'Brien 1985, Azcue et al. 1994, Freeman et al. 1986, Seyler and Martin 1989). In this study, profiles of manganese, iron, phosphorus and arsenic in the water column of Crowley Lake were obtained under stratified and unstratified conditions and examined to determine the potential for release of arsenic from Crowley Lake sediments.

5.2 Experimental Procedure

5.2.1 Sample Collection

The water column of Crowley Lake was sampled at two sites on 5 August 1998, 3 September 1998 and 11 May 1999. The reservoir stage was 2066 m on August 4 1998, and 2065 m on September 16 1998 (Ball 1999). Comparison of month-end storage (CDEC 2000) with elevation (Ball 1999) suggests that the elevation on May 11 1999 was approximately 2063 m. One site (the deepest part of the lake) was on the dam arm, approximately 150 m from the dam (N. 37° 35' 17.3", W. 118° 42' 40.7", hereafter "dam site"); the second site was in the main basin, near the chalk cliffs of the east bank (N. 37° 35' 46.8", W. 118° 43' 49.8", hereafter "basin site", Fig. 1). The dam site position was fixed by tying up to a permanent buoy line whereas the basin site position was prone to wind-driven drift on the order of 30 m southeastward during the period of sample collection on each sampling date.

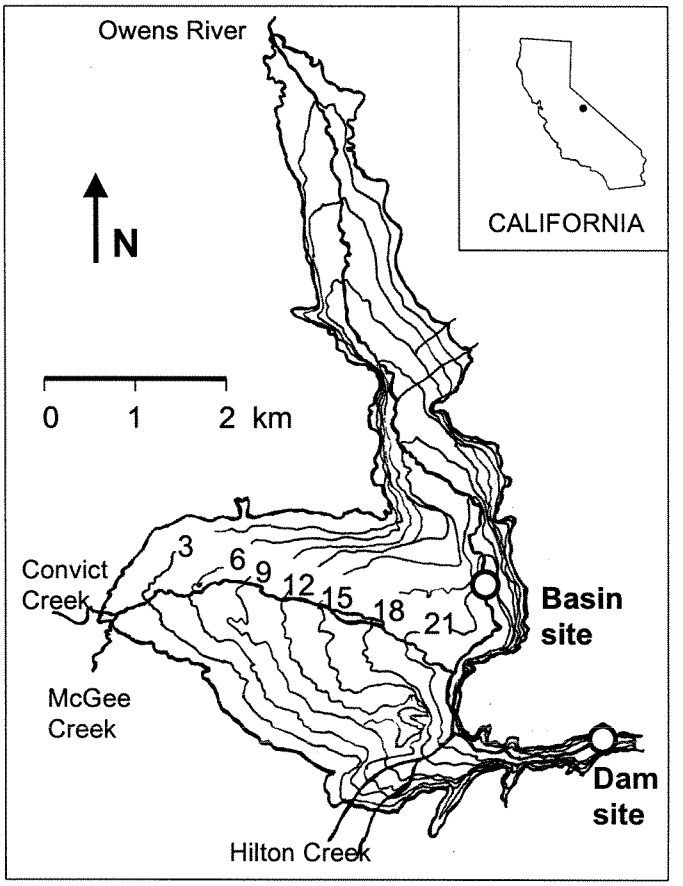

Figure 5.1: Bathymetric map of Crowley Lake with sampling sites marked. Isoclines are marked in meters, data provided by Crowley Lake Fish Camp.

A peristaltic pump was used to draw water from each depth with flow directed through a cell equipped with dissolved oxygen and combined pH/temperature electrodes (Orion, Model 1230 multimeter). When dissolved oxygen and pH readings stabilized, the flow was diverted for collection of 1 L samples in HDPE bottles. Samples with low oxygen content were collected in cubitainers flushed with nitrogen to minimize contact with air.

All laboratory and field vessels were soaked for 24 h in 10% (v/v) HCl and triple rinsed in 18 MΩcm (Millipore Milli-Q system) water before use.

5.2.2 Sample Processing

Bulk samples were processed within eight hours of collection and stored on ice before and after processing. Filtered and unfiltered aliquots were taken for anion and metal analyses. Filtered samples were obtained using syringe-tip filter units (Nucleopore) holding 0.45 μm cellulose nitrate membranes (Sartorius).

For determination of arsenic speciation, 100 mL of sample was acidified (to pH ~ 4) and passed through anion exchange columns as described by Wilkie and Hering (1998). Arsenate (pK_{a1} = 2.2, pK_{a2} = 7.0) is retained on the column and arsenite (pK_{a1} = 9.1) passes through the column and is measured in the effluent. Standard additions of DMA (Sigma Aldrich) and MMA (ChemService) to water samples collected from Hot Creek confirmed that, in this sample processing, DMA (pK_a = 6.3) passes through and MMA (pK_a = 2.6) is retained on the anion exchange columns.

Deionized water blanks were processed at the same time as samples. Samples for arsenic, phosphorus, iron and manganese analysis were acidified to 1% (v/v) nitric acid.

5.2.3 Analysis

Arsenic, iron, manganese and phosphorus were quantified by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer/Sciex Elan 5000A system). An

arsenic stock solution (0.013 M) was prepared from sodium arsenate, a phosphorus stock (0.010 M) from monosodium phosphate. Iron and manganese stocks (1.0 gL^{-1}) were obtained commercially (VWR Scientific). Calibration standards were prepared immediately prior to each analysis by dilution of the stocks. All chemicals were reagent grade or better and used without further purification.

Direct determination of MMA in samples collected in September 1998 was performed using ion chromatography (IC, Dionex DX500 with an IonPac AG11 4 mm guard column and IonPac AS11 4 mm analytical column) coupled with ICP-MS (Hewlett Packard 4500 system). Arsenic concentrations of 0.015 μM could be detected using this method.

Conductivity was measured in unacidified sub-samples (Orion, Model 1230 multimeter).

5.3 Results and Discussion

5.3.1 General Site Characteristics

The dissolved oxygen profiles for August and September reveal the oxycline around 10 m at the dam site and around 9 m at the basin site (Fig. 5.2 A, D). In May this stratification is almost completely broken down, with slight oxygen depletion in the near bottom water.

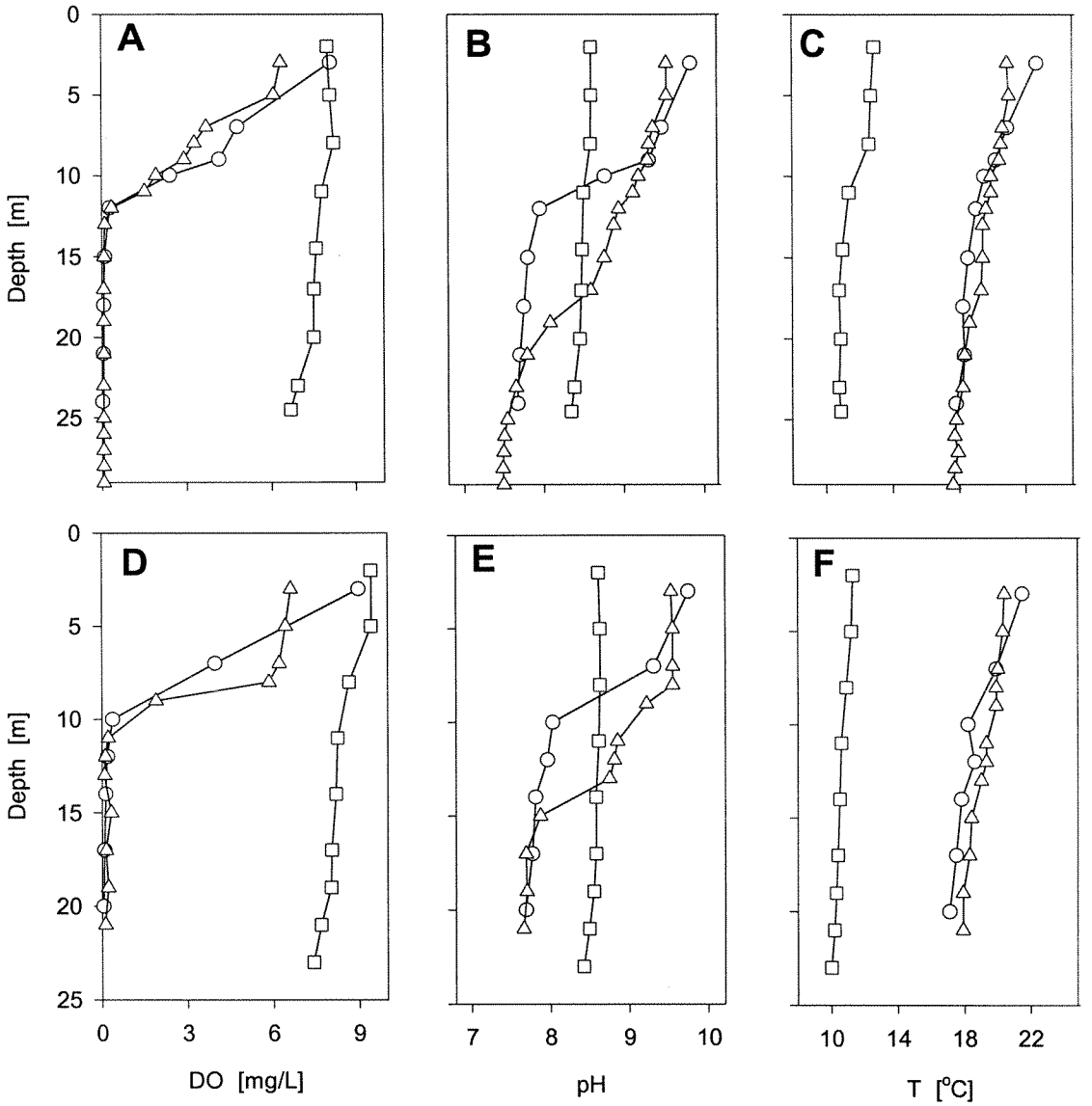

Figure 5.2: Water quality parameters measured at Crowley Lake dam site (A, B, C) and basin site (D, E, F) as a function of depth. Symbols: (○) 4 August 1998, (△) 3 September 1998, (□) 10 May 1999.

Thermal stratification is not strong in August or September (Fig. 5.2 C, F). Temperature differences between the surface and bottom waters were 4.9 °C (dam site)

and 4.4 ° C (basin site) in August and 3.3 °C (dam site) and 2.5 °C (basin site) in September. These measurements are consistent with the 2.8 °C temperature difference between surface and bottom waters measured on September 16 by the LA Department of Water and Power (LADWP) when the bottom waters still contained 0.0 mgL^{-1} dissolved oxygen (Ball 1999).

The high pH in the epilimnion in both August and September (Fig. 5.2 B, E) reflects the intense productivity during the summer months. Large flocs of phytoplankton were observed floating in the surface water at these times. These flocs were absent in May and the pH profile for this date is, correspondingly, featureless. An algal assay conducted in early June 1975 suggested Crowley Lake was nitrogen limited (Melack and Lesack 1982). An independent study of chlorophyll-*a* in Crowley Lake in 1982 showed evidence for high algal biomass and revealed nitrogen-to-phosphorus sestonic ratios below 22 and estimated loading ratios as low as 7, indicative of a lack of phosphorus limitation (Melack and Lesack 1982). The major sources of phosphorus to Crowley Lake are Big Springs (on the Owens River above its convergence with Hot Creek) and Hot Creek, evidenced by soluble reactive phosphorus in the Owens River increasing from 1.7 μM above Big Springs to 6.4 μM below this source and decreasing from 4.2 μM in Lower Hot Creek to 4.1 μM in the Owens River below Hot Creek (Melack and Lesack 1982). These phosphorus inputs make Crowley unusual, as most lakes in which arsenic cycling has been studied are phosphorus limited.

Conductivity increases gradually from □270 to □320 μScm^{-1} from the surface to the bottom at both sites in August and September with the exception of a dip in conductivity, to □200 μScm^{-1}, at 10 m at the dam site in August (data not shown).

Crowley Lake is also unusual in terms of its bathymetry and hydrology. Impounded in 1939, the reservoir consists of a broad, shallow basin with a deep channel along the eastern side following the old Owens River (Fig. 5.1). The volume of the hypolimnion is approximately 30% of the total lake volume. The reservoir outflow is regulated by the LADWP and varies dramatically on a daily, weekly and monthly basis. Residence times, calculated as month-end storage divided by total monthly outflow, varied from 0.3 to 6.7 years in 1998. Since the dam outlet is located approximately 21 m below the surface, water is withdrawn from the hypolimnion and, therefore, the chemical profile development typically observed as stratification intensifies in a lake with an *isolated* hypolimnion is likely to be significantly perturbed in Crowley Lake.

5.3.2 Manganese: Significant Release from Sediment under Stratified Conditions

The manganese profiles under stratified conditions show a strong increase in the bottom waters (Fig. 5.3 A, D). Comparison of the dissolved oxygen and manganese profiles suggests that reduced manganese diffuses upward from the sediment and is oxidized upon reaching the oxycline. A black precipitate was observed in the sample collected from a depth of 12 m at the dam site in August. Dissolution of this precipitate with hydroxylamine hydrochloride (0.04 M) in acetic acid (25% v/v) and analysis of the

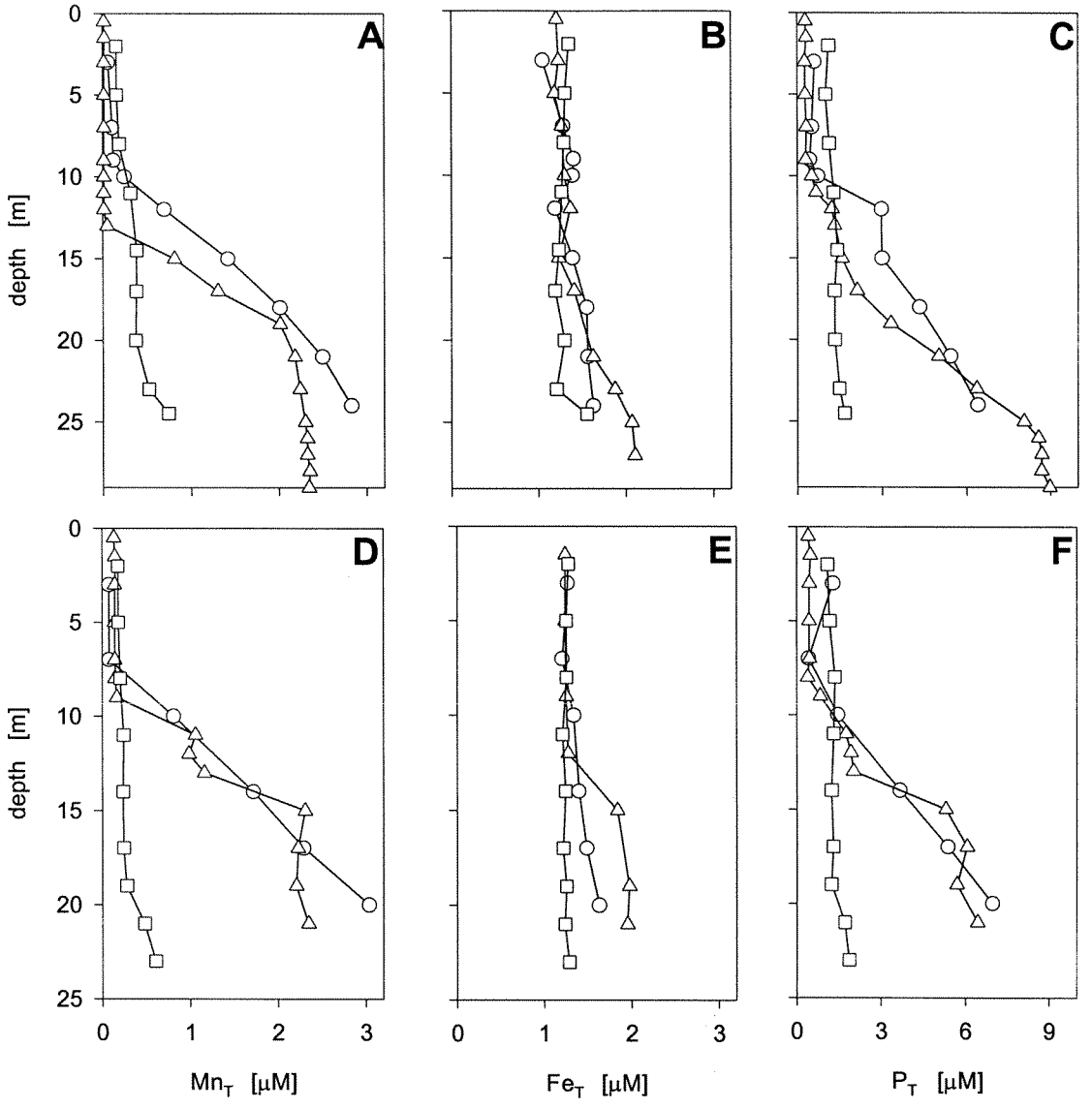

Figure 5.3: Total concentrations of manganese, iron and phosphorus measured in water samples collected from Crowley Lake dam site (A, B, C) and basin site (D, E, F). Symbols: (○) 4 August 1998, (△) 3 September 1998, (□) 10 May 1999.

leachate by ICMPS indicated that it contained arsenic, iron and manganese. This feature was not captured in the unfiltered profile as the precipitate settled rapidly in the

collection vessel and was not transferred to the sub-sample taken for analysis. No precipitates were observed at the basin site in August or at either site in September, suggesting that these precipitates are a highly localized or transient feature.

Throughout the water column in August and in the bottom waters in September, filtered and unfiltered manganese concentrations were the same within experimental error. However, in the upper 12 m at both sites in September and throughout the water column in May (when the entire water column was well oxygenated) filtered manganese concentrations were only 10-50% of the unfiltered values.

The manganese profiles at the basin site were roughly comparable in August and September whereas, at the dam site, manganese concentrations were consistently lower in September than in August. This is contrary to the increase in manganese concentration that would be expected in an isolated hypolimnion over a period of stratification. However, the hypolimnion of Crowley Lake is not isolated and the dynamics of reservoir operation can be expected to affect accumulation in the hypolimnion.

We estimate the volume of the hypolimnion to be 65 x 10^6 m^3, calculated using a lake surface area of 21 x 10^6 m^2 (USEPA 1978, and ref. cit.), defining the epilimnion as the upper 10 m based on our dissolved oxygen profiles, estimating the surface area of the hypolimnion from Fig. 1 and approximating the cross-section of the hypolimnion as triangular with a maximum depth of 28 m, justified by the deep eastern channel created by the old Owens River bed. In the three weeks preceding the August sampling, only 1.7 x 10^6 m^3 was withdrawn from the lake. However, between the August and September sampling dates, 30 x 10^6 m^3, almost half the estimated volume of the hypolimnion, was withdrawn through the outlet at 21 m (Biedelman 1998, Bagaus 1999). Storage

was decreased by only 5 x 10^6 m^3, or 3% (CDEC 1999). The water replenishing the hypolimnion must be from the epilimnion and/or surface inputs to the lake, containing essentially no manganese. For the September profile to be the same as the August profile, manganese withdrawn from the outlet must be replaced by an equivalent amount of manganese released from the sediments. The total manganese withdrawn may be estimated from the width of the selective withdrawal layer. Assuming two-dimensional flow at the outlet, the thickness of this layer is given by (after Brooks and Koh 1969)

$$(2.7)(q^{0.5})(g\varepsilon)^{0.25}$$

where q = flow per unit length of the width of the dam arm $\approx$ 11 m^3s^{-1}/100 m = 0.11 m^2s^{-1},

g = gravitational acceleration = 9.8 ms^{-2}, and

ε = density gradient parameter = $(-1/\rho_0)\, d\rho/dy = ((-1/\rho_0)(d\rho/dT))(dT/dy)$

= (0.00018 $°C^{-1}$)(4 °C / 20 m) = 3.6 x 10^{-5} m^{-1}.

Thus, the selective withdrawal layer is approximately 7 m thick. Based on the August concentration profile, withdrawal of 30 x 10^6 m^3 water from this layer would remove 7 x 10^4 mol of manganese. If there had been no withdrawal, release of manganese from the sediments equivalent to this export would have resulted in a volume-weighted average manganese concentration in the hypolimnion in September of 2.6 µM as compared with the observed value of 1.4 µM.

In May, the manganese profiles show a very small increase of approximately 0.3 µM (Fig. 5.3 A, D) near the sediment-water interface, suggesting that, even when the water column is well-oxygenated, the sediments are reducing.

5.3.3 Iron Profiles

The iron profiles are less pronounced than those of manganese during stratification (Fig. 5.3 B, E). A distinct signal of iron release from the sediments is apparent only in September. Based on samples collected in 1991, the concentration of iron in the sediments ranges from 4,000 to 11,000 ppm with an average of 7,000 ppm, while manganese ranges from 100 to 3,000 ppm with an average of 600 ppm (CA SWRCB 1993). These concentrations are low relative to crustal abundance (56,300 ppm for iron, 950 ppm for manganese) but consistent with the local geology which consists primarily of basalt, rhyolite, and andesite (Eccles 1976, refs. cit.). Despite there being more iron than manganese in the sediments, significantly more manganese than iron is released into the overlying water during stratification. Bottom water samples collected in August and September smelled strongly of sulfide and it is possible that iron is immobilized in the sediments as solid sulfide phases.

In contrast to the manganese concentrations in the hypolimnion which stayed constant, or even decreased slightly, between August and September, the iron concentrations are slightly higher in September than in August. The September iron profiles show a signal of release from the sediments that is not apparent in August. We hypothesize that the observed changes in the iron profiles may result from the introduction of oxygen associated with replacement of water withdrawn from the hypolimnion.

Although the surface water is well oxygenated, the pronounced oxycline is maintained in September, which suggests that the newly introduced oxygen must be rapidly consumed in the hypolimnion. It is possible that this dissolved oxygen promotes oxidative dissolution of iron-sulfide phases at the sediment-water interface and

subsequent release of iron to the overlying water. The surface water iron concentrations are the same within experimental error at the two sites in September, as are the bottom water iron concentrations but, at 15 to 20 m, there is 40% more iron at the basin site than at the dam site, possibly an effect of the less dynamic flow regime at the basin site.

In August, only 70% of the total iron at the oxycline at the dam site passes a 0.45 μm filter compared to 90% at the basin site. The precipitation of iron-containing solids above the oxycline at the dam site in August is corroborated by the presence of the black particulate material observed at this site.

5.3.4 Phosphorus: Uptake and Remineralization under Stratified Conditions

The phosphorus profiles under stratified conditions show significant enrichment at depth, consistent with the remineralization of algal biomass deposited on the lake floor (Fig. 5.3 C, F). Like manganese, phosphorus concentrations in the hypolimnion remain constant (or decrease slightly) between August and September. Again, only a substantial flux from the sediments could maintain these bottom water concentrations if the water withdrawn from the hypolimnion was replaced with surface water depleted in phosphorus. If the hypolimnetic water were replaced by water with elevated phosphorus concentration then accumulation of phosphorus in the hypolimnion would have been observed despite the withdrawals.

The Owens River is enriched in phosphorus as a result of inputs from Big Springs, Hot Creek and possibly other sources (Melack and Lesack 1981). Phosphorus

concentrations ranging from 4.2 to 8.1 μM with an average of 6.2 μM were measured at Benton Crossing (located 3 km north of Crowley Lake, below the confluence with Hot Creek) from January 1997 to October 1998 (Ball 1999). The low phosphorus concentrations observed in the surface water of Crowley Lake in late summer (0.3 to 0.4 μM) can be attributed to algal uptake and dilution by other tributaries that are not subject to geothermal loading. The persistence of detectable phosphorus in the surface water in late summer suggests that phosphorus does not limit primary production in Crowley Lake.

In May, the concentration of phosphorus was uniform throughout the water column (Fig. 5.3 C, F) and somewhat higher than the surface water concentrations in August and September. Estimating the total phosphorus load in the water column suggests that less than 20% of the phosphorus present in September is removed by May, probably via withdrawal of the phosphorus-enriched hypolimnetic water before turnover.

Phosphorus concentrations in filtered and unfiltered samples were the same within experimental error in the hypolimnion at both sites during the summer. In the epilimnion at 3 m at the basin site in August, the phosphorus concentration in the filtered sample was 30% of that in the unfiltered sample. In May, phosphorus concentrations in filtered samples were 70-90% of those in the corresponding unfiltered samples.

5.3.5 Total Arsenic: No Evidence for Significant Sediment-Water Exchange

The total arsenic profiles in Crowley Lake exhibit three distinct patterns. In May, concentrations were uniform throughout the water column. In August, a minimum was observed at the oxycline and, in September, concentrations decreased with depth (Fig. 5.4). Arsenic concentrations in filtered and unfiltered samples were the same within experimental error. LADWP monitoring records show fluctuations in arsenic concentration at the dam outlet. The concentrations we measured are consistent with these records for August, September and May over the four years 1996 to 1999 (Ball 1999).

The uniform concentrations measured in May are comparable to those measured in the deep water in August and the surface waters in August and September. A small (16%) loss of arsenic within Crowley Lake was indicated by a mass balance constructed in 1967 using historical, annually averaged input and withdrawal data (SCDWR 1967). A mass balance for 1998 using monthly flow estimates for each of the tributaries (Keef 1999), outlet flow data (Biedelman 1998, Bagaus 1999) and arsenic concentrations measured at Benton Crossing and Crowley Lake outlet (Ball 1999), suggests that arsenic behaves conservatively in Crowley Lake.

Neither the August nor the September arsenic profiles show evidence for substantial cycling of arsenic between the sediments and the water column, consistent with the mass balance calculation. Arsenic is not depleted in the surface waters and concentrations at depth are not elevated compared to those at the surface.

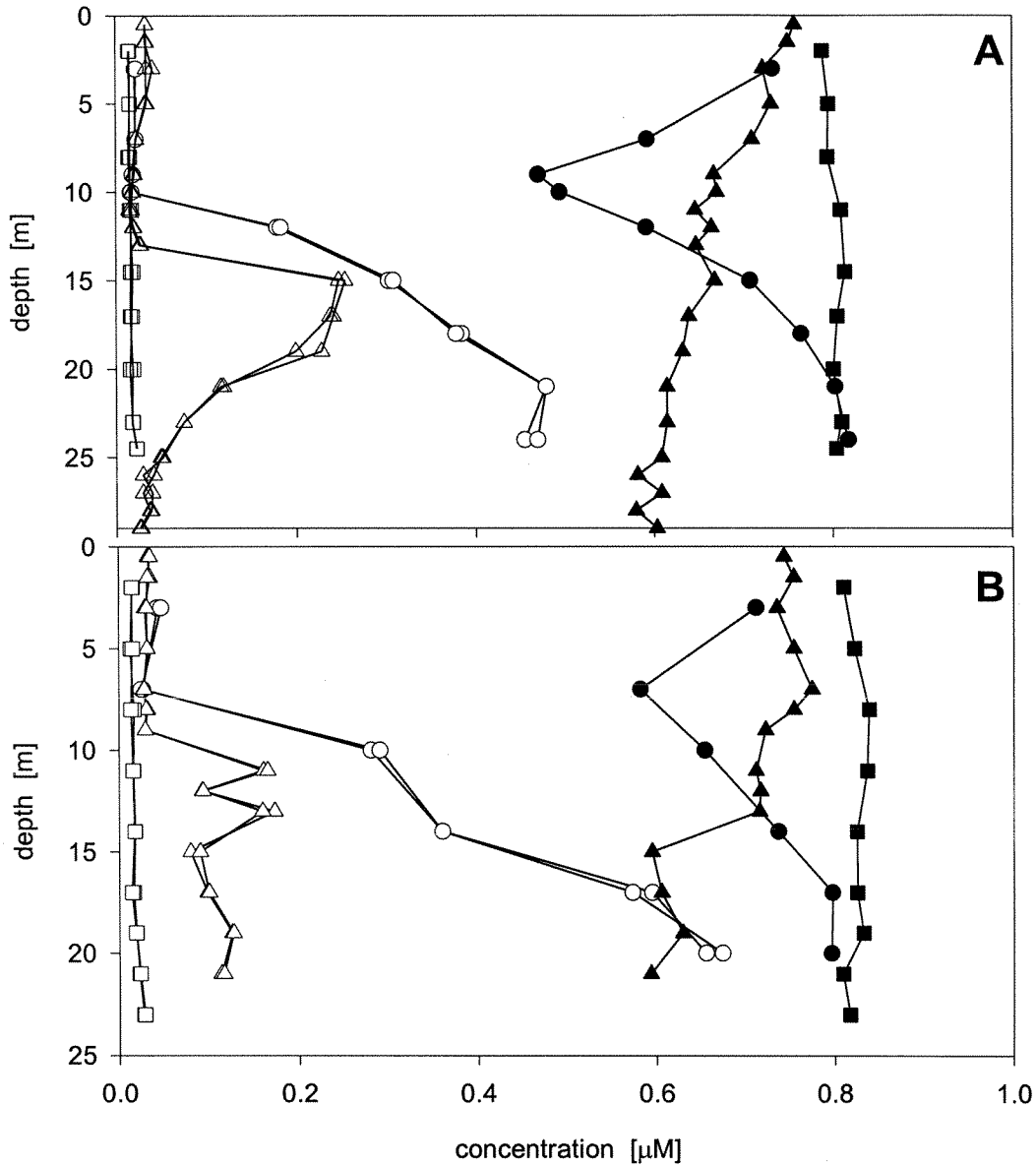

Figure 5.4: Concentrations of total arsenic (solid symbols) and arsenite (open symbols, duplicate field separations) measured in water samples collected from Crowley Lake dam site (A) and basin site (B). Samples were collected 4 August 1998 (●, ○), 3 September 1998 (▲, △), and 10 May 1999 (■, □).

The decrease in concentration with depth in September can be explained by replacement of water withdrawn from the hypolimnion by water with slightly lower total arsenic concentration. Although lower concentrations of total arsenic were observed around the oxycline in August, this effect was much less pronounced at the basin site, which is likely to be more representative of the whole lake, than at the dam site. The surface inputs to the lake in August would have had lower arsenic concentration than the hypolimnetic water since the arsenic contributed by the Owens River, with 0.8 μM arsenic (Ball 1999), was diluted approximately 1:1 in August by arsenic-free tributaries (Keef 1999).

The dip in total arsenic at the oxycline at the dam site in August is most likely due to adsorption onto the black precipitate observed in these samples. The concentration increase below this dip is probably due to release of arsenic, by reductive dissolution, from the rapidly settling particles formed at the oxycline. Thus, the shape of the August profile can be attributed to internal cycling of arsenic *within the water column* rather than to release of arsenic from the sediment. Although less pronounced, this general pattern is also observed at the basin site.

The lack of evidence for release of arsenic from the sediment under stratified conditions in spite of the significant release of manganese at the same time suggests that adsorption of arsenic to oxyhydroxide species does not result in net transport of arsenic to the sediment in this system. This is possibly a direct result of the relatively low concentrations of manganese and iron in the system.

In a 1991 survey, arsenic concentrations in Crowley Lake sediments ranged from 4 to 80 mg/kg (dry weight basis) (CA SWRCB 1993). Arsenic concentrations in

surface sediments we collected from the basin and dam sites ranged from 140 to 260 mg/kg (dry weight basis, determined by x-ray fluorescence). Arsenic sequestration by sulfides in Crowley sediments could produce this modest elevation of arsenic concentration above the local background of 8 mg/kg we measured at Benton Crossing. X-ray absorption spectra of Crowley Lake sediments indicate that arsenic is associated with a sulfide phase (Kneebone 2000).

5.3.6 Inorganic Arsenic Speciation

In August, arsenite concentrations increase with depth below the oxycline (Fig. 5.4). In the absence of release from the sediments, this may be attributed to internal recycling in the water column. Arsenic removed from the water column at the oxycline, presumably by sorption onto the rapidly settling black particulate material, is released at depth as this material undergoes reductive dissolution.

In September, the unusual arsenite profiles are most likely due to the large outflow from the reservoir prior to sample collection (Fig. 5.4). The basin site is considerably further from the outlet than the dam site and this may account for the difference between the two sites. Arsenite produced in the deep waters prior to the August sampling is withdrawn, being replaced by arsenate-bearing surface waters.

In the well-mixed conditions in May, arsenite is not an important species at any depth in the water column (Fig. 5.4).

5.3.7 Organic Arsenic Speciation

In the productive, summer months, more than 95% of the arsenic in the epilimnion was present as arsenate. Since DMA, if present, would have eluted with arsenite in the on-site sample processing, the small amount of arsenic in this fraction (Fig. 4) implies that DMA is not a significant species in the epilimnion. The IC-ICPMS method revealed no MMA in any of the samples analyzed. Thus, although the surface waters were very productive, these methylated species were not abundant.

In contrast to arsenic cycling in other productive lake systems, uptake and transformation of arsenic by phytoplankton do not appear to be important processes in Crowley Lake, perhaps because of the large input of phosphorus to the lake, which may displace arsenate from the phytoplankton cycle. In contrast to phosphorus, arsenic concentrations were the same in filtered and unfiltered samples from the epilimnion. Deposition of algal matter to the sediment does not, therefore, result in deposition of arsenic to the sediment in this system.

5.3.8 Implications for Water Quality in the Los Angeles Aqueduct

Our results indicate that arsenic is not released from the sediments of Crowley Lake during summer stratification. Neither of the two common mechanisms facilitating transport of arsenic from the water column to the sediment in freshwater lakes (adsorption to oxyhydroxides and uptake by phytoplankton), appear to be important in Crowley Lake. Arsenic is associated with a sulfide phase in the sediments which should be stable when the sediment-water interface is anoxic. The decrease in dissolved oxygen and

increase in manganese concentrations at depth in May suggest that the sediments are permanently reducing.

If upstream arsenic concentrations were decreased, concentration gradients should allow gradual release of arsenic from the sediments of Crowley Lake. However, the sediment arsenic concentrations are not extreme and arsenic is associated with a sulfide phase in these sediments. Thus, arsenic release from the sediments will be minimal while the sediment-water interface is anoxic. Crowley Lake sediments should not be a significant source of arsenic to the Los Angeles Aqueduct water supply if upstream water were treated for arsenic removal.

Crowley Lake has unique features which derive from high inputs of arsenic and phosphorus and its operation as a reservoir. These features allow observation of phenomena that would not be apparent in "normal" lakes. In contrast to other lakes, algal cycling of arsenic does not appear to be important in Crowley. This study is a clear example of how profoundly reservoir operations can influence water chemistry, an important consideration in the management of water supply systems.

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Chapter 6

THE STABILITY OF ARSENIC IN THE SEDIMENTS OF NORTH HAIWEE RESERVOIR

6.1 Introduction

6.1.1 Arsenic in the Los Angeles Aqueduct

Arsenic concentrations in the Los Angeles Aqueduct (LAA) are elevated due to geothermal inputs to tributary streams, in particular, to Hot Creek. The geothermal mass flux of arsenic in Hot Creek is relatively constant (Farrar et al. 1987). However, variable flow resulting from cycles in snowmelt and storage in the Sierra Nevada Mountains cause seasonal variations in arsenic concentrations in the LAA.

The historical annual average arsenic concentration at the LAA Filtration Plant (LAAFP) at Sylmar is 20 μg/L, well below the current 50 μg/L maximum contaminant level for arsenic in drinking water. However, this standard is under review. The new standard, to be proposed in June 2000 and finalized in January 2001, is expected to be 5 μg/L (USEPA 1999). In addition, to comply with its NPDES (National Pollutant Discharge Elimination System) permit, the Hyperion Treatment Plant is required to have less than 12 μg/L arsenic in its ocean discharge. To meet this effluent discharge stan-

dard and prepare for the future drinking water standard, the Los Angeles Department of Water and Power (LADWP) implemented an interim arsenic management plan in 1996 to reduce arsenic concentrations in the LAA to below 10 μg/L.

The Cottonwood Treatment Plant, 27 km north of Haiwee Reservoir, was historically operated to control turbidity in the LAA. Cationic polymer was added via diffusers. The aqueduct itself provided the necessary hydraulic mixing before the polymeric floc settled in North Haiwee Reservoir. The plant was operated intermittently from 1973 to the early 1980s, then continuously until the LAAFP was completed in 1987. In 1995, polymer additions at Haiwee resumed, and since 1996, as part of the interim arsenic management plan, ferric chloride has also been added at an average dose of 5.7 mg/L. Arsenic oxyanions are readily adsorbed by the iron-rich floc produced by the ferric chloride coagulant. Approximately 67% of the dissolved arsenic in the influent of the Cottonwood Treatment Plant is removed from the water by sedimentation of the arsenic- and iron-rich floc in North Haiwee Reservoir (Stolarik and Christie 1999). Since the ferric chloride additions began, the average arsenic concentration below Haiwee Reservoir has been 8.1 μg/L (Stolarik and Christie 1999). However, this efficacious arsenic removal from the dissolved phase results in extensive accumulation of arsenic in the sediments of North Haiwee Reservoir. Based on average removal and flow rates (Table 6.1), some 40 metric tons of arsenic has been deposited in the sediments of this reservoir in the four years since March 1996.

In this study, we examine the sediments of Haiwee Reservoir in an attempt to determine the stability of arsenic deposited with the iron hydroxide floc.

Table 6.1: Treatment at Cottonwood Treatment Plant - 4 year Average Parameter Values[a]

PARAMETER	4 YEAR AVERAGE VALUE
Flow at Cottonwood	17 m^3/s
As concentration above Cottonwood	24.8 mg/m^3
As concentration below N. Haiwee Reservoir	8.3 mg/m^3
$FeCl_3$ dose	5.7 g/m^3
polymer dose	1.7 g/m^3

[a] source: Stolarik and Christie 1999

6.1.2 Arsenic Mobility in Lake Sediments

In iron-rich systems, iron plays a central role in the geochemical cycling of arsenic (Davison 1985). Redox conditions may determine the stability of arsenic in the sediment. Under oxic conditions, iron oxyhydroxide phases are stable. The net surface charge of oxyhydroxide phases varies with pH. Many iron oxyhydroxides carry a net positive surface charge at the pH of their natural environment and, therefore, readily adsorb arsenic oxyanions. Arsenate (H_3AsO_4, pK_{a1}= 2.2, pK_{a2} = 6.9) is anionic in most natural systems. Due to favorable electrostatic interaction, arsenate is, in general, adsorbed to a greater extent than arsenite (H_3AsO_2, pK_{a1} = 9.3) (Manning and Goldberg 1997).

Advective processes may carry arsenic-bearing oxyhydroxide particulates to lake sediments. Subsequent burial exposes the particles to more reducing environ-

ments. In deeper, anoxic sediments, reductive dissolution of the arsenic-bearing iron oxyhydroxide releases both reduced iron and the associated arsenic to the interstitial water (Aggett and O'Brien 1985). The dissolved species will diffuse both up and down, away from the site of production, following concentration gradients.

Downward-diffusing arsenic may be sequestered by sulfide phases, if sufficient sulfide is present. Such sulfide phases are readily oxidized under aerobic conditions. Groundwater may also provide a sink for downward-diffusing species. The fate of upward-diffusing arsenic is determined by the position of the redox boundary. If the redox boundary is below the sediment-water interface, arsenic may be readsorbed on oxyhydroxide phases in the oxic surface sediment. However, if the redox boundary is at, near or above the sediment-water interface, arsenic may be released from the sediment to the water column.

The position of the redox boundary may be determined by the rate of sedimentation and the concentration of organic material. In North Haiwee Reservoir, sedimentation is accelerated due to the addition of ferric chloride and cationic polymer at the Cottonwood Treatment Plant. As particulates are deposited, overlying water trapped in the pore spaces becomes interstitial water. In this way, the growth of the sediment column effectively transports dissolved material in the water column to the pore water. If this advection is sufficiently fast and the water column is well-oxygenated, the surface sediment will remain well-oxygenated. Dissolved oxygen from the surface water may also diffuse into the pore water. Haiwee Reservoir is well-mixed year round. Therefore, the sediment-water interface is, presumably, well-oxygenated. However, exten-

sive remineralization of organic matter could promote anoxic conditions in the surface sediments.

If arsenic is primarily associated with iron oxyhydroxides in the sediment of Haiwee Reservoir, the position of the redox boundary will determine whether arsenic is immobilized in these sediments. If the redox boundary lies below the sediment-water interface, arsenic should not be released from the sediment pore water into the overlying water. However, if a strong redox gradient exists in the sediment column, the well-oxygenated surface sediment may be capping a sizeable pool of soluble arsenic in the deep, anoxic sediment pore waters. If so, physical disturbance of the sediments would release this arsenic from the pore water to the overlying water.

6.2 Experimental Methods

6.2.1 Site Description

The characteristic parameters of North and South Haiwee Reservoirs are collated in Table 6.2.

Water and sediment samples were collected at four sites from North Haiwee Reservoir (Fig. 6.1). At the NW and SW sites, orange-brown floc was visible floating in the water and was settling near the banks of the channel, where flow velocity was reduced. The surface sediment at these sites was a fine, orange-brown floc, whereas the deep sediment was fine, black and gelatinous. A fine-bore probe inserted 2 m down-

stream of the NW site suggested the sediment depth was approximately 0.4 m. At the NE site, the sediment was sandy with brown and black striations throughout.

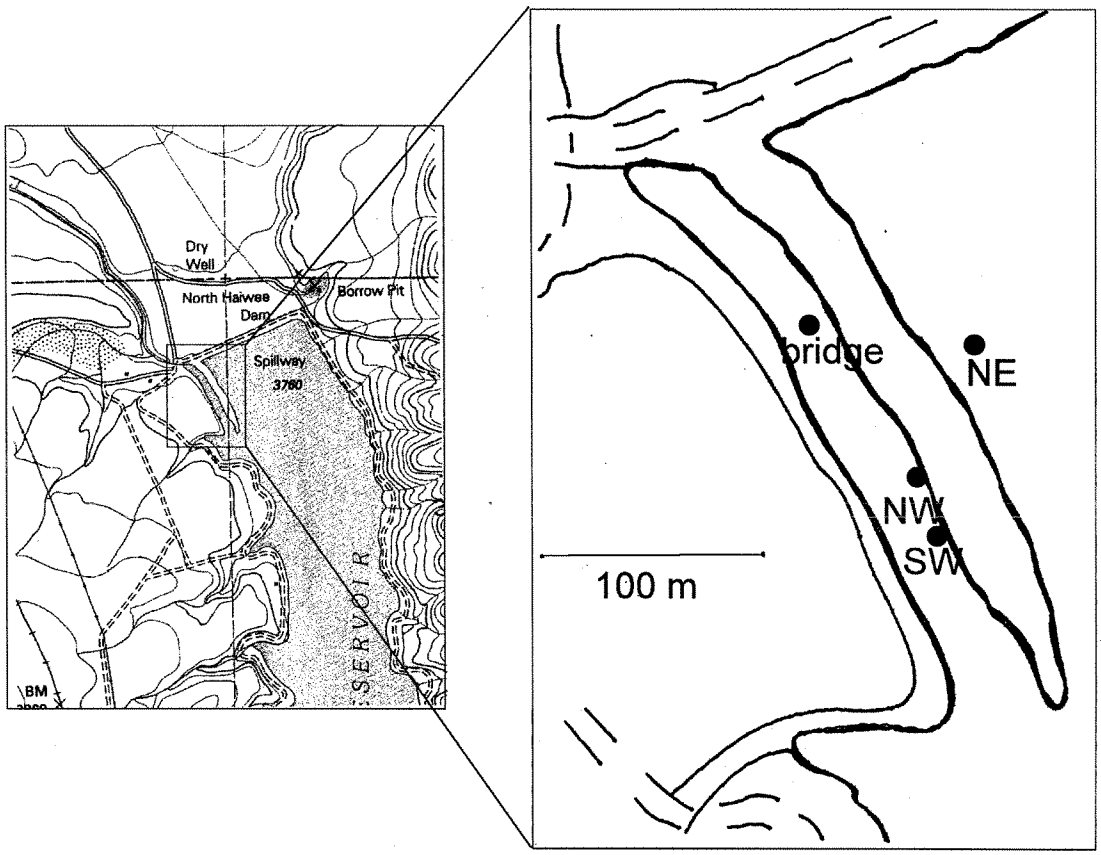

Figure 6.1: Sample collection sites in North Haiwee Reservoir, 22 December 1999. Left panel from USGS 1994.

Water samples were collected at the NE and NW sites and at the footbridge (see Fig. 6.1). Sediment samples were collected from the NE, NW and SW sites. At the NW and SW sites, water and sediment samples were collected 0.8 m from the water's edge, in water 0.2 m deep. At the NE site, water and sediment samples were collected 8 m from the bank, in water 0.8 m deep.

Table 6.2: Characteristics of Haiwee Reservoir[a]

Surface Elevation [m]	Surface Area [10^6 m^2]	Storage [10^6 m^3]	Average Depth [m]	Maximum Depth [m]
NORTH HAIWEE				
1145.1[b]	2.33	12.0	5.16	6.68
1145.3[b]	2.36	12.4	5.26	6.83
1138.5[c]	0	0	0	0
SOUTH HAIWEE				
1140.6[d]	3.76	34.3	9.12	15.4
1137.5[b]		23.4		12.3
1125.2[c]	0	0	0	0

[a] Source: W. Hopper, 2000.

[b] Typical elevation of usual operation

[c] Surface elevation at which storage = 0

[d] Maximum elevation for operation, set by State of California

6.2.2 Sample Collection

Water samples were collected from the NW, NE and bridge sites in 1L, acid washed, high density polyethylene (HDPE) jars. A hand pump was used to collect the bridge sample via tygon tubing lowered from the center of the bridge.

A gel probe sampler was used for the determination of pore water concentrations at the NW site. This device consists of polyacrylamide gel pieces (2.5 cm x 0.7 cm x 0.2 cm) of high water content (91-94%) mounted in a plexiglass ladder, covered by a 0.45 μm cellulose nitrate membrane. Upon insertion in the sediment, the water held in the gel matrix equilibrates with the pore water, allowing determination of the pore water

concentrations by back-equilibration of the gel pieces. The gel probe was stored in de-oxygenated 18.2 MΩcm water (Millipore) and bubbled with nitrogen gas for 24 h prior to being transported to the field. The gel probe sampler was inserted at the NW site for 6.5 h to ensure complete equilibration of the gel pieces with the pore water.

Sediment cores were collected using polycarbonate tubes with 9 cm internal diameter. Following sediment removal, both ends of the tubes were capped and the cores transported, upright on ice, to the laboratory. The NW sediment core, collected 0.5 m from the gel probe position following retrieval of the probe, was limited by the length of the core collector (0.44 m). (i.e., the very deepest sediment was not collected.) The length of the SW core was 0.27 m, and the NE core was 0.18 m.

Bulk sediment and water samples were collected near the SW site for use in laboratory microcosms. A second bulk water sample was collected at the NE site. The bulk water samples were filtered in the field using 0.2 μm cellulose acetate membrane filters mounted in large volume vacuum filtration units. The sediment samples were scooped into 1 L HDPE, screw-top jars. These water and sediment samples were transported on ice to the laboratory where they were frozen until use.

6.2.3 Sample Preparation

Water samples were processed in the field immediately following collection. An aliquot of the bulk sample was filtered using 0.45 μm cellulose nitrate membrane filters mounted in syringe-tip filter units. A second aliquot, unfiltered, was processed

for inorganic arsenic speciation using the anion exchange technique described Wilkie and Hering (1998). The anion exchange column influent was subsampled for total metals analyses and the effluent collected for arsenite determination. A field blank of 18 MΩcm water was processed at the same time. All samples were stored on ice. The samples for metals analysis were acidified to 1% HNO_3 in the laboratory (within 9 h of collection).

Upon retrieval of the gel probe sampler, the gel pieces were transferred to preweighed vials containing 1% HNO_3. Pore water concentrations were calculated following ICPMS analysis of the back-equilibrated solution using the equation

$$C = \frac{C_{measured}.(m_{gel}.\omega_{gel} + V_{1\%HNO3})}{m_{gel}.\omega_{gel}}$$

where C is the recovered concentration, $C_{measured}$ is the concentration measured in the back-equilibrated solution and m_{gel} is the mass of the gel piece. ω_{gel} is the fraction of gel mass which is water, determined by weight loss upon drying, and $V_{1\%HNO3}$ is the volume of 1% HNO_3 used for back-equilibration.

Sediment core samples were frozen on return to the laboratory. They were partially defrosted to allow extrusion and were sub-sectioned in a nitrogen-filled glove bag. Sections were double-bagged in zip-lock bags inside the glove bag and returned to the freezer while still frozen. Sections were defrosted and homogenized by kneading the bags. Sub-sections were taken, under a nitrogen atmosphere, for whole sediment digestion and centrifugation. Following centrifugation at 10,000 rpm for 5 minutes, the supernatant was filtered (0.45 μm, cellulose nitrate), diluted appropriately, and acidified to

1% HNO_3 for ICPMS analysis. All of these manipulations were conducted under a nitrogen atmosphere.

EPA Method 6010, modified by excluding the final addition of hydrochloric acid and using ICPMS for analysis, was used to determine the solid phase concentrations of iron, manganese, arsenic and phosphorus. This method achieves a partial digestion; the sample is heated with nitric acid and hydrogen peroxide is added. The digestate was diluted appropriately for ICPMS analysis. A blank and a standard reference soil, SRM 4711 (NIST), were analyzed with each set of digestions. The blanks consistently produced concentrations below the detection limit. Recoveries from the standard soil were within the (non-certified) range specified for leaching techniques and were approximately 80% of the (certified) x-ray fluorescence values for iron and manganese and greater than 90% for arsenic.

6.2.4 Sequential extraction

Sediment from the 2.5-4.5, 18-21.5 and 37-41 cm sections of the core collected from the NW site were subjected to a sequential extraction procedure. Extractions were run in duplicate on 1 g samples of dry sediment. The sediment was washed with 10 mL 18.2 MΩ water between extraction steps. A wrist-action shaker was used for the first and second extractions to provide continuous agitation of the samples.

In the first extraction, sediments were shaken with 8 mL of 1 M $MgCl_2$ solution, at room temperature for 1 h. This step should extract the exchangeable fraction of arse-

nic in the sample (Tessier et al. 1979). In the second extraction, the samples were shaken with 8 mL of 1 M NaOAc (adjusted to pH 5 with HOAc) at room temperature for 5 h. This solution should extract carbonate phases from the sediment (Tessier et al. 1979). The third extraction was 20 mL of 0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAc, at 96 ± 3 °C, for 6 h with occasional agitation. This extraction solution should dissolve iron and manganese oxyhydroxide phases (Tessier et al. 1979). The fourth extraction was 10 mL 0.1 M sodium pyrophosphate (pH 10), at room temperature for 12 h. This solution should extract arsenic associated with organic phases (Moore et al. 1988). For the final extraction, the sediment was combined with 1 g of $KClO_3$ per gram of sample and 10 mL concentrated HCl and left to stand for 30 min. The solution was then diluted with 10 mL of 18.2 MΩ water and mixed. This should remove arsenic associated with sulfide phases in the sediment (Chao and Sanzolone 1977). Arsenic, manganese and iron were measured in solution after each extraction.

6.2.5 Incubation of North Haiwee Reservoir Sediments

Bulk sediment collected from the SW site was homogenized and deoxygenated under an argon atmosphere. 250 mL of the wet sediment slurry, equivalent to 60 g dry sediment, was transferred to each of 6 acid-washed jars. 12 mL 37% formaldehyde solution was added to jar 4 and 20 mL Provosoli's concentrated antibiotic solution (Sigma) was added to jar 5. The lids were secured under argon, and the jars transferred to the freezer for 30 min, until a thin layer of ice had formed on the surface of the sediment. This step was an attempt to minimize sediment disturbance upon introduction of

water to the jars. Filtered water (0.2 μm, cellulose acetate) from the SW and NE sites was combined. 0.6 L of this was carefully added to jar 1 and jar 2, trying to avoid disturbing the surface sediment. The remainder was deoxygenated and 0.6 L added to jars 3 to 6. Gas dispersion tubes were inserted through pre-drilled holes in the lids of the jars. Jars 1 and 2 were bubbled continuously with air throughout the experiment. Jars 3 to 6 were bubbled with argon. Gas flow rates were controlled so that the solutions were well-mixed without disturbing the sediment. 10 mL samples were removed periodically over 48 h via teflon tubing inserted in the bleed holes in the jar lids. The pH of the samples was checked for large variations using indicator paper. Samples were acidified to pH 4 and an aliquot run through a column filled with anion exchange resin to separate arsenate from arsenite. Total arsenic, manganese and iron was measured in the influent and arsenic (arsenite) measured in the effluent.

6.2.6 Analysis

Arsenic, iron, manganese and phosphorus were quantified by inductively coupled plasma mass spectrometry (ICPMS, Perkin-Elmer/Sciex Elan 5000A system). An arsenic stock solution (1.0 g/L) was prepared from sodium arsenate, a phosphorus stock (0.010 M) from monosodium phosphate. Iron and manganese stocks (1.0 g/L) were obtained commercially (VWR Scientific). Calibration standards were prepared immediately prior to each analysis by dilution of the stocks. All chemicals were reagent grade or better and used without further purification.

Direct determination of MMA in pore water samples and inorganic arsenic speciation in the gel probe samples was performed using ion chromatography (IC, Dionex DX500 with an IonPac AG11 4 mm guard column and IonPac AS11 4 mm analytical column) coupled with ICP-MS (Hewlett Packard 4500 system).

X-ray absorption spectroscopy (XAS) was performed on beamline IV-3 at the Stanford Synchrotron Radiation Laboratory in January 2000. In XAS, a sample is scanned with x-ray photons in the range of 200 to 35,000 eV. Core photoelectrons are ejected when the incoming photon energy exceeds the electron binding energy. The fluorescence emitted by the decaying excited state is detected. The energy at which absorption occurs is determined by the core electron binding energy, and is, therefore, characteristic of the oxidation state of the absorbing atom. Neighboring atoms backscatter the emitted photoelectron wave. Deconvolution of interference patterns calculated at the central absorbing atom provides information about the identity and distance of the neighboring atoms. XAS spectra were collected at 10 K with a Si(220) monochromator. Samples were prepared under a nitrogen bleed and stored, frozen, in nitrogen-filled zip-lock bags prior to analysis.

6.3 Results and Discussion

In this study we attempt to assess the stability of arsenic in the sediments of North Haiwee Reservoir. Concentrations of arsenic, manganese and iron in the overlying water, sediments and pore waters are determined. The redox conditions persisting in the sediment column are examined by high resolution pore water sampling, XAS

spectroscopy and sequential extraction. The potential for these sediments to release arsenic to oxygenated and deoxygenated overlying water is investigated in sediment incubations. In concert, this information should allow qualitative assessment of the stability of arsenic in the sediments of North Haiwee Reservoir.

Samples used in this study were collected from four sites in the reservoir, on 22 December 1999 (Fig. 6.1). Data ancillary to those presented are available in Appendix D.

6.3.1 Effect of $FeCl_3$ Treatment on Overlying Water Concentrations

The ferric chloride treatment is effective in reducing the arsenic concentrations in the water column; arsenic concentrations in the lake water were low (< 6 μg/L) in all filtered samples and in unfiltered samples collected from the lake shore (Table 6.3). Iron, manganese and arsenic concentrations were elevated in the unfiltered water sample collected at the bridge site. Ninety percent of the iron and 80% of the manganese and arsenic in this sample was retained on a 0.45 μm filter. The bridge crosses a high flow channel, and therefore this water carries a high particulate load. Concentrations in the water column samples show that this particulate load was not carried to the NE site.

Table 6.3: Characteristics of Overlying Water, North Haiwee Reservoir, 22 December 1999

Site	T °C	pH	UNFILTERED				FILTERED		
			As_t µg/L	As(III)[a] µg/L	Mn µg/L	Fe mg/L	As µg/L	Mn µg/L	Fe mg/L
NW	6.1	7.8	5.7	1.3	9.9	0.48	2.5	6.0	0.080
bridge			17	1.8	27	1.90	3.3	5.7	0.13
NE	5.8	8.2	5.7	1.5	11	0.25	4.6	5.5	0.078
blank			0.03	0.03	<0.01	<0.001	0.06	0.7	<0.001

[a] The average result from the duplicate field separations of inorganic As(III) from As(V), which were always within 10%.

6.3.2 Effect of $FeCl_3$ Treatment on Sediment Concentrations

The NW and SW sites receive suspended solids produced by the ferric chloride additions, whereas the NE site does not; the fine, orange-brown floc observed settling on the surface sediment at the NW and SW sites was not observed at the NE site. Sediment concentrations of iron, arsenic and manganese at the NW and SW sites are significantly greater than those measured at the NE site (Fig. 6.2).

Iron, arsenic and manganese concentrations were elevated in surface sediments collected from the NW and SW sites (Fig. 6.2 A, B) with concentrations as high as 9% iron and 400 µg/g arsenic (by dry weight). This reflects the high concentrations of these elements in the well-oxygenated, orange-brown floc. Assuming all $FeCl_3$ becomes $Fe(OH)_3$, the average $FeCl_3$ dose (Table 6.1) could result in 3.8 g/m^3 of $Fe(OH)_3$. The average arsenic removal is 17 mg/m^3. This would result in a solid phase arsenic con-

centration of 3 mg/g, approximately 10 times what we observed. The arsenic concentration in the iron oxyhydroxide floc is diluted by the cationic polymer (1.7 g/m^3) and

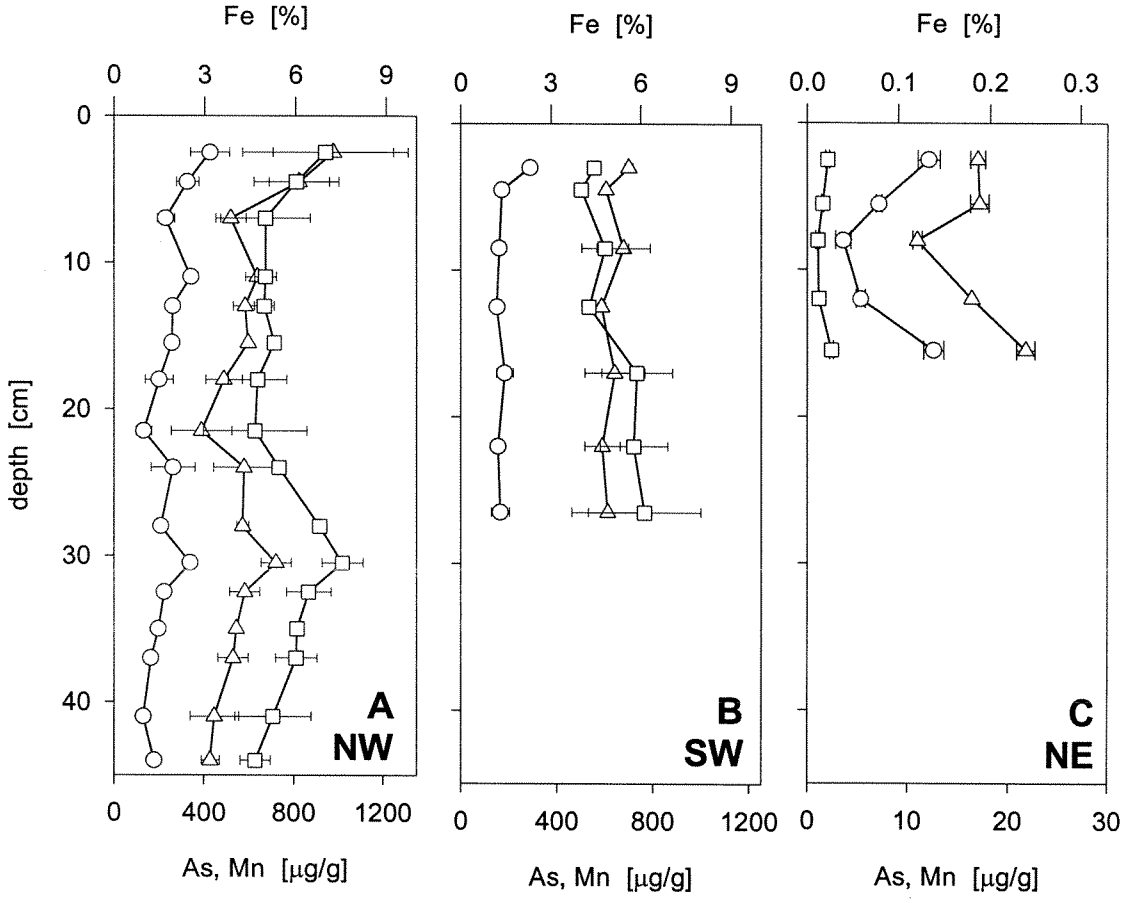

Figure 6.2: Iron (△), manganese (□) and arsenic (○) concentrations measured in sediments collected from NW (A), SW (B) and NE (C) sites in Haiwee Reservoir. Note the scale change in C. Concentrations were determined by partial digestion and are reported on a dry weight basis. The ends of the bars represent the concentration determined in duplicate digestions and the symbol sits at the average of the two determinations. Symbols are positioned at the depth of the bottom of each core section

other material such as silt. Beyond the first few centimeters, concentrations were relatively constant throughout the sediment column sampled. It should be noted that the length of the sampling tube limited the length of the sediment core collected from the NW site.

In contrast to the high concentrations measured at the NW and SW sites, iron, arsenic and manganese concentrations were uniformly low in the sediment collected at the NE site (Fig. 6.2 C). The floc produced by the ferric chloride treatment, which is rich in iron, manganese and arsenic, is not carried to the NE site. Therefore, the NE site serves as a control site in terms of establishing the effect of the ferric chloride additions on the sediment column.

6.3.3 Pore Water Chemistry

Pore water concentrations of iron, manganese and arsenic at the NW and SW sites are significantly greater than those measured at the NE site (Fig. 6.3). Manganese concentrations in the pore waters of the NW and SW cores, determined by centrifugation, are almost constant with depth. In contrast, arsenic and iron concentrations increase with depth in the first 18 cm of the NW core and throughout the entire length of the SW core.

The disruptive nature of collecting pore water by core extraction, extrusion and centrifugation makes it difficult to measure pore water profiles accurately. Colloidal material may be present in the pore water or generated during centrifugation and contribute to the pore water concentrations obtained by this technique (see §6.3.4). The gel

probe sampler deployed at the NW site is less intrusive and has better vertical resolution, and therefore should provide more informative pore water profiles.

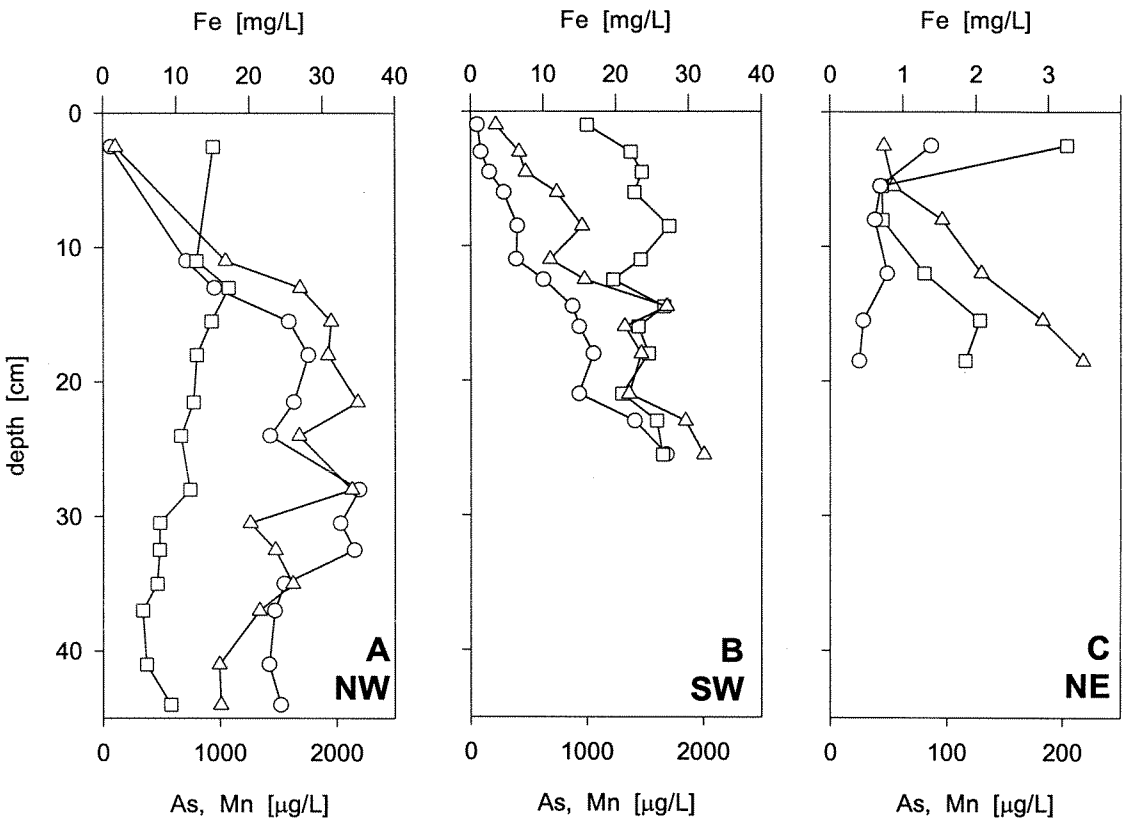

Figure 6.3: Iron (△), manganese (□) and arsenic (○) measured in pore waters extracted by centrifugation from sediments collected at Haiwee Reservoir, 22 December 1999. Note the scale change in C. Samples were filtered through 0.45 µm membrane filters; colloidal material most likely contributes to these concentrations. Symbols are positioned at the depth of the bottom of each core section.

The concentration profiles obtained with the gel probe sampler (Fig. 6.4) indicate a very strong redox gradient below the sediment-water interface. The interface was determined visually by counting the number of cells in the sampler extending above the

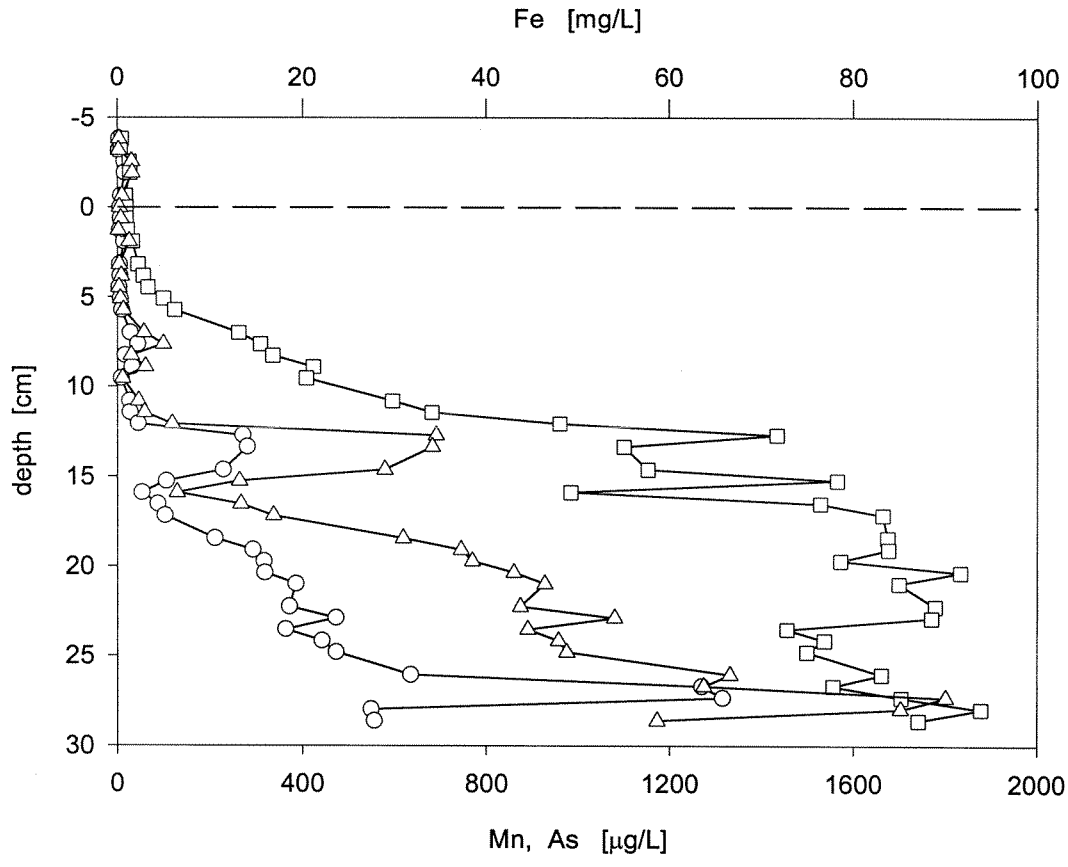

Figure 6.4: Pore water concentrations of manganese (□), iron (△) and arsenic (○) at NW site, North Haiwee Reservoir, 22 December 1999, determined using a polyacrylamide gel probe sampler. The sediment-water interface is indicated by the dashed line.

sediment surface. In the surface sediment, which is presumed to be oxic, pore water concentrations of iron, manganese and arsenic are comparable to those in the overlying water. Below 5 cm, the concentration of manganese increases, and below 10 cm the iron concentration increases. The pore water speciation of manganese and iron was not determined. However, the dissolved species are most likely Mn(II) and Fe(II) produced upon reductive dissolution of Mn(III,IV) oxides and Fe(III) oxyhydroxides in the deeper sediment. The strong correlation of arsenic and iron in the pore water (Fig. 6.5 A) implies that arsenic is associated with iron oxyhydroxide solids in the sediments; iron and arsenic are released into the pore water upon the reductive dissolution of these oxyhydroxide phases. Arsenic and manganese are less strongly correlated (Fig. 6.5 B).

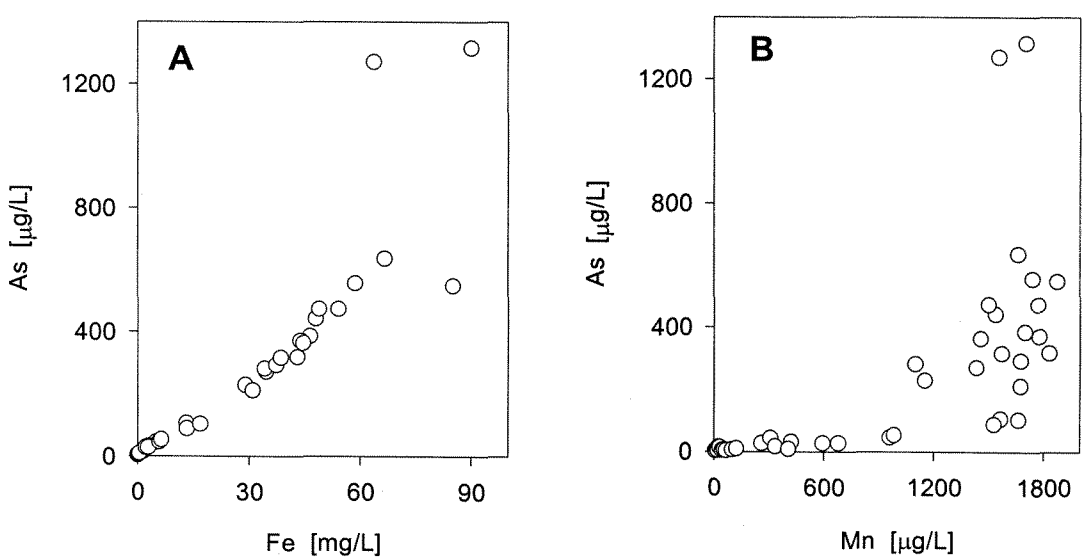

Figure 6.5: Pore water concentration correlations of iron with arsenic (A) and manganese with arsenic (B) at NW site, North Haiwee Reservoir, 22 December 1999. Concentrations were determined using a polyacrylamide gel probe sampler.

Iron and arsenic profiles obtained with the gel probe sampler have a coincident peak at 13 cm depth. This may be due to a region of high biological activity at this depth. The dramatic decrease in concentration of these species at 30 cm coincides with a region of slightly increased solid phase concentration at this site (Fig. 6.2). Dissolved iron and arsenic may be sequestered by a solid phase at this depth, possibly a sulfide phase.

We attempted to measure the speciation of arsenic in the gel probe profile by back-equilibrating every 6th gel piece in 18.2 MΩcm water and using IC-ICPMS for separation and detection of inorganic As(III) and As(V) and MMA. No MMA was detected in any of the samples. Total arsenic recovery was poor. The 18.2 MΩcm water used for back-equilibration was not deoxygenated before transport to the field because we would have no way to keep it oxygen free when transferring the gel pieces into solution. The poor recovery of arsenic may have been due to adsorption onto or co-precipitation with oxidized iron or manganese phases upon back-equilibration. The majority of the arsenic recovered was As(III).

6.3.4 Colloidal Arsenic

Comparison of the pore water profiles obtained at the NW site by centrifugation with those obtained via the gel probe shows that arsenic concentrations obtained by centrifugation are up to four times higher than those obtained with the gel probe. This may be due to the presence of colloidal material. Shear induced by centrifugation may produce colloidal material which may not be removed when passed through a 0.45 μm

membrane filter. The concentrations measured in centrifuged samples would thus overestimate the truly dissolved concentration. Colloidal material present in the sediment pore water would not diffuse freely through the membrane of the gel probe sampler. The gel probe is, therefore, a better measure of the truly dissolved pore water concentration. However, both colloidal and dissolved arsenic are equally available for transport in the overlying water. Therefore, in considering the transport of arsenic with the lake water, the colloidal and dissolved phases of arsenic are equally important.

6.3.5 Association of Arsenic in Sediments

6.3.5.1 X-ray Absorption Spectra

Selected sediment samples from the cores collected at the NW and SW site were analyzed by XAS. Two arsenic phases were identified in the XAS spectra (Fig. 6.6). The energy of the absorption maximum of one phase (the higher energy peak) indicates that it is an As(V) solid while the absorption energy maximum of the second phase corresponds to an As(III) phase. The surface section of the NW core contained a mixture of the two phases. The more oxidized arsenic phase persists only in the first few centimeters of the NW core. The second, more reduced solid phase is present in the deeper sediment. Of the model compounds considered, the XAS spectrum of the more oxidized phase is most like Na_2HAsO_4. Model compounds of As(V) or As(III) adsorbed to iron oxyhydroxides were not available for comparison with our sample spectra. The XAS spectrum for the more reduced phase is most like the spectrum for a 10 mM solution of

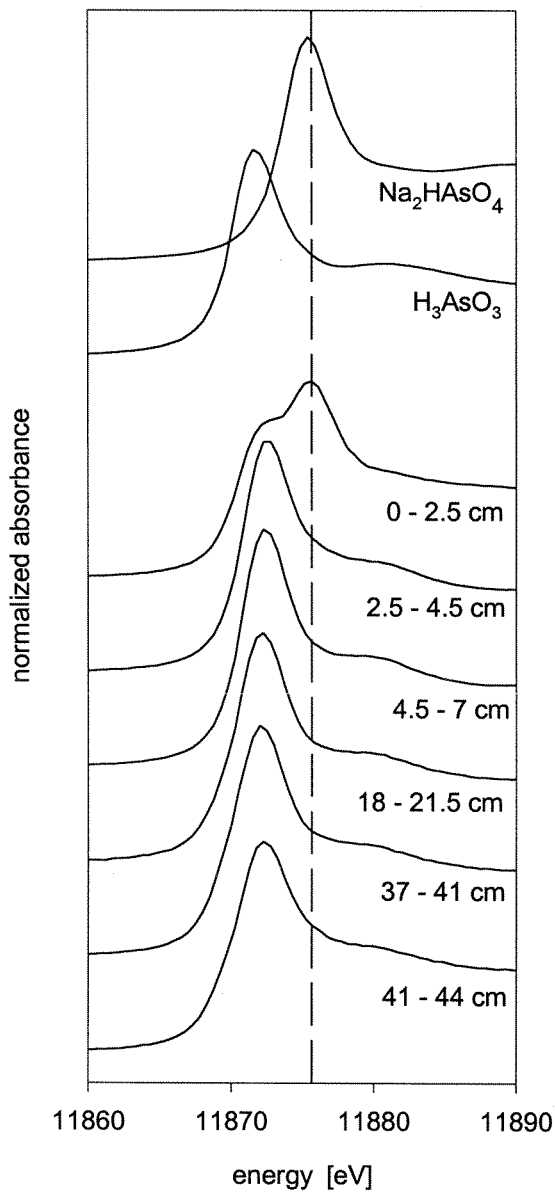

Figure 6.6: Normalized x-ray absorption spectra for model compounds Na_2HAsO_4 and H_3AsO_3 together with sediment samples collected at the NW site in North Hai-wee Reservoir.

sodium meta-arsenite, $NaAsO_2$. The $HAsO_2$ species is not known in solution. Rather, As(III) in solution exists as in H_3AsO_3 (Loehr and Plane 1969). The porosity of these

sediments (defined as the volume ratio of water to total wet sediment) varies from greater than 0.8 to 0.6. Although the pore water concentrations and porosity are high, less than 2% of the total arsenic in a wet sediment sample is in the pore water phase. Therefore, pore water arsenic should not be observed in the XAS spectra. The As(III) phase observed is most likely a surface species of the As(III) oxyanion adsorbed to iron oxyhydroxides. Spectra of scorodite, a freshly precipitated amorphous As_2S_3, and commercially obtained MMA, DMA, arsenocholine and arsenobetaine (solids and solution) did not fit the sediment spectra.

Comparison of the XAS spectra of the NW core with the gel probe pore water profile obtained at the same site suggests that the oxidized surface layer is underestimated in the XAS spectra. As noted before, the length of the NW core was limited by the length of the core collection tube. The surface sediment was slightly disturbed when the stopper was inserted into the bottom of the core tube and some surface sediment was lost. The SW site surface sediment was not disturbed, and XAS analysis showed that the surface section from this core contained only the more oxidized arsenic phase (data not shown). Improved vertical resolution would be required to determine exactly how far the oxidized layer persists, but it is certainly no thicker than a few centimeters.

Thus, the XAS spectra revealed the presence of a more oxidized form of arsenic in the surface sediment with a more reduced form dominating the solid phase speciation at depth. Presumably, the more oxidized phase is the result of As(V) in the water column adsorbing to the iron oxyhydroxide floc. Since no As(III) should be in the overlying water no As(III) should be transported to the sediments with the depositing floc.

The more reduced phase may be the product of either direct reduction of As(V) sorbed to the iron oxyhdroxide or diagenetic processes of reductive dissolution followed by readsorption. The more reduced form of arsenic does not appear to be associated with a sulfide phase.

6.3.5.2 Sequential Extraction

There are inherent limitations to interpreting the results of an operationally defined technique such as sequential extraction (Nirel and Morel 1990). The information provided by such techniques is more useful in a comparative, rather than quantitative, sense. The 2.5 to 4.5 cm (top), 18 to 21.5 cm (mid) and 37 to 41 cm (deep) sections of the NW core were subjected to a sequential extraction procedure. Extraction efficiencies for each element were determined by comparing the total extracted with the total concentration obtained by HNO_3-H_2O_2 digestion of a separate sub-sample from the same core section. The error in the extraction efficiency (or % removed) was dominated by substantial variation in the digest values. Arsenic extraction was more complete than extraction of iron or manganese; 75-120% of arsenic was removed while only 45-75% manganese and 50-80% iron was removed. This is most likely due to the fact that we did not optimize the extraction method for the unusually high iron and manganese concentrations in these sediments. Because of the limited extraction of iron and manganese, only the distribution of the total extracted between the fractions is shown for iron (Fig. 6.7 A) and manganese (Fig. 6.7 B). For arsenic, both the total arsenic removed in each extraction and the distribution between fractions is shown (Fig. 6.7 C, D).

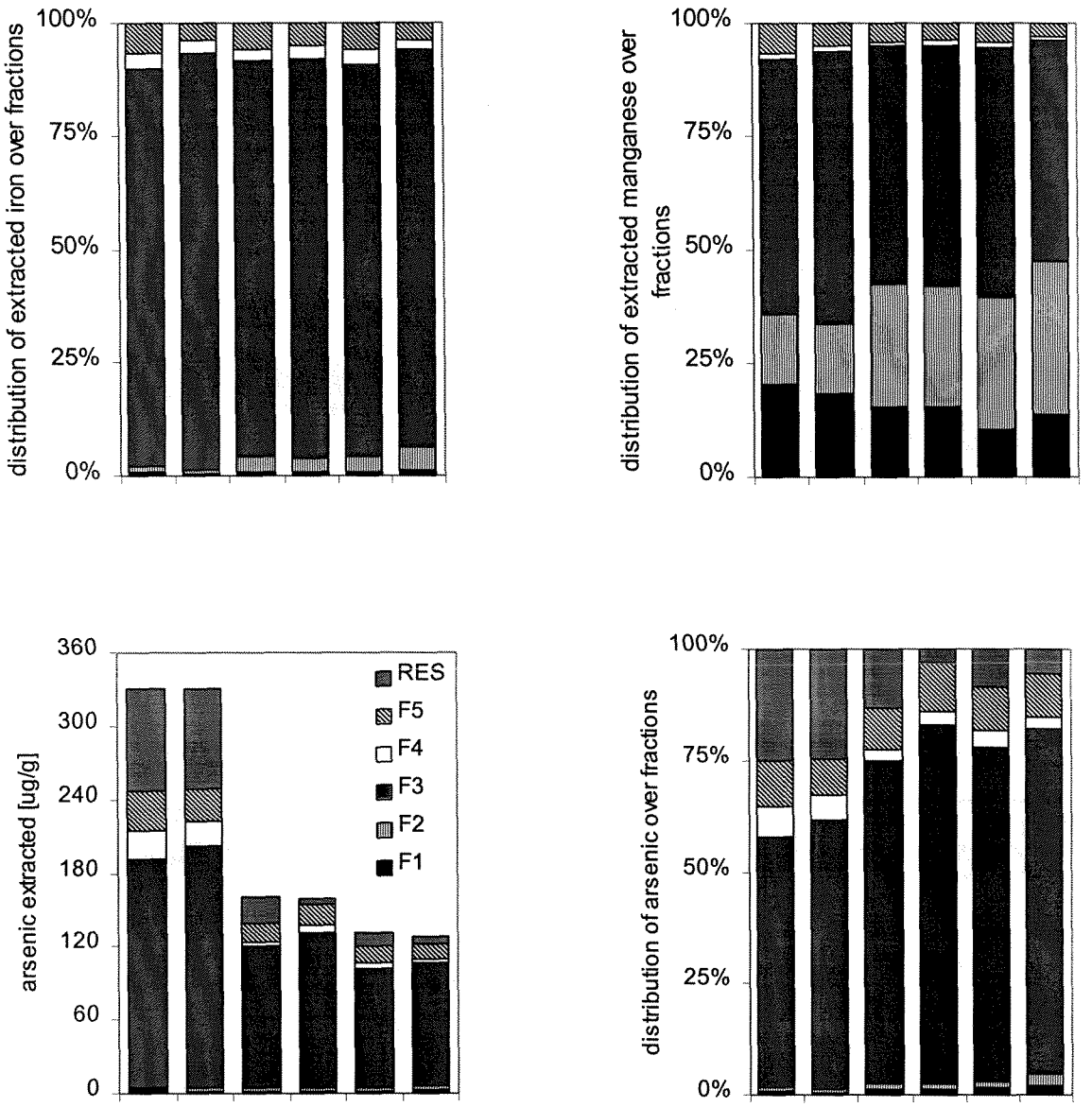

Figure 6.7: Sequential extraction of samples from NW core, Haiwee Reservoir. "top" is 2.5-4.5 cm, "mid" is 18-21.5 cm, and "deep" is 37-41 cm. Extraction solutions are $MgCl_2$ (F1); NaOAc (F2); $NH_2OH.HCl$ (F3); pyrophosphate (F4) and ClO_4-HCl (F5). A and B show iron and manganese fractionation, respectively. C and D show arsenic fractionation. In C and D, the RES fraction is the residual not extracted, calculated by subtraction of the amount extracted from the total arsenic concentration in each sample as given by sediment digestion.

Of the iron extracted from all three samples, approximately 90% was extracted in the reducing, $NH_2OH.HCl$, extraction. Approximately 50% of the extracted manganese was extracted in this fraction. The top section has higher total iron and manganese concentration than the mid and deep sections.

There is significantly more arsenic in the top sediment sample than in the middle or bottom. Most arsenic was extracted with $NH_2OH.HCl$, that is, with the dissolution of iron oxyhydroxides and manganese oxides.

Thus, the x-ray absorption spectra and sequential extraction data suggest that the top layer of the sediment is oxic and retains more arsenic in the solid phase, associated with iron oxyhydroxides and possibly manganese oxides. In the deeper sediments, a significant proportion of arsenic is lost from the solid phase by dissolution, and the predominant solid phase speciation involves an As(III) species. This As(III) species does not appear to be a sulfide phase.

6.3.6 Release of Arsenic from Sediments in Microcosms

Over the 48 h in which water samples were collected from the microcosms, several features pertinent to the different environments created were noted. As we expected, the concentrations of all elements in the filtered water increased immediately upon addition to the sediment in the jars.

In the microcosms in which the overlying water was kept well-oxygenated, the dissolved iron concentration in the overlying water decreased after 20 h (Fig. 6.8 A). Dissolved iron would be oxidized by oxygen in the water, producing solid iron oxyhy-

droxides. In contrast, the samples in which the overlying water was bubbled constantly with argon showed a continual increase in the dissolved iron concentration with time. These simple systems demonstrate the effect redox conditions have on the sediment-water transport of iron.

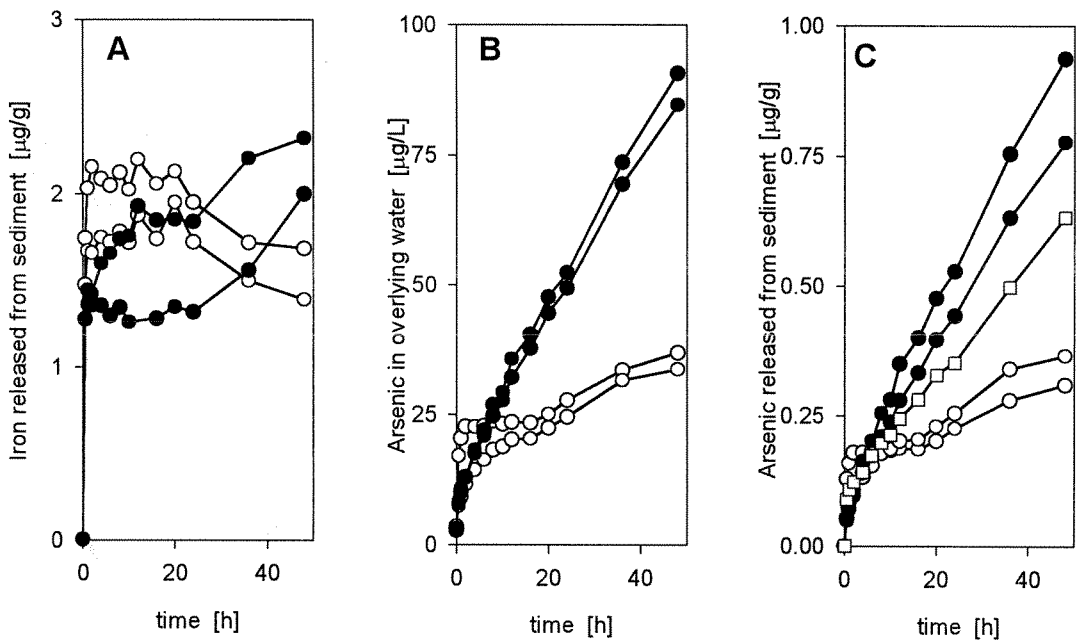

Figure 6.8: Iron (A) and arsenic (B, C) released from sediments in incubations of Haiwee Reservoir sediments, under well-oxygenated (○) and oxygen-free (●) conditions. A deoxygenated, sterile control (□) was also monitored for arsenic release. In A and C, concentrations measured in solution were corrected for initial solution concentration, then normalized to initial sediment mass and solution volume in each jar and reported here as mass of element lost from sediment per mass of dry sediment. B shows the arsenic concentration, not normalized, measured in the overlying solution. The volume of solution ranged from 0.59 to 0.68 L combined with approximately 250 mL sediment slurry, equivalent to 56 to 66 g dry sediment. The initial sediment concentrations were 5.9% iron and 225 µg/g arsenic (dry weight basis). The initial iron concentrations in the solutions were 120 to 160 mg/L; the initial arsenic concentrations were 2.6 to 3.4 µg/L.

Arsenic was released from the sediments in both the oxygenated and deoxygenated systems (Fig. 6.8 B, C). The final concentration of dissolved arsenic in the oxygenated jars was approximately half that in the deoxygenated jars (Fig. 6.8 B). This suggests that oxygenation inhibits the amount of arsenic released from the sediments. The percentage of arsenic as arsenite in the dissolved phase of all of the microcosms was approximately constant and between 60 and 80% over the duration of the experiment.

"Sterile" controls, one containing formaldehyde, the other antibiotic, were included to isolate the effect of biological activity on the release of iron and arsenic from the sediments. The formaldehyde control was confounded by a drop in pH from 8 to 6 after 20 h, which would favor abiotic dissolution of iron oxyhydroxides. In the first 24 h, the microcosm receiving the antibiotic treatment showed slightly less release of arsenic than the argon-only microcosms (Fig. 6.8 C). We had no external means of verifying that biological activity in the treated microcosm was truly inhibited. However, the similarity of arsenic release in jars 3, 4 and 6 suggests that, on the time scale of this experiment, the reductive dissolution of iron oxyhydroxides in the sediment is not biologically mediated. Freezing the sediment prior to construction of the microcosms may have inhibited biological activity in the non-sterilized systems.

6.3.7 Implications for Water Quality in Haiwee Reservoir

6.3.7.1 Long-Term Stability of Arsenic in the Reservoir Sediments

The additions of ferric chloride at Cottonwood Treatment Plant are successfully lowering the arsenic concentrations in the LAA. However, the pore waters in the deep sediments contain elevated concentrations of arsenic, as do the solid phases in the surface sediments. The low arsenic concentrations in the pore waters of the surface sediment ensure that there is no diffusive transport of arsenic from the sediments to the overlying water. As long as the surface sediments remain well-oxygenated and undisturbed, arsenic should be trapped in the deeper sediment. However, it is not clear whether diffusive or advective processes are keeping the surface sediments well-oxygenated. If the surface sediments are kept well-oxygenated solely by their contact with the overlying water, diffusion rates and the adsorptive capacity of the surface sediment will determine whether arsenic will be released from the sediment. Rapid deposition of particles entrains well-oxygenated overlying water in the growing sediment column, keeping the surface sediment well-oxygenated as long as the deposition rate is high. In this case, slowing the sedimentation rate by halting the ferric chloride treatment may cause migration of the redox boundary to the sediment-water interface, resulting in release of arsenic from the deep sediment pore waters. Extensive remineralization of organic carbon may also promote such a migration of the redox boundary.

Physical disturbance of the sediments poses a bigger risk to the water quality in Haiwee Reservoir. In the worst case, if all the arsenic stored in the sediments were released and mixed through a single volume of the reservoir, the arsenic concentration in

the outflow would be on the order of 1000 μg/L. Even from disturbed sediments, release of arsenic from the sediments to the overlying water should be more gradual. Oxidation of reduced iron and manganese species might be expected and, consequently, some removal of arsenic from the water by adsorption or co-precipitation of arsenic may occur.

6.3.7.2 Sediment Removal

An important component of the LADWP's interim arsenic management plan is the removal of the flocculated solids from Haiwee Reservoir (Stolarik and Christie 1999). This has not yet been attempted (as of April 2000). Dredging the reservoir would create turbidity in the reservoir water. The initial function of Cottonwood Treatment Plant was to reduce turbidity before the LAAFP was built and then, after 1995, to control high turbidity events. The only turbidity control downstream of Haiwee is the LAA Filtration Plant at Sylmar.

We will assume that the contaminated sediment lies in the northern-most section of North Haiwee. If the retention time in North and South Haiwee is longer than the time required for the resuspended floc to settle, then dredging may be a feasible option. The residence time in the two reservoirs may be estimated based on the average operating storage (Table 6.2), and average flow at Cottonwood (17 m^3/s). The residence time in North Haiwee is 8 days and in South Haiwee is 16 days. If we make the conservative assumptions that the specific gravity of the floc is 1.5 g/cm^3, and that the sediment particles are spherical, then the Stoke's settling velocity is determined by the size of the particles. The settling velocity for 1 μm spheres is 7 m/year, for 10 μm spheres it

is 2 m/day. If the resuspended sediment retains is floc nature, then the particles will be predominantly larger than 10 μm and should settle quickly. However, diagenesis may have altered the sediment sufficiently that it will not retain its aggregation.

Sediment disturbed by dredging may have time in the reservoirs to resettle to the sediments. The reduced pore water iron and manganese species may be rapidly oxidized on exposure to the overlying water, precipitating solid phases which may sequester arsenic.

6.3.7.3 Limitations of this Study

Haiwee Reservoir is a protected water body, in which no human contact or private boating is allowed. Therefore, only a small region of the sediments in the reservoir were accessible for our sampling. We chose to study the sediment near the inlet of the aqueduct as we anticipated that this would be the most affected by the ferric chloride additions at Cottonwood. The promontory provided a physical barrier and clear division between impacted (NW and SW) and non-impacted (NE) sites. This allowed us to collect "control" samples for identification of, and comparison with, the impacted samples.

Although it appears that no iron hydroxide floc is carried as far as the NE site, we do not know how far the floc is deposited. Deposition will occur in regions where the flow velocity is decreased, presumably in a plume around the aqueduct entrance at the north end of the reservoir. Apparently a bar, created by deposition of particulates carried by the aqueduct, runs east-west across the reservoir, just south of the aqueduct inlet (White 2000). It is possible that the bulk of the deposited floc is contained north of

this bar. Sediment transport patterns in Haiwee are not known. However, our samples most likely represent extremes of deposition in the reservoir, and are, therefore, not representative of most of the reservoir floor.

We can calculate upper and lower bounds on the volume of sediment impacted. The total arsenic deposited in the lake sediments, based on average flow and arsenic removal rates, is 40 metric tons. Our sediment concentration profiles suggest that the arsenic concentration in the impacted sediment varies from 0.1 to 0.4 mg/g (dry weight basis). Thus, the total sediment impacted is between 400×10^6 and 100×10^6 kg of dry sediment. If we make a conservative assumption that the density of the iron-rich sediment is close to that of $Fe(OH)_3$ (an upper limit on the density), 3.1×10^3 kg/m^3 (Lide 1994), then the total volume of dry sediment is 13×10^4 to 3.2×10^4 m^3. The average porosity is 0.6, giving total volume of 32×10^4 to 8.1×10^4 m^3 of sediment. The sediment depth where we sampled was approximately 0.4 m, but it is not known how deep the sediment has accumulated elsewhere in the reservoir or what area of the reservoir bottom is covered by this impacted sediment.

6.3.8 Concluding Remarks

The sediments of Haiwee Reservoir harbor some 40 metric tons of arsenic associated with iron oxyhydroxides as a result of the LADWP's interim arsenic management plan. The oxyhydroxide phases are unstable to reductive dissolution in the reducing environment a few centimeters below the sediment-water interface. This mobilizes arsenic from the solid phase in the deep sediments. Spectroscopy reveals an evolution of

the solid phase arsenic speciation in these sediments, reflecting the diagenetic processes of reductive dissolution and readsorption in the deeper sediments. Neither the long-term stability of arsenic in these sediments nor the effect of halting the ferric chloride additions at Cottonwood Treatment Plant are known. The potential for release of arsenic from the sediments to the water column in Haiwee Reservoir poses a threat to water quality in the LAA water supply.

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Chapter 7

UPTAKE AND TRANSFORMATION OF ARSENIC BY FRESHWATER PHYTOPLANKTON

7.1 Introduction

7.1.1 Occurrence of As(III) and Methylated Arsenic Species

Arsenite (As(III)) and methylated arsenic species such as monomethylarsonate (MMA) and dimethylarsenate (DMA) have been detected in well-oxygenated, productive freshwater and marine environments (Kuhn and Sigg 1993, Anderson and Bruland 1991, Riedel 1993). Abiotic production of these species from arsenate (As(V)) is thermodynamically disfavored. Except for direct, anthropogenic contamination of a surface water by methylated arsenic species, the presence of methylated arsenic species and As(III) in well-oxygenated surface water is due to algal uptake and transformation of arsenic (Phillips 1990, ref. cit.). Such uptake and transformation affects the ambient speciation of arsenic, to the extent that in some lakes, As(III) and methylated arsenic species are the dominant species in epilimnetic waters at certain times of year (Kuhn and Sigg 1993, Anderson and Bruland 1991). The ability of algae to take up and trans-

form arsenic has been studied extensively in marine systems (Sanders and Windom 1980, Andreae and Klumpp 1979, Howard et al. 1995), whereas fewer studies have considered freshwater systems.

7.1.2 Methylation and Algal Toxicity of Arsenic

Algal methylation of arsenic is believed to follow the mechanism proposed by Challenger (Fatoki 1997), in which the methyl group is transferred, as a carbocation, from S-adenosylmethionine:

$$(HO)_3As: + CH_3^+ = [(HO)_3AsCH_3]^+ = O(OH)_2AsCH_3 + H^+$$

An alternative methylation mechanism involves methylcobalamin, in which the methyl group is transferred as a carbanion. This is the probable biological methylation mechanism for many metals including mercury, and has been suggested as a possible mechanism by which bacteria methylate arsenic (Cullen and Reimer 1989).

Arsenate is electronically and sterically similar to phosphate. As(V) can mimic phosphate, becoming incorporated in arsenosugars. As(V) uptake is believed to occur via phosphate uptake systems. One suggested mechanism for As(V) toxicity is uncoupling of oxidative phosphorylation; the As-ester bond is rapidly hydrolyzed (Phillips 1990). As(III) toxicity is attributed to inactivation of sulfhydryl-containing enzymes. (See Gorby 1994, Eisler 1994 for reviews.) Some bacteria exhibit arsenic-resistance mechanisms, such as (1) the efflux pump, in which the toxin is transported out of the cell, and (2) conversion of the toxic species to a less toxic or more easily transportable moiety (Silver 1996). The genes for arsenic resistance are similar in a range of gram-

negative and gram-positive bacteria and code for arsenate reductase and arsenite cross-membrane transport proteins (Silver and Phung 1996).

Algal toxicity (i.e., inhibited growth or metabolic function) to arsenic varies between algal strains and between isolates of the same strain (Creed et al. 1990). Similarly, the ability to reduce and methylate As(V) varies between algal strains and with varying ambient conditions.

7.1.3 Observations in Crowley Lake

In Crowley Lake, arsenic concentrations are elevated relative to most freshwater lakes due to geothermal inputs to its tributaries. Arsenic concentrations in Crowley Lake range from 40 to 160 μg/L (Ball 1999) and were on the order of 50 to 60 μg/L during our sampling on August 5 and September 3, 1998. Crowley Lake also receives a relatively high input of phosphorus, also of geothermal origin. This results in high, nitrogen-limited, productivity in the epilimnion in the summer months (Melack and Lesack 1982). We did not directly measure arsenic in the phytoplankton flocs present in the surface water. However, arsenic concentrations were the same (within experimental error) in the surface water filtered and unfiltered samples, while phosphorus concentrations in filtered samples were 40 to 60% of the unfiltered samples. This suggests that although phosphorous is accumulated by algae sufficiently to perturb its distribution in the water column, arsenic is not. When we measured arsenic speciation in Crowley Lake in the summer of 1998, large flocs of phytoplankton were present in the surface

water. Despite the high levels of arsenic and productivity, less than 5% of the dissolved arsenic was As(III) or DMA, and no MMA was detected. Algal uptake and transformation did not appear to be an important factor in the arsenic cycle in Crowley Lake. In this short review of studies concerning algal uptake and transformation of arsenic, we consider possible explanations for this unexpected observation.

7.2 Factors Affecting Arsenic Uptake by Freshwater Algae

Many studies have examined the uptake and transformation of arsenic by marine phytoplankton. Fewer have concentrated on freshwater algal species. A somewhat diverse selection of studies is considered in the following sections. Characteristics of the studies are presented in Table 7.1. Some studies were undertaken to understand why methylated arsenic species are present in aquatic environments. These tend to use algal strains isolated from natural systems and cultured in the laboratory. Parameters such as arsenate, arsenite, methylated arsenic species, phosphate and nitrate are varied and the effects on growth, accumulation, and speciation are examined. Some studies of freshwater algae, notably those by Maeda, Suhendrayata and co-workers, are approached from the angle of exploiting the arsenic accumulation capability of certain species of phytoplankton to remediate contaminated water bodies. Therefore, the media used in these studies are not representative of most natural systems and the experiments are designed to test the limits of the algal species. Other studies are undertaken as monitoring

Table 7.1: Conditions of Selected Studies of Phytoplankton and Arsenic

SPECIES	MEDIUM	ARSENIC DOSE	PARAMETERS MEASURED	REFERENCE
freshwater green algae *Chlorella Vulgaris* isolated from an arsenic-polluted environment	Detmer, growth medium	10-100 mg/L As(III)	growth accumulation of As during growth speciation of accumulated As speciation of As in medium	Suhendrayatna et al. 1999
freshwater green algae *Chlorella Vulgaris* isolated from an arsenic-polluted environment	Detmer, growth medium	1-1000 mg/L As(V)	growth accumulation of As during growth effect on growth and As accumulation of change in Mn, P in media	Maeda et al. 1992
freshwater, blue-green algae *Nostoc* sp. isolated from an arsenic-polluted environment	MA growth medium	1-500 mg/L As(V)	growth accumulation of As during growth speciation of As in cells after 2 weeks effect on growth and As accumulation of change in N from 0 to 140 mg/L (as NO_3^-)	Maeda et al. 1993
Skeletonema costatum Marine alga Axenic stock culture	seawater, sterilized with 20 µM nitrate and silicate	0-25 µg/L As(V) 0-20 µg/L As(III) 0-20 µg/L DMA	growth As speciation in cells and medium change in growth with P (0.07-3.40 µM) effect on As accumulation and speciation in cells with change in P and As	Sanders and Windom 1980
unidentified	lake water, ambient	unamended	As speciation in lake water	Anderson and Bruland 1991

Table 7.1 (cont.): Conditions of Selected Studies of Phytoplankton and Arsenic

SPECIES	MEDIUM	ARSENIC DOSE	PARAMETERS MEASURED	REFERENCE
unidentified assemblages collected from lake water isolates *Chlorella* sp., *Chlamydocapsa bacillus*, *Chlamydocapsa cf. peterfii*	resuspended in defined medium, initially As free	1 ng/L - 1 mg/L As(V), As(III), DMA, MMA	effect of As concentration on photosynthesis in As amended suspensions relative to control photosynthesis	Knauer et al. 1999
unidentified	lake water, model ecosystem	5-50 µg/L As(V)	As concentration in periphyton effect on As accumulation of P (3-5 ug/L)	Reuther 1992
Clodophora glomerata	geothermally impacted river	30 µg/L (ambient)	As speciation in cells	Kaise et al. 1997
Chlorella vulgaris field isolates and cultured, reference strains	growth media	0-100 mM	effect of As on growth rate and photosynthesis effect of preconditioning with As effect of P-limitation	Creed et al. 1990
Diatoms, *Skeletonema costatum*, *Rhizosolenia delicatula* in a natural estuary	estuary	0-0.35 µg/L (ambient)	As speciation in water phytoplankton species nutrient availability	Howard et al. 1995

Table 7.1 (cont.): Conditions of Selected Studies of Phytoplankton and Arsenic

SPECIES	MEDIUM	ARSENIC DOSE	PARAMETERS MEASURED	REFERENCE
unidentified algae	hot springs environment	5-303 μg/L (ambient)	As accumulation in green algae	Koch et al. 1999
Algal assemblage	corral in a lake	1 nM - 1 mM As(V)	photosynthesis of algal community - short term changes with As(V) stress algal population - long term changes in species distribution with As(V) stress	Wängberg et al. 1991
natural marine phytoplankton assemblages stock cultures of marine phytoplankton	isolated from sea water, maintained in growth medium	0-20 pg/cell As(V)	changes in population distribution of algal species with change in As stress	Sanders and Vermersch 1982

studies of a particular water body, to determine whether algal uptake, accumulation and transformation of arsenic is important in the arsenic cycle in the particular system, or to determine the effects of arsenic stress on the algal population.

7.2.1 Growth Rates

The growth rate of the freshwater green alga *Chlorella Vulgaris*, isolated from a geothermally impacted, arsenic contaminated site in Japan, was enhanced by addition of 10-20 mg/L As(III) but inhibited at concentrations greater than 50 mg/L. Arsenic accumulation in *C. Vulgaris* increased up to 610 μg/g during the log phase of growth and then decreased in the stationary phase (Suhendrayatna et al. 1999). In a medium containing 10 mg/L As(V), arsenic accumulation in *C. Vulgaris* reached a peak during the exponential phase of growth and decreased after stationary phase was reached (Maeda et al. 1992). This is interpreted as the result of bioaccumulation, methylation and excretion of the arsenic species. The freshwater, blue-green alga *Nostoc* also accumulates most arsenic during the exponential phase of growth (Maeda et al. 1993).

Thus, we might expect to see As(V) depletion or the presence of As(III) and/or methylated species in surface waters during the exponential growth phase of an ambient algal species.

7.2.2 Ambient Arsenic Concentration

In culture studies with *C. Vulgaris*, arsenic accumulation increased with increased As(V) concentration in the growth media. Accumulation increased up to 11.3 mg/g (dry weight of cells) when the ambient As(V) concentration in the media was increased to 1000 mg/L (Maeda et al. 1992). In a similar culture study with *Nostoc*, arsenic accumulation increased with As(V) concentration up to 100 mg/L then decreased as the media concentration increased above 200 mg/L (Maeda et al. 1993).

In studies with the marine species *Skeletonema Costatum*, uptake of arsenic was also shown to increase as ambient As(V) concentrations increased through the range of 1 to 25 μg/L. With an initial concentration of 25 μg/L As(V), 30 μg/g was accumulated in the cells. 50 μg/g accumulated in cells grown in a media initially containing 20 μg/L As(III). Speciation changed dramatically in the media in these studies; in the As(V) enriched media, As(V) was reduced during the log phase of growth whereas in the As(III)-enriched media, As(III) was rapidly oxidized. In the As(V) media, the proportion of organic arsenic in the cells increased from 55% to 70%. No change in the proportion of organic arsenic in the cells was observed in As(III)- or DMA- enriched media (Sanders and Windom 1980). This suggests that As(V) is more readily taken up and transformed to organic arsenic by this species than As(III).

In ambient and amended field studies, methylated arsenic species have been detected in surface waters when total arsenic concentrations are as low as 1.5 μg/L (Anderson and Bruland 1991). In a study of a model freshwater ecosystem, ambient concentrations of 5 μg/L As(V) produced accumulation of arsenic on the surfaces and

within the cells of an unidentified algae, with toxic effects observed at concentrations greater than 50 μg/L (Reuther 1992). *Clodophora glomerata*, a freshwater green alga, accumulates As(V) from streamwater with 30 μg/L arsenic as As(V), converting 81-85% of the As(V) to dimethylated arsenic species within its tissue (Kaise et al. 1997). Phytoplankton assemblages extracted from a series of freshwater lakes were significantly more sensitive to As(V) than As(III), MMA or DMA: photosynthesis was most inhibited in the presence of As(V) (Knauer et al. 1999).

These studies suggest that, in both freshwater and marine systems, arsenic accumulation increases as the ambient arsenic concentrations increase. In Crowley Lake, the concentration of arsenic ranges from 40 to 160 μg/L (Ball 1999). The concentration ranges considered in the culture studies of freshwater alga are on the order of 1000 times greater than those encountered in Crowley Lake. However, the ambient field studies have revealed algal uptake and methylation of arsenic at concentrations similar to those observed in Crowley Lake. Thus, uptake and transformation of arsenic by algae is quite possible given the ambient concentration of arsenic in Crowley Lake.

7.2.3 Ambient Phosphate Concentration

It has been suggested that toxicity to As(V) is related to phosphate availability and uptake rates (Sanders and Vermersch 1982).

Uptake of arsenic by the freshwater alga *C. Vulgaris* decreased as phosphate concentration in the media increased from 1 to 1000 mg/L. This may be an effect of

competition between As(V) and phosphate (Maeda et al. 1992). Similarly, more arsenic accumulated in the marine species *S. Costatum* when phosphate concentrations were low; over 1 to 25 μg/L As(V) in the culture media, an increase of phosphate from 0.08 μM through to 3.4 μM decreased the extent of arsenic uptake (Sanders and Windom 1980). Phosphate-limited, arsenic tolerant, field strains of *C. Vulgaris* showed enhanced growth when As(V) was added to the growth media (Creed et al. 1990). However, for both freshwater and marine alga, phosphate limitation is often not a necessary prerequisite for arsenic uptake and transformation (Howard et al. 1995, Faye and Diamond 1996, Creed et al. 1990). The elevated phosphate concentrations in Crowley Lake will not necessarily preclude algal uptake and transformation of arsenic.

7.2.4 Ambient Nitrogen Concentration

Arsenic occupies nitrogen sites in arsenobetaine and arsenocholine, identified in the cells of higher marine organisms (Le et al. 1994, Harrington et al. 1997, Koch et al. 1999). These species have not been observed in freshwater phytoplankton.

With 100 mg/L As(V) in the medium, the accumulation of arsenic in *Nostoc* sp. decreased from 840 μg/g to 180 μg/g as nitrate in the media was increased from 0 mg/L to 140 mg/L (Maeda et al. 1993). Only trace amounts of organic arsenic species were detected in the cells at high nitrate concentration. *Nostoc* sp. contains a nitrogenase; arsenic accumulation is stimulated when the nitrogenase is activated (Maeda et al. 1993).

In contrast to phosphate-limited cells, the growth of nitrogen-limited *C. Vulgaris* cells was inhibited by As(V) (Creed et al. 1990). This suggests that freshwater algae in nitrogen-limited systems may be more sensitive to As(V), and hence, their ability to take up arsenic might be diminished. Crowley Lake is nitrogen-limited in the summer (Melack and Lesack 1982); the algal species in Crowley Lake may have a limited ability to take up arsenic.

7.3 Factors Controlling Reduction and Methylation of As(V)

Not only do different algal species have different abilities to reduce and methylate arsenic, but a single algal species which is able to methylate arsenic may only do so under certain conditions. For example, *Skeletonema* has been shown to produce mainly As(III) and DMA in culture (Andreae and Klumpp 1979, Sanders and Windom 1980), but no methylated arsenic was detected in Southampton Water during the growth of this alga (Howard et al. 1995). Therefore, the tentative identification of *Chroomonas* as a major algal species in Crowley Lake (USEPA 1978) does not imply that methylated arsenic should necessarily be observed in the surface waters of Crowley Lake, even though *Chroomonas* was implicated in the production of MMA in Chesapeake Bay (Sanders 1985).

Reduction and methylation appears to occur during the log phase of growth (Sanders and Windom 1980). The production of methylated species in Southampton

Water was observed when *S. Costatum* was decaying and *Rhizosolenia delicatula* (another diatom) was growing (Howard et al. 1995).

7.4 The Effect of Pre-Conditioning with Arsenic

There are two possible effects of As(V) pre-conditioning which may reduce the extent to which arsenic is accumulated and/or transformed by algae. As(V) stress and variability in tolerance to arsenic can induce changes in algal species composition (Wängberg et al. 1991, Sanders and Vermersch 1982, Knauer et al. 1999). Elevated ambient arsenic concentrations may favor the proliferation of those algal species which are better able to discriminate between phosphate and As(V). Thus, the major algal species would be those which do not take up As(V). Alternatively, the favored algal species may be those which are especially good at detoxifying As(V). In this case, As(V) would not be accumulated by the algae, but transformed and excreted. This would result in the presence of detoxification products, As(III) and methylated arsenic, in the ambient water (Knauer et al. 1999). We did not observe As(III), MMA or DMA in the surface waters of Crowley Lake, which suggests that the favored algal species in Crowley Lake are those able to discriminate against As(V).

The arsenic tolerance of algal assemblages taken from three lakes with different degrees of arsenic contamination increased with the arsenic concentration in the lake from which they were taken (Knauer et al. 1999). This suggests that the algae in the assemblages from the lakes with higher arsenic concentration were able either to discriminate against arsenic or to detoxify it.

The effect on arsenic uptake of pre-conditioning to elevated arsenic levels has been investigated with *C. vulgaris*. Field isolates of *C. vulgaris,* isolated from arsenic-contaminated sites, were compared with reference strains, which were cultured in an arsenic-free medium. The field isolates were more tolerant to arsenic than those with no prior exposure. The arsenic-tolerant isolates had shorter lag times and their photosynthetic rates were unaffected by As(V) concentrations in the media (Creed et al. 1990). In the presence of As(V), the field isolates had higher maximum growth rates than the reference isolates, while in the absence of As(V) the reference isolates had higher maximum growth rates. In contrast to the reference isolates, under phosphorus limitation, the field isolates showed enhanced growth with As(V) addition. It is suggested that under phosphorus limitation, the arsenic tolerant strains were able to partially substitute As(V) for phosphate in non-toxic metabolic functions (Creed et al. 1990). Crowley Lake is not phosphorus limited, so this function would not be necessary.

7.5 Freshwater vs. Marine Algae

Although it is not clear whether there are metabolic differences between freshwater and marine algae, the increased sensitivity of freshwater algae to arsenic has been ascribed to the different nutrient limitation regimes in lakes compared with the ocean (Wängberg et al. 1991). Lakes are usually phosphorus limited while the ocean is generally nitrogen limited. Ambient sea water arsenic concentrations are generally low; al-

gae which accumulate arsenic may be a significant reservoir of this element in the ocean.

7.6 Why No Evidence for Algal Cycling of Arsenic in Crowley Lake?

We sampled the surface waters in Crowley Lake twice in the summer of 1998. Methylated species are stable in surface waters and the kinetics for abiotic oxidation of As(III) are slow. These species persist in the surface waters in other lakes (Anderson and Bruland 1991, Kuhn and Sigg 1993). If As(III) or methylated species had been excreted by phytoplankton in Crowley Lake, it is likely that they would have been sufficiently persistent to be detected even in our limited sampling.

Algae in Crowley Lake must be tolerant of at least 60 μg/L As(V). Phosphate is not the limiting nutrient in this system. It is most probable that the species which proliferate are those which can either detoxify As(V) easily or those whose phosphate uptake mechanism can best discriminate between As(V) and phosphate. The former possibility would lead to the excretion of methylated arsenic species and/or As(III) in the ambient water. More than 95% of the arsenic in the surface water was As(V), suggesting that better discrimination for phosphate against As(V) is more likely.

The dominant species in Crowley in 1982 were nitrogen-fixing blue algae (Melack and Lesack 1982). The major species identified in the USEPA National Eutrophication Survey were, in June 1978, *Chroomonas* sp., *Anabaena* sp., *Asterionella* sp., *Schroederia* sp., and *Cryptomonas* sp. In November 1978, the major species were

Aphanizomenon sp., *Fragilaria* sp., *Chroomonas* sp., *Oscillatoria* sp., *Stephanodiscus* sp. (USEPA 1978). Of these algal species, two - *Anabaena* sp. and *Oscillatoria* sp. - are nitrogen-fixing algae.

In a study of the cyanobacterium *Anabaena variabilis*, As(V) was able to enter phosphate-starved cells but the presence of phosphate protected the cells from As(V) toxicity. It was suggested that in the presence of phosphate, As(V) was prevented from entering the cells. However, it was not clear in this study whether phosphate limitation was necessary for As(V) uptake (Thiel 1988). In another study, 2.6 mg/L As(V) inhibited phosphate uptake by *Chlamydomonas reinhardtii*. Very little arsenate was taken up by this species, even in the presence of such a high As(V) concentration (Planas and Healey 1978).

There is no evidence for uptake of As(V) by the algae in Crowley Lake. It is possible that species which discriminate against As(V) are favored in this lake. An alternative possibility is that, as with *A. variabilis*, phosphate protects Crowley's cyanobacteria against As(V) toxicity by inhibiting As(V) uptake.

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Chapter 8

SUMMARY, CONCLUSIONS AND IMPLICATIONS

8.1 Summary and Conclusions

In this study, the geochemistry of arsenic in the sediments of the Los Angeles Aqueduct (LAA) system has been examined. The objective was to evaluate the mechanisms by which arsenic accumulates in the sediments and the potential for release of arsenic from the sediments following treatment for arsenic removal at Hot Creek. The geochemistry of arsenic was studied in three distinct sections of the LAA system: Hot Creek, Crowley Lake and Haiwee Reservoir. The purpose of this chapter is to provide a summary of the findings of each section of the study and, in so doing, address the questions raised in §1.2.

8.1.1 Form and Association of Arsenic in the Sediments of Hot Creek and Crowley Lake

Arsenic concentrations are elevated in the sediments of Hot Creek Gorge. The dynamic flow regime in Hot Creek results in heterogeneous sedimentation and arsenic

accumulation. Concentration profiles and x-ray absorption spectra of Hot Creek sediments show that local arsenic accumulation is strongly influenced by hot springs and plants. Arsenic is associated with an organic phase in the surface sediments and a sulfide phase in the deepest sediments in Hot Creek Gorge. An As(III) solid phase is distributed throughout the sediment column. Total organic carbon and total arsenic are strongly correlated in Hot Creek sediments. Adsorption onto sediment phases and association with plant material buried in the sediment are the most probable mechanisms for arsenic accumulation in Hot Creek sediment. The sediments carry an insignificant fraction of the arsenic load exported from Hot Creek; most of the arsenic exported is in the dissolved phase in the stream water.

There is no efficient mechanism to transport arsenic from the water column to the sediments of Crowley Lake. Thus, these sediments contain only modestly elevated arsenic concentrations. X-ray absorption spectroscopy revealed the presence of an arsenic-sulfide phase in these sediments. Arsenic should be immobilized with this phase as long as the sediment-water interface remains anoxic.

8.1.2 Mobility of Arsenic in Hot Creek Sediments

High resolution profiles of arsenic concentrations in the pore waters of Hot Creek sediments indicate that the net flux of arsenic at the sediment-water interface is out of the sediment. The diffusive flux of dissolved arsenic from pore water to the overlying water is estimated to be small compared to the dissolved arsenic load carried by the stream water.

Sediment-water exchange experiments conducted in the laboratory using natural sediments and synthetic solutions indicate that sediment-water exchange of arsenic in Hot Creek Gorge is controlled by several factors. The initial arsenic concentration and grain size of the sediment affects the extent to which arsenic is released to, or sequestered from, solution. Whether arsenic is present or not present in the initial extraction solution affects the sediment-water exchange of arsenic; Hot Creek sediments are able to release arsenic to arsenic-free solution and sequester arsenic from arsenic-bearing solution. The presence of other ions in solution apparently retards the release of arsenic from Hot Creek sediments, although this may be due to aggregation of colloidal particles. Oxidation of As(III) added to the sediment-water solutions appears to be mediated by a sediment component, possibly a manganese oxide phase.

If arsenic concentrations in the stream water in Hot Creek were lowered, arsenic might be released from the sediment. However, the effect of this release on the arsenic concentration in the overlying water should be minimal due to the small reservoir of arsenic in these sediments.

8.1.3 The Behavior of Arsenic in Crowley Lake

Elevated arsenic concentrations in Crowley Lake are derived from the upstream geothermal inputs to Hot Creek. We examined the water column of Crowley Lake under stratified and unstratified conditions, seeking evidence for algal uptake and transformation of arsenic and arsenic deposition to, and release from, the sediments. Manganese and phosphorus concentrations increased with depth below the oxycline un-

der stratified conditions, consistent with a sediment source of these elements. However, these elements did not accumulate in the hypolimnion during the period of stratification. This appears to be a result of the dynamics of reservoir operation in which the outflow, withdrawn from the hypolimnion, is replaced by water from the epilimnion or surface inflow. Depletion of phosphorus in the surface water was incomplete during stratification suggesting that phosphorus is not a limiting nutrient in this highly productive lake. Vertical profiles of total arsenic during stratification did not provide evidence for release of arsenic from the sediment; concentrations were either uniform with depth or showed a mid-depth minimum at the oxycline attributable to internal recycling within the water column. There was neither depletion of arsenic in the productive surface water nor evidence for methylated arsenic species. Arsenic was present as arsenate in the epilimnion and as a mixture of arsenate and arsenite in the hypolimnion. Unlike other lakes, and perhaps because of the large input of geothermal phosphorus to Crowley Lake, algal uptake and transformation of arsenic appear to be unimportant in this system.

There was no evidence for any mechanism by which arsenic is efficiently transported to the sediment of Crowley Lake. As a result, arsenic accumulation in the sediments of Crowley Lake is modest. Spectroscopy of the solid phase shows that arsenic is associated with a sulfide phase in these sediments. Dissolved oxygen was depleted near the sediment-water interface even in May, when the remainder of the water column was well-mixed. This suggests that the sediments are permanently anoxic, and therefore the arsenic-sulfide phase should be stable. A decrease in the surface water arsenic concentration, such as would result from upstream treatment for arsenic

removal, may cause gradual release of arsenic from these sediments, but this should not have a significant impact on water quality in the LAA water supply.

8.1.4 Stability of Arsenic in the Sediments of North Haiwee Reservoir

In 1996, the Los Angeles Department of Water and Power implemented an interim management plan for arsenic removal from the Los Angeles Aqueduct water supply. Ferric chloride is added at Cottonwood Treatment Plant; the resulting iron- and arsenic-rich flocculated solids settle in North Haiwee reservoir. Effective immobilization of arsenic in these sediments requires that the surface sediments are well-oxygenated, such that arsenic will remain adsorbed to the iron oxyhydroxide phases with which it is transported to the sediment.

We measured solid and dissolved phase concentrations of arsenic, iron, manganese and phosphorus in North Haiwee Reservoir at sites impacted by and isolated from deposition of the flocculated solids. Solid phase and pore water arsenic, iron and manganese concentrations were elevated in regions receiving the flocculated solids. A high resolution pore water profile obtained using our polyacrylamide gel probe sampler revealed a strong redox gradient below the sediment-water interface in the impacted region. The profiles and strong correlation of iron and arsenic concentrations were consistent with reductive dissolution of iron oxyhydroxides and concurrent release of associated arsenic to the dissolved phase.

X-ray absorption spectroscopy revealed an inorganic As(V) form of arsenic in the solid phase in surface sediments, with transformation to an inorganic As(III) phase

in the deeper sediments. This evolution of arsenic speciation with depth reflects the influence of direct reduction of adsorbed As(V) and/or diagenetic processes of reductive dissolution and readsorption. Sequential chemical extraction confirmed that most of the arsenic in these sediments is associated with phases which may be extracted by hydroxylamine hydrochloride (i.e. iron and manganese oxyhydroxides). Sediment incubation showed that less arsenic was released from well-oxygenated sediment, consistent with release of arsenic being driven by the reductive dissolution of iron oxyhydroxide phases.

Some 40 metric ton of arsenic has been deposited in the sediments of North Haiwee Reservoir since initiation of the interim arsenic management plan in March 1996. Arsenic in the deep sediments is unstable due to reductive dissolution of the solid phase with which it is associated. Migration of the redox boundary to the sediment-water interface could result in diffusion of reduced arsenic into the overlying water. Physical disturbance of the sediments could disperse the dissolved arsenic in the pore water into the overlying water. The long-term stability of arsenic in these sediments and the effect of cessation of the ferric chloride additions is unclear, but the large amount of potentially mobile arsenic poses a threat to water quality in the LAA water supply.

8.2 Wider Implications of this Study

Information regarding the mechanisms by which arsenic accumulates in geothermally impacted sediments can be obtained via examination of concentration profiles

and x-ray absorption spectra of sediments. In geothermal systems with abundant plant growth, both the plants and springs may have significant influence on local arsenic accumulation. XAS has been shown to be an especially powerful tool in identifying changes in the solid phase form and association of arsenic in natural sediments.

The gel probe sampler allows high resolution determination of pore water concentrations with minimal sediment disturbance. Such high resolution pore water profiles can be used to determine the net flux of a species between the sediment and the overlying water.

Sediment-water exchange of arsenic in geothermally impacted systems may be influenced by the initial arsenic concentration of the sediment and water and the ionic composition of the water. Because aggregation of colloidal particles varies with ionic strength, the fraction passing a 0.45 μm filter, operationally defined as "dissolved" may include colloidal material at low ionic strength. Therefore, the importance of colloidal material must be considered in the interpretation of sediment-water exchange experiments.

A decrease in upstream arsenic concentration, as would accompany treatment for arsenic removal at Hot Creek, will not result in a dramatic release of arsenic from the sediments of Crowley Lake. If the overlying water concentration is significantly reduced, concentration gradients will require that arsenic be slowly released from the sediment to the overlying water. However, this will be a gradual process. In addition, the sediments of Crowley Lake appear to be permanently reducing; the arsenic-sulfide phase identified in the sediments should be effectively immobilized.

Crowley Lake has unique features which derive from its high input of arsenic and phosphorus and its operation as a reservoir. These features allow observation of phenomena that would not be apparent in "normal" lakes. Uptake and transformation of arsenic by phytoplankton has been invoked as the mechanism by which As(III) and methylated arsenic species are present in the surface waters of productive lakes. In contrast to other lakes, algal cycling of arsenic does not appear to be important in Crowley Lake. Crowley Lake provides a clear example of how profoundly reservoir operations can influence water chemistry, an important consideration in the management of water supply systems.

The rapid deposition of iron- and arsenic-rich flocculated solids in Haiwee Reservoir allowed us to directly observe the results of reductive diagenetic processes. The x-ray absorption spectra of these sediments change dramatically with depth, illustrating the power of this technique for determining the form and association of arsenic in arsenic-contaminated sediments. The proximity of Haiwee Reservoir to the City of Los Angeles necessitates maintenance of high water quality in the reservoir. The long-term stability of the iron- and arsenic-rich flocculated solids deposited in North Haiwee is uncertain. The striking results of our preliminary investigation will, hopefully, precipitate a more thorough investigation into the status of arsenic in these sediments.

Appendix A

ARSENIC IN THE SEDIMENTS OF HOT CREEK AND CROWLEY LAKE

A series of samples collected from Hot Creek and Crowley Lake were analyzed by x-ray absorption spectroscopy (XAS) in August 1999. A selection of these spectra were discussed in Chapter 3. The remainder of the spectra collected are collated in Fig. A.1. Reference spectra collected in August 1999 and in January 2000 are collated in Fig. A.2.

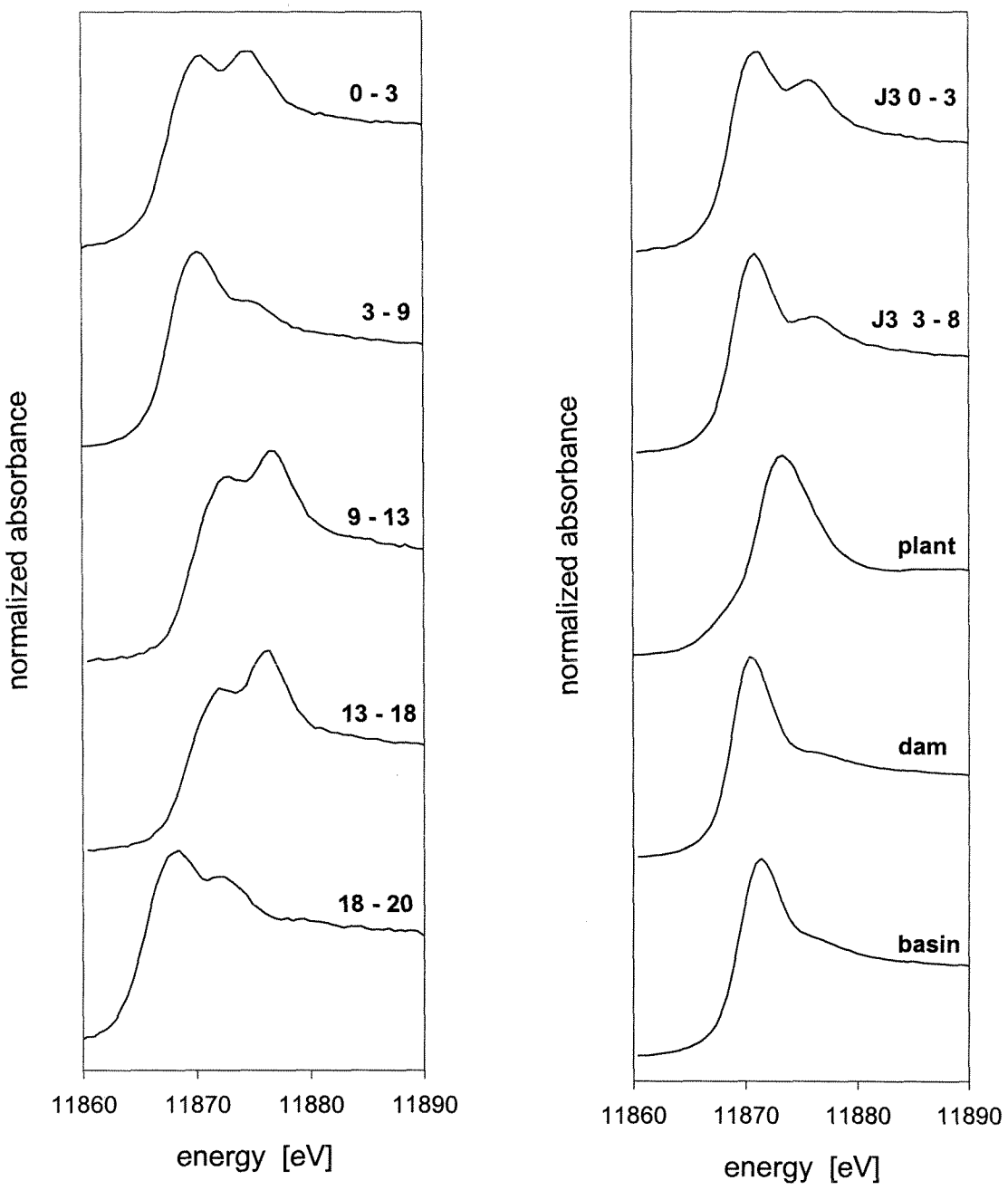

Figure A.1: X-ray absorption spectra of samples collected at Hot Creek Gorge and Crowley Lake, July 1999. Left panel shows sections of Core J1. Right panel shows Core J3 together with a sample of *potamogeton pectinatus* (plant), collected in Hot Creek, and the dam and basin samples collected in Crowley Lake. Each spectrum is normalized to the maximum absorbance.

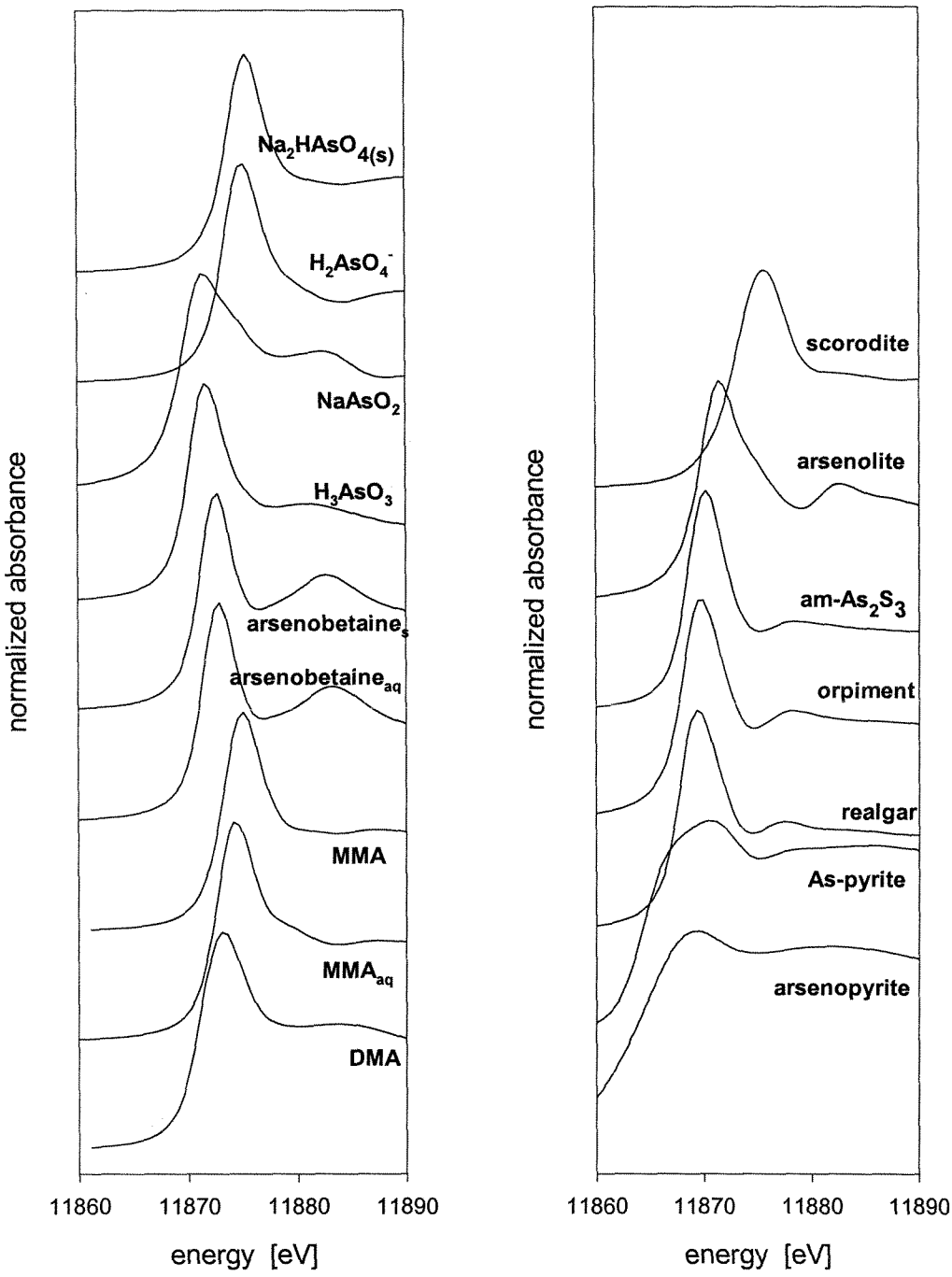

Figure A.2: X-ray absorption spectra of reference compounds. Subscripts s = solid, aq = 10 mM solution. MMA = disodium monomethylarsonate. DMA = sodium dimethylarsenate. As-pyrite = arsenic substituted pyrite. Each spectrum is normalized to the maximum absorbance.

Appendix B

SEDIMENT-WATER EXCHANGE EXPERIMENTS

The following tables contain data collected in a series of experiments to investigate the sediment-water exchange of arsenic in Hot Creek. Details regarding sample collection, experimental set-up and analysis can be found in Chapter 4 (§4.2).

Table B.1: Extractions of Hot Creek Surface Sediment Collected November 1996.

Expt. No. (Table 4.1)	extract number	$As_{T, final}$ [μg/L] 0.1 μm	$As_{T, final}$ [μg/L] 0.45μm	Mn_{final} [μg/L] 0.1 μm	Mn_{final} [μg/L] 0.45 μm	Fe_{final} [μg/L] 0.1 μm	Fe_{final} [μg/L] 0.45 μm
1	1	28	28	1.8	5.1	63	199
	1	27	29	2.8	5.9	97	198
HCH-96	2	18	19	1.7	4.2	78	179
5 g	2	19	20	1.9	3.8	73	152
50 mL	3	12	13	1.1	3.7	26	123
18	3	13	14	0.89	3.1	22	116
MΩcm	4	11	12	1.0	3.4	28	131
30 min	4	11	12	1.1	3.5	32	133
extracts	5	9.5	10	1.1	3.1	27	107
in	5	10	11	1.2	3.5	38	116
duplicate	6	9.5		1.0		30	
	6	9.9		1.1		28	
	7	7.2		1.2		38	
	7	7.8		1.3		43	
	8	6.2		0.99		30	
	8	6.6		0.95		26	
2	1	109	114	61	110	47	237
	1	114	120	58	127	59	286
HCG-96	2	91	93	29	55	31	204
5 g	2	96	100	29	134	27	428
50 mL	3	66	68	27	46	20	168
18	3	68	70	30	45	23	161
MΩcm	4	51	52	34	43	19	150
30 min	4	52	56	35	47	17	163
extracts	5	40	42	42	54	17	172
in	5	42	44	50	60	17	197
duplicate	6	36		45		16	
	6	38		46		32	
	7	29		38		28	
	7	30		41		26	
	8	22		35		23	
	8	24		36		21	

1 g sediment was shaken for 30 minutes with 50 mL 18 MΩcm water then centrifuged at 10,000 rpm for 5 minutes. Concentrations are those measured in supernatant after filtering through either a 0.45 μm or 0.1 μm membrane filter (indicated in column headings).

Table B.2: Time Series Experiments with Hot Creek Sediment Collected November 1996

Expt. No. (Table 4.1)	time [h]	As [µg/L]	Mn [µg/L]	Fe [µg/L]
3 HCG-96 40 g in 2 L 18 MΩcm $As_{T, init}$ = 0 ppb	0 0.25 0.5 0.75 1 1.5 3 22.7 46.7 116	1.5 16 23 26 29 33 37 36 35 39	0.2 19 24 25 150 89 93 128 47 12	0 44 50 58 53 62 95 121 250
4 HCH-96 40 g in 2 L 18 MΩcm $As_{T, init} \approx$ 300 ppb	0 0.25 0.5 0.75 1 1.5 2 3 6 16.7 31 50 75.5	283 288 282 276 277 266 274 257 255 225 212 203 189		
5 HCG-96 30 g in 2 L 18 MΩcm $As_{T, init} \approx$ 200 ppb	0 0.25 0.5 0.75 1 1.5 2.5 4 21.3 27 45.8	204 170 154 144 137 126 115 107 89.6 85.8 80.8		

Table B.3: Sequestration of As(III) and As(V) by Hot Creek Sediments

Expt. No. (Table 4.1)	$As(V)_{init}$ [μg/L]	$As(III)_{init}$ [μg/L]	$As_{T,final}$ [μg/L]
6	0 0	0 0	22 20
7	29 29	0 0	32 33
8	96 96	0 0	63 67
9	511 511	0 0	251 282
10	1010 1010	0 0	627 602
11	0 0	94 94	61 61
12	0 0	490 490	317 312
13	0 0	973 973	716 683

All experiments use 1 g HCH-96 in 50 mL 18 MΩcm water, spiked with As(V) or As(III), and shaken 24 h.

Table B.4: Repeated Extractions of Hot Creek Sediment Collected May 1999

Expt. No. (Table 4.1)	extract number	final pH	final k [μS/cm]	$As_{T,\ final}$ [μg/L]	$As(III)_{a,\ final}$ [μg/L]	$As(III)_{b,\ final}$ [μg/L]	P [μM]
14	1	8.55	56	281	106	108	7.6
	1	8.22	54	279	112	112	7.6
HCG-99-1	2	7.8	21	126	18	18	3.4
5 g in 50	2	7.8	23	133	23	24	3.2
mL	3	7.5	18	47.2	12	11	2.8
18 MΩcm	3	7.7	21	49.4	13	13	2.2
$As_{T,\ init}$= 0	4	7.6	37	29.6	7.9	7.9	2.5
μg/L	4	7.5	8	31.4	8.3	8.6	2.6
	5	7.2	100	21.5	6.9	6.8	3.9
	5	7.4	8	23.0	7.6	7.7	2.7
15	1	8.08	542	225	110	112	6.6
	1	8.09	540	248	118	118	6.6
HCG-99-1	2	8.2	522	87.5	22	21	3.5
5 g in 50	2	8.2	530	86.9	25	24	3.5
mL	3	8.18	507	47.9	13	13	2.7
SHC	3	8.2	507	49.7	14	14	2.6
$As_{T,\ init}$= 0	4	8.2	501	36.2	9.7	9.7	2.7
μg/L	4	8.2	500	37.1	9.8	9.7	2.7
	5	8.2	500	28.6	7.7	7.6	2.8
	5	8.2	501	27.8	7.9	7.7	2.8

k is conductivity.

5 g sediment shaken with 50 mL solution for 30 min, centrifuged and the supernatant filtered (0.45 μm). Duplicate aliquots were run through anion exchange columns for As(III) separation. Concentrations are those measured in the 50 mL supernatant following each extraction. Initial solutions contained 0 μg/L As.

Table B.5: Sediment-Water Exchange with Hot Creek Sediment Collected May 1999

Expt. No. (Table 4.1)	time [h]	final pH	k_{final} [µS/cm]	$As_{T, final}$ [µg/L]	$As(III)_{a, final}$ [µg/L]	$As(III)_{b, final}$ [µg/L]	P [µM]
16	0.5	8.7	60	500	171	169	5.8
	0.5	8.7	58	513	168	170	5.5
5 g	1	8.7	61	549	153	156	6.6
HCG-99-1	1	8.8	61	544	147	150	6.6
	2	8.2	115	587	132	132	7.6
50 mL	2	8.5	64	577	124	122	7.4
18 MΩcm	4	8.0	76	603	87	89	9.4
	4	8.1	58	598	84	81	8.3
$As_{T,init} \approx$	8	8.0	66	658	49	51	8.9
350 µg/L	8	7.9	69	659	55	54	9.0
40%	16	7.6	70	658	20	21	11
As(III)	16	7.5	71	662	23	23	12
17	0.5	8.2	540	428	167	168	5.8
	0.5	8.2	543	453	182	182	4.8
5 g	1	8.2	542	431	148	147	6.2
HCG-99-1	1	8.2	541	430	150	151	6.5
	2	8.2	543	420	125	126	6.5
50 mL	2	8.2	543	418	130	132	6.6
SHC	4	8.1	544	406	102	102	6.9
	4	8.1	538	397	96	94	6.3
$As_{T,init} \approx$	8	8.1	540	416	72	71	7.4
360 µg/L	8	8.1	540	415	66	67	7.8
40%	16	7.9	545	398	37	37	7.9
As(III)	16	7.9	543	415	43	44	8.3
18	0.5	8.4	508	469	165	167	6.2
	0.5	8.4	509	470	162	206	6.0
5 g	1	8.3	509	485	140	126	6.3
HCG-99-1	1	8.3	511	490	151	151	6.1
	2	8.4	511	494	127	128	6.5
50 mL	2	8.4	511	484	121	120	6.6
SHC-Ca	4	8.3	511	510	109	109	7.7
	4	8.3	513	495	94	93	7.5
$As_{T,init} \approx$	8	8.3	511	513	74	74	8.3
370 µg/L	8	8.3	512	531	81	81	9.2
40%	16	8.0	518	526	47	47	13
As(III)	16	8.1	517	554	57	56	11

Table B.5 (cont.): Sediment-Water Exchange with Hot Creek Sediment Collected May 1999

Expt. No. (Table 4.1)	time [h]	final pH	$k_{,final}$ [µS/cm]	$As_{T,\ final}$ [µg/L]	$As(III)_{a,\ final}$ [µg/L]	$As(III)_{b,\ final}$ [µg/L]	P [µM]
19	0.5	7.7	710	391	145	140	4.6
	0.5	7.7	707	397	450	149	4.5
5 g	1	7.8	711	400	435	133	4.3
HCG-99-1	1	7.8	710	392	130	134	4.4
	2	7.7	712	397	108	109	4.9
50 mL	2	7.7	710	398	101	102	5.5
18 MΩcm	4	7.6	714	407	88	88	5.0
+ NaCl	4	7.9	713	408	92	91	5.1
$As_{T,init} \approx$	8	7.6	717	412	73	72	6.3
330 µg/L	8	7.7	716	409	76	76	6.3
40%	16	7.2	724	367	54	56	4.9
As(III)	16	7.5	723	402	53	52	6.9
20	0.5	8.4	609	458	155	157	4.9
	0.5	8.4	609	444	157	152	4.9
5 g	1	8.3	610	447	141	144	4.6
HCG-99-1	1	8.4	609	468	153	152	4.9
	2	8.4	609	464	117	119	5.8
50 mL	2	8.4	610	458	119	118	5.4
18 MΩcm	4	8.3	611	455	95	94	5.8
$+HCO_3$	4	8.3	612	454	94	93	5.6
	8	8.3	613	488	76	76	7.8
$As_{T,init} \approx$	8	8.3	614	466	68	67	6.8
350 µg/L	16	8.1	617	495	57	59	10
40%	16	8.1	618	486	51	52	7.5
As(III)							
21	0.5	7.7	10	400	163	167	
	0.5	7.5	10	398	152	158	
0.5 g	1	7.4	11	403	155	159	
HCG-99-1	1	7.5	10	404	147	151	
	2	7.4	11	396	142	145	
50 mL	2	7.4	10	403	155	149	
18 MΩcm	4	7.2	12	396	140	141	
	4	7.3	12	395	125	123	
$As_{T,init} \approx$	8	6.9	12	393	123	123	
350 µg/L	8	7.1	12	391	128	126	
40%	16	7.1	12	384	108	108	
As(III)	16	7.1	11	391	127	128	

Table B.5 (cont.): Sediment-Water Exchange with Hot Creek Sediment Collected May 1999

Expt. No. (Table 4.1)	time [h]	final pH	$k_{,final}$ [µS/cm]	$As_{T,\ final}$ [µg/L]	$As(III)_{a,\ final}$ [µg/L]	$As(III)_{b,\ final}$ [µg/L]	P [µM]
22	0.5	8.2	461	384	149	146	
	0.5	8.2	461	383	145	145	
0.5 g	1	8.2	460	380	144	140	
HCG-99-1	1	8.2	462	384	145	151	
	2	8.2	460	382	134	136	
50 mL	2	8.2	461	381	139	141	
SHC	4	8.2	461	381	125	124	
	4	8.2	462	377	123	125	
$As_{T,init} \approx$	8	8.1	461	369	110	110	
380 µg/L	8	8.2	460	374	113	113	
40%	16	8.1	461	371	94	95	
As(III)	16	8.1		371	98	98	
23	0.5	7.7	44	442	113	112	3.7
	0.5	7.8	39	436	118	116	3.1
5 g	1	7.9	45	437	72	73	3.8
HCG-99-2	1	7.9	33	438	76	77	3.6
	2	7.8	44	421	34	34	3.6
50 mL	2	7.8	44	421	42	42	3.5
18 MΩcm	4	7.6	47	425	12	12	3.8
	4	7.6	46	437	13	13	3.8
$As_{T,init} \approx$	8	7.5	54	451	8.3	8.5	4.4
360 µg/L	8	7.6	53	444	8.8	9.4	4.9
40%	16	7.4	59	383	4.5	4.7	5.3
As(III)	16	7.4	57	413	4.9	4.9	4.8
24	0.5	8.0	478	364	123	123	3.9
	0.5	8.0	479	406	155	155	4.0
0.5 g	1	8.0	478	339	92	92	3.8
HCG-99-2	1	8.0	477	329	99	98	3.8
	2	8.0	479	319	60	60	3.8
50 mL	2	8.0	478	294	53	52	3.8
SHC	4	8.0	481	264	31	32	3.6
	4	8.0	479	301	27	26	3.9
$As_{T,init} \approx$	8	8.0	481	276	7.5	7.6	4.0
380 µg/L	8	8.1	481	277	9.4	9.2	4.0
40%	16	7.9	484	262	6.2	6.2	4.6
As(III)	16	8.0	485	265	6.5	6.7	4.9

k is conductivity.

Table B.6: Ionic Strength Experiments

Expt. No. (Table 4.1)	I [mM]	final pH	k_{final} [μS/cm]	$As_{T,\text{final}}$ [μg/L]	$As(III)_{a,\text{final}}$ [μg/L]	$As(III)_{b,\text{final}}$ [μg/L]
25	0	8.12 8.07	71 73	683 670	61 36	60 36
26	2.8	7.69 7.55	361 365	508 490	60 50	56 51
27	5.6	7.53 7.82	683 685	411 425	67 53	65 51
28	8.4	7.58 7.53	963 965	361 354	55 57	56 55

I is ionic strength; k is conductivity.

All experiments use 5 g HCG-99-1 sediment, 50 mL solution, ionic strength made up with NaCl, shaken 16 h then filtered and analyzed.

Table B.7: Experiments with Samples Collected at Benton Crossing, on the Owens River, May 1999

Expt. No. (Table 4.1)	time [h]	$As_{T, init}$ [ug/L]	$As(III)_{init}$ [ug/L]	final pH	$As_{T, final}$ [µg/L]	$As(III)_a$ [µg/L]
29	16	69.7	0.5	7.76	42.0	2.9
30	16	124 124	0.5 0.5	7.81 7.85	62.8 63.1	2.8 3.2
31	16	170 170	0.5 0.5	7.75 7.72	82.9 84.3	3.6 4.0
32	16	262 262	0.8 0.8	7.79 7.80	141 125	2.5 2.9
33	16	343 343	0.6 0.6	7.82 7.79	168 174	2.0 4.1
34 5 g BX-99 50 mL BX	0.5 0.5 1 1 2 2 4 4 9.5 16	69.7 69.7 69.7 69.7 69.7 69.7 69.7 69.7 69.7 69.7	0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	8.09 8.08 8.03 8.03 8.01 7.97 7.93 8.01 7.89 7.76	55.3 55.1 52.3 52.6 45.5 49.1 45.9 45.2 43.1 42.0	2.7 2.8 2.9 2.7 2.3 2.5 1.9 2.3 3.2 2.9

Appendix C

CROWLEY LAKE WATER COLUMN SAMPLING

August 1998, September 1998 and May 1999

C.1 Water Column Data

The data presented in the following tables pertains to samples collected from the water column of Crowley Lake, Basin and Dam sites, on 5 August 1998 (Table C.1), 3 September 1998 (Table C.2) and 11 May 1999 (Table C.3). Details regarding sample collection, preparation and analysis can be found in Chapter 5 (§5.2).

Notes to Tables:

All concentrations are in μM, except dissolved oxygen which is in mg/L.

DO dissolved oxygen

$AsIII_a$, $AsIII_b$ duplicate determinations of As(III), as the eluent from each of two anion exchange columns

As_T total arsenic (measured in influent to anion exchange columns)

Table C.1: Crowley Lake Water Samples Collected 5 August 1998

				UNFILTERED [μM]						FILTERED [uM]			
depth [m]	T [°C]	pH	DO [mg/L]	$AsIII_a$	$AsIII_b$	As_T	Mn	Fe	P	As_T	Mn	Fe	P
BASIN													
3	21.5	9.75	8.98	0.043	0.047	0.71	0.078	1.3	1.3	0.70	<0.01	1.1	0.45
7	19.9	9.31	3.96	0.027	0.025	0.58	0.079	1.2	0.42	0.59	<0.01	1.0	0.6
10	18.2	8.03	0.38	0.36	0.036	0.65	0.81	1.3	1.5	0.69	0.75	1.3	1.2
12	18.6	7.96	0.20										
14	17.8	7.81	0.14	0.28	0.29	0.74	1.7	1.4	3.7	0.86	1.7	1.5	3.5
17	18.5	7.77	0.09	0.57	0.60	0.80	2.3	1.5	5.4	0.86	2.2	1.4	4.7
20	17.1	7.69	0.06	0.67	0.66	0.80	3.0	1.6	7.0	0.82	3.0	1.6	6.5
DAM													
3	22.7	9.84	8.12	0.021	0.022	0.73	0.062	1.1	0.61	0.76	0.018	0.89	0.41
7	20.9	9.48	4.82	0.022	0.022	0.59	0.11	1.3	0.51	0.60	0.024	0.93	0.35
9	20.2	9.32	4.18	0.018	0.019	0.47	0.12	1.4	0.44	0.48	0.029	1.0	0.27
10	20.2	8.77	2.42	0.017	0.017	0.50	0.25	1.4	0.73	0.49	0.13	1.0	0.44
12	19.5	7.95	0.30	0.18	0.18	0.59	0.70	1.2	3.0	0.61	0.39	1.1	2.8
15	18.5	7.80	0.11	0.30	0.31	0.71	1.4	1.4	3.0	0.73	1.5	1.3	2.8
18	18.2	7.75	0.07	0.38	0.38	0.77	2.0	1.6	4.3	0.79	2.1	1.4	4.0
21	18.3	7.70	0.06	0.48	0.48	0.80	2.5	1.6	5.4	0.80	2.5	1.6	5.1
24	17.8	7.67	0.03	0.46	0.47	0.82	2.8	1.6	6.4	0.82	2.8	1.6	6.0

Table C.2: Crowley Lake Water Samples Collected 3 September 1998

				UNFILTERED [μM]						FILTERED [uM]			
depth [m]	T [°C]	pH	DO [mg/L]	$AsIII_a$	$AsIII_b$	As_T	Mn	Fe	P	As_T	Mn	Fe	P
BASIN													
0.5				0.032	0.034	0.74	0.14		0.42	0.74	0.031		0.18
1.5				0.034	0.032	0.75	0.15	1.2	0.49	0.72	0.032	1.2	0.33
3	20.4	9.53	6.60	0.029	0.031	0.74	0.14		0.45	0.79	0.027		0.31
5	20.3	9.55	6.42	0.032	0.031	0.75	0.14	1.2	0.44	0.73	0.025	1.1	0.37
7	20.0	9.55	6.20	0.027	0.028	0.78	0.15		0.45	0.74	0.025		0.23
8	19.9	9.55	5.84	0.031	0.030	0.75	0.15		0.39	0.75	0.025		0.42
9	19.9	9.22	1.90	0.029	0.029	0.72	0.17	1.3	0.84	0.73	0.024	1.1	0.84
11	19.3	8.85	0.23	0.16	0.17	0.71	0.11	1.3	1.8	0.72	0.049		1.7
12	19.3	8.81	0.13	0.092	0.093	0.72	0.99		1.9	0.74	0.070	1.1	1.9
13	19.0	8.75	0.10	0.17	0.16	0.72	1.2		2.0	0.70	0.99		1.9
15	18.4	7.87	0.33	0.079	0.090	0.60	2.3	1.8	5.3	0.62	2.2	1.6	5.4
17	18.3	7.69	0.15	0.098	0.10	0.61	2.2		6.1	0.61	2.2		6.1
19	17.9	7.70	0.22	0.13	0.13	0.63	2.2	2.0	5.7	0.63	2.2	1.7	7.1
21	17.9	7.66	0.12	0.11	0.12	0.60	2.3	2.0	6.4	0.62	2.3	1.8	7.2

Table C.2 (cont.): Crowley Lake Water Samples Collected 3 September 1998

				UNFILTERED [μM]						FILTERED [uM]			
depth [m]	T [°C]	pH	DO [mg/L]	$AsIII_a$	$AsIII_b$	As_T	Mn	Fe	P	As_T	Mn	Fe	P
DAM													
0.5				0.033	0.033	0.76	0.11	1.2	0.29	0.76	0.017	1.1	0.23
1.5				0.034	0.033	0.75	0.11		0.31	0.75	0.020		0.36
3	20.9	9.54	6.35	0.034	0.041	0.72	0.11	1.2	0.26	0.72	0.016	1.1	0.44
5	21.0	9.54	6.10.	0.034	0.033	0.73	0.12	1.2	0.28	0.71	0.015	1.1	0.27
7	20.6	9.37	3.71	0.022	0.022	0.71	0.14	1.3	0.32	0.71	0.014	1.2	0.35
8	20.5	9.32	3.29										
9	20.4	9.30	2.93	0.019	0.021	0.67	0.13		0.29	0.67	0.012		0.26
10	19.9	9.19	1.93	0.018	0.017	0.67	0.17	1.3	0.51	0.67	0.012	1.2	0.50
11	19.9	9.12	1.52	0.017	0.015	0.65	0.19		0.66	0.64	0.011		0.65
12	19.6	8.94	0.36	0.019	0.020	0.67	0.33	1.4	1.2	0.67	0.013	1.2	1.1
13	19.4	8.88	0.12	0.026	0.027	0.65	0.48		1.3	0.64	0.050		1.4
15	19.4	8.76	0.09	0.25	0.25	0.67	0.95	1.2	1.6	0.66	0.81	1.2	1.7
17	19.3	8.59	0.07	0.24	0.24	0.64	1.4	1.4	2.1	0.65	1.3	1.3	2.1
19	18.6	8.08	0.07	0.20	0.23	0.63	2.0		3.3	0.58	2.0		3.3
21	18.3	7.79	0.07	0.12	0.12	0.61	2.2	1.6	5.0	0.50	2.2	1.8	5.0
23	18.2	7.65	0.06	0.075	0.075	0.61	2.2	1.9	6.4	0.56	2.2	1.9	6.1
25	17.8	7.54	0.06	0.049	0.051	0.61	2.3	2.1	8.1	0.71		2.1	7.7
26	17.7	7.50	0.06	0.041	0.029	0.58	2.3	2.1	8.6	0.56	2.3		8.3
27	17.9	7.49	0.06	0.029	0.040	0.61	2.3	2.1	8.7	0.59	2.3	2.0	8.4
28	17.7	7.48	0.06	0.037	0.039	0.58	2.3		8.7	0.62	2.4		8.5
29	17.6	7.49	0.06	0.026	0.027	0.60	2.3		9.0	0.60	2.3		8.7

Table C.3: Crowley Lake Water Samples Collected 11 May 1999

				UNFILTERED [μM]						FILTERED [uM]			
depth [m]	T [°C]	pH	DO [mg/L]	$AsIII_a$	$AsIII_b$	As_T	Mn	Fe	P	As_T	Mn	Fe	P
BASIN													
2	11.3	8.61	9.41	0.015	0.014	0.81	0.18	1.3	0.78	0.83	0.034	0.95	0.63
5	11.2	8.63	9.41	0.013	0.015	0.82	0.18	1.3	0.79	0.85	0.031	0.91	0.60
8	10.9	8.63	8.64	0.017	0.013	0.84	0.21	1.3	0.84	0.87	0.035	0.94	0.77
11	10.6	8.61	8.24	0.016	0.015	0.84	0.25	1.2	0.82	0.86	0.046	0.98	0.80
14	10.5	8.58	8.19	0.018	0.017	0.83	0.24	1.2	0.76	0.85	0.046	0.97	0.72
17	10.4	8.58	8.03	0.016	0.014	0.83	0.25	1.2	0.73	0.87	0.040	0.97	0.73
19	10.3	8.55	8.01	0.019	0.019	0.83	0.28	1.3	0.80	0.87	0.056	1.01	0.71
21	10.2	8.49	7.66	0.022	0.023	0.81	0.48	1.2	1.1	0.86	0.22	0.99	0.96
23	10.0	8.42	7.40	0.028	0.028	0.82	0.61	1.3	1.3	0.84	0.34	0.99	1.2
DAM													
2	12.9	8.60	8.01	0.012	0.015	0.79	0.16	1.3	1.2	0.79	0.037	1.0	0.55
5	12.7	8.60	8.10	0.015	0.016	0.80	0.16	1.3	1.2	0.78	0.032	0.93	0.70
8	12.6	8.59	8.23	0.016	0.014	0.79	0.19	1.3	0.89	0.80	0.030	1.0	0.56
11	11.4	8.50	7.80	0.015	0.017	0.81	0.31	1.3	1.0	0.83	0.084	0.96	0.69
15	11.0	8.48	7.60	0.019	0.016	0.81	0.38	1.2	1.1				
17	10.8	8.47	7.51	0.018	0.016	0.81	0.38	1.2	1.1	0.81	0.12	0.93	0.64
20	10.9	8.45	7.50	0.016	0.019	0.80	0.37	1.3	1.1	0.82	0.11	0.96	0.55
23	10.8	8.38	6.94	0.018	0.018	0.81	0.52	1.2	1.3	0.82	0.23	1.0	0.71
25	10.9	8.34	6.68	0.022	0.023	0.80	0.74	1.6	1.5	0.82	0.41	0.96	0.78

C.2 Digestion of Black Precipitate at 12 m, Dam Site, August 5, 1998

The entire 1 L water sample collected from 12 m at the dam site in August 1998 was filtered through 0.45 μm filters upon return to the laboratory. Some of the black precipitate present in this sample was retained on the filters. Some was adhered to the walls of the collection vessel. The weight of particulates in each fraction was not determined.

Two of the filters holding particulates were added to 40 mL of 0.04 M hydroxylamine hydrochloride in 25% acetic acid. The solution was stirred and heated on a hot plate for 1 h, then diluted for ICPMS analysis. Particulate material was still present in solution, i.e., this method does not provide a complete dissolution of the particulate material. A blank was produced by heating two unused filter membranes were with a second 40 mL aliquot of the hydroxylamine hydrochloride, 25% acetic acid solution. A third 40 mL aliquot of the extraction solution was added to the (empty) bulk sample collection vessel and shaken. A sample of this wash solution was diluted for ICPMS analysis.

Table C.4: Partial Digestion of Particulate Material at Dam Site, 12 m, August 5 1998

	Fe [μg/L]	Mn [μg/L]	As [μg/L]
blank	37 ± 2	3.6 ± 0.2	12 ± 1
filter material	150 ± 8	78 ± 4	27 ± 3
vessel washings	510 ± 30	1500 ± 80	160 ± 20

The concentrations of iron, manganese and arsenic in the solutions were determined (Table C.4). The approximate molar ratios of As:Mn:Fe are 1:3:6 in the particulates on the filters and 1:9:3 in the particulates adhered to the walls of the collection vessel.

C.3 Manganese Withdrawal from Crowley Lake

The parameters used to estimate the volume of the hypolimnion (§5.3.2) and the amount of manganese withdrawn from the hypolimnion of Crowley Lake between the August 5, 1998 and September 3, 1998 sampling dates are given in Tables C.5 and C.6.

Table C.5: Calculation of Volume Withdrawn from Crowley Lake Hypolimnion

PARAMETER	VALUE	SOURCE
surface area Crowley Lake	21×10^6 m^2	USEPA 1978
depth of mixed layer (epilimnion)	10 m	our data
surface area hypolimnion	0.4 x total surface area $= 8.4 \times 10^6$ m^2	Fig. 5.1
cross section of hypolimnion	triangular, maximum depth 28 m	Approx. (Fig. 5.1)
volume hypolimnion	65×10^6 m^3	
volume withdrawn between August 5 and September 3, 1998	30×10^6 m^3 (11 m^{3}s^{-1})	Biedelman 1998, Bagaus 1999
storage July 31, 1998 (assume equal to storage on August 5, 1998)	2.01×10^8 m^3	CDEC 2000
storage August 31, 1998 (assume equal to storage on September 3, 1998)	1.96×10^8 m^3	CDEC 2000
storage change	5×10^6 m^3	
width of selective withdrawal layer	7 m	after Brooks and Koh 1969 (see §5.3.2)

Table C.6: Manganese in Horizontal Layers of Crowley Lake

DEPTH [m]	UPPER SURFACE AREA [10^6 m^2]	MANGANESE [μM][1]		MANGANESE [10^3 mol][2]	
		Aug. 5, 1998	Sept. 3, 1998	Aug. 5, 1998	Sept. 3, 1998
1	21.0	0.062	**0.11**	1.3	2.3
2	19.7	0.062	**0.11**	1.2	2.2
3	18.5	**0.062**	**0.11**	1.1	2.1
4	17.2	0.074	0.12	1.3	2.0
5	15.9	0.085	**0.12**	1.4	1.9
6	14.7	0.097	0.13	1.4	1.9
7	13.4	**0.11**	**0.14**	1.5	1.9
8	12.1	0.11	0.13	1.4	1.6
9	10.9	**0.12**	**0.17**	1.3	1.4
10	9.62	**0.24**	**0.19**	2.4	1.6
11	8.35	0.47	**0.33**	3.9	1.6
12	7.79	**0.70**	**0.48**	5.4	2.6
13	7.24	0.94	**0.71**	6.8	3.5
14	6.68	1.18	0.95	7.9	4.8
15	6.12	**1.42**	**1.18**	8.7	5.8
16	5.57	1.62	1.40	9.0	6.6
17	5.01	1.81	**1.71**	9.1	7.1
18	4.45	**2.00**	2.01	9.0	7.6
19	3.90	2.17	**2.09**	8.5	7.9
20	3.34	2.33	2.16	7.8	7.0
21	2.78	**2.50**	**2.18**	7.0	6.0
22	2.23	2.61	2.20	5.8	4.9
23	1.67	2.72	**2.24**	4.5	3.7
24	1.11	**2.83**	2.23	3.2	2.5
25	0.56	2.83	**2.31**	1.6	1.3

[1] Values in bold are measured, others are determined by linear interpolation.
[2] Calculated by multiplying concentration by volume of layer. Volume estimated as product of upper surface area and layer thickness (1 m).

We assume the outflow between August and September 1998 is from the 17 to 24 m layers (after Brooks and Koh 1969). The total manganese withdrawn is calculated as the volume of each layer multiplied by the concentration of manganese in each layer measured on August 5 1998. This assumes that the concentration at each depth remains constant throughout the month of August. This is assumption is supported by the similarity of the concentrations measured in August and September.

C.4 Arsenic Budget for Crowley Lake, 1998

Table C.7: Flow Budget for Crowley Lake, April 1998 to May 1999

month	OUT-FLOW[1] [10^6 m^3]	INFLOW[2] [10^6 m^3]					[3]Calc. month end Storage [10^6 m^3]	[4]Flow In + 100 cfs make	Calc. month end storage + 100 cfs make	[5]Re-ported month end Storage [10^6 m^3]
		Owens River	Convict Creek	McGee Creek	Crooked and Rock	Total Inflow				
Apr	36.3	5.65	0.88	1.10	0.51	8.14	146	15.5	146	146
May	31.0	6.37	1.44	1.67	0.76	10.2	118	17.8	126	130
Jun	13.1	13.2	4.33	5.13	4.84	27.5	97.2	34.8	113	153
Jul	2.4	10.6	7.96	8.34	7.58	34.5	112	42.1	135	201
Aug	29.6	8.57	3.64	3.79	2.43	18.4	144	26.0	175	196
Sep	32.1	8.15	1.98	2.06	0.95	13.1	133	20.4	171	167
Oct	40.2	8.49	1.44	1.52	0.38	11.8	114	19.4	159	151
Nov	35.3	8.22	1.10	1.32	0.29	10.9	85.6	18.2	138	136
Dec	35.8	8.04	1.21	1.21	0.23	10.7	61.2	18.3	121	151
Jan	2.2	7.96	1.14	1.06	0.23	10.4	36.1	18.0	104	168
Feb	0.34	7.19	1.03	0.82	0.27	9.32	44.3	16.2	120	167
Mar	16.8	7.43	0.99	1.06	0.15	9.63	53.3	17.2	136	155
Apr	27.4	5.36	0.66	1.10	0.29	7.41	46.1	14.8	136	158
May	17.5	8.72	1.29	2.73	1.97	14.7	26.1	22.3	123	171

[1] Values from Ball 1999.
[2] Values from Keef 1999.
[3] Month end storage calculated using month end storage for previous month minus outflow plus inflow. The starting point is the reported month end storage for April 1998, reported in CDEC 1999.
[4] Inflow does not balance outflow and produce the measured storage. It was suggested (Keef 1999) that there is a 20 to 100 cfs make in the watershed. A 100 cfs make is added to the inflow.
[5] Values from CDEC 1999.

Clearly, the storage calculated from the inflow and outflow data available do not balance to produce the measured month end storage. The 100 cfs make was invoked to better approximate the measured storage. We will assume for the sake of the arsenic budget that the 100 cfs make is entirely from the Owens River. For the sake of the arsenic budget, we have monthly measurements of arsenic at the outlet of Crowley Lake and at Benton Crossing, on the Owens River. In the absence of more detailed informa-

tion, we will use this concentration coupled with the average flow for each month and assume that, in comparison to the arsenic input with the Owens River, no arsenic is contributed by the other tributaries. Such an arsenic budget is given in Table C.8.

Table C.8: Arsenic Budget For Crowley Lake, May 1998 to April 1999

	OUTFLOW			INFLOW FROM OWENS RIVER			
MONTH	volume [10^6 m^3]	As conc. [mg/m^3]	total As [10^3 kg]	volume (+ 100 cfs make) [10^6 m^3]	As conc. [mg/m^3]	total As [10^3 kg]	As OUT - As IN [10^3 kg]
Apr	36.3	92	3.3	13.0	109	1.4	1.9
May	31.0	64	2.0	14.0	74	1.0	1.0
Jun	13.1	71	0.93	20.5	76	1.6	-0.67
Jul	2.4	61	0.15	18.2	47	0.86	-0.71
Aug	29.6	57	1.7	16.2	58	0.94	0.76
Sep	32.1	42	1.3	15.5	65	1.0	0.3
Oct	40.2	51	2.1	16.1	62	1.0	1.1
Nov	35.3	53	1.9	15.6	72	1.1	0.8
Dec	35.8	49	1.8	15.6	64	1.0	0.8
Jan	2.2	65	0.14	15.5	77	1.2	-1.1
Feb	0.34	52	0.02	14.0	79	1.1	-1.1
Mar	16.8	101	1.7	15.0			
Apr	27.4	56	1.5	12.7	60	0.76	0.74
May	17.5	57	1.0	16.3	85	1.4	-0.4
TOTALS			19.5			14.4	3.4

Even when the 100 cfs make is added entirely to the inflow from the Owens River, this very coarse budget results in 3.4 x 10^3 kg more arsenic being exported from Crowley Lake than is imported. This calculation excludes the mass of arsenic in the outflow for the month of March as the inflow arsenic concentration for this month is not known. The concentration of arsenic in the outflow of Crowley Lake and in the Owens River varies by a factor of two over the year. Clearly, more frequent determinations of arse-

nic concentration are necessary to compile an accurate arsenic budget. There is, however, no evidence for arsenic loss in Crowley Lake.

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Appendix D

NORTH HAIWEE RESERVOIR

Sediment and Pore Water Concentration Data, XAS Spectra

This appendix contains data on sediment samples collected at North Haiwee Reservoir on 22 December 1999. Presented are concentrations from whole sediment digestions (Table D.1), concentrations in pore waters by centrifugation (Table D.2), and the pore water profiles obtained using a gel probe sampler (Table D.3). Details regarding sample collection, preparation, and analysis can be found in Chapter 6. Results of a sequential extraction procedure and full results from a sediment incubation are in Tables D.4 and D.5 respectively. The spectra collected in January 2000 by x-ray absorption spectroscopy for a set of reference materials are also presented here (Fig. D.1).

Table D.1: Concentrations[a] in Haiwee Reservoir Sediments, 22 December 1999

site	depth [cm]	As [mg/g]		P [µg/g]		Fe [%]		Mn [mg/g]	
NW	0 - 2.5	0.51	0.34	1.8	1.3	9.0	5.5	1.3	0.57
	2.5 - 4.5	0.38	0.28	1.4	1.1	7.4	4.8	1.0	0.62
	4.5 - 7	0.27	0.19	0.93	1.1	3.4	4.4	0.47	0.88
	7 - 11	0.34	0.35	1.3	1.3	4.3	5.1	0.63	0.72
	11 - 13	0.26	0.27	1.2	1.2	3.9	4.7	0.62	0.71
	13 - 15.5	0.28	0.24	1.2	1.1	4.4	4.4	0.73	0.70
	15.5 - 18	0.26	0.14	1.4	0.70	4.2	3.0	0.77	0.51
	18 - 21.5	0.10	0.17	0.66	1.1	1.9	3.9	0.40	0.86
	21.5 - 24	0.16	0.36	1.1	1.3	3.3	5.3	0.72	0.75
	24 - 28	0.22	0.20	1.3	1.2	4.0	4..5	0.91	0.93
	28 - 30.5	0.36	0.32	1.6	1.5	5.8	4.9	1.1	0.93
	30.5 - 32.5	0.22	0.23	1.2	1.2	3.8	4.8	0.76	0.97
	32.5 - 35	0.21	0.19	1.2	1.1	4.2	3.9	0.84	0.80
	35 - 37	0.15	0.18	1.0	1.2	3.4	4.4	0.72	0.90
	37 - 41	0.10	0.16	0.87	1.3	2.5	4.1	0.53	0.88
	41 - 44	0.17	0.19	1.2	1.3	3.5	2.8	0.70	0.56
SW	0 - 1								
	1 - 3	0.30	0.28	1.2	1.1	5.7	5.5	0.57	0.54
	3 - 4.5	0.17	0.17	0.87	0.88	4.7	5.0	0.48	0.52
	4.5 - 6								
	6 - 8.5	0.14	0.19	0.78	1.1	4.5	6.3	0.50	0.70
	8.5 - 11								
	11 - 12.5	0.14	0.16	0.75	0.82	4.6	4.8	0.52	0.55
	12.5 - 14.5								
	14.5 - 16	0.15	0.22	0.85	1.2	4.1	6.1	0.59	0.88
	16 - 18								
	18 - 21	0.13	0.18	1.1	1.3	4.1	5.3	0.58	0.86
	21 - 23								
	23 - 25.5								
	25.5 - 26	0.20	0.13	1.5	1.0	6.1	3.7	1.0	0.53
NE	0 - 2.5	0.011	0.013	0.28	0.28	0.2	0.2	0.002	0.002
	2.5 - 5.5	0.007	0.007	0.28	0.26	0.2	0.2	0.001	0.002
	5.5 - 8	0.004	0.003	0.23	0.15	0.1	0.1	0.001	0.001
	8 - 12	0.006	0.005	0.28	0.29	<0.1	0.2		0.001
	12 - 15.5	0.012	0.014	0.71	0.46	0.3	0.2	0.002	0.003

[a] Concentrations determined by partial digestion, reported on a dry weight basis.

Table D.2: Pore Water Concentrations[a] in Haiwee Reservoir Sediments

site	depth [cm]	As		P		Fe		Mn	
		mg/L	µM	mg/L	µM	mg/L	mM	mg/L	µM
NW	0 - 2.5	0.069	0.93	0.30	9.8	1.7	0.03	0.94	17
	2.5 - 4.5								
	4.5 - 7								
	7 - 11	0.71	9.52	0.55	18	17	0.30	0.80	15
	11 - 13	0.95	12.7	0.67	22	27	0.48	1.1	20
	13 - 15.5	1.59	21.2	0.99	32	31	0.56	0.93	17
	15.5 - 18	1.76	23.5	1.0	33	31	0.55	0.80	15
	18 - 21.5	1.63	21.8	1.1	35	35	0.62	0.77	14
	21.5 - 24	1.43	19.1	0.77	25	27	0.48	0.67	12
	24 - 28	2.19	29.3	1.2	37	34	0.61	0.75	14
	28 - 30.5	2.04	27.2	0.86	28	20	0.36	0.49	8.9
	30.5 - 32.5	2.15	28.7	0.96	31	24	0.42	0.48	8.8
	32.5 - 35	1.55	20.7	0.93	30	26	0.46	0.47	8.5
	35 - 37	1.47	19.6	0.93	30	21	0.38	0.34	6.2
	37 - 41	1.42	19.0	0.94	30	16	0.28	0.37	6.8
	41 - 44	1.52	20.3	1.0	33	16	0.29	0.58	11
SW	0 - 1	0.061	0.82	0.61	20	3.5	0.06	1.0	18
	1 - 3	0.090	1.2	0.45	14	6.7	0.12	1.4	25
	3 - 4.5	0.16	2.2	0.43	14	7.6	0.14	1.5	27
	4.5 - 6	0.29	3.8	0.42	14	12	0.21	1.4	26
	6 - 8.5	0.40	5.4	0.74	24	15	0.28	1.7	31
	8.5 - 11	0.39	5.2	0.69	22	11	0.20	1.5	27
	11 - 12.5	0.63	8.3	1.1	34	16	0.28	1.2	22
	12.5 - 14.5	0.88	12	1.6	51	27	0.48	1.7	30
	14.5 - 16	0.94	13	2.0	65	21	0.38	1.4	26
	16 - 18	1.1	14	1.4	46	24	0.42	1.5	28
	18 - 21	0.93	12	1.4	46	22	0.39	1.3	24
	21 - 23	1.4	19	2.0	66	30	0.53	1.6	29
	23 - 25.5	1.7	23	2.0	63	32	0.57	1.7	30
	25.5 - 26	0.57	7.6	0.96	31	11	0.19	0.65	12
NE	0 - 2.5	0.087	0.0012	0.37	12	0.74	0.01	0.20	3.7
	2.5 - 5.5	0.043	0.0006	0.38	12	0.87	0.02	0.044	0.8
	5.5 - 8	0.038	0.0005	0.50	16	1.5	0.03	0.045	0.8
	8 - 12	0.049	0.0007	0.52	17	2.1	0.04	0.081	1.5
	12 - 15.5	0.029	0.0004	0.28	9.2	2.9	0.05	0.13	2.3

[a] Pore water extracted by centrifugation of wet sediment samples.

Table D.3: Pore Water Concentrations at NW Site Obtained with Gel Probe Sampler

depth [cm]	As		Fe		Mn	
	mg/L	μM	mg/L	mM	mg/L	μM
-3.82	0.004	0.051	0.18	0.003	0.009	0.16
-3.18	0.003	0.042	0.13	0.002	0.007	0.13
-2.54	0.015	0.20	1.54	0.028	0.026	0.47
-1.91	0.015	0.21	1.58	0.028	0.027	0.49
-0.64	0.007	0.097	0.51	0.009	0.017	0.31
0	0.005	0.073	0.23	0.004	0.019	0.34
0.64	0.007	0.088	0.39	0.007	0.019	0.34
1.27	0.005	0.063	0.12	0.002	0.022	0.40
1.91	0.014	0.19	1.27	0.023	0.033	0.59
3.18	0.005	0.067	0.21	0.004	0.044	0.81
3.82	0.006	0.078	0.44	0.008	0.056	1.01
4.45	0.004	0.051	0.18	0.003	0.066	1.2
5.09	0.006	0.086	0.34	0.006	0.10	1.8
5.72	0.009	0.13	0.65	0.012	0.12	2.3
7.00	0.028	0.37	2.86	0.051	0.26	4.8
7.63	0.044	0.59	4.96	0.089	0.31	5.6
8.27	0.017	0.23	1.50	0.027	0.34	6.1
8.90	0.032	0.42	3.03	0.054	0.42	7.7
9.54	0.009	0.12	0.56	0.010	0.41	7.4
10.81	0.027	0.36	2.30	0.041	0.60	10.8
11.45	0.028	0.37	2.93	0.053	0.68	12.4
12.08	0.045	0.61	5.91	0.11	0.96	17.5
12.72	0.27	3.6	34.5	0.62	1.43	26.1
13.36	0.28	3.7	34.1	0.61	1.10	20.0
14.63	0.23	3.1	28.9	0.52	1.15	21.0
15.26	0.11	1.4	13.2	0.24	1.57	28.5
15.90	0.053	0.71	6.45	0.12	0.98	17.9
16.54	0.088	1.2	13.3	0.24	1.53	27.8
17.17	0.10	1.4	16.8	0.30	1.66	30.3
18.44	0.21	2.8	30.9	0.55	1.67	30.5
19.08	0.29	3.9	37.2	0.67	1.68	30.5
19.72	0.32	4.2	38.5	0.70	1.57	28.6
20.35	0.32	4.2	43.0	0.77	1.83	33.4
20.99	0.39	5.1	46.4	0.83	1.70	30.9
22.26	0.37	5.0	43.7	0.78	1.78	32.4
22.90	0.47	6.3	54.0	0.97	1.77	32.2
23.53	0.36	4.9	44.5	0.80	1.46	26.5
24.17	0.44	5.9	47.9	0.86	1.54	28.0
24.80	0.47	6.3	48.8	0.87	1.50	27.3
26.08	0.64	8.5	66.6	1.12	1.66	30.2
26.71	1.27	17.0	63.7	1.14	1.56	28.3
27.35	1.31	17.6	90.0	1.61	1.70	31.0
27.99	0.55	7.3	85.1	1.52	1.88	34.2
28.62	0.56	7.4	58.6	1.05	1.74	31.7

Table D.4: Results of Sequential Extraction of Haiwee Reservoir Sediments

sample	EXTRACTION SOLUTION					
	$MgCl_2$	NaOAc	$NH_2OH.HCl$	pyro-PO_4	ClO_4-HCl	% removed[a]
Fe [mg/g]						
2.5 - 4.5	0.22 0.14	0.44 0.39	26 37	1.0 1.0	2.0 1.6	50 ± 11 69 ± 15
18 - 21.5	0.14 0.14	0.54 0.59	15 17	0.42 0.54	0.95 1.0	65 ± 22 76 ± 26
37 - 41	0.12 0.19	0.58 0.91	15 16	0.59 0.39	0.98 0.70	55 ± 13 58 ± 14
Mn [µg/g]						
2.5 - 4.5	71 64	54 54	200 210	4 4	23 18	45 ± 11 46 ± 11
18 - 21.5	59 63	100 110	200 220	4 5	15 15	69 ± 25 75 ± 27
37 - 41	42 56	120 130	220 200	6 4	16 11	61 ± 20 61 ± 20
As [µg/g]						
2.5 - 4.5	3 2	2 2	190 200	23 19	33 26	77 ± 12 77 ± 12
18 - 21.5	2 2	2 2	120 130	4 5	15 17	110 ± 30 120 ± 30
37 - 41	2 3	2 3	98 100	5 3	13 13	97 ± 22 100 ± 23

[a] calculated by comparison of total extracted with results of whole sediment extraction (Table D.1).

Table D.5: Results from Incubation of Haiwee Reservoir Sediment

	JAR 1 - AIR					JAR 2 - AIR				
time [h]	As [µg/L]	Mn [µg/L]	Fe [mg/L]	As(III) [µg/L]	pH[a]	As [µg/L]	Mn [µg/L]	Fe [mg/L]	As(III) [µg/L]	pH[a]
0	3.0	4.0	0.12	0.42	8.71	3.42	5.24	0.12	0.69	8.73
0.5	17.1	33.6	0.31	12	7.5	7.43	34.3	0.24	3.9	7.5-8
1	20.4	32.3	0.34	5.4	7.5	9.19	37.4	0.26	13	7.5
2	22.6	34.9	0.36	14	7.5-8	11.6	45.1	0.26	7.2	7.5-8
4	22.6	34.8	0.35	13	8	14.3	47.7	0.27	8.4	8
6	22.8	38.1	0.35	14	8	16.3	48.9	0.26	9.9	8
8	23.7	39.6	0.35	14	7.5	18.1	48.7	0.27	11	7.5
10	23.2	41.2	0.34	14	7.5-8	18.8	44.3	0.26	12	7.5-8
12	23.5	43.0	0.36	13	8	20.1	44.0	0.28	12	8
16	23.4	45.8	0.35	17	8	20.4	42.2	0.27	15	8
20	25.1	47.0	0.36	20	7.5	22.4	43.1	0.28	20	7.5
24	27.7	50.4	0.34	22	7.5-8	24.5	44.2	0.26	20	7.5
36	33.6	65.0	0.31	26	7.5-8	31.6	52.0	0.25	26	7.5-8
48	37.0	67.2	0.31	27	7.5	33.7	44.1	0.24	24	7.5
	JAR 3 - ARGON					JAR 4 - ARGON				
time [h]	As [µg/L]	Mn [µg/L]	Fe [mg/L]	As(III) [µg/L]	pH[a]	As [µg/L]	Mn [µg/L]	Fe [mg/L]	As(III) [µg/L]	pH[a]
0	2.64	6.95	0.16	0.45	8.72	2.93	4.29	0.12	0.42	8.58
0.5	8.25	39.6	0.29	5.3	7.5-8	7.89	41.5	0.24	5.2	7.5-8
1	10.1	40.7	0.31	6.8	7.5	10.7	42.1	0.25	6.1	7.5
2	12.8	51.5	0.31	8.5	7.5-8	13.0	52.4	0.25	8.4	7.5-8
4	17.5	62.6	0.33	11	8	18.1	55.5	0.25	11	8
6	20.8	72.3	0.33	14	7.5	21.9	58.0	0.24	14	7.5
8	24.8	80.2	0.34	17	8	26.9	59.3	0.25	18	8
10	27.7	88.4	0.34	20	7.5-8	29.3	59.4	0.24	20	7.5-8
12	32.2	94.5	0.36	21	8	35.8	59.1	0.29	22	8
16	37.8	105	0.35	26	8	40.4	55.4	0.24	26	8
20	44.4	112	0.35	32	7.5	47.5	50.1	0.25	29	7.5
24	49.3	120	0.35	35	7.5	52.4	50.2	0.25	30	7.5
36	69.4	147	0.39	48	7.5-8	73.6	59.8	0.27	43	8
48	84.6	160	0.40	63	7.5	90.6	62.9	0.31	56	7.5

Table D.5 (cont.): Results from Incubation of Haiwee Reservoir Sediment

	JAR 5 - FORMALDEHYDE					JAR 6 - ANTIBIOTIC				
time [h]	As [µg/L]	Mn [µg/L]	Fe [mg/L]	As(III) [µg/L]	pH[a]	As [µg/L]	Mn [µg/L]	Fe [mg/L]	As(III) [µg/L]	pH[a]
0	2.71	4.66	0.13	0.40	8.92	3.05	4.54	0.11	0.40	8.68
0.5	23.6	44.0	0.14	11	6.5-8	12.7	123	0.33	9.1	6.5-8
1	27.5	44.9	0.15	13	7.5	14.6	134	0.30	10	7.5
2	33.0	59.4	0.16	17	7.5-8	16.3	141	0.26	11	7.5-8
4	42.8	77.8	0.17	24	8	18.3	135	0.21	12	8
6	47.8	98.3	0.18	24	7.5	21.8	144	0.22	13	7.5
8	56.7	119	0.22	33	7.5	24.3	147	0.24	16	7.5
10	60.7	138	0.23	37	7.5-8	26.1	154	0.22	17	7.5-8
12	64.7	151	0.22	37	8	29.4	160	0.23	17	8
16	69.9	192	0.27	45	8	33.3	171	0.23	19	8
20	81.9	225	0.36	50	6.8	38.5	175	0.24	22	7.5
24	90.0	267	0.40	53	7	41.0	190	0.24	22	7.5
36	101	345	0.71	58	6.5-7	56.5	254	0.41	41	7
48	114	477	0.48	67	6-6.5	71.1	271	0.62	49	7.5-8

[a] pH at time 0 h measured by electrode in initial solution before adding to sediment in jar. All subsequent pH values are estimated from pH paper.

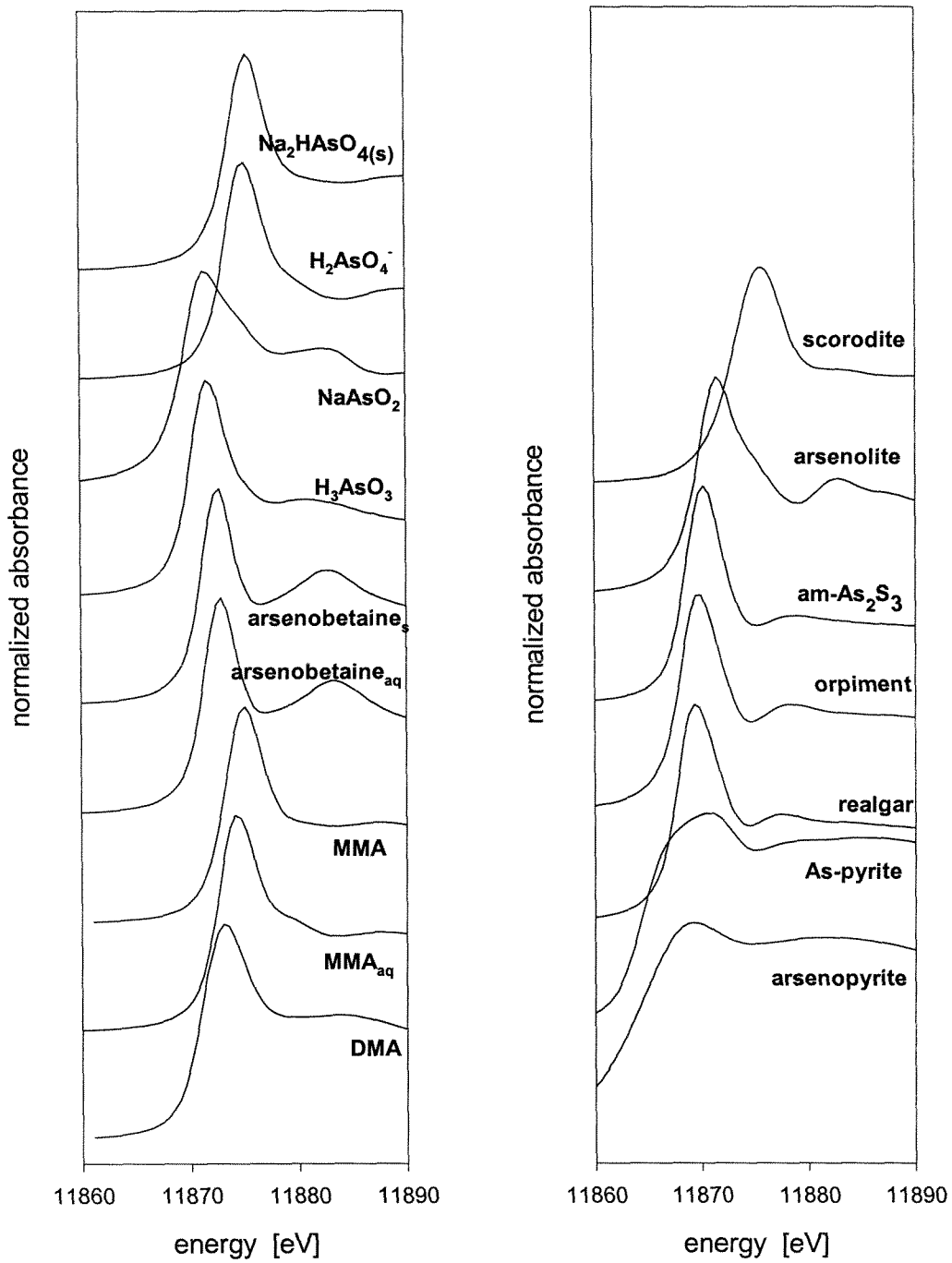

Figure D.1: X-ray absorption spectra of reference compounds. Subscripts: s = solid, aq = 10 mM solution. MMA = disodium monomethylarsonate. DMA = sodium dimethylarsenate. As-pyrite = arsenic substituted pyrite. Each spectrum is normalized to the maximum absorbance.

Appendix E

AN IC-ICPMS METHOD FOR DIRECT DETERMINATION OF As(V), As(III) and MMA

A method was developed to separate inorganic As(V) and As(III) and the organic arsenic species monomethylarsonate (MMA) and dimethylarsinate (DMA). The method involves separation of the species using ion chromatography (IC). The insensitivity of conductivity detection in IC was overcome by directing the eluent of the IC to an inductively coupled plasma mass spectrometer (ICPMS). This coupled method allows direct determination of As(V), As(III) and MMA. The IC method was designed to ensure that chloride was separated from the arsenic species since there is a known ICMPS interference for arsenic at mass-to-charge ratio of 75 caused by the formation of argon-chloride dimers in the argon plasma. IC-ICPMS methods for arsenic speciation have been reported in the literature (e.g., Sheppard et al. 1992). However, those methods are specific to the particular anion exchange resin and instrumentation used. Therefore, we needed to develop a new method for our system.

The IC system was a Dionex DX500 with an IonPac AG11, 4 mm guard column and IonPac AS11, 4 mm analytical column. Recovery of DMA was poor; it appeared

that DMA was retained on the anion exchange resin. The ICPMS was the Hewlett Packard 4500.

The flow rate of the IC eluent was pre-determined by the flow rate with which the ICPMS is compatible, 0.40 mL/min. If higher IC flow rates were used, the IC effluent would have to be split and only a fraction, 0.40 mL/min, diverted to the ICPMS, the remainder going to waste. This would cause unnecessary dilution of the sample.

The concentration of the IC eluent was optimized to achieve the best possible resolution of the peaks of interest in a reasonable time frame (Fig. E.1). A concentration gradient was used, such that for 1.5 min the eluent was 5.0 mM NaOH, then it was steadily increased to 40 mM NaOH over the next 1.0 minute, after which it remained at 40 mM NaOH for 15 minutes. The eluent concentration was then decreased to 5.0 mM and the system allowed to re-equilibrate with the lower concentration for 15 minutes before injection of the next sample. Thus, the entire run spanned 32.5 minutes. The IC eluent line was disconnected at the outlet of the anion suppressor unit and connected directly to the ICPMS. Nitric acid (25% v/v) was introduced via fine bore tubing to ensure that the final concentration entering the ICPMS nebulizer was 1% nitric acid.

The ICPMS was set to record time resolved data at mass-to-charge ratio 75. Peak areas of standard solutions of known concentrations were integrated to allow calibration and subsequent quantitative analysis of unknown samples (Fig. E.2).

Reference

Sheppard, B. S., J. A. Caruso, D. T. Heitkemper and K. A. Wolnik, **1992**, Arsenic Speciation by Ion Chromatography with Inductively Coupled Plasma Mass Spectrometric Detection, *Analyst*, 117, 971-975

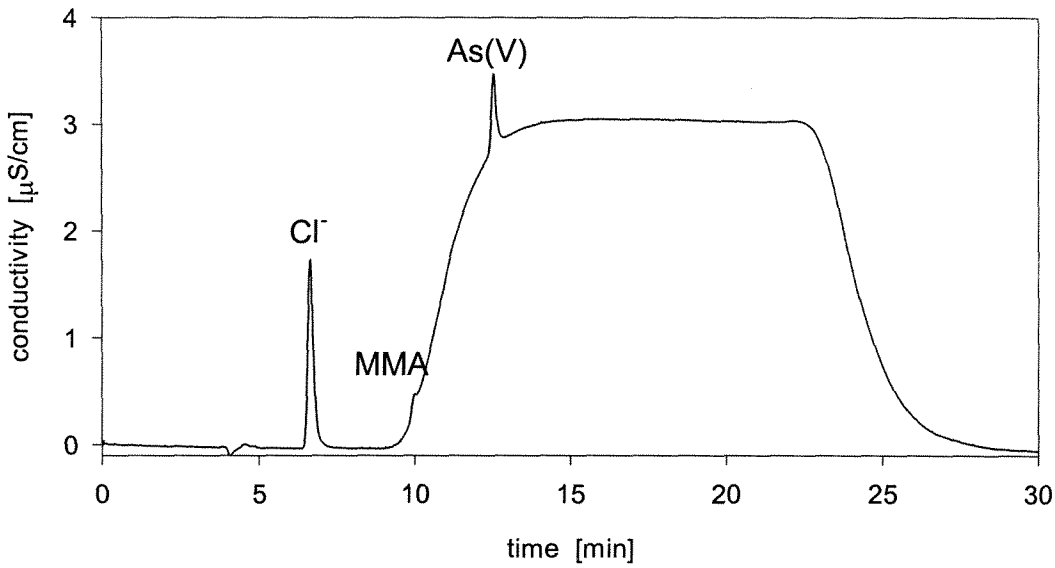

Figure E.1: Ion chromatograph of chloride, MMA and As(V) each at 1.0 mg/L. This is the chromatograph recorded by the conductivity detector of the IC, before the IC was coupled to the ICMPS. Note the very small MMA peak. Although the background introduced by the increasing concentration of NaOH seems high, the maximum background conductivity introduced by this is 3 µS/cm, which is low for conductivity detection. 1.0 mg/L is near the detection limit of the IC for As(V) and MMA.

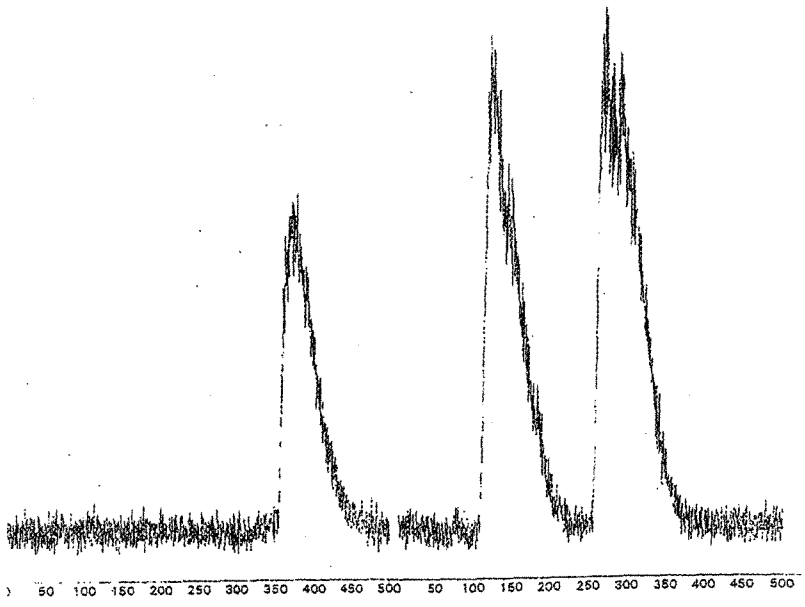

Figure E.2: IC-ICPMS chromatogram of a 5 μg/L mixture of As(III), MMA and As(V).

Appendix F

DISSOLUTION OF AMORPHOUS As_2S_3

F.1: Preparation of am-As_2S_3

A modification of Eary's method (1992) was used to prepare an am-As_2S_3. Sodium arsenite solution (0.15 M, 500 mL) was acidified to pH 4 with concentrated hydrochloric acid and deoxygenated with nitrogen for 20 minutes. Sodium sulfide (23 g) was added and hydrochloric acid added until the pH returned to 4. A bright yellow-orange solid precipitated as the pH was lowered. The solids were allowed to settle, the overlying solution removed and the solids washed with deoxygenated water. This slurry was transferred to 80 mL centrifuge tubes. Following centrifugation the supernatant was discarded, more deoxygenated water added and the washing procedure repeated twice (to remove NaCl). The wet solids were transferred to a 250 mL volumetric flask, and the volume was made up with deoxygenated water. Aliquots of this suspension were used in the initial batch dissolution experiments. Dissolution of the suspension in NaOH and analysis of total sulfur as sulfate by ion chromatography (IC) and total arsenic by inductively coupled plasma mass spectrometry (ICPMS) gave an As to S ratio of 2 to 2.8.

F.2 Dissolution Experiments

The dissolution of am-As_2S_3 can be tracked by measuring total arsenic released. Some information about the dissolution process might be obtained by consideration of the sulfur oxyanions produced. The possible oxidized sulfur species formed en route from sulfide to sulfate include sulfite, thiosulfate, polythionates and elemental sulfur. Oxidation must be quenched at the time of sampling to prevent under-recovery of these species and over-recovery of sulfate. We followed the method of Moses (1987). Formaldehyde solution (1% addition of 37% formaldehyde solution) is added to quench sulfite and thiosulfate oxidation. Potassium cyanide is added to a second aliquot of solution. Polythionates should undergo a cyanolysis reaction and be detected as SCN^-.

The methods developed for determination of sulfur oxyanions using our IC system (Dionex 500 chromatograph, AS-11 analytical column and AG-11 guard column, ED40 conductivity detector) are shown in Table F.1.

Table F.1: IC Methods for Determination of Sulfur Oxyanion Concentrations

species detected	flow rate [mL/min]	NaOH gradient [mM]	retention time[a] [min]
formate	1.0	15 - 90	1.82 ± 0.01
sulfite	1.0	15 - 90	2.89 ± 0.02
sulfate	1.0	15 - 90	3.16 ± 0.02
thiosulfate	1.0	15 - 90	5.25 ± 0.01
phosphate	1.0	30 - 90	2.27 ± 0.02
thiosulfate	1.0	30 - 90	3.23 ± 0.02
thyiocyanate	1.0	30 - 90	9.00 ± 0.05

[a] From 3 injections of each of 4 solutions with anion concentration 0.5 - 5 mg/L.

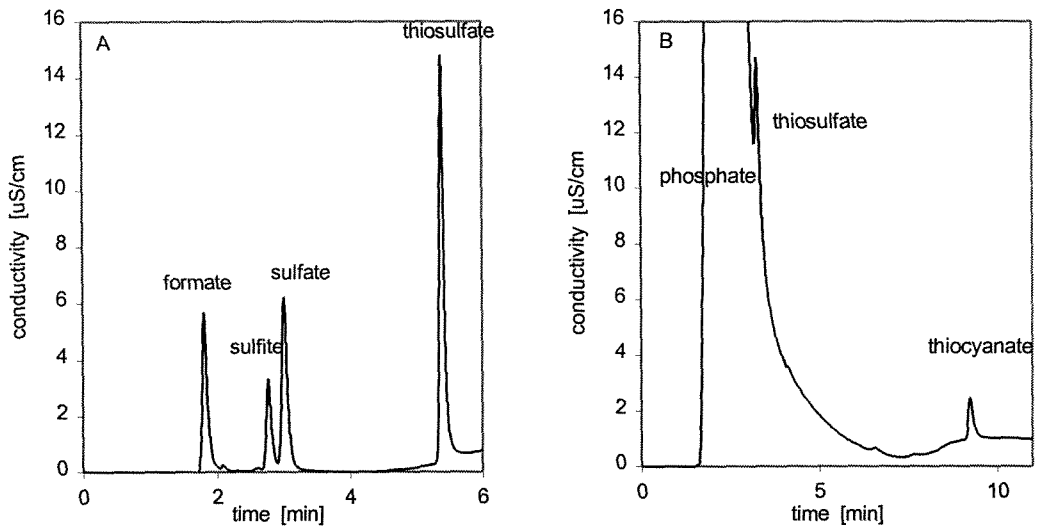

Figure F.1: Ion chromatography methods for determination of sulfur oxyanion species. Both have flow rates of 1.0 mL/min. Eluent is sodium hydroxide with gradients of 15 to 90 mM (A) and 30 to 90 mM (B). All sulfur species in A are at 1 mg/L in 1% formaldehyde solution. In B, sulfur species are at 2 mg/L in a phosphate buffer.

Arsenic was analyzed by ICPMS. Inorganic arsenic speciation was determined. An aliquot of the sample was acidified to pH 4 and passed through columns packed with an anion exchange resin which retains As(V). The effluent was collected and analyzed to determine the concentration of As(III).

Two batch dissolution studies were conducted (Fig. F.2). The first was conducted in a vessel that was open to the atmosphere but had nitrogen bubbling through it at all times. This was to determine the solubility of the am-As_2S_3 in the absence of oxygen. The second experiment was bubbled with air throughout.

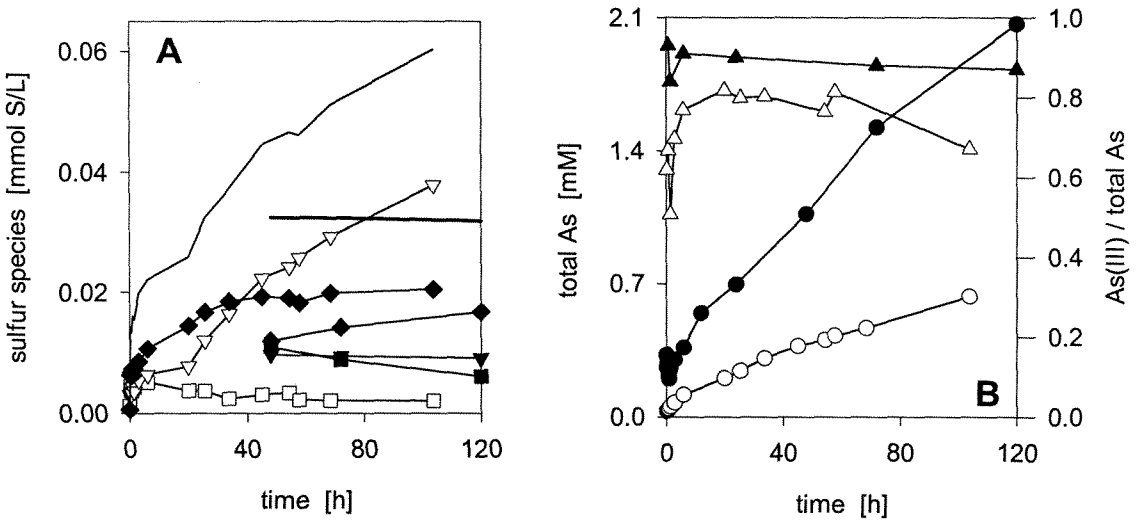

Figure F.2: Dissolution of am-As_2S_3 in oxygenated (open symbols) and deoxygenated (closed symbols) systems. A: concentrations of sulfate (▽, ▼), sulfite (□, ■), thiosulfate (◇, ◆). Lines indicate total sulfur as a sum of these three species in the oxygenated (light line) and deoxygenated (heavy line) systems. B: total arsenic (○, ●) and fraction of total arsenic which is As(III) (△, ▲, scale indicated on right hand side).

Based on the total arsenic measured, the sum of the sulfur oxyanions measured and the assumption that the arsenic-to-sulfur ratio in the solid is 2:3, these initial studies suggest that only a few percent of the sulfur released by dissolution is measured as sulfite, thiosulfate or sulfate. Polythionates were not detected; we suspected that the thiosulfate was cyanolyzed, because the thiosulfate concentration after the cyanolysis reaction was lower than before it. If polythionates had formed and been cyanolyzed there would have been an increase in the thiosulfate concentration following cyanolysis.

Some modification of this quenching step will be necessary. The discrepancy between sulfur measured and sulfur anticipated based on arsenic measured and an assumed molecular formula of As_2S_3 could be due to hydrogen sulfide evolution, formation of elemental sulfur or the presence of dissolved As_2S_3.

The same amount of solid suspension was used in each experiment. The anoxic system had total volume of 2050 mL while the oxic system had 3050 mL. Some oxidized species were detected in the nitrogen-bubbled system. This system was not isolated from the atmosphere, and contact at the surface may be responsible for the presence of the oxidized species. Some oxidation of arsenite to arsenate was also seen toward the end of the reaction, which supports the notion that the system was not sufficiently oxygen-free to study truly non-oxidative dissolution. In the oxic system the percent of total arsenic as arsenite was significantly reduced after just three hours. Higher concentrations of sulfate and thiosulfate were measured in the well-oxygenated system. Lower sulfite concentrations were also measured in the well-oxygenated system. Both systems contained sufficient solid to detect the sulfur species generated.

These preliminary batch dissolution studies illustrate the potential for determining dissolution rates in flow-through systems. Other arsenic-sulfide minerals such as realgar (AsS) and arsenopyrite (FeAsS) may be studied. The effects of the concentration of oxygen or alternative oxidants, such as iron and manganese, could be investigated.

References

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