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Enhancing reductive dechlorination of chlorinated ethenes and ethanes in a natural treatment system

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ENHANCING REDUCTIVE DECHLORINATION OF CHLORINATED ETHENES AND ETHANES IN A NATURAL TREATMENT SYSTEM

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ABSTRACT

Chlorinated solvent contamination continues to plague sites around the world. In many cases, lower chlorinated daughter products build up and remain in ground waters and soils. A Bio-Filter/Phytobed (BFP) system has been developed to replace a traditional pump and treat technology currently operating at the ReSolve Superfund site in North Dartmouth, MA.

Pilot scale testing at the facility displayed a significant acclimation period prior to microbial dechlorination, as well as delayed degradation of chlorinated ethanes. Microcosm studies suggest that acidic conditions, possibly created by the peat mixture used to construct the bio-filter, inhibited bacterial growth. The neutralization of trench pH appeared to coincide with the start of chlorinated solvent degradation in pilot scale studies.

In subsequent microcosm studies, lactate, hydrogen, and acetate were added to promote bacterial growth and enhance reductive dechlorination, yet lactate failed to enhance the degradation capabilities of either chlorinated ethenes or ethanes. In an effort to increase the availability of hydrogen, larger concentrations of hydrogen gas in the headspace replaced the lactate. Although the hydrogen eliminated chlorinated ethane lag time, the degradation rates remained lower than desired. However, the addition of acetate successfully stimulated chlorinated ethane degradation and increased degradation rates.

Recommendations for the final design include the use of carbon filtration and a two trench BFP system. A life cycle analysis depicting the BFP system as a more sustainable remediation technology as compared to the currently operating pump and treat system is included.

CHAPTER 1. INTRODUCTION

Introduction and Purpose of the Study

Soil and groundwater pollution is a global concern. In many cases, this pollution produces undesirable toxic effects to both humans and the surrounding ecosystem. Areas contaminated with chlorinated volatile organic compounds (VOCs) are of immense concern as all chlorinated VOCs are suspected or known carcinogens (Ballapragada et al 1997, Lookman et al 2005). Industries widely utilize these compounds as mechanical degreasers and solvents. Improper disposal of chlorinated VOCs has led to soil and groundwater contamination posing global health and environmental risks (Ballapragada et al 1997, Plumb 1987). Treatment of such compounds is difficult due to their affinity for environmental transport and their resistivity to degrade to non-toxic daughter products (Howard 1990, Lookman et al 2005). In many situations, treatment techniques aim at containing the transport of VOCs off-site and then treating them on site.

Pump and treat systems are often successful in halting the progression of contamination plumes toward natural waterways or property boundaries (He et al 2003). Artificial flows are created by pumping large volumes of water out of underground aquifers; as more water is pumped, the flow towards the well strengthens, ensuring that the contaminant does not travel off-site or spread to pristine areas. While successful in limiting the geographic area affected by contamination plumes, these systems have shown little effectiveness in satisfactory removal of contaminants. In many cases, chlorinated VOCs sorb onto soil particles or seep into underlying bedrock fissures making it hard to remove them from the subsurface for treatment. Due to these difficulties, pump and treat systems operate for decades without producing significant reductions in chemical contamination at high cost to the operator(s).

As technology advanced, additional techniques to remediate chemical plumes have emerged. Most of these techniques involve chemical treatments. These treatments require large amounts of chemicals and energy which adversely impact the environment and cost significantly more than processes based on natural systems. The least invasive treatment technique available to engineers is natural attenuation. In some areas, environmental factors are conducive to abiotic and biotic processes that naturally remove chlorinated solvents from the environment. Natural attenuation has proven successful in the treatment of chlorinated VOCs at such locations (Lorah et al., 1997); however, this process requires extended treatment time and is not always a suitable option due to poor environmental conditions at the facility.

One class of treatment systems relies on accelerating natural treatment processes to accomplish VOC treatment more sustainably and at greatly reduced cost. Pardue (2005) suggests utilizing engineered wetland systems (EWS) as a "passive" technology to treat VOCs. While not widely applied, this technology is particularly beneficial as VOC removal in wetlands is extremely effective and less labor is required which significantly decreases operational costs. The sustainability of such projects is also appealing as many biological treatment designs utilize far less energy and fewer chemicals than other remediation techniques.

Site History

The ReSolve superfund site, located in a rural area of North Dartmouth, Massachusetts, housed a chemical reclamation facility from 1956 until 1980. Contamination from waste solvent, oils and organic chemicals is believed to have originated from discharge into cooling ponds, unlined lagoons and oil spreading areas on the property during industrial operations (Figure 1.1). Since the ReSolve facility ceased operation, the 6.5 acre facility has undergone multiple remediation attempts to remove the chemical contamination. Multiple excavation projects took place between July 1984 and July 1993. Much of this sediment was treated on site

using thermal processes and backfilled onto the property. In September of 1987, a groundwater monitoring system and pump and treat facility were established to treat and contain aquifer contamination. After discovering the presence of dense non-aqueous phase liquids (DNAPL) in the waste management area, it became clear that the current system was inadequate to handle the pollution problems.

The groundwater pumping system was upgraded to a two tier extraction system which removes 48 gallons of groundwater per minute from eight extraction wells. Four of these wells are utilized to limit the movement of DNAPL from the contaminated areas and the remaining four wells are utilized to treat the groundwater. Treatment currently involves passing the groundwater through a variety of physical and chemical unit operations. The treated water is then discharged into the adjacent Copicut River.

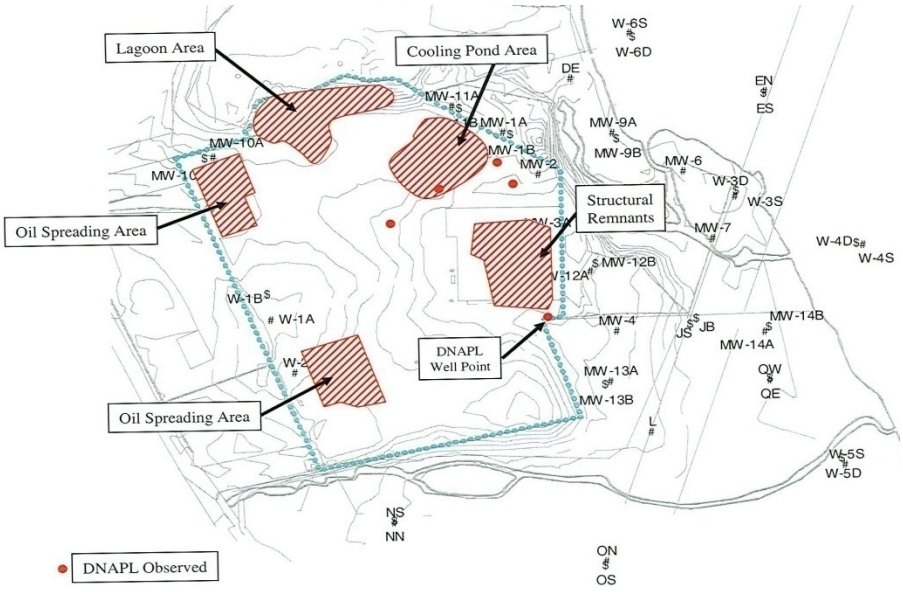

Figure 1.1. Arial depiction of ReSolve facility depicting original areas of contamination and locations where DNAPL has been observed. (ReSolve Superfund Site, 2001).

Currently significant concentrations of oils and solvents still remain in the waste management area decades after initiation of remediation projects. The remaining contamination consists of polychlorinated biphenyls (PCBs) and chlorinated solvents, specifically *cis* 1,2-

dichloroethene (DCE), 1,1,1-trichloroethane (TCA) and their daughter products vinyl chloride (VC), 1,1-dichloroethane (DCA) and chloroethane (CA). The existing pump and treat system, while highly effective in treating pumped groundwater, is costly from an operational and maintenance perspective and requires large chemical and energy input to operate. A more cost effective and sustainable treatment approach is desirable.

Bio-Filter/Phytobed System

A natural treatment system has been designed and piloted to provide a less expensive treatment option that is more sustainable over the long term. The system, termed the Bio-Filter/Phytobed system (BFP) is composed of large underground trenches filled with a peat and sand mixture to provide environmental conditions similar to that of natural wetlands. The trenches are designed with the intention of applying water at the top of the bed and allowing that water to percolate through the trench material to the bottom (Figure 1.2). As the water flows through the bed, anaerobic microbes will utilize the existing contaminants in their metabolic processes and produce non toxic daughter products ethene and ethane in a process known as reductive dechlorination (RD). Sorption of VOCs on the highly organic peat soils will ensure that the residence time within the system is long enough to accomplish treatment. When the water reaches the bottom of the bed, it will then be discharged into the Copicut River.

Sustainability

The BFP is a highly sustainable approach as it utilizes natural processes to complete chemical transformation as opposed to chemical or energy intensive processes. In many cases, this can also lead to the decrease in operational costs as fewer materials are required for facility operations. Highlighting these benefits is of interest to environmental agencies and responsible parties as the Environmental Protection Agency (EPA) requires that green treatment technologies be given preference in the selection process (EPA Green Remediation 2008). Methods to

quantify sustainability are utilized to supplement project proposals. It is believed that the proposed BFP system will be a highly sustainable treatment technology as it is based on naturally based processes and does not require massive amounts of energy or chemicals.

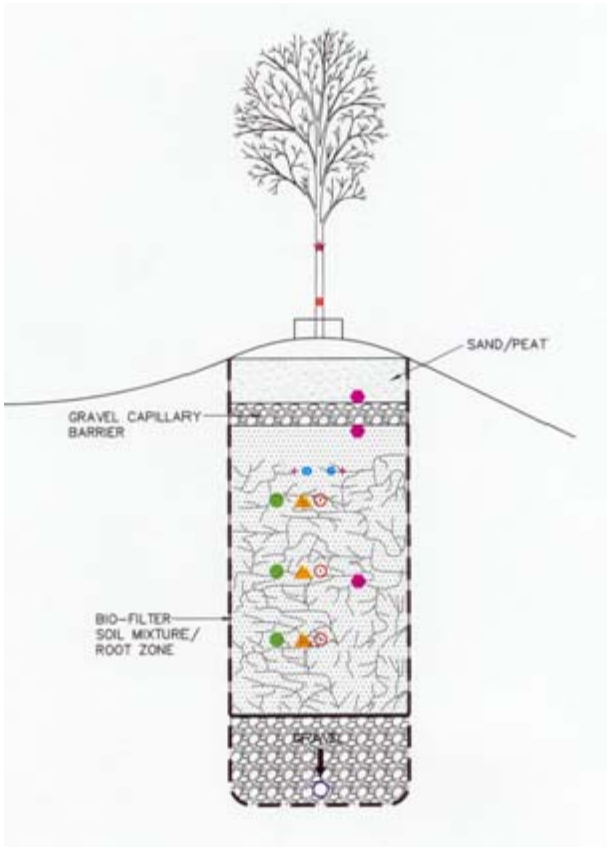

Figure 1.2. Cross sectional diagram of BFP trench (ReSolve Superfund Site, 2001).

Organization of the Thesis and Purpose of the Study

This paper is organized in five parts. The first chapter provides a basic introduction to the ReSolve facility and a literature review. The second chapter describes the BFP system and pilot scale testing of this technology at the ReSolve facility. It also highlights obstacles to the full-scale implementation of the BFP system including an initial microbial acclimation period within the trenches and the desire to optimize degradation of 1,1-DCA. The third and fourth chapters of the paper focuses on optimization of studies that identify potential solutions to

obstacles addressed in the BFP pilot scale tests. In order to optimize degradation, microcosm studies were undertaken to address the following:

1. Investigate the de-chlorination acclimation period experienced in the pilot studies to reduce or eliminate the lag time in full-scale technology implementation. (Chapter Three)
2. Investigate methods to decrease treatment time to accelerate successful treatment of DCE and DCA simultaneously via the addition of lactate, hydrogen and acetate. (Chapter Four)

The final chapter of the thesis addresses the sustainability of the BFP system. An analysis of the BFP technology was conducted in comparison to the currently operating pump and treat system in order to quantify environmental benefits of this technology versus other traditional treatment methods.

Literature Review

Biological Treatment of Chlorinated Volatile Organic Compounds

Biological treatment of chlorinated solvents is quickly becoming a desired technology for the remediation of chemical contamination. The process takes place via reductive dechlorination (RD) where bacteria use the chlorinated solvent as an electron acceptor, reducing the compound by replacing one or more chlorine molecules with hydrogen (an electron donor). Lookman et al. (2005) noted the environmental factors affecting RD: pH, temperature, presence of appropriate electron donors, and the presence of microbial communities. The pH of the environment must be fit to support microbial growth.

In many cases, microbial communities thrive in neutral (pH=7) conditions. As pH decreases the environment becomes more acidic and microbial growth rates decrease (Rousk 2009). Taconi et al (2007) showed under methanogenic conditions, acidic environments can

stimulate microbial activity suggesting each microbe may have optimum growth conditions which should be taken into account when designing biological systems. Temperature also affects microbial growth rates. Ratkowsky (2005) demonstrated that as temperature extended either above or below desirable growth ranges, microbial growth rates slowed. Friis (2007) stated that RD of higher chlorinated ethenes occurs to completion in temperatures ranging from 10 to 30^{o}C when amended with lactate. In addition to physical factors, the appropriate microbial communities and electron acceptors must be present for RD to take place (Lookman et al 2005, Doong and Wu 1996). Once these basic requirements are met, RD occurs via the removal of a chlorine atom from the original compound and hydrogen, is added to form the new compound.

There are multiple species of microbes which can perform RD. Each of these microbial species utilizes different electron donors in the RD process. Lactate, hydrogen, and acetate, among others have been found to be excellent electron donors for this process (Ballapragada et al 1997, Taconi et al 2007, Doong 1996). Lactate and acetate ferment to form hydrogen gas supplying RD species with usable electron donors. Kassenga et al (2004) stated that chlorinated ethanes can be degraded via co metabolic processes involving methanogens. Adding acetate as an electron donor to systems with high methonogenic activity gives these populations an advantage as methanogens can utilize acetate directly as opposed to waiting for hydrogen production via fermentation. This knowledge can be used to benefit researchers as often there is interspecies competition for electron donors (Kassenga et al 2006). By supplying a particular type of electron donor which favors one species over another, growth of the targeted species can be encouraged.

Just as each microbial community will thrive in certain environmental conditions, microbial communities will utilize chlorinated compounds with different affinities. Species in the *Dehalococcoides* genus have proven to play an important role in the degradation of

chlorinated ethenes. In many cases, the degradation of higher chlorinated ethenes progresses to sequentially lower chlorinated compounds and stalls. This incomplete degradation is troubling as vinyl chloride (VC), a well known product of incomplete RD, will persist in the environment and is more toxic than the parent compounds (Ritalahti 2005).

The discovery of *Dehalococcoides ethenogens* strain 195, the first strain identified as having the capability of complete dechlorination of trichloroethene (TCE) and tetrachloroethene (PCE), was particularly beneficial in promoting biological treatment. This group of organisms may play an important role in the effectiveness of the BFP system.

The degradation pathways of 1,1,1-trichloroethene (TCA) and tetrachloroethene (PCE) are depicted in Figure 1.3. In this study, *cis* 1,2-dichloroethene (DCE) is the primary chlorinated ethene present in groundwater. *cis* 1,2-DCE is transformed to vinyl chloride and then to ethene a non toxic product. Ethene is then transformed to ethane. 1,1,1-TCA is expected will degrade to 1,1-dichloroethane (DCA) in the anaerobic conditions in the BFP system. 1,1-DCA is then converted to chloroethane (CA) and finally to non-toxic ethane during the degradation process.

While much is understood about the dechlorination of ethenes, there is less information concerning the microbes that remediate chlorinated ethanes. *Dehalococcoides ethenogenes* strain 195 can RD chlorinated ethenes and 1,2-DCA (Maymo Gatell et al 1999) but not 1,1-DCA. In recent years, *Dehalobacter* species have also been identified as microbial populations that dehalogenate chlorinated ethanes (Sun 2002).

Others suggest methanogenic or sulfate reducing microbes are effective at producing acceptable remediation levels (de Best et al 1997, Kassenga et al 2004). It is possible, that multiple species are responsible for the complete degradation of chlorinated ethanes in nature. It is also hypothesized that organisms responsible for chlorinated ethane remediation function in comparable environmental conditions and utilize similar electron donors.

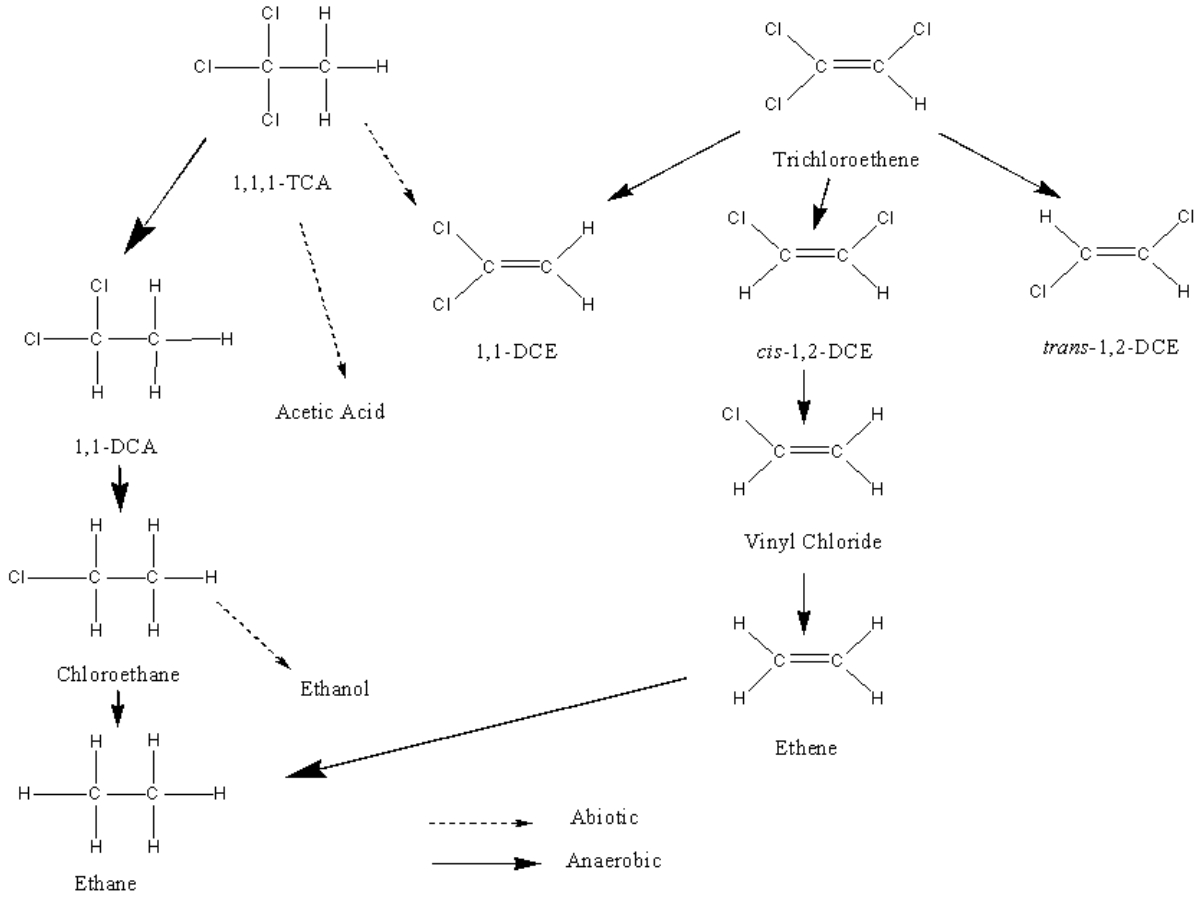

Figure 1.3. Degradation pathways for both *cis* 1,2-DCE and 1,1,1-TCA.

Engineered Wetland System (EWS)

Natural and engineered wetland systems have proven highly effective in remediating VOCs as evidenced in studies conducted by Lorah and Voytek (2004), Pardue (2005), and Kassenga et al (2003). In engineered systems, contaminated groundwater is applied at the base of the wetland bed. As water travels up through the bed, VOCs sorb onto the soil increasing their residence time within the bed. This increased residence time allows microbial populations to utilize the chemical in metabolic processes described above. As the water reaches the surface, it encounters an area dominated by the root zone of wetland plants. This area has dense populations of methanogenic bacteria (Calhoun and King, 1997). It is suggested that in this zone

complete degradation of lower chlorinated daughter products occurs to form carbon dioxide via methantrophic processes (Lorah and Olsen 1999).

In designing these EWS the choice of media is of great importance as this supports the microbial population and encourages growth throughout the remediation process (Mbuligwe 2008). The choice of substrate will significantly affect the environmental conditions and hence the success of the project. In many cases, mixing peat and sand will provide adequate substrate conditions but Kassenga et al (2003) found that adding Bion soil, an organic additive, stimulated microbial activity but decreased hydraulic conductivity which may negatively impact the success of the project.

Enhancing Biological Remediation

Researchers have identified two methods of increasing the RD capabilities of microbial communities: supplying additional micro-organisms not present in the existing population and/or supplying additional electron donors (Wenderoth et al 2003). The first method increases the amount and diversity of microbes within the treatment area to increase the rate and variety of metabolic reactions. Inoculating a groundwater aquifer is beneficial at the onset of a project as microbial populations of desired organisms will be smaller than after several days or even weeks of acclimation. In a well designed treatment process, microbial communities should flourish quickly and there would be little need to supplement the populations; however it is sometimes necessary to introduce the desired bacteria to overcome competition or other factors.

The second method of increasing degradation rates is to stimulate the existing microbes to carry out reactions at a faster rate. In many cases, RD is limited by the supply of electron donors (Kassenga 2004, Cupples 2004). In environments where carbon sources are scarce, additions can be supplied in order to reduce the limitations on the system. It is clear from previous experiments that microbes responsible for the dehalogenation of chlorinated ethenes are

successfully stimulated with additions of carbon sources such as glucose, lactate, and acetate (Bhaskar et al 1997, Maymo-Gatell 2001). These carbon sourced may need to be fermented producing hydrogen as a bi-product since RD populations often used hydrogen gas as an electron donor (Fennell and Gossett 1997).

EWS, theoretically, should not be carbon limited as peat, a major constituent of ground substrate is highly organic; however, there is concern that these electron donors may not be readily available to microbes and substrate amendment may stimulate RD in these environments. The application of hydrogen gas allows for ample and immediate application of electron donors which may not be possible in large scale facilities using lactate or other chemical additions. Chung and Rittmann (2008) developed a safe and efficient application of hydrogen gas to aquifers with the intent of stimulating RD.

The stimulation of chlorinated ethene degrading microbes is well documented in laboratory experiments. In situations where mixed organic compounds are present, there is less information available on how to effectively stimulate all bacteria responsible for the success of the technology. In previous experiments, ethane degrading bacteria are assumed to utilize the same electron donors as their ethene degrading counterparts and therefore respond positively to the additions of hydrogen or hydrogen producing compounds. In addition, chlorinated ethane degradation has been linked to co-metabolic methanogenic processes (de Best et al 1997, Kassenga et al 2004, 2006). The addition of acetate, a less common substrate addition for chlorinated ethene degradation, has been documented as an effective stimulant for chlorinated ethene and ethane RD (He et al 2002 and Doong and Wu 1996).

CHAPTER 2. PILOT STUDIES

Anaerobic Bio-Filter/Phytobed (BFP) Pilot Study

At the ReSolve site, two pilot programs have been performed to develop the design parameters and treatment concepts proposed in Chapter 1. A field pilot study, termed the Bio-Filter/Phytobed (BFP) field pilot, was initiated in 2002 and is still operating at present. A second pilot program, designed at optimizing the results from the BFP pilot was initiated in 2007 and continues to the present and is termed the Anaerobic Bioreactor or ABR pilot study. The pilot tests were conducted in concert with the experiments in this thesis, therefore, the results from the BFP and ABR pilot studies are summarized below to present the context in which the laboratory experiments were conducted.

The BFP pilot consists of two trenches, 24 feet in length, four feet wide, and eight feet deep. The trench is packed with a mixture of peat (Worcester Peat, ME) and sand. Groundwater is applied at rates ranging from 0.05-0.2 gallons per minute (gpm) to an irrigation line buried 30 inches below ground. Water percolates vertically through the trench and is then collected by a slotted pipe in a gravel layer eight feet below ground. This slotted pipe drains into a concrete sump which runs the entire depth of the trench providing control of water depth within the BFP trench. After initial attempts at running the trench in an unsaturated mode in late 2002 produced less than desirable degradation rates, the trenches have been operated in a fully saturated condition since 2003.

Initially, the BFP pilot displayed a significant acclimation period (six months) before rapid de-chlorination took place (Figure 2.1). During this lag time little RD occurred in the trenches; concentrations of chlorinated solvents in influent water remained above discharge standards. After approximately six months, RD dramatically improved and very effective reductive dechlorination rates were observed.

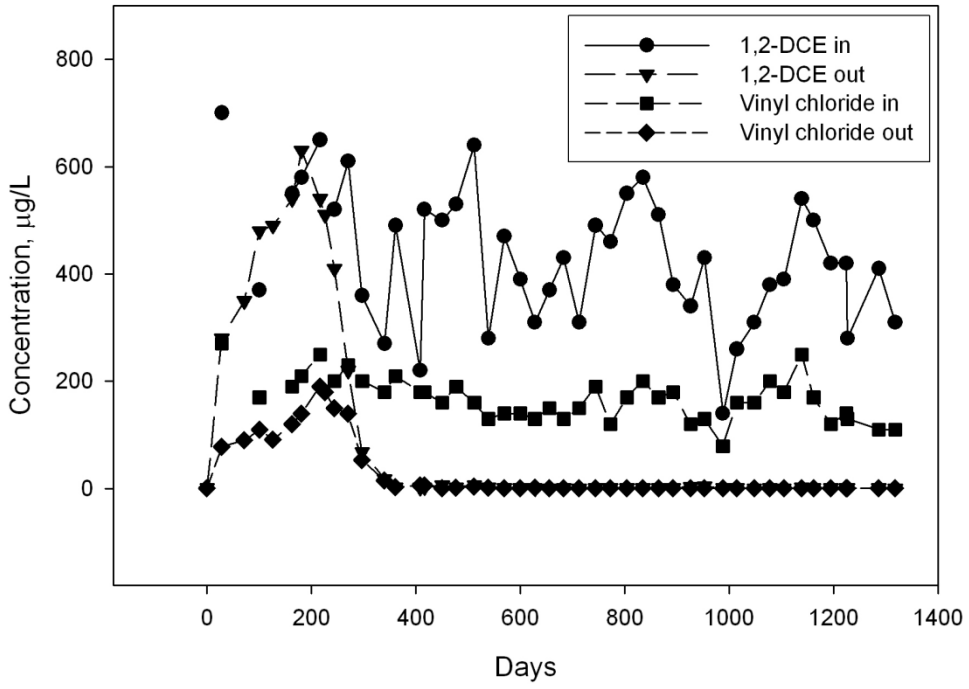

Figure 2.1. Percent removal of select chlorinated VOCs in BFP Study. Samples analyzed monthly throughout monitoring period.

Following the extended acclimation period, bacterial communities were effective at degrading chlorinated ethenes. Within the first year, parent and daughter chlorinated ethenes degraded in the first 20 inches of the bed indicating this is where most of the microbial activity would be found (Figure 2.2). In subsequent years, the removal of *cis* 1,2-DCE and VC approached 100 percent.

The treatment of chlorinated ethanes was not as successful in the BFP pilot test as the removal of chlorinated ethanes. Chlorinated ethanes only represent 10% of the VOC load in site groundwater, while chlorinated ethenes represent 80%. 1,1,1- TCA was easily transformed to 1,1-DCA, which then accumulated in the system. 1,1-DCA appeared to slowly degrade in the BFP system to produce chloroethane. On a few occasions, chloroethane concentrations in

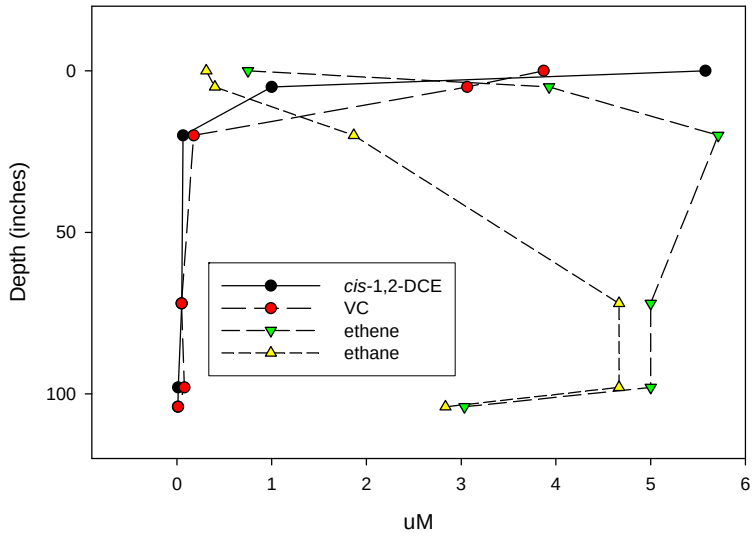

Figure 2.2. Concentrations of chlorinated ethenes versus depth in BFP system.

effluent water exceeded regulatory requirements. Concentrations of chlorinated ethanes with depth is presented in Figure 2.3. Kassenga et al (2006) suggests degradation of chlorinated ethanes is inhibited by chlorinated ethene degradation due to the low hydrogen concentrations maintained during RD. Degradation of chlorinated ethanes, most notably 1,1-DCA, requires significantly more surface area within the BFP trench and this may hinder the full scale implementation of the technology. After the initial activity of the BFP system had been assessed, other factors such as temperature and flow rate were manipulated to increase the treatment capacity of the trenches.

Temperature was monitored in both trenches. Winter temperatures (2002/2003) in the trenches reached approximately 2^{o}C, which is cooler than most microbes responsible for RD are expected to thrive (Friis 2007). During the following three winters, different methods to maintain temperatures in the trenches were investigated. From December 2003 until March 2004

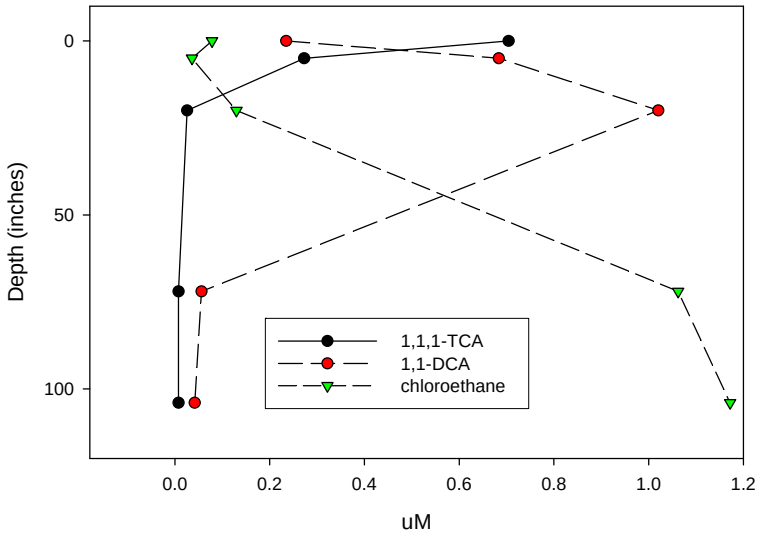

Figure 2.3. Concentrations of chlorinated ethanes versus depth in BFP system.

(second winter) Trench A influent pipes were insulated and warm water circulated through the trench. Winter temperatures in Trench A ranged from 5 to 18°C. In this same time frame, Trench B was fitted with an insulation mat in addition to the influent pipe insulation and warm water circulation. Trench B remained warmer than Trench A with a low temperature of 12°C (Figure 2.4).

Warm water circulated through both trenches throughout the third winter (2004/2005). Trench A remained slightly cooler than trench B but not by significant margins. Temperatures in both trenches remained between 5 and 20°C which did not vary significantly from those recorded during the first winter (2002/2003). During the final year of temperature testing (2005/2006), no warm water circulated through either trench and no insulation was placed on influent pipes. The only treatment applied was a thermal pad on the surface of Trench B. The pad proved effective at maintaining the temperature in the trench compared to trench A which was not insulated (Figure 2.5). The minimum recorded temperature in trench B was 8°C.

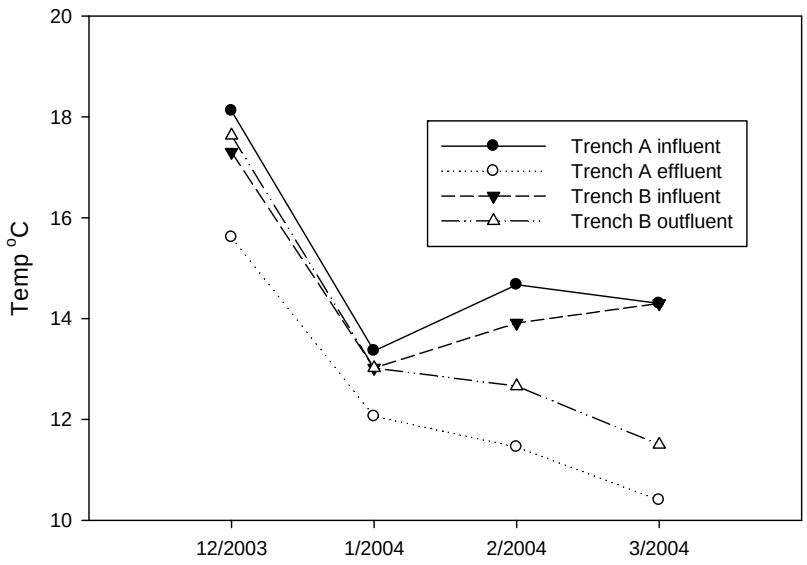

Figure 2.4. Influent and out-fluent water temperatures for both trenches A and B throughout the second winter (2003/2004).

The BFP system was designed to manage 0.20 gallons per minute (gpm) of influent water in each trench. Within three months of monitoring the trenches, the flow rate had to be decreased because of flow restrictions. In January 2004, the flow rate in trench A reached 0.05 gpm while Trench B was reduced to 0.1 gpm. By May 2006, Trench A operated at a flow rate of 0.05 gpm while Trench B was again operating at 0.2 gpm. The flow restrictions experienced during the testing period are of concern as BFP trenches must be capable of reliably treating large volumes of water without interruption. The variation in flow rates between trenches is also concerning as the capacity of the BFP system at a full scale will be difficult to determine prior to construction.

Metal leachate from the BFP trenches is also of concern. The BFP trenches operate under anaerobic/reducing conditions in which metals are highly soluble in water. Effluent concentrations of iron (Fe) and arsenic (As) exceed effluent standards, even after the trenches

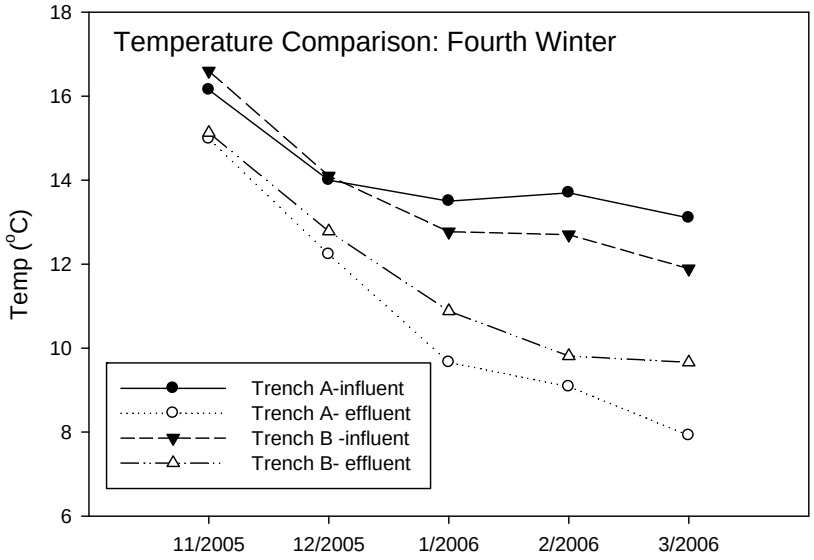

Figure 2.5. Influent and out-fluent water temperature for both trenches A and B throughout the fourth winter.

have operated for several years. As influent concentrations are lower than effluent concentrations, it is believed that additional metals are leaching from the bed material, most notably the sand. Steps must be taken to ensure metal effluent requirements are maintained in order for the BFP to succeed.

In 2007, Trench B of the BFP pilot study was forensically examined to assess the condition of the trench after four years of groundwater application. The results of the examination determined:

The roots of the willow trees did not affect remediation. Due to this finding, the willow trees were eliminated from the final implementation plans and other plants such as grasses will be utilized to supply carbon to the trenches over their lifetime (ReSolve Superfund Site, 2007).

PCBs accumulated in the trenches. Removal of measurable PCBs in the BFP system exceeded 99%. Even with the exceptional removal capacity of the BFP system, PCBs

were detected in BFP effluent above discharge limits. It is not feasible to expect the BFP system to completely handle PCB remediation at this site (ReSolve Superfund Site, 2001).

Reduced flow rates are attributed to the quantity of silt and clay present in the drainage layer at the bottom of the bed. Trench A is thought to have been more impacted than Trench B due to of natural variation in the sand and gravel distribution. It is recommended that clay and silt particles be removed from the gravel prior to construction to allow a greater hydraulic conductivity within the drainage layer to prevent clogging (ReSolve Superfund Site, 2001).

These findings, combined with the results from the BFP pilot identified five issues for optimization: 1) ensuring that PCBs are treated to the level required to avoid contaminating the trenches; 2) optimizing removal of chlorinated ethanes; 3) ensuring that metals (Fe and As) discharge limits are met; 4) confirming that improving the gravel quality will improve site drainage and 5) understanding the lag time observed prior to effective treatment via microbial degradation.

Anaerobic Bioreactor (ABR) Pilot Study

The Anaerobic Bioreactor (ABR) pilot was conducted in a tank packed with peat/sand media, application rates of groundwater were 0.12 gpm. This study was conducted to address the issues identified in the BFP pilot study. Results from this study are as follows (ReSolve Superfund Site, 2001):

1. A Granulated Activated Carbon filter was utilized to remove PCBs prior to passing water through the ABR. This treatment removed highly chlorinated VOCs (specifically 1, 1, 1-TCA) from influent water which decreased the load on the ABR system. This decreased load should

allow for more complete and reliable degradation of lower chlorinated solvents such as 1, 1-DCA and chloroethane.

2. In addition to carbon filtration, a microcosm study was initiated to investigate possible carbon additions to stimulate chlorinated ethane degradation. The results of this study are described in chapter four.

3. The sand utilized in the BFP system was determined to have high levels of metals and these metals posed a risk to meeting effluent standards. Lower metals content sand was utilized in the construction of the ABR to decrease metal contamination present in effluent water and hence providing reliable attainment of treatment standards.

4. A crushed stone drainage layer was employed to alleviate flow issues experienced in the BFP system. Variable flow rates were utilized during testing to assess treatment effectiveness to more precisely size the full scale system.

5. A microcosm experiment was initiated to better understand system limitations causing the extended lag time observed in the BFP system. The results of this study are discussed in chapter three.

Laboratory experiments were initiated to provide additional information in understanding the initial lag time as well as improving chlorinated ethane degradation within the trenches. The first study mimics the conditions present in the BFP and ABR systems. Utilizing a closed system as opposed to the ABR flow through system allows environmental conditions to be easily manipulated to determine the factor causing extended acclimation periods. The second study addresses the degradation of chlorinated ethanes. Various electron donors are added to microcosms to identify additions which will expedite the degradation of chlorinated ethanes and encourage concurrent degradation of these chemicals with chlorinated ethenes.

CHAPTER 3. UNDERSTANDING THE INITIAL TRENCH LAG TIME

Introduction

Several points of concern were identified after the BFP pilot test. The trenches required six months of acclimation before significant reductive dechlorination took place. In most biological treatment systems, it is natural for some acclimation time to occur when a system first comes online

This period is a result of relatively low microbial populations present at the start of treatment. As energy sources (chlorinated VOCs) and electron donors become available, bacteria populations increase exponentially and dechlorination takes place (Cupples et al 2004). The system will continue to acclimate and eventually reach peak efficiency levels when microbial populations approach the maximum sustainable yield. In field operations, growth rates rarely resemble models as models are often developed in lab settings with little environmental stressors such as competition and lack of resources (Cupples et al 2004, Christ 2007). The availability of electron donors and acceptors and presence of competitors significantly impacts observed growth rates. Physical-chemical properties of the environment such as pH and temperature can also impact these growth rates (Lookman et al 2005).

In the case of the BFP system, dechlorination rates were extremely low for the first six months of operation, even after inoculation attempts. It is unlikely that availability of electron acceptors or temperature is responsible for this delay as the ReSolve groundwater contains high concentrations of chlorinated VOCs and trench temperature exceed the minimum temperatures necessary for RD (Friis 2007). One possible explanation is that bacteria responsible for RD are out-competed by other microbial communities within the BFP trenches. The addition of lactate may provide increased levels of hydrogen in order to reduce effects of competition stimulating e growth of RD species (Wrenn 1996). If lactate does not produced increased growth rates, other

environmental factors such as pH must be ruled out to determine the cause of the extended acclimation period.

Materials and Methods

Microcosm Set Up

Microcosms were designed to mirror the conditions of the pilot scale BFP system operating at the ReSolve facility. Glass serum bottles (160 mL) were filled with 32 g of saturated peat and sand mixture (1:1.5 by weight) and 81 mL of de ionized water (DI). Worcester Peat Company in Cherryfield, Maine provided the peat for both this experiment and the pilot scale study at the ReSolve site. Additionally, 10 mL of slurry consisting of a reductive dechlorinating culture was added to the appropriate bottles and then spiked with chemical as appropriate (Mbuligwe 2008). The microcosms were prepared under anaerobic conditions and capped with rubber stoppers and aluminum crimp clamps to prevent exposure to oxygen during the course of experimental testing. The headspace was filled with nitrogen gas, slightly pressurizing the bottles. The microcosms were incubated in darkness at 25^{o}C.

This study incorporated six treatments, with two replicates for each treatment. The control treatments: Treatment 1 (spiked with *cis* 1,2-DCE only), Treatment 2 (spiked with 1,1-DCA only), Treatment 3 (spiked with *cis* 1,2-DCE and 1,1-DCA); and the experimental treatments: Treatment 4 (spiked with 3 mM lactate and *cis* 1,2-DCE), Treatment 5 (spiked with 3 mM lactate and 1,1-DCA), Treatment 6 (spiked with 3 mM of lactate, *cis* 1,2-DCE and 1,1-DCA).

Bottles were spiked on day zero and allowed to incubate for intervals between aqueous and gas sampling. Aqueous samples were extracted using a glass micro syringe. Gas samples were extracted using a gas tight syringe. Samples were monitored not only for the parent

compounds (*cis* 1,2-DCE and 1,1-DCA) but daughter products: vinyl chloride (VC), chloroethane (CA), ethene, and ethane.

Analytical Methods

Aqueous phase samples (0.5 mL) were diluted in 40mL of DI water and analyzed using a gas chromatograph/mass spectrometer (GC/MS) (Agilent Technologies 6890N Network GC System, Agilent Technologies 5973 Network Mass Selective Detector) coupled to an AquaTek 70 Autosampler® (Teledyne Tekmar) and Velocity XPT® purge and trap sample concentrator (Teledyne Tekmar) to detect parent and daughter compounds (*cis* 1,2-DCE, 1,1,-DCA, vinyl chloride, and chloroethane) using EPA Method 8260B.

Ethene and ethane gases were analyzed using a GC/FID. Head space sample (1 mL) was injected into a gas chromatograph with flame ionization detector (Agilent 5890 Series II) equipped with a 2.4 m x 0.32 mm ID column packed with Carbopack b/1% Sp-(Supelco, Bellefonte, PA). The column was held at 50^{o}C isothermally for 6.5 min, and the injector and detector temperatures were 375 and 325^{o}C, respectively. The carrier gas was ultra high purity nitrogen at a flow rate of 12 mL/min. Analytical standards and surrogate for the chlorinated VOCs were obtained as mixtures from Supelco Analytical. Ethene and ethane calibration gases were obtained from Supelco Analytical.

H Testing and Manipulation

The pH of the microcosms was tested by extracting 3 mL of solution from each microcosm and applying the solution to a pH test strip (range 0-14) in a test tube to determine an approximate pH of the environment within the microcosm. pH was confirmed using a combination pH electrode and meter (265A Orion pH meter). Adjustments were made with basic solutions of 40g/L NaOH and a buffer solution of 0.10 M K_2HPO_4 and KH_2PO_4.

Results and Conclusions

Results from the microcosm study displayed inhibited degradation as documented in Figures 3.1-3.6. In every replicate, the amount of contamination decreased to approximately 20 to 25 µmoles independent of treatment. While a significant decrease in parent concentration was observed, no daughter products were formed. In addition to the lack of daughter products, very little ethene and ethane were detected indicating RD did not occur. The loss of parent compound was likely due to several additional loss mechanisms including sorption and abiotic reduction from inorganic compounds present in the peat including ferric sulfide (FeS) (Kennedy et al 2006).

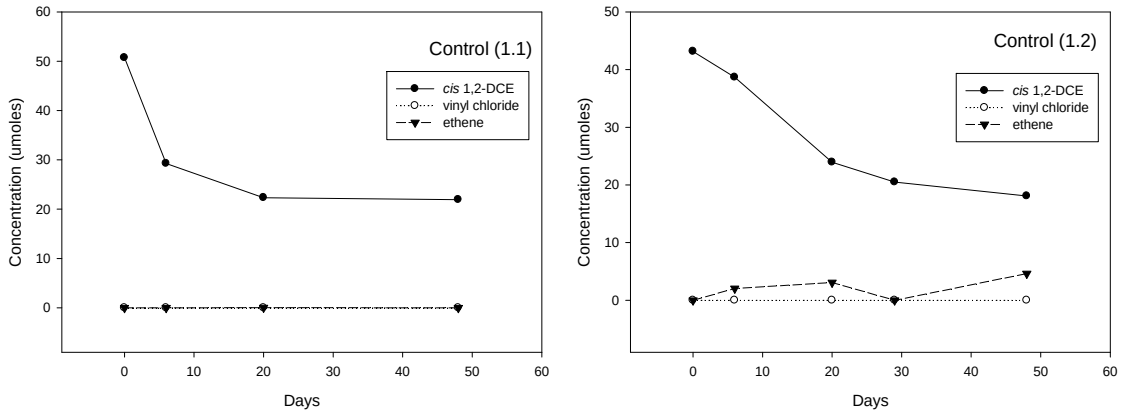

Figure 3.1. Degradation of *cis* 1,2-DCE in peat from Worcester Peat Co.

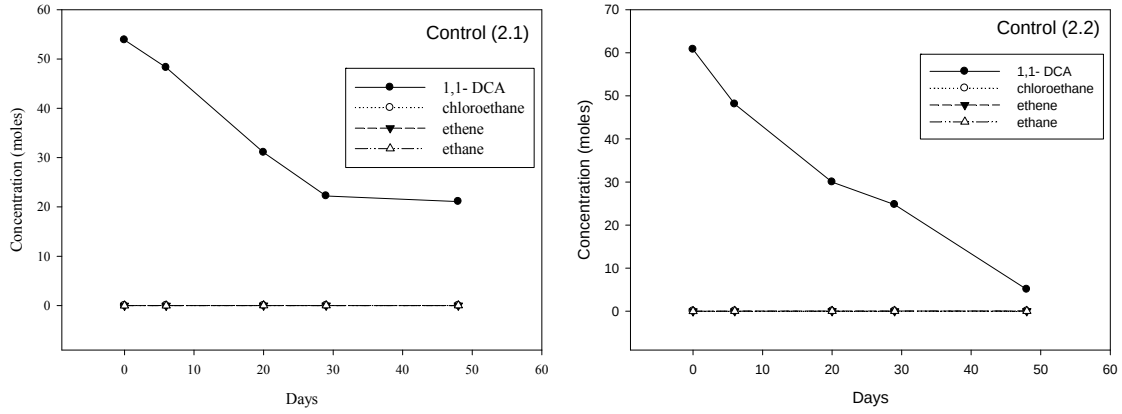

Figure 3.2. Degradation of 1,1-DCA in peat from Worcester Peat Co.

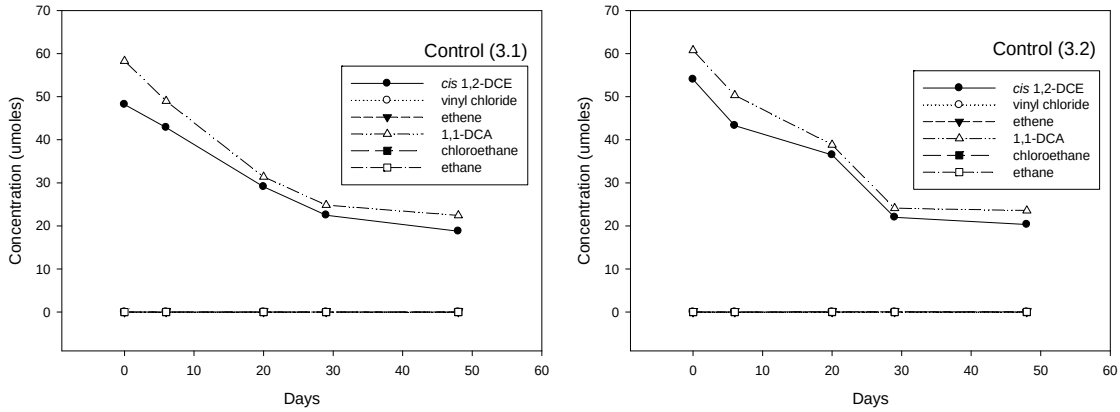

Figure 3.3. Degradation of *cis* 1,2- DCE and 1,1-DCA in peat from Worcester Peat Co.

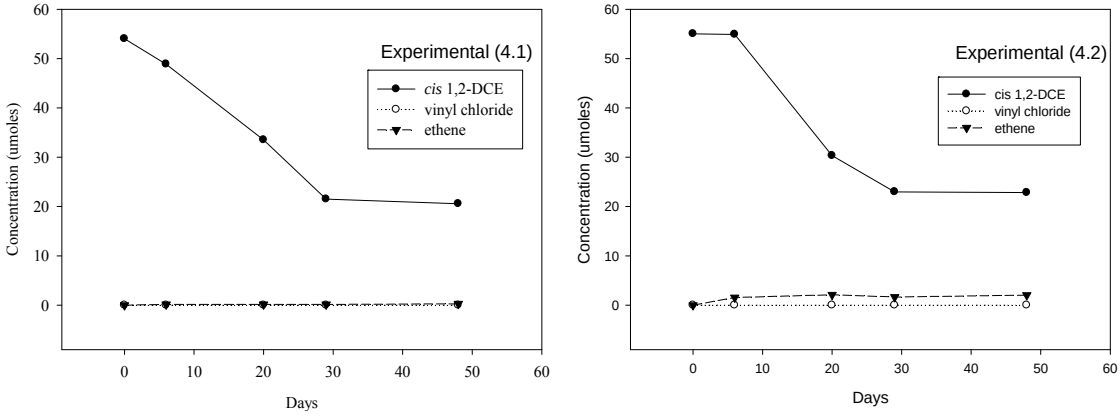

Figure 3.4. Degradation of *cis* 1,2-DCE in microcosm containing peat from Worcester Peat Co and lactate.

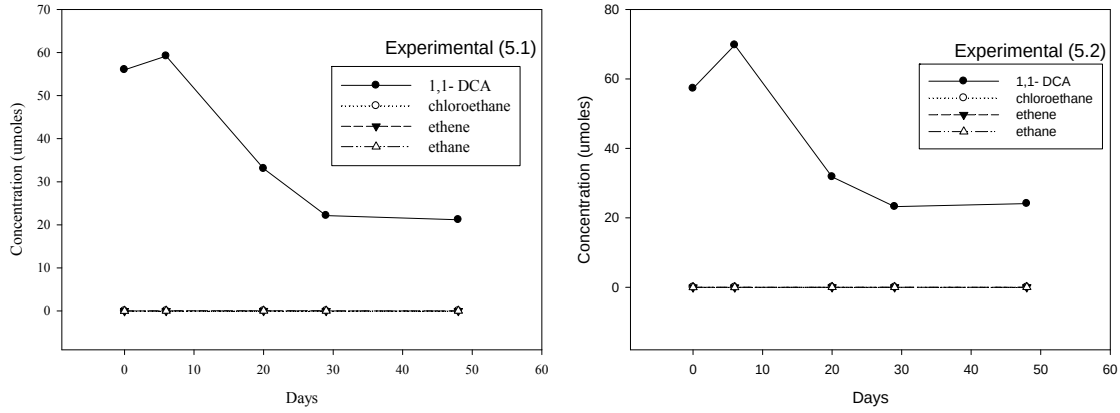

Figure 3.5. Degradation of 1,1-DCA in microcosm containing peat from Worcester Peat Co. and lactate.

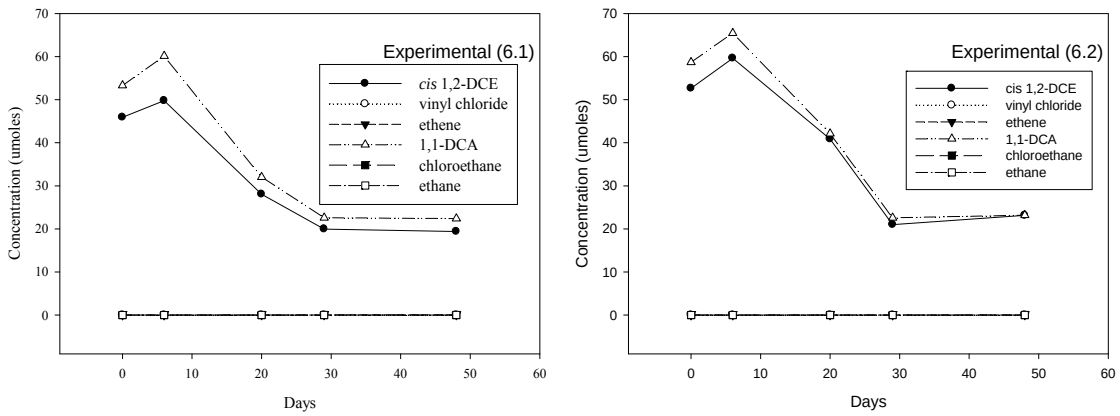

Figure 3.6. Degradation of *cis* 1,2-DCE and 1,1-DCA in microcosm containing peat from Worcester Peat Co and lactate.

It was suspected that the environmental condition of the microcosms limits RD microbial activity and not the lack of electron donors. The pH of each microcosm was measured determined to be too acidic to support microbial activity (pH=3-4). It is likely the acidic conditions of the microcosms could not support microbial growth of the desired organisms. Commercial Worcester Peat originated from a sphagnum peat bog with very acidic pH. Other commercially available peats from reed-sedge deposits are buffered near neutrality. (Mitsch and Gosselink 2000)

Microcosms were neutralized to correct the pH. After 24 hours of rest, the solutions in the bottles turned rust colored (Figure 3.7) indicating that the iron oxidized to the ferric form (+3) from the ferrous form (+2). This color change could be due to the introduction of oxygen with the buffer solution or the change in pH coupled with precipitation of iron. Bottles were allowed to incubate for several months, but no microbial activity was observed and parent compound concentrations remained the same. It is likely that the microbial populations in these microcosms perished in the presence of the acidic solution.

After the acidic pH of the microcosms was established as at least one of the limiting factors contributing to the initial acclimation time within the microcosms, data from the pilot

Figure 3.7. Color change in microcosm after pH was neutralized (right) versus acidic microcosm (left).

scale testing was re-evaluated. It was determined that the initial pH of the trenches were extremely acidic and similar to the conditions observed in the microcosm study (Figure 3.8). As time progressed, the pH of the trenches began to neutralize as groundwater with alkalinity passed through the beds. As pH approached the approximate pH of groundwater (pH=6) RD increased and the BFP pilot study has successfully dechlorinated chlorinated ethenes since that time (Figure 3.8).

Acidic conditions are assumed to be one factor attributing to the observed acclimation period. These conditions are thought to be created when the peat was saturated with water in both the microcosms and pilot scale trenches. In flow through conditions (pilot scale testing), this pH imbalance would naturally be corrected with time as the bicarbonate available in applied groundwater neutralized the system. In the microcosm environment, there was no supply of neutralizing agent to correct the imbalance and hence the bacterial populations never had an opportunity to rebound.

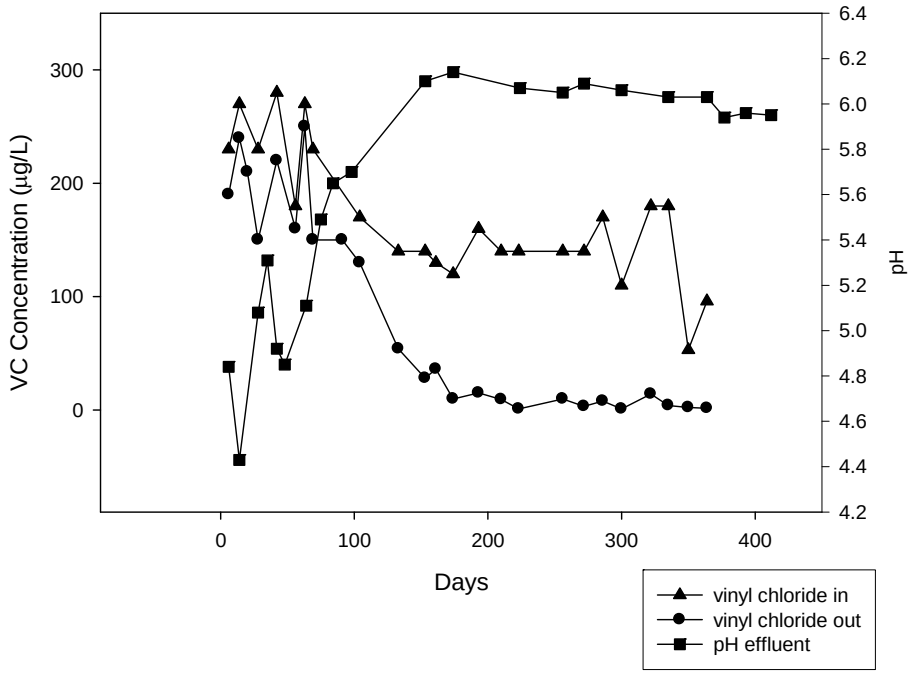

Figure 3.8. Removal of pH and VC in the ABR system.

Since the peat mixture is acidic, it is recommended that when using this particular peat, a neutralizing agent be utilized in the construction process. Applying a base to the bed during construction could neutralize the bed environment when water is applied allowing microbes to flourish immediately in contrast to the delay in microbial growth experienced until the bed naturally neutralized itself.

CHAPTER 4: STIMULATION VIA SUBSTRATE ADDITION

Introduction

Increasing the rate of biodegradation reaction of chlorinated ethenes and ethanes is important because these reaction rates control the size of the system. Therefore rate optimization studies were conducted to determine if 1) rates of dechlorination could be enhanced by additions of simple carbon substrates or hydrogen gas (H_2) and 2) to determine if degradation of chlorinated ethenes and ethanes could occur simultaneously in the bed. Both of these characteristics of the BFP pilot have a direct relationship with the size of the full-scale system. Once the BFP pilot system overcame the initial lag time, *cis* 1,2-DCE degraded prior to 1,1-DCA. This effect is thought to be caused by differing hydrogen thresholds for the different metabolic processes (Kassenga et al 2004, Kassenga et al 2006). Kassenga et al (2004) noted that hydrogen concentrations decreased abruptly before dechlorination of ethenes in wetland systems. Only after chlorinated ethene removal and hydrogen concentrations increased did chlorinated ethane degradation take place in conjunction with methanogenic reactions. Such limitations increase the treatment area necessary to remediate the contamination present at the ReSolve facility as significantly longer residence times are required. In addition to the delayed degradation of 1,1-DCA, overall degradation rates did not approach those observed in natural wetland environments (Lorah et al 1997).

In an effort to decrease required treatment area and accelerate 1,1-DCA degradation, chemical additives were proposed as amendments to the system. These amendments are expected to increase the availability of electron donors to overcome 1,1-DCA degradation lag time as well as accelerate degradation of both chlorinated species. Lactate, acetate, and hydrogen gas were chosen as additives as all three have proven successful in stimulating organisms responsible for the dehalogenation of chlorinated solvents (He et al 2003, Aluenta et

al 2006, Grostern and Edwards 2006, He et al 2002, Chung and Rittman 2008). Lactate is an effective electron donor for *cis* 1,2-DCE degrading organisms as it ferments to produce hydrogen which utilized as an electron donor by chlorinated ethene degraders (Fennell and Gossett 1997). Lactate is thought to be suitable for chlorinated ethane degrading microbes as well, as the degradation process appears to be linked to a hydrogen dependent methanogenic reaction (Kassenga et al 2006 and Debest et al 1997).

It may become necessary to provide large quantities of electron acceptors to overcome interspecies competition and stimulate growth as the partial pressure of hydrogen directly effects the degradation of chlorinated ethenes (Ballapragada et al 1997). The direct application of hydrogen gas may be a possible alternative to addition of an organic acid like lactate. H_2 is suitable for these applications as large quantities of gas can be applied easily as opposed to the liquid addition of lactate. The direct addition of hydrogen to a system is one that has not been given much credit as hydrogen is an extremely explosive gas. Safety concerns for those working at a facility as well as those nearby often rule out this option. However, Chung and Rittmann (2008) showed that the application of hydrogen gas can be utilized successfully as a microbial stimulant in a safe, effective manner. It is thought that the addition of direct hydrogen to the system could provide an electron donor that is readily available to microbes responsible for *cis* 1,2-DCE and 1,1-DCA degradation. The direct hydrogen application may allow substantially more electron donors to be easily applied to a system compared to adding chemical which must ferment to produce hydrogen. This increased concentration of electron donors should promote the degradation of both parent compounds leading to increased degradation rates.

If interspecies competition cannot be overcome via the addition of hydrogen in either the form of lactate or hydrogen gas, it may be possible to apply a carbon source which is preferentially utilized by methanogens, such as acetate. Methanogenic bacteria can utilize

acetate as an electron donor directly giving them an advantage over other hydrogen utilizing micro-organisms and have been shown to cometabolize many of these chlorinated ethanes and may provide an important role in system function (De Best et al 1999, Aluenta et al 2006).

Materials and Methods

Microcosm Set Up

Glass serum bottles (160 mL) were filled with 50g of saturated compost (Soil Builder Compost, McGill Environmental Systems) and sand mixture (1:1.5 by weight) and 81 mL of de-ionized water under. Additionally, 10 mL of slurry containing a reductive dechlorinating population was added to the microcosms and then spiked with chemical as designated under anaerobic conditions (Mbuligwe 2008). The headspace was filled with nitrogen gas, slightly pressurizing the bottles. The microcosms were incubated at 25^{o}C.

The study incorporated six treatments, two replicates of each treatment. The control treatments: Treatment 1 (spiked with *cis* 1,2-DCE only), Treatment 2 (spiked with 1,1-DCA only), Treatment 3 (spiked with *cis* 1,2-DCE and 1,1-DCA); the experimental treatments: Treatment 4 (spiked with *cis* 1,2-DCE and treatment), Treatment 5 (spiked with 1,1-DCA and treatment), Treatment 6 (spiked with *cis* 1,2-DCE and 1,1-DCA and treatment). All six treatments were utilized for the lactate study in which 3mM of lactate were applied to each microcosm.

Lactate additions were done once to acclimate the microcosms and concentrations measured intermittently over 3 months to determine if degradation had initiated (data not shown). Then, experiment was continued by respiking with VOCs and electron donors as described above to continue acclimation (data not shown) before respiking for data collection.

The hydrogen and acetate studies utilized only treatments 2,3,5, and 6. For these tests, 10 mL hydrogen gas at 20 atm and 25^{o}C, and acetate (3.5 mM) were applied to each microcosm

respectively. Additions of H_2 and acetate were performed using the same bottles used for the lactate study and the addition of these substrates was followed immediately by respiking parent compound as appropriate.

Bottles were tested to ensure neutral pH range with pH strips (range 1-14), then spiked on day zero and allowed to incubate for appropriate intervals between aqueous and gas sampling. Aqueous samples were extracted using a glass micro syringe and gas samples extracted using gas tight syringes. Samples were monitored for parent compounds (*cis* 1,2-DCE and 1,1-DCA) and daughter products: vinyl chloride (VC), chloroethane (CA), ethene, and ethane. In addition, hydrogen gas levels within the microcosms were also monitored.

Analytical Methods

Sampling and analytical methods for this study mirror those in the previous study with the exception of the use of a different model of gas chromatograph/flame ionization detector (GC/FID). Aqueous samples were sampled by analyzing 0.5 mL of aqueous samples diluted in 40mL of DI water using a gas chromatograph/ mass spectrophotometer (GC/MS) (Agilent Technologies 6890N Network GC System, Agilent Technologies 5973 Network Mass Selective Detector) coupled to an AquaTek 70 Autosampler® (Teledyne Tekmar) and Velocity XPT® purge and trap sample concentrator (Teledyne Tekmar) to detect chlorinated VOCs using EPA Method 8260B. Ethene and ethane gases were analyzed using a GC/FID. Head space samples (1 mL) were injected into the gas chromatograph with flame ionization detector (Agilent 6850), equipped with a 2 m x 0.8 in Hayes Sep D column packed with Carbopack b/1% Sp-(Supelco, Bellefonte, PA). The column was held at 80^{o}C isothermally for 3.25 min, and the injector and detector temperatures were 225^{o}C. The carrier gas was ultra high purity nitrogen at a flow rate of 12 mL/min. Analytical standards and surrogate for the chlorinated VOCs were obtained as

mixtures from Supelco Analytical. Ethene and ethane calibration gases were obtained from Supelco Analytical.

Hydrogen gas was analyzed using a reduction gas analyzer (Trace Analytical, Menlo Park, CA) equipped with a reduction gas detector. Head space samples were injected into a 1 mL gas sampling loop prior to being separated using a molecular sieve analytical column (Trace Analytical, Menlo Park, CA) at a temperature of 40^{o}C. Ultra high purity nitrogen (Capitol Welders Supply Co., Baton Rouge, LA) was used as the carrier gas. The carrier gas was first passed through a catalytic combustion converter (Trace Analytical, Menlo Park, CA) to remove traces of H_2.

Results and Conclusions

Lactate: *cis*-1,2-DCE Treatments 1 and 4

Results from microcosms treated with *cis* 1,2,-DCE alone (treatments 1 and 4) are depicted in Figures 4.1 and 4.2. Figure 4.1, depicts the degradation of *cis* 1,2-DCE to vinyl chloride in the control treatment with no lactate addition. VC was then transformed to form an end product. This end product is typically ethene which is then converted to ethane and then to CO_2. The same degradation pathway for *cis* 1,2-DCE was observed in the treatments amended with lactate (Figure 4.2). In both treatments it is important to note that VC, a known carcinogen, was not conserved.

Small quantities of ethene and ethane were measured during the experiment. The trends of the gas data are as expected with ethene levels increasing as *cis* 1,2-DCE disappears and ethane concentrations increase as ethene diminishes. This finding is concerning as the BFP and ABR pilot tests produced significant amounts of ethene and ethane during operation (ReSolve Superfund Site: Sustainability 2009). In controlled environments, ethene is often measured and compared to original concentrations of parent compound to ensure complete transformation

(Mbuligwe 2008; Kassenga et al 2003). Low ethane concentrations have been observed in the compost material in previous experiments.

It is possible that microbial communities are consuming ethene and ethane immediately (Elsgaard, 2000; Louarn et al. 2006) preventing accumulation as observed in the ABR and BFP systems. It is also possible the anomaly is due to a quality control issues with the GC-FID utilized to analyze samples as ethene and ethane concentrations increase and decrease at appropriate intervals as VC and CA degraded.

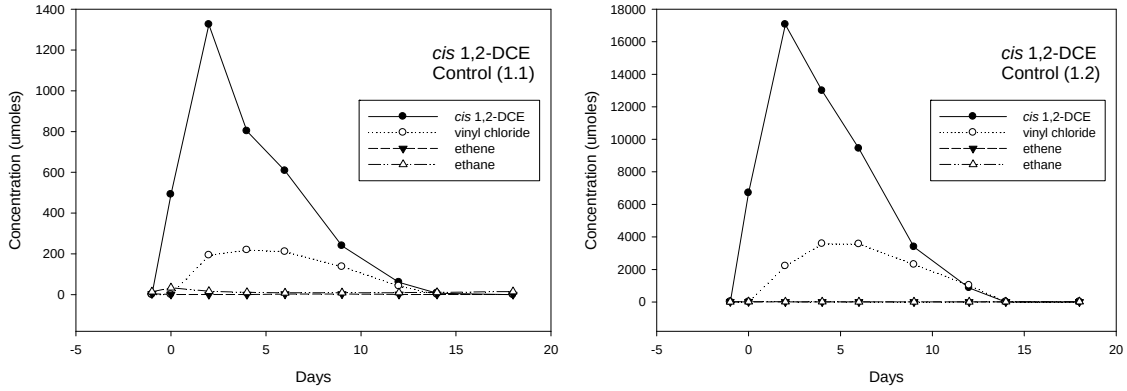

Figure 4.1. Degradation of *cis* 1,2-DCE in control microcosm.

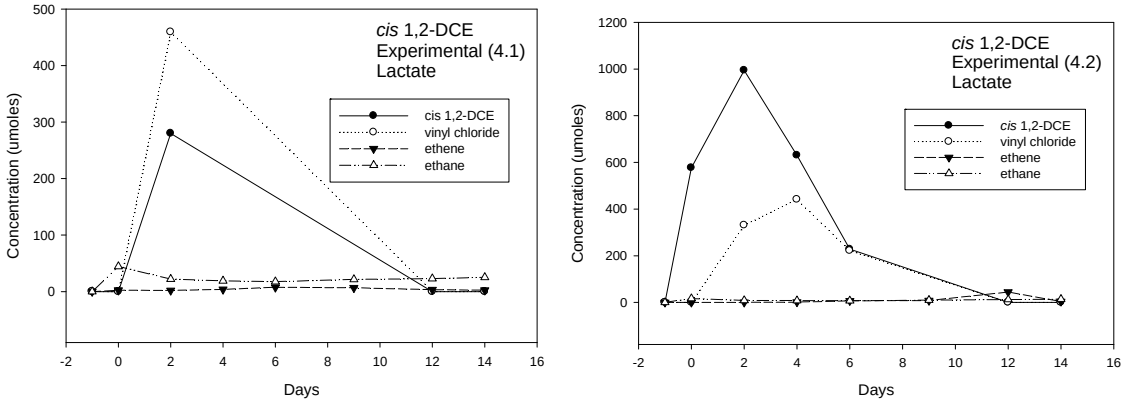

Figure 4.2. Degradation of *cis* 1,2-DCE in experimental treatment containing lactate.

Both treatments were successful in removing all of the chlorinated VOCs within the microcosms. Figure 4.3 depicts the hydrogen concentrations in the control treatments peaking within the first two days and then quickly decreasing to levels under detection limits by day four.

The experimental treatment displayed lower levels of hydrogen than the control treatment with wide variation in concentrations between the replicates (Figure 4.4). The variation in hydrogen within all of the microcosms may be due to microbial utilization of hydrogen during reductive dechlorination. As lactate ferments, hydrogen concentrations would be expected to increase and as microbes utilizes this gas, concentrations decrease respectively.

The use of hydrogen was rapid in experimental treatments resulting in the decreased observed concentrations. Hydrogen concentrations in microcosms amended with lactate peaked within the first two days of monitoring as observed in the control treatments. Concentrations decreased over the next couple days, falling below detection levels before the fourth day of observation. This trend for rapid decrease in hydrogen concentration is similar to that noted by Kassenga et al (2004); however, Kassenga noted this decrease within eight hours of introducing *cis* 1,2-DCE. The hydrogen drawdown occurred concurrently with the utilization of hydrogen during the RD of chlorinated ethenes.

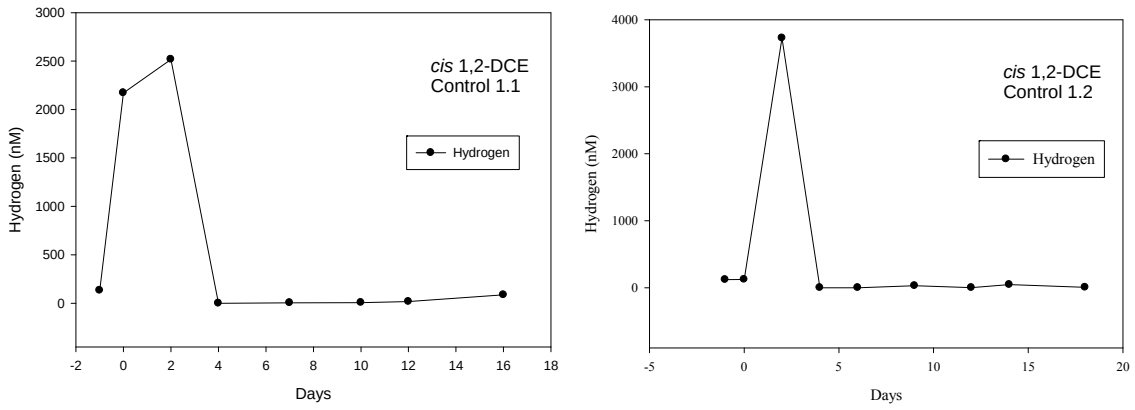

Figure 4.3. Hydrogen concentration in control treatment containing *cis* 1,2-DCE.

First order degradation rate constants for *cis* 1,2-DCE are reported in Table 4.1. *cis* 1,2-DCE control treatments display similar degradation rate constants (0.115±0.063 – 0.109±0.060).

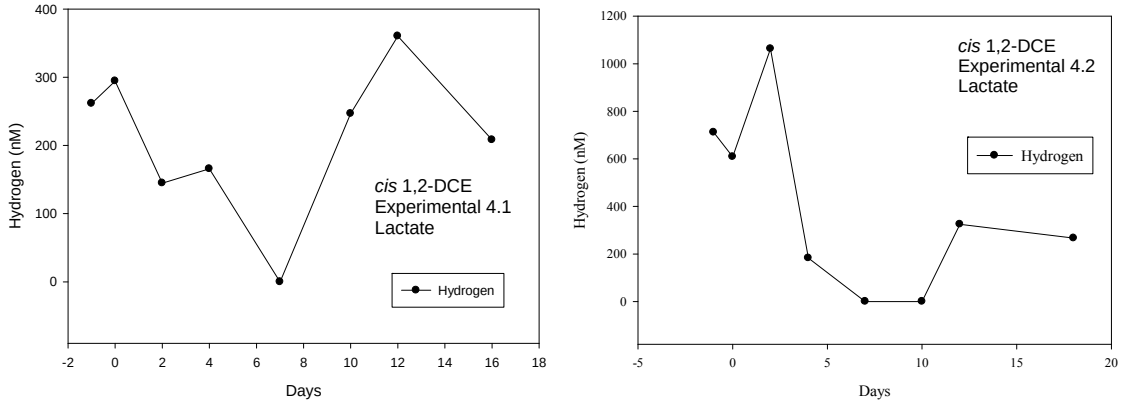

Figure 4.4. Hydrogen concentration in experimental treatment containing *cis* 1,2-DCE alone amended with lactate.

There is no statistical difference between experimental treatments which indicates lactate did not stimulate RD of *cis* 1,2-DCE and the system is limited by other factors in contrast to the findings of Ballapragada et al (1997). The high organic carbon content of the compost material may explain the lack of an effect; some other substance may be limiting for these reactions.

Table 4.1. Degradation rate constants, standard error, and half life for *cis* 1,2-DCE in lactate study.

LACTATE				
Treatment	Rate Constant (1/d)	Standard Error	DCE ½ Life (days)	Lag Time (days)
1.1 *cis* 1,2-DCE (control)	0.2409	0.0206	2.877	2
1.2 *cis* 1,2-DCE (control)	0.2118	0.0294	3.272	2
4.1 *cis* 1,2-DCE (lactate)	0.3919*	-	1.768	2
4.2 *cis* 1,2-DCE (lactate)	0.3159	0.0473	2.194	2

* Rate constants are minimum constants computed from initial two data points.
is limited by other factors in contrast to the findings of Ballapragada et al. (1997).

Lactate. 1, 1-DCA Treatments 2 and 5

Results from microcosms treated with 1,1-DCA alone, treatments 2 and 5, are depicted in Figures 4.5-4.6. 1,1-DCA degraded to chloroethane (CA) and in turn was then utilized to form a gaseous daughter product (most likely ethane) in both the control and experimental treatments; chloroethane was not conserved during this process. Note that chloroethane was elevated in the bottles initially due to a previous spike of 1,1-DCA to acclimate the samples. Similar to the *cis* 1,2-DCE treatments, little ethane was measured during the experiment; ethene is not an expected end product of 1,1-DCA degradation. The lack of observed ethane production is attributed to use by microbial populations or quality control issues with the GC/FID utilized in analyzing samples.

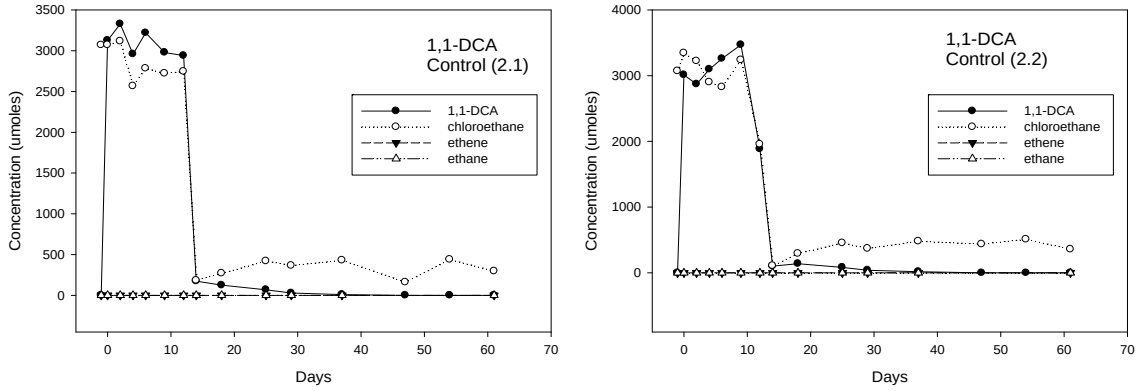

Figure 4.5. Degradation of 1,1-DCA in control microcosms.

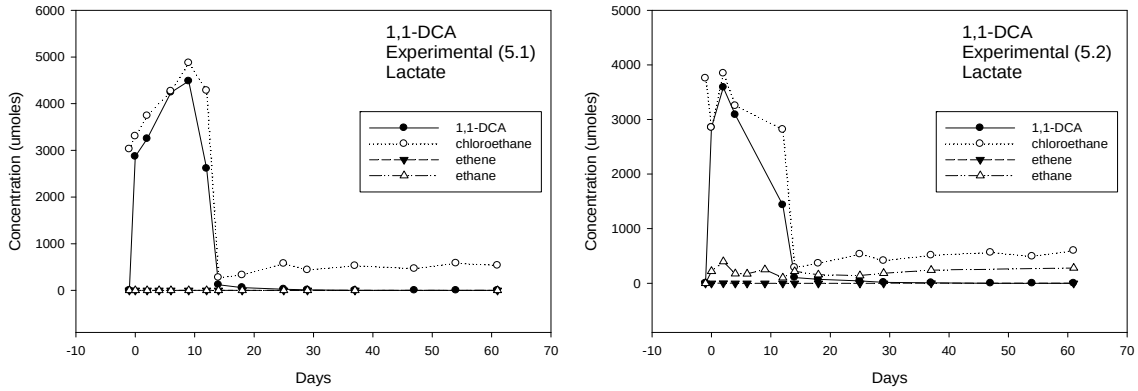

Figure 4.6. Degradation of 1,1-DCA in experimental microcosms containing lactate.

The control treatment displayed a 15 day lag time for 1,1-DCA degradation in contrast to the experimental treatment (5.2) where 1,1-DCA begins to degrade shortly after the chemical is introduced to the environment. The lag time in treatment 5.1 is unexplainable and most likely due to environmental variations between replicates. The reduction of lag time in experimental treatment 5.2 could be due to the addition of lactate and the electron donors provided via fermentation.

Hydrogen concentrations in the control replicates varied greatly during the monitoring period (Figure 4.7). The experimental treatment displayed similar levels of hydrogen, comparatively (Figure 4.8). After day four, H_2 concentrations were 309 nM and 148 nM in control 2.2 and experimental microcosm 5.2 respectively. These concentrations are higher than those observed in the treatments 1 and 4 with *cis*-1,2-DCE. This is consistent with methanogenesis as the dominant H_2 utilization process which has higher H_2 threshold than RD (Kassenga et al., 2004).

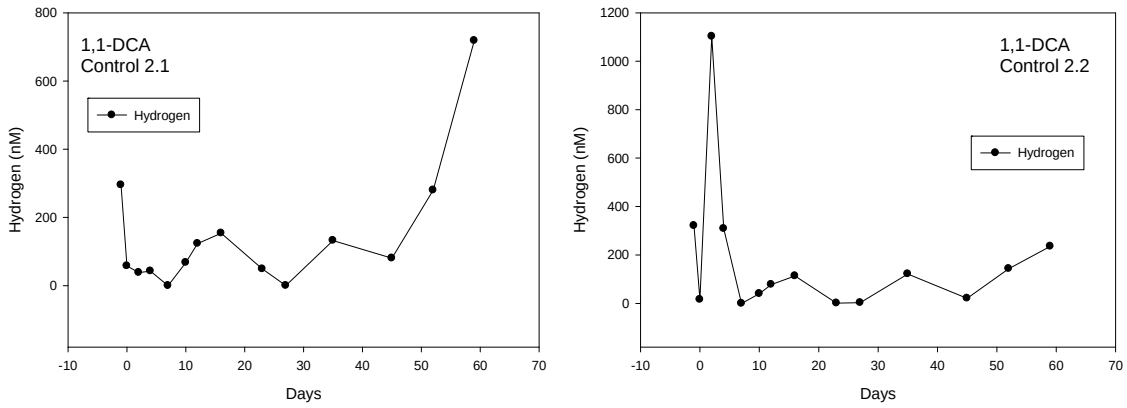

Figure 4.7. Hydrogen concentration in control treatments containing 1,1-DCA.

In Table 4.2, 1, 1-DCA degradation rate constants are reported. No significant difference was observed between the control and experimental treatments; however, one experimental microcosm did exhibit accelerated dechlorination of 1,1-DCA as compared to the control treatments. The results from these treatments are similar to those of the *cis* 1,2-DCE treatments;

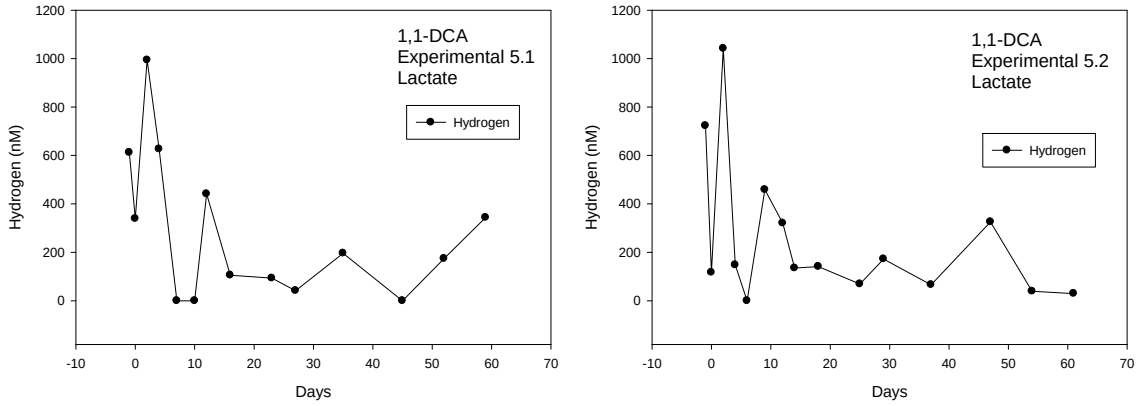

Figure 4.8. Hydrogen concentration in experimental treatments containing 1,1-DCA and lactate.

control treatments show little variability between observed degradation rates while experimental treatments vary greatly. First order rate constants for all treatments exceed that observed by Mbuligwe (2008) but do not approach those observed by Kassenga et al (2004) even with the addition of lactate.

There is no statistical evidence suggesting that lactate enhanced the degradation of 1,1-DCA. Variation in concentrations of parent compound between the two treatments may impact these results as the experimental treatment contained more parent chemical than the control treatment. Additionally, lactate does reduce 1,1-DCA RD lag time.

Lactate. *cis* 1,2-DCE and 1,1-DCA Treatments 3 and 6

Results from treatments containing both *cis* 1,2-DCE and 1,1-DCA (treatment 3 and 6) are depicted in Figures 4.9 and 4.10. The pathways remain the same as previously observed; *cis* 1,2-DCE degrades to VC and then to a final product while 1,1-DCA degrades to chloroethane and then to a final product; no daughter products were conserved in this process. As observed in the previous treatments, little ethene and ethane was measured and is attributed to either addition microbial reaction or quality control issues with sampling instruments.

Table 4.2. Degradation rate constants, standard error, and half life for 1,1-DCA in lactate study.

LACTATE				
Treatment	Rate Constant (1/d)	Standard Error	DCE ½ LIFE (days)	Lag Time (days)
2.1 1,1-DCA (control)	0.0895	0.0249	7.743	2
2.2 1,1-DCA (control)	0.1176	0.0325	5.893	4
5.1 1,1-DCA (lactate)	0.3169	0.0605	2.187	9
5.2 1,1-DCA (lactate)	0.1465	0.0228	4.730	2

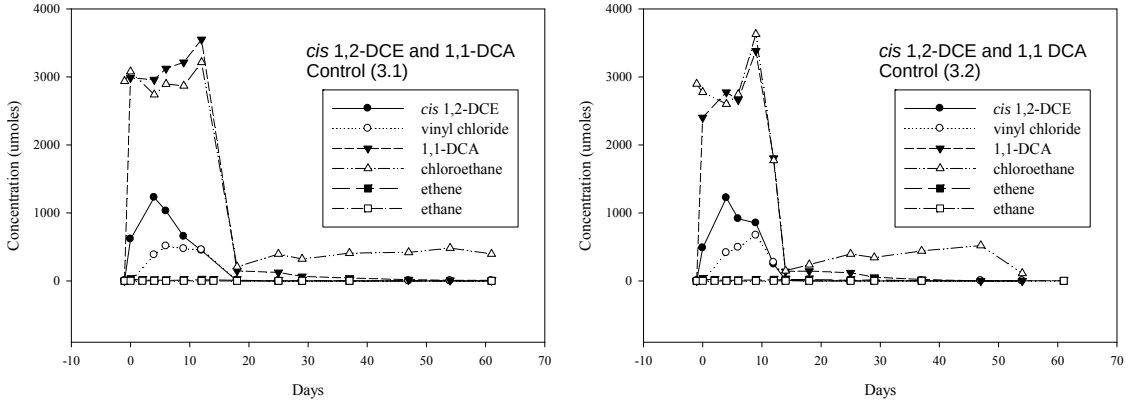

Figure 4.9. Degradation of *cis* 1,2-DCE and 1,1-DCA in control microcosms.

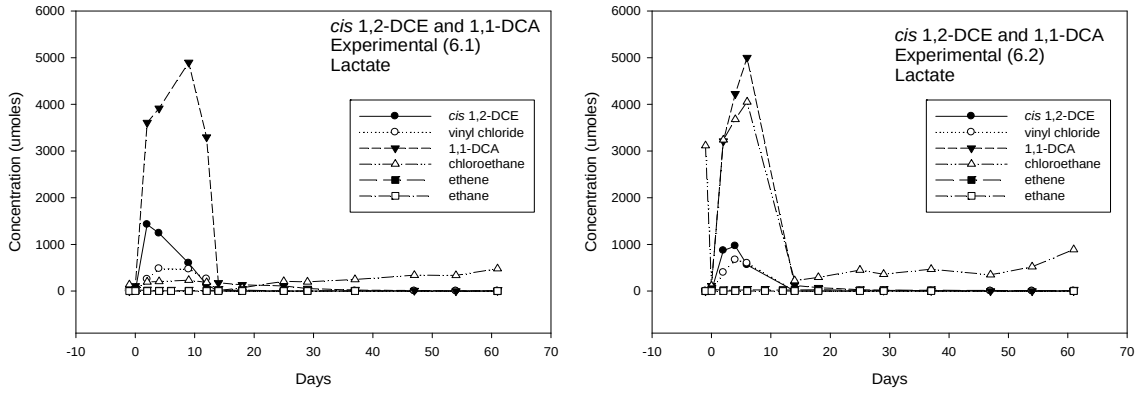

Figure 4.10. Degradation of *cis* 1,2-DCE and 1,1-DCA in experimental treatments spiked with lactate.

Figures 4.11 and 4.12 show the degradation of parent compounds in more detail. It is clear that *cis* 1,2-DCE degrades quickly with almost no lag time in both treatments. In contrast, the experimental and control treatments show similar lag times for 1,1-DCA degradation, approximately 15 days, similar to the lag time observed in the 1,1-DCA alone treatments. This may signify that 1,1-DCA degradation is not dictated by *cis* 1,2-DCE degradation as previously hypothesized and other factors limit its degradation as both *cis* 1,2-DCE and 1,1-DCA levels approached detection limits on day 18.

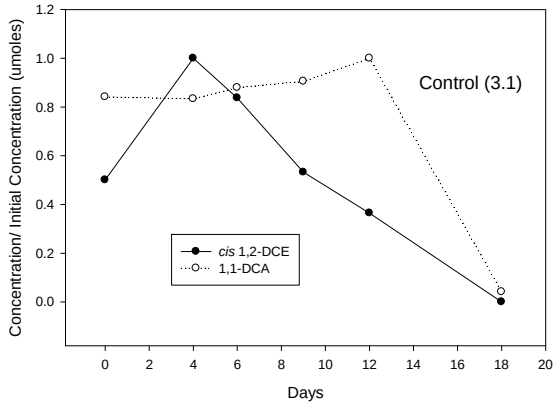

Figure 4.11. Degradation of 1,1-DCA in comparison to *cis* 1,2-DCE in a control treatment. Data for replicate 3.2 not sufficient due to rapid degradation of *cis* 1,2-DCE.

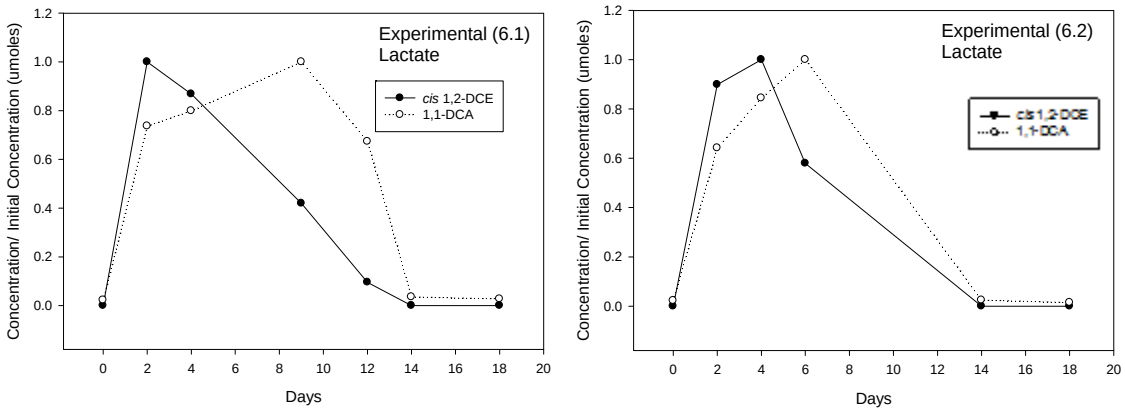

Figure 4.12. Degradation of 1,1-DCA in comparison to *cis* 1,2-DCE in a microcosm amended with lactate.

Hydrogen concentrations did not vary greatly between control replicates and experimental treatment 6.2 (Figures 4.13 and 4.14). The decreased hydrogen concentrations in experimental replicate 6.1 are not able to be explained. Concentrations in both control treatments peaked shortly after VOC addition and then quickly decreased to levels under detection limits. The experimental replicate 6.2 follows the same pattern as the control treatments; however, the hydrogen is utilized more rapidly than the control replicates. The presence of hydrogen at the beginning of the monitoring period and persistence of 1,1-DCA concentrations within the first 15 days is consistent with other findings (Kassenga et al 2004).

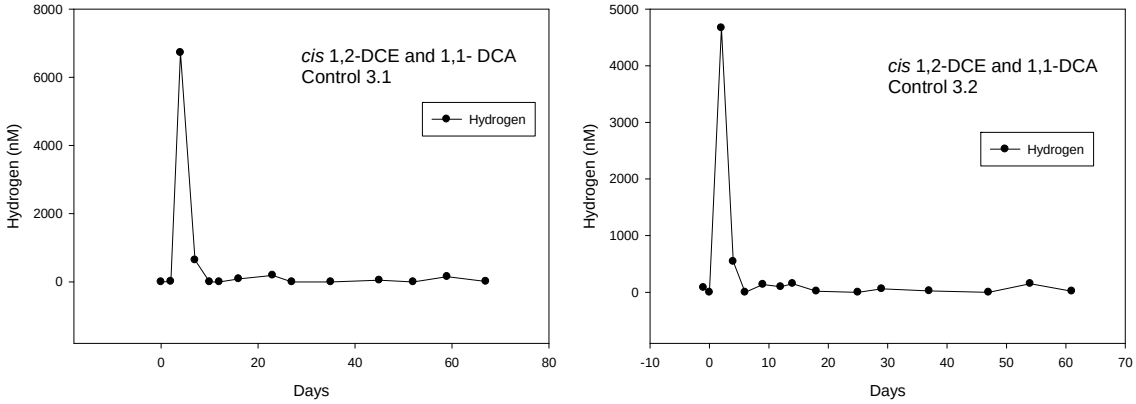

Figure 4.13. Hydrogen concentration in control treatment containing *cis* 1,2-DCE and 1,1-DCA.

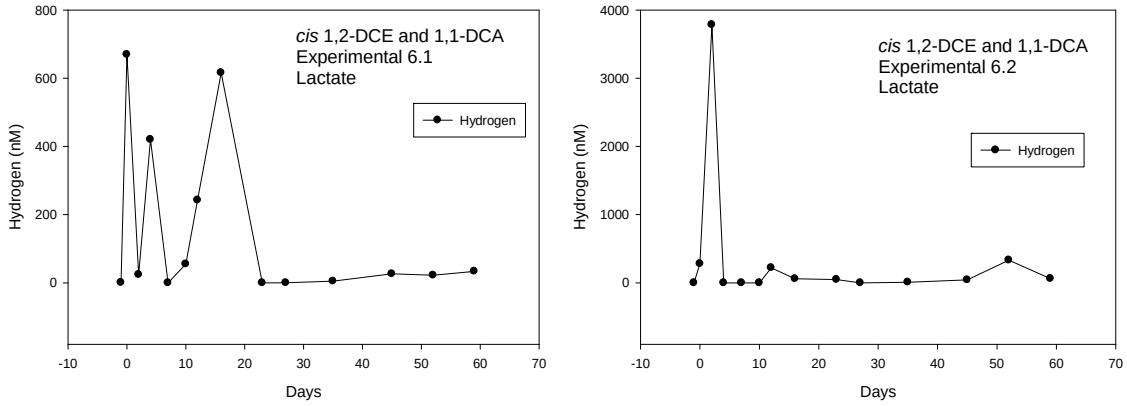

Figure 4.14. Hydrogen concentration in experimental treatments containing cis 1, 2-DCE and 1, 1-DCA spiked with lactate.

The degradation rate constants of both parent compounds (*cis* 1,2-DCE and 1,1-DCA) are reported in Table 4.3. Dechlorination rates of *cis* 1,2-DCE and 1,1-DCA did not statistically differ between control and experimental treatments indicating that the system is not limited by electron donor presence. These findings concur with those in the literature stating the degradation of chlorinated ethanes in the presence of *cis* 1,2-DCE is hindered as microbes responsible for the RD of chlorinated ethenes draw down the level of hydrogen to the point at which no methanogenesis can occur (Yang and McCarty 1998, Kassenga et al 2004). Chlorinated ethanes may not degrade during this time period if their degradation is co-metabolicaly linked to methanogenic activity which requires higher H_2 values.

Conclusions from Lactate Study

These findings clearly indicate lactate is not a suitable addition to the BFP system as a resolution for the degradation lag time identified in the pilot study. Lactate was unable to initiate concurrent degradation of 1,1-DCA with *cis* 1,2-DCE and other factors were responsible for limiting the dechlorination of 1,1-DCA. Hydrogen was utilized in the system in all six treatment scenarios indicating some RD may be occurring to degrade 1,1-DCA when it was not in the presence of chlorinated ethenes.

Table 4.3. Degradation rates, standard error, and half life for *cis* 1,2-DCE and 1,1-DCA in lactate study.

LACTATE								
Treatment	*cis* 1,2-DCE Rate Constant (1/d)	Standard Error	*cis* 1,2-DCE ½ Life (days)	Lag Time (days)	1,1-DCA Rate Constant (1/d)	Standard Error	1,1-DCA ½ Life (days)	Lag Time (days)
3.1 *cis* 1,2-DCE and 1,1-DCA (control)	0.15	0.0153	4.620	4	0.5222	0.0636	1.327	12
3.2 *cis* 1,2-DCE and 1,1-DCA (control)	0.1755	0.0323	3.949	12	0.3227	0.0556	2.148	9
6.1 *cis* 1,2-DCE and 1,1-DCA (lactate)	0.1791	0.235	3.869	2	0.2847	0.0636	2.434	9
6.2 *cis* 1,2-DCE and 1,1-DCA (lacate)	0.3007	0.019	2.305	4	0.4514	0.021	1.535	6

Hydrogen. 1, 1-DCA Treatments 2 and 5

Results from control and experimental microcosms treated with 1,1-DCA are depicted in Figures 4.15 and 4.16. The graphs show the degradation of 1,1-DCA to chloroethane and then to a final end product. No daughter products are conserved in either of the treatments. Little ethane was measured during the experiment which is consistent with the observations in the lactate study; ethene is not an expected end product of 1,1-DCA degradation. The trends of the ethane data are consistent with expected trends; ethane levels increase as 1,1-DCA is degraded. 1,1-DCA lag time is observed only in the control replicate 2.1 (Figures 4.15 and 4.16).

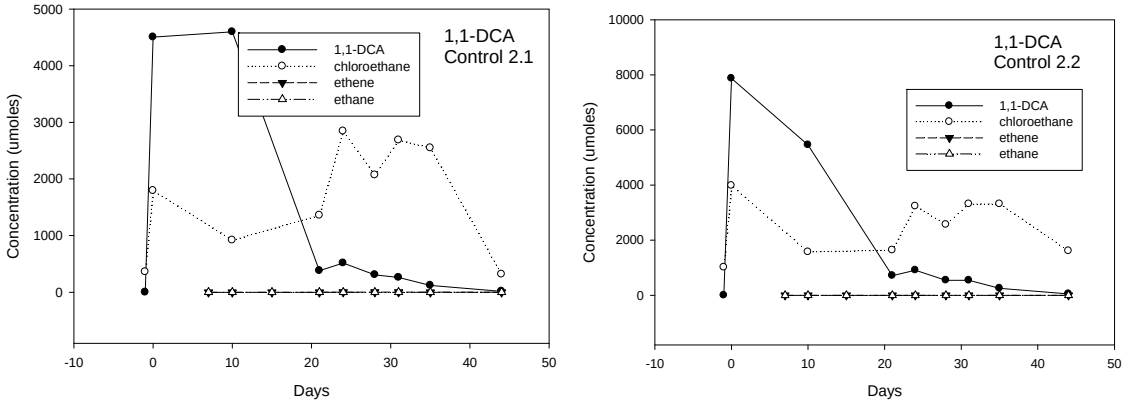

Figure 4.15. Degradation of 1,1-DCA in control treatments.

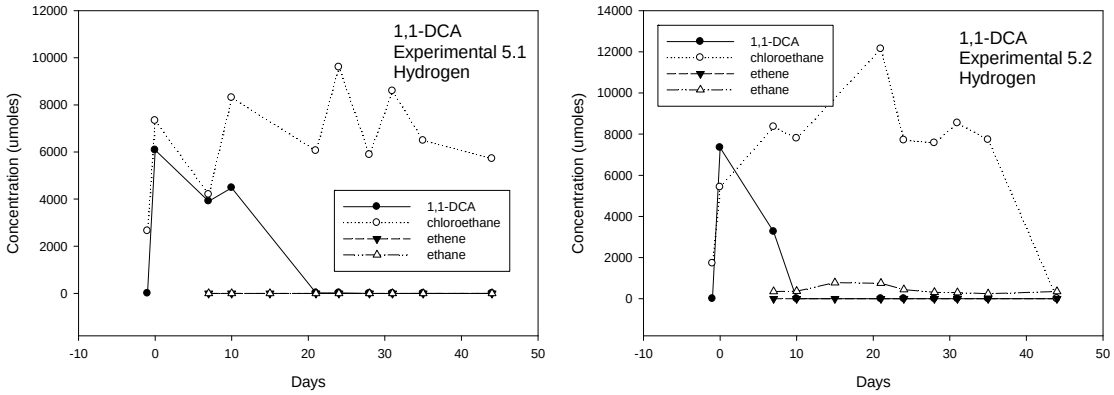

Figure 4.16. Degradation of 1,1-DCA in experimental treatments spiked with hydrogen gas.

Hydrogen concentrations in the control microcosms were significantly lower than those treated with hydrogen gas (Figure 4.17 and Figure 4.18). Figure 4.17 depicts a steady level of hydrogen in replicate 2.1 until day 20 while H_2 concentrations decrease on day 20 in replicate 2.2. The changes in concentration correlate with 1, 1-DCA is removal from the system. The experimental treatments displayed an initial peak of hydrogen during the first few days of monitoring. A dramatic drawdown of hydrogen gas occurred during the first 10 days possibly indicating that hydrogen was utilized during the degradation process as noted in the lactate study and that methanogenic co metabolism is not the only method of 1,1-DCA degradation.

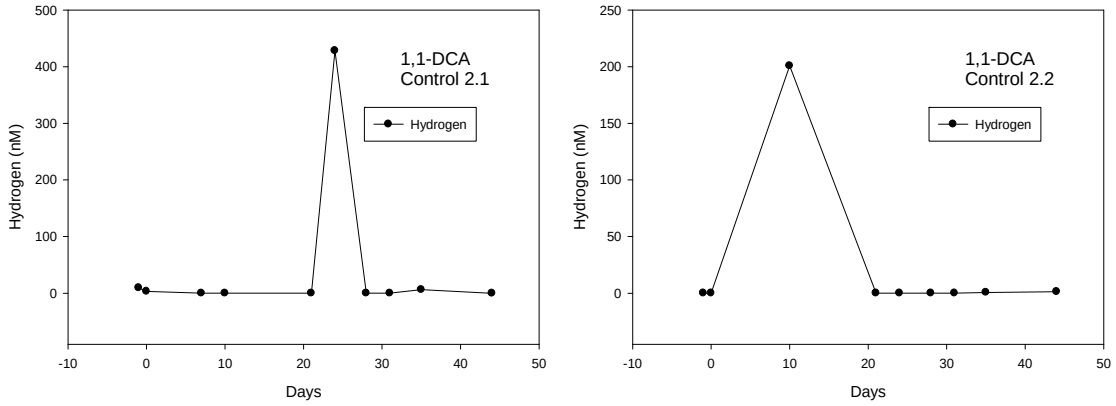

Figure 4.17. Hydrogen concentration in control treatments containing 1,1-DCA.

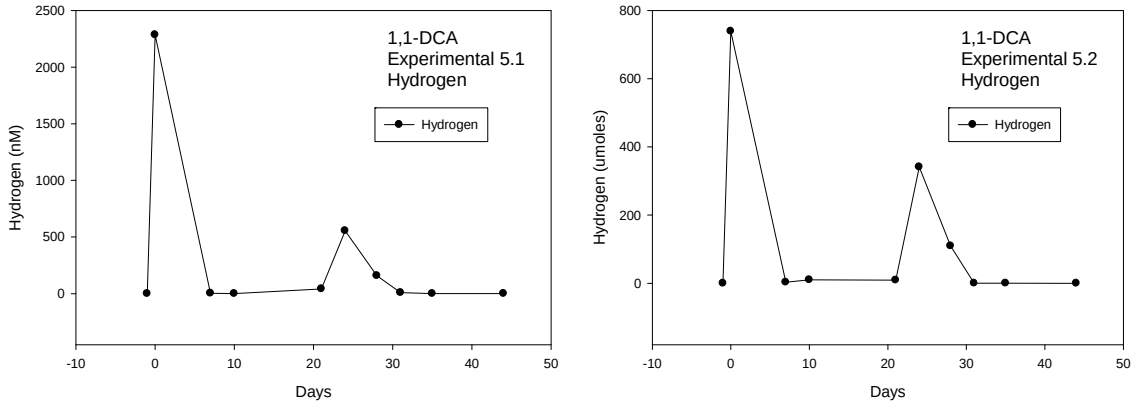

Figure 4.18. Hydrogen concentration in an experimental treatments containing 1, 1-DCA.

Degradation rates for 1, 1-DCA are reported in Table 4.4. Degradation rates of 1, 1-DCA in experimental treatments are not significantly faster than those in the control treatments. Control rates in this study are not significantly different from those observed in the lactate study (0.075/0.077) indicating there were no major changes to the conditions of the microcosms between treatments. These rates again do not approach those observed by Kassenga et al. (2004) but do exceed those observed by others (Klecka et al., 1998). It is possible that not enough hydrogen gas was applied to experimental treatments and completely saturating the environment with hydrogen gas throughout the degradation process might enhance results; however, this may not be feasible at full scale operations as massive amounts of hydrogen would need to be applied to the trenches increasing safety concerns and cost.

Hydrogen. *cis* 1,2-DCE and 1,1-DCA Treatments 3 and 6

Results from microcosms treated with *cis* 1,2-DCE and 1,1-DCA are depicted in Figures 4.19 and 4.20. Degradation pathways are consistent with previous lactate studies and display the same uncharacteristically low levels of ethene and ethane. Chloroethane persisted in these samples longer than the lactate treatments.

Table 4.4. First order degradation rate constant, standard error, and half life for 1,1-DCA in hydrogen study.

HYDROGEN				
Treatment	Rate Constant (1/d)	Standard Error	½ LIFE (days)	Lag Time (days)
2.1 1,1-DCA (control)	0.182	0.0175	3.808	10
2.2 1,1-DCA (control)	0.0784	0.0128	8.839	0
5.1 1,1-DCA (hydrogen)	0.0882	0.0199	7.857	0
5.2 1,1-DCA (hydrogen)	0.1781	0.0335	3.891	0

Figures 4.21 and 4.22 depict the degradation of both parent compounds in more detail. Figure 4.21 depicts *cis* 1,2-DCE degrading immediately. 1,1-DCA lags behind until approximately day 10 when degradation begins. Only after *cis* 1,2-DCE is completely degraded does 1,1-DCA degradation begin. This is similar to observations in the lactate study. Degradation in the experimental replicates show immediate degradation of *cis* 1,2-DCE and no lag time for 1,1-DCA (Figure 4.22); although degradation of 1,1-DCA appears to be hindered until day 10. This hindered degradation does not correlate with findings from other studies. Injections providing

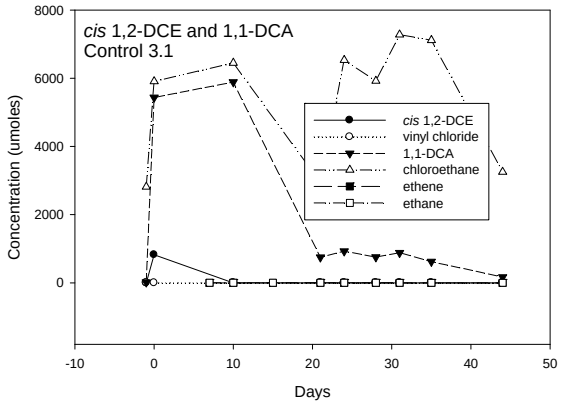

Figure 4.19. Degradation of *cis* 1,2-DCE and 1,1-DCA in control replicate 3.1. Data from replicate 3.2 was removed from the study due to error.

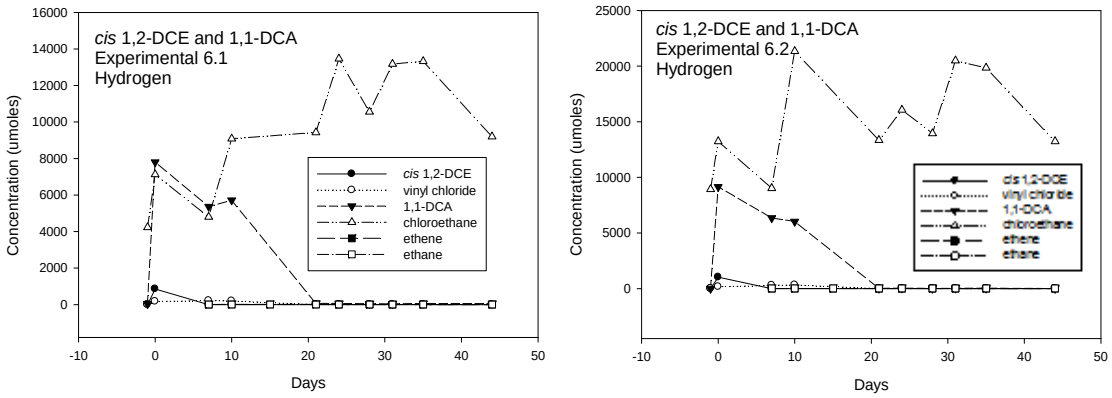

Figure 4.20. Degradation of *cis* 1,2-DCE and 1,1-DCA in experimental treatments spiked with hydrogen gas.

increased H_2 concentrations may have increased degradation rates and proved to be a successful treatment option.

Examining hydrogen concentrations within the treatments may explain the hindered, co-metabolism of 1,1-DCA during *cis* 1,2-DCE degradation (Figures 4.23 and 4.24). The control treatment displayed somewhat consistent hydrogen concentrations until approximately day 25 when they peaked to 250 nM and 107 nM respectively (Figure 4.23). This heightened hydrogen concentration quickly decreased within five days. The increase in H_2 corresponds to the

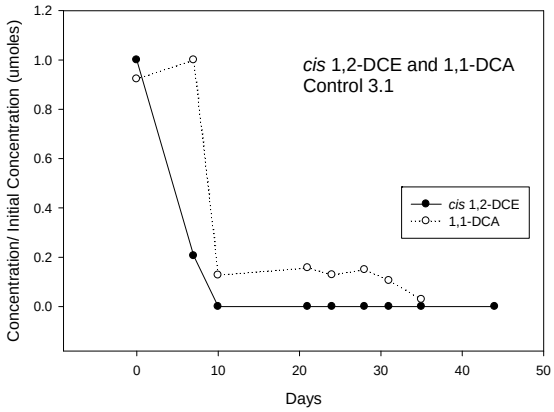

Figure 4.21. Degradation of 1,1-DCA in comparison to *cis* 1,2-DCE in a control treatment.

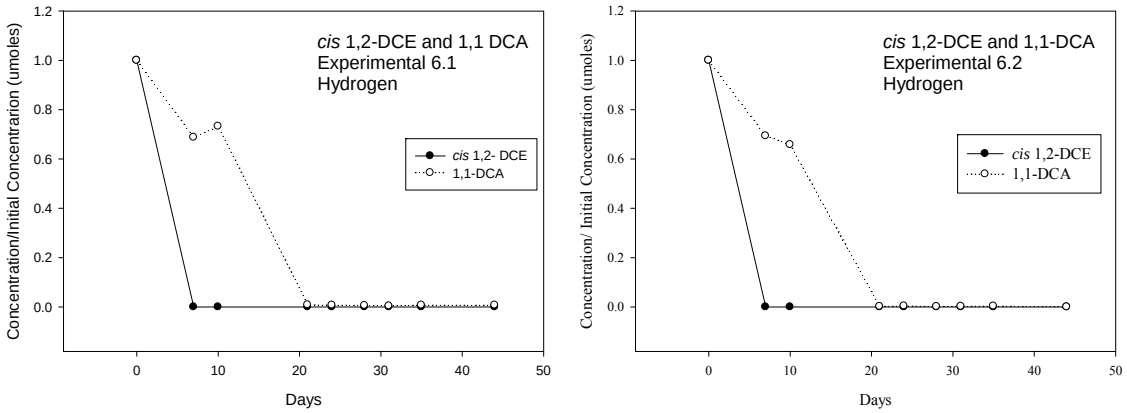

Figure 4.22. Degradation of 1,1-DCA in comparison to *cis* 1,2-DCE in the experimental treatments spiked with hydrogen gas.

disappearance of both parent compounds (*cis*-1,2-DCE and 1,1-DCA). The increase in H_2 may represent the transition of one H_2 utilizing process to another (example: RD to methanogenesis).

The hydrogen in experimental replicates varied in concentration but followed the same general pattern: hydrogen peaked almost immediately and dramatically fell prior to day 10 (Figure 4.24). The dramatic drop in hydrogen concentrations correlate with *cis* 1,2-DCE degradation patterns previously described (Yang and McCarty 1998). Hydrogen concentrations cease to fall as *cis* 1,2-DCE is completely removed from the system. These concentrations then rise, as predicted, as 1,1-DCA degrades.

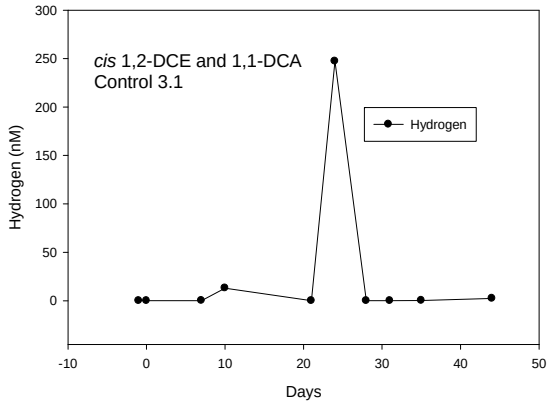

Figure 4.23. Hydrogen concentration in control treatment containing *cis* 1, 2-DCE and 1, 1-DCA.

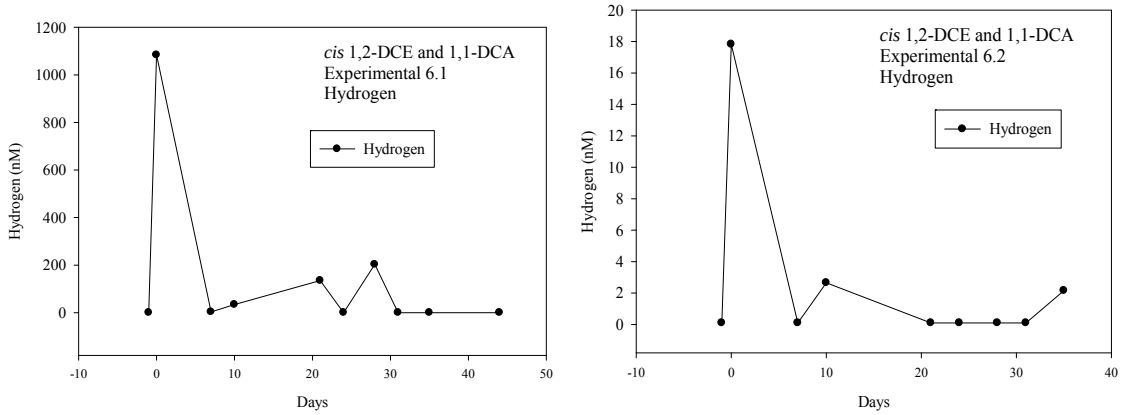

Figure 4.24. Hydrogen concentration in an experimental treatment containing *cis* 1,2-DCE and 1,1-DCA.

The degradation rates of both parent compounds (*cis* 1,2-DCE and 1,1-DCA) are reported in Table 4. Dechlorination rates of *cis* 1,2-DCE did not differ between control and experimental treatments indicating the addition of hydrogen gas did not affect the microbial population's ability to remediate *cis* 1,2-DCE. *cis* 1,2-DCE dechlorination rates in the control treatments were much higher than those observed in the lactate study. The de-chlorination of 1,1-DCA was not statistically faster in experimental treatments compared to the degradation in control treatments and continue to fail to meet those reported by Kassenga et al (2004). Additional hydrogen application may separate these results to give clear statistical meaning to the research.

Table 4.5. First order degradation rate constants, standard error, and half life for *cis* 1,2-DCE and 1,1-DCA in hydrogen study.

HYDROGEN								
Treatment	*cis* 1,2-DCE Rate Constant (1/d)	Standard Error	*cis* 1,2-DCE ½ LIFE (days)	Lag Time (days)	1,1-DCA Rate Constant	Standard Error	1,1-DCA ½ LIFE (days)	Lag Time (days)
3.1 *cis* 1,2-DCE and 1,1-DCA (control)	0.2259*	-	3.068	0	0.1334	0.0184	5.195	10
3.2 *cis* 1,2-DCE and 1,1-DCA (control)	-	-	-	-	-	-	-	-
6.1 *cis* 1,2-DCE and 1,1-DCA (hydrogen)	0.652*	-	1.063	0	0.086	0.019	8.03	0
6.2 *cis* 1,2-DCE and 1,1-DCA (hydrogen)	0.677*	-	1.023	0	0.09	0.018	7.734	0

**Rate constants are minimum constants computed from initial two data points.*

Degradation trends of 1,1-DCA in co-treatment microcosms mimicked those of microcosms containing only 1,1-DCA with no observed lag time of 1,1-DCA degradation, but no significant improvements in first order degradation rate constants. Dosing the microcosms with greater concentrations of hydrogen gas may increase degradation rates, but it is unlikely that rates would improve enough to significantly benefit BFP implementation.

Conclusions from Hydrogen Study

While the addition of hydrogen gas did reduce the initial lag time of 1,1-DCA degradation in microcosms with 1,1-DCA alone and co-treatment microcosms, the degradation of 1,1-DCA did not improve significantly. Utilizing hydrogen as an amendment for the BFP system does not attain treatment goals in the BFP system. It is possible that with increased hydrogen gas applications, the problem could be resolved although cost may hinder the feasibility. Hydrogen may be part of the solution to decreasing the lag time of 1,1-DCA degradation, but it may be possible to stimulate degradation further with other amendments.

Acetate. 1,1-DCA Treatments 2 and 5

Results from control and experimental microcosms treated with 1,1-DCA are depicted in Figures 4.25 and 4.26. The graphs depict the degradation of 1,1-DCA to chloroethane and then to a final end product, most likely ethane. Chloroethane was not conserved in either treatment. Very little ethane was measured during the experiment which is consistent with the findings from the lactate and hydrogen experiments.

Neither control replicate displays lag time for 1,1-DCA degradation which is in contrast to the findings in the lactate and hydrogen studies (Figure 4.25). This is likely due to acclimation since this represented the fourth feeding of the bottles with 1,1-DCA. Similarly, experimental replicate 5.1 does not display 1,1-DCA lag time; however replicate 5.2 does display a lag time of approximately 15 days (Figure 4.26).

As expected, initial hydrogen concentrations in the control microcosms were significantly lower than those treated with hydrogen gas with the exception of replicate 6.2 (Figure 4.27 and Figure 4.28). In both control and experimental treatments hydrogen trends varied greatly and is most likely due to variations in the microcosm environment. Figure 4.27 depicts the hydrogen

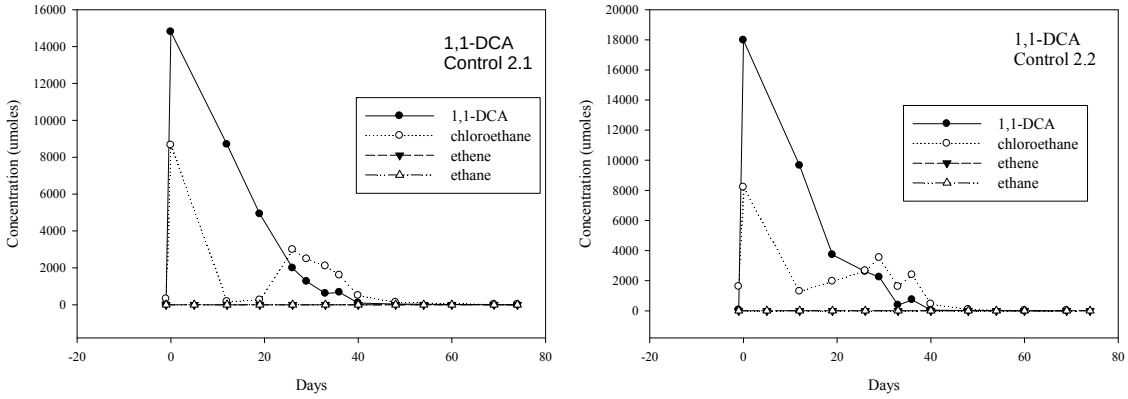

Figure 4.25. Degradation of 1,1-DCA in control treatments.

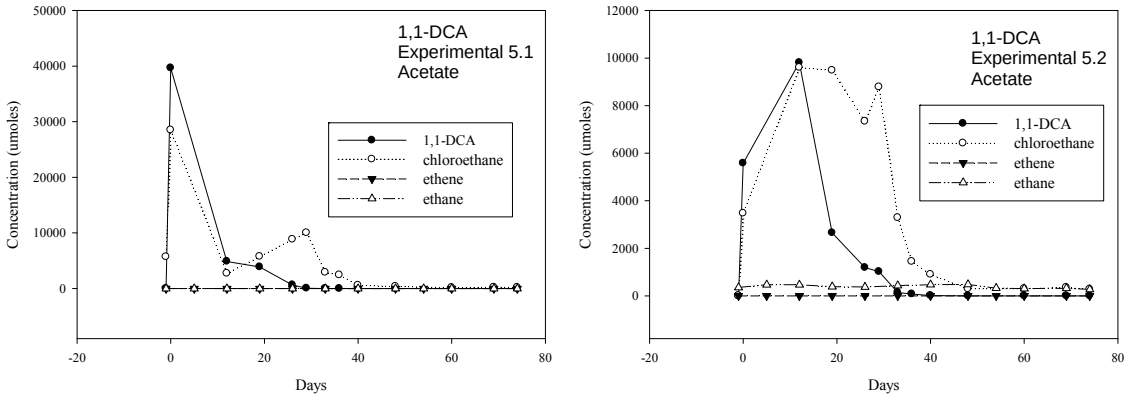

Figure 4.26. Degradation of 1,1-DCA in experimental treatments spiked with acetate.

levels in replicate 2.1 near or below detection limits until approximately day 55. Concentrations appear to rebound when all of the 1,1-DCA and most of the CA have been biodegraded and are no longer present. Conversely, the experimental replicate 5.1 displays a dramatic increase in hydrogen levels at the beginning of the monitoring period (Figure 4.28). This peak in hydrogen may be attributed to the fermentation of organic acids present in the peat mixture. H_2 drawdown appeared to coincide with the degradation of 1,1-DCA, despite Kassenga et al (2004) measuring higher hydrogen concentrations during chlorinated ethane degradation; however, hydrogen concentrations do remain above published threshold limits for dehalorespiring organisms (Kassenga et al., 2004).

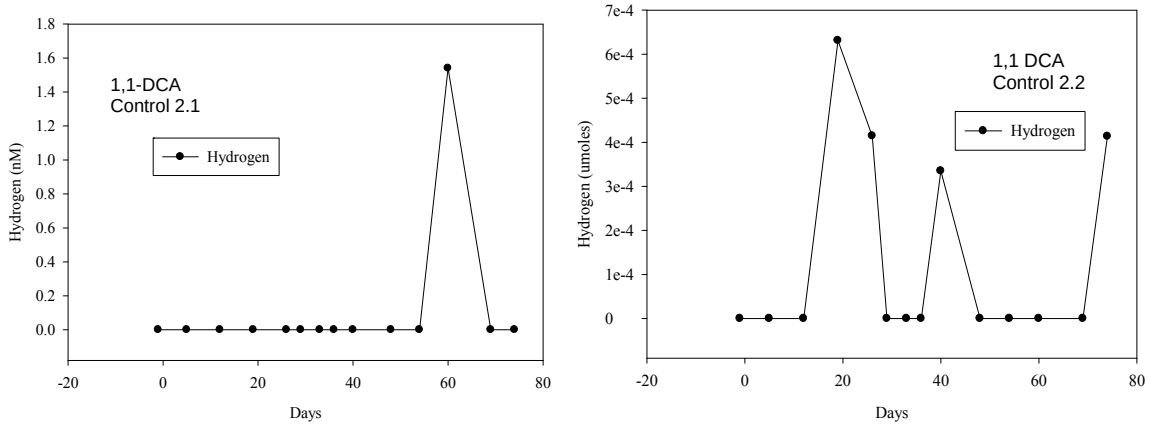

Figure 4.27. Hydrogen concentration in control treatments containing 1,1-DCA.

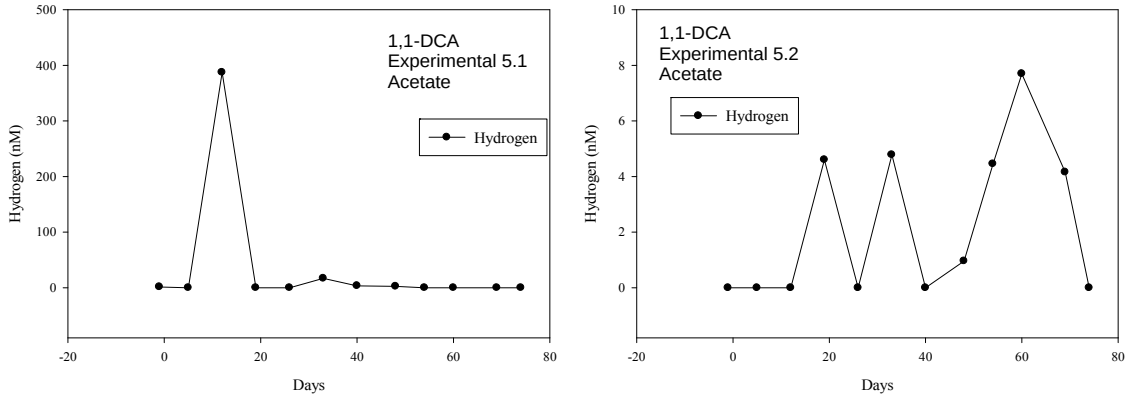

Figure 4.28. Hydrogen concentration in acetate experimental treatments containing 1,1-DCA.

Degradation rates and half life for the parent compounds are reported in Table 4.6. 1,1-DCA control degradation rates were similar to those of the hydrogen study. Degradation rates of 1,1-DCA in one experimental treatment rivals that reported in Kassenga et al (2004) and is statistically greater than those rates observed in the control treatments.

Acetate appears to stimulate 1,1-DCA, as no lag time in degradation was observed. It is interesting that only one experimental treatment responded to the acetate treatment with increased degradation rate while the other displayed half life of double that of the control treatments. Acetate did stimulate the degradation of 1,1-DCA in one microcosm, but did not

produce similar results in the replicate microcosm suggesting there may be other factors limiting the progression of 1,1-DCA in the replicate microcosm.

Table 4.6. First order degradation rate constants, standard error, and half life for 1,1- DCA in acetate study.

ACETATE				
Treatment	Rate Constant (1/d)	Standard Error	½ LIFE (days)	Lag time (days)
2.1 1,1-DCA (control)	0.069	0.006	10.043	0
2.2 1,1-DCA (control)	0.075	0.006	9.277	0
5.1 1,1-DCA (acetate)	0.16	0.0088	4.331	0
5.2 1,1-DCA (acetate)	0.17	0.086	4.076	12

Acetate: *cis* 1,2-DCE and 1,1-DCA Treatments 3 and 6

Results from microcosms treated with *cis* 1,2 DCE and 1,1-DCA are depicted in Figures 4.29 and 4.30. Degradation pathways are consistent with lactate and hydrogen studies, and display uncharacteristically low levels of ethene and ethane as described previously. Again, no measured daughter products were conserved in this process.

Figures 4.31 and 4.32 depict 1,1-DCA degrading concurrently with *cis* 1,2-DCE. It is possible that during the first 10 day of monitoring, the *cis* 1,2-DCE degraded first and then the 1,1-DCA was able to progress through the degradation reactions. In any case this lag time is small but may impact continuous flow through systems if *cis* 1,2-DCE is always present as would be the case in the BFP system. Frequent monitoring would be necessary to create an

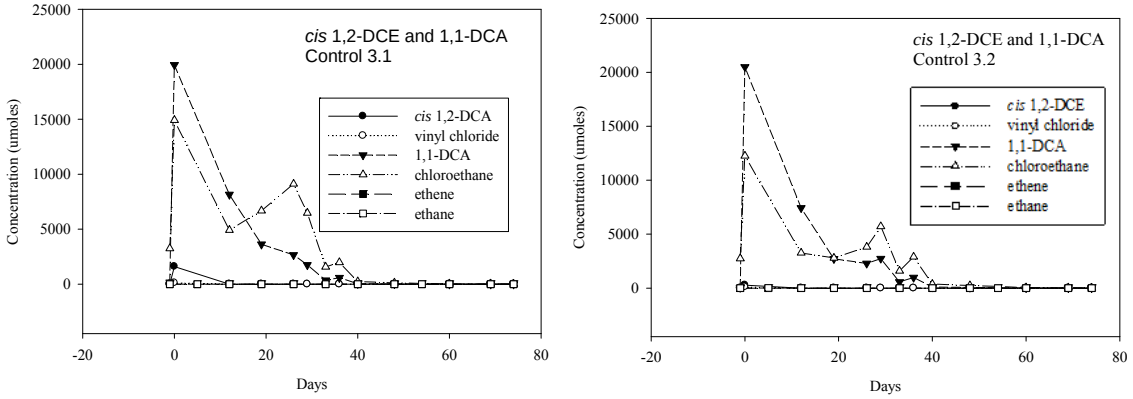

Figure 4.29. Degradation of *cis* 1,2-DCE and 1,1-DCA in control treatments.

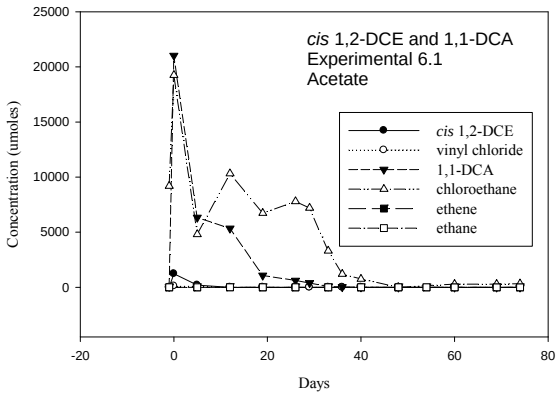

Figure 4.30. Degradation of *cis* 1,2-DCE and 1,1-DCA in experimental treatment spiked with acetate. Data from replicate 6.2 was eliminated from this study as no *cis* 1,2-DCE was recorded during testing due to sampling error.

accurate degradation profile for *cis* 1,2-DCE and may be problematic with microcosm studies as the frequent removal of samples from small test environments may disrupt the study. A bench scale flow through system would be a good choice of experimental design to further investigate these findings.

Initial hydrogen concentrations in the control treatment replicates remained significantly lower than observed in the previous studies (Figure 4.33). Hydrogen concentrations in control replicates vary dramatically and cannot be explained. Figure 4.34 depicts hydrogen concentrations in the experimental treatment. Replicate 6.2 displays hydrogen concentrations peaking immediately to approx 18 nM, above the methanogenesis threshold of 5 nM. Hydrogen

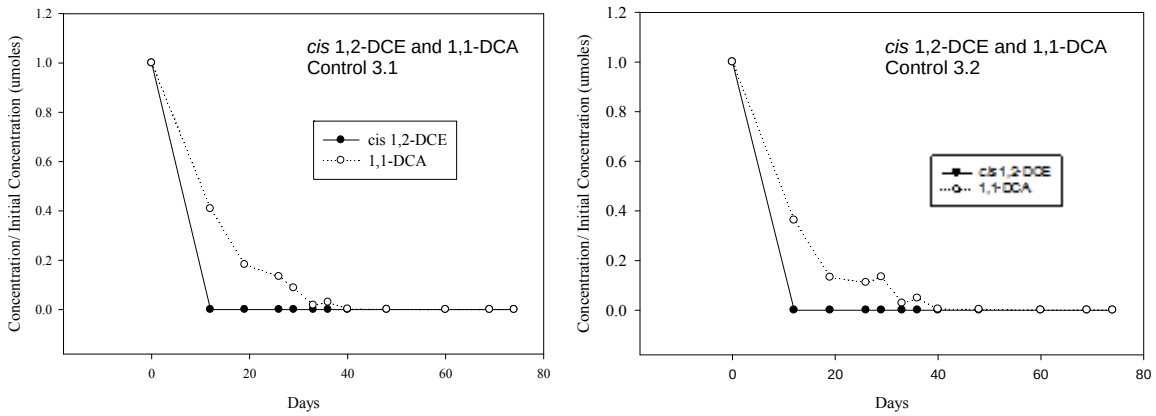

Figure 4.31. Degradation of 1,1-DCA in comparison to *cis* 1,2-DCE in control treatments.

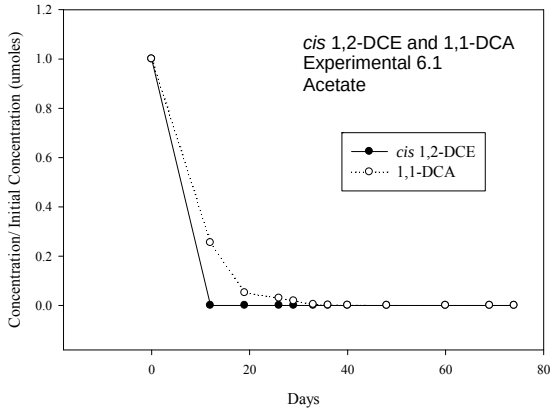

Figure 4.32. Degradation of 1,1-DCA in comparison to *cis* 1,2-DCE in an experimental treatment spiked with acetate. Data from replicate 6.2 was eliminated from this study as no *cis* 1,2-DCE was recorded during testing due to sampling error.

results from replicate 6.1 are not readily explained. The degradation of *cis* 1,2-DCE and VC occurs so rapidly that it is hard to distinguish changes in hydrogen concentration, due to the degradation of these chlorinated ethenes; however, hydrogen concentrations mostly follow the same trends as reported in the hydrogen study with both chlorinated ethenes and ethanes present.

The degradation rates of both parent compounds (*cis* 1,2-DCE and 1,1-DCA) are reported in Table 4.6. Dechlorination rates of *cis* 1,2-DCE did not differ significantly between control and experimental treatments indicating the addition of acetate did not greatly affect the microbial population's ability to remediate *cis* 1,2-DCE, although *cis* 1,2-DCE degradation was not monitored in one experimental replicate due to sampling error.

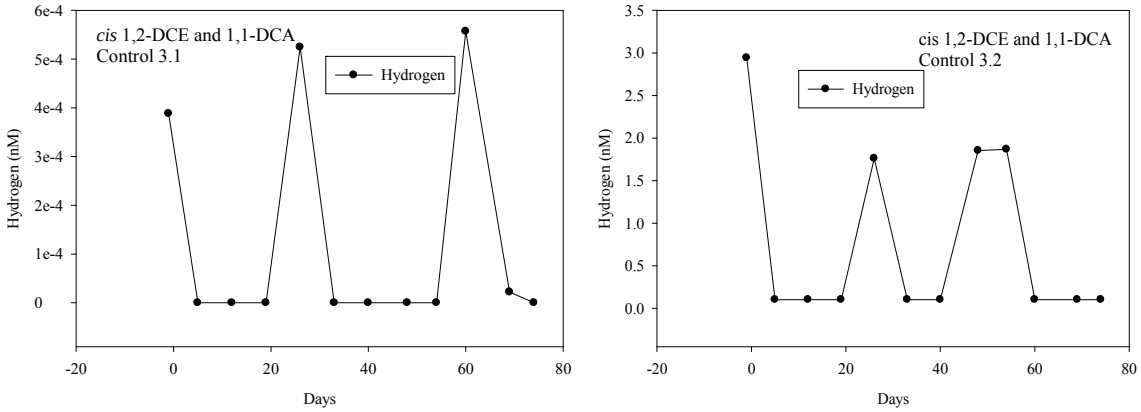

Figure 4.33. Hydrogen concentration in control treatments containing *cis* 1,2-DCE and 1,1-DCA.

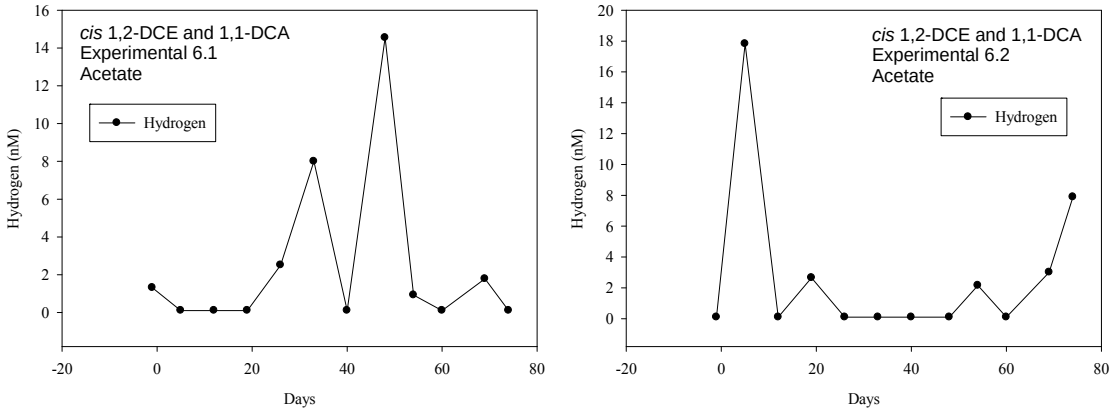

Figure 4.34. Hydrogen concentration in acetate experimental treatments containing *cis* 1,2-DCE and 1,1-DCA.

The dechlorination rates of *cis* 1,2-DCE in the control treatments did not vary significantly from those observed in the hydrogen study. 1,1-DCA degraded faster in experimental treatments compared to the degradation in control treatments suggesting 1,1-DCA dechlorinating bacteria are influenced by acetate availability. Rate constants far exceed those published by Klecka et al (1998). The observed dechlorination rates and the lack of 1,1-DCA lag time are sufficient to prompt further flow through studies to determine if this addition will be successful in full scale BFP installations.

The 1,1-DCA degradation lag time and degradation rates appear to be affected by acetate amendment in microcosms containing both *cis* 1,2-DCE and 1,1-DCA. This is encouraging, as

Table 4.7. First order degradation rate constants, standard error, and half life for *cis* 1,2-DCE and 1,1-DCA in acetate study. Data from replicate 6.2 was eliminated as no *cis* 1,2-DCE was recorded due to sampling error.

ACETATE								
Treatment	*cis* 1,2-DCE Rate Constant (1/d)	Standard Error	*cis* 1,2-DCE ½ LIFE (days)	Lag Time (days)	1,1-DCA Rate Constant (1/d)	Standard Error	1,1-DCA ½ LIFE (days)	Lag time (days)
3.1 *cis* 1,2-DCE and 1,1-DCA (control)	0.462*	-	1.5		0.085	0.004	8.182	0
3.2 *cis* 1,2-DCE and 1,1-DCA (control)	0.316*	-	2.195		0.089	0.004	7.752	0
6.1 *cis* 1,2-DCE and 1,1-DCA (acetate)	0.440*	-	1.577	0	0.175	0.022	3.96	0
6.2 *cis* 1,2-DCE and 1,1-DCA (acetate)	-	-	-	-	-	-	-	-

* Rate constants are minimum constants computed from initial two data points.

acetate may prove to be the chemical addition appropriate to stimulate the BFP system. More testing is necessary to determine if this treatment will be successful in the BFP system, as the degradation *cis* 1,2-DCE occurred so rapidly that it was difficult to monitor its degradation without the possibility of disrupting the microcosm environment.

Conclusions from Acetate Study and Recommendations for Project

Acetate does appear to be a viable treatment to resolve BFP pilot co-treatment issues identified in pilot scale studies. However, this will require extensive testing in the lab and

possibly another pilot scale test at the facility to ensure the success of the treatment. Since it is clear that the degradation of *cis* 1,2-DCE can be accomplished quickly and efficiently, without the use of large surface areas, it is suggested that the ReSolve treatment system utilize two trenches in series. The first trench would be intended to treat *cis* 1,2-DCE in the presence of 1,1-DCA.

After complete *cis* 1,2-DCE degradation has occurred, and its daughter products are consumed, water from the first trench can be applied to the second for the treatment of 1,1-DCA. To maximize degradation, the second trench could be amended with acetate. Utilizing this method, it is hypothesized that there would be no concern of 1,1-DCA degradation lag time and the acetate would stimulate the degradation of 1,1-DCA to levels at which the system can function with a minimal surface area.

CHAPTER 5. QUANTIFYING SUSTAINABILITY ENHANCEMENTS TO THE RESOLVE SITE REMEDIATION SYSTEM

Introduction

Sustainability and the Life Cycle Analysis

In recent years, the desire for sustainable, green technologies has become increasingly important to consumers. In response, many companies are re-designing operations to accommodate environmentally friendly practices. This shift in focus is particularly noticeable in chemical remediation projects where traditional treatment approaches are far from eco-friendly in their use of chemicals and energy. As the drive to utilize more sustainable techniques increases, quantifying and assessing sustainability enhancements to existing technologies is important. The same holds true for newly developed technologies. The first step in evaluating the sustainability of a treatment process is to perform a life cycle analysis (LCA).

Life cycle analyses identify, categorize, and calculate the impacts of inputs (required materials) and outputs (wastes) associated with a process, such as groundwater remediation. Assessing the entire life cycle of a product/process allows attention to be focused on one of three general phases: production, use, and disposal. The production phase incorporates a variety of stages including what raw materials are used, how these materials are processed before manufacturing, as well as the manufacturing process itself. The use phase of a product considers how that product will be utilized and what resources are consumed during this use. The final phase, disposal, can also be detrimental to the environment. Corporations interested in reducing environmental impacts can then identify phases and impacts where the most improvement can be made.

An LCA can generally be performed via two different methods: the process based method or the economic input/output method. The process based method requires the

identification of all inputs to the process, including raw materials. Inputs to these products must also be considered. Incorporating these secondary inputs can be relatively easy for basic products; the process for more complicated products utilizing many inputs and materials is complex. Difficulty occurs when establishing boundaries of the assessment and determining circularity effects. The second method, the economic input/output life cycle analysis (EIO-LCA) method, relates all materials, resources, and emissions to economic inputs and outputs in the 420 economic sectors in the US economy. Knowing how much is spent on these materials and resources allows for the calculation of different impacts on the environment, such as greenhouse gas and toxic emissions.

Pump and Treat Facility

The pump and treat operation at the ReSolve facility extracts groundwater from the aquifer. This water is then passed through a series of treatments including phase separation, oxidizing and precipitation, filtration and air stripping (Figure 1.1). A review of these procedures identified energy (electricity and propane), chemicals, carbon regeneration, and waste transportation as areas attributing to environmental impacts. Electricity, propane, and chemicals are considered inputs into the system. Currently, 19,700 kilowatt-hour (kwh) of electrical energy are used each month and 2,600 gallons of propane are utilized each year to maintain operations at the ReSolve facility.

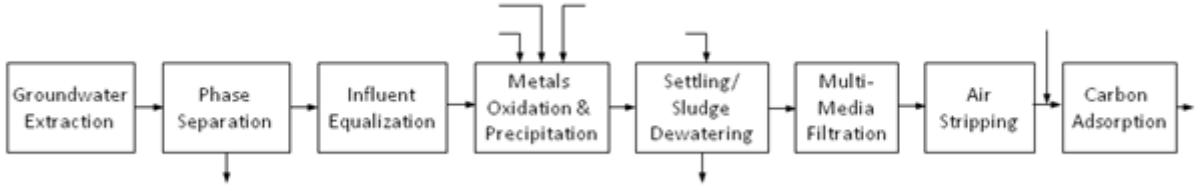

Figure 5.1. Current treatment process at the ReSolve facility.

The facility also produces 56,000 pounds of waste which is transported from the facility each year. Ten thousand pounds of carbon are re-generated each year utilizing heat production

to strip chemicals from activated carbon granules before the product can be re-used. In addition, 150 pounds of VOCs are discharged into the air each year (Table 1.1). Finally, the use of chemicals at the ReSolve facility is of interest as they contribute to environmental impacts (Table 5.1).

Table 5.1. Environmental impacts associated with the pump and treat system operating at the ReSolve facility.

Environmental Impact	**Existing System**
Electricity Use	19,700 KWH/Month
Propane Use	2600 Gallons/Year
Off-Site Transportation and Disposal of Sludge	56,000 lbs/year
Spent Carbon Regeneration	10,000 lbs/year
Discharge of VOCs to the Environment	Approx. 150 lbs/yr
25% Sodium Hydroxide	38,000 lbs
Sulfuric Acid	5,400 lbs
Potassium Permanganate	2,200 lbs
Aluminum Chlorhydrate	7,100 lbs
Sodium Hypochlorite	6,300 lbs
Polymer	330 lbs

BFP Design

The proposed BFP system incorporates carbon filtration for the removal of PCBs and biological filtration beds for chlorinated solvent removal. During the use phase, water is to be

pumped from groundwater aquifers and sent to activated carbon filters. Next, the water will be sent to two anaerobic biological filtration beds in series. Water applied at the top of the bed percolates to the bottom. As the water flows through the first bed, anaerobic microbes will utilize chlorinated ethenes as food sources and produce non toxic daughter products. The water will then be applied to the second bed where a different microbial community will utilize chlorinated ethanes. When the water reaches the bottom of the second bed, it will pass through another activated carbon filter system for final polishing and the water will then be discharged into the Copicut River (Figure 1.2).

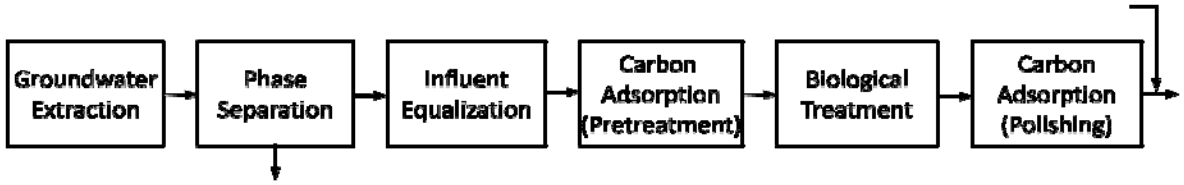

Figure 5.2. Proposed BFP treatment process.

This process utilizes far less chemicals, even eliminating the need for some products and is much more energy efficient. Table 1.2 depicts the environmental impacts associated with the BFP treatment process.

Purpose of Study

The environmental protection agency (EPA) has initiated plans for the business sector based on the Energy Policy Act (EPA primer). These goals aim to minimize environmental impacts incurred during business operations associated with energy and water use. Best management practices associated with green remediation are vital to operations seeking to meet these goals; hence, the EPA requires that green technologies be given preference in the design of future remediation plans (EPA Green Remediation).

Determining which technologies benefit the environment can be a taxing process. It requires the quantification of environmental impacts of each process involved in the construction, operation and decommissioning of a technology. Often, focus is centered on

Table 5.2. Environmental impacts associated with the proposed BFP system.

Environmental Impact	**BFP System**
Electricity Use	13,600 KWH/Month
Propane Use	2,300 Gallons/Year
Off-Site Transportation and Disposal of Sludge	5,000 lbs/year
Spent Carbon Regeneration	14,000 lbs/year
Discharge of VOCs to the Environment	<10 lbs/yr
25% Sodium Hydroxide	7,600 lbs
Sulfuric Acid	0 lbs
Potassium Permanganate	0 lbs
Aluminum Chlorhydrate	0 lbs
Sodium Hypochlorite	0 lbs
Polymer	60 lbs

reducing one environmental impact to reduce the complexity of the investigation. In this study, we strive to quantify the sustainability of the BFP system versus the existing pump and treat system operating at the ReSolve facility. Carbon dioxide (CO_2) emissions will be the focus

environmental impact in this study as CO_2 attributes to global warming and recent legislative action suggests that CO_2 emissions will be highly regulated in the future.

Literature Review

The EPA Green Remediation initiative focuses on achieving remediation goals at a facility with efficient, cost effective technologies that consume fewer natural resources, decrease environmental pollution burdens and enhance the environmental health of the ecosystem (EPA primer). The process of developing a green remediation technology involves the evaluation of the system in several areas: energy use, materials use, and the production of wastes. Groundwater remediation technologies are notorious for high energy consumption. Electric power generation in the US is responsible for over one third of all carbon dioxide (CO_2) emissions in the energy sector (EPA Technology Primer 2008). Reducing energy consumption and alleviating CO_2 emissions is a key EPA priority.

The use of more passive technologies may be ideal to attain this goal, but these technologies are not always capable of feasibly treating existing contamination. The energy requirements of more active processes can be minimized with the implementation of efficient mechanical mechanisms such as water pumps and maintaining equipment to optimize efficiency throughout the course of treatment. Facilities with abundant wind or solar resources may consider installing equipment to harness this energy and reduce the use of fossil fuel based energy (EPA Green Remediation).

Materials use is also of importance and many treatment processes utilize land, water, and manmade products which inherently carry environmental impacts of their own. Minimizing the use of land and water resources reduces ecological disturbance to natural ecosystems and protects the natural hydrology of an area (EPA Technology Primer 2008). In some areas, fresh water is scarce; in these areas it is particularly desirable to preserve reservoirs for community

use. In many operations, potable water can be replaced with non potable water and relieve stress on the drinking water supply (EPA Technology Primer 2008). In addition to natural material use, the manufacturing of secondary items used for construction and operations may carry significant environmental burdens (Suer et al 2004).

Remediation technologies also produce wastes associated with the operation of mechanical equipment and chemical processes. The emissions of particulates and priority pollutants can be reduced by utilizing energy efficient technologies. Clean fuel options in machinery and vehicles will increase these efforts (EPA Technology Primer 2008). It is imperative to ensure air quality is not impacted as these effects can be felt at local, regional and global levels (Suer et al 2004, Diamond et al 1999).

In addition to air pollutants, solid waste production should be minimized and re-used whenever possible to decrease the amount of waste disposed of in landfills. Items such as demolished concrete can be utilized as road paving and recyclable materials disposed of at appropriate facilities (EPA Technology Primer 2008). Finally, long term treatment processes should incorporate sustainable operations to reduce greenhouse gas emissions and allows for adaptations in the treatment process as they become available (EPA Technology Primer 2008). In doing so, long term operations will not significantly add to the effects of global warming and the treatment process can easily maintain its effectiveness with little difficulty.

In order to address these concerns, engineers utilize the LCA process to quantify the inputs and outputs associated with available technologies. The scope of such an investigation is paramount as the more comprehensive an LCA is, the larger the data set becomes. To limit the complexity of studies often boundaries are drawn to focus of impacts associated in a given spatial area and given time frame (Suer et al 2004, Cadotte et al 2007). Results of studies will vary according to the boundaries applied. Regardless of variability in results, LCAs are a proven

tool in the quantitative assessment of environmental impacts (Blanc et al 2004, Page et al 1999, Worlen et al).

LCAs applied to groundwater remediation technologies span a wide range of topics. The most basic of these investigations determine risk assessments for contaminated sites. Godin et al. (2004) stated that allowing contaminated facilities to be treated via natural attenuation alone is often the option with the least environmental impacts; however, these sites will continue to contain large concentrations of contaminants well above treatment standards. It is for this reason that many suggest incurring some environmental impacts to minimize public risk now and in the future (Lessage et al., 2007; Godin et al., 2004).

Taking LCA applications further, remediation technologies were evaluated on a site specific basis. These studies focus mainly on soil treatment processes such as vapor extraction and excavation. These technologies are very aggressive at removing chemical contamination from soils in short time periods. They are also associated with high environmental impacts. Passive groundwater technologies are often more environmentally friendly but require extensive treatment times (Cadotte et al., 2007). In situ bioremediation is predominantly described as a passive system with energy being the primary cause of environmental impact (Diamond et al., 1999) with the exception of Suer et al. (2004) who notes that the inclusion of electron donor production is associated with significant environmental impacts. The development of a case study for the BFP system will be beneficial to quantitatively establish the technology as an environmentally friendly technology and increase its use in the field.

Methods

Calculations

EIO-LCA Method

This method operates by assessing the products and/or processes involved in a project.

This assessment follows a basic logic pattern to include all activities associated with a particular product. For example, raw materials are mined and refined to produce finished materials. These materials are then manufactured into a final product which is then utilized by the consumer. Once the product is exhausted, it must be disposed.

The EIO-LCA method considers each step involved in a products development as described above as well as an additional factor, the transportation of goods between steps. Each of these steps requires energy and materials as well as producing wastes and emissions which are quantified for the user. The process operates on the basic function:

$$X_{dierct} = (I+A)*y$$

where A is a matrix relating how different sectors of the economy directly relate to each other, I represents an identity matrix accounting for circularity effects in the economy, y represents a vector describing how much money is used to purchase inputs in a process and X_{direct} represents the output from the entire economy.

This equation does not account for output from secondary and tertiary suppliers. For example, the production of cars increases the demand for steel and the production of steel creates a demand for energy. The requirements for secondary suppliers (steel manufacturer in the example) are calculated via A*A*y. Many suppliers may exist beyond the secondary supplier. All supplier requirements can be expressed mathematically via:

$$X = (I+A)^{-1}*y$$

The use of these economic principles were then transformed to include matrices for environmental impacts using government records of items such as greenhouse gas emissions, energy, toxic release and more. Using these matrices it is possible to calculate the environmental effects produced given the amount of money spent in an economic sector. The CO_2 impacts

from electricity, carbon regeneration, transportation and chemicals were calculated via the EIO-LCA method (Carnegie Mellon University Green Design Institute. 2008).

Direct Chemical Balance Calculations

Impacts associated with propane use and VOC discharges were calculated using the appropriate chemical equations:

Propane: $C_3H_8+5O_2 \rightarrow 3CO_2+4H_2O+heat$

VOC: $C_XH_Y+ZO_2 \rightarrow XCO_2$

Assumptions

The scope of the LCA analysis was limited to simplify the process. The only phase considered in the pump and treat facility was the use phase as the technology was already in operation. Impacts associated with the disposal of the equipment were negated as this system would operate for many decades if left undisturbed. Similarly, due to the extensive treatment time predicted for the BFP system, environmental impacts from construction and disposal of the system were not incorporated into the analysis. In addition, CO_2 emissions were identified prior to the study as a major environmental impact associated with the BFP system. For this reason, CO_2 emissions were chosen as the basis of this LCA.

Results and Discussion

Comparison of Treatment Plans

The proposed BFP treatment process will significantly decrease the amount of energy and chemicals needed to operate the system as well as the amount of waste produced (Tables 1.3 and 1.4). One of the major components of the BFP system attributing to CO_2 emissions is electricity use (Table 1.3). Solar energy may be an appropriate alternative energy source which will reduce the production of CO_2 at the facility. The addition of solar panels could potentially provide

enough energy to operate the BFP system during the summer months. In addition to the decreased emissions, the facility would save a significant amount in operational costs.

The BFP decreases propane use by just 300 gallons per year and hence does not significantly contribute to a decrease in carbon dioxide emissions (Table 1.3). The same is true for polymer use (Table 1.4). In contrast, the BFP system produces significantly less waste than the pump and treat system. This decrease in wastes prevents two metric tons of carbon dioxide emissions each year (Table 1.3).

Chemical use also decreases with the implementation of the BFP system reducing CO_2 emissions by more than 300 metric tons each year (Table 1.4). The BFP system does require larger volumes of activated carbon for PCB removal than the pump and treat system. The regeneration of this carbon results in an additional five metric tons of carbon dioxide emissions each year (Table 1.3).

When the proposed BFP system is implemented, CO_2 emissions will be reduced by 88% (Table 1.5). This decrease in emissions is primarily due to the decrease in chemical use. The reduction will also lead to decreases in CO_2 emissions associated with chemical transport which are not included in the calculation.

In addition to the environmental benefits associated with the BFP system discussed above, other benefits which are not easily quantified also contribute to environmental impact. Natural grasses currently cover most of the ReSolve facility. With the exception of construction, these grasses will remain and the property will appear to be a natural grass bed during operations. The BFP system will not require the construction of additional overlying structures which will alter the hydrology of the area and wildlife will only temporarily be displaced. In addition, the BFP system consists of lined trenches which will prevent the alteration of natural microbial communities on the property.

Table 5.3. Comparison of environmental impacts of the pump and treat system and BFP systems.

Environmental Impact	Existing System (Pump and Treat)	CO_2 (metric ton)	Proposed BFP System	CO_2 (metric ton)
Electricity Use	19,700 KWH/Month	31.7 Equivalents	13,600 KWH/Month	21.9 Equivalents
Propane Use	2600 Gallons/Year	17.27 Equivalents	2300 Gallons/Year	15.26 Equivalents
Off-Site Transportation and Disposal of Sludge	56,000 lbs/year	2.51 Equivalents	5000 lbs/year	0.501 Equivalents
Spent Carbon Regeneration	10,000 lbs/year	16.1 Equivalents	14,000 lbs/year	22.5 Equivalents
Discharge of VOCs to the Environment	Approx. 150 lbs/yr	0	< 10 lbs/yr	0

* Complete calculations determining CO_2 emissions are included in Appendix A.

Table 5.4. Comparison of environmental impacts from chemical and polymer use in the pump and treat and BFP systems.

Environmental Impact		Existing System (Pump and Treat)	CO_2 (metric tons)	Proposed BFP System	CO_2 (metric tons)
Annual Chemical Use		$337,026	665 Equivalents	$13,784	27.4 Equivalents
	25% Sodium Hydroxide	38,000 lbs		7,600 lbs	
	Sulfuric Acid	5,400 lbs		0 lbs	
	Potassium Permanganate	2,200 lbs		0 lbs	
	Aluminum Chlorhydrate	7,100 lbs		0 lbs	
	Sodium Hypochlorite	6,300 lbs		0 lbs	
Polymers			1.35 Equivalents	60 lbs	0.246 Equivalents

* Complete calculations determining CO_2 emissions are included in Appendix A.

Table 5.5. Total yearly CO_2 emissions from the pump and treat system and proposed BFP system.

	CO_2 Emissions/Year
Pump and Treat System	733.93 metric tons
BFP System	87.35 metric tons

Special Considerations in Understanding the Data

During the LCA process of these two remediation process, the only environmental impact assessed during the analysis was CO_2 emissions. This is not the only environmental impact associated with chemical remediation activities in either treatment plan discussed. For example, the release of VOCs into the air is considered an emission of greenhouse gasses as these VOCs will attribute to the detrimental addition of ozone in the lower atmosphere. However, because these VOCs are not combusted, they do not produce CO_2 and therefore register zero environmental impact in this study.

In addition to evaluating only CO_2 impacts, the analysis considered the environmental impacts of all chemicals used in the remediation processes as equal. This is not the case because each chemical is manufactured using different processes, some producing more environmental impacts than others. For example, the production of sulfuric acid involves a simple oxidation and dilution processes. Compounds such as sodium hydroxide (NaOH) and potassium permanganate involve simple hydrolysis processes (energy intensive) while sodium hypochlorite and aluminum chlorhydrate are produced in temperature controlled electrolysis processes. The varying energy requirements alone are sure to alter the emissions associated with each process.

The EIO-LCA cannot calculate environmental impacts for each chemical not only because manufacturing processes differ, but also because transportation from the manufacturer to

each facility will differ. In order to perform a full investigation of environmental impacts from chemical use, the specific manufacturing process would need to be identified and then assessed. In addition, the distance between supplier and use facility would need to be established as well as method of transport (air or ground). Once this information is identified, the individual aspects of each process can be evaluated using the EIO-LCA method.

For a full scale LCA, it would be important to investigate the manufacturing process of all chemicals utilized in a process to understand the specific environmental impacts produced via the chemicals manufacturing process. In addition, the source of such chemicals should be chosen based on local supply and alternative options should be considered to decrease transportation effects. While the scope of this LCA does not encompass all environmental impacts associated with the remediation technologies discussed, it is important to note that the new, proposed system dramatically reduces inputs and outputs throughout the entire remediation process which will reduce environmental impacts in a broader LCA analysis.

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APPENDIX :SUSTAINABILITY CALCULATIONS

ELECTRICITY: The carbon footprint of electricity use can be calculated using the average cost of electricity ($0.1605/kwh for industries in Massachusetts) and using this amount as the economic input using the EIO-LCA method. The pump and treat system utilizes 19,700 kwh/month while the proposed system utilizes 13,600 kwh/month.

PUMP AND TREAT

(19700 kwh/month) * $0.1605/kwh = $3161.85/month

31.7 CO_2 Equivalents associated with $3162 of economic input into power generation and supply (EIO-LCA sector # 221100).

ABR SYSTEM

(13600 kwh/month) * $0.1605/kwh = $2183/month

21.9 CO_2 Equivalents associated with $3162 of economic input into power generation and supply (EIO-LCA sector # 221100).

PROPANE

Propane calculations follow a different format as propane combusts to produce CO_2. According to the following equation, when one mole of propane combusts, it produces three moles of CO_2. The current system utilizes 2,600 gallons each year while the proposed system would utilize 2,300 gallons per year.

$$C_3H_8+5O_2 \rightarrow 3CO_2+4H_2O+heat$$

PUMP AND TREAT

(2,600 gal C_3H_8/year)*(3.785L/gal)*(585g/L)*(1mol C_3H_8/44.094 g)*(3mol CO_2/1 mol C_3H_8) =391,685 moles of CO_2

ABR SYSTEM

(2,300 gal C_3H_8/year)*(3.785L/gal)*(585g/L)*(1mol C_3H_8/44.094 g)*(3mol CO_2/1 mol C_3H_8)

=346,033 moles of CO_2

CARBON REGENERATION

During the operation of the pump and treat system, 10,000 pounds of carbon need to be regenerated each year. Implementing the proposed system increases this amount to 14,000 pounds per year. Carbon regeneration involves massive amounts of heat production to produce water vapor which will lift adsorbent material from the carbon, allowing the carbon to be utilized in filters again. The energy requirement for such a process is the most significant input to the process. According to Liu and Wagner, 1.0 kwh are necessary to regenerate one pound of activated carbon.

PUMP AND TREAT

(10,000 lbs-Carbon/year)*(1 kwh/1.0 lbs-Carbon) = 10,000 kwh

(10,000 kwh/year)*$0.1605/kwh = $1605 /year

16.1 CO_2 Equivalents associated with $1605 of economic input into power generation and supply (EIO-LCA sector # 221100).

ABR SYSTEM

(14,000 lbs-Carbon/year)*(1 kwh/1.0 lbs-Carbon) = 14,000 kwh

(14,000 kwh/year)*$0.1605/kwh = $2247 /year

22.5 CO_2 Equivalents associated with $2,247 of economic input into power generation and supply (EIO-LCA sector # 221100).

CHEMICALS

Considerable amounts of sodium hydroxide, sulfuric acid, potassium permanganate, aluminum chlorhydrate, and sodium hypochlorite are utilized. For this paper's purpose, the environmental impact of all chemicals is treated as equal.

PUMP AND TREAT

Sodium Hydroxide is sold in 55 pound containers for $100.40.

(38,000 lbs/yr) * ($100.40/55 lbs) = $69,368/yr

Sulfuric Acid is sold in 55 pound bags at $800.40 per bag.

(5400 lbs/yr) * (453g/1 lbs) * (1L/184g) * (1 gal/3.785L) * ($800.40/55lbs) = $51,116/yr

Potassium Permanganate is sold in 55 pound bags at $313.25.

(2200 lbs/yr) * ($313.25/55 lbs) = $12,530

Aluminum Chlorhydrate (assumed 99%) is available at $32.80 per 500g.

(7100 lbs/yr) * (435g/1 lbs) * ($32.80/500g) = $202,606

Sodium Hypochlorite (assumed 5%) is assumed to be sold at $2/gallon.

(6300 lbs/yr) * (435g/1lbs) * (1ml/1.030g) * (1L/1000ml) * (1gal/3.785L) * ($2/gal) = $1,406

Sum of chemical costs= $337,026

665 CO_2 equivalents associated with $337,026 of economic input into other basic inorganic chemical manufacturing (EIO-LCA sector # 325180).

ABR SYSTEM

Sodium Hydroxide is sold in 55 pound containers for $100.40.

(7,600 lbs/yr) * ($100.40/55 lbs) = $13,874/year

Sulfuric Acid is sold in 55 pound bags at $800.40 per bag.

(0 lbs/yr) * (453g/1 lbs) * (1L/184g) * (1 gal/3.785L) * ($800.40/55lbs) = $0/year

Potassium Permanganate is sold in 55 pound bags at $313.25.

(0 lbs/yr) * ($313.25/55 lbs) = $0/year

Aluminum Chlorhydrate (assumed 99%) is available at $32.80 per 500g.

(0 lbs/yr) * (435g/1 lbs) * ($32.80/500g) = $0/year

Sodium Hypochlorite (assumed 5%) is assumed to be sold at $2/gallon.

(0 lbs/yr) * (435g/1lbs) * (1ml/1.030g) * (1L/1000ml) * (1gal/3.785L) * ($3/gal) = $0/year

Sum of chemical costs= $13,874/year

27.4 CO_2 equivalents associated with $13,874 of economic input into other basic inorganic chemical manufacturing (EIO-LCA sector number 325180).

POLYMER

The environmental effects of polymer use are relatively small compared to those of other activities associated with the remediation processes discussed. The existing technology only utilizes 330 pounds of polymer each year and the proposed system decreases that number to less than half (60 pounds per year). According to EIO-LCA calculations, 1.35 CO_2 equivalents are associated with one thousand dollars worth of economic activity in plastics materials and resin manufacturing (EIO-LCA sector # 325211). For this comparison, it is assumed that 330 pounds of polymer produce roughly the CO_2 emission from one thousand dollars of economic activity and 60 pounds of polymer results in 0.246 CO_2 equivalents respectively.

WASTE TRANSPORTATION

The pump and treat system at the Re-Solve facility produces 56,000 pounds of waste which needs to be transported from the facility each year. The biological system produces only 5,000 pounds a year. Sludge waste is transported from the facility in 55 gallon drums which are estimated to weigh approximately 490 pounds. 20 drums are expected to fit on each truck and it is estimated each removal costs $250.

PUMP AND TREAT

(490 lbs/drum) * (20 drums/truck) * ($250/truck) = 9800 lbs/truck

56,000 lbs/(9800 lbs/truck) =5.7 or 6 trucks per year

(6 trucks/year) * $250 = $1250/year

2.51 CO_2 equivalents associated with $13,874 of economic input into truck transportation (EIO-LCA sector #484000).

ABR SYSTEM

(490 lbs/drum)*(20 drums/truck)*($250/truck) = 9800 lbs/truck

(5,000 lbs/year) / (9800 lbs/truck) = 0.51 or 1 truck per year

(1 truck/year) * $250= $250/year

0.501 CO_2 equivalents associated with $13,874 of economic input into truck transportation (EIO-LCA sector #484000).

VOC EMISSIONS

VOCs combust to produce CO2 via:

$$C_XH_Y+ZO_2 \rightarrow XCO_2$$

The pump and treat facility emits 150 pounds of VOCs each year while the proposed system emits less than 10 pounds per year. Because the remediation processes do not combust these VOCs, there is no CO_2 output associated with this release. However, VOCs are chemicals which produce ozone (O_3) and attribute to detrimental atmospheric impacts and should be considered in a broader LCA analysis.

VITA

Caroline Burda was born and raised in Houston, Texas. She attended Eckerd College in Saint Petersburg, Florida, and received a Bachelor of Science in marine science in 2006. In 2007, after completing a year of offshore rotation for the oil and gas industry, she began her studies at Louisiana State University in Baton Rouge, Louisiana, under Dr. John Pardue. She will graduate in December 2009 and pursue a career as an environmental specialist in an industry setting.