Chapter 1

INTRODUCTION

1.1 Motivation

Arsenic (As) can cause a variety of skin, neurological, and cardiovascular disorders, and it has recently been confirmed as a human carcinogen. It is naturally present in the earth's crust, so weathering reactions or geothermal activity can cause elevated As concentrations in groundwater and surface water. Although a greater fraction of surface waters have detectable levels of As compared to groundwaters, those groundwaters that do contain measurable As tend to have higher concentrations (Frey and Edwards 1997). Due to differences in underlying bedrock composition and weathering conditions, groundwater As concentrations can change dramatically not only over large geologic regions but also at the local level.

Because drinking water is a primary exposure pathway for As, the United States drinking water standard for As has been lowered to 10 μg L^{-1}. Even this new standard presents significantly higher health risks than standards for other regulated contaminants, but economic and analytical considerations constrain further reduction of the standard. High levels of As in groundwater in regions throughout the U.S. (Figure 1.1) will require thousands of water distribution systems that rely on groundwater sources to implement As removal procedures. Most of the affected systems serve less than 10,000 people.

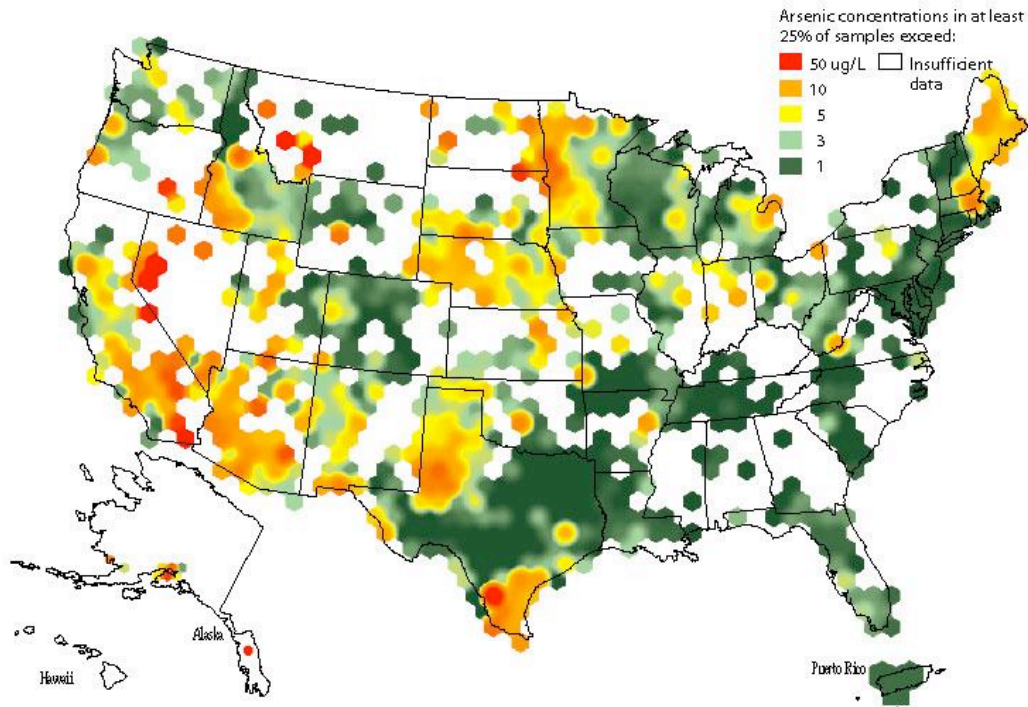These small systems face additional challenges for meeting the standard due to their limited financial bases.

Figure 1.1. Groundwater As concentrations in the United States (Ryker 2001).

Although many As treatment technologies are available, most are less effective for As(III) removal than for As(V) removal, thus necessitating a pre-oxidation step for source waters containing substantial As(III). Several oxidation methods currently used by water treatment facilities, including chlorination, permanganate addition, and ozonation, are effective for transforming As(III) to As(V) (Ghurye and Clifford 2001). However, chlorination and permanganate addition involve handling and storage of

hazardous chemicals, and both chlorination and ozonation generate harmful reaction byproducts such as trihalomethanes and bromate. Moreover, ozonation is not typically used by small systems. Therefore, a low-cost, environmentally benign technology capable of preoxidizing As(III) to As(V) prior to As removal by standard water treatment methods is needed. Titanium dioxide (TiO_2) photocatalysis could potentially serve as a solution to this problem.

TiO_2 photocatalysis has been used for decades to promote redox degradation or transformation of various organic and inorganic compounds. Recent studies have shown rapid oxidation of As(III) to As(V) in the presence of TiO_2, UV light and air. There is a need to characterize this reaction and to assess whether such a system would be appropriate in water treatment applications.

1.2 Research Objectives and Scope

The primary objectives of this research are to understand the parameters affecting the efficiency of TiO_2-photocatalyzed As(III) oxidation and to assess the feasibility of applying this technology to water treatment. To achieve this, laboratory studies involving both TiO_2 slurries and a fixed-bed, flow-through TiO_2 reactor were designed and conducted. Results from these experiments were combined with model analysis and compared to current As pre-oxidation technologies.

Since most experiments involved measuring losses of As(III) and corresponding gains of As(V), the speciation and quantitation of As was central to this research. Multiple analytical techniques were employed, including anion exchange filters, a liquid

chromatograph anion exchange column (LC) coupled to inductively coupled plasma mass spectrometry (ICP-MS), and high resolution ICP-MS. The anion exchange filters were used to distinguish As(III) from total As in batch studies performed with TiO_2 slurries (Chapter 3). This work addressed the extent and kinetics of As(III) and As(V) adsorption to TiO_2 and how that sorption affected the apparent reaction rates. Moreover, experiments using hydroxyl radical quenchers, alternate electron acceptors, and superoxide dismutase were carried out to elucidate the mechanism of As(III) oxidation on TiO_2.

Fixed-bed, flow-through studies were designed to investigate parameters relevant to system performance in a water treatment context, such as residence time, propensity for catalyst poisoning, and the effect of common ions found in groundwater (Chapter 4). LC-ICP-MS was used to separate As(III) from As(V) in this study due to the improved time resolution it allowed. Also in this chapter, a reactive transport model is used to model the steady-state effluent As(III) concentrations during UV irradiation.

In Chapter 5, the discrepancies between the enforceable As standard and the health and analytical standards for As are addressed. The current enforceable standard for As remains much higher than the corresponding health standard due to the cost of treatment and analytical detection ability, but as these two factors decrease the enforceable standard is expected to be lowered as well. High resolution ICP-MS was considered as one of several analytical approaches that have low As detection limits and demonstrate potential for becoming more widespread, resulting in a decrease in the standard analytical limit for As detection.

Chapter 6 synthesizes information from the previous three chapters to assess whether TiO_2-photocatalyzed As(III) oxidation could be plausibly integrated into water distribution systems, focusing on cost efficiency and recommended changes to the reactor. Finally, in Chapter 7 the major results of this research are summarized and areas for future research are identified.