Chapter 1

Introduction and Motivation

1.1 Arsenic as a world-wide health concern

One of the most challenging environmental problems today is arsenic (As)-contaminated drinking water, which currently affects millions of people world-wide. The greatest exposure to As occurs through ingestion, which can lead to acute or chronic arsenic poisoning. Chronic As exposure can result in skin lesions, melanosis (skin discoloration), keratosis, cancer, and possible reproductive effects (Bhattacharyya et al. 2003; Ng et al. 2003). An estimated 41-57 million people are potentially exposed to elevated levels of arsenic, from 10 to 10,000 µg/L, especially in the Bengal Delta (Bangladesh and West Bengal, India), Taiwan, China, and parts of South America and Southeast Asia (Nordstrom 2002; Smedley and Kinniburgh 2002). The current drinking water standard in the United States is 10 µg/L, decreased from 50 µg/L in 2002 by the US Environmental Protection Agency (EPA). However, there is a greater challenge to find acceptable treatment options in less developed regions where the affected population is primarily rural and large scale treatment is prohibitively expensive.

Although there are some anthropogenic sources of arsenic to the environment through mining, pesticide application, wood preservation, and combustion of some coal deposits, elevated concentrations of As are often derived from natural sources. Arsenic occurs naturally in alluvial and deltaic sediments, as well as volcanic rocks and thermal springs (Welch et al. 2000; Nordstrom 2002; Smedley and Kinniburgh 2002; Ng et al. 2003), and the weathering of such deposits can lead to mobilization of As. The situation in Bangladesh is an example of As occurring naturally in alluvial sediments that is being mobilized into the groundwater. A significant rural population relies upon this groundwater for its drinking water supply and consequently exhibits extreme health effects of chronic arsenic exposure (Bhattacharyya et al. 2003).

The causes of As mobilization are complex, and not well understood. In order to identify and treat the problem of elevated As concentrations in groundwater, it is necessary to understand the specific biogeochemical controls of As mobility in subsurface environments. By understanding the processes that govern mobilization, it may be possible to predict future problems of As contamination and design effective treatment methods. A field site in California (CA) has been selected to study the processes that influence arsenic release to groundwater.

1.2 Arsenic in the Los Angeles Aqueduct System

The City of Los Angeles imports water from several different sources, including the Sierra Nevada Mountains in Northern California. Approximately 70% of drinking water in the City of Los Angeles is delivered via the Los Angeles Aqueduct (LAA). The remaining 30% comes from the Colorado River Aqueduct, the California Aqueduct, and local groundwater wells. The main tributary to the LAA is the Owens River (Fig 1.1). Natural geothermal springs in Hot Creek, California, contribute large As loads to the LAA source waters, resulting in a long-term average As concentration in the LAA of 22 µg/L (yearly averages from 1940-1991). Although the hot springs contribute <5% of the total water flow, they contribute >60% of the total As load to the LAA. The remaining As comes from smaller sources such as alkali lake discharge. The geothermal water has elevated concentrations of strontium (Sr), barium (Ba), zinc (Zn), manganese (Mn), aluminum (Al), and germanium (Ge) in addition to As, and significant amounts of chromium (Cr), copper (Cu), lead (Pb), molybdenum (Mo), tin (Sn), titanium (Ti), and vanadium (V). The As flux from the hot springs is relatively constant throughout the year, but changes in flow from snowmelt and aqueduct operations create seasonal fluctuations of As concentrations in the LAA (Willets et al. 1967; Stolarik and Christie 1999).

Pilot tests of optimizing coagulation treatment to remove As at the LAA filtration plant (LAAFP) in Sylmar, CA, resulted in early turbidity breakthrough and filter backwash solids requiring hazardous solid waste disposal and was, therefore, an unacceptable treatment option. The LA Department of Water and Power (LADWP) developed an interim management plan to remove arsenic from the LAA at Haiwee Reservoir, which went into effect in March, 1996 (Stolarik and Christie 1999). A better site for a treatment facility might be Hot Creek, which is close to the geothermal As source and upstream of dilution by the Owens River. However, construction of a facility in this location is not feasible. As an alternative, an existing treatment plant in the Owens Valley, the Cottonwood Treatment Plant, was modified to inject ferric chloride ($FeCl_3$) as a coagulant directly into the LAA about 27 km upstream of Haiwee reservoir (Figure 1.1). Cationic polymer (diallyldimethyl ammonium chloride, DADMAC) is also added as a flocculent aid to remove glacial silts that can clog filters at the LAAFP. The polymer dose does not affect As removal. The ferric chloride forms an amorphous iron (Fe) oxyhydroxide floc in the aqueduct channel. Dissolved arsenic readily adsorbs and/or co-precipitates with the Fe floc, and is subsequently deposited in the inlet channel to Haiwee reservoir (see Figure 1.1 in Chapter 6 for a map of the study area). The treatment results in an average As concentration of 5.1 µg/L at the South Haiwee Reservoir outlet. Since the treatment removes ~67% of the incoming As in the LAA, occasionally the water downstream of Haiwee Reservoir has >10 µg/L As because of seasonal fluctuations. However, some of the remaining As is removed at the LAAFP. Another result of this treatment is substantial deposition of iron- and arsenic-rich sediments in the Haiwee Reservoir. These sediments are a natural laboratory for an investigation of biogeochemical controls on arsenic mobilization.

1.3 Research Scope and Objectives

The objective of this work is to answer the following questions:

1. What are the mechanisms controlling the partitioning of As and Fe between the sediments and porewaters?
2. What circumstances cause mobilization of As, Fe, and other elements into porewater?
3. What processes determine the fraction of the total As and Fe in the solid phase that is mobilized into the porewater?

These questions have been addressed by investigating the conversion of Fe- and As-bearing mineral phases, porewater chemistry, and the role of microbially-mediated redox transformations of As and Fe phases.

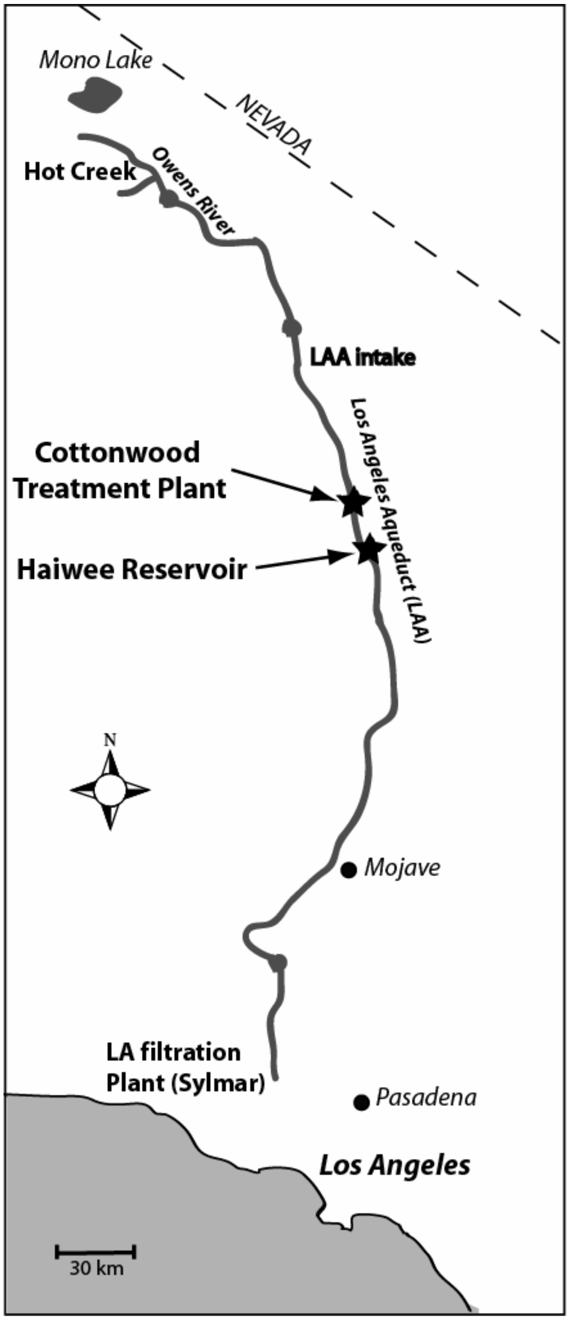

Figure 1.1. Map of the Los Angeles Aqueduct (LAA) system. Ferric chloride injections at Cottonwood Treatment plant result in Fe- and As- enriched sediment deposition at Haiwee Reservoir, the research site for this study.

1.4 Brief Overview of Chapters

A literature review and background information can be found in Chapter 2. A gel probe equilibrium sampler was developed for *in situ* measurement of porewater composition and As adsorption behavior by doping polyacrylamide gels with Fe(III) oxide. Laboratory development, gel properties, and As sorption performance in the presence and absence of competing ions are presented in Chapter 3. Chapter 3 also contains an X-ray absorption spectroscopy (XAS) calibration for quantifying As speciation on the Fe-doped gels. Gel probes were deployed at Haiwee reservoir on several dates. The results from the gel probe deployment and solid phase (core) analyses are discussed in Chapter 4. The field studies highlight how mineral transformation and porewater composition affect the accumulation of dissolved As in the sediment porewater. Microbiological studies of As(V) and Fe(III) reduction using an ambient bacterial population from Haiwee Reservoir sediments and a pure culture strain of bacteria are presented in Chapter 5. Further investigation into how the presence of adsorbed As affect bacterial Fe(III) reduction was performed by imaging the solid phase with light and electron microscopy as well as studying bacterial adhesion to surfaces (Chapter 6). Chapter 7 summarizes the information from the previous chapters and discusses the implications for Haiwee Reservoir sediment stability. Additional field and experimental data can be found in the appendices.