Laboratory and Field Studies Directed toward Accelerating Arsenic Remediation at a Major US Superfund Site in New Jersey

Karen Wovkulich

Submitted in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2011

ABSTRACT

Laboratory and Field Studies Directed toward Accelerating Arsenic Remediation at a Major US Superfund Site in New Jersey

Karen Wovkulich

Arsenic is a prevalent contaminant at a large fraction of US Superfund sites. Therefore, establishing techniques for accelerating As remediation could benefit many contaminated sites. Remediation of As contaminated groundwater by conventional methods, i.e. pump and treat (P&T), can be impeded by slow desorption of As from Fe and Al (hydr)oxides in aquifer solids. Through experimentation at different physical scales (grain, bench, and field scale), the potential for chemical additions to increase As release from sediments and possibly accelerate P&T remediation is examined.

The work described here focuses on As contamination and remediation at the Vineland Chemical Co. Superfund site in southern NJ. The site is extensively contaminated with As resulting from decades of poor chemical storage and disposal practices by the Vineland Chemical Co., which manufactured As-based biocides from 1949-1994. Despite significant intervention, including groundwater remediation by P&T and treatment of solids via soil washing, sufficient site clean up could require many decades with current technologies.

Chemical amendments that either compete with As for sorption sites or dissolve Fe and Al (hydr)oxides can increase As mobility and potentially improve P&T remediation efficiency. Simple extrapolations from bench scale column experiments based on pore volumes suggest that treatment with 10 mM oxalic acid could lower the time necessary for clean up at the Vineland site from 600 years (with current techniques

involving just groundwater) to potentially on the order of 4 years. Small scale (<1 mm^2) X-ray fluorescence maps from columns performed within the synchrotron beamline showed As release during oxalic acid treatment that was consistent with the bulk column materials and suggested that microscale processes can be predictive of the larger system.

Finally, during a 3-month pilot study at the Vineland site, oxalic acid was injected into a section of the aquifer via an injection manifold system that was designed and built for the experiment. Groundwater samples indicate that introduction of oxalic acid led to increased As release at a sampling well and pump and treat recovery well in the study area. Addition of oxalic acid shows promise for accelerating treatment of a highly contaminated site.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

It takes a village to write a thesis; without the contributions of many individuals in my life, this thesis could have never happened. I cannot possibly thank everyone by name in this space so I will extend a big thank you here to all who made this body of work possible. I gratefully acknowledge and thank my scientific advisors, Jim Simpson, Steve Chillrud, Brian Mailloux, and Martin Stute, who provided me with the tools to start this journey and support and guidance along the way. Each has offered their particular expertise and unique perspective, which has been a great benefit to my thesis and to myself as a person and scientist. I cannot thank them enough for their dedication to the project and for all of their assistance. The other members of my dissertation committee, Bob Anderson and Zoltan Szabo, provided helpful insights and a fresh outlook on the work in its final stages. I must also acknowledge the financial support for my work from NIEHS through grants ES010349 and ES0090890. Additionally, the site managers and staff from EPA, USACE, and Sevenson Environmental at the Vineland Chemical Co. Superfund site provided ongoing assistance in obtaining data and samples and supplied invaluable support during the field studies.

I owe many thanks to all of the folks at Lamont and Columbia involved in arsenic research and beyond, especially Karrie Radloff, Alison Keimowitz, Jamie Ross, and Beth O’Shea, who listened to random musings on arsenic, gave feedback on drafts of papers, taught me various techniques, and generally made my time at Lamont all the more pleasant. Extending back further in time I want to acknowledge my undergraduate mentors at Vassar College, Curt Beck, Edie Stout, and Chris Smart, who made me excited about science, encouraged me to go to graduate school, and cheered me on to the

finish. Kristin Rule Gleitsman also played a big role in shaping my interests in science, from healthy competition in general chemistry to choreographing a dance piece based on organic chemistry.

Finally, I have to thank my family for all of their support in this process. My parents, Sally and Pete Wovkulich, have always fostered my interests and given encouraging words when the going got tough. My in-laws, Terrie and Peter Walker, also remained some of my biggest cheerleaders and have helped me see the light at the end of the tunnel. And, of course, none of this could have happened without my husband and companion in life, Tyler Walker, who has always jumped in with a hug, words of inspiration and motivation, or tough love just when I need it.

DEDICATION

For Tyler,

who makes the impossible,

possible

CHAPTER 1
Arsenic at the Vineland Chemical Company Superfund Site: Arsenic Contamination and Remediation

1.1 Overview: As toxicity, occurrence, and geochemistry

Arsenic is a toxic metalloid with an average crustal abundance of 1-3 mg/kg, though widely varying concentrations are possible depending on the mineral and sediment types present (Cullen and Reimer, 1989; Oremland and Stolz, 2003; Vaughan, 2006). Arsenic occurs naturally in the environment as a component of soils, sediments, and rocks or can result from anthropogenic inputs such as swine and poultry farming, As-based pesticides, mining operations, CCA treated wood, etc (Leist, et al., 2000; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Arsenic can present a problem for the human population when it leaches into drinking water supplies. The current US drinking water standard and the World Health Organization (WHO) guideline for As is 10 μg/L. However, millions of people drink waters in excess of 10 μg/L; the highest density of individuals drinking water with elevated As live in the Bengal Basin, with an estimated 40+ million people affected (BGS and DPHE, 2001; Smedley and Kinniburgh, 2002; Smith, et al., 2000). Groundwater with elevated As concentrations has also been identified in Vietnam, China, Hungary, Argentina, Chile, Mexico and parts of the USA (Berg, et al., 2001; Del Razo, et al., 1990; Mandal and Suzuki, 2002; Sancha and Castro, 2001; Smedley and Kinniburgh, 2002; Sun, et al., 2001; Varsányi, et al., 1991; Welch, et al., 2000).

Both acute and chronic exposure to As can lead to ill effects. Acute exposure to a high dose can result in death (preceded by abdominal cramping and vomiting) (ATSDR, 2007; Vaughan, 2006). In fact, As has been implicated in poisoning deaths since imperial Rome (Vaughan, 2006). Chronic mid to low dose exposure can cause skin lesions and increased risk of cancers of the skin, liver, bladder, and lungs as well as cardiovascular and respiratory effects (Argos, et al., 2010; ATSDR, 2007; Balakumar and Kaur, 2009; Parvez, et al., 2010). Epidemiological studies in populations with poor diet are also beginning to suggest potential for impacts on neurological development and increased incidence of certain eye disorders (Chen, et al., 2009; Lin, et al., 2008). The most common route of chronic exposure is through contaminated groundwater used as drinking water; in most of these cases the As is naturally occurring but has been mobilized into the water supply.

Naturally occurring As is found distributed in the environment in waters, soils, sediments, rocks and minerals; As concentrations in these environmental components can cover a huge range. Arsenic concentrations in soils, sediments, and rocks vary depending on minerals present. Arsenic minerals (orpiment, realgar, arsenopyrite) will necessarily contain high concentrations of As, however, As can also substitute for other elements such as S in S-mineral structures; this substitution can result in weight percent values of As in minerals such as galena, pyrite, and marcasite (Smedley and Kinniburgh, 2002). Arsenic has also been known to substitute for P (notably in apatite), Si^{+4}, Al^{+3}, Fe^{+3}, etc. Aside from As presence within the mineral structure, As concentrations in solids may be elevated due to adsorbed As. Arsenic is commonly adsorbed to Fe, Al, and Mn oxides as well as clays and calcite; if these oxides or minerals are present in aquifer materials, water As concentrations may be elevated as a result of episodic, pulsed, or near continuous desorption (De Vitre, et al., 1991; EPA, 2002; Mandal and Suzuki, 2002; Sullivan and Aller, 1996).

Concentrations of As in natural waters can be widely variable as well and can range from less than 0.5 µg/L to greater than 5,000 µg/L (Smedley and Kinniburgh, 2002). Additionally, high As concentrations in groundwater are not necessarily found solely in aquifers with high As aquifer materials. Aquifer solids with 1-20 mg/kg still contain a sufficient mass of As to cause elevated groundwater concentrations under the right geochemical conditions. Some of the factors that impact As mobilization from solids into the water include Eh, pH, presence of certain anions and ligands, and microbial activity (Barringer, et al., 2010; EPA, 2002; Kuhlmeier, 1996; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Though As can exist as As (-III), As (0), As (III), and As (V), the latter two are most common in the environment; in natural waters, typical forms are ions of the inorganic As compounds, arsenite ($H_3As(III)O_3$) and arsenate ($H_3As(V)O_4$). Organic forms of As are also possible though they tend to indicate the presence of biological activity or industrial inputs (Oremland and Stolz, 2003).

Oxidation-reduction potential can greatly impact the mobility of As in the environment; reducing conditions can lead to As mobilization in multiple ways. Conversion of As (V) to As (III) can result in As mobilization since As (III) is often, but not always, more mobile in the environment (Dixit and Hering, 2003). Additionally, reduction of Fe (III) to Fe (II) and subsequent dissolution of Fe species can lead to release of adsorbed As. However, several studies have indicated a decoupling between Fe and As release under reducing conditions (Horneman, et al., 2004; Keimowitz, et al., 2005a; Radloff, et al., 2007; van Geen, et al., 2004). High pH conditions can also cause As release as electrostatic repulsion between As oxyanions and surface adsorption sites increase with increasing pH (Dixit and Hering, 2003). Several anions or ligands can impact As mobilization. Phosphate, for which arsenate is an analog, bicarbonate, silicate and organic matter can all compete with As for sorption sites (Bauer and Blodau, 2006; Dixit and Hering, 2003; Smedley and Kinniburgh, 2002). Furthermore, As transport is generally retarded by adsorption to Fe, Al, and Mn oxides and so the presence of compounds that dissolve these species, such as organic acids, may also lead to As mobilization (Zhang, et al., 2005).

Finally, microbial activity can impact As mobility by altering redox conditions of a system, by acting on As compounds individually, or by inducing As release during mineral weathering for nutrient acquisition. Microbial activity in an aquifer can help to induce reducing conditions and potentially lead to As release (Radloff, et al., 2007). In addition, various microbes have been found to take part in oxidation, reduction, or methylation of As compounds directly (Barringer, et al., 2010; Oremland and Stolz, 2003; 2005). Arsenic methylation is often used as a detoxification process to remove As from cells more easily; the mechanism depends on the type of cell involved (Oremland and Stolz, 2003). Arsenic reducing microbes, which can gain energy from coupling As reduction with oxidation of organic matter, have been isolated from a number of environments (freshwater, estuaries, hot springs, aquifers, etc.) (Herbel, et al., 2002; Oremland, et al., 2002). Arsenic oxidizing prokaryotes have also been identified; these microbes can couple As oxidation with reduction of oxygen or nitrate (Ehrlich, 2002; Oremland and Stolz, 2003). Finally, studies have shown mobilization of As from As containing minerals, such as apatite, as microbes weather the minerals to gain access to nutrients (Mailloux, et al., 2009).

1.2 Industrial uses and anthropogenic induced contamination

Through the years, As and As-based compounds have found many uses in industry. Organic arsenic compounds have been used as digestive aids and anti-parasitic compounds in swine and poultry farming (Arai, et al., 2003). Organic and inorganic As compounds have been used as insecticides and pesticides (Walsh and Keeney, 1975); for instance, lead arsenate was applied to apple orchards to combat apple maggots and other pests and calcium arsenate found use in eradicating boll weevils in cotton fields (Peryea, 1998). As of 2005, organic arsenic compounds were still being used as pesticides in cotton fields, however, inorganic arsenic compounds are no longer used for agricultural pest control (ATSDR, 2007). Various pigments in wallpapers, paints, and ceramics have made use of As compounds (Vaughan, 2006). Gallium arsenide has been used in the semi-conductor industry and copper chromated arsenic was used for many years as a wood preservative but was phased out for residential uses in 2003 (ATSDR, 2007).

Though As has proven useful in many applications, unacceptable levels of As have found their way onto certain sites and into water bodies as a result. Sometimes the route to As accumulation is obvious; for instance, purposeful application of As compounds to orchards for pest control has led to As contaminated soils at some former orchard sites. However, other times, the reason for As accumulation is less obvious or potentially due to neglect or improper usage and storage of As chemicals. Additionally, anthropogenic activities, such as mining, have resulted in mobilization of As from previously stable minerals. Arsenic is often associated with ores of valuable metals such as Cu, Ag, Pb, and Au and can be released when these metals are mined (Nriagu, 2002;

Smedley and Kinniburgh, 2002). Additionally, smelting activities of ore materials can lead to atmospheric release and fallout of arsenic near the smelter (Pershagen, 1985).

Due to its prevalence as an environmental contaminant As is the second most common contaminant of concern at EPA National Priority List (NPL) sites (after Pb) (EPA, 2002). It is found at over 500 of the NPL sites that have filed a Record of Decision (EPA, 2007; 2010a), ~47% of all such sites as of 1999 (EPA, 2002). Additional As contaminated sites may have been discovered but did not have a Record of Decision at the time. According to an As report released by EPA in 2002, the most commonly contaminated media were groundwater, soils, and sediments; however, sites also reported contamination in surface waters, sludge, leachate, air, etc. (EPA, 2002). The majority, nearly 40%, of As contaminated sites were landfill or other disposal sites with the next largest category, chemical and allied products, making up less than 8% of the total. Other categories of contaminated sites included lumber, groundwater plume, metal fabrication, and batteries and scrap metal (EPA, 2002). Solidification and stabilization techniques were most frequently used to treat As contaminated soils. Pump and treat coupled with precipitation/coprecipitation was most commonly used for treating contaminated water (EPA, 2002).

1.3 Arsenic contamination at the Vineland Chemical Company Superfund site

The work described in this dissertation focuses on As contamination at the Vineland Chemical Company Superfund site. The Vineland Chemical Company site in Southern New Jersey was listed on the National Priority List as a Superfund site in 1984. The company produced As-based biocides from 1949-1994 (EPA, 1989a; 2006). During that time, hundreds of tons of As were released into the environment due to poor chemical storage and disposal practices. This resulted in contamination of the groundwater and sediments under the site as well as offsite transport via groundwater discharge to a small stream, the Blackwater Branch, at the north end of the site. The timeline of investigatory and remedial activities is outlined in the Appendix. Since 2001, the site has been undergoing extensive remediation to contain the contaminated groundwater plume as well as treat the contaminated groundwater and vadose zone and floodplain sediments. Prior to the start of remediation, As concentrations in the groundwater could exceed 10,000 μg/L, three orders of magnitude greater than the current drinking water standard for As (10 μg/L); contaminated sediments in the unsaturated zone could have As concentrations in excess of 500 mg/kg, while uncontaminated background levels are likely to be <5 mg/kg. Remediation is ongoing and expected to cost upwards of $160 million (Funderburk, 2009).

The Vineland Chemical site is situated on 54-acres (0.22 km^2) in Southern New Jersey. The site is bordered to the north by a small stream, Blackwater Branch, which feeds into the Maurice River and further downstream, Union Lake. The Maurice River continues below Union Lake into the Delaware Bay. Impacts from the As discharged from Vineland Chemical have been noted in the Blackwater Branch, Maurice River, and Union Lake (EPA, 2006). Vineland Chemical is located within an industrial zone in the city of Vineland but is bordered by residential zones. At the time the Record of Decision was published (1989), 12 residences were in the immediate vicinity of the plant; other residences were nearby (EPA, 1989a). In 1977, one well owner near the site was cautioned not to use his well water for drinking or irrigation due to high As concentrations (~2 mg/L). Approximately 57,000 people in the area depend on groundwater for drinking water purposes (either private or municipal wells) (EPA, 2001b). Portions of Maurice River and Union Lake were and are used for recreational purposes including swimming and fishing (EPA, 1989a; 2001b; USACE, 1996a).

Vineland Chemical produced organoarsenical compounds to be used as pesticides, typically for cotton, sugar cane, soybeans and other crops. Records indicate that Vineland Chemical also produced cadmium based herbicides and used other inorganics on site such as lead and mercury (USACE, 1996b). However, the main contaminant remaining following the company's closure was As. The company predominantly manufactured monosodium acid methanearsonate (MSMA) and disodium acid methanearsonate (DSMA), which are sodium salts of monomethyl arsonic acid (MMA) (EPA, 1989b; OSR, draft). They also produced smaller quantities of amine methane arsonate, amine methane arsonate +2,4-D, cacodylic acid (dimethyl arsonic acid or DMA), and calcium acid methanearsonate. Starting materials for formation of MSMA and DSMA include arsenic trioxide, sodium hydroxide, methyl chloride, and sulfuric acid (OSR, draft). During the manufacturing process, a byproduct waste salt was formed which contained sodium chloride, sodium sulfate, and up to 1-2% arsenic. Each week ~20 metric tons of this waste salt were generated or over 1000 metric tons per year (EPA, 1989a). These waste salts were stored in uncontrolled piles on the site and in abandoned chicken coops on site. A combination of the high permeability of the site's quartzose sand sediments with limited fine-grained materials or organic matter and the high solubility of the waste salts allowed for percolation of As into the subsurface. In addition, As contaminated process water, storm run off, and contaminated cooling water were discharged into unlined lagoons on site; both seepage into the ground under the lagoons as well as overflow resulted in further As contamination on site. Smoke stacks on site also emitted As associated dusts or mists during operation, which could have led to deposition of As dusts on land and surface water bodies (OSR, draft). At the time the site's Record of Decision was published (1989), Vineland Chemical was listed in the top 10 hazardous waste sites in NJ and was ranked #42 on the National Priority List (NPL); these numbers guide the EPA in investigation and remediation of contaminated sites (EPA, 1989a).

1.4 Vineland Superfund site geology

The Atlantic Coastal Plain area of New Jersey is formed by a seaward dipping wedge of unconsolidated sediments and contains clay, silt, sand, and gravel (Zapecza, 1989). These sediments accumulated between the Cretaceous to Quaternary periods and include continental, coastal, and marine-type deposits (Zapecza, 1989). Portions of the coastal plain area near Vineland, NJ contain surficial deposits of Holocene age alluvium and colluvium or the Miocene age Bridgeton Formation, which is an arkosic sand with some fine gravel material (Cauller and Carleton, 2006; Zapecza, 1989). However, these are likely limited under the Vineland Chemical site. The Vineland Chemical Company site itself is underlain by the unconsolidated sands of the Cohansey Formation, which is a marginal marine deposit from the middle Miocene (Szabo, et al., 1997; USACE, 1996a). The Cohansey Formation is largely composed of medium to coarse grained quartzose sands with some gravel and silt as well as thin interbedded clay layers (Cauller and Carleton, 2006; Szabo, et al., 1997; Zapecza, 1989). The Cohansey Sands contain very limited amounts of weatherable silicate minerals, minimal potassium and sodium feldspars, and include secondary kaolinite, gibbsite, and silica (Szabo, et al., 1997). Locally perched groundwater tables and semiconfined aquifer conditions are possible within the Cohansey Formation. Beneath the Cohansey Formation lies the Kirkwood Formation, a middle Miocene marine unit with micaceous deposits and calcareous shell materials. The Kirkwood Formation consists of fine to medium grained quartz sand as well as silty sands (Cauller and Carleton, 2006; Szabo, et al., 1997; Zapecza, 1989). The basal potion of the Kirkwood Formation contains dark grey, massive clays of the Alloway Clay Member; this marine clay member is thick and regionally extensive (Szabo, et al., 1997; Szabo, et al., 1996). There is direct hydraulic communication between the upper sands of the Kirkwood Formation with the Cohansey Formation; these form the Kirkwood-Cohansey aquifer system (Skelley and Loy, 2003). In the study area, the Kirkwood-Cohansey aquifer system is predominantly a water table aquifer with the Alloway Clay Member as the basal boundary of the aquifer (Szabo, et al., 1996; Zapecza, 1989). Even within an aquifer that seems fairly uniform hydrogeologically, like the Kirkwood-Cohansey, redox conditions and other geochemical parameters can be quite variable. This chemical heterogeneity can influence groundwater characteristics and contaminant transport. For instance, there are possibilities for wide variations in the dissolved oxygen, Fe, and organic carbon content in Atlantic Coastal Plain aquifers (Ryan and Gschwend, 1990). Ryan and Gschwend discovered significant differences in the presence of colloidal materials in groundwater, with substantially greater incidence of colloids under anoxic conditions in the Atlantic Coastal Plain aquifers studied (Ryan and Gschwend, 1990). The potential for heterogeneity and variability both in physical and chemical properties is important to acknowledge and highlights the need for careful characterization of field sites.

The relevant sediments under the Vineland Chemical Company site can also be described by informal stratigraphic units (Figure 1.1) – Upper Sand, Banded Zone, Middle Sand. The Upper Sand, which begins at the ground elevation (60-70 ft or 18.3-21.3 m above mean sea level), is well sorted and contains light brown sands that range from ~40 ft (~12 m) thick in the northwest of the site to ~80 ft (~24 m) thick in the southeast (USACE, 1996a). An unconfined aquifer exists in the highly permeable Upper Sand with the water table approximately 15 ft (4.6 m) below ground surface; it is this aquifer, part of the Kirkwood-Cohansey aquifer system, whose groundwater was contaminated by the Vineland Chemical Co. Flow in this aquifer generally follows a westward direction, becoming northwestward toward the north of the site near Blackwater Branch. Hydraulic conductivity values typically range from 292 ft/d ($1.0\text{x}10^{-3}$ m/s) to 537 ft/d ($1.9\text{x}10^{-3}$ m) and specific yield ranges from 0.018-0.068 (Skelley and Loy, 2003). Beneath the Upper Sand lies the Banded Zone, which acts as a semi-confining layer between the Upper Sand and the Middle Sand. The Banded Zone is composed of interbedded sand, silt, and clay and is between 13 and 26 ft (4 and 7.9 m) thick (thickest at the NW part of the site) (USACE, 1996a; 2007). Its exact structure is unknown. Hydraulic head gradients indicate that groundwater flow can be upward through the Banded Zone from the sand units below. The Middle Sand, a well-sorted sand layer, lies below the banded zone and monitoring wells screened in this stratigraphic unit suggest it is largely uncontaminated by As.

1.5 Description of on site plume and distribution of As

The final design report for the wastewater treatment facility describes the groundwater As contamination under the site as occurring in two plumes (USACE, 1996a). One plume was migrating in a west-northwest direction toward Blackwater Branch from the northern part of the site, the other was moving in a westerly direction from the southern part of the site. The first plume was described as smaller and contained high levels of organic As (MMA with lesser quantities of DMA) while the other plume was predominantly composed of inorganic As. Figure 1.2 shows isolines for As concentrations in both the shallow and intermediate aquifer prior to the start of treatment; both shallow and intermediate wells (both located within the Upper Sand) on site show As contamination. The Record of Decision noted that a groundwater Cd plume also existed in the same general location as the As plume. However, Cd was not listed as a soil contaminant. Elevated groundwater levels of Pb, certain pesticides, and TCE (TCE presence was likely not related to Vineland Chemical) were also noted, however, the major contaminant was As. The As contamination is limited to the unconfined aquifer of the Upper Sand; As levels below the Banded Zone were generally undetected to very low, with a maximum of 28 μg/L (EPA, 1989a).

1.6 Inventory of As in the aquifer beneath Vineland Chemical

Site literature states that approximately 1000 metric tons of waste salts were produced each year during manufacture of the organoarsenical biocides (EPA, 1989a). Vineland Chemical stored their waste salts in open piles and in chicken coops until 1978, making these waste salts a major source of As to the subsurface. If the waste salts contained between 1 and 2% As, then between 290 and 580 metric tons of As could have entered the environment by 1978. This figure does not include As inputs to the system from As-based starting materials, storm water run off, or wastewater and/or process waters discharged to the unlined lagoons (could have 67 mg/L As); there is little information available to enable quantification of these other potential inputs. Additionally, discharge of contaminated groundwater to Blackwater Branch provided a means for transporting As offsite. Since the inputs are difficult to define, it is necessary to evaluate the quantity of contaminant beneath the Vineland site itself in other ways. We discuss three ways of evaluating the pre-remediation aquifer sediment As load under the site and one technique for estimating the total mass of groundwater As. In the next section, we discuss estimations of offsite transport and As quantities present downstream from the site.

The assumptions for site aquifer As sediment inventory #1 are listed in Table 1.1. This allows a rough approximation based on site dimensions and an assumed average As concentration. The total quantity of As estimated by this method is 200 metric tons of As.

Table 1.1. Assumptions for calculating sediment As inventory #1

Site Area	54 acres = 0.22 km^2
Thickness of aquifer [a]	45 ft = 13.7 m
Bulk density	1750 kg/m^3
Sediment As concentration [b]	30-40 mg/kg

[a] Aquifer thickness estimate based on thickness of Upper Sand (40-80 ft) minus typical depth to water table (15 ft); minimum and maximum thickness were averaged.

[b] The median As concentration for aquifer solids in pilot study area (see Chapter 5) was 35 mg/kg. Concentrations are expected to be higher near the source area and lower further from the source area.

The second estimate of site sediment As inventory relies on the same assumption of aquifer thickness (adapted from undergraduate thesis (McMahon, 2009)). However, sediment As concentrations were based on EPA surveys of 20 aquifer sediment depth profiles, which measured As concentrations at depths of 15-35 ft (4.6-10.7 m) below ground surface (bgs) in February and March of 2005. Sediment concentrations were evaluated every 5 ft or 1.52 m in depth from 4.6 to 10.7 m bgs. The average concentration per depth was then summed over the volume the depth interval represented across the site. Sediments located deeper than 10.7 m were assumed to have the same As concentration as the average value at 10.7 m. These calculations were carried out using GIS software and estimate the aquifer sediment As inventory as 3,900 metric tons. Since several of the sediment concentration data points (~75%) are in the former "hot zone," this approximation may overestimate the total inventory.

Finally, an estimate of total As mass in sediments and groundwater was included in the wastewater treatment facility final design appendices (USACE, 1996b). For these calculations, the site was divided into grid cells and a groundwater As concentration for each cell was determined from a groundwater model. Mass of As in groundwater was calculated assuming a porosity of 0.3. The mass of As in groundwater was determined to be approximately1.4 metric tons. The Langmuir isotherm equation was then used to calculate the mass of As in sediments (USACE, 1996b). Using this method, the total mass of As in sediments under the site was determined to be approximately 62 metric tons.

Though the three methods for calculating the aquifer sediment As inventory under the site produce differing results, they do help to constrain the quantity of As in the aquifer solids. Since Inventory #2 was based on solids data mostly from within the former “hot zone,” this method may overestimate the total As inventory of the aquifer solids. The other two estimates, however, differ only by a factor of ~3; this is decent agreement considering the uncertainties in extrapolating a limited number of solid and liquid measurements that was required for expanding As estimates to the full site. Therefore, approximately 100 metric tons of As are likely to lie within the aquifer solids under the Vineland site. Additionally, comparing the predicted dissolved mass of As with the mass of As in the sediments suggests that the dissolved As concentration at any given time may represent a very small percentage (<3%) of total As inventory under the site.

1.7 Offsite Transport of As and Maurice River basin

Due to continued discharge of contaminated waters from the site to Blackwater Branch prior to the start of remediation, significant quantities of As were released to Blackwater Branch and impacted the Maurice River and Union Lake as well. The Record of Decision presents clear evidence that the As within the Maurice River Basin, at least that downstream of Vineland Chemical, is a result of the contamination on the Vineland Chemical site. Blackwater Branch, Maurice River, and Union Lake all showed evidence of As contamination. Arsenic concentrations in upstream surface waters and sediments of Blackwater Branch were low to undetected, but were elevated downstream. Additionally, As concentrations in the Maurice River were low to undetected above the junction with Blackwater Branch but elevated below it. According to the Record of Decision, there was a decrease in surface water As concentrations in the Upper Maurice

River traveling downstream from Vineland Chemical; however, concentrations did not drop below 50 μg/L (the drinking water standard at the time of the Record of Decision). Arsenic concentrations of the Lower Maurice River (below Union Lake) decreased gradually downstream of Union Lake but did not consistently drop below 50 μg/L until >20 river miles (>32 river km) further downstream at the tidal front. All tributaries between the Blackwater Branch and Union Lake had very low to undetected As. Taken together, this concentration distribution implicates Vineland Chemical as the only significant source of As to the Maurice River Drainage Basin between the Vineland Chemical site and Union Lake (EPA, 1989a).

It has been estimated from historical stream data that 500 metric tons of As were discharged from Vineland Chemical to the Maurice River watershed over time (EPA, 1989c). The maximum release was estimated to occur around 1978 with >63 metric tons released in that year; releases decreased substantially from 1979-1984, most likely due to remedial actions recommended by NJDEP. The Remedial Investigation Report indicated that between 2 and 11 metric tons of As per year were carried offsite via groundwater discharge based on data from summer 1987 (EPA, 1989c). The Remedial Investigation Report also provided estimates of sediment As inventory for the various water bodies impacted by Vineland Chemical (EPA, 1989c). Sediments in Blackwater Branch and the Upper Maurice River (above Union Lake) were estimated to contain 6 metric tons of As. Union Lake sediments were estimated to contain 140 metric tons (~30% of the As mass transported offsite). Tidal influences and resulting reactions within the Lower Maurice can complicate determination of fate and transport of As below Union Lake. However, sediments in the Lower Maurice (below Union Lake) were reported as ranging from ~9 mg/kg in As to 234 mg/kg, with a mean value of 30 mg/kg and river water concentrations (total and dissolved) declined by more than 70% across the salt front. Therefore, a crude estimate of sediment bound As in the Lower Maurice River was developed and approximated at 175 metric tons (EPA, 1989c); this is estimated to be nearly half of the As that had passed through the lake.

In absence of other hydrological controls (i.e., pump and treat system) Blackwater Branch is a gaining stream, meaning that groundwater discharges to the surface water system. Blackwater Branch and the Upper Maurice River acted as conduits, passing As to Union Lake. This is supported by the relatively low mass of As in the sediments of Blackwater Branch and the Upper Maurice (6 metric tons) as compared with the As discharged from the site (500 metric tons). Cessation of discharge of contaminated water should therefore lead to a relatively rapid decrease in surface water As concentrations in Blackwater Branch and the Upper Maurice. In the past, Union Lake may have acted as a sink for As. It was unclear, however, exactly what was controlling the dissolved As concentrations in Union Lake and whether stopping As input into Blackwater Branch would lead to quick decline in surface water As in Union Lake (EPA, 1989a; c). However, bacterial action during summer months could release As to the lake water from bottom-water sediments (Keimowitz, et al., 2005b), which could result in elevated surface water As even without continued upstream input.

In 1982-1983 and 1986, EPA and NJDEP carried out studies of Union Lake waters and found total As concentrations (unfiltered) up to 267 μg/L. In 1986, lakeshore sediments submerged in less than 10 ft (3 m) of water were tested (N=193) by NJDEP; As concentrations varied from undetected to 1273 mg/kg. Lake sediment samples taken for the Remediation Investigation/Feasibility study, however, found generally lower concentrations of As; sediments of the upper lake had As concentrations between 36-65 mg/kg, in the mid lake ~12 mg/kg, and in the lower lake 14-107 mg/kg. Highest concentrations were detected in a submerged dam at the north of the lake and near the main dam at the south (EPA, 1989a). Arsenic mobility in Union Lake is thought to be iron-controlled, indicating that reducing conditions in the lake could lead to release of As sorbed to iron oxides in the lake sediments (Keimowitz, et al., 2005b). Fish were tested and found to have levels of As considered normal for US fish and shellfish; PCBs and some pesticides were elevated but this is not likely related to Vineland Chemical (EPA, 1989a). Studies were also conducted to evaluate the surface water and sediment As concentrations of Blackwater Branch and the Upper Maurice River. Shallow sediments (0-1 ft or 0-0.3 m) in these water bodies had up to 3760 mg/kg As and surface waters had up to 6200 μg/L (EPA, 1989a). Arsenic mobility in Blackwater Branch is thought to be sulfur-controlled; therefore, oxic conditions could lead to As mobilization via release from sulfur-minerals (Keimowitz, et al., 2005b). One fish sample from the Upper Maurice and crab and oyster samples from the Lower Maurice (below Union Lake) had detectable levels of As but were still considered within normal background limits (EPA, 1989a; b).

Blackwater Branch is currently monitored at several locations along its pathway between Vineland Chemical and its confluence with the Maurice River. Between March 2007 and March 2010, detectable As levels were measured in 12% of the samples taken and the maximum As concentration reported was 19 μg/L. However, since the flood plain area of Blackwater Branch has been undergoing remediation, which has included diverting the stream itself and cleaning the sediments beneath it, the environmental health and As contents of Blackwater Branch will need to be reassessed following completion of the floodplain cleanup. Phase I of the 3-phase project (east of Mill Rd) was completed in December 2007 (EPA, 2010b).

Additionally, recent Union Lake data (Summers 2007-2008) indicate that even though bottom sediment concentrations can be high, up to 1125 mg/kg, lake water As concentrations remain fairly low even at depth and during periodic anoxia; the maximum As concentration seen during those sampling periods was ~30 μg/L at 7.5 m depth during an anoxic event. Surface waters, however, remained low in concentration, generally 6 μg/L or less (Keimowitz, et al., submitted 2011).

1.8 Remediation activities

Several court orders were required to prompt cleanup actions during Vineland Chemical's manufacturing lifetime. These actions included containerizing and removing piles of waste salts, lining two of the lagoons, and installing a wastewater treatment facility to treat process water, storm runoff and the shallow aquifer. However, the wastewater treatment facility built by Vineland Chemical had its difficulties. It was only able to treat ~35,000 GPD (132 m^3/d) while an estimated ~150,000 GPD (568 m^3/d) left the site. Additionally, the treatment system did not consistently decrease arsenic concentrations to permissible levels. Eventually, Vineland Chemical stopped treating groundwater and process water (claiming that all water used in manufacture was now utilized in the herbicide product) and only treated storm water runoff intermittently. NJDEP allowed the cessation due to worries that discharge of treated water into the aquifer could lead to groundwater mounding and subsequently encourage offsite transport and/or migration of the contaminant plume deeper within the aquifer.

Vineland Chemical was listed as a Superfund site in 1984 and following a Remedial Investigation/Feasibility Study, the Record of Decision was issued in 1989, which discussed the site's contamination and provided a plan for remediation (EPA, 1989a). The cleanup plan was broken into 4 sections or "operable units." Operable unit 1 is concerned with source control on the plant site, both minimizing exposure to contaminated site solids and preventing As release into the groundwater. Operable unit 2 deals with containment and cleanup of the contaminated aquifer waters. Operable unit 3 addresses river area sediments and flood plain cleanup of the Blackwater Branch to decrease public exposure. Operable unit 4 is concerned with minimizing human health risks related to the sediments of Union Lake.

OU1 The Record of Decision called for soil flushing in order to accomplish the objectives for operable unit 1 (source control) (EPA, 1989a). Approximately 41,000 m^3 of sediments on site were to be excavated and consolidated with another 55,000 m^3 of contaminated sediments (undisturbed) prior to flushing (total = 96,000 m^3). Additionally two lined surface impoundments were to be closed and chicken coops and storage buildings were to be decontaminated. An Explanation of Significant Differences document was later released providing an alternate solution to soil flushing – soil washing (EPA, 2001b). Soil flushing is an *in situ* cleaning method involving injection of groundwater through the contaminated sediments in an effort to flush As from the solids. Soil washing would involve excavating sediments and cleaning them at a soil washing plant before returning cleaned sediments to the site. Based on laboratory column studies, 17-20 years of soil flushing would be necessary to decrease soil As concentrations to 20 mg/kg when starting concentrations were 178 mg/kg; 38-43 years of flushing would be necessary if the starting As concentrations were higher (1720 mg/kg). Follow up testing by the EPA showed that soil As concentrations could be decreased to 27 mg/kg with ~15 pore volumes of flushing but ~460 pore volumes would be needed to reach the target cleanup level of 20 mg/kg (EPA, 2001b).

Soil washing was chosen as a preferred alternative and a 70-ton per hour (~64 metric ton per hour) soil washing facility was constructed (EPA, 2010b). It was predicted that soil flushing could have taken 40 years and cost $120 M, while soil washing would require ~2 years and $34 M (Grzyboski and Leiser, 2001). The soil washing facility has further been used for treatment of flood plain area soils.

Site soils and sediments in the most contaminated region of the site were excavated from the vadose zone and ~1-3 ft (~0.3-1 m) into the aquifer. Oversized particles and fines were removed and remaining sands were chemically leached. A slurry of sand and water was formed which moved through a series of four tanks for washing; sodium carbonate was the main washing agent (Voight and USACE, 2005). The slurry was mixed aggressively at high-temperature (130 ^{o}F or 54 ^{o}C) to remove As and Fe coatings from the sands. Sands were typically blended prior to soil washing to create a feed stream with approximately 80 mg/kg As; the target cleanup level at the soil washing facility was 20 mg/kg As. However, recent sediment extraction experiments indicate that the As remaining following treatment may still be fairly mobile. Up to ~75% of the As on the cleaned sands was mobilized with a 24 hr, 1 M phosphate leach and is therefore considered easily extractable. Most of the sand was returned to the site following soil washing, however, oversized materials, fines, and waste sludge were shipped to a hazardous waste landfill (Voight and USACE, 2005). Soil washing of vadose zone sediments was completed in 2007. From 2004-2007, approximately 372,000 metric tons of materials were processed at the soil washing facility including ~109,000 metric tons of floodplain materials which are further discussed below (86,000 metric tons in 2004, 100,000 metric tons each in 2005 and 2006 and 86,000 metric tons in 2007). Nearly 8% of that was sent to landfills for disposal; this includes nearly 17,000 metric tons of sludge and filter cake and 12,000 metric tons of oversized materials. Based on the average As concentration of the sludge (3,000 mg/kg) and the quantity of sludge (17,120 metric tons), an estimated total of 51.3 metric tons of As was removed from the subsurface over 4 years of soil washing or ~12.8 metric tons per year (Table 1.2) (Creighton, 2007). An alternate estimate based on the amount of material treated (~372,000 metric tons) and estimated average input concentration of 80 mg/kg, would predict removal of 22-26 metric tons of As, assuming a final concentration of 10-20 mg/kg for treated soils. However, it is possible that once the soil washing plant was established it was able to process sediments with higher starting concentrations. For instance, if the average input concentration was instead 150 mg/kg, approximately 48-52 metric tons of As would have been removed during this time, which would be consistent with removal estimates provided by the facility managers. The soil washing facility costs approximately $9M/year to operate (Grzyboski, 2004).

In addition to the change from soil flushing to soil washing, EPA decided to demolish and remove the buildings and structures on site rather than attempt to decontaminate. Once Vineland Chemical indicated they intended to abandon the site, EPA assessed the buildings and structures on site and discovered high levels of As both within the building materials (e.g., highest reported level of 11,000 mg/kg in the brick floors below building #9) and beneath the structures (e.g., 471 mg/kg at a depth of 8 ft or 2.4 m below ground surface under building #9) (EPA, 2001b).

OU2 To mitigate offsite migration of the As plume and address the contaminated aquifer under the site, the Record of Decision called for installation of a pump and treat system. Once the water was treated the Record of Decision recommended injection of effluent into the aquifer at a maximum practical rate (using some for soil flushing) and releasing the rest to the Maurice River (EPA, 1989a). The As waste sludge created as a byproduct of the water treatment would be disposed in a hazardous waste facility.

The final design of the pump and treat system consisted of 13 extraction wells. Placement of wells and pump rates were evaluated using groundwater modeling with MODFLOW and MT3D (USACE, 1996a). Combining that information with geochemical data lead to an optimized design scenario of 2 MGD from 13 wells; this would allow hydraulic control of the As plume while keeping the treatment plant to a manageable size. The extraction wells were installed in two lines – one approximately parallel to Blackwater Branch, one approximately parallel to N. Mill Rd (with one well further west – RW 11) (Figure 1.3). Following further groundwater modeling studies using FEMWATER, additional wells, RW 2a, 2b and 9a were installed in 2006 to aid in plume capture (2a and 2b) or replace wells not pumping to capacity (9a) (Figure 1.3) (USACE, 2007).

The water treatment process consists of several steps to oxidize and precipitate As. Initially, the treatment influent was separated into two streams – inorganic and organic. The organic stream received additional treatment steps (notably repetition of oxidation, coagulation, flocculation, and clarification steps) prior to being combined with the inorganic stream for final processing. Currently (2011), all incoming groundwater is directed through the inorganic influent train. The treatment steps for both influent trains are as follows (USACE, 1996a):

Organic Train

1) Oxidation with hydrogen peroxide
2) Coagulation with ferric chloride and sodium hydroxide*
3) Flocculation with potassium permanganate and polymer addition
4) Clarification with dissolved air flotation
5) Repeat steps 1-4
6) Blend with pre-treated inorganic As stream

Inorganic Train

1) Oxidation with hydrogen peroxide
2) Coagulation with ferric chloride and sodium hydroxide*
3) Flocculation with potassium permanganate and polymer addition
4) Clarification with dissolved air flotation
5) Blend with pre-treated organic As stream

*Laboratory studies determined effective treatment conditions to be Fe:As ratio > 5:1 and pH 6.5.

Blended streams receive final processing

1) Addition of sodium hydroxide and potassium permanganate
2) Addition of polymer
3) Filtration

The treated effluent waters are ultimately discharged to Blackwater Branch and at present adhere to the current US drinking water standard of 10 µg/L. The original Record of Decision had called for discharge of as much water as practical back to the aquifer. However, it was noted in the wastewater treatment plant final design documentation that, at least initially, reinjection of only 15% or less would be possible. Reinjection of a higher percentage had the potential to cause groundwater mounding and possibly flood basements of nearby residences; further impacts could be an increase in contaminant flow to Blackwater Branch and/or travel of contaminated groundwater upgradient (USACE, 1996a).

Groundwater models were employed to define the necessary extraction rate for plume capture; the models used the maximum probable site hydraulic conductivity for these calculations (USACE, 1996a). Extraction rates of 0.5 MGD (1900 m^3/d) or 1 MGD (3800 m^3/d) did not hydraulically control the As plume so that concentration values above 50 µg/L (drinking water standard at the time of the wastewater treatment plant final design publication) were contained on site. However, models indicated that an extraction rate of 1.87 MGD (7080 m^3/d) captured and hydraulically controlled the contaminant plume such that waters with As concentrations above 50 µg/L were not transported off site. A design specification of 2 MGD (7600 m^3/d) was suggested to allow for a margin of error in model calculations. As of March 2009, approximately 3.5 billion gallons (13 million m^3) of contaminated water had been treated (Funderburk, 2009) indicating that the pump and treat plant has not maintained maximum pumping conditions and had a 9-yr average of ~1 MGD (3800 m^3/d). Site documents mirror the figures published by the popular press indicating over 3.6 billion gallons had been treated by February 2010 (EPA, 2010b). Well fouling and clogging of wells with biological materials or oxidized iron, downtime for maintenance, and other factors may contribute to less than maximum pump rates. Further optimization of pumping scenarios and hydrological models have given site managers confidence in the lower pumping rates. Additionally, a Classification Exception Area-Well Restriction Area was established to prohibit groundwater well installation (for drinking, irrigation, or industrial uses) near the site and protect human health.

According to a 1996 study, the pump and treat system has been successful in significantly decreasing but not eliminating off site transport to the Blackwater Branch, from ~4 kg/day to ~1.7 kg/day (Miller, et al., 1996) and lowering surface water concentrations considerably (~100 µg/L to ~20 µg/L). A 2004 study still showed evidence for offsite transport of 1.64 kg/day of As from the site into Blackwater Branch (Keimowitz, et al., 2005b). Four plausible sources of As to the Blackwater Branch were discussed: 1) erosion and overland transport, 2) As discharged in the pump and treat plant effluent, 3) remobilization of sediment bound As, and 4) groundwater discharge. Overland transport was eliminated as an unlikely source, pump and treat effluent was calculated to account for <3% of the total mass released offsite, and remobilization from sediments accounted for another ~1.6% based on diffusive flux calculations. The study concluded, therefore, that the only logical and likely source of the bulk of the As to the stream was discharge of contaminated groundwater (Keimowitz, et al., 2005b). Since that study three additional pump and treat wells have been installed on site to aid in more efficient plume capture. A recent hydrological modeling study (USACE, 2007) evaluated plume capture under site pumping conditions (~0.9 MGD or 3400 m^3/d); in this model, the main portion of the As plume was captured in the pump and treat wells. However, in 2006 there was some evidence of elevated As concentrations in the northwest of the site (across Blackwater Branch), which was thought to be outside of the capture zones of the pump and treat wells. The study reported a need for additional investigation and monitoring to determine the routes of As migration to that portion of the site (USACE, 2007). EPA continues to assess this area and considers it no risk for human exposure, especially since establishing a well restriction area (i.e., no new drinking water wells can be placed in a designated area around the site) (USACE, 2007). The site's remediation activities are re-examined every 5 years through Remedial Site Evaluations and efforts are ongoing to ensure more efficient plume capture while decreasing costs and exploring new ways to bring the site toward the clean-up goals.

The As contaminated sludge (~3,000 mg/kg in As) remaining after treatment is disposed of in a hazardous waste landfill. Approximately 295 metric tons of sludge are formed from the pump and treat process each year. Therefore, ~900 kg of As are removed each year through groundwater extraction and cleaning (Creighton, 2007), for a total of ~9,900 kg over the 11 years (2000-2011) that groundwater treatment plant has been operational (Table 1.2). The average cost would be roughly $2000-4000/kg As removed according to average operating and maintenance costs for the pump and treat system. The removal of As per year via pump and treat is at least an order of magnitude smaller than the removal achieved by soil washing, however, soil washing is not a feasible remediation tool for sediments within the aquifer (Table 1.2).

Since the aquifer sediments beneath the site have been estimated to hold on the order of ~100 metric tons of As, the amount removed via pump and treat over 11 years represents <10% of the sediment inventory. The low recovery of As is likely due to slow desorption of As from the Al and Fe (hydr)oxides within the sediments. Additionally, declines in As removal rates have been noted in several pump and treat recovery wells over time. There were large initial decreases in As concentration at several pump and treat wells once the wells were turned on, which could have resulted from flushing As out of the system or from movement of the As plume. However, over time the As concentrations at some of the wells began to level off, and they leveled off at concentrations of hundreds of μg/L. This leveling off or “tailing effect” is not unique to Vineland Chemical and has been noted as a problem that arises with many pump and treat systems; tailing can make it difficult to reach cleanup goals even with very long treatment times (Palmer and Fish, 1992). The majority of the As inventory remains on the solids; therefore, remediation via pump and treat is limited by the ability to move As from solids to the liquid phase for treatment. The following chapters discuss methods for accelerating As release from the solids to increase the efficiency of pump and treat remediation.

The original Record of Decision called for pump and treat to remain active until the maximum As concentration in the groundwater plume fell below 350 μg/L (EPA, 1989a). The EPA reasoned that the groundwater discharge rate to Blackwater Branch and stream flow rates would make it necessary to decrease groundwater As to these levels in order to keep the surface water As concentrations of Blackwater Branch below 50 μg/L (the standard at the time). It has not been determined if and how this target will be changed now that the federal drinking water standard has been lowered to 10 μg/L and the NJ state standard to 5 μg/L. Blackwater Branch waters are not used for human consumption. However, if the lower standards are taken into account and one assumes the same As dilution and retardation as originally calculated, groundwater As concentrations would need to be 5-10 times lower than 350 μg/L (i.e., 70 or 35 μg/L) to keep Blackwater Branch below these lower standards.

The wastewater treatment facility final design document indicates that it may be necessary to utilize the pump and treat system for over 20 years depending on actual pumping rates and the geochemistry of the site (USACE, 1996a) while the EPA fact sheet indicated that 15 years of pump and treat were anticipated (EPA, 2006). In 2009, the popular press reported that site managers indicated the pump and treat system may be in operation for 20-25 more years and the endpoint was uncertain (Kornbluh, 2009). The wastewater treatment facility final design appendices also included calculations regarding the expected groundwater As concentrations after varying lengths of time spent pumping and treating (USACE, 1996b). After 10 years of pump and treat, they predict maximum inorganic As concentrations to be 429 μg/L and maximum organic As concentration to be 405 μg/L (USACE, 1996b). The site remediation managers no longer consistently speciate their As samples, however, we can compare those figures with recovery well data from Jan 2009-March 2010, approximately 9-10 yrs after pump and treat started. In practice, the organic As concentrations decreased faster than expected while the inorganic species decreased slower than anticipated; all waters extracted by the pump and treat system are currently handled by the inorganic treatment train. Adding the predicted inorganic and organic As values gives 834 μg/L and 24% of the samples collected at the pump and treat recovery wells (n=135) exceed that value. Approximately 58% of the samples have total As values that exceed the 429 μg/L value predicted from maximum inorganic As concentration. Even if the site remediation were following predictions, calculations in the wastewater treatment facility final design appendices indicate that 50-70 years of pump and treat could be required before maximum groundwater concentrations would decline to 350 μg/L (USACE, 1996b). Of the samples collected at the pump and treat recovery wells between January 2009 and March 2010 (n=135), 61% have As concentrations greater than 350 μg/L and 91% have As concentrations greater than 35 μg/L.

At the time of a 2001 survey, the pump and treat system at Vineland Chemical cost $4 M per year for operation and maintenance, the most expensive pump and treat system of the 79 which reported costs; the average cost of those surveyed was $570 K per site and the median cost was $350 K (EPA, 2001a). Operation and maintenance expenses have been reduced at Vineland through continued optimization of the system and are reported to be $1.7 M/yr (Naman, 2010), but the costs still remain high. Prolonged periods of pump and treat may be an expensive proposition.

Table 1.2. Arsenic removal from the Vineland site via soil washing and pump and treat

	Soil Washing[a,b]	Pump and Treat[b]	Total
Mass As removed per year (kg/yr)	12,800 kg/yr	900 kg/yr	13,700 kg/yr
Operation and maintenance cost per year ($/yr)	$9 M/yr	$1.7-4 M/yr[c]	$10.7-13.7 M/yr
Approx. cost per kg As removed ($/kg)	~$700/kg	~$1900-4400/kg	~$2600-5100/kg
Mass As removed (metric tons)[b]	51.3	9.9	61.2

[a] Soil washing values used here are from the figures provided by Vineland site managers.
[b] Soil washing values include data between 2004 and 2007. Soil washing beyond 2007, when the facility was used primarily for flood plain materials, is not included. Pump and treat values include data and projections for 2000-2011.
[c] Operation and maintenance costs for the pump and treat facility were reported to be $4 M/yr in 2001 (EPA, 2001a) and $1.7 M/yr in 2010 (Naman, 2010).

OU3 Operable unit 3 addresses the river area sediments. The Record of Decision detailed a plan to excavate and treat As-contaminated sediments of the Blackwater Branch floodplain as well as submerged sediments. Additionally, after cessation of the discharge of As contaminated groundwater to Blackwater Branch, the Record of Decision suggested the Maurice River be monitored for a period of three years to allow for natural flushing. The monitoring results would dictate the next steps – whether remediation of submerged river sediments would be necessary or not.

In 2006, the floodplain cleanup was begun; this remediation was separated into three phases (EPA, 2010b). In Phase I, floodplain materials east of Mill Rd were excavated and treated at the soil washing plant while peat and organic materials were separated and shipped to a landfill offsite (Creighton, 2007). In addition to cleaning sediments surrounding Blackwater Branch, the stream itself was diverted and the sediments beneath it cleaned before redirecting the stream to its original channel. As mentioned above, 109,000 metric tons of floodplain sands were treated at the soil washing plant. Approximately 39,000 metric tons of floodplain materials were untreatable peat and organic matter and were disposed of at an offsite landfill. Phase II and III of the floodplain cleanup concentrate on materials to the west of Mill Rd up to the point where Blackwater Branch joins the Maurice River (Mill Rd to Route 55 and Route 55 to Maurice River); these phases of cleanup are on going (2010). There are an estimated 150,000 metric tons of contaminated soils and sediments in the Phase II section; these materials are made up of ~70% peat and organics and 30% sands. After the floodplain cleanup is complete, site managers will allow a 3-year natural flushing period to determine whether sediments in the Maurice River can naturally return to acceptable levels.

OU4 Operable unit 4 involves the sediments of Union Lake. This part of the remediation has not yet been started and plans have not yet been finalized. The beaches on the Maurice River and Union Lake are tested annually and continue to be regarded as safe for swimming (Kornbluh, 2009). The Record of Decision suggested sampling and treatment of As-contaminated sediments at the periphery of the lake after the 3-year flushing period and any Maurice River remediation had taken place. The Record of Decision noted that if Union Lake remediation is necessary, this could involve over 76,000 m^3 of sediments (EPA, 1989a). Large loads of As deposited in lake bottoms can remain a source of As to surface waters through remobilization for decades (Tanner and Clayton, 1990).

1.9 Chapter Summaries

It is clear that the extensive remediation on the Vineland Superfund site has been successful in many regards. Soil washing has removed tens of metric tons of As from the site, thereby preventing continued contamination of the site via that source. In addition, the pump and treat plant has successfully decreased the off site transport of As to the Blackwater Branch. However, pump and treat operation without additional modifications could require substantial investments in resources as well as a long remediation timeframe if it is to ultimately clean the groundwater to acceptable levels where offsite transport will no longer be an issue. Based on recovery well data and the tailing seen at a number of the wells, alternate remediation strategies should be considered. In the following chapters, we discuss one such potential method for accelerating remediation, namely continuing pump and treat but adding a chemical amendment to the subsurface to maximize the amount of As released from the solids into the liquid phase where it can be managed via pump and treat.

The work described here is specifically focused on the As contamination and remediation of the Vineland Chemical Co. Superfund site in southern New Jersey. However, the results will hopefully be useful for numerous sites. A multi-scale approach was taken to investigate As release from the solids; studies were performed on the bench scale, subgrain scale, and field scale. At each scale, we investigate chemical addition as a way to release As from the solids and potentially accelerate pump and treat remediation.

Bench scale work investigating optimal chemical amendments for accelerating As release are described in Chapter 2. Chemical amendments that either compete with As for sorption sites or dissolve Fe and Al (hydr)oxides can increase As mobility and improve pump and treat remediation efficiency. Extraction and column experiments were performed using As contaminated aquifer solids (81 ± 1 mg/kg), site groundwater, and either phosphate ($NaH_2PO_4 \cdot H_2O$) or oxalic acid ($C_2H_2O_4 \cdot 2H_2O$); phosphate can compete with As for sorption sites while oxalic acid can dissolve Fe and Al species in sediments and may also vie with As for sorption sites. In column experiments, phosphate additions induced more As mobilization early in the experiments but oxalic acid was more effective at mobilizing As overall and at lower amendment concentrations. Simple extrapolations of the column experiments based on pore volumes suggest that treatment with 10 mM oxalic acid could lower the time necessary for cleanup at the Vineland site from 600 years (with current techniques involving just groundwater) to potentially on the order of 4 years. Since oxalic acid additions yielded the most promising results for accelerating As release, further research focused on mobilization of As by oxalic acid. This work included both small-scale experiments (<1 mm^2 of sediment) to investigate mechanistic and kinetic issues (Chapter 3) and large-scale experiments (~50 m^2) to evaluate the efficiency of oxalic acid for As release in a field setting (Chapter 5).

In Chapter 3, a new method is discussed for integrating the use of microfocused synchrotron techniques with column transport experiments. This combination allows simultaneously monitoring of grain-scale solid phase reactions and column scale transport in order to better understand As release and transport processes. Microfocused synchrotron X-ray techniques (X-ray fluorescence and X-ray absorption near edge spectroscopy) were used in conjunction with laboratory column and batch experiments and geochemical modeling to investigate As release by oxalic acid. Small scale (<1 mm^2) X-ray fluorescence maps showed As release during oxalic acid treatment that was consistent with the bulk column materials. Additionally, As release rate constants were calculated from the X-ray fluorescence maps and used to create a one dimensional transport model. The effluent As data generated by the transport model agreed fairly well with effluent As vs. pore volume plots for both a small column (4.25 cm x 0.635 cm ID) and a larger column (23.5 cm x 4.2 cm ID), showing that microscale processes can be predictive of the larger system.

Finally, Chapters 4 and 5 detail field experiments investigating As release by oxalic acid in a pilot study at the Vineland site. In a 3-month field experiment, approximately 2000 kg of oxalic acid were dissolved and injected into a section of the aquifer. An injection manifold system was designed and built for this experiment in order to evenly and consistently distribute oxalic acid and tracer solutions to the 15 injection wells during the three-month pilot scale injection experiment (Chapter 4). In Chapter 5, As release resulting from the oxalic acid injection was investigated. Groundwater samples suggest that introduction of oxalic acid led to increased As release at a sampling (observation) well and pump and treat recovery well in the study area. Furthermore, following the oxalic acid treatment, As concentrations in the sampling well decreased ~45% relative to initial concentrations, indicating As removal from the aquifer system. Further decreases were not realized since groundwater coming into the pilot study area was still high in As. Conservatively, a total of 2.9 kg of As was removed from the combined efforts of the sampling well and the pump and treat well above initial background levels and as a result of the 3-month oxalic acid treatment. A comparison of median and average As concentrations on a small number of sediment cores collected before and after treatment and analyzed using X-ray fluorescence spectroscopy suggested a reduction in As solid concentrations of ~34% (median difference) to 48% (mean difference). While further study is warranted, addition of oxalic acid, shows promise for accelerating treatment of a highly contaminated site and offers the potential to decrease the As remediation time-scale.

1.10 References

Arai, Y., Lanzirotti, A., Sutton, S., Davis, J.A., Sparks, D.L., 2003. Arsenic speciation and reactivity in poultry litter. Environ. Sci. Technol. 37, 4083-4090.

Argos, M., Kalra, T., Rathouz, P., Chen, Y., Pierce, B., Parvez, F., Islam, T., Ahmed, A., Rakibuz-Zaman, M., Hasan, R., Sarwar, G., Slavkovich, V., van Geen, A., Graziano, J., Ahsan, H., 2010. Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study. Lancet. 376, 252-258.

ATSDR, 2007. Toxicological profile for arsenic. US Department of Health and Human Services.

Balakumar, P., Kaur, J., 2009. Arsenic Exposure and Cardiovascular Disorders: An Overview. Cardiovasc. Toxicol. 9, 169-178.

Barringer, J.L., Mumford, A., Young, L.Y., Reilly, P.A., Bonin, J.L., Rosman, R., 2010. Pathways for arsenic from sediments to groundwater to streatms: Biogeochemical processes in the Inner Coastal Plain. Water Res. 44, 5532-5544.

Bauer, M., Blodau, C., 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Sci. Total Environ. 354, 179-190.

Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. Environ. Sci. Technol. 35, 2621-2626.

BGS, DPHE. 2001. Arsenic contamination of groundwater in Bangladesh. In: British Geological Survey (Technical Report, WC/00/19. 4 Volumes), Kinniburgh, D.G. and Smedley, P.L. (Eds.), vol. British Geological Survey, Keyworth.

Cauller, S.J., Carleton, G.B., 2006. Hydrogeology and simulated effects of groundwater withdrawals, Kirkwood-Cohansey aquifer system, upper Maurice River Basin area, New Jersey. U.S. Geological Survey Scientific Investigations Report 2005-2528.

Chen, Y., Parvez, F., Gamble, M., Islam, T., Ahmed, A., Argos, M., Graziano, J., Ahsan, H., 2009. Arsenic exposure at low-to-moderate levels and skin lesions, arsenic metabolism, neurological functions, and biomarkers for respiratory and cardiovascular diseases: Review of recent findings from the Health Effects of Arsenic Longitudinal Study (HEALS) in Bangladesh. Toxicol. Appl. Pharmacol. 239, 184-192.

Creighton, S., 2007. Personal communication.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713-764.

De Vitre, R., Belzile, N., Tessier, A., 1991. Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. Limnol. Oceanogr. 36, 1480-1485.

Del Razo, L.M., Alrellano, M.A., Cebrián, M.E., 1990. The oxidation states of arsenic in well-water from a chronic arsenicism area of northern Mexico. Environ. Pollut. 64, 143-153.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environ. Sci. Technol. 37, 4182-4189.

Ehrlich, H.L. 2002. In: Environmental Chemistry of Arsenic, Jr., W.T.F. (Ed.) vol. Dekker, New York, pp. 313-322.

EPA, 1989a. Record of Decision, Vineland Chemical Co., Inc.

EPA, 1989b. Vineland Chemical Company site final draft, . Feasibility study report, River areas, Vineland NJ.

EPA, 1989c. Vineland Chemical Company site, Final draft, Remedial investigation report, River areas, Vineland, NJ.

EPA, 2001a. Groundwater pump and treat systems: summary of selected cost and performance information at Superfund-financed sites. (EPA 542-R-01-021a).

EPA, 2001b. Vineland Chemical Superfund Site. Explanation of Significant Differences. EPA/ESD/R02-01/555.

EPA, 2002. Arsenic treatment technologies for soil, waste, and water. http://www.clu-in.org/download/remed/542r02004/arsenic_report.pdf.

EPA, 2006. Vineland Chemical Co., Inc National Priority List site fact sheet. http://www.epa.gov/Region2/superfund/npl/0200209c.pdf.

EPA, 2007. EPA Basic query for National Priorities List, Superfund, US EPA.

EPA, 2010a. EPA Basic query - Annual Status Report Remediation Database, http://cfpub.epa.gov/asr/index.cfm.

EPA, 2010b. Vineland Chemical Co., Inc National Priority List site fact sheet update. http://www.epa.gov/Region2/superfund/npl/0200209c.pdf.

Funderburk, K., 2009, Officials: Superfund site progress slow, but effective, in *The Daily Journal*, edited, Vineland, NJ.

Grzyboski, L., 2004, Vineland Chemical Co.'s Superfund site, in *The Daily Journal*, edited, Vineland, NJ.

Grzyboski, L., Leiser, M., 2001, EPA changes chemical plant cleanup plans, in *The Daily Journal*, edited, Vineland, NJ.

Herbel, M., Blum, J., Hoeft, S., Cohen, S., Arnold, L., Lisak, J., Stolz, J., Oremland, R., 2002. Dissimilatory arsenate reductase activity and arsenate-respiring bacteria in bovine rumen fluid, hamster feces, and the termite hindgut. FEMS Microbiol. Ecol. 41, 59-67.

Horneman, A., Van Geen, A., Kent, D.V., Mathe, P.E., Zheng, Y., Dhar, R.K., O'Connell, S., Hoque, M.A., Aziz, Z., Shamsudduha, M., Seddique, A.A., Ahmed, K.M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part 1: Evidence from sediment profiles. Geochim. Cosmochim. Acta. 68, 3459-3473.

Keimowitz, A.R., Mailloux, B.J., Wovkulich, K., Ross, J., Chillrud, S.N., submitted 2011. Chemical and microbial controls on arsenic cycling in a contaminated lake. Environ. Sci. Technol.

Keimowitz, A.R., Simpson, H.J., Chillrud, S.N., Stute, M., Tsang, M., Datta, S., Ross, J. 2005a. Oxidation of groundwater arsenic and iron. In: Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation, O'Day, P.A., Vlassopoulos, D., Meng, D. and Benning, L.G. (Eds.), vol. 915. American Chemical Society, Washington, DC.

Keimowitz, A.R., Zheng, Y., Chillrud, S.N., Mailloux, B., Jung, H.B., Stute, M., Simpson, H.J., 2005b. Arsenic redistribution between sediments and water near a highly contaminated source. Environ. Sci. Technol. 39, 8606-8613.

Kornbluh, A., 2009, Hazardous waste cleanup: Who will pay?, in *The Grapevine*, edited, Vineland, NJ.

Kuhlmeier, P.D., 1996. Partitioning of arsenic species in fine-grained soils. Journal of Air and Waste Management Association. 47.

Leist, M., Casey, R.J., Caridi, D., 2000. The management of arsenic wastes: problems and prospects. J. Hazard. Mater. 76.

Lin, W., Wang, S., Wu, H., Chang, K., Yeh, P., Chen, C., Guo, H., 2008. Associations between arsenic in drinking water and pterygium in southwestern Taiwan. Environ. Health Perspect. 116, 952-955.

Mailloux, B.J., Alexandrova, E., Keimowitz, A.R., Wovkulich, K., Freyer, G.A., Herron, M., Stolz, J.F., Kenna, T.C., Pichler, T., Polizzotto, M.L., Dong, H., Bishop, M., Knappett, P.S.K., 2009. Microbial Mineral Weathering for Nutrient Acquisition Releases Arsenic. Appl. Environ. Microbiol. 75, 2558-2565.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta. 58, 201-235.

McMahon, E. (2009), Arsenic budgets and plume migration at the Vineland Superfund site, NJ, Barnard College, New York.

Miller, D., Kuo, M., Gabry, J., Sachder, D. 1996, Remedial planning activities at selected uncontrolled hazardous substance disposal sites within EPA Region 2: updated draft arsenic mass balance for the Blackwater Branch, Foster Wheeler Environmental Corp.

Naman, R., 2010. EPA Region 2, Regional Project Manager, Personal communication.

Nriagu, J.O. 2002. In: Environmental Chemistry of Arsenic, Jr., W.T.F. (Ed.) vol. Dekker, New York, pp. 1-26.

Oremland, R.S., Newman, D.K., Wail, B.W., Stolz, J.F. 2002. In: Environmental Chemistry of Arsenic, Jr., W.T.F. (Ed.) vol. Dekker, New York, pp. 273-296.

Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. Science. 300, 939-944.

Oremland, R.S., Stolz, J.F., 2005. Arsenic, microbes, and contaminated aquifers. TRENDS in Microbiology. 13, 45-49.

OSR. draft. Arsenic in the Maurice River: Aquatic studies of the environmental fate and chemical transformations of industrial arsenic contaminating the Maurice River. In: Environmental Fate, Belton, T.J. (Ed.) vol. I.

Palmer, C.D., Fish, W., 1992. Chemical enhancements to pump-and-treat remediation. EPA Ground Water Issue. http://www.epa.gov/ada/download/issue/chemen.pdf.

Parvez, F., Chen, Y., Brandt-Rauf, P., Slavkovich, V., Islam, T., Ahmed, A., Argos, M., Hassan, R., Yunus, M., Haque, S., Balac, O., Graziano, J., Ahsan, H., 2010. A prospective study of respiratory symptoms associated with chronic arsenic exposure in Bangladesh: findings from the Health Effects of Arsenic Longitudinal Study (HEALS). Thorax. 65, 528-533.

Pershagen, G., 1985. Lung cancer mortality among men living near an arsenic emitting smelter. Am. J. Epidemiol. 122, 684-694.

Peryea, F.J. (1998), Historical use of lead arsenate insecticides, resulting soil contamination and implications for soil remediation, paper presented at 16th World Congress of Soil Science, Montpellier, France.

Radloff, K., Cheng, Z., Rahman, M., Ahmed, K., Mailloux, B., Juhl, A., Schlosser, P., van Geen, A., 2007. Mobilization of arsenic during one-year incubations of grey aquifer sands from Araihazar, Bangladesh. Environ. Sci. Technol. 41, 3639-3645.

Ryan, J.N., Gschwend, P.M., 1990. Colloid Mobilization in two Atlantic Coastal Plain aquifers: Field studies. Water Resour. Res. 26, 307-322.

Sancha, A.M., Castro, M.L. 2001. Arsenic in Latin America: occurrence, exposure, health effects and remediation. In: Arsenic Exposure and Health Effects IV, Chappell, W.R., Abernathy, C.O. and Calderon, R.I. (Eds.), vol. Elsevier, Amsterdam, pp. 87-96.

Skelley and Loy 2003, Draft report of hydrogeologic investigations/capture zone analysis, The Vineland Chemical Superfund site, Vineland, NJ.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517-568.

Smith, A., Lingas, E., Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bulletin of the World Health Organization. 78, 1093-1103.

Sullivan, K.A., Aller, R.C., 1996. Diagenetic cycling of arsenic in Amazon shelf sediments. Geochim. Cosmochim. Acta. 60, 1465-1477.

Sun, G.F., Pi, J.B., Li, B., Guo, X.Y., Yamauchi, H., Yoshida, T. 2001. Progresses on research of endemic arsenism in China: population at risk, intervention actions, and related scientific issues. In: Arsenic Exposure and Health Effects IV, Chappell, W.R., Abernathy, C.O. and Calderon, R.I. (Eds.), vol. Elsevier, Amsterdam, pp. 79-85.

Szabo, Z., Rice, D.E., MacLead, C.L., Barringer, T.H., 1997. Relation of distribution of radium, nitrate, and pesticides to agricultural land use and depth, Kirkwood-Cohansey aquifer system, New Jersey Coastal Plain, 1990-91. U.S. Geological Survey Water-Resources Investigations Report 96-4165A.

Szabo, Z., Rice, D.E., Plummer, L.N., Busenberg, E., Drenkard, S., Schlosser, P., 1996. Age dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3 and flow path analysis, southern New Jersey coastal plain. Water Resour. Res. 32, 1023-1038.

Tanner, C.C., Clayton, J.S., 1990. Persistence of arsenic 24 years after sodium arsenite herbicide application to Lake Rotoroa, Hamilton, New Zealand. N. Z. J. Mar. Freshwat. Res. 24, 173-179.

USACE 1996a, Design Analysis Report Wastewater Treatment Facility, Final Design, Malcom Pirnie, Inc. and Woodward-Clyde Federal Services.

USACE, 1996b. Specifications for Remediation of Vineland Chemical Company site Superfund project: Wastewater Treatment Facility Final Design, Appendices.

USACE, 2007. Classification Exception Area and Well Restriction Area Report. Vineland Chemical Company Superfund Site, Vineland, NJ., Prepared for USEPA, Region II.

van Geen, A., Rose, J., Thoral, S., Garnier, J.M., Zheng, Y., Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. Geochim. Cosmochim. Acta. 68, 3475-3486.

Varsányi, I., Fodré, Z., Barha, A., 1991. Arsenic in drinking water and mortality in the southern Great Plain, Hungary. Environ. Geochem. Health. 13, 14-22.

Vaughan, D.J., 2006. Arsenic. Elements. 2, 71-75.

Voight, E., USACE, 2005. Soil washing proves innovations in remediation. The Corps Environment.

Walsh, L.M., Keeney, D.R. 1975. Behavior of organoarsenicals in plants and soils. In: Arsenical Pesticides, Woolson, E.A. (Ed.) vol. 7. American Chemical Society, pp. 32-52.

Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in ground water of the United States-- occurence and geochemistry. Ground Water. 38, 589-604.

Zapecza, O.S., 1989. Hydrogeologic framework of the New Jersey Coastal Plain. U.S. Geological Survey Professional Paper 1404-B.

Zhang, S.Z., Li, W., Shan, X.Q., Lu, A.X., Zhou, P.J., 2005. Effects of low molecular weight organic anions on the release of arsenite and arsenate from a contaminated soil. Water Air Soil Pollut. 167, 111-122.

1.11 Figures

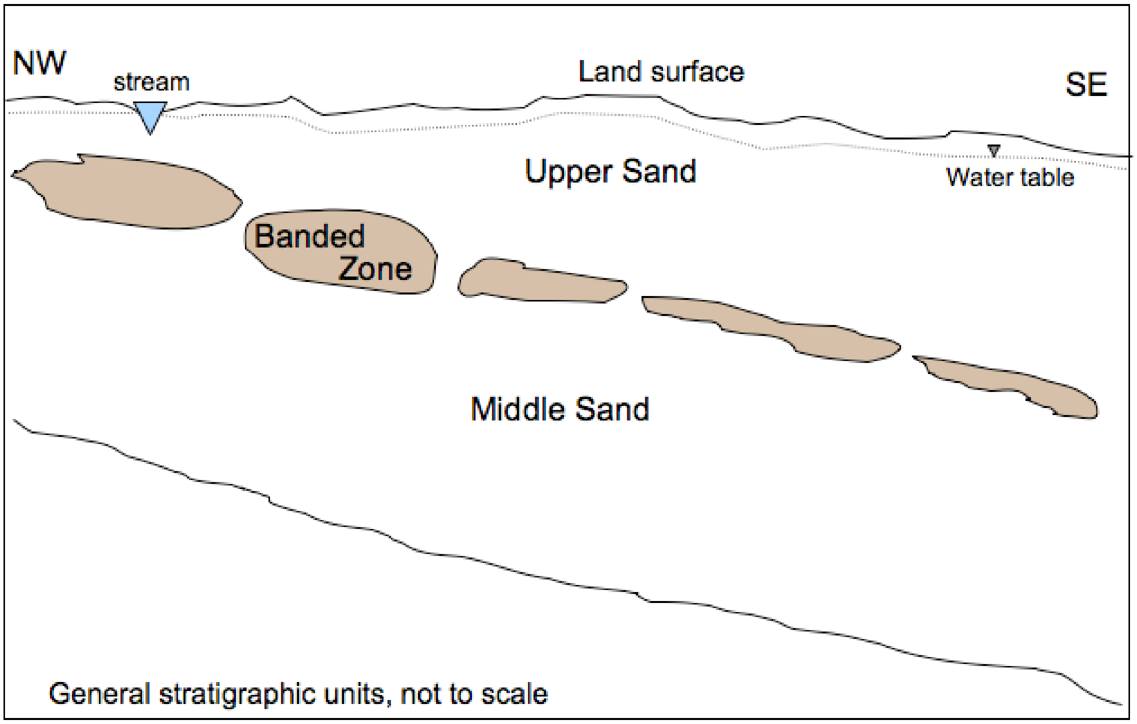


Figure 1.1 General description of the geology under the Vineland Superfund site, showing the informal stratigraphic units – Upper Sand, Banded Zone and Middle Sand.

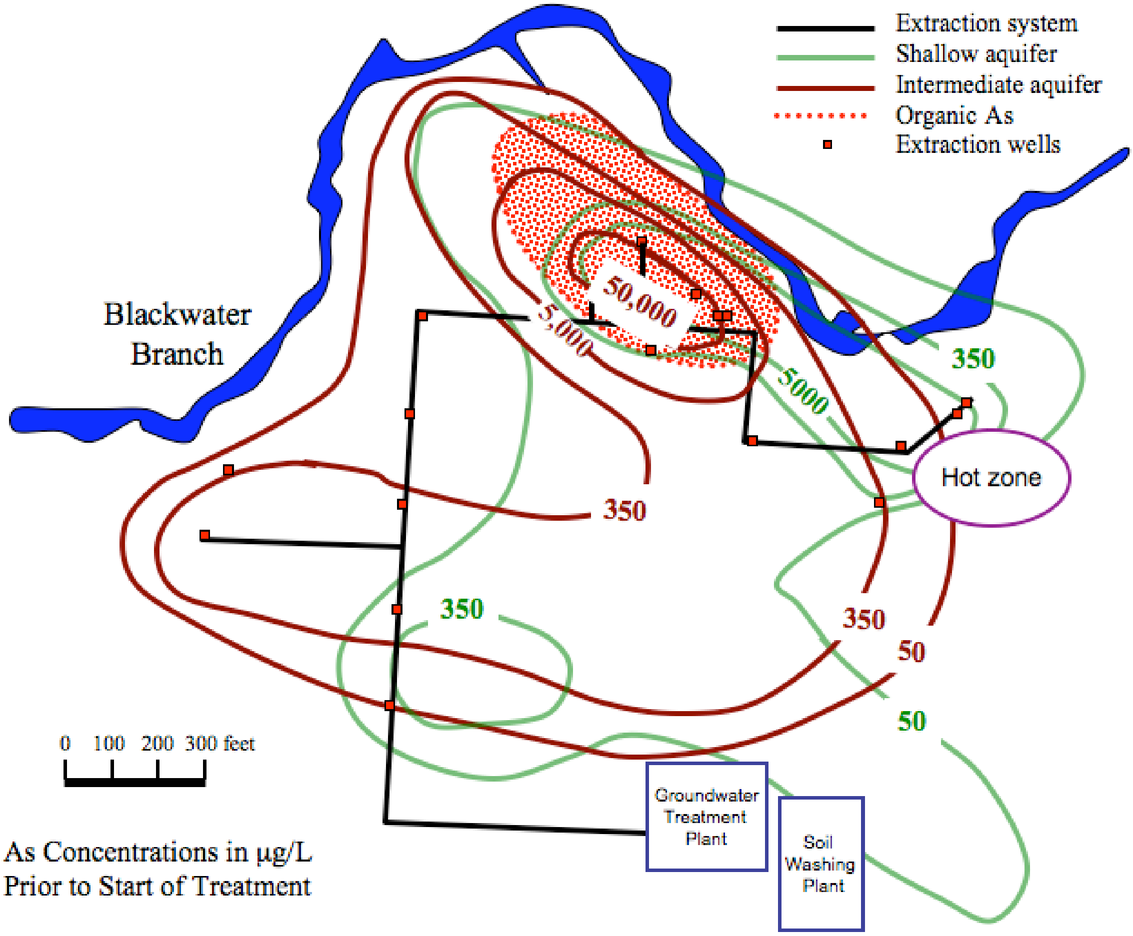


Figure 1.2. Schematic of the Vineland site displaying the organic As plume as well as As isolines for measurements taken in the shallow and intermediate wells of the Upper Sand. (Adapted from M. Stute)

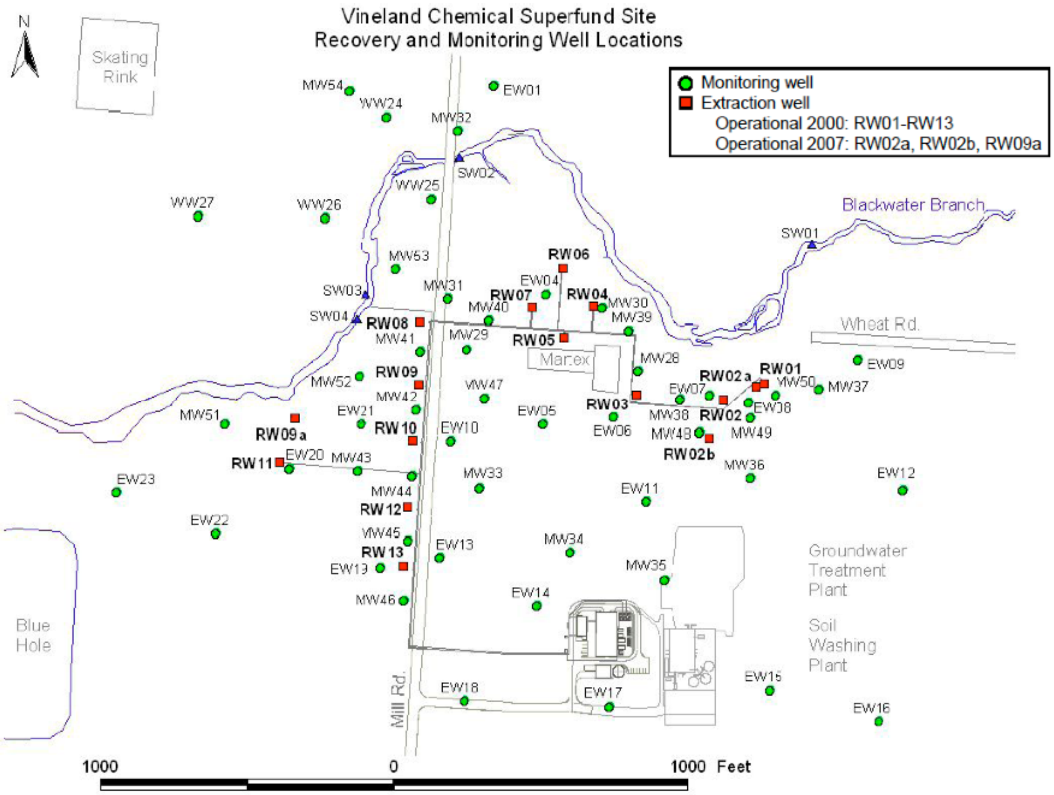


Figure 1.3. Monitoring well and extraction well locations on the Vineland site (USACE, 2007).

USACE, 2007. Classification Exception Area and Well Restriction Area Report. Vineland Chemical Company Superfund Site, Vineland, NJ., Prepared for USEPA, Region II.

1.12 Appendix

1.12.1 History of production and remediation activities at Vineland Chemical

Vineland Chemical began production of organoarsenicals in 1949 and stopped in 1994, a few years after the death of the company's owner. Currently (2010) the site is undergoing extensive remediation to deal with the contamination resulting from poor chemical handling practices during manufacturing operations. Below is a timeline of events concerning As contamination, intervention and remediation from the company's inception to the present day.

Table 1.3. Timeline of production and remediation activities at the Vineland site

Year	**Month**	**Who**	**What**
1949		ViChem	Began manufacture of organoarsenical biocides
1965	May	Vineland Health Department	Requested that the NJ Occupational Health Program inspect ViChem (nothing very serious listed in the violations)
1966	January	NJDEP	Discovered ViChem was releasing untreated wastewater into unlined lagoons with As concentrations of ~67 mg/L
1971	January	NJDEP	Ordered ViChem to deal with air pollution issues
1971	February	NJDEP	Ordered ViChem to install wastewater treatment and/or disposal facilities
1975	October	NJDEP	Performed "Macroinvertebrate Analysis" in BWB and found evidence of a stressed ecosystem

1975		ViChem	Began fixing waste salts by mixing with ferric chloride and soda ash to decrease solubility; fixed wastes were sent to Kin-Buc Landfill
1976		Kin-Buc Landfill	Stopped accepting all chemical wastes. Vichem resumed disposing of waste salts in piles on site.
1977	January	US Supreme Court	Ordered removal of waste salts from piles and chicken coops for storage in drums in off site warehouse. ViChem complied.
1977	May		Potable wells near ViChem tested for As content; one well owner was told not to use his well water for drinking or irrigation as it contained ~2 mg/L As
1977	September	OSHA	Investigated the site following complaint by a worker; among the violations – lunchroom contaminated with arsenic
1977	November	ViChem	Began sending wastes from the warehouse to the Robert H. Grove Landfill
1978	June	ViChem	Hired a consulting company to examine the groundwater plume (part of one the court orders); plume is delineated and well placement for wastewater treatment is suggested
1979	January	NJDEP	Approved plans for ViChem waste treatment plant

1979	June	US Supreme Court	Ordered disposal of drums in approved landfill.
1979	July	Vineland Mayor	Closed the Almond Rd beach on the Maurice River following a newspaper story detailing the As contamination of the watershed
1979	July		Heavy rains caused overflow of a lagoon at ViChem; lagoon waters flowed onto the floodplain of Blackwater Branch
1979	September		Starting in Sept 1979, aerial photos of the site showed evidence of vegetative damage and vegetative stress along Blackwater Branch
1979			Soil survey on site (surface and at depth) showed As concentrations ranged from undetected to 864 mg/kg
1980	March	ViChem	Began operation of wastewater treatment facility
1981			Geophysical survey on site estimated 40 ft (12 m) as the maximum probable depth of As plume
1982			ViChem employee was diagnosed with subacute As poisoning; other employees showed elevated hair and urine As concentrations but showed only minor symptoms associated with As trioxide dust on skin and mucous membranes.
1982	July	ViChem	Sent remaining drums to licensed facility for

			disposal.
1984		EPA	Listed ViChem as a Superfund site
1985-1986			Beavers constructed a dam on Blackwater Branch leading to flooding with As contaminated waters and deposition of As containing sediments in the floodplain
1987			Beaver dam was removed
1988		EPA	Conducted a Remedial Investigation/Feasibility Study to examine the site contamination as well as evaluate plans for remediation.
1989		EPA	Record of Decision for Vineland Chemical was filed detailing a plan for remediation.
1990	October	ViChem	Slowed biocide production following the death of the company's owner.
1991		NJDEP	Investigated complaints by residents near ViChem regarding a garlic odor – which could have resulted during cleaning of a tank in building #9; it is likely the odor resulted from unwitting production of the highly toxic arsine gas. Building #9 was sealed and signs posted.
1992-1993		EPA	Secured buildings and chicken coops and installed fences around the high As areas on site and around the site, removed hazardous

			chemicals in storage.
1994		ViChem	Ceased production and abandoned site.
1995		EPA/USACE	Completed demolition and removal of 8 highly contaminated buildings
1997	September	Black & Veatch	Received the contract to construct a new groundwater pump and treat remediation system
2000	Spring	EPA	Began operation of the pump and treat system
2001	September	EPA	Published Explanation of Significant Differences which detailed a change from soil flushing to soil washing as part of the remediation effort, contract awarded for construction of soil washing plant.
2004		EPA/USACE	Began full-scale operation of soil washing plant.
2004	Spring	EPA/USACE	Demolished/removed 2 remaining site buildings.
2006		EPA/USACE	Installed 3 additional pump and treat wells to aid in plume capture.
2006		EPA/USACE	Began remediation in the flood plain area of Blackwater Branch (from the site to point where BWB meets Maurice River); this has included excavating and cleaning sediments in the flood plain as well as redirecting the stream and cleaning sediments beneath it.
2007		EPA/USACE	Completed soil washing of the vadose zone

			sediments near the former manufacturing areas of the site.
2007	December	EPA/USACE	Completed 1st phase of flood plain clean up (east of Mill Rd); 2nd phase begun
2011		EPA/USACE	Investigation of Maurice River and Union Lake sediments to be started
Future		EPA/USACE	Hand-over of pump and treatment operations to the state of NJ

From: (EPA, 1989; 2001; 2010; Funderburk, 2009; OSR, draft)

1.12.2 References

EPA, 1989. Record of Decision, Vineland Chemical Co., Inc.

EPA, 2001. Vineland Chemical Superfund Site. Explanation of Significant Differences. EPA/ESD/R02-01/555.

EPA, 2010. Vineland Chemical Co., Inc National Priority List site fact sheet update. http://www.epa.gov/Region2/superfund/npl/0200209c.pdf.

Funderburk, K., 2009, Officials: Superfund site progress slow, but effective, in *The Daily Journal*, edited, Vineland, NJ.

OSR. draft. Arsenic in the Maurice River: Aquatic studies of the environmental fate and chemical transformations of industrial arsenic contaminating the Maurice River. In: Environmental Fate, Belton, T.J. (Ed.) vol. I.

CHAPTER 2
Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation

Wovkulich, K., Mailloux, B.J., Lacko, A., Keimowitz, A.R., Stute, M., Simpson, H.J., Chillrud, S.N., 2010. Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation. Appl. Geochem. 25, 1500-1509.

2.1 Abstract

Arsenic is a prevalent contaminant at US Superfund sites where remediation by pump and treat systems is often complicated by slow desorption of As from Fe and Al (hydr)oxides in aquifer solids. Chemical amendments that either compete with As for sorption sites or dissolve Fe and Al (hydr)oxides can increase As mobility and improve pump and treat remediation efficiency. The goal of this work was to determine optimal amendments for improving pump and treat at As contaminated sites such as the Vineland Chemical Co. Superfund site in southern New Jersey. Extraction and column experiments were performed using As contaminated aquifer solids (81 ± 1 mg/kg), site groundwater, and either phosphate ($NaH_2PO_4 \cdot H_2O$) or oxalic acid ($C_2H_2O_4 \cdot 2H_2O$). In extraction experiments, phosphate mobilized between 11% and 94% of As from the aquifer solids depending on phosphate concentration and extraction time (1 mM-1 M; 1-24 h) and oxalic acid mobilized between 38% and 102% depending on oxalic acid concentration and extraction time (1-400 mM; 1-24 h). In column experiments, phosphate additions induced more As mobilization in the first few pore volumes but oxalic acid was more effective at mobilizing As overall and at lower amendment concentrations. At the end of the laboratory column experiments, 48% of As had been mobilized from the aquifer sediments with 100 mM phosphate and 88% had been

mobilized with 10 mM oxalic acid compared with 5% with ambient groundwater alone. Furthermore, simple extrapolations based on pore volumes suggest that chemical treatments could lower the time necessary for clean up at the Vineland site from 600 years with ambient groundwater alone to potentially as little as 4 years with 10 mM oxalic acid.

2.2 Introduction

2.2.1 Background

Arsenic is present at more than 500 US Superfund sites and is the second most common contaminant of concern after Pb (EPA, 2002; 2007). Elevated groundwater As can be the result of mobilization of As naturally occurring in minerals, sediments, and soils or the result of anthropogenic inputs from As-based biocides, swine and poultry farming, mine tailings, coal combustion, wood treated with chromated copper arsenate, etc. (Leist, et al., 2000; Mandal and Suzuki, 2002; Oremland and Stolz, 2003; Smedley and Kinniburgh, 2002). Sites with contaminated groundwater commonly use pump and treat remediation technologies (Mackay and Cherry, 1989; Palmer and Fish, 1992). However, aquifer conditions (pH, oxidation-reduction potential, etc.) impact As mobility and the slow desorption of As from Fe and Al (hydr)oxides in solids can decrease the effectiveness of pump and treat systems (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Chemical amendments have the potential to accelerate As mobilization from soils and sediments and thus improve the efficiency of pump and treat remediation (Palmer and Fish, 1992). By increasing As mobilization, more As contaminant would be removed from the aquifer system with each volume of groundwater extracted by the pump and treat system. This study examines the potential impact of phosphate and oxalic acid to accelerate As release from contaminated aquifer solids using laboratory extraction and column experiments.

Pump and treat is a widely used remediation option; the US EPA estimates there are more than 700 such systems in operation in the USA (EPA, 2003). However, pump and treat remediation can sometimes require decades to reach target clean up levels and systems tend to have high operation and maintenance costs; in a recent survey, the mean annual cost per site was $570,000 for 79 sites reporting costs (EPA, 2001; 2003; Palmer and Fish, 1992). During remediation, the rate of decline in contaminant concentration can progressively decrease, a phenomenon sometimes referred to as tailing, making it difficult to reach target cleanup levels even with long treatment times (Kuhlmeier, 1997; Mackay and Cherry, 1989; Palmer and Fish, 1992). At sites where contaminant removal from the aquifer is controlled largely by chemical processes (adsorption, precipitation), it may be possible to enhance pump and treat remediation by altering aquifer chemistry (Palmer and Fish, 1992). Arsenic mobility can depend on adsorption-desorption reactions between As and Al, Fe, and Mn oxides in soils and sediments; these sorption processes can be impacted by a variety of factors including As speciation, pH, groundwater oxidation-reduction potential, microbial activity, and the presence of chemical species such as anions or ligands (EPA, 2002; Kuhlmeier, 1996; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Here the focus is on adding chemical species in order to increase As mobilization with the ultimate goal of improving the pump and treat operation efficiencies at As contaminated Superfund sites. The presence of various chemical anions or ligands can promote As release by competing with As for soil and sediment sorption sites or can lead to complexation reactions that mobilize As (Darland and Inskeep, 1997; Hongshao and Stanforth, 2001; Klarup, 1997; Panias, et al., 1996; Tao, et al., 2006; Zeng, et al., 2008). Though it is recognized that chemical additions could positively impact pump and treat remediation (i.e., the principles behind the methods are understood), the authors know of few other studies that have investigated potential applications of chemical additions at sites contaminated with As (Keimowitz, et al., 2005b; Palmer and Fish, 1992).

Two promising chemical amendments for As release are phosphate ($NaH_2PO_4 \cdot H_2O$) and oxalic acid ($C_2H_2O_4 \cdot 2H_2O$), both of which are often included in As sequential soil extraction schemes (Keon, et al., 2001; Swartz, et al., 2004; Wenzel, et al., 2001). Phosphate and arsenate are chemically analogous and numerous studies have shown that the presence of phosphate inhibits the adsorption of arsenate (As V) and arsenite (As III) by competing for suitable surface binding sites in soils and sediments and on Al and Fe (hydr)oxides (Darland and Inskeep, 1997; Dixit and Hering, 2003; Jain and Loeppert, 2000; Jeong, et al., 2007). Additionally, phosphate fertilizers have been shown to increase As release from orchard soils that were previously treated with lead arsenate pesticides (Peryea, 1991). Oxalic acid is a low molecular weight organic acid found naturally in soil solutions, typically at concentrations of 0-50 μM but has been observed at concentrations as high as 1 mM (Fox and Comerford, 1990; Strobel, 2001; van Hees, et al., 2000). Oxalic acid is effective at dissolving Al and Fe (hydr)oxides and is involved in the vertical transport of Al and Fe in soils (van Hees, et al., 2000). Arsenic is often associated with or adsorbed to Al and Fe (hydr)oxides (De Vitre, et al., 1991; Jain and Loeppert, 2000; Sullivan and Aller, 1996); therefore, oxalic acid treatments should mobilize As co-precipitated or associated with amorphous Al and Fe (hydr)oxides (Keon, et al., 2001). A study by Zhang et al. showed that As mobilization by low molecular weight organic acids (including oxalic) was significantly correlated with Fe, Al, and Mn mobilization in extraction experiments; they suggested a possible mechanism of As release from Fe, Al, and Mn (hydr)oxides (Zhang, et al., 2005). Other studies suggest low molecular weight organic acids may lead to As release through competitive sorption mechanisms or suggest that both mechanisms may play a role (Shi, et al., 2009).

Through extraction and column experiments the ability of phosphate and oxalic acid for mobilizing As from contaminated aquifer solids was explored. Extractions were performed first and used to guide the design of column experiments. All experiments were performed with aquifer solids from the Vineland Superfund site. Though the chemical mechanisms are different, both phosphate and oxalic acid have the potential to increase As mobilization, making these chemical amendments promising candidates for accelerating pump and treat remediation at As contaminated sites.

2.2.2 Site overview

The Vineland Chemical Company site is located in southern New Jersey, overlying the unconsolidated sands of the Cohansey Formation, which are interbedded with thin silt and clay layers. The Vineland Chemical Company produced As-based biocides from 1950-1994, during which time hundreds of tons of waste As were released into the environment due to improper chemical storage and disposal practices (EPA, 2006; Keimowitz, et al., 2005c). This resulted in extensive contamination of subsurface solids and groundwater with both organic and inorganic As species. Prior to the start of treatment groundwater concentrations exceeded the current US EPA drinking water standard for As (10 μg/L) by up to three orders of magnitude. Discharge to an adjacent stream, Blackwater Branch, caused significant contamination of the stream's floodplain as well as bottom sediments of the nearby Maurice River and Union Lake (EPA, 2006). Site remediation includes a large groundwater pump and treat facility, designed to treat up to 7.5×10^6 L/d (2 million gallons), as well as excavating, cleaning, and replacing unsaturated zone sands and flood plain area soils. The pump and treat system has an estimated annual operation and maintenance cost of $4 million (EPA, 2001). Soil washing at the Vineland Superfund site has significantly decreased the amount of As in the unsaturated zone; contaminated unsaturated zone sediments (~0-4.6 m below ground surface) in the former "hot" zone had a maximum >500 mg As/kg while cleaned sediments have As concentrations of <20 mg/kg. In comparison, offsite samples suggest that a representative background As concentration of these sandy sediments is less than 5 mg/kg. Only unsaturated zone sediments and the top 0.3-1 m of materials found below the water table were treated at the soil washing plant (maximum excavation to depths of ~4.9-5.6 m below ground surface). Since aquifer materials below this depth can still have elevated As, with typical As concentrations of 20-250 mg/kg, this reservoir of As can continue to contaminate the groundwaters; recent measurements at the recovery wells show As concentrations can still be several hundred μg/L.

2.3 Methods

2.3.1 Field methods

Aquifer solids were obtained from a pit freshly dug down below the water table with a backhoe in the most contaminated region of the site (with As concentrations in the aquifer sediments typically 20-250 mg/kg). This section of the site is composed of medium to coarse-grained sands. The subsurface materials are largely oligotrophic and composed of quartz sand with a thin layer of topsoil or fill in places. At the time of sampling, the majority of the unsaturated zone sediments had been removed from the most contaminated region of the site to be processed to remove As at a soil washing facility; the backhoe removed the remaining ~1 m depth of the unsaturated zone before sampling the aquifer sediments. The sandy aquifer solids were sealed in new metal paint cans (0.004 m^3 each) and kept refrigerated until use. Groundwater for the column experiments was collected from a pump and treat well (RW 11) approximately 500 m from the sediment collection location; previous sampling suggested this well had low As and low Fe concentrations (7 μg/L and 230 μg/L, respectively). Groundwater parameters (pH, oxidation-reduction potential, electrical conductivity, and dissolved O_2) were monitored and allowed to stabilize to ensure the well was sufficiently flushed before collecting water in plastic cubitainers (Fisher Scientific). The water was allowed to equilibrate with the atmosphere for several days before moving it to cold storage to minimize subsequent microbial activity.

2.3.2 Extraction experiments

Approximately 2 g of wet contaminated aquifer sediment (~80 mg/kg in As), equivalent to an average of ~1.9 g dry sediment, was combined with 10 mL of the desired extraction solution. The following solutions were used in separate extraction trials: 1 mM, 100 mM, and 1 M sodium phosphate monobasic monohydrate ($NaH_2PO_4{\cdot}H_2O$) and 1 mM, 10 mM, 100 mM, and 400 mM oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$). The pH of each solution was measured (Figure 2.1) but not adjusted. Samples were extracted for 1, 2, 4 or 24 h and were agitated on an adjustable rocker table (Cole-Parmer). Suspensions were centrifuged at 3000 rpm (Damon/IEC Division) for 10 min and the supernatants were decanted into acid washed bottles. Additional batch experiments were carried out to test the efficacy of increasing pH or inducing reducing conditions on the mobilization of As from Vineland aquifer sediments (see Supplementary Information).

2.3.3 Column experiments

Contaminated aquifer sediments were used for the five column experiments. The sandy aquifer materials were wet packed into a section of Geoprobe Macro-Core® liner approximately 25 cm x 4.2 cm ID. Glass wool (0.25-1.5 cm) was packed into each end to help distribute solution over the full cross sectional area of the column; the columns were sealed with PVC end caps. The columns were run in upflow mode at 2-3 m/d using a peristaltic pump (Rainin Instrument Co.) to control the flow rate. The flow velocity was in the range of estimated average groundwater flow under the study site during active pumping for treatment (estimate based on site dimensions and pump and treat plant design parameters). For initial experiments, solutions of ambient groundwater (column 1), ~1 mM phosphate in groundwater (column 2), and 1 mM oxalic acid in groundwater (column 3) were pumped through separately prepared columns for ~3 days (between 22 and 34 pore volumes depending on the column). Once results from those experiments were obtained, two other column experiments were designed, one involving introduction of a 100 mM phosphate solution in groundwater in three pulses of ~2 pore volumes each and groundwater washes between each pulse (column 4), and the other involving an influent solution of 10 mM oxalic acid in groundwater for ~21 pore volumes, followed by several more pore volumes of groundwater alone (column 5). A Br tracer test was used to constrain the porosity of each column. Bromide was measured with a portable Br electrode (Thermo Scientific); effective porosity was calculated using bromide breakthrough curves and was estimated to be 0.27-0.33 depending on the column (typical porosity values at the field site are 0.2-0.4). The average influent As concentration was <10 μg/L for all experiments. For all oxalic acid and phosphate trials, unamended groundwater was flowed through the column initially until the effluent was visually clear of fine solids, at least ~1.4 pore volumes. Effluent samples were collected and monitored for pH and electrical conductivity, trace metals, and anions. A fraction collector (LKB Bromma) was used to collect effluent samples for the oxalic acid and phosphate trials (columns 2-5). Trace metal samples were acidified to 1% acid using either HCl (groundwater alone, 1 mM oxalic acid, and 1 mM phosphate columns) or HNO_3 (10 mM oxalic acid and 100 mM phosphate columns) and filtered through a 0.45 μm PES syringe filter (Whatman) prior to analysis; the acid used (HCl vs. HNO_3) should not impact the results as the goal for preserving the samples was to lower the pH below 2 (EPA, 1996; van Geen, et al., 2003). Anion samples were filtered through a 0.45 μm PES syringe filter into non-acid washed bottles.

2.3.4 Sediment digests

Samples of contaminated aquifer solids (N=5) were digested using HNO_3, H_3ClO_4, and HF and analyzed for total As, Fe, Al and Mn concentration (Fleisher and Anderson, 1991). After completion of the 100 mM phosphate column (column 4) and 10 mM oxalic acid (column 5) experiments, the columns were divided into 2-3 cm sections (10-11 sections per column) and one sample per section (~2 g dry) was digested and analyzed to evaluate the distribution of As along the columns following the experiments.

2.3.5 Analytical techniques

Samples were analyzed for As, Fe, Mn Al, S, and P content using inductively coupled plasma mass spectrometry (ICP MS) with a high-resolution Axiom Single Collector instrument (Thermo Elemental, Germany). In-115 was added to each sample as an internal response standard and was used to correct for instrument drift prior to quantification. ^{27}Al, ^{31}P, ^{34}S, ^{55}Mn, ^{57}Fe, ^{75}As and ^{115}In were determined with the instrument set at >8500 resolving power, which is sufficient to resolve the ^{75}As peak from $Ar\text{-}Cl^+$ interference. Each sample and standard was run three times and averaged. Three to four point calibration curves were run at least once every 30 samples; calibration curves used for analysis of the data presented here had $R^2 > 0.98$.

Samples were analyzed for oxalic acid concentrations using a Dionex ICS-2000 (Sunnyvale, CA) ion chromatography system with an IonPac AS-11 HC column. Samples were run in gradient mode with eluent concentrations increasing from 5 to 60 mM KOH over the course of the sample run. Four point calibration curves were used for quantification; calibration curves used for analysis had $R^2>0.99$.

X-ray diffraction (XRD) was performed at The Mineral Lab, Inc (Lakewood, CO). The detection limit for an average mineral is ~1-3%.

Arsenic X-ray absorption near edge spectroscopy (XANES) was performed at the Stanford Synchrotron Radiation Lightsource (Palo Alto, CA) on beam line 11-2.

2.4 Results

2.4.1 Aquifer sediment characterization

Complete digestion of the aquifer sediments collected for these experiments averaged (±1 standard deviation): total As = 81 ± 1 mg/kg (N=5), total Fe = 1050 ± 180 mg/kg (N=5), total Al = 1070 ± 110 mg/kg (N=3), and total Mn = 12 ± 2 mg/kg (N=5). All subsequent calculations of percent of an element mobilized from the aquifer solids are based on these average concentrations. Based on X-ray diffraction (XRD) measurements, both the bulk and clay-sized fraction of the aquifer sediment samples are >95% quartz with the remaining <5% unidentified. X-ray absorption near edge spectroscopy (XANES) indicates that As in these aquifer solid samples may be >95% arsenate.

2.4.2 Extraction experiments

In the phosphate batch experiments, 1 mM phosphate extractions mobilized 11-20% of As, 100 mM mobilized 32-50%, and 1 M mobilized 89-94% of As from the aquifer solids depending on extraction time (Figure 2.1). Increasing extraction time led to increased As release for 1 mM and 100 mM trials; 1, 2, and 4 h extractions all yielded 89-90% As release for the 1 M extractions. Less than 5% of the Fe was released during these extractions, less than 2% of the Mn was released, and Al was not measured (Fe and Mn data not shown).

In the oxalic acid batch experiments, 1 mM oxalic acid extractions mobilized 38-56% of As from the aquifer sediment, 10 mM mobilized 83-93%, 100 mM mobilized 86-99%, and 400 mM mobilized 90-102% of the As (Figure 2.1). Arsenic release increased with extraction time. Although oxalic acid is known to be effective at dissolving Fe and Al (hydr)oxides (van Hees, et al., 2000), the % Fe and Al mobilized tended to be low. Less than 7% of the Fe was mobilized in the 1 and 2 h extractions. The amount of Fe mobilized was 12% or less except for the 24 h extractions with 100 mM and 400 mM oxalic acid where the Fe mobilized from the aquifer solids was 27% and 41%, respectively. Additionally, the amount of Al mobilized was less than 19% except for the 24 h extractions with 100 mM and 400 mM oxalic acid where the Al mobilized was 27% and 29%, respectively. The amount of Mn mobilized was always 6% or less (Fe, Al, and Mn data not shown).

2.4.3 Groundwater column

Column experiment 1 using ambient groundwater from the site was performed to establish a baseline of As mobilization with no amendments. The effluent As concentration started high, approximately 6000 μg/L, but dropped below 1000 μg/L after 9 pore volumes and continued to fall through the rest of the experiment (Figure 2.2a). The As release rate had stabilized after 9 pore volumes and As concentration began to stabilize at 270 μg/L by the end of 29 pore volumes. The effluent pH decreased from ~8 to ~5.5 over the course of the experiment; influent pH increased from 4.8 to 5.5, presumably as the influent water equilibrated with atmospheric CO_2.

2.4.4 Phosphate columns

During the ~1 mM phosphate trial (column 2), unamended groundwater was flowed through the column for 1.6 pore volumes, followed by phosphate for the remainder of the experiment. The effluent P concentrations leveled off to match the influent concentration at 5.4 pore volumes (data not shown). The actual influent phosphate concentration was 0.85 mM based on P data from the ICP MS. Approximately 90% of the influent P was captured in the effluent. The effluent As concentrations increased to ~21,000 μg/L, with a peak at 3.5 pore volumes, soon after initially introducing the phosphate solution to the column (Figure 2.2b). Effluent As then decreased and remained below 2000 μg/L from 8.5 pore volumes until the end of the experiment. The effluent pH decreased from ~7.1 to 5.6 over the course of the experiment; influent pH was between 4.8 and 4.9.

Because of the decrease in effectiveness for removing As after ~5 pore volumes with the ~1 mM phosphate treatment, two changes were introduced for the subsequent phosphate column (column 4). The influent phosphate concentration was increased to 100 mM and the phosphate solution was introduced to the column as three pulses with groundwater washes between each pulse. The shaded areas in the background of Figure 2.2b show the timing of the phosphate pulses. The effluent P showed three peaks, one for each pulse of phosphate introduced (data not shown). Comparison of influent and effluent P data indicates that there was no significant adsorption of P to the solids in this experiment. A peak in effluent [As] occurred following each introduction of phosphate. The first pulse of phosphate started at 1.5 pore volumes and the peak in As occurred at 2.7 pore volumes with an effluent [As] of ~120,000 μg/L. The second pulse of phosphate started at 11.0 pore volumes and the peak in As occurred at 12.5 pore volumes with an effluent [As] of ~29,000 μg/L. The third pulse of phosphate started at 20.2 pore volumes and the peak in As occurred at 21.7 pore volumes with an effluent [As] of ~16,000 μg/L. The effluent pH started at 7.2 but varied between 6.1 and 4.6 for the rest of the experiment; the pH of the phosphate influent was ~4.2 and the pH of the groundwater influent was ~5.7.

2.4.5 Oxalic acid columns

During the 1 mM oxalic acid column (column 3), unamended groundwater was flowed through the column for 1.6 pore volumes followed by 1 mM oxalic acid for the remainder of the experiment. Approximately 85% of the oxalic acid introduced to the column was collected in the effluent. Effluent As concentrations showed a small peak at ~4.1 pore volumes with a concentration of ~2700 μg/L and then fell to ~2000 μg/L (Figure 2.2c). The [As] began to increase substantially from ~7 to 13 pore volumes; for the remainder of the experiment, [As] was ~8000-10,000 μg/L. Iron and Al data are also shown with the 1 mM oxalic acid column (column 3) because oxalic acid was expected to mobilize these elements. The effluent Al increased rapidly after 3.7 pore volumes and remained above 13,000 μg/L from 6.0 pore volumes through the rest of the experiment (Figure 2.3). The Fe concentration started relatively low, less than 200 μg/L, until about

15 pore volumes at which time the concentration began to increase and finally leveled off ~8000 µg/L at ~30 pore volumes (Figure 2.3). Amounts of Fe and Al mobilized from the aquifer sediments by the end of the experiments were 1% and 8%, respectively. There was also little Mn release (<1%) from the solids. The effluent pH decreased from 7.2 to 3.6 over the course of the experiment; influent pH was between 2.9 and 3.0 for the duration of the experiment.

Based on the extraction data, increasing oxalic acid concentrations above 10 mM made little additional improvement in terms of fraction of As mobilized; therefore, the 10 mM concentration was chosen for the next oxalic acid column (column 5). For this experiment (Figure 2.2c), unamended groundwater was flowed through the column until 1.5 pore volumes, followed by 10 mM oxalic acid until 21.1 pore volumes, and then unamended groundwater again. Approximately 99% of the influent oxalic acid was recovered in the effluent. The effluent As concentration peaked at 5.8 pore volumes with a maximum of nearly 100,000 µg/L. The effluent [As] decreased below 2000 µg/L after 14 pore volumes. At the end of the experiment (30 pore volumes), the effluent As concentration stabilized around 40 µg/L; 88% of the As had been mobilized. Effluent Fe and Al (data not shown) also exhibited peaks in concentration following the introduction of 10 mM oxalic acid; effluent Fe reached a maximum of ~100,000 µg/L at 5.8 pore volumes and effluent Al reached a maximum of ~150,000 µg/L at 4.4 pore volumes. Due to instrumental limitations, the Al data for this column has greater uncertainty; several samples exceeded the replicate %RSD threshold for acceptance of 10%. Therefore, the Al numbers for this one column should only be used as a first-order guide. Effluent Fe and Al concentrations remained above 10,000 µg/L until the influent was switched to ambient groundwater. Though effluent As and Fe reached their maximum values at the same time, the initiation of As release preceded that of Fe release. Based on effluent concentrations, total percentages of Fe and Al mobilized were 9% and 16%, respectively. Since 98% of the influent Mn was recovered in the effluent, there was no indication of Mn release from the sediment. The effluent pH fell from 6.5 to 2.2 after the introduction of the 10 mM oxalic acid and increased to pH 4, within the range found at the Vineland site, after 8 pore volumes of groundwater had been washed through the column. The 10 mM oxalic acid influent solution had pH 2.2 and the pH of the groundwater influent was 5.8.

2.4.6 Cumulative percentage As mobilized

At the end of the experiments, 5% of the As was mobilized from the aquifer solids after 29 pore volumes with ambient groundwater (column 1), 12% after 22 pore volumes with ~1 mM phosphate (column 2), 44% after 34 pore volumes with 1 mM oxalic acid (column 3), 48% after 28 pore volumes with pulsed 100 mM phosphate (column 4), and 88% after 30 pore volumes with 10 mM oxalic acid (21 pore volumes) and groundwater (9 pore volumes) (column 5). The ~1 mM phosphate column had a higher cumulative percentage As mobilized than the 1 mM oxalic acid column until 14 pore volumes, beyond which 1 mM oxalic acid values were higher (Figure 2.4). The 100 mM phosphate had higher cumulative percentage As mobilized than the 10 mM oxalic acid until 5 pore volumes, after which the 10 mM oxalic acid values were always higher (Figure 2.4). Samples prior to ~1.4 pore volumes, before the effluent solution was clear of fine particles, were not included in the percentage mobilization calculations.

After the 100 mM phosphate (column 4) and 10 mM oxalic acid (column 5) experiments were complete, sediment was separated into approximately 2-3 cm sections and one sample (~2 g dry) from each section was digested and analyzed for total As content. The average As concentration after the 100 mM phosphate experiment was 45.2 mg/kg with a standard deviation of 5.7 mg/kg, indicating 44% of the As had been removed from the aquifer sediment. The average As concentration after the 10 mM oxalic acid experiment was 8.5 mg/kg As ±1.5 mg/kg; 89% of the As had been removed from the aquifer solids. The results for percentage mobilization obtained from the solids data agree well with percentages estimated from the effluent solution data for As. However, variability in solid Fe, Al and Mn concentrations in the starting aquifer material, together with the relatively small amount of mobilization of these elements during the 10 mM oxalic acid column experiment, indicates it may be better to assess the mobilization with effluent solution chemistry; solution chemistry suggested 9% Fe mobilization,16% Al mobilization and 0% Mn**.**

2.5 Discussion

2.5.1 Description of supporting information

In addition to the extraction and column experiments discussed here, mobilization of As was also investigated by stimulating microbial respiration to induce reducing conditions (28 day and 49 day incubations) and by incrementally increasing pH in a batch reaction vessel from 4.1 to 9.4 to maximize the electrostatic repulsions between arsenate and surface binding sites. These methods and results are reported in the Supporting

Information. A much higher degree of As mobilization was generally achieved using chemical amendments than for microbial respiration or pH adjustment experiments.

2.5.2 Batch extraction experiments

At the same molar concentrations, oxalic acid extractions consistently mobilized a higher percent of As from the aquifer sediment than phosphate extractions. The 1 mM oxalic acid extractions mobilized more As (38-56%) than the 100 mM phosphate extractions (32-50%). Greater than 80% As mobilization was achieved with 10 mM oxalic acid or 1 M phosphate suggesting that addition of oxalic acid or phosphate could lead to significant increases in As release from contaminated sediments. The greater effectiveness of oxalic acid at lower concentration may be attributed to differences in the mechanism or kinetics of mobilization. While phosphate acts through anion exchange for arsenate and arsenite species, oxalic acid is thought to complex and dissolve Fe and Al, thereby also dissolving any As that is co-precipitated with or adsorbed to Fe and Al (hydr)oxides (though competitive sorption mechanisms may also play a role in As release by oxalic acid).

In batch and column experiments, Darland and Inskeep show that adsorption of phosphate or arsenate can be slow to reach equilibrium even though the actual chemical adsorption step is quick (milliseconds) and suggest that the kinetics of phosphate exchange for arsenate may be limited by arsenate desorption (Darland and Inskeep, 1997). In the phosphate extractions presented here, As release increased with extraction time suggesting that an equilibrium state may not yet have been attained and perhaps further As mobilization would occur with longer extraction times. Additionally, phosphate may not entirely out-compete arsenate for binding sites even when phosphate concentrations exceed the calculated binding site capacity (Darland and Inskeep, 1997). This idea is mirrored by Jain and Loeppert who performed batch adsorption experiments on ferrihydrite and suggest that while some adsorption sites are common to both phosphate and arsenate, some are more suited to one or the other (Jain and Loeppert, 2000). Other batch sorption studies have shown that arsenate can bind more strongly than phosphate on goethite (Hongshao and Stanforth, 2001). It is possible therefore that some binding sites in the Vineland aquifer materials favor As species over phosphate, and until there is an extremely large excess of phosphate (1 M phosphate or more) there is not complete exchange.

Previous studies have shown a positive correlation between As mobilized by low molecular weight organic acids (0-10 mM, including oxalic) and mobilized Fe, Al, and Mn; Zhang et. al. suggested that the As was released from Fe, Al and Mn (hydr)oxides (Zhang, et al., 2005). In the oxalic acid extractions presented here (1-400 mM), there was also a positive correlation between mobilized As and mobilized Fe, Al, and Mn at each extraction time. The R^2 values for the 1 and 2 h extractions fit with linear regressions were all >0.8 (except the relationship between Mn and As in the 1 h extraction where R^2=0.48 which may be related to the low overall percentage of Mn mobilized). The 24-h extractions also showed a positive correlation but were better fit by exponential curves and had $R^2 \geq 0.75$. The batch extraction data are consistent, therefore, with As mobilization occurring as a result of Fe, Al, and Mn (hydr)oxide dissolution despite the low percentages of Fe, Al and Mn mobilized. However, the oxalic acid column data discussed later call this simple mechanism into question.

Even though oxalic acid was shown to be more effective at mobilizing As than phosphate at lower concentrations in the extraction experiments, the applicability of these experiments to *in situ* conditions is hindered by the low solid to water ratio (1:~5). This concern was addressed using column experiments.

2.5.3 As release from phosphate columns

In the ~1 mM phosphate column (column 2), the effluent As concentration increased rapidly shortly after the introduction of phosphate; the peak was at 3.5 pore volumes with a concentration of ~21,000 μg/L. The effluent As concentration decreased quickly but still remained higher than the effluent As concentrations of the unamended groundwater column (column 1), indicating greater As removal from the system compared with groundwater alone. Similar results have been seen in other studies involving a sand column treated with arsenate first and then phosphate; there was a peak in effluent As after phosphate was introduced but the effluent As concentration began to show tailing after ~5 pore volumes (Darland and Inskeep, 1997). While the two experiments were somewhat different in design, both show a decrease in effluent As concentration even with continuous phosphate input. This decrease in As mobilization may indicate that the remaining As was adsorbed more strongly and/or that some of the available binding sites were more suited to As species than phosphate. The incomplete exchange of phosphate for arsenate may also suggest a kinetic limitation for As desorption (Darland and Inskeep, 1997). Despite the incomplete exchange of phosphate for arsenate, both phosphate columns discussed in this paper, ~1mM phosphate (column

2) and 100 mM pulsed phosphate (column 4), showed increased As release compared to groundwater alone (column 1).

2.5.4 Phosphate adsorption

Previous studies have shown that Fe and Al (hydr)oxides can be significant sinks for phosphate (Darke and Walbridge, 2000). Our results show that in this system and with the concentrations of phosphate used here, there was minimal phosphate adsorption. Effluent P concentrations quickly approached their influent levels after introduction of phosphate solutions (data not shown) suggesting fast exchange of phosphate for arsenate on surface sites. The lack of phosphate adsorption limits concerns over nutrient pollution and subsequent eutrophication of downstream surface water bodies in hydrological systems controlled by pump and treat; the phosphate would be collected and processed by the pump and treat operation, leaving little residual phosphate in the aquifer system. It is reiterated, however, that the authors are only considering use of these types of chemical amendments *in situ* at sites that currently use pump and treat technologies to ensure capture of amendments and mobilized As.

2.5.5 As mobilization and Fe, Al, and Mn release from oxalic acid columns

Arsenic, Fe and Al were all mobilized by the oxalic acid treatments. Both oxalic acid columns (column 3 and 5) showed substantial release of As compared with groundwater alone (column 1) (Figures 2.2 and 2.4). In the 1 mM oxalic acid column, the order of element release occurred as Al, then As, then Fe. The effluent Al concentration began to increase after ~3.7 pore volumes, the effluent As concentration had a small peak around 4.1 pore volumes then began to increase substantially after ~7.6 pore volumes, and finally the effluent Fe concentration began to increase after ~17.5 pore volumes (Figure 2.3). The order of element release was the same for the 10 mM oxalic acid column (though there was no visible small peak in As before the large increase), however, the process was accelerated and the maximum effluent concentrations were ~10x higher due to the higher concentration of oxalic acid. The relative timing of Al and Fe release, Al early and Fe later, may be related to the differences in the mechanisms of Al and Fe mobilization by oxalic acid (Li, et al., 2006; Panias, et al., 1996). The relative timing may also indicate that the Al (hydr)oxides in these aquifer materials were more amorphous and thus more easily dissolved than the Fe (hydr)oxides. Since the oxalic acid treatment performed here mimics soil podzolization to an extreme degree, the earlier release of Al than Fe could be thought of in terms of the proto-imogolite theory of podzolization, in which Al-rich proto-imogolites dissolve more readily than Fe oxides (Lundstrom, et al., 2000). The podzolization process is characterized in a soil profile by a weathered soil horizon, depleted of Fe and Al, underlain by a horizon enriched in Fe and Al. One mechanism that explains this phenomenon involves complexation of Fe and Al species with organic acids (produced by decaying organic matter, etc.) and subsequent transport and precipitation of Fe and Al in a lower soil horizon (Lundstrom, et al., 2000). In these experiments, a significant quantity of organic acid was introduced, in this case oxalic acid, to enhance the leaching process and we maintained oxalic acid concentrations to avoid the re-precipitation process. While these techniques mimic podzolization in many ways, there would certainly be differences between introduction of oxalic acid during an *in situ* experiment vs. podzolization. If oxalic acid were introduced into the aquifer on site, predominant transport would occur horizontally (vs. vertically in podzolization) with higher flow rates, shorter time frames, and would lack the solid materials being subjected to cycles of wet and dry (as would occur in natural soil podzolization).

A small peak in effluent As in the 1 mM oxalic acid column coincided with the increase in Al concentration and may indicate that just a small portion of the As in these solids was associated with Al (hydr)oxides; when the Al (hydr)oxides began dissolving that portion of the As was also released. Because there was little to no effluent Mn beyond what was introduced in the influent, it seems unlikely that As release was related to dissolution of Mn (hydr)oxides in these columns. Presumably, therefore, the majority of the As would be associated with Fe (hydr)oxides since they can serve as major As adsorption sites in soils and sediments. However, the significant increase in [As] did not coincide with the increase in Fe. Therefore, these results suggest that while a small amount of As may be released as Al was dissolved, As release may have been largely decoupled from the release of Al and Fe. Previous studies have also shown As mobilization decoupled from Fe release, although those studies looked at As release under reducing conditions (Horneman, et al., 2004; Keimowitz, et al., 2005a; van Geen, et al., 2004). In the experiments presented here, the dissolution of Al and Fe (hydr)oxides may not entirely account for the mobilization of As in these column experiments. Other mechanisms may be at play; perhaps there was secondary Fe mineral formation which prevents Fe from being released in the effluent with the As or perhaps oxalic acid was acting on the As itself or competing with As for sorption sites in order to induce mobilization. Another possibility is that the initial release of As was coincident with the dissolution of Al and Fe hydr(oxides), but that there were differences in retardation of the three elements making transport and ultimate export from the column vary due to differences in partitioning. Current work is focused on elucidating mechanisms by which oxalic acid mobilizes As.

2.5.6 Oxalic acid adsorption

In the oxalic acid columns, between 85% and 99% of the oxalic acid introduced in the influent was collected in the effluent. This indicates that there is little sorption or degradation of oxalic acid within the column over the limited time period of the experiments; 0.1 - 0.5 mmol oxalic acid were degraded or remained in the oxalic acid columns discussed here. The lack of oxalic acid sorption is an asset when considering application to a contaminated site because the oxalic acid will not remain in the environment; it will be removed with the contaminated groundwater delivered to the pump and treat facility. Even if a small amount of oxalic acid remains sorbed to the sediments, microbes are known to degrade this small organic compound (Sahin, 2003). Concentrations up to 1 mM oxalic acid have been found in certain natural soils (Fox and Comerford, 1990).

2.5.7 Columns – cumulative percentage As mobilized

In comparing the cumulative percentage As mobilized, it is clear that each chemical amendment was able to mobilize more As than ambient groundwater alone (groundwater mobilized just 5%) with a maximum of 88% As mobilized from the aquifer sediments with the 10 mM oxalic acid treatment (Figure 2.4). Phosphate was able to initiate As mobilization faster but oxalic acid resulted in greater cumulative mobilization by the end of the experiments and did so with lower amendment concentrations. The 1 mM oxalic acid treatment mobilized a similar amount As (44% after 34 pore volumes) as the 100 mM phosphate treatment (48% after 28 pore volumes) but required much lower amendment concentration. Additionally, the 10 mM oxalic acid treatment mobilized nearly twice as much total As from the aquifer solids (88%) as the 100 mM phosphate column (48%).

2.5.8 Implications for site remediation

Based on an estimation of the aquifer volume, the groundwater beneath the Vineland site has a residence time of ~200 days if the pump and treat plant operates at full capacity, 7.5 x 10^6 L per day (2 million gallons); therefore, each pore volume in a simplified field scale study would require 200 days of injection and pumping. The groundwater column experiment was designed to simulate the current situation on site, i.e., groundwater flushing through the system. Based on the results from this experiment and using a pore-volume-in-column to pore-volume-in-field extrapolation, the 15-year time frame (27 pore volumes) that the site information reports for pump and treat remediation (EPA, 2006), would release ~5% of the As from the aquifer sediments and leave behind a substantial reservoir of As to continue to contaminate the groundwaters (e.g. effluent As concentrations at the end of the groundwater only column experiment were ~270 μg/L). Five percent As removal in 15 years is consistent with onsite estimates based on a comparison between the mass of As removed by pump and treat and estimates of the mass of As within the contaminated aquifer. Using the current As removal rates by the Vineland pump and treat system, 4-9% of the As would be removed from the contaminated aquifer with a total of 15 years of pump and treat remediation. If the As release rate continued as extrapolated from the groundwater column experiment, almost 600 years could be required to reach the site's soil washing clean up target of 20 mg/kg. Similar extrapolations were performed for the 1 mM oxalic acid, 10 mM oxalic acid, and ~1 mM phosphate experiments. Assuming uniform exposure of all site aquifer solids with elevated As concentrations to the chemical treatment, using 10 mM oxalic acid could decrease the cleanup timeframe to ~4 years (Table 2.1). If instead a clean up goal of 5 mg/kg is used (closer to the uncontaminated background As concentration), longer clean up times are calculated based on each of the column experiments; however, 10 mM oxalic acid treatment still shows dramatic decrease vs. groundwater alone (24 years for 10 mM oxalic acid vs. 750 years for groundwater alone) (Table 2.1). For ease of calculation, these projections were based on clean up goals of a certain As concentration on the solids. It could take longer than this to decrease groundwater concentrations below the current US drinking water standard of 10 μg/L; for instance, the concentration at the end of the 10 mM oxalic acid column (column 5) was still 40 μg/L even with 88% of the As removed (final solid concentration of As of 8.5 mg/kg). One can also use similar extrapolations to estimate the percentage clean up goal reached (using 20 mg/kg as the goal) after 5 or 15 years (Table 2.1). After 15 years with ambient groundwater, the site would only be 7% closer to the clean up goal and still have very elevated groundwater As concentrations. In less than 5 years the treatment goal of 20 mg/kg would be surpassed using the 10 mM oxalic acid treatment. These calculations have assumed As concentrations in the aquifer sediments to be the same as those used in the column experiments (~80 mg/kg). While the As concentrations in the aquifer sediments of the most contaminated region on site are variable (typically 20-250 mg/kg), these calculations allow for approximations of clean up times as well as comparisons between treatment methods. Additionally, the column experiments did not account for the contribution of fine particles to As mobility; fine particles were eluted in the first ~1.4 pore volumes and these data were not included in the mobilization calculations. Fine particles may play a role in As mobility *in situ*, which could impact necessary treatment times. Even with the limitations for extrapolating laboratory data to the field, the results and calculations presented here clearly suggest 1) pump and treat alone is not likely to be an effective means of remediation on a reasonable time scale for the Vineland site and 2) adding chemical amendments could substantially decrease the cumulative time necessary for remediation provided injection methods can be developed for delivering the amendment to all of the contaminated aquifer sediments.

Table 2.1. Extrapolations to the study site

Amendment	Length of remediation (years) based on clean up target of X mg/kg [a, b]		Percent clean up goal reached after Y years [e]	
	20 mg/kg	5 mg/kg	5 years	15 years
Unamended groundwater	590	750	4%	7%
1 mM phosphate	180	230	12%	18% [f]
1 mM oxalic acid	28	34	7%	46%
100 mM pulsed phosphate	-- [c]	-- [c]	41%	64% [f]
10 mM oxalic acid	4 [d]	24	111% [f]	118% [g]

-- Estimate not made for this experiment.

[a] Two remediation endpoints were examined for these calculations. The first is based on the time it would take to the clean the solids to 20 mg/kg; that is the clean up target for the soil being treated at the site’s soil washing plant. The second is based on the time it would take to clean the solids to 5 mg/kg; the uncontaminated background As concentration is <5 mg/kg.

[b] We have assumed that the arsenic release rate would continue to be similar to that at the end of each column experiment.

[c] The design for the 100 mM phosphate experiment was different; three pulses of phosphate were introduced instead of a continuous flow. Therefore, this calculation would not be as straightforward.

[d] The clean up goal was reached during the course of the experiment so it was not necessary to assume that the release rate would continue to be similar to that at the end of the column experiment.

[e] The clean up goal used for this calculation was an As concentration on the solids of 20 mg/kg.

[f] The 1 mM phosphate experiment hadn’t proceeded to the number of pore volumes equivalent to 15 years in the field. Therefore, the percent clean up goal reached after 15 yrs of treatment was calculated by assuming the arsenic release rate to be similar to the release rate at the end of the experiment. The 100 mM phosphate experiment also had not proceeded to the number of pore volumes equivalent to 15 years in the field; it was short by <1 pore volume. The same assumptions described above were used.

[g] Values greater than 100% indicate that the As concentration of the solids had been decreased below the target clean up level of 20 mg/kg.

2.6 Conclusions

Both phosphate and oxalic acid can accelerate release of As from contaminated solids. Based on results from extraction and column experiments, oxalic acid appears to be more effective at mobilizing As at lower amendment concentrations. Significant As mobilization by oxalic acid was decoupled from Fe and Al release, indicating that an As release mechanism independent of Fe or Al may be significant. For As contaminated sites using pump and treat as part of clean up, chemical amendments like phosphate or oxalic acid could improve remediation efficiency and thus could significantly decrease the cumulative treatment time.

2.7 Acknowledgements

The authors would like to thank James Ross for his assistance and input, Benjamin Bostick for x-ray absorptions spectroscopy analysis, and the US EPA, the US Army Core of Engineers, and Sevenson Environmental at the Vineland Superfund Site for access to samples and support on site. This work was primarily supported by the Superfund Research Program (NIEHS Grant ES010349). Additional support was provided by NIEHS Grant ES0090890. This is LDEO publication 7384.

2.8 References

Darke, A.K., Walbridge, M.R., 2000. Al and Fe biogeochemistry in a floodplain forest: Implications for P retention. Biogeochemistry. 51, 1-32.

Darland, J.E., Inskeep, W.P., 1997. Effects of pH and phosphate competition on the transport of arsenate. J. Environ. Qual. 26, 1133-1139.

De Vitre, R., Belzile, N., Tessier, A., 1991. Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. Limnol. Oceanogr. 36, 1480-1485.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environ. Sci. Technol. 37, 4182-4189.

EPA, 1996. Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Method 1669. Office of Water, Washington, DC.

EPA, 2001. Groundwater pump and treat systems: summary of selected cost and performance information at Superfund-financed sites. (EPA 542-R-01-021a).

EPA, 2002. Arsenic treatment technologies for soil, waste, and water. http://www.clu-in.org/download/remed/542r02004/arsenic_report.pdf.

EPA, 2003. Improving nationwide effectiveness of pump-and-treat remedies requires sustained and focused action to realize benefits report. EPA Office of Inspector General, Memorandum Report 2003-P-000006.

EPA, 2006. Vineland Chemical Co., Inc National Priority List site fact sheet. http://www.epa.gov/Region2/superfund/npl/0200209c.pdf.

EPA, 2007. EPA Basic query for National Priorities List, Superfund, US EPA.

Fleisher, M.Q., Anderson, R. (1991), Particulate matter digestion (from mg to 10's of g) and radionuclide blanks, paper presented at Marine Particle Analysis and Characterization; American Geophysical Union, Washington, DC.

Fox, T.R., Comerford, N.B., 1990. Low-molecular-weight organic-acids in selected forest soils of the southeastern USA. Soil Sci. Soc. Am. J. 54, 1139-1144.

Hongshao, Z., Stanforth, R., 2001. Competitve adsorption of phosphate and arsenate on goethite. Environ. Sci. Technol. 35, 4753-4757.

Horneman, A., Van Geen, A., Kent, D.V., Mathe, P.E., Zheng, Y., Dhar, R.K., O'Connell, S., Hoque, M.A., Aziz, Z., Shamsudduha, M., Seddique, A.A., Ahmed, K.M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part 1: Evidence from sediment profiles. Geochim. Cosmochim. Acta. 68, 3459-3473.

Jain, A., Loeppert, R.H., 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J. Environ. Qual. 29, 1422-1430.

Jeong, Y.R., Fan, M.H., Van Leeuwen, J., Belczyk, J.F., 2007. Effect of competing solutes on arsenic(V) adsorption using iron and aluminum oxides. J. Environ. Sci. China. 19, 910-919.

Keimowitz, A.R., Simpson, H.J., Chillrud, S.N., Stute, M., Tsang, M., Datta, S., Ross, J. 2005a. Oxidation of groundwater arsenic and iron. In: Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation, O'Day, P.A., Vlassopoulos, D., Meng, D. and Benning, L.G. (Eds.), vol. 915. American Chemical Society, Washington, DC.

Keimowitz, A.R., Simpson, H.J., Stute, M., Datta, S., Chillrud, S.N., Ross, J., Tsang, M., 2005b. Naturally occurring arsenic: Mobilization at a landfill in Maine and implications for remediation. Appl. Geochem. 20, 1985-2002.

Keimowitz, A.R., Zheng, Y., Chillrud, S.N., Mailloux, B., Jung, H.B., Stute, M., Simpson, H.J., 2005c. Arsenic redistribution between sediments and water near a highly contaminated source. Environ. Sci. Technol. 39, 8606-8613.

Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. Environ. Sci. Technol. 35, 2778-2784.

Klarup, D.G., 1997. The influence of oxalic acid on release rates of metals from contaminated river sediment. Sci. Total Environ. 204, 223-231.

Kuhlmeier, P.D., 1996. Partitioning of arsenic species in fine-grained soils. Journal of Air and Waste Management Association. 47.

Kuhlmeier, P.D., 1997. Sorption and desorption of arsenic from sandy soils: column studies. Journal of Soil Contamination. 6, 21-36.

Leist, M., Casey, R.J., Caridi, D., 2000. The management of arsenic wastes: problems and prospects. J. Hazard. Mater. 76.

Li, J.Y., Xu, R.K., Tiwari, D., Ji, G.L., 2006. Mechanism of aluminum release from variable charge soils induced by low-molecular-weight organic acids: Kinetic study. Geochim. Cosmochim. Acta. 70, 2755-2764.

Lundstrom, U.S., van Breemen, N., Bain, D., 2000. The podzolization process. A review. Geoderma. 94, 91-107.

Mackay, D.M., Cherry, J.A., 1989. Groundwater contamination: Pump-and-treat remediation. Environ. Sci. Technol. 23, 630-637.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta. 58, 201-235.

Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. Science. 300, 939-944.

Palmer, C.D., Fish, W., 1992. Chemical enhancements to pump-and-treat remediation. EPA Ground Water Issue. http://www.epa.gov/ada/download/issue/chemen.pdf.

Panias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A., 1996. Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. Hydrometallurgy. 42, 257-265.

Peryea, F.J., 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55, 1301-1306.

Sahin, N., 2003. Oxalotrophic Bacteria. Res. Microbiol. 154, 399-407.

Shi, R., Jia, Y.F., Wang, C., Shuhua, Y., 2009. Mechanism of arsenate mobilization from goethite by aliphatic carboxylic acid. J. Hazard. Mater. 163, 1129-1133.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517-568.

Strobel, B.W., 2001. Influence of vegetation on low-molecular-weight carboxylic acids in soil solution - a review. Geoderma. 99, 169-198.

Sullivan, K.A., Aller, R.C., 1996. Diagenetic cycling of arsenic in Amazon shelf sediments. Geochim. Cosmochim. Acta. 60, 1465-1477.

Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C.F., 2004. Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data, and mineralogical characterization. Geochim. Cosmochim. Acta. 68, 4539-4557.

Tao, Y.Q., Zhang, S.Z., Jian, W., Yuan, C.G., Shan, X.Q., 2006. Effects of oxalate and phosphate on the release of arsenic from contaminated soils and arsenic accumulation in wheat. Chemosphere. 65, 1281-1287.

van Geen, A., Rose, J., Thoral, S., Garnier, J.M., Zheng, Y., Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. Geochim. Cosmochim. Acta. 68, 3475-3486.

van Geen, A., Zheng, Y., Versteeg, R., Stute, M., Horneman, A., Dhar, R., Steckler, M., Gelman, A., Small, C., Ahsan, H., Graziano, J.H., Hussain, I., Ahmed, K.M., 2003. Spatial variability of arsenic in 6000 tube wells in a 25 km(2) area of Bangladesh. Water Resour. Res. 39,

van Hees, P.A.W., Lundstrom, U.S., Giesler, R., 2000. Low molecular weight organic acids and their Al-complexes in soil solution - composition, distribution and seasonal variation in three podzolized soils. Geoderma. 94, 173-200.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta. 436, 309-323.

Zeng, H., Fisher, B., Giammar, D.E., 2008. Individual and competitive adsorption of arsenate and phosphate to a high-surface-area iron oxide-based sorbent. Environ. Sci. Technol. 42, 147-152.

Zhang, S.Z., Li, W., Shan, X.Q., Lu, A.X., Zhou, P.J., 2005. Effects of low molecular weight organic anions on the release of arsenite and arsenate from a contaminated soil. Water Air Soil Pollut. 167, 111-122.

2.9 Figures

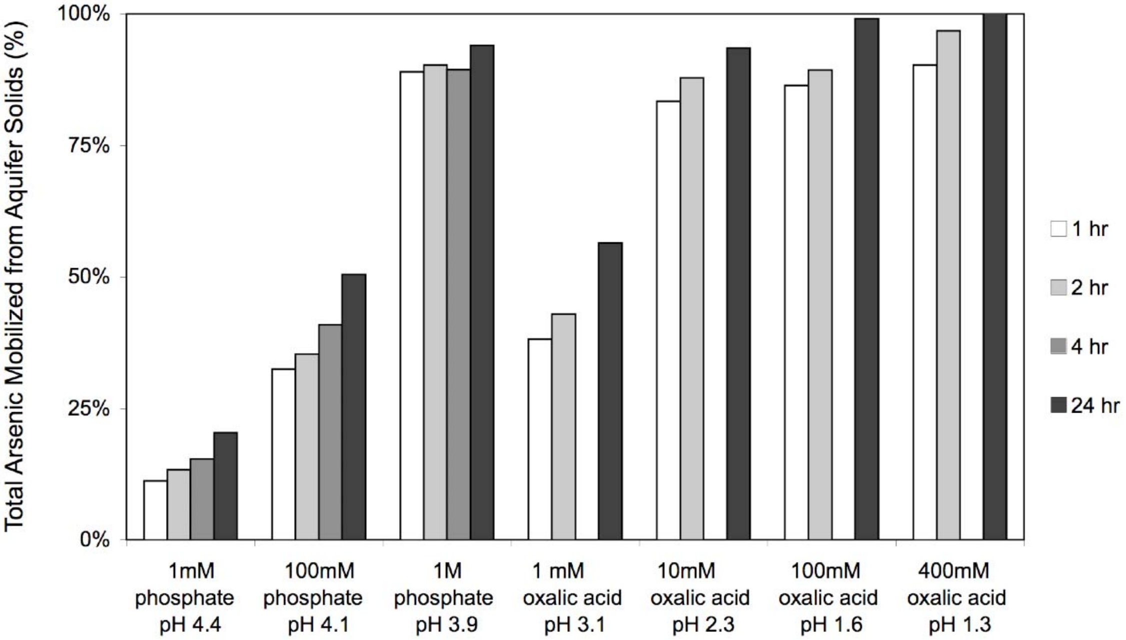
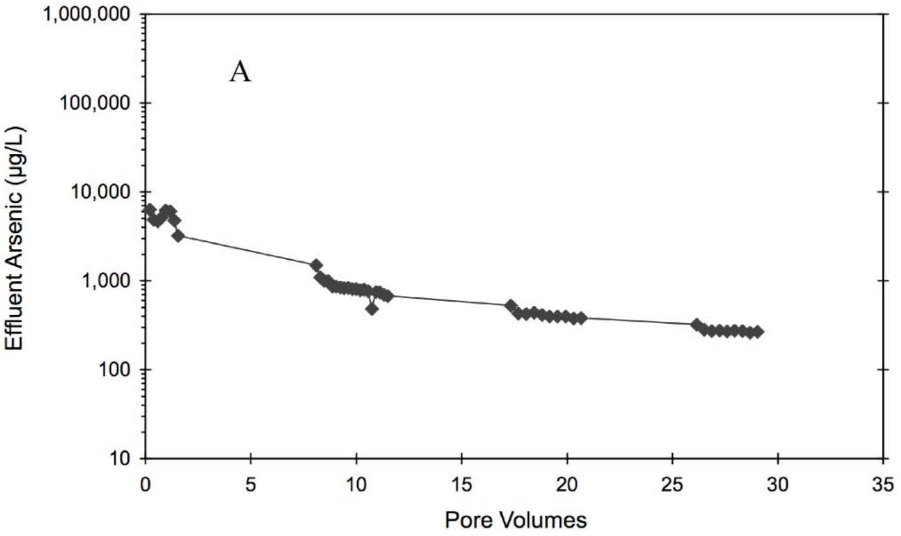
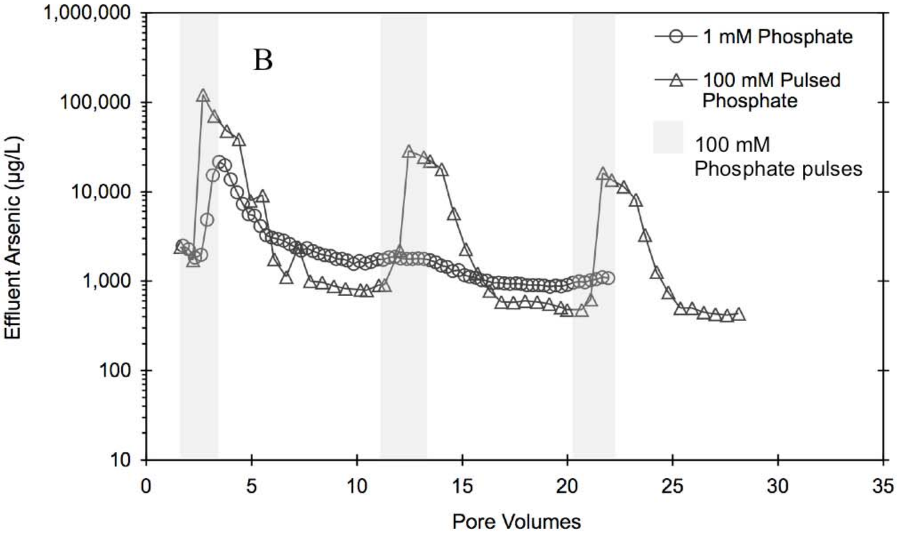


Figure 2.1. Batch extraction experiments using three different concentrations of phosphate (1 mM, 100 mM and 1 M) and four different concentrations of oxalic acid (1 mM, 10 mM, 100 mM, and 400 mM) as the chemical amendment. The pH of the extraction solution is also listed. There were no 4 h extractions for the oxalic acid experiments.


A
Effluent Arsenic (µg/L)
1,000,000
100,000
10,000
1,000
100
10
0
5
10
15
20
25
30
35
Pore Volumes


B
1 mM Phosphate
100 mM Pulsed Phosphate
100 mM Phosphate pulses
Effluent Arsenic (µg/L)
1,000,000
100,000
10,000
1,000
100
10
0
5
10
15
20
25
30
35
Pore Volumes

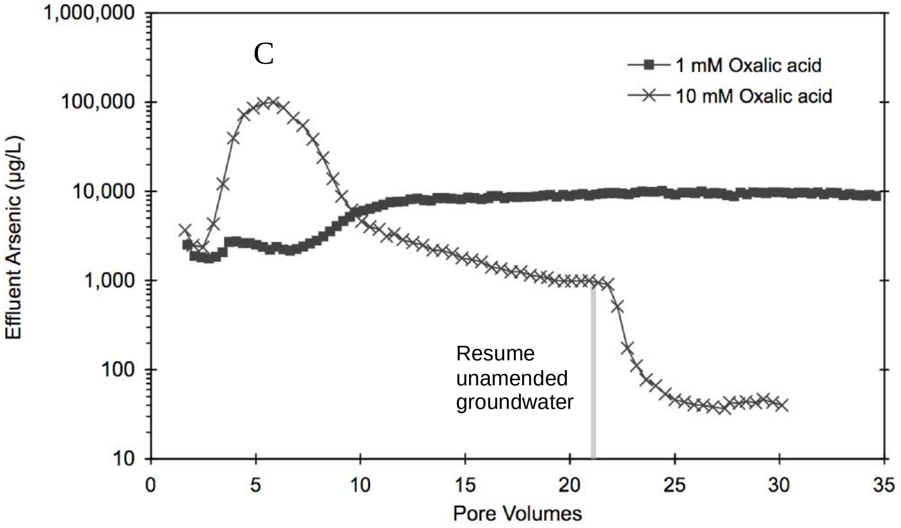

C
1 mM Oxalic acid
10 mM Oxalic acid
Resume unamended groundwater
Effluent Arsenic (µg/L)
1,000,000
100,000
10,000
1,000
100
10
0
5
10
15
20
25
30
35
Pore Volumes

Figure 2.2. Results from column experiments shown as effluent arsenic concentration on a log scale versus number of pore volumes that had passed through the column. Influent solutions were (a) unamended groundwater, (b) phosphate (1 mM and pulsed 100 mM phosphate introductions shown), and (c) oxalic acid (1 mM and 10 mM oxalic acid). A fraction collector was used to collect samples for all columns except the unamended groundwater column (a). Gaps in sampling points exist for the unamended groundwater column (a) during overnight periods when composite samples were taken. The pulses of phosphate in (b) are shown by the shaded regions. The switch from an influent solution of 10 mM oxalic acid to groundwater in (c) is shown by the vertical line on the x-axis.

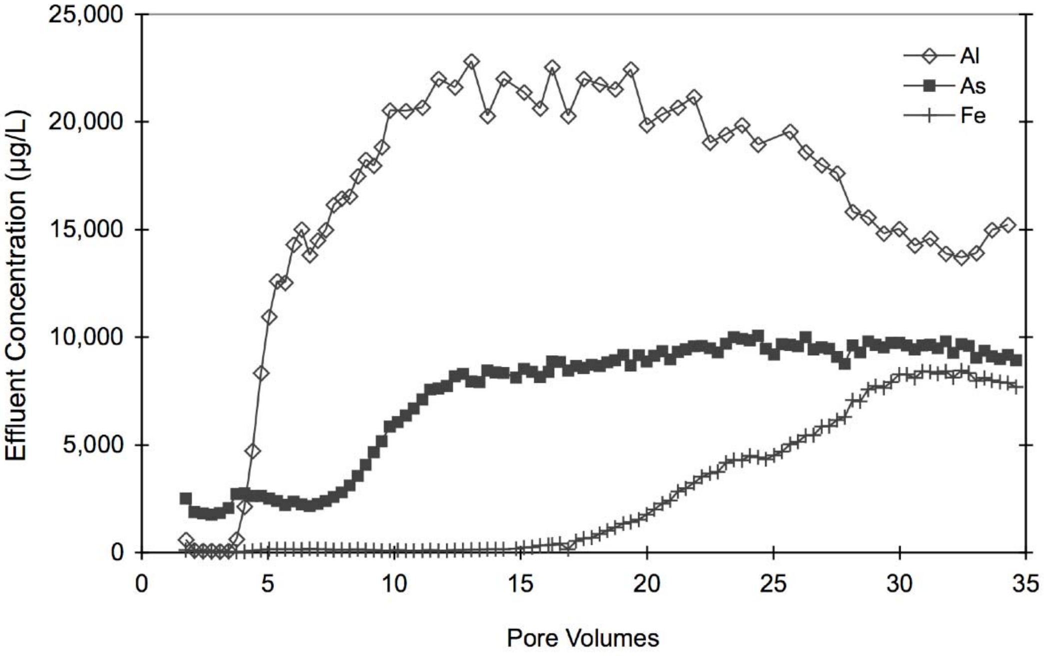


Figure 2.3. Effluent Al, As, and Fe versus number of pore volumes for the 1 mM oxalic acid column experiment. Note that the element concentrations are not on a log scale as in Figure 2.2.

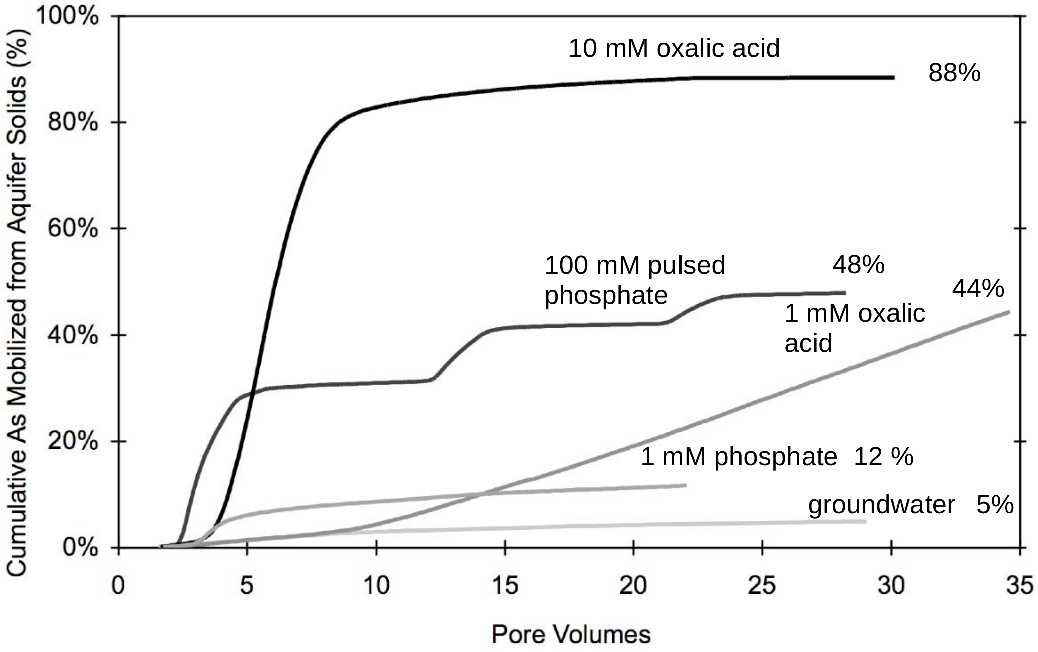


Figure 2.4. Cumulative percentage arsenic mobilized from the aquifer solids as a function of pore volume for each of the column experiments. Samples prior to ~1.4 pore volumes, before the effluent solution was visually clear of fine particles, were not included.

2.10 Supporting Information

2.10.1 Overview

In addition to arsenic mobilization laboratory experiments presented in the main manuscript, we have also explored promoting arsenic mobilization by stimulating microbial activity and by increasing the pH of the system. Increased microbial activity should induce reducing conditions leading to a mobilization of arsenic both because As(III) tends to be more soluble than As(V) and because Fe reduction can lead to mobilization of adsorbed As (Ahmann, et al., 1997; Smedley and Kinniburgh, 2002; van Geen, et al., 2004). Increasing the pH of the system should also lead to As mobilization (Dixit and Hering, 2003); raising the pH can result in increased electrostatic repulsions between arsenate oxyanions and surface binding sites.

Additional phosphate and oxalic acid experiments were also conducted and are detailed below.

2.10.2 Methods

Stimulating microbial activity - incubation experiments

Wet aquifer solids (~210 ppm As) were combined with a liquid phase with solid to water ratio of ~1:5. Three liquid phases were used, (1) nutrient media containing vitamins, minerals, pH 7 HEPES buffer, and 20 mM acetate as a carbon source for the microbes (Kostka and Nealson, 1998), (2) artificial groundwater containing major anions and cations but no nitrate and no acetate (therefore, no added food for the microbes), and (3) artificial groundwater plus incremental additions of acetate, reaching a maximum concentration of ~2 mM acetate. No microbes were intentionally added to any of the three incubation types; these experiments rely on the native soil microbial community. Nutrient media and artificial groundwater solutions were sterilized by autoclaving prior to use. Incubations using (1) and (2) above were carried out in 60 mL glass incubation bottles fitted with blue butyl rubber stoppers and aluminum crimp tops and the incubations lasted a total of 28 days. Duplicate bottles were sacrificed at each sampling time point. The incubation using (3) above was carried out in a reaction vessel, a 1 L plastic container fitted with a rubber stopper and the incubation lasted a total of 49 days. There were ports in the stopper for collecting samples and for oxidation-reduction potential (ORP) and dissolved oxygen (DO) probes. The reaction vessel was kept in a nitrogen filled glove bag for the duration of the experiments and was only removed from the glove bag for collection of water samples. All incubation bottles/vessels were kept in the dark. Incubations using (1) as liquid phase will subsequently be referred to as "nutrient media," (2) as "artificial groundwater," and (3) as "reaction vessel."

On day 6, 14, 21, and 28 duplicate bottles of the nutrient media and artificial groundwater incubations were sacrificed. Water samples of 5 mL were also removed from the reaction vessel on these days and subsequently 0.5 mL of 1 M acetate was added to the reaction vessel, increasing the acetate concentration in the reaction vessel by ~0.5 mM at each time point. Two additional samples were taken from the reaction vessel, on day 38 and day 49, with no further acetate addition.

All water samples were filtered through 0.45 μm syringe filters and acidified to 1% HCl prior to analysis for As, Mn, and Fe by ICP MS. ICP MS procedures were the same as discussed in the main manuscript.

Increasing pH - titration experiments

Wet aquifer solids (~80 ppm As) were combined with distilled, deionized water with a solid to water ratio of ~1:5. The experiment was carried out in a reaction vessel similar to that described above; pH and ORP were monitored over the course of the experiment. The pH of the system was adjusted to 4 with 0.5 M HCl and the vessel was placed on a shaker table for 1 hour. After the 1 hour equilibration, a water sample was removed, filtered through a 0.45 μm syringe filter and acidified to 1% HNO_3. Then the pH of the reaction vessel was increased using NaOH. The pH of the system was incrementally increased to 9.4 over the course of the experiment allowing for 1 hour of equilibration before each sample was taken and more base was added.

Water samples were analyzed for As, Mn, and Fe by ICP MS; procedures were the same as discussed in the main manuscript.

Adding phosphate and oxalic acid - titration experiments

Titration experiments were also conducted in which either phosphate or oxalic acid was added to a reaction vessel filled with aquifer solids. Experiments were carried out similarly to those described for the pH experiments. Wet aquifer solids (~80 ppm As) were combined with distilled, deionized water with a solid to water ratio of ~1:5. In separate experiments, phosphate or oxalic acid was incrementally added to the reaction vessel allowing about 1 hour for equilibration before each sample was taken and more phosphate or oxalic acid added. Phosphate was incrementally increased to 1 M over the course of the experiment; oxalic acid was increased to 390 mM. Both pH and ORP were monitored over the course of the experiment. The reaction vessel was agitated on a shaker table during equilibration. After the 1 hour equilibration, a water sample was removed, filtered through a 0.45 μm syringe filter and acidified to 1% HNO_3. Water samples were analyzed for As, Mn, and Fe by ICP MS; procedures were the same as discussed in the main manuscript.

2.10.3 Results and discussion

Stimulating microbial activity - incubation experiments

The percentage of arsenic mobilized increased from 11% to 25% between 6 and 28 days for the nutrient media incubations, from 2% to 3% for the artificial groundwater incubations, and from 3% to 19% for the reaction vessel (Figure 2.5). The percent arsenic mobilized further increased to 27% at the end of 49 days of incubation for the reaction vessel. The two sample types with acetate added (nutrient media and reaction vessel) showed greater arsenic mobilization after 28 days than the samples without acetate (artificial groundwater). We attribute the increased arsenic mobilization to increased activity of the native soil microbes; however, no abiotic controls were performed. Therefore, it is also possible that arsenic mobilization was motivated by abiotic redox reactions resulting from the addition of a reduced carbon source.

The dissolved oxygen (DO) in the reaction vessel decreased steadily after the vessel was closed and fell to ~0 ppm at 12 days and remained there for the rest of the experiment (Figure 2.6). The oxidation-reduction potential (ORP) decreased through the course of the experiment reaching two plateau regions before it became negative and finally began to level off around -400 mV at day 22 (Figure 2.6). From the ORP and DO measurements it is clear that the redox conditions were altered through the course of the incubation experiment; the reaction vessel went anoxic and the system became quite reducing.

As mentioned above, there were two plateaus in the ORP measurements as the values decreased. Previous studies have indicated that plateaus of this type may result from redox buffering as one electron acceptor is being consumed (Christensen, et al., 2000; Scott and Morgan, 1990). Once the target electron acceptor has been exhausted, ORP falls to the level of the next redox pair. Each of the plateaus could therefore coincide with the consumption of one particular electron acceptor. The first plateau seemed to coincide with the steady decrease of dissolved oxygen (Figure 2.6). Once the dissolved oxygen decreased sufficiently (below ~1 ppm), ORP values began to decline again. The second plateau may coincide with the consumption of another electron acceptor, such as soil bound nitrate or Mn. After that plateau, ORP values decreased further and began to level off around -400 mV at day 22, perhaps indicating Fe reduction as there was also a strong increase in dissolved Fe between day 21 and 28 (data not shown).

The DO began to decrease at a steady rate after the reaction vessel was closed and before any acetate was added. Furthermore, after the initial acetate addition, there was no appreciable change in the rate of DO decrease indicating that the system may have gone anoxic even without the input of a carbon source as added food for the microbes. However, the initial decrease in oxygen did not result in much arsenic mobilization and ORP readings were still positive until after the second acetate addition at day 14. At day 6, the reaction vessel showed only 3% of As mobilized from the solids and only 5% at day 14. These results were similar to mobilization in the artificial groundwater incubations with 2% mobilization at day 6 and 3% at day 14. The reaction vessel incubation and artificial groundwater incubation diverged in terms of arsenic mobilization at the next sampling point, day 21, where the artificial groundwater incubation remained at ~3% mobilization and the reaction vessel incubation increased to 12%. This suggests that the second acetate addition was necessary to induce sufficiently reducing conditions to mobilize more arsenic, which is supported by the onset of negative ORP shortly after the second acetate addition. Therefore, it appears the microbial community may have been carbon limited and benefited from an added carbon source. However, only a relatively small amount of carbon (~1 mM acetate) was required to make a difference in the mobilization of arsenic.

The nutrient media samples had at least 10x the acetate concentrations as the reaction vessel at all time points, however, only 6% more arsenic was mobilized from the aquifer solids in the nutrient media samples compared with the reaction vessel after 28 days. Although the microbes did appear to benefit from added carbon, supplementing with much higher concentrations of carbon, as in the case of the nutrient media samples, resulted in little additional As mobilization.

Increasing pH – titration experiments

Over the course of the pH titration experiment, there was only minor increase in percent arsenic released, with a total of 9% mobilized by the end of the experiment (Figure 2.7). Calculating the percent mobilization for each pH change (i.e., by subtracting the percent mobilized at previous sampling points), the greatest mobilization increments were at pH 4.1 (3%), pH 8.5 (2.1%), and pH 9.4 (1.3%). The 3%

mobilization at pH 4.1 was possibly caused by As desorption upon contact with a liquid water phase and might occur at almost any initial pH. For comparison, this was a similar percent mobilization as for the first sampling time point for the artificial groundwater incubations described above. The other two pH values with somewhat increased mobilization were probably due to electrostatic repulsions between arsenate oxyanions and surface binding sites at high pH; iron (hydr)oxides can have a zero point of charge at pH ~7.8-8.5 and aluminum oxides at pH 8-9 (Davis and Leckie, 1978; Sparks, 1995). This experiment was repeated using Na_2CO_3 as the added base with similar results.

Adding phosphate and oxalic acid - titration experiments

During the phosphate titration experiments, between 84% and 104% of the As was mobilized from the aquifer solids (Figure 2.8). As the phosphate concentration increased, so did the percentage of As released. The pH decreased from at least 5.8 to less than 4 over the course of the experiments as phosphate was added. During the oxalic acid titration experiments, between 56% and 63% of the As was mobilized from the aquifer solids (Figure 2.9). Again, as the oxalic acid concentration increased, the percentage of As released also increased. The pH decreased from about 6 to 1.5 over the course of the experiments as oxalic acid was added.

Comparing the data from the titration experiments to results from the extraction experiments discussed in the main manuscript, the percentage of As mobilized was substantially lower for all amendment concentrations except the 1 M phosphate (Table 2.2). It is possible, therefore, that the titration experiments were not as well mixed as the extraction experiments.

Although the titration experiments may not have allowed for sufficient mixing, it is still possible to compare the phosphate and oxalic acid titrations with the pH titrations. Such comparisons suggest that phosphate and oxalic acid additions promote greater As release than increasing pH.

Table 2.2. Comparison between percent As mobilized by 1 hr extractions and titration experiments at the same amendment concentrations.

	Percent As Mobilized (%)			
	Phosphate		Oxalic Acid	
Approx. concentration	1 hr Extraction	Titration[a]	1 hr Extraction	Titration[a]
1 mM	11%	2%	38%	14-18%
10 mM	--	--	83%	20-29%
100 mM	32%	12-13%	86%	28-41%
400 mM	--	--	90%	56-63%
1 M	89%	84-104%	--	--

-- Data not available for both extraction and titration experiments, hence no comparison can be made.

[a] Percentages for both trials of the titration experiments are given.

2.10.4 Conclusions

Both stimulating microbial activity and increasing pH, resulted in As mobilization as would generally be expected. However, the pH experiments presented here suggest that As mobilization associated with increasing system pH was small and not likely to be very useful as part of a remediation scheme. The incubations experiments showed a higher proportion of arsenic mobilization than increasing pH, but could require a longer time frame to effect arsenic mobilization than making chemical additions as discussed in the main manuscript.

2.10.5 References

Ahmann, D., Krumholz, L.R., Hemond, H.F., Lovley, D.R., Morel, F.M.M., 1997. Microbial mobilization of arsenic from sediments of the Aberjona Watershed. Environ. Sci. Technol. 31, 2923-2930.

Christensen, T.H., Bjerg, P.L., Banwart, S.A., Jakobsen, R., Heron, G., Albrechtsen, H.J., 2000. Characterization of redox conditions in groundwater contaminant plumes. J. Contam. Hydrol. 45, 165-241.

Davis, J.A., Leckie, J.O., 1978. Surface ionization and complexation at oxide-water interface .2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal-ions. J. Colloid Interface Sci. 67, 90-107.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environ. Sci. Technol. 37, 4182-4189.

Kostka, J., Nealson, K. 1998. Isolation, cultivation and characterization of iron- and manganese-reducing bacteria. In: Techniques in microbial ecology, Burlage, R., Atlas, R., Stahl, D., Geesey, G. and Sayler, G. (Eds.), vol. Oxford University Press, New York.

Scott, M.J., Morgan, J.J. 1990. Energetics and conservative properties of redox systems. In: ACS Symposium Series: Chemical Modeling of Aqueous Systems II, Melchior, D.C. and Bassett, R.L. (Eds.), vol. 416. American Chemical Society, Washington, DC, pp. 368-378.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517-568.

Sparks, D.L., 1995. Environmental soil chemistry, Academic Press, San Diego, CA.

van Geen, A., Rose, J., Thoral, S., Garnier, J.M., Zheng, Y., Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. Geochim. Cosmochim. Acta. 68, 3475-3486.

2.10.6 Supporting figures

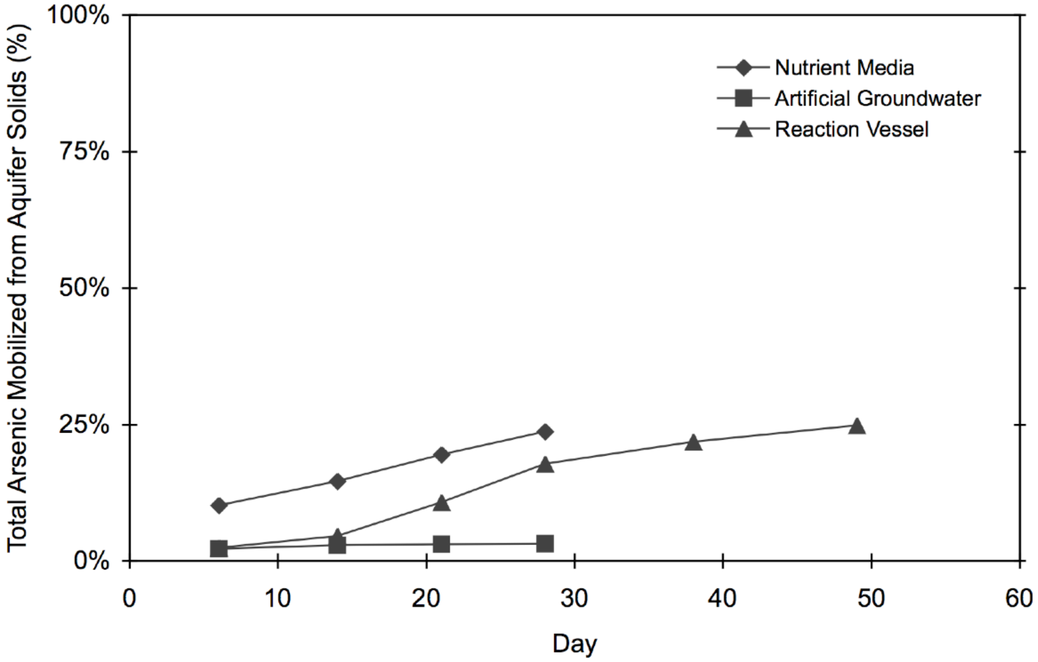


Figure 2.5. Percent arsenic mobilized from the aquifer solids over time for the nutrient media, artificial groundwater, and reaction vessel incubations. Nutrient media and artificial groundwater incubations were carried out in 60 mL glass incubation bottles fitted with blue butyl rubber stoppers and aluminum crimp tops. Reaction vessel incubations were carried out in a reaction vessel, a 1 L plastic container fitted with a rubber stopper.

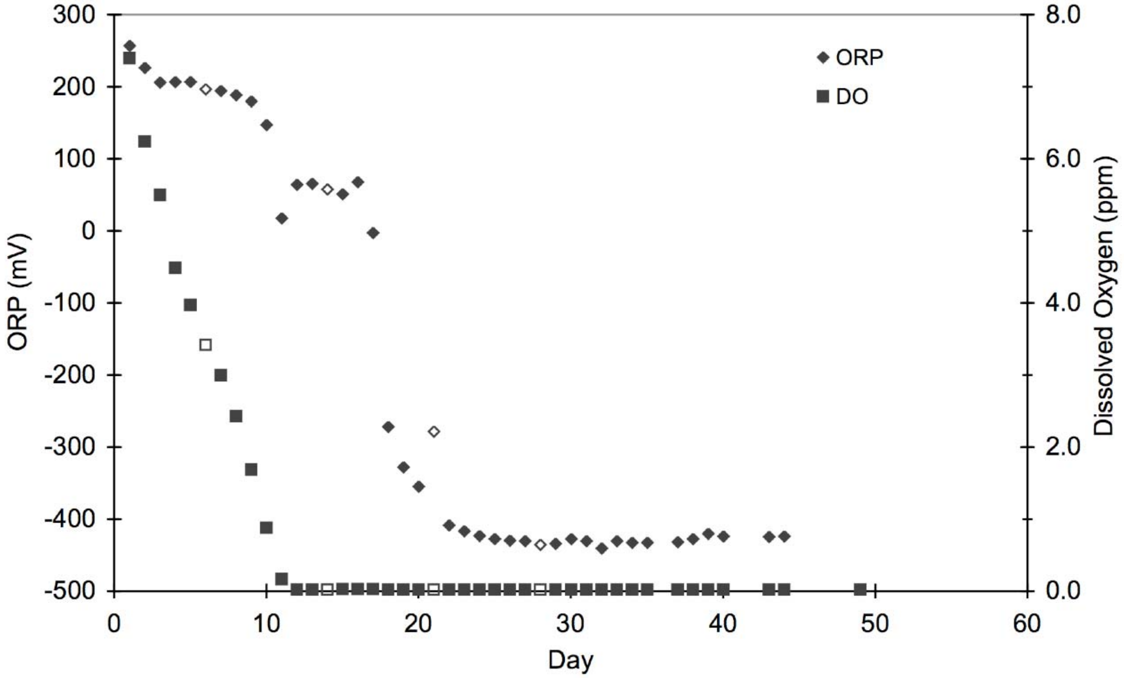


Figure 2.6. Oxidation-Reduction potential (ORP) and Dissolved Oxygen (DO) in the reaction vessel over time. The open symbols represent days on which acetate was added to the system.

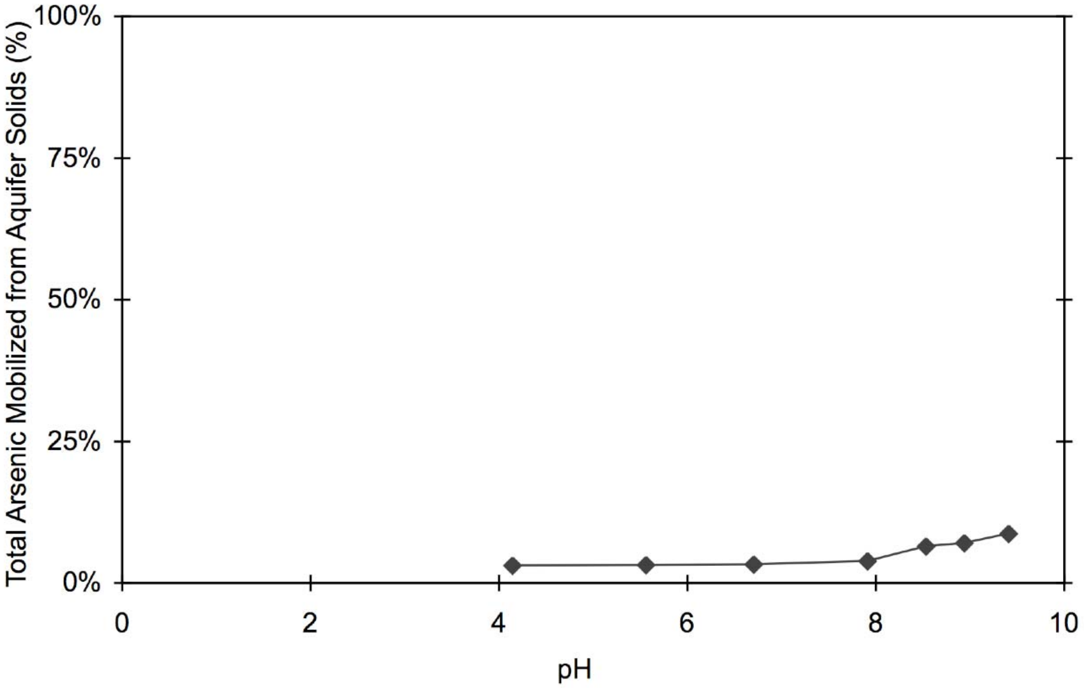


Figure 2.7. Percent arsenic mobilized from the aquifer solids over pH range 4.1-9.4. The system was equilibrated at each pH for 1 hr prior to sampling.

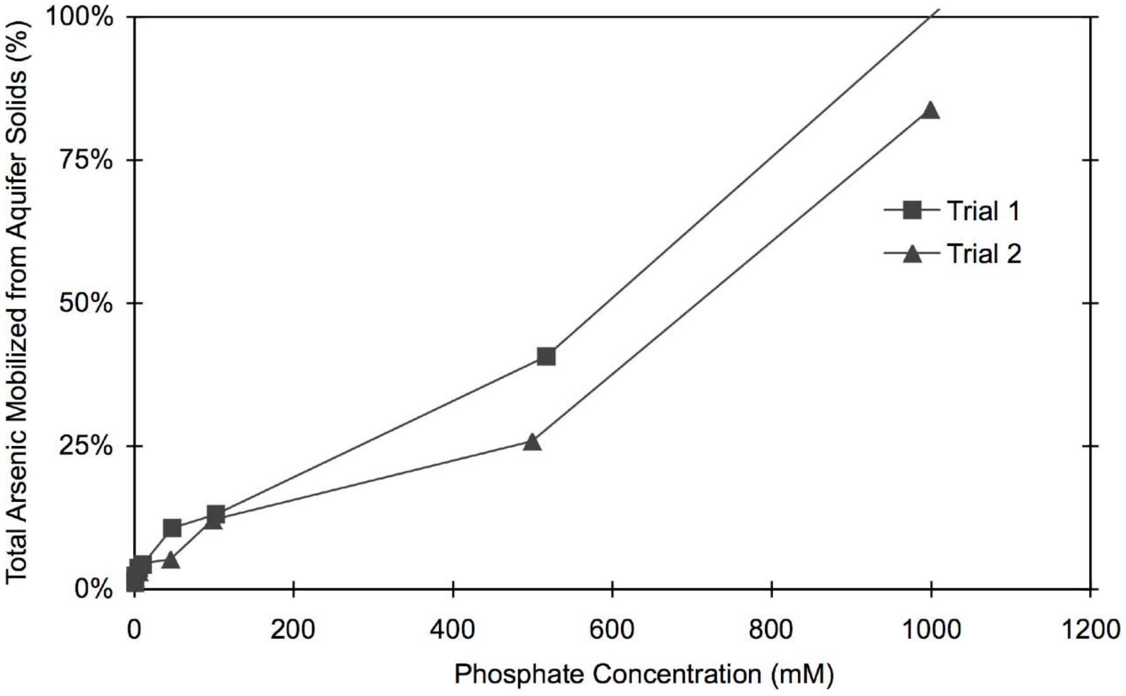


Figure 2.8. Percent arsenic mobilized from the aquifer solids during the phosphate titration experiments. The final point in Trial 1 reaches 104%. Maximum phosphate concentrations were approximately 1 M.

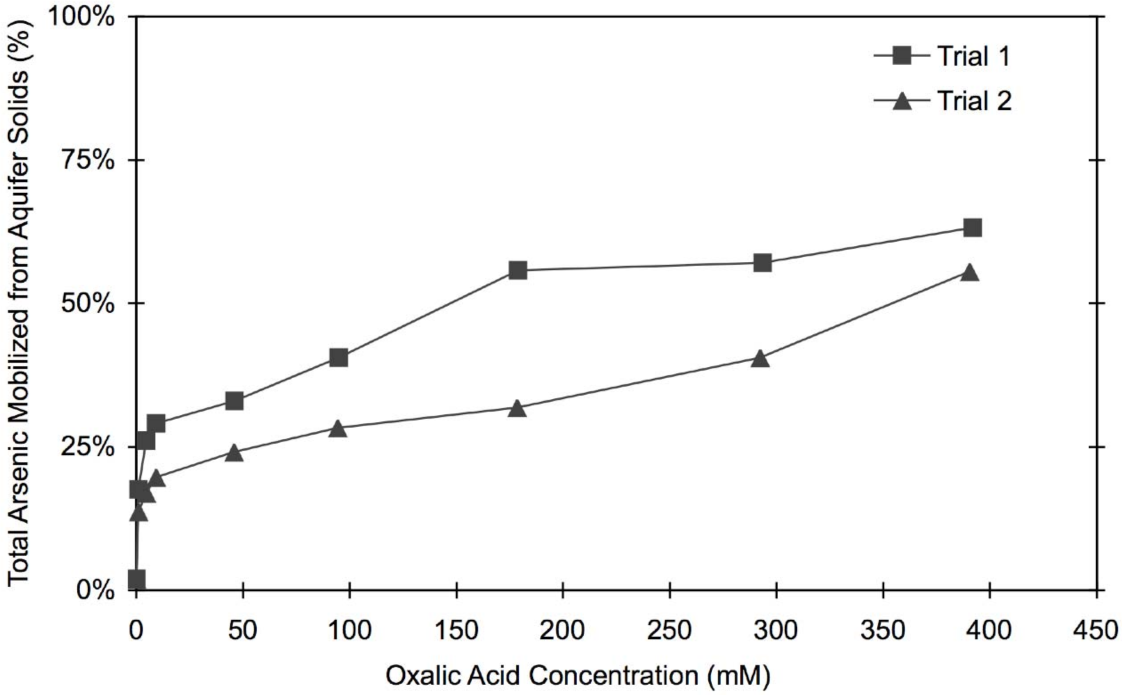


Figure 2.9. Percent arsenic mobilized from the aquifer solids during the oxalic acid titration experiments. Maximum oxalic acid concentrations were 390 mM.

CHAPTER 3
Use of Microfocused X-ray Techniques to Investigate the Mobilization of As by Oxalic Acid

Wovkulich, K., Mailloux, B.J., Bostick, B.C., Dong, H., Bishop, M.E., Chillrud, S.N., Use of Microfocused X-ray Techniques to Investigate the Mobilization of As by Oxalic Acid, submitted to Geochim. et Cosmochim. Acta, 2011.

3.1 Abstract

Improved linkages between aqueous phase transport and solid-phase reactions are needed to better predict and model transport of contaminants through the subsurface. Here we develop and apply a new method for measuring As mobilization *in situ* within soil columns that utilizes synchrotron-based X-ray fluorescence. By performing these measurements *in situ* during column transport experiments, we simultaneously monitor grain-scale solid phase reactions and column-scale transport. Arsenic may be effectively mobilized by oxalic acid but the geochemical and mineralogical factors that influence the rate and extent of mobilization are not well understood. Column experiments (~4 cm long x 0.635 cm ID) using As contaminated sediments from the Vineland Chemical Company Superfund site were performed on the laboratory bench as well as in the synchrotron beamline. Microfocused synchrotron X-ray fluorescence (μSXRF) maps for As and Fe were collected at the same location in the columns (<1 mm^2) before and during treatment with 10 mM oxalic acid. The fraction of As and Fe removed by oxalic acid treatment was calculated from the change in flux-normalized counts for each pixel in the map images, and these data were used to calculate kinetic parameters over the studied area. Between 79% and 83% of the As was removed from the sediments by the oxalic acid treatment based on μSXRF data; these removal percentages agreed well with laboratory data based on column effluent (88-95%). Considerably less Fe was removed

by oxalic acid treatment, 14-25% based on μSXRF counts, which is somewhat higher than the 7-9% calculated from laboratory column effluent concentrations. Fe speciation did not change appreciably over the course of the experiments based on a subset of points examined by microfocused X-ray absorption near edge spectroscopy (μXANES). Kinetics information extracted from μSXRF data compared favorably with rates of As removal from observed As breakthrough curves. The average pseudo-first order As removal rate constant was calculated to be 0.015 min^{-1} ± 0.002 (± average standard error, N=400) based on changes in μSXRF counts over time. The spatial variation observed in the rate constant is likely a result of differences in the mineral substrate or As retention mechanism. Geochemical models created using the calculated As removal rate constants showed agreement with As breakthrough curves for both a small column (4.25 cm x 0.635 cm ID) and a larger column (23.5 cm x 4.2 cm ID), indicating that the processes studied using the microprobe are representative and often can be predictive of larger systems. While this work was used to understand the processes that regulate As release and transport, the methods developed here could be used to study a wide variety of reaction processes, including contaminant removal due to chemical treatment, mineral precipitation due to changing redox characteristics, and solid phase transformations.

3.2 Introduction

Transport of chemicals and contaminants through the subsurface are controlled by interactions with the solid phase, including adsorption-desorption and mineral dissolution/precipitation (Bone, et al., 2006; Johannesson and Tang, 2009; Kaste, et al., 2006; O'Day, et al., 2004; Polizzotto, et al., 2006). Hydrogeologic investigations attempt to parameterize these processes to describe reactive transport, however, the reactions are rarely examined directly within the solid-phase. In most traditional transport experiments at the column or field scale, measurements of aqueous compositions are made over time and these are used to infer reactions in the solid phase with little or no direct measurement of the solid phase materials (Kuhlmeier, 1997; Roden, et al., 2000; Wovkulich, et al., 2010). Even when solids are analyzed, the characterization methods used usually examine mineral phases at the micron-scale before or after experiments to infer potential reactions that could occur within solutions (Arai, et al., 2006; Singer, et al., 2009). In both cases, the different scales and phases of these measurements can complicate attempts to link the data. In this work, we develop a method in which column transport experiments are conducted within a microfocused X-ray beam to simultaneously monitor grain-scale solid phase reactions and column scale transport in order to better understand element release and transport processes. This method provides a valuable tool to link time-series measurements on the solid and liquid phases while reactions are taking place.

X-ray microprobe analysis can be a powerful tool for investigating the spatial distribution of target elements at the micron scale as well as giving insight into the speciation of those elements. Microfocused synchrotron X-ray fluorescence (μSXRF) can provide information regarding relative element abundance, distribution, and correlations between elements with micron to sub-micron spatial resolution sufficient to investigate small-scale differences and heterogeneities within a sample. These data can be integrated with spectroscopic measurements performed using X-ray absorption near edge spectroscopy (μXANES) to determine oxidation state and speciation at the grain scale. To date, numerous X-ray microprobe studies have been used to examine distribution and speciation of many elements in diverse environmental samples, including investigating As speciation and mobility in poultry litter (Arai, et al., 2003), mapping toxic elements in nematodes (Jackson, et al., 2005), and examining Pb distribution and correlations in forest soils (Kaste, et al., 2006) as well as other applications and studies (Arai, et al., 2006; Denecke, et al., 2007; Freeman, et al., 2006; Hettiarachchi, et al., 2006; Moberly, et al., 2009; Negra, et al., 2005; Polizzotto, et al., 2005; Ryser, et al., 2006; Schroth, et al., 1998; Singer, et al., 2009; Tokunaga, et al., 2008). While these studies have provided invaluable information concerning the distribution of elements and mineral phases in solids, few link these observations to measures of dissolved concentrations directly, nor do they examine dynamic systems undergoing mineralogical changes that would influence solid-solution partitioning. To fully relate aqueous and solid-phase composition, it is preferable to directly study both the solid and the solution, and to examine their evolution over time.

Concurrent study of solids and solutions in a single experiment is complicated by the fact that the measurements used for each can differ considerably in scale and frequency. Solid-phase measurements often must be performed at the grain-scale to yield mechanistic information while aqueous concentrations are not simple to analyze at the same scale. Additionally, it may only be feasible to characterize the solid phase before and after a particular treatment, providing information on the end points of the reaction but not the progress of geochemical reactions over time. This is especially problematic for column studies, since columns generally need to be sacrificed for solid phase characterization, thereby ending the experiment (Gu, et al., 2005). Even when the endpoints are evaluated, it may be difficult to quantify changes due to the heterogeneous nature of environmental samples. We extend the use of microfocused synchrotron methods to study column solids *in situ* during reaction to directly observe the evolution of elemental composition, mineralogy, and speciation over time during reaction. As part of this work, we compare reaction parameters derived at various measurement scales (microprobe solid-phase measurements and cm-scale column experiments examining effluent composition) to determine if micron-scale kinetic measurements are representative of the column-scale.

Other researchers have studied column materials using microfocused X-ray techniques, but those studies have seldom performed analyses *in situ* or during reactions. Notably, μXANES has been used to study slow changes in U, Fe, and Mn speciation over a long time period (>1 yr) as a result of organic carbon input; this study quantified mineralogical changes along the column but couldn't guarantee that the exact same spots were evaluated each time (Tokunaga, et al., 2008). As a result, it was not possible to directly measure the transformation of specific phases with the data collected, nor could they quantify the rates of those transformations or link mineralogical transformations to transport properties of relevant aqueous species. We instead make repeated microfocused synchrotron X-ray measurements during chemical treatment while maintaining sample configuration; by doing so, we evaluate changes in distribution and correlation of elements due to treatment in the same sample location over time. The strength in this approach is that it quantifies relatively small changes in fluorescence intensity at the same location during the experiment. Since fluorescence intensity is proportional to concentration, these changes can be used to determine concentration changes in the solid-phase substrates over time, and thus insight into their rates of reaction. Changes in element abundance and speciation as well as correlation between elements can be evaluated on a pixel-by-pixel basis; each pixel is essentially its own kinetics experiment allowing hundreds or thousands of such experiments to take place simultaneously. The fine scale resolution of microfocused synchrotron methods also separates mineral phases into their component parts, in principle, allowing us to link variation in kinetic parameters to their underlying mineralogy. Such an approach may be useful for studying a wide variety of reaction processes in natural sediments, including contaminant removal due to chemical treatment, mineral precipitation due to changing redox characteristics, solid phase transformations, etc. In the application described here, we focus on As transport.

Arsenic is a prevalent contaminant found in drinking water supplies and at US Superfund sites (Cullen and Reimer, 1989; EPA, 2002; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). The mobility of As is highly dependent on its interactions with oxide bearing minerals making it critical to understand mineral scale processes in order to predict field scale transport (Dixit and Hering, 2003), and make informed decisions about managing this contaminant. Numerous studies examining As fate and transport in sediment-water mixtures have focused on adsorption and surface properties (Arai, et al., 2006; Moberly, et al., 2009), microcosms (Keimowitz, et al., 2005; Radloff, et al., 2007; van Geen, et al., 2004), columns (Kocar, et al., 2006; Kuhlmeier, 1997; Masue-Slowey, et al., 2010), or field scale observations (van Geen, et al., 2003) but few have examined the linkages between the scales. In this study, microfocused synchrotron X-ray fluorescence (μSXRF) spectroscopy was used to monitor the removal of Fe and As from sediments in column experiments during oxalic acid treatment. Laboratory work has suggested that oxalic acid, a naturally occurring soil acid, may be a useful part of field remediation schemes for As where pump and treat remediation is used for groundwater treatment (Wovkulich, et al., 2010), though more information is needed to understand the processes and fully evaluate the utility of oxalic acid to an As remediation scheme. Using μSXRF and μXANES, we investigate changes in As and Fe distribution in As contaminated sands during oxalic acid treatment as well as the rate of As removal. The goals of the work presented here are threefold: (1) to show that it is possible to run sediment column experiments in the synchrotron beamline and gather information about a particular part of the column at multiple time points during the experiment thus integrating microfocused techniques with column transport studies, (2) to use such techniques to investigate As release by oxalic acid, and (3) to use μSXRF data collected at the grain scale to calculate As release rates and determine if this rate information can be used to make predictions in larger scale systems.

3.3 Methods

3.3.1 Field methods

Aquifer solids were obtained from a pit freshly dug down below the water table with a backhoe in the most contaminated region of the Vineland Chemical Company Superfund site, a former As-based biocide manufacturing plant. The field site has been described in detail elsewhere (Wovkulich, et al., 2010). The sandy aquifer sediments used in these experiments were collected and then stored sealed in new metal paint cans at 4^{o}C until use. Groundwater used in the column experiments was collected from a pump and treat well on site with historically low As and low Fe concentrations (7 μg/L and 230 μg/L, respectively). The unfiltered groundwater was equilibrated with the atmosphere for several days, thereby further lowering As and Fe concentrations via precipitation, before moving it to cold storage (4°C) prior to use to minimize subsequent microbial activity.

3.3.2 Column experiments

Four small column experiments were performed (~4 cm x 0.635 cm ID). Three columns were run in the beamline; two of the three (#87-2 and #90) were analyzed by microfocused synchrotron X-ray fluorescence (μSXRF) and two of the three (#87-1 and #87-2) were evaluated before and after transport experiments with X-ray absorption near edge spectroscopy (μXANES). Configuration of each column was maintained for repeated measurements to ensure that the analysis window was identical. The fourth small column was run in the laboratory (#73) and not in the beamline to allow for frequent effluent measurements. Each of the column experiments was performed in a similar way with only minor alterations in column length and sediment packing efficiency.

For each column, the sandy aquifer material was wet packed into a section of clear polycarbonate tube with 0.635 cm ID (McMaster-Carr). Column lengths packed with sediments were between 4.0 and 4.6 cm (#73=4.25 cm, #87-1=4.6 cm, #87-2=4.3 cm, #90=4.0 cm). A small amount of glass wool was packed into each end to help distribute solution over the full cross sectional area of the column; the columns were sealed with nylon end caps. The columns were oriented vertically and solutions flowed upward through the columns at a groundwater velocity of ~3.4 m/d using a peristaltic pump (Rainin Instrument Co.). The flow velocity was comparable to the estimated average groundwater flow at the study site during active pumping for treatment (2-3 m/d estimated based on site dimensions and pump rates for optimal pump and treat parameters for the site). For columns experiments performed in the beamline, the polycarbonate walls were too thick for efficient penetration of fluorescence X-rays to the solids within the column. To address this, spectroscopy was performed through a Kapton window in the column. A section of the polycarbonate material was thinned, then covered with a layer of Kapton tape and/or X-ray transparent epoxy to prevent potential leakage.

Columns were initially treated with unamended groundwater to establish baseline conditions and allow collection of μSXRF and μXANES data within the region of interest in the beamline columns (#87-1, #87-2, #90) and to flush fine solids for the lab bench column (#73), ~1 pore volume for the lab bench column. Solutions of 10 mM oxalic acid in groundwater were then pumped through the columns for several pore volumes (approximately 17 pore volumes for #73, 39 for #87-1, 31 for #87-2, and 15 for #90). Each pore volume took approximately 17-20 minutes depending on the column length. For the experiment performed on the lab bench (#73), the oxalic acid treatment was followed by 4 pore volumes of groundwater. A fraction collector (LKB Bromma) was used to collect effluent samples for the lab bench experiment (#73), approximately one sample per pore volume. No effluent subsampling was performed on the columns carried out in the synchrotron beamline; however, effluent subsampling should be possible in future beamline experiments. For the lab bench experiment, samples were prepared for trace metal analysis directly following the experiment. Because of the small volume of sample in each pore volume, effluent samples were not filtered. We do not believe this biased our results since effluent Fe concentrations were smooth (suspended colloids would produce concentration spikes) and were consistent with results from larger columns where samples were filtered through 0.45 μm filters. Effective porosity of the columns was estimated to be 0.27, based on wet packed column weight and volumetric water content as determined from previous work on similar sediments (Wovkulich, et al., 2010); this porosity is also within the range determined for larger columns based on bromide tracer breakthrough curves.

3.3.3 Sediment digests

Samples of contaminated aquifer solids before and after column experiments with oxalic acid treatment were digested using concentrated nitric, perchloric, and hydrofluoric acids and analyzed for total As, Fe, Al, and Mn concentration (Fleisher and Anderson, 1991). Total As concentrations were corrected for recovery of a standard reference material.

3.3.4 Inductively coupled plasma mass spectrometry

Effluent samples and sediment digests were analyzed for As, Fe, Mn, and Al content using inductively coupled plasma mass spectrometry (ICP MS) with a high-resolution Axiom Single Collector instrument (Thermo Elemental). ^{115}In was added to each sample as an internal response standard and was used for drift correction. ^{27}Al, ^{55}Mn, ^{57}Fe, ^{75}As, and ^{115}In were analyzed with the instrument set at >8500 resolving power, which is sufficient to resolve the ^{75}As peak from Ar-Cl^{+} interference. Each sample and standard was run three times and averaged. Three to four point calibration curves were run at least once every 30 samples; calibration curves used for analysis of the data presented here had $R^2 > 0.98$.

3.3.5 Synchrotron analyses

Microfocused X-ray fluorescence (μSXRF) and X-ray absorption studies were conducted on beam X26A at the Brookhaven National Laboratory, National Synchrotron Light Source. μSXRF scans and maps were collected in focused monochromatic mode with a Si(111) monochromator using 13 keV incident X-rays. Elemental intensities of As and Fe were recorded using a Canberra 9-element Ge Array detector with integrated count times of 2 seconds per pixel. The fluorescence spectra at each pixel were normalized to incident photon intensity, I_0. The normalized fluorescence intensity is proportional to the amount of a given element in the pixel; within a constant volume, this fluorescence intensity is also proportional to a concentration. μSXRF scans covered an area of 0.168 x 0.168 mm with step size of 8 μm (400 pixels for column #90) or 0.3 x 0.3 mm with step size of 10 μm (930 pixels for #87-2).

For each experiment a baseline scan was taken before oxalic acid treatment, during introduction of water. Scans were taken approximately every 20 minutes during oxalic acid treatment (#90) or once before and once after treatment with oxalic acid (#87-2). The scan intervals for #90 correspond with the time required to collect the image. Although the reaction continues throughout data collection, the interval between collection at each pixel is constant, allowing a measured change in concentration to be related directly to a change in time at a given point. The columns were not moved for the duration of the experiments to ensure that each scan and pixel was reproducibly analyzed at the same location during the course of the reaction. Several points within two of the columns (#87-1 and #87-2) were chosen for microfocused X-ray absorption near edge spectroscopy (μXANES) to examine the forms of Fe present before and after oxalic acid treatment. Data were collected at the Fe K-edge over the energy range 7050 to 7220 eV. Background correction and normalization of the μXANES spectra were performed using WinXAS software (http://www.winxas.de/). Sample spectra were compared with standard spectra; linear combination fitting was performed using sixPACK software (http://ssrl.slac.stanford.edu/~swebb/sixpack.htm) to determine the percentage of various components. Samples were fit with a combination of a representative Fe (II) mineral (siderite), a representative Fe (III) mineral (ferrihydrite), and a representative Fe silicate (biotite). Data were not sufficiently robust to identify and quantify individual iron(III) (hydr)oxides.

3.3.6 PHREEQCI

One-dimensional transport and kinetic simulations were performed using PHREEQCI Version 2 (Charlton and Parkhurst, 2002). Using As removal rate constants derived from the μSXRF data and column parameters from laboratory experiments, PHREEQC models were constructed to predict the effluent As concentrations over time for column experiments of different lengths.

3.4 Results

3.4.1 Sediment characterization

Sediments used for the small laboratory column experiment #73 had a total of 86 ± 1 mg/kg for As, 540 ± 79 mg/kg for Fe, and 750 ± 16 mg/kg for Al (N=2). Sediments used for synchrotron column experiments (#87-1, #87-2, #90) had a total of 80 ± 4 mg/kg for As, 555 ± 15 mg/kg for Fe, and 788 ± 71 mg/kg for Al (N=3).

3.4.2 Arsenic and Fe removal from columns

Microfocused synchrotron X-ray fluorescence (μSXRF) data from scans taken before and during 10 mM oxalic acid treatment of column #90 indicate significant removal of As from the sediment column due to oxalic acid (Figure 3.1). Each map image has been matched with the closest corresponding effluent data point in terms of pore volumes for a column performed outside of the radiation hutch, column #73 (Figure 3.1). Arsenic released from column #73 in a large peak after introduction of 10 mM oxalic acid in the influent solution; maximum effluent As concentration was 92 mg/L. Arsenic counts for each map pixel were evaluated before and after oxalic acid treatment for the column experiments performed in the beamline (#90 and #87-2) and the percent removal at each pixel was averaged, which suggests that 79 ± 9% (± 1σ) and 83 ± 8% of the As was removed from each column, respectively (Table 3.1). Arsenic distribution in the scan area in column #90 varied spatially, with the lower portion of the analysis area (pixels 1-250) generally having higher starting As counts (average ~40% higher) than the upper portion of the image (pixels 251-400) (Figure 3.1). The upper portion of the image tended to have slightly higher average percent As removed (82% vs. 77%), though the difference is not statistically significant. Small increases in normalized As counts were observed at specific map points early in the reaction process; these increases may be due to spectral noise or may reflect precipitation or retardation within the column. However, by the end of the experiment all points showed a significant decrease in As counts. Based on complete digest data on sediments from before and after oxalic acid treatment, percent As removal was 88% for #90 and 88% for #87-2, very similar to the 79± 9% and 83± 8% predicted by comparison of μSXRF counts. Following the oxalic acid treatment, between 80% and 95% of the As had been removed from the aquifer solids of lab bench column #73; approximately 80% As removal was calculated based on digest of materials before and after treatment of column #73 while the 95% value is based on effluent concentrations and volume collected compared with the starting solids concentration according to sediment digest.

The μSXRF data from scans taken before and during 10 mM oxalic acid treatment suggest considerably less Fe removal from the sediments than As (Figure 3.1). Based on complete digestions performed on sediments from before and after oxalic acid treatment, percent Fe removal was 12% for column #90 while μSXRF data predicted an average of 25% removal. Evaluating the raw normalized Fe counts for each map pixel before and after oxalic acid treatment for the column experiments performed in the beamline (#90 and #87-2) and averaging the percent removal at each pixel suggests removal of 25± 32% (column #90) and 14± 14% (column #87-2) of the Fe; however, the values of individual pixels are often negative indicating precipitation or re-adsorption rather than removal (Table 3.2). Fe distribution in the scan area in column #90 varied spatially, with the lower portion of the analysis area (pixels 1-250) generally having higher starting Fe counts (~35% higher, 12833 ± 9403 vs. 8359 ± 5391 counts) than the upper portion of the image (pixels 251-400) (Figure 3.1). Points 251-400 also tended to have somewhat higher average percent Fe removed (30% vs. 22%), though there was a large spread in the data (standard deviation was on the order of the average). Bulk sediment digestions for column #87-2 actually suggest overall increases in Fe concentrations, which is not possible as Fe was eluted from the column but is possibly an artifact of sample heterogeneity since different sediment sub-samples were used to characterize initial and final Fe concentrations. The μSXRF measurements in this experiment were taken in the exact same location before and during oxalic acid treatment, which can alleviate the difficulties in making comparative measurements on different sub-samples and in fact represents an advantage for microscopic measurements rather than whole column estimates of loss. The mass of Fe collected in column effluent also can be used independently to determine the quantity of Fe mobilized in the experiment and provides a somewhat independent check of Fe loss, although it still depends on the either initial or final Fe concentrations determined by digestion. Based on effluent data, approximately 7% of the Fe was mobilized from the aquifer materials of lab bench column #73, comparable to the 9% of the Fe mobilized from a larger column experiment (Wovkulich, et al., 2010). Both are somewhat lower than the average Fe removal values predicted by μSXRF measurements, 14-25%.

Correlations between Fe and As counts at each pixel were also examined for column #90 before and after oxalic acid treatment (Figure 3.2). Arsenic and Fe are expected to be spatially related due to As adsorption to Fe phases, with varying strength of adsorption or association. Depending on the system being studied, multiple types of associations can be present and changes in correlations following treatment can indicate preferential removal of one or more of these phases. Within a correlation plot, a single compositionally-homogeneous phase of uniform thickness would form a point; Fe and As concentrations would correspond to the relative content of each element within that homogeneous phase. However, in samples such as these that have variable thickness and are heterogeneous, a single phase would form a line. The line would start near the origin (where the sample is thin or diluted by other phases) and would extend to some maximum level, which corresponds to the thickest portion of the purest phase. Prior to oxalic acid treatment, the As vs. Fe correlation plot has a cone-shaped appearance (broad divergence at the high end of concentration ranges for both constituents) indicating presence of at least two types of As/Fe associations, one with a much higher As:Fe ratio than the other. Following the oxalic acid treatment, the linear correlation between Fe and As is stronger (R^2=0.82); the slope decreases, indicating that the As:Fe ratio is lower in residual phases, consistent with the preferential removal of As from the column.

Table 3.1. Percent As removed on the basis of μSXRF data in columns undergoing 10 mM oxalic acid treatment

	Percent As Removed Based on μSXRF Data (%)			
Experiment	**Median**	**Mean**	**Standard Deviation**	**Mode**[c]
#90[a]	80%	79%	9%	80-85%
#87-2[b]	84%	83%	8%	85-90%

[a] Each scan took approximately 20 minutes and covered an area of 0.168 mm x 0.168 mm. Total number of pixels = 400.

[b] One scan was performed before and one after oxalic acid treatment. The scans covered an area of 0.3 mm x 0.3 mm. Total number of pixels = 930.

[c] Most common value was based on histogram transformation of the data points. Data were collected into bins of 5 percentage points.

Table 3.2. Percent Fe removed on the basis of μSXRF data in columns undergoing 10 mM oxalic acid treatment

	Percent Fe Removed Based on μSXRF Data (%)			
Experiment	**Median**	**Mean**	**Standard Deviation**	**Mode**[c]
#90[a]	30%	25%	32%	≤ 0 %[d]
#87-2[b]	15%	14%	14%	15-20%

[a] Each scan took approximately 20 minutes and covered an area of 0.168 mm x 0.168 mm. Total number of pixels = 400.

[b] One scan was performed before and one after oxalic acid treatment. The scans covered an area of 0.3 mm x 0.3 mm. Total number of pixels = 930.

[c] Most common value was based on histogram transformation of the data points. Data were collected into bins of 5 percentage points. All numbers ≤ 0 % were lumped into one bin.

[d] Percent Fe removed less than 0 indicate precipitation or re-adsorption of Fe at those pixels, rather than removal.

3.4.3 μXANES

Select points in columns #87-1 and #87-2 (4 points in each) were evaluated by Fe microfocused X-ray absorption near edge spectroscopy (μXANES) both before and after oxalic acid treatment. μXANES spectra from each point were fit by linear combinations of spectra of a representative Fe (II) species, Fe (III) species, and Fe silicate (Figure 3.3a, b). Percentages of Fe silicate were 8% or less except for one point following treatment (87-1a after). All points regardless of whether analysis was done before or after treatment consisted of approximately 60% Fe (III) or more, except for one point in #87-2 after treatment (87-2a after) which was best represented by ~50% Fe (II) and 50% Fe (III). Slight changes in distribution of Fe species exist from before to after treatment but the changes tend to be minor; the maximum change in Fe species for #87-1 is 14% and the maximum change for #87-2 is 11%. In several of the sample points, there is a slight increase in Fe silicate following treatment, which may represent removal of Fe(II) and

Fe(III) phases. In #87-1, sample points 87-1a and 87-1b show a slight drop in Fe (II) after treatment and in #87-2, sample point 87-2a shows a slight increase in Fe (II) after treatment. Overall, no significant differences were observed in the μXANES from before to after treatment, which is also consistent with SEM images (Supporting Information, Figure 3.7).

3.4.4 As and Fe removal rate

For column #90, μSXRF scans were taken every ~20 minutes; this is approximately equal to the time it takes for 1 pore volume to travel through the column (17 min). Arsenic counts for each map pixel were recorded at these time points. Normalized As counts over time are shown for several representative pixels in Figure 3.4. Three of the four pixel plots clearly show a lag period after oxalic acid is first introduced where As counts do not change appreciably during the initial scans. This is followed by a steady decline in As counts and then another plateau at which point the reaction reaches some form of steady-state. These points were chosen to show the range in As removal rates and variability with time after injections were initiated.

To extract kinetics information from the decreases in As concentrations, it is necessary to derive a rate expression for the mobilization/dissolution of surface bound As by oxalic acid. However, the nature of this mobilization mechanism is not completely clear and could be explained by competitive adsorption/desorption or As release prompted by the dissolution of species to which it is sorbed (Shi, et al., 2009; Zhang, et al., 2005). Both of these are adequately described by a second-order reaction rate equation.

$$d/dt\ (As)_{aq} = -k[As_{adsorbed}][\text{oxalic acid}]$$

This generalized equation applies to either mechanism since both involve the concentration of the same species and intrinsically, both depend on the surface area of adsorbing mineral phases, presumably primarily Fe- and Al-oxides. For rate calculations, oxalic acid concentrations can be assumed constant near input values (10 mM); previous column experiments (10 mM influent) indicated 99% recovery of oxalic acid (Wovkulich, et al., 2010). The second order equation can therefore be simplified to a pseudo first-order kinetic expression for the generalized reaction,

$$As_{adsorbed} \rightarrow As_{dissolved}$$

with an integrated rate law of

$$Ln[As_{adsorbed}] = -k't + Ln[As_{adsorbed}]_0$$

where $[As_{adsorbed}]$ is taken as normalized As counts, k' is the rate constant, and t is time. $Ln[As_{adsorbed}]$ vs. time should yield a straight line with slope of $-k'$, with k' referring to the pseudo first-order rate constant for As desorption. The natural log (Ln) of normalized As counts (proportional to concentration) was plotted against time (data not shown) and a desorption rate constant was calculated from the linear region. The first few time points yielded fairly stable normalized As counts as did the last few time points. We interpret these stable periods as an initial lag in As removal occurring in the first few pore volumes and then the reaction finishing before the final scan, likely due to removal of nearly all of the extractable As. The length of the lag-phase was not uniform for each pixel, and only the linear range for each pixel was utilized to determine rates. A range of rate constants were observed that appeared to be separated spatially based on these different map (sediment) regions (Figure 3.5). The lower portion of the map (points 1-250; closer to the inlet) had an average As removal rate constant of 0.011 ± 0.001 min^{-1} (average ± average standard error); the upper portion of the map (further from the inlet; points 251-400) had a somewhat higher average As removal rate constant of 0.022 ± 0.004 min^{-1} (Figure 3.5). The bulk average removal rate constant for the entire map area was 0.015 ± 0.002 min^{-1}; the bulk average rate constant was converted from a time based rate to a pore volume based rate by accounting for column dimensions, porosity, and flow rates and this pore volume based rate constant was used for PHREEQCI modeling.

A similar exercise was performed for μSXRF Fe data. Normalized Fe counts over time are shown for several pixels in Figure 3.4b. These plots indicate that while some pixels show slight decreases in Fe, others show no significant change, or even small increases. Pseudo-first order kinetics were applied and Fe removal rate constants were calculated from the slope of $\text{Ln}[\text{Fe}_{\text{absorbed}}]$ vs. time. All scans taken during the oxalic acid treatment were used in the rate constant calculations. The average Fe removal rate constant was 0.001 ± 0.0002 min^{-1} (average ± average standard error). Some pixels showed negative Fe removal rate (i.e., re-precipitation or re-adsorption) (Supporting Information, Figure 3.8).

3.4.5 PHREEQCI

Using basic column parameters from laboratory columns and a pore volume based rate derived from the bulk As removal rate constant calculated above, one-dimensional transport and As release kinetics were modeled with PHREEQCI (Table 3.3). Expected effluent As concentrations were calculated and compared with the effluent As concentrations from the small (4.25 cm x 0.635 cm ID) laboratory column #73 (Figure

3.6a). The time based rate constant derived from μSXRF data was converted to a pore volume based rate constant by multiplying the time based rate constant, k′ (min^{-1}), by the number of minutes per pore volume in column #90, the column for which the rate was originally calculated. Although the average rate constant used in these calculations is independent of As release mechanism, local variations in mechanism may locally impact release rates. A four-pore volume lag, during which no As was released, was introduced into the model to better represent the data; the lag is presumed to relate to equilibration with oxalic acid. The model data was also averaged such that there was one effluent data point per pore volume to match the sampling frequency of the small column run on the laboratory bench (#73). The PHREEQCI model calculates As release at each time step, recalculating for subsequent steps based on mass of As remaining in the sediments. In the PHREEQCI modeled small column, the maximum effluent As concentration occurred at 6 pore volumes with a magnitude of 116 mg/L; in the laboratory column (#73), the maximum effluent As concentration occurred 6.3 pore volumes after oxalic acid introduction with a magnitude of 92 mg/L (Figure 3.6a).

The same bulk average As removal rate constant derived from the μSXRF data was applied to describe As breakthrough in a larger sediment column (referred to as large column here). This column contained sediments collected at the same time and same location as materials used in the small columns; the column was approximately 23 cm long (23.5 cm x 4.2 cm ID) and was treated with 10 mM oxalic acid. Details regarding that laboratory column are reported elsewhere (Wovkulich, et al., 2010). A three-pore volume lag, during which no As was released, was introduced into the model to better represent the data. The model data was averaged such that there was one effluent data points per 0.1 pore volumes to more closely match the sampling frequency of the column run in the laboratory. In the PHREEQCI modeled large column, the peak in effluent As occurred at 4.2 pore volumes with a magnitude of 88 mg/L; in the laboratory column, the peak in effluent As occurred 4.3 pore volumes after oxalic acid introduction with a magnitude of 100 mg/L (Figure 3.6b). In the PHREEQCI modeled column with pore-volume based rate, it took approximately 9 pore volumes to reach 80% As removal while in the laboratory column, it took 7 pore volumes after oxalic acid introduction.

Table 3.3. Parameters for PHREEQC Models

Relative Column Size	Small (#73)[a]	Large[b]
Sediment Properties		
As concentration (mg/kg)	86	81
Porosity	0.27	0.33
Column Properties		
Total column length (cm)	4.25	23.5
Time/pore volume (min)	18	158
Other PHREEQC inputs		
# Cells	20	20
# Shifts	400	400
Length/cell (cm)	0.2125	1.175
Time step (s)	54	475
Total # pore volumes	20	20
# Pore volumes lag	4	3
As removal rate (pv^{-1})	0.2608	0.2608

[a] Small column parameters are based on lab bench column #73, except for As removal rate which was derived from synchrotron column #90.

[b] Large column parameters are based on a 23.5 cm long lab bench column (Wovkulich, et al., 2010), except for As removal rate which was derived from synchrotron column #90.

3.5 Discussion

3.5.1 As removal from columns

Performing column experiments within the microfocused synchrotron beamline has allowed integration of data from the solid phase with column transport information and shows that microscale processes observed within a small portion of the column are, at least in this case, predictive of the larger system. Microfocused synchrotron X-ray fluorescence (μSXRF) data indicate that an average of 79-83% of As is removed by 10 mM oxalic acid treatment over the course of the experiment based on the change in normalized As counts at individual pixels over time. Initial experiments where sediment sub-samples from columns were scanned before and after oxalic treatment had significant limitations. It was clear from those results that As counts had decreased, but changes in As/Fe correlations were not clear; results indicated overall Fe counts increased due to a local hotspot in the after treatment sample and no rate data could be obtained. Therefore, a method was developed where a column experiment could be performed real-time within the microfocused beam. In the experiments described here, the extent of Fe and As removal was consistent between μSXRF scans, column effluent, and column solids. This agreement indicates that relative concentrations determined from μSXRF scans in the same location of a sediment core over the course of a reaction can be related to macroscopic removal. Moreover, it suggests that As and Fe dissolution and transport observed within a very small (<1 mm^2) scan area can be representative of larger scale transport and that variation in removal rates observed at the micron-scale is representative of chemical or physical heterogeneity in the sediment.

Throughout the scan region, As and Fe counts decreased over the course of the experiment corresponding to the decrease in As and Fe concentrations on the solids. In initial scans of beamline column #90 (each scan took ~20 minutes), most pixels displayed near constant or modestly increasing As counts. This increase in As counts suggests that As was not removed, and actually may have locally increased over that short time interval. This may result from random noise in As counts or may indicate that advected As is accumulating, at least transiently due to initial redistribution processes. However, by the end of the experiment, no pixel showed increased As counts compared to the initial scan. Arsenic re-adsorption is likely limited due to competitive sorption between oxalic acid and arsenate (Shi, et al., 2009) and removal of reactive Fe surfaces.

Although experiment #87-2 included more pore volumes of oxalic acid than #90 (31 vs. 15), cumulative As mobilization was similar in both columns (79-83%). Thus only ~80% of the As in these aquifer sediments appears to be mobilized by oxalic acid treatment; further treatment did not yield full As removal. However, this process results in fairly rapid release of a significant portion of the sediment As and may be well suited for extraction-based remediation strategies.

3.5.2 Fe removal from columns

There are several interesting components to the Fe data that provide mechanistic information about the mineralogy of adsorption, and the control of the underlying substrate on As removal. There is evidence for Fe re-precipitation based on the μSXRF data, which may contribute to the relatively low overall net Fe removal from the columns. Following the addition of oxalic acid to the columns, a significant number of data points or pixels consistently show Fe accumulation (an increase in normalized Fe counts over time) rather than Fe removal. For column #90, nearly 20% of the data points had $\leq 0\%$ Fe removal (12% for #87-2). The accumulation of Fe observed within these pixels appears to be real, and indicates that while Fe is mobilized within the column, it is not effectively advected through the column and instead re-precipitates or re-adsorbs in other areas. Because re-precipitation of Fe is evident on the sub millimeter scale (scan area <1 mm^2) in the small columns, it is likely that re-precipitation or re-adsorption of Fe is also taking place throughout the small and large columns. The re-precipitation and re-adsorption of Fe may help to explain the limited extent of net Fe removal even though oxalic acid has been shown to complex and dissolve Fe species (Baumgartner, et al., 1983; Blesa, et al., 1987; Lee, et al., 2007; Panias, et al., 1996). SEM data also indicates that Fe removal was limited as Al and Fe coatings on quartz grains are still present following oxalic acid treatment (Supporting Information).

Previous work has shown that in the large oxalic acid columns, Al, As and Fe breakthrough did not occur at the same time; Al began to release first, then As, followed by Fe (Wovkulich, et al., 2010). This difference in breakthrough prompted us to question whether As release was predicated on Fe dissolution and transport since Fe transport appears to occur following As release. However, the μSXRF data provides direct evidence for Fe re-precipitation or re-adsorption and offers an alternate possibility; As and Fe release do happen concurrently, at least to some extent, but Fe re-precipitation, re-adsorption, and retardation within the column delay and/or suppress Fe appearance in the effluent solution.

Correlations between As and Fe counts as measured by μSXRF were examined before and after oxalic acid treatment (Figure 3.2). Before oxalic acid treatment, the As vs. Fe plot shows a fair amount of scatter in a cone shaped pattern, which could indicate the presence of multiple types of As/Fe associations. Following oxalic acid treatment the As vs. Fe plot shows a stronger linear correlation (R^2=0.82). Several factors could contribute to the increased correlation between As and Fe after oxalic acid treatment.

The oxalic acid treatment may have preferentially mobilized certain types of As (weakly sorbed) and/or Fe, leaving behind one type of well correlated Fe and As, perhaps a more crystalline form. It is clear that As was removed preferentially over Fe based on the percent removal for each, though a fraction of Fe is re-adsorbed or re-precipitated. Since the As in these solids is largely As(V) based on bulk XANES data (not shown), it is unlikely that the stronger correlations are the result of one oxidation state of As being preferentially removed. However, the adsorption of As(V) to certain Fe binding sites could have been stronger than to others, allowing weaker adsorption sites to release As preferentially and leaving behind As which is more strongly adsorbed to Fe. In addition, it is possible that there was preferential removal of certain Fe phases (amorphous oxides) or minerals (labile) and therefore, the As associated with those. The scatter in the data prior to oxalic acid treatment could also have been the product of As interactions with other phases such as Mn or Al oxides; these oxides can provide sorption sites for As (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002; Sullivan and Aller, 1996). If the As was released from these sites preferentially, the correlation between As and Fe could have strengthened following oxalic acid treatment. Moreover, the association of As with low percentage Fe minerals such as silicates would cause them to have higher As:Fe ratios than observed for Fe oxides, suggesting that the As was preferentially removed from Fe silicates.

3.5.3 μXANES

The μXANES spectra provide insight into how Fe mineralogy changes during re-precipitation and extraction with oxalic acid, and could help determine if redox transformations have occurred within the column (Templeton, et al., 2003). Data from Fe μXANES scans taken before and after oxalic acid treatment in columns #87-1 and 87-2 on 4 points each indicate that Fe at these points exist predominantly as Fe (III) and the spectra most closely resemble some mixture of ferrihydrite and hematite; however, it is difficult to differentiate between the Fe (III) minerals with the data collected. Differentiation may have been possible if we had performed spectral averaging of several scans at each point before and after reaction, but this was not possible to complete within the allotted beamline time. Therefore, formation of secondary minerals during the leaching experiment is possible; original Fe could have existed as goethite and re-precipitated, redistributed, or otherwise transformed Fe could exist as ferrihydrite, but we cannot confirm this with the present data. There is no evidence for significant change (always <14%) in oxidation state from before to after the oxalic acid treatment.

3.5.4 Rates of As removal and comparisons with PHREEQCI models

Net As removal modeled by PHREEQCI for small and large columns agree well with effluent data from the laboratory columns when using a pore volume based As removal rate (Figure 3.6). The size of the column is not important and based on these results, one would expect similar results on a per pore volume basis for 4 cm columns or field scale "columns." Contact time appears not to be important as 4 cm columns require ~20 min per pore volume while 23 cm columns require ~2.5 hrs per pore volume, yet columns still quickly achieved nearly equivalent As removal rates indicating rapid equilibrations of the removal reactions.

A lag time, where no significant As release is seen in the first few pore volumes, was necessary to include in the models to improve the match; we believe this is related to the buffering capacity and pH within the column. Oxalic acid is known to mobilize Al and Fe (Lee, et al., 2007; Li, et al., 2006). Therefore, one may hypothesize that removal of Al and Fe sorption sites leads to As release and As release is related to Fe release. Since Fe release occurs optimally at a pH of 2-3 (Lee, et al., 2007; Panias, et al., 1996), there is a lag initially in As release as the buffer capacity of the sediment is overcome. Once sediment pH is low enough and oxalic acid is therefore predominantly found as $HC_2O_4^-$, Fe and thus As release occurs (Figure 3.6b). In the large column, As release begins to increase ~2 pore volumes after the introduction of oxalic acid when the effluent pH is still 4.5-5. The buffer capacity of sediments early in the column may have been overcome within a short time frame leading to the initiation of As release while pH buffering in the later sediments kept the effluent pH high until additional effluent passed. The peak in As concentration occurs when the pH is ~2.5-3. This suggests that pH 2-3 is optimal for As release as well, perhaps because As release is linked to Fe release. Since pKa_1 for arsenate is 2.15, desorption of uncharged As species may also play a role. While we know pH to be important to the release of As by oxalic acid, we do not believe the sole mechanism of release to be pH based, i.e. As release by oxalic acid is not simply proton promoted. Extraction experiments using similar pH of inorganic acids (HCl or HNO_3) do not show as much As release as oxalic acid; at the 1 mM (pH 3) and 10 mM (pH 2) level, oxalic acid mobilized at least double the As as HCl (Chapter 5, Appendix C).

A longer lag time in the models is necessary for the small column than the large, which may be partly explained by the differences in pore volume size and the volume in the tubing leading up to the laboratory columns. The small column (#73) has a pore volume of just ~0.4 mL while the large column has a pore volume closer to 100 mL. Oxalic acid introduction was marked from the time the tubing entered the oxalic influent bottle; the volume held by the tubing leading up to the bottom of the columns would be a much larger percentage of a pore volume for the small column than the large.

It is worth considering that other factors, besides As concentration (or counts), may be important to the removal rate on scales larger than microscale. Studies have investigated oxalic acid removal rates of Fe in various systems and have suggested that other parameters such as pH and oxalate concentration may need to be considered in rate equations (Lee, et al., 2007; Lee, et al., 2006). Including such parameters in transport models could further improve agreement between modeled data and laboratory data, especially for larger columns and larger systems. Similar considerations may also prove useful in creating a more accurate As removal rate equation but are beyond the scope of this study.

3.6 Conclusions

We have shown that it is possible to run sediment column experiments in the synchrotron beamline and gather information about a particular part of the column at multiple time points during the experiment and integrate microfocused synchrotron techniques with column transport studies. The decrease in overall As and Fe counts over the treatment time showed that oxalic acid mobilized these species, with net As removal being greater than Fe removal. Arsenic and Fe release based on μSXRF counts from before and after oxalic acid treatment were consistent with laboratory column effluent data. The small scale (<1 mm^2) μSXRF maps, therefore, provide information regarding net removal and removal rates consistent with the bulk material (small column and large column).

We used a combination of μSXRF data and PHREEQCI models to investigate As release rate information. Columns modeled with a pore volume based As removal rate agreed fairly well with laboratory effluent data for both small and large columns. This would suggest one could expect similar results in the field on a per pore volume basis. However, extrapolating the rate information to larger systems may be complicated by other factors that impact large-scale transport (diffusion, dispersion, preferential transport pathways, increased variability in concentrations and matrix composition, etc.); a more complete and more effective rate equation might require information on additional parameters such as pH or oxalic acid concentration.

Performing column studies within a microfocused synchrotron beamline offers a powerful approach for studying microscale changes in element abundance and distribution over time and relating these changes to column transport. Since the same area of sediment is examined each time, reaction rate information can also be obtained for each pixel in the map area; this precisely focused approach essentially allows study of hundreds of reactions at once and provides more statistically relevant reaction rates. These microfocused synchrotron techniques should find application for studying a wide variety of reaction processes.

3.7 Acknowledgements

The authors would like to thank the US EPA, the US Army Core of Engineers, and Sevenson Environmental at the Vineland Superfund Site for access to samples and support on site. Portions of this work were conducted at beamline X26a National Synchrotron Light Source (NLSL), Brookhaven National Laboratory. X26a is supported by the U.S. Department of Energy (DOE) - Geosciences (DE-FG02-92ER14244 to The University of Chicago - CARS) and DOE - Office of Biological and Environmental Research, Environmental Remediation Sciences Div. (DE-FC09-96-SR18546 to the University of Kentucky). Use of the NSLS was supported by DOE under Contract No. DE-AC02-98CH10886. The authors would like to thank Antonio Lanzirotti for assistance with microprobe work on beamline X26a. This work was supported by the Superfund Research Program (NIEHS Grant ES010349). Additional support was provided by NIEHS Grant ES0090890. This is LDEO publication xxxx.

3.8 References

Arai, Y., Lanzirotti, A., Sutton, S.R., Newville, M., Dyer, J., Sparks, D.L., 2006. Spatial and temporal variability of arsenic solid-state speciation in historically lead arsenate contaminated soils. Environ. Sci. Technol. 40, 673-679.

Baumgartner, E., Blesa, M.A., Marinovich, H.A., Maroto, A.J.G., 1983. Heterogeneous Electron-Transfer as a Pathway in the Dissolution of Magnetite in Oxalic-Acid Solutions. Inorg. Chem. 22, 2224-2226.

Blesa, M.A., Marinovich, H.A., Baumgartner, E.C., Maroto, A.J.G., 1987. Mechanism of Dissolution of Magnetite by Oxalic Acid-Ferrous Ion Solutions. Inorg. Chem. 26, 3713-3717.

Bone, S.E., Gonneea, M.E., Charette, M.A., 2006. Geochemical cycling of arsenic in a coastal aquifer. Environ. Sci. Technol. 40, 3273-3278.

Charlton, S.R., Parkhurst, D.L., 2002. PHREEQCI: A graphical user inerface to the geochemical model PHREEQC. USGS Survey Fact Sheet. FS-031-02.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713-764.

Denecke, M.A., Somogyi, A., Janssens, K., Simon, R., Dardenne, K., Noseck, U., 2007. Microanalysis (micro-XRF, micro-XANES, and micro-XRD) of a tertiary sediment using microfocused synchrotron radiation. Microsc. Microanal. 13, 165-172.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environ. Sci. Technol. 37, 4182-4189.

EPA, 2002. Arsenic treatment technologies for soil, waste, and water. http://www.clu-in.org/download/remed/542r02004/arsenic_report.pdf.

Fleisher, M.Q., Anderson, R. (1991), Particulate matter digestion (from mg to 10's of g) and radionuclide blanks, paper presented at Marine Particle Analysis and Characterization; American Geophysical Union, Washington, DC.

Freeman, J.L., Zhang, L.H., Marcus, M.A., Fakra, S., McGrath, S.P., Pilon-Smits, E.A.H., 2006. Spatial imaging, speciation, and quantification of selenium in the hyperaccumulator plants Astragalus bisulcatus and Stanleya pinnata. Plant Physiol. 142, 124-134.

Gu, B.H., Wu, W.M., Ginder-Vogel, M.A., Yan, H., Fields, M.W., Zhou, J., Fendorf, S., Criddle, C.S., Jardine, P.M., 2005. Bioreduction of uranium in a contaminated soil column. Environ. Sci. Technol. 39, 4841-4847.

Hettiarachchi, G.M., Scheckel, K.G., Ryan, J.A., Sutton, S.R., Newville, M., 2006. mu-XANES and mu-XRF investigations of metal binding mechanisms in biosolids. J. Environ. Qual. 35, 342-351.

Johannesson, K.H., Tang, J., 2009. Conservative behavior of arsenic and other oxyanion-forming trace elements in an oxic groundwater flow system. Journal of Hydrology. 378, 13-28.

Kaste, J.M., Bostick, B.C., Friedland, A.J., Schroth, A.W., Siccama, T.G., 2006. Fate and speciation of gasoline-derived lead in organic horizons of the northeastern USA. Soil Sci. Soc. Am. J. 70, 1688-1698.

Keimowitz, A.R., Simpson, H.J., Stute, M., Datta, S., Chillrud, S.N., Ross, J., Tsang, M., 2005. Naturally occurring arsenic: Mobilization at a landfill in Maine and implications for remediation. Appl. Geochem. 20, 1985-2002.

Kocar, B.D., Herbel, M.J., Tufano, K.J., Fendorf, S., 2006. Contrasting effects of dissimilatory iron (III) and arsenic (V) reduction on arsenic retention and transport. Environ. Sci. Technol. 40, 6715-6721.

Kuhlmeier, P.D., 1997. Sorption and desorption of arsenic from sandy soils: column studies. Journal of Soil Contamination. 6, 21-36.

Lee, S.O., Tran, T., Jung, B.H., Kim, S.J., Kim, M.J., 2007. Dissolution of iron oxide using oxalic acid. Hydrometallurgy. 87, 91-99.

Lee, S.O., Tran, T., Park, Y.Y., Kim, S.J., Kim, M.J., 2006. Study on the kinetics of iron oxide leaching by oxalic acid. Int. J. Miner. Process. 80, 144-152.

Li, J.Y., Xu, R.K., Tiwari, D., Ji, G.L., 2006. Mechanism of aluminum release from variable charge soils induced by low-molecular-weight organic acids: Kinetic study. Geochim. Cosmochim. Acta. 70, 2755-2764.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta. 58, 201-235.

Masue-Slowey, Y., Kocar, B.D., Bea Jofré, S.A.s., Mayer, K.U., Fendorf, S., 2010. Transport Implications Resulting from Internal Redistribution of Arsenic and Iron within Constructed Soil Aggregates. Environ. Sci. Technol. 45, 582-588.

Moberly, J.G., Borch, T., Sani, R.K., Spycher, N.F., Sengor, S.S., Ginn, T.R., Peyton, B.M., 2009. Heavy Metal-Mineral Associations in Coeur d'Alene River Sediments: A Synchrotron-Based Analysis. Water Air Soil Pollut. 201, 195-208.

Negra, C., Ross, D.S., Lanzirotti, A., 2005. Soil manganese oxides and trace metals: Competitive sorption and microfocused synchrotron X-ray fluorescence mapping. Soil Sci. Soc. Am. J. 69, 353-361.

O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. Proceedings of the National Academy of Sciences. 101, 13703-13708.

Panias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A., 1996. Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. Hydrometallurgy. 42, 257-265.

Polizzotto, M.L., Harvey, C.F., Li, G., Badruzzman, B., Ali, A., Newville, M., Sutton, S., Fendorf, S., 2006. Solid-phases and desorption processes of arsenic within Bangladesh sediments. Chem. Geol. 228, 97-111.

Polizzotto, M.L., Harvey, C.F., Sutton, S.R., Fendorf, S., 2005. Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. Proceedings of the National Academy of Sciences of the United States of America. 102, 18819-18823.

Radloff, K., Cheng, Z., Rahman, M., Ahmed, K., Mailloux, B., Juhl, A., Schlosser, P., van Geen, A., 2007. Mobilization of arsenic during one-year incubations of grey aquifer sands from Araihazar, Bangladesh. Environ. Sci. Technol. 41, 3639-3645.

Roden, E.E., Urrutia, M.M., Mann, C.J., 2000. Bacterial reductive dissolution of crystalline Fe(III) oxide in continuous-flow column reactors. Appl. Environ. Microbiol. 66, 1062-1065.

Ryser, A.L., Strawn, D.G., Marcus, M.A., Fakra, S., Johnson-Maynard, J.L., Moller, G., 2006. Microscopically focused synchrotron X-ray investigation of selenium speciation in soils developing on reclaimed mine lands. Environ. Sci. Technol. 40, 462-467.

Schroth, M.H., Istok, J.D., Conner, G.T., Hyman, M.R., Haggerty, R., O'Reilly, K.T., 1998. Spatial variability in in situ aerobic respiration and denitrification rates in a petroleum-contaminated aquifer. Ground Water. 36, 924-937.

Shi, R., Jia, Y.F., Wang, C., Shuhua, Y., 2009. Mechanism of arsenate mobilization from goethite by aliphatic carboxylic acid. J. Hazard. Mater. 163, 1129-1133.

Singer, D.M., Zachara, J.M., Brown, G.E., 2009. Uranium Speciation As a Function of Depth in Contaminated Hanford Sediments - A Micro-XRF, Micro-XRD, and Micro- And Bulk-XAFS Study. Environ. Sci. Technol. 43, 630-636.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517-568.

Sullivan, K.A., Aller, R.C., 1996. Diagenetic cycling of arsenic in Amazon shelf sediments. Geochim. Cosmochim. Acta. 60, 1465-1477.

Templeton, A.S., Trainor, T.P., Spormann, A.M., Brown, G.E., 2003. Selenium speciation and partitioning within Burkholderia cepacia biofilms formed on alpha-Al2O3 surfaces. Geochim. Cosmochim. Acta. 67, 3547-3557.

Tokunaga, T.K., Wan, J., Kim, K., Sutton, S.R., Lanzirotti, A., Rao, W., 2008. Real-time x-ray absorption spectrscopy of uranium, iron, and manganese in contaminated sediments during bioremediation. Environ. Sci. Technol. 42, 2839-2844.

van Geen, A., Horneman, A., Aziz, Z., Hoque, M.A., Shamsudduha, M., Cheng, Z.Q., Dhar, R.K., Versteeg, R., Steckler, M., Mailloux, B., Zheng, Y., Stute, M., Goodbred, S.L., Ahmed, K.M., 2003. Spatial variability of arsenic concentrations and sediment properties in Bangladesh aquifers. Abstracts of Papers of the American Chemical Society. 226, U583-U583.

van Geen, A., Rose, J., Thoral, S., Garnier, J.M., Zheng, Y., Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. Geochim. Cosmochim. Acta. 68, 3475-3486.

Wovkulich, K., Mailloux, B.J., Lacko, A., Keimowitz, A.R., Stute, M., Simpson, H.J., Chillrud, S.N., 2010. Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation. Appl. Geochem. 25, 1500-1509.

Zhang, S.Z., Li, W., Shan, X.Q., Lu, A.X., Zhou, P.J., 2005. Effects of low molecular weight organic anions on the release of arsenite and arsenate from a contaminated soil. Water Air Soil Pollut. 167, 111-122.

3.9 Figures

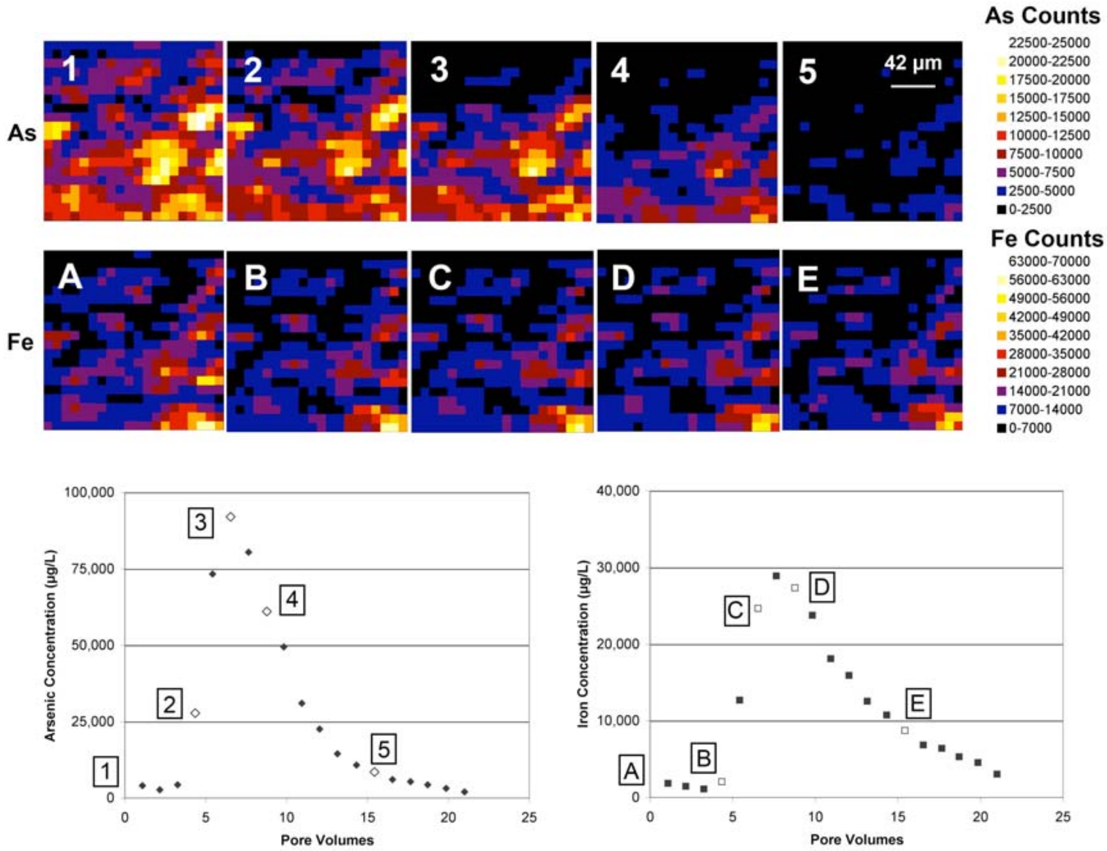


Figure 3.1. µSXRF maps showing As and Fe counts in a 0.168 mm x 0.168 mm section of column #90 before (1 for As and A for Fe) and (2-5 for As and B-E for Fe) during treatment with 10 mM oxalic acid. Flow direction is from the bottom of the map to the top. For reference, maps are correlated with points on the effluent concentration vs. pore volumes graph of laboratory column #73. Arsenic map #1 and Fe map A were collected prior to introduction of oxalic acid. Arsenic maps #2-5 and Fe maps B-E were matched with the closest effluent measurement in column #73 based on number of pore volumes (open symbols).

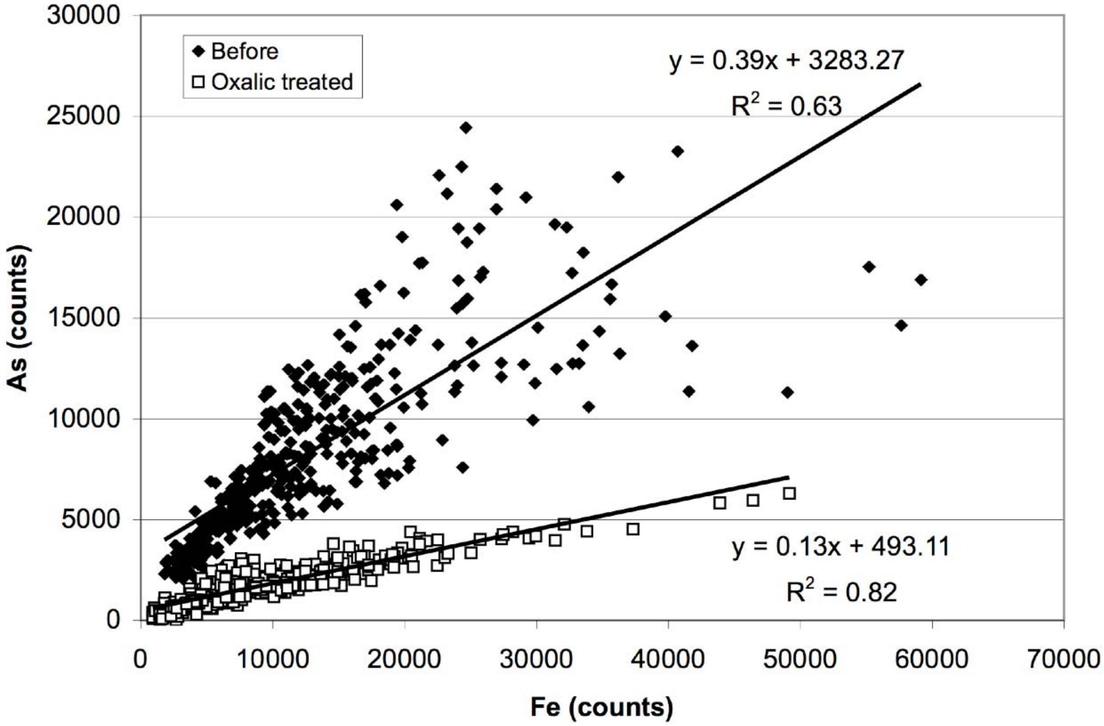


Figure 3.2. Correlations between As and Fe counts from μSXRF measurements before and after oxalic acid treatment. The equation for each line and the R^2 values are shown.

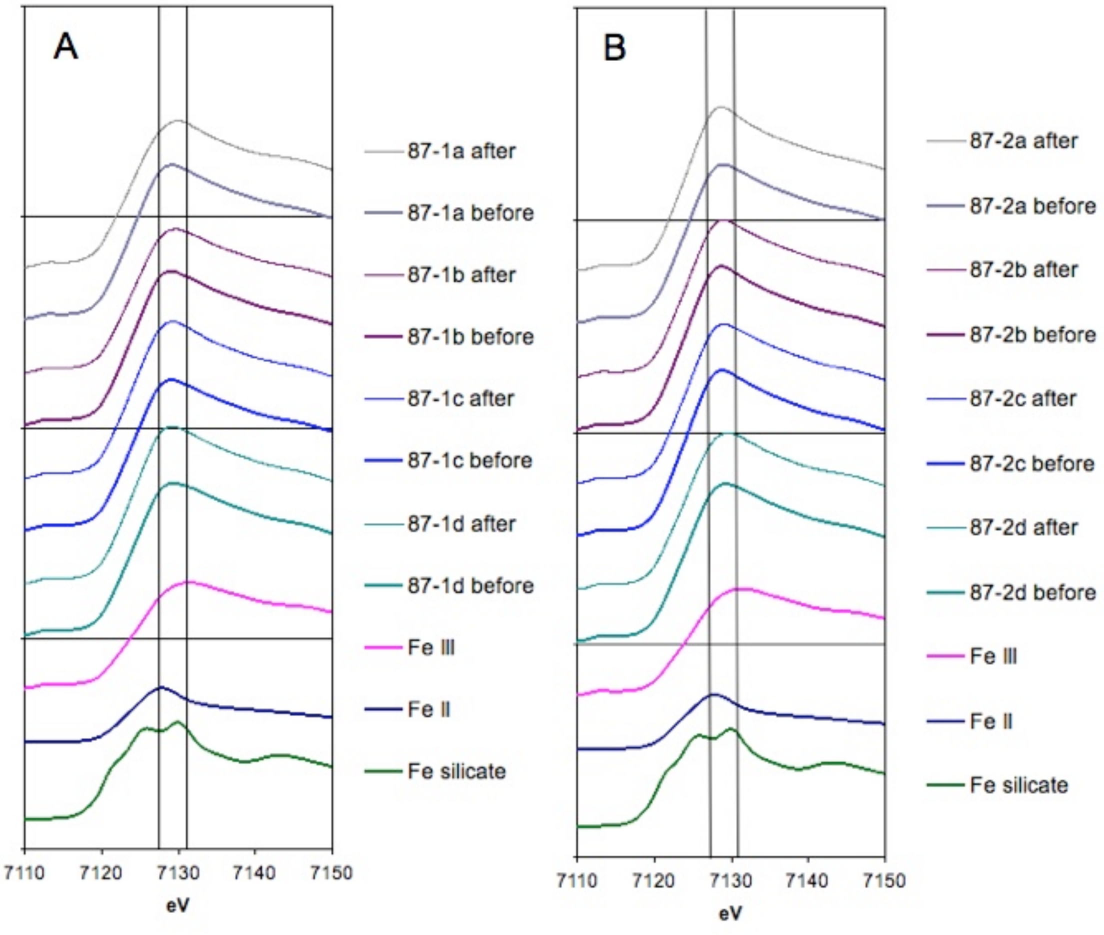
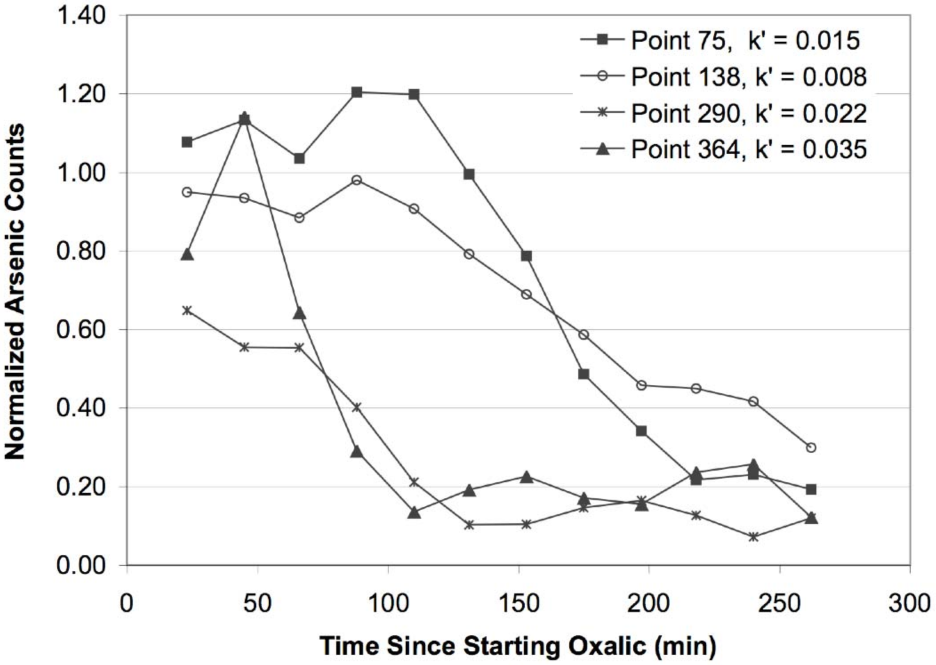


Figure 3.3. μXANES fits for selected points before and after oxalic acid treatment as well as Fe standards for comparison. The two vertical lines show approximate locations for maximum signal in Fe II (right) and Fe III (left) species. (a) Fits for column #87-1. (b) Fits for column #87-2. Minimal change in Fe species occurred as a result of oxalic acid treatment.

A


1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Normalized Arsenic Counts
0
50
100
150
200
250
300
Time Since Starting Oxalic (min)
Point 75, k' = 0.015
Point 138, k' = 0.008
Point 290, k' = 0.022
Point 364, k' = 0.035

B

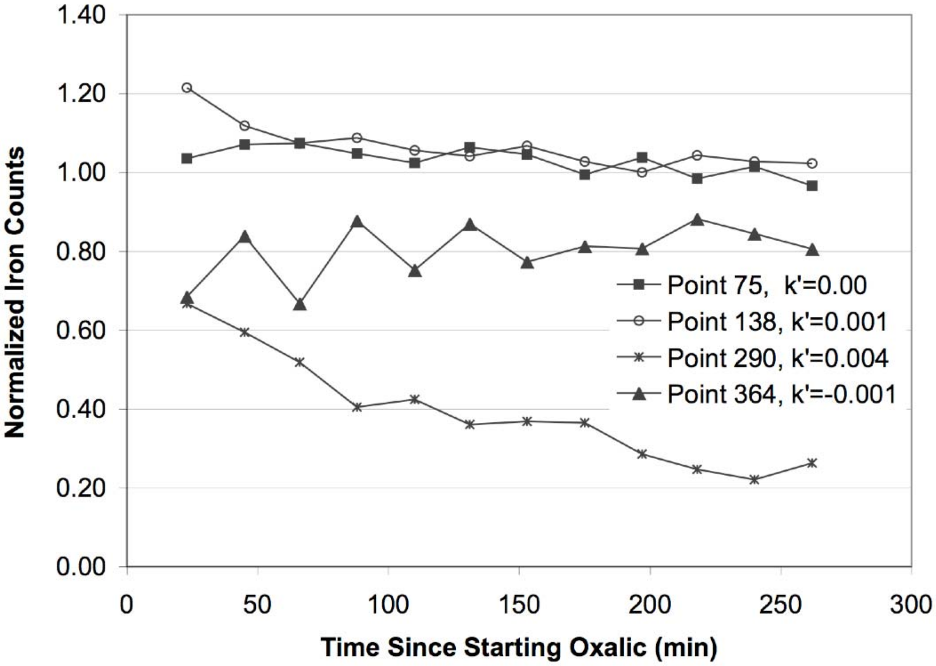

1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Normalized Iron Counts
0
50
100
150
200
250
300
Time Since Starting Oxalic (min)
Point 75, k'=0.00
Point 138, k'=0.001
Point 290, k'=0.004
Point 364, k'=-0.001

Figure 3.4. (a) Normalized As counts over time as measured by μSXRF. Arsenic counts were normalized to values of the scan taken prior to oxalic acid introduction. Arsenic removal rate constants (min^{-1}) are shown for reference. The rate constants were calculated from the linear portion of graphs of Ln normalized counts vs. time.
(b) Normalized Fe counts over time as measured by μSXRF. Fe counts were normalized to values of the scan that was taken prior to oxalic acid introduction. Fe removal rate constants (min^{-1}) are shown for reference. The rate constants were calculated from the linear portion of graphs of Ln normalized counts vs. time.

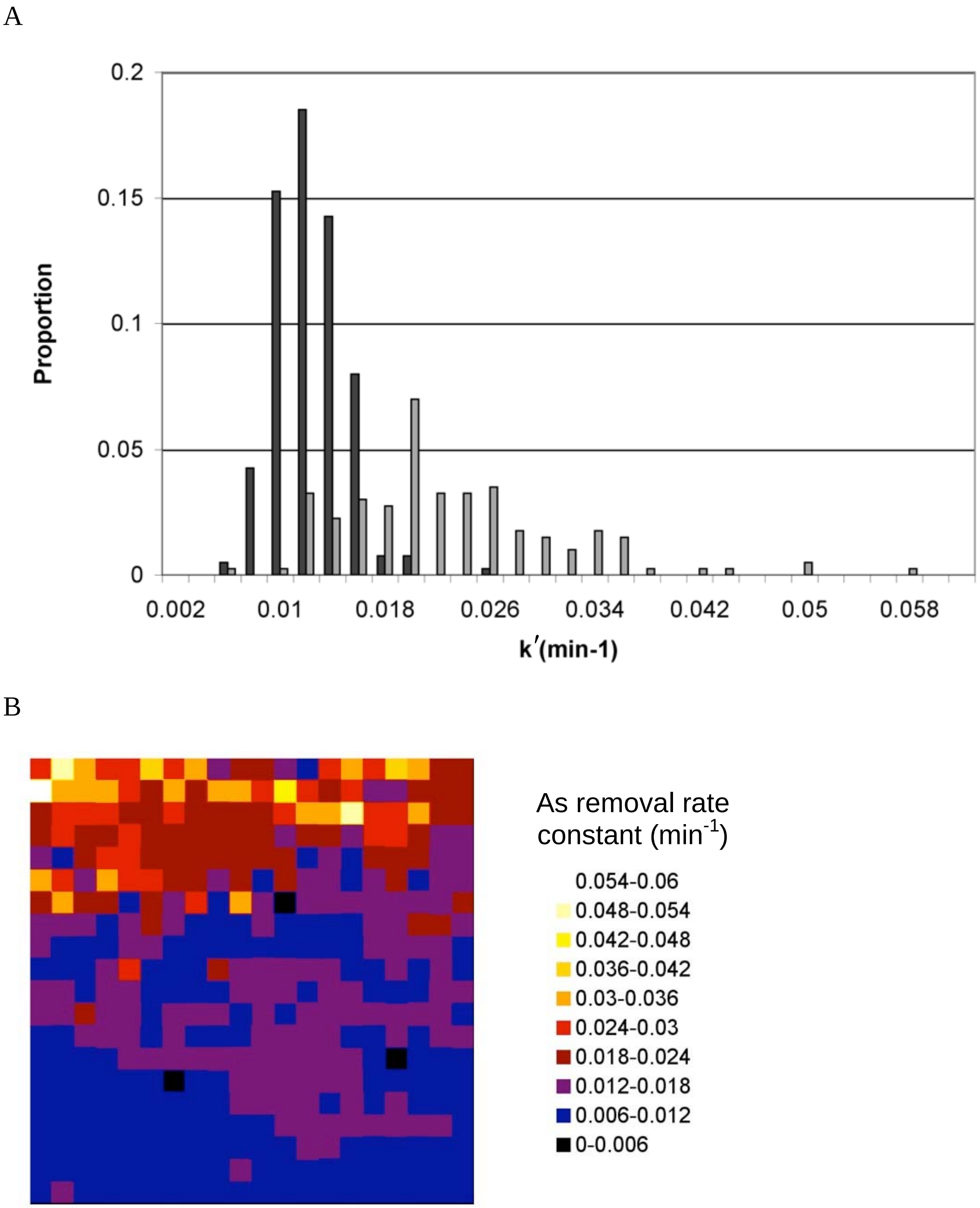
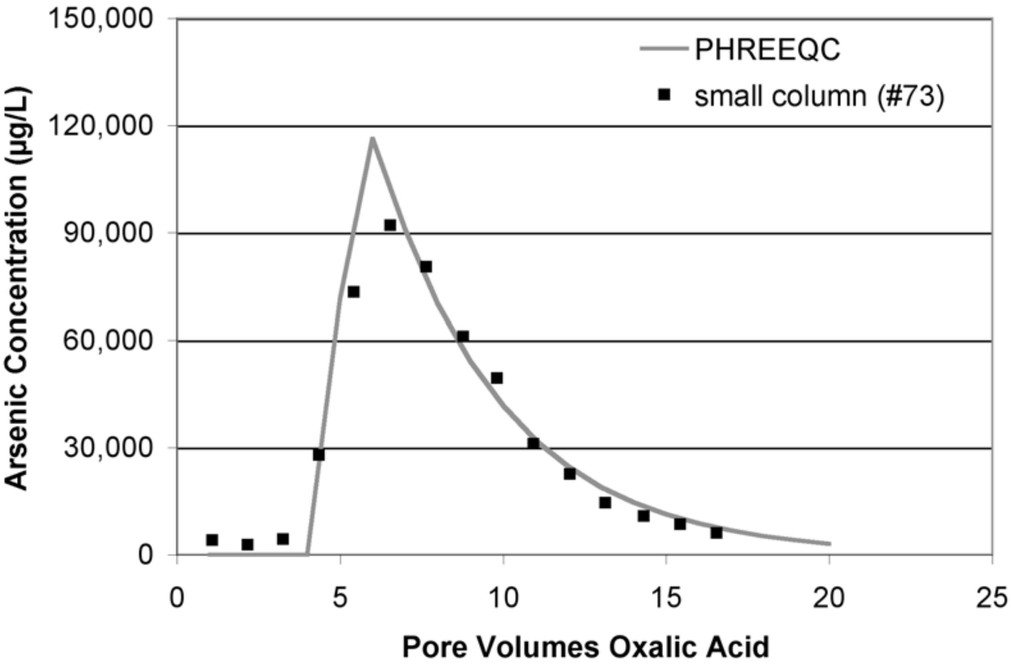


Figure 3.5. Distribution of rate constants for As removal. (a) Histogram showing the proportion of different rate constants of As removal in the section of column #90 analyzed by μSXRF. The darker grey bars show data for pixels #1-250 and the lighter grey for pixels #251-400. All frequency values were divided by the total number of pixels (400) to calculate the proportion. (b) Map showing the same data. Average standard error is 0.002 in the rate constant calculations.

A


150,000
120,000
90,000
60,000
30,000
0
Arsenic Concentration (µg/L)
PHREEQC
small column (#73)
0
5
10
15
20
25
Pore Volumes Oxalic Acid

B

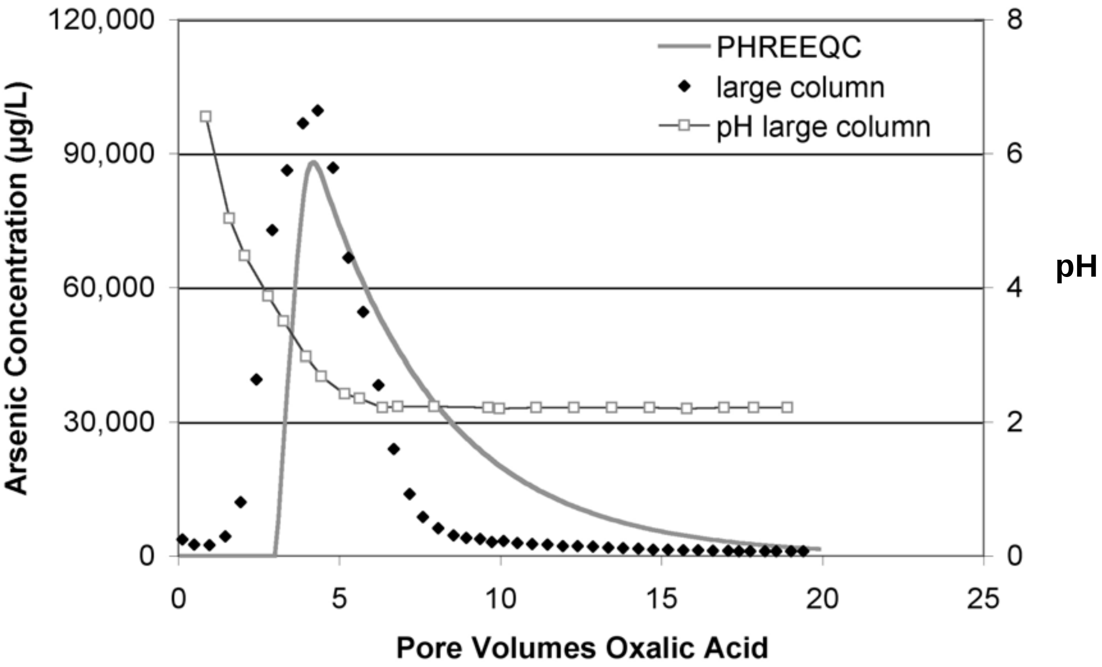

120,000
90,000
60,000
30,000
0
Arsenic Concentration (µg/L)
PHREEQC
large column
pH large column
8
6
4
2
0
pH
0
5
10
15
20
25
Pore Volumes Oxalic Acid

Figure 3.6. (a) Comparison between PHREEQC simulated effluent As concentrations and laboratory data for a small column (#73) over several pore volumes of oxalic acid treatment. A bulk average As removal rate (pv^{-1}) was calculated from the μSXRF data and used in the PHREEQC simulation; a 4 pore volume lag period was applied in the simulation. (b) Comparison between PHREEQC simulated effluent As concentrations and laboratory data for a large column (~23 cm) over several pore volumes of oxalic acid treatment. A bulk average As removal rate (pv^{-1}) was calculated from the μSXRF data and used in the PHREEQC simulation; a 3 pore volume lag period was applied in the simulation. Effluent pH values were also plotted for the large column.

3.10 Supporting information

3.10.1 SEM methods

Scanning electron micrograph images of solids were obtained before and after treatment with oxalic acid. Images were collected using a Zeiss Supra 35 VP FEG SEM that was operated at an accelerating voltage of 21-22 kV. The instrument was equipped with energy dispersive spectroscopy (EDS); EDS spectra of specific grains allowed qualitative evaluation of dominant elements in the grain.

3.10.2 SEM results

Scanning electron microscopy (SEM) was used to visualize sand grains from samples with and without oxalic acid treatment (Figure 3.7a before treatment, Figure 3.7b, sediments from column #90 after treatment). Micrographs show no gross morphological changes in the coatings on the quartz grains. Furthermore, energy dispersive spectroscopy (EDS) results show that Fe and Al coatings were present in samples both with and without oxalic acid treatment (data not shown).

3.10.3 Supporting figures

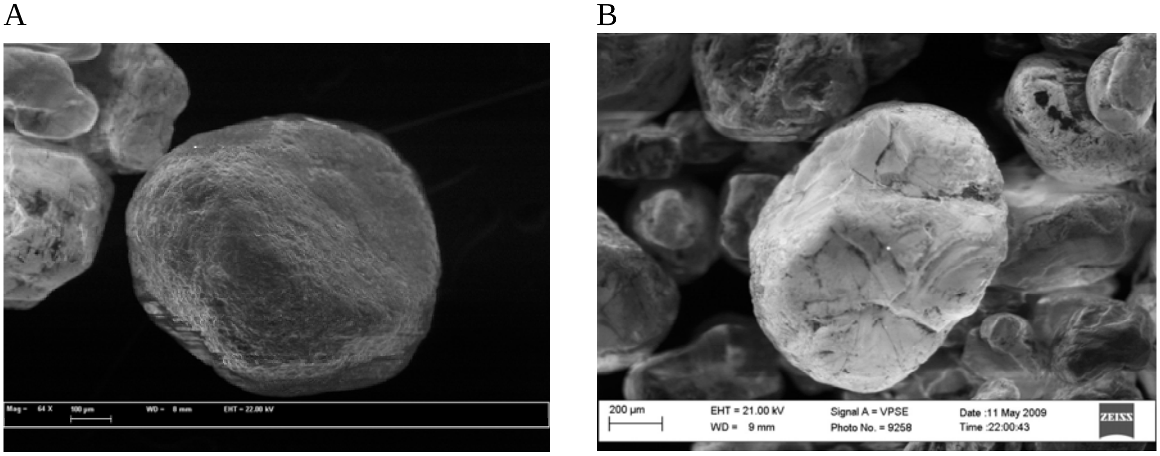


Figure 3.7. Scanning electron micrograph images of aquifer sediments (a) prior to treatment with oxalic acid and (b) following treatment with oxalic acid. The image in (b) shows sediments following column experiment #90, which took place at the synchrotron beamline. Both samples were also analyzed by energy dispersive spectroscopy (EDS); while Al and Fe peaks decreased in size from before to after oxalic acid treatment, the peaks were still present. Arsenic was not present in high enough concentrations to be detected by EDS.

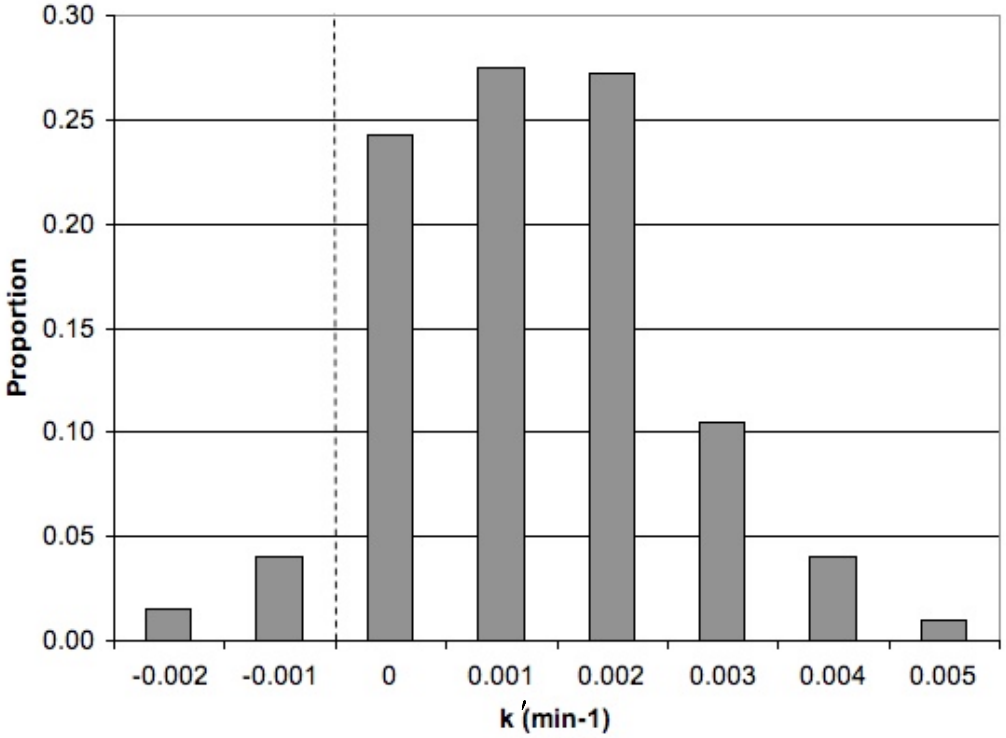


Figure 3.8. Distribution of rate constants of Fe removal. Histogram showing the proportion of different rate constants for Fe removal in the section of column #90 analyzed by μSXRF. The average removal rate constant is 0.001 min^{-1}.

CHAPTER 4
Injection System for Multi-Well Injection Using a Single Pump

Wovkulich, K., Stute, M., Protus, T.J.,Sr., Mailloux, B.J., Chillrud, S.N., 2011. Injection System for a Multi-Well Injection Using a Single Pump. Ground Water Monit. Rem. 31, 79-85.

4.1 Abstract

Many hydrological and geochemical studies rely on data resulting from injection of tracers and chemicals into groundwater wells. The even distribution of liquids to multiple injection points can be challenging or expensive, especially when using multiple pumps. An injection system was designed using one chemical metering pump to evenly distribute the desired influent simultaneously to 15 individual injection points through an injection manifold. The system was constructed with only one metal part contacting the fluid due to the low pH of the injection solutions. The injection manifold system was used during a three-month pilot scale injection experiment at the Vineland Chemical Company Superfund site. During the two injection phases of the experiment (Phase I = 0.27 L/min total flow, Phase II = 0.56 L/min total flow), flow measurements were made 20 times over three months; an even distribution of flow to each injection well was maintained (RSD <4%). This durable system is expandable to at least 16 injection points and should be adaptable to other injection experiments that require distribution of air-stable liquids to multiple injection points with a single pump.

4.2 Introduction

Many field-scale experiments involve introduction of tracers and other liquids to the subsurface via injection wells for the purpose of defining hydrological parameters or aquifer heterogeneities at a field site, enhancing microbial activity, transforming contaminants into less toxic forms, etc. (Gouze et al. 2008; Istok et al. 2004; Mailloux et al. 2003a; Schroth et al. 1998). In particular, recent experiments have involved injection of tracers, biotracers, nutrients, microorganisms, etc. to the subsurface at multiple injection points (Harvey and Garabedian 1991; Kennedy et al. 2006; Mailloux et al. 2007; Mailloux et al. 2003b; Sandrin et al. 2004). When multiple injection wells are used, it can be difficult to introduce chemicals and tracers consistently and evenly over time. The use of multiple pumps or pump heads is a common method for influent introduction to multiple wells (Harvey and Garabedian 1991; Mailloux et al. 2007; Mailloux et al. 2003b; Sandrin et al. 2004) but this can become logistically complicated or cost prohibitive. As an alternative to using multiple pumps one can perform sequential experiments (Istok et al. 2004), yet, this is not always feasible due to time constraints or desired experimental design. Therefore, injection manifold systems for distribution of liquids to multiple injection wells are a potential solution; however, the design of injection systems is rarely published in detail (Gouze et al. 2008; Mailloux et al. 2003b; Schroth et al. 1998).

Here we describe an injection manifold system that can simultaneously and evenly distribute liquids to many injection points with a single pump. The motivation for design of this injection system was the need to introduce a solution of reagents and tracers to 15 individual wells at a total injection rate of 0.27 (Phase I) to 0.56 L/min (Phase II) during a three-month pilot experiment using a single chemical metering pump. While the data presented here describe use of the injection system at one specific site, this type of system could be adapted to many other field locations and to other experimental designs using multi-well configurations and where even flow distribution is desired.

4.3 Design considerations

Division of flow from a single source to multiple outlets is a common engineering problem used in applications such as irrigation systems, gas burners, water supply systems, and sewage disposal (McNown 1954; Rawn et al. 1961; Roberson et al. 1998). To design a system that maintains even distribution of flow, it is important to consider the various factors that impact flow through pipes or tubes and work to minimize differences in discharge at each outlet point. For a system with laminar pipe flow (like the one in our design), Hagen-Poiseuille's law states that the flow rate is proportional to $r^4 l^{-1} \mu^{-1} \Delta h$, with r and l being the radius and length of the pipe, respectively, Δh the difference in hydraulic head, and μ the viscosity (Hornberger et al. 1998). Consequently, flow out of individual ports is very sensitive to the radius of the tubes and somewhat sensitive to temperature-controlled changes in viscosity, the length of individual tubes and the hydraulic head distribution in a manifold system, which is a function of elevation, for example.

By keeping the system small, variations in r, l, Δh, and μ (which is a function of temperature) can be minimized. Also, leveling of the manifold and its input and outputs will equalize the hydraulic head differences between the individual ports. By keeping the inner diameter of the manifold large compared to that of the individual discharge tubes, the head loss due to friction along the manifold is negligible compared with that in the small diameter discharge tubing, resulting in a relatively uniform hydraulic gradient along the small diameter tubes.

Finally, surface effects may also play a role in creating flow rate differences at the multiple outlet points. By pulsing the pressure in the manifold, water is ejected rapidly out of the individual ports (versus constant dripping), reducing the effects of surface tension. Additionally, the high flow velocity in individual pulses minimizes opportunity for precipitation of dissolved salts, which could change the diameter of the outlet point and thus impact flow rates.

4.4 Materials and methods

4.4.1 Overview

This injection manifold system was used as part of a pilot scale injection experiment at the Vineland Chemical Company Superfund site. The site is located in southern New Jersey and is underlain by the sandy sediments of the Kirkwood-Cohansey aquifer system. Due to years of improper chemical storage and disposal by the Vineland Chemical Co., the site’s groundwater and subsurface soils are extensively contaminated with As. Despite nearly 10 years of pump and treat remediation, groundwater As concentrations at the recovery wells can be several hundred μg/L while the US drinking water standard is 10 μg/L. Additionally, the aquifer sediments have become contaminated with typical As concentrations of 20-250 mg/kg; these sediments act as a source of As to the groundwater. Laboratory work has been conducted which shows that introducing oxalic acid to As contaminated sediments can increase As release and may potentially accelerate As remediation at sites using pump and treat technologies

(Wovkulich et al. 2010). The injection system was used during a pilot scale injection experiment where the ability of oxalic acid to release As was tested in a field setting (Wovkulich et al. in preparation).

The injection system needed to run continuously for three months to inject chemicals and tracers. In the pilot area, five injection well nests, with three 1" wells per nest, were installed for a total of 15 wells. In each well nest, the wells were screened at 27-28 ft (8.2-8.5 m), 29-30 ft (8.8-9.1 m), and 31-32 ft (9.4-9.8 m) below ground surface (bgs); the water table is approximately 15 ft (4.6 m) bgs. The injection manifold was mounted on top of one of the well casings and was used to inject chemical solutions and tracers (pH ~1, density up to 1.018 kg/L) to 15 wells over the course of the three-month experiment. The total flow rate was 0.27 L/min (18 mL/min per well) for the first 34 days (Phase I) and 0.56 L/min (37 mL/min per well) for the next 56 days (Phase II). During the three-month experiment, flow rates were measured 20 times at a subset of the wells to ensure the even distribution of solutions; the flow at each outflow point was collected into a graduated cylinder for two minutes and the volumes recorded. Additionally, at the end of the injection experiment, the pump settings (speed and stroke) were varied and the flow rates were monitored to evaluate the distribution of flow at each outflow point.

4.4.2 Description of injection system

A model C131-26S, LMI Milton Roy chemical metering pump (Ivyland, PA) was chosen for the experiment because of its ability for continuous pumping over long time periods (months), chemical resistant design, and desirable output flow range; pump function is based on movement of a diaphragm which is driven by an electromagnetic solenoid. The goals for the design of the injection system were (1) use a single pump, (2) evenly distribute flow from that pump to 15 outflow ports, and (3) use inexpensive and readily available materials. Because of the low pH of the solutions being injected in this experiment, the injection system was designed such that no metal parts would come in contact with the fluids (except for one small, replaceable metal spring in the pump). The system can only be used with fluids that can come in contact with the atmosphere. Photographs of the injection system set up can be found in the Supporting Information (Figure 4.3).

The chemical metering pump was mounted above a 300-gallon (1136 L) polyethylene tank with the pump's polyethylene tubing and foot valve extending into the tracer reservoir through a hole cut in the cap of the tank. In this design, liquid flows from the chemical metering pump through approximately 40 ft (12.2 m) of 3/8" PVC tubing (Figure 4.1, A-7) to a tube fitting tee (Figure 4.1, A-8) where the liquid is split evenly to either side of the injection manifolds (Figure 4.1, A-5); liquid reaches the manifolds after passing through tube-to-pipe elbows (Figure 4.1, A-6). Hose clamps were used to secure tubing to the tube fitting tee and the tube-to-pipe elbows that led to the manifolds. The liquid is then pushed from the manifolds through pipe-to-tubing adapters (Figure 4.1, A-2) to narrow diameter tubes (1/16") that are 8.7" (22.2 cm) in length (Figure 4.1, A-1). As mentioned in Design Considerations, the inner diameter of the individual discharge tubes were small compared with that of the manifold; this kept the frictional head loss along the manifold negligible compared with that in the 1/16" tubing and allowed for a relatively uniform hydraulic gradient along the 1/16” tubes once maximum tubing height and tubing length were made consistent.

The manifolds come with 4 or 8 outlets; outlets can be fitted with a hex hollow plug (no flow) (Figure 4.1, A-3) or pipe-to-tubing adapters (flow) (Figure 4.1, A-2) to achieve the desired number of outflow points. Additionally, two manifolds can be joined (Figure 4.3B and Figure 4.1A) with a pipe hex nipple (Figure 4.1, A-4) for applications requiring more than 8 outflow ports. The manifolds are mounted to a horizontal PVC plate (Figure 4.3C). The 1/16” tubes are threaded through holes in a vertical PVC plate (Figure 4.1, B-16) such that the height of each tube is identical; differences in tube height could lead to uneven distribution of flow. The 1/16” tubing is then threaded through holes cut in plastic plugs (Figure 4.3C; Figure 4.1, B-17); vent holes are also cut in these plastic plugs. The plastic plugs are fitted into thru-wall adapters (Figure 4.1, B-21), which have been tapped into the horizontal PVC plate (the manifolds are also mounted to this plate). The pieces of 1/16” tubing end at the bottom of the thru-wall adapters; each piece of tubing ends at the same height to ensure even distribution of flow. The 1/16” tubes were kept in the center of the thru-wall adapters by winding electrical tape around the 1/16” tubes; siphoning effects could result if the 1/16” tubing is in contact with the sides of the thru-wall adapters or the 1/2" tubing (Figure 4.1, B-22). Liquid flows from the 1/16” tubing into 1/2” tubing, then passes from the 1/2” tubing into the injection wells using reducing couplings (Figure 4.3D; Supporting Table 4.2, #23) to secure the tubing to the top of the wells.

The injection manifolds were mounted high enough to allow for continuous downward flow through the 1/2” tubing toward the injection wells; this ensures liquid won’t back up or collect in the 1/2” tubing, which could lead to inconsistencies in the flow (Figure 4.3A and B). The following details provide one example of a successful way of mounting and stabilizing the system. Other injection experiments or sites may require some alterations to this method. The injection manifolds were installed ~1 m above the top of the well casings (Figure 4.3A). Angle brackets (Figure 4.1, B-14) were mounted to each side of the horizontal PVC plate (Figure 4.3B) to which the manifolds had been affixed (hereafter called the upper horizontal PVC plate) and were attached to 10’ aluminum strut channels (Figure 4.1, B-9). For added stability, a second horizontal PVC plate (lower horizontal PVC plate) was bolted to the top of the well casing of the middle injection well nest (Figure 4.3E) and was also fitted with angle brackets that connected to the 10’ aluminum strut channels. The strut channels were sunk approximately 1 m into the ground; this gave support and kept the injection system stable while the pump was running. For another level of added stability, bolts were tapped into the sides of the well cap (Figure 4.3E; Supporting Table 4.2, #10) to brace the well cap against the well casing. A 3” (7.6 cm) diameter hole was cut into the top of the well cap of the middle injection well nest and lower horizontal PVC plate (Figure 4.3E) to allow room for tubing to pass to the top of the wells.

To level the injection system, which helps maintain even distribution of fluids to each outlet port, a hole for a 3/8” threaded rod (Figure 4.1, B-15) was tapped into each corner of the upper and lower horizontal PVC plates. Locknuts (Figure 4.1B-12) securing the 6-foot rods to the plates were adjusted until the upper horizontal PVC plate was level as measured by two horizontal-mount levels (we recommend a bull’s eye level for greater accuracy, Figure 4.1, B-18, 19, 20). After leveling, the plates were screwed down (Figure 4.1, B-10, 11, 12, 13, 14) into the aluminum strut channels (Figure 4.1, B-9) for greater stability.

This system is easily adaptable to other field sites; the number of injection points can be adjusted by choosing a manifold with 4 or 8 outlets (or a combination thereof, linked with a hex nipple and unused outlets blocked with hex hollow plugs). The key features to successfully using the system are (1) keeping the manifold mounted high enough that liquid always flows downward through the 1/2" tubing toward the injection wells, (2) precisely leveling the manifold, (3) ensuring enough stability (by mounting to aluminum strut channels, etc.) that the pulsations from the pump or disturbances from environmental conditions do not significantly alter the leveling during the experiment, and (4) ensuring that the 1/16" tubing has the same maximum height and end point height for each port.

It may be necessary to include a venting system if the liquids being pumped are prone to degassing; formation of bubbles can lead to air being trapped within the manifold or the 1/16" tubing. Trapped air can result in uneven distribution of liquid to the outflow ports. The liquids and tracers used in these experiments did not degas so a venting system was not used. To accomplish venting, one could insert pipe-to-tubing adapters (1/4" pipe to 1/2" ID tube) with a length of 1/2" tubing in the ports at the outer edges of the manifold. The 1/2" tubing should be secured with the opening upwards; therefore, gasses can escape.

4.5 Results and discussion

During the pilot experiment, the flow rate was measured 20 times over 13 weeks. Between 4 and 12 of the ports were measured each time; it was not feasible to measure the ports going to the middle wells, to which the injection system was mounted, due to the relatively small clearance between the tubing and the edge of the well cap opening. Two injection rates were used during the injection experiment; the injection rate is proportional to both the speed and stroke settings of the pump. The speed setting has units of strokes/unit-time. The number corresponds to strokes/min within 10% error. The stroke setting is related to how much the pump diaphragm moves with each pulse, with the number corresponding to percent of maximum displacement. Though we only present results for use of the system with a chemical metering pump, the concept of the system should still be valid with other pump types.

In Phase I, the total flow rate was 0.27 L/min and stroke and speed of the pump were set at 83 and 50, respectively. There were 46.5 strokes/min and average volume per stroke was 5.8 mL. The average volume per port per minute was between 17.4 and 18.5 mL in Phase I with a relative standard deviation (RSD) < 4% (Figure 4.2). This data is also illustrated in tabular format in the Supporting Information (Table 4.3). Over the course of Phase I (34 days), the average volume per port showed an incremental increase from 17.4 to 18.5 mL per minute, (6% over 34 days). The slight increase over time could have been caused by loosening of the pump diaphragm as the pump was breaking in; this was the first time the pump was used for any significant period of time (i.e., >8 hrs). In Phase II, the total flow rate was 0.56 L/min and stroke and speed of the pump were set at 83 and 95, respectively. There were 94 strokes/min and average volume per stroke was

6.0 mL. The average volume per port per minute was between 36.7 and 38.1 mL with a RSD < 3% (Figure 4.2). This data can also be found in tabular format in the Supporting Information (Table 4.3). There was no systematic change in flow rate over the 56 days of Phase II. The results from flow monitoring during the pilot experiment show that there is even distribution of liquid between the different outflow ports throughout the three months of the injection.

Additionally, samples were obtained via peristaltic pump from within the well bore of one of the injection wells during Phase I and Phase II of injection. Samples were analyzed by ion chromatography (Dionex ICS-2000, Sunnyvale, CA). During Phase I, the tracer and oxalic acid concentrations measured in the well bore were 4% and 14% different, respectively, compared with the influent concentration on that day. During Phase II, the tracer and oxalic acid concentrations measured in the well bore were 7% and 2% different, respectively, compared with the influent concentration on that day. This suggests a high degree of consistency between injected concentrations and well bore concentrations and thus sufficient mixing within the well bore.

Following the injection experiment, the robustness of the system was tested. The effect of stroke, speed, and tubing stiffness were evaluated. The stroke and speed were varied and tested with the bulk of the 3/8" flexible PVC tubing from the pump to the tube fitting tee replaced with 1/4" braided reinforced tubing to examine whether tubing size and wall strength would impact the flow results. For these tests, 5 or 15 outflow ports were measured (one from each well nest or all outflow ports). With the pump speed set at 95, the relative standard deviations for the average volume per port per minute were less than 3% for both tubing types for the three stroke settings tested - 83, 60, and 30 (Table

4.1). Except for the tests with pump speed at 95 and stroke at 30, the volumes per port per minute were significantly different for the two tubing types ($p<0.05$). The discrepancy could indicate that using more rigid tubing leads to slightly larger flow output; the rigid walls of the tubing could cause less dampening of each pulse of the chemical metering pump.

To examine how changes in pump speed would impact distribution of solution among the outflow ports, the stroke was set at 60 and the speed varied (Table 4.1). With the 3/8" tubing, the speed was set at 70, 40, and 30 in successive trials. Percent relative standard deviation for average volume per port per minute was <5% for speeds of 70 and 40. However, when the speed setting was reduced to 30, there was greater variation in the distribution of liquid; relative standard deviation was 13.9%. At slower speeds it became evident that air was pulled back into the 1/16" tubing between each pulse of the pump. The horizontal-mount levels used in the field design were not sensitive enough for extremely precise leveling; therefore, air was pulled back further into the 1/16" tubing on the left side of the injection manifold than on the right. This issue only seems to be a problem at the lower speeds; however, this is the reason we recommend using a bull's-eye level (Supporting Table 4.2, #18, 19, 20) rather than horizontal-mount levels.

Using the 1/4" braided, reinforced tubing, speeds of 60, 50, and 40 were tested (stroke = 60 in each case). We again observed that at lower speeds the relative standard deviation for average volume per port per minute would increase; for speed settings of 60 and 50 the relative standard deviations were <8%. However, when the speed setting was lowered to 40, the relative standard deviation climbed to 20.8%. Note that the relative standard deviation exceeded 10% with the speed setting at 30 with the 3/8" tubing and 40 with the 1/4" braided, reinforced tubing. A possible reason for this difference is that the 1/4" braided, reinforced tubing has a smaller opening and less flexible walls, which could lead to stronger pulses from the pump (the more flexible walls of the 3/8" tubing could dampen the pulses). Stronger pulses would also lead to more air being pulled back into the 1/16" tubing between pulses. Therefore, very precise leveling becomes more important when slower speed settings are used as well as smaller diameter, more rigid tubing.

Table 4.1. Flow tests with varying stroke and speed

Tube Type[a]	Stroke	Speed	Total rate (L/min)	Average volume per port per minute (mL)	Standard Deviation	% RSD	N
1	83	95	0.55	36.8	0.25	0.68	5
1	60	95	0.42	28.0	0.64	2.28	15
1	30	95	0.24	15.8	0.47	2.97	5
1	60	70	0.29	19.5	0.52	2.67	15
1	60	40	0.18	11.8	0.50	4.26	5
1	60	30	0.13	8.8	1.21	13.9	5
2	83	95	0.56	37.6	0.37	0.99	5
2	60	95	0.43	28.8	0.66	2.30	15
2	30	95	0.24	16.2	0.45	2.76	5
2	60	60	0.27	18.1	0.58	3.18	5
2	60	50	0.23	15.3	1.09	7.15	5
2	60	40	0.18	12.0	2.49	20.8	5

N= Number ports tested

[a] Tube type describes the tubing used between the pump and tube fitting tee. Tube type 1 refers to 3/8" flexible PVC tubing. Tube type 2 refers to 1/4" braided reinforced tubing (McMaster part # 52375K12).

4.6 Conclusions

An injection manifold system was designed that uses a single pump to evenly distribute flow to 15 ports using inexpensive and readily available materials. Except for one metal spring, the system is made of plastic and allows the injection of chemically aggressive fluids. Injected fluids do come in contact with air due to venting in the system. Over the course of a three-month experiment during which the system was used, even flow distribution was maintained across the injection manifold. Relative standard deviations for average flow rate were <4% for both phases of the experiment (Phase I = 0.27 L/min total flow, Phase II = 0.56 L/min total flow) throughout the three-month experiment. This injection system is adaptable for varying numbers of injection points and can be used for a wide array of multi-well injection scenarios.

4.7 Acknowledgements

The authors would like to thank Sevenson Environmental, US EPA, and US Army Core of Engineers at the Vineland Superfund Site for support at the site. The authors would also like to thank: Alison Keimowitz, James Ross, Patrick McNamara, Nathan Rollins, Bethany O'Shea, and Kamini Doobay. The authors also thank Matt Becker and anonymous reviewers for their insightful comments. This work is supported by NIEHS Grants ES010349 and ES0090890. This is LDEO publication 7427.

4.8 References

Gouze, P., Le Borgne, T., Leprovost, R., Lods, G., Poidras, T., and Pezard, P., 2008, Non-Fickian dispersion in porous media: 1. Multiscale measurements using single-well injection withdrawal tracer tests: *Water Resources Research*, 44, 6, W06426.

Harvey, R. W., and Garabedian, S. P., 1991, Use of Colloid Filtration Theory in Modeling Movement of Bacteria through a Contaminated Sandy Aquifer: *Environmental Science & Technology*, 25, 1, 178-185.

Hornberger, G. M., Raffensperger, J. P., Wiberg, P. L., and Eshleman, K. N., 1998, Elements of Physical Hydrology: Baltimore, The Johns Hopkins University Press.

Istok, J. D., Senko, J. M., Krumholz, L. R., Watson, D., Bogle, M. A., Peacock, A., Chang, Y. J., and White, D. C., 2004, In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer: *Environmental Science & Technology*, 38, 2, 468-475.

Kennedy, L. G., Everett, J. W., Becvar, E., and Defeo, D., 2006, Field-scale demonstration of induced biogeochemical reductive dechlorination at Dover Air Force Base, Dover, Delaware: *Journal of Contaminant Hydrology*, 88, 1-2, 119-136.

Mailloux, B. J., Devlin, S., Fuller, M. E., Onstott, T. C., DeFlaun, M. F., Choi, K. H., Green-Blum, M., Swift, D. J. P., McCarthy, J., and Dong, H., 2007, The limited role of aquifer heterogeneity on metal reduction in an Atlantic coastal plain determined by push-pull tests: *Applied Geochemistry*, 22, 5, 974-995.

Mailloux, B. J., Fuller, M. E., Onstott, T. C., Hall, J., Dong, H. L., DeFlaun, M. F., Streger, S. H., Rothmel, R. K., Green, M., Swift, D. J. P., and Radke, J., 2003a, The role of physical, chemical, and microbial heterogeneity on the field-scale transport and attachment of bacteria: *Water Resources Research*, 39, 6.

Mailloux, B. J., Fuller, M. E., Rose, G. F., Onstott, T. C., DeFlaun, M. F., Alvarez, E., Hemingway, C., Hallet, R. B., Phelps, T. J., and Griffin, T., 2003b, A modular injection system, multilevel sampler, and manifold for tracer tests: *Ground Water*, 41, 6, 816-827.

McNown, J. S., 1954, Mechanics of Manifold Flow: *Transactions of the American Society of Civil Engineers*, 119, 1103-1142.

Rawn, A. M., Bowerman, F. R., and Brooks, N. H., 1961, Diffusers for disposal of sewage in sea water: *Transactions of the American Society of Civil Engineers*, 126, 344-388.

Roberson, J. A., Cassidy, J. J., and Chaudhry, M. H., 1998, Hydraulic Engineering: New York, John Wiley & Sons, Inc.

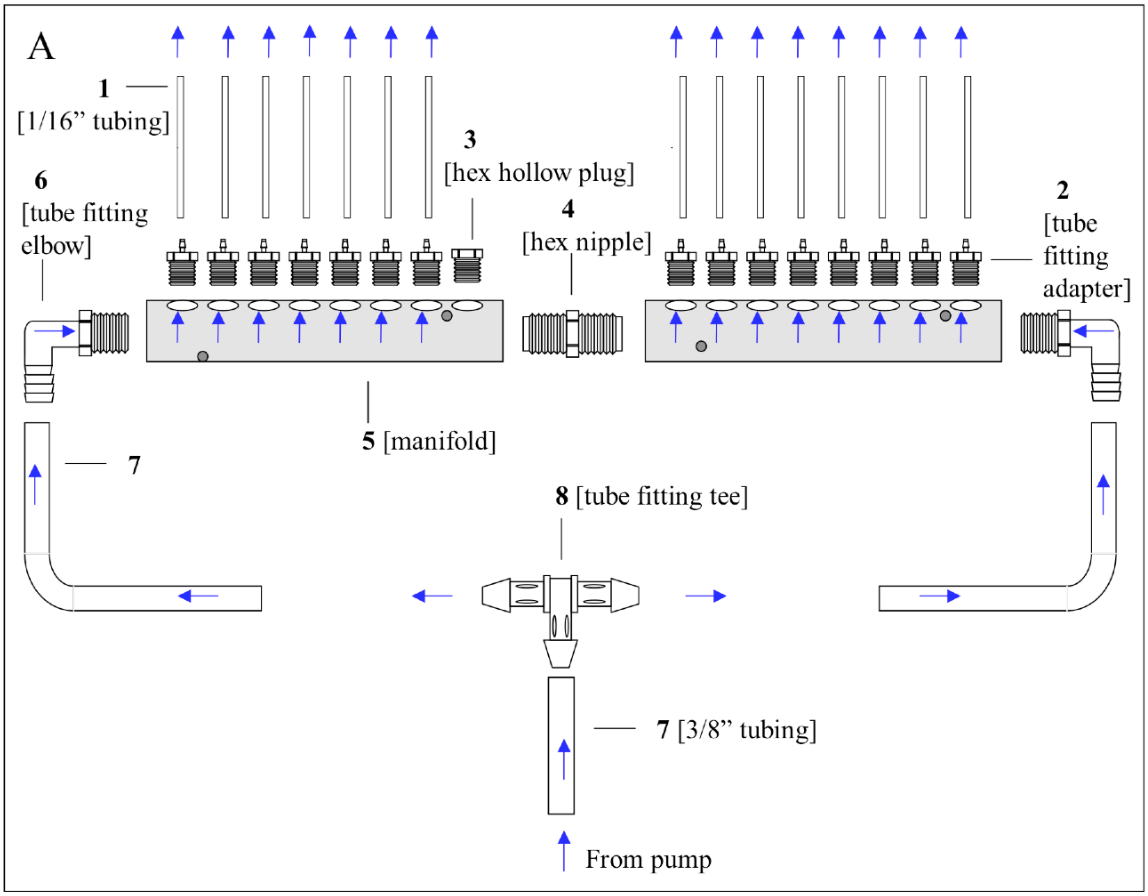
Sandrin, S. K., Brusseau, M. L., Piatt, J. J., Bodour, A. A., Blanford, W. J., and Nelson, N. T., 2004, Spatial variability of in situ microbial activity: Biotracer tests: *Ground Water*, 42, 3, 374-383.

Schroth, M. H., Istok, J. D., Conner, G. T., Hyman, M. R., Haggerty, R., and O'Reilly, K. T., 1998, Spatial variability in in situ aerobic respiration and denitrification rates in a petroleum-contaminated aquifer: *Ground Water*, 36, 6, 924-937.

Wovkulich, K., Mailloux, B. J., Lacko, A., Keimowitz, A. R., Stute, M., Simpson, H. J., and Chillrud, S. N., 2010, Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation: *Applied Geochemistry*, 25, 10, 1500-1509.

Wovkulich, K., Stute, M., Mailloux, B. J., Keimowitz, A. R., Ross, J., and Chillrud, S. N., in preparation, In Situ Oxalic Acid Injection to Accelerate Arsenic Remediation at a Superfund Site in NJ.

4.9 Figures


A
1
[1/16” tubing]
6
[tube fitting
elbow]
3
[hex hollow plug]
4
[hex nipple]
2
[tube
fitting
adapter]
5 [manifold]
7
8 [tube fitting tee]
7 [3/8” tubing]
From pump

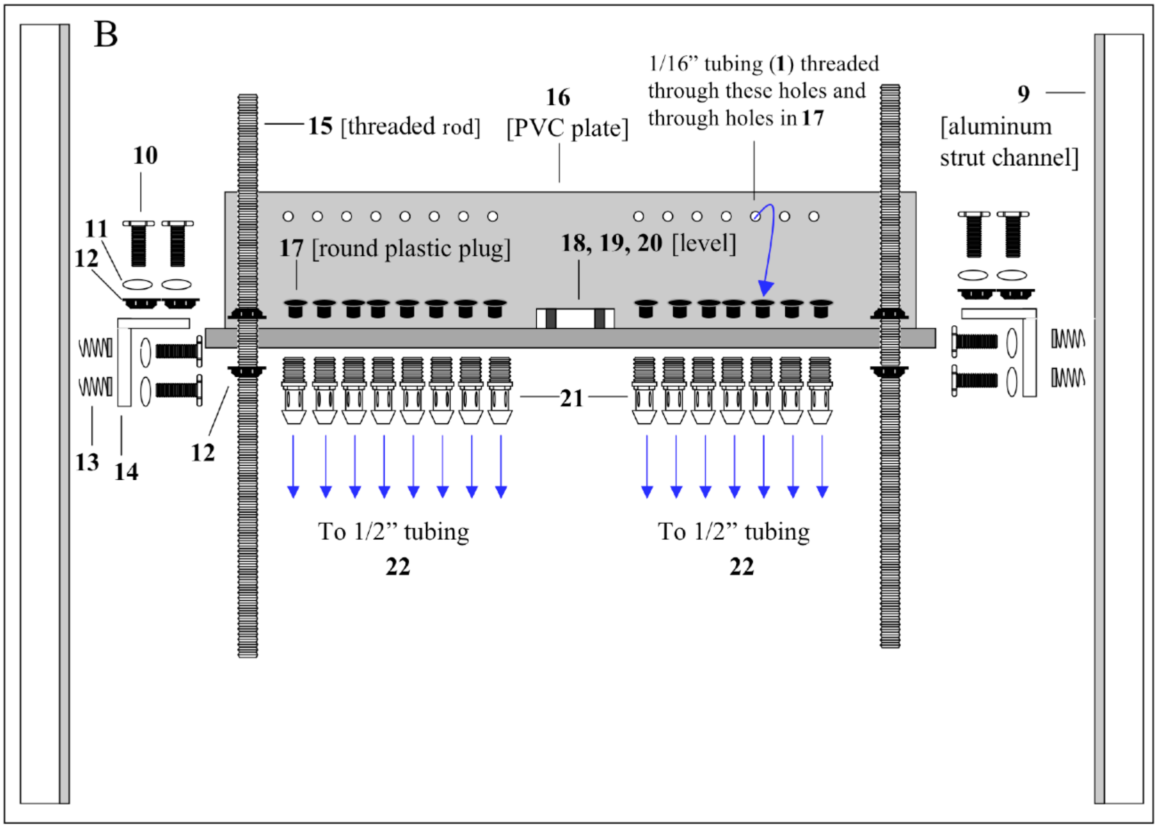


Figure 4.1. (A) and (B) show schematic diagrams of the injection system. The parts are listed in Table 4.2 in the Supporting Information. Blue arrows indicate flow direction. Briefly, the liquid flows from the pump through 3/8" tubing (1A-7) and is split by a tube fitting tee (1A-8). Liquid then passes through a short length of 3/8" tubing on either side of the manifolds; liquid flows through tube-to-pipe elbows (1A-6) to the manifolds (1A-5) and up through the tube-to-pipe adapters (1A-3) to the 1/16" tubing (1A-1). The 1/16" tubing is threaded through holes in the vertical PVC plate (2B-16) and through holes cut in plastic plugs (1B-17), stopping at the bottom of the thru-wall adapters (1B-21). Liquid passes from the bottom of the 1/16" tubing into 1/2" tubing (1B-22), which is connected to the thru-wall adapters and leads to the top of the injection wells.

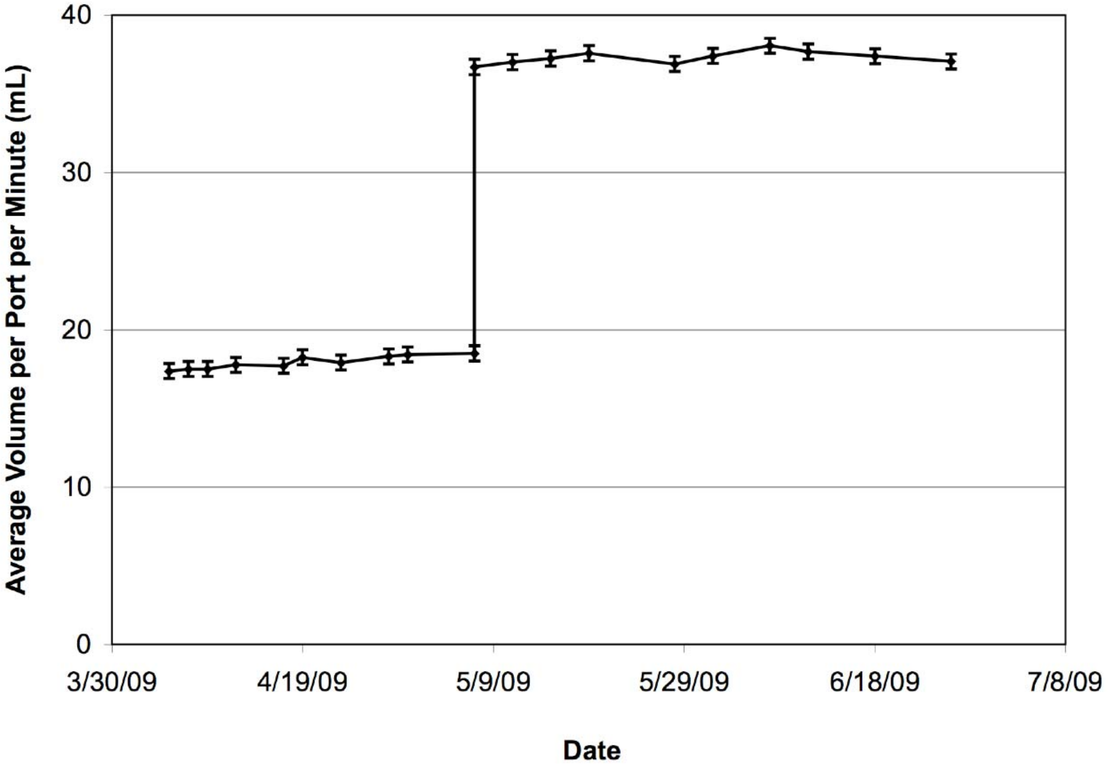


Figure 4.2. Flow rates during the Vineland injection. The error bars show 1 standard deviation above and below the average value. During Phase I, the total output was 0.27 L/min. The pump settings were Stroke = 83, Speed = 50; for these settings, stroke/min = 46.5 and average mL/stroke = 5.8 mL. During Phase II, total output was 0.56 L/min. The pump settings were Stroke = 83, Speed = 95. For these settings, stroke/min = 94 and average mL/stroke = 6 mL.

4.10 Supporting information

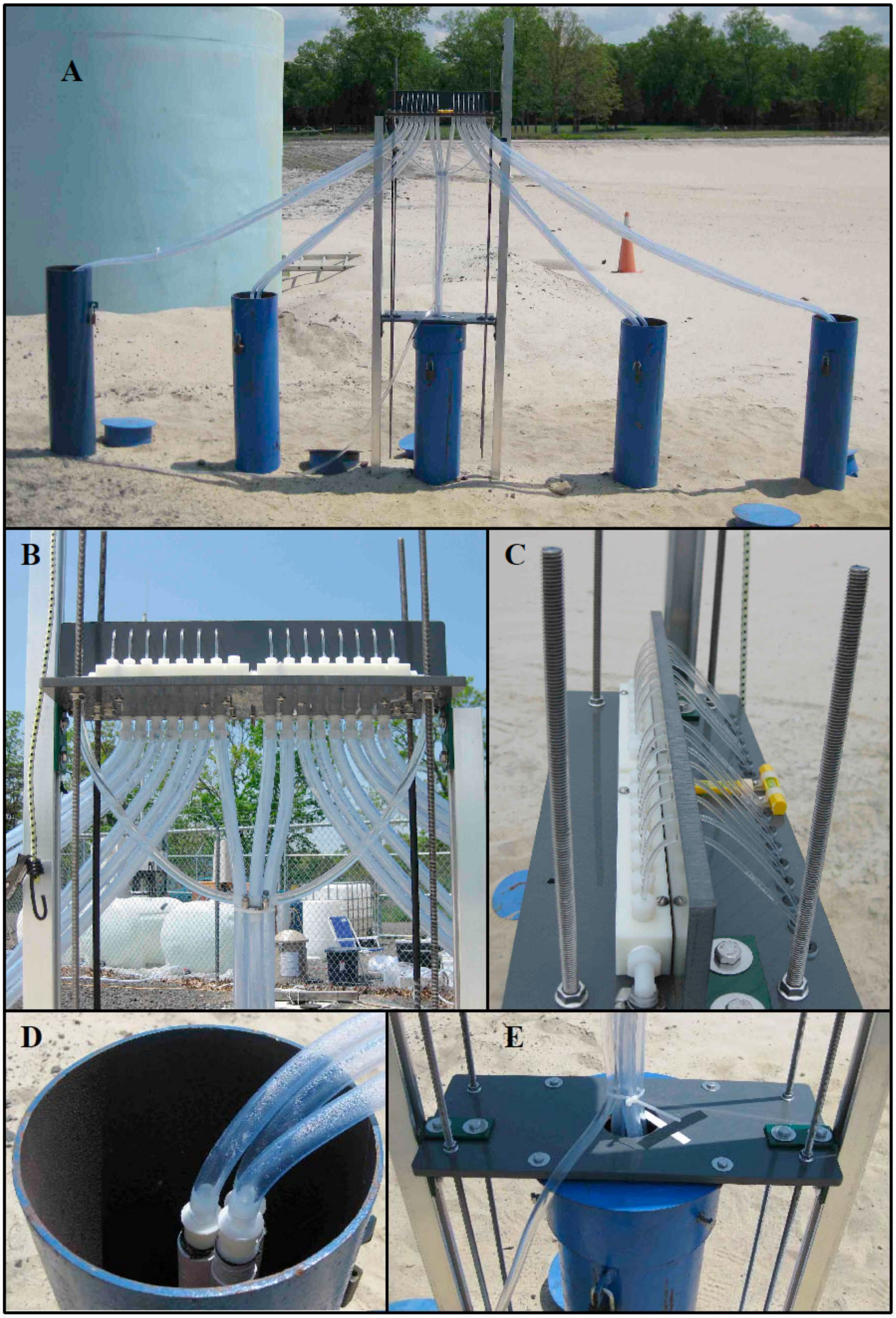


Figure 4.3. Photographs of various views of the injection system in use at the Vineland site. (A) View of the whole injection system and mounting to the middle well casing. (B) Closer view of the back of the injection system highlighting the pipe-to-tubing adapters, which carry liquid from the manifold to the 1/16” tubing, and the thru-wall adapters that are tapped into the upper horizontal PVC plate. (C) Side view of the injection manifold, which shows how the 1/16” tubing is threaded through the vertical PVC plate. (D) Connection between 1/2" tubing and the top of the injection wells via reducing coupling (Table S1, #23). (E) View of the lower PVC plate mounted to the top of the well cap.

Table 4.2. List of parts used for injection system

List of Parts Used for Injection System
All part numbers refer to the McMaster-Carr Catalog (www.mcmaster.com)*

#	Description	Part #
1	Tubing, Ultra-Clear Tygon PVC , 1/16" ID, 1/8" OD X 1/32" Wall	8339K12
2	Tube Fitting Adapter for 1/16" Tube ID X 1/4" NPT Male Pipe	5116K84
3	Hex Hollow plug, Threaded Pipe Fitting, 1/4" Pipe Size	48335K152
4	Hex Nipple, Threaded Pipe Fitting 1/4" Pipe Size	48335K171
5	Nylon Manifold 8 Outlets, 3/8" NPT Inlet X 1/4" NPT outlet	5253K332
5 *alt*	Nylon Manifold 4 Outlets, 3/8" NPT Inlet X 1/4" NPT Outlet	5253K312
6	Tube Fitting 90 Degree Elbow for 3/8" Tube ID X 3/8" NPT Male Pipe	5372K318
7	Tubing, Masterkleer PVC, 3/8" ID, 9/16" OD X 3/32" Wall	5233K64
8	Tube Fitting Tee for 3/8" Tube ID	2808K172
9	Aluminum Strut Channel Solid, 1-5/8" X 1-5/8", 10' Length	3230T66
10	Hex Head Cap Screw 3/8"-16 Thread, 1" Length, stainless steel	92240A624
11	Large-OD Flat Washer 3/8", stainless steel	90313A114
12	Serrated-Flange Hex Locknut 3/8"-16, stainless steel	93776A461
13	Nut for Strut Channel W/Spring, for 1-5/8" Deep Strut, 3/8"-16 Thread	3259T14
14	90 Degree Angle Bracket for strut channel, 4-Hole,	33125T33
15	Threaded Rod 3/8"-16 Thread, 6' Length, stainless steel	98920A031
16	PVC (Type 1) Sheet 1/2" Thick, 12" X 24" Sheet, Gray *(cut to size)*	8747K128
17	Push-in Round Plastic Plug Fits 3/8" ID, 15/32" Head Diameter *(add holes for tube and vents)*	85985K14
18	*Recommend:* Bull's-Eye Level, 21/32" Base Diameter, 21/64" Height	2147A61
19	*Recommend:* Mounting Flange for 2147A61 Bull's-Eye Level	2147A71
20	*Recommend:* Sheet Metal Screw No 4 Size, 3/8" Length, stainless steel	90065A108
21	Thru-Wall Adapter for 1/2" Tube X 1/4" NPSM	5463K86
22	Tubing, Clear PVC, 1/2" ID, 3/4" OD X 1/8" Wall	5231K375
23	Tube Fitting Reducing Coupling for 1" X 1/2" Tube ID	53415K134

NPSM= National Straight Mechanical Pipe Thread
NPT= National Pipe Thread
*Part numbers are listed only for reference and do not constitute an endorsement.

Table 4.3. Results From Flow Monitoring During Vineland Injection

Phase I: 0.27 L/min total output
Stroke = 83; Speed = 50; Stroke/min = 46.5; Average mL/stroke = 5.8 mL

Date	Average volume per port per minute (mL)	Standard Deviation	% RSD	N
4/5/09	17.4	0.48	2.8	4
4/7/09	17.5	0.00	0.0	4
4/9/09	17.5	0.35	2.0	4
4/12/09	17.8	0.42	2.4	12
4/17/09	17.7	0.54	3.1	12
4/19/09	18.3	0.29	1.6	4
4/23/09	17.9	0.62	3.5	12
4/28/09	18.3	0.55	3.0	4
4/30/09	18.4	0.38	2.1	12
5/7/09	18.5	0.41	2.2	4
Mean	**17.9**			

Phase II: 0.56 L/min total output
Stroke = 83; Speed = 95; Stroke/min = 94; Average mL/stroke = 6 mL

Date	Average volume per port per minute (mL)	Standard Deviation	% RSD	N
5/7/09	36.7	0.71	1.9	12
5/11/09	37.0	1.81	2.5	12
5/15/09	37.3	1.41	1.9	12
5/19/09	37.6	0.94	1.2	12
5/28/09	36.9	1.51	2.1	12
6/1/09	37.4	0.94	1.3	12
6/7/09	38.1	0.61	0.8	12
6/11/09	37.7	0.68	0.9	12
6/18/09	37.4	0.54	0.7	12
6/26/09	37.1	0.91	1.2	12
Mean	**37.3**			

N= number of ports tested; %RSD= % Relative Standard Deviation

CHAPTER 5

In Situ Oxalic Acid Injection to Accelerate Arsenic Remediation at a Superfund Site in NJ

Wovkulich, K., Stute, M., Mailloux, B.J., Keimowitz, A.R., Ross, J., Chillrud, S.N., In Situ Oxalic Acid Injection to Accelerate Arsenic Remediation at a Superfund Site in NJ, in preparation.

5.1 Abstract

Arsenic is a prevalent contaminant at a large fraction of US Superfund sites; establishing techniques that accelerate As remediation could thus benefit many contaminated sites. Hundreds of tons of As were released into the environment by the Vineland Chemical Co. in southern NJ during its manufacturing lifetime, resulting in extensive contamination of surface and subsurface soils and sediments, groundwater, and the downstream watershed. Despite extensive intervention at this Superfund site, sufficient site aquifer cleanup could require many decades with current pump and treat technologies. Slow desorption of As from aquifer solids appears to contribute to progressively decreased effectiveness of the pump and treat (P&T) system. Laboratory column experiments have suggested that addition of oxalic acid to contaminated aquifer solids could be a promising way to release As from the solid phase and thus could significantly accelerate As removal by pump and treat remediation. To evaluate the potential of chemical additions for increasing As release *in situ* and boosting the efficiency of the P&T approach, a pilot scale forced gradient study was conducted on the Vineland site. During spring/summer 2009, oxalic acid and tracers (bromide and SF_6) were injected into a small portion (~50 m^2) of the Vineland site for 3 months. Groundwater samples from a sampling well and pump and treat recovery well indicate that introduction of oxalic acid led to increased As release. Between 2.9 and 3.6 kg of As

were removed (depending on the background corrections used) from the sampled wells as a result of the oxalic acid treatment during the 3-month injection. However, with some evidence for preferential flow paths and a sinking injection plume, the size and shape of the impacted area are not well defined. A comparison of median and average As concentrations on a small number of sediment cores collected before and after treatment and analyzed using X-ray fluorescence spectroscopy suggested a reduction in As solid concentrations of ~34% (median difference) to 48% (mean difference). Overall, the addition of oxalic acid shows promise for accelerating treatment of a highly contaminated site offering the potential to lower the As remediation time-scale.

5.2 Introduction

Arsenic is a common contaminant in the environment, present at hundreds of US Superfund sites (EPA, 2002; 2007). One of the most frequently used and widely-accepted technologies at sites with contaminated groundwater is pump and treat (P&T) remediation (Mackay and Cherry, 1989; Palmer and Fish, 1992). Of the approximately 78 As contaminated sites that were in the design phase or were actively being remediated as of October 2006, ~58% of the sites listed P&T remediation as part of their clean up plan (EPA, 2011). However, P&T remediation can be costly. Additionally, remediation of As sites via P&T can require extended periods of treatment to reach As cleanup goals, at least in part, due to limitations on desorption of As from iron and aluminum (hydr)oxides in sediments (Palmer and Fish, 1992; Smedley and Kinniburgh, 2002). It may be possible to accelerate As release and improve remediation efficiency at sites using P&T technologies by making judicious chemical additions. Laboratory column experiments suggest that introducing a 10 mM oxalic acid solution can release ~88% of the As from the contaminated solids while groundwater alone released only 5% of the As (Wovkulich, et al., 2010). Here we extend these laboratory studies to a field setting and investigate the possibility of using oxalic acid to increase As mobilization and potentially accelerate remediation by P&T in a 3-month pilot scale study at the Vineland Chemical Co. Superfund site.

The US EPA estimates that there are over 700 P&T systems in operation at US Superfund sites (EPA, 2011). However, a growing body of evidence indicates that P&T is often ineffective, especially as contaminant removal can decrease over time in a process known as tailing (EPA, 1996; Mackay and Cherry, 1989; Palmer and Fish, 1992; Voudrias, 2001). Pump and treat generally has two functions in a remediation plan: (1) to contain the contaminant plume by influencing the hydrology and (2) to remove contaminant from the aquifer and lower dissolved contaminant concentrations to acceptable levels (EPA, 1996; Voudrias, 2001). Through careful planning and well placement, the first objective can generally be reached. However, aquifer conditions and the geochemistry of the contaminant can lead to limitations for reaching the second objective. Arsenic mobility is often controlled by sorption-desorption processes, which can be influenced by pH, oxidation-reduction potential, presence of anions and ligands, microbial activity, and presence of binding sites on solid surfaces (Ahmann, et al., 1997; Anawar, et al., 2004; Darland and Inskeep, 1997; Dixit and Hering, 2003; Jeong, et al., 2007; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). At As contaminated sites using P&T, cleanup procedures may be prolonged by slow desorption of As from soil or sediment surface sites, resulting in decreases in contaminant removal over time.

Systems in which tailing is caused by chemical processes may be amenable to P&T enhancement by chemical additions (Palmer and Fish, 1992).

For As contaminated sites using P&T, additions of oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) have the potential to help accelerate As release from solids and thus improve P&T efficiency (more As removed with each volume of groundwater pumped from the subsurface). Oxalic acid is a low molecular weight organic acid found in natural soil environments; typical concentrations in soil solutions are 0-50 μM, though concentrations up to 1 mM have been reported (Fox and Comerford, 1990; Strobel, 2001; van Hees, et al., 2000). Oxalic acid is involved in the vertical transport of Al and Fe through soils; sources of organic acids (including oxalic acid) in soil solutions include decay of plant materials, exudation from plant roots, and products of microbial degradation (Jones, 1998; van Hees, et al., 2000). Studies suggest that dissolution of Al and Fe species by organic acids leads to As release or that there is competitive sorption between organic acids and As (or a combination of the two processes play a role) (Luo, et al., 2006; Shi, et al., 2009; Zhang, et al., 2005). Oxalic acid is often included in sequential soil extraction schemes investigating As phases (Keon, et al., 2001; Slowey, et al., 2007; Swartz, et al., 2004; Wenzel, et al., 2001). Additionally, studies have shown As release in the presence of oxalic acid (Klarup, 1997; Mohapatra, et al., 2005; Wovkulich, et al., 2010; Zhang, et al., 2005) and inhibition of As sorption in the presence of oxalic acid under certain conditions (Shi, et al., 2009).

In this work, we examine the possibility of using oxalic acid in a field setting to increase release of As from contaminated aquifer solids and potentially improve P&T remediation. A small pilot scale study was conducted at the Vineland Chemical Co.

Superfund site in which two different concentrations of oxalic acid were introduced to a small portion of the study site over the course of three months. Groundwater samples were taken throughout the pilot study to evaluate oxalate concentrations and As release at a sampling well and P&T recovery well and to assess the potential for using chemical injection methods in a field setting.

5.3 Site overview

The Vineland Chemical Co. Superfund site is located in Southern New Jersey, USA. The site is underlain by the unconsolidated sands of the Cohansey Formation. Between 1949 and 1994, Vineland Chemical manufactured As-based biocides, predominantly monosodium acid methanearsonate (MSMA) and disodium acid methanearsonate (DSMA), which are sodium salts of monomethyl arsonic acid (MMA) (EPA, 1989). Waste salts including up to 1-2% As were stored on site in open piles and in abandoned chicken coops on site prior to 1978. These poor chemical storage and disposal practices led to the release of hundreds of tons of As into the environment (EPA, 2006). The groundwater and sandy subsurface materials of the site were contaminated with high levels of organic and inorganic As species. Groundwater concentrations of total As exceeded 10,000 μg/L before remediation began; the US drinking water standard is currently set at 10 μg/L (EPA, 2001b). Additionally, discharge of contaminated water into an adjacent stream, Blackwater Branch, resulted in impacts on the flood plain soils as well as bottom sediments of the Maurice River and Union Lake further downstream (EPA, 2006; Keimowitz, et al., 2005).

A large-scale cleanup operation onsite includes pump and treat (P&T) for managing groundwater contamination as well as soil washing of the unsaturated zone sediments in the “hot” zone (most contaminated region of the site) and flood plain areas. The P&T system consists of 16 extraction wells situated around the site. Up to 2 million gallons (7.5 million liters) of contaminated water are extracted from the subsurface each day and cleaned at the treatment facility; treated water ([As]<10 μg/L) is currently discharged to the Blackwater Branch (EPA, 2001a). Contaminated unsaturated zone sands in the former “hot” zone had a maximum of >500 mg As/kg; soil washing procedures decreased soil As concentrations to <20 mg/kg. Offsite samples suggest that a representative background As concentration of the aquifer sediments is less than 5 mg/kg. Additionally, only unsaturated zone sediments and the top layer of aquifer solids were excavated (maximum excavation depth of ~4.9-5.6 m below ground surface) and treated at the soil washing plant. Aquifer materials below this depth can still have elevated As (typically 20-250 mg/kg), making the aquifer solids a reservoir of As that can continue to contaminate the groundwater. Recent measurements at the P&T recovery wells show groundwater As concentrations can still be several hundred μg/L. A Classification Exception Area-Well Restriction Area was established to prohibit groundwater well installation and protect human health.

5.4 Hydrogeological modeling

Groundwater numerical modeling was performed prior to well installation and prior to the oxalic acid injection experiment to help determine optimal well placement, dilution factors, and other hydrological parameters (Appendix B). The models were created using GMS, a graphical interface for groundwater modeling (Aquaveo Water Modeling Solutions, Provo, UT). MODFLOW, MODPATH, and MT3D packages were used to model flow, particle tracking, and transport, respectively. The models examined a small portion of the Vineland site near one of the pump and treat recovery wells (RW 2a). The initial model was based on outputs from the USACE FEMWATER models for the area around Vineland Chemical and evaluated well configurations for injection and sampling wells. Subsequent model simulations attempted to replicate the tracer data collected in 2008 and were then used to evaluate injection and pumping scenarios for the oxalic acid injection experiment.

5.5 Field methods

5.5.1 Well installation

For the purpose of the pilot field experiment, injection and monitoring wells were installed within the cone of depression of an existing well (RW 2a) on the Vineland site (Figure 5.1). There were two primary reasons for installing the wells within the cone of depression: the P&T recovery well focuses water toward it creating a forced gradient, therefore, (1) simplifying the groundwater flow regime in that area and (2) ensuring that any chemicals injected and any As mobilized should be captured by the combination of the sampling well and the high-volume P&T recovery well. Five injection well nests (CW 2-6), with three 1” wells per nest, were installed for a total of 15 injection wells. In each well nest, the wells were screened at 27-28 ft (8.2-8.5 m), 29-30 ft (8.8-9.1 m), and 31-32 ft (9.4-9.8 m) below ground surface (bgs); the water table is approximately 15 ft (4.6 m) bgs. One 2” monitoring well (referred to as CW 1 or sampling well) was also installed; this well was screened at 27-40 ft bgs (8.2-12.2 m). The nearby P&T recovery well, RW 2a, is screened 25-45 ft bgs (7.6-13.7 m) (Figure 5.2a). During installation of CW 1, a coarser layer of pebbles and gravel was discovered approximately 36-38 ft bgs (11.0-11.6 m). A core obtained midway between the injection wells and CW 1 also showed evidence for coarser materials (pebbles and gravel) approximately 38-39 ft (11.6-11.9 m) bgs. It is not clear whether the coarse materials found at each of these locations form one continuous layer. No coarse sections were noted in the cores taken during installation of two of the injection wells; maximum core depths were 40 ft (12.2 m) bgs. To test whether injected materials would travel primarily within the coarse zones, a screen interval was chosen for the sampling well that would include the depths of the coarse materials and a 1.8” low pressure pneumatic well packer (Model 800, Solinst, Canada) was used to sample different parts of CW 1 during the initial tracer tests and oxalic injection experiments (Figure 5.2b).

The wells were installed by SGS Environmental (West Creek, NJ) in June 2008. Boreholes were made by hollow stem auger (4.25”) driven by direct push equipment (Geoprobe, Salina, KS). Injection wells were sand-packed using sand from the site (15 ft bgs and below) and A1 sand (above 15 ft bgs). The sampling well was sand-packed with A1 sand. For all wells, the well tubes were threaded PVC construction. Prior to well installation several cores were obtained using direct push methods with a maximum depth of 40 ft (12.2 m) bgs (Macro-Core© Soil Sampling tools with 2.25” OD sampler tube, Geoprobe, Salina, KS); cores taken at the end of the oxalic acid injection experiment were obtained by the same method and had maximum depths of 50 ft (15.2 m) bgs (Figure 5.1).

5.5.2 Tracer experiment (field experiment #1), June 24 – July 2, 2008

The 2008 forced gradient tracer experiment (field experiment #1) involved injection of inert tracers to confirm that significant amounts of the injected materials were captured in the sampling well and to help calibrate the hydrological models. The inert chemicals used in the tracer experiment (field experiment #1) included sodium bromide (NaBr) and sulfur hexafluoride (SF_6) (see Appendix A for SF_6 data and information). The tracers were added in line to groundwater from a nearby P&T recovery well (RW 2a, ~1000 μg/L As) and were injected over the course of 3 hours. Tracer was pumped to each of the 15 injection wells at 10 L/min for 12 min for a total of ~1800 L. A piston pump (Series I pump, SSI Lab Alliance, College Park, PA) was used to add tracer-spiked water to the stream of RW 2a water at a flow rate of 3 mL/min; concentrations of tracers injected into the wells were approximately 123 mg/L bromide and 3.4×10^{-10} ccSTP SF_6/cc. The sampling well (CW 1) and P&T well (RW 2a) were monitored over the course of ~9 days for tracer breakthrough as well as As concentration and other groundwater parameters (pH, ORP, conductivity, etc.). Samples at the sampling well (CW 1) were taken from the entire screened well interval and above and below an inflatable packer (labeled all, above, and below, respectively, Figure 5.2b). When the packer was in place in the well screen, sampling below it would sample the coarse layer while sampling above it would exclude groundwater flowing through the coarse layer. During the tracer experiment (field experiment #1), water was continuously extracted from the sampling well at an average of 4.8 L/min with a 12 V submersible plastic pump (Water Spout, Groundwater Essentials, Sarasota, FL); a total volume of ~60,000 L were extracted. Through most of the experiment (>90% of the time), water was pumped from the entire well, with periodic sampling from above and below the packer when the packer was placed within the well screen. The extracted water was pumped into a ~35,000 L tank, which was emptied every few days. The water was transferred to the groundwater treatment plant using a stainless steel tanker truck (~19,000 L). An automated sampler (Teledyne Isco, Lincoln, NE) was used for obtaining water samples during the night from the pumped flow at CW 1 and was linked to the outflow line by T-connection. Samples were also obtained from the P&T recovery well (RW 2a) daily (typically 3 per day); no samples were taken overnight. Flow rates at the P&T recovery well averaged 312 L/min during the tracer experiment (field experiment #1); maximum of 332 L/min and minimum of 300 L/min based on daily averages.

Samples to be analyzed by inductively coupled plasma-mass spectrometry (ICP MS) for metal concentrations were filtered through 0.45 μm PES filters (Whatman) into acid washed HDPE bottles and acidified to 1% acid with trace metal grade or better nitric acid and then kept cold (4°C). Samples to be analyzed for bromide concentration by ion chromatography were filtered into HDPE bottles and kept cold (4°C).

5.5.3 Oxalic acid injection (field experiment #2), April 3 – July 2, 2009

Prior to injection of any bromide or oxalic acid, SF_6 tracer was again injected to the pilot study site (Appendix A). Injection of oxalic acid and a bromide tracer were begun 4/4/09, the day after the SF_6 injection, and lasted 90 days. Two phases of oxalic acid injection were performed. The total flow rate was 0.27 L/min (18 mL/min per injection well) for the first 34 days starting 4/4/09 (Phase I) and 0.56 L/min (37 mL/min per injection well) for the next 56 days starting 5/7/09 (Phase II). In Phase I, target concentrations of injection solutions were 100 mM oxalic acid (oxalic acid dihydrate technical grade, 99.5%, Univar in Redmond, WA and Chemical Distributors, Inc. in Buffalo, NY) and 50 mg/L Br (sodium bromide anhydrous, 99+%, Acros Organics); in Phase II target concentrations were 400 mM oxalic acid and 100 mg/L Br. Hydrological modeling had suggested that input of 50 mg/L of a conservative tracer like Br would result in 3.5 mg/L measured at the sampling well (Appendix B). If we assume that the oxalic acid will behave conservatively as well, then one would expect 7 mM oxalic acid at the sampling well, CW 1, during Phase I. To make the influent solutions, oxalic acid and sodium bromide solids were mixed in 300-gallon (1136 L) polyethylene tanks (McMaster-Carr) with groundwater from a P&T recovery well (RW 2) outside of the pilot study area and screened deeper within the aquifer (54-74 ft bgs or 16.5-22.6 m bgs) than the injection and sampling (CW 1) wells in the pilot area. Mixing was accomplished by both manually stirring and with the help of a 12 V submersible plastic pump (Water Spout, Groundwater Essentials, Sarasota, FL). The influent solutions were pumped from the tanks using a chemical metering pump (model C131-26S, LMI Milton Roy, Ivyland, PA) through an injection manifold system, which split the flow evenly to each of the 15 injection wells. Details regarding the design and testing of the injection manifold system have been presented elsewhere (Wovkulich, et al., 2011).

The sampling well (CW 1) and P&T well (RW 2a) were monitored over the course of the 90 days of injection as well as 69 days after injection was stopped; samples were taken to monitor for tracer and oxalate breakthrough as well as changes in As, Fe, Al, and Mn concentrations and other groundwater parameters (pH, ORP, conductivity, etc). A packer was placed within the well screen for the duration of the experiment (Figure 5.2b). Samples at the sampling well (CW 1) were taken above and below the inflatable packer. Water was continuously extracted from above the packer at the sampling well while the oxalic and bromide influent solutions were being injected and for 13 days afterward; extraction was accomplished using a 12 V submersible plastic pump and low flow controller (Typhoon, Groundwater Essentials) and the extraction rate was kept as close to 2.5 L/min as possible. Samples taken beyond that time were obtained from the sampling well after purging the well for at least 60 minutes at 2.5 L/min prior to sampling (more than 30 well volumes). Samples taken below the packer were obtained using a peristaltic pump (Master Flex Environmental Sampler, Cole Parmer) set to extract water at a rate of ~100 mL/min; the well was purged for at least 60 minutes before sampling (more than two well volumes below the packer). The water extracted from above the packer was pumped into the ~35,000 L tank, as discussed above. The water extracted from below the packer was also containerized and taken to the P&T plant for treatment. Flow rates at the P&T recovery well averaged 301 L/min during the oxalic acid injection experiment (field experiment #2).

Daily influent samples were taken and tested for oxalic acid, bromide, and As concentration. Periodic samples were also taken at one of the injection wells (CW 3.2) using the peristaltic pump (and dedicated tubing).

Samples to be analyzed by inductively coupled plasma-mass spectrometry (ICP MS) for metal concentrations were filtered through 0.45 μm PES or PP filters (Whatman) into acid washed HDPE bottles and acidified to 1% acid with trace metal grade or better nitric acid. Samples to be analyzed for oxalate and bromide concentration by ion chromatography were filtered into HDPE bottles and kept cold (4^{o}C or frozen).

5.6 Analytical techniques

5.6.1 Inductively coupled plasma mass spectrometry

Water samples were analyzed for As, Fe, Mn, Al, S, and P content using inductively coupled plasma mass spectrometry (ICP MS) with a high-resolution Single Collector instrument (Axiom, Thermo Elemental, Germany). ^{115}In was added to each sample as an internal response standard and was used to correct for instrument drift prior to quantification. Each sample and standard was run three times and averaged with percent relative standard deviations (%RSD) of less than 10% and typically less than 5%, except where noted. Three to four point calibration curves were run at least once every 30 samples; calibration curves used for analysis of the data presented here had R^2 >0.98.

5.6.2 Ion chromatography

Water samples were analyzed for oxalate and bromide concentrations using a Dionex ICS-2000 (Sunnyvale, CA) ion chromatography system with an IonPac AS-11 HC column. Samples were run in gradient mode with eluent concentrations increasing from 5 to 60 mM KOH over the course of the sample run. Four to five point calibration curves were used for quantification and were analyzed throughout each batch of samples; calibration curves used for analysis had R^2>0.98. Replicate standards analyzed with each batch had %RSD of less than10%.

5.6.3 Bromide selective electrode

A bromide specific electrode (Orion, Thermo Scientific, Waltham, MA) was used to make field measurements of Br concentrations. An ionic strength adjustment solution was added to each sample prior to analysis (0.1 mL of 5 M $NaNO_3$ solution for every 5 mL sample). Separate samples were obtained for electrode measurements and ion chromatography measurements. The bromide electrode was calibrated daily before use; calibration curves used for analysis had $R^2>0.98$. Replicate standards measured each day had %RSD of 5% or less.

5.6.4 Measurement of groundwater parameters

Groundwater parameters were measured in the field with the aid of portable meters. These parameters included pH (pH 20 series pH meter, Cole Parmer, Vernon Hills, IL or YSI 556 MPS Multi-Parameter Instrument, Yellow Springs, OH), conductivity, dissolved oxygen, and oxidation-reduction potential (YSI 556 MPS Multi-Parameter Instrument, Yellow Springs, OH). Dissolved oxygen content was also monitored with the use of portable field kits (self filling ampules, Chemetrics, Calverton, VA).

5.6.5 X-ray fluorescence spectroscopy

Arsenic concentrations on the sediment core materials were determined by X-ray fluorescence (XRF) spectroscopy with a Spectro Xepos desktop instrument (Spectro Analytical Instruments, Germany). Samples were sieved to remove particles >2 mm (greater than sand sized) and powdered using an Angstrom TE-110 shatterbox

(Angstrom, Inc; IL). Larger particles were removed because As likely exists as coatings on the solids and including larger particles could create a low As concentration bias in the results. A quality control sample was measured after every 11 unknown samples; percent relative standard deviation for these replicate analyses were 10% or less for all elements measured (except V at 13%) and typically less than 5%. A calibration curve specific to these sands was created by performing complete digestion procedures on a subset of the samples. Oven dried samples were digested using nitric, perchloric, and hydrofluoric acids and analyzed for total As, Fe, Al, and Mn concentration by ICP MS (Fleisher and Anderson, 1991).

5.7 Safety precautions

While making up influent solutions of oxalic acid, care was taken to avoid exposure to oxalic acid powders with the use of proper personal protective equipment, i.e, gloves, goggles, Tyvek suit, and a respirator. Oxalic acid exposure can lead to burns of the skin, respiratory system and eyes and can cause kidney damage (NJDHSS, 2010).

During the oxalic acid injection experiment (field experiment #2), we monitored for production of arsine gas, a toxic gas that can form in the presence of As, acid, and a strong reductant (Baghel, et al., 2007). We did not expect to see arsine gas under the conditions present in this experiment and indeed saw no indication of arsine gas formation. Arsine gas production was monitored using the arsine sensitive test strips from a portable groundwater As testing kit (0-500 ppb, with 10 ppb detection limit, Hach, Loveland, CO). When used to evaluate groundwater As, the test strips are place over the opening of a small reaction vessel in which the groundwater sample is mixed with reagents to evolve arsine gas. The test strips change color in proportion to the concentration of arsine gas. To monitor for arsine gas in the field, the test strips were placed over the openings of well bores at the injection, sampling, and P&T wells in addition to the holding tank and the tanker truck used for transporting water to the treatment facility. The test strips were watched for color change and were changed on a regular basis. Portable arsine gas sensors and dosimeter badges can also be used to monitor for arsine gas formation. Further information regarding the health effects of arsine gas can be found through the Agency for Toxic Substances and Disease Registry (ATSDR, 2007).

5.8 Results - Tracer experiment (field experiment #1)

5.8.1 Arsenic, Fe, and Al mobilization

Throughout the tracer experiment (field experiment #1, 6/24/08-7/3/08), water samples were obtained from the sampling well (CW 1) from the coarse layer (below packer), excluding the coarse layer (above packer), and from the entire well. In addition, samples were obtained from the nearby pump and treat (P&T) recovery well, RW 2a.

Arsenic, Fe, and Mn concentrations for each of these sample types did not show a significant or systematic change over the course of the experiment (Table 5.1). Aluminum concentrations averaged less than 100 μg/L for each of the sample types; accurate quantification in that range was difficult with the method used due to elevated background Al levels in blanks.

Table 5.1. Element concentrations in groundwater samples during the 2008 tracer experiment (field experiment #1), with no oxalic acid injection [a]

	Average concentration ± 1 standard deviation (μg/L)		
Sample Type	As	Fe	Mn
CW1 – coarse layer	441 ± 77	30 ± 31[b]	30 ± 2
CW1 – excluding coarse layer	3620 ± 130	504 ± 25	7 ± 1
CW1 – entire well	2820 ± 210	371 ± 74	11 ± 4
RW 2a	952 ± 35	102 ± 11[c]	46 ± 2

[a] Al concentrations averaged <100 μg/L for each sample type.

[b] Poor data quality due to low signal

[c] Samples for which %RSD of replicate measurements were >10 % were excluded from average

5.8.2 Bromide recovery

Bromide was introduced into the injection wells on 6/24/08. The average influent bromide concentration was 123 ± 13 mg/L. Throughout the tracer experiment (field experiment #1, 6/24/08-7/3/08), water samples were obtained from CW 1 (the sampling well) from the coarse layer, excluding the coarse layer, and from the entire well.

Bromide concentrations were analyzed for each of these sample types. Groundwater extraction from CW 1 most often occurred from the entire well screen (>90% of the time) and most samples were taken from this well configuration. Bromide concentration at CW 1 (entire well) began at levels not detectable by the IC. Bromide breakthrough formed a relatively Gaussian-shaped peak; concentrations began to rise on 6/25/08 and reached a maximum of 4.1 mg/L on 6/29/08. Bromide concentrations then fell, returning to non-detectable levels on 7/3/08 (see Appendix A, Figure 5.10). Approximately 28% of the injected bromide was recovered at the sampling well (entire well); this estimate is adjusted for times when the well pump was off or when pumping from other configurations, but does not include the mass of Br captured as a result of pumping from the other configurations (which constituted <10% of the pumping time).

Samples were also obtained from the coarse layer and from the zones excluding the coarse layer. Within the coarse layer, bromide concentrations averaged 0.2x the entire well concentration; when the coarse layer was excluded, bromide concentrations averaged 1.5x the entire well concentration as measured by the Br selective electrode.

5.9 Results - Oxalic acid injection (field experiment #2)

5.9.1 As, Fe, and Al in influent solutions

Daily influent samples were taken throughout the injection experiment. Samples were obtained from the tank connected to the injection pump. Average influent As concentration during the injection experiment was 358 ± 17 µg/L; Fe concentration was 1240 ± 990 µg/L and Al concentration averaged <150 µg/L.

5.9.2 As, Fe, and Al at CW 1(sampling well) – above packer

Introduction of ~100 mM oxalic acid into the injection wells began 4/4/09 at ~5:30 pm. Daily sampling (except for 1 or 2 days) was performed for the duration of the injection. At the sampling well, CW 1, samples that were collected above the packer initially had As concentrations of 3080 ± 150 µg/L (mean ± 1 standard deviation; 4/4/09-4/9/09). There was an oxalic acid induced peak in As concentration of 6250 µg/L on 4/18/09 (Figure 5.3). After this peak, As concentrations declined gradually, remaining above the baseline concentration, until after the introduction of the higher concentration of oxalic acid (~350 mM) on 5/7/09, 4pm. With the higher concentration of oxalic acid came a more sustained increase in the As concentration at CW1; the average value was 5780 µg/L between 5/11/09 and 6/12/09. The large variability in As concentration is, in part, due to disruptions of the forced gradient flow because of shutdowns of the P&T plant (5/25-5/26 and 6/1-6/5). After the concentration plateau from 5/11/09-6/12/09, As concentrations fell despite continued input of oxalic acid until 7/2/09, 4:30 pm. After the injection ended, samples were collected until 9/9/09. The As concentration at CW 1 decreased to an average of 1700 ± 100 μg/L (7/28/09-9/9/09), a 45% decrease from the initial average. Further decreases were not realized because groundwater coming into the pilot study area from upgradient was still high in As. A total of 1.5 kg of As was mobilized and captured at CW 1 (above packer) between 4/13/09 and 7/9/09, the time when As concentrations became consistently elevated above initial background levels; 0.5 kg was mobilized as a result of the oxalic acid injection. The calculation for mass of As mobilized by oxalic acid includes a background correction for initial As concentration of 3080 μg/L (average value from 4/3/09-4/9/09) at CW 1 and therefore, only includes the mass of As released as a result of the oxalic acid treatment.

Aluminum and Fe also showed increases in concentration after introduction of oxalic acid to the system (Figure 5.3). Aluminum concentrations began <100 μg/L (4/4/09-4/7/09); concentrations increased gradually between 4/8/09 and 5/8/09 and increased further when the higher concentration of oxalic acid was started, with a maximum concentration of 101,000 μg/L (5/26/09). When sampling was stopped on 9/9/09, Al concentrations were leveling off ~100 μg/L. Fe concentrations began at 292 ± 27 μg/L (4/4/09-4/8/09). There was a fairly gradual increase in Fe concentration until 5/8/09. When the higher concentration of oxalic acid was started, Fe concentrations increased more sharply; maximum concentration was 299,000 μg/L (6/2/09). When sampling was stopped on 9/9/09, Fe concentrations were leveling off ~1500 μg/L.

5.9.3 As, Fe, and Al at CW 1(sampling well) – below packer

A subset of samples were also collected below the packer at the sampling well, CW 1. These samples evaluate conditions in the aquifer deeper than the injected depths and where coarser sands exist. Collection of below packer samples began 6/3/09. On 6/3/09 and 6/4/09, while the P&T wells were turned off, the As concentrations at the sampling well below the packer were low, ~60 µg/L (Figure 5.4). Once the pumps were turned on again on 6/5/09, As concentrations increased rapidly, peaking at 8460 µg/L on 6/6/09. After the As peak, concentrations decreased and began to plateau with an average As concentration of 721 ± 138 µg/L between 6/21/09 and 7/1/09. There was another increase in As concentration following the 7/2/09 – 7/3/09 shutdown. After 7/8/09 As concentrations declined and remained low for the rest of sampling; As concentration averaged 129 ± 83 µg/L between 7/12/09 and 9/9/09.

Aluminum and Fe showed similar patterns (increases and declines) as groundwater As (Figure 5.4). On 6/3/09 and 6/4/09, while the P&T wells were turned off, the concentrations at the sampling well below the packer were ~1240 µg/L for Al and ~1030 µg/L for Fe (Figure 5.4). Once the pumps were started again on 6/5/09, concentrations increased rapidly, with Al peaking at 161,000 µg/L on 6/6/09 and Fe peaking at 220,000 µg/L on the same day. After that peak, concentrations decreased and began to plateau with an average Al concentration of 12,200 ± 1890 µg/L and average Fe concentration of 18,500 ± 2000 µg/L between 6/21/09 and 7/1/09. There was another increase in concentration after the P&T system was turned on following the 7/2/09 –

7/3/09 shutdown. After 7/8/09 concentrations declined and remained low for the rest of sampling; both Al and Fe concentration were <100 µg/L between 7/20/09 and 9/9/09.

5.9.4 As, Fe, and Al at RW 2a (pump and treat recovery well)

Daily sampling at the P&T recovery well, RW 2a, was performed for the duration of the injection (except for 1 or 2 days or when the P&T wells were shut off). Samples initially had As concentrations of 454 ± 18 µg/L (mean ± 1 standard deviation; 4/4/09-5/8/09). There was no significant increase in As concentration while the lower concentration of oxalic acid was being injected (Figure 5.5). Substantial increase in As concentrations began on 5/9/09 and there was a peak in concentration at 726 µg/L on 5/12/09 (Figure 5.5). Following this peak, As concentrations declined until after a plant shutdown (6/1/09-6/5/09) when As concentrations increased again to a maximum for the experiment of 770 µg/L on 6/5/09. Arsenic concentrations again showed a gradual overall decline until after another plant shutdown between 7/6/09 and 7/12/09, when As concentrations reached a plateau. Oxalic acid injection ended on 7/2/09; samples were collected until 9/9/09. The As concentration at RW 2a decreased to an average of 417 ± 18 µg/L (7/13/09 - 9/9/09), an 8% decrease from the initial average. A total of 12.8 kg of As was captured at RW 2a between 5/9/09 and 7/12/09 (when As concentrations were elevated above initial background levels); 2.4 kg of that total was mobilized and captured at RW 2a as a result of the oxalic acid injection. It is important to note that the 12.8 kg captured at RW 2a includes the entire capture zone and not just the pilot area treated by oxalic acid. The calculation for mass of As mobilized by oxalic acid included a background correction for initial As concentration of 454 µg/L (average value from

4/4/09-5/8/09) at RW 2a and therefore, only accounts for the mass of As released as a result of the oxalic acid treatment. The total mass of As mobilized and captured through the combined efforts of CW 1 and RW 2a was 2.9 kg. The 2.4 kg captured at RW 2a as a result of oxalic acid treatment represents a conservative estimate, subtracting out background As based on just the initial background average at RW 2a. Since there is historical evidence for a declining background As concentration at RW 2a, we also calculated mass of As mobilized as a result of oxalic acid using a declining background for the background subtraction; doing so suggests As mobilization of 3.1 kg at RW 2a as a result of oxalic acid treatment, bringing the total As mobilization due to oxalic acid treatment to 3.6 kg between CW 1 and RW 2a. These calculations are described further in the discussion.

Aluminum and Fe also showed increases in concentration after introduction of oxalic acid to the system (Figure 5.5). Aluminum concentrations began <100 μg/L (4/4/09-4/8/09); concentrations increased gradually between 4/9/09 and 5/8/09 to ~600 μg/L and increased further when the higher concentration of oxalic acid was started. Maximum Al concentration was 7070 μg/L on 6/5/09 (just after the pumps were turned on following a plant shutdown). Aluminum concentrations then showed an overall decrease (aside from a spike when the pumps were turned on briefly on 7/10/09 during the 7/6/09-7/12/09 shutdown) and were leveling off at ~100 μg/L between 7/28/09 and 9/9/09, the end of sampling. Fe concentrations began at 205 ± 9 μg/L (4/4/09-4/10/09); Fe concentrations increased gradually between 4/10/09 and 5/9/09 to ~800 μg/L and increased further after the higher concentration of oxalic acid influent was started. Maximum Fe concentration was 9240 μg/L on 6/9/09. Fe concentrations then showed an overall decrease (aside from a spike when the pumps were turned on again briefly during the 7/6/09-7/12/09 shutdown) and were leveling off at ~200 µg/L between 7/28/09 and 9/9/09, the end of sampling.

5.9.5 Oxalic acid and bromide in influent solutions

During Phase I of the experiment (4/4/09 – 5/7/09), the average influent concentrations were 93 ± 11 mM for oxalic acid and 48 ± 5 mg/L for bromide. On 5/7/09 the oxalic acid and bromide concentrations were increased; during Phase II (5/7/09-7/2/09) the average oxalic acid concentration was 351 ± 30 mM and bromide was 92 ± 10 mg/L.

5.9.6 Oxalic acid and bromide at CW 1 (sampling well) – above packer

Introduction of ~100 mM oxalic acid into the injection wells began 4/4/09 at ~5:30 pm. Daily sampling (except for 1 or 2 days here and there) was performed for the duration of the injection. Less than 0.02 mM oxalate was detected in the sampling well prior to injection of the influent solution. After 4/8/09, oxalate concentrations began to increase and reached a rough plateau between 4/26/09 and 5/9/09, which averaged 2.1 mM (Figure 5.6). The oxalic acid influent concentration was increased to ~350 mM on 5/7/09 and the concentration at the sampling well increased rapidly between 5/9/09 and 5/18/09. The oxalate concentration began to plateau at an average of 11.9 mM (5/18/09-5/23/09) until P&T plant shutdowns disrupted the forced gradient flow and caused greater variations in the concentrations at CW 1. This average value represents a 44-fold dilution of the injected solutions. Oxalate concentrations decreased sharply following the 6/1/09-

6/5/09 shutdown, but were increasing again until the next shutdown and end of injection. Injection of the influent solutions was stopped on 7/2/09 and concentrations of oxalate decreased to <0.02 mM after 8/3/09.

Bromide concentrations showed similar patterns to oxalate in CW 1 (above packer). Introduction of ~50 mg/L Br into the injection wells began 4/4/09 at ~5:30 pm. Bromide concentration in CW 1 began at undetectable levels. The Br concentrations increased gradually and reached a plateau averaging 1.4 mg/L between 4/15/09 and 5/9/09, which represents a 35-fold dilution from injected Br concentrations (Figure 5.6). The Br influent concentration was increased on 5/7/09 to ~100 mg/L and the Br concentration at the sampling well increased between 5/9/09 and 5/25/09. The Br concentration had not yet reached a plateau before P&T plant shutdowns disrupted the forced gradient flow; Br concentration reached ~3 mg/L before the 5/25/09 shutdown. After the 6/1/09-6/5/09 shutdown, the Br concentration dropped sharply as the groundwater flow was changed. Br concentrations then increased until the next shutdown and end of injection. Injection of the influent solutions was stopped on 7/2/09 and concentrations of Br fell back to undetected levels by 8/10/09, remaining there until sampling was stopped on 9/9/09.

The ratio of oxalate (mM) to Br (mg/L) in the influent during Phase I was 1.9. Oxalate:Br ratios in CW 1 (above packer) plateau at approximately 1.3 between 4/20/09 and 5/16/09. The ratio of oxalate to Br in the influent during Phase II was 3.8. Oxalate:Br ratios in CW 1 (above packer) were somewhat variable between 5/16/09 and 7/2/09 but averaged 3.3. Approximately 13% of the injected oxalic acid and 15% of the injected Br were recovered at the sampling well, CW 1 above packer.

5.9.7 Oxalic acid and bromide at CW 1 (sampling well) - below packer

Samples were obtained from below the packer at the sampling well and measured from 6/6/09 – 9/9/09; these samples reflect the groundwater solution in a coarser layer of the aquifer than above the packer. Between 6/6/09 and 7/1/09 the oxalate and bromide concentrations were rather variable but averaged 11.6 ± 3.0 mM and 4.7 ± 3.5 mg/L, respectively. After 7/1/09 oxalate and bromide concentrations below the packer decreased and reached non-detectable levels by 7/28/09. The ratio of oxalate to Br in the influent during Phase II is 3.8. Oxalate:Br ratios at CW 1 (below packer) averaged 3.3 between 6/6/09 and 7/1/09 in Phase II of injection, however, there is considerable variation.

5.9.8 Oxalic acid and bromide at RW 2a (pump and treat recovery well)

Introduction of ~100 mM oxalic acid into the injection wells began 4/4/09 at ~5:30 pm. Daily sampling (except for 1 or 2 days here and there and when the P&T wells were off) was performed for the duration of the injection. Less than 0.01 mM oxalate was detected in the recovery well prior to injection of the influent solution. From 4/8/09-5/8/09, the oxalate concentrations increased gradually to ~0.06 mM (average 4/23/09-5/8/09), reaching a rough plateau at ~1500-fold dilution from injected solutions (Figure 5.7). The oxalic acid influent concentration was increased to ~350 mM on 5/7/09 for Phase II and the concentration at the recovery well increased rapidly between 5/9/09 and 5/15/09. The oxalate concentration averaged 0.38 mM (5/15/09-6/1/09), approximately 930-fold dilution from injection solutions, until P&T plant shutdowns disrupted the forced gradient flow and caused greater variations in the concentrations at RW 2a. Maximum concentration of oxalate reached was 0.8 mM on 6/11/09, a few days after the 6/1/09-6/5/09 shutdown. After the maximum on 6/11/09, concentrations decreased sharply. The oxalate concentrations then showed a general increasing trend until the subsequent plant shutdown and end of injection. Injection of the influent solutions was stopped on 7/2/09; concentrations of oxalate decreased sharply after 7/10/09, falling below to 0.01 mM by 7/23/09.

Introduction of ~50 mg/L Br into the injection wells began 4/4/09 at ~5:30 pm. Bromide concentration in RW 2a began at undetectable levels. Through all of Phase I (4/4/09 – 5/7/09), bromide concentrations remained below 0.1 mg/L except for a few concentration spikes (maximum 0.27 mg/L) (Figure 5.7). The Br influent concentration was increased on 5/7/09 to ~100 mg/L and the Br concentration at the recovery well increased after 5/9/09, reaching a plateau averaging 0.15 mg/L between 5/16/09 and 6/1/09, when the plant was shutdown; this is a 630-fold dilution vs. injected materials. The Br concentration reached another plateau between 6/13/09 and 7/10/09 at 0.25 mg/L, ~360-fold dilution from injected materials. Injection of the influent solutions was stopped on 7/2/09 and concentrations of Br decreased sharply after 7/10/09; remaining undetected after a concentration spike 7/28/09 until sampling was stopped on 9/9/09.

The ratio of oxalate (mM) to Br (mg/L) in the influent during Phase I was 1.9. Oxalate:Br ratios in RW 2a did not remain steady in Phase I; many of the points have non-detectable levels of Br. The ratio of oxalate to Br in the influent during Phase II was 3.8. Oxalate:Br ratios at RW 2a average 2.8 between 5/18/09 and 6/12/09 in Phase II of injection, however, there is considerable variation.

Approximately 46% of the injected oxalic acid was recovered at the P&T recovery well; a total of 59% of the oxalic acid was recovered by the sampling and P&T wells. Between ~90 and 125% of the injected Br was recovered at the recovery well, RW 2a, depending on whether a lower limit cut off value is applied to the data. Therefore, between ~105 and 140% of the Br is recovered between the sampling and P&T well.

5.9.9 Oxalic acid and bromide at injection well CW 3.2

Samples were also taken at one of the injection wells during the experiment. A sample taken 4/28/09, during Phase I of injection, had an oxalic acid concentration of 91 mM and bromide concentration of 47 mg/L (14% and 4% different, respectively, than the influent concentrations on that day). A sample taken 6/11/09, during Phase II of injection, had an oxalic acid concentration of 323 mM and bromide concentration of 74 mg/L (2% and 7% different, respectively, than the influent concentrations on that day). Samples taken following the injection period had oxalate concentrations < 0.02 mM and bromide concentrations < 0.25 mg/L.

5.9.10 Arsenic concentrations on the solids

X-ray fluorescence spectroscopy (XRF) was used to evaluate As concentrations of sediment cores obtained in 2008 (prior to the oxalic acid injection) and in 2009 (at the end of the oxalic acid injection experiment, field experiment #2). An XRF calibration specific to Vineland sands was created based on complete digestion of a subset of samples and As was adjusted for low recovery of a standard reference material. Pairs of data points (N=50 pairs) were compared for 2008 and 2009 sediments; pairs were matched for depth and location and covered depths of approximately 27-40 ft (8.2-12.2 m) bgs, the depth range of the screened region of sampling well, CW 1. Sediment samples were collected from three locations for these comparisons: at/near the injection wells, midway between injection and sampling wells, and at/near the sampling well in 5 ft (1.5 m) sections. The sections were subsampled in roughly 20 cm increments. Following oxalic acid treatment, the solids over the 27-40 ft depth range showed a decrease in As concentration by 28-36% depending on whether the median or mean values, respectively, were used to make the comparison (Table 5.2). The two populations of samples, 2008 cores and 2009 cores, which were matched for similar location and depth, show a statistically significant difference in As concentration (paired t-test, $p<0.001$).

Additionally, the As data was grouped by depth; doing so indicates that there was little As removal from the shallowest depths, 27-30 ft (8.2-9.1 m) bgs, compared with deeper samples, 30-35 ft (9.1-10.7 m) or 35-40 ft (10.7-12.2 m) bgs (Table 5.2). When data for the 30-40 ft depths (9.1-12.2 m) was combined, an As removal of 34-48% was calculated depending on whether the median or mean values, respectively, were used to make the comparison. This data is also presented in histograms in Figure 5.8 (5.8a shows all available data for depths of 27-40 ft and 5.8b shows the matched pairs).

Aluminum and Fe concentrations were also examined in this way. Following oxalic acid treatment, the solids over the 30-40 ft depth range did not show a statistically significant change in Al (paired t-test, $p>0.05$). Fe concentrations decreased by 10-30% depending on whether the median or mean values, respectively, were used to make the comparison; this difference was statistically significant when the two populations of samples, 2008 cores and 2009 cores, were matched for similar location and depth and were compared (paired t-test, $p<0.02$).

Table 5.2. Arsenic concentrations and percent As removal based on XRF data.[a] Data is shown for matched pairs for the full depth range of the sampling well, CW 1, or 27-40 ft bgs, as well as depth sections 27-30 ft, 30-35 ft, 35 ft-40 ft and 30-40 ft.

	2008 Cores (before oxalic acid treatment)	**2009 Cores (after oxalic acid treatment)**	**Percent Difference 2008 – 2009 (%)[b]**	**N (pairs)**
27-40 ft bgs[c]				50
Mean (mg/kg)	40	26	36%	
% RSD	59%	34%		
Median (mg/kg)	35	25	28%	
27-30 ft bgs[d]				16
Mean (mg/kg)	33	32	3%	
% RSD	18%	23%		
Median (mg/kg)	33	30	8%	
30-35 ft bgs[e]				15
Mean (mg/kg)	52	25	52%	
% RSD	71%	27%		
Median (mg/kg)	42	25	40%	
35-40 ft bgs[e]				19
Mean (mg/kg)	37	21	43%	
% RSD	40%	39%		
Median (mg/kg)	30	24	21%	
30-40 ft bgs[f]				35
Mean (mg/kg)	43	23	48%	
% RSD	63%	33%		
Median (mg/kg)	37	25	34%	

[a] These values are based on XRF data using a calibration specific to the Vineland sands and adjusted for low As recovery of a standard reference material in the digestion procedure.

[b] Percent difference was calculated based on comparison between the average or median value for 2008 and 2009.

[c] If all available data for the 27-40 ft depth range are included, not just matched pairs, the mean and median values are nearly identical. For 2008 data, the mean and median values were 40 and 35 mg/kg, respectively (N=51); for 2009 data, the mean and median values were 25 and 25 mg/kg, respectively (N=80). The matched pairs for this depth range are statistically different (paired t-test, $p<0.001$).

[d] The matched pairs for this depth range are not statistically different (paired t-test, $p>0.05$).

[e] The matched pairs for each of these depth ranges are statistically different (paired t-test, $p<0.02$).

[f] The matched pairs for this depth range are statistically different (paired t-test, $p<0.001$).

5.10 Discussion

5.10.1 Comparison between 2008 and 2009 Br tracers

Bromide tracers were used in both the 2008 and 2009 field experiments. In the 2008 tracer experiment (field experiment #1), Br was introduced into the subsurface in a short pulse (3 h) while in the 2009 oxalic acid injection experiment (field experiment #2) Br was introduced with the oxalic acid over the course of 3 months.

In the 2008 tracer experiment (field experiment #1), Br recovery at CW 1 (samples taken from the full well) was calculated to be 28%. Measurements for Br content at RW 2a were not made as samples were expected to be too dilute. Br recovery at CW 1 (above packer) was calculated to be 15% for the 2009 oxalic acid injection experiment (field experiment #2). The difference in Br recoveries at CW 1 for the two experiments may be explained in part by the higher extraction rate used during the 2008 experiment (4.8 L/min vs. 2.5 L/min in 2009); the higher extraction rate could result in a larger cone of depression around the well, faster groundwater flow velocity near the well, and therefore, greater capture of Br. Additionally, there was higher than normal precipitation during the 2009 experiment, which could have led to increased recharge and rainwater input into the subsurface and thus diluted the tracer signal. Precipitation was ~25% higher than normal during the 3-month Br injection period in 2009 (April, May, and June); precipitation during June alone was ~75% higher than normal (NOAA, 2011).

The results of the 2008 tracer experiment (field experiment #1) indicated that little of the injected materials traveled through the coarser layer found deeper within CW 1. Br concentrations in samples obtained above the packer were at least 7x higher than samples obtained below the packer. However, during the 2009 experiments there was evidence for transport of injected materials down through this layer. This discrepancy is discussed in more detail later, however, it is possible that differences in the experimental design of the 2008 and 2009 experiments could also explain the disparity. Most notably, the greater duration of the 2009 experiment could have allowed time for the injected materials to travel vertically and access the coarser layer. A longer period of altered flow gradient may have caused water to advect along more conductive zones.

A value for days/pore volume can be calculated using the tracer data. For the 2008 experiment, there were 4.9 days per pore volume between injection wells and sampling well based on the time to capture half of the recovered Br. For the 2009 experiment, there were 7.6-8.0 days per pore volume between injection wells and sampling well based on the time until the Br concentration reached half of the plateau value during Phase I of injection. The increased pore volume time in 2009 was unexpected especially in light of the fact that the pumping rates at RW 2a had remained so similar. However, a nearby pump and treat well, RW 1, had been turned on during the 2008 experiment (~380 L/min) but was off during the 2009 experiment. Although RW 1 is screened lower in the aquifer (~55-75 ft or 16.8-22.9 m bgs) than RW 2a (~25-45 ft or 7.6-137 m), its spatial location (xy) is within 40 ft (12.2 m) of RW 2a and its pumping rate could potentially have an impact on the flow regime in the pilot area. Additionally, the increased precipitation in 2009 could impact recharge and flow velocities within the pilot area.

5.10.2 Bromide and oxalic acid recovery (field experiment #2)

Approximately 15% of the injected Br was captured at the sampling well and approximately 90-125% was captured at the P&T well, for a total of 105-140% Br recovery. The percentage Br recovery for each well was estimated using trapezoidal integration to calculate the area under the concentration vs. volume curve (=mass Br captured) and comparing with the mass of Br injected. The excess Br at RW 2a may be related to measurement uncertainty since the Br concentrations at the P&T well tended to be at the very low end or below the calibrated range. Restricting the recovery calculation to exclude concentration values less than half of the lowest standard (i.e., <0.15 mg/L), results in a Br recovery estimate of 101% for RW 2a and 116% between the two wells. The data suggest that complete capture of Br was likely through the combined efforts of the sampling well and the P&T well.

Approximately 13% of the injected oxalic acid was captured at the sampling well and approximately 46% was captured at the P&T well, for a total of 59% oxalic acid recovery. Since complete capture of Br was likely, it is possible that the remaining oxalate was adsorbed to the aquifer solids, precipitated as insoluble oxalate salts (e.g., calcium oxalate) at the fringes of the oxalic acid plume, or was degraded by microbial activity. Concentrations of oxalate at the sampling well, CW 1, decreased and remained below 0.05 mM by 7/20/09, indicating that adsorption and re-release of oxalate may be limited. Adsorption and degradation or just degradation by microbes seems to be the most plausible explanation, with the possibility of some salt precipitation as well. Certain microbes can utilize oxalate for metabolic activities and it is believed biodegradation may play a role in removal of organic acids from soil solutions in various ecosystems (Jones, 1998; Sahin, 2003).

5.10.3 Sampling well, CW 1, during field experiment #2

At the sampling well, CW 1, As concentrations increased after the introduction of oxalic acid, reaching a maximum of 6250 μg/L in the first phase of oxalic acid injection and exhibiting the ability of oxalic acid to increase As mobilization (Figure 5.3). However, despite the continued input of ~100 mM oxalic acid, As concentrations began to decrease. One explanation for the decrease in As concentration at the sampling well could be related to the pH distribution within the pilot study area during the first phase of oxalic acid injection. Previous research has shown that the optimal pH for Fe release by oxalic acid is 2-3, at which point the dominant form of oxalic acid would be $HC_2O_4^-$ (Lee, et al., 2007; Panias, et al., 1996). If we assume that As mobilization is related to Fe release as suggested in several studies (Klarup, 1997; Tao, et al., 2006; Zhang, et al., 2005), then low pH would be needed for optimal As release as well. Near the injection wells it is possible that the pH in the aquifer was low enough and As was efficiently being released from this portion of the pilot area. However, minor amounts of reactive components within the sandy sediments closer to the sampling well may have continued to buffer the solution and the pH at the sampling well decreased but never fell below 4.5 during the first phase of oxalic acid injection. Therefore, although there was As release early in the oxalic flow path there may have been some re-precipitation or adsorption closer to the sampling well because of decreased oxalate concentration (dilution along the flow path) and slightly higher pH (buffer capacity not exceeded in the sediments closer to the sampling well). There was evidence of Fe precipitation in the pump tubing (red/orange staining and precipitate) during the first phase of oxalic acid injection; this precipitation of Fe could generate As sorption sites and result in further removal of As from solution (Dixit and Hering, 2003; Hongshao and Stanforth, 2001; Jain and Loeppert, 2000; Jeong, et al., 2007; Jia, et al., 2006). Additionally, it is possible that the first phase of oxalic acid injection may have moved most or all of the As that is easily mobilized or available at that oxalic acid level from that low pH region. Since the pH later in the flow path was still not low enough for optimum release, overall As release, as monitored at CW 1, declined. Therefore, it is important to keep the pH low and the concentration of oxalate high enough in order to maximize As release and transport and minimize re-precipitation/sorption.

Arsenic concentrations at the sampling well fell to ~3300 μg/L before increasing again as a result of the introduction of the higher oxalic acid influent concentration, ~350 mM, and higher injection flow rate. Approximately three days following introduction of the higher oxalic acid influent, As concentrations increased to 5000 μg/L at which point the pH measured in the sampling well had dropped to 3.3; the next day the As concentrations had increased further to 6900 μg/L and the pH fell to 2.5. The pH fell fairly quickly after introduction of the higher oxalic acid influent because the buffer capacity of the sediments had been partly overcome in the first phase of injection. Additionally, the pump tubing became clear of Fe precipitates due to the decreased pH. Arsenic concentrations increased concurrently with the pH decrease; this trend lends credence to the notion that maintaining a low pH in the system is important for maintaining As release. However, we do not believe that the pH alone is responsible for

As release, i.e., the release mechanisms are not solely proton-promoted. Based on batch laboratory extractions, simply acidifying the system with an inorganic acid such as hydrochloric or nitric acids resulted in less As mobilization than the same concentration and similar pH of oxalic acid (Appendix C); for instance, depending on extraction time 1 mM HCl mobilized 5-6% of the As from aquifer solids vs. 41-56% with 1 mM oxalic acid and 10 mM HCl mobilized 11-45% of As vs. 80-93% with 10 mM oxalic acid.

During the second phase of oxalic acid injection, there was a more sustained increase in As concentration than in the first phase, with concentrations averaging 5780 μg/L between 5/11/09 and 6/12/09. There was some variation in As concentration in large part due to P&T plant shutdowns, which disrupted the forced gradient flow in the subsurface. However, even though the injection of oxalic acid was continued until 7/2/09, the As concentrations began to decrease on 6/12/09. This decrease could indicate that most or all of the As that could be mobilized with that level of oxalic acid had been removed from the system. This decrease was also seen in laboratory column studies with 10 mM oxalic acid treatment; a large pulse of As was released from column with effluent As concentrations decreasing after reaching a peak of 100 mg/L and >40 % of the As had been removed from the solids (Wovkulich, et al., 2010).

Fe and Al showed steady increases in concentration at the sampling well in Phase I of the oxalic acid injection, despite evidence of Fe precipitation in the pump tubing. It is possible, therefore, that Fe concentrations (and possibly Al concentrations as well) would have been even more elevated if the pH at the sampling well had been lower. During Phase II of the injection, there was a sharper increase in Fe and Al concentrations due to the lower pH value and higher oxalate concentration. Similar to As, concentrations of Fe and Al decreased before the oxalic acid injection was stopped. Fe and Al concentrations appeared to decrease somewhat earlier than As, possibly as early as 6/3 or 6/4; however, the timing is difficult to discern as this was during a plant shutdown. The decline in Fe and Al concentrations indicates the possibility that most of the oxalic leachable Fe and Al had already been released. The Fe and Al concentrations remained above their background levels at the end of sampling (9/9/09), which could indicate greater retardation in Fe and Al transport than As. In the original column experiments Al appeared in the effluent solutions first, then As, then Fe (Wovkulich, et al., 2010). Relative retardation factors of Al, As, and Fe are being studied further through laboratory experiments.

At the sampling well, CW 1, As concentrations averaged 3080 μg/L before oxalic acid treatment and concentrations showed an overall decrease of 45% after oxalic acid injections (average of 1700 μg/L). This marked decrease in As concentration indicates that As was moved out of the system as a result of the oxalic acid treatment. Further decrease in As concentration following the oxalic acid treatment may have been prevented because water coming into the pilot study area already had elevated As concentrations, which would not be impacted by the oxalic acid injection. For instance, As concentrations at one of the injection wells could be >8000 μg/L. A total of 0.5 kg of As (above initial background levels) were captured at CW 1 during the oxalic acid injection experiment (field experiment #2).

5.10.4 Pump and treat well, RW 2a, during field experiment #2

At the pump and treat well (P&T), RW 2a, As concentrations did not increase significantly or systematically in the first phase of oxalic acid injection. This absence of change could be caused by a combination of dilution and Fe precipitation; dilution could impact both the oxalate concentration and thus, the ability to maintain Fe and As in solution, and the As concentration itself. In contrast to As, the Fe and Al concentrations showed a steady increase at RW 2a in the first phase of oxalic acid injection. The level of increase of Fe and Al in the sampling well, CW 1, was much higher than for As. Therefore, even if there were dilution of Fe and Al along the flow path from CW 1 to RW 2a, an increase in Fe and Al concentrations may still be evident at the P&T well, RW 2a. By the end of Phase I, Fe and Al at CW 1 had increased to ~50,000 μg/L and ~30,000 μg/L, respectively while As reached a maximum of 6250 μg/L.

In the second phase of oxalic acid injection, the As concentration at the P&T well increased to a maximum of ~726 μg/L on 5/12/09. As with the sampling well, it is possible that the increase in As occurred rapidly following the introduction of the higher oxalic acid influent because of a relatively rapid drop in aquifer pH as the buffer capacity of the solids was partly spent during the first phase of oxalic acid injection. This drop in pH could allow for re-dissolution of precipitated As, Fe, and Al as well as release of previously undissolved species, thus the increase in concentrations at the P&T recovery well, RW 2a. Perhaps mobilization would have been higher (and opportunities for re-precipitation and re-adsorption lower) if the pH at the P&T well, RW 2a, had been decreased further; the pH at the well averaged 3.4 during Phase II of the oxalic acid injection.

The use of Redux 333, a proprietary mixture containing HCl and phosphonates, in the P&T well, RW 2a, somewhat complicates interpretation of pH effects at RW 2a; Redux 333 is used as an anti-well fouling agent at some of the P&T wells. Redux 333 input was not constant at RW 2a, but the presence of Redux 333 can be monitored at RW 2a because P levels are high when Redux 333 is in use. It should be noted that P levels can be influenced (i.e., increased) by the presence of oxalic acid; this may be related to Fe release by oxalic acid since Fe can provide significant sorption sites for P species. However, the P and Fe concentrations at the pump and treat well, RW 2a, do not seem to be correlated (R^2=0.01); P concentrations are, therefore, not likely to be significantly controlled by oxalate or Fe at this well. Phosphorus levels at RW 2a (and therefore Redux 333 levels) increased on 5/7/09, the same day the higher oxalic influent was started; the pH decreased from 5.5 to 4.5. A peak in P occurred on 5/9/09 with pH falling to 3.6. Arsenic concentrations at the P&T well, RW 2a, began increasing on 5/9/09. The oxalate concentration also increased from 0.06 mM on 5/9/10 to 0.21 mM on 5/10/09. The pH remained in the 2.8-3.9 range from 5/9-7/10 despite variable P until early June and very low P from 6/14-7/15 (indicating Redux 333 addition may have ceased). The fact that pH stayed low even with low P suggests that pH, which hovered ~3.6, may be controlled by presence of oxalate during this time. Oxalate averaged ~0.2 mM from 6/14-7/15; the Henderson Hasselbach equation would predict a pH of ~3.7 for 0.2 mM oxalate. Oxalic acid input ended on 7/2/09; on 7/12/09, pH increased to 5 while P didn’t show strong increase until 7/20 (7/20 pH remains at 4.7). These considerations suggest that the As and overall pH effects seen at RW 2a were predominantly a result of oxalic acid input and Redux 333 input was not much of a factor.

Similar to what was seen in the sampling well, As, Fe, and Al concentrations at the pump and treat well, RW 2a, decreased before oxalic acid injection was stopped. The general decline was interrupted by peaks in concentration around 6/5/09 and 7/10/09, which resulted from changes to the forced gradient flow by P&T plant shutdowns and restarts. Again the decrease in concentrations despite input of oxalic acid could indicate that all of the As, Fe, and Al that could be mobilized at that level of oxalic acid had been mobilized. Arsenic, Fe, and Al concentrations at RW 2a track together during this time (6/5/09-7/10/09). Concentrations decreased consistently after 7/12/09; the oxalic acid injection had been stopped by that time.

By the end of sampling, As and Fe concentrations had decreased below their initial values at the pump and treat well, RW 2a, while Al concentrations remained slightly elevated. Ending As and Fe concentrations averaged ~8% and 20% lower than initial averages, respectively. Though the As concentrations showed a slight decrease from before to after oxalic acid treatment, it is likely due to a background decline in As concentration at that well since it was turned on in 2006. Based on the slope of decline in As concentration at RW 2a between Jan 2008 and March 2009, an As concentration of 409 μg/L would be expected on 9/9/09; it was measured as 428 μg/L. Since the capture zone of RW 2a is much larger than just the pilot study area and the well has such a high extraction rate (301 L/min), it may be difficult to see an oxalic acid prompted decline in As concentration at that well after the injection experiment; it is estimated from extraction rates and the size of the pilot area that P&T well, RW 2a, can pump the equivalent of the volume of the pilot area in <2 hrs. A total of 2.4 kg of As (above initial background levels) were captured at RW 2a during the oxalic acid injection experiment (field experiment #2), for a total of 2.9 kg captured between the combination of CW 1 and RW 2a. However, this mass of As would represent a conservative estimate since the background correction is based on the average initial As concentration. The RW 2a data from Jan 2008-March 2009 suggest a gradual decrease in As concentrations within that well, therefore, the background correction should account for this gradual decrease. To estimate the declining background at RW 2a, we assumed an initial As value of 454 μg/L (average concentration 4/4/09-5/8/09), an ending As value of 417 μg/L (average concentration 7/13/09-9/9/09), and interpolated linearly in between; the mass of As captured at RW 2a as a result of the oxalic acid treatment was then calculated to be 3.1 kg, an increase of approximately 30% compared to the conservative estimate. The total quantity of As captured between the two wells would be 3.6 kg. Although the overall concentrations of As at the P&T recovery well were lower than in the sampling well, the majority of the mass of As was captured there due to the high volume of water pumped. It is clear from this data that oxalic acid treatment led to mobilization of As at both the sampling well, CW 1, and the P&T recovery well, RW 2a.

5.10.5 Effects of P&T plant shutdowns during oxalic acid injection (field experiment #2)

During the 4/10-4/11/09 P&T plant shutdown, the oxalic acid injection was turned off. However during the 5/25-5/26/09 and 6/1-6/5/09 shutdowns, injection remained on. The injection pumps were also left on during the 7/2-7/3/09 shutdown until the end of the day on 7/2/09 when the injection was stopped for good. There was another shutdown from 7/6-7/12/09 after the injection phases were over. Since the groundwater flow under the site is controlled by the pumping at the P&T wells, pumping well shutdowns change the flow regime in the subsurface; groundwater velocity in the pilot area decreases and flow directions may also change. Much of the variability in concentrations seen during the oxalic acid injection experiment (field experiment #2) could likely be explained by P&T plant shutdowns.

One might expect that in a fairly permeable sand aquifer, groundwater elevations would recover to their natural levels rapidly. However, aquifer tests performed in 2002 and 2003 indicated that while groundwater elevations began to recover soon after pump and treat wells were shutdown, full recovery was not attained at monitoring wells even after 9 days (Skelley and Loy, 2003). Three separate shutdowns of varying lengths (3, 8, and 9 days) were monitored and investigated; static equilibrium conditions were not achieved during any of the shutdowns. The consultants performing the study concluded that several factors, namely the site's fairly uniform ground surface elevation, the considerably transmissive aquifer and extensive zones of capture, could contribute to delay in reaching steady-state conditions (Skelley and Loy, 2003). However, they noted that more study would be needed to determine the causes with more confidence. In light of this information, it is unlikely that the aquifer system was able to fully recover to non-pumping groundwater elevations during the relatively short shutdowns (maximum of 6 days) experienced during the oxalic acid injection experiment (field experiment #2), although changes to groundwater flow directions and a decrease in groundwater velocities would occur. These changes could also result in increased contact time between oxalic acid and sediments and may lead to contact between oxalic acid and some sediments not impacted under pumping conditions.

Samples taken at CW 1 (above packer) during the P&T shutdowns typically showed an increase in As, Fe, and Al concentrations. One could argue that the lower flow velocities during the shutdowns would allow more time for reaction between sediments and oxalic acid. However, Br tracer and oxalate concentrations also tended to increase during the shutdowns. Therefore, it seems more likely that there is less dilution and mixing during the P&T shutdowns. Less water is being pulled through the pilot area to cause dilution. Additionally, there is less dispersion, and consequently less spreading and less mixing when flow velocities decrease, as would be the case during the shutdowns.

Samples were taken at sampling well, CW 1, below the packer starting 6/3/09, during one of the plant shutdowns. The samples taken during the shutdown had low As, Fe, and Al concentrations and low oxalate and Br. When the wells were restarted, the concentrations of all of these analytes increased rapidly to a peak. The As, Fe, and Al concentrations similarly dropped during the 7/2-7/3/09 shutdown (unfortunately, oxalic acid and Br samples were not analyzed for those dates) and increased again when the pumps were turned back on. It would seem, therefore, that under pumping conditions groundwater is pulled downward as well as laterally through the pilot area. When the P&T wells are off, the oxalic acid and elements released by oxalic acid, are not mixed downward levels to below the packer as much. Interestingly, As, Fe, and Al concentrations increased during the 7/6-7/12/09 shutdown and the reason for this increase is unclear.

It was generally not possible to take samples from RW 2a during P&T shutdowns. One sample was obtained during the 7/6-7/12/09 shutdown when wells were turned on briefly; As, Fe, and Al concentrations increased as did oxalate concentrations (Br concentrations increased only modestly). Concentrations of As, Fe, and Al typically increased at RW 2a after the pumps were turned back on following a shutdown. This may be the result of the plug of water with elevated As, Fe, and Al seen at CW 1 during the shutdown traveling toward RW 2a once the pumps were restarted.

5.10.6 Comparison between laboratory column experiments and field experiment #2

The field oxalic acid injection experiment was undertaken as a means to test the efficacy of oxalic acid for mobilizing As in a field setting. Laboratory column experiments had shown very promising results. Approximately 88% of sediment As had been removed from a sediment column (starting As = 81 mg/kg) when the column was treated with 10 mM oxalic acid (Wovkulich, et al., 2010). A comparison of sediment cores taken before and after the oxalic acid field injection would suggest that 34-48% of the As (30-40 ft bgs) had been released by the oxalic acid injection depending on whether the median or mean values, respectively, were compared; this is somewhat less than anticipated from the laboratory data (the difference is discussed further in the next section). It can be difficult to directly compare field results with laboratory results because it is not possible to control as many variables during field experiments. Influent solutions must be injected to the field study area with dilution factors in mind and a gradient of injection solution concentrations will exist across the study area (in contrast to a single uniform concentration that can be achieved in laboratory experiments). In addition, there is a much larger volume of sediments involved in a field experiment, which increases the potential for heterogeneities in physical properties of sediments, in mineralogy, and in contaminant concentrations. However, comparisons between field and laboratory studies can still provide useful insight.

In the laboratory experiment, 10 mM oxalic acid was introduced to the column for 21 pore volumes followed by several pore volumes of water; much of the As (and Fe and Al) release occurred within the first 10 pore volumes. In the field experiments, oxalic acid was introduced in two phases. Phase I injection took place for ~4 pore volumes in the field; phase II for ~7 pore volumes. In Phase I, influent oxalic acid was ~100 mM and the average concentration at sampling well, CW 1, was ~2 mM; in phase II, influent oxalic acid was ~350 mM and the average concentration at CW 1 was ~8 mM. The goal was to introduce enough oxalic acid at the injection wells such that much of the aquifer between the injection wells and the sampling well would be at least 10 mM. Hydrological modeling (Appendix B) had predicted approximately 14x dilution from injection wells to sampling well while field results suggest ~40x dilution of oxalic acid and Br during Phase I (44x for oxalic acid and 35x for Br). Therefore, the oxalate concentrations at the sampling well were somewhat less than the target values. However, oxalate concentrations early in the flow path (i.e., before substantial transport along the flow path) would have been much higher than those measured at the downgradient sampling well, CW 1.

In laboratory columns using 10 mM oxalic acid treatments, As and Fe concentrations peaked at 100,000 μg/L and Al concentrations peaked at ~150,000 μg/L; one might have expected similar concentrations to be possible at the sampling well, CW 1, during the field experiment. While Fe and Al levels in the field experiment were similar to those seen in the column experiments with field concentrations between 5/11/09 and 6/12/09 (before As concentrations started to decrease in Phase II) averaging

111,000 µg/L for Fe and 62,600 µg/L for Al, the average As value was substantially smaller at 5780 µg/L (~17x lower than the maximum level in the laboratory column). The lower As concentration could be due, in part, to the lower average starting As concentration of the solids in the field experiment than the laboratory experiments (mean value of 40 mg/kg from 27-40 ft bgs vs. 81 mg/kg for laboratory column experiments); iron and Al concentrations in sediments in the field experiment tended to be higher than those used in the laboratory column although standard deviations were much greater for the field sediments (Table 5.3). Additionally, dispersion of oxalic acid into low As zones in the subsurface may help explain the lower groundwater As concentrations in the field. Similarly high Al and Fe groundwater concentrations could be explained by the higher sediment concentrations. Arsenic concentrations would also be impacted by heterogeneities (both in concentration and in physical properties) as well as mixing, dispersion, and specific flow paths, etc., all of which have greater variability in the field experiments and may contribute to lower groundwater As concentrations in the field.

Percent Al and Fe removal were also compared between column and field experiments. Laboratory columns with 10 mM oxalic acid indicated 16% Al removal while XRF data from the field experiments (30-40 ft bgs) suggested that the difference in sediment Al concentrations before and after the oxalic acid treatment was not statistically significant (paired t-test, $p>0.05$). There was considerable variability in Al concentrations. Fe mobilization was similarly low with 9% Fe removal from the laboratory 10 mM oxalic acid columns and 10% (median difference) to 30% (mean difference) Fe removal from sediments based on XRF data from paired cores (30-40 ft bgs) in the field experiments. The difference between sediment Fe concentrations before and after oxalic acid treatment in the field was statistically significant (paired t-test, $p<0.02$).

Table 5.3. Comparison between sediments used in lab and field experiments

	Laboratory Column Sediments[a]			Field Sediments[b]		
	mg/kg			mg/kg		
	Average concentration	Standard deviation	N	Average concentration	Standard deviation	N
As	81	1	5	40	23	51
Fe	1050	180	5	2880	1460	51
Al	1070	110	3	8120	5080	45

[a] Vineland aquifer solids used for column experiments had been obtained in 2006 (Wovkulich, et al., 2010). These values are based on complete digestion of sediments and analysis by ICP MS.

[b] Samples from sediment cores obtained in 2008 with depths of 27-40 ft bgs. These values are based on XRF data using a calibration curve specific to Vineland sands.

5.10.7 Percent As mobilized from aquifer solids

Two methods can be used to quantify the percent As mobilized from the aquifer solids: (1) comparison of concentrations on the solids from cores taken before and after oxalic acid treatment in the zone thought to be impacted and (2) comparison of mass of As removed with mass of As in the oxalic impacted aquifer. Both methods ideally require knowledge of the volume of aquifer impacted by the oxalic acid treatment. Simple hydrological modeling performed in preparation for the field experiment (Appendix B) suggested that the injected materials would be focused as they moved from injection wells to the sampling well and P&T well; a pie-shaped geometry would result. Similar shapes, something of a modified pie, would also be predicted if one used models and methods like those for delineating well head protection areas around a pumping well (Spayd and Johnson, 2003). Based on data from the sediment cores, it appeared that most of the As was mobilized from the 30-40 ft depth range; therefore, the oxalic impacted depth was taken to be 10 ft (3 m). One can estimate the inventory of As in the targeted areas using this impacted depth, the dimensions of the pilot area (12 ft x 42.83 ft or 3.7 m x 13.1 m), and the median starting As concentration on the solids of 35 mg/kg (27-40 ft bgs); the total mass of As in the pie wedge between the injection wells and P&T well, RW 2a, would be 4.4 kg. Therefore, 11% of the As in the aquifer solids of the pilot area would have been mobilized and captured at CW 1 and 53% at RW 2a, for a total of 64% (using the conservative estimate of 2.9 kg total As mobilized and captured). However, because the size and shape of the oxalic acid plume were not experimentally determined, alternate geometries should be considered. Geometries considered were pie-shaped wedges and rectangular sections including aquifer solids between injection wells and the P&T well; calculations using these two shapes should lead to upper and lower bounds for percent mobilization. The results are summarized in Table 5.4 and indicate that between 33% and 64% of the As could have been mobilized from the aquifer solids and captured as a result of the oxalic acid injection (using the conservative estimate of 2.9 kg of As mobilized). If instead we use the estimate for As mobilization at RW 2a that accounts for the declining background concentration at that well (3.1 kg As at RW 2a and total from both wells of 3.6 kg As), the total percent As mobilized would be calculated as 41-80% (Table 5.4).

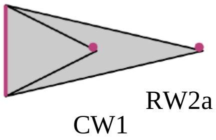
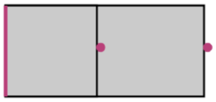
While As mobilization of 33-80% (as noted in Table 5.4) represents quite a large range, the lower value of 33% mobilization is still substantial considering the short time frame of the experiment (3 months). Additionally, 33% mobilization is consistent with comparisons of sediment concentrations on cores taken before and after the oxalic acid treatment (Table 5.2). The XRF data from the 2008 and 2009 Geoprobe cores suggested between 28% (median) - 36% (mean) As removal overall (27-40 ft bgs). However, no significant concentration differences were observed from before to after oxalic acid treatment at the 27-30 ft interval; this would suggest little interaction between sediments and oxalic acid at that depth and would be consistent with hypothesized oxalic acid plume sinkage. Restricting the sediment comparison to the 30 to 40 ft depth range one observes 34% (median) to 48% (mean) reductions in As concentrations (Table 5.2). Core samples deeper than 40 ft (40-50 ft range) in 2009 have an average and median As concentration of 45 mg/kg and 37 mg/kg, respectively (N=45), values which are more similar to the average and median for 2008 samples (40 and 35 mg/kg) than 2009 samples (26 and 25 mg/kg) at 27-40 ft bgs. These data may suggest limited oxalate exposure for sediments deeper than 40 ft. However, no direct comparison can be made to 2008 samples at the same depth range (40-50 ft).

In laboratory miniature column experiments using solids collected from one of the 2008 sediment cores and treated with two phases of oxalic acid with concentrations similar to those seen at CW 1, similar As mobilization was reported, between ~35-45%. Details on how these column experiments were performed are listed in Appendix D (updated from (Doobay, 2010)). Previous laboratory experiments involving larger columns had indicated 88% removal of As when treated with 10 mM oxalic acid (Wovkulich, et al., 2010). One may interpret this difference in percent removal by suggesting that the As in the 2008 sediment core and thus in the pilot area of the site may be more strongly sorbed than the As on aquifer solids in other areas of the site. However, the starting As concentration used in the larger column experiment was significantly higher (81 mg/kg) than sediments used in the miniature column (28 mg/kg). Arsenic removal of 35-45% brought the miniature column sediments down to 16-18 mg/kg; arsenic removal of 88% would decrease the large column sediments to ~10 mg/kg. It is possible that the final 10-20 mg/kg As is difficult to remove from the sediments via oxalic acid treatment. It is clear, however, that the oxalic acid treatment was able to accelerate As release in each case.

To further assess the success of the oxalic acid injection experiment (field experiment #2), one can compare the As removed as a result of the oxalic acid treatment with various estimates of the amount that was removed from the pilot area by the pump and treat system alone. Site managers have indicated that As removal from the site by the pump and treat plant is ~885 kg/yr (Creighton, 2007). The full site has an area of ~0.22 km^2 (EPA, 2006) while the pilot experiment took place in an area of ~50 m^2 (rectangular section between injection wells and pump and treat well, RW 2a); the pilot area is therefore 0.02% of the full site. If As removal is assumed to occur evenly across the site, then one would expect removal of approximately 0.2 kg As/yr or 0.05 kg over a three-month period from the pilot area; the amount would be less if we consider the pie-shaped geometry. Since the oxalic acid injection experiment (field experiment #2) induced mobilization of ~3 kg (conservatively) from the pilot area with just three months of oxalic acid injection, the treatment represents a clear improvement in terms of As removal as compared to pump and treat alone.

One can also approach this evaluation in another way. We can consider a simple circular capture zone area for pump and treat well RW 2a with a radius of ~40 ft, equivalent to the length of the pilot area; within this circular capture zone the pilot area with pie-shaped geometry makes up 4.5% of the RW 2a capture zone. This scenario dramatically underestimates the size of the RW 2a capture zone from which As is being mobilized based on the high As concentrations measured pre-experiment at the injection wells and thus overestimates the fraction made up by the pilot area. Based on the pump rate at the recovery well RW 2a during the oxalic acid injection experiment (field experiment #2), the average As concentration at that well prior to treatment, and the fraction of the circular RW 2a capture zone represented by the pilot area, one would calculate As removal of ~0.8 kg As per three-month period from the pilot study area. The expected removal is much larger than calculated above, presumably both because As removal does not occur evenly across the site and we have overestimated the fraction of the RW 2a capture zone represented by the pilot area. If we doubled the radius of the circular RW 2a capture zone to ~80 ft, which is still probably a significant underestimation, then the pilot area would make up an even smaller fraction of the RW2a capture zone and the amount of As mobilized from just the pilot area in 3 months without oxalic acid would be 0.2 kg. In the oxalic acid injection experiment (field experiment #2), approximately 3 kg As (conservatively) was removed during the three-month experiment, again indicating that oxalic acid can substantially improve As removal compared with pump and treat alone.

Table 5.4. Percent As mobilized during the oxalic acid injection experiment (field experiment #2) based on various geometries

		Conservative estimate for As mobilized			Estimate accounting for declining background at RW 2a		
		Mass As Captured (kg)			Mass As Captured (kg)		
		CW 1	RW 2a	Total	CW 1	RW 2a	Total
		0.5	2.4	**2.9**	0.5	3.1	**3.6**
Geometry[a]		Percent As Captured (%)[b]			Percent As Captured (%)[b]		
Visual	Description[c]	CW1	RW 2a	Total	CW1	RW 2a	Total
	Pie-shaped wedge	11%	53%	**64%**	11%	69%	**80%**
	Rectangle	6%	27%	**33%**	6%	35%	**41%**

[a] Assumed 10 ft (3 m) depth section
[b] Starting concentration on soils taken as 35 mg/kg based on the median As value from 2008 sediment cores (27-40 ft bgs).
[c] Both geometries include the area between injection wells and P&T well, RW 2a.

5.10.8 Consideration of alternate flow regimes

Even though the subsurface sediments at this site appear to consist of fairly homogeneous medium sands it is important to consider unexpected flow paths due to local heterogeneities in physical and chemical properties of the solids; there may be plume sinkage, preferential flow paths, or other complicated flow regimes that do not conform to our simple geometries above.

Since a coarser layer at 36-38 ft bgs (11.0-11.6 m) was discovered during installation of the sampling well and another coarse section at 38-39 ft bgs (11.6-11.9 m) midway between injection and sampling wells, samples were taken to evaluate the possibility for preferential flow through these more permeable regions. In the 2008 tracer experiment (field experiment #1), SF_6 and Br were introduced to the pilot area in a short pulse, and samples were collected at the sampling well to evaluate transport time and dilution factors. Concentrations of Br from samples within the coarser layer averaged at least 7 times lower than samples excluding the coarser layer, suggesting limited transport of injected materials through the coarser layer during the tracer experiment (field experiment #1). However, samples obtained from the coarser layer during the 2009 injection experiment indicated that there was transport of injected materials through this layer. Samples were collected in the coarse layer starting 6/3/09 (during a plant shutdown) through the end of sampling on 9/9/09. Arsenic concentrations were low in the coarse layer (<100 μg/L) while the plant was shutdown; however, a large pulse of As was seen in the coarse layer when the P&T wells were turned back on (maximum of 8460 μg/L on 6/6/09). This could indicate groundwater solutions being pulled downward through the coarse layer by the influence of the P&T well. Additionally, there is evidence for elevated oxalate and Br in the coarse layer; average concentrations were 11 mM and 4 mg/L, respectively, between 6/10/09 and 7/1/09. Since these concentrations are similar to those seen in samples that excluded the coarser layer (average of 8 mM oxalate and 3 mg/L Br for the same time frame), it is clear that injected solutions did travel through that coarser layer and this contradicts the information gained in the 2008 tracer experiment (field experiment #1).

A few explanations are possible for this apparent discrepancy between 2008 tracer data and 2009 injection experiment data. First, one might consider plume sinkage; the coarser layer is deeper than the injection points: coarser layers at 36-38 ft (11.0-11.6 m) bgs and 38-39 ft (11.6-11.9 m) bgs and the injection wells are screened at 27-32 ft (8.2-9.8 m) bgs. The density of the oxalic acid injection solution is greater than that of the background water; the Phase II injection influent was 1.57% more dense than background water (determined experimentally). Assuming a porosity of 0.3, a vertical hydraulic conductivity of 1.1 x 10^{-4} m/s, a groundwater transit time from injection wells to CW 1 of ~8 days, and an average dilution of the injected fluid in the aquifer by a factor of >10, the vertical displacement would be <1.3 ft (0.4 m), less than the necessary 4 ft (1.2 m) vertical change from injection wells to sampling well (Holzbecher, 1998). If a dilution factor of 35 is used instead, which is more realistic to the field data collected, the vertical displacement is only 0.4 ft (0.12 m). To investigate the sensitivity of this calculation to various parameters (porosity, hydraulic conductivity, groundwater transit time, etc.), each parameter was altered in turn to obtain the vertical change of 4 ft. Base values were as follows: porosity of 0.3, groundwater transit time of 8 days (derived from field data), dilution factor of 35 (derived from field data), and vertical hydraulic conductivity of 1.1 x 10^{-4} m/s. To achieve the 4 ft vertical shift, porosity would need to be decreased to 0.027 (~10x decrease), groundwater transit would need to be increased to 85 days (~10x increase), the dilution factor would need to be decreased to 3.3 (~10x decrease), or the vertical hydraulic conductivity would need to be increased by ~10x. None of these changes would be physically reasonable based on the field conditions and collected data. The hydraulic conductivity values used in these calculations were based on values used in the USACE FEMWATER groundwater model, which in turn were based on available hydrologic data (Skelley and Loy, 2003). Horizontal hydraulic conductivities in the model regions nearest the pilot area had values of 1.06 x 10^{-3} to 1.59 x 10^{-3} m/s. Vertical hydraulic conductivities were assumed to be 10x lower than horizontal, which is a standard assumption. From the available hydrologic data, hydraulic conductivity values ~5x higher are possible on site; however, these high hydraulic conductivity areas are to the far northwest and one point east of the pilot area. It, therefore, seems unlikely that density induced sinking can fully explain the difference between the 2008 and 2009 data.

Possibly more important to the discrepancy between 2008 and 2009 data are differences in the duration and set up of the experiments. In the 2008 tracer experiment (field experiment #1), the tracers were introduced in a short (~3 h) pulse with sampling for ~9 days, while in the 2009 experiment the injection of oxalic acid and bromide influents and sampling took place over 3 months. It is possible, therefore, that the tracer experiment (field experiment #1) was not long enough to see significant transport of injected materials into the coarse layer. The probability for alternate flow paths to become available increases with increasing experiment time. For instance, there may have been a barrier to vertical flow down to the coarse layer during the tracer experiment (field experiment #1) such as particle size (perhaps a narrow silt layer above sections of the coarse layer). Nine days in the tracer experiment (field experiment #1) was simply not sufficient for a substantial mass of injectant to disperse to a flow path around such a barrier. Additionally, because vertical hydraulic conductivity tends to be lower than horizontal (usually by a factor of 10 or more), increased experiment time could be required to see substantial vertical transport. Furthermore, injection rates were greater in 2009, but pumping rates at the sampling well, CW 1, were lower, and the 2009 experiment was continued later into the summer season when heads may decline naturally; all of these could contribute to the differences. It is clear, however, that injected materials did make it into the coarse layer during the oxalic acid injection experiment (field experiment #2), and this flow path was unanticipated prior to the oxalic acid injection experiment.

Sediment cores obtained at the end of the oxalic acid injection experiment (field experiment #2) allude to another unanticipated flow regime and suggest that the oxalic acid solutions may have been traveling along preferential flow paths. Some cores show evidence for substantial oxalic acid leaching in small sections. In the most visually pronounced case, a sediment core appears “bleached” at 34 ft (10 m) bgs and has correspondingly low As concentrations, 2-7 mg/kg while the mean and median values for that core are 21 and 25 mg/kg, respectively (Figure 5.9).

Even though the pilot area of this site had appeared to be a rather homogeneous sandy system with a clear gradient enforced by the P&T well, transport of oxalic acid through the subsurface was probably at least partly controlled by preferential flow paths as evidenced by the As concentration distribution in cores obtained at the end of the oxalic acid injection experiment (field experiment #2). The lack of a uniform concentration front could have limited the mobilization potential in this pilot experiment. In this experiment, injection was accomplished with three injection depths over a 5 ft depth interval with injection well nests placed 3 ft apart. Perhaps a different injection configuration could have helped overcome this issue of preferential flow paths; alternate injection schemes could include closer spacing of the injection well nests or a trench approach. Circular pumping methods, in which liquids could be pumped from the sampling well and re-injected to the injection wells, could also be employed to ensure better mixing in the subsurface and could decrease the overall mass of oxalic acid injected.

For future oxalic acid injection studies, it will be important to better define the size, shape and extent of the oxalic acid plume. To that end, geophysical resistivity surveys should be conducted on the field site both before and during oxalic acid injection. Several transects through the pilot area, parallel and perpendicular to flow directions, should be done to examine resistivity in the subsurface and develop a 3D image of the oxalic acid plume; the oxalic acid plume would appear as an area of low resistivity or high conductivity. Some geophysical measurements were made during the oxalic acid injection described above (data not shown) which serve as proof of concept; there are clear differences in resistivity in the subsurface due to presence of oxalate. However, no pre-injection surveys had been conducted and the data were not sufficient to adequately describe the plume. Being able to visualize the plume in the subsurface would allow for more accurate estimates of percent As mobilized.

For large-scale use on a Superfund site, it is imperative to maximize the oxalic acid concentration to the desired areas while minimizing wasted oxalic acid. Therefore, chemical additions may be well suited to targeting small areas of the site where As concentrations are known to be high. This must be carefully planned, as it is necessary to ensure capture of oxalic acid and mobilized As by a P&T extraction well. In addition, it is necessary to maintain a low pH and sufficiently high oxalate concentration so as to minimize risk of Fe or As re-precipitation.

5.11 Conclusions

Oxalic acid solutions were injected into a small section (~50 m^2) of an As contaminated site over the course of 3-months to evaluate its potential for As release in a field setting. Complete capture of the Br tracer was likely between the combination of the sampling well and the pump and treat recovery well. However, only ~60% of the oxalic acid was recovered indicating that some of the oxalic acid may have been adsorbed to sediments and degraded by microbes in the subsurface. The oxalic acid treatment resulted in 1) increased As mobilization at the sampling well during treatment with both concentrations of oxalic acid (~100 mM and ~350 mM), 2) increased As mobilization at the pump and treat well during treatment with the higher concentration of oxalic acid, 3) a decrease in As concentration at the sampling well following treatment, and 4) a conservative estimate of approximately 3 kg of As (33-64% of As inventory in the pilot area) removed from the system. It was difficult to determine the shape and extent of the oxalic acid impacted portion of the aquifer, therefore, future studies should make use of geophysical measurements to help define the oxalic plume. While further study is certainly necessary, oxalic acid application shows promise for As release and therefore, potential for improving the efficiency of pump and treat remediation of As contaminated aquifers.

5.12 References

Ahmann, D., Krumholz, L.R., Hemond, H.F., Lovley, D.R., Morel, F.M.M., 1997. Microbial mobilization of arsenic from sediments of the Aberjona Watershed. Environ. Sci. Technol. 31, 2923-2930.

Anawar, H.M., Akai, J., Sakugawa, H., 2004. Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. Chemosphere. 54, 753-762.

ATSDR, 2007. Toxicological profile for arsenic. US Department of Health and Human Services.

Baghel, A., Singh, B., Pandey, P., Sekhar, K., 2007. A rapid field detection method for arsenic in drinking water. Anal. Sci. 23, 135-137.

Creighton, S., 2007. Personal communication.

Darland, J.E., Inskeep, W.P., 1997. Effects of pH and phosphate competition on the transport of arsenate. J. Environ. Qual. 26, 1133-1139.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environ. Sci. Technol. 37, 4182-4189.

Doobay, K. (2010), The use of oxalic acid to mobilize arsenic from contaminated aquifer solids from Vineland, NJ, Barnard College, New York.

EPA, 1989. Vineland Chemical Company site final draft, . Feasibility study report, River areas, Vineland NJ.

EPA, 1996. Pump-and-Treat Ground-Water Remediation: A Guide for Decision Makers and Practitioners. Office of Research and Development, EPA/625/R-95/005.

EPA, 2001a. Groundwater pump and treat systems: summary of selected cost and performance information at Superfund-financed sites. (EPA 542-R-01-021a).

EPA, 2001b. Technical fact sheet: Final rule for arsenic in drinking water. EPA 815-F-00-016.

EPA, 2002. Arsenic treatment technologies for soil, waste, and water. http://www.clu-in.org/download/remed/542r02004/arsenic_report.pdf.

EPA, 2006. Vineland Chemical Co., Inc National Priority List site fact sheet. http://www.epa.gov/Region2/superfund/npl/0200209c.pdf.

EPA, 2007. EPA Basic query for National Priorities List, Superfund, US EPA.

EPA, 2011. EPA basic query - Annual status report remediation database (data through Oct 2006), http://cfpub.epa.gov/asr/search.cfm.

Fleisher, M.Q., Anderson, R. (1991), Particulate matter digestion (from mg to 10's of g) and radionuclide blanks, paper presented at Marine Particle Analysis and Characterization; American Geophysical Union, Washington, DC.

Fox, T.R., Comerford, N.B., 1990. Low-molecular-weight organic-acids in selected forest soils of the southeastern USA. Soil Sci. Soc. Am. J. 54, 1139-1144.

Holzbecher, E.O., 1998. Modeling density-driven flow in porous media: principles, numberics, software, Springer, New York.

Hongshao, Z., Stanforth, R., 2001. Competitve adsorption of phosphate and arsenate on goethite. Environ. Sci. Technol. 35, 4753-4757.

Jain, A., Loeppert, R.H., 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J. Environ. Qual. 29, 1422-1430.

Jeong, Y.R., Fan, M.H., Van Leeuwen, J., Belczyk, J.F., 2007. Effect of competing solutes on arsenic(V) adsorption using iron and aluminum oxides. J. Environ. Sci. China. 19, 910-919.

Jia, Y.F., Xu, L.Y., Fang, Z., Demopoulos, G.P., 2006. Observation of surface precipitation of arsenate on ferrihydrite. Environ. Sci. Technol. 40, 3248-3253.

Jones, D.L., 1998. Organic acids in the rhizosphere - a cricial review. Plant Soil. 205, 25-44.

Keimowitz, A.R., Zheng, Y., Chillrud, S.N., Mailloux, B., Jung, H.B., Stute, M., Simpson, H.J., 2005. Arsenic redistribution between sediments and water near a highly contaminated source. Environ. Sci. Technol. 39, 8606-8613.

Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. Environ. Sci. Technol. 35, 2778-2784.

Klarup, D.G., 1997. The influence of oxalic acid on release rates of metals from contaminated river sediment. Sci. Total Environ. 204, 223-231.

Lee, S.O., Tran, T., Jung, B.H., Kim, S.J., Kim, M.J., 2007. Dissolution of iron oxide using oxalic acid. Hydrometallurgy. 87, 91-99.

Luo, L., Zhang, S., Shan, X.-Q., Zhu, Y.-G., 2006. Effects of oxalate and humic acid on arsenate sorption by and desorption from a Chinese red soil. Water, Air, Soil Pollut. 176, 269-283.

Mackay, D.M., Cherry, J.A., 1989. Groundwater contamination: Pump-and-treat remediation. Environ. Sci. Technol. 23, 630-637.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta. 58, 201-235.

Mohapatra, D., Singh, P., Zhang, W., Pullammanappallil, P., 2005. The effect of citrate, oxalate, acetate, silicate, and phosphate on stability of synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite. J. Hazard. Mater. B124, 95-100.

NJDHSS, 2010. NJ Department of Health and Senior Services. Right to Know, Hazardous Substance Fact Sheet, Oxalic Acid.

NOAA, 2011. Annual Climatological Summary, Millville Municipal Airport Station, NJ. National Climatic Center Database search, http://cdo.ncdc.noaa.gov/ancsum/ACS.

Palmer, C.D., Fish, W., 1992. Chemical enhancements to pump-and-treat remediation. EPA Ground Water Issue. http://www.epa.gov/ada/download/issue/chemen.pdf.

Panias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A., 1996. Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. Hydrometallurgy. 42, 257-265.

Sahin, N., 2003. Oxalotrophic Bacteria. Res. Microbiol. 154, 399-407.

Shi, R., Jia, Y.F., Wang, C., Shuhua, Y., 2009. Mechanism of arsenate mobilization from goethite by aliphatic carboxylic acid. J. Hazard. Mater. 163, 1129-1133.

Skelley and Loy 2003, Draft report of hydrogeologic investigations/capture zone analysis, The Vineland Chemical Superfund site, Vineland, NJ.

Slowey, A.J., Johnson, S.B., Newville, M., Brown Jr., G.E., 2007. Speciation and colloid transport of arsenic from mine tailings. Appl. Geochem. 22, 1884-1898.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517-568.

Spayd, S.E., Johnson, S.W., 2003. Guidelines for dilineation of well head protection areas in New Jersey. New Jersey Geological Survey, Open File Report OFR 03-1.

Strobel, B.W., 2001. Influence of vegetation on low-molecular-weight carboxylic acids in soil solution - a review. Geoderma. 99, 169-198.

Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C.F., 2004. Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data, and mineralogical characterization. Geochim. Cosmochim. Acta. 68, 4539-4557.

Tao, Y.Q., Zhang, S.Z., Jian, W., Yuan, C.G., Shan, X.Q., 2006. Effects of oxalate and phosphate on the release of arsenic from contaminated soils and arsenic accumulation in wheat. Chemosphere. 65, 1281-1287.

van Hees, P.A.W., Lundstrom, U.S., Giesler, R., 2000. Low molecular weight organic acids and their Al-complexes in soil solution - composition, distribution and seasonal variation in three podzolized soils. Geoderma. 94, 173-200.

Voudrias, E.A., 2001. Pump-and-treat remediation of groundwater contaminated by hazardous waste: Can it really be achieved? Global Nest Int J. 3, 1-10.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta. 436, 309-323.

Wovkulich, K., Mailloux, B.J., Lacko, A., Keimowitz, A.R., Stute, M., Simpson, H.J., Chillrud, S.N., 2010. Chemical Treatments for Mobilizing Arsenic from Contaminated Aquifer Solids to Accelerate Remediation. Appl. Geochem. 25, 1500-1509.

Wovkulich, K., Stute, M., Protus, T.J., Sr., Mailloux, B.J., Chillrud, S.N., 2011. Injection System for a Multiwell Injection Using a Single Pump. Ground Water Monit. Rem. 31, 79-85.

Zhang, S.Z., Li, W., Shan, X.Q., Lu, A.X., Zhou, P.J., 2005. Effects of low molecular weight organic anions on the release of arsenite and arsenate from a contaminated soil. Water Air Soil Pollut. 167, 111-122.

5.13 Figures

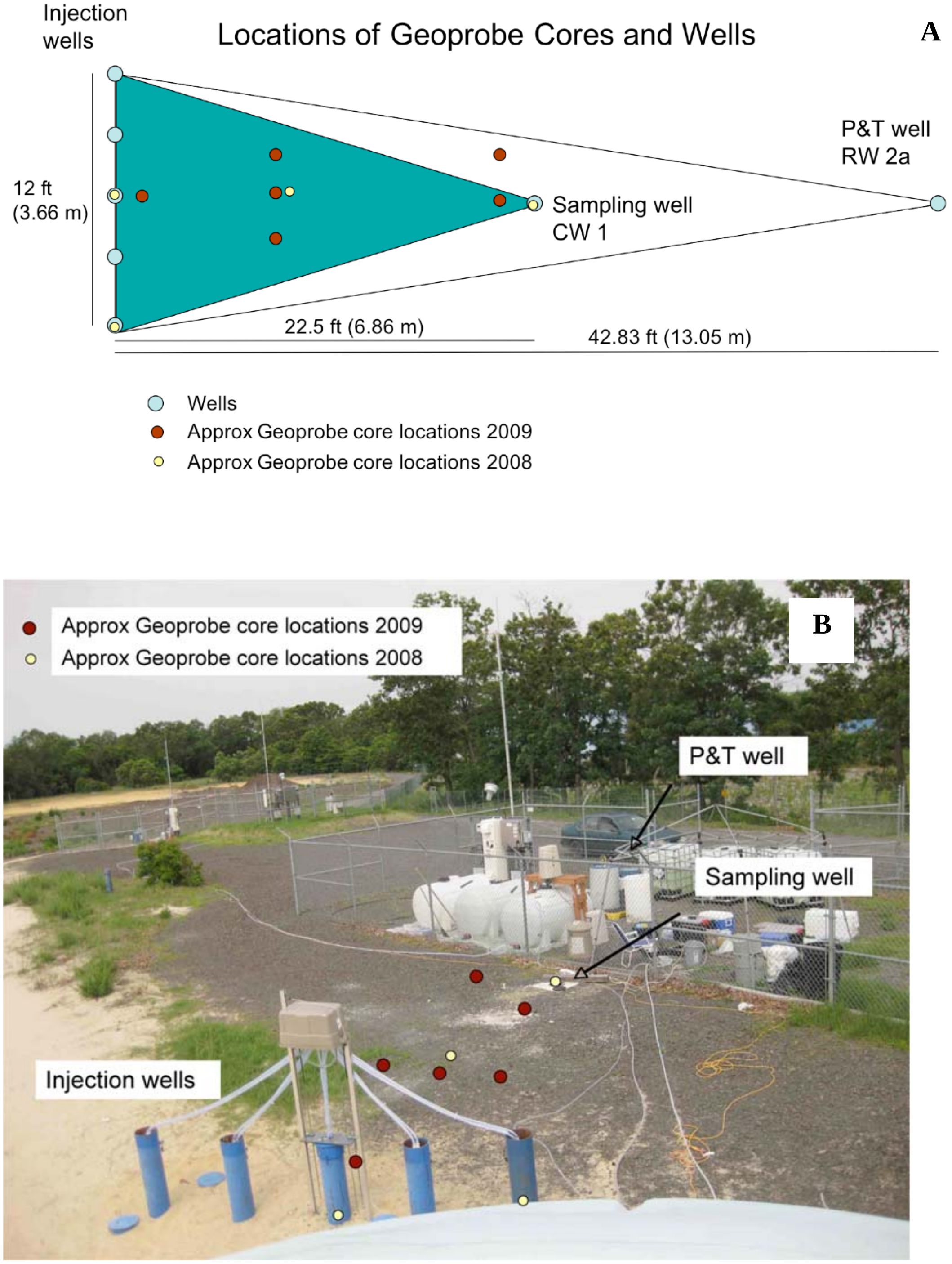
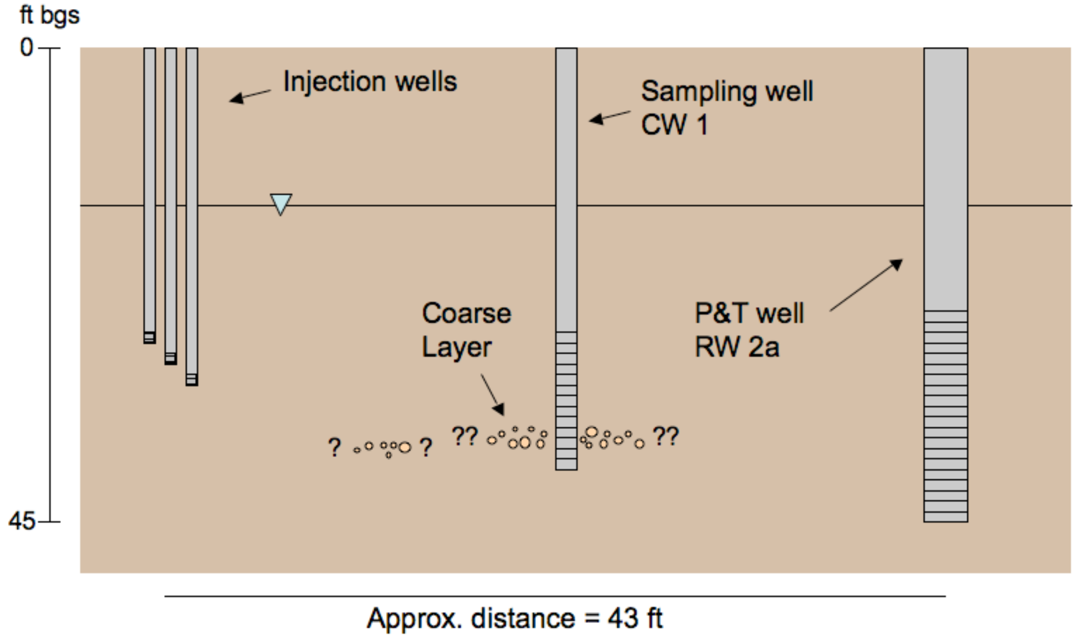


Figure 5.1. Schematic and photograph showing the pilot study area with wells and approximate Geoprobe core locations. The injection wells and sampling well were installed in 2008. (A) The schematic shows a map view of the distances between wells and approximate Geoprobe locations for 2008 and 2009. (B) Geoprobe locations have been overlain on a photograph of the pilot study area with injection, sampling, and P&T wells.

A



B

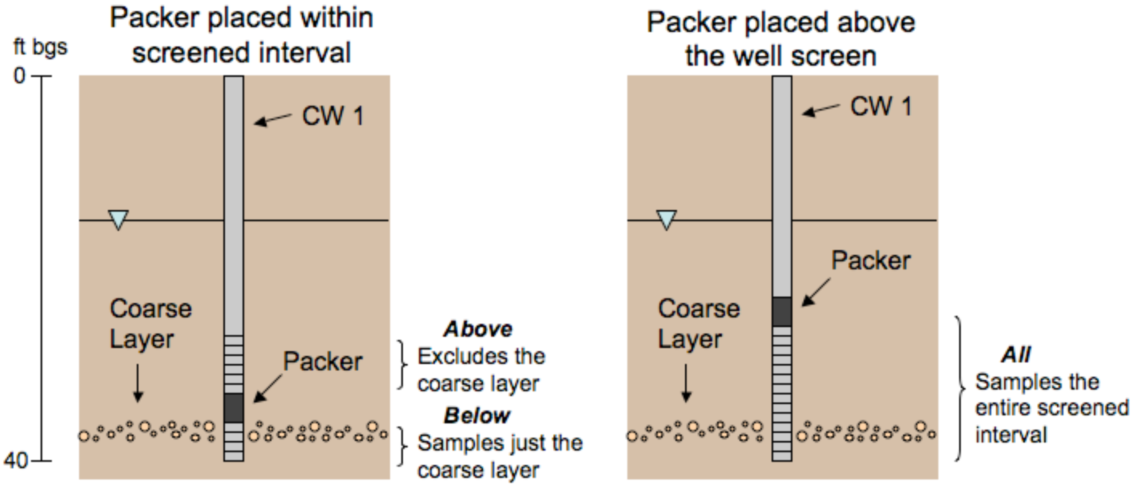


Figure 5.2. Schematics showing cross-sections in the pilot area. (A) This cross-section includes one of the injection well nests and the both the sampling well and pump and treat well. Screened intervals are shown for each well. A coarse section was discovered at ~36-38 ft bgs while installing CW 1. A coarse section was also found at ~38-39 ft bgs in a core taken midway between injection wells and the sampling well. (B) Different packer positions were used when obtaining samples from the sampling well, CW 1. With the packer placed within the screened interval, samples were taken above the packer,

excluding the coarse layer, and below the packer, sampling the coarse layer. With the packer placed above the well screen, samples included the entire screened interval.

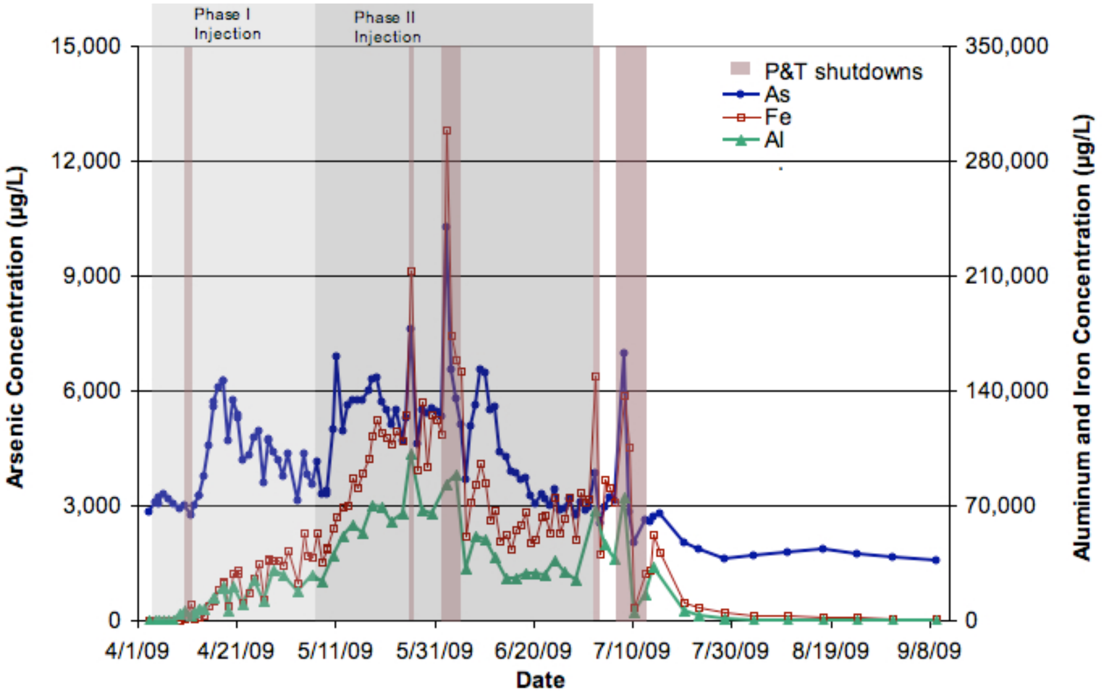


Figure 5.3. Concentrations of Al, Fe, and As over the course of the oxalic acid injection experiment at the sampling well, CW 1, above the packer (and therefore excluding the coarser layer). The target concentrations for oxalic acid influent were 100 mM in Phase I and 400 mM in Phase II.

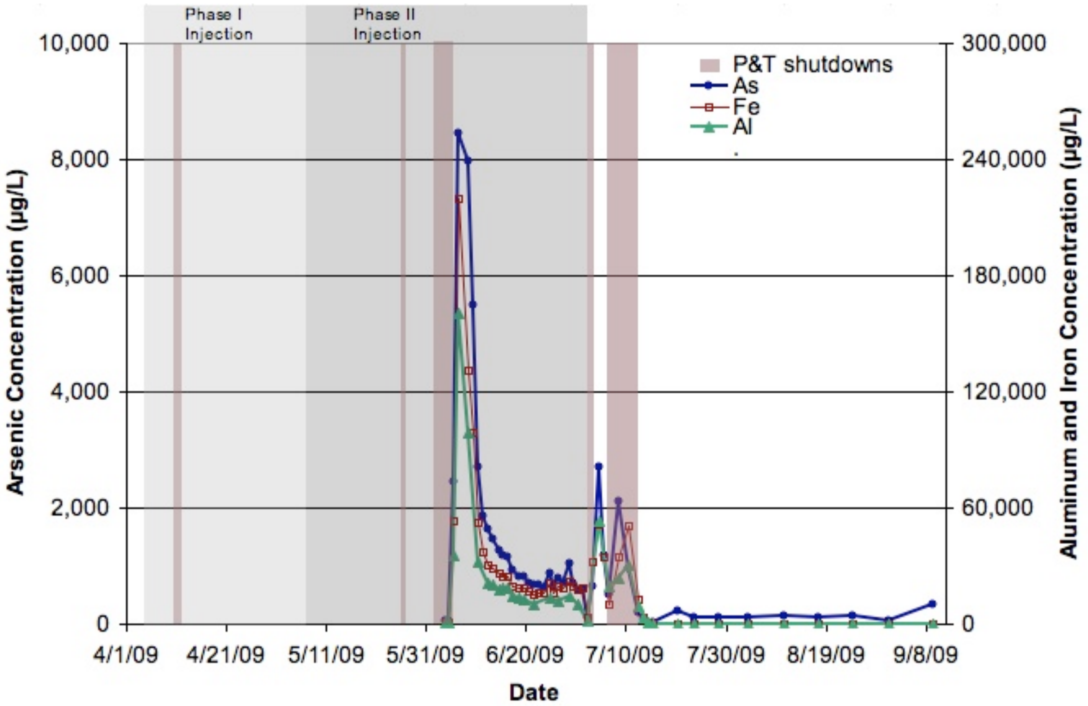


Figure 5.4. Concentrations of Al, Fe, and As over the course of the oxalic acid injection experiment at the sampling well, CW 1, below the packer (and therefore sampling the coarser layer). No samples were collected below the packer prior to 6/3/09. The target concentrations for oxalic acid influent were 100 mM in Phase I and 400 mM in Phase II.

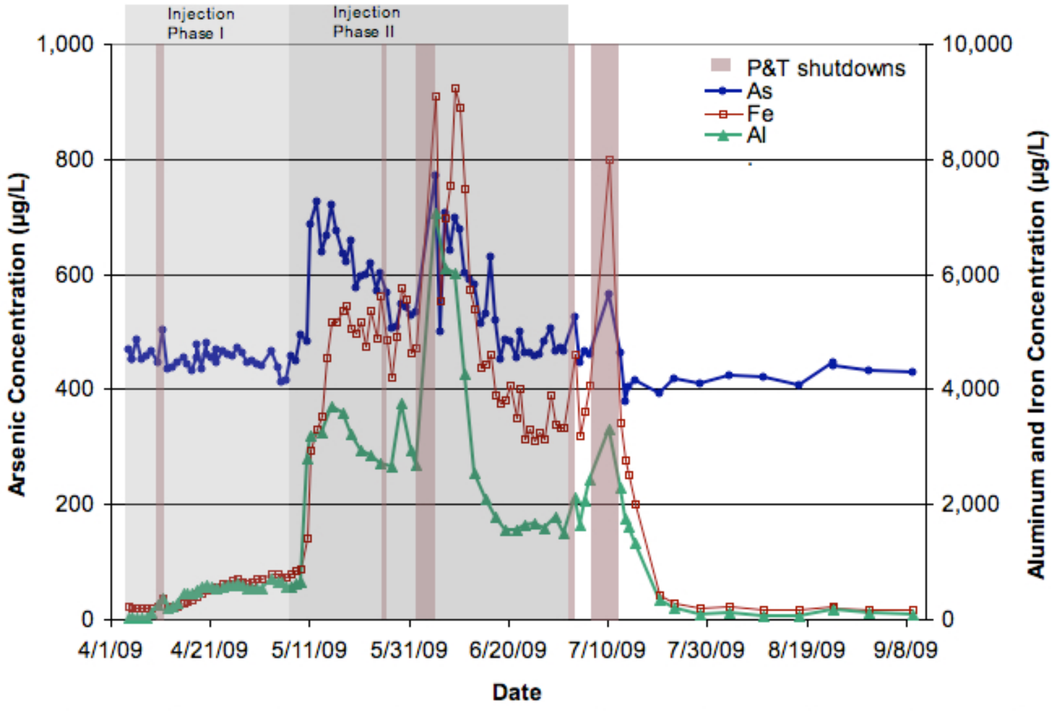


Figure 5.5. Concentrations of Al, Fe, and As at the pump and treat recovery well, RW 2a, over the course of the oxalic acid injection experiment. The target concentrations for oxalic acid influent were 100 mM in Phase I and 400 mM in Phase II.

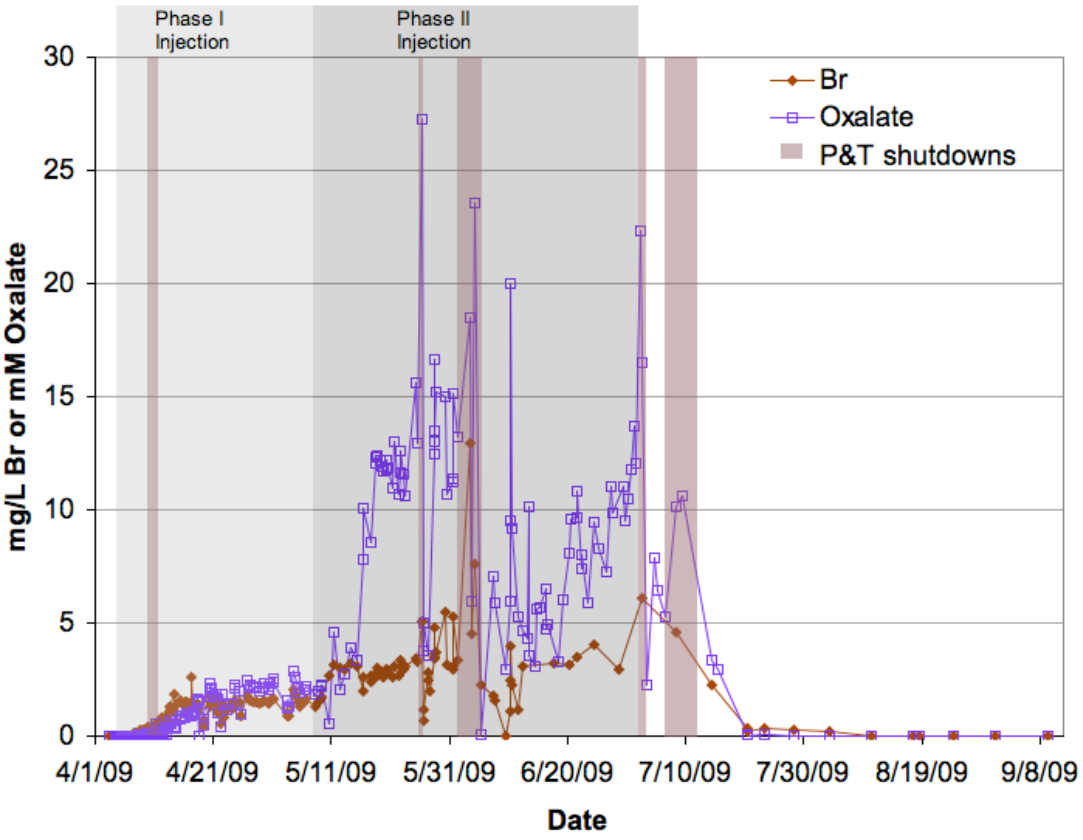


Figure 5.6. Concentrations of Br and oxalate over the course of the oxalic acid injection experiment at the sampling well, CW 1, above the packer (and therefore excluding the coarser layer). The target concentrations for oxalic acid influent were 100 mM in Phase I and 400 mM in Phase II. Actual average influent concentrations were 93 ± 11 mM during Phase I and 351 ± 30 mM during Phase II.

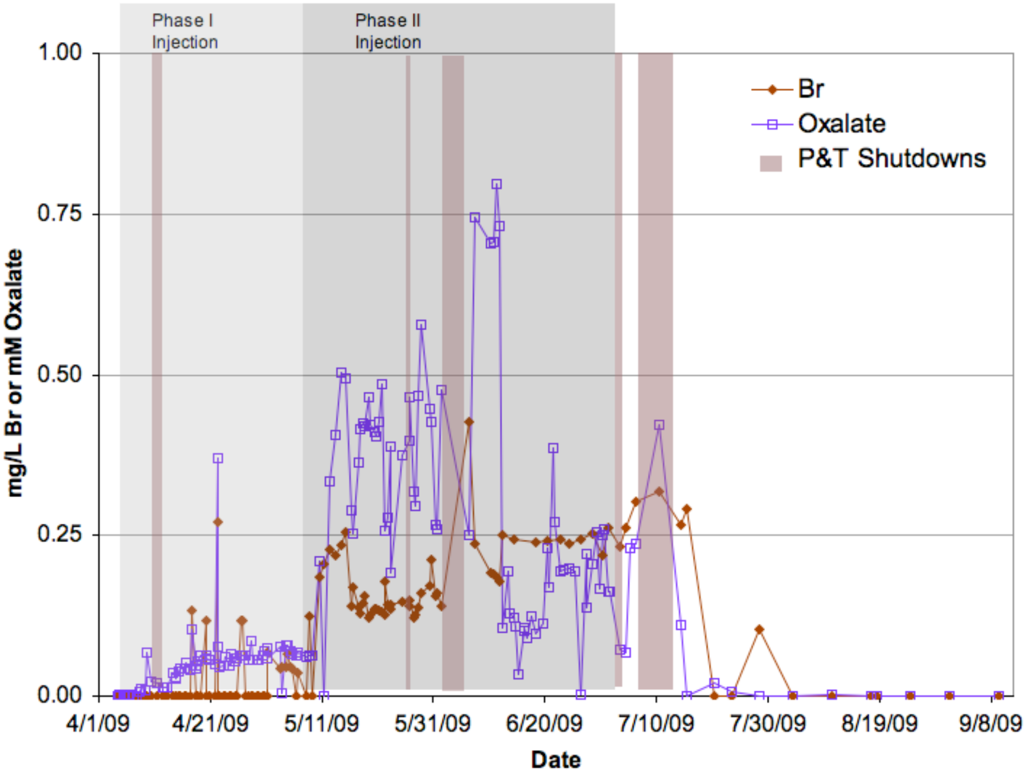
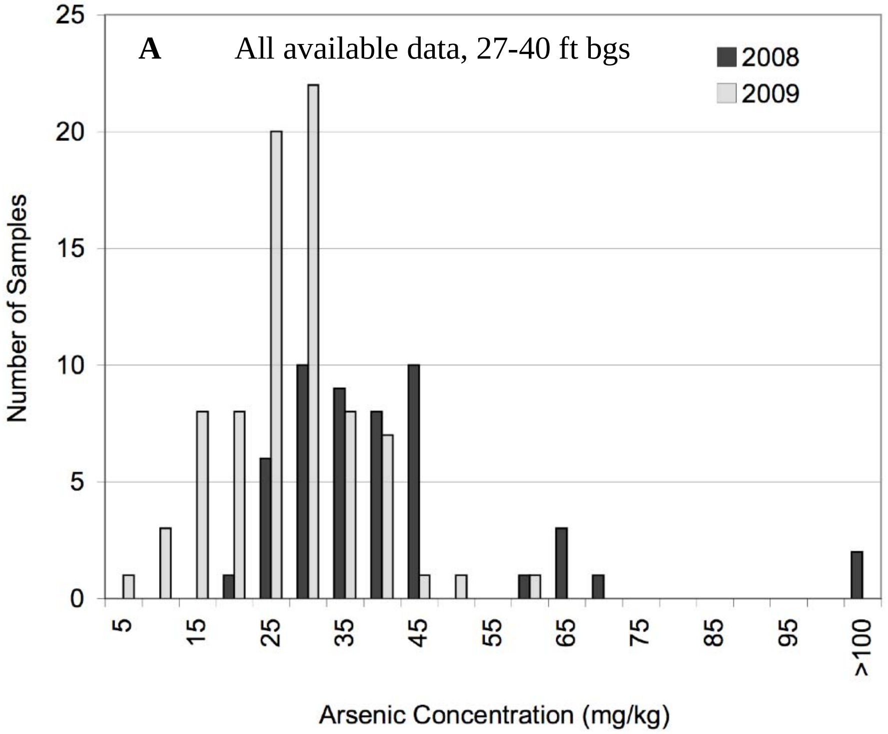


Figure 5.7. Concentrations of Br and oxalic acid at the pump and treat recovery well, RW 2a, over the course of the oxalic acid injection experiment. The target concentrations for oxalic acid influent were 100 mM in Phase I and 400 mM in Phase II. Actual average influent concentrations were 93 ± 11 mM during Phase I and 351 ± 30 mM during Phase II.


A
All available data, 27-40 ft bgs
2008
2009
Number of Samples
0
5
10
15
20
25
5
15
25
35
45
55
65
75
85
95
>100
Arsenic Concentration (mg/kg)

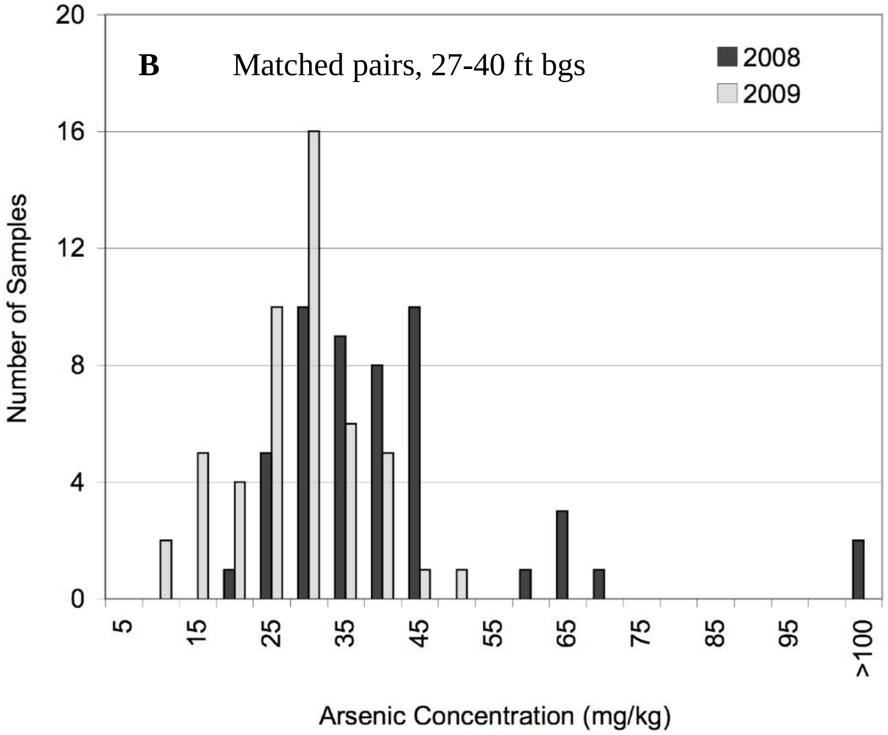

B
Matched pairs, 27-40 ft bgs
2008
2009
Number of Samples
0
4
8
12
16
20
5
15
25
35
45
55
65
75
85
95
>100
Arsenic Concentration (mg/kg)

Figure 5.8. Histograms showing As concentrations on sediments in the pilot area in 2008 (before oxalic acid treatment) and 2009 (after oxalic acid treatment) in the depth range 27-40 ft bgs. (A) All available data between depths 27-40 ft bgs in the pilot area are included. (B) Only data with matched depth/location pairs for 2008-2009 are included. The x-axis displays the bins for each concentration; the bin marked 5 includes all values greater than 0 and up to 5, the bin marked 15 includes values greater than 10 and up to 15.

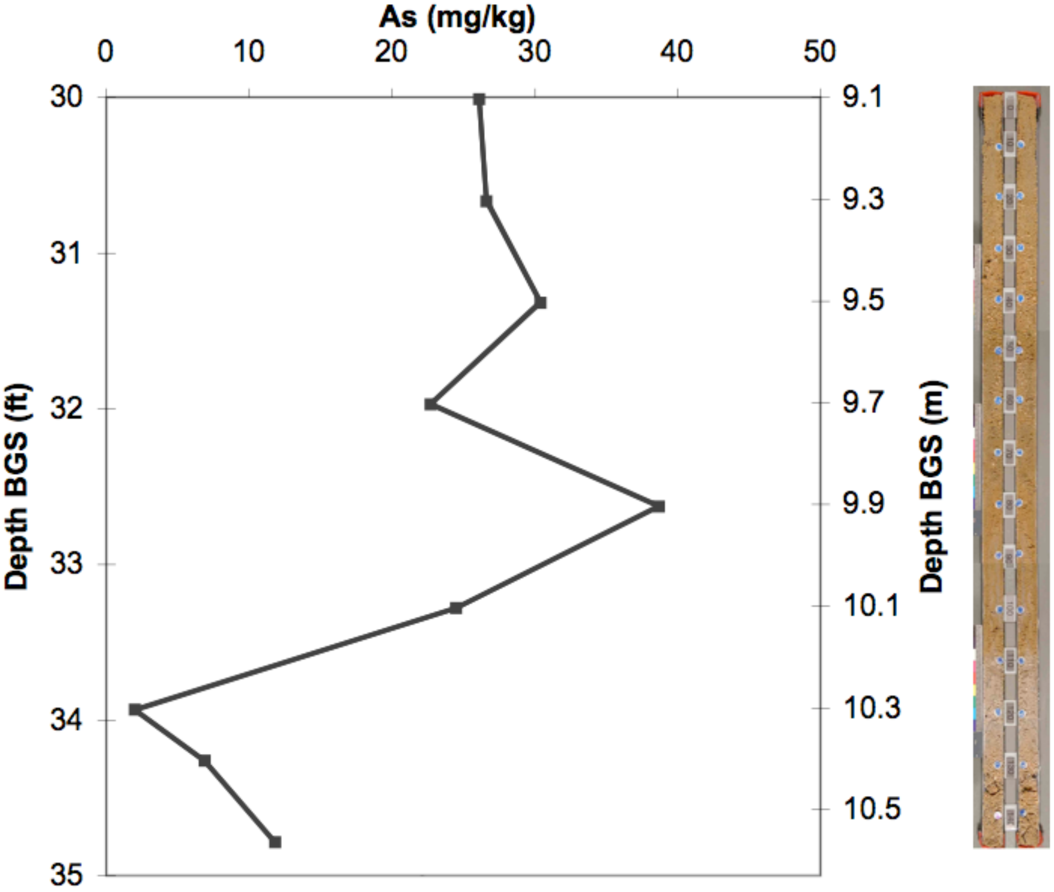


Figure 5.9. Arsenic concentration as a function of depth for one of the soil cores collected at the end of the oxalic acid injection experiment. Of the points sampled, maximum As concentration is 39 mg/kg. The minimum As concentration is 2 mg/kg; the minimum corresponds to the section of the column which appears “bleached” around 34 ft (10.3 m).

5.14 Appendix A – SF_6 measurements

5.14.1 Methods

Tracer experiment (field experiment #1), June 24 – July 2, 2008

The forced gradient tracer experiment (field experiment #1) involved injection of inert tracers to confirm that significant amounts of the injected material were captured in the sampling well and to help calibrate the hydrological models. The inert chemicals used in the tracer experiment (field experiment #1) included sodium bromide (NaBr) and sulfur hexafluoride (SF_6). The tracers were added in line to groundwater from a nearby pump and treat recovery well (RW 2a, ~1000 μg/L As) and injected over the course of 3 hours. Tracer was pumped to each of the 15 injection wells at 10 L/min for 12 min for a total of ~1800 L; concentrations of tracers injected into the wells were approximately 123 mg/L bromide and 3.4×10^{-10} ccSTP SF_6/cc. A piston pump (Series I pump, SSI Lab Alliance, College Park, PA) was used to add tracer spiked water to the stream of RW 2a water. The sampling well (CW 1) and pump and treat well (RW 2a) were monitored over the course of ~9 days for tracer breakthrough. Samples at the sampling well (CW 1) were taken from the entire screened well interval and above and below an inflatable packer (labeled all, above, and below, respectively, Figure 5.2b). When the packer was in place in the well, sampling below it would exclusively sample the coarse layer while sampling above it would exclude groundwaters flowing through the coarse layer. During tracer experiment (field experiment #1), water was continuously extracted at the sampling well at an average of 4.8 L/min using a 12 V plastic pump (Groundwater Essentials, Florida); a total volume of ~60,000 L were extracted. Through most of the experiment, water was pumped from the entire well, with periodic sampling from above and below the packer when the packer was placed within the well screen.

SF_6 injection prior to oxalic acid injection (field experiment #2), April 3, 2009

A higher concentration of SF_6 was used than the previous year to ensure significant SF_6 signal at the pump and treat well (RW 2a) even with the extensive dilution from injection wells to pump and treat recovery well. This tracer test did not involve use of Br, as Br was to be injected with the oxalic acid. The SF_6 tracer was added in-line to groundwater from a nearby pump and treat recovery well (RW 2a, ~450 μg/L As) and injected over the course of 4.4 hours at an average rate of 6.8 L/min; concentration of SF_6 tracer injected into the wells was approximately 5.6×10^{-8} ccSTP SF_6/cc. Each of the 15 injection wells received ~120 L of the tracer spiked solution for a total of ~1800 L injected. A piston pump (Series I pump, SSI Lab Alliance, College Park, PA) was used to add concentrated tracers to the stream of RW 2a water that was ultimately injected at the injection wells.

A packer was placed within the well screen for the duration of the experiment. Water was continuously extracted from above the packer at the sampling well while the oxalic and bromide influent solutions were being injected and for 13 days afterward; extraction was accomplished using a Typhoon pump and low flow controller (Groundwater Essentials) and the extraction rate was kept as close to 2.5 L/min as possible. Water samples were obtained for SF_6 analysis between 4/4/09 and 6/15/09 from CW 1 (the sampling well) excluding the coarse layer and from the nearby pump and treat recovery well, RW 2a. Samples could not be obtained from the coarse layer at CW 1 during this experiment because a peristaltic pump was being used for those samples, which can lead to degassing of dissolved SF_6.

Collection of SF_6 samples

SF_6 samples were collected from the sampling well, CW 1, and the pump and treat well, RW 2a, into glass bottles in such a way as to minimize gas loss (i.e., bottles were capped under water) capped with blue butyl rubber stoppers and aluminum crimp tops, and kept cold (4^oC).

SF_6 measurement by gas chromatography

Water samples were analyzed for dissolved SF_6 content by gas chromatography using a Shimadzu GC-8a (Japan). Standards and nitrogen blanks were run several times each day to ensure instrument stability and consistency.

5.14.2 SF_6 tracer results and discussion

Tracer experiment (field experiment #1)

Sulfur hexafluoride (SF_6) was introduced into the injection wells on 6/24/08. The total quantity of SF_6 injected was 0.001 ccSTP. Throughout the tracer experiment (field experiment #1, 6/24/08-7/3/08), water samples were obtained from CW 1 (the sampling well) from the coarse layer, excluding the coarse layer, and from the entire well. In addition, samples were obtained from the nearby pump and treat recovery well, RW 2a.

SF_6 concentrations were analyzed for each of these sample types. Extraction from CW 1 most often occurred from the entire well (>90% of the time) and most samples were taken from this well configuration. A peak in SF_6 concentration occurred on 6/29/08 (Figure 5.10). The rising flank in the breakthrough curve occurred between 6/24/08 and 6/29/08 and the falling flank between 6/29/08 and 7/2/09. Approximately 22% of the injected SF_6 was recovered at the sampling well (entire well); this estimate is adjusted for well pump being off or pumping from other configurations and assumes an extraction rate of 4.8 L/min. Based on the time to capture half of the recovered SF_6 there were ~5 days per pore volume between injection wells and sampling well. This is in agreement with the value calculated using the Br data (4.9 days). Samples were also obtained from the coarse layer and excluding the coarse layer. Within the coarse layer, SF_6 concentrations averaged 0.15x the entire well concentration; when the coarse layer was excluded, SF_6 concentrations averaged 1.3x the entire well concentration. These figures are similar to those seen for Br where coarse layer concentrations were 0.2x the entire well concentration and samples excluding the coarse layer were 1.5x more concentrated than those sampling the entire well.

Concentrations of SF_6 were too low at the pump and treat well, RW 2a, to confidently quantify percent recovery; samples were obtained between 6/26/08 and 7/11/08. Total recovery at RW 2a was estimated to be 172%, clearly much higher than is possible. This estimate was calculated assuming a constant pumping rate of 312 L/min, the average for the duration of the experiment and no background correction was applied. The plot of SF_6 concentration over time is quite noisy and duplicate samples often did not agree well; at least 40% of the time, samples differed from their corresponding duplicates by more than 20% (this included all SF_6 samples, not just samples at RW 2a). Therefore, the data indicate that full recovery of the injected SF_6 was possible; however, full quantification is limited by the quality of the data.

Oxalic acid injection experiment (field experiment #2)

Sulfur hexafluoride (SF_6) was introduced into the injection wells on 4/3/09. The total quantity of SF_6 injected was 0.102 ccSTP. Water samples were obtained for SF_6 analysis between 4/4/09 and 6/15/09 from CW 1 (the sampling well) excluding the coarse layer and from the nearby pump and treat recovery well, RW 2a.

At the sampling well, a peak in SF_6 concentration occurred on 4/9/09, with a spike occurring on 4/11/09 just after the pump and treat well was turned on following a shut down. The SF_6 breakthrough curve showed a rising flank between 4/4/09 and 4/9/09 and a falling flank between 4/9/09 and 4/26/09 (Figure 5.11). Approximately 66% of the injected SF_6 was recovered at the sampling well (above packer). The percent recovery calculation assumed an extraction rate at the sampling well of 2.5 L/min. Based on the time to capture half of the recovered SF_6 there are 7.8 days per pore volume between injection wells and sampling well. This agrees with the days per pore volume calculated based on the Br data (7.6-8.0 days).

At the pump and treat recovery well, RW 2a, a peak in SF_6 concentration occurred on 4/12/09-4/13/09. The rising flank in the SF_6 breakthrough curve occurred between 4/4/09 and 4/12/09 or 4/13/09 and the falling flank between 4/12/09 or 4/13/09 and 4/23/09 (Figure 5.12). Assuming a constant pumping rate of 300 L/min and adjusting for times when the pump and treat well was off, approximately 65% of the injected SF_6 was recovered at the pump and treat well. Based on the time to capture half of the recovered

SF_6, there are 9.8 days per pore volume between injection wells and pump and treat recovery well.

Adding the percent recoveries for the sampling well and pump and treat recovery well gives a total recovery of 131%. However, the SF_6 recovery at the sampling well, CW 1, is high compared with the Br recovery of ~15%. Additionally, it is much higher than the Br and SF_6 recoveries calculated at CW 1 during the 2008 tracer experiment (field experiment #1), which were 28% and 22%, respectively. The extraction rate at CW 1 during the tracer experiment (field experiment #1) was nearly double that during the oxalic acid injection experiment (field experiment #2), which may help explain the higher Br recovery during the 2008 tracer experiment. An SF_6 recovery of 66% at CW 1 during the oxalic acid injection experiment (field experiment #2), however, seems inordinately high.

Compounding the problem of a suspiciously high SF_6 recovery at CW 1 is poor reproducibility in duplicate samples. For the RW 2a data, the reproducibility issues are more pronounced with the low signal samples. However, the CW 1 samples, which had much higher signal, also had problems with reproducibility of duplicates. Nearly half of the time, CW 1 samples differed from their duplicates by more than 20%. Perhaps because the concentrations were so much higher in these samples, error was introduced during dilution. Regardless of the reason, it seems likely that absolute percent recoveries from the SF_6 data are not reliable. Rather this data should be used for timing of breakthrough curve only.

5.14.3 Appendix A figures

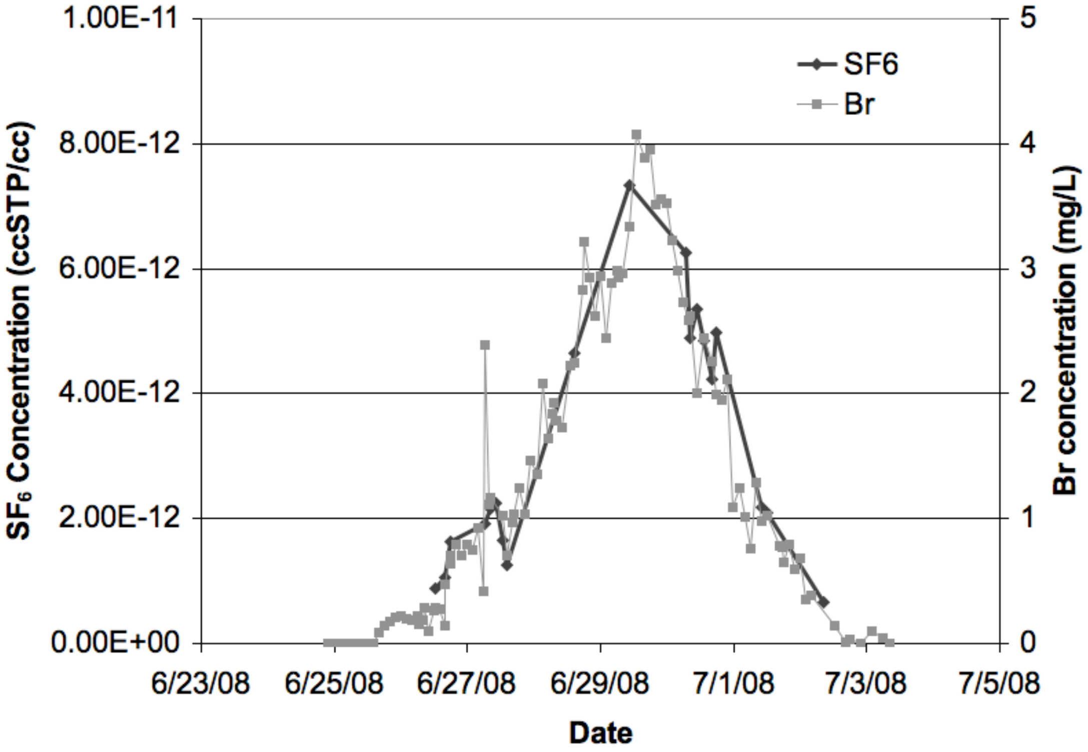


Figure 5.10. SF_6 breakthrough curve at the sampling well, CW 1, following injection of inert tracers in June 2008. The Br breakthrough curve is included for comparison.

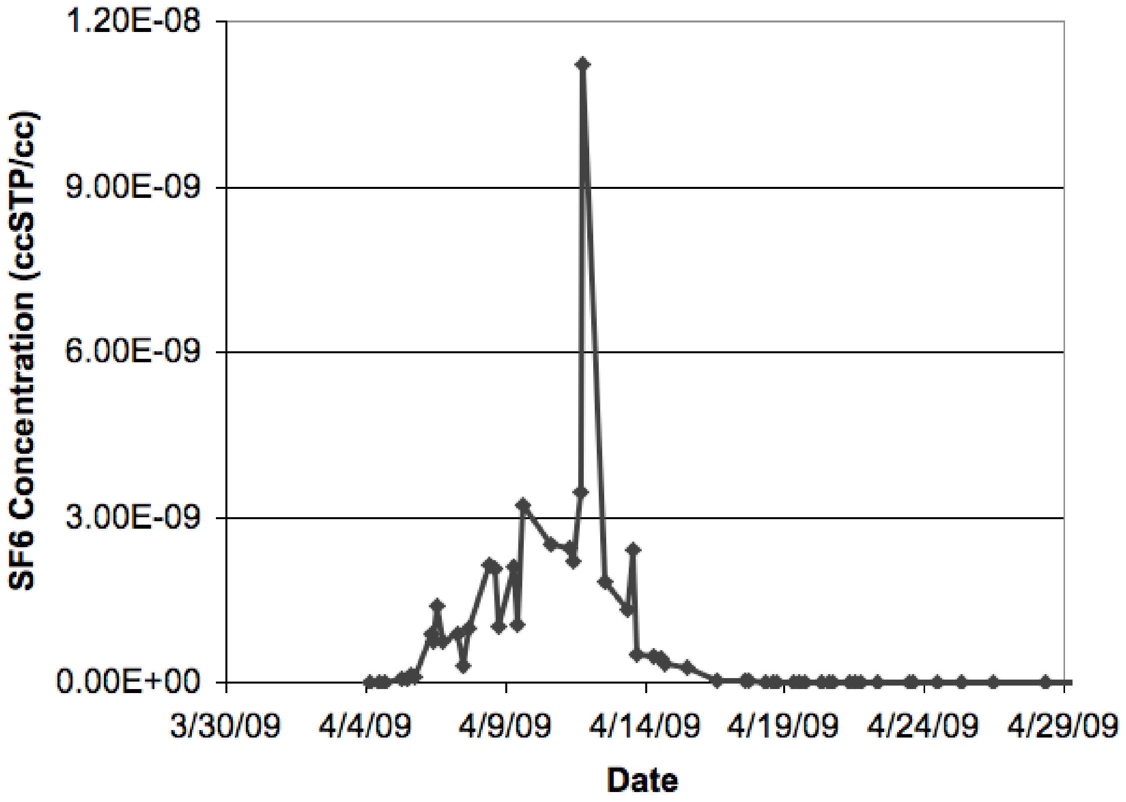


Figure 5.11. SF_6 breakthrough curve at the sampling well, CW 1, following injection on April 3, 2009.

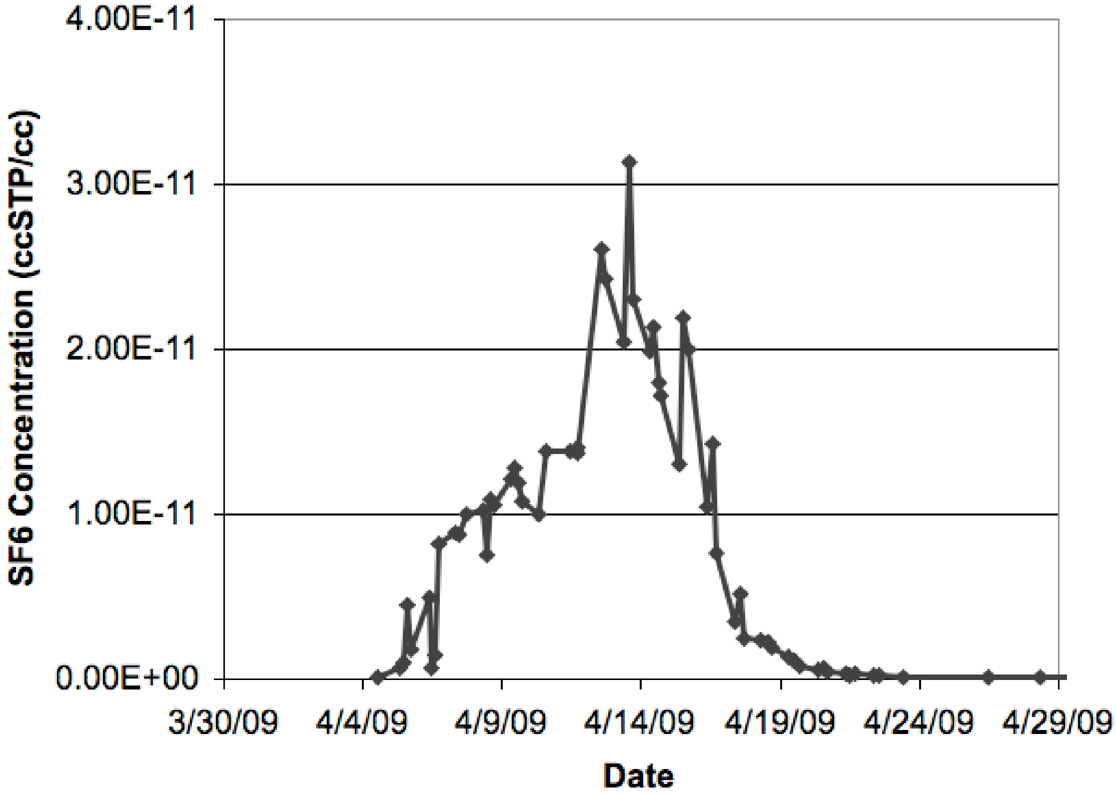


Figure 5.12. SF_6 breakthrough curve at the pump and treat well, RW 2a, following injection on April 3, 2009.

5.15 Appendix B – Hydrological modeling

5.15.1 Initial model prior to well installation

Groundwater numerical modeling was used to help derive several important parameters for the planned well installation fieldwork. These include placement of wells in space (x,y,z), distance between injection and sampling wells, injection and pumping rates, well screen depth, and dilution factor for injected materials. An initial groundwater model was developed prior to installation of the injection and sampling wells. It was designed to represent a small sub-area of the Vineland site and was created using output files from the United States Army Core of Engineers (USACE) FEMWATER model for the area around the Vineland site (Figure 5.13). The numerical model was created with GMS, a graphical interface for groundwater modeling; the MODFLOW package was used for flow modeling, MODPATH for particle tracking and MT3D for transport modeling (Aquaveo Water Modeling Solutions, Provo, UT). The initial model described a small sub area of the Vineland site just to the east of pump and treat well RW 2a and within the capture zone of RW 2a (Figure 5.14). The model contained a small portion of the aquifer in the z direction; it was 25 ft (7.6 m) thick, 55 ft - 30 ft (16.8 – 9.1 m) elevation relative to sea level (~20-45 ft bgs; 6.1-13.7 m bgs). Hydrological parameters were kept the same as in the USACE model; hydraulic conductivity was 300 ft/d (1.1 x 10^{-3} m/s) and porosity = 0.3.

In the USACE model, RW 2a was assumed to be pumping at 80 GPM (303 L/min); RW 2a was not included in our initial model. The hydraulic head output from the USACE model was used to define the boundaries and hydraulic head gradient in our initial model. The east and west boundaries were modeled as specified head boundaries;

the north and south boundaries were modeled as no flow boundaries but hydraulic head values were specified at points along the boundary so that the correct hydraulic head gradient would be maintained (Figure 5.14).

The hydraulic head output from the initial MODFLOW model agreed well with the USACE FEMWATER model as shown in Figure 5.15. Once this result was obtained, the injection and sampling wells were added to the model (Figure 5.14). The injection and sampling wells were screened at 45-40 ft (13.7-12.2 m) elevation in the model, within the screened interval of RW 2a. Based on the head gradient, hydraulic conductivity, and porosity for the system, the flow velocity should be ~ 10 ft/d (3.0 m/d) near the injection wells and should increase to ~12.5 ft/d (3.8 m/d) near the sampling well.

For transport modeling calculations, we simulated injection of a 100 mmol/L solution at a rate of 0.1 L/min at each injection well for a total injection rate of 0.5 L/min. The injection wells were modeled with 5 ft (1.5 m) continuous screens for simplicity, although it was ultimately decided to install three wells per nest each with a 1 ft (0.3 m) screened interval over a total of 5 ft (1.5 m). The sampling well had an extraction rate of 5 L/min. Figure 5.16 shows the predicted concentrations at the sampling well. The graph represents a 20-day experiment in which injection was turned on for 10 days and off for 10 days. The longitudinal dispersivity was 1 ft (0.3 m) in this model, transverse dispersivity was 0.1 ft (0.03 m), and vertical dispersivity was 0.1 ft (0.03 m). No retardation factor was input into the model. After ~3.5 days, the concentration in the sampling well reached a plateau at ~8 mmol/L, a dilution factor of ~12.5. Once injection was turned off, it took another ~3.5 days for the concentration in the sampling well to decrease back to 0 mmol/L. Based on these results we would need to inject our solutions 10-25x more concentrated than the target concentration at the sampling well when using a 0.5 L/min total injection rate and 5 L/min extraction rate. These parameters helped us plan the well installation and future experiments.

5.15.2 Model simulation using tracer data

Additionally, the results of the tracer experiments (2008) were used to create a simplified groundwater flow model surrounding pump and treat well, RW 2a. This model was then used to predict dilution factors for conservative tracers (no adsorption, retardation, or chemical reactions included) at the sampling (CW 1) and pump and treat recovery (RW 2a) wells under different injection and extraction scenarios. Flow and transport models were created using MODFLOW, MODPATH, and MT3D computer codes with a GMS interface (Aquaveo Water Modeling Solutions, Provo, UT).

The boundary of this model was a specified head boundary, which formed a circle (r=75 ft or 22.9 m) surrounding the pump and treat well, RW 2a (Figure 5.17). The model depth covered 77 ft -20 ft elevation (23.5-6.1m). The well screen for RW 2a was placed at 52-32 ft elevation (15.8-9.8 m) or 25-45 ft bgs (7.6-13.7 m bgs). The sampling well was screened 27-40 ft bgs (8.2-12.2 m bgs) and the injection wells were screened 27-32 ft bgs (8.2-9.8 m bgs) to mimic the wells installed on the field site. Five injection wells were modeled with 5 ft (1.5 m) continuous screens for simplicity, although it was decided to install three wells per nest each with a 1 ft (0.3 m) screened interval over a total of 5 ft (1.5 m); total number of injection wells on the field site was 15. Porosity was set at 0.3, hydraulic conductivity at 300 ft/d (1.1 x 10^3 m/s), and the ratios of longitudinal to transverse dispersivity and longitudinal to vertical transpersitvity were both set to 10. A transport model using MT3D was set up with a series of stress periods, injection of tracer at each injection well and pumping at the sampling well, to mimic the tracer experiment. The injection of tracer occurred for 36 min at each modeled injection well at a rate of 10 L/min. The pump rate at the sampling well was set to 5 L/min. The injection concentration was input as 94 mg/L, which was the expected injection concentration based on flow rates and stock tracer solution concentration; the concentration was later measured to have an average of 123 mg/L Br. However, the discrepancy is not expected to impact the results of the modeling exercise to a significant degree. Pump rate at RW 2a and longitudinal dispersivity, which impact timing and concentration in the breakthrough curve, were then varied in the model to try to match the Br breakthrough curve at the sampling well during the tracer experiment. The goal was to create a model that could reasonably match the tracer data and then use it to make predictions for the longer injection experiment.

The simulation that yielded the best match, i.e. the best compromise in transport timing and peak shape for the tracer experiment was modeled with a pumping rate of 32 GPM (121 L/min) at RW 2a and a longitudinal dispersivity of 1.1 ft (0.34 m) (Figure 5.18). These parameters were used for simulations of different field injection scenarios for a long injection experiment. Using the results of the various models, we chose an injection scheme involving injection of oxalic acid and bromide at a total injection rate of ~0.25 L/min (actual rate in field = 0.27 L/min) during Phase I and a pumping rate at the sampling well at 2.5 L/min for the entire experiment (actual rate in field was the same). Using these parameters, the model predicted that injected solutions would be focused toward the sampling well and the average impacted thickness would be ~8 ft (2.4 m). Since the model did not include reaction or retardation, it could only predict general dilution factors and concentrations for a conservative tracer like Br; it would not be predictive of a potentially reactive species such as oxalic acid. With continuous injection of Br, the model predicted a plateau concentration of 3.5 mg/L Br at the sampling well, CW 1, for Phase I when the injected concentration was 50 mg/L (field measurements showed an average Br concentration of 1.4 mg/L from 4/15/09-5/9/09); the model predicted a concentration of 0.05 mg/L Br at the pump and treat well, RW 2a (field measurements showed values <0.1 mg/L during Phase I). Hydrological modeling, therefore, predicted less dilution of injected materials between injection and sampling wells than was seen in the field experiment. Modeling predicted approximately 14x dilution from injection wells to sampling well while ion chromatography results for Br concentrations suggest ~40x dilution of oxalic acid and Br during Phase I (44x for oxalic acid and 35x for Br). The presence of Br at RW 2a during Phase I was largely undetected; accurately quantifying concentrations in the 0.05 mg/L range is difficult with the instrument set up used. The greater dilution factors at CW 1 could have resulted from inaccuracies in the model inputs such as hydraulic conductivity, longitudinal dispersivity, etc. or from factors relevant in the field study that the simplistic model would not take into account, such as preferential flow paths and other heterogeneities in the subsurface.

5.15.3 Appendix B figures

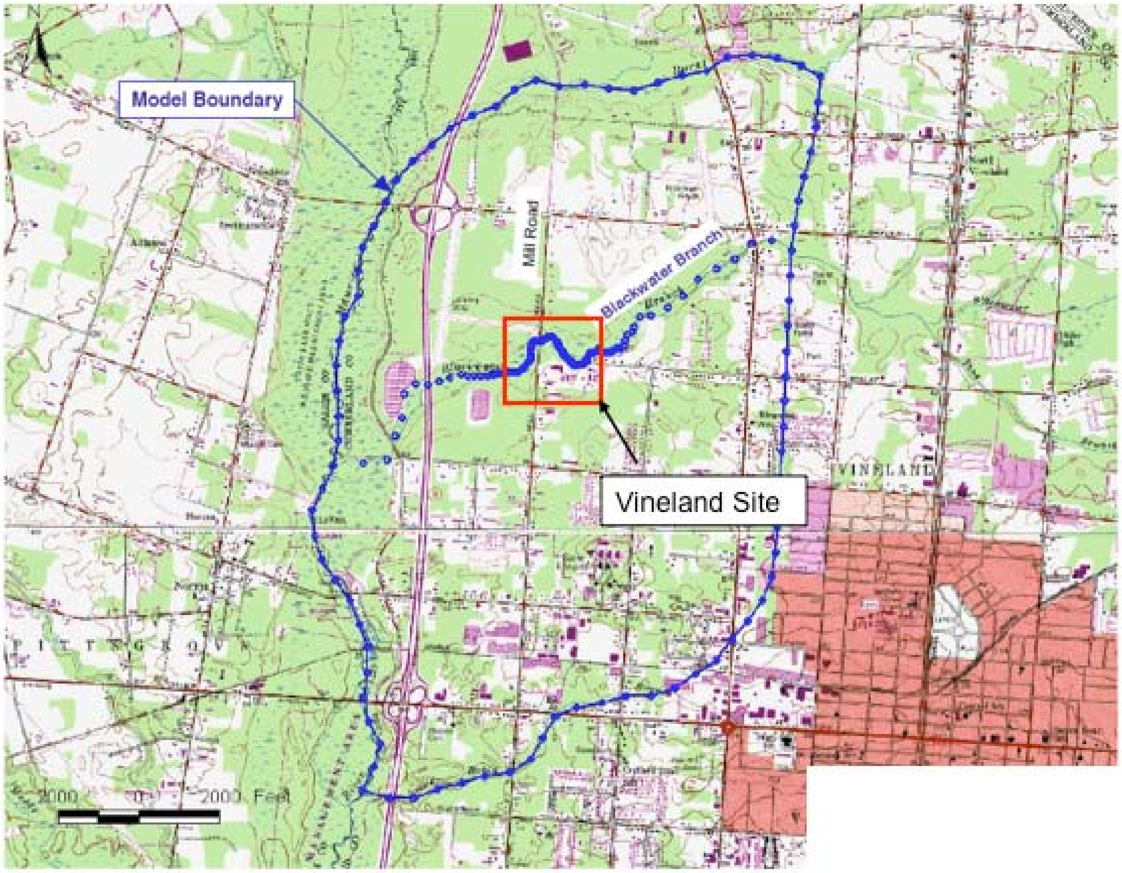


Figure 5.13. Map of the area around the Vineland site showing the location of the Vineland site (red box) as well as the USACE FEMWATER model boundary (blue) (USACE, 2007).

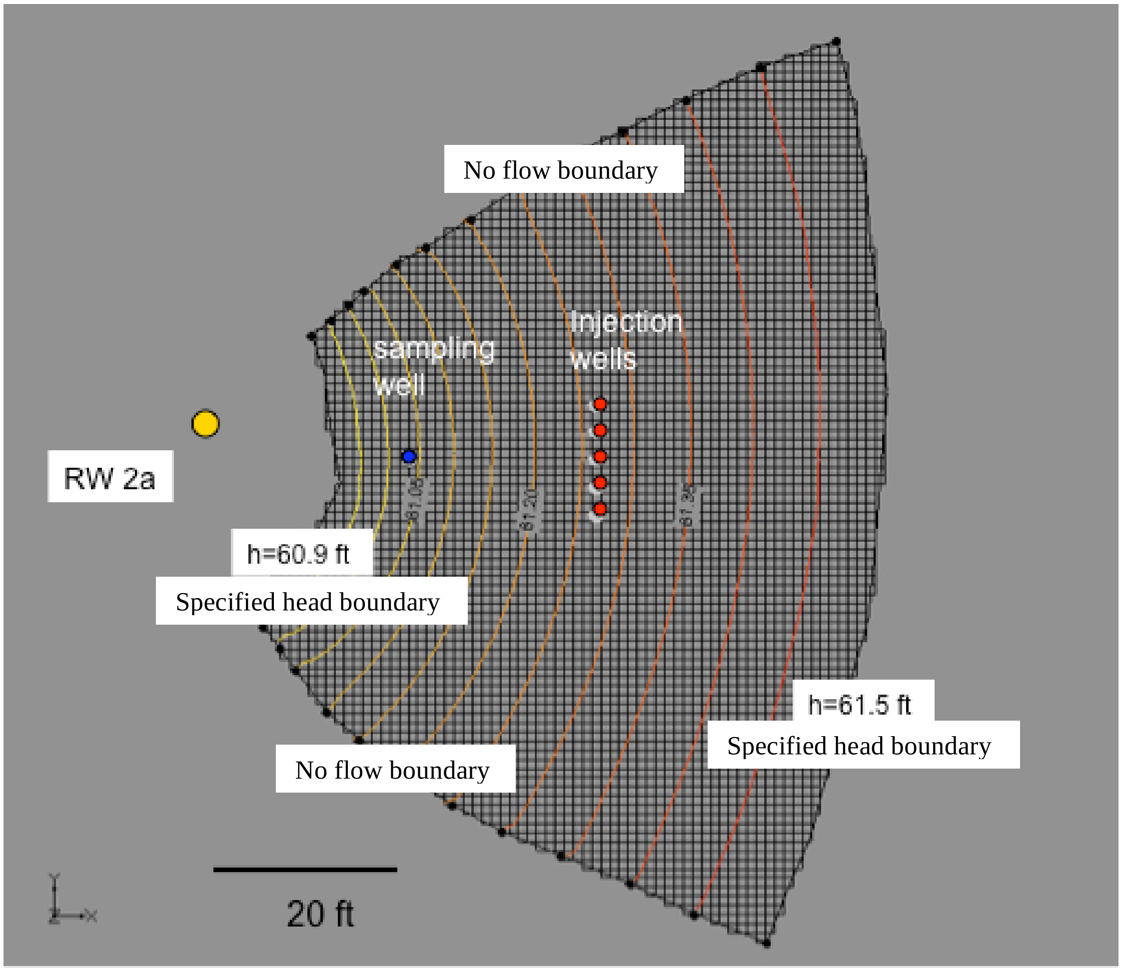


Figure 5.14. Initial MODFLOW model of sub-area near RW2a. RW 2a is shown in yellow and was not part of the model. The injection wells are shown in red and sampling well in blue. Hydrological parameters were kept the same as in the USACE model; hydraulic conductivity was 300 ft/d (1.1 x 10^{-3} m/s) and porosity = 0.3. Each square in the grid above represents one cell in the model.

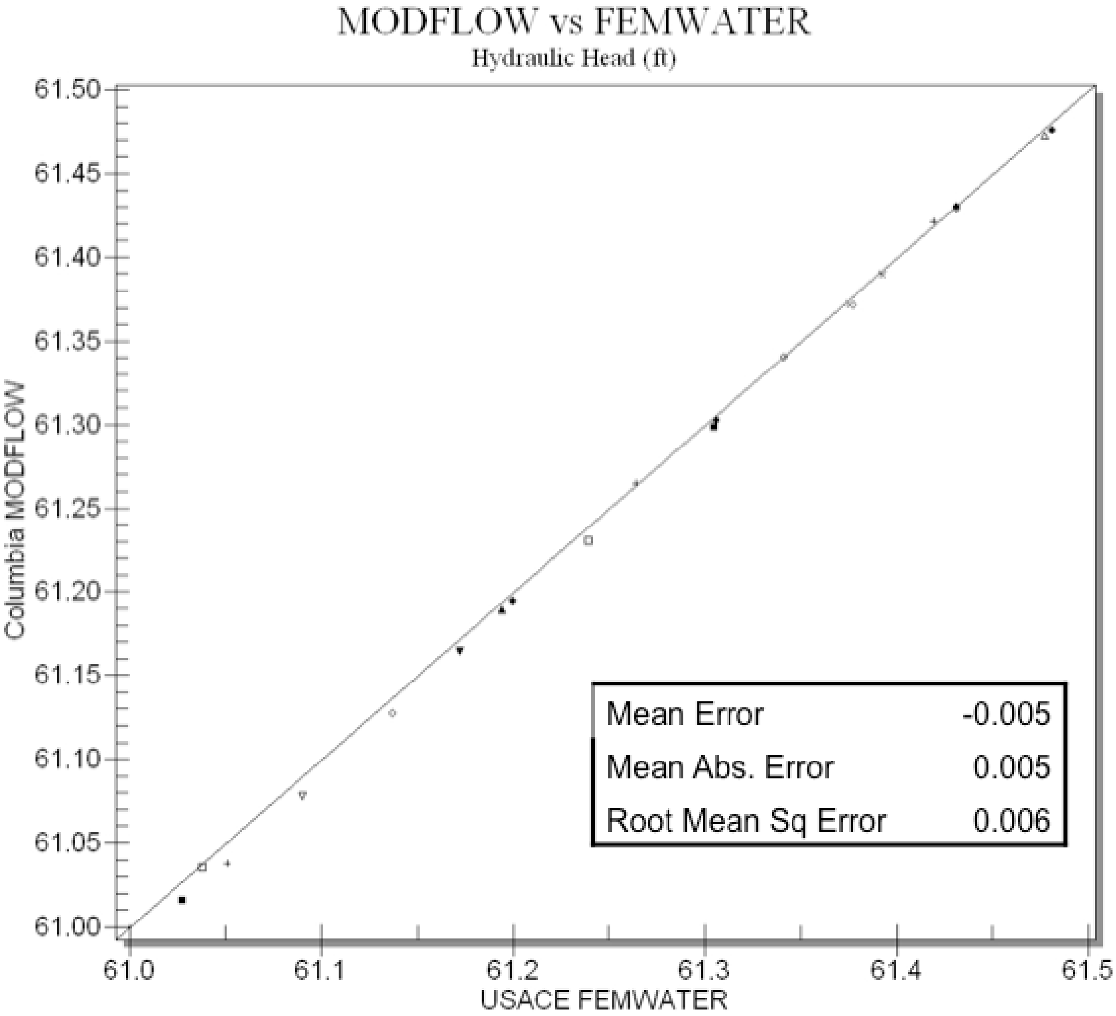


Figure 5.15. A comparison of the hydraulic head output for our initial MODFLOW model and the USACE FEMWATER model.

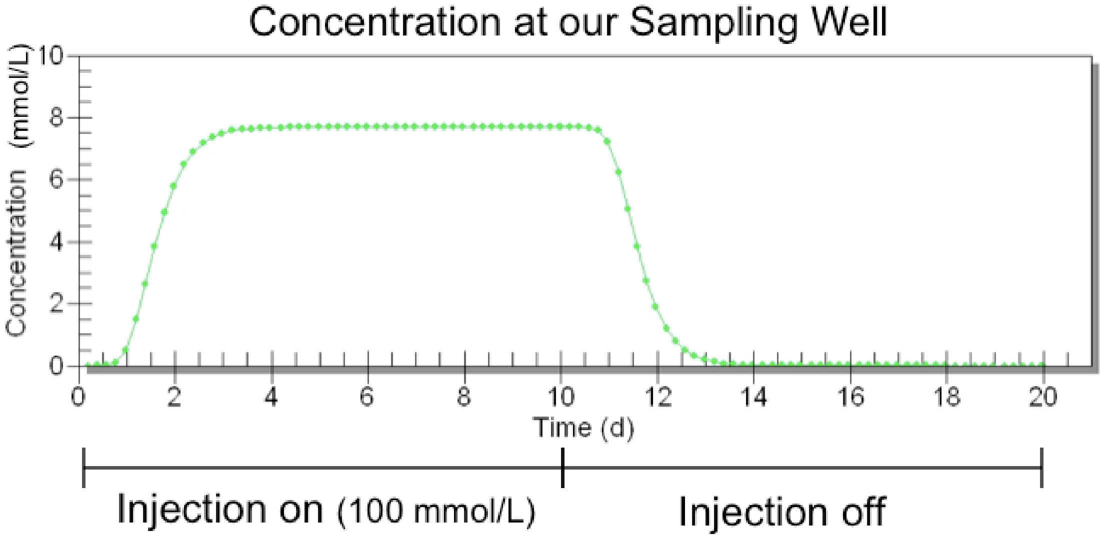


Figure 5.16. Concentration at the sampling well as obtained from transport modeling in which injection was turned on for 10 days at 100 mmol/L and off for 10 days.

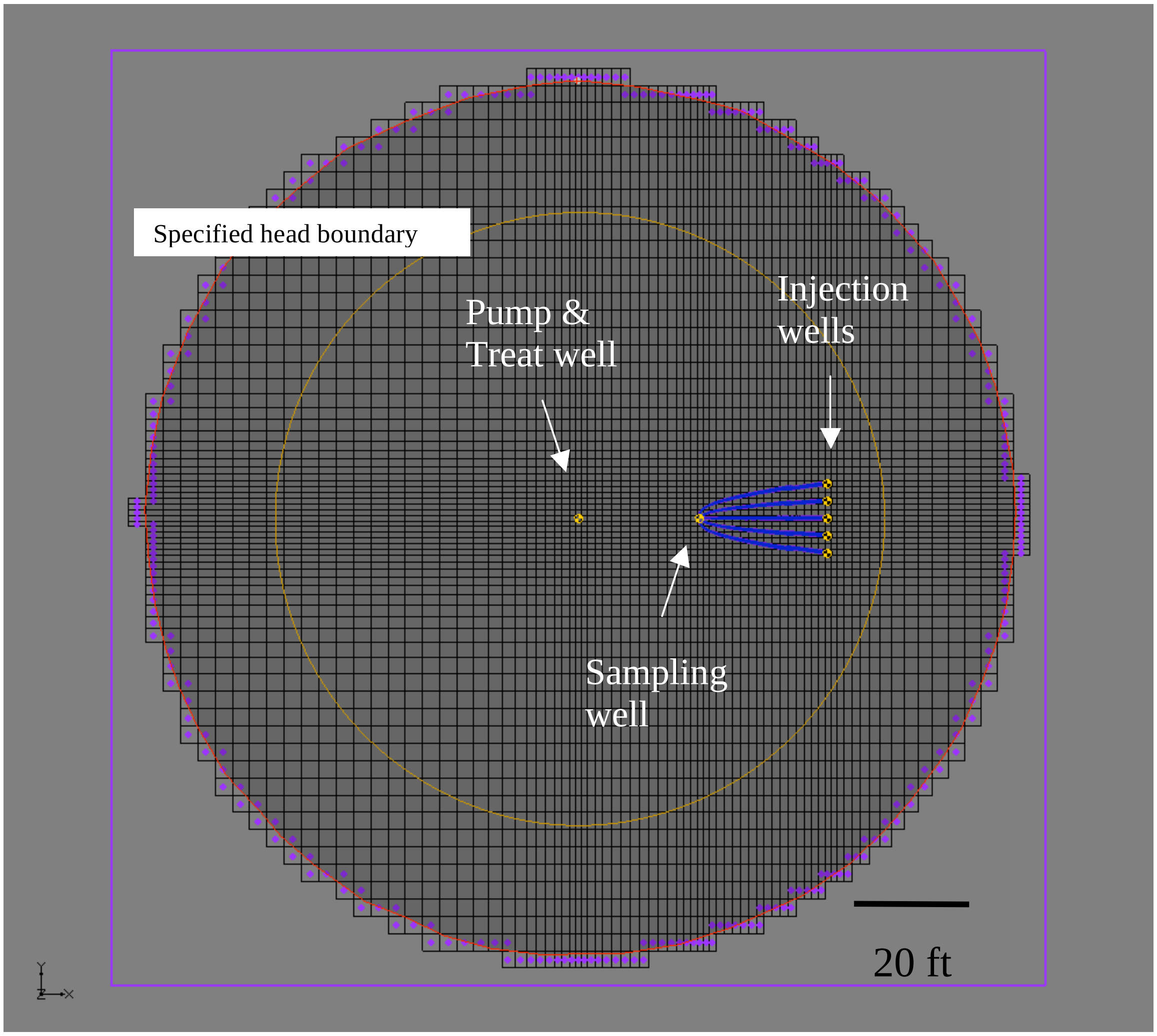


Figure 5.17. Model of area around the pump and treat well, RW2a. The pump and treat well, sampling well, and injection wells are shown. The blue lines extending from the injection wells to the sampling well are the result of a particle tracking exercise. Porosity was set at 0.3, hydraulic conductivity at 300 ft/d (1.1 x 10^3 m/s), and the ratios of longitudinal to transverse dispersivity and longitudinal to vertical transpersitvity were both set to 10. The radius of the circular model was 75 ft or 22.9 m. Each square or rectangle in the grid above represents one cell in the model; a finer grid was used around the wells than in the rest of the model.

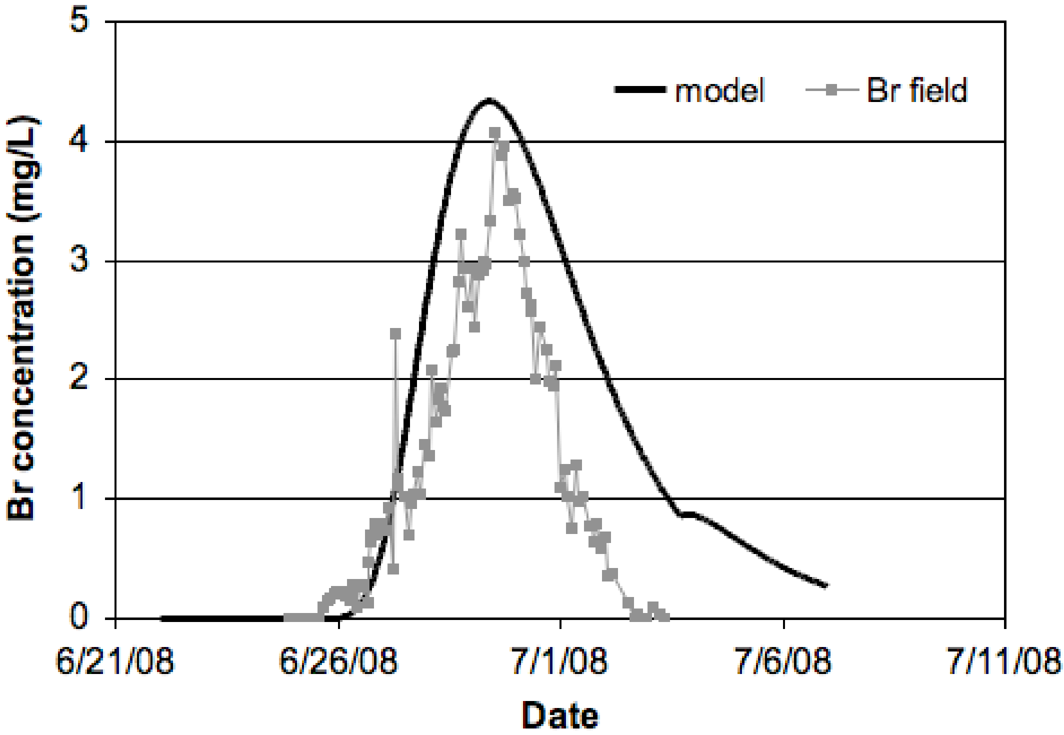


Figure 5.18. Comparison of model data and Br breakthrough from the field tracer experiment. The Br samples from the field experiment were measured by ion chromatography.

5.15.4 References

USACE, 2007. Classification Exception Area and Well Restriction Area Report, Appendix A. Vineland Chemical Company Superfund Site, Vineland, NJ., Prepared for USEPA, Region II.

5.16 Appendix C – Sediment extractions

5.16.1 Methods

Extraction Experiments

Approximately 2 g of wet contaminated aquifer solids (~80 mg/kg in As), equivalent to an average of ~1.7 g dry sediment, was combined with 10 mL of the desired extraction solution. The following solutions were used in separate extraction trials: 1 mM, 10 mM, and 100 mM HCl; 100 mM HNO_3; 10 mM and 100 mM ammonium oxalate; 1 mM, 10 mM, and 100 mM ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA); 1 mM nitriloacetic acid (NTA). Extractions were performed in duplicate and averaged. These batch experiments were intended to investigate impacts of various extraction types on As mobilization: efficacy of acidity alone (HCl and HNO_3), efficacy of an oxalate salt compared with oxalic acid (ammonium oxalate), and effect of chelating agents (EDTA and NTA). Extractions with 1 mM, 10 mM, and 100 mM oxalic acid have been reported elsewhere (Wovkulich, et al., 2010). The pH of the solutions was measured but not adjusted. Samples were extracted for 2 or 24 hours (ammonium oxalate extractions were 2 hrs only) and were agitated on an adjustable rocker table (Cole-Parmer). Suspensions were centrifuged at 3000 rpm (Damon/IEC Division) for 10 minutes and the supernatants were decanted into acid washed bottles.

5.16.2 Results

Sediment Characterization

Sediments that were used for batch extractions have been described elsewhere (Wovkulich, et al., 2010). Briefly, complete digestion of the aquifer sediments collected for these experiments averaged (±1 standard deviation): total As = 81 ± 1 mg/kg (N=5), total Fe = 1050 ± 180 mg/kg (N=5), total Al = 1070 ± 110 mg/kg (N=3), and total Mn = 12 ± 2 mg/kg (N=5).

Extraction Experiments

Oxalic acid extractions have been reported elsewhere (Wovkulich, et al., 2010) and reproduced in Figure 5.19. Briefly, 1 mM oxalic acid (pH=3.1) mobilized 43-56% of the As from the aquifer solids depending on extraction time (2 or 24 hrs), 10 mM oxalic acid (pH=2.3) mobilized 88-93%, and 100 mM oxalic acid (pH=1.6) mobilized 89-99%.

HCl and HNO3 were used as extractants to test for effectiveness of acidity alone for mobilizing As. Depending on extraction time (2 or 24 hrs), 1 mM HCl (pH=3.1) mobilized 5-6% of the As from the aquifer sediments, 10 mM HCl (pH=2.2) mobilized 11-45%, 100 mM HCl (pH=1.4) mobilized 53-72%, and 100 mM HNO3 (pH=1.4) mobilized 55-73% of the As from the sediments (Figure 5.19).

Ammonium oxalate extractions were performed at the 10 mM and 100 mM levels with only a 2 hr extraction. The 10 mM ammonium oxalate extraction (pH=6.3) mobilized 14% of the As from the aquifer solids and the 100 mM (pH=6.5) extraction mobilized 22% in 2 hrs (Figure 5.19).

Finally, the chelators EDTA and NTA were tested for their effect on As mobility. The 1 mM EDTA extraction (pH=5.1) mobilized 10-26% of the As from the solids depending on extraction time (2 or 24 hrs), 10 mM EDTA (pH=4.7) mobilized 11-31%, 100 mM EDTA (pH=4.5) mobilized 14-36%. The 1 mM NTA extraction (pH=2.7) mobilized 22-66% of the As from the solids (Figure 5.19); 10 mM and 100 mM extractions were not possible with NTA due to limited solubility.

5.16.3 Discussion

Extraction Experiments

A series of extractions were conducted to gain further insight into the mechanism by which oxalic acid can mobilize As. Three types of extractions were performed besides the oxalic acid extractions: acidity extractions (HCl and HNO3), oxalate salt (ammonium oxalate), and chelating agents (EDTA and NTA). The acidity extractions were performed to evaluate whether low pH alone could explain the efficacy of the oxalic acid treatments. As seen in these extraction experiments, oxalic acid tended to be more effective at mobilizing As than either HCl or HNO_3. At the 1 mM (pH 3) and 10 mM (pH 2) levels, oxalic acid mobilized at least double the As as HCl. At the 100 mM (pH 1) level, oxalic acid still mobilized more As (89-99%) than either HCl or HNO3 (53-73%), although the difference between the extractant efficacy was decreasing. However, it seems clear from these extractions that acidity alone cannot explain the As mobilization by oxalic acid.

The oxalate salt extraction with ammonium oxalate showed mobilization of 14-22% of the As compared with 88-89% with oxalic acid (10 and 100 mM with 2 hr extraction). The ammonium oxalate extraction was meant to investigate whether an oxalate salt could be as effective as oxalic acid at mobilizing As; these extractions suggest that ammonium oxalate is not as effective as oxalic acid. However, the pH values of the extraction solutions were not adjusted and this difference would play a role in effective mobilization. Even though acidity alone does not seem to be the dominant mechanism for inducing As mobilization, the pH will determine the level of protonation of the acid. The pKa values for oxalic acid are 1.27 and 4.14. Therefore, the dominant form of oxalic acid in the extractions described is singly protonated. This may be an important feature in the oxalic acid mechanism. For instance, it has been suggested that optimal Fe release by oxalic acid occurs at pH 2-3, where oxalic acid is predominantly singly protonated. This optimal pH is in the range of observed pH for 1 mM and 10 mM oxalic acid extractions. However, the ammonium oxalate extractions took place at their unadjusted pH of ~6. The oxalate ions would likely be unprotonated at this pH and this may make them less effective for mobilizing As.

Finally, because oxalic acid can act as a chelating agent, extractions were performed with other chelating agents (EDTA and NTA) to evaluate whether other chelators in similar molar amounts could be just as effective as oxalic acid. EDTA was not particularly effective at mobilizing As, with a maximum of 36% with 100 mM EDTA for 24 hours, which is less effective than the 2 hour extraction with 1 mM oxalic acid. Oxalic acid (1 mM) was more effective than 1 mM NTA for the 2 hour extraction (43% vs. 22%). However, 1 mM NTA mobilized somewhat more As than 1 mM oxalic acid in the 24 hour extraction (66% vs. 56%). Chelation, depending on the chelating agent, may be a useful mechanism for As removal. Although NTA may show promise for As mobilization, low solubility makes it less useful for field applications. In these extractions, 3% or less of the sediment Fe was mobilized by EDTA or NTA while oxalic acid mobilized somewhat more Fe, 3-27%. It is possible that EDTA and NTA get used in this system to chelate “easier” targets such as calcium or sodium and little is left to complex Fe. However, Fe mobilization is still relatively low in the oxalic acid extractions as well. Mobilization of 88% of the sediment As was possible with a 2-hr 10 mM oxalic acid treatment, despite only 5% Fe mobilization. This may indicate re-precipitation of Fe in the system and/or may indicate a role for competitive sorption between As and oxalic acid as part of the release mechanism.

5.16.4 Appendix C figures

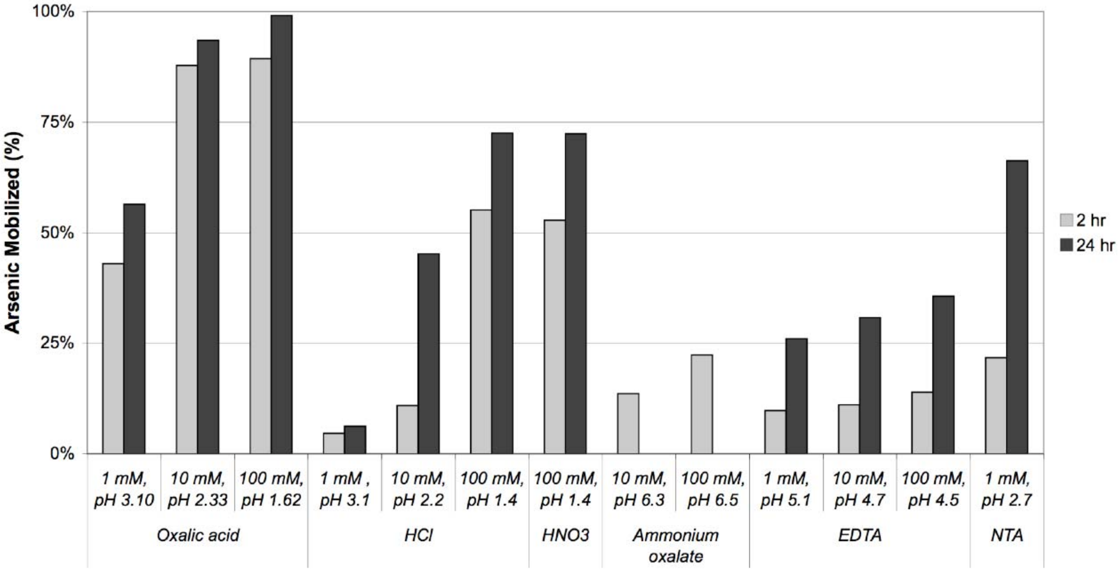


Figure 5.19. Several types of batch extractions were performed. Extractants included oxalic acid, inorganic acids (HCl and HNO_3), an oxalate salt (ammonium oxalate) and chelating agents (EDTA and NTA). Other extractants typically did not perform as well as oxalic acid in terms of percent As mobilized from the aquifer sediments except for 24-hr NTA extraction.

5.17 Appendix D – Miniature laboratory columns to mimic the field oxalic injection (updated from (Doobay, 2010), undergraduate thesis)

5.17.1 Methods

Duplicate small column experiments were performed in the laboratory to mimic the field experiment. Sandy aquifer material was wet packed into a section of clear polycarbonate tube with 0.635 cm ID (McMaster-Carr). Column lengths packed with sediments were approximately 6 cm long. A small amount of glass wool was packed into each end to help distribute solution over the full cross sectional area of the column; the columns were sealed with nylon end caps. The columns were run in upflow mode at ~1 m/d using a peristaltic pump (Rainin Instrument Co.) to control the flow rate. The flow velocity was similar to calculated average values for the pilot study area based on Br breakthrough curves. Each of the duplicate columns was assumed to have a porosity of 0.34. Influent solutions were flowed into the columns as follows: approximately one to three pore volumes of groundwater alone (obtained from a pump and treat recovery well near the pilot study area, RW2), then six pore volumes of ~ 2 mM oxalic acid influent, then 9 pore volumes of ~ 18 mM oxalic acid influent, and finally groundwater (RW2). The higher concentration oxalic acid influent used in the laboratory experiment was somewhat higher than the field experiment Phase II plateau of ~12 mM since the laboratory experiments were started before completion of the field experiments. The number of pore volumes used for each phase of oxalic acid introduction in the columns was also slightly different than in the field experiment (6 and 9 pore volumes in the columns as opposed to 4 and 7 pore volumes in the field). The sediment used in the column experiments was sub-sampled from the 2008 sediment core taken at the sampling well (CW 1) and had an As concentration of 28 mg/kg.

5.17.2 References

Doobay, K. (2010), The use of oxalic acid to mobilize arsenic from contaminated aquifer solids from Vineland, NJ, Barnard College, New York.

5.18 Appendix E – Data tables for 2008 and 2009 field experiments

5.18.1 ICP MS data from 2008 tracer experiment (field experiment #1)

Field experiment #1 - groundwater concentrations over time at the sampling well, CW 1 – (full well)

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
6/25/08 8:05	14	11	419	3032
6/25/08 14:00	20	11	359	2681
6/25/08 18:00	20	10	413	3018
6/26/08 6:25	21	11	365	3207
6/26/08 10:05	16	12	356	2619
6/26/08 10:05	20	10	364	2734
6/26/08 14:05	13	10	327	2793
6/26/08 17:45	20	11	346	3003
6/27/08 6:30	27	25	95	3144
6/27/08 6:30	19	27	-	3050
6/27/08 10:05	11	9	209	2863
6/27/08 14:15	10	9	288	2730
6/28/08 6:35	13	11	338	2771
6/28/08 10:20	14	9	355	2523
6/28/08 17:35	13	10	415	2752
6/28/08 17:35	9	9	399	2902
6/29/08 6:30	17	13	366	2737
6/29/08 10:25	11	11	387	2490
6/29/08 10:25	11	10	410	2837
6/29/08 15:45	19	11	417	2675
6/30/08 8:20	20	11	367	2682
6/30/08 13:25	15	8	518	2776
6/30/08 16:15	16	10	422	2597
7/1/08 8:05	21	12	383	3431
7/1/08 10:20	18	11	405	2743
7/1/08 16:20	17	10	397	2665
7/1/08 16:20	16	11	429	2710
7/2/08 8:20	22	11	416	2864
7/2/08 16:15	17	10	-	2867
7/3/08 8:10	22	11	398	3022
7/3/08 16:10	16	10	407	2750
7/3/08 16:10	7	9	371	2542

- %RSD >10
Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #1 - groundwater concentrations over time at the sampling well, CW 1 – (above packer)

Date/Time	**Al (µg/L)**	**Mn (µg/L)**	**Fe (µg/L)**	**As (µg/L)**
6/28/08 11:45	24	7	-	3457
6/28/08 16:35	19	6	497	3478
6/29/08 9:45	27	7	528	3645
6/29/08 13:50	26	7	517	3706
6/30/08 11:55	21	7	493	3531
7/1/08 13:50	30	7	465	3783

- %RSD >10

Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #1 - Groundwater concentrations over time at the sampling well, CW 1 – (below packer)

Date/Time	**Al (µg/L)**	**Mn (µg/L)**	**Fe (µg/L)**	**As (µg/L)**
6/25/08 11:20	15	23	129	680
6/26/08 9:25	22	32	*56*	470
6/26/08 13:30	30	32	45	405
6/26/08 15:30	31	31	*35*	375
6/27/08 9:05	7	30	*15*	405
6/27/08 9:05	16	30	*17*	422
6/27/08 13:20	15	30	*17*	411
6/27/08 13:20	11	30	*17*	448
6/27/08 15:25	9	32	*19*	426
6/28/08 9:35	15	34	*9*	374
6/28/08 13:50	27	29	*24*	476
6/29/08 11:30	15	29	*11*	410
6/29/08 16:35	11	30	*17*	426
6/30/08 10:00	9	30	*9*	375
7/1/08 14:35	10	27	23	515

Grey = questionable Fe data, small peaks and %RSD >10
Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #1 - Groundwater concentrations over time at the pump and treat well, RW 2a

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
6/25/08 7:25	25	46	104	938
6/25/08 7:25	149	47	-	986
6/25/08 14:00	103	47	-	936
6/25/08 18:00	101	45	118	974
6/26/08 6:25	53	45	-	950
6/26/08 10:05	40	46	-	950
6/26/08 10:05	84	47	102	1013
6/26/08 14:05	252	48	106	969
6/26/08 17:45	49	49	108	962
6/27/08 8:05	47	47	131	978
6/27/08 10:05	36	45	-	974
6/27/08 14:15	39	45	103	951
6/28/08 6:35	26	48	98	945
6/28/08 10:20	23	45	-	957
6/28/08 17:35	32	49	-	983
6/29/08 6:30	30	46	-	912
6/29/08 10:25	31	46	103	984
6/29/08 10:25	42	46	99	940
6/29/08 15:45	31	45	-	980
6/30/08 8:20	27	49	-	927
6/30/08 13:25	26	47	93	906
6/30/08 16:15	50	47	-	995
7/1/08 8:05	31	44	84	860
7/1/08 10:20	75	54	-	983
7/1/08 16:20	36	45	94	925
7/2/08 8:20	96	38	-	863
7/2/08 16:15	31	47	-	960
7/2/08 16:15	34	46	-	976
7/3/08 8:10	41	46	-	956
7/3/08 16:10	21	44	94	957
7/10/08 10:20	32	48	96	920

- Fe values unreliable due to small peaks and %RSD >10

Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

5.18.2 ICP MS data from oxalic acid injection experiment (field experiment #2)

Field experiment #2 - groundwater concentrations over time at the sampling well, CW 1 – (above packer)

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
4/3/09 9:30	46	4	274	2828
4/4/09 10:45	48	3	267	3089
4/5/09 7:20	47	11	272	3058
4/5/09 7:20	47	10	274	3226
4/6/09 8:30	49	6	299	3281
4/7/09 7:20	50	14	284	3179
4/8/09 7:20	160	11	321	3054
4/9/09 10:50	4321	83	341	2919
4/10/09 7:45	6016	119	803	3015
4/11/09 16:15	3037	221	9491	2751
4/12/09 8:40	5381	74	881	2980
4/13/09 8:20	6631	120	1571	3246
4/13/09 8:20	7007	120	1711	3266
4/14/09 7:35	6942	108	3179	3766
4/15/09 11:20		133	8728	4571
4/16/09 7:55	13847	156	12026	5570
4/16/09 7:55	14027	156	12209	5714
4/17/09 8:15		136	18836	6095
4/18/09 7:35	19558	117	22821	6240
4/18/09 7:35	20941	124	23937	6250
4/19/09 7:35	5920	25	9087	4710
4/20/09 7:45	21083	119	28419	5732
4/21/09 8:00		127	30508	5363
4/21/09 8:00		121	28990	5293
4/22/09 7:45	9853	41	10982	4166
4/23/09 10:25		69	16403	4291
4/24/09 11:15	25107	104	25903	4784
4/25/09 8:35		135	34640	4940
4/26/09 11:00	12036	44	13013	3578
4/27/09 8:00		158	36662	4694
4/27/09 8:00		160	37427	4719
4/28/09 8:05	30106	155	36766	4379
4/29/09 8:40		159	36790	4192
4/30/09 8:25	27990	137	33253	3748
5/1/09 6:30		178	42609	4370
5/3/09 10:30	18155	98	23039	3138
5/4/09 13:50		191	52855	4341
5/5/09 8:15		158	39341	3789
5/6/09 8:55	27896	142	38676	3567
5/7/09 8:20		177	52758	4135

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
5/8/09 8:15	24132	119	35910	3311
5/9/09 7:55		167	43135	3366
5/9/09 7:55		175	44779	3301
5/10/09 14:45	39767	204	56252	4996
5/11/09 7:15		248	63528	6901
5/12/09 8:40	50815	263	69423	4941
5/13/09 8:50		247	70236	5606
5/14/09 8:10	58623	275	86878	5759
5/15/09 8:45		258	81125	5760
5/16/09 8:20	53249	252	89263	5743
5/17/09 15:00		262	98594	6019
5/18/09 8:45	69949	301	112679	6313
5/19/09 8:10		303	122149	6339
5/20/09 8:35	68915	293	114352	5688
5/21/09 8:45		271	111260	5476
5/22/09 8:30	59902	253	107837	5130
5/23/09 7:05		269	115693	5477
5/24/09 11:15	64774	259	109370	4687
5/25/09 8:50		264	125325	5296
5/26/09 7:15	101433	458	213250	7594
5/27/09 9:00		212	91808	4604
5/28/09 8:45	67440	298	132792	5474
5/29/09 12:15		216	93408	5409
5/30/09 7:55	64888	297	125182	5515
5/31/09 12:15		276	122676	5465
6/1/09 7:15		247	113511	5309
6/2/09 8:15	82868	623	299160	10274
6/3/09 9:10		380	173888	6552
6/4/09 8:40	88639	365	159048	5775
6/5/09 8:55		375	151641	5116
6/6/09 8:10	31506	126	50807	3686
6/7/09 10:00		191	71599	5068
6/8/09 8:05	51177	245	82544	5631
6/9/09 10:00		282	95651	6561
6/10/09 8:15	49007	240	83312	6456
6/11/09 7:55		157	60645	5475
6/12/09 8:10	38524	168	66553	5587
6/13/09 7:40		113	48098	4399
6/14/09 12:40	25144	119	52499	4282
6/15/09 8:35		104	43124	3882
6/16/09 7:45	25525	129	55631	3847
6/17/09 8:15		134	57795	3679
6/18/09 10:30	28977	149	66135	3732
6/19/09 9:00		111	46882	3274

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
6/20/09 7:50	28939	110	49496	3058
6/21/09 12:30		133	62819	3297
6/22/09 8:20	27510	135	64037	3166
6/23/09 8:10		127	53419	3011
6/24/09 9:00	36618	165	74708	3421
6/25/09 8:40		120	52868	2864
6/26/09 7:55	29778	140	62102	2929
6/27/09 8:20		167	75089	3148
6/28/09 14:30	24807	109	48852	2753
6/29/09 8:40		182	77743	3100
6/30/09 8:15		164	72301	2874
7/1/09 7:15		163	73769	2964
7/2/09 7:00	67301	301	148822	3857
7/3/09 9:05		95	39942	2526
7/4/09 12:00	46202	180	86075	2956
7/5/09 9:10		185	80722	3200
7/6/09 12:50	37677	159	72087	3119
7/8/09 11:00	74477	306	137306	6989
7/9/09 7:55		202	105530	2822
7/10/09 9:25	4542	42	8250	2033
7/12/09 12:25	16158	77	28820	2607
7/13/09 11:25		92	30974	2585
7/14/09 8:15	32580	148	52313	2723
7/15/09 9:00		122	41102	2779
7/20/09 11:00	5740	41	10592	2008
7/23/09 10:55	3285	34	7512	1864
7/28/09 11:10	1212	24	4594	1610
8/3/09 11:00	276	21	3247	1708
8/10/09 11:40	435	18	2552	1788
8/17/09 11:05	279	17	2057	1848
8/24/09 11:15	153	15	1608	1726
8/31/09 11:20	154	17	1452	1664
9/9/09 11:35	107	14	1408	1576

Blank = no data available (Usually this means that the signal switched detectors during analysis and only a subset of samples were re-diluted and re-run.)
Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #2 - groundwater concentrations over time at the sampling well, CW 1 – (below packer)

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
6/3/09 17:10	1250	33	1147	62
6/4/09 10:05	1230	36	912	52
6/5/09 10:05	35726	165	53097	2456
6/6/09 9:50	160777	470	220140	8459
6/8/09 9:25	98956	345	130835	7981
6/9/09 10:10		242	99262	5483
6/10/09 9:40	32426	116	52101	2710
6/11/09 9:30		93	37545	1851
6/12/09 9:40	20984	90	30499	1640
6/13/09 8:55	20581	91	28618	1478
6/14/09 13:50	18062	91	26131	1271
6/15/09 9:35	18205	89	24395	1191
6/16/09 9:20	18426	98	24172	1144
6/17/09 9:45	14663	101	19248	930
6/18/09 16:40	13535	103	18947	829
6/19/09 9:50	12989	108	18415	815
6/20/09 9:20		90	16686	712
6/21/09 13:45	10478	99	15579	669
6/22/09 9:35		99	16422	689
6/23/09 9:50		100	16139	632
6/24/09 16:50	13883	120	20785	875
6/25/09 9:50		101	15757	638
6/26/09 9:20	11801	109	19807	785
6/27/09 9:30		97	18435	701
6/28/09 14:40	14493	113	21617	1053
6/29/09 10:05		98	19646	708
6/30/09 9:30	10456	91	17831	588
7/1/09 8:15		92	18331	591
7/2/09 9:30	1898	38	3040	104
7/3/09 10:00		95	31775	636
7/4/09 13:30	52864	262	51929	2693
7/5/09 11:30		117	34996	1173
7/6/09 12:55	19525	27	10554	521
7/8/09 11:05	23672	141	34281	2110
7/10/09 9:35	30133	99	50589	958
7/12/09 13:10	9168	54	12730	194
7/13/09 11:35	3524	44	3793	76
7/14/09 9:15	835	34	456	33
7/15/09 10:15	329	35	299	23
7/20/09 11:15	32	27	59	225
7/23/09 11:05	26	38	88	122
7/28/09 11:20	18	43	32	118

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
8/3/09 11:10	20	50	22	108
8/10/09 11:50	15	55	68	148
8/17/09 11:15	14	58	15	105
8/24/09 11:25	14	63	15	142
8/31/09 11:30	5	20	6	60
9/9/09 11:45	12	38	17	328

Blank = no data available (Usually this means that the signal switched detectors during analysis and only a subset of samples were re-diluted and re-run.)
Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #2 - groundwater concentrations over time at injection well, CW 3.2

Date/Time	**Al (µg/L)**	**Mn (µg/L)**	**Fe (µg/L)**	**As (µg/L)**
4/3/09 8:55	359	5	237	8150
4/9/09 14:50	265	89	1458	372
4/17/09 17:15	626	276	4464	426
4/28/09 12:00	1979	52	3447	489
5/15/09 15:30	501	47	1517	415
5/28/09 16:30	2138	84	3132	405
6/11/09 16:40	1550	44	1004	325
7/15/09 10:50	4827	21	2225	12653
7/20/09 12:30	2747	14	1210	13893
7/23/09 12:00	1858	10	777	13191
7/28/09 12:15	1892	11	820	13680
8/3/09 12:05	1664	10	675	14361
8/10/09 12:40	1576	14	899	13391
8/17/09 12:30	1924	18	1155	13604
8/24/09 12:25	725	8	358	11718
8/31/09 12:30	374	4	121	12472
9/9/09 12:40	394	5	165	10543

Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #2 - groundwater concentrations over time at pump and treat well, RW 2a

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
4/4/09 12:05	40	55	218	470
4/5/09 7:25	36	56	200	453
4/5/09 7:25	33	53	191	452
4/6/09 8:35	34	58	201	485
4/7/09 7:25	38	55	201	452
4/8/09 7:25	36	57	205	459
4/9/09 7:30	121	57	208	466
4/10/09 7:50	254	59	217	446
4/11/09 10:30	364	55	363	503
4/12/09 8:45	200	58	225	435
4/13/09 8:25	215	56	225	438
4/14/09 7:40	294	57	236	445
4/15/09 16:45	443	63	286	455
4/16/09 8:00	463	60	321	445
4/17/09 8:20	461	58	341	432
4/18/09 7:40	466	57	389	453
4/18/09 7:40	499	65	444	477
4/19/09 7:40	552	61	449	434
4/20/09 7:50	593	61	538	481
4/20/09 7:50	555	61	518	461
4/21/09 8:05	564	61	535	455
4/22/09 7:50	550	59	574	469
4/22/09 7:50	539	62	557	447
4/23/09 10:30	554	60	607	465
4/24/09 11:20	589	63	622	459
4/25/09 8:40	590	60	677	457
4/26/09 11:05	628	59	712	473
4/27/09 8:05	606	61	655	464
4/28/09 8:10	525	59	623	446
4/29/09 8:45	540	56	653	450
4/30/09 8:30	535	58	693	443
5/1/09 6:35	550	54	718	442
5/3/09 10:35	697	61	778	467
5/4/09 13:55	652	58	788	439
5/5/09 8:20	656	58	744	412
5/6/09 9:00	556	60	721	416
5/7/09 8:25	557	58	794	458
5/8/09 8:20	624	59	858	449
5/9/09 8:00	645	57	870	494
5/10/09 14:50	2794	73	1400	484
5/11/09 7:20	3190	72	2942	686
5/12/09 8:45		68	3308	726

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
5/13/09 8:55	3248	67	3536	638
5/14/09 8:15		69	4546	666
5/15/09 8:50	3693	71	5163	720
5/16/09 8:25		69	5183	674
5/17/09 15:05	3594	66	5371	634
5/18/09 8:50		68	5450	622
5/19/09 8:15	3224	59	5065	658
5/20/09 8:40		60	4981	577
5/21/09 8:50	2949	64	5178	595
5/22/09 8:35		65	4735	599
5/23/09 7:10	2852	65	5356	617
5/24/09 11:20		61	4899	571
5/25/09 8:55	2716	62	5611	603
5/26/09 15:00		62	4861	567
5/27/09 9:05	2645	58	4220	505
5/28/09 8:50		63	4915	509
5/29/09 9:00	3754	64	5767	547
5/30/09 8:00		64	5569	544
5/31/09 12:20	2937	55	4631	527
6/1/09 7:20	2680	57	4726	534
6/5/09 10:00	7065	84	9104	770
6/6/09 8:15		65	5547	500
6/7/09 10:05	6113	77	6985	707
6/8/09 8:10		75	7556	643
6/9/09 10:05	6026	78	9243	699
6/10/09 8:20		76	8885	677
6/11/09 8:00	4280	71	7479	602
6/12/09 8:15		61	5739	591
6/13/09 7:45	2538	62	5395	582
6/14/09 12:45		53	4390	514
6/15/09 8:40	2080	56	4430	531
6/16/09 7:50		62	4616	631
6/17/09 8:20	1773	57	3908	521
6/18/09 10:35		53	3746	452
6/19/09 9:05	1566	54	3805	485
6/20/09 7:55		59	4063	482
6/21/09 12:35	1563	53	3511	456
6/22/09 8:25		57	4002	500
6/23/09 8:15	1650	51	3144	462
6/24/09 9:05		51	3294	462
6/25/09 8:45	1666	52	3104	456
6/26/09 8:00		53	3239	462
6/27/09 8:25	1589	55	3138	484
6/28/09 14:35		53	3906	505
6/29/09 8:45	1783	52	3385	465

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
6/30/09 8:20		51	3339	471
7/1/09 7:20	1498	51	3334	466
7/3/09 9:10	2122	56	4592	526
7/4/09 12:05	1642	54	3200	448
7/5/09 9:15	2054	54	3603	467
7/6/09 9:40	2428	51	4079	460
7/10/09 9:30	3316	71	7998	564
7/12/09 12:30	2286	55	3424	464
7/13/09 11:30	1755	51	2758	379
7/14/09 8:20	1600	50	2525	405
7/15/09 9:05	1317	51	2001	414
7/20/09 11:05	350	48	433	394
7/23/09 11:00	198	46	293	419
7/28/09 11:15	95	43	211	410
8/3/09 11:05	121	47	232	424
8/10/09 11:45	66	47	182	421
8/17/09 11:10	58	45	163	408
8/24/09 11:20	176	47	212	446
8/24/09 11:20	165	45	198	440
8/31/09 11:25	110	46	156	431
9/9/09 11:40	78	44	160	428

Blank = no data available (Usually this means that the signal switched detectors during analysis and only a subset of samples were re-diluted and re-run.)
Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

Field experiment #2 - groundwater concentrations over time in influent solutions

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
4/4/09 16:30	144	45	1118	376
4/6/09 17:45	158	45	1137	388
4/8/09 15:05	154	43	909	375
4/11/09 17:25	124	194	1885	389
4/12/09 14:40	115	159	1636	372
4/14/09 15:00	121	767	6693	383
4/16/09 14:45	101	282	3448	372
4/18/09 16:45	103	167	2088	387
4/20/09 13:20	110	150	1877	383
4/22/09 13:30	116	72	990	378
4/24/09 16:20	118	46	655	374
4/26/09 16:40	116	47	640	366
4/28/09 16:50	118	40	572	365
4/30/09 16:55	117	38	527	362
5/3/09 17:50	114	40	665	373
5/5/09 17:00	115	42	707	372
5/7/09 14:05	110	41	730	364
5/7/09 17:35	269	53	2066	350
5/8/09 16:55	315	55	2152	357
5/10/09 14:55	245	53	1926	350
5/12/09 16:40	209	54	1596	365
5/14/09 17:05	179	54	1207	368
5/16/09 12:45	136	49	1010	367
5/18/09 17:25	124	48	952	357
5/20/09 17:10	118	46	828	345
5/22/09 17:05	124	49	943	332
5/24/09 16:55	138	50	1066	339
5/26/09 15:05	135	51	1114	353
5/28/09 17:10	145	48	1127	368
5/30/09 15:20	145	48	994	348
6/2/09 13:25	125	46	882	360
6/4/09 16:25	125	47	865	355
6/6/09 15:30	122	47	817	354
6/8/09 17:25	122	46	744	340
6/10/09 17:00	114	44	637	340
6/12/09 16:50	118	44	682	338
6/14/09 17:10	125	45	723	342
6/16/09 16:45	127	46	888	343
6/18/09 16:45	139	50	1165	338
6/20/09 15:00	143	47	1007	334
6/22/09 17:25	139	54	1011	361
6/24/09 16:55	123	48	925	339
6/26/09 17:20	120	47	876	345

Date/Time	Al (µg/L)	Mn (µg/L)	Fe (µg/L)	As (µg/L)
6/28/09 14:45	125	46	849	331
6/30/09 17:05	126	46	906	331
7/2/09 16:55	131	48	1004	335

Due to elevated Al in blanks, values of <100 µg/L Al are not trustworthy.

5.18.3 Br data from 2008 tracer experiment (field experiment #1)

Field experiment #1 - groundwater concentrations over time at the sampling well, CW 1 – (full well)

Date	Br selective electrode Br (mg/L)	IC Br (mg/L)
6/24/08 21:53	0.20	U
6/24/08 23:53	0.25	U
6/25/08 1:53	0.20	U
6/25/08 3:53	0.25	U
6/25/08 5:53	0.19	U
6/25/08 7:53	0.23	U
6/25/08 9:53	0.20	U
6/25/08 11:53	0.18	U
6/25/08 13:53	0.20	U
6/25/08 15:53	0.23	0.09
6/25/08 17:55	0.31	0.15
6/25/08 19:55	0.37	0.17
6/25/08 21:55	0.39	0.21
6/25/08 23:55	0.39	0.22
6/26/08 1:55	0.40	0.20
6/26/08 3:55	0.44	0.19
6/26/08 5:55	0.40	0.22
6/26/08 6:25	0.45	0.16
6/26/08 7:55	0.40	0.19
6/26/08 8:15	0.37	0.29
6/26/08 10:05	0.31	0.10
6/26/08 11:55	0.46	0.26
6/26/08 12:30	0.56	0.28
6/26/08 14:05	0.46	0.27
6/26/08 15:55	0.38	0.14
6/26/08 16:05	0.61	0.47
6/26/08 17:45	0.88	0.70
6/26/08 17:55	0.94	0.64
6/26/08 19:55	1.08	0.80
6/26/08 21:55	1.08	0.71
6/26/08 23:55	1.18	0.79
6/27/08 1:55	1.14	0.74
6/27/08 3:55	1.33	0.92
6/27/08 5:55	0.76	0.42
6/27/08 6:30	2.26	2.39
6/27/08 7:55	1.43	1.11
6/27/08 8:05	1.30	1.17
6/27/08 12:30	1.32	1.02
6/27/08 14:15	1.04	0.71

Date	Br selective electrode Br (mg/L)	IC Br (mg/L)
6/27/08 16:05	1.15	0.97
6/27/08 16:55	1.09	1.04
6/27/08 18:55	1.18	1.24
6/27/08 20:55	1.13	1.04
6/27/08 22:55	1.47	1.46
6/28/08 0:55	1.49	1.36
6/28/08 2:55	1.77	2.09
6/28/08 4:55	1.64	1.65
6/28/08 6:35	1.60	1.83
6/28/08 6:55	1.93	1.93
6/28/08 8:10	1.64	1.79
6/28/08 10:20	1.77	1.73
6/28/08 13:15	2.42	2.23
6/28/08 14:30	2.13	2.25
6/28/08 17:35	3.14	2.83
6/28/08 18:00	2.89	3.22
6/28/08 20:00	2.81	2.93
6/28/08 22:00	2.76	2.62
6/29/08 0:00	2.83	2.94
6/29/08 2:00	2.65	2.45
6/29/08 4:00	2.84	2.89
6/29/08 6:00	3.02	2.99
6/29/08 6:30	2.80	2.93
6/29/08 8:05	2.50	2.96
6/29/08 10:25	3.20	3.33
6/29/08 12:50	3.56	4.08
6/29/08 15:45	3.41	3.89
6/29/08 17:55	3.27	3.95
6/29/08 19:55	2.99	3.51
6/29/08 21:55	3.00	3.56
6/29/08 23:55	3.02	3.53
6/30/08 1:55	2.60	3.23
6/30/08 3:55		2.98
6/30/08 5:55	2.50	2.73
6/30/08 7:55	2.41	2.58
6/30/08 8:20	2.20	2.62
6/30/08 10:35	2.06	2.01
6/30/08 13:25	2.29	2.44
6/30/08 16:15	2.63	2.25
6/30/08 17:55	2.09	1.99
6/30/08 19:55	1.91	1.95
6/30/08 21:55	2.05	2.12
6/30/08 23:55	1.51	1.09
7/1/08 1:55	1.43	1.25

Date	Br selective electrode Br (mg/L)	IC Br (mg/L)
7/1/08 3:55	1.35	1.01
7/1/08 5:55	1.01	0.76
7/1/08 8:05	0.89	1.28
7/1/08 10:20	1.15	0.98
7/1/08 12:05	0.98	1.03
7/1/08 16:20	0.96	0.78
7/1/08 17:35	0.84	0.77
7/1/08 17:56	0.98	0.65
7/1/08 19:56	1.11	0.79
7/1/08 21:56	0.73	0.60
7/1/08 23:56	1.00	0.68
7/2/08 1:56	0.63	0.36
7/2/08 3:56	0.64	0.38
7/2/08 12:10	0.53	0.14
7/2/08 16:15	0.37	0.01
7/2/08 17:55	0.33	0.03
7/2/08 21:55	0.28	U
7/3/08 1:55	0.24	0.10
7/3/08 5:55	0.22	0.05
7/3/08 8:10	0.17	U

U = undetected (sample run undiluted)

Field experiment #1 - groundwater concentrations over time at the sampling well, CW 1 – (above packer)

Date	**Br selective electrode Br (mg/L)**
6/28/08 11:45	2.92
6/28/08 16:35	3.49
6/29/08 9:45	4.26
6/29/08 13:50	5.16
6/30/08 11:55	3.40
7/1/08 13:50	1.22

Field experiment #1 - groundwater concentrations over time at the sampling well, CW 1 – (below packer)

Date	**Br selective electrode Br (mg/L)**
6/25/08 11:20	0.18
6/25/08 15:00	0.22
6/26/08 9:25	0.22
6/26/08 13:30	0.25
6/26/08 15:30	0.28
6/27/08 9:05	0.33
6/27/08 13:20	0.37
6/27/08 15:25	0.37
6/28/08 9:35	0.50
6/28/08 13:50	0.63
6/29/08 11:30	0.61
6/29/08 16:35	0.65
6/30/08 10:00	0.36
6/30/08 15:25	0.40
7/1/08 14:35	0.26

Field experiment #1 - Bromide concentration of influent solutions

Date	**IC Br (mg/L)**
Influent 1	128.58
Influent 2	97.85
Influent 3	124.46
Influent 4	123.43
Influent 5	127.85
Influent 6	133.66

5.18.4 IC data from oxalic acid injection experiment (field experiment #2)

Field experiment #2 - groundwater concentrations over time at the sampling well, CW 1 – (above packer)

Date	Br (mg/L)	Oxalate (mM)
4/3/09 9:30	U	0.00
4/4/09 10:45	U	U
4/4/09 15:50	U	0.00
4/5/09 1:39	U	0.01
4/5/09 5:39	U	U
4/5/09 7:20	U	U
4/5/09 7:20	U	U
4/5/09 10:30	U	U
4/5/09 14:35	U	0.00
4/5/09 17:20	U	U
4/5/09 21:39	U	U
4/5/09 22:44	U	U
4/6/09 2:44	U	U
4/6/09 6:44	U	U
4/6/09 8:30	U	U
4/6/09 10:30	U	U
4/6/09 13:50	U	U
4/6/09 13:50	U	U
4/6/09 17:25	U	0.00
4/6/09 22:46	U	U
4/7/09 2:46	U	U
4/7/09 6:46	U	U
4/7/09 7:20	U	U
4/7/09 16:20	U	0.00
4/7/09 16:20	0.12	U
4/7/09 22:15	0.15	0.00
4/8/09 2:15	0.14	0.02
4/8/09 6:15	0.14	0.03
4/8/09 7:20	0.16	0.04
4/8/09 10:20	0.16	0.03
4/8/09 14:25	U	0.00
4/8/09 14:25	U	0.00
4/8/09 17:30	0.24	0.04
4/9/09 2:41	0.25	0.07
4/9/09 6:41	0.25	0.06
4/9/09 7:25	0.30	0.10
4/9/09 10:50	0.26	0.10
4/9/09 14:10	0.28	0.12
4/9/09 14:10	0.29	0.10
4/9/09 17:15	0.30	0.14

Date	Br (mg/L)	Oxalate (mM)
4/9/09 22:41	0.42	0.06
4/10/09 2:03	0.12	0.01
4/10/09 6:03	0.13	0.00
4/10/09 7:45	0.44	0.16
4/10/09 14:25	0.42	0.10
4/10/09 14:25	0.39	0.13
4/10/09 22:03	0.30	0.11
4/11/09 7:45	0.57	0.53
4/11/09 10:25	0.59	0.35
4/11/09 16:15	0.45	0.20
4/12/09 2:43	0.26	0.04
4/12/09 6:43	0.30	0.03
4/12/09 8:40	0.84	0.19
4/12/09 10:43	0.78	0.22
4/12/09 13:35	0.65	0.17
4/12/09 17:00	0.84	0.35
4/12/09 22:43	0.48	0.10
4/13/09 8:20	0.96	0.38
4/13/09 13:05	1.08	0.54
4/13/09 17:00	1.27	0.68
4/14/09 7:35	1.83	0.41
4/14/09 10:50	1.12	0.36
4/14/09 14:25	0.69	0.32
4/14/09 17:00	1.36	0.67
4/15/09 8:00	1.48	0.78
4/15/09 11:20	1.59	0.92
4/15/09 16:40	1.46	0.90
4/16/09 7:55	1.35	0.88
4/16/09 7:55	1.50	0.84
4/16/09 14:05	1.49	1.00
4/16/09 17:10	1.21	1.00
4/17/09 8:15	1.53	1.06
4/17/09 8:15	2.59	0.89
4/17/09 13:05	1.38	0.94
4/17/09 16:45	1.44	1.13
4/18/09 7:35	1.26	1.50
4/18/09 7:35	1.34	1.62
4/18/09 13:15	1.38	0.02
4/18/09 17:00	1.22	1.59
4/19/09 7:35	0.54	0.78
4/19/09 7:35	0.40	0.50
4/19/09 11:35	0.69	1.01
4/20/09 7:45	1.32	1.77
4/20/09 7:45	1.49	1.90
4/20/09 13:10	1.75	2.31

Date	Br (mg/L)	Oxalate (mM)
4/20/09 17:00	1.71	2.13
4/20/09 17:10	1.52	2.07
4/21/09 8:00	1.39	1.72
4/21/09 8:00	1.40	1.72
4/21/09 12:15	1.44	1.83
4/21/09 17:05	1.00	1.00
4/22/09 7:45	0.57	0.44
4/22/09 13:15	1.41	1.83
4/22/09 17:00	0.83	1.35
4/23/09 10:25	1.16	1.17
4/23/09 14:15	1.31	1.45
4/24/09 11:15	1.25	1.43
4/24/09 16:50	1.59	2.27
4/24/09 16:50	1.49	2.11
4/25/09 8:35	1.52	2.01
4/25/09 17:00	0.87	0.93
4/25/09 17:00	0.89	0.93
4/26/09 16:30	1.76	2.46
4/27/09 8:00	1.55	2.19
4/27/09 8:00	1.59	2.28
4/27/09 16:25	1.51	2.09
4/28/09 8:05	1.53	2.13
4/28/09 8:05	1.52	2.22
4/28/09 16:50	1.41	2.00
4/29/09 8:40	1.50	2.14
4/29/09 16:40	1.59	2.31
4/30/09 8:25	1.50	2.18
4/30/09 8:25	1.43	2.07
4/30/09 17:50	1.54	2.30
5/1/09 6:30	1.66	2.52
5/1/09 6:30	1.61	2.39
5/3/09 10:30	0.87	1.25
5/3/09 10:30	1.05	1.56
5/3/09 17:40	0.90	1.31
5/4/09 13:50	2.05	2.90
5/4/09 17:35	1.77	2.60
5/5/09 8:15	1.51	2.09
5/5/09 8:15	1.50	2.09
5/5/09 16:50	1.31	1.95
5/6/09 8:55	1.50	2.06
5/6/09 16:50	1.63	2.22
5/8/09 8:15	1.33	1.82
5/8/09 16:45	1.51	1.99
5/9/09 7:55	1.69	2.19
5/9/09 7:55	1.72	2.28

Date	Br (mg/L)	Oxalate (mM)
5/10/09 14:45	2.64	0.53
5/11/09 7:15	3.17	4.61
5/12/09 8:40	3.03	2.08
5/13/09 8:50	2.96	2.73
5/14/09 8:10	3.23	3.87
5/15/09 8:45	3.06	3.34
5/16/09 8:20	2.02	7.80
5/16/09 12:35	2.62	10.08
5/17/09 15:00	2.39	
5/17/09 17:40	2.67	8.56
5/18/09 8:45	2.73	12.06
5/18/09 8:45	2.73	12.06
5/18/09 14:15	2.63	12.30
5/18/09 17:15	2.98	12.39
5/19/09 8:10	2.86	12.19
5/19/09 12:55	2.69	11.94
5/19/09 16:55	2.58	11.72
5/20/09 8:35	2.92	11.79
5/20/09 8:35	2.97	12.21
5/20/09 17:00	2.78	11.84
5/21/09 8:45	2.62	10.95
5/21/09 17:05	3.10	13.04
5/22/09 8:30	2.64	10.72
5/22/09 14:30	3.05	11.65
5/22/09 16:55	3.37	12.63
5/23/09 7:05	2.93	11.55
5/23/09 9:45	3.06	10.59
5/25/09 8:50	3.41	15.63
5/25/09 15:40	3.29	12.94
5/26/09 7:15	5.08	27.27
5/26/09 14:55	0.72	3.78
5/26/09 17:20	1.19	4.98
5/27/09 9:00	2.83	3.59
5/27/09 9:00	2.46	
5/27/09 17:00	1.97	
5/28/09 8:45	3.44	12.48
5/28/09 8:45	3.66	12.98
5/28/09 10:00	4.80	16.64
5/28/09 10:00	3.51	13.50
5/28/09 17:00	3.71	15.20
5/30/09 7:55	5.50	15.01
5/30/09 15:10	3.14	10.70
5/31/09 12:15	2.94	11.25
5/31/09 12:15	3.12	11.39
5/31/09 17:00	5.31	15.14

Date	Br (mg/L)	Oxalate (mM)
6/1/09 7:15	3.36	13.20
6/3/09 9:10	12.98	18.49
6/3/09 15:15	4.50	5.97
6/4/09 8:40	7.60	23.59
6/5/09 9:25	2.23	0.05
6/7/09 10:00	1.77	7.03
6/7/09 16:00	1.58	5.92
6/9/09 10:00	0	2.97
6/10/09 7:55	1.07	5.99
6/10/09 8:15	2.47	9.55
6/10/09 9:40	3.98	19.99
6/10/09 16:45	2.28	9.18
6/11/09 17:15	1.15	5.24
6/12/09 8:10	3.10	4.63
6/13/09 7:40		4.34
6/13/09 7:40		4.31
6/13/09 8:55		10.13
6/13/09 14:00		3.55
6/14/09 12:40		3.07
6/14/09 16:55		5.60
6/15/09 8:35		5.68
6/16/09 7:45		6.51
6/16/09 8:15		4.74
6/16/09 16:30		4.94
6/17/09 16:30	3.21	
6/18/09 10:30		3.30
6/19/09 9:00		6.00
6/20/09 7:50	3.13	8.09
6/20/09 14:45		9.61
6/21/09 12:30	3.47	9.67
6/21/09 17:00		10.80
6/22/09 8:20		7.37
6/22/09 8:20		8.02
6/23/09 8:10		5.90
6/24/09 9:00	4.04	9.48
6/25/09 8:40		8.29
6/26/09 17:05		7.24
6/27/09 8:20		11.01
6/27/09 12:25		9.85
6/28/09 14:30	2.98	
6/29/09 8:40		11.01
6/29/09 16:45		9.55
6/30/09 8:15		10.51
6/30/09 16:50		11.76

Date	Br (mg/L)	Oxalate (mM)
7/1/09 7:15		13.69
7/1/09 16:25		12.07
7/2/09 7:00		22.36
7/2/09 16:45	6.12	16.51
7/3/09 9:05		2.28
7/4/09 16:50		7.88
7/5/09 9:10		6.43
7/6/09 12:50		5.27
7/8/09 11:00	4.61	10.12
7/9/09 7:55		10.61
7/14/09 8:15	2.28	3.36
7/15/09 9:00		2.97
7/20/09 11:00	0.35	0.08
7/20/09 11:15	0.21	U
7/23/09 10:55	0.32	0.05
7/28/09 11:10	0.25	0.03
8/3/09 11:00	0.23	0.02
8/10/09 11:40	U	0.01
8/17/09 11:05	U	0.00
8/24/09 11:15	U	0.00
8/24/09 11:15	U	0.00
8/31/09 11:20	U	0.00
9/9/09 11:35	U	U

U = undetected (sample run undiluted); different from 0.00 which has a value in the 3rd or 4th decimal place.
Blank = sample dilution either too much or too little to quantify properly

Field experiment #2 - groundwater concentrations over time at the sampling well, CW 1 – (below packer)

Date	**Br (mg/L)**	**Oxalate (mM)**
6/6/09 9:50	18.9	16.7
6/10/09 16:50	2.98	15.31
6/11/09 9:30	2.50	14.85
6/11/09 16:20	3.09	12.39
6/13/09 14:10	4.70	9.47
6/14/09 13:50	9.79	18.77
6/14/09 17:05	8.98	18.51
6/16/09 9:20	4.96	11.07
6/16/09 16:40	4.89	9.29
6/17/09 9:45	4.21	7.98
6/17/09 16:40	5.36	10.14
6/19/09 9:50	4.66	12.18
6/20/09 9:20	1.31	9.83
6/20/09 14:55	1.36	9.34
6/21/09 13:45	1.34	10.16
6/21/09 17:10	1.61	8.49
6/25/09 16:50	4.19	9.81
6/27/09 9:30	4.51	10.90
6/27/09 12:35	4.41	11.16
6/28/09 14:40	4.44	12.30
6/29/09 10:05	4.31	11.57
6/29/09 16:55	4.29	10.98
6/30/09 9:30	4.10	10.69
6/30/09 17:00	4.51	11.87
7/1/09 8:15	4.23	10.66
7/1/09 16:35	3.57	7.69
7/8/09 11:05	2.88	3.08
7/15/09 10:15	0.14	0.00
7/20/09 11:15	0.14	0.00
7/23/09 11:05	0.00	0.00
7/28/09 11:20	U	U
8/3/09 11:10	U	U
8/3/09 11:10	0.13	0.00
8/17/09 11:15	U	U
8/31/09 11:30	U	U
9/9/09 11:45	U	U

6/3 and 6/4 samples too dilute
U = undetected (sample run undiluted); different from 0.00 which has a value in the 3rd or 4th decimal place.
Blank = sample dilution either too much or too little to quantify properly
Red = bordering on too dilute for Br

Field experiment #2 - groundwater concentrations over time at injection well, CW 3.2

Date	Br (mg/L)	Oxalate (mM)
4/3/09 8:55	U	U
4/28/09 12:00	46.8	91.2
6/11/09 16:40	74.1	322.9
7/15/09 10:05	0.17	0.00
7/20/09 12:30	0.13	0.02
7/23/09 12:00	0.22	0.00
7/28/09 12:15	0.22	0.00
8/3/09 12:05	0.22	0.00
8/24/09 12:25	U	0.00
8/31/09 12:30	U	0.00
9/9/09 12:40	U	U

U = undetected (sample run undiluted); different from 0.00 which has a value in the 3rd or 4th decimal place.
The 4/28 sample was taken during Phase I injection; the 7/15 sample was taken during Phase II injection. All other samples were taken before or after injection periods.

Field experiment #2 - groundwater concentrations over time at the pump and treat well, RW 2a

Date	Br (mg/L)	Oxalate (mM)
4/4/09 12:05	U	0.00
4/4/09 16:00	U	0.00
4/5/09 7:25	U	0.00
4/5/09 7:25	U	0.00
4/5/09 10:40	U	0.00
4/5/09 17:25	U	0.00
4/6/09 8:35	U	0.00
4/6/09 13:55	U	0.00
4/6/09 13:55	U	0.00
4/7/09 7:25	U	0.00
4/7/09 16:25	U	0.00
4/8/09 7:25	U	0.00
4/8/09 14:25	U	0.00
4/9/09 7:30	U	0.00
4/9/09 14:15	U	0.00
4/10/09 7:50	U	0.00
4/11/09 10:30	U	0.00
4/12/09 8:45	U	0.00
4/12/09 17:05	U	0.00
4/13/09 8:25	U	0.00
4/14/09 7:40	U	0.00
4/14/09 17:05	U	0.00
4/14/09 17:05	U	0.00
4/15/09 8:05	U	0.00
4/15/09 16:45	U	0.00
4/16/09 8:00	U	0.00
4/16/09 17:15	U	0.00
4/17/09 8:20	U	0.00
4/17/09 16:50	0.13	0.00
4/18/09 7:40	U	0.00
4/18/09 7:40	U	0.00
4/18/09 17:05	U	0.00
4/19/09 7:40	U	0.00
4/20/09 7:50	0.12	0.00
4/20/09 7:50	U	0.00
4/20/09 17:05	U	0.00
4/20/09 17:15	U	0.00
4/21/09 17:10	0.00	0.00
4/22/09 7:50	0.27	0.27
4/22/09 7:50	U	0.00
4/22/09 17:05	U	0.00
4/23/09 10:30	U	0.00

Date	Br (mg/L)	Oxalate (mM)
4/23/09 14:20	U	0.00
4/24/09 11:20	U	0.00
4/24/09 16:55	U	0.00
4/25/09 8:40	U	0.00
4/25/09 17:05	U	0.00
4/26/09 11:05	0.12	0.00
4/26/09 16:35	0.12	0.00
4/27/09 8:05	U	0.00
4/27/09 16:30	U	0.00
4/28/09 8:10	U	0.00
4/28/09 16:55	U	0.00
4/29/09 8:45	U	0.00
4/29/09 16:45	U	0.00
4/30/09 8:30	U	0.00
4/30/09 17:55	U	0.00
5/1/09 6:35	U	0.00
5/1/09 6:35	0.07	0.00
5/3/09 10:35	0.04	0.00
5/3/09 17:45	0.05	0.00
5/4/09 13:55	0.04	0.00
5/4/09 17:40	0.07	0.00
5/5/09 8:20	0.04	0.00
5/5/09 16:55	0.04	0.00
5/6/09 9:00	U	0.00
5/6/09 16:55	0.04	0.00
5/8/09 8:20	U	0.00
5/8/09 16:50	0.12	0.00
5/9/09 8:00	U	0.00
5/10/09 14:50	0.18	0.18
5/11/09 7:20	0.21	0.21
5/12/09 8:45	0.23	0.23
5/13/09 8:55	0.22	0.22
5/14/09 8:15	0.23	0.23
5/15/09 8:50	0.26	0.26
5/16/09 8:25	0.14	0.00
5/16/09 12:40	0.17	0.17
5/17/09 15:05	0.14	0.00
5/17/09 17:45	0.13	0.00
5/18/09 8:45	0.14	0.00
5/18/09 17:20	0.15	0.15
5/19/09 8:15	0.12	0.00
5/19/09 17:00	0.13	0.00
5/20/09 8:40	0.14	0.00
5/20/09 17:05	0.14	0.00
5/21/09 8:50	0.13	0.00

Date	Br (mg/L)	Oxalate (mM)
5/21/09 17:10	0.13	0.00
5/22/09 8:35	0.13	0.00
5/22/09 8:35	0.18	0.18
5/22/09 17:00	0.14	0.00
5/23/09 7:10	0.13	0.00
5/23/09 9:50	0.14	0.00
5/25/09 8:55	0.15	0.00
5/26/09 15:00	0.14	0.00
5/26/09 17:25	0.15	0.00
5/27/09 9:05	0.12	0.00
5/27/09 17:05	0.13	0.00
5/28/09 8:50	0.14	0.00
5/28/09 17:05	0.16	0.16
5/30/09 8:00	0.17	0.17
5/30/09 15:15	0.21	0.21
5/31/09 12:20	0.16	0.16
5/31/09 17:05	0.16	0.16
6/1/09 7:20	0.14	0.00
6/6/09 8:15	0.43	0.43
6/7/09 10:05	0.24	0.24
6/10/09 8:20	0.19	0.19
6/10/09 16:50	0.19	0.19
6/11/09 8:00	0.19	0.19
6/11/09 17:20	0.18	0.18
6/12/09 8:15	0.25	0.25
6/13/09 7:45		
6/13/09 14:05		
6/14/09 12:45	0.24	0.24
6/14/09 17:00		
6/15/09 8:40		
6/16/09 7:50		
6/16/09 8:20		
6/16/09 16:35		
6/17/09 16:35		
6/18/09 10:35	0.24	0.24
6/19/09 16:50		
6/20/09 7:55	0.24	0.24
6/20/09 14:50		
6/21/09 12:35		
6/21/09 17:05		
6/22/09 17:15	0.24	0.24
6/23/09 8:15		
6/24/09 9:05	0.24	0.24
6/25/09 8:45		

Date	Br (mg/L)	Oxalate (mM)
6/26/09 8:00	0.24	0.24
6/27/09 8:25		
6/27/09 12:30		
6/28/09 14:35	0.25	0.25
6/29/09 8:45		
6/29/09 16:50		
6/30/09 8:20	0.22	0.22
6/30/09 16:55		
7/1/09 7:20	0.26	0.26
7/1/09 16:30		
7/3/09 9:10	0.23	0.23
7/4/09 12:05	0.26	0.26
7/5/09 9:15		
7/6/09 9:40	0.30	0.30
7/10/09 9:30	0.32	0.32
7/14/09 8:20	0.27	0.27
7/15/09 9:05	0.29	0.29
7/20/09 11:05	U	0.00
7/23/09 11:00	U	0.00
7/28/09 11:15	0.10	0.00
8/3/09 11:05	U	0.00
8/10/09 11:45	U	0.00
8/17/09 11:10	U	0.00
8/18/09 11:25	U	0.00
8/24/09 11:20	U	0.00
8/24/09 11:20	U	0.00
8/31/09 11:25	U	0.00
9/9/09 11:40	U	0.00

U = undetected (sample run undiluted); different from 0.00 which has a value in the 3rd or 4th decimal place.
Blank = One sample run was not good for quantifying Br in RW 2a samples due to overlap in Br and NO_3^- peaks.

Note: There is little to no Br in the Phase I samples at the pump and treat well, RW 2a, and the recovery of Br is still very high at that one well (> 90%). However, it is worth noting that only ~13% of the total injected mass of Br was injected during Phase I with ~87% injected during Phase II.

5.18.5 SF_6 concentrations during 2008 tracer experiment (field experiment #1)

Field experiment #1 - SF_6 concentrations over time at the sampling well, CW 1 – (entire well)

Note: No bubble corrections were included as they were determined to have only a minor impact on calculations.

Sample Date/Time	SF_6 Conc. (ccSTP/cc)	Decision for use in calculations
6/26/08 10:05	1.82E-12	delete sample point, replicates >40% different
6/26/08 10:05	4.81E-13	
6/26/08 12:30	8.80E-13	
6/26/08 16:05	1.05E-12	
6/26/08 17:45	1.59E-12	
6/26/08 17:45	1.67E-12	
6/27/08 6:30	1.91E-12	
6/27/08 8:05	2.22E-12	
6/27/08 8:05	2.12E-12	
6/27/08 10:05	2.25E-12	
6/30/08 10:35	5.35E-12	
6/27/08 12:30	1.64E-12	
6/27/08 14:15	1.25E-12	
6/28/08 14:45	4.66E-12	
6/29/08 10:25	7.34E-12	
6/30/08 6:40	6.25E-12	
6/30/08 8:20	4.90E-12	
6/30/08 13:25	4.85E-12	
6/30/08 16:15	4.23E-12	
6/30/08 17:45	4.97E-12	
7/1/08 10:20	2.19E-12	
7/1/08 12:05	2.02E-12	
7/1/08 12:05	2.18E-12	
7/2/08 8:20	6.62E-13	
7/3/08 16:10	3.78E-13	delete sample point, replicates >40% different
7/3/08 16:10	2.24E-13	

Field experiment #1 - SF_6 concentrations over time at the sampling well, CW 1 – (above packer)

Note: Sample points from above and below packer were not included in SF_6 recovery calculations. No bubble corrections were included as they were determined to have only a minor impact on calculations.

Sample Date/Time	**SF_6 Conc. (ccSTP/cc)**	**Note**
6/30/08 11:55	7.06E-12	
7/1/08 13:50	2.29E-12	

Field experiment #1 - SF_6 concentrations over time at the sampling well, CW 1 – (below packer)

Note: Sample points from above and below packer were not included in SF_6 recovery calculations. No bubble corrections were included as they were determined to have only a minor impact on calculations.

Sample Date/Time	**SF_6 Conc. (ccSTP/cc)**	**Note**
6/26/08 13:30	1.60E-13	
6/27/08 9:05	3.22E-13	
6/27/08 9:05	1.96E-13	replicates >40% different
6/27/08 13:20	3.13E-13	
6/27/08 13:20	2.55E-13	
6/27/08 15:25	3.42E-13	
6/30/08 10:00	5.37E-13	
6/30/08 15:25	7.38E-13	
7/1/08 14:35	1.78E-13	
7/1/08 14:35	2.60E-13	

Field experiment #1 - SF_6 concentrations over time at the pump and treat well, RW 2a

Note: No bubble corrections were included as they were determined to have only a minor impact on calculations.

Sample Date/Time	**SF_6 Conc. (ccSTP/cc)**	**Decision for use in calculations**
6/26/08 6:25	1.17E-13	
6/26/08 8:15	7.85E-14	
6/26/08 10:05	2.02E-13	delete sample point, replicates >40% different
6/26/08 10:05	8.16E-14	
6/26/08 16:05	1.12E-13	
6/26/08 17:45	2.24E-13	
6/27/08 8:05	1.14E-13	
6/28/08 6:35	2.72E-13	
6/28/08 17:35	2.10E-13	delete sample point, replicates >40% different
6/28/08 17:35	1.40E-13	
6/29/08 12:50	1.40E-13	
6/29/08 12:50	1.44E-13	
6/29/08 15:45	1.47E-13	
6/29/08 15:45	1.31E-13	
6/30/08 6:40	1.56E-13	
6/30/08 6:40	1.62E-13	
6/30/08 8:20	1.74E-13	
6/30/08 8:20	1.76E-13	
6/30/08 17:45	2.85E-13	avg replicates
6/30/08 17:45	2.19E-13	
7/1/08 6:20	1.95E-13	
7/1/08 6:20	2.32E-13	
7/1/08 16:20	1.65E-13	delete sample point, replicates >40% different
7/1/08 16:20	3.31E-13	
7/1/08 17:35	2.70E-13	
7/2/08 10:10	2.33E-13	
7/2/08 10:10	2.32E-13	
7/2/08 16:15	2.00E-13	
7/2/08 16:15	2.25E-13	
7/3/08 6:25	4.32E-14	delete sample point, replicates >40% different
7/3/08 6:25	9.06E-14	
7/3/08 10:05	0.00E+00	
7/3/08 10:05	1.25E-13	use this replicate

Sample Date/Time	**SF_6 Conc. (ccSTP/cc)**	**Decision for use in calculations**
7/3/08 12:30	2.18E-13	delete sample point, most replicates >40% different
7/3/08 12:30	1.02E-13	
7/3/08 12:30	1.88E-13	
7/3/08 12:30	1.10E-13	
7/3/08 14:15	2.28E-13	
7/3/08 14:15	2.16E-13	
7/3/08 16:10	9.63E-14	
7/3/08 16:10	1.13E-13	
7/3/08 17:45	2.11E-13	
7/3/08 17:45	1.84E-13	
7/10/08 10:20	4.90E-14	avg replicates
7/10/08 10:20	6.44E-14	

5.18.6 SF$_6$ concentrations during oxalic acid injection experiment (field experiment #2)

Field experiment #2 - SF$_6$ concentrations over time at the sampling well, CW 1 – (above packer)

Notes: Green text indicates the sample replicate with lower dilution factor. That sample was considered more reliable. Red text indicates replicates with the same or similar dilution but >20% difference between them. A decision for each set of replicates as to how to use them in the calculations is listed in the final column. In general, the sample point was deleted from calculations if replicates that were greater than 40% different. Sample points with no note indicate that either there was only 1 replicate and that point was used or there were multiple replicates but one was chosen as more reliable (i.e., one had a lower dilution factor). No bubble corrections were included as they were determined to have only a minor impact on calculations.

Sample Date/Time	SF$_6$ Conc. (ccSTP/cc)	Dilution factor	Decision for use in calculations
4/4/09 3:50	4.43E-12	1	
4/4/09 10:45	2.41E-13	1	
4/4/09 15:50	**7.05E-12**	**1**	
4/4/09 15:50	9.43E-12	5	
4/5/09 7:20	4.90E-11	1	avg the replicates
4/5/09 7:20	7.66E-11	1	
4/5/09 10:50	6.84E-11	28	
4/5/09 14:35	**1.24E-10**	**1**	*sample and dup within ~10%
4/5/09 14:35	1.37E-10	5	
4/5/09 17:15	7.61E-11	25	avg the replicates
4/5/09 17:15	1.14E-10	25	
4/6/09 8:30	**8.54E-10**	**25**	*sample and dup within ~10%
4/6/09 8:30	9.17E-10	106	
4/6/09 10:30	7.34E-10	104	
4/6/09 13:50	**1.38E-09**	**1**	*sample and dups within ~10%
4/6/09 13:50	1.35E-09	5	
4/6/09 13:50	1.44E-09	25	
4/6/09 17:25	7.61E-10	100	
4/7/09 7:20	**8.97E-10**	**265**	
4/7/09 7:20	1.13E-09	360	
4/7/09 11:15	**2.89E-10**	**1**	
4/7/09 11:15	1.20E-09	5	
4/7/09 11:15	1.22E-09	25	
4/7/09 16:20	7.93E-10	250	avg the replicates
4/7/09 16:20	1.18E-09	281	
4/8/09 7:20	1.16E-09	1000	delete sample point, replicates >40% different
4/8/09 7:20	2.76E-09	1000	

Sample Date/Time	**SF_6 Conc. (ccSTP/cc)**	**Dilution factor**	**Decision for use in calculations**
4/8/09 10:20	2.15E-09	900	
4/8/09 14:25	**2.07E-09**	**5**	
4/8/09 14:25	2.53E-09	25	
4/8/09 17:30	1.40E-09	2500	
4/8/09 17:30	**1.02E-09**	**1000**	
4/9/09 7:25	1.99E-09	1000	avg the replicates
4/9/09 7:25	2.25E-09	1000	
4/9/09 10:50	1.05E-09	1000	
4/9/09 14:10	**3.32E-09**	**5**	*sample and dups within ~10%
4/9/09 14:10	3.12E-09	25	
4/9/09 17:15	1.67E-09	1000	delete sample point, replicates >40% different
4/9/09 17:15	1.09E-08	1000	
4/10/09 7:45	1.10E-08	1000	delete sample point replicates >40% different
4/10/09 7:45	2.25E-09	1000	
4/10/09 14:25	**2.59E-09**	**5**	*sample and dups within ~10%
4/10/09 14:25	2.45E-09	25	
4/11/09 7:45	2.33E-09	999	avg sample and dup; discard redilutions
4/11/09 7:45	2.56E-09	1000	
4/11/09 7:45	1.90E-09	1025	(discard)
4/11/09 7:45	8.45E-10	1050	(discard)
4/11/09 10:25	2.46E-09	980	avg sample and dup; discard redilutions
4/11/09 10:25	1.98E-09	1000	
4/11/09 10:25	1.18E-09	980	(discard)
4/11/09 10:25	1.84E-09	1000	(discard)
4/11/09 16:15	3.22E-09	5	avg all replicates
4/11/09 16:15	3.18E-09	25	
4/11/09 16:15	3.74E-09	5	
4/11/09 16:15	3.69E-09	25	
4/11/09 17:30	1.12E-08	1000	
4/12/09 8:40	5.81E-10	1000	delete, most replicates >40% different
4/12/09 8:40	1.52E-09	1000	
4/12/09 8:40	7.97E-10	1000	
4/12/09 8:40	1.12E-09	980	
4/12/09 13:35	1.82E-09	25	avg all replicates
4/12/09 13:35	**1.79E-09**	**5**	*sample and dups within ~10%
4/12/09 13:35	1.91E-09	25	
4/12/09 17:00	8.07E-10	1000	delete sample point, replicates >40% different
4/12/09 17:00	1.75E-09	1000	
4/12/09 17:00	5.57E-09	1000	

Sample Date/Time	SF_6 Conc. (ccSTP/cc)	Dilution factor	Decision for use in calculations
4/13/09 8:20	1.30E-09	1000	avg sample and dup; discard redilutions and reinsertions
4/13/09 8:20	1.37E-09	1000	
4/13/09 8:20	9.74E-10	1000	(discard)
4/13/09 8:20	9.88E-10	1000	(discard)
4/13/09 8:20	1.31E-09	1000	
4/13/09 8:20	6.77E-10	1000	(discard)
4/13/09 8:20	7.76E-10	1000	(discard)
4/13/09 13:05	**2.44E-09**	**5**	*sample and dups within ~10%
4/13/09 13:05	2.39E-09	25	
4/13/09 17:00	5.14E-10	1000	avg all replicates
4/13/09 17:00	3.74E-10	1000	
4/13/09 17:00	7.58E-10	1025	
4/13/09 17:00	4.10E-10	980	
4/14/09 7:35	4.78E-10	50	avg all replicates
4/14/09 7:35	4.84E-10	50	
4/14/09 7:35	4.40E-10	50	
4/14/09 14:25	4.28E-10	50	avg all replicates
4/14/09 14:25	4.23E-10	50	
4/14/09 17:00	3.40E-10	50	avg all replicates
4/14/09 17:00	3.21E-10	50	
4/14/09 17:00	3.52E-10	50	
4/14/09 17:00	3.59E-10	50	
4/15/09 8:00	1.64E-10	50	delete sample point
4/15/09 8:00	1.40E-10	50	
4/15/09 8:00	1.08E-10	50	
4/15/09 8:00	1.28E-10	50	
4/15/09 11:20	**2.65E-10**	**5**	
4/15/09 11:20	3.17E-10	25	
4/16/09 7:55	2.83E-11	5	delete sample point, most replicates >40% different
4/16/09 7:55	2.99E-11	5	
4/16/09 7:55	4.96E-11	5	
4/16/09 7:55	5.97E-11	5	
4/16/09 14:05	**4.95E-11**	**1**	
4/16/09 14:05	2.19E-11	50	
4/16/09 14:05	1.23E-11	50	
4/16/09 17:10	3.83E-11	5	delete sample point, most replicates >40% different
4/16/09 17:10	2.64E-11	5	
4/16/09 17:10	2.25E-11	5	

Sample Date/Time	SF$_6$ Conc. (ccSTP/cc)	Dilution factor	Decision for use in calculations
4/17/09 8:15	2.48E-11	5	delete sample point, most replicates >40% different
4/17/09 8:15	2.65E-11	5	
4/17/09 8:15	1.70E-11	5	
4/17/09 8:15	1.73E-11	5	
4/17/09 13:05	2.22E-11	1	
4/17/09 16:45	1.93E-11	4.3	avg all replicates
4/17/09 16:45	1.85E-11	5	
4/17/09 16:45	1.92E-11	5	
4/18/09 7:35	9.27E-12	5	avg sample, redil, dup redil
4/18/09 7:35	9.23E-12	5	
4/18/09 7:35	6.35E-12	5	(discard)
4/18/09 7:35	7.83E-12	5	
4/18/09 13:15	7.62E-13	1	
4/18/09 17:00	9.03E-12	5	avg all replicates
4/18/09 17:00	9.08E-12	5	
4/18/09 17:00	1.15E-11	5	
4/18/09 17:00	1.29E-11	5	
4/19/09 7:35	4.70E-12	5	avg all replicates
4/19/09 7:35	4.75E-12	5	
4/19/09 7:35	6.28E-12	5	
4/19/09 7:35	7.33E-12	5	
4/19/09 11:45	3.05E-12	1	
4/19/09 17:10	4.68E-12	1	
4/20/09 7:45	3.30E-12	1	avg all replicates
4/20/09 7:45	2.73E-12	1	
4/20/09 13:10	2.29E-12	1	
4/20/09 17:00	2.26E-12	1	avg all replicates
4/20/09 17:00	2.41E-12	1	
4/21/09 8:00	1.69E-12	1	avg all replicates
4/21/09 8:00	1.35E-12	1	
4/21/09 12:15	1.20E-12	1	
4/21/09 17:05	1.01E-12	1	avg all replicates
4/21/09 17:05	1.01E-12	1	
4/22/09 7:45	5.69E-13	1	avg all replicates
4/22/09 7:45	8.16E-13	1	
4/23/09 10:25	7.11E-13	1	avg all replicates
4/23/09 10:25	7.49E-13	1	
4/23/09 14:15	3.94E-13	1	avg all replicates
4/23/09 14:15	6.54E-13	1	
4/24/09 11:15	4.18E-13	1	
4/25/09 8:35	3.95E-13	1	avg all replicates
4/25/09 8:35	3.75E-13	1	

Sample Date/Time	SF$_6$ Conc. (ccSTP/cc)	Dilution factor	Decision for use in calculations
4/26/09 11:00	2.63E-13	1	avg all replicates
4/26/09 11:00	1.98E-13	1	
4/28/09 8:05	2.60E-13	1	avg all replicates
4/28/09 8:05	2.57E-13	1	
4/29/09 8:40	1.79E-13	1	avg all replicates
4/29/09 8:40	1.85E-13	1	
4/30/09 8:25	2.22E-13	1	avg all replicates
4/30/09 8:25	1.93E-13	1	
5/1/09 6:30	2.30E-13	1	avg all replicates
5/1/09 6:30	1.66E-13	1	
5/3/09 10:30	1.26E-13	1	avg all replicates
5/3/09 10:30	1.03E-13	1	
5/5/09 8:15	1.20E-13	1	
5/7/09 8:20	1.28E-13	1	
5/9/09 7:55	1.12E-13	1	avg all replicates
5/9/09 7:55	1.20E-13	1	
5/11/09 7:15	1.08E-13	1	avg all replicates
5/11/09 7:15	1.00E-13	1	
5/13/09 8:50	2.17E-13	1	avg all replicates
5/13/09 8:50	2.37E-13	1	
5/15/09 8:45	2.13E-13	1	delete sample point, replicates >40% different
5/15/09 8:45	1.32E-13	1	
5/18/09 8:45	1.15E-13	1	avg all replicates
5/18/09 8:45	1.46E-13	1	
5/25/09 8:50	1.92E-13	1	avg all replicates
5/25/09 8:50	1.38E-13	1	
6/1/09 7:15	3.38E-13	1	delete sample point, most replicates >40% different
6/1/09 7:15	1.12E-13	1	
6/8/09 8:05	1.01E-13	1	avg all replicates
6/8/09 8:05	1.66E-13	1	
6/15/09 16:40	1.19E-13	1	avg all replicates
6/15/09 16:40	1.39E-13	1	

Field experiment #2 - SF_6 concentrations over time at the pump and treat well, RW 2a

Notes: All replicates were averaged and used in calculations unless otherwise noted. No bubble corrections were included as they were determined to have only a minor impact on calculations.

Sample Date/Time	**SF_6 Conc. (ccSTP/cc)**	**Decision for use in calculations**
4/4/09 12:05	1.00E-13	
4/4/09 16:00	8.72E-14	delete sample point, replicates >40% different
4/4/09 16:00	1.51E-13	
4/5/09 7:25	6.53E-13	
4/5/09 10:40	9.58E-13	
4/5/09 14:45	4.54E-12	
4/5/09 17:20	1.81E-12	
4/6/09 8:35	4.77E-12	
4/6/09 8:35	5.03E-12	
4/6/09 10:35	7.25E-13	
4/6/09 13:55	1.49E-12	
4/6/09 17:30	8.24E-12	
4/6/09 17:30	8.11E-12	
4/7/09 7:25	9.25E-12	
4/7/09 7:25	8.39E-12	
4/7/09 11:20	8.79E-12	
4/7/09 16:25	1.00E-11	
4/7/09 16:25	9.39E-12	
4/8/09 7:25	1.02E-11	
4/8/09 7:25	1.03E-11	
4/8/09 10:20	7.50E-12	
4/8/09 14:30	1.09E-11	
4/8/09 17:35	1.06E-11	
4/8/09 17:35	1.04E-11	
4/9/09 7:30	1.20E-11	
4/9/09 7:30	1.22E-11	
4/9/09 10:55	1.28E-11	
4/9/09 14:15	1.19E-11	
4/9/09 17:20	1.08E-11	
4/9/09 17:20	1.06E-11	
4/10/09 7:50	9.75E-12	
4/10/09 7:50	1.03E-11	
4/10/09 14:30	1.39E-11	
4/11/09 10:30	1.40E-11	
4/11/09 10:30	1.37E-11	
4/11/09 16:20	1.40E-11	
4/11/09 17:35	1.37E-11	

Sample Date/Time	SF_6 Conc. (ccSTP/cc)	Decision for use in calculations
4/12/09 13:40	2.61E-11	
4/12/09 17:05	2.44E-11	
4/12/09 17:05	2.42E-11	
4/13/09 8:25	2.27E-11	
4/13/09 8:25	1.81E-11	
4/13/09 13:10	3.14E-11	
4/13/09 17:05	2.27E-11	
4/13/09 17:05	2.33E-11	
4/14/09 7:40	2.02E-11	
4/14/09 7:40	1.96E-11	
4/14/09 10:55	2.14E-11	
4/14/09 14:30	1.80E-11	
4/14/09 17:05	1.87E-11	
4/14/09 17:05	1.57E-11	
4/15/09 8:05	1.30E-11	
4/15/09 8:05	1.32E-11	
4/15/09 11:25	2.19E-11	
4/15/09 16:45	2.03E-11	
4/15/09 16:45	1.96E-11	
4/16/09 8:00	9.74E-12	
4/16/09 8:00	1.11E-11	
4/16/09 14:10	1.43E-11	
4/16/09 17:15	7.55E-12	
4/16/09 17:15	7.63E-12	
4/17/09 8:20	3.69E-12	
4/17/09 8:20	3.30E-12	
4/17/09 13:10	5.14E-12	
4/17/09 16:50	2.47E-12	
4/17/09 16:50	2.42E-12	
4/18/09 7:40	2.25E-12	
4/18/09 7:40	2.42E-12	
4/18/09 13:20	2.21E-12	
4/18/09 17:05	1.89E-12	
4/18/09 17:05	1.86E-12	
4/19/09 7:40	1.32E-12	
4/19/09 11:50	1.17E-12	
4/19/09 17:15	8.95E-13	
4/19/09 17:15	7.82E-13	
4/20/09 7:50	6.17E-13	
4/20/09 13:15	6.20E-13	
4/20/09 17:05	4.93E-13	
4/20/09 17:05	4.00E-13	

Sample Date/Time	SF_6 Conc. (ccSTP/cc)	Decision for use in calculations
4/21/09 8:05	3.86E-13	
4/21/09 8:05	3.24E-13	
4/21/09 12:20	2.77E-13	
4/21/09 17:10	3.01E-13	
4/21/09 17:10	3.23E-13	
4/22/09 7:50	2.07E-13	
4/22/09 7:50	1.83E-13	
4/22/09 13:20	1.92E-13	
4/23/09 10:30	1.20E-13	
4/23/09 10:30	1.16E-13	
4/23/09 14:20	4.84E-13	delete sample point, replicates >40% different
4/23/09 14:20	1.16E-13	
4/24/09 11:20	1.71E-13	delete sample point, replicates >40% different
4/24/09 11:20	3.39E-13	
4/25/09 8:40	2.50E-13	delete sample point, replicates >40% different
4/25/09 8:40	8.63E-14	
4/26/09 11:05	7.05E-14	
4/28/09 8:10	7.34E-14	
4/28/09 8:10	8.19E-14	
4/29/09 8:45	1.74E-13	delete sample point, replicates >40% different
4/29/09 8:45	6.50E-14	
4/30/09 8:30	6.37E-14	
4/30/09 8:30	6.85E-14	
5/1/09 6:35	5.26E-14	
5/1/09 6:35	5.40E-14	
5/3/09 10:35	7.34E-14	
5/3/09 10:35	6.73E-14	
5/5/09 8:20	1.57E-13	delete sample point, replicates >40% different
5/5/09 8:20	2.30E-13	
5/7/09 8:25	1.55E-13	delete sample point, replicates >40% different
5/7/09 8:25	2.63E-13	
5/9/09 8:00	1.59E-13	
5/9/09 8:00	2.28E-13	
5/11/09 7:20	1.13E-13	
5/11/09 7:20	9.24E-14	

Sample Date/Time	SF_6 Conc. (ccSTP/cc)	Decision for use in calculations
5/13/09 8:55	5.73E-14	delete sample point, replicates >40% different
5/13/09 8:55	9.99E-14	
5/15/09 8:50	6.75E-14	delete sample point, replicates >40% different
5/15/09 8:50	4.44E-14	
5/18/09 8:50	1.13E-13	
5/18/09 8:50	1.18E-13	
5/25/09 8:55	1.01E-13	
5/25/09 8:55	1.04E-13	
6/1/09 7:20	1.18E-13	
6/1/09 7:20	1.07E-13	
6/8/09 8:10	1.93E-13	delete sample point, replicates >40% different
6/8/09 8:10	8.81E-14	
6/15/09 16:45	9.52E-14	delete sample point, replicates >40% different
6/15/09 16:45	1.64E-13	

5.18.7 Groundwater parameters during 2008 tracer experiment (field experiment #1)

Field experiment #1 – groundwater parameters over time at the sampling well, CW 1 – (entire well)

Date/Time	**T (ºC)**	**Cond (mS/cm)**	**DO (mg/L)**	**pH**	**ORP (mV)**	**DO (mg/L; Chemets)**
6/25/08 12:30	13.54	0.130	5.04	6.26	-4.5	2
6/25/08 14:15	13.41	0.130	2.72	6.39	19.6	2
6/25/08 16:00	13.46	0.132	2.31	6.33	24.5	
6/26/08 8:58	13.46	0.132	2.65	6.36	17.0	
6/26/08 12:50	13.54	0.131	3.58	6.43	-6.2	
6/26/08 16:15	13.57	0.134	2.22	6.37	16.0	2
6/27/08 8:29	13.29	0.134	2.29	6.43	3.9	
6/27/08 12:47	13.5	0.135	2.03	6.48	-14.7	
6/27/08 16:25	13.57	0.135	2.01	6.43	-5.3	
6/28/08 8:20	13.87	0.137	2.43	6.65	1.2	
6/28/08 13:30	14.12	0.140	2.14	6.62	-5.8	
6/29/08 8:25	13.28	0.138	2.46	6.45	6.7	2-3
6/29/08 16:00	14.16	0.142	2.28	6.54	13.0	
6/30/08 8:45	13.65	0.140	2.29	6.44	5.8	
6/30/08 16:50	13.41	0.142	2.16	6.46	21.6	
7/1/08 8:35	13.47	0.139	2.35	6.74	14.7	~1.5
7/2/08 8:42	13.48	0.138	2.43	6.61	19.4	
7/3/08 9:14	14.3	0.139	2.05	6.35	25.2	

Measurements taken with YSI 556 MPS Multi-Parameter Instrument

Field experiment #1 - groundwater parameters over time at the sampling well, CW 1 – (above packer)

Date/Time	T (ºC)	Cond (mS/cm)	DO (mg/L)	pH	ORP (mV)	DO (mg/L; Chemets)
6/28/08 12:00	13.53	0.146	0.92	6.82	-35.2	~1
6/28/08 16:52	13.55	0.148	1.15	6.9	-22.2	
6/29/08 9:55	14.18	0.150	1.23	6.79	-13.2	~1
6/30/08 12:10	13.85	0.150	1.17	6.72	-12.3	
7/1/08 14:10	13.50	0.147	1.75	6.98	-30.8	~1

Measurements taken with YSI 556 MPS Multi-Parameter Instrument

Field experiment #1 - Groundwater parameters over time at the sampling well, CW 1 – (below packer)

Date/Time	T (ºC)	Cond (mS/cm)	DO (mg/L)	pH	ORP (mV)	DO (mg/L; Chemets)
6/25/08 14:50	13.45	0.106	6.11	5.65	53.7	
6/26/08 9:35	13.48	0.103	6.52	5.69	52.2	5-6
6/26/08 15:40	13.83	0.104	6.58	5.66	29.4	
6/27/08 9:21	13.54	0.104	6.38	5.48	63.8	
6/27/08 13:42	13.77	0.104	6.51	5.56	56.2	5
6/28/08 9:50	13.73	0.103	6.79	5.45	78.2	
6/29/08 11:47	13.87	0.106	6.63	5.63	50.8	~6
6/30/08 10:15	13.87	0.105	6.50	5.49	69.3	
6/30/08 15:47	13.51	0.113	5.95	5.73	59.2	
7/1/08 14:55	13.76	0.110	5.98	5.75	65.9	~5

Measurements taken with YSI 556 MPS Multi-Parameter Instrument

Field experiment #1 - groundwater parameters over time at the pump and treat well, RW 2a

Date/Time	**T (ºC)**	**Cond (mS/cm)**	**DO (mg/L)**	**pH**	**ORP (mV)**	**DO (mg/L; Chemets)**
6/25/08 12:30	13.28	0.162	7.23	5.91	9.4	4.5
6/25/08 16:00	13.40	0.161	5.04	5.79	15.2	
6/26/08 9:12	12.94	0.16	4.30	5.80	19.0	
6/26/08 13:05	15.13	0.162	4.31	5.84	9.6	2
6/26/08 16:25	14.07	0.162	4.07	5.80	21.1	4
6/27/08 8:40	14.25	0.163	4.16	5.83	23.6	
6/27/08 13:01	15.12	0.163	4.15	5.89	-1.9	
6/28/08 8:42	13.68	0.161	4.14	5.93	39.3	
6/28/08 13:40	13.98	0.162	4.19	5.95	6.9	
6/29/08 8:40	13.76	0.161	4.14	5.92	5.6	3-4
6/29/08 16:15	14.36	0.162	4.28	5.98	26.0	
6/30/08 8:55	13.76	0.162	4.14	5.84	3.5	
6/30/08 17:05	14.77	0.161	3.92	6.03	19.8	
7/1/08 8:50	13.34	0.161	4.18	5.92	3.2	~4
7/2/08 8:50	13.59	0.161	4.21	5.95	16.6	
7/3/08 9:24	14.08	0.160	4.45	5.97	24.0	

Measurements taken with YSI 556 MPS Multi-Parameter Instrument

5.18.8 Groundwater parameters during oxalic acid injection experiment (field experiment #2)

Field experiment #2 - groundwater parameters over time at the sampling well, CW 1 – (above packer)

Date/Time	T (ºC)[1]	Cond (mS/cm)[1]	DO (mg/L)[1]	pH[2]	ORP (mV)[1]	DO (mg/L; Chemets)
4/5/09 8:35	13.44	0.185	1.14	7.03	3.8	0.8
4/6/09 9:00	13.43	0.186	1.63	6.97	7.9	1
4/7/09 8:00	13.17	0.182	1.60	6.82	29.6	1
4/7/09 16:45	13.3	0.183	1.52	6.78	24.7	
4/8/09 7:50	12.85	0.186	1.45	6.33	43.8	1
4/9/09 8:10	12.85	0.196	1.37	6.72	51	1
4/10/09 8:10	13.17	0.204	1.38	6.4	72.9	
4/11/09 16:25	13.14	0.175	2.20	6.09	133	1
4/12/09 13:55	13.66	0.204	1.18	6.41	82.1	
4/13/09 10:50	13.67	0.215	1.23	6.22	176.1	1
4/14/09 11:00	12.85	0.227	0.99	6.28	35.3	
4/15/09 11:30	12.83	0.247	1.09	6.14	32.2	
4/16/09 11:15	13.71	0.263	1.11	6.18	38.6	1
4/17/09 11:20	13.88	0.266	1.23	6.02	41.9	
4/19/09 12:10	13.92	0.235	0.76	6.23	-4.8	
4/21/09 8:30	13.08	0.249	1.11	5.67	104.5	
4/22/09 8:15	12.94	0.261	0.95	6.08	35.2	0.5, 0.6
4/23/09 11:10	13.72	0.228	0.85	6.04	4.3	0.1
4/24/09 11:50	14.17	0.257	1.18	6	63.3	0.2
4/25/09 9:20	13.63	0.264	1.09	5.49	115.8	
4/27/09 8:30	13.65	0.246	1.5	5.15	125.3	>1 (0-1), 4 (1-12)
4/28/09 8:40	13.82	0.247	1.28	5.09	129.3	>1 (0-1), ~3 (1-12)
4/29/09 9:25	13.02	0.242	1.41	5.11	147.1	
4/30/09 9:05	13.32	0.251	1.3	4.94	159.7	
5/1/09 7:00	13.21	0.255	1.71	4.77	180.2	
5/3/09 11:00	13.1	0.286	0.84	4.56	191	>1 (0-1)
5/4/09 14:15	12.94	0.256	1.36	4.64	186.7	
5/5/09 9:00	13.01	0.234	1.73	4.81	169.1	
5/6/09 9:35	13.17	0.223	1.63	4.8	163.6	
5/7/09 9:15	13.63	0.238	1.2	4.65	198.9	~5 *
5/8/09 8:30	13.69	0.224	1.06	4.88	167.7	
5/9/09 8:45	13.92	0.244	1.72	4.71	180.4	
5/10/09 16:20	13.76	0.369	0.95	3.33	228	8 *
5/11/09 8:20	13	1.16	1.71	2.46	216.1	
5/12/09 8:55	13.35	1.488	1.39	2.62	182.7	

Date/Time	**T (ºC)[1]**	**Cond (mS/cm)[1]**	**DO (mg/L)[1]**	**pH[2]**	**ORP (mV)[1]**	**DO (mg/L; Chemets)**
5/13/09 9:25	13.29	1.388	1.22	2.64	177.1	
5/14/09 9:40	13.25	1.976	1.36	2.46	204.7	
5/15/09 9:25	13.49	0.788	0.78	2.41	186.4	
5/15/09 9:35	13.5	0.504	0.71		178.4	
5/16/09 8:45	13.36	2.285	1.26	2.3	197.8	
5/17/09 15:35	13.22	2.847	1.4	2.25	190.1	
5/18/09 9:25	13.04	3.169	1.78	2.11	186	
5/19/09 8:30	13.09	2.964	1.49	2.04	180.7	
5/20/09 8:55	13.48	3.588	1.60	2.07	174	
5/21/09 9:15	13.57	3.626	1.52	2.16	171.9	
5/22/09 9:05	13.73	3.57	1.37	2.17	174	
5/23/09 7:25	13.32	3.89	1.41	2.19	180.3	
5/24/09 11:40	13.8	3.964	1.72	2.15	171.2	
5/25/09 9:30	13.66	4.184	1.47	2.08	175.4	
5/26/09 7:35	13.33	6.536	3.11	2.03	199.4	
5/27/09 9:20	13.14	3.09	1.14	2.21	186	
5/28/09 8:55	13.78	4.328	1.90	2.07	184.5	
5/29/09 12:25	13.55	2.682	0.92	2.25	167.5	
5/30/09 8:30	13.41	4.078	1.32	2.17	175.4	
6/1/09 7:50	13.26	4.267	1.29	2.12	172.8	
6/2/09 8:30	13.75	8.648	4.51	1.97	203.7	
6/3/09 9:25	13.56	4.874	2.86	2.09	197	
6/4/09 9:05	13.27	4.13	3.07	2.11	204.7	
6/5/09 9:10	13.1	0.156	1.04	5.92	25	
6/6/09 8:40	13.19	1.175	1.24	2.63	211.8	
6/7/09 10:30	13.92	1.997	2.50	2.57	185.6	
6/8/09 8:55	13.61	2.32	0.98	2.44	199	
6/9/09 11:50	13.54	2.887	1.40	2.23	191.3	
6/10/09 8:40	13.6	2.985	1.34	2.28	175	
6/11/09 8:30	13.45	2.107	1.07	2.37	175.5	
6/12/09 8:35	13.72	3.235	1.78	2.32	164.4	
6/13/09 8:05	13.8	2.164	1.35		154.2	
6/14/09 13:00	13.88	2.615	1.32		145.6	
6/15/09 8:55	13.66	2.364	1.07	2.63	146.6	
6/16/09 9:05	13.56	3.75	1.54	2.15	158.8	
6/17/09 8:35	13.49	3.43	1.45	2.25	153.8	
6/18/09 10:45	13.71	3.471	2.35	1.97	159.7	
6/19/09 9:15	13.74	3.714	2.50	2.07	156.2	
6/20/09 8:10	13.59	3.728	2.31	1.99	154.9	
6/21/09 12:50	13.71	4.105	2.05	2.05	152.6	
6/22/09 8:45	13.78	4.127	2.25	1.93	153	
6/22/09 8:45	13.78	4.127	2.25	1.93	153	
6/23/09 8:30	13.65	3.817	1.82	2.09	156.2	

Date/Time	T (ºC)[1]	Cond (mS/cm)[1]	DO (mg/L)[1]	pH[2]	ORP (mV)[1]	DO (mg/L; Chemets)
6/24/09 9:30	13.82	4.522	2.60	1.95	153.7	
6/25/09 9:05	13.62	3.89	2.05	2.13	156.8	
6/26/09 8:15	13.69	4.021	1.97	1.99	159.4	
6/27/09 8:45	13.7	5.07	2.50	1.98	155.2	
6/28/09 15:05	14.16	3.2	1.88	2.24	134.8	
6/29/09 9:05	13.78	5.05	2.00	1.94	151.4	
6/30/09 8:35	13.9	5.036	1.90	2.02	152	
7/1/09 7:40	13.65	5.454	1.90	2.08	158.4	
7/1/09 7:40	13.65	5.454	1.90	2.08	158.4	
7/2/09 7:15	13.73	9.263	3.57	1.91	164.6	
7/3/09 9:25	13.88	2.44	1.50	2.19	139.9	
7/4/09 12:30	14.32	4.016	2.46	2.04	149.1	
7/5/09 9:30	14.32	3.241	3.02	2.14	156.5	
7/6/09 13:00	14.73	7.65	4.30	1.77	157.6	
7/8/09 11:15	17.9	2.909	2.87	2.26	131.2	
7/10/09 9:50	14.42	0.194	1.55	5.91	94.8	
7/12/09 12:15	14.69	0.296	1.57	3.62	122.4	
7/13/09 11:45	14.23	0.627	1.76	2.68	151.6	
7/14/09 8:30	14.07	1.05	1.83	2.68	163.4	
7/15/09 9:20	14.18	0.602	1.82	3.07	173.9	
7/20/09 11:25	14.45	0.201	1.52	6.15	40.5	
7/23/09 11:10	14.16	0.19	1.42	6.35	3.8	
7/28/09 11:25	14.83	0.188	1.48	6.32	-107.3	
8/3/09 11:15	14.45	0.18	1.83	6.71	-141.3	~1
8/10/09 12:00	15.06	0.176	1.85	6.82	-82.9	
8/17/09 11:15	15.11	0.172	2.26	6.67	-48.9	
8/24/09 11:30	15.26	0.168	2.12	6.82	-87.8	<1
8/31/09 11:35	15.50	0.173	1.89	7.05	-91	0.3
9/9/09 11:50	15.29	0.172	1.63	6.81	-44	0.6

[1] YSI 556 MPS Multi-Parameter Instrument

[2] pH 20 series pH meter, Cole Parmer

* Interference with DO measurement by Chemets due to high Fe content in groundwater

Field experiment #2 - groundwater parameters over time at the sampling well, CW 1 – (below packer)

Date/Time	**T (ºC)**[1]	**Cond (mS/cm)**[1]	**DO (mg/L)**[1]	**pH**[2]	**ORP (mV)**[1]	**DO (mg/L; Chemets)**
6/4/09 10:30	16.14	0.12	6.85	4.08	164	
6/5/09 10:30	14.97	2.082	4.20	2.25	164	
6/6/09 10:05	18.65	9.778	5.53	1.98	117.9	
6/8/09 9:20	19.46	10.99	6.29	1.8	95.5	
6/9/09 12:00	18.58	9.058	5.92	1.86	130.8	
6/10/09 10:05	19.85	6.23	6.20	1.88	95.5	
6/11/09 9:45	17.39	5.48	6.34	1.86	138.8	
6/12/09 9:55	19.57	4.932	6.46	2.37	145.3	
6/13/09 9:10	20.19	5.014	6.17		99	
6/14/09 14:05	22.34	4.585	4.76		76.2	
6/15/09 9:50	17.95	4.588	6.31	2.11	98.3	
6/16/09 9:35	17.30	4.906	5.96	2.06	106.5	
6/17/09 10:01	18.51	3.78	5.05	2.03	84.2	
6/18/09 16:50	17.78	4.036	6.13	1.91	158.5	
6/19/09 10:00	19.61	3.744	4.78	1.91	89.2	
6/20/09 9:20	17.44	3.73	6.13	1.98	144.9	
6/21/09 13:55	18.46	3.636	4.93	2.04	100.8	
6/22/09 9:50	19.74	3.78	4.72	1.92	100.6	
6/22/09 9:50	19.74	3.78	4.72	1.92	100.6	
6/23/09 10:00	18.22	3.633	5.47	1.9	115.9	
6/24/09 11:10	20.09	4.99	5.16	1.87	108.6	
6/25/09 10:00	20.13	4.18	3.70	2.02	80.5	
6/26/09 9:30	20.58	4.699	5.52	1.9	103.5	
6/27/09 9:40	20.58	4.687	4.38	1.9	82.6	
6/28/09 15:30	22.19	4.991	4.87	1.81	94	
6/29/09 10:15	21.27	4.658	3.87	1.88	77.6	
6/30/09 9:40	21.16	4.232	3.90	1.94	88.2	
7/1/09 8:30	18.13	4.46	5.67	1.99	121.1	
7/1/09 8:30	18.13	4.46	5.67	1.99	121.1	
7/2/09 9:45	20.80	0.517	5.51	3.14	139.9	
7/3/09 10:05	21.06	3.61	4.40	1.99	71.7	
7/4/09 13:30	21.20	7.717	4.60	1.71	66	
7/5/09 11:45	21.41	3.991	4.24	2.08	60.8	
7/6/09 13:15				2.61		
7/8/09 11:25	24.11	0.705	3.56	2.89	211.6	
7/10/09 10:15	20.77	1.94	2.70	2.2	65.8	
7/12/09 13:10	22.40	0.623	0.99	2.7	73.7	
7/13/09 12:05	22.97	0.237	2.80	3.18	170.8	
7/14/09 9:25	19.31	0.149	4.40	3.9	182.3	
7/15/09 10:20	21.40	0.137	4.16	4.13	214.5	

Date/Time	**T (°C)**[1]	**Cond (mS/cm)**[1]	**DO (mg/L)**[1]	**pH**[2]	**ORP (mV)**[1]	**DO (mg/L; Chemets)**
7/20/09 11:50	22.83	0.12	4.53	5.01	50.3	
7/23/09 11:30	21.07	0.13	5.22	4.93	29.4	
7/28/09 11:45	25.70	0.142	5.03	5.11	39.7	
8/3/09 11:45	23.59	0.144	5.70	5.05	37.4	~7
8/10/09 12:20	25.25	0.152	6.46	5.26	110.2	
8/17/09 11:40	24.58	0.154	6.09	5.24	130	
8/24/09 11:55	22.60	0.157	6.41	5.2	85.7	~5
8/31/09 11:55	18.95	0.158	7.12	5.24	100.5	
9/9/09 12:10	18.40	0.152	7.31	4.8	86.2	

[1] YSI 556 MPS Multi-Parameter Instrument
[2] pH 20 series pH meter, Cole Parmer
* Interference with DO measurement by Chemets due to high Fe content in groundwater

Field experiment #2 - groundwater parameters over time at injection well, CW 3.2

Date/Time	**T (ºC)**[1]	**Cond (mS/cm)**[1]	**DO (mg/L)**[1]	**pH**[2]	**ORP (mV)**[1]	**DO (mg/L; Chemets)**
7/20/09 12:40	16.84	0.266	1.53	9.61	-112.5	
7/23/09 12:10	15.83	0.263	1.25	9.66	-38	
7/28/09 12:30	18.65	0.248	1.60	9.76	-88	
8/3/09 13:00	19.00	0.25	0.83	9.57	-1.5	0-1
8/10/09 13:00	17.97	0.26	1.83	9.82	-42	
8/17/09 12:25	19.04	0.263	0.26	9.52	-6.9	
8/24/09 12:35	17.92	0.241	1.55	9.38	13.4	~1
8/31/09 12:35	16.41	0.228	1.49	9.83	6.34	
9/9/09 12:55	15.94	0.213	4.40	9.46	-45.2	

[1] YSI 556 MPS Multi-Parameter Instrument
[2] pH 20 series pH meter, Cole Parmer
* Interference with DO measurement by Chemets due to high Fe content in groundwater
Red = fog on screen made deciphering readings difficult

Field experiment #2 - groundwater parameters over time at pump and treat well, RW 2a

Date/Time	**T (°C)[1]**	**Cond (mS/cm)[1]**	**DO (mg/L)[1]**	**pH[2]**	**ORP (mV)[1]**	**DO (mg/L; Chemets)**
4/5/09 8:50	13.87	0.177	5.46	5.76	157.2	4
4/6/09 9:15	13.71	0.176	5.61	5.71	151.9	4-5
4/7/09 8:15	13.14	0.179	5.58	5.54	115.8	4
4/8/09 8:00	13.16	0.178	5.51	5.53	121.2	
4/9/09 8:20	13.1	0.176	5.62	5.81	136.8	4-5
4/10/09 8:15	13.52	0.176	5.97	6.35	147.6	
4/11/09 16:35	13.46	0.17	5.69	5.43	132.5	4
4/12/09 14:02	13.71	0.174	5.87	5.62	156	
4/13/09 11:00	13.44	0.175	5.79	5.42	672	4
4/14/09 11:10	13.33	0.176	5.89	5.3	20.5	
4/15/09 11:35	12.86	0.178	5.81	5.33	181.8	
4/15/09 17:20				5.44		
4/16/09 11:20	13.5	0.177	5.93	5.35	194.2	4-5
4/17/09 11:25	13.61	0.176	5.97	5.17	172.4	
4/18/09 13:35	14.08	0.179	6.02	4.73	181.2	4.5
4/18/09 17:20				5.34		
4/19/09 12:20	14.03	0.176	5.91	5.49	130.2	
4/19/09 12:21	13.86	0.176	5.83		149.9	
4/20/09 8:15				5.42		
4/21/09 8:40	13.38	0.175	6.02	5.4	169.1	
4/22/09 8:25	13.38	0.175	5.96	5.46	150.9	4
4/23/09 11:20	13.43	0.175	5.94	5.48	131	
4/24/09 12:00	13.81	0.175	6.12	5.45	140.5	4
4/25/09 9:25	13.62	0.174	6.15	5.42	145.7	
4/26/09 12:59				5.23		
4/27/09 8:35	13.72	0.174	5.77	5.16	143.5	4
4/28/09 8:50	14.04	0.175	6.02	5.2	154.6	
4/29/09 9:30	13.31	0.172	5.63	5.22	169.5	
4/30/09 9:20	13.53	0.173	5.72	5.24	169.5	
5/1/09 7:10	13.45	0.172	5.77	5.14	174.8	
5/3/09 11:05	13.37	0.172	6.1	5.21	178.3	4
5/4/09 14:20	13.33	0.173	5.85	5.22	182.6	
5/5/09 9:10	13.34	0.171	5.85	5.3	186.9	
5/6/09 9:45	13.48	0.171	5.78	5.49	178.3	
5/7/09 9:25	13.73	0.176	5.8	4.43	178	4
5/8/09 8:40	13.52	0.181	5.820	4.53	193.3	
5/9/09 8:55	13.78	0.221	5.680	3.63	193.3	
5/10/09 16:25	14.02	0.201	5.710	3.95	164.6	
5/11/09 8:30	13.37	0.203	5.610	3.94	195.8	
5/12/09 9:05	13.56	0.227	5.540	3.53	171.8	
5/13/09 9:30	13.53	0.233	5.520	3.47	170.3	

Date/Time	**T (ºC)[1]**	**Cond (mS/cm)[1]**	**DO (mg/L)[1]**	**pH[2]**	**ORP (mV)[1]**	**DO (mg/L; Chemets)**
5/14/09 9:50	13.42	0.272	5.590	3.42	186.5	
5/15/09 9:45	13.66	0.284	5.400	3.33	181.9	
5/16/09 8:55	13.45	0.185	5.640	3.90	198.7	
5/17/09 15:45	13.37	0.194	5.600	3.66	187.3	5
5/18/09 9:35	13.36	0.198	5.440	3.55	175.6	
5/19/09 8:40	13.35	0.387	5.650	2.82	171.3	
5/20/09 9:05	13.64	0.385	5.57	3.01	167	5
5/21/09 9:25	13.56	0.38	6.05	3.11	167.6	
5/22/09 9:15	13.73	0.334	6.27	2.97	169.2	5-6
5/23/09 7:35	13.54	0.285	5.41	3.12	173.5	
5/24/09 11:55	13.84	0.232	6.28	3.51	161.6	
5/25/09 9:40	14.12	0.237	5.32	3.56	145.8	
5/26/09 15:25	13.26	0.211	5.67	3.28	184.6	
5/27/09 9:35	13.27	0.201	6.23	3.73	178.7	
5/28/09 9:10	13.75	0.263	6.54	3.30	160.9	
5/29/09 9:10	13.35	0.336	5.90	3.05	177.3	
5/30/09 8:40	13.46	0.294	5.48	3.33	169.8	
6/1/09 8:00	13.63	0.303	5.16	3.18	151.2	
6/5/09 10:15	13.28	0.247	6.03	3.26	243.5	
6/6/09 8:50	13.32	0.192	6.02	3.91	196.3	
6/7/09 10:40	14.26	0.409	5.64	3.24	168.5	
6/8/09 9:05	13.58	0.45	6.16	3.07	180.4	
6/9/09 11:55	13.54	0.469	5.83	3.03	189.5	
6/10/09 8:55	13.85	0.427	5.72	3.03	164.7	
6/11/09 8:40	13.33	0.399	5.88	3.09	179.8	
6/12/09 8:45	13.86	0.298	5.83	3.14	159.3	
6/13/09 8:20	13.81	0.278	6.18		143.8	
6/14/09 13:10	13.59	0.274	6.05		152.9	
6/15/09 9:05	13.44	0.274	5.83	3.65	153.5	
6/16/09 9:10	13.48	0.269	5.86	3.47	160.0	
6/17/09 8:45	13.53	0.26	5.85	3.04	148.7	
6/18/09 10:55	13.53	0.26	5.95	3.32	165.8	
6/19/09 9:30	13.37	0.252	6.43	3.52	153.9	
6/20/09 8:20	13.52	0.255	6.22	3.47	152.5	
6/21/09 13:00	13.35	0.251	6.16	3.55	156.5	
6/22/09 8:55	13.52	0.255	5.99	3.49	151.1	
6/22/09 8:55	13.52	0.255	5.99	3.49	151.1	
6/23/09 8:40	13.39	0.256	6.4	3.37	156.6	
6/24/09 9:40	13.59	0.261	6.09	3.34	143.3	
6/25/09 9:15	13.5	0.265	6.14	3.30	148.3	
6/26/09 8:25	13.55	0.272	5.95	3.55	157.8	
6/27/09 8:55	13.58	0.272	5.97	3.53	147.4	
6/28/09 15:15	13.67	0.301	6.08	3.31	147.6	

Date/Time	**T (ºC)**[1]	**Cond (mS/cm)**[1]	**DO (mg/L)**[1]	**pH**[2]	**ORP (mV)**[1]	**DO (mg/L; Chemets)**
6/29/09 9:15	13.55	0.276	5.93	3.48	143.7	
6/30/09 8:45	13.57	0.281	6	3.38	141.8	
7/1/09 7:50	13.54	0.284	5.78	3.49	149.3	
7/1/09 7:50	13.54	0.284	5.78	3.49	149.3	
7/3/09 9:35	13.51	0.249	6.26	3.45	150.3	
7/4/09 12:40	15.80	0.259	5.7	3.61	120.0	
7/5/09 9:40	14.16	0.275	6.26	3.51	111.3	
7/6/09 9:45	14.79	0.289	5.81	3.42	121.2	
7/10/09 10:00	13.66	0.223	6.82	3.63	185.8	
7/12/09 12:50	13.86	0.151	6.53	5.07	172.8	
7/13/09 11:55	13.84	0.156	6.74	4.74	153.6	
7/14/09 8:40	13.57	0.156	6.14	5.17	162.5	
7/15/09 9:30	13.50	0.157	6.71	5.47	157.2	
7/20/09 11:35	13.80	0.173	5.54	4.74	56.1	
7/23/09 11:20	13.77	0.169	5.39	5.00	33.8	
7/28/09 11:35	13.87	0.164	5.43	5.63	-22.6	
8/3/09 11:25	13.79	0.201	6.06	4.00	89.3	~5
8/10/09 12:10	13.96	0.166	6.7	5.86	57.8	
8/17/09 11:25	14.33	0.168	6.48	5.8	70.5	
8/24/09 11:45	14.00	0.174	6.78	5.65	12.3	~5
8/31/09 11:45	13.87	0.172	6.86	5.93	57.7	4-5
9/9/09 12:00	14.13	0.175	6.60	6.31	25.5	4-5

[1] YSI 556 MPS Multi-Parameter Instrument

[2] pH 20 series pH meter, Cole Parmer

* Interference with DO measurement by Chemets due to high Fe content in groundwater

5.18.9 XRF data for 2008 sediments cores

Location	Depth (ft)	Depth (m)	Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	As (mg/kg)
CW4-Injection well	26.0	7.9	7679	28	2397	28
	26.7	8.1	6825	18	2056	26
	27.3	8.3	8676	28	2534	30
	28.0	8.5	7889	23	2170	25
	28.6	8.7	8197	33	2825	29
	29.3	8.9	6806	24	2183	35
	29.6	9.0	6165	52	3051	43
	31.7	9.7	7143	64	3522	42
	32.2	9.8	7564	63	3733	44
	32.8	10.0	7286	42	3035	45
	33.5	10.2	16550	38	5987	130
	34.2	10.4	5405	14	1733	25
	34.8	10.6	8079	23	2440	42
	35.0	10.7	20	17	1539	32
	35.7	10.9	2322	30	2310	44
	36.3	11.1	1852	24	2435	59
	37.0	11.3	20	21	1972	40
	37.6	11.5	20	33	3341	62
	38.3	11.7	3814	50	3778	63
	38.9	11.9	3121	9	1707	39
	39.8	12.1	20	30	1929	60
CW 1 - Sampling well	25.0	7.6	5765	15	1652	28
	25.3	7.7	5450	13	1833	33
	26.0	7.9	8210	28	2687	31
	26.6	8.1	6159	15	1842	22
	27.3	8.3	11630	44	3658	34
	28.0	8.5	12140	40	3467	32
	28.6	8.7	11740	35	3185	40
	29.3	8.9	9404	29	2542	27
	29.6	9.0	7967	19	2088	23
	35.0	10.7	20	26	2097	22
	35.7	10.9	2391	35	2388	24
	36.3	11.1	2606	27	2745	29
	37.0	11.3	2821	25	2585	30
	37.6	11.5	3849	34	2614	28
	38.1	11.6	5965	10	1140	16
	38.8	11.8	7199	35	2348	26
	39.5	12.0	5363	5	1232	23

Location	Depth (ft)	Depth (m)	Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	As (mg/kg)
CW 1 – sampling well	39.8	12.1	4285	7	1103	20
Middle	25.0	7.6	6207	13	1559	23
	25.3	7.7	6782	18	2016	29
	26.0	7.9	6259	17	1876	28
	26.6	8.1	5632	10	1515	27
	27.3	8.3	7511	19	2070	28
	28.0	8.5	9042	29	2764	32
	28.6	8.7	10280	21	2572	36
	29.3	8.9	10660	45	3307	42
	29.6	9.0	8791	22	2423	35
	30.0	9.1	10730	35	3200	36
	30.7	9.3	10710	19	2313	33
	31.3	9.5	12490	16	3203	42
	32.0	9.7	11160	22	2893	37
	32.6	9.9	12700	26	2861	39
	33.3	10.1	18850	93	6204	65
	33.9	10.3	18370	56	4948	36
	34.8	10.6	26110	93	10350	151
	37.3	11.4	2086	42	2780	30
	37.9	11.6	2131	36	2301	28
	38.6	11.8	2951	42	2985	41
	39.2	12.0	2423	33	2452	31
	39.8	12.1	20	15	1725	28
	Min		20	5	1103	16
	Max		26110	93	10350	151

5.18.10 XRF data for 2009 sediment cores

Location	Depth (ft)	Depth (m)	Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	As (mg/kg)
CW4 - Injection well	25.0	7.6	5083	25	1806	33
	25.3	7.7	5716	25	1937	40
	26.0	7.9	5162	20	1474	35
	26.6	8.1	5751	23	1776	34
	27.3	8.3	7414	23	2374	25
	28.0	8.5	6960	18	2163	22
	28.6	8.7	7469	16	1992	25
	29.3	8.9	10340	36	3242	37
	29.6	9.0	11990	32	3264	37
	30.0	9.1	6487	28	2366	35
	30.7	9.3	6015	12	1986	18
	31.3	9.5	6722	20	1970	26
	32.0	9.7	5856	45	2702	30
	32.6	9.9	8032	34	2709	33
	33.3	10.1	9386	16	2326	24
	33.9	10.3	7611	34	2666	29
	34.8	10.6	6395	29	2391	20
	35.0	10.7	4933	38	2469	20
	35.7	10.9	7330	56	3271	30
	36.3	11.1	6631	64	3482	30
	37.0	11.3	6320	60	3901	32
	37.6	11.5	4793	32	2680	25
	38.3	11.7	5160	43	2545	25
	38.9	11.9	20780	49	5216	25
	39.8	12.1	6562	11	1521	24
	40.0	12.2	11630	78	7890	51
	40.3	12.3	13700	83	9030	61
	41.0	12.5	19220	15	3628	36
	41.6	12.7	28350	48	5518	54
	42.3	12.9	27850	23	3266	31
	43.0	13.1	26340	50	6552	46
	43.6	13.3	30050	49	11780	112
	44.3	13.5	27370	17	4551	48
	44.6	13.6	30060	39	6381	75
CW 1 - Sampling well	25.0	7.6	22.3	22	1369	24
	25.3	7.7	4271	20	1371	23
	26.0	7.9	4947	26	1812	27
	26.6	8.1	7024	19	1841	35
	27.3	8.3	7915	26	2399	43

Location	Depth (ft)	Depth (m)	Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	As (mg/kg)
CW 1 - Sampling well	28.0	8.5	5392	16	1687	30
	28.6	8.7	5789	15	1767	28
	29.3	8.9	10710	41	4064	39
	29.8	9.1	10280	58	4265	45
	30.0	9.1	4527	21	1505	22
	30.7	9.3	5311	19	1469	26
	31.3	9.5	6070	17	1525	26
	32.0	9.7	4792	13	1287	24
	32.6	9.9	5280	27	1977	19
	33.3	10.1	7197	29	2380	25
	33.9	10.3	9545	46	3161	28
	34.8	10.6	5639	12	1376	10
	35.0	10.7	5096	13	1355	24
	35.7	10.9	6223	13	1443	28
	36.3	11.1	6591	26	1996	18
	37.0	11.3	7698	50	2970	29
	37.6	11.5	5158	12	1401	8
	38.3	11.7	5175	29	1876	5
	38.9	11.9	11080	27	2410	26
	39.8	12.1	6290	9	1442	20
	40.0	12.2	6134	27	2017	10
	40.3	12.3	6169	20	3671	16
	41.0	12.5	8578	12	2291	26
	41.6	12.7	10050	13	1875	24
	42.3	12.9	9831	12	1437	17
	43.0	13.1	14360	63	5047	46
	43.6	13.3	15970	21	2638	34
	44.3	13.5	8838	9	2237	41
	44.6	13.6	17180	45	6652	77
	45.0	13.7	13850	23	3692	47
	45.3	13.8	10600	24	3226	41
	46.0	14.0	12450	20	2835	22
	46.6	14.2	15720	41	4031	37
	47.3	14.4	13690	31	3967	41
	48.0	14.6	9461	10	1579	33
	48.6	14.8	8018	9	1893	28
	49.3	15.0	24210	283	23790	167
	49.6	15.1	8610	14	1971	23
Middle centered	25.0	7.6	5117	16	1244	26
	25.3	7.7	3883	13	1336	23

Location	Depth (ft)	Depth (m)	Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	As (mg/kg)
Middle centered	26.0	7.9	5004	18	1502	27
	26.6	8.1	5458	17	1397	31
	27.3	8.3	6387	21	1717	34
	28.0	8.5	7497	26	2321	39
	28.6	8.7	6766	23	2248	29
	29.3	8.9	6675	13	1634	22
	29.6	9.0	8933	29	2847	31
	30.0	9.1	<20	14	1047	25
	30.7	9.3	<20	21	1306	27
	31.3	9.5	<20	21	1430	30
	32.0	9.7	3350	48	2798	38
	32.6	9.9	<20	21	1723	20
	33.3	10.1	3026	75	3312	25
	33.9	10.3	3612	36	1861	12
	34.8	10.6	<20	59	2969	17
	35.0	10.7	6191	23	1841	18
	35.7	10.9	7726	18	2123	23
	36.3	11.1	7550	40	2563	13
	37.0	11.3	6403	53	2869	10
	37.6	11.5	5702	36	2358	12
	38.3	11.7	5429	22	1765	15
	38.9	11.9	6462	15	1487	22
	39.8	12.1	6492	14	1162	14
	40.0	12.2	11910	18	3075	48
	40.3	12.3	7507	9	2149	30
	41.0	12.5	10210	8	3238	45
	41.6	12.7	16630	75	6171	50
	42.3	12.9	13500	15	1622	13
	43.0	13.1	12300	28	3856	36
	43.6	13.3	9782	31	3764	43
	44.3	13.5	6276	30	2626	22
	44.6	13.6	5902	28	2259	11
Middle - off axis (CW 2 side)	30.0	9.1	5011	25	1561	26
	30.7	9.3	4465	18	1377	27
	31.3	9.5	6251	23	1876	30
	32.0	9.7	5977	22	2082	23
	32.6	9.9	7368	41	2928	39
	33.3	10.1	12110	66	3634	25
	33.9	10.3	6956	32	1302	2
	34.3	10.4	6854	25	1549	7

Location	Depth (ft)	Depth (m)	Al (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	As (mg/kg)
Middle - off axis (CW 2 side)	34.8	10.6	6983	79	4089	12
	35.0	10.7	5545	43	3178	22
	35.7	10.9	6066	39	2912	20
	36.3	11.1	5850	42	2947	18
	37.0	11.3	5570	33	4020	22
	37.6	11.5	6312	35	2578	23
	38.3	11.7	7378	49	3017	30
	38.9	11.9	7343	55	3324	30
	39.8	12.1	27600	31	4923	56
	45.0	13.7	6534	22	1834	19
	45.3	13.8	11150	28	3114	32
	46.0	14.0	11820	28	3286	40
	46.6	14.2	9227	18	2875	35
	47.3	14.4	6875	19	2826	37
	48.0	14.6	7313	15	1739	19
	48.6	14.8	15850	102	8543	65
	49.3	15.0	13540	13	1503	23
	49.6	15.1	18050	287	35090	203
	Min		22	8	1047	2
	Max		30060	287	35090	203