DISSERTATION

REMEDIATION OF ARSENIC
AND PERSISTENT ORGANIC CONTAMINANTS
USING ENHANCED IN-SITU METHODS

Submitted by:

Mary Elizabeth Sullivan

Civil and Environmental Engineering

In partial fulfillment of the requirements

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Colorado State University

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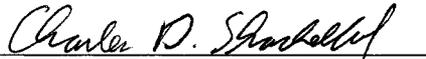
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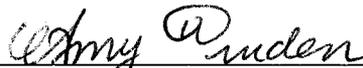
Dr. Amy Pruden
Co-Advisor
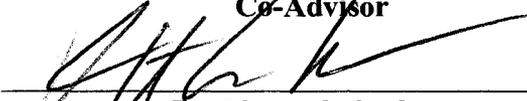
Dr. Kenneth Carlson
Advisor
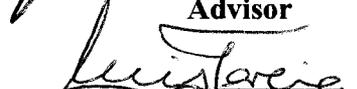
Dr. Luis Garcia
Department Head

ABSTRACT OF DISSERTATION

REMEDIATION OF ARSENIC AND PERSISTENT ORGANIC CONTAMINANTS USING ENHANCED IN-SITU METHODS

The demand for inexpensive and reliable water treatment technologies continues to increase as the number of contaminants grows and their associated fate and transport mechanisms become more complex. Advances in public health have contributed to the implementation of more stringent drinking water standards for compounds such as arsenic. Furthermore, advances in analytical chemistry have contributed to the detection of previously immeasurable compounds including endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and other bioactive chemicals in wastewater effluents and surface waters around the world. This research examined the use of enhanced in-situ methods for the remediation of arsenic and several persistent organic contaminants. Unamended and amended electrokinetic remediation (ER) column studies conducted to determine the impact on arsenic revealed arsenic removal from the soil column due to the electrolysis of water and electromigration of the charged species. Column studies also examined the impact of amended aquifer recharge and recovery (ARR) treatment on persistent organic compounds. Water treatment residual-amended ARR columns were utilized to promote an environment capable of reducing flame retardants. The results indicated that the presence of water treatment residuals created a reducing environment and provided ideal adsorption sites and sources of organic matter in the form of leached carbon. Unamended and amended ER column studies were completed to examine the impact on two pharmaceuticals (sulfamethoxazole and carbamazepine) and three organophosphorus flame retardants (tris-(2-chloroethyl)

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phosphate, tris-(2-chloro-, 1-methylethyl)phosphate, and tris-(2-chloro-, 1-chloromethyl-ethylphophate). Results indicated that the highest removal results occurred in the significant redox zones of the ER column. Oxidizing conditions at the anode and reducing conditions at the cathode had significant impacts on the compounds' concentrations in the column's pore water. Lastly, critical characterization of the compounds' affinity for aqueous, colloidal, and solid phases was determined for the five organic compounds. These results, as well as sources of flame retardant contamination in the experimental design, was useful (and necessary) in interpreting the treatment results from the amended ARR and electrokinetic column studies.

Mary Elizabeth Sullivan
Civil and Environmental Engineering
Colorado State University
Fort Collins, CO 80523
Spring 2008

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List of Abbreviations

ARR	Aquifer recharge and recovery
As	Arsenic
CBZ	Carbamazepine
EI	Electrokinetic injection
EM	Electromigration
EO	Electroosmosis
ER	Electrokinetic remediation
IS	Internal Standard
POC	Persistent organic compounds
RBF	River bank filtration
SMX	Sulfamethoxazole
TCEP	tris-(2-chloroethyl) phosphate
TCPP	tris-(2-chloro-, 1-methyl-ethyl) phosphate
TDCP	tris-(2-chloro, 1-chloromethyl-ethyl) phosphate
WTR	Water treatment plant residuals
WWTP	Wastewater treatment plant

1.0 Introduction

1.1 Background

The demand for clean drinking water continues to grow as the challenge to provide safe potable water becomes increasingly complex and costly. The drinking water community is faced with new obstacles in meeting customer demand in an environment where water quality can be affected by many variables (Figure 1-1). As a result, there is a major effort to develop passive treatment technologies (including electrokinetic remediation) which utilize engineered microbiological systems for complete contaminant removal or to act as an integral process in a multiple barrier treatment scheme. Passive treatment is gaining interest in areas where access to conventional water treatment technologies is limited by local economics, geographic location, and access to power and other raw materials. Passive treatment is also emerging as a potential approach to remove or breakdown contaminants prior to conventional treatment in an effort to remove or alter contaminants for better removal results in downstream processes and to minimize concentrated waste streams from conventional treatment processes.
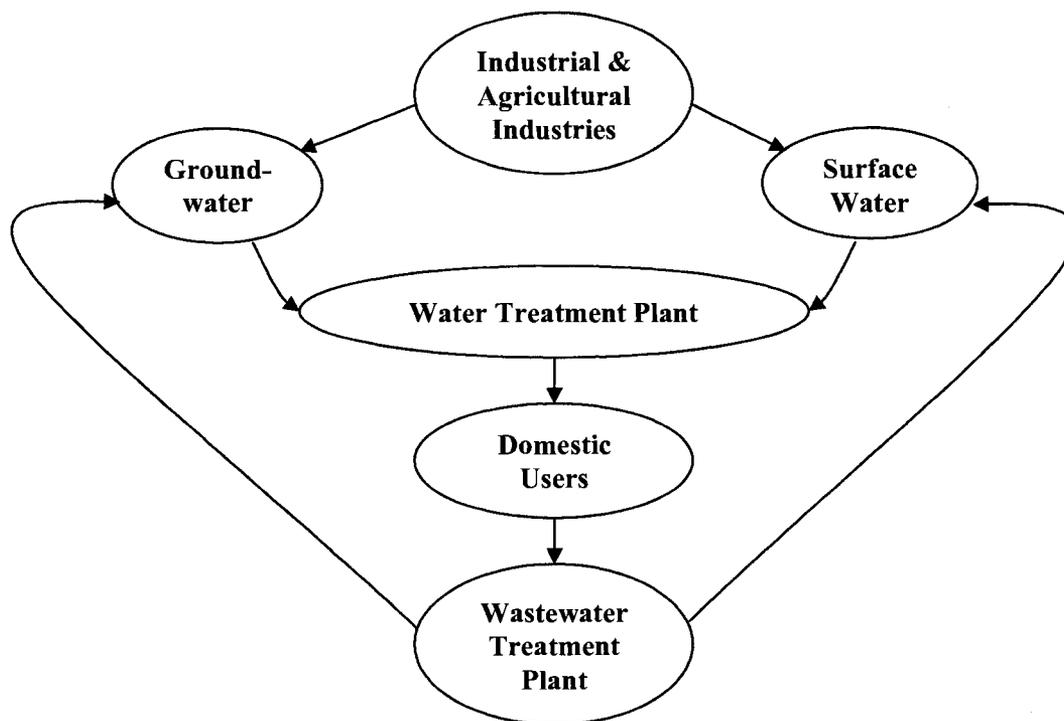
Figure 1-1: Inter-related pathways of drinking water sources, water users, and treated effluent

1.2　Contaminants of Interest

As interest in alternative treatment technologies grows, with simplicity and low-cost as major driving factors, existing and new compounds are altering the playing field for water treatment professionals. Advances in public health have contributed to the implementation of more stringent drinking water standards for compounds such as arsenic (from 50 to 10 μg L^{-1}). This water contaminant, although previously known to be detrimental to human health, is now recognized as a direct cause to certain types of cancer and to other health problems at concentrations as low as 100 parts per billion (ppb) (WHO 2003). Furthermore, advances in analytical chemistry have contributed to the detection of previously immeasurable compounds including endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and other

bioactive chemicals in wastewater effluents and surface waters around the world (Kolpin et al. 2002). Although researchers do not currently know the extent to which these compounds in drinking water impact human health, water treatment professionals generally agree that additional research must be conducted.

Although the occurrence, transport, and ultimate impact of these emerging contaminants on humans and the aquatic ecosystems are not completely understood, concern that these ubiquitous compounds may contribute to the increased incidences of reproductive and physiological abnormalities, cancer rates, and strains of antibiotic-resistant bacteria has prompted researchers to examine their presence and persistence throughout the water supply, treatment, and re-use cycle (Kolpin et al. 2002; Petrovic et al. 2003). Research is also underway to determine if the exposure to multiple organic compounds at low concentrations has synergistic human-health consequences (Stackelberg et al. 2004; Pomati et al. 2006). Additionally, as "pure" water sources are becoming rare, the need for water treatment professionals to implement indirect potable reuse practices is becoming more common. The presence of these new compounds in wastewater effluents creates a new area of concern for indirect potable water reuse utilities because there is little knowledge regarding the presence, concentrations, and toxicities of these compounds.

This research was developed to focus on several compounds, selected to provide a cross-section based on their occurrence and persistence in the environment. Arsenic above the new drinking water standard of 10 μg L^{-1} has been found in potable ground water resources in many parts of the world (WHO 2003). In the United States, drinking water aquifers in the Great Lakes Region, New England, and West have documented

arsenic levels greater than 10 μg L^{-1}(Welch et al. 2000). With half the population of the United States relying on ground water for drinking water, arsenic has been increasingly viewed as an important, lethal contaminant present in drinking water sources. The other selected contaminants (sulfamethoxazole (SMX), carbamazepine (CBZ), tris-(2-chloroethyl) phosphate (TCEP), tris-(2-chloro-, 1-methylethyl) phosphate (TCPP), and tris-(2-chloro-, 1-chloromethyl-ethylphophate (TCDP)) are organic compounds which are suspected endocrine disruptors and remain relatively unaffected by conventional wastewater and water treatment processes (Snyder et al. 2003; Heberer et al. 2004; Meyer et al. 2004; Zuehlke et al. 2004; Marklund et al. 2005; Westerhoff et al. 2005).

1.3   Treatment

Many in-situ treatment methods have been employed to remove or reduce contaminants in surface and groundwater including river bank filtration, aquifer recharge and recovery, and electrokinetic remediation. River bank filtration (RBF), which has been practiced for over 100 years, is an effective and mostly inexpensive natural process for removing inorganic, microbial, and some organic contaminants from river water (Grunheid et al. 2005). The river water is drawn through the aquifer using a production well and is filtered through the sand and sediments in the stream bank and purified via different mechanisms: physical filtration, chemical adsorption, and biodegradation.

Aquifer recharge and recovery (ARR) is another natural process which occurs within the groundwater aquifer. In ARR treatment, water is transferred to an independent aquifer typically via a piping network. The water then percolates into this independent aquifer (Bouwer 1996). As in RBF treatment, the transport of the water through the aquifer is dictated by production wells located at set distances from the infiltration point

based on desired hydraulic detention times. In both treatment scenarios, as the water travels through the aquifer the water quality is improved. Recently, ARR filtration systems have been modified in order to treat contaminants which were not successfully removed in conventional ARR systems. The modifications involve the use of engineered material including saw dust and water treatment plant residuals (Carlson, 2006). The type of material is selected based on the target contaminant and subsurface conditions.

Electrokinetic remediation (ER) is a technology that has been successfully applied in the removal, reduction, and stabilization of groundwater contaminants such as heavy metals, dense non-aqueous phase liquids (DNAPL), chlorinated solvents and other contaminants (Acar et al. 1993; Acar et al. 1995; Acar et al. 1996; Gent et al. 2003; Jackson et al. 2004).

This research includes both unamended and amended electrokinetic remediation column studies. Unamended ER uses mechanisms such as electromigration, electroosmosis, and electrolysis of water to remediate the compounds of concern. In amended ER, amendments are introduced to the subsurface through the use of an electrical potential. Depending on the selected amendment (e.g., acetic acid or potassium permanganate), the electrolyte can assist in pH control, promote chemical oxidation or stimulate microbial communities.

An enhanced ARR system could be an alternative or addition to a conventional water treatment process. Additionally, ER may be used as a supplement to a riverbank filtration site. This method of treatment for persistent compounds may be more effective than adding additional treatment barriers within a water treatment plant. However, ER-RBF and engineered-ARR treatment systems have yet to be studied for the breakdown or

removal of arsenic or persistent emerging contaminants and is the key aspect of the research project.

This research tests the hypothesis that ER can be used to create a severe redox and pH environment that will increase the removal efficiency of bank filtration for the breakdown of persistent emerging contaminants and efficiently remove arsenic from groundwater through mechanisms including reduction and oxidation of the original compound and formation of complexes and precipitates.

1.4   Dissertation Format

The format of this dissertation has been organized in the following manner: Chapter 2 "Literature Review" provides an extensive review on the sources, human health risks, and current removal technologies pertaining to arsenic, SMX, CBZ, TCEP, TCPP, and TDCP. Additionally, a detailed explanation of river bank filtration, electrokinetic remediation, and enhanced-ARR and the mechanisms behind the technologies is provided. The research hypotheses and objectives are also identified in Chapter 2. Chapter 3 "Amendment Transport Study" is organized as a typical manuscript. The research summarized in this chapter tests the hypothesis that charged amendments can be successfully and uniformly introduced to varying soil conditions at low current levels. Chapter 4 "Arsenic Removal in an Electrokinetic Remediation System" is also organized as a conventional manuscript. This chapter summarizes arsenic sources, chemistry, and current treatment technology. It also defines the materials and methods used to conduct the arsenic ER column tests, the results, and summary of the test findings. Chapter 5 "QA Characterization for the Analyses of Organic Compounds" describes in detail the method development for the measurement of

SMX, CBZ, TCEP, TCPP, and TDCP. In addition, this chapter addresses the quantification of the compounds' affinity to partition to the aqueous, solid, and colloidal phases. Chapter 6 "Remediation of Persistent Organic Compounds" is formatted as a conventional manuscript. The paper summarizes the findings of remediating SMX, CBZ, TCEP, TCPP, and TDCP in three different column studies including enhanced ARR and RBF supplemented with unamended and amended electrokinetic remediation. Chapter 7 summarizes the conclusions of the research. Chapter 8 lists the references and Chapter 9 includes the associated appendices.

2.0   Literature Review

2.1   Background

The demand for clean drinking water continues to grow as the challenge to provide safe potable water becomes increasingly complex and costly. As interest in alternative treatment technologies grows, with simplicity and low-cost as major driving factors, existing and new compounds are forcing water treatment professionals to provide treatment schemes for varying and complex scenarios. The following is an extensive review on the sources, human health risks, and current removal technologies as it pertains to arsenic, SMX, CBZ, TCEP, TCPP, and TDCP. Additionally, a detailed explanation of two treatment alternatives, enhanced ARR and RBF supplemented with electrokinetic remediation, is provided.

2.2   Arsenic

The U.S. Environmental Protection Agency (EPA 2002) proposed an interim maximum contaminant level (MCL) for arsenic in drinking water of 50 μg L^{-1} as part of the National Interim Primary Drinking Water Standards under the Safe Drinking Water Act. The U.S. Public Health Service originally established the 50 ppb standard in 1942 (Council 1999). Due to the increased findings of arsenic effects on public health, the United States EPA recently adopted a new maximum contaminant level for arsenic in drinking water at 10 ppb. The extensive contamination of drinking water sources with arsenic as presented in Figure 2-1 and the growing concern over the adverse effects small concentrations of arsenic have on public health has brought arsenic to the forefront for public health and water treatment professionals. Sources of arsenic in natural waters can originate from natural and anthropogenic sources and can contaminate both ground and

surface waters (Council 1999; Safety 2001). The distribution of arsenic and its

speciation is mainly dependent on the pH and reduction-oxidation (redox) potential

conditions. Common arsenic removal technologies require a pre-oxidation step to

oxidize As(III) to As(V). The addition of chemical reagents such as hydrogen peroxide,

ozone, potassium permanganate, or chlorine promotes the transformation of As(III) to

As(V). Subsequent treatment technologies may include chemical precipitation,

adsorption (ferric chloride addition), and/or membrane separation.
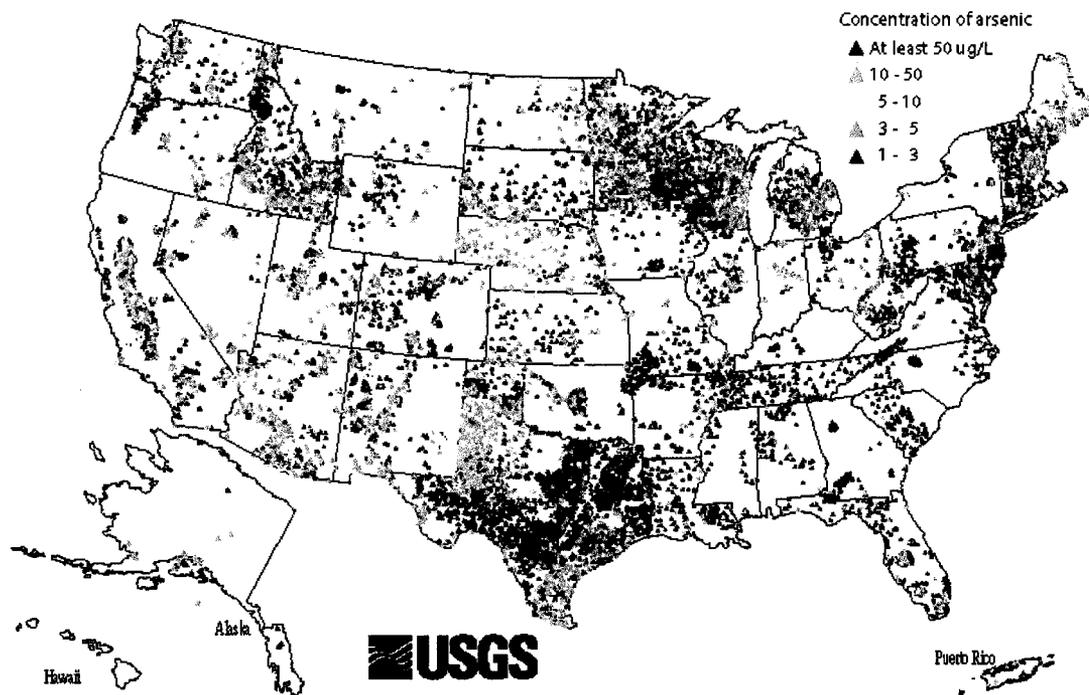
Figure 2-1: Arsenic in U.S. Ground Waters (Ryker 2001)

Arsenic occurs naturally and is widely distributed throughout the earth's soil and

water bodies. The metalloid is the 20th most abundant element in the earth's crust at 1.5-

2 parts per million. Arsenic is found in organic and inorganic forms, however, the organic forms are considerably less harmful. Organic arsenic is present in soils as cocodylic acid, also known as dimethylarsenic acid (DMA) and may also be found at low concentrations in some foods. The primary source of arsenic in the environment is due to the release of arsenic due to weathering and dissolution of As-enriched rocks, minerals, and ores (Wang et al. 2006). The main anthropogenic sources of arsenic include energy production, mining, smelting, and refining of the ores, industrial processes, and agricultural processes. Agricultural processes include the application of herbicides and insecticides to fields. As such, arsenic can enter drinking water via both groundwater and surface water sources. Approximately 100,000 tons of arsenic is produced worldwide. The majority of this is produced as a by-product of the smelting of copper, lead, cobalt, and gold ores. The amount of arsenic associated with lead and copper ores and gold ores is approximately 2-3% and 11%, respectively (Welch et al. 2000).

Arsenic trioxide, As_2O_3, is the chief commercial compound. Approximately 90% of the United States' arsenic demand is for use as a wood preservative. Lesser demands for arsenic are used in the production of agricultural chemicals including insecticides, herbicides, algicides, and growth stimulants for plants and animals. Additionally, other small demand areas include the glass and nonferrous alloy production fields and in the electronics industry (Safety 2001). Extremely high-purity arsenic (99.999%) is used in the manufacture of semiconductors. Gallium arsenide is used in light-emitting diodes (LEDs) and solar cells. Indium arsenide is used to produce infrared devices and lasers. Prior to the introduction of DDT in the 1940s, most pesticides were made from inorganic arsenic compounds. As a result, some agricultural soils have arsenic concentrations in

excess of 100 ppm, but most studies suggest that this arsenic is confined to the topsoil. In comparison, most soils unaffected by human activities contain less than 10 ppm arsenic (WHO 1996). Of the arsenic trioxide produced, approximately 75% is used as agricultural pesticides and feed additives.

For most people, food is the largest source of arsenic exposure (about 25 to 50 micrograms per day [μg d^{-1}]), with lower amounts coming from drinking water and air (Safety 2001; WHO 2003). Among foods, some of the highest levels are found in fish and shelfish; however, this arsenic exists primarily as organic compounds, which are essentially nontoxic. However, in areas (i.e., Texas, New England and the Great Lakes regions) that are prone to high levels of arsenic due to natural geothermal and geo-hydrological processes and anthropogenic activities, water is the most vital media which provides a pathway into the human body. Airborne arsenic, due to occupational exposure, can also negatively contribute to health problems. Human exposure to arsenic can have both short and long-term effects on human health depending on the arsenic dose and duration of exposure to the pollutant. Complications arising from chronic exposure can include dermatological problems including melanosis (pigmentation) and keratosis (rough, dry skin lesions), reproductive, neurological, cardiovascular, respiratory, hepatic, hematological, and diabetic effects in humans (Council 1999). Studies have reported that consumption of groundwater contaminated with arsenic at concentrations as low as 100 ug L^{-1} can cause skin, lung, and urinary bladder cancers. Additionally, increased risks of kidney and liver cancer have been reported (Council 1999). The U.S. EPA requested the National Academy of Sciences to review worldwide studies of arsenic health effects to determine the health risks of arsenic at various levels of exposure. The Academy

concluded the risk level at a 50 ug L^{-1} was greater than previously determined and that the level should be lowered.

There are over 200 different mineral forms of naturally occurring arsenic. The approximate breakdown of these arsenic forms is as follows: 60% arsenates, 20% sulfides and sulfosalts, and 20% including arsenides, arsenites, oxides, silicates, and elemental arsenic (Onishi 1969-1978). Contaminated surface and ground waters may also contain organic forms of arsenic including mono methyl arsenate (MMA) and dimethyl arsenate (DMA). The major arsenic species found in the environment are arsenite As(III), arsenate As(V), arsenious acids, and arsenic acids (Figure 2-2). The pH and redox conditions determine the distribution of arsenic species in natural waters as either As(III) or As(V). In surface waters or oxidizing conditions, arsenate is predominant, whereas in groundwaters where mildly reducing conditions exist, arsenic is typically found in its thermodynamically stable and soluble form, arsenite. However, both oxidation states have been detected in oxic and anoxic conditions (Oremland et al. 2003). Arsenite is the most toxic of the arsenic compounds and unfortunately, more soluble than arsenate and hence, more mobile. Although arsenate can exist in four forms in aqueous solutions (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}), the oxyanionic species $H_2AsO_4^-$ or $HAsO_4^{2-}$ are the most common forms detected in the environment. The equilibrium expressions for these arsenate forms are as follows:

$$H_3AsO_4 \rightarrow H^+ + H_2AsO_4^- \qquad \text{(Eq. 2.1)}$$

$$pK_1 = 2.2$$

$$H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-} \qquad \text{(Eq. 2.2)}$$

$$pK_2 = 6.98$$

$$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$$ (Eq. 2.3)

$$pK_3 = 11.6$$

At pH values typically found in most natural waters, As(III) is present at the non-ionic

form of arsenious acid (H_3AsO_3). As(III) may also exist as $H_2AsO_3^-$ and $HAsO_3^{2-}$

depending on pH. The equilibrium expressions for all arsenite species are as follows:

$$H_3AsO_3 \rightarrow H^+ + H_2AsO_3^-$$ (Eq. 2.4)

$$pK_1 = 9.2$$

$$H_2AsO_3^- \rightarrow H^+ + HAsO_3^{2-}$$ (Eq. 2.5)
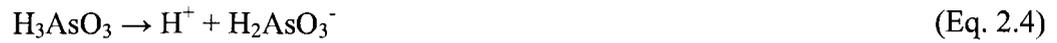
$$pK_2 = 13.41$$
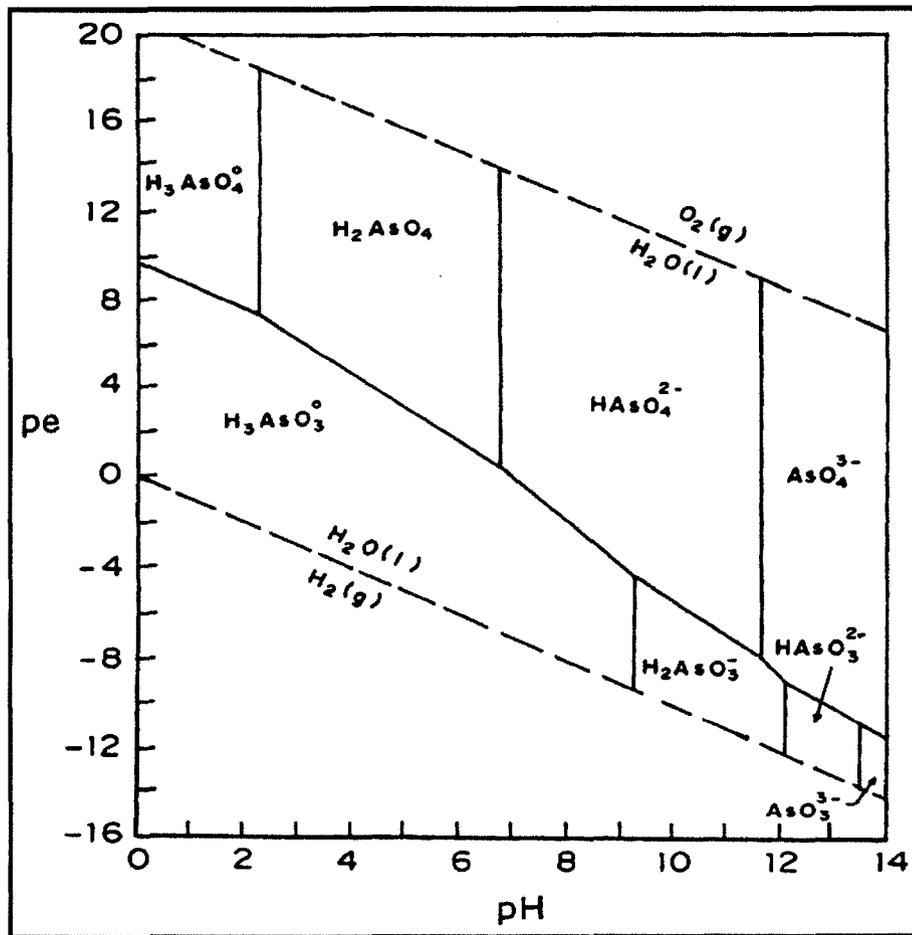
Figure 2-2: pe-pH diagram of arsenic in water at 25° (Pourbaix 1966)

Physico-chemical processes and biological processes can remove arsenic from water. Physico-chemical processes include: chemical coagulation-precipitation, adsorption using chemical reagents such as ferric chloride, membrane separation, and ion exchange. Biological processes for the removal of arsenic can include: phytoremediation and treatment with living microbes or biofiltration (Mondal et al. 2006). Since As(III) is most commonly found in its nonionic form, it likely does not often interact with solid surfaces, and therefore cannot be removed with such common removal technologies such as adsorption or precipitation (Torrens 1999). Common arsenic removal technologies involve oxidizing As(III) to As(V) using the addition of chemical oxidants such as potassium permanganate, ozone, hydrogen peroxide, or chlorine. Unfortunately, the addition of oxidants increases the cost of arsenic removal and may also create unwanted residuals and byproducts.

Natural attenuation of arsenic-contaminated soils and groundwater has also been considered an option for a cost efficient in situ remedial option. The principal mechanism for in situ remediation relies on arsenic's ability to adsorb to a solid phase. The sorption is directly influenced by the arsenic speciation and the site's geochemical characteristics such as pH, redox potential and other existing ions. Essentially, arsenic (in the As (V) form) would adsorb onto an adsorbent such as hydroxides of iron, aluminum, and manganese, clay and sulfide minerals, and organic matter and lead to immobilizing arsenic in soils and removing it from groundwater (Wang et al. 2006).

Electrokinetic remediation (unamended and amended) is a viable treatment means to remove arsenic from groundwater. Electromigration could be used to transport

charged arsenic ions to the anode. Additionally, electroosmosis could be used to transport neutral arsenic species from the anode region to the cathode region. And lastly, the electrolysis of water at both electrodes will create reducing and oxidizing conditions capable of manipulating conditions within the soil column and consequently impacting the form of arsenic species.

2.3   Emerging Organic Contaminants

The occurrence, fate, and transport of pharmaceuticals, personal healthcare products, and bioactive chemicals in the aquatic environment have become important environmental issues and have attracted significant attention. There is major concern that these ubiquitous compounds may contribute to the increased incidences of reproductive and physiological abnormalities(Tyler et al. 1998), cancer rates(Fenton 2006), and strains of antibiotic-resistant bacteria (Pruden et al. 2006). It is believed that some of these compounds can have major effects on the endocrine systems of humans and wildlife. The endocrine system is made up of glands throughout the body; hormones are synthesized and secreted by the glands into the bloodstream, and receptors in the various target organs and tissues recognize and respond to the hormones. The function of the system is to regulate a wide range of biological processes, including control of blood sugar, growth and function of reproductive systems, regulation of metabolism, brain and nervous system development, and development of an organism from conception through adulthood and old age. Disruptions in hormonal balance at critical life stages may have long-lasting effects (Campbell 1993).

Although the impact of EDCs and PPCPs on public health and the aquatic ecology continues to be studied, many aspects surrounding this emerging issue lack

complete understanding (Daughton et al. 1999). One approach to minimizing the number and volume of compounds entering the environment is to eliminate the use of all suspected endocrine-disrupting compounds. This may be a potential solution for personal healthcare products and bioactive chemicals which could theoretically be replaced with less toxic substitutes. Although this may ultimately occur, it is not a sound solution for the contaminants currently in the environment. Additionally, this approach does not address pharmaceuticals that are predominantly excreted by humans and animals and generally enter the environment via treatment plant point discharges or as the result of non-point sources such as land application of biosolids or surface runoff from agricultural sites.

Some EDCs and PPCPs can be naturally attenuated in the stream or river through physical processes including mixing, dilution, and diversion and also through environmental removal processes such as volatilization, sorption, precipitation, photolysis, biodegradation, and biotransformation (Barber et al. 2006; Gurr et al. 2006). However, not all compounds can be naturally attenuated in streams and therefore, research efforts need to address the presence of these persistent compounds in surface, drinking and ground waters and determine the best method for removing the compounds at the sewage treatment and/or the drinking water treatment plant. Water treatment professionals are striving to be proactive by designing treatment systems with multiple treatment barriers (including indirect potable reuse) that will remove the emerging contaminants. In order to accomplish this, the potentially harmful compounds currently found in water sources need to be fully researched. This includes determining the source(s), concentration, and fate of the compound in water treatment processes.

Intentional indirect potable reuse is accomplished through augmenting raw drinking water sources with treated effluent. This method is an alternative in which communities are turning to in order to meet their water demands in times of shrinking, dependable water resources and increased growth. Recent research has determined that the occurrence and concentration of some PPCPs are highly seasonally dependent, and reach maximums when river flows are low and imported reclaimed nonpotable wastewater volumes are high (Loraine et al. 2006). This data magnifies the reason for concern in areas that depend on water sources influenced by indirect potable reuse.

Previous studies have already determined that several organic compounds, specifically carbamazepine, tris(2-chloroethyl)-phosphate, and sulfamethoxazole, continue to persist in wastewater treatment effluent, downstream of bank filtration sites, and in treated drinking water (Snyder et al. 2003; Heberer et al. 2004; Zuehlke et al. 2004; Westerhoff et al. 2005). The reported persistence of these compounds in the environment was the basis for their selection in this study. The following section summarizes the current status of research regarding the occurrence, removal, and ultimate fate of the compounds selected in this study and describes the motivation for an alternative treatment method.

2.3.1 Regulatory Review

A well-cited study by Kolpin et al. surveyed 139 streams within the U.S. analyzing samples for the occurrence of ninety five pharmaceuticals, hormones, and personal healthcare products. The researchers detected the compounds in eighty percent of the surveyed streams (Kolpin et al. 2002). Although the concentrations of the compounds were below drinking water standards or aquatic-life criteria, many of the

compounds do not have established guidelines, as opposed to more conventional compounds such as arsenic, which is regulated under the Safe Drinking Water Act (SDWA). In 1995 US legislation specifically mentioned endocrine disruption in the amendments to the SDWA (bill number S.1316) and in the Food Quality Protection Act (bill number P.L. 104-170). Essentially these bills require that chemicals be tested for endocrine-disrupting activity before being manufactured or used in processes where drinking water or food has the potential of becoming contaminated. The Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) was formed during 1996 in order to make recommendations to the EPA on how to develop the screening and testing program mandated by Congress. The Committee was composed of representatives from industry, government, environmental and public health groups, worker safety groups, and academia. The EDSTAC addressed the health effects on humans and wildlife by focusing attention on estrogenic, androgenic, and thyroid hormone systems. The committee recommended that EPA consider pesticides, industrial chemicals, and environmental contaminants. The committee's recommendations included setting priorities, Tier 1 screening, and Tier 2 testing. EPA outlined the Endocrine Disruptor Screening Program (EDSP), which incorporated many of EDSTAC's recommendations, in two Federal Register Notices published in 1998.

The EPA formed the Standardization and Validation Task Force (SVTF) to coordinate and conduct the scientific and technical work necessary to validate the recommendations by the EDSTAC. In 2001, the SVTF was replaced by the Endocrine Disruptor Methods Validation Subcommittee (EDMVS). The mission of this group is to provide technical input to the EPA for the assays recommended by EDSTAC. The

outcomes of the EDMVS will be critical to the water industry in the long term because EDCs will ultimately be identified; however, the current legislation only regulates the industries using or producing the compounds (34). In 2004, the Endocrine Disruptor Methods Validation Advisory Committee (EDMVAC) was established in accordance with the Federal Advisory Committee Act (5 U.S.C. App. 2 Section 9c) and was formed to replace the EDMVS. The EDMVAC will provide advice and recommendations to the EPA on scientific and technical aspects of the Tier I screens and Tier II assays being considered for the Endocrine Disruptor Screening Program similar to the EDMVS. The committee will evaluate relevant scientific issues, protocols, data, and interpretations of the data for the assays during the validation process. EDMVAC will also provide advice on the composition of the Tier I screening battery (EPA 2006). In 2005, the EPA published the Chemical Selection Approach for Initial Round of Screening. This document presents the EPA's method for the selection of the initial group of 50 to 100 chemicals to be screened under Tier 1 of the Agency's Endocrine Disruptor Screening Program (EDSP). The Food and Drug Administration (FDA) generally requires ecological testing and evaluation of a pharmaceutical only if an environmental concentration in water or soil is expected to exceed 1 ug L^{-1} or 100 ug kg^{-1}, respectively (USFDA 1998). California has modified its draft regulations for indirect potable reuse to include language covering monitoring recycled water for EDCs and pharmaceuticals specified by the State (Snyder et al. 2003).

2.3.2 Pharmaceuticals in the Environment

The United States annually produces approximately fifty million pounds of antibiotics, with approximately 40% used in animal production to treat diseases and increase animal weight gain (non-therapeutic use) (Batt et al. 2006). The antibiotics

administered to the animals are excreted in un-metabolized and metabolized forms, making the soil and water susceptible to contamination through cropland application of animal wastes and overland flow. Pharmaceuticals used to treat medical conditions in humans are excreted from the body in the parent compound form or as metabolites. The compounds are subject to metabolic reactions in both humans and animals such as hydroxylation, cleavage, or glucuronidation (Daughton et al. 1999; Hirsch et al. 1999). Some metabolites have reversible reactions and are able to transform back to the parent compound after excretion from the body (Hirsch et al. 1999). These compounds and their metabolites enter the domestic wastewater treatment plant via human excretions or as unused products discarded in toilets. These compounds may have unintended health outcomes on the aquatic ecology due to the pharmacological functions of the compounds. Most pharmaceuticals do not pose a toxic threat to the aquatic environment, but instead they have a significant cumulative effect on the metabolism of non-target organisms and the aquatic ecology as a whole (Daughton et al. 1999). The behavior of the compound in the environment will depend on chemical properties such as water solubility, pH of the matrix, volatility, and sorption potential (Boxall et al. 2003). Most pharmaceutically active compounds (PhACs) are polar and neither volatile nor biodegradable, which explains why the compounds are not removed during a WWTP's sedimentation and biological treatment processes. In addition, some PhACs may transform into conjugates that can be hydrolyzed in the future to revert back to the parent compound.

Reports of antibiotic contamination of soil, surface water, and groundwater (Kolpin et al. 2002; Yang et al. 2003; Bendz et al. 2005; Castiglioni et al. 2006) have raised public concern because low levels of antibiotics will promote the propagation of

antibiotic-resistant bacteria. It is estimated that there are more than eighty

pharmaceutically active compounds from various therapeutic classes at concentrations in

the ug L^{-1} range in sewage, surface and groundwaters (Heberer 2002). Current research

regarding the effect of therapeutic drug mixtures on human embryonic kidney cells

suggests that the proliferation of cells is inhibited through adverse effects on their

physiology and morphology. This study was conducted using a drug mixture containing

thirteen drugs including such drugs as carbamazepine and sulfamethoxazole in the ng L^{-1}

concentration range which is typical of environmental levels. The decrease in cell

proliferation compared to the controls was reported to be between ten and thirty

percent(Pomati et al. 2006).

The ultimate fate of micropollutants in water treatment plants depends on their

physico-chemical properties, such as lipophilicity or acidity. Historically, the

compound's sorption effectiveness and its affinity for organic matter were estimated by

the octanol-water partition coefficient (K_{ow}) and the organic carbon partition coefficient

(K_{oc}) (Carballa et al. 2005). The K_{ow} is the ratio between the equilibrium concentrations

of a compound in octanol and water at a specific temperature. K_{oc} relates the

compound's concentration sorbed to organic carbon and the concentration dissolved in

water. Typically, pharmaceuticals can be divided into three main groups depending on

their physico-chemical properties: lipophilic (high K_{ow} values), neutral (non-ionic) and

acidic (hydrophilic and ionic) (Carballa et al. 2005). Researchers have found some

limitation in applying these indicators in the determination of a PPCPs sorption behavior

and ultimate fate in the environment (Holbrook et al. 2004). A parameter known as the

solid-water distribution coefficient (K_d) has been proposed (Ternes et al. 2004)as an

acceptable alternative. It is defined as the ratio of the concentration of a compound in the solid to aqueous phase under equilibrium conditions. This coefficient addresses absorption and adsorption which are the two main sorption mechanisms. Absorption is defined as hydrophobic interactions characterized by K_{oc} values, whereas adsorption is defined as electrostatic interactions related to the compound's tendency to be ionized or dissociated in the aqueous phase (typically characterized by the dissociation constant pKa) (Carballa et al. 2005).

2.3.2.1 Sulfamethoxazole

The antibiotic group sulfonamide (sulfa drugs) is a group of synthetic antimicrobials used for therapeutic treatment of infectious disease in humans and for treating and protecting the health of animals (Boxall et al. 2003). When used at sub-therapeutic levels in livestock production, the sulfa drugs will improve feeding efficiency. In human and veterinary medicine, these drugs are used in the treatment of infections (Perez et al. 2005). Sulfa drugs are designed to compete with p-aminobenzoic acid in the enzymatic synthesis of dihydropholic acid. This action leads to a decreased availability of the reduced folates which are essential in the synthesis of nucleic acids (Bogialli et al. 2003). Up to ten different sulfonamides are used in veterinary medicine to treat bacterial and protozoan infections in cattle, swine, and poultry. Some sulfonamides are also active against some viruses (Bogialli et al. 2003). Sulfonamides have two nitrogen functional groups as noted in Figure 2-3. Sulfamethoxazole (SMX) which belongs to the sulfonamide group, contains two functional moieties at both sides of the sulfonamide linkage ($-NH-S(O_2)-$). Thus, SMX exhibits two dissociation constants, one involving the protonation of the primary aromatic

amine –NH2 and the other corresponding to the deprotonation of the sulfonamide –NH (Nghiem et al. 2005). The speciation of SMX over the entire pH range includes anionic species at pH above 5.7, uncharged between 1.7 and 5.7, and positive species below pH of 1.7. The presence of these persistent compounds in surface water and soil has created public concern due to the low levels of antibiotics which can favor the proliferation of antibiotic resistant bacteria.

In published studies, data indicated that surface waters impacted by wastewater treatment effluent and confined animal feeding operation (CAFOs) contained sulfonamides that appeared to persist in the environment and not biodegrade (Daughton et al. 1999; Hirsch et al. 1999; Heberer 2002; Kolpin et al. 2002; Boxall et al. 2003; Bendz et al. 2005; Carballa et al. 2005; Batt et al. 2006; Cunningham 2006; Kinney et al. 2006; Pei et al. 2006). Studies have found the presence of sulfa drugs at levels of 0.04-6.47 mg L^{-1} at landfill sites (Daughton et al. 1999). Sulfonamides approved strictly for veterinary medicine have been detected in private water wells in proximity to a CAFO at concentrations of 46-68 ng L^{-1} (Batt et al. 2006) which underscores the impact CAFOs have on groundwater sources. Sulfamethoxazole is a 4-amino-*N*-(5-methyl-3-isoxazolyl)benzenesulfon-amide. It is an off-white, odorless, tasteless compound with a molecular weight of 253.28 and a molecular formula of $C_{10}H_{11}N_3O_3S$. Typically the medical formulation is a combination of sulfamethoxazole with trimethoprim, a broad-spectrum antimicrobial. Trimethoprim optimizes the impact of SMX's major active ingredient (Perez et al. 2005). Generally, the drugs are absorbed into the body and are subject to metabolic reactions (protonation/de-protonation) as mentioned earlier.

However, it has been proven that up to 15% of sulfamethoxazole and 60% of trimethoprim leave the body through urine and feces unaltered (Hirsch et al. 1999). Detections of SMX and trimethoprim in rivers and streams were found at frequencies of up to 27%. The presence of sulfamethoxazole was found in Boulder Creek, the watershed of which is located along Colorado's Northern Front Range. In this instance, the per capita dissolved mass loading of the antimicrobial SMX into the Boulder Creek from the WWTP was 0.27 mg/person-day, which is higher than the median value of 0.15 mg/person-day reported by Canadian WWTPs. Additionally, concentrations of trimethoprim were detected in WWTP effluent and in Boulder Creek (Barber et al. 2006). Other studies have detected sewage treatment plant removal rates of approximately 20% (Ternes 1998; Castiglioni et al. 2006). Perez et al. determined definite levels of SMX biodegradability testing sewage obtained during different stages of wastewater treatment(Perez et al. 2005).

Molecular Wt: 253.3 g/mol
Solubility: 600 mg L-1
Log K_{ow}: 0.89
pK_{a1}: 1.7
pK_{a2}: 5.6
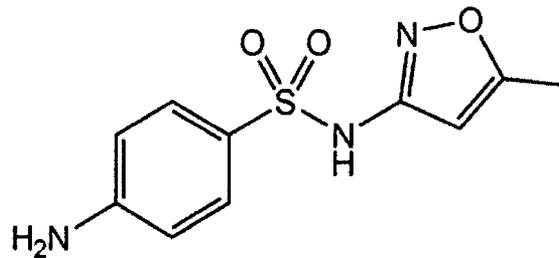
Figure 2-3: Sulfamethoxazole (SMX)

Water treatment plants have also been proven to have difficulty in removing SMX. Adams found that coagulation/flocculation/sedimentation with alum and iron salts or excess lime/soda ash softening did not result in significant removal of antibiotics including SMX (Snyder et al. 2003). Jar test experiments have also been conducted

simulating coagulation with aluminum and ferric sulfate (Vieno et al. 2006). Results from this experiment determined that under varying amounts of dissolved organic matter, neither coagulant had any effect on removal. Westerhoff reported minimal removal of SMX (less than twenty percent) in samples treated with 1 mg L^{-1} powdered activated carbon (PAC) (Westerhoff et al. 2005). In the same study, samples treated with 5 mg L^{-1} of PAC resulted in a thirty six percent removal of SMX. Sharma reported results which suggest that Ferrate(VI) has the potential to serve as a chemical oxidant in the removal of sulfonamides including sulfamethoxazole (Sharma et al. 2006; Sharma et al. 2006).

Westerhoff also concluded that SMX was completely removed with chlorine and 88% removed with ozone using doses similar to those experienced at a WTP (Westerhoff et al. 2005). It was noted that oxidation of some endocrine disruptors and PPCPs will result in transformations of certain compounds and the creation of metabolites, which are largely unknown and occasionally more harmful than the original compound. Similar SMX removal in ozone-treated samples have also been reported (Huber et al. 2003; Snyder et al. 2006). Huber determined second order rate constants for the reaction of sulfamethoxazole with ozone and OH radicals in bench scale experiments (Huber et al. 2003). High reactivities with ozone were found for SMX among others indicating these compounds rapidly transform during ozonation. Researchers concluded that nanofilters retained SMX in laboratory studies mainly due to the size (for tight nanofilters) and charge of the compound (for loose nanofilters) at test conditions of pH 8 and higher (Nghiem et al. 2005). Other laboratory studies using micelles pre-adsorbed on montmorillonite clay resulted in approximately ninety eight percent removal of SMX at initial concentrations of 10 mg of SMX L^{-1} (Polubesova et al. 2006).

2.3.2.2 Carbamazepine

Carbamazepine is a hydrophilic compound consisting of three rings of carbon with double bonds and an amine group attached and a double bond as shown in Figure 2-4. It is a base which is found mostly uncharged in the environment. The molecule's structure makes it susceptible to fracturing under certain conditions. CBZ is an important drug for the treatment of seizure disorders such as epilepsy, which is ranked second for the most common central neuron system disease. CBZ has been available for more than thirty years and has recently replaced phenobarbitol as the most common anticonvulsant drug (Miao et al. 2003). CBZ has also been used to treat cases of schizophrenia because of the drug's ability as a mood-stabilizer (Okuma 1993). The drug has also been prescribed for the treatment of bipolar disorder (Dilsaver et al. 1996) and can be combined with other drugs for the treatment of alcohol withdrawal (Franz et al. 2001).

CBZ has several pathways of elimination which leads to over 30 different metabolites. In humans, approximately 70% of the CBZ dose is excreted in urine and only 2% is excreted as unchanged drug (Amore et al. 1997) . The biotransformation of CBZ is characterized by four pathways of elimination. The first step of the major pathway is oxidative formation of carbamazepine-10, 11-epoxide (CBZE). CBZE is largely eliminated by hydrolysis to CBZ-10,11-*trans*-dihydrodiol and conjugation to form *O*-glucuronides. Some researchers believe CBZE is an intermediate in the formation of substituted acridine metabolites from CBZ. Acridine is a known human carcinogen. In addition, this pathway may also involve minor CBZ metabolites formed by aromatic hydroxylations of CBZE. The remaining three pathways of CBZ elimination include: *N*-glucuronidation, aromatic hydroxylation, and thioether formation (Amore et al. 1997).

- 26 -

Molecular Wt: 236.3 g/mol
Solubility: 17.7 mg L-1
Log K_{ow}: 2.45
pK_a: 2.3
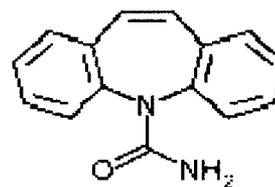
Figure 2-4: Carbamazepine (CBZ)

Research conducted by the United States Geological Survey (USGS) and the

Centers for Disease Control and Prevention was performed on two streams which feed a

drinking water treatment plant. One of the seven compounds that was found in every

sample taken from the stream water and raw water was CBZ (Stackelberg et al. 2004).

The same study concluded that CBZ persisted in a drinking water treatment plant that

included processes such as filtration with granulated activated carbon (GAC). It is

estimated that sorption efficiencies are negatively impacted when there is competition

with other organic compounds. Essentially, a WTP using GAC which treats water with

high amounts of organic compounds (both natural and anthropogenic) will have less of an

adsorption capacity for CBZ (Stackelberg et al. 2004). A different study reported that jar

tests using ferric chloride (Ternes et al. 2002), aluminum and ferric sulfate with varying

amounts of dissolved organic matter had no effect on initial CBZ concentrations (Vieno

et al. 2006). In addition, reports of little or no removal of CBZ in bank filtration sites

have been reported (Drewes et al. 2001),(Heberer et al. 2004), which is also supported by

laboratory tests focused on the water/sediment relationship (Loffler et al. 2005).

Research conducted by Kinney et al. determined that CBZ and other wastewater-derived

pharmaceuticals were present in soil irrigated with reclaimed water throughout the

irrigation season and months after irrigation(Kinney et al. 2006). Studies conducted on

the effect of CBZ on riverine biofilm communities indicated that at concentrations of 10

ug CBZ L^{-1}, a loss of cyanobacteria and an increase in algal biomass occurred, thus suggesting that the presence of CBZ may have toxicological impacts on microbial community structure and function (Lawrence et al. 2005).

Benchtop experiments (and pilot scale studies (Hua et al. 2006; Jasim et al. 2006; Snyder et al. 2006)) testing the removal of CBZ with ozone demonstrated that removal of the parent compound was achieved under conditions similar to ozone processes within a water treatment plant (Andreozzi et al. 2002; Ternes et al. 2002; Huber et al. 2003; Westerhoff et al. 2005). Huber et al. determined second order rate constants for the reaction of CBZ with ozone and OH radicals in bench scale experiments (Huber et al. 2003; McDowell et al. 2005). OH radicals are the main oxidants during advanced oxidation processes (AOPs). Results from the rate constants suggested complete transformation during ozonation process. Chlorine has also been studied for the oxidation and removal of CBZ under similar conditions found in WTPs with results indicating removal greater than seventy five percent (Westerhoff et al. 2005). However, additional research has concluded that treatment of these compounds with conventional oxidation methods such as chlorine and ozone can result in transformations of certain compounds such as acridine and the creation of metabolites, which are largely unknown and occasionally more harmful than the original compound (Snyder et al. 2003). The formation of similar metabolites was reported by Doll in studies using photocatalysis (TiO$_2$) to degrade CBZ (Doll et al. 2005). Nanofilters were reported to retain CBZ in laboratory studies mainly due to the size and charge of the compound at the test condition of a pH of 8 (Nghiem et al. 2005).

In another study, researchers observed zero percent removal of CBZ in several Italian sewage treatment plants (Castiglioni et al. 2006). Clara found that neither traditional activated sludge plants nor a membrane bioreactor had any effect on CBZ concentrations (Clara et al. 2005). Carballa determined that the addition of ferric chloride, aluminum sulfate, and aluminum polychloride had no effect on CBZ removal (Carballa et al. 2005). The same study also looked at CBZ removal using dissolved air flotation (DAF) under varying fat concentrations in the sample water. CBZ experienced twenty and thirty five percent removal using DAF under low and high fat containing solutions, respectively. The removal may be explained due to CBZ's solubilization in the lipid fractions or sorption onto smaller aggregates(Carballa et al. 2005). Others have reported less than seven percent removal of CBZ in sewage treatment plants with maximum effluent and surface water concentrations reported at 6.3 ug L^{-1} and 1.1 ug L^{-1}, respectively (Ternes 1998). Wetland pilot tests found that up to 77% of the initial CBZ concentration was retained on the gravel bed of the wetland (Matamoros et al. 2005). This may be explained by the compound's sorption onto the biofilm coating the gravel bed. Due to CBZ's persistent nature in waters impacted by wastewater effluent, it has been proposed that CBZ act as a molecular biomarker of sewage (Clara et al. 2004). Lastly, researchers have reported higher CBZ values in the treated effluent of wastewater treatment plants than the influent with consideration of the effect of the plant's hydraulic retention time (Vieno 2007). This increase has been explained through the conversion of carbamazepine glucuronides and other conjugated metabolites to the parent compound CBZ by enzymatic processes occurring within the treatment plant. It has been reported that activated sludge has glucuronidase activity thus the cleavage of the glucuronic acid

moiety is possible within the activated sludge treatment plant (Ternes et al. 1999; Miao et al. 2003).

There is little research data on the existence of metabolites for carbamazepine and other organic compounds in wastewater effluent and surface waters. One researcher has reported a successful method for the simultaneous determination of CBZ and its five metabolites. The analytical method was validated with data from WWTP influent, effluent, and receiving surface waters (Miao et al. 2003). Miao et al found CBZ and its five metabolites in WWTP influent and effluent. The influent and effluent concentrations of CBZ and its metabolites were approximately the same, indicating that the drug and its metabolites remain unaffected by conventional wastewater treatment. The receiving surface waters only contained CBZ and 10, 11-dihydro-10, 11-dihydroxycarbamazepine (Miao et al. 2003). Interestingly enough, the metabolite 10, 11-dihydro-10, 11-dihydroxycarbamazepine was found at concentrations three times higher than the parent compound, carbamazepine, in all of the samples (Miao et al. 2003). Research has indicated that some CBZ metabolites which exist in the conjugated form in urine are possibly transformed in wastewater treatment plants through the cleavage of the glucuronide conjugates. This would release CBZ and its metabolites into the free forms (Miao et al. 2003).

2.3.3 Flame Retardants

The presence of bioactive compounds such as organophosphorus compounds which are manufactured by the chemical industry for use as pesticides, flame retardants, plasticizers, hydraulic fluids and solvents has been detected in the aquatic environment (Fries et al. 2001; Andresen et al. 2006). Organophosphorus compounds (OPs) are manufactured world-wide for many industries and end-users. More than half of the

compounds manufactured are pesticides and the remainder are flame retardants, plasticizers, hydraulic fluids and solvents (Fries et al. 2001). The chlorinated OPs such as tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) and tris-(2-chloroethyl) phosphate (TCEP) are predominantly used as flame retardants in polyurethane foams. As with other additives, OPs are mixed and are not chemically bonded with the containing materials, and therefore are easily released into the environment (Rodriguez et al. 2006).

$C_6H_{12}Cl_3O_4P$
TCEP
Molecular Wt: 285.49 g/mol
Solubility: 8,000 mg L^{-1} at 20°C
Log K_{ow}: 1.7
pK_a: 7.8

(a)
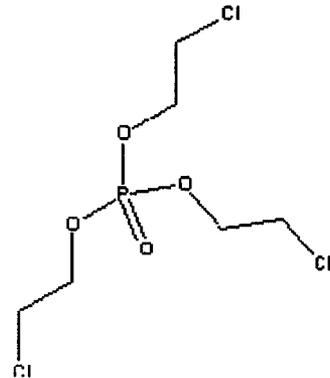
$C_9H_{18}Cl_3O_4P$
TCPP
Molecular Wt: 327.55 g/mol
Solubility: 1600 mg L^{-1} at 20 C
Log K_{ow}: 2.59
pK_a: NA

(b)
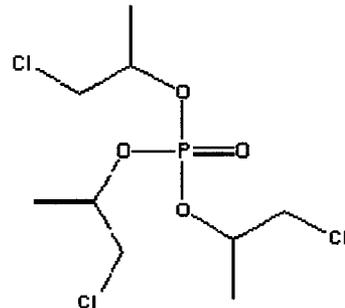
$C_9H_{15}Cl_6O_4P$
TDCP
Molecular Wt: 430.91 g/mol
Solubility: 100 mg L^{-1} at 30 C
Log K_{ow}: 3.8
pK_a: NA
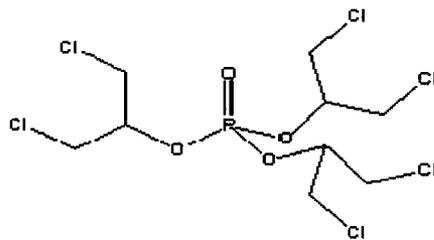
(c)

Figure 2-5: (a) TCEP, **(b)** TCPP, **(c)** TDCP

Organophosphates have been detected in indoor air samples, surface waters, wastewater treatment plant effluent, snow deposition, and finished drinking water (Fries et al. 2001; Kolpin et al. 2002; Stackelberg et al. 2004; Marklund et al. 2005; Andresen et al. 2006). TDCP appears to be most toxic among the three flame retardants to aquatic organisms. The 96-hour LC_{50} for rainbow trout is 1.1 mg L^{-1} of TDCP (WHO 1998). TCPP and TCEP pose less of a threat to aquatic organisms based on their 96-hour LC_{50} concentrations of 51 mg L^{-1} for fathead minnows and 90 mg L^{-1} for goldfish, respectively (WHO 1998). TCEP, a known carcinogen to animals, and other chlorinated organophosphates is currently undergoing a re-evaluation by several European regulatory groups on environmental issues (Andresen et al. 2006). There is additional concern for the presence of OPs and other chemicals and personal health care products in our waters because these products, unlike pharmaceuticals, were never made to be ingested.

The detection and quantification of OPs at concentrations ranging from low ug L^{-1} to ng L^{-1} in wastewater treatment plant effluent, reclaimed wastewater, and surface waters has been reported in many studies (Acar et al. 1995; Fries et al. 2001; Heberer et al. 2002; Kolpin et al. 2002; Snyder et al. 2003; Meyer et al. 2004; Stackelberg et al. 2004; Bendz

et al. 2005; Marklund et al. 2005; Westerhoff et al. 2005; Loraine et al. 2006). Research conducted by the United States Geological Survey (USGS) and the Centers for Disease Control and Prevention was performed on two streams that feed a drinking water treatment plant. Two of the seven compounds that was found in every sample taken from the stream water and raw water were TCEP and TCPP (Stackelberg et al. 2004). The same study concluded that TCEP concentrations were consistent across the sampling events and throughout the drinking water treatment plant. This may suggest temporally constant concentrations in source streams and little or no removal of the compounds within the WTP (Stackelberg et al. 2004). A Swedish study determined that there was little to no removal of chlorinated organophosphates during the wastewater treatment process where both effluent and anaerobic sludge were examined from several different wastewater treatment plants with varied capacities and influent sources (Marklund et al. 2005).

Other Swedish research found only 19% removal of TCEP in a sewage treatment plant upon comparing the influent and effluent concentrations (Bendz et al. 2005). In research conducted at wastewater treatment plants in Germany (and other western Europe countries (Reemtsma et al. 2006)), similar results indicate little to no removal of chlorinated OPs throughout the treatment process (Meyer et al. 2004). In other German research, a study comparing OP concentration data from 1985 and 2000 have indicated that concentrations in surface, rain, and groundwater have decreased overall; however, the use of these compounds is still affecting the water quality (Fries et al. 2001). Results also indicated elevated concentrations in wastewater effluent leading to river water contamination and in groundwaters impacted by nearby rivers infiltrating into the aquifer.

Researchers examining the successfulness of activated sludge processes and membrane bioreactors (MBR) in the removal of TCEP and TCPP concluded that removal rates ranged between 0% - 35% and 0% - 25% for activated sludge plants and MBR, respectively (Bernhard et al. 2006).

Studies conducted on TCEP removal using simulated drinking water treatment processes indicated zero percent removal after treatment with alum (Westerhoff et al. 2005). The same study also tested TCEP removal using powdered activated carbon (PAC). Little removal (less than fifteen percent) was accomplished at a PAC concentration of 1 mg L^{-1}, however, at PAC concentrations of 20 mg L^{-1}, removal was greater than eighty percent. It was also theorized in this study that a linear relationship existed between the log octanol/water partition coefficient (log K_{ow}) of the neutral compound and the observed percent removal of TCEP (and other compounds including SMX and CBZ). Westerhoff reported zero removal in ozone and chlorine-treated samples (Westerhoff et al. 2005). Research on different simulated water treatment processes including RBF, determined TCEP and TCPP were not significantly reduced by river bank filtration (Heberer et al. 2004). Figure 2-6 represents data from a laboratory - simulated natural treatment system for three commonly found persistent chlorinated flame retardants, TCEP, TCPP, and TDCP. The soil columns were constructed to mimic an actual aquifer recharge site in Aurora, CO. As noted, there is approximately seventy five percent removal of TCEP over twenty five days and negligible removal of TCPP and TDCP over the same time frame.
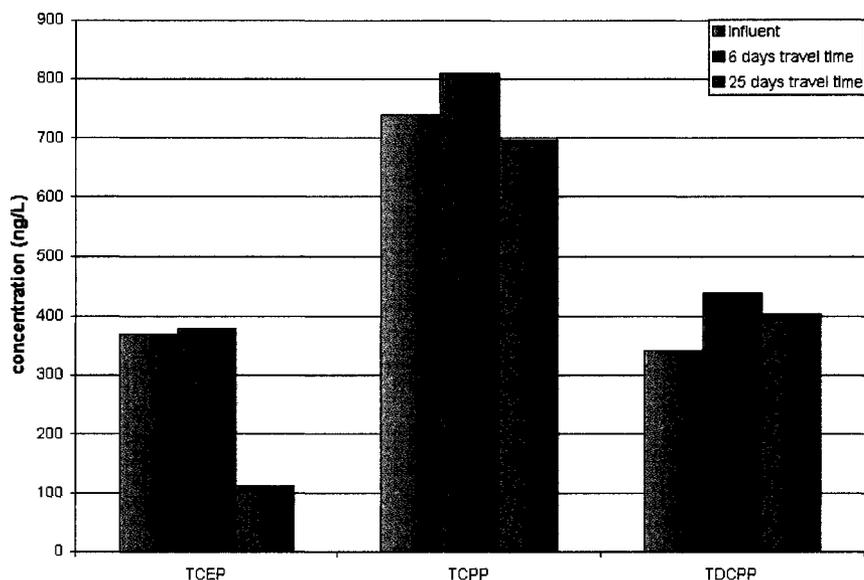
Figure 2-6: Flame retardant data in soil columns modeling aquifer recharge **(Drewes**

2006)

Although some endocrine-disrupting compounds and personal care products can

be reduced in wastewater and water treatment plants and through natural attenuation

processes, the persistent compounds remain minimally reduced or completely unaffected.

Enhanced or engineered in-situ processes such as amended aquifer recharge and recovery

and electrokinetically-enhanced river bank filtration systems may reduce the persistent

compounds in the groundwater. Severe oxidizing and reducing conditions within the

systems may directly break down the contaminants or alter the compound's structure

allowing for microbial degradation to take place.

2.4   River Bank Filtration

Bank filtration, which has existed for over 100 years, is an effective and mostly

inexpensive natural process for removing inorganic, microbial, and some organic

contaminants from groundwater. River bank filtration occurs when raw water is drawn

through an aquifer by a production well located alongside a river. The production well induces a hydraulic gradient drawing the river water through the river bank's native alluvial sand into the neighboring groundwater aquifer. The treated water at the production well, is returned to the surface where it can be subjected to additional treatment or used directly.

The quality of bank-filtered water depends upon the contaminant to be removed, the hydraulic and chemical characteristics of the bottom sediment, the aquifer, local recharge-discharge conditions, and biochemical processes (Heberer et al. 2004). As shown in Figure 2-7, a water production well is set in fine, sandy sediments next to a lake or stream. The water pumped from the well is filtered through the sediments in the stream bank and purified via different mechanisms: physical filtration, chemical adsorption, and biodegradation. Physical treatment involves the river bank's ability to filter and remove large suspended particles from the river water. Additionally, dilution may occur as the river water mixes with local groundwater that may be of higher or lower water quality, depending on the constituent of interest. Chemical processes may include adsorption of hydrophobic compounds onto organic and charged clay particles. Adsorbed compounds on particulates are readily available for microbial degradation. A few undesirable effects of bank filtration on water quality can include increases in concentrations of hardness, ammonium, dissolved iron and manganese. Additionally, hydrogen sulfide and other malodorous sulfur compounds can form due to the result of changing redox conditions (Hiscock et al. 2002).

The two main zones where the treatment mechanisms occur are in the biologically active colmation layer and along the main flow path between the river and production

well (Hiscock et al. 2002). The colmation layer or biofilm has a reduced hydraulic

conductivity due to the clogging from the input and precipitation of sediment particles,

microorganisms and colloids, precipitation of manganese and iron oxy-hydroxides and

calcium carbonates. Within this layer, intensive degradation and adsorption processes

occur within a short residence time (Hiscock et al. 2002). Degradation rates and sorption

capacities are lower and mixing processes are greater along the main flow path.

The number of utilities in the United States obtaining bank-filtered water is

slowly increasing as cities continue to develop along major waterways. Surface waters

that receive treated effluent from wastewater treatment plants are commonly the same

source waters used to indirectly feed downstream drinking water utilities. Essentially

these cities use groundwater wells in close proximity to the surface water body to obtain

raw water for ultimate drinking water treatment and distribution. Locations such as

Berlin, Germany obtain 100% of the public water supply from groundwater in which

70% originates from bank filtration and artificial ground water replenishment (Heberer et

al. 2004).
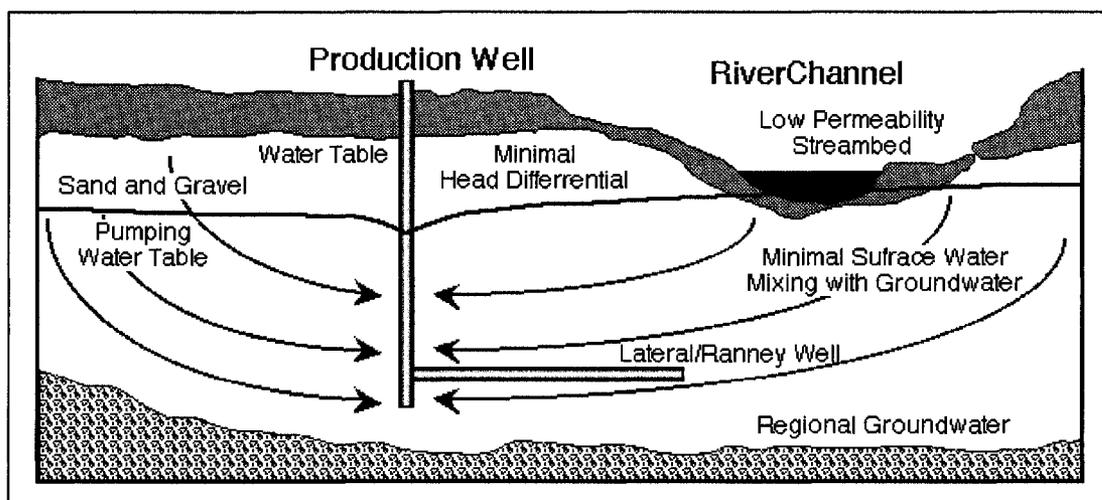
Figure 2-7: Bank filtration **(Ray 2000)**

Research conducted on the removal of hormones at bank filtration sites in Germany indicated that bank filtration is capable of removing these compounds (Zuehlke et al. 2004). However, known recalcitrant compounds such as CBZ (Heberer 2002) and selected flame retardants (Fries et al. 2003) persist during infiltration through vadose and saturated soil zones. Similar findings also reported some removal (or dilution) of CBZ at other bank filtration sites, while TCEP showed no signs of removal (Heberer et al. 2004). Unsaturated laboratory column studies indicated zero removal of CBZ and little retardation of the compound within the column(Scheytt et al. 2006). Additional studies using saturated columns, determined the concentration distribution of pharmaceuticals in bank filtration sites was controlled by sorption-desorption and input variation, as opposed to contaminant degradation (Scheytt et al. 2004).

The proposed research presents an opportunity to strengthen the existing bank filtration process by adding an additional water treatment barrier. This additional barrier, electrokinetic soil processing (ESP), could effectively breakdown the EDCs and PPCPs that are currently passing unchanged through traditional bank filtration sites. Contaminant removal could be accomplished directly by the physiochemical changes in the soil caused by ESP or through subsequent biodegradation of the ESP-altered parent compounds. Utilities using bank filtration as a preliminary treatment method would benefit by removing the EDCs and PPCPs via bank filtration to eliminate the risk of being untreated in the treatment plant and to prevent unwanted compound metabolites from forming as the result of conventional water treatment processes. Additionally, the successful use of electrokinetic remediation used in conjunction with bank filtration may result in optimizing the overall water treatment process and therefore potentially decrease

the amount of land typically required to effectively treat surface water at conventional bank filtration sites.

2.5   Aquifer Recharge and Recovery

Aquifer Recharge and Recovery (ARR) uses the same physical, chemical and biological mechanisms for water treatment as river bank filtration. However, source water is introduced to the aquifer via pipelines as opposed to being fed by a nearby river as depicted in Figure 2-8. The water introduced into the aquifer percolates through soil where it mixes with native groundwater and is removed by a recovery well located at a specific distance from the injection point in order to maintain a sufficient residence time. The recovery well draws the water through the aquifer and in doing so the water is subjected to physical, chemical and biological processes. Once the water is pumped from the recovery well, it can be used directly or piped to a treatment plant for additional treatment.
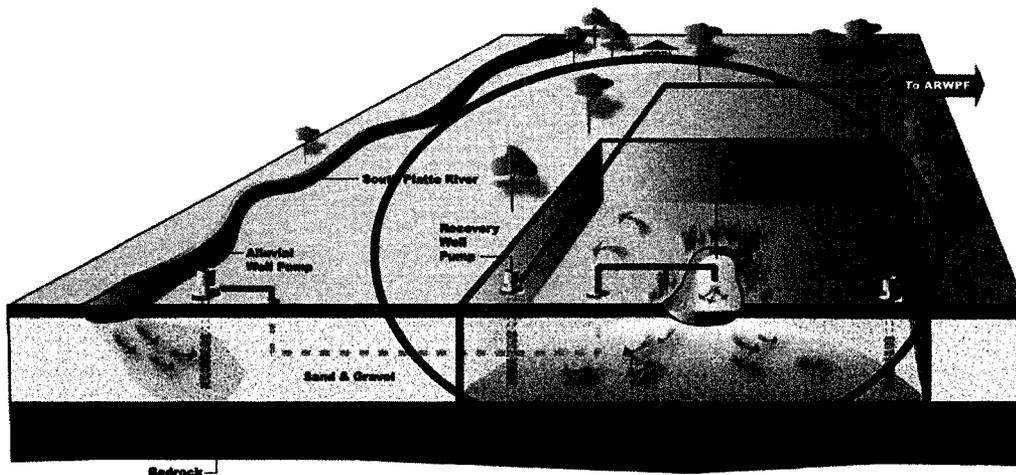
Figure 2-8: Aquifer recharge and recovery schematic **(Ray 2000; Brauer 2006)**

ARR sites can be located in aquifers with or without barriers on the perimeter in order to minimize or promote ARR mixing with local groundwaters. In the United

States, ARR is typically used for tertiary treatment of wastewater effluent. However, in

Europe and in arid regions of Asia, variations of aquifer recharge and recovery are used

for both water and wastewater treatment. In both scenarios, the aquifer is used to reduce

nutrients, pathogens, and trace organics.

Data from sites where wastewater effluent is used to recharge aquifers indicate

that pharmaceuticals, specifically triiodinated benzene derivatives, were partially

removed in groundwater aquifer recharge systems (Drewes et al. 2001). Figure 2-9

shows sulfamethoxazole biodegradation results along the transect (x-axis) of a bank

filtration site with extended travel times (ARR simulation) in Germany. The results are

plotted as box plots with the median value (center line), 25-75% quartiles (box), and the

minimum and maximum values (vertical line).
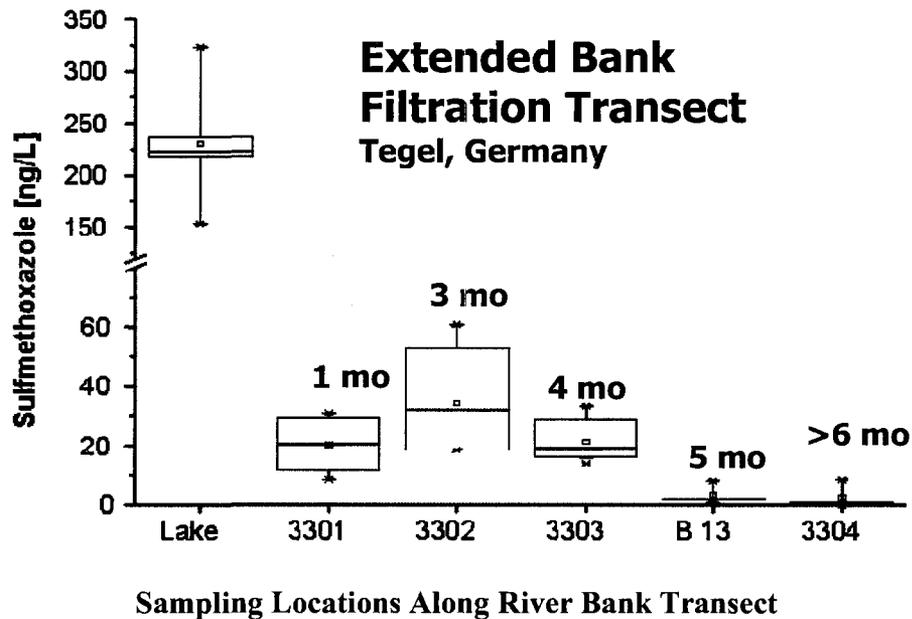
Figure 2-9: Effect of extended travel time in soil aquifer treatment on SMX
biodegradability(Grunheid et al. 2005)

2.5.1   Enhanced Aquifer Recharge and Recovery

A unique approach of utilizing waste byproduct to enhance a passive treatment process is the use of water treatment residuals at an aquifer recharge and recovery site. Drinking water treatment plants typically add iron or aluminum salts to process water to remove colloids, color, sediment, and other contaminants from surface and groundwater supplies. The byproducts in the process are drinking water treatment residuals (WTRs). The WTRs are typically a mixture of either iron or aluminum hydr(oxides) or $CaCO_3$ and also natural organic matter, activated carbon, and polymer. Water treatment plants in the United States produce up to 2 million tons of WTRs per day (Prakash et al. 2003). WTRs have been successful in reducing excess soluble phosphorus concentrations in poorly P-sorbing soils (Makris et al. 2004). The use of WTRs (both aluminum and ferric-based) has also been determined to be highly effective in removing As(V) and As(III) with little desorption (Makris et al. 2006).

Column studies using ARR amended with WTRs for the removal of phosphorus and other compounds were conducted by researcher Carlson, K. at Colorado State University (2006). In addition to the phosphorus removal data, researchers determined the WTRs are leaching an active electron donor, organic carbon. This donor has contributed to an increase in microbial activity in the reduced conditions within the column. The presence of a strong absorbent such as WTRs, whose characteristics promote reducing conditions and an increase in microbial activity, in an aquifer recharge and recovery system could be suitable conditions for the breakdown of persistent compounds.

2.6   Electrokinetic Remediation

Electrokinetic remediation (ER), which is also referred to as electroreclamation and electrokinetic soil processing, has been successfully used in groundwater treatment applications for the breakdown and extraction of many contaminants.   The low-level direct current across the soil results in physiochemical and hydrological changes in the subsurface soil mass, leading to species transport by coupled mechanisms such as electrolysis of water, electrophoresis, electromigration, electroosmosis, and to a lesser extent, diffusion (Acar et al. 1996).

The electrolysis of water, which predominantly occurs at the electrodes, produces hydrogen ions in the anode compartment and hydroxide ions in the cathode compartment. Electrophoresis is the transport of charged particles under an electric field (Acar et al. 1993). Electromigration is the transport of ions and polar molecules in the pore fluid under an electric field and electroosmosis is the flow of an ionic liquid resulting from the applied electric field that acts on the charged interface between the water and the soil particles' surface. Diffusion is the mechanism in which species are transported due to concentration gradients. The electromigration, electroosmosis, and electrophoresis mechanisms are depicted in Figure 2-10.
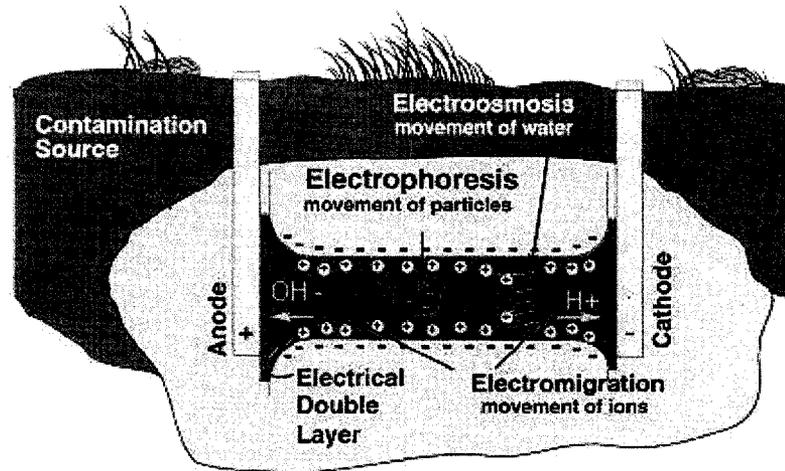
Figure 2-10: Electrokinetic remediation (Re-drawn from (Lindgren 1998))

Groundwater or an externally introduced fluid is used as the conductive medium in the ER process. This fluid is allowed to flow in and out of the electrode compartment through a porous barrier at the electrode. The conduction phenomena in the soil which is influenced by the electric field will promote species transport across the porous media. Since most contaminant transport occurs in the pore fluid, ER is not effective unless the species are soluble or are converted to a soluble form. Therefore, physico-chemical reactions such as acid/base reactions, sorption, precipitation/dissolution, and oxidation/reduction reactions are the principal means under which electrokinetic remediation technology operates (Acar et al. 1993). In unamended electrokinetic remediation (when the electrolytic fluid is not externally influenced) application of direct electric current via electrodes immersed in a saturated soil results in oxidation at the anode and reduction at the cathode. This process known as electrolysis generates oxidized and reduced species which will aid in the degradation of contaminants. This process is defined by Equations 2.6 and 2.7.
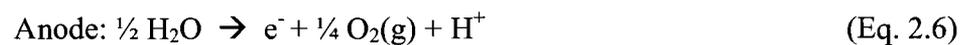
$$\text{Anode: } \frac{1}{2} H_2O \rightarrow e^- + \frac{1}{4} O_2(g) + H^+ \hspace{2cm} \text{(Eq. 2.6)}$$

$$\text{Cathode: } H_2O + e^- \rightarrow \frac{1}{2} H_2(g) + OH^- \qquad\qquad \text{(Eq. 2.7)}$$

Due to the above reactions, an acid front will be created at the anode and an alkaline front created at the cathode. The acid front will proceed to the cathode by transport mechanisms including migration and electroosmotic flow (Acar et al. 1993). Unless the buffering capacity of the soils is high enough to retard the flow, the chemistry across the soil will be dominated by the hydrogen ion. This is because the mobility of the hydrogen ion is approximately twice the mobility of the hydroxyl ion under an electric field (Acar et al. 1995). The protons generated at the anode are transported across the soil and meet the hydroxyl ions close to the cathode. This will result in the generation of water in this zone (Acar et al. 1993). The acid front across the soil will promote the desorption of cationic species concentrated on the soil surface (Acar et al. 1995). The base front created at the cathode due to the reduction of water, will retard the migration of cationic ions to the cathode by precipitating them as oxides and hydroxides in the region of the cathode (Acar et al. 1996). The simplest approach for electrokinetic remediation uses groundwater as the electrolyte in both electrode wells. In this case, the acid front would be established at the anode and move toward the cathode where the base front exists, resulting in significant precipitation of contaminants in the soil as hydroxides and oxides (Acar et al. 1993). This unenhanced ER approach is essentially delivering hydroxide ions as an amendment to the contaminated soil zone resulting in the retardation and stabilization of mobile cationic contaminants.

Electrophoresis, the transport of charged particles through the pore fluid under an electric field, becomes a main transport mechanism only when surfactants are introduced into the electrolytic solution to form charged particles (micelles) with other species.

Electromigration is the movement of charged chemical species relative to the movement of pore fluid (Alshawabkeh et al. 1999). Electromigration occurs when mobile ions are subjected to an electric field. The velocity of electromigration will depend the on the field strength, the charge on the ions, and the drag the ions are subjected to during migration. Anions, the negatively charged ions move to the anode, the positive electrode, while the cations, the positively charged ions, move to the cathode which is negatively charged.

Electromigration is typically the predominant transport mechanisms in soils under an electrical gradient(Acar et al. 1996; Alshawabkeh et al. 1999). The ionic mobility of a charged species is at least one order of magnitude higher than the diffusion coefficient of the same species. Additionally, the ratio of the effective ionic mobility of a charged species under a electrical gradient to the effective diffusion coefficient of the same species is approximately 40 times the charge on the species (Acar et al. 1993). The ratio of electromigration flux to electroosmotic flux is approximately 10-100.

Electroosmosis is the flow of an ionic liquid resulting from the applied electric field that acts on the charged interface between the water and the soil particles' surface. This mechanism of transport is generally from the anode to the cathode because the species in the diffuse double layer are often positively charged (Acar et al. 1996). However, under certain circumstances (which cannot be thoroughly explained) this direction of flow may be reversed (Alshawabkeh et al. 1999). It is hypothesized that this occurs when the electrolyte concentration is high and the pH of the pore fluid is low(Acar et al. 1993). Simply stated, electroosmotic flow is produced because locally existing excess ions migrate in a parallel plane to the soil particle surface toward the oppositely

charged electrode, and as the ions migrate, the ions transfer momentum to the surrounding fluid molecules via viscous forces. The relationship between the electoosmotic volume flow rate and electric gradient is defined by the following equation,

$$Q = k_e i_e A_T \qquad (Eq.\ 2.8)$$

Where Q = electroosmotic flow rate ($m^3\ s^{-1}$); k_e = coefficient of electroosmotic conductivity ($m^2\ V\text{-}s^{-1}$); i_e = electric potential gradient across the system ($V\ m^{-1}$); and A_T = total cross-sectional area perpendicular to the flow direction (m^2).

Electroosmosis has been theoretically explained by the Helmholtz-Smoluchowski theory. This theory introduces the coefficient of electroosmotic permeability, defined as the volume rate of water flowing through a unit cross-sectional area due to a unit electrical potential difference. The coefficient, k_e, has units of $cm^2\ (V\text{-}s)^{-1}$ (Acar et al. 1993). Electroosmotic flow under an electric potential is largely dependent on the soil's porosity and zeta potential and is independent of the soil's pore size distribution and the presence of macropores (Acar et al. 1993). The zeta potential of a soil particle is defined as the electrical potential at the junction of the Stern and diffuse layer. It is related to the particle's mobility which is determined by the dielectric constant and viscosity of the suspending liquid. The impact of electroosmotic flow and its direction is mainly important when remediating soil contaminated by nonionic species, including organics.

Minimizing premature species precipitation at the cathode and maintaining an optimal pH range over the soil column can be accomplished through the use of an enhancement in the cathode compartment (Acar et al. 1993). Neutralization of the cathode area will also assist in decreasing the electrical potential difference across the

electrodes, thereby, decreasing overall energy demand. This enhancement can also be used to extract species collected in the electrode compartments. The addition of the enhancement modifies the chemical reactions at the electrodes and can assist in the desorption of species and dissolution of carbonates and hydroxides(Acar et al. 1995). For example, when acetic acid is added to the cathode compartment, it neutralizes the hydroxide ions at the cathode which are created during the electrolysis of water. Without the precipitation, the cationic species can migrate into the cathode well and become concentrated for periodic removal from the system. The presence of acetate anions into the system creates soluble complexes across the soil sample as it migrates to the anode.

Electrokinetic soil processing has been effective in uniformly introducing process additives and nutrients into the biologically active zones where microorganisms have been unsuccessful due to nutrient deficiency. These rate-limiting conditions would therefore restrict the microbial community's ability to reproduce. Other attempts to provide nutrients and other necessary process additives have been accomplished through hydraulic means. Hydraulic introduction of amendments has proven to be inefficient in varied soil types. This process also has the tendency to overdose which can result in areas with excessive biological growth, therefore clogging the soil system (Acar et al. 1996).

In addition to controlling the pH of the soil system, amended electrokinetic remediation has been used as a means for uniform delivery of amendments to the subsurface for the stabilization of several groundwater contaminants. Subsurface electrodes are used to induce a potential across contaminated soil systems, mobilizing amendments through the contaminated zone and resulting in a stimulation of in-situ

remediation (Acar et al. 1993; Gent et al. 2003; Jackson et al. 2004). This is

accomplished by using an electron donor such as acetate or citrate as the electrolyte

amendment in the cathode well. The negatively charged acetate or citrate ion will

migrate toward the anode in a uniform manner even in low permeability soils, allowing

microbial communities to develop. Researchers have demonstrated the efficacy of this

approach for delivering amendments to the subsurface for the reduction or stabilization of

perchlorate, DNAPLs, and metals (Acar et al. 1993; Gent et al. 2003; Jackson et al.

2004; Bejankiwar et al. 2005; Luo et al. 2005; Jiradecha et al. 2006).

Acetic acid (CH_3COOH) is a weak acid that undergoes partial dissociation in

water

$$CH_3COOH = CH_3COO^- + H^+ \qquad\qquad (Eq.\ 2.9)$$

It has a pKa of 4.76, resulting in acetate being the main species at near-neutral pH. The

dissociation of the weak acid will result in a low concentration of ions generated at the

cathode. It is an important commonly used as a chemical reagent in the production of

vinegar, soft drink bottles, photographic film, wood glue and many synthetic fibers and

fabrics. Diluted acetic acid is commonly used as a descaling agent and also as a food

additive. Acetic acid has been selected as the additive to depolarize hydroxyl ions

generated at the cathode because of its chemical characteristics. Some of these

advantages of using acetic acid are: most of its metal acetates are highly soluble in water,

the increase in conductivity in soil will not be drastically increased, it is non-toxic and

biodegradable, it is as an organic electron donor compound in remediation environments,

and it will prevent the creation of other insoluble salts near the cathode that may increase

the resistance in this area (Alshawabkeh et al. 1999).

The RBF-ER application for persistent organic compounds will not heavily rely on electromigration as a potential remedial process since these (in the parent form) are uncharged. Although electroosmosis may contribute slightly to the movement of the uncharged compounds to the cathode region, it is not viewed as an efficient process by itself. The main ER mechanism as applied for the reduction of persistent organic contaminants, focuses on the electrolysis of water as defined by equations 2.6 and 2.7.

Essentially, reducing or oxidizing species generated from the electrolysis of water could potentially be used to remediate the persistent organic contaminants. For instance hydroxyl radical species are products of a series of reactions beginning with electrolysis of water. These strong oxidizing species are relatively non-selective oxidizers which could break down the contaminants within the electrochemical cell. First, hydrogen peroxide (H_2O_2) is electrochemically formed by the two-electron reduction of dissolved oxygen at the cathode as noted in (Do et al. 1994) :

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \hspace{2cm} \text{(Eq. 2.10)}$$

The hydrogen peroxide reacts with Fe^{2+} known as the classical Fenton reaction and generates hydroxyl radicals ($OH\cdot$) which in turn may react with an organic compound (Pignatello 1992):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + HO^- \hspace{2cm} \text{(Eq. 2.11)}$$

In many soils, naturally occurring iron is sufficient to initiate this process. The reaction of $OH\cdot$ with organic compounds may result in dehydrogenated or hydroxylated derivatives of the original compound or ideally, ultimate degradation to CO_2. Research on the electrochemical degradation of a chlorinated solvent using stainless steel electrodes and synthetic groundwater have reported significant removal rates under

varying experimental conditions (Bejankiwar et al. 2005). Research involving the remediation of persistent organic compounds with hydroxyl radicals (in a non-ER setting) reported second-order rate constants for the successful reaction of CBZ and SMZ with OH radicals in bench scale experiments (Huber et al. 2003).

In addition, research examining the treatment of EDCs and PPCPs in water treatment plants has determined that removal could potentially occur if the compounds partition onto particulate matter or partition/adsorb onto metal (hydr)oxides (Westerhoff et al. 2005). As mentioned above, a proven result of electrokinetic remediation is the removal of inorganic metals as metal hydroxides. In removing background charged species in the groundwater, it is possible that persistent organic compounds will also be stabilized. In addition, ER has successfully been used to remove the organic compound phenol due to its solubility in water and because phenol protonates in an acid to produce positively charged species(Acar et al. 1995).

2.7   Potassium Permanganate

The use of potassium permanganate ($KMnO_4$) as an oxidizing agent for the in situ chemical oxidation of organic compounds has been reported to be an effective means of remediation. $KMnO_4$ was initially used in water treatment as a strong oxidant for the removal of iron and manganese and for taste and odor control (Cherry 1962). There are many reaction mechanisms proposed to define the complex oxidation reactions for $KMnO_4$. The following summarizes the primary permanganate reactions.

In systems with pH values greater than 12, a single electron transfer occurs as explained in the following equation:

$$MnO_4^- + e- \rightarrow MnO_4^{-2}$$ (Eq. 2.12)
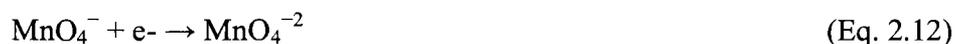
In alkaline systems with pH >9, the permanganate ion (MnO_4^-) reacts with hydroxyl ions and to form HO· radicals in lieu of directly reacting with other oxidizable materials (Gates-Anderson et al. 2001) as defined in Equation 2.13. The hydroxyl radical HO· is the neutral form of the hydroxide ion. Hydroxyl radicals are highly reactive and short-lived and are the principal oxidizing entities in high pH systems.

$$MnO_4^- + H_2O \rightarrow MnO_4^- + HO· + H^+ \qquad \text{(Eq. 2.13)}$$
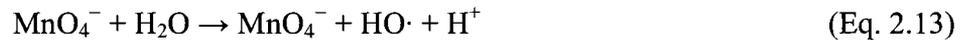
Equation 2.14 indicates the reaction in which manganese can be reduced to form a manganese oxide through a three electron transfer in systems with pH values between 3.5 and 12.

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^- \qquad \text{(Eq. 2.14)}$$

In slightly acidic conditions, the Mn(IV) atom in MnO_2 can be slowly reduced to form Mn^{+2} as seen in the following equation.

$$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad \text{(Eq. 2.15)}$$
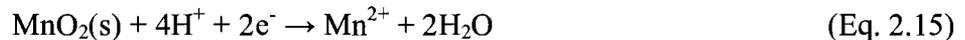
Additionally, the Mn(IV) ion in slightly acidic solutions can be slowly reduced to form manganese dioxide while also releasing oxygen (Eq. 2.16). The MnO_2 solids produced in both acidic and alkaline systems are believed to further catalyze oxidation reactions by providing additional surface area where complexes may form.

$$4MnO_4^- + 2H_2O \rightarrow 3O_{2(g)} + 4MnO_2(s) + 4OH^- \qquad \text{(Eq. 2.16)}$$
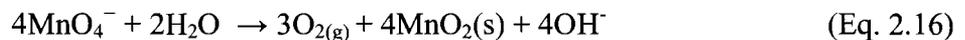
Systems with pH values below 3.5 can produce Mn^{2+} cations as seen in Equation 2.17 through a five electron transfer. Excess permanganate can further oxidize the Mn^{2+} cations to manganese dioxide (Eq. 2.18)

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{(Eq. 2.17)}$$

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+ \qquad \text{(Eq. 2.18)}$$
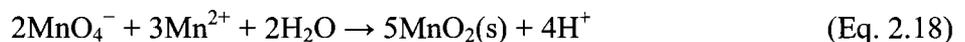
Hazardous waste sites in the United States are increasingly applying in situ chemical oxidation methods for the reduction of dissolved chlorinated ethenes (e.g., TCE, PCE) in aqueous environments. Oxidants employed for in-situ chemical oxidation include ozone, hydrogen peroxide, and permanganate (Crimi et al. 2004). Uniform delivery of the oxidants to the contaminated zone in the subsurface is essential for successful treatment. Current oxidant delivery technologies including the use of injection probes, fracturing, and wells are typically not effective in heterogeneous soils or soils with low hydraulic conductivity. Electrokinetic injection of permanganate could be an efficient method for uniformly introducing the negatively charged permanganate to the subsurface. In addition to using electrokinetics as an efficient transport method, an electrokinetic system with potassium permanganate as the cathode electrolyte could potentially be used to reduce the concentration of persistent organic compounds through direct oxidation by the permanganate ion or indirectly through the creation of hydroxyl radicals at the cathode.

2.8   Research Hypothesis

This research will test the hypotheses that:

1.   Electrokinetic injection is a viable means to introduce amendments to the subsurface,

2.   ER will efficiently remove arsenic from groundwater through transport mechanisms such as electromigration and through the combined processes of complexation and precipitation,

3. Determining a compound's affinity for the solid or aqueous phase will promote comprehensive data interpretation and will provide additional information on the compound's fate and transport characteristics,

4. Amended aquifer recharge and recovery will create a reducing environment which promotes the reduction of certain flame retardants,

5. Electrokinetic remediation (ER) will significantly alter the redox conditions thereby increasing the removal efficiency of bank filtration for the breakdown of persistent emerging contaminants including sulfamethoxazole, carbamazepine, and several chlorinated flame retardants (TCEP, TCPP, TDCP), and

6. Reversing the polarity in an amended ER system with permanganate as the cathode electrolyte will promote oxidation of previously reduced manganese.

Bench-top column studies will be conducted to test the efficacy of introducing two different amendments to the subsurface: acetate and permanganate. Electrokinetic soil processing column tests will be used to determine the efficacy of an ER system in unamended and amended modes for the remediation of arsenic and persistent organic compounds from groundwater. Laboratory column studies will be conducted to test the efficacy of amended ARR on the removal of several flame retardants. Laboratory studies will be designed and conducted to determine compound partitioning between aqueous, colloidal, and solid phases.

3.0 Transport of Acetate Using Electrokinetic Injection

3.1 Abstract

The efficiency of using electrokinetic injection (EI) for the uniform transport of acetate, a negatively charged biodegradable additive, from the cathode to the anode in sand, clay, and mixed media beds under an electric potential is investigated. Traditional transport methods of nutrient delivery to the subsurface typically involve hydraulic technologies such as the use of wells and injection probes. These methods can be inefficient and non-uniform in soils with low hydraulic conductivities or in heterogeneous soils. This paper summarizes the results when a low-level direct current, at constant current densities of 1.33 A m$^{2-1}$ and 5.33 A m$^{2-1}$ in various media, is used for the ionic injection of acetate. EI experiments were run on sand, clay, and mixed sand and clay columns using acetic acid (5,000 mg L^{-1}) as the catholyte in all experiments. The movement of acetate in the sand was successful under both low and high current densities. The migration of acetate in clay soils was most successful under the higher current densities; however, the presence of high electroosmotic flows may have impacted final acetate concentrations.

3.2 Background

The demand for efficient and inexpensive in-situ remediation of contaminated soils and groundwater continually grows as conventional treatment methods prove to be cost prohibitive. Electrokinetic remediation (ER), which is also referred to as electroreclamation and electrokinetic soil processing, has been successfully used in groundwater treatment applications for the breakdown and extraction of many contaminants. The various ions, suspended soil particles and water in a saturated soil

specimen move in a specific direction depending upon the charge of ions and particles. The movement of particles, ions and water in the wet soil medium is referred to as electrokinetics. The low-level direct current across the soil results in physiochemical and hydrological changes in the subsurface soil mass, leading to species transport by coupled mechanisms such as electrolysis of water, electrophoresis, electromigration, electroosmosis, and to a lesser extent, diffusion (Acar et al. 1996).

The electrolysis of water, which predominantly occurs at the electrodes, produces hydrogen ions in the anode compartment and hydroxide ions in the cathode compartment. Electrophoresis is the transport of charged particles under an electric field (Acar et al. 1993). Electromigration is the transport of ions and polar molecules in the pore fluid under an electric field, and electroosmosis is the flow of an ionic liquid resulting from the applied electric field that acts on the charged interface between the water and the soil particles' surface. Diffusion is the mechanism in which species are transported due to concentration gradients. The mechanisms electromigration and electroosmosis are depicted in Figure 3-1.
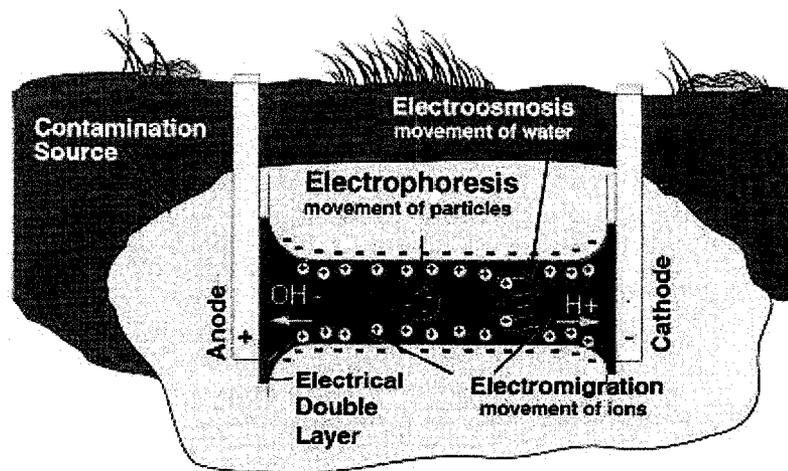
Figure 3-1: Electrokinetic remediation (Re-drawn from (Lindgren 1998))

Electrokinetic Theory

Groundwater or an externally introduced fluid is used as the conductive medium

in the ER process. This fluid is allowed to flow in and out of the electrode compartment

through a porous barrier at the electrode. The conduction phenomena in the soil which is

influenced by the electric field will promote species transport across the porous media.

Physico-chemical reactions such as acid/base reactions, sorption,

precipitation/dissolution, and oxidation/reduction reactions are the principal means under

which electrokinetic remediation technology operates (Acar et al. 1993). In unamended

electrokinetic remediation (when the electrolytic fluid is not externally influenced)

application of direct electric current via electrodes immersed in a saturated soil results in

oxidation at the anode and reduction at the cathode. This process known as electrolysis

generates oxidized and reduced species which can aid in the degradation of contaminants.

This process is defined by equations:

$$\text{Anode: } \tfrac{1}{2}\,H_2O \rightarrow e^- + \tfrac{1}{4}\,O_2(g) + H^+ \qquad\qquad \text{(Eq. 3.1)}$$
$$\text{Cathode: } H_2O + e^- \rightarrow \tfrac{1}{2}\,H_2(g) + OH^- \qquad\qquad \text{(Eq. 3.2)}$$

Due to the above reactions, an acid front will be created at the anode and an

alkaline front created at the cathode. The acid front will proceed to the cathode by

transport mechanisms including electromigration and electroosmotic flow (Acar et al.

1993). Unless the buffering capacity of the soils is high enough to retard the flow, the

chemistry across the soil will be dominated by the hydrogen ion which has a mobility

approximately twice the mobility of the hydroxyl ion under an electric field (Acar et al.

1995). The protons generated at the anode are transported across the soil and meet the

hydroxyl ions close to the cathode. The acid front across the soil will promote the

desorption of cationic species concentrated on the soil surface (e.g., Cd, Cr, Cu, Pb) (Acar et al. 1995; Suer et al. 2003). The base front created at the cathode due to the reduction of water, will retard the migration of cationic ions to the cathode by precipitating them as oxides and hydroxides in the region of the cathode (Acar et al. 1996).

Electro-migration of ions is quantified by the effective ionic mobility u_k^*. Effective ionic mobility is defined as the velocity of the ion in the soil under the influence of a unit electrical potential gradient. The ionic mobility and the diffusion coefficient of an ion in dilute solution are related by the Nernst–Townsend – Einstein equation (Acar et al. 1993) assuming the relation is applicable for ions in the pore fluid of soils;

$$u_k^* = \frac{D_k^* z_k F}{RT}$$
(Eq. 3.3)

where D_k^* (cm^2 s^{-1}) is the effective diffusion coefficient in porous mediums, z_k is the charge of the chemical species, F is Faraday's constant (96,484 C mol^{-1} electrons), R is the universal gas constant (8.314 J mol^{-1}K^{-1}) and T is absolute temperature (K). The effective diffusion coefficient in the porous medium is related to the respective diffusion coefficient in free solution, D_k by (Acar et al. 1993)

$$D_k^* = D_k \tau n$$
(Eq. 3.4)

where τ is an empirical coefficient accounting for the tortuosity of the medium and n is for the porosity. Typical values of τ range from 0.01 to 0.84 for saturated soils (Shackelford et al. 1991).

In order to understand electroosmotic flow rates (q$_e$), the coefficient of electroosmotic conductivity k$_e$ (cm^2 V^{-1}s^{-1}) must be addressed. k$_e$ is a soil property that indicates hydraulic flow velocity under a unit electrical gradient. The mathematical

model presented by Helmholtz and later refined by Smoluchowski is the basis in which k_e is described theoretically. It can be explained by the following relation (Mitchell 1993)

$$k_e = \frac{\varepsilon \xi}{\eta} n \qquad\qquad \text{(Eq. 3.5)}$$

where ε is the permittivity of the medium or dielectric constant of the pore fluid, ζ is the zeta potential, η is the viscosity, and n is the porosity. Electroosmotic conductivity based on the above theory is dependent mainly on porosity and zeta potential. Zeta potential is the electrical potential at the boundary between the moving particle and the liquid. This boundary (slip plane) is the point where the Stern layer and the diffuse layer meet (Mitchell 1993). The pH of the soil determines the zeta potential and since the soil pH changes as the electroosmotic front moves across the column, the zeta potential is not a constant. Although hydraulic conductivities, which are significantly influenced by pore size and distribution in the medium, can range from 10^{-3} to 10^{-9} m s^{-1}, the electroosmotic conductivity is generally in the small range of 10^{-9} to 10^{-8} m^2 s^{-1} V^{-1} (Mitchell 1993).

The rate of species transport under an electric field which accounts for ionic migration and electoosmotic transport processes is given by the following equation (Alshawabkeh et al. 1999):

$$\upsilon = (nu\tau + k_e) \, \nabla(-\Phi) \qquad\qquad \text{(Eq. 3.6)}$$

where υ = rate of species transport (cm/s); n = porosity of the soil (dimensionless); u = ionic mobility of the species (cm^2/V-s); τ = factor that accounts for soil tortuosity and species concentration (dimensionless); $\nabla(-\Phi)$ = the applied potential gradient; and k_e = coefficient of electroosmotic conductivity (cm^2/V-s). The time, t, required for ions of interest to travel from the cathode to anode electrode assuming the space between the electrodes is L, can be estimated by (Alshawabkeh et al. 1999):

$$t = \frac{L}{(nu\tau + k_e)\nabla(-\Phi)}$$

(Eq. 3.7)

Amended Electrokinetic Remediation

Minimizing premature species precipitation at the cathode and maintaining an optimal pH range over the soil column can be accomplished through the use of an enhancement in the cathode compartment (Acar et al. 1993). The addition of the enhancement modifies the chemical reactions at the electrodes and assists in the desorption of species and dissolution of carbonates and hydroxides(Acar et al. 1995). For example, when acetic acid is added to the cathode compartment, it neutralizes the hydroxide ions at the cathode which are created during the electrolysis of water. The main reaction at the cathode becomes the reduction of proton and the evolution of hydrogen. Without precipitation occurring at the cathode, the cationic species can migrate into the cathode compartment and become concentrated for periodic removal from the system. The presence of acetate anions into the system creates soluble complexes across the soil sample as the acetate migrates to the anode.

Additionally, electrokinetic soil processing has been effective in uniformly introducing process additives and nutrients into the biologically active zones where microorganisms have been unsuccessful due to nutrient deficiency. These rate-limiting conditions would therefore restrict the microbial community's ability to reproduce. Other attempts to provide nutrients and other necessary process additives have been accomplished through hydraulic means. Hydraulic introduction of amendments has proven to be inefficient and non-uniform in low permeability and mixed media soils leading to incomplete in-situ remediation. This process also has the tendency to over

dose which can result in areas with excessive biological growth, therefore clogging the soil system (Acar et al. 1996).

In addition to controlling the pH of the soil system, amended electrokinetic remediation has been used as a means for uniform delivery of amendments to the subsurface for the stabilization of several groundwater contaminants. Subsurface electrodes are used to induce a potential across contaminated soil systems, mobilizing amendments through the contaminated zone and resulting in a stimulation of in-situ remediation (Acar et al. 1993; Gent et al. 2003; Jackson et al. 2004). This is accomplished by using an electron donor such as acetate or citrate as the electrolyte amendment in the cathode well. The negatively charged acetate or citrate ion will migrate toward the anode in a uniform manner even in low permeability soils, allowing microbial communities to develop. Researchers have demonstrated the efficacy of this approach for delivering amendments to the subsurface for the reduction or stabilization of perchlorate, DNAPLs, and metals (Acar et al. 1993; Gent et al. 2003; Jackson et al. 2004; Bejankiwar et al. 2005; Luo et al. 2005; Jiradecha et al. 2006).

This paper evaluates the electrokinetic injection of acetate a commonly used electron donor for microbial degradation. Acetic acid transport column studies were conducted in order to determine if ER could uniformly transport acetic acid under a controlled setting in sand, clay, and mixed media. If successful, the method will be used in further electrokinetic remediation column studies focusing on contaminants of concern.

3.3   Materials and Methods
Acetic acid (CH_3COOH) is a weak acid that undergoes partial dissociation in water (Snoeyink et al. 1980):

$$CH_3COOH = CH_3COO^- + H^+ \qquad \text{(Eq. 3.8)}$$

It has a pKa of 4.76, resulting in acetate being the main species at near-neutral pH. The dissociation of the weak acid will result in a low concentration of ions generated at the cathode. It is a commonly used chemical reagent in the production of vinegar, soft drink bottles, photographic film, wood glue and many synthetic fibers and fabrics. Diluted acetic acid is commonly used as a descaling agent and also as a food additive. Acetic acid was chosen as the additive to neutralize hydroxyl ions generated at the cathode because of its chemical characteristics. Some of the advantages of using acetic acid are: most of its metal acetates are highly soluble in water, the increase in conductivity in soil will not be drastically increased, it is non-toxic, it is an important organic electron donor compound in remediation environments, and it will prevent the creation of other insoluble salts near the cathode that may increase the resistance in this area (Alshawabkeh et al. 1999). A 5,000 mg L^{-1} solution of acetic acid was made from glacial acetic acid (Fisher Scientific, Pittsburgh, PA) and used as the electrolyte in the cathode compartment.

The experiments were conducted in soil columns as depicted in Figure 3-2. The acrylic column is separated into three sections: anode, soil column, and cathode. Both electrode compartments were approximately three inches long by six inches high. The soil column section measured approximately sixteen inches long by six inches deep. The soil column was separated from the electrode compartments by an acrylic plate with over fifty percent perforation. Filter paper (Whatman No. 4) was positioned within the soil column along the perforated acrylic plate in order to minimize media entering the electrode compartment. The column had twelve sample ports across the face of the

column for sample withdrawal. Both of the electrode compartments had ports on the top

and the bottom which are used for electrolyte circulation. The top port on each of the

electrode compartments was also used for connecting power to the electrode. The soil

columns were sealed with silicone and water tested before the commencement of each

test. The columns had six carbon reference electrodes evenly spaced across the top of the

column. The reference electrodes were carbon rods with a diameter of 0.242" and an

approximate length of 5". The electrical equipment used for the experiment was a GW

Instek GPR Middle Series DC laboratory power supply. The anode was a platinum mesh

plate where the cathode electrode was a titanium plate. The titanium commercial grade

sheet had dimensions of 6.25" x 2" x 0.063". The platinum electrode had the same outer

dimensions as the titanium sheet; however, it was comprised of 0.032" platinum wire

with a maximum mesh spacing of 0.04".

Figure 3-2: Experimental electrokinetic remediation cell (Re-drawn from (Kim et al. 2000))

The peristaltic pump used to circulating the electrolyte solution was a Cole

Parmer, Masterflex 7550-20. The pump tubing was Tygon 1.14 mm ID. The two liter

electrolyte recirculating reservoir containers were high density polyethylene (HDPE) and

were graduated for electrolyte level monitoring. The pH and conductivity of the

electrolyte was monitored daily with a bench-top meter. The voltage drop across the

column was measured daily using a Fluke 112 multi-meter and the six carbon reference

electrodes on top of the column.
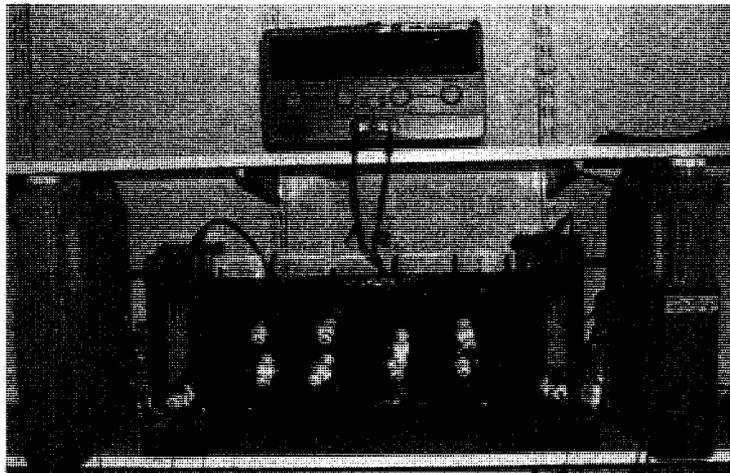
Figure 3-3: Laboratory bench-top electrokinetic remediation column

The sand and clay used in the column were obtained from US Silica (OK-110)

and Thiele Kaolin Company (Kaofine 90), respectively. Although research has

determined that extrapolating laboratory results using industrial kaolinite for field

applications can be misleading (Shackelford et al. 1995), the Georgia clay was used to

prevent introduction of unnecessary variables into the transport study and to provide

comparison with other studies. Table 3-1 and 3-2 list the properties of the sand and clay used in the column testing.

Table 3-1: Properties of soil materials

Parameter	US Silica (OK-110)	Thiele Kaolin Co. (Kaofine 90)
Principal Mineralogy	Quartz	Kaolin
USCS Class	SW	CL
pH	7.2	7.2
Specific Gravity	2.65	2.63
Moisture Content (%)	<0.2	0.9
Size (%)	99.8 <0.212 mm	98.9 <0.2μ
K_h (cm/s)	2.5×10^{-4}	1×10^{-8}

Table 3-2: Kaolin sample XRF results

Compound	%
Al_2O_3	37.94
SiO_2	44.82
P_2O_5	0.10
K_2O	0.17
TiO_2	1.10
Fe_2O_3	0.38
SO_3	0.05
Na_2O	0.16
CaO	0.01
MgO	0.03
Total	84.8

Tap water was used in lieu of DI water at the anode because it is already ionized to a suitable level. A 5,000 mg L^{-1} solution of acetic acid was used as the electrolyte in the cathode compartment. The soil was mixed with tap water at thirty five percent water content and was added to the column in one-half inch lifts using a rubber mallet on the

column's sides to evenly compact the media. The columns testing clay were filled in one inch lifts and were compacted using a five pound hammer modified for the column which had a twelve inch drop. The mixed media column had a middle layer of sand surrounded by kaolin. The soil tap water mixture had a moisture content of thirty five percent.

Samples were taken from the sample ports periodically to measure acetate levels across the column. A spectrometric method was developed to measure acetate in the samples (Roche R-Biopharm). Standard solutions were measured and used to create a calibration curve each day the spectrometer was used for analysis. The acetic acid UV test kits were obtained from R-Biopharm and determined acetate concentrations based on the formation and UV measurement of nicotinamide-adenine dinucleotide (NADH). Acetic acid standards measured with the UV test kits were compared with standards measured using an ion chromatograph (IC). The results from the IC were similar to the values from the UV test kit. The UV spectrometer method was selected because samples could be analyzed within the laboratory as opposed to be out-sourcing the samples.

The recirculation pump continually circulated acetic acid within the electrode and the electrolyte reservoir. The anode's pH was manually regulated on a daily basis through the addition of sodium hydroxide. The tests were conducted at two different constant current settings. The low and high settings were 1.33 A/m^2 and 5.33 A/m^2, respectively. The duration of the tests ranged from fourteen to twenty nine days, similar to other transport studies using EK (Acar et al. 1997; Budhu et al. 1997; Thevanayagam et al. 1998). Table 3-3 summarizes the experimental set-up. Laboratory restrictions prevented the clay test to continue beyond 14 days.

Table 3-3: Experimental column summary

Column Type	Current (A/ m^2)	Duration (days)	Electrode Condition	
			Anode	Cathode
Sand	1.33	29	pH Adjust (7-8) w/NaOH	Acetic Acid (5,000 mg/L)
Kaolin	5.33	14	pH Adjust (7-8) w/NaOH	Acetic Acid (5,000 mg/L)
Sand/Clay Mix	1.33	27	pH Adjust (7-8) w/NaOH	Acetic Acid (5,000 mg/L)

3.4 Results and Discussion

The column containing only sand was tested at the low current setting of 1.33 A/m^2. The experiment was not run at the high setting due to the large resistance across the column at the beginning of the experiment. The maximum voltage output of the bench-top DC power supply was below the voltage required to overcome the resistance through the column. Additionally, the successful acetate transport results under the low current settings indicated that higher current settings were not necessary. The number of samples retrieved from the sample ports on the face of the column were minimized due to the loss of media while sampling.

The clay column was tested under a constant current of 0.04 amps or 5.33 A/m^2. The low current setting was not attempted on the clay column due to findings from other researchers who had minimal success in attempting electrokinetic injection in clay columns at low current settings. A power outage and consequently a major leak in the column experiment shortened the length of testing to approximately half of the other

column tests. The clay column experiment was fourteen days where the other sand and mixed media test were roughly twenty nine days. It was not possible to retrieve a large enough volume of pore water samples from the sample ports during the experiment due to the nature of the hydraulic properties of the clay in the column and therefore samples were only retrieved upon the completion of the test. Since the voltage drop continued to decrease across the column during the experiment, it was assumed that acetate migration was occurring and mid-experiment sampling was not necessary.

Column testing was also performed on a column layered with clay and sand. This experiment was conducted at the lower current level of 1.33 A/m^2. The experiment verified that electronic injection would be successful in uniformly introducing amendments to a non-homogeneous subsurface.

3.4.1 pH

Maintaining a pH across the soil column in the range of 5-9 is desirable for the optimization of biological activity and for achieving reasonable transport rates for target species (Acar et al. 1997). The initial pH of the soil column was 7.2. A peristaltic pump circulated anode electrolyte between the 2-L anode reservoir and the 0.5-L anode electrode compartment. The pH of the anode was manually adjusted with sodium hydroxide to an optimal pH of 7-8. A peristaltic pump circulated a 0.5% acetic acid solution between the 2-L reservoir and the 0.5-L cathode compartment. The pumping rate was maintained in order that the electrode compartments were completely circulated several times per day. The pH in the cathode compartment throughout all of the tests ranged from 3.5 to 4.0. The pH of the pore fluid was measured at the completion of the experiment from four sample points across the column. The measured pH values were consistently in the range of 4.8-5.0 for all column experiments.

3.4.2 Conductivity and Voltage Drop

As mentioned earlier, all of the tests were run at constant current values of either

1.33 A/m^2 (sand and mixed medium columns) or 5.33 A/m^2 (clay column). Monitoring

of the electrical gradient and conductivity throughout the test indicated that the two

parameters were inversely proportional to each other. During the introduction of acetate

to the soil, the conductivity across the column increased at the same time the voltage drop

between the anode and cathode decreased. This continued until the columns approached

steady state conditions.

Figure 3-4 depicts how the voltage across the sand column dropped within the

first ten days of the experiment. At the conclusion of the test, the initial voltage across

the column decreased by approximately a factor of three, from 47V to 14V due to the

increase in conductivity across the column.
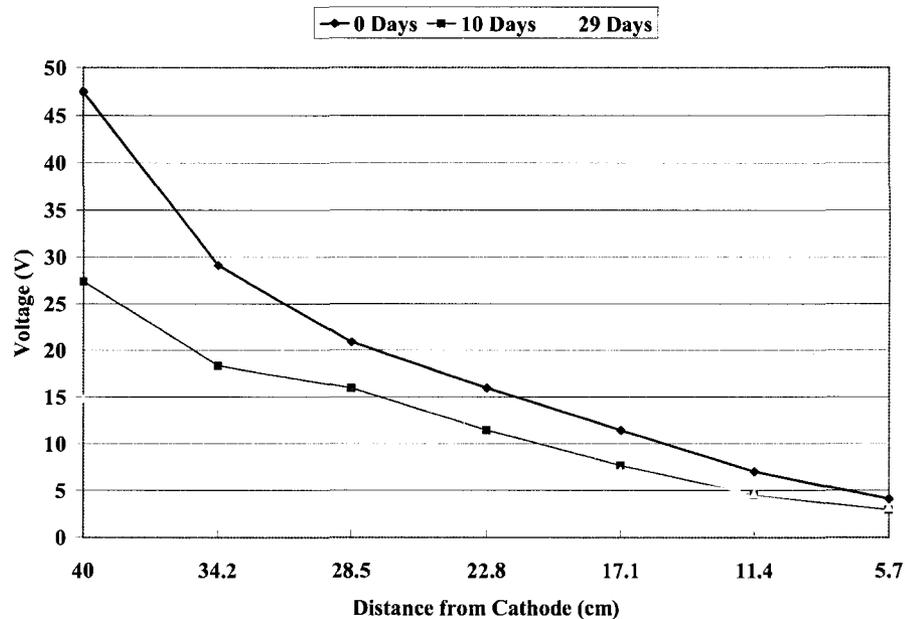
Figure 3-4: Electric potential distribution across sand column from t=0 days to t=29 days

The 14-day column test resulted in a linear decrease of electric potential across

the kaolin soil column. The overall drop in the cell's voltage of 20 V corresponds with

the column's increase in conductivity from approximately 1,500 μS cm^{-1} to 1,900 μS cm^{-1}. The voltage drop across the column (V/cm) appears to be uniform horizontally across

the kaolin column. The electric potential readings on the clay column throughout the

fourteen day test continued to decrease each day and did not indicate the system was

approaching steady state. Under steady state conditions, the electric potential across the

column would eventually level-off and be roughly equal between reference electrodes

across the column.
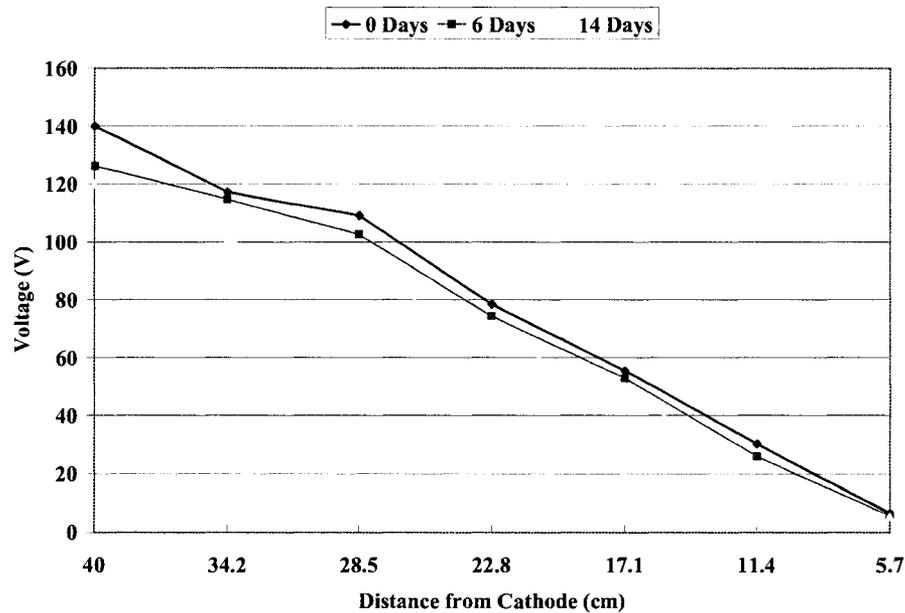
Figure 3-5: Electric potential distribution across kaolin column from t=0 days to t =14 days

As noted in Figure 3-6 the voltage drop across the mixed media column decreased

dramatically over the course of the experiment (27 days), indicating an increase in system

conductivity. The initial voltage applied to the system was nearly 115 volts and the voltage at the completion of the experiment was 40V, a decrease by approximately a factor of three. The voltage drop between each reference electrode is approximately equal which indicates uniform soil conductance horizontally across the column. The voltage drop readings across the column during the final seven days of the column test suggested the system was approaching steady state. The increase in conductivity across the column from approximately 600 μS cm^{-1} to 1,700 μS cm^{-1} is correspondingly inversely proportional to the decrease in voltage drop. The mixed media column's decrease in electric potential and increase in conductivity data was a positive indicator that acetate was being transported across the heterogeneous soil column.
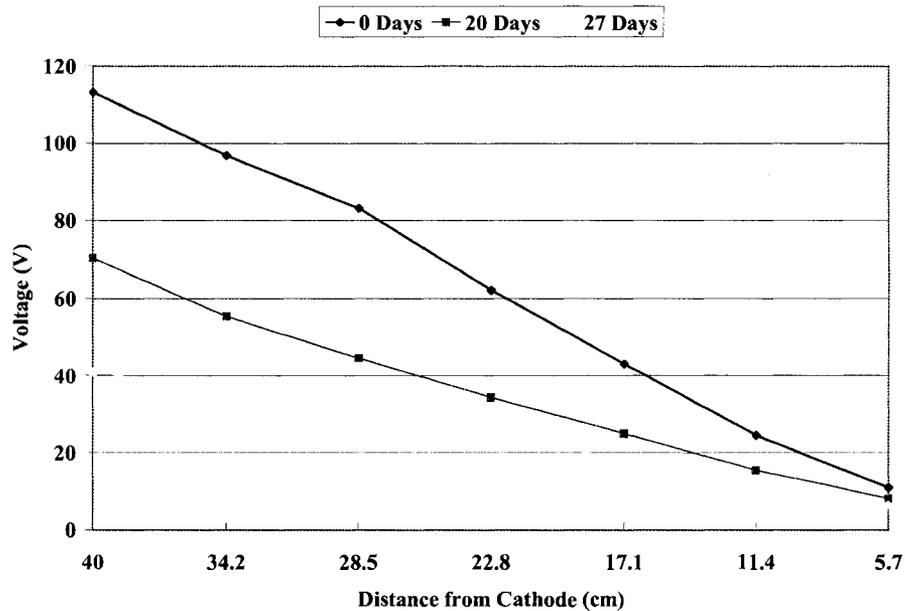
Figure 3-6: Electric potential distribution across mixed media column from t = 0 days to t = 27 days

3.4.3 Acetate Transport

Migration of acetate into the sand column was noted within the first 48 hours of the experiment. Soil columns under an electric potential will transport ions primarily due to electromigration and not diffusion (Acar et al. 1993). Figure 3-7 represents the concentration of acetate horizontally across the column at the completion of the experiment. Concentrations varied from approximately 1,100 mg L^{-1} to 1,700 mg L^{-1} after 29 days of testing. There was no measurable amount of electroosmotic flow at the cathode during this test at 1.33 A/m^2. Assuming that acetate reached the first sample port closest to the cathode by the 2nd day, the transport rate of acetate under 1 V cm^{-1} was 4 cm day^{-1} with an effective ionic mobility of 8.4 cm^2 $V^{-1}d^{-1}$. Researchers examining the EI of ammonium into sand beds reported transport rates of approximately 9 cm day^{-1} (Acar et al. 1997).
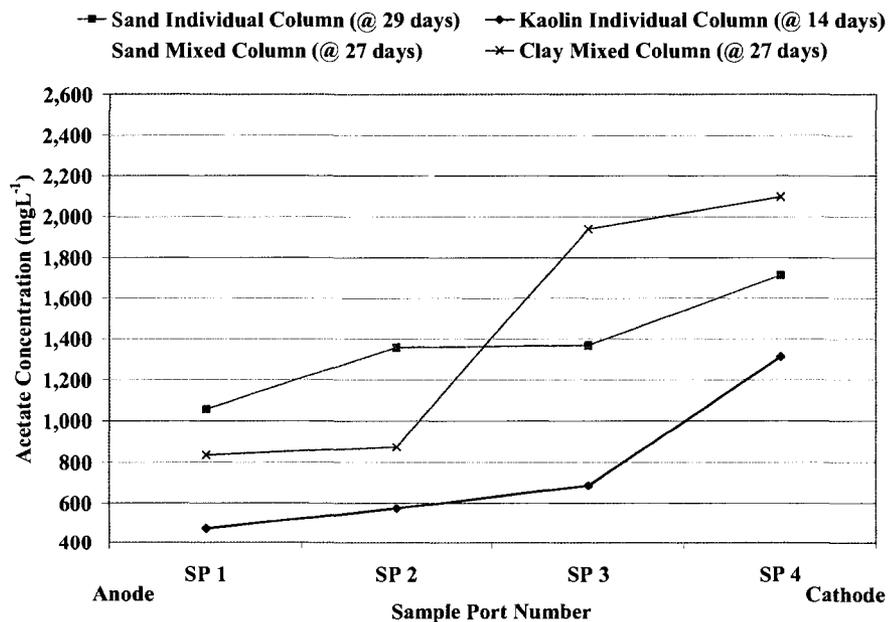
Figure 3-7: Final acetate concentrations across the sand, kaolin, and mixed columns

Acetate concentrations from the kaolin column upon the completion of the experiment verified the successful distribution of acetate across the column as seen in Figure 3-7. Although the concentration of acetate in the pore fluid samples from the column was lower than found in the sand column, successful migration was observed across the column based on the concentrations of acetate across the column at only 14 days. Concentrations remained relatively steady from the anode to SP3 and then tripled to 1,300 mg L^{-1} at SP4. This could indicate that the column had not reached steady state at the end of the experiment and further acetate transport could be anticipated.

The amount of electroosmosis flow was measured throughout all of the column experiments. Evidence of electroosmosis was only detected at the cathode. Electroosmotic flow rates of up to 75 ml d^{-1} were observed during the kaolin column experiment at the cathode as depicted in Figure 3-8. EO flow rates were calculated based on the daily measurement of excess water in the cathode which overflowed into the EO beaker. The presence of high EO flow rates from the anode to the cathode has a direct impact on the migration of acetate in the opposite direction. Additionally, non-uniform EO flows across the ER column have been detected where higher flows existed at the anode end of the column in comparison to the cathode end. This non-uniform EO may contribute to the smaller acetate concentrations at the sample ports closest to the anode. Because samples were only taken at the completion of the experiment, the migration rate of acetate cannot be determined from field data, however, the coefficient of electroosmotic conductivity k_e in kaolinite is approximately 5.7 x 10^{-5} cm^2 $s^{-1}V^{-1}$ (Mitchell 1993). It is possible that lengthening the experiment duration would have a significant effect on the final acetate concentrations within the column; however, the

major drop off in concentration in sample ports closest to the anode would hint that

acetate transport is limited in kaolin under these conditions.
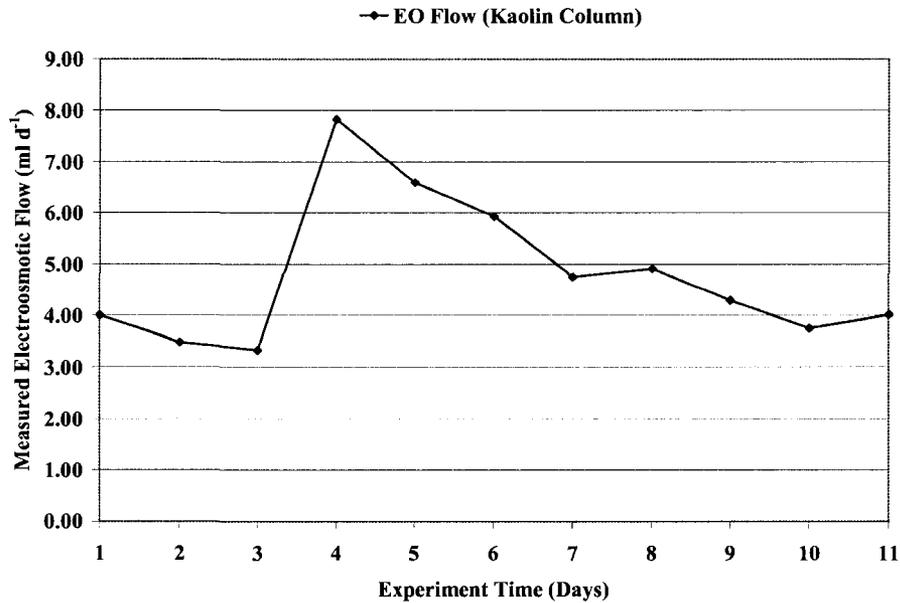
Figure 3-8: Measured electroosmotic flow at the cathode of the kaolin column

The acetate concentrations across the mixed media column within the individual

sand and kaolin layers followed similar trends to the individual sand and kaolin column

experiments, verifying the success of EI in mixed media as noted in Figure 3-7.

Electroosmotic flows measured daily at the cathode indicated a rate of approximately 35

ml d^{-1}. Interestingly, the distribution of acetate in the kaolin layer dramatically dropped

off at the two sample ports closest to the anode. The presence of non-uniform

electroosomotic flows causing dilution in this region could explain this phenomenon.

Results from this task indicate that amendments can be adequately added to subsurfaces

with varying hydraulic conductivities for nutrient addition or system neutralization.

Traditional means of introducing amendments to the subsurface for in-situ treatment such as pumping are ineffective and inconsistent due to preferential flow paths, soil heterogeneities, and adsorption (Acar et al. 1997). Due to the uniformity of the acetate across the columns, electrokinetic injection appears to be a successful means to uniformly introduce a compound into the subsurface. Because actual sites will have native soil and groundwater and not industry grade sand and tap water, the resistance in the subsurface between electrodes will likely remain minimal and a lower current setting should provide ample power.

3.5   Conclusions

The electrokinetic injection of acetate was tested under sand, clay, and heterogeneous soil conditions. A major portion of the transport of the acetate ion in the sand column would be to due its ionic mobility under the electrical gradient, since no measurable amount of electroosmotic flow was detected. The majority of the transport of acetate in the kaolin column is likely due to acetate's ionic mobility since the electroosmotic flow within the column was in the opposite direction of the migration of the negatively charged ion. The findings of the tests are summarized as follows:

- Effective transport rates of acetate can be achieved in sand columns under current densities as low as 1.33 A/m^2. No electroosomotic flow was detected in the sand column under the test conditions.

- Clay columns operated under a current density of 5.33 A/m^2 indicated successful distribution of acetate across the column. Large electroosmotic flows were detected in the cathode at rates as high as 75 ml d^{-1}. The presence of non-uniform

EO flows may contribute to the non-uniform distribution of acetate across the column.

- Mixed media columns containing layered sand and clay and under a current density of 1.33 A/m^2 achieved effective transport of acetate. Acetate concentrations followed the same trends as seen in the individual sand and clay column tests. Electroosmotic flow rates of 35 ml d^{-1} were measured at the cathode.

- Results from the mixed media columns may be indicative of conditions of aquifers in the field (mostly sand with clay lenses). EI appears to be a successful method to introduce charged amendments to the subsurface, which could include pH neutralizers, oxidizers, or nutrient supplements.

- EO flow in an electrokinetic process is significant. In soils with increasing clay amounts (or soils with high surface charge density) EO flows could be substantial and could possibly work against the electromigration of amendments. However, EO flow is also a useful mechanism for the movement of species across the soil column.

4.0   Arsenic Removal in an Electrokinetic Remediation System

4.1   Abstract

The efficacy of using unamended and amended electrokinetic remediation for the removal of arsenic from groundwater was examined through a series of laboratory column experiments. Electrokinetic remediation has been successful in removing metals in laboratory experiments and field applications. Aqueous and solid samples across the bench-top soil column were analyzed for arsenic in order to determine the effects of ER on the system. Unamended ER tests used groundwater as the electrolyte at both electrodes, where amended ER tests used pH-conditioned groundwater at the anode and an acetic acid solution at the cathode. The distribution of arsenic and the characteristics of the pore water across the column in the unamended mode indicated removal was solely due to the electromigration and precipitation mechanisms within the column. Amended electrokinetic remediation studies were conducted using pH-adjusted groundwater at the anode and acetic acid as the electrolyte at the cathode. The distribution of arsenic and the characteristics of the pore water across the column in the amended mode indicated removal was due to electroosmosis and electromigration mechanisms within the column. Arsenic speciation within the column was estimated using column pH and redox data.

4.2   Background

Due to the increased findings of arsenic effects on public health, the United States EPA recently adopted a new maximum contaminant level for arsenic in drinking water at 10 ppb. The extensive contamination of drinking water sources with arsenic and the growing concern over the adverse effects small concentrations of arsenic have on public health has brought arsenic to the forefront for public health and water treatment

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professionals. Sources of arsenic in natural waters can originate from natural and anthropogenic sources and can contaminate both ground and surface waters(Council 1999; Safety 2001). The distribution of arsenic and its speciation is mainly dependent on the pH and reduction-oxidation (redox) potential conditions. As such, arsenic can be found in natural waters as the more toxic and soluble form, As (III), or as As(V) depending on pH and redox conditions. Common arsenic removal technologies require a pre-oxidation step to oxidize As(III) to As(V). The addition of chemical reagents such as ozone, potassium permanganate, or chlorine promote the transformation of trivalent arsenic to pentavalent arsenic. Subsequent treatment technologies may include chemical precipitation, adsorption (using ferric chloride), or membrane separation.

Arsenic occurs naturally and is widely distributed throughout the earth's soil and water bodies. The primary source of arsenic in the environment is due to the release of arsenic from weathering and dissolution of As-enriched rocks, minerals, and ores (Wang et al. 2006). The main anthropogenic sources of arsenic include energy production, mining, smelting, and refining of the ores, industrial processes, and agricultural processes. Agricultural processes include the application of herbicides and insecticides to fields. As such, arsenic can enter drinking water via both groundwater and surface water sources. The majority of the arsenic produced worldwide is created as a by-product of the smelting of copper, lead, cobalt, and gold ores. Approximately 90% of the United States' arsenic demand is for use as a wood preservative. Arsenic is also used for the production of agricultural chemicals including insecticides, herbicides, algicides, and growth stimulants for plants and animals, but on a much smaller scale. Additionally, other small demand areas include the glass and nonferrous alloy production fields and the

electronics industry (Safety 2001). Prior to the introduction of DDT in the 1940s, most pesticides were made from inorganic arsenic compounds. As a result, some agricultural soils have arsenic concentrations in excess of 100 ppm, but most studies suggest that this arsenic is confined to the topsoil. In comparison, most soils unaffected by human activities contain less than 10 ppm arsenic (WHO 1996).

For most people, food is the largest source of arsenic exposure (about 25 to 50 micrograms per day [$\mu g\ d^{-1}$]), with lower amounts coming from drinking water and air (Safety 2001; WHO 2003). Among foods, some of the highest levels are found in fish and shellfish; however, this arsenic exists primarily as organic compounds, which are essentially nontoxic. In areas that are prone to high levels of arsenic due to natural geothermal and geo-hydrological processes and anthropogenic activities, water is the most vital media providing a pathway into the human body. Airborne arsenic, due to occupational exposure, can also negatively contribute to health problems. Human exposure to arsenic can have both short and long-term effects on human health depending on the arsenic dose and duration of exposure to the pollutant. Complications arising from chronic exposure can include dermatological problems including melanosis (pigmentation) and keratosis (rough, dry skin lesions), reproductive, neurological, cardiovascular, respiratory, hepatic, hematological, and diabetic effects in humans (Council 1999). Studies have reported that consumption of groundwater contaminated with arsenic at concentrations as low as 100 ug L^{-1} can cause skin, lung, and urinary bladder cancers. Additionally, increased risks of kidney and liver cancer have been reported (Council 1999). The U.S. EPA requested the National Academy of Sciences to review worldwide studies of arsenic health effects to determine the health risks of arsenic

at various levels of exposure. The Academy concluded the risk level at a 50 ug L^{-1} was greater than previously determined and that the level should be lowered.

There are over 200 different mineral inorganic forms of naturally occurring arsenic (Onishi 1969-1978). The approximate breakdown of these arsenic forms is as follows: 60% arsenates, 20% sulfides and sulfosalts, and 20% including arsenides, arsenites, oxides, silicates, and elemental arsenic (Onishi 1969-1978). Contaminated surface and ground waters may also contain organic forms of arsenic including mono methyl arsenate (MMA) and dimethyl arsenate (DMA). The major arsenic species found in the environment are arsenite As(III), arsenate As(V), arsenious acids, and arsenic acids (Figure 4-1). The pH and redox conditions determine the distribution of arsenic species in natural waters as either As(III) or As(V). In surface waters or oxidizing conditions, arsenate is predominant, whereas in groundwaters where mildly reducing conditions exist, arsenic is typically found in its thermodynamically stable and soluble form, arsenite. However, both oxidation states have been detected in oxic and anoxic conditions (Oremland et al. 2003).
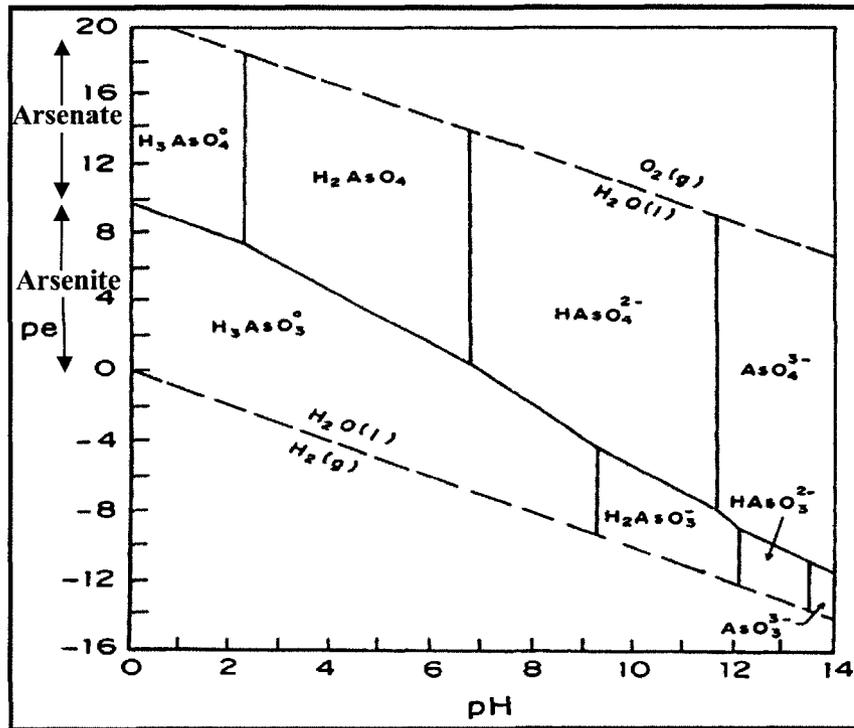
Figure 4-1: pe-pH Diagram of arsenic in water at 25° (Pourbaix 1966)

Arsenite is the most toxic of the arsenic compounds, more soluble than arsenate

and hence, more mobile. Although arsenate can exist in four forms in aqueous solutions

(H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}), the oxyanionic species $H_2AsO_4^-$ or $HAsO_4^{2-}$

are the most common forms detected in the environment. The equilibrium expressions

for these arsenate forms are as follows:

$$H_3AsO_4 \rightarrow H^+ + H_2AsO_4^-$$ (Eq. 4.1)

$$pK_1 = 2.2$$

$$H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-}$$ (Eq. 4.2)

$$pK_2 = 6.98$$

$$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$$ (Eq. 4.3)

$$pK_3 = 11.6$$

At pH values typically found in natural waters, As(III) is present as the non-ionic form of arsenious acid (H_3AsO_3). As(III) may also exist as $H_2AsO_3^-$ and $HAsO_3^{2-}$. The equilibrium expressions for all arsenite species are as follows:

$$H_3AsO_3 \rightarrow H^+ + H_2AsO_3^- \tag{Eq. 4.4}$$

$$pK_1 = 9.2$$

$$H_2AsO_3^- \rightarrow H^+ + HAsO_3^{2-} \tag{Eq. 4.5}$$

$$pK_2 = 12.7$$

$$HAsO_3^{2-} \rightarrow H^+ + AsO_3^{3-} \tag{Eq. 4.6}$$

$$pK_3 = 13.4$$

Physico-chemical processes and biological processes can remove arsenic from water. Physico-chemical processes include: chemical coagulation-precipitation, adsorption, membrane separation, and ion exchange. Biological processes for the removal of arsenic can include: phytoremediation and treatment with microbes or biofiltration (Mondal et al. 2006). Since As(III) is most commonly found in its nonionic form, it likely does not significantly interact with solid surfaces, and therefore cannot be removed with such common removal technologies as adsorption with ferric chloride or precipitation (Torrens 1999). Common arsenic removal technologies involve oxidizing As(III) to As(V) using the addition of chemical oxidants such as potassium permanganate, ozone, hydrogen peroxide, or chlorine. Unfortunately, the addition of oxidants increases the cost of arsenic removal and may also create unwanted residuals and byproducts.

Natural attenuation of arsenic-contaminated soils and groundwater is also being considered as a cost efficient alternative. The principal mechanism for in situ remediation relies on arsenic's ability to adsorb to a solid phase. The sorption is directly influenced by the arsenic speciation and the site's geochemical characteristics such as pH, redox potential and other existing ions. Essentially, arsenic (in the As(V) form) will adsorb to an adsorbent such as hydroxides of iron, aluminum, and manganese, clay and sulfide minerals, and organic matter leading to immobilization of arsenic in soils and removal from groundwater (Wang et al. 2006).

Electrokinetic remediation (ER) is a technology that has been successfully applied in the removal, reduction, and stabilization of groundwater contaminants such as heavy metals, dense non-aqueous phase liquids (DNAPL), chlorinated solvents and other contaminants (Acar et al. 1993; Acar et al. 1995; Acar et al. 1996; Gent et al. 2003; Jackson et al. 2004). The low-level direct current across the soil results in physiochemical and hydrological changes in the subsurface soil mass, leading to species transport by coupled mechanisms such as electrolysis of water, electrophoresis, electromigration, electroosmosis, and to a lesser extent, diffusion (Acar et al. 1996). These mechanisms are depicted in Figure 4-2.
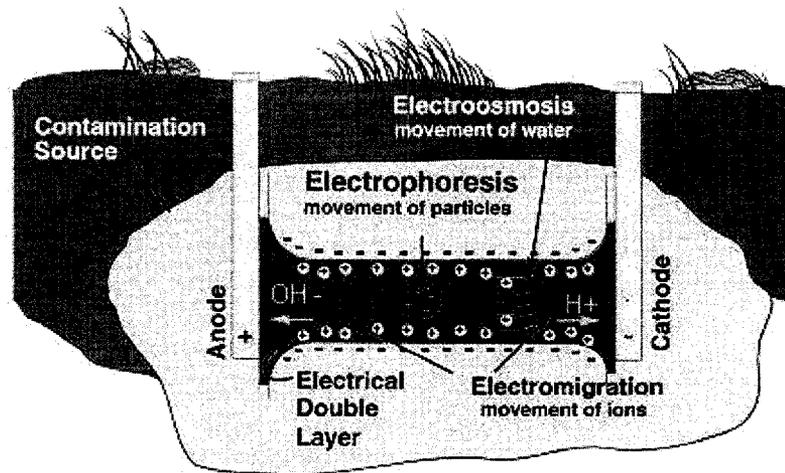
Figure 4-2: Electrokinetic remediation (Re-drawn from (Lindgren 1998))

The electrolysis of water, which predominantly occurs at the electrodes, produces hydrogen ions in the anode compartment and hydroxide ions in the cathode compartment. Electrophoresis is the transport of charged particles under an electric field (Acar et al. 1993). Electromigration is the transport of ions and polar molecules in the pore fluid under an electric field and electroosmosis is the flow of an ionic liquid resulting from the applied electric field that acts on the charged interface between the water and the soil particles' surface. Diffusion is the mechanism in which species are transported due to concentration gradients.

Electrokinetic Theory

Groundwater or an externally introduced fluid is used as the conductive medium in the ER process. This fluid is allowed to flow in and out of the electrode compartment through a porous barrier at the electrode. The conduction phenomena in the soil which is influenced by the electric field will promote species transport across the porous media. Physico-chemical reactions such as acid/base reactions, sorption,

precipitation/dissolution, and oxidation/reduction reactions are the principal means under which electrokinetic remediation technology operates (Acar et al. 1993). In unamended electrokinetic remediation (when the electrolytic fluid is not externally influenced) application of direct electric current via electrodes immersed in a saturated soil results in oxidation at the anode and reduction at the cathode. This process known as electrolysis generates oxidized and reduced species which will aid in the transformation of contaminants. This process is defined by equations:

$$\text{Anode: } \frac{1}{2} H_2O \rightarrow e^- + \frac{1}{4} O_2(g) + H^+ \qquad \text{(Eq. 4.7)}$$
$$\text{Cathode: } H_2O + e^- \rightarrow \frac{1}{2} H_2(g) + OH^- \qquad \text{(Eq. 4.8)}$$
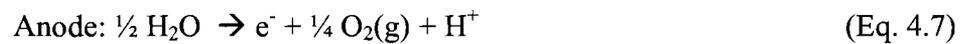
As shown in the above reactions, an acid front will be created at the anode and an alkaline front created at the cathode. The acid front will proceed to the cathode by transport mechanisms including migration and electroosmotic flow (Acar et al. 1993). Unless the buffering capacity of the soils is high enough to retard the flow, the chemistry across the soil will be dominated by the hydrogen ion which has a mobility approximately twice the mobility of the hydroxyl ion under an electric field(Acar et al. 1995). The protons generated at the anode are transported across the soil and meet the hydroxyl ions close to the cathode. The acid front across the soil will promote the desorption of cationic species concentrated on the soil surface (Acar et al. 1995). The base front created at the cathode due to the reduction of water will retard the migration of cationic ions to the cathode by precipitating them as oxides and hydroxides in the region of the cathode (Acar et al. 1996).

Electro-migration of ions is quantified by the effective ionic mobility u_k^*. Effective ionic mobility is defined as the velocity of the ion in the soil under the influence

of a unit electrical potential gradient. The ionic mobility and the diffusion coefficient of

an ion in dilute solution are related by the Nernst–Townsend – Einstein equation (Acar et

al. 1993) assuming the relation is applicable for ions in the pore fluid of soils;

$$u_k^* = \frac{D_k^* z_k F}{RT}$$ (Eq. 4.9)

where D_k^* (cm^2 s^{-1}) is the effective diffusion coefficient in porous mediums, z_k is the

charge of the chemical species, F is Faraday's constant (96,484 C mol^{-1} electrons), R is

the universal gas constant (8.314 J $mol^{-1}K^{-1}$) and T is absolute temperature (K). The

effective diffusion coefficient in the porous medium is related to the respective diffusion

coefficient in free solution, D_k by (Acar et al. 1993)

$$D_k^* = D_k \tau n$$ (Eq. 4.10)

Where τ is an empirical coefficient accounting for the tortuosity of the medium and n is

for the porosity. Typical values of τ range from 0.01 to 0.84 for saturated soils

(Shackelford et al. 1991).

In order to understand electroosmotic flow rates (q_e), the coefficient of electroosmotic

conductivity k_e (cm^2 $V^{-1}s^{-1}$) must be addressed. The electroosmotic-induced water flux is

proportional to the voltage gradient in a manner analogous to the flux dependence on the

hydraulic gradient under Darcy's law.

k_e is a soil property that indicates hydraulic flow velocity under a unit electrical

gradient. The mathematical model presented by Helmholtz and later refined by

Smoluchowski is the basis in which k_e is described theoretically. It can be explained by

the following relation (Acar et al. 1993)

$$k_e = \frac{\varepsilon \xi}{\eta} n$$ (Eq. 4.11)

Where ε is the permittivity of the medium or dielectric constant of the pore fluid, ζ is the

zeta potential, η is the viscosity, and n is the porosity. Electroosmotic conductivity based

on the above theory is dependent mainly on porosity and zeta potential. Zeta potential is

the electrical potential at the boundary between the moving particle and the liquid. This

boundary (slip plane) is the point where the Stern layer and the diffuse layer meet

(Mitchell 1993). The pH of the soil determines the zeta potential and since the soil pH

changes as the electroosmotic front moves across the column, the zeta potential is not a

constant.The pH of the soil determines the zeta potential and since the soil pH changes as

the electroosmotic front moves across the column, the zeta potential is not a constant.

Although hydraulic conductivities, which are significantly influenced by pore size and

distribution in the medium, can range from 10^{-3} to 10^{-9} m s^{-1}, the electroosmotic

conductivity is generally in the small range of 10^{-9} to 10^{-8} m^2 s^{-1} V^{-1} (Mitchell 1993).

The rate of species transport under an electric field which accounts for ionic

migration and electroosmotic transport processes is given by the following equation

(Alshawabkeh et al. 1999):

$$\upsilon = (nu\tau + k_e)\; \nabla(-\Phi) \tag{Eq. 4.12}$$

where υ = rate of species transport (cm/s); n = porosity of the soil (dimensionless); u =

ionic mobility of the species (cm^2/V-s); τ = factor that accounts for soil tortuosity and

species concentration (dimensionless); $\nabla(-\Phi)$ = the applied potential gradient; and k_e =

coefficient of electroosmotic conductivity (cm^2/V-s). The time, t, required for ions of

interest to travel from the cathode to anode electrode assuming the space between the

electrodes is L, can be estimated by (Alshawabkeh et al. 1999):

$$t = \frac{L}{(nu\tau + k_e)\nabla(-\Phi)} \tag{Eq. 4.13}$$

Amended Electrokinetic Remediation

Minimizing premature species precipitation at the cathode and maintaining a pH range of 6-9 for optimal microbial activity across the soil column can be accomplished through the use of an acidic enhancement in the cathode compartment (Acar et al. 1993). The addition of the acid enhancement modifies the chemical reactions at the electrodes and assists in the desorption of species and dissolution of carbonates and hydroxides(Acar et al. 1995). For example, when acetic acid is added to the cathode compartment, it neutralizes the hydroxide ions at the cathode which are created during the electrolysis of water. The main reaction at the cathode becomes the reduction of water and the creation of hydrogen gas and hydroxide ions. Without precipitation occurring at the cathode, the cationic species can migrate into the cathode well and become concentrated for periodic removal from the system. In the case of metals and metalloids, precipitation may be desirable considering the metals are immobilized and in-situ therefore, alleviating the need for future treatment. However, over time this creates a blockage in the soil which requires an increase in power to overcome the resistance. The injection of acetate anions into the system results in the creation of soluble complexes across the soil sample as the acetate migrates to the anode.

Other attempts to provide nutrients and other necessary process additives have been accomplished through hydraulic means. Hydraulic introduction (e.g., using wells, injection probes, fracturing) of amendments has proven to be inefficient and non-uniform in low permeability and mixed media soils leading to incomplete in-situ remediation. This process also has the tendency to overdose which can result in areas with excessive biological growth, therefore clogging the soil system (Acar et al. 1996). Researchers

have demonstrated the efficacy of using electrokinetic injection for delivering amendments to the subsurface for the reduction or stabilization of perchlorate, DNAPLs, and metals (Acar et al. 1993; Gent et al. 2003; Jackson et al. 2004; Bejankiwar et al. 2005; Luo et al. 2005; Jiradecha et al. 2006).

This paper evaluates the efficacy of using unamended and amended electrokinetic remediation for the removal of arsenic from groundwater and soil systems. Unamended and amended ER column studies were conducted in order to determine if electrokinetic mechanisms could remove arsenic from a simulated riverbank filtration system under a controlled setting. Conventional riverbank filtration systems are unable to successfully remove arsenic from the groundwater; however, supplementing the system with ER may result in positive results. If successful, this method could be employed as an engineered in-situ method for the removal of a lethal contaminant.

4.3   Methodology

The experiments were conducted in two identical soil columns as depicted in Figure 4-3. The acrylic column was separated into three sections: anode, soil column, and cathode. Both electrode compartments were approximately three inches long by six inches high. The soil column section measured approximately sixteen inches long by six inches deep. The soil column was separated from the electrode compartments by an acrylic plate with over fifty percent perforation. Filter paper (Whatman No. 4) was positioned within the soil column along the perforated acrylic plate in order to minimize media from entering the electrode compartment. The column had twelve sample ports across the face of the column for sample withdrawal. Both of the electrode compartments had ports on the top and the bottom which were used for electrolyte

circulation. The top port on each of the electrode compartments was also used for connecting power to the electrode.

Figure 4-3: Experimental bench-top electrokinetic remediation cell schematic (Re-drawn from (Kim et al. 2000))

The soil columns were sealed with silicone and water tested before the commencement of each test. The columns had six carbon reference electrodes evenly spaced across the top of the column as noted in Figure 4-4. The reference electrodes were carbon rods with a diameter of 0.242" and an approximate length of 5". The electrical equipment used for the experiment was a GW Instek GPR Middle Series DC laboratory power supply. The anode was a platinum mesh plate where the cathode electrode is a titanium plate. The titanium commercial grade sheet had dimensions of 6.25" x 2" x 0.063". The platinum electrode had the same outer dimensions as the titanium sheet; however, it was comprised of 0.032" platinum wire with a maximum mesh spacing of 0.04".
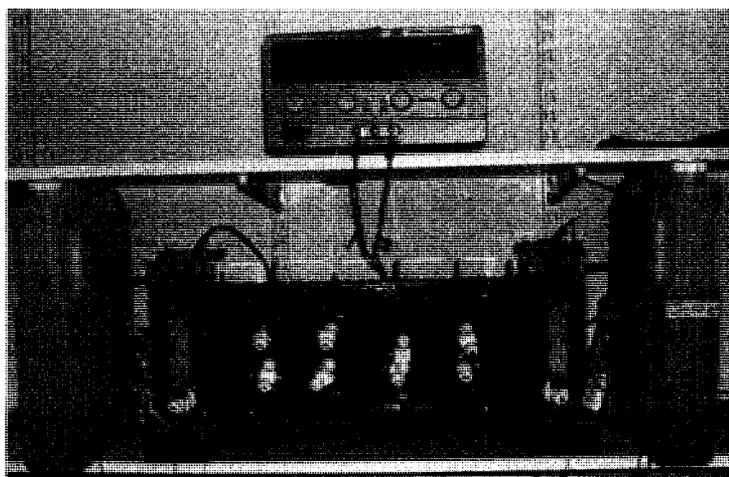
Figure 4-4: Laboratory bench-top ESP column

The peristaltic pump used in circulating the electrolyte solution was a Cole

Parmer, Masterflex 7550-20. The pump tubing was Tygon with an internal diameter of

1.14 mm. The two liter electrolyte recirculating reservoir containers were high density

polyethylene (HDPE) and were graduated for electrolyte level monitoring. The pH and

conductivity of the electrolyte was monitored daily with a bench-top meter. The voltage

drop across the column was measured daily using a Fluke 112 multi-meter and the six

carbon reference electrodes on top of the column.

The soil in the arsenic remediation experiments was native alluvial material from

a site along the South Platte River in Brighton, Colorado. Table 4-1 lists the properties of

the soil. The material was sieved with a 10 mm sieve and air dried. An arsenic solution

of 10 mg L^{-1} was made using sodium arsenate and South Platte River water. (Analysis of

the river water showed less than 0.001 mg L^{-1} of arsenic in the water.) The native

alluvial material and the arsenic solution was mixed with a stainless steel mechanical

mixer for 30 minutes and placed in the soil columns in one-half inch lifts. A rubber

mallet was used on the sides of the column in order to promote even compaction within the column. The soil-water mixture had a moisture content of thirty five percent. Unamended tests used South Platte River water as the electrolyte in both the anode and cathode compartments. The amended tests used river water as the anode electrolyte and a 10,000 mg L^{-1} solution of acetic acid as the cathode electrolyte. The acetic acid solution was made from glacial acetic acid (Fisher Scientific, Pittsburgh, PA).

Table 4-1: Properties of soil materials

Soil Properties	Value
pH	7.4
Conductivity, mmhos/cm	0.4
Organic Matter, %	0.1
Nitrate, as N, ppm	0.7
Phosphorus, as P, ppm	9
Potassium, ppm	15.6
Zinc, ppm	4.3
Iron, ppm	19.6
Manganese, ppm	1.8
Copper, ppm	2.1
Total Organic Carbon, %	0.051
Texture	Sand
Sand, %	94
Silt, %	0
Clay, %	6

Acetic acid (CH_3COOH) is a weak acid that undergoes partial dissociation in water (Snoeyink et al. 1980):

$$CH_3COOH = CH_3COO^- + H^+ \qquad \text{(Eq. 4-14)}$$

It has a pKa of 4.76, resulting in acetate being the main species at near-neutral pH. The dissociation of the weak acid will result in a low concentration of ions generated at the

cathode. Diluted acetic acid is commonly used as a descaling agent and also as a food additive. Acetic acid was chosen as the additive to neutralize hydroxyl ions generated at the cathode because of its chemical characteristics. Some of these advantages of using acetic acid are: most of its metal acetates are highly soluble in water, the increase in conductivity in soil will not be drastically increased, it is non-toxic and biodegradable, it is as an organic electron donor compound in remediation environments, and it will prevent the creation of other insoluble salts near the cathode that may increase the resistance in this area (Alshawabkeh et al. 1999). A 10,000 mg L^{-1} solution of acetic acid was made from concentrated acetic acid from Fisher Scientific and used as the electrolyte in the cathode compartment. This concentration was used based on other amended ER studies using weak organic acids acetic acid at the cathode (Jackson et al. 2001; Gent et al. 2003).

Two sets of unamended and amended tests were conducted for approximately thirty days at a constant current level of 20 mA (2.67 A/m^2). Daily monitoring of the electrode compartments' pH, conductivity, and solution level was conducted. The voltage drop across the soil column was also monitored daily. Samples were retrieved from the electrode compartments and from sample ports along the column several times throughout the experiment. The samples were immediately measured for pH, conductivity, and redox potential and refrigerated for subsequent analysis. In the amended tests, the pH of the anode was adjusted to a neutral pH with sodium hydroxide on a daily basis. At the conclusion of the experiments, the soil columns were disassembled and samples were retrieved from the column for arsenic analysis. Samples

were acid digested and analyzed for total arsenic by the CSU Soil, Water, and Plant

Testing Laboratory. The lab uses a Thermal Solutions ICP for metal analysis.

Table 4-2: Experimental arsenic column summary

Column Type	Soil Type	Current (A/ m^2)	Duration (days)	Electrode Condition Anode	Cathode
Unamended ER	Alluvial Material	2.67	30	Groundwater	Groundwater
Amended ER	Alluvial Material	2.67	30	pH Adjust (7-8) w/NaOH	Acetic Acid (5,000 mg/L)

4.4   Results and Discussion

The arsenic remediation experiments were run in both the unamended and

amended mode in order to observe and compare the removal efficiency between the two

conditions. Parameters such as pH, electric potential, and conductivity were measured

for both column systems and analyzed in order to completely understand the soil

environment. This data is used in conjunction with the arsenic data to determine the ideal

conditions for arsenic remediation.

4.4.1 Unamended ER Column Tests

4.4.1.1 pH

The unamended soil column used only river water (pH of 7) as the electrolyte in

both electrode compartments. The pH of the anode remained essentially uniform

throughout the test, in the range of 2.2 to 2.8. Figure 4-5 depicts the pH distribution

across the column from the anode to the cathode at t=0, 10, 20, and 30 days. The pH at

the cathode also remained relatively constant throughout the test in the range of 10.5 to

11.2. The oxidizing and reducing of water at the anode and cathode, respectively, resulted in the creation of hydrogen ions at the anode and hydroxide ions at the cathode. These reactions explain the extreme pH values at each respective electrode.
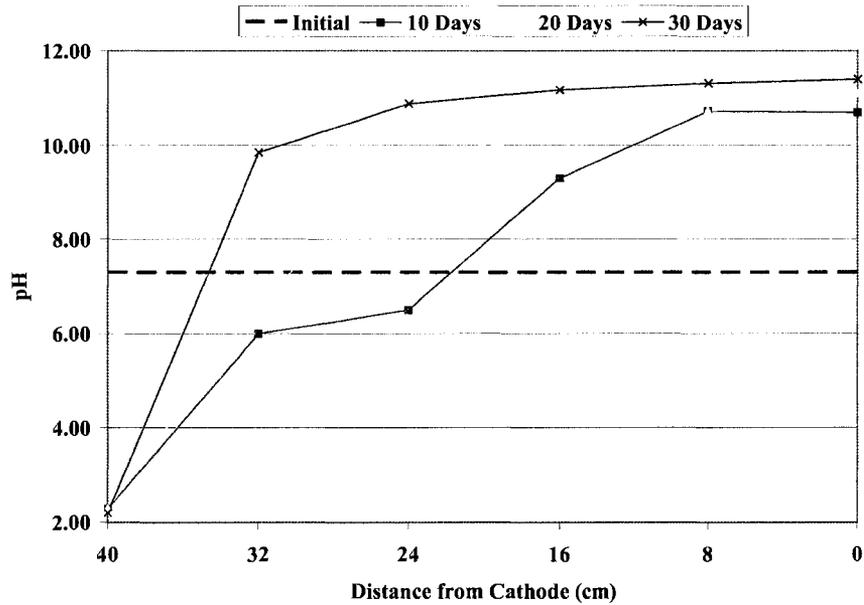
Figure 4-5: Unamended ER column pH distribution from t = 0 to t = 30 days

The pH values across the experimental column are not typical for unamended ER column experiments which analyze cationic heavy metals (Acar et al. 1990; Alshawabkeh et al. 1992). Typically, an acid front in the direction from cathode to anode due to the transport of hydrogen ions across the cell dominates the cell pH. In Figure 4-5, the pH at ten days appears to be dropping at the two sample ports closest to the anode. This trend would typically continue (and become increasingly acidic) as the acid front moves from the anode to the cathode during the experiment. It is typical to see an acid front move from the anode and an alkaline front from the cathode flow in opposite directions, with the acid front moving quicker due to the higher mobility of the hydrogen ion. However, in the unamended ER column, the alkaline front appeared to dominate. It is likely that

the large ionic migration of negatively charged arsenic ions moved towards the anode and collected in the region. This in turn caused a major resistance in the column within the anode region which created a large voltage drop. As such, the hydroxide ion and the alkaline front freely migrated towards the anode region, while the acidic front was suspended shortly outside the anode.

4.4.1.2 Conductivity and Voltage Gradient

The current remained at 0.02 amps throughout the test with voltages ranging from forty five to forty. The electric potential across the column from the anode to the cathode at t=0, 10, 20, and 30 days is presented in Figure 4-6. The electrical potential across the column at the beginning of the experiment is linear across the column from electrode to electrode, indicating the ionic composition of the pore water is uniform across the column. As the column test progresses, the region from the anode to the second reference electrode had a steep electric potential gradient. This trend is apparent at the 10, 20, and 30-day sampling event as noted in Figure 4-6. Since the electric potential was fixed from the anode to the cathode, the gradient change is due to the decrease in pore water conductivity.
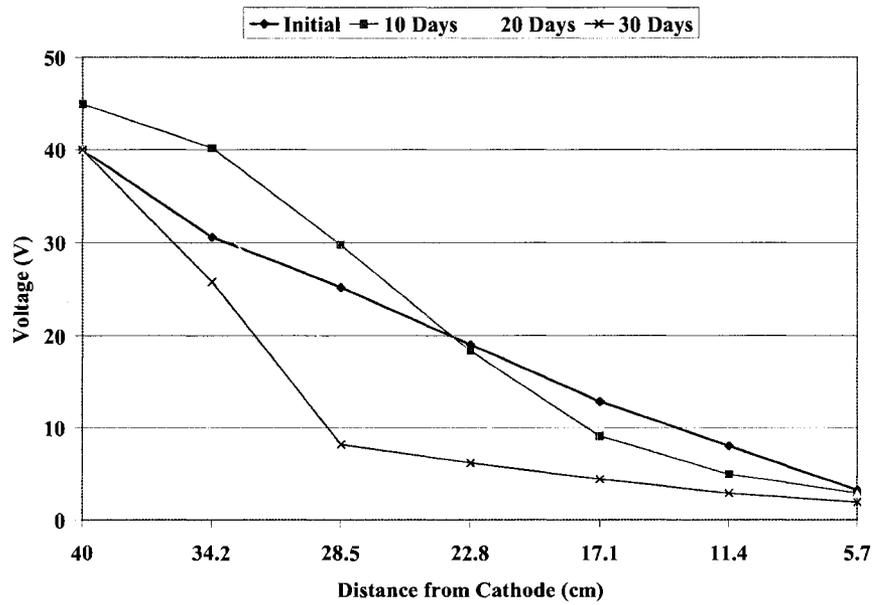
Figure 4-6: Unamended ER column electric potential distribution from t=0 to t=30d

Figure 4-7 graphically depicts the voltage drop across the column using the evenly-spaced reference carbon electrodes. The largest voltage drop is recorded in a region between two reference electrodes at the anode end of the column. This large drop is explained by the inversely steep conductivity drop in the region.
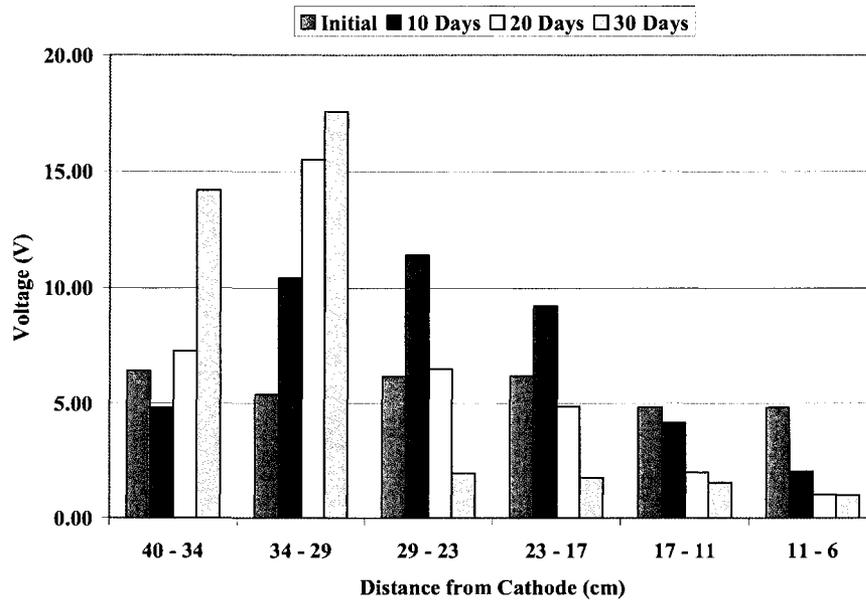
Figure 4-7: Unamended ER column voltage drop from t=0 to t=30 days

The conductivity of the anode electrolyte remained at approximately 2.3 mS m^{-1} throughout the experiment. The conductivity across the column from the anode to the cathode at t=0, 10, 20, and 30 days is presented in Figure 4-8. The conductivity of the cathode remained at approximately 1.25 mS m^{-1} for the initial twenty days and increased to approximately 2.5 mS m^{-1} by the end of the experiment. The conductivity across the column decreased in the region approximately 16 cm from the anode. This region experienced the highest amount of arsenic in the soil and also the largest voltage drop within the column. The migration of arsenic species towards the anode and the consequent precipitation of arsenic in this region directly contributed to this trend.
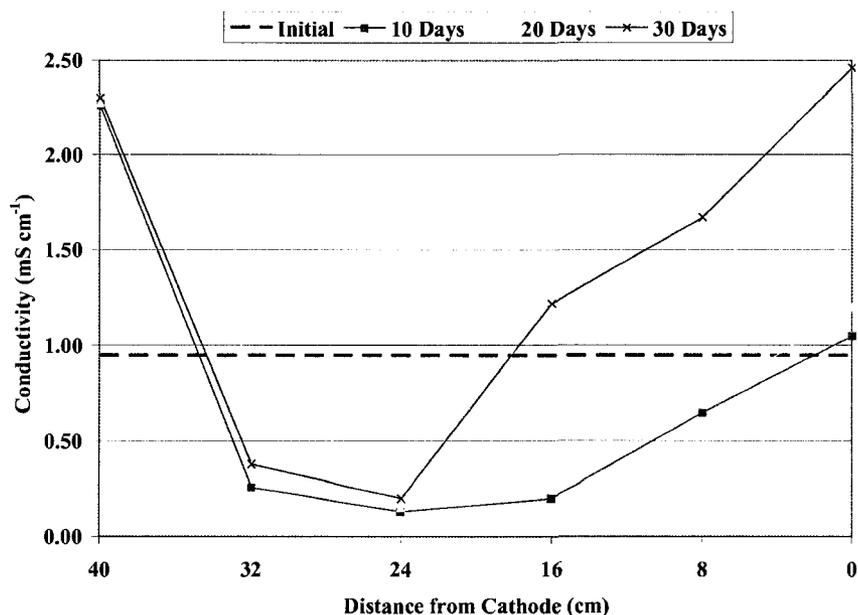
Figure 4-8: Unamended ER column conductivity distribution from t=0hrs to t=30days

The results from the routine monitoring of water quality parameters (pH and conductivity) and the electric potential across the column appear to indicate successful transport and precipitation of arsenic. The characterization of the column's pore fluid ultimately assists in determining the specific species of the contaminant present in the soil column and which ER mechanisms assisted in contaminant transport.

4.4.1.3 Arsenic

In both the unamended and amended experiments arsenic was measured every ten days at the electrode compartments and from sample ports extending across the ER column. The arsenic distribution in the pore fluid at t=10, 20, and 30 days and soil at t=30 days from the anode to the cathode is presented in Figure 4-9. At the completion of the unamended ER experiment, column concentrations of arsenic ranged from 2 mg L^{-1} to below the detection limit. The amount of arsenic in the sediment indicated that the highest values were in the anode region in the range of 3.6 – 4.6 mg kg^{-1} as noted on the

second y-axis in Figure 4-9. The fairly alkaline pH across the column appears to trend with the amount of arsenic in the soil. The alkaline front was likely desorbing the arsenic species in the soil and accelerating the ionic migration towards the anode. Column samples obtained during the experiment at 10 and 20-days indicated a peak arsenic value in the sample port closest to the anode and drastically smaller values for the other three sampling ports and non-detect values at the cathode. The concentration of arsenic in the anode increased ten-fold from 10 to 20 days. Although a laboratory error prevented an anode sample from being analyzed for arsenic, it is assumed that the aqueous arsenic concentration would have continued to increase as more arsenic migrated to the anode. The electromigration of the negatively charged arsenic species towards the anode is likely the main reason for this arsenic distribution in the column. Since there was no evidence of electroosmotic flow in either direction throughout the experiment, the movement of the arsenic species across the column toward the anode electrode was solely due to electromigration.
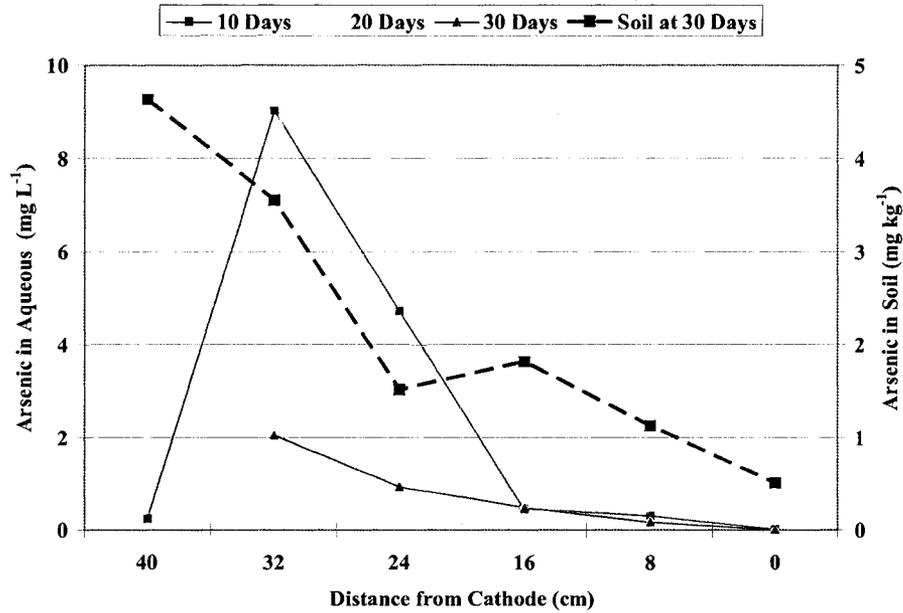
Figure 4-9: Unamended ER column arsenic distribution; aqueous As (t=0 to t=30days) and As soil (t=30 days)

The likely predominant form of arsenic in the column was arsenite due to the saturated conditions of the column. However, arsenate could have been present in a region close to the anode where an oxidizing environment existed. Positive oxidation reduction potential (ORP) values at the anode and pH values of 2.5 – 3.5 suggest that arsenate ($H_2AsO_4^-$) was the predominant form at the anode. The negatively charged ion naturally attracted to the anode remained in the anode region. However, ORP values in the range of -100 to -300 mV and pH values of 11 at the cathode indicate that arsenite (As III) may also be present in the cathode region as ($H_2AsO_3^-$). Since the pH across the column continued to increase to nearly ten at the completion of the experiment, the predominant form of arsenic was negatively charged as either arsenite or arsenate. Since there was no measurable electroosmosis flow at the cathode (or anode), the anionic forms

of arsenic were able to migrate toward the anode region under the imposed electrical potential.

Reddish-brown discoloration of the soil in the column in the region of high solid arsenic values indicates potential ferric hydroxide formation due to naturally occurring iron in the soil and alkaline conditions across most of the column. It is likely that arsenic co-precipitated with ferric hydroxide in this region. Considerable reddish-brown scaling on the anode electrode and similar deposits accumulated in the anode indicates the presence of additional arsenic complexes formed with naturally occurring iron bearing minerals.

Arsenic concentrations normalized to initial spiked values in the column's pore fluid and soil at the completion of the experiment are presented in Figure 4-10. Values for arsenic in the soil at 0 and 40 cm represent arsenic values in the soil immediately adjacent to the electrode compartments. Arsenic appears to have been almost completely removed from the column's pore fluid as seen in Figure 4-9 with C/Co values of 0.05 to below detectable levels. The arsenic in the soil appears to have been desorbed due to the alkaline conditions across most of the column, with the exception of the area near the anode.
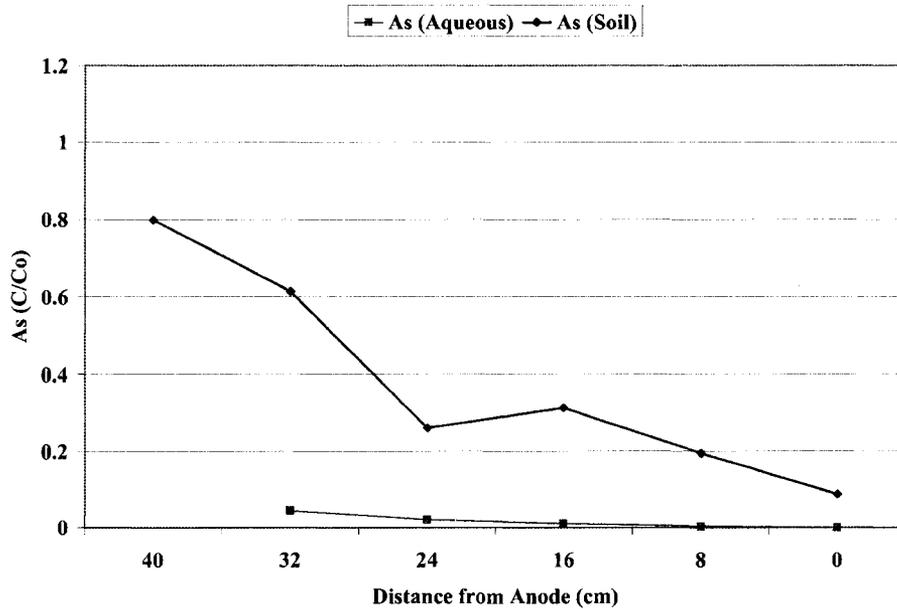
Figure 4-10: Unamended ER column arsenic distribution (C/Co) in aqueous and soil phases at t=30 days

A mass balance performed on the column, accounted for only 61% of the initial spiked arsenic, with 53% being accounted for in the soil alone. The remaining 39% is likely due to the precipitates in the anode and the anode electrolyte. A sample of the anode electrolyte was not analyzed due to laboratory error. If the arsenic concentration in the anode electrolyte continued to increase in a similar trend as seen in values at t=10 and 20 days, an additional 37% of the total arsenic would be accounted for leaving only 3% unaccounted for of the total arsenic mass. In addition, the precipitates within the anode compartment (as seen in Figure 4-11) were not characterized or quantified and could account for the remaining mass.

Figure 4-11: Unamended ER column: plan view of the anode compartment at t=20 days

An attempt to characterize the solid arsenic species in the soil column by performing a compositional analysis of the solid substrate using electron microscopy did not yield any useful results. The soil column was disassembled in an anaerobic glove box equipped with nitrogen gas supply. Representative soil samples from six regions of the column were collected, mixed, and prepared for analysis. Soil samples were analyzed using X-ray Photoelectron Spectroscopy (XPS) in the Central Instrumentation Facility in Colorado State University's Chemistry Department. XPS is an extremely powerful surface sensitive technique used to semi-quantitative and qualitative analysis of thin film and powder samples and consequently the equipment's magnification was too great for the size of the soil particles. This method could potentially be resolved by grinding sample specimens to a powder-like substance. The sample could also be measured using

other spectroscopic techniques which have been used for chemical speciation such as infrared and x-ray absorption (Welch et al. 2000).

The distribution of arsenic in the unamended ER column is exactly opposite to results from unamended ER studies conducted on cationic species. In these reported studies, the cationic metal species migrate toward the cathode and precipitate out in the cathodic region. This occurs when the positively charged species meets the alkaline front created by the electromigration of the hydroxide ion and precipitates out as a metal hydroxide.

4.4.2 Amended ER Column Tests

4.4.2.1 pH

The amended electrokinetic experiment was set up similar to the unamended test except for the type of electrolytes. The anode electrolyte was South Platte River water with daily additions of sodium hydroxide for pH adjustment. The cathode electrolyte was a 10,000 mg L^{-1} solution of acetic acid. Figure 4-12 presents the pH distribution across the column from the anode to the cathode at t=0, 10, 20, and 30 days. The pH of the anode and cathode throughout the experiment were in the range of 5 – 6.5 and 4 – 4.9, respectively. The pH across the column appeared to fluctuate during the first 10 days; however, for the majority of the experiment, the pH remained at approximately 5 across the soil column versus the unamended column where the pH was predominantly alkaline except for the region closest to the anode. The use of sodium hydroxide at the anode was successful in neutralizing the hydrogen ions created during the electrolysis of water, where the acetic acid at the cathode was successful in neutralizing the hydroxide ions.
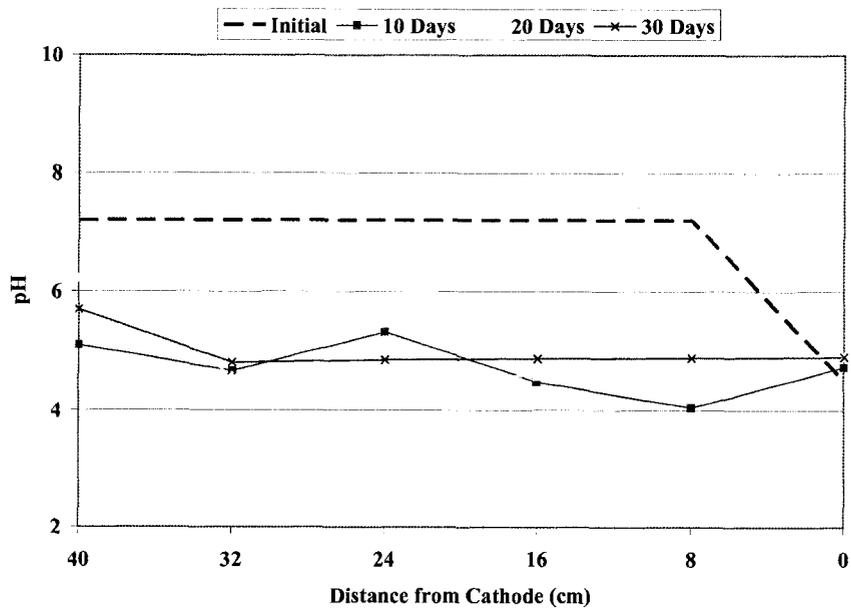
Figure 4-12: Amended ER column pH distribution from t = 0 to t = 30 days

4.4.2.2 Conductivity and Voltage Gradient

The current remained at 0.02 amps throughout the test with voltages ranging from forty to eleven volts as show in Figure 4-13, which presents the conductivity distribution across the column from the anode to the cathode at t=0, 10, 20, and 30 days. The initial electric potential across the column was essentially linear, indicating a uniform ionic distribution in the pore water across the column.
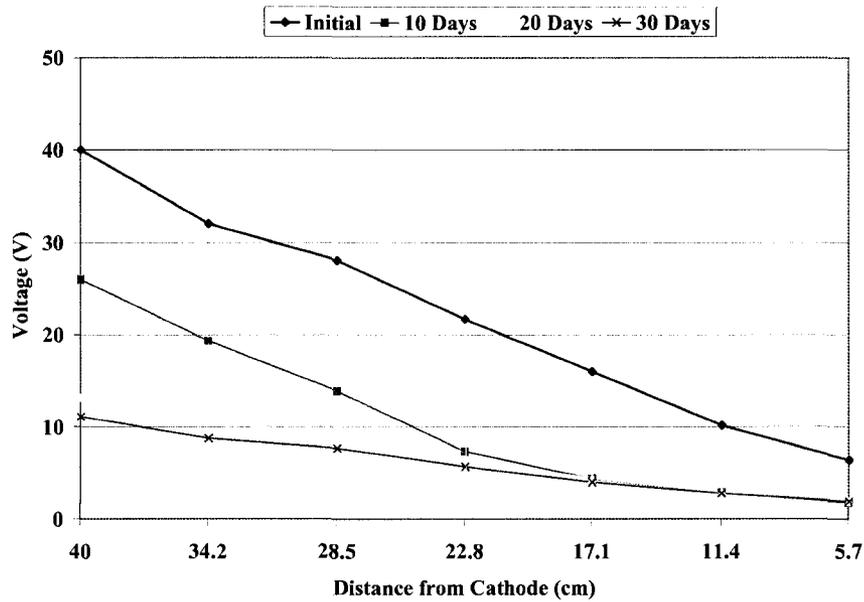
Figure 4-13: Amended ER column electric potential distribution from t=0 to t=30 days

Subsequent voltage readings indicated a near-uniform electric potential across the column. Figure 4-14 presents voltage drop data across the column at t=0, 10, 20, and 30 days. At the completion of the experiment the voltage drop between the electrodes and adjacent reference electrodes were as low as 1-2 volts as depicted in Figure 4-14.
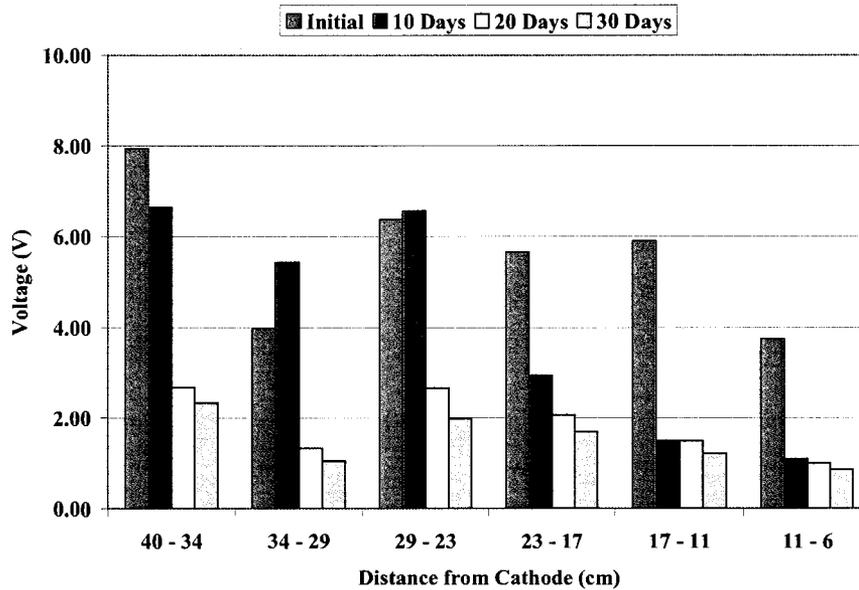
Figure 4-14: Amended ER column voltage drop distribution from t=0 to t=30 days

Figure 4-15 presents conductivity distribution data across the column at t=0, 10, 20, and 30 days. The conductivity of the anode and cathode compartments increased throughout the experiment with final values of 4.1 and 5.3 mS m^{-1} for the anode and cathode respectively. This increase in conductivity was likely due to the pH adjustment at the electrodes and the transport of ions to the anode and cathode. The conductivity readings across the column at Day 10 looked similar to that of the unamended column conductivity distribution. A drop in conductivity in the region 16 cm from the anode with major increases at either end of the column looked very similar to the trends reported throughout the unamended experiment. However, the conductivity values at 20 and 30 days indicate that the neutralizing of the anode and cathode was successful and a more consistent, increasing conductivity gradient persisted across the column.
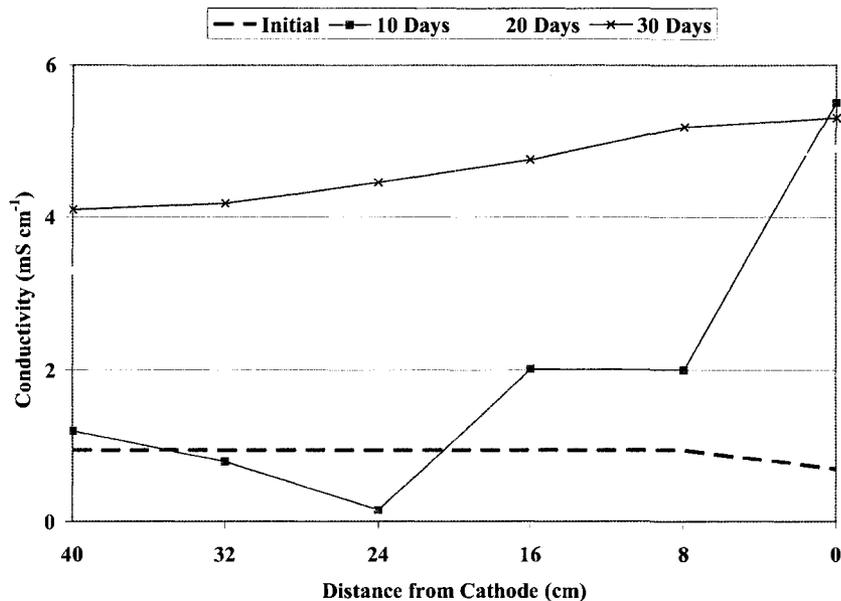
Figure 4-15: Amended ER column conductivity distribution from t=0 to t=30 days

4.4.2.3 Arsenic

The amended mode used acetic acid as the electrolyte in the cathode and pH-adjusted river water (using NaOH) as the electrolyte in the anode compartment. The arsenic distribution in the pore fluid at t=10, 20, and 30 days and soil at t=30 days from the anode to the cathode is presented in Figure 4-16. The pH control within the column maintained the entire column pH near 5 during the experiment indicating the major form of arsenic under oxidized and reduced conditions were dihydrogen arsenate as $H_2AsO_4^-$ and arsenite as $H_3AsO_3^\circ$ (arsenious acid), respectively. Highly positive ORP readings at the anode and highly negative ORP values at the cathode confirm that both forms were present within the column. The significant overall reduction of arsenic in the pore water across the soil column is depicted in Figure 4-16. Aqueous arsenic concentrations of 0.76 to 0.06 mg L^{-1} were obtained across the column, with exception to the anode compartment where higher arsenic values were measured. Minimal scaling was detected

on the anode and no settled particulates were visible in the anode compartment. In addition, the presence of gas bubbles on the cathode was visible throughout the entire experiment which was not seen in the unamended mode. A major difference between the column experiments was the presence of electroosmotic flow at 11 days in the amended column in the direction of anode to cathode. This flow was measured at the cathode's overflow beaker. The maximum flow was measured at approximately 50 ml d^{-1} and appeared to taper off towards the end of the experiment. Consequently, a substantial amount of reddish-brown particles began to appear at the cathode at the same time EO flow was initially noticed. The presence of the particulates in the cathode and the likeliness of the non-ionic (acid or fully protonated) form of arsenite being present in the column indicates that the transport of arsenic was due to both electroosmosis and electromigration. The combination of these two transport mechanisms is significant in the removal of arsenic because both electromigration (ionic As forms) and electroosmosis (non-ionic As forms) aide in the movement of arsenic across the cell. EO flow can hinder the transport of cathodic conditioning agents electromigrating in the opposite direction; however, the electromigration of acetic acid in the amended ER tests appeared to have overcome the opposing EO flow. This was determined based on the relatively constant pH of 5 across the soil column.

An effort (as was attempted with the unamended column) to characterize the solid arsenic species in the cathode and deposits across the column by performing a compositional analysis of the solid substrate using electron microscopy did not yield any useful results.
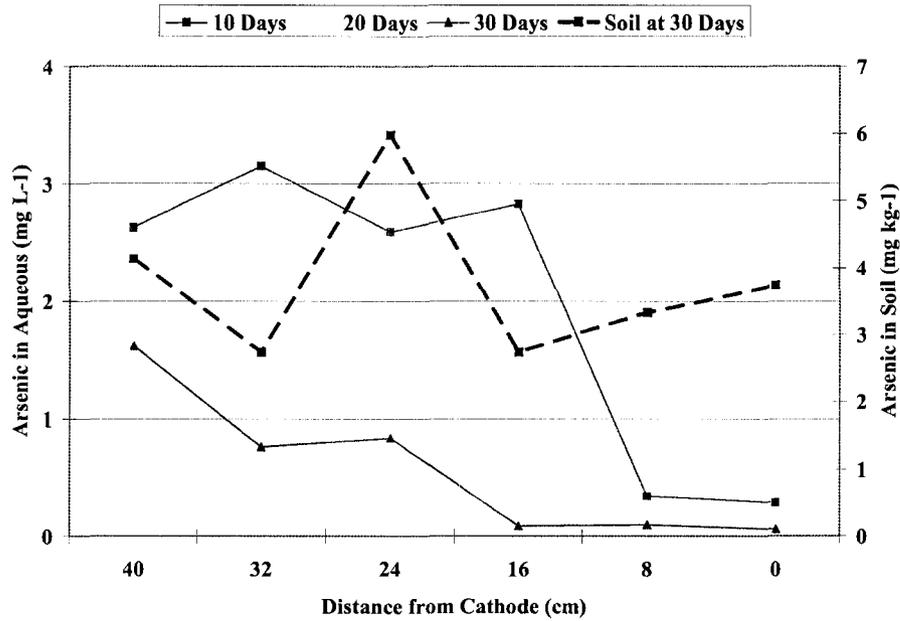
Figure 4-16: Amended ER column arsenic distribution; aqueous As (t=0 to t=30days) and As Soil (t=30 days)

The arsenic values in the pore water and in the soil appeared to peak 16 cm from the anode. This trend also occurred in the unamended column experiment, however, with much higher arsenic values and at a distance of 8 cm from the anode. The trend in the amended column is likely due to the electromigration of $H_2AsO_4^-$ towards the anode. The location along the column of the peak arsenic values may be due to the extent of the oxidized zone at the anode end of the column. Arsenic concentrations normalized to initial spiked values in the column's pore fluid and soil at the completion of the experiment are presented in Figure 4-17. Values for arsenic in the soil at 0 and 40 cm represent arsenic values in the soil immediately adjacent to the electrode compartments. Arsenic appears to have been almost completely removed from the column's pore fluid as seen in Figure 4-17 with C/Co values of 0.04 to not detectable levels across half of the column. Arsenic C/Co values in the soil are higher than unamended values across the

column. This is likely due to the pH of the pore fluid in the amended column which was not alkaline, but closer to 5 throughout the column. The pore fluid pH in the amended tests did not promote dissolution of the arsenic associated with the soil particles as experienced in the unamended column which had higher alkaline pore fluid pH values. The C/Co value of >1 at 24 cm from the anode could be due to localized precipitation of arsenic.
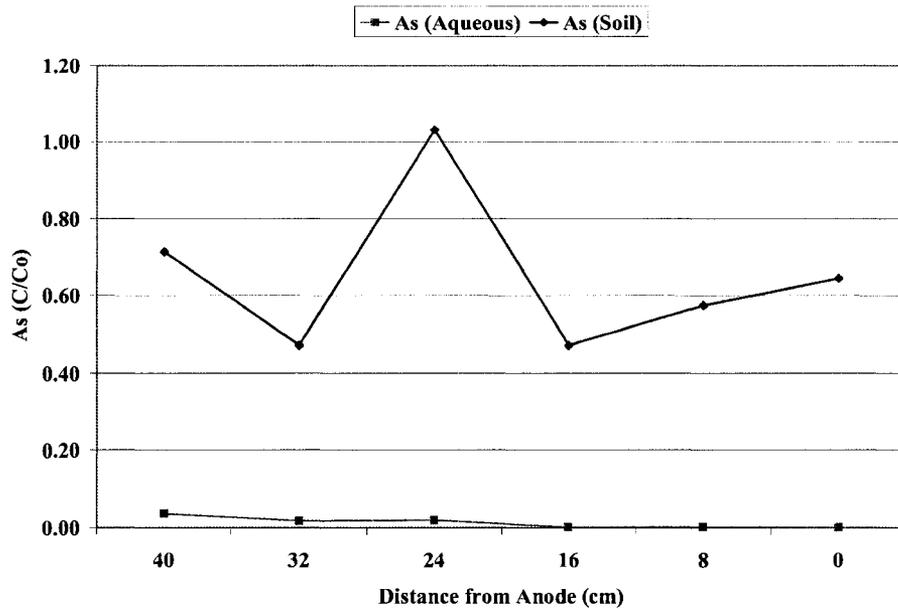
Figure 4-17: Amended ER column arsenic distribution (C/Co) in aqueous and soil phases at t=30 days

A mass balance performed on the column, accounted for 106% of the initial spiked arsenic, with 92% and 14% being accounted for in the soil and pore fluid, respectively. Although the total mass balance is slightly higher than the initial mass introduced to the column, the error is within acceptable limits. The additional 6% could be due to potential analytical errors. Lastly, the reddish-precipitates within the cathode

compartment (as seen in Figure 4-18) were not characterized and could account for a small increase in the overall arsenic mass balance.
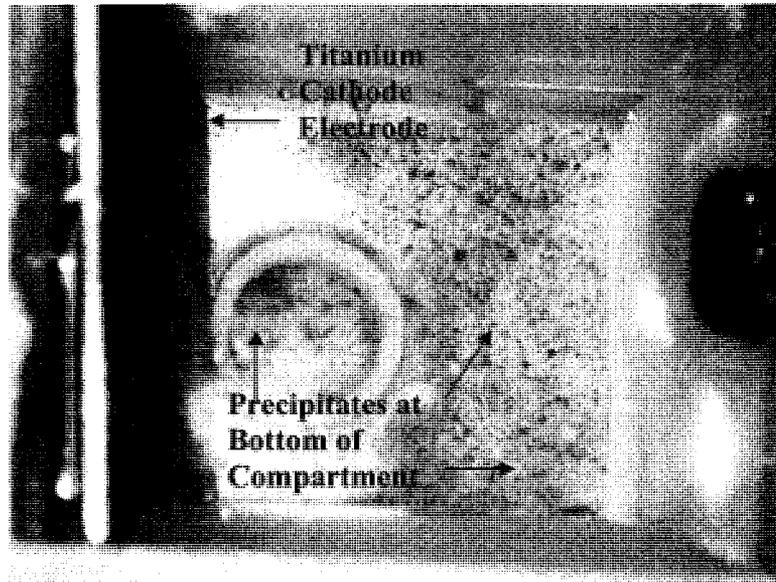
Figure 4-18: Amended ER column: plan view of cathode compartment at t=20 days

Overall mass removal varied between the unamended and amended column studies. The unamended column had a lower amount of arsenic remaining in most of the soil, except for areas near the anode which were close to the values in the same location in the amended columns. Final pore water arsenic values across the column in both the unamended and amended columns were in similarly quite low with average C/Co values of 0.08 and 0.05 for the unamended and amended columns, respectively. Although final aqueous arsenic values in the anode for the unamended test are unknown it is likely that they continued to increase from values reported ten days before the end of the experiment. This would conclude that electromigration is an adequate means to transport arsenic to the anode for ultimate removal in the unamended column. Most importantly, the presence of the hydroxide ion from the cathode region was useful in desorbing the

arsenic from the soil particles in the unamended column. The amended column succeeded in removing the arsenic from the aqueous form, however, the amount of arsenic in the soil phase remained high. Although it is sometimes desirable to immobilize the contaminant and precipitate the compound in the soil, ultimate removal from the system would be most ideal to prevent potential reversible reactions which would promote the dissolution of arsenic back into the groundwater.

4.5   Applications

Prior to the installation of a full-scale ER system, it would be prudent to install and run a small pilot demonstration system at the test site. This would result in valuable installation and operational information that could be incorporated into the large-scale system. An ER system would generally consist of an array of anode and cathode electrodes, a power distribution system, master control center, monitoring equipment, and process piping. The piping would be necessary to transport amendments to the electrode wells and for contaminant extraction.

Electrode material, configuration, and spacing are three important components of an ER system requiring considerable planning. The material for the electrodes needs to be chemically inert and electrically conductive. In addition, the electrode should be porous and hollow to allow the exchange of solution between the electrode and the subsurface environment. Availability, cost, fabrication limits, and ease of installation must be considered when selecting electrodes (Alshawabkeh et al. 1999). Most researchers have used 1-dimensional electrode configurations in laboratory and field studies. The easiest method to install and the most cost-effective approach for in situ remediation uses lines of rod electrodes placed in boreholes (Alshawabkeh et al. 1999).

However, this configuration of electrodes may develop spots of inactive electric fields between electrodes of the same polarity (Alshawabkeh et al. 1999). Factors affecting the spacing between electrodes are cost and processing time required. A larger electrode spacing will reduce the number of boreholes and installation costs, but will increase the processing time and operational costs. The processing time required for ER is a function of the rate of contaminant transport and electrode spacing (Alshawabkeh et al. 1999). Typical relationships between processing time and electric field strength under varying electrode spacing have been established by assuming ionic mobilities of the contaminant, coefficient of electroosmotic conductivity of the soil, a tortuosity factor, and the lack of retardation. Although these are simplified estimations, this provides a starting point for pilot field test installation. Using the published relationship (Alshawabkeh et al. 1999), for a electric field of 100 V/m and a processing time required of 30 days, an electrode spacing of 2 meters is required. A test cell layout and the corresponding electrode well locations are depicted in Figure 4-19.

Figure 4-19: Test cell layout and electrode well locations along the South Platte River in Brighton, CO (Google 2005)

4.6 Conclusions

The electrokinetic remediation of soil contaminated with arsenic was tested under unamended and amended conditions. Electromigration was the main mechanism responsible for arsenic removal in the unamended column tests due to the increased concentrations of arsenic (aqueous and in soil) located in the anode and anode region of the column. Electroosmosis and electromigration transport mechanisms were both responsible for the arsenic removal in amended column tests as indicated by arsenic concentrations in the anode and cathode. The findings of the tests are summarized as follows:

- Unamended ER promoted electromigration of anionic arsenic species toward the anode region, however, premature precipitation of the arsenic complexes created a large resistance in the column in the anode region which increased the voltage drop. Therefore, the applied voltage needed to be increased in order to continue the experiment.

- The alkaline front in the unamended test appeared to dominate across the column. The high pH values of the pore water across the column appeared to promote dissolution of solid arsenic species and promote the electromigration towards the anode.

- Amended ER promoted arsenic removal from the pore fluid through both electromigration and electroosmosis mechanisms. Only five percent of the original arsenic concentration remained in the pore fluid upon completion of the experiment. Negatively charged arsenic species migrating to the anode region likely were precipitated or sorbed before reaching the anode based on the increase in arsenic in the soil in this region. Arsenic was also likely transported to the cathode due to EO flow.

- Mass balances were performed on both columns. The results for the unamended column only accounted for 61% of the initial spiked arsenic, with 53% and 8% being accounted for in the soil and pore fluid, respectively. The remaining unaccounted for 39% is likely due to the precipitates in the anode which could not be measured, and the arsenic concentration in the anode electrolyte (also not measured) which was increasing throughout the experiment. The mass balance results for the

amended column, accounted for 106% of the initial spiked arsenic, with 92% and 14% being accounted for in the soil and pore fluid, respectively. The increased amount of percent arsenic in the solid phase in the amended experiments is likely due to the absence of the hydroxide ion which promotes arsenic dissolution.

- The presence of the hydroxide ion in the unamended column was useful in desorbing the arsenic from the soil particles. Although it is sometimes desirable to immobilize and precipitate the contaminant in the soil, ultimate removal from the system would be most ideal to prevent potential reversible reactions which would promote the dissolution of arsenic back into the groundwater.

- Due to the neutralization of the electrolysis of water at both electrodes, the voltage drop across the amended column was considerably less than in the unamended column suggesting that less power is required for ER operation.

- Periodic electrode compartment flushing and electrode cleaning appears to be necessary for column maintenance.

- Based on the experimental data, the most practical approach for using ER in the removal of arsenic would include amendments, but only at the anode. In applying sodium hydroxide to the anode the low pH created due to the electrolysis of water would be neutralized and the hydroxide ion would dominate across the entire column. This would be beneficial because the hydroxide ion would promote complete arsenic desorption

across the column and uninhibited electromigration would allow complete transport of arsenic to the anode electrode compartment.

- Use of ER as a remediation strategy for arsenic removal would require less power and materials than other remediation techniques such as pump and treat methods. These methods involve large pumping systems to remove the water, chemicals to convert the arsenic to As(V), and physico-chemical processes to remove the As(V) such as chemical coagulation-precipitation, adsorption, and membrane separation. ER for the removal of arsenic appears to be more passive than other popular arsenic removal methods. Unfortunately, in most remediation methods (including ER), the process results in an arsenic byproduct which must be disposed of in a safe and controlled manner.

5.0 Quality Assurance Characterization for the Analyses of Organic Compounds

5.1 Abstract

Significant, undocumented challenges were encountered during the quantification and determination of certain organic compounds from an experimental treatment study. A thorough examination of compound partitioning characteristics and potential sources of contamination was conducted. Analytical methods were developed for the measurement of two pharmaceuticals, sulfamethoxazole (SMX) and carbamazepine (CBZ) and three flame retardants tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) and tris-(2-chloroethyl) phosphate (TCEP) in aqueous and solid samples. Solid phase extraction (SPE) was used to clean-up and concentrate the samples. The pharmaceuticals were analyzed using high performance liquid chromatography equipped (HPLC) with a tandem mass spectrometer (MS-MS). The flame retardants were analyzed on a gas chromatograph (GC) equipped with a mass spectrometer (MS). The range of recoveries for the flame retardants and pharmaceuticals in river water were 50-104% and 56-109%, respectively. The limit of quantification (LOQ) was determined for each compound using the single-to-noise ratio method. The LOQs for CBZ, TCEP, and TDCP were 0.01 μg L^{-1} and 0.05 μg L^{-1} for SMX and TCPP. In addition, each compound was examined in the aqueous, solid, and colloidal phases. Lastly, sources of contamination relative to the measurement of the flame retardants were addressed. Concentrations of TDCP in HPLC water and river water stored in low-grade plastic containers for one week to several months were approximately five to ten times higher than values measured from volumes stored in glass containers. Also, aqueous extracts from control soil samples dried in front of an electric heater contained two to

fifty times of TCEP, TCPP, and TDCP than was found in the samples re-run using only ambient air drying techniques. The accurate analysis of organic compounds found in natural waters at low $\mu g\ L^{-1}$ concentrations require strict handling procedures and a methodical approach to sample clean-up, preparation, and method development in order to incorporate the data into meaningful results.

5.2   Background
Advances in analytical chemistry have contributed to the detection of previously immeasurable compounds including endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and other bioactive chemicals in wastewater effluents and surface waters around the world (Kolpin et al. 2002). The occurrence, fate, and transport of these compounds in the aquatic environment have become important environmental issues and have attracted significant attention. It is believed that some of these compounds can have major effects on the endocrine systems of humans and wildlife. Researchers have determined that several organic compounds, specifically sulfamethoxazole (SMX), carbamazepine (CBZ), tris(2-chloroethyl)-phosphate (TCEP), tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), and tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) continue to persist in wastewater treatment effluent, downstream of bank filtration sites, and in treated drinking water (Snyder et al. 2003; Heberer et al. 2004; Zuehlke et al. 2004; Westerhoff et al. 2005).

Pharmaceuticals used to treat medical conditions in humans are excreted from the body in the parent compound form or as metabolites. The antibiotics administered to the animals are excreted in un-metabolized and metabolized forms, which can make the soil and water susceptible to contamination through cropland application of animal wastes

and overland flow. The compounds are subject to metabolic reactions in both humans and animals such as hydroxylation, cleavage, or glucuronation. Some metabolites have reversible reactions and are able to transform back to the parent compound after excretion from the body (Hirsch et al. 1999). These compounds and their metabolites enter the domestic wastewater treatment plant via human excretions or as unused products discarded in toilets. The behavior of the compound in the environment will depend on chemical properties such as water solubility, pH of the matrix, volatility, and sorption potential(Boxall et al. 2003).

The antibiotic group sulfonamide (sulfa drugs) is a group of synthetic antimicrobials used for therapeutic treatment of infectious disease in humans and for treating and protecting the health of animals (Boxall et al. 2003). Sulfamethoxazole (SMX) which belongs to the sulfonamide group, contains two functional moieties at both sides of the sulfonamide linkage (-NH-S(O$_2$)-). The structure of SMX is presented in Figure 5-1. Thus, exhibiting two dissociation constants, one involving the protonation of the primary aromatic amine –NH2 and the other corresponding to the deprotonation of the sulfonamide –NH (Nghiem et al. 2005). The speciation of SMX over the entire pH range includes anionic species at pH above 5.7 (typical of natural waters), uncharged between 1.7 and 5.7, and positive species below pH of 1.7. The presence of these persistent compounds in surface water and soil has created public concern due to the low levels of antibiotics which can favor the proliferation of antibiotic resistant bacteria.

Sulfamethoxazole is a 4-amino-N-(5-methyl-3-isoxazolyl)benzenesulfon-amide. It is an almost white, odorless, tasteless compound with a molecular weight of 253.28 and a molecular formula of $C_{10}H_{11}N_3O_3S$. Typically the medical formulation is a combination

of sulfamethoxazole with trimethoprim, a broad-spectrum antimicrobial. Trimethoprim

optimizes the impact of SMX's major active ingredient (Perez et al. 2005). Generally,

the drugs are absorbed into the body and are subject to metabolic reactions as mentioned

earlier.

Molecular Wt: 253.3 g/mol
Solubility: 600 mg L-1
Log K_{ow}: 0.89
pK_{a1}: 1.7
pK_{a2}: 5.6
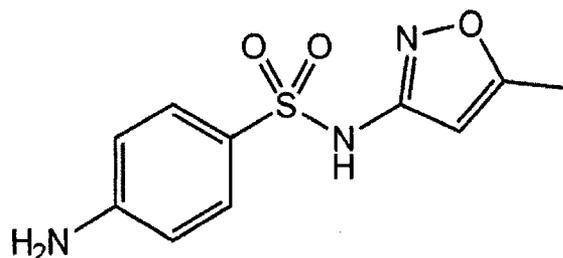
Figure 5-1: Sulfamethoxazole (SMX)

Carbamazepine is a hydrophilic compound consisting of three rings of carbon

with double bonds and an amine group attached and a double bond as presented in Figure

5-2. It is a base which is found mostly uncharged in the environment. The molecule's

structure makes it susceptible to fracturing under certain conditions. CBZ is an important

drug for the treatment of seizure disorders such as epilepsy, which is ranked second for

the most common central neuron system disease. CBZ has been available for more than

thirty years and has recently replaced phenobarbitol as the most common anticonvulsant

drug (Miao et al. 2003). CBZ has also been used to treat cases of schizophrenia because

of the drug's ability as a mood-stabilizer (Okuma 1993). The drug has also been

prescribed for the treatment of bipolar disorder (Dilsaver et al. 1996) and can be

combined with other drugs for the treatment of alcohol withdrawal (Franz et al. 2001).

Molecular Wt: 236.3 g/mol
Solubility: 17.7 mg L-1
Log K_{ow}: 2.45
pK_a: 2.3

Figure 5-2: Carbamazepine (CBZ)

The presence of organophosphorus compounds which are manufactured by the

chemical industry for use as pesticides, flame retardants, plasticizers, hydraulic fluids and

solvents have been detected in the aquatic environment (Fries et al. 2001; Andresen et al.

2006). Organophosphorus compounds (OPs) are manufactured world-wide for many

industries and end-users. More than half of the compounds manufactured are pesticides

and the remainder are flame retardants, plasticizers, hydraulic fluids and solvents (Fries et

al. 2001). The chlorinated OPs presented in Figure 5-3 such as TCEP, TCPP, and TDCP

are predominantly used as flame retardants in polyurethane foams. As with other

additives, OPs are mixed and are not chemically bonded with the containing materials,

and therefore are easily released into the environment (Rodriguez et al. 2006). The

compounds' structures and associated chemical information is presented in Figure 5-3.

$C_6H_{12}Cl_3O_4P$
Molecular Wt: 285.49 g/mol
Solubility: 8,000 mg L^{-1} at 20°C
Log K_{ow}: 1.7
pK_a: 7.8

(a)
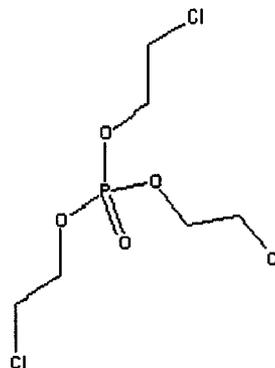
$C_9H_{18}Cl_3O_4P$
Molecular Wt: 327.55 g/mol
Solubility: 1600 mg L^{-1} at 20 C
Log K_{ow}: 2.59

(b)
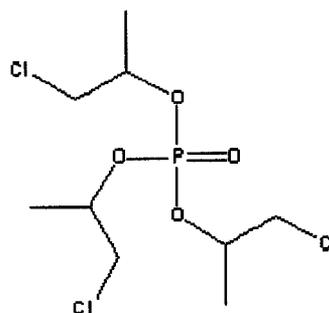
$C_9H_{15}Cl_6O_4P$
Molecular Wt: 430.91 g/mol
Solubility: 100 mg L^{-1} at 30 C
Log K_{ow}: 3.8

(c)
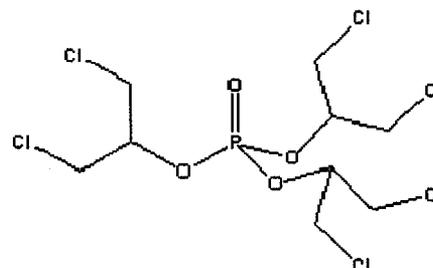
Figure 5-3: (a) TCEP, (b) TCPP, (c) TDCP

Organophosphates have been detected in indoor air samples, surface waters,

wastewater treatment plant effluent, snow deposition, and finished drinking water (Fries

et al. 2001; Kolpin et al. 2002; Stackelberg et al. 2004; Marklund et al. 2005; Andresen et

al. 2006). TCEP, a known carcinogen to animals, and other chlorinated

organophosphates is currently undergoing a re-evaluation by the European regulatory

groups on environmental issues (Andresen et al. 2006). TCEP is included in the

European Commission second priority list, while TCPP and TDCP are included in the

fourth priority list (Marklund et al. 2005). There is additional concern for the presence of

OPs and other chemicals and personal health care products in our waters because these

products, unlike pharmaceuticals, were never made to be ingested.

Solid phase extraction (SPE) is the most widely used sample preparation technique in the analysis of pharmaceutical compounds and many other compounds in water. In order to quantify compounds down to the ng L^{-1} level, it is necessary to remove interfering matrix constituents while retaining the analyte of interest. SPE plays an important role in sample preparation by concentrating the compound and removing contaminants which could interfere or mask the compound of interest during quantification. In its simplest form, SPE uses a packing material such as bonded silica or polymeric media packed into a plastic syringe-like tube. There are several different stationary phases that can be used in SPE cartridges including reversed-phase (C-18), ion-exchange, or normal-phase. Hydrophilic-lipophilic balance (HLB) materials have been commonly used for the extraction of both polar and non-polar environmental contaminants. The SPE process consists of four general steps: conditioning, sample addition, washing and elution. The conditioning step prepares the bonded phase so that it can accept the sample, the washing step removes interferences and the elution step involves the use of a strong solvent to elute the analyte of interest. The eluent may be further concentrated by evaporating the solvent using heat or nitrogen gas.

In addition to determining the selected pharmaceuticals and flame retardants from water samples, methods were also developed to extract the compounds from sediment samples. Few studies have been reported on the extraction of these compounds from sediments. Ishikawa et al. (1985) used an acetone-based extraction method for select flame retardants from solid samples which resulted in recovery rates of 80 to 94% (Ishikawa et al. 1985). Other researchers reported using an acetonitrile/water mix in an accelerated solvent extraction method for the extraction of SMX and CBZ from solid

samples resulting in recovery rates of 81-85% and 68-74%, respectively (Kinney et al. 2006). Due to differences in analytical methodology, modified versions of these methods were used in the development of unique methods for the extraction of the compounds from sediment.

Chromatography is the range of physical methods used to separate complex mixtures based upon their relative affinity for partitioning between different phases. The components to be separated are distributed between two phases: a stationary phase (liquid or solid) and a mobile phase (liquid or gas) which percolates through the stationary bed (Ahuja 2003). In this process one phase is held in place while one phase moves past it. Mass spectrometry sorts out charged gas molecules or ions according to their masses. The substance to be analyzed is vaporized and converted to positive ions by bombardment with rapidly moving electrons. The formed ions are pulled from the gas stream by an electrical field and are separated based on their mass-to-charge ratio. A positive identification of the analyte can be made by comparing the mass-to-charge ratio and the density of fragments of the unknown to that of known materials (Ahuja 2003). Gas chromatographs (GC) and high performance liquid chromatographs (HPLC) equipped with mass spectrometers (MS) or tandem mass spectrometers (MS/MS) are the most widely used analytical equipment employed to separate and quantify environmental compounds.

In liquid chromatography, a sample mixture is passed through a column packed with solid particles which may or may not be coated with another liquid. Using the proper solvents and column for the compound of interest, ions in the sample will travel the column more slowly than others resulting in optimal separation (Ahuja 2003). In gas

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chromatography, the sample is vaporized and injected onto head of chromatographic column. The sample is then transported through column by flow of inert, gaseous mobile phase. The column in a GC contains a liquid stationary phase which is adsorbed onto the surface of an inert solid (Ahuja 2003).

This paper examines the partitioning characteristics of SMX, CBZ, TCEP, TCPP, and TDCP in the aqueous, solid, and colloidal, of which no published literature exists for flame retardants in colloidal phase. In addition, a series of tests were conducted in order to determine the contamination sources encountered during initial laboratory column experiments. Results from these studies will allow a more thorough and accurate data interpretation in future remediation studies. Determining a compound's fate and extent of potential contamination will lead to more accurate scientific studies.

5.3   Experimental Methods and Materials
5.3.1 Materials

Stock solutions (1 g L^{-1}) of the flame retardants TCEP (Sigma Aldrich, Dallas, TX) and TCPP and TDCP (Pfaltz and Bauer, Waterbury, CT) were made in HPLC-grade ethyl acetate (Fisher Scientific, Pittsburgh, PA) and stored at 4°C. The pharmaceuticals SMX and CBZ (Sigma Aldrich, Dallas, TX) were made in HPLC-grade methanol (Fisher Scientific, Pittsburgh, PA). Monthly standards (100 mg L^{-1}) were made in HPLC-grade ethyl acetate and methanol and also stored at 4°C. All standards were stored in amber glass bottles which were cleaned with acetone and triple rinsed with de-ionized (DI) water. Working solutions of 5 mg L^{-1} were made on a weekly basis from the monthly standard solutions. Samples from this stock were measured with HPLC and GC analysis in order to assure that degradation of the standards did not occur. The control water

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selected for method optimization was obtained from a pristine section of the Poudre River. This section is upstream from major development, wastewater treatment plants, and agricultural activity. Analysis on this water confirmed the absence of pharmaceutical or flame retardant pollutants.

5.3.2 Solid Phase Extraction

Solid phase extraction for the flame retardants was accomplished by using 3cc 60 mg Oasis HLB cartridges (Waters Corporation, Milford, MA) and a twelve-port vacuum manifold (Fisher Scientific, Pittsburgh, PA). Cartridges were preconditioned using successive 2-mL volumes of ethyl acetate, methanol, and HPLC-grade water. Samples (100 ml with pH 6-8) were filtered using 0.2 micron glass fiber filters (colloidal samples used 1.2 and 2.7 micron filters). Filtered samples were drawn through the cartridges in the vacuum manifold at a vacuum of approximately 8 inches of mercury and a rate of 1.5-2 mL min^{-1}. When all of the sample volume had been passed through the cartridge, approximately 20 mL of methanol/water solution (1:3) was added to each flask. After this solution was passed through the cartridges, air was drawn through the cartridges for five minutes. The cartridges were eluted with 2 mL of ethyl acetate using a vacuum of 5 inches of mercury. The extract was collected in 15 mL vials which each contained the 100 μL of 10 ppm internal standard squalane. The internal standard squalane has been used successfully in the examination of flame retardants by previous researchers (Fries et al. 2001). Water was removed from the extract by passing the solution over 2 grams of pre-washed (ethyl acetate) sodium sulfate crystals and into fresh 15-ml vials. An additional 2 mL of ethyl acetate was passed over the sodium sulfate as a final rinse and was collected with the initial extract in the 15-ml vials. The final solution volume was

reduced to 0.1 mL in a warm water bath under a gentle stream of high purity nitrogen (Organomation Associates, Inc., Berlin, MA). The sample was transferred to a 0.150 mL poly spring insert which was placed in a 2-mL amber vial.

The SPE method for CBZ and SMX followed a modified version of published methods by Yang (Yang et al. 2004). Solid phase extraction for the pharmaceuticals was accomplished by using 3cc 60 mg Oasis HLB cartridges (Waters Corporation) and a twelve-port vacuum manifold (Fisher Scientific). Cartridges were preconditioned using successive 3 mL volumes of methanol, 0.5N hydrochloric acid, and HPLC-grade water. Samples were filtered using 0.2 micron glass fiber filters (colloidal samples were filtered using 1.2 and 2.7 micron filters). The samples (120 ml) were acidified to a pH of approximately 2.3-2.5 using 40% sulfuric acid. The acidified samples were drawn through the cartridges at a vacuum of approximately 8 inches of mercury and a rate of 1.5-2 mL min^{-1}. When all of the sample volume had been passed through the cartridge, the cartridges were rinsed three times with successive 3 ml volumes of HPLC water. The cartridges were eluted with 5 mL of ethyl acetate using a vacuum of 5 inches of mercury. The extract was collected in 15 mL vials which each contained the 50 μL of the internal standard simatone (0.24 mg L^{-1}). Simatone was selected as the internal standard due to its successful results in previous studies (Lindsey et al. 2001). The final solution volume was reduced to 0.05 mL in a warm water bath under a gentle stream of high purity nitrogen (Organomation Associates, Inc., Berlin, MA). The sample was transferred to a 0.150 mL poly spring insert and combined with 0.070 ml of mobile phase A (99.9% HPLC water/0.1% Formic Acid, v/v) which was placed in a 2-mL amber vial. Colloidal fractions were samples

5.3.3 Sediment Extraction

Fifty grams of air-dried sediment was weighed and placed into a 250-ml glass beaker. Two hundred ml of acetone (flame retardants) or acetonitrile/water 70/30 v/v (pharmaceuticals) was added to the flask and Parafilm was used to cover the beaker. The beaker was placed on a horizontal shaker table (Lab-Line 4626) and shaken for sixty minutes at 400 rpm. The liquid sample was centrifuged and then filtered with a 0.2 micron glass filter. The filtrate was evaporated under a gentle stream of nitrogen to a final volume of 1 ml. The sample was reconstituted with HPLC water to final volume of 100 ml (flame retardants) or 120 ml (pharmaceuticals). The SPE method used for final sample clean-up and concentration was the same as the SPE method detailed above for each respective compound.

5.3.4 GC Analysis

All samples were analyzed using an Agilent 6890 series gas chromatograph (GC) equipped with an Agilent 7683 autosampler and interfaced to an Agilent 5973 mass selective detector. Samples were injected in 1 μL volumes in splitless mode and were separated on a Supelco SPB-1 methyl silicone capillary column (0.25 μm film thickness) 30m in length and 0.25mm inside diameter. The separation used the following temperature program: 90°C [2 minutes] $\rightarrow$ 10°C min^{-1} $\rightarrow$ 280°C [15 minutes] using helium as the carrier gas at a rate of 1.5 ml min^{-1}. The mass spectrometer began acquiring at 3 minutes and was operated in selected ion monitoring (SIM) mode. The flame retardants were detected by means of their mass spectral data and retention time. Mass spectral data from the internal MS database software was used to verify the identification. TCPP gives three peaks in the ratio 9:3:1. In this study, only the main isomer was used for quantification. Table 5-1 summarizes the compounds' SIM

parameters and retention times. Chromatograms of the three flame retardants and the

internal standard (5 µg L^{-1} standards) are presented in Figure 5-4.

Table 5-1: Gas Chromatograph Mass Spectral Parameters

Compound	Analytical Ion	SIM Ions	Retention Time(min)
Squalane	207	57, 71, 85, 207	22.4
TCEP	249	63, 205, 249	14.3
TCPP	277	125, 99, 157, 277	14.7
TDCP	381	75, 99, 191, 381	19.7
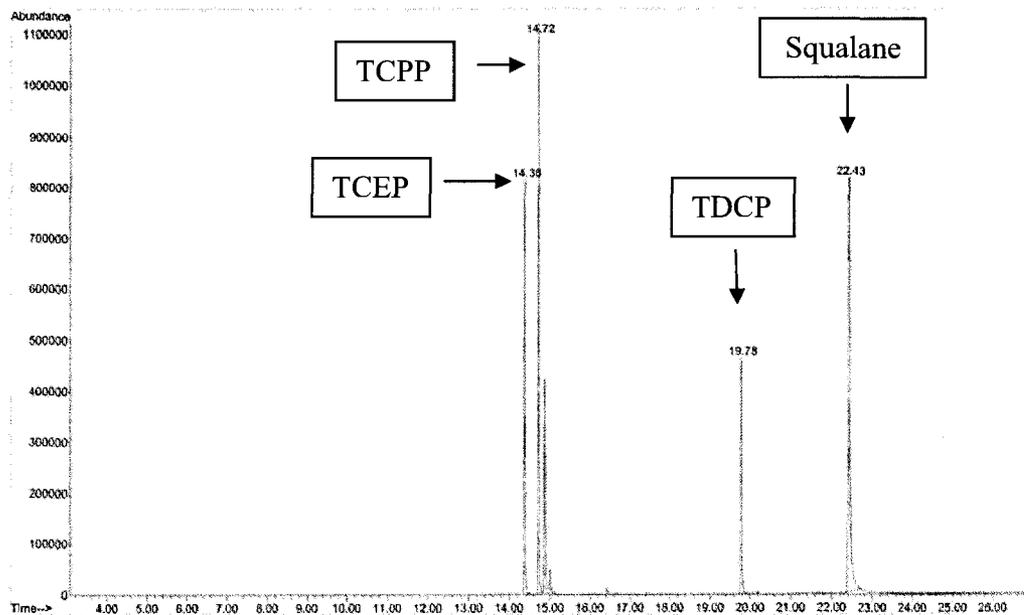
Figure 5-4: GC/MS Chromatograms of TCEP, TCPP, and TDCP (5 µg L^{-1})

Mass spectral data from the internal MS database software was used to verify the

identification of TCEP, TCPP, and Squalane (IS). The mass spectral data from the mass

spectrometer's database software was compared to the mass spectral obtained from actual

standards of the compounds (5 μg L^{-1}) and presented in Figure 5-5. Unfortunately, the

mass spectral library software has not been updated in many years and did not have

information on the compound TDCP.
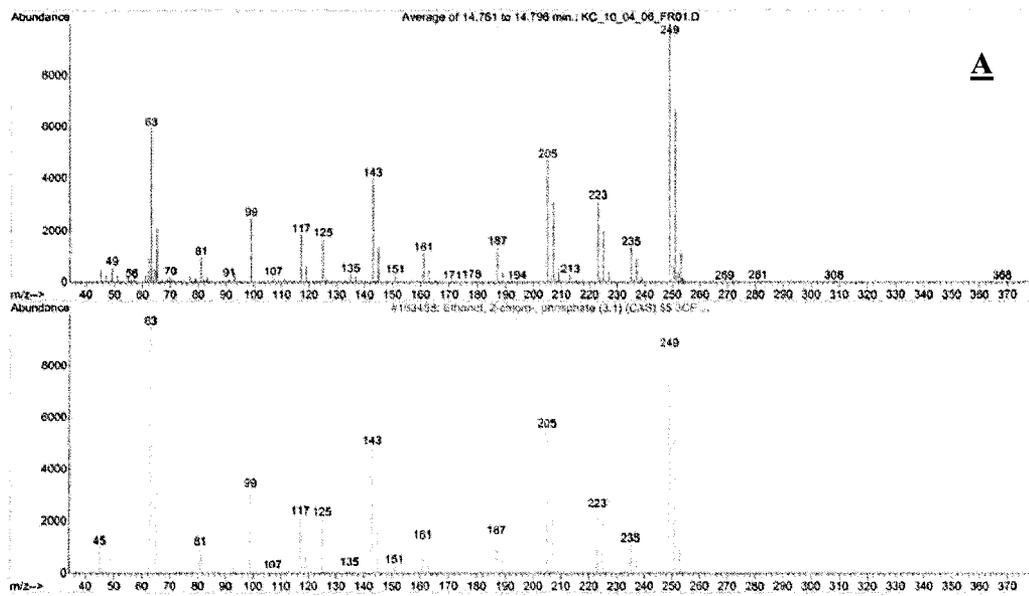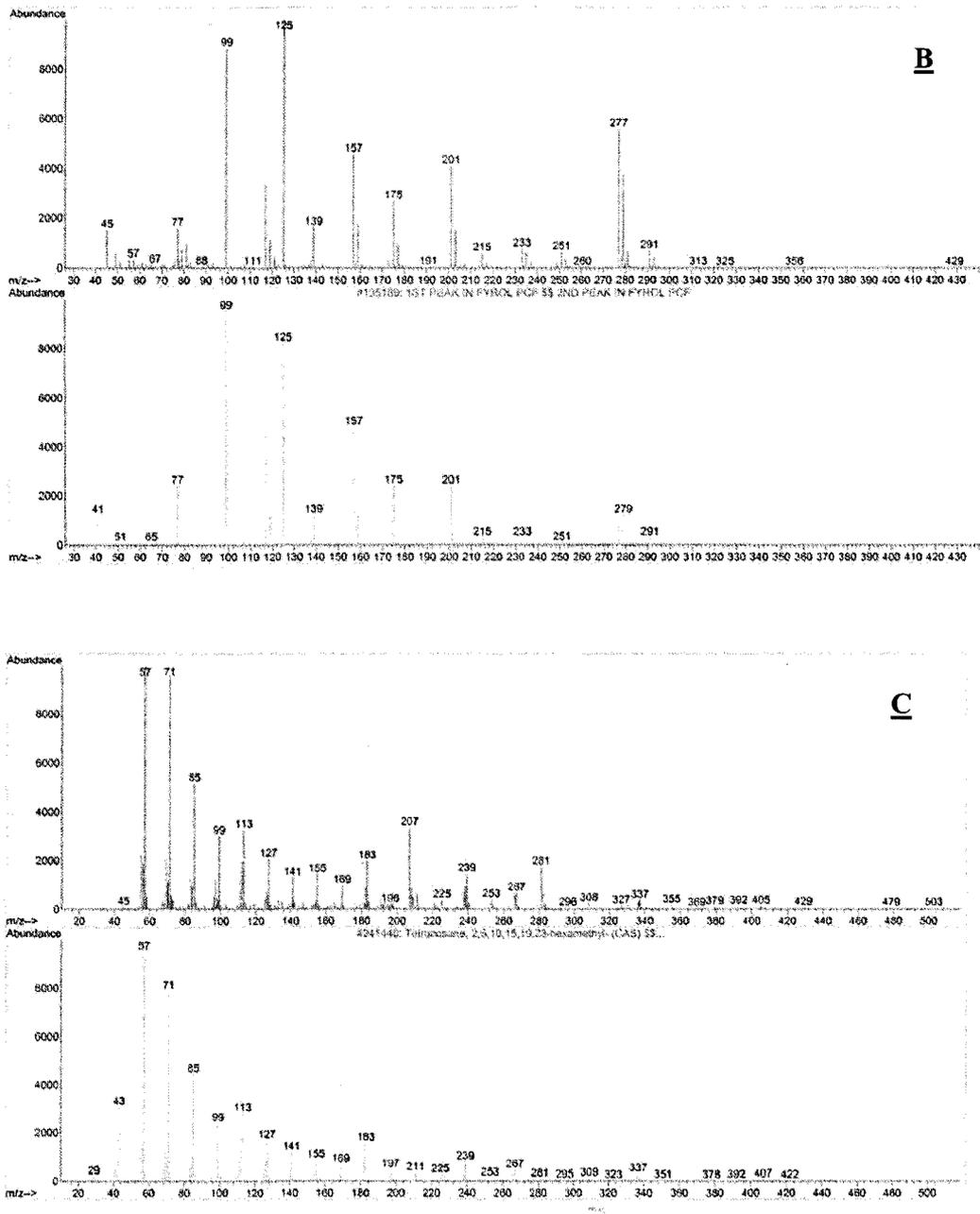
Figure 5-5: (a) TCEP, (b) TCPP, and (c) IS GC/MS Spectrum vs. Library Spectrum

5.3.5 HPLC Analysis

The HPLC system was an HP 1100 Series Liquid Chromatograph equipped with

an Agilent 1100 Series Thermostatted Auto Sampler and a variable wavelength UV

detector. The column used was a Phenomenx Gemini C_{18} 50 x 2.00 mm (5μ pore size) end capped reversed-phase column. A Phenomenx C_{18} guard column was used upstream of the main column to remove any particulates from the sample. Mobile phase A consisted of HPLC water with 0.1% formic acid (v/v) and mobile phase B consisted of pure acetonitrile. The autosampler enclosure was maintained at a temperature of 4°C and the column temperature was maintained at 15°C. The sample volume was 20 μL. The eluent gradient was programmed for 20 minutes beginning with 5% mobile phase B and 95% mobile phase A and increasing to 95% mobile phase B and 5% mobile phase A. A ten minute post-run time was included after each run in order for the column to equilibrate. The eluent flow remained constant over the run at 0.38 ml min^{-1}. SMX, CBZ, and the internal standard are eluted in under 15 minutes.

A ThermoFinnigan LCQ Duo ion trap mass spectrometer equipped with a heated capillary interface and electrospray ionizer (ESI) was used to obtain mass spectral data. Standard solutions (10 μM) of each compound in HPLC water were injected into the system at a flow rate of 5 μL min^{-1} using the LCQ Duo syringe pump to optimize individual MS parameters. Nitrogen gas was used for drying and nebulizing. The spray voltage was set to 4.5 kV and the capillary voltage was set to 21V. The capillary temperature was set to 165°C. The electrospray ionizer was operated in the positive ion mode. The sheath gas flow rate was set at 40 and the auxiliary gas was not used. The tune files created during the optimization will be used for compound quantification during LC/MS/MS mode. The product ion producing the highest intensity will be used for quantification to maximize analytical sensitivity and selectivity. The compounds' precursor and product ions obtained through the MS optimization are summarized in

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Table 2. Chromatograms showing the separation of standard solutions of the internal standard and two compounds are presented in Figure 5-6. Full-scale tandem mass spectra of CBZ and SMX are depicted in Figure 5-7. The fragmentation data is unique for each compound, therefore, the potential is minimized for collecting incorrect data due compounds in the solution with similar protonated or de-protonated masses or compounds that have close retention times.

Table 5-2: HPLC MS/MS Optimized Parameters

Compound	Precursor Ion [M+H]$^+$ (m/z)	Fragment Ions	Isolation Width	Collision Energy (%)
Simatone	198	(SIM)	2	26
CBZ	237	**193**, 219	2	36
SMX	254	**156**, 187	2	36
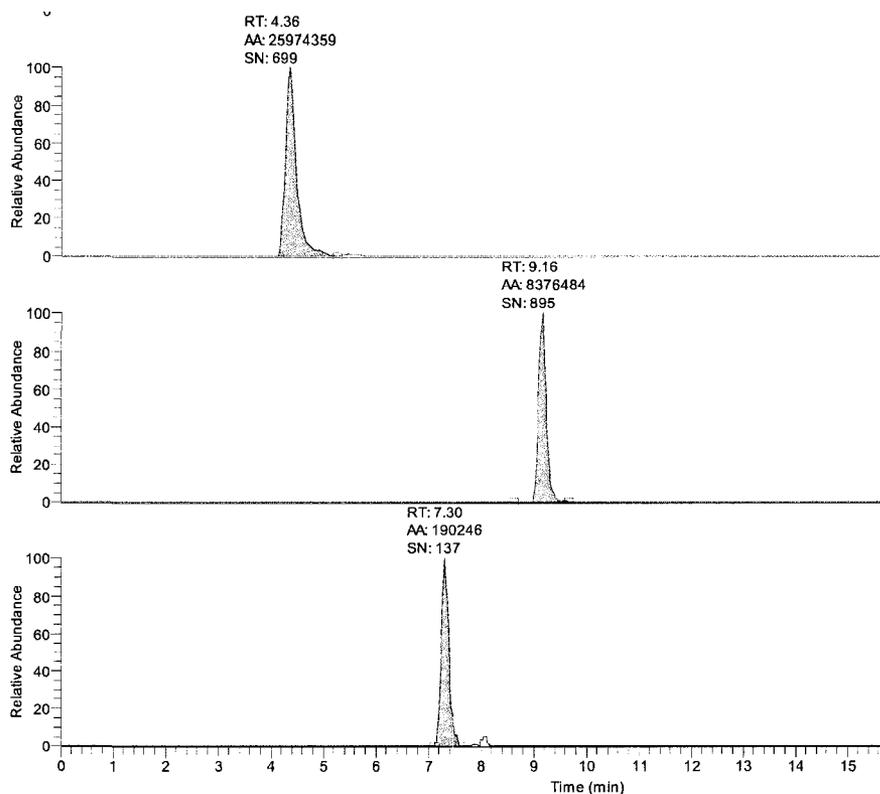
Figure 5-6: Chromatograms of 10 μM Simatone, SMX, and CBZ

5.4 Results

5.4.1 Recovery and Calibration Studies

The solid phase extraction method was studied in order to determine the contaminant recovery efficiency. This was achieved by comparing two sets of SPE results. First, pristine river water samples were spiked with known concentrations of contaminant solutions before the SPE process. The river water selected for use in the calibration and recovery studies was obtained from the upper reaches of the Poudre River. The river water from these reaches has non detectable levels of common pollutants and was considered "pristine" river water for purposes of the recovery study. River water for the calibration and recovery studies was selected in order to mimic

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background interferences which are likely to be encountered in the experimental samples. These spiked river water samples were extracted and analyzed using the SPE protocol described above.

Secondly, clean river water samples were run through the SPE process. The ethyl acetate extract (for flame retardants) or methanol (for pharmaceuticals) was spiked with known concentrations of contaminant solutions. Both sets of samples were processed and analyzed identically. The recovery ratio was calculated using the area response values given by the GC or HPLC:

$$\text{Recovery (\%)} = \frac{\text{Response pre-SPE Spiked Sample}}{\text{Response post-SPE Spiked Sample}} * 100 \qquad \text{(Eq. 5.1)}$$

where the response is the area of each contaminant divided by the average area of the internal standard for the set of recovery samples. The calculated recoveries for the varying compounds and concentrations are shown in Table 5-3. The range of recoveries for the flame retardants and pharmaceuticals in river water were 50-104% and 56-109%, respectively. The lowest recovery results for the compounds were reported at concentrations of 100 ng L^{-1}. Recoveries above and below 100% may be due to impurities in the sample or analytical column that creates a false ion enhancement or may mask the compound of interest.

Table 5-3: Persistent Organic Compound Recoveries at Varied Concentrations

	Compound Recovery (%)		
	$10\ \mu g\ L^{-1}$	$1\ \mu g\ L^{-1}$	$0.1\ \mu g\ L^{-1}$
CBZ	109	77	80
SMX	98	68	56
TCEP	91	100	104
TCPP	79	82	48
TDCP	89	77	50

Three point calibration curves were constructed for each compound (in triplicate) for the concentrations of 10 $\mu g\ L^{-1}$, 1.0 $\mu g\ L^{-1}$, and 0.01 $\mu g\ L^{-1}$ for the pharmaceuticals and flame retardants. In order to incorporate the recovery data into future reported data, the calibration curves were established by plotting the response (the ratio of the area under the analyte peak to the area of the internal standard) from the recovery calibration standards versus the target concentration. All calibration curves were linear with a $R^2 > 0.99$. In order to account for the matrix effects, calibration curves were constructed using contaminant-spiked pristine river water instead of HPLC-grade water.

The limit of quantification (LOQ) is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy. Determining the LOQ involved using the signal-to-noise (S/N) which is measured directly using the instrument's software and the internal standard contained in every sample analyzed. Essentially, the lowest point of the calibration curve with a S/N of greater than three was determined as the limit of quantification of that respective analyte. The LOQs for CBZ, TCEP, and TDCP were 0.01 $\mu g\ L^{-1}$ and 0.05 $\mu g\ L^{-1}$ for SMX and TCPP. Other researchers have reported LOQs for SMX and CBZ of 2 ng L^{-1} to 40 $\mu g\ L^{-1}$ (Ternes et al. 2002; Huber et al. 2003) and 0.01 $\mu g\ L^{-1}$ for the flame retardants (Meyer et al. 2004; Snyder et al. 2006).

5.4.2 Mass Recovery Experiments

Mass recovery experiments were conducted to observe the partitioning of the compounds between the aqueous, colloidal, and solid phases. To date, no reported literature contains information on flame retardant partitioning data, nor colloidal pharmaceutical data. The degree of adsorption is dependent on the soil's organic content, clay content, ion exchange capacity, and pH (Mitchell 1993). The compound's solubility and octanol-water partition coefficient also play an important role in determining the extent of adsorption. Therefore, several of the mechanisms that may be responsible for sorption of these compounds to soil include hydrophobicity, ion exchange, and surface bridging (Mitchell 1993). Compounds with an affinity to colloidal fractions could potentially be transported in the subsurface by mobile colloidal particles. Analyzing only aqueous and solids samples may only provide a portion of the compound's presence in the environment. This lack of colloidal data will provide inaccurate, low levels of the compounds. Also, delineating between aqueous, colloidal, and solid phases will provide additional information on the compounds modes of transport in the subsurface.

Known concentrations of the contaminants were added to the control river water and stirred for one hour as noted in Figure 5-7 as the first step. A portion of the contaminant solution was set aside for analytical measurement. The contaminant solution was added to 50 grams (sieved <2 μm) alluvial material, placed in flasks, covered with Parafilm® , and placed on a horizontal shaker table for 24 hours. Samples from the aqueous portion were removed from the beakers, centrifuged (IEC, Centra) for 10 minutes at 4,800 rpm and sequentially filtered using 2.7, 1.2, and 0.2 μm glass fiber filters. These samples were subsequently prepared for analysis as described above.

To determine the desorption of the compound from soil, approximately 50 grams

of each sample of the soil material was air-dried and placed in 250 ml beakers with 200

ml of acetone (flame retardants) or acetonitrile/water 70/30 v/v (pharmaceuticals). The

beakers were covered with Parafilm®, placed on a horizontal shaker table (Lab-Line

4626), and shaken for sixty minutes at 400 rpm. The aqueous portion was retrieved from

each of the beakers, centrifuged, filtered (0.45 micron glass fiber), and reduced to 1 ml in

a warm water bath under a gentle stream of high-purity nitrogen (Organomation

Associates, Inc.). The samples were then reconstituted to 100 ml (flame retardants) or

120 ml (pharmaceuticals) by addition of HPLC-grade water and prepared for analysis as

described in the standard SPE protocol.

Step 1:
Mix Contaminant Solution and Soil
on Shaker Table for 24 hrs

↓

Step 2:
Centrifuge Aqueous Portion

↓

Step 3:
Sequentially Filter Aqueous Sample Thru
2.7, 1.2, and 0.2 μm Filters

↓

Step 4:
Prepare Samples Using SPE Protocol for
Pharmaceuticals and Flame Retardants
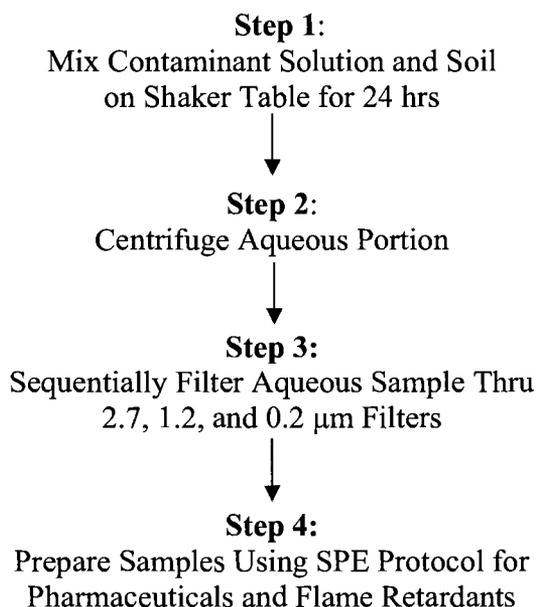
Fig. 5-7: Schematic diagram of mass partitioning process

As presented in Table 5-4, TDCP, TCEP, and CBZ had a higher affinity for the

soil surface than the other compounds with mass recoveries in the solid phase of

approximately 64, 26, and 25 percent, respectively. All of the five compounds tested had

minimal affinities for colloidal particles of greater than 0.2 micron, with TCEP having

the greatest affinity (8%) for colloids between 0.2 and 1.2 μm. The compound

partitioning results presented in Table 5-4 has not been reported in published literature.

TDCP which appeared to be the most hydrophobic and sorptive compound, did not

appear likely to be significantly transported via colloidal particles. The dissolved fraction

contained the majority of the compounds' mass, with the exception of TDCP.

Incomplete absolute mass recovery percentages could be due to the inability to extract

compound fractions which were strongly sorbed on the soil particle.

Table 5-4: Compound Sorption Results

| | % Mass Recovery | | | | |
	TCEP	TCPP	TDCP	CBZ	SMX
Soil	26.31	15.06	64.00	24.89	5.20
Colloidal 1.2<>2.7	0.75	1.26	0.37	0.00	0.45
Colloidal 0.2<>1.2	8.11	4.65	2.17	5.28	0.27
Dissolved <0.2	79.82	66.92	9.61	55.40	51.42
Total Recovery	114.98	87.90	76.16	85.56	57.33

The high percent of sorbed TDCP and the relatively high K_{ow} value from Figure

5-3 indicates that hydrophobicity may be the primary sorption mechanism. All of the

other compounds had relatively low percent sorbed values, indicating that the partitioning

characteristics of these compounds favored the aqueous phase. The compound sorption

results can aide in further understanding of a compound's transport in groundwater. A

reactive solute will travel at a slower rate than the groundwater flow because of the affect

of adsorption. Based on the compounds' sorption results in Table 5-4, it is assumed that

with the exception of TDCP, the impact of adsorption on contaminant flow is minimal.

5.4.3 Sample Contamination

At the initial method development stage, unexplainable increases in the flame retardants were detected. After many additional tests, the sources of the background contamination were identified. Concentrations of TDCP in HPLC water and river water stored in low-grade (non low density or high density polyethylene) plastic containers for one week to several months were approximately five to ten times higher than values measured from volumes stored in glass containers. An additional source of contamination was located during the water/soil partitioning experiments. In this case the blank or control soil sample was placed in front of a small, plastic electric heater to expedite drying of the control sample. The aqueous extract from the control soil sample contained two to fifty times of TCEP, TCPP, and TDCP than was found in the samples re-run using only ambient air drying techniques. Due to the nature of the sources of pharmaceuticals (vs. flame retardants) no external sources of contamination of CBZ or SMX were found. As a sidebar, an attempt was taken to find out the chemical make-up of the plastic containers used in the field and laboratory however, the plastic container company was not willing to release such information.

Organophosphate flame retardants have been detected in sewage effluent, surface, ground, rain, and drinking waters, sludge, soil, and indoor air (Fries et al. 2001; Meyer et al. 2004; Marklund et al. 2005; Loraine et al. 2006). Sources of flame retardants in indoor air were contributed to electrical equipment, including computer screens (Meyer et al. 2004). In addition, the broad application of these compounds and the fact they are often used as additives may result in a wide dispersion into the environment by multiple means. The ubiquitous nature of flame retardants makes it absolutely necessary to

methodically plan each step involved with sample retrieval, experimental setup, and sample analysis. Reporting data that is inflated up to 50 times the actual value due to sample contamination by seemingly innocuous experimental sources can have major impacts on successfully proving research hypotheses.

5.5   Conclusions

Analytical methods were developed for the measurement of two pharmaceuticals, sulfamethoxazole (SMX) and carbamazepine (CBZ) and three flame retardants tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) and tris-(2-chloroethyl) phosphate (TCEP) in aqueous and solid samples. Solid phase extraction (SPE) was used to clean and concentrate the sample. The pharmaceuticals were analyzed using high performance liquid chromatography equipped (HPLC) with a tandem mass spectrometer (MS-MS). The flame retardants were analyzed on a gas chromatograph (GC) equipped with a mass spectrometer (MS). The following summarizes the findings of these experiments:

- The measurement of the degree of sorption of each compound in the aqueous, solid, and colloidal phases was determined. TDCP had the highest affinity for soil surfaces of all five compounds.

- All five compounds tested had minimal affinities for colloidal particles between 2.7 and 0.2 micron, which is significantly important when studying transport behaviors of organic compounds.

- Incomplete mass balances may be associated with inadequate sample clean-up methods at the low concentrations measured for colloidal and solid phases.

- For reliable partitioning results, tests should be run using varying concentrations and pH levels (within range experienced in the field) and at controlled temperatures in order to develop adsorption isotherms.

- Sources of flame retardant background contamination were traced to two sources. HPLC laboratory water and experimental laboratory water stored in low-grade plastic containers contained considerably higher concentrations than the same water stored in glass containers. Soil extracts from soil samples placed in front of a plastic heater contained extremely high concentrations of flame retardants vs. soil samples that were air-dried.

- The broad application of flame retardants results in wide environmental contamination by multiple transport means. The ubiquitous nature of flame retardants requires thorough planning compound sampling and analyzing. Reporting data that is inflated up to 50 times the actual value due to sample contamination by seemingly innocuous experimental sources can have major impacts on successfully proving research hypotheses.

6.0 Remediation of Persistent Organic Compounds Using Enhanced In-Situ Processes

6.1 Abstract

The remediation of five persistent contaminants, two pharmaceuticals and three flame retardants, was investigated in three different column studies including simulated enhanced amended aquifer recharge and recovery (ARR), unamended electrokinetic remediation (ER), and amended ER. In addition, a study was conducted to determine the efficacy of using electrokinetics to introduce the proposed amendment, potassium permanganate, to the subsurface. The persistent contaminants examined were the pharmaceuticals carbamazepine (CBZ) and sulfamethoxazole (SMX) and the flame retardants tris(2-chloroethyl)-phosphate (TCEP), tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), and tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP). Enhanced ARR was successful in reducing the flame retardants, with the complete removal of TDCP. Unamended ER created a reducing zone at the cathode which reduced all of the compounds to some extent within this area. Sulfamethoxazole was completely removed across the entire column after 72 hours. Amended ER columns used a pH-neutralized groundwater and potassium permanganate solution as the electrolyte in the anode and cathode compartments, respectively. Although there was evidence of permanganate transport within the column, the presence of the oxidant did not improve contaminant removal results. Based on the experimental column data, lower contaminant levels in the simulated groundwater were detected in the unamended ER and amended ARR columns. These results indicate that unamended ER and amended ARR are successful in-situ methods used in the reduction of persistent organic compounds which have historically been difficult to remove using traditional treatment methods.

6.2 Background

Advances in analytical chemistry have contributed to the detection of previously immeasurable compounds including endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and other bioactive chemicals in wastewater effluents and surface waters around the world (Kolpin et al. 2002). The occurrence, fate, and transport of these compounds in the aquatic environment have become important environmental issues and have attracted significant attention. It is believed that some of these compounds can have major effects on the endocrine systems of humans and wildlife. Researchers have determined that several organic compounds, specifically sulfamethoxazole (SMX), carbamazepine (CBZ), tris(2-chloroethyl)-phosphate (TCEP), tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), and tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) continue to persist in wastewater treatment effluent, downstream of bank filtration sites, and in treated drinking water (Snyder et al. 2003; Heberer et al. 2004; Zuehlke et al. 2004; Westerhoff et al. 2005).

Many in-situ treatment methods have been employed to remove or reduce contaminants in groundwater including bank filtration and electrokinetic remediation. Bank filtration, which has existed for over 100 years, is an effective and mostly inexpensive natural process for removing inorganic, microbial, and some organic contaminants from groundwater. The raw water is drawn through the aquifer using a production well and is purified through the sediments in the stream bank via different mechanisms: physical filtration, chemical adsorption, and biodegradation. Aquifer Recharge and Recovery (ARR) uses the same physical, chemical and biological mechanisms for water treatment as river bank filtration. However, source water is introduced to the aquifer via pipelines as opposed to being fed by a nearby river. The

water introduced into the aquifer percolates through soil where it mixes with native groundwater and is removed by a recovery well located at a specific distance from the injection point in order to maintain a sufficient residence time. Recently, ARR systems have been modified in order to treat contaminants which were not successfully removed in conventional ARR systems. The modifications involve the use of engineered river bank material such as saw dust and water treatment plant residuals. The type of material is selected based on the target contaminant and subsurface conditions.

Electrokinetic remediation (ER) is a technology that has been successfully applied in the removal, reduction, and stabilization of groundwater contaminants such as heavy metals, DNAPL, chlorinated solvents and other contaminants (Acar et al. 1993; Acar et al. 1995; Acar et al. 1996; Gent et al. 2003; Jackson et al. 2004). This technology could serve as an alternative or addition to conventional water treatment processes. ER uses mechanisms such as electromigration, electroosmosis, and electrolysis of water to remediate or remove the compounds of concern. Electromigration is not being considered as a primary remedial process since the compounds of interest are uncharged. Electroosmosis may contribute slightly to the movement of the uncharged compounds to the cathode region, however, it is not viewed as an efficient process by itself. The main ER mechanism this research focuses on is the electrolysis of water which is defined by equations:
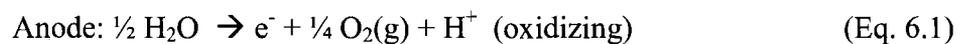
$$\text{Anode: } \tfrac{1}{2} H_2O \rightarrow e^- + \tfrac{1}{4} O_2(g) + H^+ \text{ (oxidizing)} \qquad \text{(Eq. 6.1)}$$

$$\text{Cathode: } H_2O + e^- \rightarrow \tfrac{1}{2} H_2(g) + OH^- \text{ (reducing)} \qquad \text{(Eq. 6.2)}$$

Reducing or oxidizing species generated from the electrolysis of water could potentially be used to remediate the persistent organic contaminants through chemical reactions. For instance hydroxyl radical species are products of a series of reactions beginning with

electrolysis of water. These strong oxidizing species are relatively non-selective oxidizers which could break down the contaminants within the electrochemical cell. First, hydrogen peroxide (H_2O_2) is electrochemically formed by the two-electron reduction of dissolved oxygen at the cathode as noted in (Do et al. 1994) :

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \text{(Eq. 6.3)}$$

The hydrogen peroxide reacts with Fe^{2+} known as the classical Fenton reaction and generates hydroxyl radicals ($OH\cdot$) which in turn may react with an organic compound (Pignatello 1992):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + HO^- \qquad \text{(Eq. 6.4)}$$

In many soils, naturally occurring iron is sufficient to initiate this process. The reaction of $OH\cdot$ with organic compounds may result in dehydrogenated or hydroxylated derivatives of the original compound or ideally, ultimate degradation to CO_2. Huber et al. determined second-order rate constants for the reaction of CBZ and SMZ with OH^- radicals in bench scale experiments (Huber et al. 2003).

There are two types of ER depending on the type of electrolyte used in the electrode compartments: unamended and amended electrokinetic remediation. Unamended ER uses groundwater as the electrolyte in both the anode and cathode electrode compartment. Amended ER involves the use of varied electrolytes to manipulate the reactions at the electrodes and also to uniformly introduce amendments into the subsurface to promote biotic and abiotic reactions. Minimizing premature species precipitation at the cathode and maintaining an optimal pH range over the soil column can be accomplished through the use of an enhancement in the cathode compartment (Acar et al. 1993). Neutralization of the cathode area will also assist in

decreasing the electrical potential difference across the electrodes, thereby, decreasing overall energy demand. Electrokinetic soil processing has been effective in uniformly introducing process additives and nutrients into the biologically active zones where biodegradation approaches have been unsuccessful due to non-uniform nutrient injection. Subsurface electrodes are used to induce a potential across contaminated soil systems mobilizing amendments uniformly through the contaminated zone resulting in a stimulation of in-situ remediation (Acar et al. 1993; Gent et al. 2003; Jackson et al. 2004). This can be accomplished by using a negatively-charged electron donor as the electrolyte amendment in the cathode well. The negatively-charged ions ion will migrate toward the anode in a uniform manner even in low permeability soils, allowing microbial communities to develop. In the case of acetate, the compound serves as the electron donor and a neutralizer for the hydroxide ions at the cathode. Researchers have demonstrated the efficacy of this approach for delivering amendments to the subsurface for the reduction or stabilization of perchlorate, DNAPLs, and metals (Acar et al. 1993; Gent et al. 2003; Jackson et al. 2004; Bejankiwar et al. 2005; Luo et al. 2005; Jiradecha et al. 2006). In amended ER charged amendments can also be introduced to the subsurface to promote chemical oxidation through the use of an oxidant such as potassium permanganate.

The use of potassium permanganate ($KMnO_4$) as an oxidizing agent for the in situ chemical oxidation of organic compounds has been reported to be an effective means of remediation (Gates-Anderson et al. 2001; Crimi et al. 2004). $KMnO_4$ was initially used in water treatment as a strong oxidant for the removal of iron and manganese and for taste and odor control (Cherry 1962). There are many reaction mechanisms proposed to define

the complex oxidation reactions for $KMnO_4$. In alkaline systems with pH >9, the permanganate ion (MnO_4^-) reacts with hydroxyl ions to form $HO\cdot$ radicals in lieu of directly reacting with other oxidizable materials (Gates-Anderson et al. 2001) as defined in Equation 6.5. The hydroxyl radical $HO\cdot$ is the neutral form of the hydroxide ion. Hydroxyl radicals are highly reactive and short-lived and are the principal oxidizing entities in high pH systems.

$$MnO_4^- + H_2O \rightarrow MnO_4^- + HO\cdot + H^+ \tag{Eq. 6.5}$$
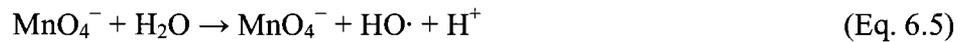
Equation 6.6 shows the reaction in which manganese can be reduced to form a manganese oxide through a three electron transfer in systems with pH values between 3.5 and 12 (Gates-Anderson et al. 2001).

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^- \tag{Eq. 6.6}$$

In slightly acidic or reducing conditions, the Mn (IV) species in MnO_2 can be slowly reduced to form Mn^{+2} as seen in the following equation (Siegrist et al. 2001).

$$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \tag{Eq. 6.7}$$
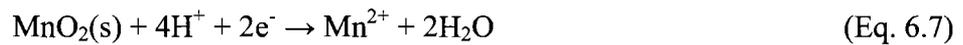
Additionally, the Mn(VII) species is reduced to Mn(IV) in slightly acidic solutions to form manganese dioxide while also releasing oxygen (Eq. 6.8). The MnO_2 solids produced in both acidic and alkaline systems are believed to further catalyze oxidation reactions by providing additional surface area where complexes may form.

$$4MnO_4^- + 2H_2O \rightarrow 3O_{2(g)} + 4MnO_2(s) + 4OH^- \tag{Eq. 6.8}$$
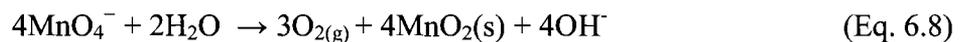
Systems with pH values below 3.5 can produce Mn^{2+} cations as seen in Equation 6.9 through a five electron transfer (Siegrist et al. 2001). Excess permanganate can further oxidize the Mn^{2+} cations to manganese dioxide (Eq. 6.10) (Gates-Anderson et al. 2001)
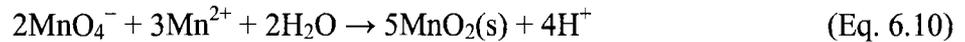
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \tag{Eq. 6.9}$$

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+ \qquad \text{(Eq. 6.10)}$$

The use of potassium permanganate as the electrolyte for the cathode in an ER system could potentially be a successful method to introduce an oxidant to the subsurface which can directly lead to the oxidation and breakdown of the organic contaminant or react with hydroxyl ions to create hydroxyl radicals which will degrade the contaminant.

Persistent contaminants or bioactive compounds which are unaffected by conventional water treatment processes can be potentially harmful to humans and the ecology because of their ability to mimic natural hormones in living systems. In addition, some researchers believe there is potential for an increase in negative impact due to the cumulative effect many of these bioactive compounds may collectively have on humans and the environment. There is additional concern for the presence of toxic organophosphorus compounds and other chemicals and personal health care products in our waters because these products, unlike pharmaceuticals, were never made to be ingested. CBZ in waters impacted by wastewater effluent is so persistent, that some have proposed that CBZ act as a molecular biomarker of sewage (Clara et al. 2004).

Pharmaceuticals used to treat medical conditions in humans are excreted from the body in the parent compound form or as metabolites. The antibiotics administered to the animals are excreted in un-metabolized and metabolized forms, which make the soil and water susceptible to contamination through cropland application of animal wastes and overland flow. The compounds are subject to metabolic reactions in both humans and animals such as hydroxylation, cleavage, or glucuronation. Some metabolites have reversible reactions and are able to transform back to the parent compound after excretion from the body (Hirsch et al. 1999). These compounds and their metabolites enter the

domestic wastewater treatment plant via human excretions or as unused products discarded in toilets. The behavior of the compound in the environment will depend on chemical properties such as water solubility, pH of the matrix, volatility, and sorption potential (Boxall et al. 2003).

The antibiotic group sulfonamide (sulfa drugs) is a group of synthetic antimicrobials used for therapeutic treatment of infectious disease in humans and for treating and protecting the health of animals (Boxall et al. 2003). Sulfamethoxazole (SMX) which belongs to the sulfonamide group, contains two functional moieties at both sides of the sulfonamide linkage (-NH-S(O₂)-) is presented in Figure 6-1. The speciation of SMX over the entire pH range includes anionic species at pH above 5.7, uncharged between 1.7 and 5.7, and positive species below pH of 1.7. The presence of these persistent compounds in surface water and soil has created public concern due to the low levels of antibiotics which can favor the proliferation of antibiotic resistant bacteria.

Molecular Wt: 253.3 g/mol
Solubility: 600 mg L-1
Log K_{ow}: 0.89
pK_{a1}: 1.7
pK_{a2}: 5.6
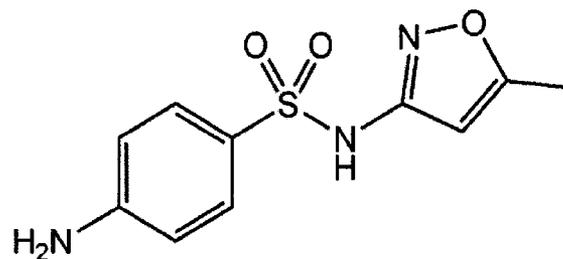
Figure 6-1: Sulfamethoxazole (SMX)

Studies on SMX removal in conventional wastewater treatment plants have reported removal rates of approximately twenty percent (Ternes 1998; Castiglioni et al. 2006). Water treatment plants have also been proven to have difficulty in removing SMX. Researchers have found that coagulation/flocculation/sedimentation with alum

and iron salts or excess lime/soda ash softening, treatment with 1 mg L^{-1} powdered

activated carbon did not result in significant removal of antibiotics including SMX

(Snyder et al. 2003; Westerhoff et al. 2005). However, researchers have concluded that

SMX was completely removed with chlorine and eighty eight percent removed with

ozone using doses similar to those experienced at a WTP (Huber et al. 2003; Westerhoff

et al. 2005; Snyder et al. 2006).

Carbamazepine is a hydrophilic compound consisting of three rings of carbon

with double bonds and an amine group attached and a double bond as presented in Figure

6-2. It is a base which is found mostly uncharged in the environment. The molecule's

structure makes it susceptible to fracturing under certain conditions. Carbamazepine is

an important drug for the treatment of seizure disorders such as epilepsy, which is ranked

second for the most common central neuron system disease. Carbamazepine (CBZ) has

been available for more than thirty years and has recently replaced phenobarbitol as the

most common anticonvulsant drug (Miao et al. 2003). CBZ has also been used to treat

cases of schizophrenia because of the drug's ability as a mood-stabilizer (Okuma 1993).

The drug has also been prescribed for the treatment of bipolar disorder (Dilsaver et al.

1996) and can be combined with other drugs for the treatment of alcohol withdrawal

(Franz et al. 2001).

Molecular Wt: 236.3 g/mol
Solubility: 17.7 mg L-1
Log K_{ow}: 2.45
pK$_a$: 2.3
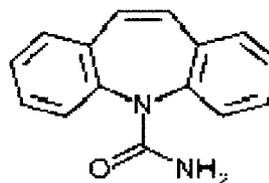
Figure 6-2: Carbamazepine (CBZ)

Researchers have reported findings of minimal removal in conventional wastewater treatment plants and increased removal in the disinfection stage of conventional water treatment plants. Researchers observed zero percent removal of CBZ in several Italian sewage treatment plants (Castiglioni et al. 2006). Clara found that neither traditional activated sludge plants nor a membrane bioreactor had any effect on CBZ concentrations (Clara et al. 2005). Carballa determined that the addition of ferric chloride, aluminum sulfate, and aluminum polychloride had no effect on CBZ removal(Carballa et al. 2005). The same study also had marginal results using dissolved air flotation (DAF) for the removal of CBZ. CBZ experienced twenty and thirty five percent removal using DAF under low and high fat containing solutions, respectively. Others have reported less than seven percent removal of CBZ in sewage treatment plants with maximum effluent and surface water concentrations reported at 6.3 ug/l and 1.1 ug/l, respectively (Ternes 1998).

In addition, reports of little or no removal of CBZ in bank filtration sites have been reported (Drewes et al. 2001; Heberer et al. 2004), which is also supported by laboratory tests focused on the water/sediment relationship (Loffler et al. 2005). Benchtop experiments (and pilot scale studies (Hua et al. 2006; Jasim et al. 2006; Snyder et al. 2006)) testing the removal of CBZ with ozone demonstrated that removal of the parent compound was achieved under conditions similar to ozone processes within a water treatment plant (Andreozzi et al. 2002; Ternes et al. 2002; Huber et al. 2003; Westerhoff et al. 2005). Huber et al. determined second order rate constants for the reaction of CBZ with ozone and OH⁻ radicals in bench scale experiments (Huber et al. 2003; McDowell et al. 2005). OH⁻ radicals are the main oxidants during advanced

oxidation processes (AOPs). Results from the rate constants suggested complete transformation during typical ozonation process. Chlorine has also been studied for the oxidation and removal of CBZ under similar conditions found in WTPs with results indicating removal greater than seventy five percent (Westerhoff et al. 2005). However, additional research has concluded that treatment of these compounds with conventional oxidation methods such as chlorine and ozone can result in transformations of certain compounds such as acridine and the creation of metabolites, which are largely unknown and occasionally more harmful than the original compound (Snyder et al. 2003).

The presence of bioactive compounds such as organophosphorus compounds which are manufactured by the chemical industry for use as pesticides, flame retardants, plasticizers, hydraulic fluids and solvents have been detected in the aquatic environment (Fries et al. 2001; Andresen et al. 2006). Organophosphorus compounds (OPs) are manufactured world-wide for many industries and end-users. More than half of the compounds manufactured are pesticides and the remainder are flame retardants, plasticizers, hydraulic fluids and solvents (Fries et al. 2001). The chlorinated OPs such as tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) and tris-(2-chloroethyl) phosphate (TCEP) are predominantly used as flame retardants in polyurethane foams. As with other additives, OPs are mixed and are not chemically bonded with the containing materials, and therefore are easily released into the environment (Rodriguez et al. 2006). The compounds' structures and pertinent chemical information is presented in Figure 6-3.

$C_6H_{12}Cl_3O_4P$ (TCEP)
Molecular Wt: 285.49 g/mol
Solubility: 8,000 mg L^{-1} at 20°C
Log K_{ow}: 1.7
pK_a: 7.8
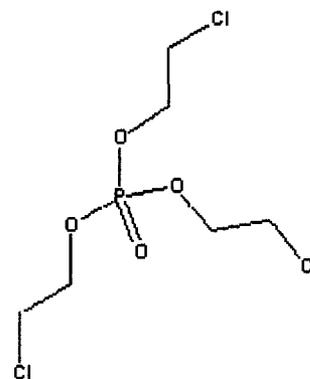
(a)

$C_9H_{18}Cl_3O_4P$ (TCPP)
Molecular Wt: 327.55 g/mol
Solubility: 1600 mg L^{-1} at 20 C
Log K_{ow}: 2.59

(b)
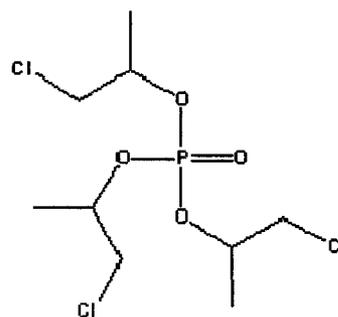
$C_9H_{15}Cl_6O_4P$ (TDCP)
Molecular Wt: 430.91 g/mol
Solubility: 100 mg L^{-1} at 30 C
Log K_{ow}: 3.8

(c)
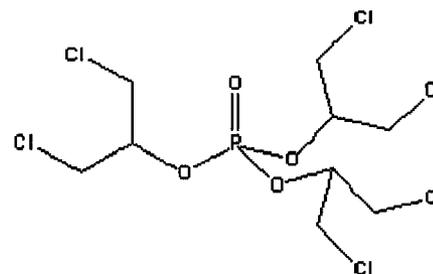
Figure 6-3: (a) TCEP, (b) TCPP, (c) TDCP

The detection and quantification of OPs at concentrations ranging from low ug L^{-1} to ng L^{-1} in wastewater treatment plant effluent, reclaimed wastewater, and surface waters has been reported in several studies (Acar et al. 1995; Fries et al. 2001; Heberer et al. 2002; Kolpin et al. 2002; Snyder et al. 2003; Meyer et al. 2004; Stackelberg et al. 2004; Bendz et al. 2005; Marklund et al. 2005; Westerhoff et al. 2005; Loraine et al. 2006).

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Research conducted by the United States Geological Survey (USGS) and the Centers for Disease Control and Prevention was performed on two streams that feed a drinking water treatment plant. Two of the seven compounds that was found in every sample taken from the stream water and raw water were TCEP and TCPP (Stackelberg et al. 2004). The same study concluded that TCEP concentrations were consistent across the sampling events and throughout the drinking water treatment plant. This may suggest temporally constant concentrations in source streams and little or no removal of the compounds within the WTP (Stackelberg et al. 2004). A Swedish study determined that there was little to no removal of chlorinated organophosphates during the wastewater treatment process where both effluent and anaerobic sludge were examined from several different wastewater treatment plants with varied capacities and influent sources (Marklund et al. 2005).

Other Swedish research found only 19% removal of TCEP in a sewage treatment plant upon comparing the influent and effluent concentrations (Bendz et al. 2005). In research conducted at wastewater treatment plants in Germany (and other western Europe countries (Reemtsma et al. 2006)), similar results indicate little to no removal of chlorinated OPs throughout the treatment process (Meyer et al. 2004). In other German research, comparative data have indicated that OP concentrations have decreased overall, however, the use of these compounds is still affecting the quality of surface, rain, and ground water (Fries et al. 2001). Results also indicated elevated concentrations in wastewater effluent leading to river water contamination and in groundwaters impacted by nearby rivers infiltrating into the aquifer. Researchers examining the successfulness of activated sludge processes and membrane bioreactors (MBR) in the removal of TCEP

and TCPP concluded that removal rates ranged between 0% - 35% and 0% - 25% for activated sludge plants and MBR, respectively (Bernhard et al. 2006).

Studies conducted on TCEP removal using simulated drinking water treatment processes indicated zero percent removal after treatment with alum (Westerhoff et al. 2005). The same study also tested TCEP removal using powdered activated carbon (PAC). Little removal (less than fifteen percent) was accomplished at a PAC concentration of 1 mg L^{-1}; however, at PAC concentrations of 20 mg L^{-1}, removal was greater than eighty percent. Westerhoff reported zero removal in ozone and chlorine-treated samples (Westerhoff et al. 2005). Conflicting research determined both no removal and substantial removal of flame retardants in bank filtration processes (Heberer et al. 2004; Andresen et al. 2006).

Although some endocrine-disrupting compounds and personal care products can be reduced in wastewater and water treatment plants and through natural attenuation processes, the persistent compounds remain minimally reduced or completely unaffected. Enhanced or engineered in-situ processes such as amended aquifer recharge and recovery and electrokinetically-enhanced river bank filtration systems may reduce the persistent compounds in the groundwater. Severe oxidizing and reducing conditions within the systems may directly break down the contaminants or alter the compounds structure allowing for microbial degradation to take place.

This paper evaluates whether enhanced in-situ methods such as amended ARR and unamended and amended ER-enhanced RBF can promote reduction of certain persistent compounds such as CBZ, SMX, TCEP, TCPP, and TDCP. In addition, the polarity in an amended ER system will be reversed in order to see the impacts on

permanganate in the system. If successful, these methods could be used as enhanced in-situ treatment methods for the removal of contaminants which have been unsuccessfully removed in traditional treatment schemes.

6.3   Materials and Methods

6.3.1 Chemicals

Stock solutions (1 g L^{-1}) of the flame retardants TCEP (Sigma Aldrich, Dallas, TX) and TCPP and TDCP (Pfaltz and Bauer, Waterbury, CT) were made in HPLC-grade ethyl acetate (Fisher Scientific, Pittsburgh, PA) and stored at 4°C. The pharmaceuticals SMX and CBZ (Sigma Aldrich) were made in HPLC-grade methanol (Fisher Scientific). Monthly standards (100 mg L^{-1}) were made in HPLC-grade ethyl acetate and methanol and also stored at 4°C. Groundwater was obtained from a production well located near the South Platte River in Brighton, CO. Potassium permanganate solutions were made with HPLC water and 1N certified potassium permanganate concentrated solution (Fisher Scientific).

6.3.2 Solid Matrices

The native alluvial material was obtained from the banks of the South Platte River in Brighton, CO, air-dried, and sieved using a 2 mm brass sieve. This material was used in the electrokinetic remediation columns and the enhanced ARR columns. The enhanced ARR columns contained seventy percent native alluvial material and thirty percent water treatment residual from the Wellington Water Treatment Plant. A control ARR column contained 100% native alluvial material. The properties of the soil and the water treatment residual (WTRs) used in the column experiments are listed in Table 6-1.

Table 6-1: Column material characterization

	Alluvial Material	WTR[c]
pH	7.4	7.4
Conductivity (mmhos/cm)	0.4	2.2
Lime estimate	Low	Low
Organic Matter (%)	0.1	11.4
NO_3-N (mg/kg)	0.7	51.5
P (mg/kg)	9.0	0.3
K (mg/kg)	15.6	73.6
Zn (mg/kg)	4.3	2.0
Fe (mg/kg)	19.6	34.3
Mn (mg/kg)	1.8	36.3
Cu (mg/kg)	2.1	2.4
Sand (%)	94	37
Silt (%)	0	47
Clay (%)	6	16
Texture	Sand	Loam
Bulk Density (g/cm^3)	1.46[b]	1.43[a]

[a] Based on the American Bulk Density Calculator (Pedosphere.com).
[b] Based on laboratory measurement of dry density.
[c] WTR = Water Treatment Plant Residuals

6.3.3 Experimental Methods

The remediation of five persistent contaminants, two pharmaceuticals and three flame retardants, were investigated in three different column studies including simulated enhanced ARR, unamended electrokinetic remediation, and amended electrokinetic remediation. In addition, a study on the introduction of permanganate to the subsurface using electrokinetic injection (EI) was studied without the presence of contaminants. The EI study focused on the transport of permanganate, the pH neutralization of

permanganate, and the effect of reverse polarization on the column. Table 6-2 summarizes the different experimental column studies.

Table 6-2: Experimental column summary

Column Description	Column Type	Compounds Studied	Sample Frequency	Purpose
Amended ARR (Using Standard ARR as Control)	Continuous Flow-thru	TCPP and TDCP	Monthly (08/06-01/07)	Effect of Water Treatment Residuals on Compound Removal
Amended ARR (Using Amended ARR as Control)	Continuous Flow-thru	TCEP, TCPP, and TDCP	Weekly (05/07-06/07)	Effect of Water Treatment Residuals on Compound Removal
Unamended ER Simulating Enhanced RBF	Batch	TCEP, TCPP, TDCP, CBZ, and SMX	24, 48, 72, 168, and 504 hrs	Effect of Electrokinetic Remediation on Compound Removal
Electrokinetic Injection	Batch	$KMnO_4^-$	1st Set: 144 & 288 hrs 2nd Set: Daily for 10 d	EI Transport of MnO_4^- and Effect of Polarity Reversal
Amended ER Simulating Enhanced RBF	Batch	TCEP, TCPP, TDCP, CBZ, and SMX	144 and 298 hours	Effect of MnO_4^- in ER System on Compound Removal

6.3.3.1 ARR Columns

Column testing simulating aquifer recharge and recovery were constructed to test removal efficiencies for several different groups of compounds; however this study only examined flame retardant removal. The acrylic columns were four feet in length with an internal diameter of six inches. There were sample ports located along the length of the column at one-foot intervals; however, all samples for this study were drawn from the sample port at the bottom of the column. The fittings were stainless steel with the exception of the top and bottom fittings which were brass. The influent, effluent, and sampling tubing were Teflon with the exception of the pump head tubing, which was Tygon. The columns were initially conditioned for one month from bottom to top at 1 ml

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min^{-1} with production well water. Upon completion of the column conditioning, the contaminant feed was loaded on the column in a top to bottom direction at a flow rate of 1 ml min^{-1} maintaining column saturation. The feed solution to the control columns (one with only alluvial material and the other with 70/30% alluvial/WTR material) contained 2 mmol of sodium azide in order to maintain abiotic conditions. The original amended ARR column experiment used a control column which contained 100% native soil. Realizing that this was not a true control for amended ARR, a new control column was constructed. This second control column consisted of the 70/30 % alluvial/WTR material Figure 6-4 depicts the ARR-simulated columns.
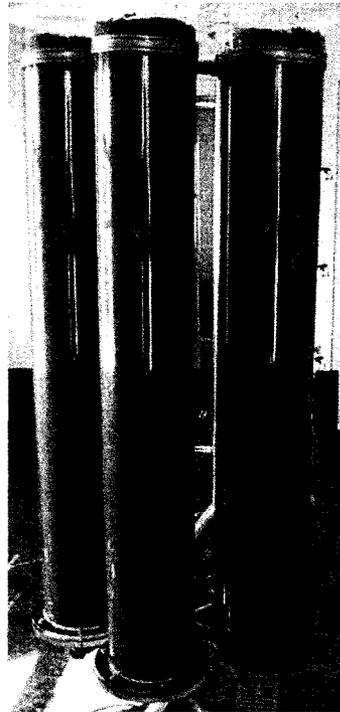
Figure 6-4: ARR-simulated columns

6.3.3.2 Electrokinetic Remediation Columns

Two sets of batch electrokinetic experiments were conducted using a soil column with river alluvium contaminated with flame retardants and pharmaceutical solution.

Additionally, control columns using uncontaminated soil were run coincidently under the same respective test conditions for both sets of experiments. The first set of tests was conducted using groundwater as an electrolyte in both the anode and cathode electrode compartments. The second set of experiments used a pH-controlled groundwater as the anode electrolyte and potassium permanganate as the cathode electrolyte. Flame retardant and pharmaceutical removal efficiencies were examined for each set of experiments.

The acrylic columns used in this experiment were separated into three sections: anode, soil column, and cathode as presented in Figure 6-5. Both electrode compartments were approximately three inches long by six inches high. The soil column section measured approximately sixteen inches long by six inches deep. The soil column was separated from the electrode compartments by an acrylic plate with over fifty percent perforation. Filter paper (Whatman No. 4) was positioned within the soil column along the perforated acrylic plate in order to minimize media from entering the electrode compartment. The column had twelve sample ports across the face of the column for sample withdrawal. Both of the electrode compartments had ports on the top and the bottom which were used for electrolyte circulation. The top port on each of the electrode compartments was also used for connecting power to the electrode. The soil columns were sealed with silicone. The columns had six carbon reference electrodes evenly spaced across the top of the column. The reference electrodes were carbon rods with a diameter of 0.242" and an approximate length of 5". The electrical equipment used for the experiment was a GW Instek GPR Middle Series DC laboratory power supply. The anode was a platinum mesh plate where the cathode electrode was a titanium plate. The

titanium commercial grade sheet had dimensions of 6.25" x 2" x 0.063". The platinum electrode had the same outer dimensions as the titanium sheet, however, it was comprised of 0.032" platinum wire with a maximum mesh spacing of 0.04". The peristaltic pump used in circulating the electrolyte solution was a Cole Parmer, Masterflex 7550-20. The pump tubing material was Tygon with an internal diameter of 1.14 mm. The two liter electrolyte circulating reservoir containers were graduated glass beakers.

Water originating from a production well along the South Platte River was mixed with contaminant solutions and mixed for two hours. The solution and the soil were mechanically mixed for one hour. The soil-water mixture was added to the column in one-half inch lifts using a rubber mallet on the column's sides to evenly compact the media. Amended pH-controlled experiments used a 10,000 mg L^{-1} solution of neutralized (with acetic acid) potassium permanganate solution as the cathode electrolyte. Pump discharge water was used as the electrolyte in the anode compartment. The anode's pH was manually regulated on a daily basis through the addition of sodium hydroxide. The tests were conducted at the constant current settings of 1.33 A/m^2. The duration of the tests ranged from one to twenty one days.
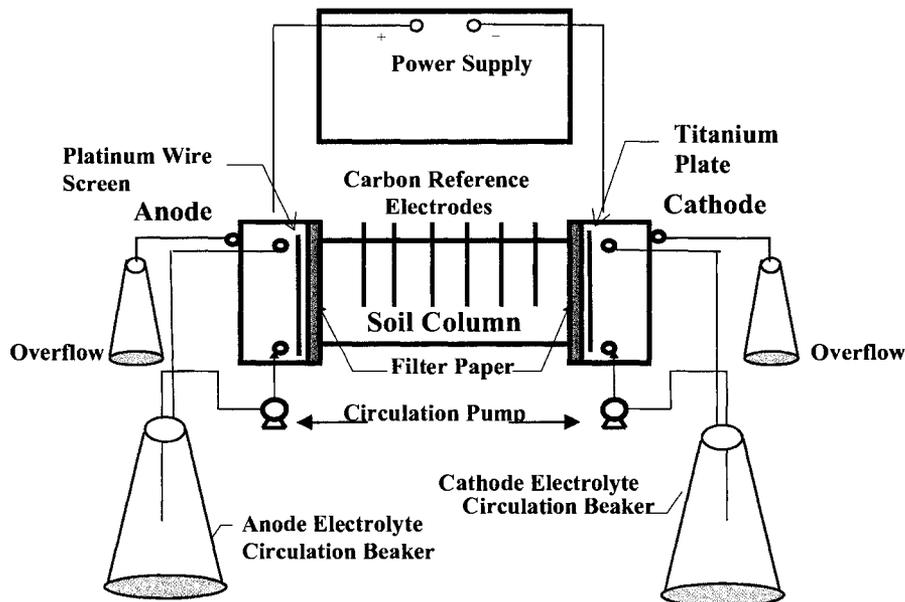
Figure 6-5: Experimental bench-top electrokinetic remediation cell schematic (Re-drawn from (Kim et al. 2000))

6.3.4 Sampling Methods

Samples were taken monthly from August 2006 to January 2007 from the ARR

columns which included the abiotic ARR control column without WTR amendments.

Once the second control column was on-line (simulating abiotic amended ARR) samples

were retrieved on a weekly basis (May - June 2007). All samples from the ARR columns

were retrieved from the effluent port at the bottom of the columns. Samples from the

electrokinetic remediation columns were taken at approximately 24, 48, 72, 168, and 504

hours. All samples were stored in acetone-cleaned amber, glass bottles at 4°C for a

maximum of 24 hours. The pH and oxidation reduction potential (ORP) of the samples

and electrolytes were monitored with a bench-top Accumet AR25 meter while the

conductivity of the samples and electrolytes were monitored with a Thermo Scientific

Orion 150+ bench-top meter. The voltage drop across the column was measured daily

using a Fluke 112 multi-meter and the six carbon reference electrodes on top of the column.

6.3.5 Analysis

Carbamazepine and sulfamethoxazole were analyzed by high performance liquid chromatography and quantified by tandem mass spectrometry (Bendz et al. 2005), (Petrovic et al. 2003), (Richardson et al. 2005), (Yang et al. 2004). The compounds were extracted from the water sample and then concentrated using Oasis 60mg/3ml polymeric hydrophilic-lipophylic balance (HLB) solid phase extraction (SPE) cartridges. The SPE method followed a modified version of published methods by Yang et al. (Yang et al. 2004). After preconditioning the cartridges with methanol, hydrochloric acid, and water the samples were passed through the cartridges. The samples were initially pH-adjusted to a pH below the pKa in order to increase retention of the compounds on the SPE cartridges. Adsorbed compounds were rinsed with water and then eluted with methanol into a test tube. The internal standard, simatone was (Ray 2000; Yang et al. 2004) added to the sample prior to concentration using a nitrogen bath. Mobile phase A (water with 0.1% formic acid) was added to the sample prior to introduction into the HPLC.

The method for the HPLC/MS-MS followed a modified version of the method as described in the work of Yang et al. (Yang et al. 2004). The LC system was a HP 1100 system with a variable wavelength UV detector. The mass spectrometer was a Finnigan LCQ Duo ion trap equipped with a heated capillary interface and an ESI source. ThermoQuest Xcalibur software was employed to control the mass spectrometric conditions. The column used for compound separation was a 2.0 x 50 mm Phenomenex Gemini 5 micron C18 column in combination with a 2.1 x 4mm guard column of the same type. An injection volume of 20 ul and a gradient introduction of eluents at 0.38

ml/min was used. Separations were achieved by a gradient program which began with 95% of Mobile Phase A and 5% of Mobile Phase B. The gradient program continued to increase to 5% of Mobile Phase A and 95% Mobile Phase B over twenty minutes. The LC column temperature was maintained at 15° Celsius. Mobile Phase A was water with 0.1% formic acid and Mobile Phase B was pure acetonitrile. SMX, CBZ, and the internal standard were eluted in under 15 minutes.

Mass spectral data, precursor and product ions (relative to the compounds) which have been previously obtained by the LCQ Duo ion trap with an ESI source in the positive mode were used. The tune files created during the initial optimization were used for compound quantification during LC/MS/MS mode. The product ion producing the highest intensity was used for quantification to maximize analytical sensitivity and selectivity.

Determination of TCEP, TCPP, and TDCP were performed on a gas chromatograph with mass spectrometric detection. Derivatization of the compound was not necessary, however, samples were prepared for analysis using solid phase extraction. The SPE and GC method was a modified version to that of published methods, (Fries et al. 2001) (Meyer et al. 2004) (Rodriguez et al. 2006). In summary, the SPE cartridges were conditioned with ethyl acetate, methanol, and water. The filtered samples (pH-adjusted to a neutral pH when necessary) were passed through the Oasis HLB polymer cartridge. After the concentration step was complete, the beaker containing the sample and SPE conductions were rinsed with a methanol/water mixture (which also passed through the cartridge). Cartridges were then dried and eluted with ethyl acetate. The cartridges were eluted with 2 mL of ethyl acetate using a vacuum of 5 inches of mercury.

The extract was collected in 15 mL vials which each contained the 100 µL of 10 ppm internal standard squalane. The internal standard squalane has been used successfully in the examination of flame retardants by previous researchers (Fries et al. 2001). Water was removed from the extract by passing the solution over 2 grams of pre-washed (ethyl acetate) sodium sulfate. An additional 2 mL of ethyl acetate was passed over the sodium sulfate crystals as a final rinse and added to the sample extract in the 15 mL-vials. The final solution volume was reduced to 0.1 mL in a warm water bath under a gentle stream of high purity nitrogen (Organomation Associates, Inc.). The sample was transferred to a 0.150 mL poly spring insert which was placed in a 2-mL amber vial.

The extracts were introduced into the gas chromatograph as 1 uL injected aliquots via the autosampler using a pulsed splitless mode. The injector temperature was maintained at 280° Celsius. Separation of the analytes was performed on a 30 m FS-Supreme capillary column with a film thickness of 0.25 micron. Helium served as the carrier gas. The GC oven temperature was initially held at 80° Celsius for one minute and then increased to 300° Celsius at a rate of 4 degrees per minute and kept at this temperature for twenty minutes. Mass spectrometric analyses were operated in select ion monitoring (SIM) mode. Data acquisition, processing, and instrumentation control were performed using the instrument's software. The concentrations of the analytes in all samples were calculated by measuring the peak area of each compound relative to the peak area of the internal standard squalane. This internal standard has successfully been used by other researchers in the determination of chlorinated flame retardants (Rodriguez et al. 2006).

The limit of quantification (LOQ) was determined using a signal to noise S/N value of greater than three measured directly by the instrument's software and the internal standard contained in every sample analyzed. In addition, recovery tests were run to determine the accuracy of the SPE method. Known concentrations of the compounds were spiked into surface water samples prior to SPE and directly into SPE extract of only river water. The samples were cleaned and concentrated using the defined SPE method. Recovery was calculated using:

$$\text{Recovery (\%)} = \frac{\text{Extract Concentration Prior to Extraction}}{\text{Extract Concentration Post Extraction}} \qquad \text{(Eq. 6-11)}$$

The range of recoveries for the flame retardants and pharmaceuticals in river water were 50-104% and 56-109%, respectively,

A daily internal QC check was performed on all equipment. Standard concentrations of compounds were measured daily to confirm compound shelf life and instrument's accuracy. Replicate analyses or duplicates were analyzed as part of the lab's QC program. Sample blanks were also incorporated into the lab's QC program.

The determination of permanganate in the electrokinetic injection transport study and in the amended electrokinetic remediation study was performed using a UV spectrometer (Standard Methods 4500). Residual manganese in the soil column was determined by digesting the soil samples using nitric acid/perchloric acid digestion and analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (EPA Method 6010).

6.4   Results and Discussion

The completion of this study resulted in column treatment data indicating the impact of engineered ARR and electrokinetic methods have on the remediation of persistent compounds. Concentrations of the compounds within the soil column were analyzed to determine variability within the column.

6.4.1 ARR Columns

Column studies simulating aquifer recharge and recover initially included an abiotic control column with 100% alluvial material fed with a contaminant solution which included sodium azide to assure minimized microorganism activity. The aquifer recharge and recovery (ARR) column consisted of 100% alluvial material fed with a contaminant solution identical to the control except for the sodium azide. Both columns had hydraulic detention times of thirty days. The ARR-WTR column consisted of mixed media in a 70/30 (v/v) proportion ratio of alluvial material and water treatment plant residuals. The contact time in the ARR-WTR columns was approximately six days. The flame retardants TCPP and TDCP were analyzed in the effluent from these columns. As shown in Figure 6-6 and Figure 6-7, there was 64% and 70% removal of TCPP and TDCP, respectively, from the ARR column and a 78% and 100% removal of TCPP and TDCP, respectively, from the ARR-WTR column. Since there was negligible TCPP removal from the control column, the TCPP removal within the ARR and enhanced ARR columns was due to microbial degradation under anaerobic conditions. Figure 6-7 indicates some TDCP removal from the control column. The decrease in TDCP from the control column effluent is likely due to the compound's affinity to partition to the solid phase.
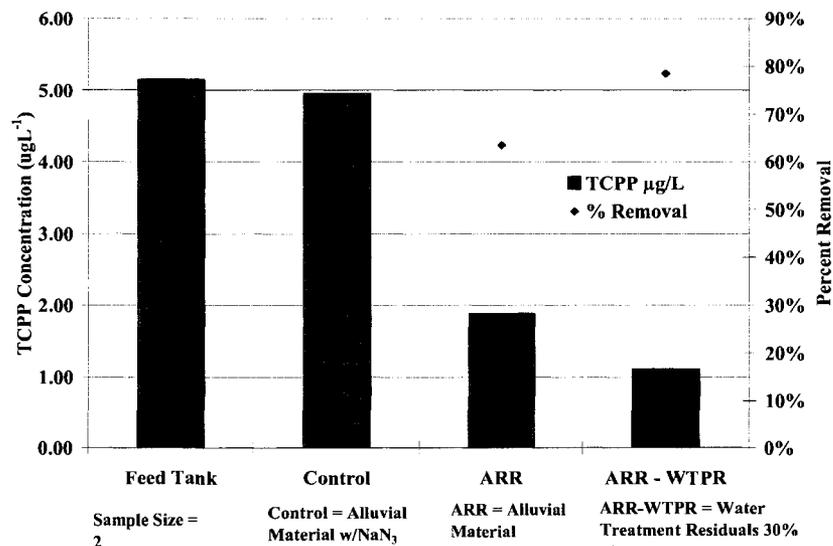
Figure 6-6: Conventional and enhanced ARR-simulated columns: TCPP removal data
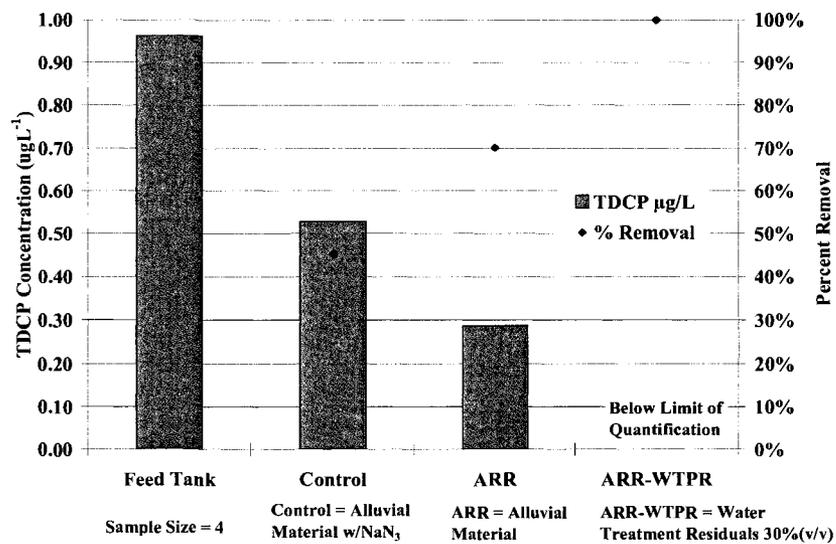
Figure 6-7: Conventional and enhanced ARR-simulated columns: TDCP removal data

Figure 6-8 normalizes the removal concentrations to the initial contaminant

concentration in the spiked feed water. It is clear that there is an increase in removal of

both TCPP and TDCP within the enhanced ARR column. This reduction in contaminant

in the effluent is attributed to several benefits associated with the presence of the water

treatment plant residual. The residuals are an excellent adsorbent with the high amount

of aluminum (up to 15% of the total). In addition, its hypothesized that the residuals are

leaching organic matter that is promoting very active microbial activity. The leaching of

organic matter was assumed due to a twenty percent increase in the TOC level.

Additional studies proved that increasing the amount of WTR in the column increased in

the level of TOC.
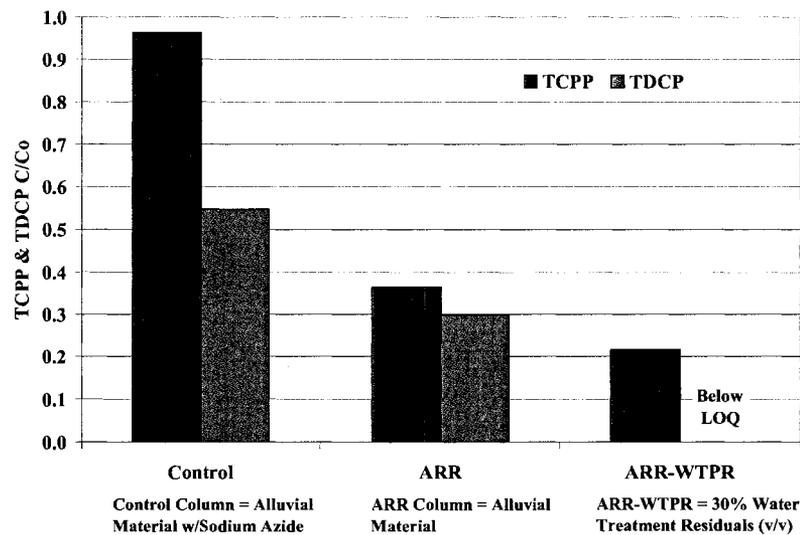
Figure 6-8: ARR-simulated column flame retardant removal data

In addition, severe reducing conditions exist within the amended column. The

elevated reduced conditions with the column were verified with data supporting sulfate

reduction. The severe reducing conditions likely reduced the contaminants which were

adsorbed on the water treatment residual and to a lesser effect, the alluvial material.

Figure 6-9 indicates the location of sulfate reduction on the oxidation-reduction ladder.
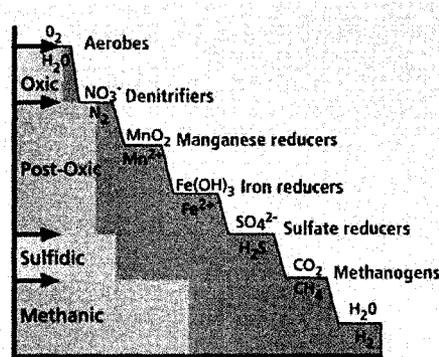
Figure 6-9: Oxidation-reduction ladder (Bilal et al. 1979)

The control column data in Figures 6-6, 6-7, and 6-8 were obtained from a

column with 100% alluvial material simulating abiotic conditions. Since this was not a

true control column for the amended ARR column, a new control column was

constructed. The new control column consisted of 70% alluvial material and 30% WTR

and was fed with a contaminant solution containing 2 mmol of sodium azide to promote

abiotic conditions. Figure 6-10 depicts flame retardant data from the new control column

and the amended ARR column. TCPP indicated zero removal in the control column and

over 70% removal in the WTR-amended column. These results indicate that microbial

degradation combined with the reducing conditions in the biotic column was the primary

mechanism in which TCPP was reduced in the column.
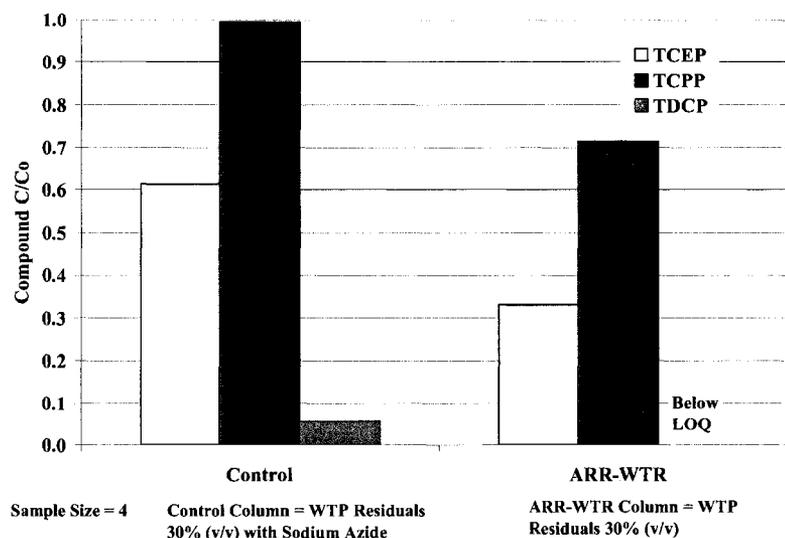
Figure 6-10: Enhanced ARR-simulated column: flame retardant data

TCEP showed some removal in both the control and biotic columns. The lower

TCEP concentration in the effluent of the control (abiotic) column could be due to

adsorption onto the alluvial material or water treatment plant residual. Previous

partitioning studies determined that approximately 26% of the compound's mass was

recovered from extraction methods performed on the solid material (Chapter 5). There

also may be the possibility that sodium azide was not completely successful in inhibiting

all microbiological activity in the column. The effluent from the amended column

revealed a reduction in TCEP of 67% from the original concentration of the compound in

the feed solution. And lastly, TDCP once again showed its affinity for the solid phase in

the results from the control column. Approximately 95% of the compound was removed

in the abiotic column. The enhanced ARR column effluent contained levels of TDCP

that were below the limit of quantification. These results once again indicate the effect of

the WTR in the removal of TDCP. Removal rates between the first set of columns

(Figures 6-6, 6-7, and 6-8) and the second set of columns (Figure 6-10) have the potential to vary in ultimate removal results due to the varying water treatment residual factor. The second set of columns was constructed nearly two years after the initial set of columns. Chemical characterization of the water treatment residuals from these two time periods revealed varying chemical compositions. This is likely due to the continually changing raw water quality and therefore, changing coagulant and polymer dose. The potential difference in the chemical characterization of the WTR in the different columns may have unknown impacts on column treatment results.

Enhanced ARR was successful in reducing the flame retardants due to the adsorption qualities of the WTR and the reduced conditions within the column. TCPP had over 30% removal in the WTR-amended column and TCEP was reduced to 33% of the original concentration. The results from the control column indicated that TDCP showed an affinity for the solid phase. Approximately 95% of the compound was removed in the abiotic column which led to effluent TDCP levels below the limit of quantification in the biotic column.

6.4.2 Unamended Electrokinetic Remediation Columns

The column studies testing unamended electrokinetic remediation for the removal of persistent compounds resulted in conditions characterized by extreme pH and redox values and varying degrees of compound removal. Groundwater was used as the electrolyte in both the anode and cathode compartment and therefore pH was not buffered during this experiment. The three week experiment studied unamended ER removal of CBZ, SMZ, TCEP, TCPP and TDCP.

The pH distribution across the column (from anode to cathode) was monitored throughout the experiment. Figure 6-11 depicts the typical acidic and alkaline zones in

the anode and cathode regions, respectively. The acid and alkaline fronts are due to the electrolysis of water as defined in Equations 6.1 and 6.2. Hydrogen ions are created at the anode and hydroxide ions at the cathode. Both ions attempt to migrate to the opposite electrode. The pH at the anode and the cathode remained within the range of 1.8-2.5 and 11.2-11.5, respectively. Typically the acid front dominates within poorly buffered soils because the mobility of the hydrogen ion is approximately twice the mobility of the hydroxyl ion under an electric field (Acar et al. 1995). However, based on Figure 6-11 the acid front did not appear to dominate until 72 hours into the experiment.
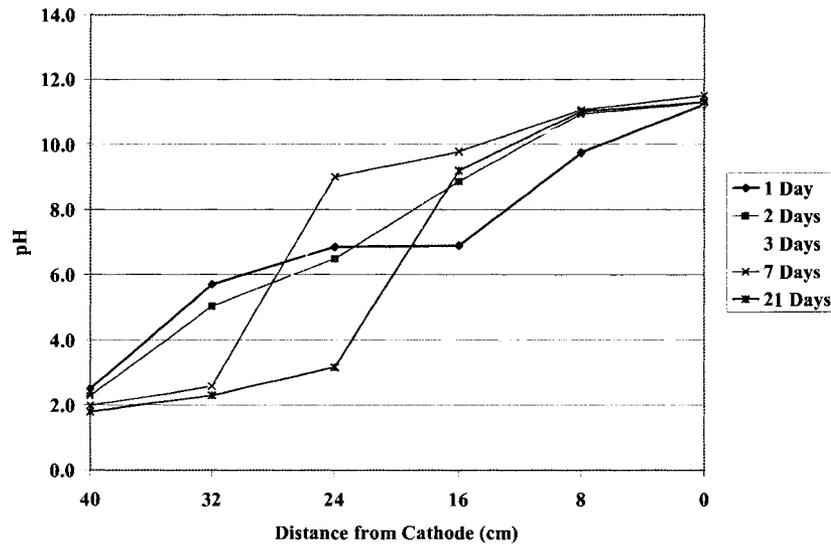
Figure 6-11: Unamended ER column: pH distribution across column

The conductivity in the anode and cathode electrode compartments and across the soil column was monitored during the experiment and presented in Figure 6-12. An increase in conductivity at both electrodes is likely due to the creation of hydrogen and hydroxide ions due to electrolysis and to the migration of ions in the groundwater to either electrode. Each pH unit is an order of magnitude of hydrogen ion concentration.

As shown in Figure 6-12, the decrease in conductivity at 8 and 16cm from the cathode

are likely due to anion depletion, the formation of water in that region, and or the

deposition of species in this area which results in an increase in resistance (Alshawabkeh

et al. 1992). The conductivity is higher at the anode than the cathode due to the increase

in the electrolyte concentration.
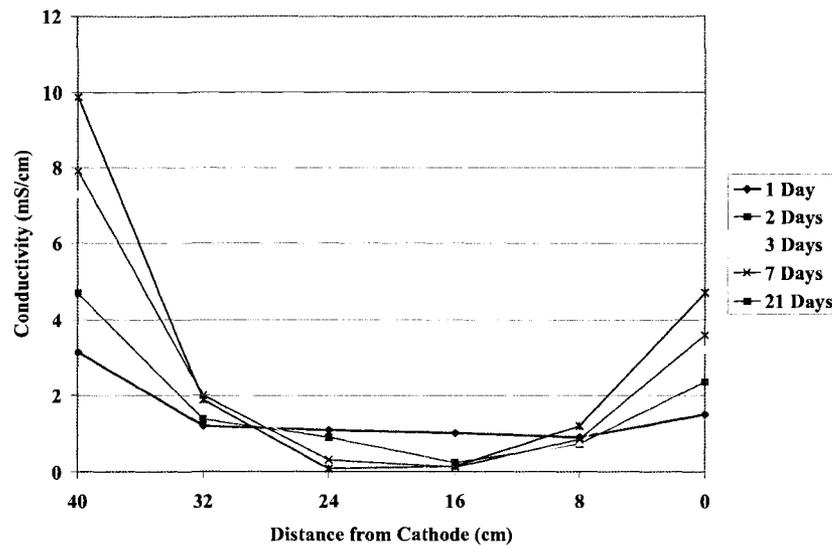
Figure 6-12: Unamended ER column: conductivity distribution across soil column

The oxidation-reduction potential was monitored across the soil column

throughout the length of the experiment and the results are presented in Figure 6-13. As

expected, the anode and cathode region exhibits strong oxidizing and reducing values,

respectively. A decrease in redox values at the completion of the study (at t=504 hours)

implied the cathode area (e.g. 32 cm from the anode) may have experienced a significant

drop in redox potential. This daily reduction in redox suggests the reduced region is

migrating from the cathode and is dominant over a greater region in the soil column. The

data shown in Figure 6-13 indicates that the system had not come to steady state with

respect to redox potential, even after three weeks of operation. The region at the cathode

did not show a varying redox potential, most likely because the aqueous solution at this

point would reach an equilibrium much faster than a mineral matrix.
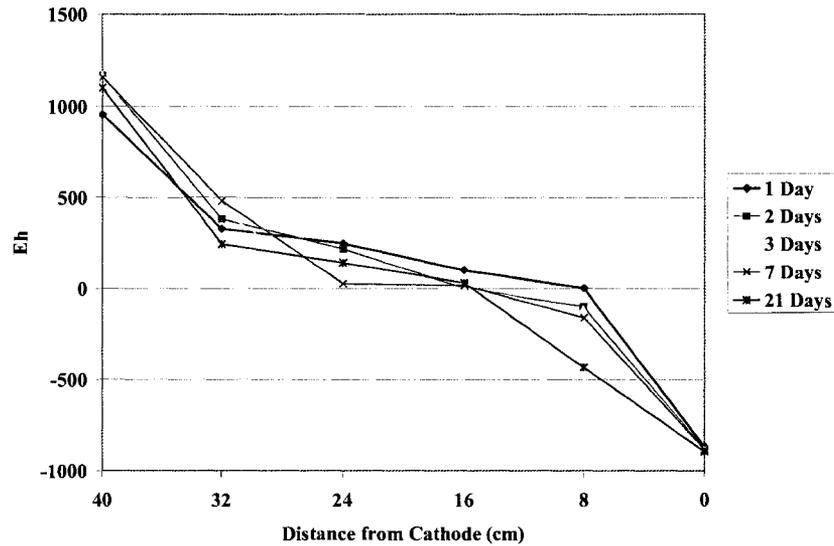
Figure 6-13: Unamended ER column: redox distribution across soil column

Concentrations of the five persistent compounds were monitored within the soil

column over the duration of the study and the results are presented in Figure 6-14. The

figure depicts the concentration distribution (normalized to the initial spiked

concentration) of each compound across the column throughout the study.
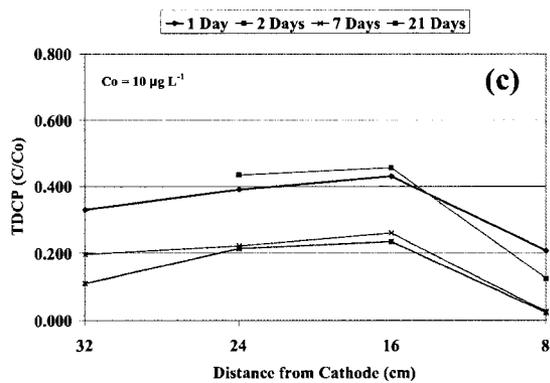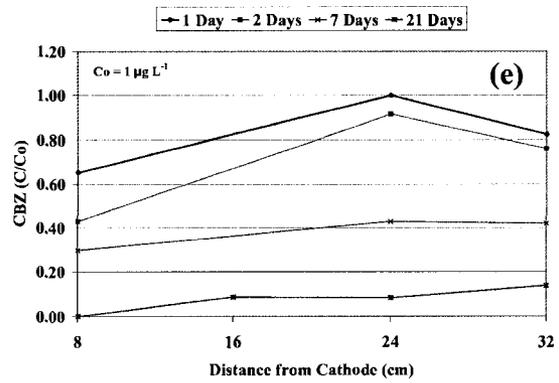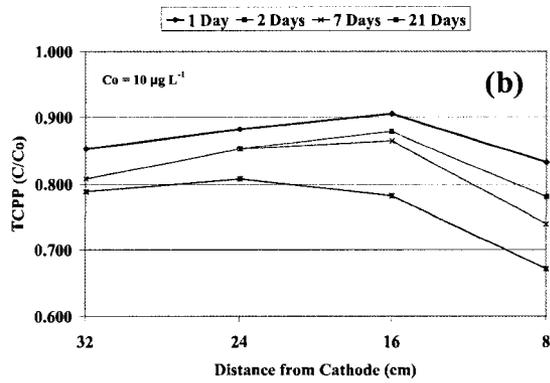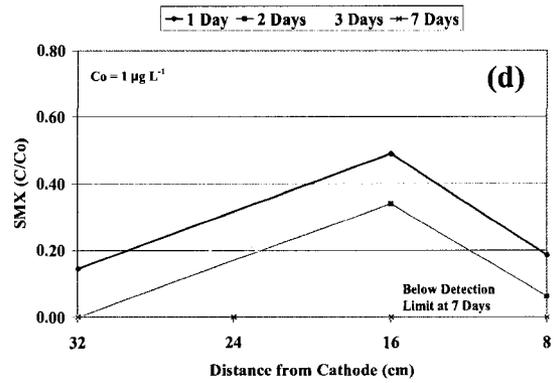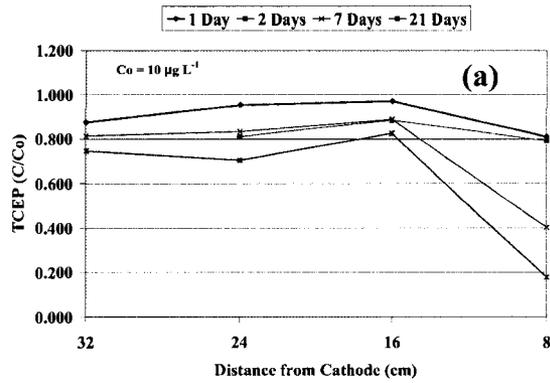
Figure 6-14: Unamended ER data (C/Co) across the soil column for compounds (a) TCEP, (b) TCPP, (c) TDCP, (d) SMX, and (e) CBZ.

Half-lives were calculated for each compound at the anode and cathode region using

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

(Eq. 6-12)

where k is the rate constant (day $^{-1}$) obtained from the slope of the plot of ln (C/Co) versus t. The compounds' half-lives and coefficient of determination (r^2) are presented in Figure 6-15 and Table 6-3. The R^2 value is the proportion of variability in a data set and is used by many to test how well the statistical model fit the set of observations. TCEP appeared to exhibit its greatest reduction at the cathode region where its half live was 9 days as compared to its half life at the anode which was an order of magnitude longer at 96 days. The reaction rates for TCPP were almost the identical reverse of what was seen for TCEP. TCPP's half-life at the cathode (72.2 days) was approximately an order of a magnitude slower than the reaction rate at the anode ($t_{\frac{1}{2}}$ = 8.8 days). CBZ had shorter half –lives at both electrodes with calculated reaction rates of 4 and 7.8 days for the anode and cathode, respectively. The substantial reducing conditions at the cathode region are likely the more effective redox condition for transformation of these compounds in an ER system because of the electrophilic nature of chlorinated functional groups.

(a)

$y = -0.0077x - 0.1367$
$R^2 = 0.9704$

$y = -0.0762x - 0.1793$
$R^2 = 0.9655$

Anode — Cathode

ln (Co/C)

Time (days)

(b)

$y = -0.0094x - 0.2102$
$R^2 = 0.8998$

$y = -0.0473x - 0.0165$
$R^2 = 0.9429$

Anode — Cathode

ln (Co/C)

Time (days)

(c)

$y = -0.0526x - 1.1386$
$R^2 = 0.9636$

$y = -0.1028x - 1.9648$
$R^2 = 0.7789$

Anode — Cathode

ln (Co/C)

Time (days)

(d)

$y = -0.0883x - 0.1427$
$R^2 = 0.9923$

$y = -0.2532x - 0.038$
$R^2 = 0.97$

Anode — Cathode

ln (Co/C)

Time (days)

(e)

$y = -0.6616x - 1.2223$
$R^2 = 0.9865$

$y = -3.843x + 1.8769$
$R^2 = 1$

Anode — Cathode

ln (Co/C)

Time (days)

Figure 6-15: Half-life data for anode and cathode regions of unamended ER experiments (ln C/Co vs. time) (a) TCEP, (b) TCPP, (c) TDCP, (d) CBZ, and (e) SMX.

Table 6-3: Unamended ER compound half-lives ($t_{1/2}$) for anode and cathode regions

	Anode		Cathode	
	$t_{1/2}$ (d)	R^2	$t_{1/2}$ (d)	R^2
CBZ	5.4	0.97	7.8	0.99
SMX	na	na	1.0	0.99
TCEP	96.3	0.97	9.0	0.97
TCPP	8.8	0.94	72.2	0.90
TDCP	13.1	0.96	6.7	0.78

TDCP was found to have the highest removal during ER, with the exception of SMX. However, previous partitioning studies indicated TDCP has a high affinity for adsorbing onto the surface of solids. Therefore, TDCP concentrations in the pore water were likely primarily due to TDCP's affinity for solid surfaces which occurred within the initial 24 hours and secondly, the reducing conditions within the soil. The calculated half-lives for TDCP of 13.1 and 6.7 days for the anode and cathode region, respectively, still give an a clear indication that TDCP is removed twice as faster under reducing conditions as opposed to oxidizing conditions. The reducing zone at the cathode resulted in the greatest removal of TDCP with values at the completion of the study near the limit of quantification.

Although the flame retardant data (TCEP and TDCP) showed less removal at the anode end, it is believed that some fraction of the original spiked compound was oxidized. The oxidation of the flame retardants could be due to the presence of hydroxyl radicals formed through a series of reactions as noted in Equations 6.1 – 6.4. The strong chlorine odors at the anode end of the column were likely due to the oxidation of the chlorinated flame retardants. Although chlorine may be a product in electrochemical processes due to the natural occurrence of the chloride ion, previous ER testing of other

non-chlorinated compounds using the same source water and soil were never encountered. The oxidization of the compounds may be due to the formation of hydroxyl radicals from hydrogen peroxide due to the classical electro-Fenton's reaction. Hydroxyl radicals are powerful oxidizing species which can degrade organic compounds into dehydrogenated or hydroxylated byproducts. Studies have confirmed the success of this process in the reduction chlorinated solvents (Bejankiwar et al. 2005).

Results of the two pharmaceuticals studied in the unamended electrokinetic soil columns are also presented in Figure 6-14. SMX was removed to a level below the limit of quantification at 168 hours. Since the amount of SMX at the anode was below the detection limit after the initial sampling, a half life could not be calculated. SMX which historically is not as persistent as the compounds in this study had C/Co levels of below 0.2 within the first 24 hours of the study and a half-life at the cathode of only 1 day. Westerhoff concluded that SMX was completely removed with chlorine and eighty eight percent removed with ozone using doses similar to those experienced at a WTP(Westerhoff et al. 2005). Huber determined second order rate constants for the successful removal reactions of sulfamethoxazole with ozone and OH· radicals in bench scale experiments (Huber et al. 2003).

However, carbamazepine proved to be more difficult to reduce than SMX in the ER column. As seen in Figure 6-14, CBZ resulted in consistently lower C/Co values in the anode region or oxidized area compared to other locations along the soil column. The half-life of CBZ at the anode was 4 days while the half-life at the cathode was twice as long (7.8 days). CBZ's reaction rate at the anode is 2 to 24 times faster than the other compounds (excluding SMX). Assuming a 24 hour contact time, which is approximately

the rate of groundwater flow in this soil type at 1 ft day⁻¹, only SMX will be removed at

both the anode and cathode.

It appears that CBZ is more readily oxidized than reduced in the ER column. The

presence of chlorine in the anode region due to the slight oxidation of the chlorinated

flame retardants and the presence of hydroxyl radicals may have contributed to the

oxidation of CBZ. Chlorine has been studied for the oxidation and removal of CBZ

under similar conditions found in WTPs with results indicating removal greater than

seventy five percent (Westerhoff et al. 2005).

Figure 6-16 depicts the relationship between the compound concentrations

(normalized to the initial spiked concentrations) in the cathode region throughout the

length of the experiment to the Eh values. The decrease in contaminant levels at the

cathode end appears to trend with both increasing experimental length and the increase in

reducing conditions in the cathode region.
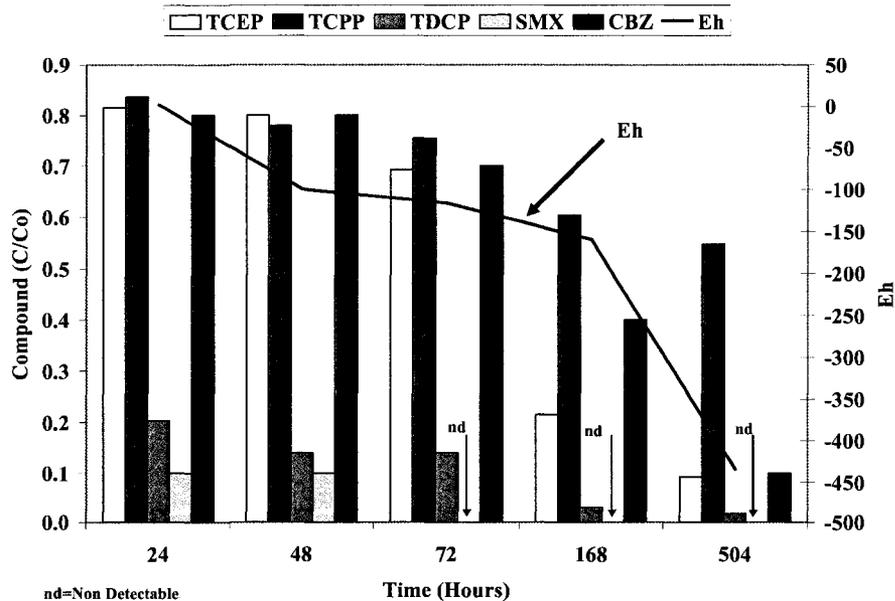
Figure 6-16: Unamended ER column cathode region: redox and compound relationship

6.4.3 Potassium Permanganate Electrokinetic Injection Experiment

Amended electrokinetic studies involve the use of varied electrolytes to manipulate the reactions at the electrodes and to also uniformly introduce amendments into the subsurface. The introduction of selected electrolytes to the subsurface can serve many purposes in an ER column including: pH neutralization of electrolysis reactions at the electrodes, nutrient supplements for microbial processes, contaminant conditioners such as chelating agents, or oxidizers for contaminant breakdown. An electrokinetic study using potassium permanganate as the cathode electrolyte and non-contaminant spiked groundwater was conducted to examine the transport efficiency of using electrokinetic injection (EI) for the introduction of the oxidizer permanganate. The transport study examined the effects of electrode neutralization on the transport efficiency. The study also examined the use of reverse polarization on the ER column and its effect on the redox cycling of manganese in the cathode electrolyte. The use of potassium permanganate as the electrolyte for the cathode in an ER system could potentially be a successful method to introduce an oxidant to the subsurface which can directly lead to the breakdown of the organic contaminant or react with hydroxyl ions to create hydroxyl radicals which will degrade the contaminant. A major issue with using permanganate oxidation for in-situ processes is non-uniform delivery to the subsurface. Electrokinetic injection was examined as an alternative delivery method.

The initial two column tests were conducted using groundwater as the electrolyte in the anode and a permanganate solution as the electrolyte in the cathode. The unamended column did not have pH adjustment at the electrodes, whereas the amended column used daily additions of sodium hydroxide at the anode and acetic acid at the cathode. The columns were operated at 1 V cm^{-1} for approximately six days. After 144

hours, the polarity was reversed on both columns by switching the positive and negative

leads from the power supply on each column. The columns were operated in the scenario

for an additional 144 hours. Bulk water quality parameters (pH, conductivity, redox, and

voltage drop) were measured at the completion of the standard power test (t=144 hours)

and after 144 hours of reversed polarity (t=288 hours).

Table 6-4: Electrokinetic injection (EI) experimental column summary

	Initial Simultaneous Column Tests		Final Simultaneous Column Tests	
	1	2	3	4
Anode Electrolyte	Groundwater	pH-adjusted Groundwater	pH-adjusted Groundwater	pH-adjusted Groundwater
Cathode Electrolyte	MnO_4^-	pH-adjusted MnO_4^-	pH-adjusted MnO_4^-	pH-adjusted MnO_4^-
Total Test Duration (hrs)	288	288	298	144
Reverse Polarization Frequency	Once @ 144 hrs	Once @ 144 hrs	5 x's over 298 hrs	None

The pH of the unamended standard polarity test was typical of pH values

dominated by the electrolysis of water reactions. The pH values of the unamended

reversed polarity tests were almost mirror opposites (Figure 6-17) as would be expected

since the polarity was reversed. The amended standard and reversed polarity columns

appeared to have consistent pH values between 6 and 9 which were due to the pH

adjustment at both electrodes. The conductivity in the unamended and the amended

standard tests had higher values at the anode and cathode most likely due to the

electromigration of ions within the column and due to pH adjustments for the amended

column (amended only). The conductivity in both the unamended and amended reversed

polarity column appeared to increase along the soil column and in the electrode

compartments.
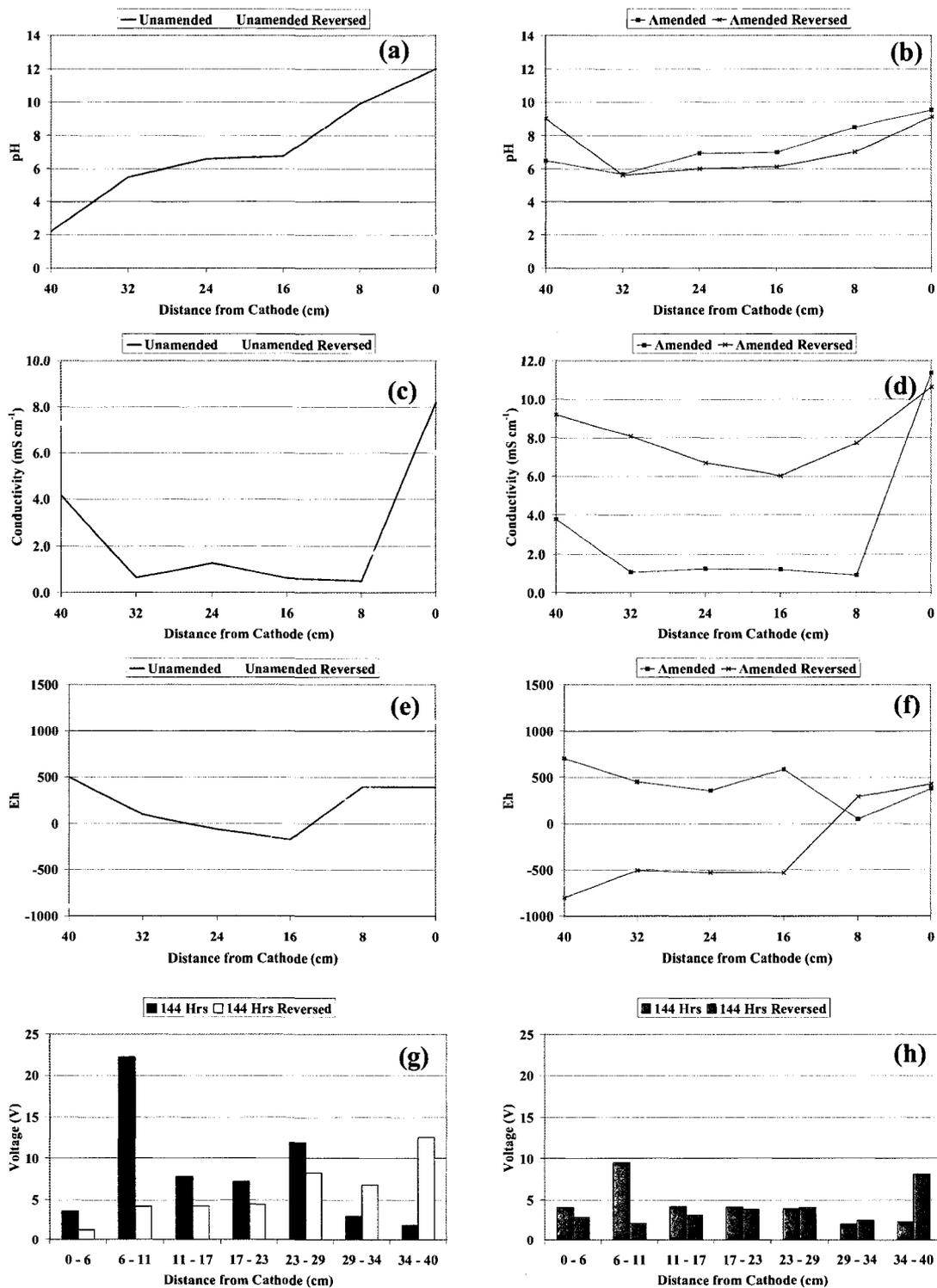
Figure 6-17: Bulk water quality parameter data for unamended (not pH-adjusted) and amended (pH-adjusted) KMnO₄ electrokinetic injection columns in standard and reversed Polarity scenarios: (a) unamended pH, (b) amended pH, (c) unamended conductivity, (d) amended conductivity, (e) unamended Eh, (f) amended Eh, (g) unamended voltage drop, (h) amended voltage drop

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The redox potential in the unamended standard polarity column indicates typical oxidation values at the anode and instead of reduced conditions at the cathode, oxidized conditions exist likely due to the presence of the oxidant permanganate. In the reverse polarized unamended column the anode-end experienced substantial reducing conditions because of the polarity reversal and the cathode-end experienced an even higher oxidizing environment. In the amended columns, the standard polarity test appeared to maintain highly oxidized values at the anode end. The oxidized region continued from the anode to approximately 2/3 of the way down the soil column toward the cathode end where the Eh dropped, but still maintained oxidized conditions. The amended reversed polarity exhibited a reversal at the anode from oxidized to reduced conditions as experienced in the unamended column scenarios. The amended reversed polarity increased the oxidizing environment at the cathode, but not as dramatically as in the unamended scenario which cannot be explained.

The voltage drop at the completion of the unamended standard polarity test revealed a large drop in the anode vicinity. This voltage drop is likely due to the migration of the negatively charged permanganate ion toward the anode and subsequent precipitation. The unamended reversed polarity voltage drop appeared to even out along the column except at the cathode region where voltage drop values increased likely due to migration and precipitation of manganese compounds immediately outside of the cathode electrode. The amended standard and reversed polarity columns tended to have minimal voltage drops across the column with the exception of higher values at the anode (standard polarity) and cathode (reversed polarity) similar to that of the unamended

columns, but not as severe. This may indicate the increased in voltage drop at the electrodes is due to the precipitation of manganese compounds due to redox reactions as opposed to pH conditions within the column. The pH-adjusted columns resulted in lower voltage readings than the unamended which resulted in lower power required for column operation.

Permanganate distribution was monitored by measuring the concentration of manganese along the column at 144 hours in the unamended and amended modes for the standard polarity tests (immediately before reversing the polarity) and 144 hours after reversing the polarity of the original columns. At the completion of the experiment (t=288 hours), soil samples were removed from the unamended and amended columns, digested, and analyzed for manganese. Background manganese concentrations in the groundwater and soil were less than 0.1 mg L^{-1} and 2 mg kg^{-1}, respectively.

Figure 6-18 indicates transport of permanganate under unamended and amended conditions, with the amended column having slightly more uniform results across the column. Visual inspection of the column noted the transport of manganese across the soil column within the first 24 hours of both the unamended and amended column tests. The coloration originally was pink-purple in color but turned brown within 48-72 hours in both unamended and amended columns.
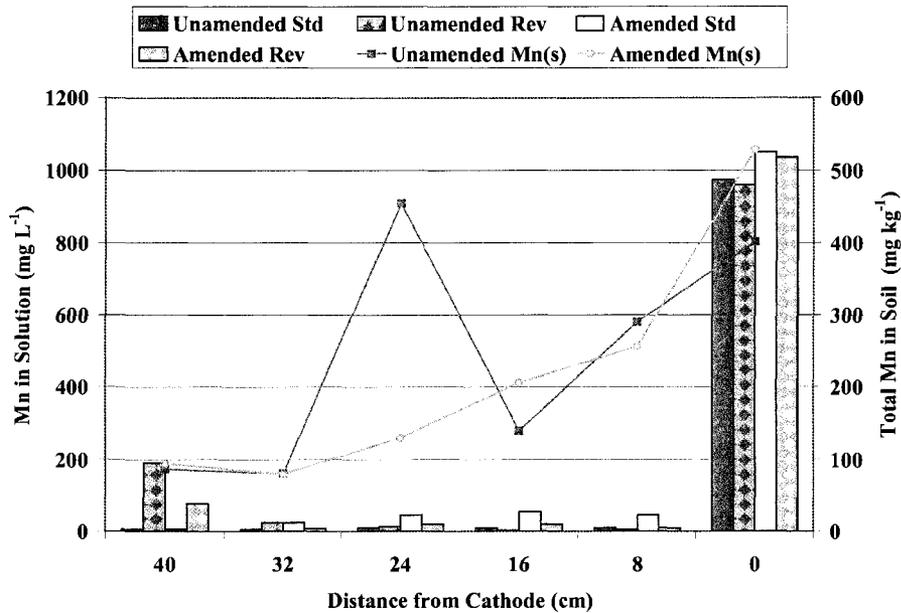
Figure 6-18: Unamended and amended ER columns under standard and reversed polarity: Mn distribution (aqueous and soil) across the column

The cathode also contained a large amount of dark deposits at the bottom of the electrode compartment which continually increased over the length of the unamended and amended standard polarity column testing. It is likely that the permanganate ions in the cathode accepted the electrons introduced by the power supply and were consequently reduced to MnO_2 solids in the cathode and in the cathode-impacted region. This likely reaction would prohibit the efficient transport of permanganate because the solid would likely precipitate out and cause excessive resistance within the column. In addition, MnO_2 is not charged and therefore would not be transported using electromigration. The effect of the polarization reversal appeared to decrease the aqueous manganese concentration in the cathode region and increase the concentration in the anode region. The presence of electroosmotic flow in the direction from the anode to the cathode may have negatively impacted the electromigration of the permanganate ion in the opposite

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direction. Potential future studies on transport should involve permanganate as the electrolyte in the anode to use electroosmotic flow to transport the ion across the column.

The polarity reversal in the initial studies was performed after 144 hours of operation and continued in the reversed setting for an additional 144 hours. A second set of tests using two separate columns was performed to determine the impact on permanganate concentration in the catholyte under a more frequent polarity reversal scenario. Figure 6-19 displays data from two electrokinetic columns: one operated at the uniform, standard polarity scenario and a second operated under an alternating polarity reversal scenario. The column operated under the standard polarity scenario completely reduced the initial permanganate catholyte solution within 144 hours. The alternating polarity column was able to continue operating for an additional 120 hours with permanganate solution in the cathode. The permanganate solution in the uniform polarity column appeared to have an average half-life of one day.
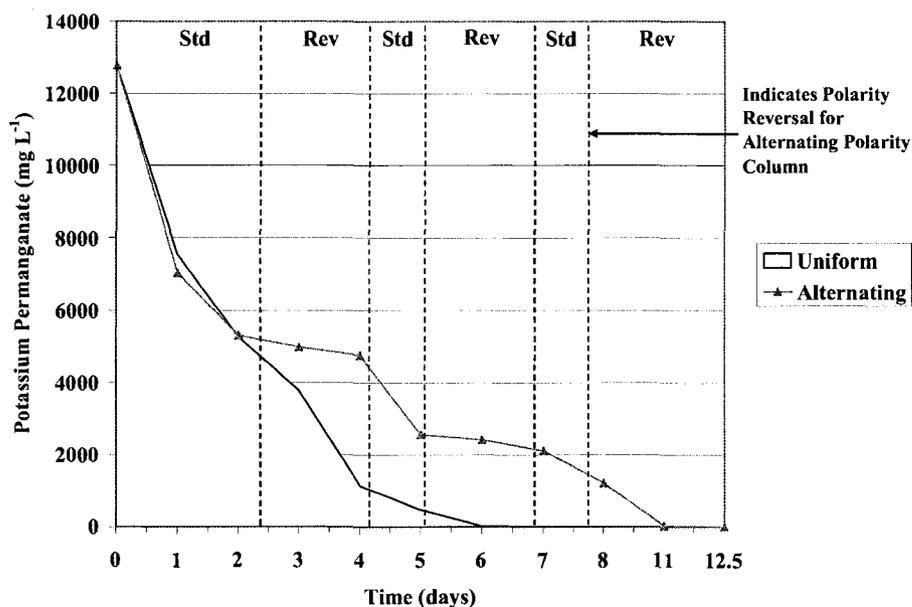
Figure 6-19: ER columns under uniform and alternating standard/reversed polarity scenarios: cathode electrolyte potassium permanganate concentration

The results in Figure 6-19 indicate that polarity reversal appears to lengthen the duration between necessary additions to the cathode electrolyte by oxidizing previously reduced manganese. It is possible that an increase in reversals, or lengthening reversal intervals and shortening standard intervals could preserve the permanganate solution in the cathode even longer than exhibited in this study.

Results from the transport study indicate that the pH-adjusted electrokinetic columns appeared to have greater and more uniform concentrations of manganese across the column. The presence of electroosmotic flow in the opposite direction of the electromigration of the oxidant may have negatively impacted overall permanganate transport. A potential remedy to this problem would be to utilize the EO flow and have permanganate as the electrolyte in the anode in order to optimize both electromigration and electroosmosis mechanisms in the transport of the oxidant. Reverse polarization

proved to re-oxidize previously reduced forms of permanganate to minimize the rate at which permanganate decreased in the cathode.

6.4.4 Amended Electrokinetic Remediation Columns

Amended electrokinetic remediation column studies were conducted to determine the effect of using a permanganate solution as the cathodic electrolyte. This column study used a manual pH neutralized anode electrolyte (groundwater) and an acidified permanganate solution in the cathode. As displayed in Figure 6-20, the addition of permanganate did not appear to have a major effect on the removal of the persistent compounds. Removal results from this set of column experiments were not greater than the results from unamended column experiments as noted in Figure 6-14. It is likely that the transport of permanganate across the column was not adequate to have permanganate react directly with the organic compound or with hydroxyl ions to form the strong oxidizing species, hydroxyl radicals. Since the columns were only sampled twice during the experiment, half-lives were not able to be calculated for this test.
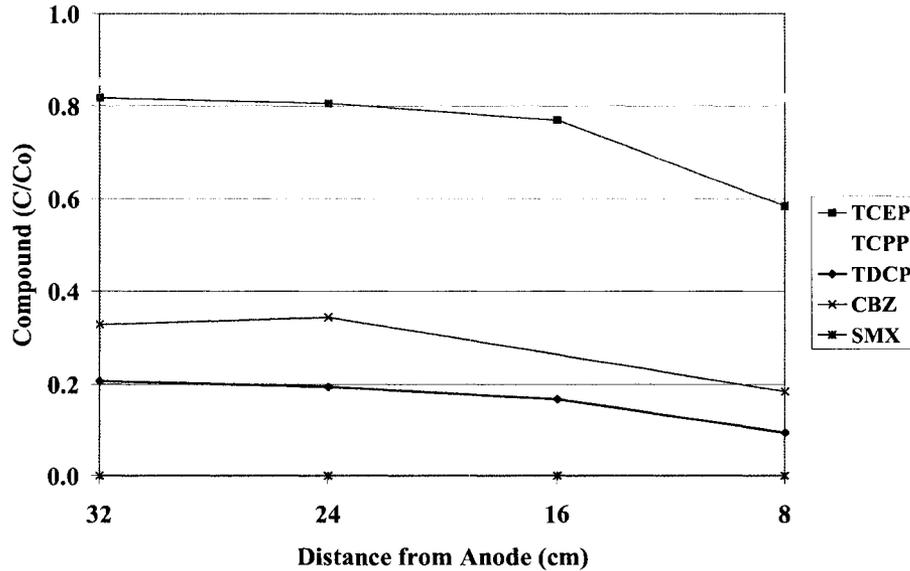
Figure 6-20: Amended ER columns data (C/Co) across the soil column for compounds TCEP, TCPP, TDCP, SMX, and CBZ using pH-adjusted permanganate and groundwater in the cathode and anode, respectively

6.5 Conclusions

The remediation of five persistent contaminants, two pharmaceuticals and three flame retardants, were investigated in three different column studies including simulated enhanced ARR, unamended electrokinetic remediation (ER), and amended electrokinetic remediation. In addition, a study was conducted to determine the efficacy of using electrokinetics to introduce the proposed amendment, potassium permanganate, to the subsurface. The persistent contaminants examined were the pharmaceuticals carbamazepine and sulfamethoxazole and the flame retardants tris(2-chloroethyl)-phosphate, tris-(2-chloro-, 1-methyl-ethyl)phosphate, and tris-(2-chloro, 1-chloromethyl-ethyl)phosphate.

- Enhanced ARR was successful in reducing the flame retardants due to the adsorption qualities of the WTR and the reduced conditions within the column.
  - TCPP and TCEP had over 70 and 33% removal in the WTR-amended column
  - TDCP showed its affinity for the solid phase in the results from the control column. Approximately 95% of the compound was removed in the abiotic column which led to effluent TDCP levels below the limit of quantification in the biotic column.
- Unamended electrokinetic remediation created a reducing zone at the cathode which reduced all of the compounds within this area and an oxidized region at the anode which had some effect on compound levels.
  - Based on the half-lives of CBZ, SMX, TCEP, TCPP, and TDCP (7.8, 1, 9, 72.2, and 6.7 days, respectively) at the cathode region only SMX will be reduced to half of the initial level within 24 hours contact time (approximately 1 ft/day in this soil type).
  - Sulfamethoxazole was removed across the entire column (below the limit of quantification) at 168 hours.
  - TCEP and TDCP showed less reduction at the anode end, however, based on their cathode half-lives of 9 and 6.7 days, respectively, considerable reduction of the compounds can occur within reasonable RBF contact time. The oxidization of the compounds at

the anode may be due to the formation of hydroxyl radicals from

hydrogen peroxide due to the classical electro-Fenton's reaction.

- CBZ resulted in consistently lower C/Co values in the anode

  region or oxidized area compared to other locations along the soil

  column. At the completion of the study, CBZ values at the anode

  were near the limit of quantification. CBZ values across the

  remainder of the column were below 20% of the originally-spiked

  solution. The calculated half life of CBZ at the anode (4 days)

  indicates that considerable reduction of the initial compound

  concentration can occur within several days.

- An electrokinetic transport study on the delivery of the oxidant

  permanganate to the subsurface (using non-spiked groundwater) was

  conducted to examine transport efficiency, the neutralization of the anode

  and cathode electrolytes (groundwater and permanganate), and effects of

  reverse polarization on the ER column.

  - The pH-adjusted electrokinetic columns appeared to have higher

    and more uniform concentrations of manganese across the column.

  - Reverse polarization proved to re-oxidize previously reduced

    forms of permanganate to minimize the rate at which

    permanganate decreased in the cathode.

- Amended electrokinetic remediation columns used a pH-neutralized

  groundwater and potassium permanganate solution as the electrolyte in the

  anode and cathode compartments, respectively. Although there was

evidence of permanganate transport within the column, the presence of the oxidant did not improve contaminant removal results when compared to the unamended ER column results.

- Compound removal values across the column (C/Co) ranged from TCPP with 0.8-0.9 to SMX (below LOQ). TCEP and TDCP C/Co values across the column ranged from 0.8-0.6 and 0.2-0.1, respectively. CBZ removal rates within the column at the completion of the study were approximately 30-20% of the originally spiked concentration.

7.0   Conclusion

The demand for inexpensive and reliable water treatment technologies continues

to increase as the number of contaminants grows and their associated fate and transport

mechanisms become more complex. The primary objective for this research was to

examine the use of enhanced in-situ methods for the remediation of arsenic and several

persistent organic contaminants. The tasks for fulfilling this objective involved

developing an experimental bench-top design capable of successfully running

electrokinetic experiments, completing unamended and amended arsenic electrokinetic

remediation experiments, conducting amended aquifer recharge and recovery-simulated

column experiments, completing unamended and amended electrokinetic remediation on

several persistent organic contaminants, and lastly simulating electrokinetic transport of

permanganate within an ER column. The following sections summarize the findings of

the research.

7.1   Acetate Transport

The electrokinetic injection of acetate was tested under sand, clay, and

heterogeneous soil conditions. Electromigration was the main mechanism responsible for

the uniform transport of acetate across the soil columns. Effective transport rates of

acetate can be achieved in sand columns under current densities as low as 1.33 A/m^2.

There was no measurable electroosomotic flow in the direction of anode to cathode and

therefore, the electromigration of acetate proceeded uninhibited in the sand column.

Large electroosmotic flows were detected in the cathode (75 ml d^{-1}) in the clay columns

which were operated under a current density of 5.33 A/m^2. Although the concentration of

acetate was detected in all sample ports across the column, the presence of non-uniform

EO flows may contribute to the slightly non-uniform distribution of acetate across the column. Mixed media columns containing layered sand and clay under a current density of 1.33 A/m^2 achieved effective transport of acetate. Acetate concentrations followed the same trends as exhibited in the individual sand and clay column tests. Electroosmotic flow rates of 35 ml d^{-1} were measured at the cathode and had some impact on the variability of acetate within the column. Results from the mixed media columns are indicative of conditions of aquifers in the field (mostly sand with clay lenses). The hypothesis that EI is an effective method for introducing charged amendments to the subsurface, which could include pH neutralizers, oxidizers, or nutrient supplements, was supported.

7.2   Arsenic Removal

The electrokinetic remediation of soil contaminated with arsenic was tested under unamended conditions (no pH conditioning at the electrodes) and amended conditions (pH neutralization at the electrodes). Electromigration was the main mechanism responsible for arsenic removal in the unamended column and both electroosmosis and electromigration transport mechanisms were responsible for arsenic removal in amended column tests.

Unamended ER promoted electromigration of anionic arsenic species toward the anode region, however, premature precipitation of the arsenic complexes created a large resistance in the column's anode region which increased the voltage drop and consequently, power demand. The alkaline front in the unamended test appeared to dominate across most of the column. The high pH values of the pore water across the column promoted dissolution of solid arsenic species and promoted electromigration of

arsenic towards the anode. Although it is sometimes desirable to immobilize and precipitate the contaminant in the soil, ultimate removal from the system would be most ideal to prevent potential reversible reactions which would promote the dissolution of arsenic back into the groundwater.

Amended ER promoted arsenic removal from the pore fluid through both electromigration and electroosmosis mechanisms. Only five percent of the original arsenic concentration remained in the pore fluid upon completion of the experiment, however, since the hydroxide ions were neutralized at the cathode, significant dissolution of arsenic species on the soil did not occur, and arsenic species in the soil remained high. Due to the neutralization of the electrolysis of water at both electrodes, the voltage drop across the amended column was considerably less than in the unamended column suggesting that less power is required for amended ER operation.

Based on the experimental data, the most practical approach for using ER in the removal of arsenic would include amendments, but only at the anode. In applying sodium hydroxide to the anode the low pH created due to the electrolysis of water would be neutralized and the hydroxide ion would dominate across the entire column. This would be beneficial because the hydroxide ion would promote complete arsenic desorption across the column and uninhibited electromigration would allow complete transport of arsenic to the anode electrode compartment. In addition, the arsenic species would not precipitate out near the anode region and cause a large source of resistance. Therefore, an increase in power would not be necessary. Periodic electrode compartment flushing and electrode cleaning would be required to remove the arsenic and maintain good electrode conductivity. The hypothesis that ER can be successfully used to

remediate arsenic-contaminated soils using electromigration and electrolysis of water mechanisms was supported.

7.3   QA Characterization for the Analyses of Organic Compounds

Analytical methods were developed for the measurement of two pharmaceuticals, sulfamethoxazole (SMX) and carbamazepine (CBZ) and three flame retardants tris-(2-chloro-, 1-methyl-ethyl)phosphate (TCPP), tris-(2-chloro, 1-chloromethyl-ethyl)phosphate (TDCP) and tris-(2-chloroethyl) phosphate (TCEP) in aqueous and solid samples. Solid phase extraction (SPE) was used to clean and concentrate the sample. The pharmaceuticals were analyzed using high performance liquid chromatography equipped (HPLC) with a tandem mass spectrometer (MS-MS). The flame retardants were analyzed on a gas chromatograph (GC) equipped with a mass spectrometer (MS). Method development involved a methodical process in which acceptable compound recoveries during sample preparation were achieved, adequate limit of quantifications were established, and acceptable chromatography and spectrometry method programs were created. This process is a critical first step that all subsequent data interpretation will rely upon.   Additional analytical analyses including the measurement of the compound affinity for the aqueous, solid, and colloidal phases was completed. This data is helpful in determining behaviors of organic compounds. If the compound has the ability to partition to colloidal particles, colloidal-facilitated transport would increase the mobility of the compound and enhance the level of containment or treatment of the substance. Interpreting data without this crucial information could lead to inaccurate or misleading results, which could lead to a lack of treatment or over-engineered treatment

schemes for the wrong phase (aqueous vs. solid). No colloidal-sized partitioning data for flame retardants or CBZ has yet to be reported in literature.

And lastly, sources of flame retardant background contamination were traced to low-grade plastic water storage containers and a plastic electric heater. Initial data from ER experiments contained inflated and inconsistent values and led to a study to determine the source. The broad application of flame retardants results in wide environmental contamination by multiple transport means. The ubiquitous nature of flame retardants requires careful planning regarding compound sampling and analyzing. Reporting inaccurately-inflated data can have major impacts on successfully proving research hypotheses or even simply acquiring data which has any semblance of meaning. The hypothesis that determining a compound's partitioning characteristics is essential for successful experimental research is accurate.

7.4   Remediation of Persistent Organic Contaminants Using Enhanced In-situ Methods

The remediation of five persistent contaminants, two pharmaceuticals (SMX and CBZ) and three flame retardants (TCEP, TCPP, and TDCP) were investigated in three different column studies including simulated enhanced ARR, unamended electrokinetic remediation (ER), and amended electrokinetic remediation. In addition, a study was conducted to determine the efficacy of using electrokinetics to introduce the proposed amendment, potassium permanganate, to the subsurface. Enhanced ARR was successful in reducing the flame retardants due to the adsorption qualities of the WTR and the reduced conditions within the column. Unamended electrokinetic remediation created a reducing zone at the cathode which reduced all of the compounds within this area and an oxidized region at the anode which also reduced compound levels. Conventional

treatment methods have had little success with obtaining any considerable reduction in flame retardant concentrations. Sulfamethoxazole was removed across the entire column (below the limit of quantification) at 168 hours. At the completion of the study, CBZ values at the anode were near the limit of quantification. CBZ values across the remainder of the column were below 20% of the originally-spiked solution.

An electrokinetic transport study on the delivery of the oxidant permanganate to the subsurface (using non-spiked groundwater) was conducted to examine transport efficiency, the neutralization of the anode and cathode electrolytes (groundwater and permanganate), and effects of reverse polarization on the ER column. Reverse polarization proved to re-oxidize previously reduced forms of permanganate to minimize the rate at which permanganate decreased in the cathode. Amended electrokinetic remediation columns used a pH-neutralized groundwater and potassium permanganate solution as the electrolyte in the anode and cathode compartments, respectively. The presence of the oxidant did not significantly improve contaminant removal results in comparison to the unamended ER column results.

The hypothesis that implementation of unamended electrokinetic remediation would be effective in removing persistent compounds at a river bank filtration site with sufficient hydraulic detention times is true with varying degrees of contaminant removal. However, the hypothesis that utilizing permanganate as the electrolyte in amended ER would increase removal of persistent organic contaminants did prove to be accurate.

7.5   Closing Remarks
The world's increasing need for safe, aesthetically-pleasing drinking water, has prompted interest in natural, in-situ treatment approaches for water purification. This

research has focused on enhancing traditional in-situ methods to remove persistent inorganic and organic contaminants. These enhanced methods included electrokinetic remediation-supplemented river bank filtration and water treatment residual-amended aquifer recharge and recovery. Results of this research allow us to conclude that electrokinetic remediation is a promising approach for the removal of arsenic from contaminated soil and groundwater. Electrokinetic remediation was also successful in remediating (to varying degrees) groundwater contaminated with pharmaceuticals SMX and CBZ and flame retardants TCEP, TCPP, and TDCP. These compounds are continually reported to be the most persistent compounds repeatedly found in surface, ground, and drinking waters. And lastly, water treatment residual- amended ARR was successful in reducing persistent flame retardants due to the residuals' adsorption characteristics and the microbial active, reducing region within the soil. This successful treatment method is a passive in-situ technology utilizes a readily-available waste product that is often disposed of in municipal landfills.

8.0 References

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9.0   Appendix

This appendix contains information and data pertinent to the main experimental activities discussed in Chapters 3, 4, 5, and 6. The appendix is divided into three sections: acetate transport data, arsenic removal data, and persistent organic contaminants removal data.

9.1 Acetate Transport Data

Spl	VA	V1	V2	V3	V4	V5	V6	pA	pC	CA	CC	Ac	Sample	IC	DF	Calc	Adj
SL1	34.90	19.78	17.48	13.36	9.98	5.75	3.04	3.64	2.87	123	595	1,057	C2SP1	1714	1	1,714	1,715
SL2	47.50	29.10	20.88	15.95	11.45	6.99	4.08	3.28	2.89	199	559	1,357	C2SP2	1357	1	1,357	1,357
SL3	39.80	23.77	17.55	11.25	7.95	4.55	2.66	3.35	2.85	195	564	1,369	C2SP3	1369	1	1,369	1,370
SL4	37.90	23.25	18.22	11.85	8.37	4.97	2.88	4.58	2.90	203	542	1,714	C2SP4	1057	1	1,057	1,058
SL5	33.50	19.50	16.60	10.58	7.32	4.32	2.35	3.65	2.84	169	585	---	C2SP5	760	1	760	761
SL6	37.70	24.45	21.38	14.56	9.85	5.65	2.80	3.73	2.96	220	538	---	C2SP6	741	1	741	741
SL7	27.40	18.35	15.95	11.45	7.65	4.53	2.91	4.06	2.90	186	621	---	C2SP7	649	1	649	649
SL8	35.80	27.58	23.66	17.15	11.26	6.37	3.08	4.95	2.82	227	594	---	C2SP8	690	1	690	690
SL9	36.00	24.32	21.42	15.99	11.22	6.41	3.79	4.24	3.13	191	540	---	C2SP9	810	1	810	810
SL10	38.30	26.20	23.00	17.55	12.35	7.08	3.75	4.04	2.92	198	555	---	C2SP10	750	1	750	750
SL11	37.70	25.98	22.83	17.33	12.40	7.49	4.30	3.94	2.90	200	535	---	C2SP10	733	1	733	733
SL12	35.70	23.52	20.87	15.32	11.02	6.71	4.10	3.63	2.91	198	524	---	C2SP11	744	1	744	744
SL13	42.40	29.83	26.55	19.30	13.68	8.16	4.80	3.80	2.99	208	518	---	C2SP12	627	1	627	627
SL14	34.10	27.47	24.55	18.35	13.02	7.79	4.57	4.79	3.04	340	518	---	C1SP1	94	5	471	471
SL15	33.60	26.70	24.18	18.49	12.90	7.55	4.11	4.70	2.92	333	523	---	C1SP2	115	5	574	574
SL16	37.70	28.18	25.65	20.35	14.84	8.55	4.58	4.33	3.04	292	515	---	C1SP3	96	7	687	688
SL17	37.10	27.55	24.65	19.67	15.14	9.30	5.11	4.02	3.13	260	523	---	C1SP4	79	17	1,312	1,313
SL18	46.50	29.88	24.25	19.05	14.68	9.88	6.03	3.46	3.22	252	575	---	C1C 4.09	78	100	7,752	7,754
SL19	28.80	20.68	17.95	12.52	9.39	6.14	3.98	3.86	3.01	275	508	---	C1C 4.09	90	100	8,989	8,992
SL20	39.30	33.32	29.54	20.62	13.88	8.62	5.29	4.82	3.11	513	531	---	C1C 4.11	80	100	7,975	7,977
SL21	33.40	26.22	23.77	19.65	15.44	9.75	5.40	4.15	3.19	447	560	---	C1C 4.12	84	100	8,405	8,408
SL22	29.30	22.70	20.47	16.17	12.50	8.22	4.98	4.27	3.45	471	587	---	STD 4	31	1	31	31
SL23	35.40	21.60	18.82	14.70	11.66	7.02	4.42	4.20	3.10	374	548	---	C1C 4.14	81	100	8,111	8,113
SL24	31.20	17.62	15.98	12.00	9.08	5.75	3.80	4.94	3.30	572	600	---	C2A 3.18	8	10	82	82
SL25	23.54	18.36	16.90	13.12	9.80	6.30	4.40	5.10	3.36	610	655	---	C2A 3.19	11	10	109	109
SL26	22.90	18.80	17.40	13.86	10.25	6.50	4.00	3.93	3.86	680	558	---	C2A 3.20	12	10	124	124
SL27	14.80	11.98	11.17	9.20	7.08	4.63	3.16	5.56	3.20	691	578	---	C2A 3.21	13	10	132	132
SL28	24.30	18.92	17.45	14.50	11.70	7.04	4.33	4.81	3.10	571	556	---	C2A 3.23	20	10	198	198
SL29	23.60	17.74	15.83	12.80	10.15	6.40	4.05	4.31	3.27	469	625	---	C2A 3.22	15	10	146	146
SL30	23.80	17.19	15.50	11.95	9.40	6.18	3.99	4.54	3.06	530	524	---	C2A 3.24	23	10	225	225
SL31	24.70	18.12	16.35	12.60	9.70	6.50	4.40	4.34	3.26	499	602	---	C2A 3.24	23	10	226	226
CL1	55.10	47.32	31.55	19.92	15.88	10.35	5.20	2.50	3.70	1456	1463	471	C2A 3.25	26	10	260	260
CL2	80.80	74.10	60.00	27.28	16.66	9.93	4.87	2.41	3.80	1256	1781	574	C2A 3.27	35	10	348	348
CL3	140.00	117.20	109.30	78.50	55.40	30.21	6.50	2.36	4.39	1169	1543	687	C2A 3.29	34	10	344	344
CL4	126.50	118.10	102.40	75.60	52.50	22.40	4.90	2.57	3.56	1124	1077	1312	C2A 3.30	35	10	349	349
CL5	126.20	119.10	103.10	72.80	46.80	19.70	3.60	2.78	3.70	1255	1292	---	STD 4	36	1	36	36
CL6	126.20	114.80	102.70	74.40	52.80	25.95	5.70	3.32	3.55	1265	983	---	C1A 4.11	3	1	3	3
CL7	126.20	119.50	106.70	79.80	57.66	28.25	6.70	3.72	3.68	1310	977	---	C1A 4.12	2	1	2	2
CL8	126.20	93.40	80.10	47.90	34.56	17.77	5.14	3.24	3.22	247	634	---	C1A 4.14	4	1	4	4
CL9	126.20	89.80	80.05	58.50	42.75	20.39	5.29	4.45	3.37	144	705	---	C2A 3.18	8	10	82	82
CL10	124.00	111.90	101.60	68.20	42.08	16.28	4.50	3.07	3.35	419	680	---	C2A 3.20	11	10	114	114
CL11	123.00	110.30	100.20	74.50	51.50	25.35	7.35	3.19	3.16	327	583	---	C2A 3.22	14	10	145	145
CL12	120.00	100.50	89.50	66.80	47.30	22.39	5.40	3.43	3.19	151	604	---	C2A 3.24	24	10	243	243
SC1	113.40	96.80	83.20	62.20	43.07	24.60	11.00	2.87	3.45	475	936	835	C2A 3.27	32	10	320	320
SC2	112.00	98.30	85.70	57.00	41.53	24.38	11.17	2.86	3.32	607	715	875	C2A 3.29	32	10	321	321
SC3	93.00	85.40	76.30	55.00	37.90	25.30	11.80	10.95	3.12	1584	603	1940	C2A 4.01	48	10	483	483
SC4	70.00	58.92	49.00	36.85	25.60	15.20	7.97	4.37	3.42	790	836	2097	C2A 4.01	51	10	513	513
SC5	71.00	58.50	49.30	30.60	26.80	16.28	9.00	4.23	3.37	628	780	1544	C2A 4.11	43	10	431	430
SC6	88.00	67.00	52.50	29.50	18.30	13.00	7.44	3.09	3.66	569	1045	2095	C2A 4.12	41	10	415	415
SC7	107.00	88.00	71.00	42.50	27.12	16.30	8.70	2.84	3.67	685	1167	2259	C2A 4.14	49	10	487	486
SC8	79.50	67.40	58.00	44.00	30.30	18.60	9.30	4.00	3.61	791	970	2302	C3A 4.25	185	1	185	185
SC9	69.60	61.90	54.75	40.38	29.50	19.00	10.40	4.43	3.32	1250	758	2043	C3A 4.28	378	1	378	378
SC10	70.40	55.40	44.60	34.40	25.00	15.50	8.20	3.52	3.56	1038	1052	2153	C3A 4.29	405	1	405	405
SC11	64.50	56.40	49.20	33.30	25.20	16.50	8.90	4.38	3.40	1347	860	2410	C3A 5.02	911	1	911	911
SC12	62.50	54.55	47.43	35.20	23.80	15.25	8.22	4.37	3.59	1344	1090	2483	C3A 5.03	981	1	981	981
SC13	60.00	50.80	45.80	34.35	24.45	15.13	8.23	4.40	3.15	1281	845	---	C3A 5.06	104	10	1,044	1,043
SC14	60.50	52.52	46.75	35.10	25.25	16.27	9.07	4.23	3.38	1410	1074	---	C3A 5.09	135	10	1,351	1,350
SC15	46.00	39.45	35.45	27.00	19.30	12.87	8.30	4.50	3.20	1635	866	---	C3A 5.09	138	10	1,380	1,379
SC16	41.00	35.92	32.20	25.20	17.90	11.68	6.46	4.43	3.69	1595	1240	---	STD	16	1	16	16
													C3A 5.11	142	10	1,421	1,420
													C3A 5.12	142	10	1,420	1,420

U.S. SILICA
Sands of Time

OK-110

UNGROUND SILICA

PLANT: MILL CREEK, OKLAHOMA

TYPICAL VALUES
(% RETAINED ON SIEVE)

U. S. A. SIEVE ANALYSIS
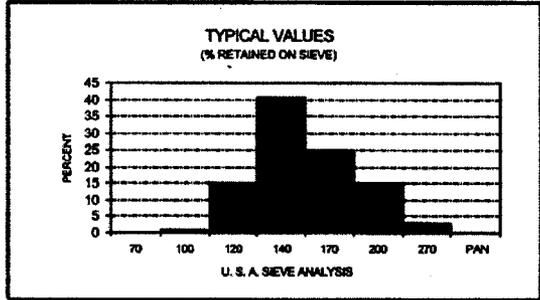
USA STD SIEVE SIZE		TYPICAL VALUES		
		% RETAINED		% PASSING
MESH	MILLIMETERS	INDIVIDUAL	CUMULATIVE	CUMULATIVE
70	0.212	0.2	0.2	99.8
100	0.150	1.0	1.2	98.8
120	0.125	15.0	16.2	83.8
140	0.106	40.8	57.0	43.0
170	0.088	25.0	82.0	18.0
200	0.075	15.0	97.0	3.0
270	0.053	3.0	100.0	0.0
PAN		0.0	100.0	

$AFS^{(1)}$ ACID DEMAND (@pH 7) 0.5
AFS GRAIN FINENESS 119
COLOR.. WHITE
GRAIN SHAPE .... ROUND
HARDNESS (Mohs) 7

(1) AMERICAN FOUNDRYMEN'S SOCIETY

MELTING POINT (Degrees F).................................... 3100
MINERAL .... QUARTZ
MOISTURE CONTENT (%)... <0.2
pH 7.2
SPECIFIC GRAVITY.. 2.65

SiO_2 (Silicon Dioxide).................................... 99.7
Fe_2O_3 (Iron Oxide)................................... 0.018
Al_2O_3 (Aluminum Oxide)................................. 0.10
TiO_2 (Titanium Dioxide)............................... <0.01
CaO (Calcium Oxide) .... <0.01

MgO (Magnesium Oxide)... <0.01
Na_2O (Sodium Oxide)... <0.01
K_2O (Potassium Oxide)... <0.01
LOI (Loss On Ignition).. 0.1

DISCLAIMER: The information set forth in this Product Data Sheet represents typical properties of the product described; the information and the typical values are not specifications. U.S. Silica Company makes no representation or warranty concerning the Products, expressed or implied, by this Product Data Sheet.

WARNING: The product contains crystalline silica - quartz, which can cause silicosis (an occupational lung disease) and lung cancer. For detailed information on the potential health effect of crystalline silica - quartz, see the U.S. Silica Company Material Safety Data Sheet.

March 16, 2000

U.S. Silica Company   P.O. Box 187, Berkeley Springs, WV 25411-0187   (304) 258-2500

Thiele Kaolin Company
Reedy Creek Division
P.O.Box 337
Wrens, GA 30833-0337
706-547-2593
FAX 706-547-2786

Thiele

August 1, 2005

Ms. Mary Beth Talty
Colorado State University
Civil Engineering Department
1320 Campus Delivery – A211 ERC
Ft. Collins CO 80523

As requested by you, we are forwarding the materials listed below at no charge and look forward to your comments when your evaluation is completed. Please contact us if you need more information or samples. We appreciate your interest in our clays.

GRADE	Kaofine 90		Ref. 535847	
FORM	Spray Dried			
SAMPLE IDENTIFICATION	Lot #129-R			
DATE SHIPPED	8/2/2005			
AMOUNT	2 lbs.			
BRIGHTNESS, G.E.	91.1			
MOISTURE, %	.9			
SOLIDS, %	70.0			
PARTICLE SIZE, % < 2μ	98.9			
pH (Dry clay tested at 20% solids, Slurry tested at solids shipped)	7.2			
SCREEN RESIDUE, % RETAINED 325 MESH	.0010			
BROOKFIELD VISCOSITY, cP	220			
HERCULES VISCOSITY	1.1 dynes			
Sample Request No. 7-29-2005-171811				

Salesman:
Enclosures: MSDSheet
   C: Customer Service
     QC
     S. Ahrens
     File

Sincerely,

C.

Quality Control Supervisor
Reedy Creek Division
Thiele Kaolin Company

Thiele

FORM PC

MATERIAL SAFETY DATA SHEET

THIELE KAOLIN COMPANY
P.O. Box 1056
520 Kaolin Road
Sandersville, Georgia 31082

Name of Preparer: Sam J. Smith
Date Prepared: January 22, 1990
Revision Date: October 20, 2003
Telephone No.: 478-552-3951

SECTION I - MATERIAL IDENTIFICATION

Trade Name: Kaowhite, Kaowhite S, SP, Kaofill, Kaogloss, Kaogloss 90, Kaobrite, Kaobrite 90, Kaofine, Kaofine 90

Chemical Identity, Common Names: Hydrous aluminum silicate; Kaolin

CAS Number: 1332-58-7

SECTION II - HAZARDOUS INGREDIENTS/IDENTITY INFORMATION

Hazardous Ingredient	Weight% (Approx.)	CAS No.	MSHA PEL	OSHA PEL	ACGIH TLV
Kaolin	100%	1332-58-7	10mg/m^3 Total	15mg/m^3 Total 5mg/m^3 Respirable	2mg/m^{3}Respirable

SECTION III - PHYSICAL/CHEMICAL CHARACTERISTICS

Note: Kaolin is produced in a dry form and as an aqueous slurry. The information in this section is characteristic of the dry form.

Boiling Point:	Solid	**Specific Gravity (H_2O = 1):**	2.63
Vapor Pressure (mm Hg.):	Solid	**Melting Point:**	1735° C
Vapor Density (AIR = 1):	No Vapor	**Evaporation Rate**	
		(Butyl Acetate = 1):	0
Solubility in Water:	Insoluble		
Appearance and Odor:	Off-white color, odorless		

SECTION IV - FIRE AND HAZARD DATA

Flash Point (Method Used): None   **Flammable Limits:** None   LEL: None   UEL: None
Extinguishing Media: Not Applicable, will not burn

8/1/2005

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9.2 Arsenic Removal Data

Spl	As	Spl	As	Spl	As	Spl	As	Spl	As	Spl	As
S14-1	0.004	S16-2	0.040	S16-26	0.678	S16-50	<0.001	W763	0.288	W787	<0.001
S14-2	0.001	S16-3	0.042	S16-27	0.679	S20-1	0.095	W764	2.73	W788	2.03
S14-3	<0.001	S16-4	0.029	S16-28	0.760	S20-2	0.200	W765	0.404	W789	9.22
S14-4	<0.001	S16-5	0.049	S16-29	0.694	S20-3	0.054	W766	1.84	W790	0.751
S14-5	<0.001	S16-6	0.036	S16-30	0.803	S20-4	0.572	W767	0.957	W791	0.486
S14-6	0.006	S16-7	0.051	S16-31	0.818	S20-5	0.007	W768	1.59	W792	0.202
S14-7	0.003	S16-8	0.047	S16-32	0.781	S20-6	0.101	W769	0.422	W793	<0.001
S14-8	<0.001	S16-9	0.039	S16-33	0.374	S20-7	0.010	W770	0.168	W794	2.06
S14-9	0.002	S16-10	0.045	S16-34	0.645	S20-8	0.208	W771	0.151	W795	1.27
S14-10	<0.001	S16-11	0.070	S16-35	0.563	S20-9	0.067	W772	1.62	W796	0.484
S14-11	<0.001	S16-12	0.060	S16-36	0.528	S20-10	0.264	W773	1.16	W797	0.168
S14-12	<0.001	S16-13	0.064	S16-37	0.295	S20-11	0.059	W774	0.835	R1694	4.63
S14-13	<0.001	S16-14	0.051	S16-38	6.465	S20-12	0.415	W775	0.087	R1695	3.56
S14-14	<0.001	S16-15	0.032	S16-39	0.060	S20-13	0.069	W776	0.099	R1696	1.52
S14-15	<0.001	S16-16	0.044	S16-40	0.087	S20-14	0.093	W777	0.061	R1697	1.82
S14-16	<0.001	S16-17	0.022	S16-41	0.678	S20-15	0.063	W778	1.10	R1698	1.13
S14-17	<0.001	S16-18	0.138	S16-42	0.196	S20-16	0.293	W779	0.035	R1699	0.51
S14-18	0.007	S16-19	0.548	S16-43	45.29	W756	2.59	W780	0.250	R1700	4.14
S14-19	<0.001	S16-20	0.559	S16-44	0.346	W757	0.199	W781	9.03	R1701	2.74
S14-20	0.007	S16-21	0.562	S16-45	0.467	W758	2.63	W782	4.74	R1702	5.98
S14-21	<0.001	S16-22	0.598	S16-46	0.077	W759	3.15	W783	0.459	R1703	2.74
S14-22	<0.001	S16-23	0.611	S16-47	0.109	W760	0.595	W784	0.310	R1704	3.33
W339	368	S16-24	0.632	S16-48	0.243	W761	2.83	W785	0.013	R1705	3.74
S16-1	0.040	S16-25	0.665	S16-49	0.111	W762	0.348	W786	1.14		

Spl	V1	V2	V3	V4	V5	V6	pA	pC	CA	CC	RA	RC	V
CIU1	33.78	29.83	25.50	17.53	11.92	6.52	2.8	10.4	1.56	1.06	174	-180	40
CIU2	36.80	31.26	24.97	19.38	13.21	5.45	2.6	11.1	2.26	1.31	170	173	40
CIU3	37.95	31.25	26.13	19.76	11.27	4.10	2.4	11.1	2.79	1.63	173	173	40
CIU4	38.45	32.50	27.29	18.42	9.09	3.20	2.3	11.3	3.41	1.90	1095	71	41
CIU5	38.36	32.09	25.82	18.04	6.96	2.70	2.2	11.3	3.54	1.85	1097	-83	41
CIU6	38.50	32.12	24.08	15.12	6.85	2.68	2.2	11.3	3.76	1.81	1120	-110	41
CIU7	38.75	34.10	24.55	17.05	5.67	2.53	2.2	11.3	4.27	2.10	1113	-91	41
CIU8	38.85	34.14	21.92	12.31	5.27	2.33	2.3	11.3	3.69	2.10	173	171	41
CIU9	38.68	33.44	20.77	12.25	5.44	2.55	2.2	11.3	4.36	2.00	1120	-40	41
CIU10	38.58	33.40	23.38	11.33	4.86	2.64	2.2	11.3	4.40	2.05	1103	-5	41
CIU11	38.85	35.13	20.26	10.88	4.94	2.96	2.2	11.3	4.65	2.20	1098	0	41
CIU12	37.89	34.35	21.18	11.09	4.22	2.98	2.2	11.3	4.69	2.00	1113	10	41
CIU13	38.11	35.02	21.79	9.27	4.20	2.37	2.3	11.3	5.50	2.10	1027	154	41
CIU14	38.12	35.10	22.12	9.25	4.90	2.90	2.3	11.3	4.93	2.01	1083	5	41
CIU15	37.83	36.05	24.76	9.20	4.91	2.45	2.2	11.2	4.88	2.06	1105	-28	41
CIU16	38.20	35.85	24.67	9.24	4.60	2.52	2.3	11.4	4.95	1.90	1107	16	41
CIU17	37.73	35.47	25.46	8.35	4.20	2.32	2.3	11.5	4.42	1.80	173	173	41
CIIA18	30.75	27.08	20.85	14.32	8.58	5.45	4.68	3.08	1.19	0.87	170	169	39
CIIA19	25.90	22.15	15.90	11.28	7.39	5.13	2.88	3.18	1.35	0.85	688	234	39
CIIA20	25.96	21.15	16.15	12.03	8.24	5.04	5.64	3.27	1.17	0.95	427	-393	32
CIIA21	23.90	19.95	15.85	12.35	9.20	5.40	4.35	3.27	1.18	0.94	605	236	29
CIIA22	22.50	19.08	15.08	12.08	8.57	4.66	4.92	3.36	1.41	1.08	451	39	27
CIIA23	26.08	23.12	19.12	14.35	9.24	4.84	4.33	3.18	1.12	1.47	768	140	33
CIIA24	28.28	21.10	20.90	15.90	10.04	4.86	4.71	3.30	1.53	1.54	634	-364	32
CIIA25	28.48	25.69	21.11	15.62	9.58	4.50	5.38	3.43	2.40	1.70	424	-378	32
CIIA26	27.62	24.80	19.98	14.36	8.28	3.76	5.02	3.68	2.55	1.99	420	172	31
CIIA27	25.86	22.66	17.82	12.55	7.50	3.68	5.81	3.73	3.48	2.30	386	-355	29
CIIA28	17.03	14.82	11.58	8.25	5.13	2.89	4.98	3.87	3.22	2.60	433	-163	20
CIIA29	21.90	18.80	11.80	8.65	4.97	2.70	5.19	4.29	4.21	3.96	406	-129	22
CIIA30	29.10	22.18	17.32	12.43	8.45	5.20	3.45	3.26	1.05	1.28	720	-387	39
CIIA31	33.00	26.30	19.30	14.30	9.85	5.51	5.02	3.42	1.56	1.38	414	-337	39
CIIA32	34.34	27.40	20.62	14.66	9.83	5.11	4.35	3.55	1.52	1.58	431	-339	41
CIIA33	41.00	30.86	22.96	15.54	8.91	4.48	2.89	3.75	1.56	2.16	518	-349	50
CIIA34	25.10	33.80	22.00	13.86	7.10	2.88	2.39	4.01	2.41	2.93	725	-340	54
CIU2-1	30.60	25.22	19.05	12.87	8.05	3.25	5.50	9.70	0.85	0.86	376	-178	40
CIU2-2	32.10	27.48	23.39	18.72	14.09	9.31	3.14	10.38	0.99	0.81	448	-227	40
CIU2-3	32.31	27.29	23.98	20.11	15.22	7.62	2.89	10.95	1.50	0.86	732	-447	40
CIU2-4	34.83	28.91	25.72	21.94	15.62	6.60	2.55	10.73	1.53	0.94	765	-480	41
CIU2-5	38.39	32.27	29.08	24.85	13.95	5.03	2.41	10.75	1.84	0.89	814	-229	41
CIU2-6	38.95	34.43	31.88	26.72	12.25	4.25	2.50	10.60	2.03	0.94	755	-167	41
CIU2-7	42.17	38.18	35.52	28.73	12.15	4.15	2.46	10.60	2.15	1.00	820	-104	44
CIU2-8	43.35	38.21	34.77	25.18	11.41	4.81	2.49	10.60	2.22	1.02	910	-125	45
CIU2-9	43.25	37.77	33.90	23.28	9.74	3.72	2.30	10.74	2.26	1.05	680	-133	45
CIU2-10	35.26	28.94	20.16	13.05	10.05	8.77	---	---	---	---	---	---	45
CIU2-11	40.20	29.78	18.36	9.14	5.00	2.94	7.00	10.90	0.70	1.15	---	-130	45
CIU2-12	43.16	29.31	18.61	9.85	5.03	2.41	6.90	10.88	0.89	1.09	360	-25	50

Spl	V1	V2	V3	V4	V5	V6	pA	pC	CA	CC	RA	RC	V
CIU2-13	45.40	27.08	17.95	9.64	4.96	2.37	6.76	9.99	0.86	1.15	320	-80	50
CIU2-14	45.90	27.02	17.32	10.12	4.95	2.34	6.53	11.00	0.87	1.07	410	-12	50
CIU2-15	46.02	26.34	17.22	9.81	4.94	2.44	6.00	11.08	0.85	1.10	432	-46	50
CIU2-16	54.75	24.00	29.24	16.55	4.36	2.51	5.72	10.98	0.78	1.05	325	1	60
CIU2-17	36.01	18.68	11.00	5.50	3.08	2.00	4.72	10.85	0.75	1.11	410	-15	40
CIU2-18	35.35	17.35	10.35	5.06	3.03	1.99	3.63	10.80	0.77	1.04	518	8	40
CIU2-19	34.55	16.65	9.80	4.86	3.10	2.16	3.38	10.87	0.85	1.12	555	-18	40
CIU2-20	33.29	16.41	9.69	4.89	3.40	2.39	3.10	10.85	0.91	1.19	560	-52	40
CIU2-21	29.51	15.32	9.16	5.00	3.49	2.69	3.00	10.83	0.95	1.08	564	-20	40
CIU2-22	32.74	17.23	10.75	5.88	3.86	2.82	2.93	11.11	1.03	1.19	490	-54	40
CIU2-23	31.03	15.58	9.51	5.83	3.83	2.34	2.79	11.00	9.36	1.21	420	-165	40
CIU2-24	29.39	15.58	10.48	6.76	4.33	2.60	2.78	11.01	1.08	1.29	400	-265	40
CIU2-25	27.66	14.27	10.05	6.82	4.40	2.68	2.67	11.06	1.07	1.42	415	-120	40
CIU2-26	26.25	12.85	9.18	6.32	4.03	2.56	2.70	11.00	1.08	1.49	405	-16	40
CIU2-27	26.48	15.92	14.75	10.66	6.68	3.75	3.10	11.20	864	1.57	456	-48	40
CIU2-28	25.79	8.82	6.85	4.97	3.17	2.00	2.60	11.30	1811	2.03	490	-516	40
CIU2-29	25.80	8.23	6.25	4.47	2.92	1.92	2.50	11.40	2.06	2.46	482	-802	40
CIIA2-30	32.06	28.08	21.70	16.05	10.15	6.39	5.20	2.80	0.87	0.59	560	-15	40
CIIA2-31	23.28	19.58	14.41	10.71	7.43	4.99	3.07	2.90	0.12	0.57	783	-222	40
CIIA2-32	23.78	17.95	13.68	10.62	7.71	5.18	2.77	3.23	1.35	0.61	815	-229	40
CIIA2-33	26.32	19.26	14.72	11.38	8.00	5.38	2.70	2.99	1.36	0.64	820	-174	41
CIIA2-34	26.91	19.04	14.63	11.45	7.91	5.33	2.76	3.11	1.31	0.68	820	-263	41
CIIA2-35	27.15	19.25	14.24	11.13	7.68	5.01	2.83	3.20	1.28	0.77	938	-373	41
CIIA2-36	33.19	24.34	17.38	13.52	9.24	5.95	3.06	3.17	1.10	0.83	944	-381	44
CIIA2-37	28.18	22.50	15.32	11.96	7.49	5.16	3.53	3.38	1.05	1.03	867	-404	38
CIIA2-38	23.28	18.12	10.69	7.65	4.57	2.79	3.04	3.94	1.12	3.17	826	-434	36
CIIA2-39	20.52	16.45	10.12	6.77	3.97	2.40	3.63	4.60	1.09	4.68	702	208	27
CIIA2-40	19.35	13.92	7.35	4.40	2.90	1.80	3.30	4.73	1.17	5.52	865	-462	26
CIIA2-41	14.60	11.46	7.02	4.85	2.80	1.80	10.70	4.78	2.02	5.48	113	-474	19
CIIA2-42	12.96	8.94	6.77	4.70	2.80	2.00	5.01	4.58	1.72	4.55	385	-437	17
CIIA2-43	12.82	10.92	7.05	4.90	3.00	2.20	5.00	4.46	1.74	4.00	580	-451	17
CIIA2-44	12.57	10.88	7.34	5.06	3.10	2.15	4.92	4.40	1.86	3.91	694	-460	16
CIIA2-45	12.09	10.45	7.15	4.95	3.17	2.13	4.80	4.40	1.94	4.03	725	-463	15
CIIA2-46	11.97	10.36	7.16	4.95	3.22	2.12	5.26	4.41	2.26	4.04	683	-463	15
CIIA2-47	12.92	11.10	7.85	5.32	3.54	2.26	10.50	4.55	2.84	4.25	140	-465	16
CIIA2-48	11.62	10.15	7.13	4.88	3.22	2.09	5.51	4.72	2.73	4.58	438	-474	15
CIIA2-49	11.60	10.12	7.12	4.89	3.22	2.09	5.70	4.69	2.81	4.85	434	-479	15
CIIA2-50	10.21	8.92	6.30	4.30	2.89	1.90	5.31	4.74	2.87	4.86	638	-483	13
CIIA2-51	10.52	9.18	6.51	4.45	2.96	1.95	6.22	4.86	3.25	4.90	377	-480	13
CIIA2-52	10.01	8.74	6.23	4.23	2.48	2.12	5.94	4.81	3.38	4.98	398	-473	11
CIIA2-53	8.25	7.05	4.75	3.04	1.95	1.55	5.12	4.84	3.24	5.05	446	-471	12
CIIA2-54	9.50	8.30	5.06	4.30	2.84	1.90	5.25	4.88	3.27	5.24	660	-487	12
CIIA2-55	9.30	8.09	5.88	4.08	2.83	1.81	5.17	4.98	3.43	5.32	647	-490	12
CIIA2-56	6.19	5.45	4.00	2.80	2.11	1.55	5.21	4.95	3.80	5.60	620	-496	8
CIIA2-57	8.78	7.72	5.71	4.03	2.81	1.94	5.85	4.90	4.03	5.17	407	-485	11
CIIA2-58	8.76	7.70	5.72	4.03	2.81	1.94	5.73	4.86	4.14	5.29	413	-484	11

9.3 Persistent Organic Contaminants Removal Data

SMP	SQ	TCEP	TCPP	TDCP	SIM	SMX	CBZ
3-30 UC1	18,597,059	8,564,091	13,184,867	5,064,832	308,716,395	67,433,791	341,491,923
3-30 PD1	16,981,421	90,534	3,337,975	269,102	264,500,149	nd	132,099,577
3-30 PD2	18,185,894	90,392	3,500,061	249,699	266,751,691	6,007,454	100,361,288
3-30 UC2	27,321,640	13,255,281	17,040,667	5,882,434	453,622,555	35,034,781	335,060,596
3-30 US1	17,322,059	685,990	4,196,524	341,231	319,918,025	9,830,401	210,805,026
3-30 US2	18,678,776	767,249	4,623,726	383,362	174,754,913	7,304,005	107,692,312
3-30 US3	16,295,517	636,102	4,308,944	331,028	174,754,913	7,304,005	107,692,312
3-30 US4	19,105,803	650,427	5,393,795	486,218	276,492,800	nd	nd
3-30 US5	15,637,642	7,802,988	10,559,238	4,121,453	191,802,999	nd	71,735,916
3-30 US6	18,018,697	6,119,887	10,340,293	736,165	226,096,558	9,046,409	135,406,677
3-30 US7	24,419,380	8,572,428	9,697,741	1,090,746	438,604,135	1,837,497	131,827,530
3-30 US8	18,711,730	4,485,068	6,266,881	597,120	228,557,632	3,190,034	139,155,280
3-30 US9	19,095,967	13,711,572	18,218,591	6,745,153	21,550,897	nd	nd
3-30 US10	20,885,097	2,207,409	3,839,021	1,690,000	8,171,633	nd	3,119,232
3-30 US11	20,512,317	8,890,710	11,784,117	1,810,238	17,329,881	365,190	9,058,175
3-30 US12	23,106,120	7,213,223	9,015,915	1,561,716	16,221,195	nd	4,054,761
3-30 US13	23,821,074	8,300,796	10,427,962	1,926,758	21,245,306	nd	7,204,341
3-30 US14	16,201,584	6,684,563	9,383,577	997,487	11,239,399	nd	7,792,470
3-30 US15	21,395,715	1,711,957	6,430,434	3,016,331	156,254,111	nd	nd
3-30 US16	19,998,337	8,006,122	7,760,607	4,871,673	282,542,336	nd	83,519,232
3-30 US17	23,443,853	2,048,896	2,928,889	572,911	453,622,555	nd	104,054,761
3-30 US18	23,829,330	7,569,414	10,173,152	2,030,761	389,918,025	nd	82,804,341
3-30 US19	26,822,669	7,631,108	10,350,055	791,685	374,754,913	nd	107,792,470
3-30 US20	23,712,689	4,091,316	10,507,993	2,158,573	17,329,881	365,190	9,058,175
3-30 US21	15,480,777	2,499,839	7,013,654	1,052,183	16,221,195	nd	4,054,761
3-30 US22	19,605,305	4,413,259	6,625,494	492,551	21,245,306	nd	7,204,341
3-30 US23	21,589,729	5,439,690	7,260,815	583,281	11,239,399	nd	7,792,470
3-30 US24	23,126,394	5,570,028	7,329,261	560,021	324,660,975	nd	3,345,498
3-30 US25	33,262,642	6,607,364	10,433,188	870,426	324,660,975	nd	3,345,498
3-30 US26	64,056,305	10,340,959	43,297,021	8,225,103	98,967,240	nd	6,376,040
3-30 US27	31,930,978	1,998,755	4,288,104	438,170	165,494,474	nd	10,064,869
3-30 US28	23,225,632	5,502,338	11,952,952	1,282,384	232,612,991	nd	48,345,510
3-30 US29	23,464,480	801,104	1,666,831	200,324	139,175,731	nd	7,792,470
3-30 US30	24,435,348	3,492,789	14,040,717	535,101	453,622,555	nd	104,054,761
3-30 US31	10,372,109	517,192	3,963,548	87,163	389,918,025	nd	82,804,341
3-30 US32	27,984,533	9,168,986	15,520,899	1,618,877	374,754,913	nd	107,792,470
3-30 US33	20,283,458	1,745,739	4,003,986	279,745	239,513,804	nd	275,060,667
3-30 US34	27,601,269	3,367,693	8,256,177	900,033	141,055,206	7,814,181	154,803,317
3-30 US35	28,384,328	1,529,947	3,154,312	379,036	284,617,288	10,374,380	147,607,468
3-30 US36	19,458,693	1,182,037	9,906,678	394,400	103,790,854	5,002,827	18,302,397
3-30 US37	29,851,609	1,642,062	19,319,749	498,997			

SMP	PH	EH	SMP	SQ	TCEP	TCPP	TDCP	SIM	CBZ	SMX
1D-40	2.5	955	P-C	18,259,620	7,997,476	11,309,782	4,736,797	26,145,976	20,009,883	3,076,904
1D-32	5.7	325	P-1	16,994,153	6,285,933	8,239,371	888,379	21,874,884	10,895,536	1,646,369
1D-24	6.9	244	P-2	22,089,739	7,279,839	10,170,926	1,157,042	80,455,808	42,113,286	3,627,333
1D-16	6.9	98	P-3	16,984,420	6,573,405	8,399,666	1,008,481	43,703,610	24,080,023	2,445,112
1D-8	9.7	2	P-4	19,505,971	7,476,724	9,736,964	1,194,280	32,477,713	17,237,639	2,112,247
1D-0	11.2	-870	P-5	18,581,859	7,353,787	9,396,422	1,196,014	65,238,278	32,190,912	3,882,527
2D-40	2.3	1167	P-6	17,995,280	6,858,861	9,019,590	1,061,514	97,986,389	55,540,672	6,126,950
2D-32	5.0	380	P-7	27,699,784	1,063,793	4,638,402	3,491,696	20,547,462	5,702,682	nd
2D-24	6.5	215	P-8	26,638,710	778,698	3,390,966	1,010,469	36,017,578	7,329,984	nd
2D-16	8.9	2.3	P-9	26,973,629	617,576	3,452,837	1,054,902	31,004,374	3,681,360	101649
2D-8	10.9	-100	P-10	32,092,646	14,414,141	12,549,673	7,137,328	4,052,226	55,174,712	6,883,480
2D-0	11.3	-880	P-11	35,731,106	403,885	5,462,003	1,052,839	1,476,214	36,487,418	3,494,098
3D-40	2.1	1170	P-12	28,445,395	620,891	4,175,969	973,116	1,243,467	24,379,624	2,731,060
3D-32	2.7	428	P-13	45,057,571	1,505,945	6,464,365	1,841,710	1,841,446	44,953,179	3,418,612
3D-24	7.8	-31	P-14	26,004,421	785,842	3,508,515	1,194,287	1,859,577	38,199,726	3,021,322
3D-16	9.4	4	P-15	50,164,595	1,057,847	7,178,585	1,608,397	3,759,543	33,884,170	2,869,111
3D-8	10.8	-117	P-16	43,563,398	1,095,762	6,309,473	1,187,356	8,896,946	37,238,877	3,562,285
3D-0	11.3	-886	P-17	23,763,326	388,217	3,233,329	861,024	19,221,589	11,504,627	765,011
7D-40	2.0	1156	P-18	25,206,166	919,913	6,334,111	633,262	23,706,362	17,917,733	717,275
7D-32	2.6	480	P-19	18,259,620	7,997,476	11,309,782	4,736,797	16,896,218	9,379,340	870,383
7D-24	9.0	27	P-20	16,994,153	6,285,933	8,239,371	888,379			
7D-16	9.8	16	P-21	22,089,739	7,279,839	10,170,926	1,157,042			
7D-8	11.1	-160	P-22	16,984,420	6,573,405	8,399,666	1,008,481			
7D-0	11.5	-883	P-23	19,505,971	7,476,724	9,736,964	1,194,280			
21D-40	1.8	1100	P-24	18,581,859	7,353,787	9,396,422	1,196,014			
21D-32	2.3	242	P-25	17,995,280	6,858,861	9,019,590	1,061,514			
21D-24	3.2	140	P-26	27,699,784	1,063,793	4,638,402	3,491,696			
21D-16	9.2	30	P-27	26,638,710	778,698	3,390,966	1,010,469			
21D-8	11.0	-434	P-28	26,973,629	617,576	3,452,837	1,054,902			

SMP	SQ	TCEP	TCPP	TDCP
UC1	17,322,059	685,990	4,196,524	341,231
UC2	18,678,776	767,249	4,623,726	383,362
UC3	16,295,517	636,102	4,308,944	331,028
UC4	19,105,803	650,427	5,393,795	486,218
UC5	15,637,642	7,802,988	10,559,238	4,121,453
UC6	18,018,697	6,119,887	10,340,293	736,165
UC7	24,419,380	8,572,428	9,697,741	1,090,746
UC8	18,711,730	4,485,068	6,266,881	597,120
UC9	19,095,967	13,711,572	18,218,591	6,745,153
US10	20,885,097	2,207,409	3,839,021	1,690,000
US11	20,512,317	8,890,710	11,784,117	1,810,238
US12	23,106,120	7,213,223	9,015,915	1,561,716
US13	23,821,074	8,300,796	10,427,962	1,926,758
US14	16,201,584	6,684,563	9,383,577	997,487
US15	21,395,715	1,711,957	6,430,434	3,016,331
US16	19,998,337	8,006,122	7,760,607	4,871,673
US17	23,443,853	2,048,896	2,928,889	572,911
US18	23,829,330	7,569,414	10,173,152	2,030,761
US19	26,822,669	7,631,108	10,350,055	791,685
US20	23,712,689	4,091,316	10,507,993	2,158,573
US21	15,480,777	2,499,839	7,013,654	1,052,183
US22	19,605,305	4,413,259	6,625,494	492,551
US23	21,589,729	5,439,690	7,260,815	583,281
US24	23,126,394	5,570,028	7,329,261	560,021
US25	33,262,642	6,607,364	10,433,188	870,426
US26	64,056,305	10,340,959	43,297,021	8,225,103
US27	31,930,978	1,998,755	4,288,104	438,170
US28	23,225,632	5,502,338	11,952,952	1,282,384
US29	23,464,480	801,104	1,666,831	200,324
US30	24,435,348	3,492,789	14,040,717	535,101
US31	10,372,109	517,192	3,963,548	87,163
US32	27,984,533	9,168,986	15,520,899	1,618,877
US33	20,283,458	1,745,739	4,003,986	279,745
US34	27,601,269	3,367,693	8,256,177	900,033
US35	28,384,328	1,529,947	3,154,312	379,036
US36	19,458,693	1,182,037	9,906,678	394,400
US37	29,851,609	1,642,062	19,319,749	498,997

SPL	Mn	ABS	CONC	SPL	ABS	CONC	SPL	ABS	CONC	SPL	ABS	CONC
R3780	81.3	0.00529	0.1	U5-03-01	-0.0195	-1.6	UR48-01	0.00275	-0.1	A120R-01	0.0155	0.7
R3781	455	0.01056	0.4	U5-03-02	0.0017	-0.2	UR48-02	0.00313	-0.1	A120R-02	0.003	-0.1
R3782	140	0.07191	4.6	U5-03-03	0.00484	0.0	UR48-03	0.01418	0.7	A120R-03	0.50238	33.6
R3783	291	0.00417	0.0	U5-03-04	0.02542	1.4	UR48-04	0.0523	3.2	A120R-04	0.07142	4.5
R3784	80.5	0.02028	1.1	U5-03-05	0.0904	5.8	UR48-05	0.09122	5.9	A120R-05	0.0031	-0.1
R3785	130	1.1091	74.6	U5-03-06	1.0226	68.8	UR48-06	1.1895	80.1	A120R-06	0.76891	51.6
R3786	206	0.00336	-0.1	U5-04-01	-0.00403	-0.6	UR120-01	0.0032	-0.1			
R3787	257	0.03471	2.0	U5-04-02	-0.00294	-0.5	UR120-02	0.01088	0.4			
R3788	86.9	0.08855	5.7	U5-04-03	0.00948	0.3	UR120-03	0.00926	0.3			
R3789	402	0.08353	5.3	U5-04-04	0.07383	4.7	UR120-04	0.01736	0.9			
R3790	94.6	0.00287	-0.1	U5-04-05	0.18269	12.0	UR120-05	0.04329	2.6			
R3791	529	0.86456	58.1	U5-04-06	0.42979	28.7	UR120-06	0.57748	38.7			
R3996	89.6	0.00307	-0.1	U5-05-01	-0.00005	-0.3	A120-01	0.0029	-0.1			
R3997	177	0.00882	0.3	U5-05-02	0.00486	0.0	A120-02	0.05491	3.4			
R3998	106	0.03172	1.8	U5-05-03	0.03018	1.7	A120-03	0.08727	5.6			
R3999	158	0.03018	1.7	U5-05-04	0.08813	5.7	A120-04	0.06995	4.4			
R4000	258	0.06068	3.8	U5-05-05	0.17985	11.8	A120-05	0.12907	8.4			
R4001	268	0.83713	56.3	U5-05-06	0.4011	26.8	A120-06	1.0041	67.5			
R4002	370	0.00658	0.1	U5-07-01	0.00269	-0.1	A24R-01	0.00435	0.0			
R4003	179	0.01053	0.4	U5-07-02	0.00491	0.0	A24R-02	0.05225	3.2			
R4004	219	0.02371	1.3	U5-07-03	0.02854	1.6	A24R-03	0.09324	6.0			
R4005	912	0.02193	1.2	U5-07-04	0.11754	7.6	A24R-04	0.27152	18.0			
R4006	137	0.06775	4.3	U5-07-05	0.18553	12.2	A24R-05	0.0374	2.2			
R4007	51.5	0.68749	46.1	U5-07-06	0.36991	24.7	A24R-06	1.2192	82.1			
R4008	104	0.01262	0.5	UR24-01	0.00305	-0.1	A48R-01	0.0215	1.1			
R4009	100	0.00465	0.0	UR24-02	0.00436	0.0	A48R-02	0.00339	-0.1			
R4010	224	0.01797	0.9	UR24-03	0.0129	0.6	A48R-03	0.04556	2.8			
R4011	NA	0.01365	0.6	UR24-04	0.04514	2.7	A48R-04	0.04083	2.5			
R4012	NA	0.04941	3.0	UR24-05	0.09644	6.2	A48R-05	0.01208	0.5			
R4013	NA	1.0992	74.0	UR24-06	0.4514	30.2	A48R-06	2.369	159.8			

SMP	40	34.2	28.5	22.8	17.1	11.4	5.7
U-N48 EP	57.5	52.62	45.8	35.82	25	10.17	2.63
U-N72 EP	57.5	53.85	35.33	28.94	19.59	7.92	2.85
U-N96 EP	57.5	49.72	29.42	24.63	16.75	6.68	2.01
U-N120 EP	57.5	52.63	27.52	23.06	15.35	6.28	1.83
U-N144 EP	57.5	53.90	31.69	23.92	16.73	4.83	1.86
U-R72 EP	63.3	5.94	42.8	49.36	53.45	57.42	60.67
U-R96 EP	63.3	4.31	38.4	48.35	52.84	56.63	60.09
U-R120 EP	63.3	2.74	23.91	37.24	43.42	48.42	55.07
U-R144 EP	41.7	1.29	5.45	9.67	14.12	22.35	29.15
U-N48 VD	4.88	6.82	9.98	10.82	14.83	7.54	2.63
U-N72 VD	3.65	18.52	6.39	9.35	11.67	5.07	2.85
U-N96 VD	7.78	20.30	4.79	7.88	10.07	4.67	2.01
U-N120 VD	4.87	25.11	4.46	7.71	9.07	4.45	1.83
U-N144 VD	3.60	22.21	7.77	7.19	11.90	2.97	1.86
U-R72 VD	5.94	36.86	6.56	4.09	3.97	3.25	2.63
U-R96 VD	4.31	34.09	9.95	4.49	3.79	3.46	3.21
U-R120 VD	2.74	21.17	13.33	6.18	5.00	6.65	8.23
U-R144 VD	1.29	4.16	4.22	4.45	8.23	6.80	12.55
A-N48 EP	63.1	58.66	52.67	42.25	29.25	15.65	4.9
A-N72 EP	63.1	56.37	46.38	40.11	32.06	19.89	5.32
A-N96 EP	63.1	59.03	52.18	43.04	32.95	18.33	3.87
A-N120 EP	63.1	55.85	29.5	18.8	11.16	5.55	3.15
A-N144 EP	30	25.95	16.45	12.28	8.19	4.3	2.3
A-R72 EP	50.3	6.7	17	27.45	33.4	38.61	40
A-R96 EP	49.01	4.01	11.18	19.48	25.92	30.80	33.72
A-R120 EP	47.4	3.00	7.25	12.48	18.22	23.34	27.06
A-R144 EP	26.4	2.85	4.93	8.04	11.84	15.88	18.32
A-N48 VD	4.44	5.99	10.42	13.00	13.60	10.75	4.90
A-N72 VD	6.73	9.99	6.27	8.05	12.17	14.57	5.32
A-N96 VD	4.07	6.85	9.14	10.09	14.62	14.46	3.87
A-N120 VD	7.25	26.35	10.70	7.64	5.61	2.40	3.15
A-N144 VD	4.05	9.50	4.17	4.09	3.89	2.00	2.30
A-R72 VD	6.70	10.30	10.45	5.95	5.21	1.39	10.3
A-R96 VD	4.01	7.17	8.30	6.44	4.88	2.92	15.29
A-R120 VD	3.00	4.25	5.23	5.74	5.12	3.72	20.34
A-R144 VD	2.85	2.08	3.11	3.80	4.04	2.44	8.08
U-NPH-1		2.19	5.5	6.6	6.77	9.9	12.02
U-NCON-1		4.2	0.6	1.272	0.623	0.511	8.2
U-NRED-1		500.0	97.0	-66	-171	399	394
A-NPH-1		6.5	5.7	6.94	7	8.5	9.5
A-NCON-1		3.8	1.1	1.25	1.22	0.907	11.35
A-NRED-1		705.0	450.0	360	586	50	380
U-RPH-1		11.8	10.77	11.25	10.93	6.34	1.88
U-RCON-1		7.3	1.2	2.41	1.755	0.93	6.02
U-RRED-1		-895	-826	-792	83	320	1100
A-RPH-1		9	5.63	6	6.13	7	9.1
A-RCON-1		9.2	8.1	6.68	6.02	7.72	10.63
A-RRED-1		-800.0	-507.0	-532	-530	295	429