3-2007

Characterization of Chlorinated Ethene Degradation in a Vertical Flow Constructed Wetland

James M. Waldron

CHARACTERIZATION OF CHLORINATED ETHENE DEGRADATION IN A VERTICAL FLOW CONSTRUCTED WETLAND

THESIS

James M. Waldron, Civ, USAF

AFIT/GEM/ENV/07-M17

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the United States Government.

AFIT/GEM/ENV/07-M17

CHARACTERIZATION OF CHLORINATED ETHENE DEGRADATION IN A VERTICAL FLOW CONSTRUCTED WETLAND

THESIS

Presented to the Faculty

Department of Systems and Engineering Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Engineering Management

James M. Waldron, BS

Civ, USAF

March 2007

AFIT/GEM/ENV/07-M17

CHARACTERIZATION OF CHLORINATED ETHENE DEGRADATION IN A VERTICAL FLOW CONSTRUCTED WETLAND

James M. Waldron, BS
Civ, USAF

Approved:

Abinash Agrawal (Chairman)	28 Feb '07 Date
Charles A. Bleckmann (Member)	28 Feb 07 Date
Carl G. Enfield (Member)	28 Feb 07 Date

Abstract

Chlorinated solvents, including perchloroethene (PCE) and trichlorethene (TCE), are among the most common groundwater contaminants found in the United States. Once released into the environment, chlorinated solvents are extremely persistent and often require costly and lengthy remedial actions. The use of constructed wetlands has shown promise as an effective and less costly alternative for the treatment of chlorinated solvent contaminated groundwater.

This study characterized and evaluated the concentration of chlorinated ethenes within a vertical flow constructed wetland, fed with PCE contaminated groundwater, at Wright-Patterson Air Force Base (WPAFB), Ohio. Chlorinated ethene concentrations were characterized within three distinct layers of the wetland cell, as well as within the influent, and effluent. In addition, a pore-water sampler prototype was designed and developed for this research effort in order to obtain a more detailed contaminant profile.

PCE concentrations declined from an average of 46.5 μg/L in the influent to an average of 0.5 μg/L in the upper layer, a 98.9% decrease. The chlorinated ethene concentration profiles indicate that the lower half of the wetland provides favorable conditions for the complete anaerobic reductive dechlorination of the PCE. Within the upper half of the wetland, contaminant profiles indicate dominant degradation processes other than anaerobic reductive dechlorination, possibly including aerobic or anaerobic oxidation or direct volatization. The limited data generated from the implementation of the pore-water sampler prototypes was inclusive, requiring the need for further testing and research.

To my wife and children

Acknowledgments

I would like to express my sincere appreciation to my thesis committee members, Dr. Abinash Agrawal, Dr. Charles Bleckmann, and Dr. Carl Enfiled. Their guidance and support throughout the course of this thesis effort was invaluable. I would also like to thank Mr. Jan LaValley and Mr. Daniel Ryan of the AFIT Model Shop. Their professionalism and excellent craftsmanship were paramount in the successful development of the pore-water sampler prototype.

I am also indebted to many of the graduate students at Wright State University who are also involved in the wetland remediation research project, including Yussuf Mohamud, Raghaven Parthasarathy, Christina Smith, and Sarah Tritschler. The assistance and training they provided to me in both the field and laboratory were greatly appreciated.

Finally, I would like to thank my wife and children for their support and love. Your encouragement and patience gave me the strength to complete thesis research effort.

James M. Waldron

Table of Contents

Page

List of Figures

List of Tables

CHARACTERIZATION OF CHLORINATED ETHENE DEGRADATION IN A VERTICAL FLOW CONSTRUCTED WETLAND

I. Introduction

Overview

The purpose of this study is to characterize and evaluate the concentration of chlorinated ethenes within a vertical flow constructed wetland cell at Wright-Patterson Air Force Base (WPAFB), Ohio. The WPAFB wetland cell has been a source of research for evaluating the remediation of chlorinated ethene contaminated groundwater since its construction in September 2000. This effort will follow up on the research performed by Bryan Opperman (2002), Nathan Clemmer (2003) and Teresa Sobolewski (2004). Their research collected water samples from the wetland cell using a three layer stratified sampling grid and analyzing for tetrachloroethene (PCE) and its degradation products. In order to obtain a more detailed contaminant profile within the wetland cell, a sampling method enabling the collection of a closely-spaced vertical sampling interval using pore-water samplers was introduced in this research effort. With a more detailed contaminant profile a better understand of the degradation pathways of the organic contaminants is possible.

This effort will determine a vertical profile concentration of chlorinated ethene contaminants to demonstrate the effectiveness of the WPAFB vertical flow constructed wetland cell as a viable remediation technology. This research will also evaluate pore-

water sampling as compared to the previous sampling methodology in order to validate and further develop the pore-water sampling methodology. Since it has been over five years since the WPAFB cell was constructed, this research effort will also evaluate the maturation of the wetland cell and the impact this maturation has on the ability of the cell to treat the contaminants.

The results of this research will spur more focused evaluation of the effectiveness of constructed vertical flow wetlands as a viable remediation technology. Through this and future research an understanding of the degradation of chlorinated solvent contamination within a constructed wetland cell will aid in the validation and development of this alternative remediation technology.

Background

The chlorinated ethenes tetrachloroethene (perchloroethene or PCE), and trichloroethene (TCE) are commonly used as industrial cleaning and degreasing solvents. Their use in the United States (U.S.) began in the 1923 and increased significantly from the 1940s to the 1970s when their combined production peaked at approximately 600 million kilograms (Pankow and Cherry, 1996). PCE and TCE are still widely used within U.S. industries. The demand for PCE in 2004 was estimated to be 152 million kilograms (HSIA, 2005) while the demand for TCE in 1998 was estimated to be 78 million kilograms (HSIA, 2001). The application of chlorinated solvents crosses many industrial sectors. The primary uses of PCE are as a chemical intermediate in the manufacture of other chemicals, such as the refrigerant hydrofluorocarbon (HFC) 134a, and it is also used in over 70% of the commercial dry cleaners (HSIA, 2005). TCE is also widely used

as a chemical intermediate, as in the production of polyvinyl chloride (PVC), and also as a metal cleaner/degreaser within many industries (HSIA, 2001). Table 1 list some of the industries and industry processes that are often associated with the use of chlorinated solvents (ITRC, 2005).

Table 1. Industries associated with the use of chlorinated solvents

Industries	Industrial Processes
• timber treatment • coal gasification • electronics manufacturing • solvent or paint production • pesticide/herbicide manufacturing • airplane maintenance and engine manufacturing • military bases and rocket fuel production • dry cleaning • instrument manufacturing • transformer oil production • transformer reprocessing • steel industry cooking • vehicle manufacturing • pipeline compressor stations	• metal cleaning and degreasing • metal machining and plating • tool and die operations • paint removing • solvent storage above and below ground • solvent transmission through pipeline • solvent loading and unloading • mixed waste disposal in landfills • storage of liquid waste in lagoons

Due to their prevalent use and material handling and disposal practices during the past century, chlorinated solvents have been released into underlying groundwater aquifers. From 1987 to 1993, according to EPA's Toxic Chemical Release Inventory, PCE releases to land and water totaled over 1 million pounds (EPA, 2006a), while TCE releases total over 291,000 pounds (EPA, 2006b). Chlorinated solvents are among the most common groundwater contaminants found in the U.S. TCE and PCE are ranked as the first and fourth most common contaminants at National Priority List (NPL) sites, with the remaining chlorinated ethenes, trans-1,2-dichloroethene (trans-DCE), cis-1,2-

dichloroethene (cis-DCE), 1,1-dichloroethene (DCE), and vinyl chloride (VC), all within the top 33 most common contaminants at NPL sites (EPA, 2006c). Since liquid chlorinated solvents are denser than water and have relatively low solubilities, they are commonly referred to as dense non-aqueous phase liquids (DNAPLs). Once a DNAPL has been released to the subsurface in sufficient quantity it has the ability to penetrate the groundwater table where it can remain in its pure form and provide a long-term source of contamination to the groundwater. Although chlorinated solvents have relatively low solubilities, they can easily result in a groundwater dissolved phase concentration in excess of the established groundwater standards. Table 2 identifies some of the physical and chemical properties of the chlorinated ethenes (ITRC, 2005).

Table 2. Physical and Chemical Properties of Chlorinated Ethenes

Chemical	Weight Molecular	Molecular Formula	Specific Gravity	Log Kow	Koc	Color / Form	Boiling Point °C	Solubility mg/L
PCE	165.834	Cl2C=CCl2	1.6230	2.88	665	Colorless Liquid	121	150
TCE	131.3889	ClCH=CCl2	1.4694	2.29	160	Colorless Liquid	86.7	1,550
cis-DCE	96.9439	ClCH=CHCl	1.2837	1.86	35	Colorless Liquid	60.3	3,500
Trans-DCE	96.9439	ClCH=CHCl	1.2565	2.09	59	Colorless Liquid	47.5	6,300
DCE	96.9439	CH2=CCl2	1.218	2.13	65	Colorless Liquid	31.9	2,250
VC	62.4988	CH2=CHCl	0.9106	1.38	8.2	Colorless Gas	13.37	1,100

It was not until the mid-to-late 1970s, after decades of significant use, that the severity of chlorinated solvent contamination of important aquifers was discovered (Pankow and Cherry, 1996). Possible health effects of exposure to chlorinated ethenes include liver damage, birth defects, respiratory problems, kidney damage, central nervous

system disorders, and cancer (ATSDR, 1997 and 2003). The EPA has determined that VC is a carcinogen while both PCE and TCE are probable carcinogens (EPA, 2006d).

With over 81 percent of today's communities deriving their drinking water from groundwater sources (Sullivan, 2005), the protection of these drinking water sources is essential. In 1974, Congress passed the Safe Drinking Water Act, with amendments to the act in 1986 and 1996. This law requires EPA to determine safe levels of chemicals in drinking water which do or may cause health problems. These non-enforceable levels, based solely on possible health risks and exposure, are called Maximum Contaminant Level Goals (MCLGs). Based on these MCLGs, EPA has set an enforceable standard called a Maximum Contaminant Level (MCL). MCLs are set as close to the MCLGs as possible, considering the ability of public water systems to detect and remove contaminants using suitable treatment technologies (Sullivan, 2005). The MCLs and MCLGs for the chlorinated ethenes are shown in Table 3 (EPA, 2006e).

Table 3. MCLs and MCLGs for Chlorinated Ethenes

Chlorinated Ethene	MCL (mg/L)	MCLG (mg/L)
PCE	0.005	0
TCE	0.005	0
cis-DCE	0.07	0.07
trans-DCE	0.1	0.1
DCE	0.007	0.007
VC	0.002	0

The Clean Water Act is the primary federal law governing water pollution in the U.S. Congress first passed the statute as the Federal Water Pollution Control Act

Amendments of 1972. It became known as the Clean Water Act after Congress passed a significant set of amendments to it in 1977. The act was further amended in 1987. The stated objectives of the law are to "restore and maintain the chemical, physical, and biological integrity of the nation's waters" (Sullivan, 2005). The Clean Water Act established discharge prohibitions on toxic chemicals, and a permit program to authorize and regulate discharges in compliance with the Act. Although, not directly applicable to groundwater, the Clean Water Act has played a role in minimizing the release of chlorinated ethenes into the environment.

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund, was enacted by Congress on December 11, 1980, with a significant amendment to the law passed in 1986. The major provision of the law is to address the problems associated with hazardous waste sites caused by the release of hazardous substances to the environment. The law established the procedures and standards that are to be followed in remediating hazardous waste sites. CERCLA also authorizes the EPA to perform Potentially Responsible Party searches to identify those parties responsible for the contamination at hazardous waste sites. The law also required the reporting of hazardous substances releases to federal and local authorities when such a release exceeded the reportable quantity (RQ) established by CERCLA (Sullivan, 2005). The RQ for both PCE and TCE is 100 pounds.

In general, remediation of aquifers contaminated by PCE and its daughter products are extremely difficult and costly. The initial process of accurately characterizing a site contaminated by a chlorinated solvent with a DNAPL component can be difficult. A large DNAPL spill will migrate vertically through the groundwater

until it reaches a geological confining layer where it will "pool" and migrate due to gravity along the slope of the confining layer, possibly migrating in the opposite direction of the groundwater flow. If the subsurface contains multiple layers of non-contiguous confining layers, the DNAPL could "pool" on one confining layer and then "spill over" to deeper confining layer, often changing its horizontal direction. Therefore, lateral movement from the spill location can be large. Due their low viscosities and interfacial tension between DNAPLs and water, DNAPLs can also penetrate into deeper aquifers by migrating along tiny fractures in confining layers. In addition, drilling into or through a DNAPL zone can cause further mobilization of the DNAPL, making contaminate distribution even more complex. Figure 1 provides a conceptual site model of a DNAPL site with multiple DNAPL "pools". (Huling and Weaver, 1991)

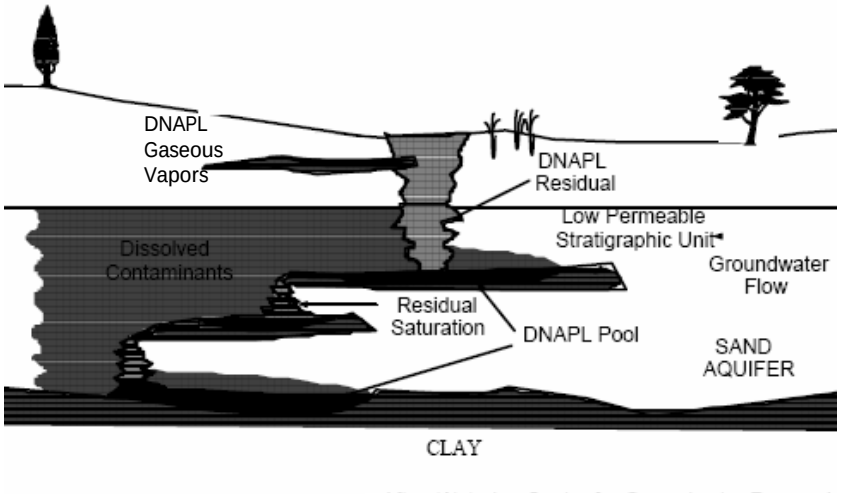


Figure 1. Conceptual Site Model of DNAPL Site

Also shown in Figure 1 are the four phases of DNAPL that may exist at a site. The DNAPL may partition onto the soil solid phase, and be retained in the soil matrix as

residual DNAPL, or it could volatize into the soil gas, dissolve into the surrounding groundwater, or remain in an immiscible phase. The need to understand the distribution of the contaminant among the phases and due to fact that a "pooled" DNAPL can continue to provide a source of groundwater contamination for several decades contributes to the difficulty in characterizing and remediating chlorinated ethene sites.

In the last 10 years alone the Department of Defense (DoD) has spent over $20 billion investigating and remediating hazardous waste sites located on military installations (DoD, 2005). Due to the difficulties and often technical impracticality of completely remediating DNAPL source zones, the benefits of source zone remediation efforts have been debate. Despite the removal of large masses of DNAPL from high cost source zone remediation efforts, responsible parties are often faced with little or no reduction in risk or regulatory relief. Therefore, often at DNAPL sites the primary objective, instead of actively treating the source area, is to contain and prevent the further migration of the dissolved contaminant plume. Containment technologies have typically been based on groundwater extraction and treatment systems (i.e., pump and treat). Given the time frame these systems are expected to be operational the cost to maintain and operate a pump and treatment system can be exorbitant. Although more passive containment technologies, including permeable reactive barriers and in-situ enhanced bioremediation zones, have been developed they still require continued long term maintenance. (ITRC, 2002)

The use of engineered wetlands for the treatment of groundwater contaminated with chlorinated ethenes has shown to be effective based on past research performed at the engineered wetland cell at WPAFB, OH (Sobolewski, 2004). Wetland treatment is an

attractive alternative because of its passive nature and potential low operation and maintenance costs. Wetlands can offer an ideal environment for the natural attenuation of chlorinated ethenes through complete anaerobic degradation. The anaerobic conditions and naturally high concentration of organic carbon within wetland soils allows for the biodegradation of chlorinated ethenes through reductive dehalogenation pathways (Lorah and Olsen, 1999). As a follow up on the work performed by Sobolewski, this effort will determine a vertical profile concentration of chlorinated ethene contaminants within the WPAFB wetland in an attempt to provide further support of the biodegradation potential of engineered wetlands. A sampling method enabling the collection of a closely-spaced vertical sampling interval, using a pore-water sampler, will be introduced in this research and compared to previous data. The collection of samples from the existing three layer stratified sampling grid will also be continued. Since it has been over five years since the WPAFB cell has been constructed, this research effort will also attempt to evaluate the maturation of the wetland cell and the impact this maturation has on the ability of the cell to treat the contaminants.

Research Questions

1. Do the vertical profile concentrations of PCE and its degradation products within the wetland cell provide further evidence of the biodegradation potential of an engineered wetland?
2. As the WPAFB wetland cell has matured, is there evidence to support an increase or decrease in the wetland cells capability to degrade the contaminants?

3. Are the analytical results obtained from the pore-water sampling methodology consistent with previous analytical results?

II. Literature Review

Natural Attenuation

As defined by EPA, the natural attenuation (NA) processes "include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater" (EPA, 1999). There are many different potential physical, chemical, or biological processes taking place within a contaminated aquifer. However, bioremediation is generally considered the most important of these processes for groundwater remediation because it can completely destroy the contaminant, as compared to sorption, dilution, or volatilization processes where the contaminant is simply transferred from one media to another or simply diluted (Wiedemeier et al., 1998).

Natural attenuating processes are generally occurring at all sites, but to different degrees of effectiveness, depending upon the contaminants involved and the characteristics of the soils and groundwater. Wetland environments appear to be favorable for the NA of chlorinated ethenes (Lorah and Olsen, 1999), through reductive biodegradation and phytoremediation, and are the subject of much research.

The implementation of NA as a remedy to address a hazardous waste site offers many advantageous compared to more intrusive remedial technologies. NA generates less remediation wastes, and significantly reduces the potential for cross-media contamination. NA also reduces the risk of human exposure to the contaminants, as well as to other toxic chemicals and safety hazards associated with the implementation of other more intrusive technologies. Often hazardous waste sites are located on or adjacent to sensitive habitats; the implementation of a NA remedy prevents the disturbance of

such habitats. Another advantage of NA is that there are no down times associated with equipment failures. And finally, NA is typically more cost effective than other more intrusive technologies (EPA, 1999).

However, NA as a sole remedy for a site is not always appropriate. Besides the fact that natural attenuation processes may not be actively taking place at a site, there are other disadvantageous to a NA remedy. Longer time frames to reach cleanup objectives are generally associated with NA remedies. Site characterization is usually more detailed and expensive when attempting to prove the effectiveness of NA. An extensive long-term monitoring program is typically needed to track the progress of NA. And a final disadvantage of NA is that the hydrologic and geochemical conditions favorable to NA may change over time and could result in the mobilization of previously stabile contaminants (EPA, 1999).

Phytoremediation

Phytoremediation is a remediation technology that uses plants to remove, degrade, or contain contaminants in soils, sediments, groundwater, surface water, or air. Phytoremediation of organic contaminants primarily occurs by one or more of the following five mechanisms:

- Phytoextraction: the uptake and translocation of dissolved-phase contaminants from groundwater into plant tissue;
- Phytovolatilization: the transfer of the contaminant to air via plant transpiration;
- Rhizosphere degradation: the breakdown of organic contaminants within the microbe-rich rhizosphere (soil surrounding the root);
- Phytodegradation: the breakdown of organic contaminants within plant tissue.

- Hydraulic control: the use of trees to intercept and transpire large quantities of groundwater or surface water in order to contain or control the migration of contaminants (RTDF, 2005).

Besides the hydraulic control mechanism, all the phytoremediation mechanisms are likely participants in the remediation of chlorinated ethenes in a wetland environment. Phytoextraction is the simple uptake and relocation of contaminants from the groundwater to the plant as the plant takes in water and nutrients from the soil. The extent of phytoextraction depends on many factors related to the plant and subsurface; to include pH, clay content, water content, and organic matter content (RTDF, 2005). Phytovolatilization of chlorinated volatiles from plant tissues to the atmosphere, via plant transpiration, is a major pathway for chlorinated volatiles in phytoremediation applications. Although transpiration of chlorinated solvents has been confirmed in studies, researchers predict that transpiration from vegetation will not result in unacceptable levels of airborne contaminants in the surrounding area (Davis et al., 1998; Narayanan et al., 1999; and McCutcheon and Schnoor, 2003).

Rhizosphere degradation is the breakdown of organic contaminants within the rhizosphere - a zone of increased microbial activity and biomass at the root-soil interface. Plant roots secrete substances such as carbohydrates, enzymes, and amino acids that microbes can utilize as a substrate (RTDF, 2005). Walton and Anderson (1990) showed that microbial activity is greater in unsaturated rhizosphere soils and that TCE degradation occurs faster in the rhizosphere than in nonvegetated soils. Plants do not transport oxygen to the subsurface through their root system, except for wetland plants and some other flood adapted plants (Pivetz, 2001). Therefore, in wetland environments,

contaminant degradation within the rhizosphere may also occur due to the delivery of oxygen causing enhanced aerobic mineralization of organics and the stimulation of co-metabolic transformation of chemicals (Anderson et al., 1993). Phytodegradation refers to the decay of contaminants within the plant tissue. Although the attenuating mechanisms of phytodegradation are not fully understood, it appears that the plant and its associated microbial communities contribute to the degradation of the communities. Research has shown that enzymes produced by plants may be able to degrade PCE and TCE to lesser chlorinated ethenes (RTDF, 2005).

Biodegradation

Biodegradation is the most important process in the removal of contaminants from ground water (Wiedemeier et al., 1998). Over the past three decades extensive research has demonstrated that subsurface microorganisms can degrade a variety of chlorinated solvents. Biodegradation of chlorinated solvents may take place via three different pathways; (1) through use as an electron acceptor (reductive dechlorination), (2) through use as an electron donor, or (3) through co-metabolism (Wiedemeier et al., 1998). In uncontaminated aquifers, native organic carbon is used as an electron donor, and dissolved oxygen, when available, is the primary electron acceptor. When carbon sources from contaminants are present they too may be used as elector donors. As the DO is consumed, anaerobic microorganisms typically use additional electron acceptors such as nitrate, iron, sulfate, and carbon dioxide. And in anaerobic conditions anthropogenic sources of carbon can also be used as an electron acceptor. Evaluation of the distribution of these electron acceptors can provide evidence of where and how chlorinated ethenes biodegrade (Wiedemeier et al., 1998).

Reductive Dechlorination

Under anaerobic conditions, the biodegradation of the highly chlorinated ethenes, such as PCE and TCE, can readily be accomplished through reductive dechlorination. During this process, the chlorinated ethene is used as an electron acceptor and a chlorine atom is removed and replaced with a hydrogen atom, producing a less chlorinated product (Lorah and Olsen, 1999). This form of anaerobic respiration is known as direct dehalorespiration where microorganisms (halorespirers) take advantage of the energy released during reductive dechlorination and use the energy for growth and reproduction. If electron donors are depleted from the environment, reductive dechlorination will stop, and the accumulation of PCE intermediates may result. This reductive dechlorination process is known to occur under a range of anaerobic conditions (nitrate reducing, iron reducing, sulfate reducing, and methanogenic) but is believed to be faster and more likely to result in the complete dechlorination to ethylene under the highly reducing methanogenic conditions (McCarty and Semprini, 1994). As chlorinated ethenes become less chlorinated and further reduced, a greater concentration of hydrogen (electron donor) and more strongly reducing conditions are required to reduce them further. The reduction of PCE and TCE to DCE can occur under mild nitrate or Fe(III) reducing conditions, whereas the reduction of DCE to VC requires sulfate reducing conditions, but the reduction occurs more readily under methanogenic conditions. Finally, the reduction of VC to ethylene, can be extremely slow and requires highly reducing methanogenic conditions (Vogel et al., 1987). Figure 2 provides the sequencing of the complete reductive dechlorination of PCE to ethylene. According to Bouwer, of the three possible

DCE isomers, cis-1,2-DCE predominates over trans-1,2-DCE and 1,1-DCE is the least significant of the intermediaries (Bouwer, 1994).

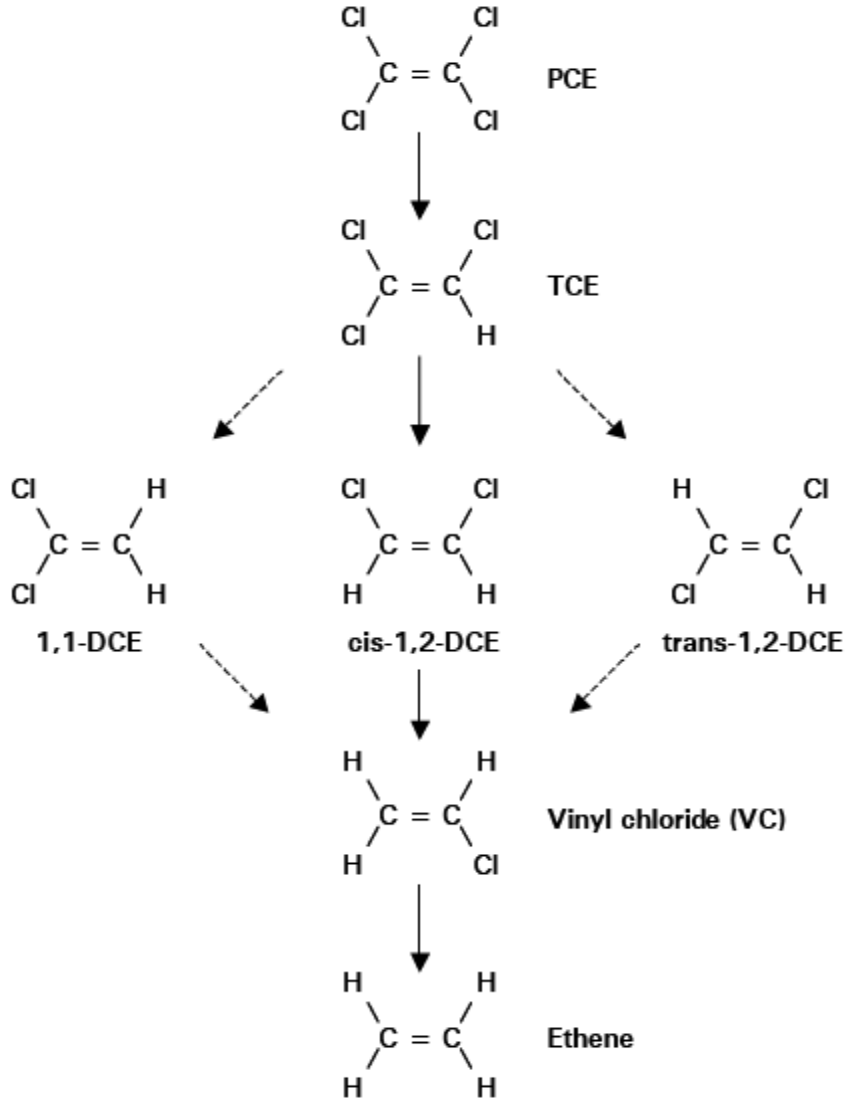


Figure 2. Anaerobic Reductive Dechlorination Pathway of PCE

A significant issue regarding the effectiveness of reductive dechlorination is the competition for hydrogen and other electron donors between dehalorespiring bacteria and

other anaerobic microorganisms (Yang and McCarty, 1998). The reducing condition within an aquifer, which drives reductive dechlorination, is determined by the dominant electron acceptor (Chapelle, 2001). Nitrate reducers, iron reducers, sulfate reducers, methanogens, and dechlorinating bacteria all have different affinities for consuming hydrogen. The order of affinity, in anaerobic systems, for hydrogen in descending order is nitrate, iron, sulfate, and carbon dioxide. As nitrate concentrations are depleted, iron reducing conditions become dominant. Sulfate reducers will take over when iron is depleted, and methanogens will follow sulfate exhaustion (Chapelle, 2001). When nitrate, iron, and sulfate have been exhausted, or remain in low concentrations, dechlorinating bacteria can successfully compete for electron donors and reductive dechlorination will readily take place. As chlorinated ethenes become less chlorinated and more reduced, greater concentrations of hydrogen and more strongly reducing conditions are required for them to be dechlorinated. Ultimately, the success of reductive dechlorination depends on the presence of dechlorinating microorganisms, an ample organic substrate to donate electrons, and favorable environmental conditions such as temperature and pH (Lee et al., 1998).

Wetland environments offer ideal conditions for the complete anaerobic reductive dechlorination of chlorinated solvents. Due to the limited diffusion of oxygen into the waterlogged soils and the rapid depletion of oxygen due to the high concentration of natural organic substrates available for microbial respirations, anaerobic conditions typically exist in wetland environments. In addition, the significant supply of natural organic carbon within a wetland provides an abundant source of electron donors for the reductive dechlorination of the chlorinated ethenes (Lorah and Olsen, 1999). The

fermentation of the organic carbon generates hydrogen, which acts as the primary electron donor in the reductive dechlorination process. Other fermentation products, such as acetate, may serve as electron donors but hydrogen appears to be the most important electron donor for anaerobic dechlorination of chlorinated ethenes (Maymo-Gatell et al., 1997a).

Oxidation

As the tendency for chlorinated ethenes to be reduced decreases as the number of chlorine atoms decreases in the molecule, the tendency to undergo oxidation increases (Vogel et al., 1987). Therefore, VC has the greatest potential to undergo oxidation. Under aerobic and in some anaerobic cases, the less-oxidized chlorinated ethenes can be used as an electron donor in biologically mediated redox reactions (Wiedemeier et al., 1998). Bradley and Chapelle have observed in laboratory cultures and aquifer samples the rapid microbial degradation of VC, including mineralization, under aerobic conditions. In their continuing research they also showed that VC, and to a lesser extent DCE, could be oxidized to carbon dioxide under the anaerobic Fe(III)-reducing conditions (Bradley and Chapelle, 1996 and 1997). The results indicated that vinyl chloride can be mineralized under anaerobic, Fe(III)-reducing conditions, and that the bioavailability of Fe(III) is an important factor affecting the rates of mineralization. More importantly, microbial oxidation of VC under Fe(III)-reducing conditions can provide a potential anaerobic alternative to the slow and inefficient reductive dechlorination of VC to ethene.

The dechlorination of cis-DCE and VC appear to be the rate limiting steps in the complete reductive dechlorination of PCE. Due to the highly reducing conditions need to

reduce cis-DCE and VC to ethene, it is common to witness their accumulation at PCE sites. VC is the most toxic of the chlorinated ethenes, thus their accumulation is of concern. Clemmer (2003) hypothesized that aerobic oxidation plays a role in the biodegradation of VC and cis-DCE at the WPAFB wetland cell. Due to the transport of oxygen into the rhizospheres of the wetland plant root system, VC and cis-DCE can be aerobically oxidized in the tiny microenvironments.

Co-metabolism

Degradation of a chlorinated ethene via a co-metabolic reaction occurs when the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by a microorganism for other purposes. The organism receives no benefit from the degradation (Wiedemeier et al., 1998). Co-metabolism may occur under both anaerobic and aerobic conditions, however, under aerobic conditions chlorinated ethenes, with the exception of PCE, are more susceptible to co-metabolic degradation.

Microbial Cultures

The first observed pure microbial cultures to catalyze reductive dechlorination reactions were methanogens that did not gain energy or grow by using the chlorinated ethenes as an electron acceptor. These methanogens caused only slow and partial dechlorination of PCE and TCE to yield DCE. Based on these initial studies, reductive dechlorination was thought to be a cometabolic process where the methanogenic microorganisms were not believed to obtain any direct benefits from the process (Chapelle, 2001).

However, through the works of DiStefano, Hollinger, Maymo-Gatell and others in the early 1990s, it was shown that reductive dechlorination can be carried out by

microorganisms that used chlorinated ethenes as terminal electron acceptors for their own growth and reproduction. These microorganisms, known as halorespirers, are able to grow using chlorinated ethenes as sole terminal electron acceptors (Chapelle, 2001). The complete dechlorination of PCE to ethene under anaerobic conditions and in the absence of methanogenic conditions was first reported by DiStefano (1991). Although the complete reductive dechlorination of PCE has been shown to occur in mixed microbial communities, pure bacterial isolates taken from these communities typically only dechlorinate PCE to cis-DCE (Flynn et al., 2000). To date only one pure isolate, *Dehalococoides ethenogenes,* completely dechlorinates PCE to ethene (Maymo-Gatell et al. 1997). However, the reduction of VC to ethene is still the rate limiting step while using *D. ethenogenes;* the growth of *D. ethenogenes* increased during the reduction of PCE, TCE, and DCE but it appears that the reduction of VC does not support the growth of this microorganism (Flynn et. al., 2000). The VC was consumed with first order kinetics while the other chlorinated ethenes disappeared with zero-order kinetics (Maymo-Gatell et al., 1999).

The discovery of *D. ethenogenes* is significant to enhanced remediation technologies, however in natural environments, as in the subject wetland cell, bacteria do not exist as stand alone pure isolates, but instead as mixed diverse cultures. Flynn et al. (2000) "suggest that different sites have different chloroethene dechlorinating communities and that communities specialized in cis-DCE and VC dechlorination can be different from those involved in PCE dechlorination." The wetland cell may be host to several halorespirers acting together in the complete dechlorination of the PCE contaminate.

Constructed Wetlands

Natural wetlands have the ability to improve the quality of water that flows through them by filtering out impurities, actively degrading waste matter, and removing some chemicals that flow through them. The discovery of this attribute led to the idea of intentionally using wetlands to treat wastewater. The cleansing processes identified in natural wetlands can be mimicked in constructed wetlands. Constructed treatment wetlands are designed to maximize the natural abilities of wetlands to remove pollutants from a variety of wastewater and contaminated groundwater sources. The use of constructed wetlands to treat domestic wastewater has been in use for over 50 years and was first used in Europe (Ramsar, 2005). Once the advantages of constructed wetlands for the treatment of domestic wastewater were realized, the application on their use has broadened in recent years. Constructed wetlands are now used to treat acid mine drainage, pulp mill wastewater, swine waste, poultry rendering wastes, landfill leachate, urban runoff, textile wastewater, and effluent from the photography industry (Moore, 1993). The use of constructed wetlands for treatment of contaminated groundwater from hazardous waste sites is the most recent application of this treatment technology. The research and development of constructed wetlands for the treatment of contaminated groundwater has been limited and has only been initiated in the last 10-15 years.

Researchers most widely recognize the work of Dr. Michelle Lorah, with the U.S. Geological Survey, as spearheading the research and development of using wetlands for the treatment of contaminated groundwater. Her work with Dr. Olsen during the early and mid 1990s at Aberdeen Proving Grounds, a U.S. Army post in Maryland, provided evidence that anaerobic biodegradation naturally attenuated a chlorinated solvent

contaminated groundwater plume as it passed through natural wetland sediments (Lorah and Olsen, 1999a, and Lorah and Olsen, 1999b). They concluded that the enhanced reductive dechlorination of chlorinated organics in the wetland sediments could be attributed to the favorable anaerobic, naturally high dissolved organic carbon concentrations, and highly reducing conditions of the wetlands (Lorah and Olsen, 1999a). The rapid attenuation observed in the natural wetland systems suggests that a constructed treatment wetland approach based on the presence of reductive dechlorinating microbial populations known to degrade chlorinated solvents may be possible. This work has spurred other field and laboratory research assessing the ability of wetlands to effectively treat chlorinated solvent contaminated groundwater as well as the development of constructed wetlands for the treatment of such contaminated groundwater.

Research conducted by Kassenga has focused on the impact of hydrogen threshold concentrations and terminal electron acceptor competition as indicators of deholorespiration in constructed treatment wetlands. Using laboratory-scale upflow treatment wetland systems Kassenga et al. concluded "rapid dechlorination potential was distributed throughout the wetland bed, both within and below the rhizoshpere, indicating that reductive dechlorination pathways can be active in anaerobic environments located in close spatial proximity to aerobic environments and plants in treatment wetland systems" and regardless of the initial H_2 concentration, dehalorespirators competed successfully for H_2 with methanogens (2004). In addition, there have been several other case study publications and conference presentations providing support for the use of constructed wetlands for the treatment of chlorinated solvent contaminated groundwater;

however they all point toward the need for further research in order to understand the underlying processes producing the favorable results.

Even as the research continues, the use of constructed wetlands for the treatment of contaminated groundwater at hazardous waste sites is gaining in popularity. Table 4 provides a list of hazardous waste sites implementing a constructed treatment wetland at different stages of development. These sites are working towards the acceptance of constructed wetlands as a component of their formal remedial action. Regulatory agencies are realizing the benefits of constructed wetlands and are approaching this developing technology with optimism.

Table 4. Implementation of Constructed Treatment Wetland Technology

Site	Application	Status
Superfund site in North Dartmouth, MA	Treatment of groundwater to replace an existing pump and treat system	Pilot initiated 12/2002—3 year pilot
22nd Street Landfill Site, Aberdeen Proving Ground, Md (Superfund)	Protection of Southern Bush River, Chesapeake Bay, Md from discharge of contaminated groundwater	Proposed as primary remedial option for the site-regulatory approval pending
Superfund site in Southington, CT	Treatment of groundwater to replace an existing pump and treat system	Pilot proposed and designed in 2001-regulatory delays have delayed start of program
3 additional coastal sites at Aberdeen Proving Ground, Md (Superfund)	Protection of Southern Bush River, Chesapeake Bay, Md from discharge of contaminated groundwater	Treatability studies and conceptual designs completed
Hazardous Waste Site in North Carolina	Protection of drinking water reservoir	Design completed, system will be built in summer 2006
ETTP, Oak Ridge, Tennessee	Interception of plume prior to reaching stream	Conceptual design completed, treatability studies in progress
Industrial facility in Louisiana	Treatment of groundwater	Preliminary design in progress
Industrial facility in Minnesota	Protection of small pond	Pilot in progress
Hazardous Waste Site in central Michigan	Treatment of groundwater	Full-scale system operating

III. Materials and Methods

Treatment Wetland Design

A small, experimental wetland was built and completed in August of 2000 in Area A of WPAFB to evaluate the degradation potential of chlorinated ethenes (CEs) in a wetland environment. The pilot-scale treatment wetland was constructed in an excavated pit or cell (120 feet x 60 feet, & 5 feet deep), lined with a 12-inch thick clay layer and PVC geomembrane for hydraulic isolation from the underlying soil/aquifer and from the sides, and it was located in an area overlying an aquifer contaminated with chlorinated solvents. The excavated pit was filled with soil relocated from a drained wetland area on WPAFB, and the contaminated groundwater was withdrawn from the underlying aquifer and pumped into the constructed wetlands, as described below.

Three 3" parallel, perforated PVC supply lines run along the bottom of the cell encased in a 9" thick bed of gravel consisting of crushed limestone. These lines provide a continuous supply of CE-contaminated groundwater into the treatment wetland at a rate of approximately 4.2 gallons per minute. The gravel layer was placed to allow the water entering the wetland cell to get evenly distributed across the bottom layer. A 54" thick fill, consisting mainly of soil obtained from a drained wetland nearby, was then placed on top of the gravel layer. The treatment wetland design and imposed hydraulics allows the contaminated groundwater to move upward through the soil layer to the surface, and then flow through an exit weir.

The weir is located at the opposite end of the wetland cell from the water inlet pipe (Figure 3) and it can be adjusted to control the depth of standing water on the wetland surface. The water exiting the wetland through the weir is discharged to the local sanitary sewer. A drawing of the wetland cell depicting the flow of water is provided in Figure 3.

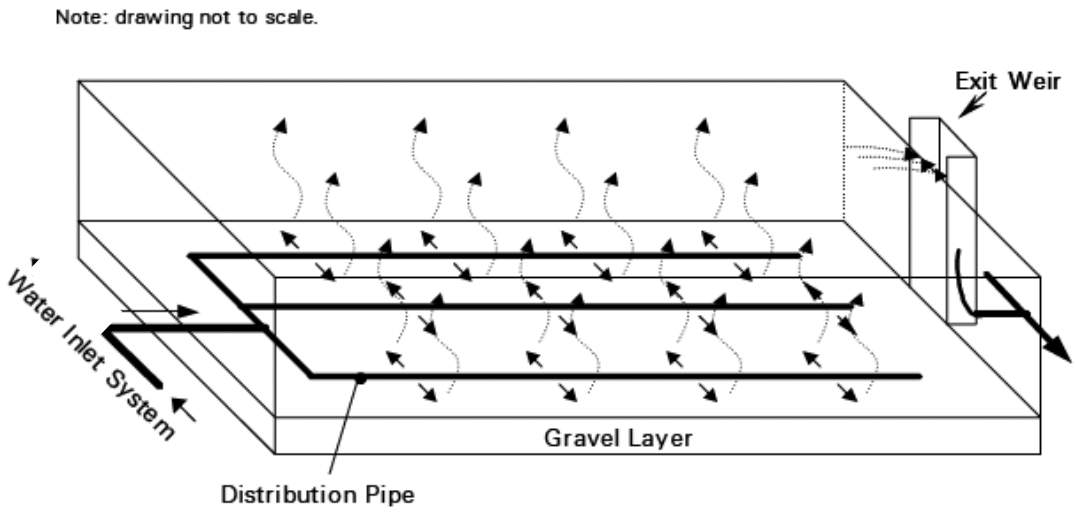


Figure 3. Water Flow Through Constructed Wetland (Enting, 2002)

The soil fill within the constructed wetland overlies the bottom gravel layer, and it is divided into three layers (Figure 4), as follows: (a) Lower Layer – 18 inches of wetland soil fill was amended with 10% wood chips (v/v) at the time of construction, to provide a source of organic carbon for inducing anaerobic (reducing) conditions quickly; (b) Middle Layer – 18 inches of un-amended wetland soil fill; (c) Upper Layer – 18 inches of un-amended wetland soil fill in which wetland vegetation was planted. Typical wetland vegetation, such as *Carex hystercina*, *Acorus calamus*, and *Juncus effusus*, was planted on the ground surface within the cell. The original assumption was that the thickest part

of the plant roots would only penetrate through the top 18 inches. However, soil cores from the field site and greenhouse experiments conducted at Wright State University have shown that the roots have penetrated to a depth greater than 5 feet (Bugg, 2002). Although oxygen is likely to be transported to the deeper interval of the soil layer by the root system, it is not known how much oxygen may be transported, and how the oxygen may affect microbial processes occurring in the generally anaerobic environment (Anderson et al., 1993).

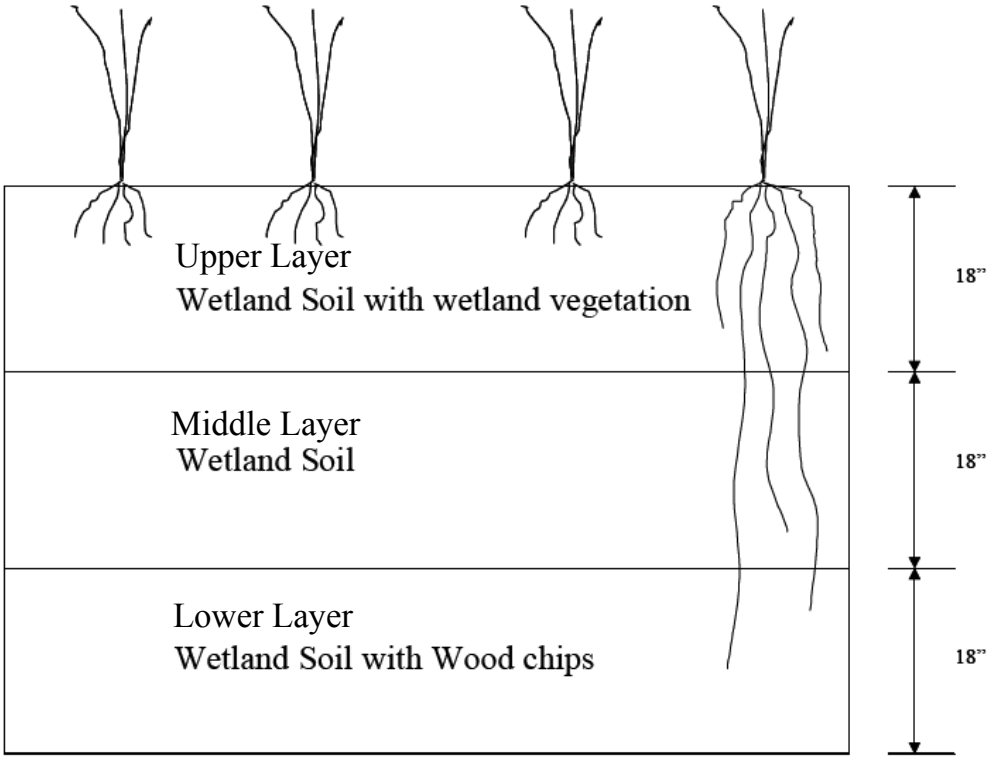


Figure 4. Constructed Wetland Cross Section

Sampling Design

Sixty-six nests of multi-level piezometers were installed in the summer of 2001 in a regular grid pattern (6 rows x 11 columns, as shown in Figure 5) for the sampling of

groundwater from the three soil layers, and water flow analysis. In addition, six nests of 2¼" diameter monitoring wells were installed in September of 2002. These wells were installed to allow a sonde/probe to be lowered below the water level for the *in situ* measurement of key parameters at various depths within the soil fill. In Figure 5 the small circles represent the piezometer nest locations and the large circles represent the 2 ¼ inch well nest locations.

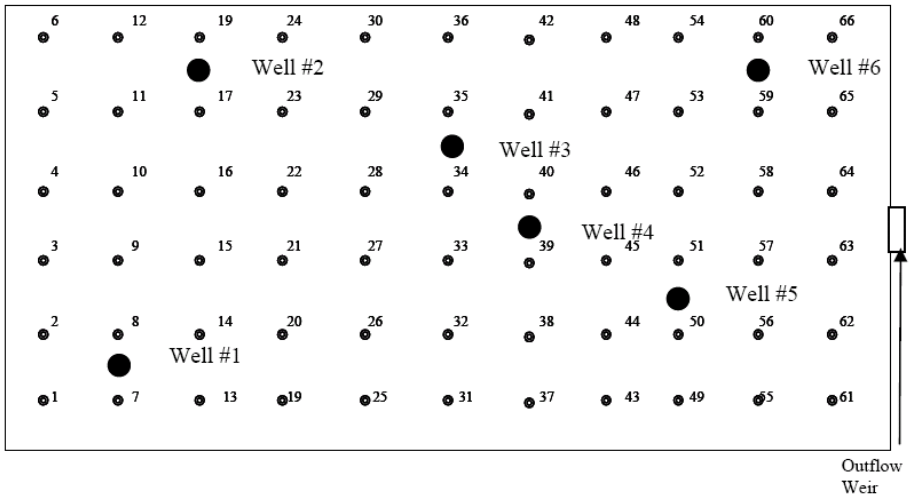


Figure 5. Plan view of wetland cell showing 6 rows each with 11 piezometers

Each piezometer nest consists of three piezometers, one screened in each of the lower, middle, and upper layer (Figure 6) of the constructed wetland cell. The piezometers were installed so that their 6-inch screen depths were positioned in the middle of the target layer. Therefore, the average depths of the piezometers in the lower, middle, and upper layers are 45, 27, and 9 inches, respectively (Figure 6).

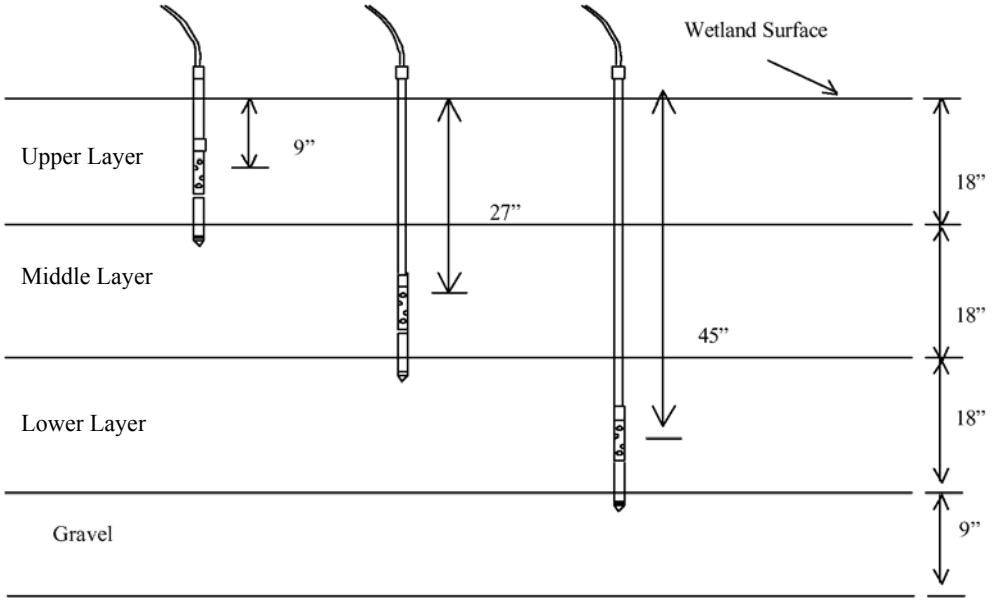


Figure 6. Piezometer Depths

Field Groundwater Sampling Approach

Four sampling events were completed in support of this research. Sampling events took place in September, October, November, and December of 2006. These months were chosen to examine any variability in the efficiency of the wetland cell due to seasonal changes from the late summer months to the early winter months as the wetland vegetation gradually underwent senescence through the fall season. Twenty-two out of the total 66 piezometer nests, as well as influent and effluent waters, were planned for sampling in each month during September-December 2006, and the location of the piezometers nests selected for sampling were distributed throughout the cell (Figure 7). Two piezometer nests per column, alternating between even and odd number nests, were considered representative sampling points (Figure 7), and it resulted in a staggered

sampling grid. However, due to a damaged lower layer piezometer in nest number 35, piezometer nest number 36 was selected instead.

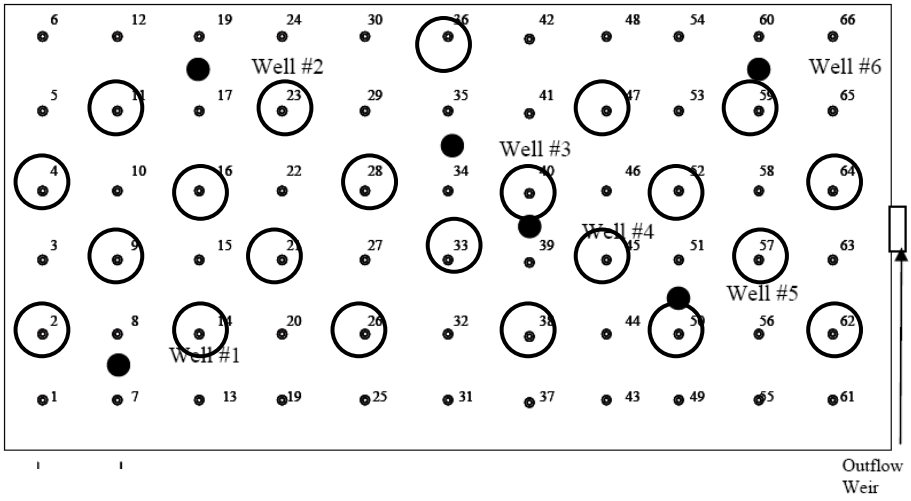


Figure 7. Location of selected piezometer nests (shown with circular outline)

A total of 66 water samples (22 piezometer nests x 3 levels) were scheduled to be collected each month, in addition to samples from the influent and effluent points. However, due to unforeseen weather conditions, as well as unexpected laboratory equipment maintenance, only 11 out of the 22 planned piezometer nests were sampled in October 2006. The piezometer nests sampled during October 2006 were numbers 2, 4, 14, 16, 26, 28, 38, 40, 50, 52, and 62 (see Table 5, for monthly details).

Due to the time requirement in the laboratory analysis of groundwater samples and the constrain to limit the hold time of the samples to less than 24 hours before GC analysis, all 22 piezometer nests could not be sampled and analyzed on the same day, and therefore, the sampling effort for each month was split into two or three sub-events.

However, in order to reflect a "snap shot" of the conditions of the wetland cell each month, the sampling events were scheduled as close to each other as possible. In September 2006, three sampling events were completed (Table 5), with the first and last events separated by 11 days. All 11 of the piezometer nests sampled in October 2006 were collected and analyzed on the same day. In November 2006, two sampling events were completed separated by seven days; and in December 2006, three sampling events were conducted over a 3 day period.

Table 5. Sampling/Analysis Schedule

September 2006 Sampling Events	
Date	**Piezometer Nests Sampled and Analyzed**
9/15/2006	2, 4, 14, 16, 26
9/20/2006	9, 11, 28, 38, 40, 50, 52, 62, 64
9/26/2006	59, 57, 47, 45, 36, 33, 23, 21
October 2006 Sampling Event	
Date	**Piezometer Nests Sampled and Analyzed**
10/11/2006	2, 4, 14, 16, 26, 28, 38, 40, 50, 52, 62
November 2006 Sampling Events	
Date	**Piezometer Nests Sampled and Analyzed**
11/10/2006	9, 11, 21, 23, 33, 36, 45, 47, 57, 59, 64
11/18/2006	2, 4, 14, 16, 26, 28, 38, 40, 50, 62
December 2006 Sampling Events	
Date	**Piezometer Nests Sampled and Analyzed**
12/12/2006	2, 4, 9, 11, 14, 16, 21
12/14/2006	23, 26, 28, 33, 36, 38, 40, 45
12/15/2006	47, 50, 52, 57, 59, 62, 64

The above data (collected during September-December 2006) may be combined with similar data collected previously (dating back to 2001-'04), and can be useful to understand the biogeochemical evolution of the constructed wetland and its VOC treatment efficiency/performance since its construction.

Groundwater Field Sampling Procedure

Prior to collection of the groundwater samples, the piezometers were purged to remove the stagnant water inside each piezometer, and then allowed to recharge with fresh pore-water from the surrounding soil matrix. The purging was accomplished with a 60 ml polypropylene syringe (Becton Dickinson syringe, part # 301035) attached with a Teflon tubing that was lowered to the bottom of the piezometer. It was possible to completely empty or evacuate the standing water within the piezometers screened in the upper and middle layers of the wetland cell. However, the water level in the piezometers screened in the lower layer recovered very quickly during purging due to a fast recharge rate from the surrounding soil, and could not be completely emptied by the syringe suction technique. Therefore, for the piezometers screened in the lower layer, a minimum of 4 syringe volumes (approximately 240 mL) of water were removed from the piezometers. The internal volume of the lower layer piezometers is approximately 154 mL, therefore, the purging of 240 mL ensures an adequate purge of the piezometer. The water levels were allowed to recover and recharge the piezometers for approximately 24 hours before collection of water samples from all three soil depths. Samples of the purged water from each piezometer were used to obtain the field parameters of pH, temperature, and conductivity. The use of the purged water to obtain the field parameters raises concerns regarding the quality and acceptability of the field data collected. Standing water from the piezometers should not be used for field measurements; therefore, in the future the procedures will be revised to ensure the quality of field parameter measurements.

All three layers at a piezometer nest were sampled during the same sampling event in order to get a snapshot of the concentration values and measurements at that location. However, the review of the research completed during 2001-2004 by AFIT students (Bugg, 2002; Clemmer, 2003; Sobolewski, 2004) indicate that water samples were collected by layer, i.e., all the piezometers screened in a layer were sampled in one discrete sampling event, and thus there were time gaps between field and lab data collected for each of the soil layers. For the present investigation, however, each layer of a piezometer nest was sampled during the same sampling event, starting with the upper layer.

The actual groundwater sampling was carried out with a 60 mL polypropylene syringe, connected to a ¼-inch OD Teflon tubing, identical to the device used earlier from purging of the piezometers. For extracting the water samples from each piezometer, the Teflon tube attached to the large syringe was lowered inside its narrow (1/2-inch diameter) stainless steel casing all the way to the piezometer bottom. The extracted water from the syringe was then immediately transferred into a pre-labeled 15 ml glass serum bottle (part #223742; Wheaton); the loss of the dissolved volatiles organics from the sample and contact with atmospheric oxygen was minimized by transferring the water from the syringe down the side of the serum bottle with as little turbulence as possible, and until the serum bottle overflowed, thus leaving a meniscus of water above. A Teflon-lined grey butyl rubber stopper (part #224100-081; Wheaton) was then immediately pushed into place to close the serum bottle, minimizing the exposure of the water sample to the atmosphere, and also ensuring that there were no bubbles or headspace in the vial.

Soon after, the bottle was sealed with an aluminum crimp (part #27222-U; Supelco) and stored in dark at 4 degree C in a cooler. Then the middle layer of the same piezometer nest was sampled, followed by a similar sampling for the upper layer. A minimum of 30 mL was first extracted from the middle piezometer using the same syringe, and discarded; this syringe rinsing procedure was adapted in order to reduce any potential contamination of the sample by the droplets of residual water remaining in the tubing and syringe from earlier sampling. Further, the sampling was continued in the lower layer of the same nest using the same procedures; however, prior to sampling, the syringe was rinsed with a minimum of 120 ml of the standing water from within the piezometer

The sampling procedures for the influent and effluent water in the wetland cell were different. The influent water samples were collected in the pump-house through a valve in the pipe feeding the wetland cell. The valve was turned open and allowed to flow for about 10 seconds before the sample was collected. The effluent water sample was collected from the pool of surface water within the wetland cell, just inside the outlet weir. After the sample collection for the day was accomplished, the samples were stored in a cooler with an ice pack, and then transferred to the Environmental Geochemistry laboratory of Wright State University within 1 hour after collection. All the samples were analyzed on the same day for PCE, TCE, trans-DCE, cis-DCE, VC, ethylene, and ethane in the Environmental Geochemistry Laboratory at Wright State University.

Analysis - Gas Chromatography with Purge-and-Trap

All groundwater samples collected from the field site were analyzed by gas chromatography equipped with a purge and trap sample concentrator. A Hewlett Packard 6890 Series gas chromatograph (GC) and the HP Chemstation software were used to analyze the aqueous samples collected from the field site. The GC was equipped with an Electron Capture Detector (ECD) and a Flame Ionization Detector (FID). The chlorinated compounds (including PCE, TCE, and trans and cis-DCE) were separated by 30m VOC capillary column (part #19091V-413; Agilent Technologies), and quantified by the ECD detector. Other analytes of interest (vinyl chloride, ethane, ethene, etc.) were separated by a 30m GS-GasPro capillary column (part# 113-4332; J&W). The operating parameters for the GC are listed on the following page in Table 6. The HP Chemstation software allows plotting and integration of the chromatographic peaks. Although the program was set to auto-integrate the peaks, manual integration was used occasionally for small peaks. The operating conditions of the purge and trap concentrator (Velocity XPT Accelerated Purge-and-Trap System; manufacturer: Teledyne, Tekmar) attached to the GC is given in Table 7.

Five mL of an aqueous sample was manually injected into the purge-and-trap system that gently extracts volatile compounds from the aqueous samples. Purge gas is bubbled through the aqueous sample in the purge tube and collected on a trap column containing a solid adsorbent. After a predetermined amount of purge time (Table 7), the temperature of the trap is raised so that the volatile compounds that were adsorbed on the trap are released and injected into the GC.

Table 6. GC Operating Parameters

Oven	**Front Inlet**
Initial Temp (deg C) 50	Mode: Splitless
Initial Time (min) 2.00	Initial Temp (deg C) 200
Ramp (deg C/min) 10.00	Pressure (psi) 9.85
Final Temp (deg C) 160	Gas Saver: Off
Post Temp (deg C) 50	Gas Type: Helium
Total Run Time (min) 13.0	
Column 1 (J&W 113-4332 GS-GasPro)	**Column 2 (Agilent 19091V-413)**
Max Temp (deg C) 230	Max Temp (deg C) 260
Nominal Length (m) 30	Nominal Length (m) 30
Nominal Diameter (µm) 320	Nominal Diameter (µm) 320
Nominal Film Thickness (µm) N/A	Nominal Film Thickness (µm) 1.8
Mode Const Flow	Mode Const Flow
Pressure (psi) 9.85	Pressure (psi) 9.85
Nominal Initial Flow (mL/min) 2.1	Nominal Initial Flow (mL/min) 2.0
Average Velocity (cm/sec) 34	Average Velocity (cm/sec) 34
Inlet Front	Inlet Front
Outlet Front	Outlet Back
Outlet Pressure Ambient	Outlet Pressure Ambient
Front Detector (FID)	**Back Detector (µECD)**
Temp (deg C) 250	Temp (deg C) 250
N_2 Makeup Flow (mL/min) 45.0	Anode Flow (mL/min) 6.0
H_2 Flow (mL/min) 40	N_2 Makeup Flow (mL/min) 60.0
Air Flow (mL/min) 450	Electrometer On
Flow & Electrometer On	
Lit Offset 2.0	

Table 7. Purge and Trap Operating Parameters

Sample Volume (mL)	5	Purge Gas	Helium
Valve Oven Temp (°C)	150	Transfer Line Temp (°C)	150
Sample Mount Temp (°C)	90	Purge Ready Temp (°C)	45
Dry Flow Standby Temp (°C)	175	Standby Flow (mL/min)	10
Pre Purge Time (min)	0	Pre Purge Flow (mL/min)	40
Sample Heater	Off	Sample Pre Heat Time (min)	1
Pre Heat Temp (°C)	40	Purge Time (min)	11
Purge Flow (mL/min)	40	Dry Purge Time (min)	0
Dry Purge Temp (°C)	40	Dry Purge Flow (mL/min)	200

The GC method used in the analyses was developed, and the standard solutions for each analyte were prepared in the Environmental Geochemistry lab. Calibration curves were created from the various standard concentrations and are included in Appendix B. The curves were forced through zero to result in an improved R-squared value for each of the analytes. The calibration curves were then used to convert the peak areas of individual analytes of interest to determine their concentrations.

Development of Pore-Water Sample Chamber

The biogeochemical and hydrogeological conditions within a wetland can change drastically over small vertical intervals. Therefore, a sampling approach offering a greater vertical resolution was desired as compared to the current nested piezometer system. After evaluating the literature on the various pore-water sampling techniques (Hesslein, 1976; LeForce et al., 2000; Laor et al., 2003, Lorah et al., 2003) and with the knowledge and experience of the thesis committee members regarding pore water

samplers, it was determined that a more rigid design of the pore-water sampler (PWS) than the commonly used peepers (Hesslein, 1976) would be necessary at this site due to the compact nature of the soil interval. The design of the PWS incorporated the advantage of dialysis bags placed inside a well at discrete depths. The conceptual design of the PWS includes small cylindrical units, each a few inches in length and housing a sample chamber and open on one side by a porous stainless steel plate. Further, the units may be assembled in series (end-to-end) to a desired length, and can be easily lowered/pushed within the PVC casing of a well, and positioned at the screened interval of the well (see Figure 8). Dr. Carl Enfield offered a basic design for a PWS utilizing solid PVC rod and porous stainless steel plates, and the mechanical workshop at AFIT was able to fabricate 10 units of the PWS.

PWS Design

Solid PVC rod of 1.75-inch diameter was used as the foundation raw material providing the structural support desired. The solid PVC rod was machined to a length of 4 3/8-inchs, and a cylindrical 1.25-inch diameter (internal volume: 19.5 mL) cavity was bored into the PVC rod from one side to create the sample cavity. The cylindrical cavity was rounded at the bottom in order to maximize the volume of the cavity. A 1.5-inch square porous stainless steel plate (Mott Corporation, Farmington, CT) fastened with four #4-40 screws using standard helical inserts covers the sample cavity. A 1/16 inch thick viton O-ring (1.25 inch inside diameter x 1.375 inch outside diameter) was used under the porous stainless steel plate to provide a watertight seal. Sampling ports into the cavity of each chamber were provided on both ends of the pore-water sampler with septa material

covering the ports being held in place with ¼ inch-20 vented screws and washers. The vented screws allowed access to the sample collection cavity with a sampling syringe and needle.

The samplers were designed to be chained together, using ¼ inch-20 screws, for insertion into a 2 inch monitoring well, enabling a pore-water sample to be obtained approximately every 3 5/8 inches. A 2-inch outer diameter, 1/8 inch thick viton washer placed between each sampler provides a tight fit against the well casing and therefore prevents vertical migration of the wetland water within the monitoring well. The viton washer isolates each pore-water sampler and ensures that only the water within each targeted interval has contact with the respective pore-water sampler. Figure 9 provides design drawings and photographs of the pore-water sampler prototype. The AFIT model shop fabricated 10 prototypes of the samplers for laboratory and field testing.

Bench-scale evaluation of the PWS

Laboratory testing was conducted to estimate the diffusion rate of the subject contaminants through the porous stainless steel plates. The results of this laboratory testing will help determine the length of time that the pore-water must stay in place within the monitoring well in order to reach equilibrium with the surrounding groundwater.

A 12 liter aqueous solution of Calcium Sulfate ($CaSO_4$), Magnesium Chloride ($MgCl_2$), Sodium Sulfate (Na_2SO_4), and Potassium Nitrate (KNO_3) was built to test the pore-water samplers. The 19.5 ml sample cavities of eight (8) pore water samplers were

filled with de-ionized water and covered with 5 micrometer pore sized stainless steel porous plates. Prior to placing the pore-water samplers in the salt solution test bath, each of the samplers were placed in a vacuum chamber filled with de-ionized water. A vacuum was pulled on the chamber for approximately 2.5 hours in order to evacuate the air from the porous stainless steel plates. Evacuating the air from the pores of the porous plates and thus infusing the pores with water enabled a more efficient diffusion process through the plates. After evacuating the air from the plates, the eight (8) samplers were immediately placed in the 12 liter salt test solution. The solution and samplers were housed in large cooler with a tight fitting lid to minimize evaporation of the solution.

Two of the pore-water samplers were removed from the test solution at intervals of 1, 3, 9, and 30 days. Samples of the water from the removed pore-water samplers' cavity were then analyzed to determine the concentration of the subject cations in the samples. In addition, at each of the sampling intervals two samples of the test bath solution were also collected and analyzed for the subject cations.

Field evaluation of the PWS

In addition, the pore-water sampler was also tested in the field at the WPAFB experimental wetland cell. The number 4 - 2 ¼ inch monitoring well (MW4) nest (see Figure 5) was used to test the pore-water sampler in the field. Since the 2 ¼ inch monitoring wells only have a 6-inch screened interval, only two pore-water samplers could be chained together and used in these wells. The middle depth monitoring well of the number 4 - 2 ¼ inch monitoring well nest was used to field test the pore-water

sampler. The total depth of this well was 33 inches below grade surface (bgs) and the 6-inch screened interval extended from 27 inches bgs to 33 inches bgs.

Two pore-water samplers, filled with deionized water and covered with 5 micrometer porous plates, were inserted into the well on December 15, 2006. Prior to placing the samplers in the well they were first placed in a vacuum chamber filled with deionized water. A vacuum was pulled on the chamber for approximately 2.5 hours in order to evacuate the air from the porous stainless steel plates. The samplers were then transported to the field submerged in deionized water to avoid the evaporation of the deionized water from the pores of the stainless steel plates. The monitoring well was first purged and allowed to recharge before inserting the pore-water samplers. In addition, a grab sample was obtained from the well, following procedures similar to the sampling of the piezometers, prior to installing the pore-water samplers. A handle fabricated of solid PVC stock attached to the two pore-water samplers was used to place the samplers at the bottom of the well. Given the dimensions of the pore-water sampler, the center of the sampling cavity of the bottom pore-water sampler was 2 5/16 inches from the bottom of the well and therefore 30 11/16 inches bgs. The center of the sampling cavity of the top pore-water sampler was 6 inches from the bottom of the well and thus 27 inched bgs. Since the well was only screened 6 inches (27 – 33 inches bgs), only half of the sampling cavity of the top pore-water sampler was within the screened interval, however, due to the hydrostatic pressure within the well the entire sampling interval of the top pore-water sampler was filled with water. Viton seals were placed between the samplers and at the top of the second sampler in order to prevent vertical migration of the water within the well casing.

The pore-water samplers were retrieved on January 4, 2007 and therefore were in the well for 20 days. After retrieving the pore-water samplers the well was purged, allowed to recover, and another grab sample was obtained from the well. The pore-water samplers and the grab sample were transported to the lab in a cooler and immediately analyzed.

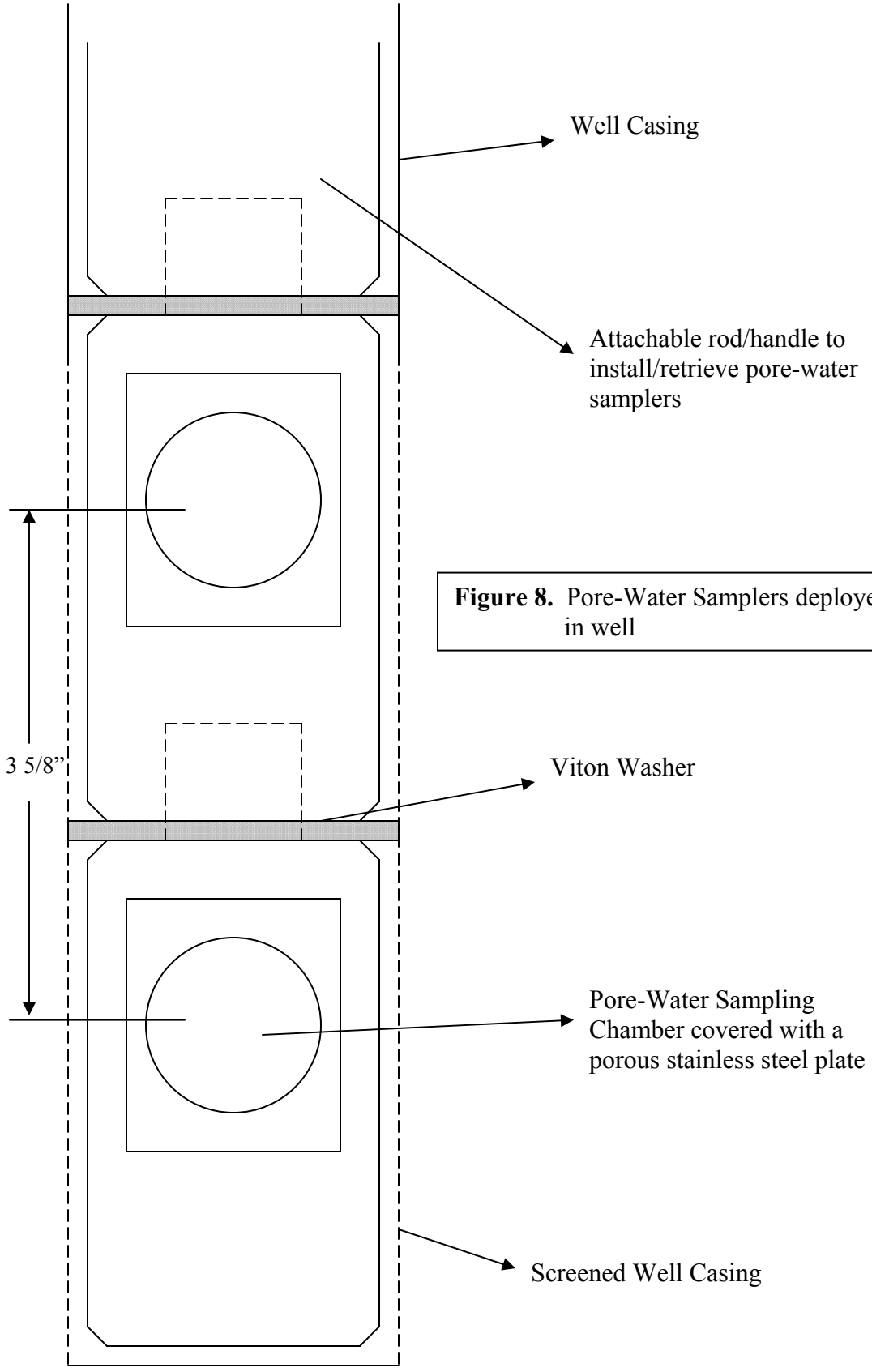


Figure 8. Pore-Water Samplers deployed in well

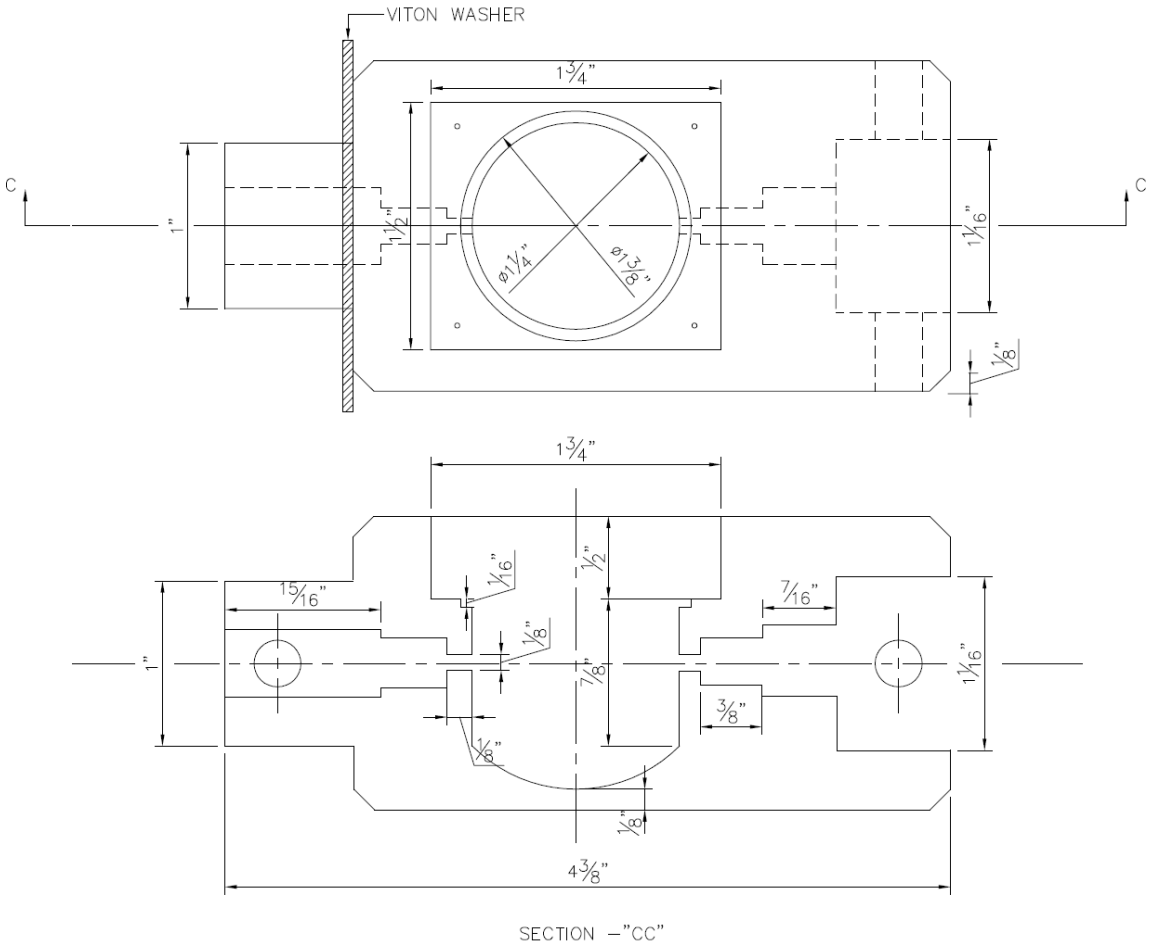


Figure 9. Pore-Water Sampler

Figure 9. Pore-Water Sampler (continued)

IV. Results and Discussion

This chapter presents the results of the sampling and laboratory analytical procedures described in Chapter III. A detailed analysis of the PCE contamination and its degradation products within the engineered wetland cell is presented in this chapter. This analysis will provide evidence of the wetland cell's ability to effectively treat chlorinated solvent contaminated groundwater as well as insight into the processes taking place in the wetland resulting in the degradation of the contamination. Where possible, the analytical results obtained from this research effort are compared to previous results compiled by past researchers of the WPAFB wetland cell. In addition, this chapter will present the results of the laboratory test and field deployment of the pore-water sampler prototype.

Chlorinated ethene contamination was found throughout the wetland cell. As discussed in Chapter III, the analytes for each collected sample were PCE, TCE, trans-DCE, cis-DCE, VC, ethylene, and ethane. The raw data, in a Microsoft Excel spreadsheet format, for each of the sampling points is provided in Appendix A. For the four month sampling period (September 2006 – December 2006), the analytical results show a significant reduction in PCE concentration as the water passes through the wetland cell. This is consistent with previous findings from earlier researchers.

Average Chlorinated Ethene Concentrations in the Wetland Cell

Figure 10(a-f), shown on the next three pages, presents a set of graphs showing average contaminant concentrations as the water passed through the wetland cell for each month of collected data. Data collected for this most recent research effort (Sep-Dec 2006) is shown with solid symbols and previous data collect (Dec 2001, Jan 2003,

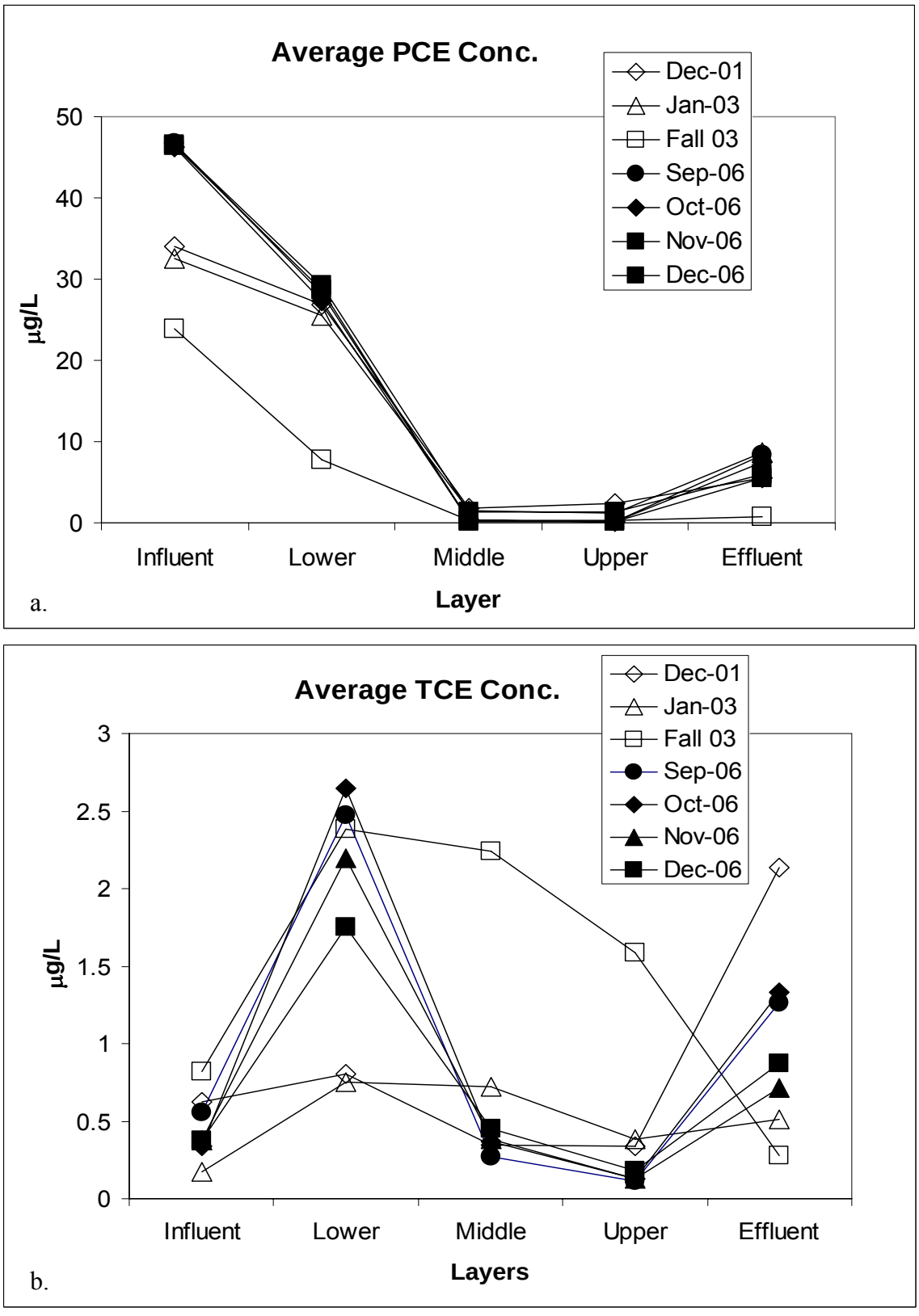
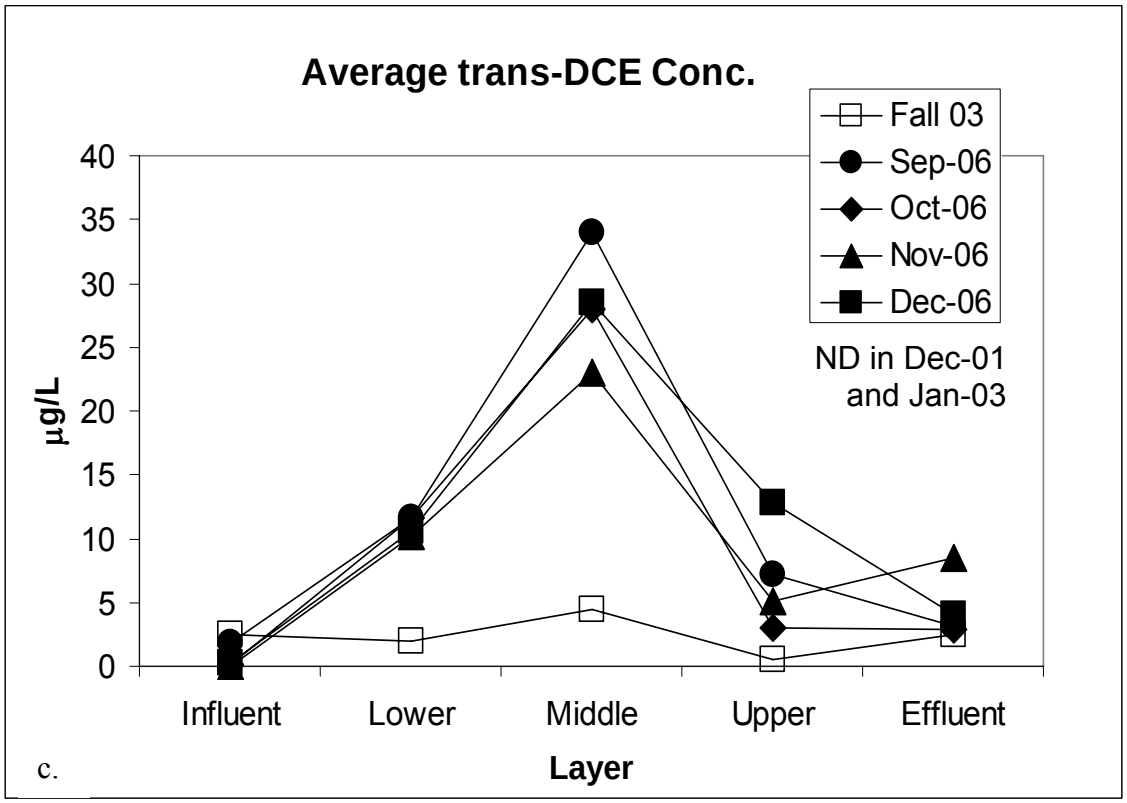


Figure 10 a. & b. Average PCE and TCE Contaminant Concentrations



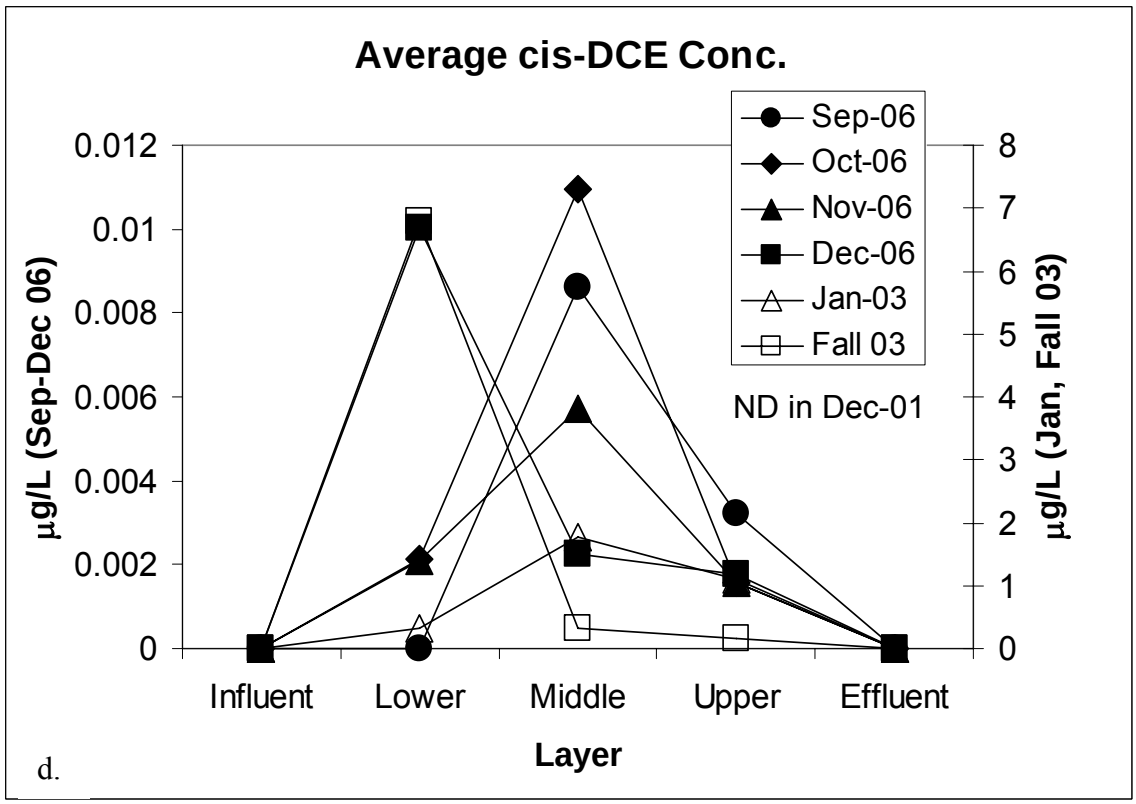
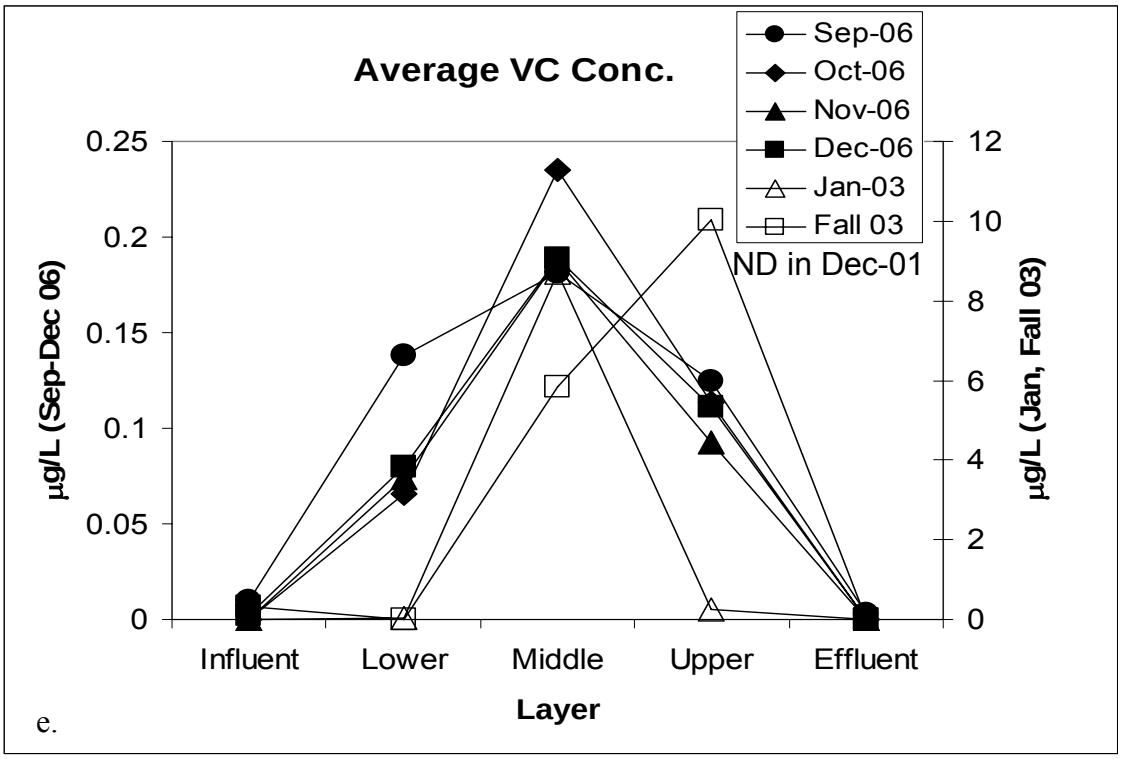
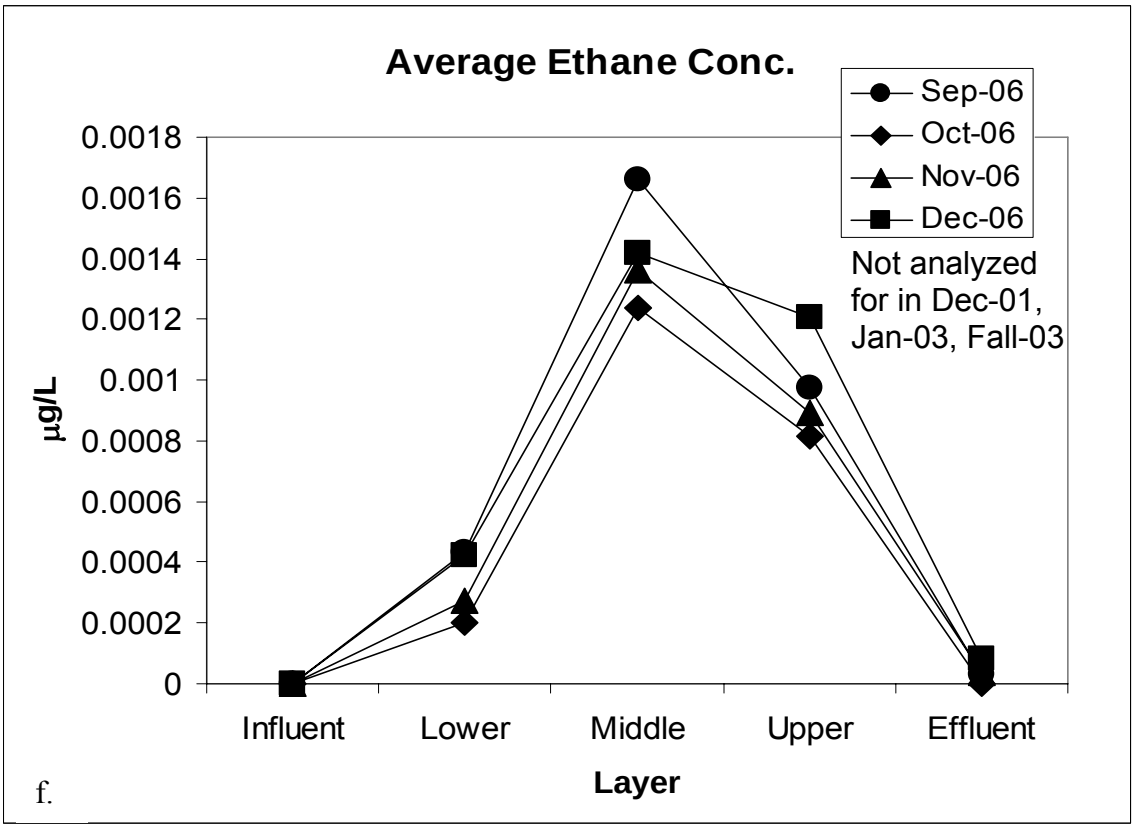


Figure 10 c. & d. Average trans-DCE and cis-DCE Concentrations



e.



f.

Figure 10 e. & f. Average VC and Ethane Concentrations

and Fall 2003) is shown with hollow symbols. Ethylene was not analyzed for in the previous research efforts and was not detected in any sample collected in this most recent research effort and therefore an ethylene graph is not presented in Figure 10. It should be noted that although measurements for ethane and cis-DCE concentrations were collected in the parts per trillion (ppt) range the reliability of those extremely small measurements is uncertain. An accurate method detection limit (MDL) could not be calculated with the available data. Regardless, the general trends represented in the ethane and cis-DCE graphs are still significant.

Figure 11 presents the average chlorinated ethene concentrations by wetland cell layer for the entire set of data collected from September through December 2006. The concentrations are presented in micro moles (μM) to allow for the tracking of the total number of chlorinated ethene moles as the water flows through the wetland. Since the ethane and cis-DCE concentrations were extremely small, they were not included on the graph but are included in the Total line shown on the graph. Figure 10 a. and 11 clearly show a significant decrease in the parent PCE contaminant as it passes through the wetland cell. Also evident from Figure 11 is the sequential accumulation of PCE daughter products taking place between the influent and middle layer of the wetland cell. With the decrease in PCE concentrations between the influent and lower layer there is a corresponding increase in the TCE concentrations over the same interval. As the TCE concentrations decrease between the lower and middle layers an increase in the DCE isomer concentrations as well as VC and ethane concentrations takes place. This sequential accumulation of PCE daughter products supports evidence of biological degradation processes, specifically anaerobic reductive dechlorination. Evidence of the

complete step wise dechlorination pathway from PCE to ethane supports the hypothesis that the lower half of the wetland cell offers favorable anaerobic environmental conditions such as pH and temperature, as well as sufficient quantities of dechlorinating microorganisms and organic material necessary for the complete anaerobic reductive dechlorination of PCE. In the upper half of the wetland cell the sequential degradation pattern is no longer evident; instead all contaminant levels are decreasing, suggesting degradation patterns other than reductive dechlorination.

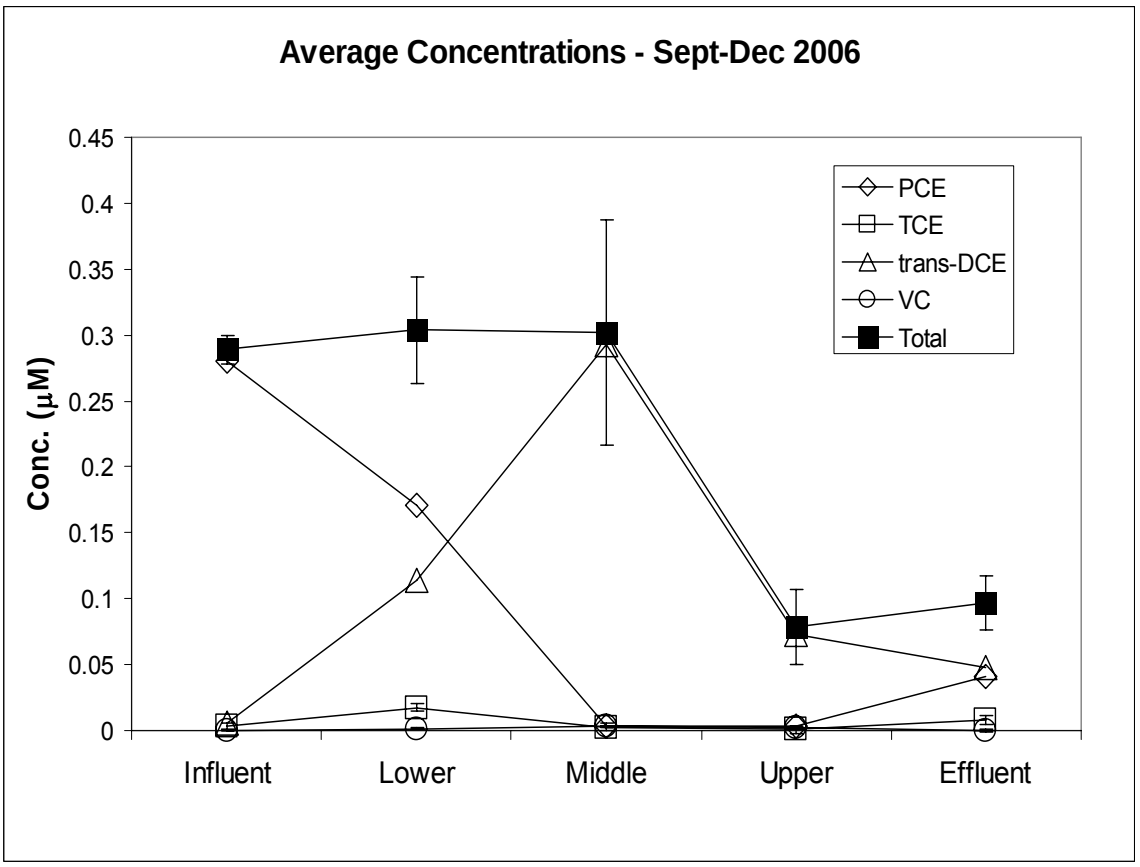


Figure 11. Average Chlorinated Ethene Concentrations

In Figure 11, although the Total chlorinated ethene concentration shown in the lower and middle layers are unrealistically greater than the influent Total concentration,

the differences are small. The Total average concentration in the lower layer was only 0.015 μM greater than the influent and the Total average concentration in the middle layer was only 0.013 μM greater than the influent. The 95% confidence interval error bars included on the Total line in Figure 11 show that the variance within the lower and middle layer could account for the Total concentration within these layers exceeding the original Total concentration in the influent.

As evident from the graphs in Figure 10 (a-f), there was little variation in average contaminant concentrations throughout the wetland cell from September 2006 through December 2006. The PCE concentrations observed throughout the four month period were extremely consistent, with the most variation observed in the effluent concentrations. The maximum monthly effluent average PCE concentration was 8.39 μg/L in September and the minimum was 5.49 μg/L in November. Variation from month to month in contaminant concentrations increased slightly for the lighter chlorinated ethenes. cis-DCE reflected the most varied concentrations from one month to another. This general observation of minimal variation leads to a general conclusion that the seasonal change from late summer to early winter for the year 2006 had a minimal effect on the overall capability of the wetland cell to treat the contaminated groundwater.

The graphs presented in Figure 10 are also presented in tabular format in Table 8. Table 8 presents the average concentration of each analyte for each layer of the cell and its particular confidence interval. Previous data collected in December 2001 (Opperman, 2002), January 2003 (Clemmer, 2003), and Fall 2003 (Sobolewski, 2004) is also included in Table 8 and allows for an easy comparison of the data over the five year period. Averages and confidence levels for the December 2001, January 2003, and Fall 2003 data

were computed with 66 samples from each wetland layer, whereas for the September, November, and December 2006 data the averages and confidence levels were computed from 22 samples, and only 11 samples where used for the October 2006 data. Therefore, since more data points where used for the December 2001, January 2003, and Fall 2003 data sets, their confidence intervals are smaller.

Significant changes were observed between the most recent data collect and the previous collect data. Influent PCE concentrations for the months of September 2006 through December 2006 have nearly doubled as compared to the average PCE influent concentrations observed in the Fall of 2003. After being below the MCL (i.e., 5 μg/L) in the Fall of 2003, the PCE effluent concentrations from September to December 2006 are now above the MCL and consistent with the concentrations found in Dec 2001 and Jan 2003 (5.5 to 8.6 μg/L). PCE was the only chlorinated ethene detected above its MCL in the effluent for the September through December 2006 sampling events.

Another observed difference between previously collected data and the most recent data is in regards to the TCE concentrations. The September-December 2006 data shows the TCE concentration rapidly increasing between the influent and lower layer and then rapidly decreasing between the lower and middle layers. Whereas for the Fall 2003 data the TCE concentration also rapidly increase between the influent and lower layer, but then more slowly, gradually declines through the middle and upper layers. This suggest that the environmental conditions within the bottom of the cell are ideal for the anaerobic dechlorination of the PCE to TCE, for both time periods, but that conditions have changed in the September-December 2006 period to allow the rapid decrease in the TCE concentrations between the lower and middle layers. The conditions may have

become more reducing favoring the rapid destruction of the TCE, or other TCE degradation pathways have developed.

After previously not being detected in Dec 2001 and Jan 2003, and then at low levels in the Fall 2003, trans-DCE concentrations increased significantly during this research effort. The accumulation of trans-DCE is maximized in the middle layer, following the accumulation of TCE in the lower level, and therefore represents the product of the reductive dechlorination of the TCE. This accumulation of trans-DCE over cis-DCE observed in the September through December 2006 data is contrary to published research which shows that cis-DCE is the dominant DCE isomer resulting from the reduction of TCE (Bouwer, 1994).

A final observation in the maturation of the wetland cell is in regards to the observed VC concentrations. The VC concentrations were significantly less in the September-December 2006 data set as compared to the January 2003 and Fall 2003 data sets. The maximum average concentration for the September-December 2006 data was 0.2 μg/L (middle layer) as compared to 8.7 μg/L (middle layer) and 10.0 pbb (upper layer), for the January 2003 and Fall 2003 data respectively. This change in VC concentration supports a change in the underlying degradation process of the wetland. The accumulation of VC is often a concern in the remediation of PCE contaminated groundwater, and therefore not experiencing a significant build-up of VC during this research effort is a significant highlight in the maturation of the wetland cell.

Table 8. Average Contaminant Concentrations

Average Concentrations (μg/L ± 95% Confidence Interval)						
		Influent	Lower	Middle	Upper	Effluent
PCE	Dec-01	33.97±0.92	26.82±0.38	1.79±0.17	2.42±0.56	5.59±0.62
	Jan-03	32.59±0.70	25.53±1.73	1.49±0.74	1.18±0.94	8.64±0.81
	Fall-03	23.93±1.14	7.79±1.78	0.29±0.38	0.29±0.42	0.80±0.49
	Sep-06	46.71±1.17	28.25±6.66	0.23±0.15	0.21±0.05	8.39±1.64
	Oct-06	46.33±0.35	27.32±8.48	0.25±0.16	0.16±0.06	7.47±1.71
	Nov-06	46.42±0.78	27.32±8.48	0.16±0.05	0.20±0.03	5.49±2.57
	Dec-06	46.49±0.27	29.25±5.86	1.37±1.54	1.41±1.16	6.03±0.57
TCE	Dec-01	0.63±0.19	0.81±0.03	0.35±0.03	0.34±0.34	2.14±2.18
	Jan-03	0.17±.0.01	0.75±0.19	0.72±0.27	0.38±0.19	0.51±0.04
	Fall-03	0.28±0.11	1.58±0.30	2.24±1.91	2.38±2.16	0.82±1.13
	Sep-06	0.56±0.22	2.48±0.67	0.27±0.25	0.11±0.05	1.26±0.11
	Oct-06	0.34±0.03	2.65±0.94	0.36±0.33	0.13±0.095	1.33±0.12
	Nov-06	0.37±0.08	2.19±0.65	0.38±0.28	0.13±0.07	0.71±0.04
	Dec-06	0.37±0.08	1.75±0.54	0.45±0.28	0.18±0.11	0.87±0.02
trans-DCE	Dec-01	ND	ND	ND	ND	ND
	Jan-03	ND	ND	ND	ND	ND
	Fall-03	2.44±2.70	1.98±0.66	4.47±0.53	0.48±0.32	2.44±2.70
	Sep-06	1.81±2.39	11.66±6.95	34.02±21.42	7.20±3.46	3.19±1.42
	Oct-06	0.11±0.22	11.62±8.23	28.0±22.06	3.05±2.02	2.85±0.48
	Nov-06	ND	10.26±6.52	22.94±11.36	5.04±2.27	8.51±5.5
	Dec-06	0.19±0.39	10.58±6.63	28.51±12.75	12.88±8.10	4.05±1.68
cis-DCE	Dec-01	ND	ND	ND	ND	ND
	Jan-03	ND	0.311±0.275	1.770±0.724	1.105±0.585	ND
	Fall-03	ND	6.780±1.716	0.330±0.322	0.150±0.211	ND
	Sep-06	ND	ND	0.009±0.005	0.003±0.004	ND
	Oct-06	ND	0.002±0.004	0.01±0.006	0.002±0.002	ND
	Nov-06	ND	0.002±0.004	0.006±0.004	0.002±0.002	ND
	Dec-06	ND	0.01±0.02	0.002±.003	0.0018±0.0019	ND
VC	Dec-01	ND	ND	ND	ND	ND
	Jan-03	ND	0.02±.002	8.70±6.69	0.26±0.13	ND
	Fall-03	0.31±0.61	ND	5.85±3.09	10.03±9.54	ND
	Sep-06	0.01±0.02	0.14±0.09	0.18±0.07	0.12±0.059	0.003±0.006
	Oct-06	ND	0.07±0.06	0.24±0.16	0.11±0.09	ND
	Nov-06	ND	0.07±0.06	0.19±0.09	0.09±0.04	ND
	Dec-06	0.002±0.004	0.08±0.07	0.19±0.08	0.11±0.05	ND
Ethane	Dec-01	NA	NA	NA	NA	NA
	Jan-03	NA	NA	NA	NA	NA
	Fall-03	NA	NA	NA	NA	NA
	Sep-06	ND	0.0004±0.0004	0.002±0.0006	0.001±0.0002	0.00003±0.00006
	Oct-06	ND	0.0002±0.0003	0.001±0.0005	0.0008±0.0002	ND
	Nov-06	ND	0.0003±0.0003	0.001±0.0004	0.0009±0.0003	0.00004±0.00007
	Dec-06	ND	0.0004±0.0005	0.001±0.0004	0.0012±0.0003	0.00008±0.00006

In the remainder of this chapter a more detailed analysis of the results is presented. The analysis is presented in an order that follows the flow of the contaminated water through the wetland cell. First, the influent results are presented and discussed, followed by the lower layer, middle, layer, upper layer, and finally the effluent. Then, looking at the system as a whole, data is presented and discussed identifying where in the wetland cell the majority of the remediation is taking place. Finally, the chapter concludes with an analysis of the results obtained from the development of the pore-water samplers.

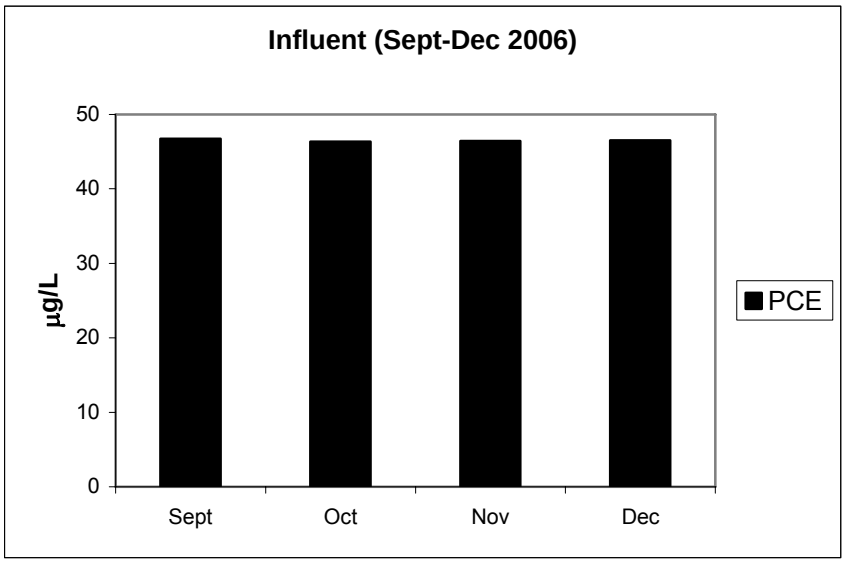
Monthly Variation in Chlorinated Ethene Concentrations by Wetland Layer

Influent

As previously mentioned, the influent concentration of PCE detected from September to December 2006 was extremely consistent; concentrations ranged from a maximum average of 46.7 μg/L in September to a minimum average of 46.3 μg/L in October. As also addressed above, the influent PCE concentrations were significantly higher than those detected in the Fall of 2003. The average PCE influent concentration for the months September through December 2006 (46.5 μg/L) represents a 94.6% increase from the Fall 2003 PCE influent concentrations (23.9 μg/L). This drastic increase will make comparisons of subsequent wetland cell results between the Fall 2003 data and current 2006 data difficult, given the difference in starting PCE concentrations. The PCE influent concentrations for Dec 01 (33.9 μg/L) and Jan 03 (32.6 μg/L) are more consistent with the 2006 data.

From the observed influent concentrations, there is minimal evidence of any natural PCE degradation taking place in the underlying aquifer. Few daughter products of PCE degradation were detected in the influent. Small amounts of TCE were detected in the influent (monthly averages ranging from 0.37 μg/L to 0.56 μg/L) possibly representing small releases of TCE product into the groundwater, or small amounts of PCE being reduced to TCE. Sporadic detections at very low levels of trans-DCE and VC where also observed in the influent. No cis-DCE or ethane was observed in the influent. Typical of most PCE contaminated aquifers, the underlying PCE contaminated groundwater sourcing the wetland test cell does not appear to provide the favorable anaerobic reducing conditions for the degradation of the PCE. Figure 12 provides a summary of the influent concentrations for the September-December 2006 data.

Of particular note regarding the influent concentrations are the slight variations between the September 2006 and October through December 2006 data. The September influent TCE concentrations were approximately 35% higher as compared to the October through December 2006 influent data. Also the trans-DCE influent concentration in October through December 2006 was approximately 95% lower compared to the September data. Although, as previously mentioned, any natural degradation of the PCE taking place in the aquifer was minimal; the decrease in temperature after September could have also limited any natural biodegradation processes (Whitkamp and Frank, 1969) and thus resulting in the lower TCE and DCE concentrations.



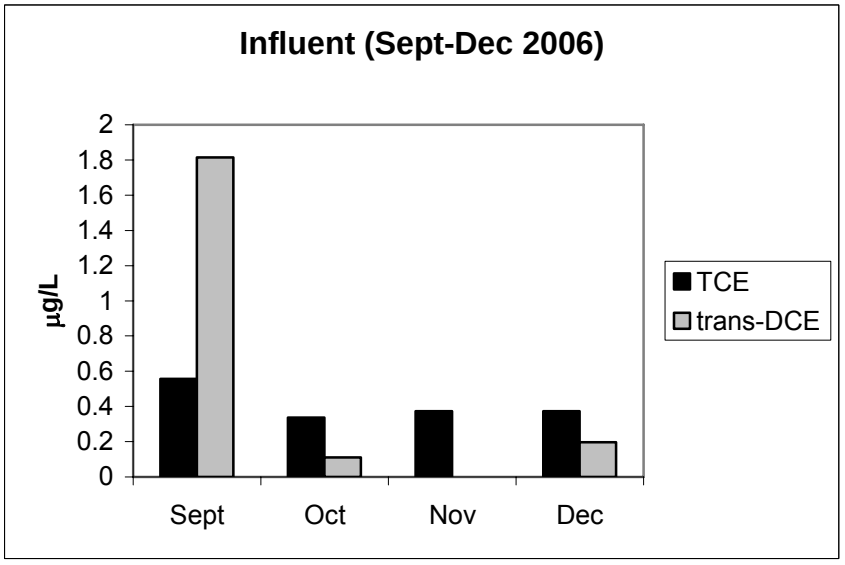
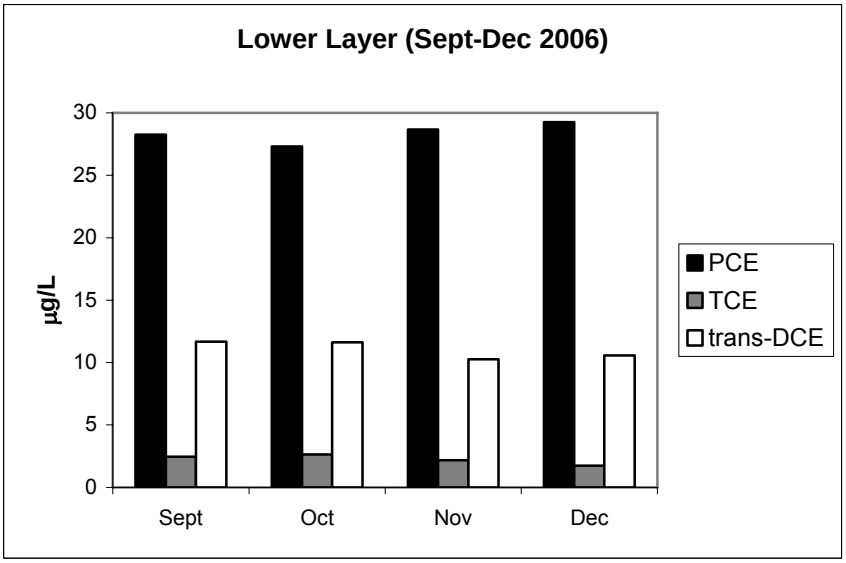


Figure 12. Average Monthly Influent Concentrations

Lower Layer of Wetland Cell

In the lower layer of the wetland cell significant changes in contaminant levels are observed. Figure 13 provides a summary of the concentrations detected in the lower



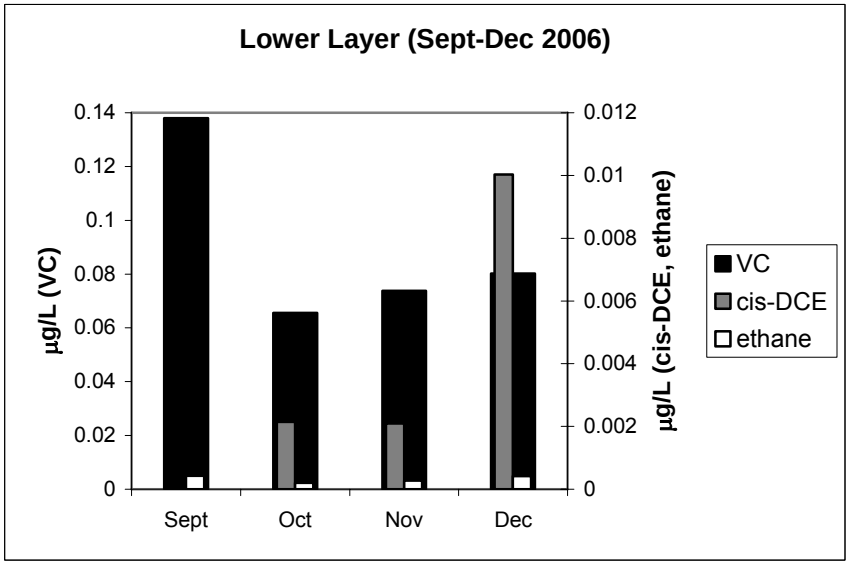


Figure 13. Average Monthly Lower Layer Concentrations

layer of the wetland cell form September through December 2006. As the PCE concentrations drop the TCE concentrations are increasing, as compared to their influent concentrations. For September through December 2006 the average monthly PCE concentration decreased from 46.5 µg/L in the influent to 28.4 µg/L in the lower layer

(39% decrease) while the average TCE concentrations increased from 0.4 μg/L to 2.3 μg/L (475% increase). A significant increase is also observed in the trans-DCE concentration from the influent to the lower layer concentrations. trans-DCE went from a monthly average concentration of 0.5 μg/L in the influent to 11.0 μg/L in the lower layer (2100% increase). The concentration of VC also increased by 2900% in the lower layer of the wetland cell, from a monthly September to December average of 0.003 μg/L in the influent to 0.09 μg/L in the lower layer. In addition, cis-DCE and ethane, which were not detected in the influent, were detected at low levels in the lower layer, 0.004 μg/L and 0.0003 μg/L monthly averages, respectively.

The decrease in PCE concentration and detection of PCE daughter products in the lower layer provides evidence of reductive dechlorination processes taking place in the lower part of the wetland cell. The decrease in PCE concentrations and increase in TCE and trans-DCE concentrations in the lower layer, suggest that the reducing conditions are favorable for the reduction of PCE to DCE. The anaerobic reduction of the highly chlorinated chemicals of PCE and TCE requires only nitrate or Fe(III) reducing conditions (Vogel et al., 1987). As shown through the inorganic wetland cell data, collected by Yussuf Mohamud, nitrates are being readily reduced to nitrites while the sulfate concentrations are remaining relatively constant between the influent and lower layer of the wetland cell. Any available dissolved oxygen has been consumed and microorganisms are utilizing nitrates as terminal electron acceptors for their energy and growth. PCE and TCE compete well with the nitrates as an electron acceptor under these conditions (Vogel et al., 1987) and the PCE is therefore being reduced to TCE and then

the TCE is being reduced to trans-DCE. The accumulation of TCE in the lower layer suggests that the dechlorinating microorganisms may preferentially degrade PCE to the exclusion of TCE because they gain more energy from dechlorination of the more highly chlorinated PCE. Thus, the dechlorination of TCE may not proceed until the PCE has been depleted. However, as previously mentioned, there are other PCE intermediates present in the lower level including cis-DCE, VC, and ethane. The presence of ethane provides evidence of the complete anaerobic dechlorination of the PCE, thus suggesting a consortium of bacteria within the wetland cell promoting the complete dechlorination of the PCE even at the lower level (Bradley, 2000).

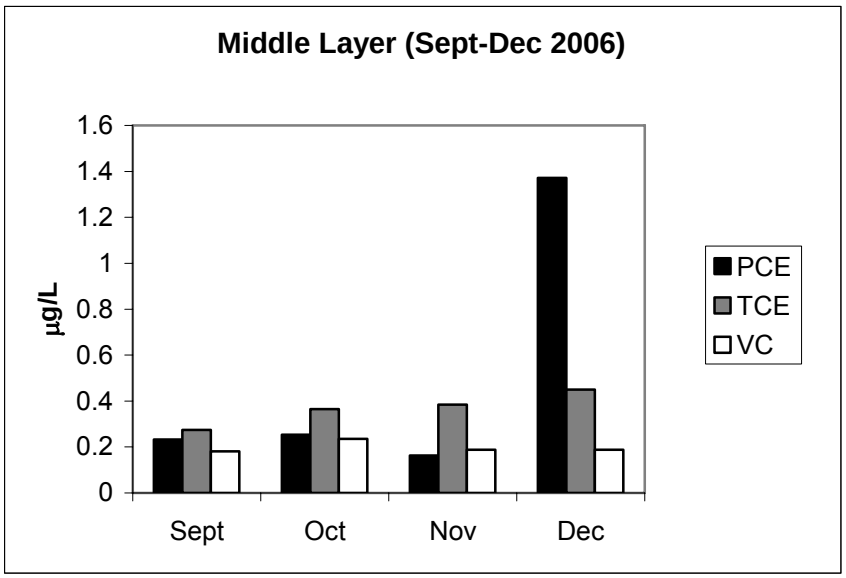
Variation from month to month, between September and December 2006, in the lower layer was minimal. Most notable variations from month to month in lower layer are the TCE and cis-DCE concentrations. The average December TCE concentration in the lower layer was 31% lower than the average September and October TCE concentrations and 25% lower than the average November TCE concentrations. The colder temperatures (See Appendix C), experienced after the November sampling round, may be a contributor to a decrease in microbial activity and therefore a slower degradation rate in the reduction of PCE to TCE (Parsons, 2004). The average December cis-DCE concentration was 5 times greater than the average October and November cis-DCE concentrations and no cis-DCE was detected in September. A cold resistant bacteria strain may possibly be responsible for this increase in cis-DCE concentrations in December. The bacteria responsible for the reduction of the TCE to cis-DCE in December could be more resistant to the cold than other bacteria. These cold resistant

bacteria, which may not compete well in the warmer months, are able to out-compete the other bacteria in the colder temperatures.

Middle Layer of Wetland Cell

In the middle layer of the wetland cell we continue to see changes in chlorinated ethene concentrations, suggesting the sequential dechlorination of PCE. Figure 14 provides a summary of the concentrations found in the middle layer for the September through December 2006 data.

For the data collected between September and December 2006 the average monthly PCE concentration decreased by 98% from the lower layer to the middle layer of the wetland cell, from 28.4 μg/L to 0.51 μg/L. Also, the TCE concentrations have decreased in the middle layer following its increase between the influent and lower layer. The TCE concentrations decreased by 83% between the lower and middle layer, decreasing from a monthly average of 2.3 μg/L in the lower layer to a monthly average of 0.4 μg/L in the middle layer. The trans-DCE concentrations increased significantly in the middle layer of the wetland cell. The average monthly trans-DCE concentration in the lower layer was 11.0 μg/L as compared to 28.4 μg/L in the middle layer, a 158% increase. VC concentrations peak in the middle layer at 0.2 μg/L, a 122% increase over the VC concentrations in the lower layer. cis-DCE and ethane concentrations also peaked in the middle layer, although at very low concentrations. cis-DCE increased from 0.004 μg/L in the lower layer to 0.007 μg/L in the middle layer, and ethane concentrations increased from 0.0003 μg/L in the lower layer to 0.001 μg/L in the middle layer.



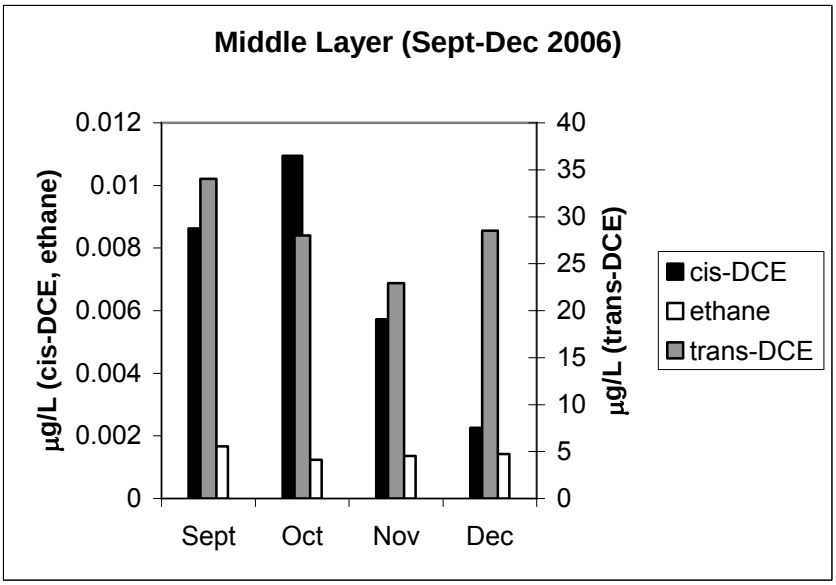


Figure 14. Average Monthly Middle Layer Concentrations

Between the lower and middle layers we continue to see a decline in the PCE concentrations, almost to its complete elimination, as well as a decline in TCE concentrations. As the amount of PCE available to act as an electron acceptor decreases, TCE becomes a favorable electron acceptor and therefore is reduced to DCE. This results in a reduction in the TCE that was accumulated in the lower layer and a

subsequent accumulation of trans-DCE in the middle layer. The middle layer of the wetland cell is where the highest concentrations of trans- and cis-DCE are found. As shown by Yussuf Mohamud's data, the conditions of the wetland cell become more reducing between the lower and middle layer. Along with the continued decline in nitrates, Mohamud also shows a significant increase in ferrous iron concentrations, as well as a significant decrease in sulfates, between the lower and middle layers. Thus it appears that nitrates and ferric iron have been depleted and sulfates are now being utilized as electron acceptors. In these increased sulfate reducing conditions, DCE becomes more readily reduced to VC. This therefore, helps explain the significant increase in VC concentrations between the lower and middle layer.

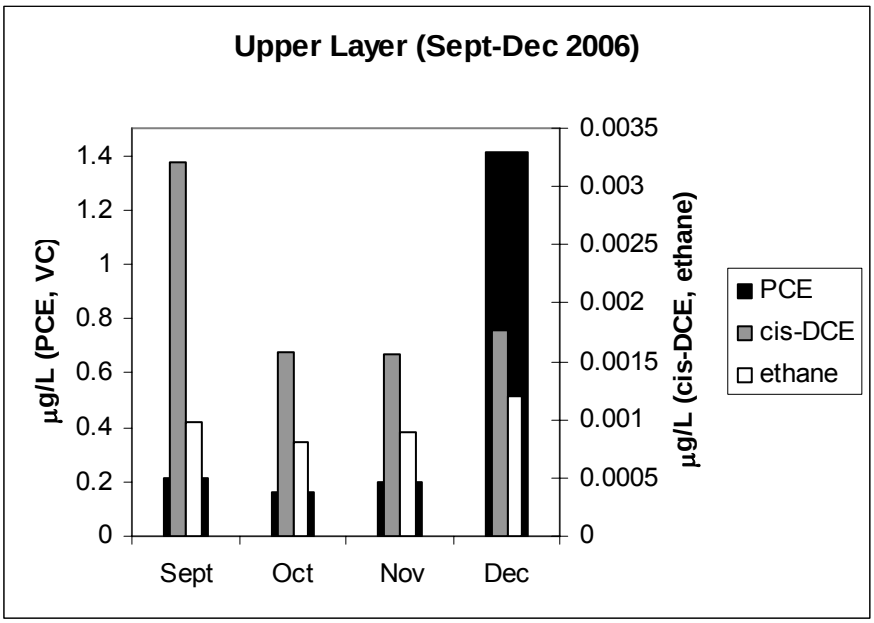
As the tendency for chlorinated ethenes to be reduced decreases, as the number of chlorine atoms decreases in the molecule, the tendency to undergo oxidation increases. Therefore, DCE and VC have the greatest potential to undergo oxidation. Although sulfate reducing conditions may be sufficient for the anaerobic reduction of DCE and VC to ethylene and eventually to ethane, oxidation of DCE and VC may represent another pathway for the degradation of these chlorinated ethenes in the wetland. The increase in VC and ethane concentrations in the middle layer, although at very low concentrations, identifies the end products of the complete stepwise anaerobic reduction of the parent PCE. However, the low concentrations of VC and ethane possibly suggest that the DCE and VC are being degraded by other than anaerobic reduction. Alternatively, the VC may be undergoing anaerobic reduction but it is occurring so rapidly that it is not accumulating at significant concentrations. The introduction of oxygen through the rhizospheres of the plant material could be contributing to the aerobic oxidation of the

DCE and VC. In addition, VC, and to a lesser extent DCE, could be oxidized to carbon dioxide under the anaerobic Fe(III)-reducing conditions (Bradley and Chapelle, 1996 and 1997). Bradley and Chapelle's results indicated that vinyl chloride can be mineralized under anaerobic, Fe(III)-reducing conditions, and that the bioavailability of Fe(III) is an important factor affecting the rates of mineralization. Thus, between the lower and middle layer it appears that anaerobic reductive dechlorination of PCE to TCE and from TCE to DCE is taking place. Also, the presence of VC and ethane in the middle layer provides evidence of the complete stepwise reduction of the parent PCE compound. However, given the small quantities of VC and ethane present other pathways, including aerobic and anaerobic, oxidation of the DCE and VC may be taking place.

Of particular note, in regards to monthly variations in the middle layer, is the higher PCE concentrations detected in December as compared to the previous months. The average PCE concentration in the middle layer in December was 1.37 μg/L as compared with 0.23 μg/L in September, 0.25 μg/L in October, and 0.16 μg/L in November (0.21 μg/L avg – 552% increase). December marked a sharp decrease in the temperature of the water in the various layer of the wetland cell (See Appendix C), perhaps surpassing a threshold temperature for a particular microbial strain. The average temperature of the middle layer water during December was 7.9 deg C, as compared with 19.6 deg C in September, 19.0 deg C in October, and 13.9 deg C November. This lower temperature likely resulted in decreased microbial activity and therefore reduced the degradation rate of the PCE (Parsons, 2004).

Upper Layer of Wetland Cell

Figure 15 provides a summary of the concentrations detected in the upper layer of the wetland cell for the data collected between September and December 2006. The average monthly PCE concentration decreased by only 2% between the middle and



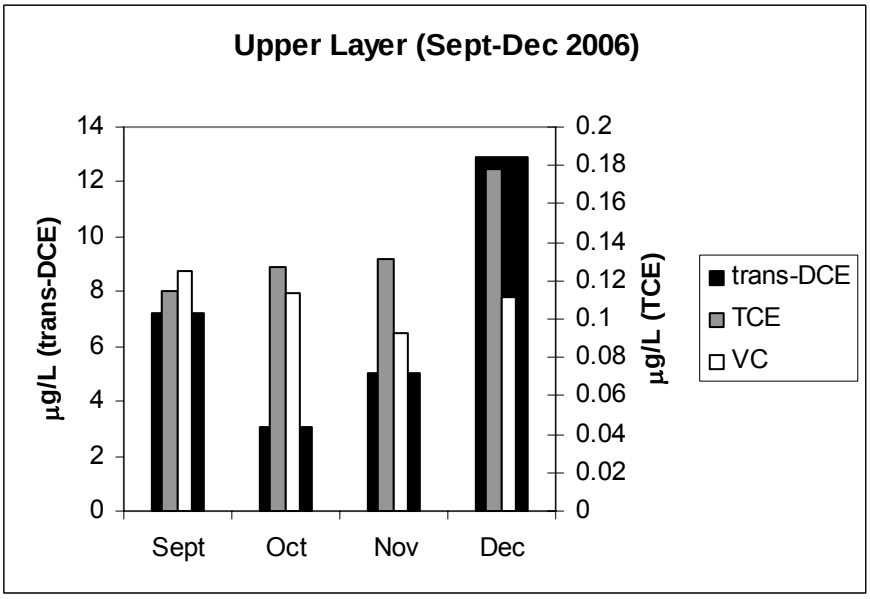


Figure 15. Average Monthly Upper Layer Concentrations

upper layer, from 0.51 μg/L in the middle layer to 0.50 μg/L in the upper layer. Compared to the average PCE influent concentrations, the average 0.50 μg/L found in the upper layer represents an overall 98.9% reduction in the PCE levels. Due to a high root density, promoting the influx of oxygen, and proximity to the open atmosphere, the upper layer is more likely to be aerobic. PCE cannot degrade aerobically and therefore we see very little reduction in the PCE concentrations in the upper layer.

The other lighter chlorinated ethenes experience more significant reductions between the middle and upper layer. TCE concentrations were reduced by 63% from 0.37 μg/L in the middle layer to 0.14 μg/L in the upper layer. The trans-DCE concentrations sharply decreased from 28.4 μg/L in the middle layer to 7.0 μg/L in the upper layer, a 75% reduction. cis-DCE concentrations remained at very low levels in the upper layer, but are now decreasing after peaking in the middle layer. cis-DCE concentrations decreased from 0.007 μg/L in the middle layer to 0.002 in the upper layer, a 71% reduction. The VC concentrations also start to decrease between the middle and upper layers decreasing by 44%, from 0.20 μg/L in the middle layer to 0.11 in the upper layer. These lighter less chlorinated ethenes are more likely being degraded through aerobic oxidation or aerobic cometabolism, given the likely aerobic conditions of the upper layer. Ethane concentrations also show their first decline in the upper layer, from 0.00142 μg/L in the middle layer to 0.00097 μg/L, a 32% reduction. Since there is not a subsequent accumulation of DCE following the sharp decrease in TCE concentrations, as well as no accumulation of VC or ethane, this also supports the hypothesis of aerobic oxidation or aerobic cometabolism taking place in the upper layer.

Of particular note again, in regards to monthly variations in the upper layer, is the higher PCE concentrations detected in December as compared to the previous months. The average PCE concentration in the upper layer in December was 1.41 μg/L as compared with 0.21 μg/L in September, 0.16 μg/L in October, and 0.20 μg/L in November (0.19 μg/L average – 642% increase). December marked a sharp decrease in the temperature of the water in the various layer of the wetland cell (See Appendix C). The average temperature of the upper layer water during December was 6.8 deg C, as compared with 20.0 deg C in September, 18.8 deg C in October, and 13.6 deg C November (See Appendix C for temperature data). This lower temperature likely resulted in decreased microbial activity and therefore reduced the degradation rate of the PCE (Parsons, 2004).

Effluent

Concentrations monitored at the outlet weir from September through December 2006 provided insight into the overall physical flow of water through the cell. At the outlet, the average monthly PCE concentration for the months of September through December 2006 was 6.8 μg/L, approximately 1300% higher than the concentrations measured in the upper layer of the wetland cell (0.50 μg/L). This 6.8 μg/L PCE concentration also represents an overall 85.4% reduction compared to the average PCE influent concentration. TCE concentrations were 660% higher in the effluent as compared to the concentrations detected in the upper layer; the TCE concentrations increased from 0.14 μg/L in the upper layer to 1.0 μg/L in the effluent. These significantly higher concentrations in the effluent, as compared to the upper layer, provide evidence that a

portion of the contaminated water being injected into the wetland cell is not being treated. Contaminated water must be by-passing or short circuiting the wetland system. A portion of the injected contaminated water is not receiving the residence time within the wetland cell to be effectively treated. Due to variations in the influent distribution lines or through the establishment of preferential pathways, portions of the injected water is rising too rapidly in the system and is not being treated.

cis-DCE was not detected in the effluent during any of the months. A very low (0.003 μg/L) detection of VC was observed in the effluent, occurring during the month of September, and no other detections of VC were observed in the effluent. Extremely low concentrations (order of 10^{-5} μg/L) of ethane were detected in September, November, and December, no detections in October. At the surface of the wetland, where these effluent samples are collected just prior to the water exiting over the effluent weir, there is a highly interactive zone between the wetland surface and atmosphere. At this interface, oxygen from the atmosphere is entering the surface waters of the wetland. Here the less chlorinated/reduced ethenes are more likely to be aerobically oxidized, and thus supports the absence of cis-DCE, VC, and ethane in the effluent. Figure 16 provides a summary of the concentrations detected in the effluent of the wetland cell for the data collected between September and December 2006.

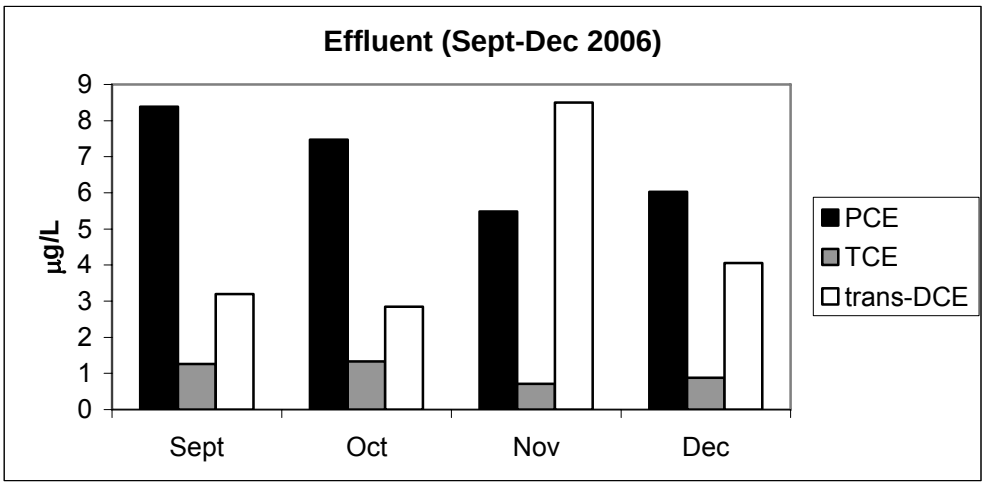
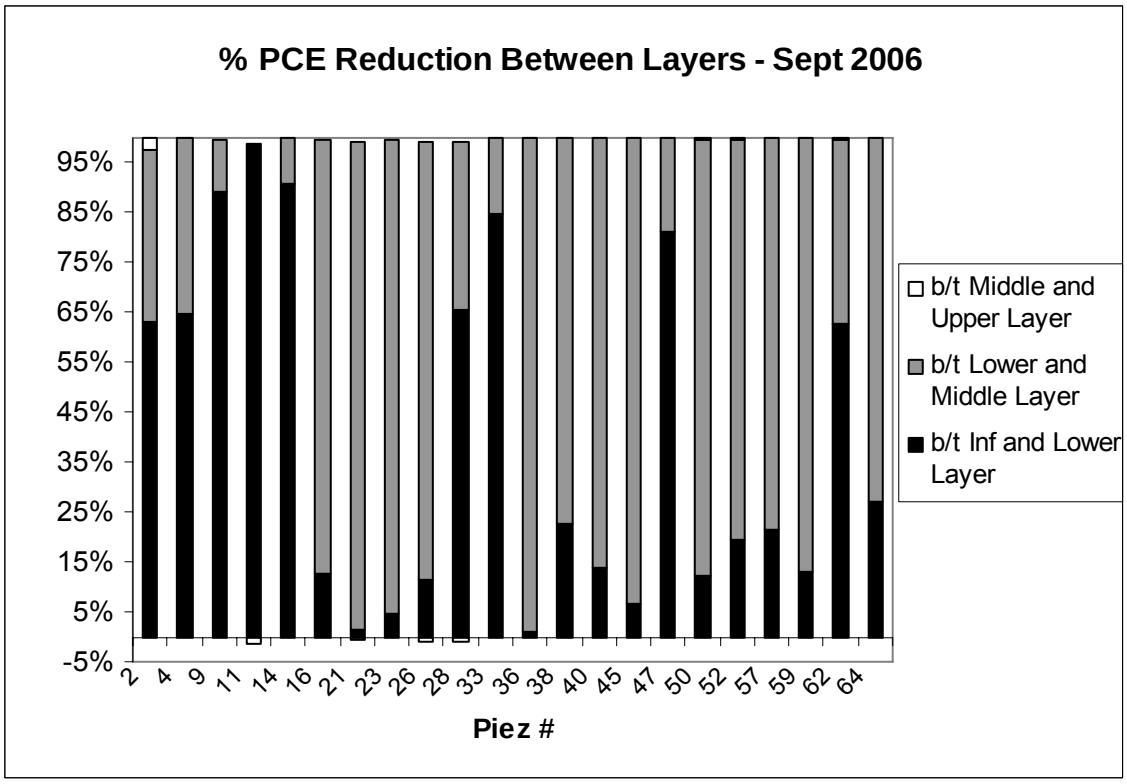


Figure 16. Average Monthly Effluent Concentrations

Overall Chlorinated Ethene degradation within the Wetland Cell

In this section, the data will be presented to evaluate where in the wetland cell the parent PCE contamination is being degraded. Figure 17 presents a set of graphs showing the percent reduction in PCE concentrations occurring between the various stages of water flow in wetland cell (i.e., between the influent and lower layer, between the lower layer and middle layer, and between the middle layer and upper layer). The data is presented on a monthly basis for each piezometer sampled. As shown in the graphs, the PCE is almost completely destroyed within each piezometer set. The average reduction in PCE concentrations, comparing the influent PCE concentrations to the upper layer PCE concentrations for all piezometers over the four month sampling period was 98.9%. The majority of the PCE reduction took place either between the influent and lower layer or between the lower layer and the middle layer, as shown in Figure 17. There was at least a 97% PCE reduction through the middle layer of each piezometer except for



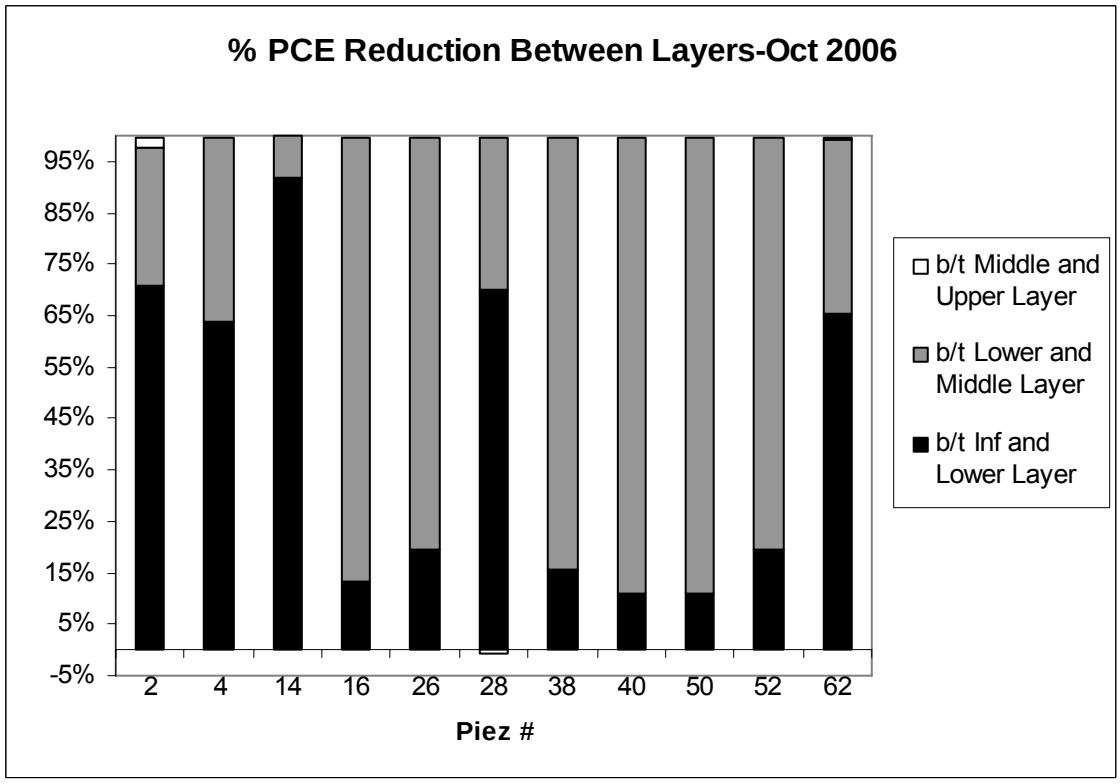
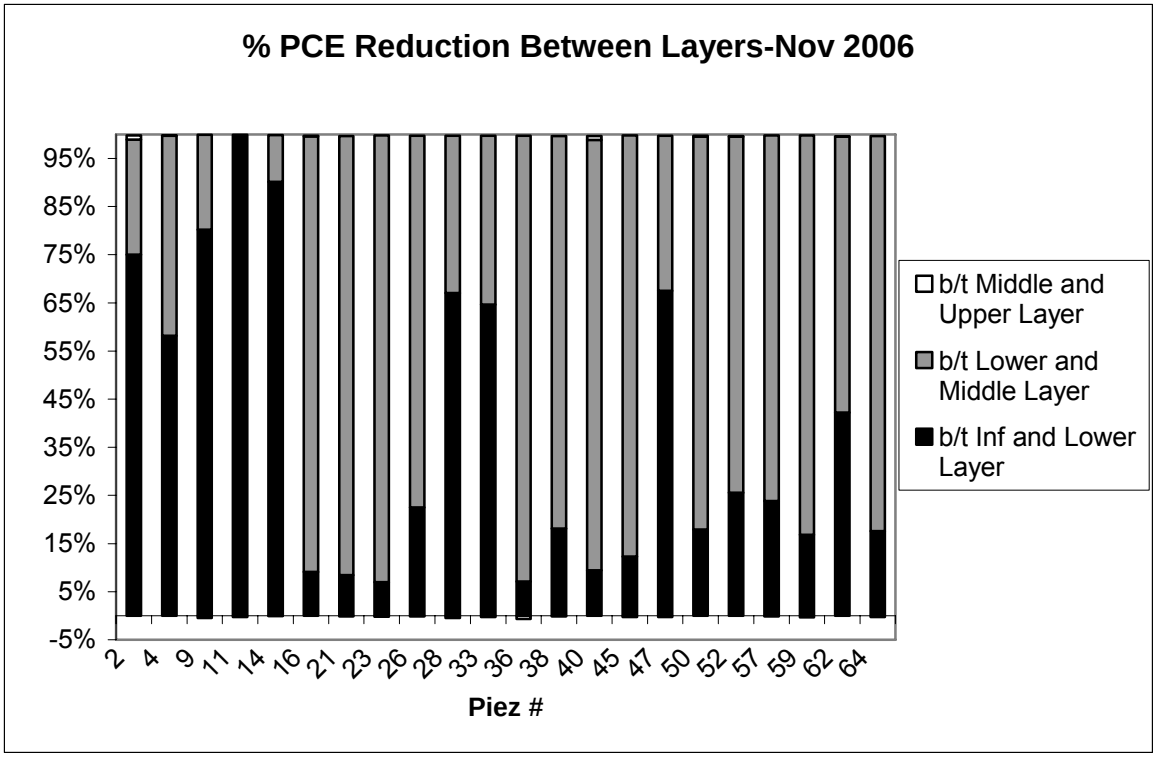


Figure 17. Percent Reduction in PCE Concentration Between Layers



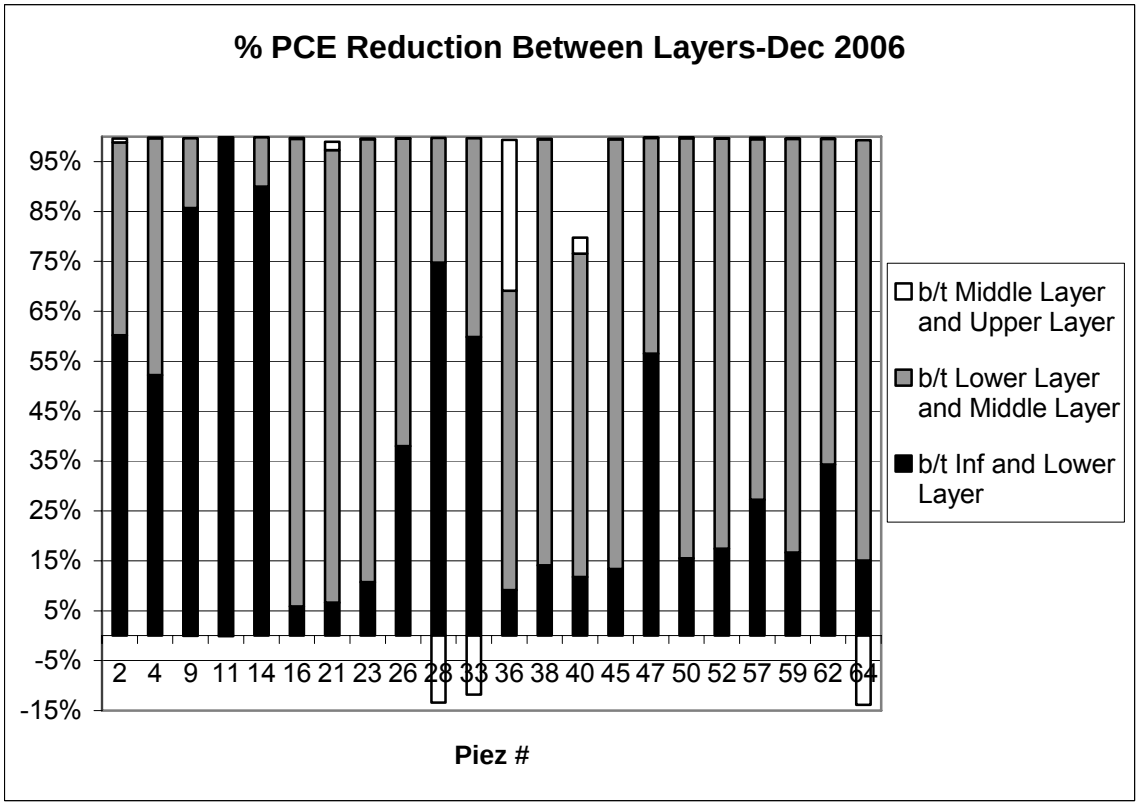


Figure 17. Percent Reduction in PCE Concentration Between Layers (continued)

piezometer nest #2 during September and piezometer nest's 36 and 40 in December. The small amount of PCE remaining in the middle layer did not degrade any further between the middle and upper layers, and in some instances the PCE concentration increased (represented by a negative percentage in Figure 17) between the middle and upper layer (e.g., piezometer nest's 28, 33, and 64 in December). These increases in PCE concentration between the middle and upper layers could be due to the preferential pathways within the wetland cell where the injected water is directly migrating to the top of the wetland cell without the required residence time for treatment. In addition, during the month of December a thin film of ice covering the wetland in some areas may have prevented the natural volatization of PCE from the surface and thus resulted in anincrease in PCE concentrations in the upper layer.

From month to month (Sept-Dec 2006) there was little variation in the amount of PCE degraded in each layer of the wetland cell within in each piezometer nest. Consistently, from month to month relatively the same amount of PCE was being degraded in each layer within each piezometer nest. The most variation occurred in piezometer nest #s 36 and 40. In piezometer nest #36 the percentage of PCE being reduced between the lower layer and middle layer decreased from 96% in September, 93% in November to only 60% in December. And in piezometer nest #40 the percentage of PCE being reduced between the lower and middle layer decreased from 86% in September, 89% in October and November to only 64% in December. These decreases in the amount of PCE being reduced in the middle layer again could be attributed to the lower temperatures and thin layer of ice present during the December sampling round.

Based upon a four month average, Figure 18 depicts the piezometer nests where greater than 60% of the PCE degradation takes place between the influent and lower layer (solid black circles) and those where more than 72% of the degradation takes place between the lower layer and middle layer (concentric circles). The four month average for piezometer nest #62 represented a 51% PCE reduction between the influent and lower layer and a 48% PCE reduction between the lower layer and the middle layer and is therefore not highlighted in Figure 18. The end of the wetland cell opposite of the outlet weir shows an area where the bulk of the PCE degradation takes place between the influent and lower layer. However, the half of the wetland cell towards the outlet weir is an area where the majority of the PCE degradation takes place between the lower and middle layer. The area where the bulk of the PCE degradation takes place between the influent and lower layer is also an area where the amount of standing water is greater than other areas of the wetland cell. The standing water may create favorably increasing anaerobic reducing conditions, therefore promoting the degradation of the PCE at greater depths. In addition, the various wetland vegetation found throughout the wetland cell, with their various root depths, may also impact where the majority of the PCE reduction takes place.

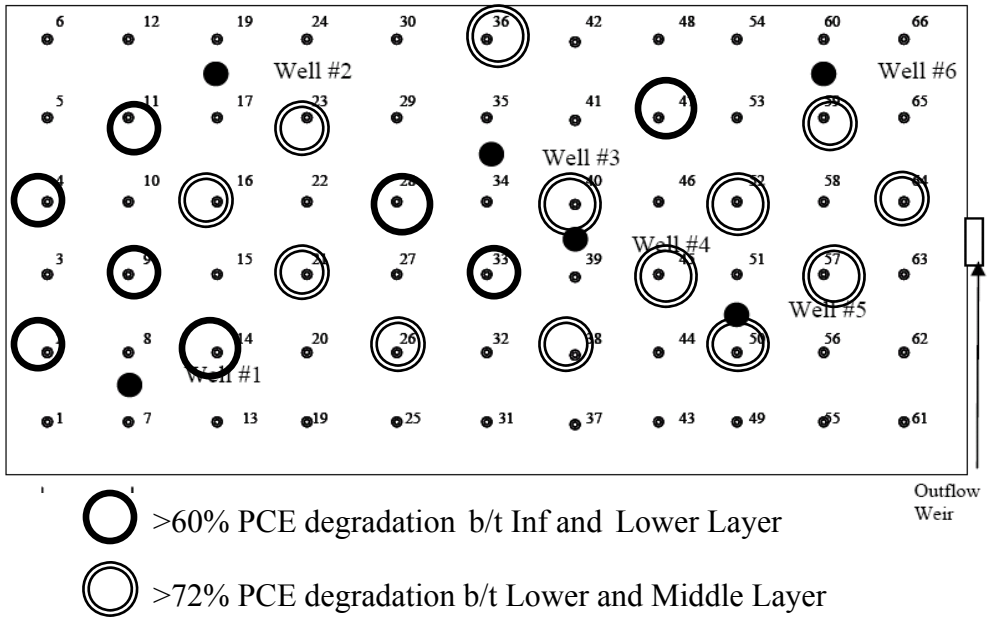


Figure 18. PCE Reduction within the Wetland Cell

Pore-Water Sampler Results

Laboratory Testing

The laboratory test to evaluate the diffusion rate through the 5 micrometer porous membrane of the pore-water sampler prototype provided some useful information. As explained in Chapter 3, eight (8) pore-water samplers were placed in an aqueous salt solution of calcium sulfate ($CaSO_4$), magnesium chloride ($MgCl_2$), sodium sulfate (Na_2SO_4), and potassium nitrate (KNO_3). Two pore-water samplers, as well as two samples taken from the bath solution, were removed after 1, 3, 9, and 30 days. The water from the pore-water samplers' cavity and the samples of the bath solution were analyzed for the various cations using an ion chromatograph. Figure 19 presents the results of the laboratory test. Figure 19 shows the percentage of the cation concentrations found in the pore-water samplers as compared to the surrounding test solution.

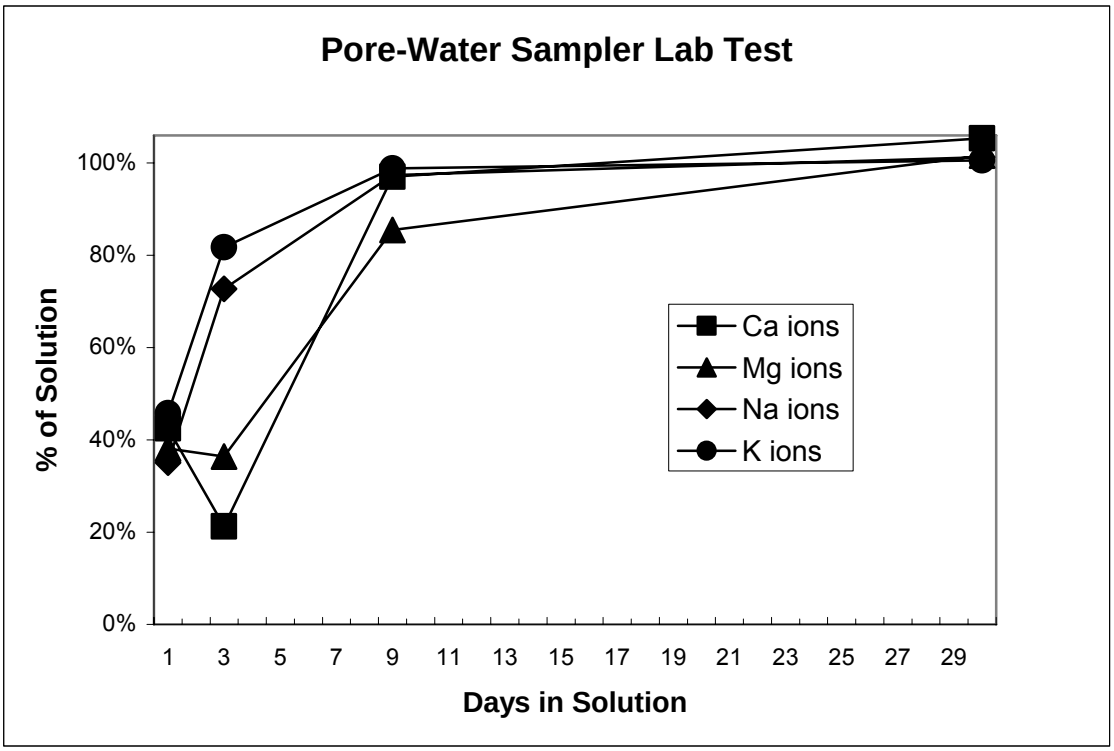


Figure 19. Pore-Water Sampler Lab Test Results

After 9 days the concentration of the Ca, Na, and K cations found in the pore-water samplers were at least 97% of the concentration found in the surrounding solution, whereas the concentration of the Mg cations in the pore-water samplers was only at 85%. From an interpolation of the graph, the concentration of Ca, Na, and K cations within the samplers reached 100% of the concentration found in the test solution after approximately 17 days. The Mg cations took approximately 28 days to reach 100% of the concentration in the test solution.

The laboratory test correlated well with the analytical solution derived from Fick's Second Law of Diffusion:

$$\partial C/\partial t = D\, \partial^2 C/\partial x^2,$$

where C is the concentration of the diffusion substance, x is the space coordinate measured normal to the referenced section, D is the diffusion coefficient, and t is time.

In applying Fick's law of diffusion to the pore-water sampler prototype, first an estimation of the diffusion time scale through the porous stainless steel plate covering the sampling chamber is determined. The diffusion through the thin plate can be ignored, if the time scale through the plate is small relative to the time scale of diffusion through the sampling chamber. The time scale through the porous plate can be expressed as L^2/D_{eff}, where L is the thickness of the plate (0.16 cm), and D_{eff} is the effective diffusion coefficient. The effective diffusion coefficient accounts for the structure of the porous medium. Helfferich (1966) estimated the effective diffusion coefficient to be a function of the porosity of the porous media, ranging from

$$D_{eff} = (n/2)D \quad \text{to} \quad D_{eff} = (n/(2\text{-}n))^2 D,$$

where n equals the porosity of the media. Through a set of laboratory procedures, the bulk dry weight and fully saturated weight of the 5 micron porous plate were determined. Knowing the dry weight and saturated weight, the porosity of the 5 micron plate was calculated to be 0.36. Table 9 summarizes the calculated diffusion time scale through the porous plate for the cations used in the laboratory test.

Table 9. Diffusion time scale through porous plate

Cation	Diffusion Coefficient (D) in water (cm^2/s)*	Range D_{eff} thru plate (cm^2/s), n=0.36		Range Diffusion time scale thru plate (L^2/D_{eff}), L=0.16 cm		
		$(n/2)D$	$(n/(2-n))^2D$	min (hrs)	max (hrs)	Avg (hrs)
K^+	1.96E-05	3.53E-06	9.44E-07	2.02	7.53	4.77
Na^+	1.30E-05	2.34E-06	6.26E-07	3.04	11.35	7.20
Ca^{2+}	7.93E-06	1.4274E-06	3.82E-07	4.98	18.61	11.80
Mg^{2+}	7.05E-06	1.27E-06	3.40E-07	5.60	20.93	13.27

* From Li and Gregory (1974)

As shown in Table 9, the diffusion time through the porous plate is relatively short compared to the days required for the diffusion to occur through the sampling chamber of the pore-water sampler. The diffusion time through the porous plate is relatively short, therefore it will be ignored.

Ignoring the porous plate, the diffusion into the sampling cavity can be simply expressed as diffusion through a single plane sheet medium (i.e., water) of thickness l (i.e., distance from the opening/face of the sampling cavity to the back wall of the sampling cavity) with the following boundary conditions:

$$C = C_0, \quad x = 0, \quad t \geq 0,$$

$$\partial C/\partial x = 0, \quad x = l, \quad t \geq 0,$$

where C_0 represents a constant concentration at the face of the plane (i.e., at the opening to the sampling cavity). Through the application of the Laplace transform and with the above boundary conditions, a solution to Fick's Second Law of Diffusion can be obtained. The solution is an infinite series of complimentary error functions:

$$(C = C_o \sum_{n=0}^{\infty} (-1)^n erfc \frac{(2n+1)l - x}{2\sqrt{Dt}} + C_o \sum_{n=0}^{\infty} (-1)^n erfc \frac{(2n+1)l + x}{2\sqrt{Dt}}),$$

which converges on a solution quite rapidly. For example, considering only the first three terms of the series, we have for the concentration at $x = l$ (i.e, at the back wall of the sampling cavity) when $Dt/l^2 = 1$ to be

$$C = 0.89C_0.$$

(Crank, 1975)

The results of applying the above analytical solution to the diffusion of the same cations used in the laboratory test are summarized in Table 10. Table 10 also compares the obtained analytical solution to the results obtained from the laboratory test.

Table 10. Analytical Diffusion Calculations compared with Laboratory Results

Cation	**Diffusion Coefficient (*D*) in water (cm^2/s)***	**Time (days) when $C=0.89C_o$ at back wall of cavity****	**Est. Time (days) when $C=0.89C_o$ from lab test*****
K^+	19.6×10^{-6}	4.97	5.0
Na^+	13.3×10^{-6}	7.32	7.0
Ca^{2+}	7.93×10^{-6}	12.27	8.5
Mg^{2+}	7.05×10^{-6}	13.81	12.5

* From Li and Gregory (1974)
** Derived from $Dt/l^2 = 1$, where $l = 2.9$ cm, distance from the opening/face of the sampling cavity to the back wall of the sampling cavity.
*** Estimated from the results shown in Figure 18.

Using the solution provided by Crank (1975), the analytical model diffusion curves for K^+ and Na^+ are provided in Figure 20 and compared with the diffusion curves from the laboratory results. Since the laboratory results for the Ca^{2+} and Mg^{2+} included an unrealistic decrease between days one and three, the diffusion curves for Ca^{2+} and Mg^{2+} are not included in Figure 20. The analytical results correspond well with the laboratory results, and thus adding a degree of certainty to the laboratory results. An assumption made in

this comparison of the analytical and laboratory results, is that the time it takes for the concentration at the back wall of the cavity to reach a particular value (used in the analytical solution) is the same amount of time it takes for the entire cavity to reach the same concentration (used in the laboratory test).

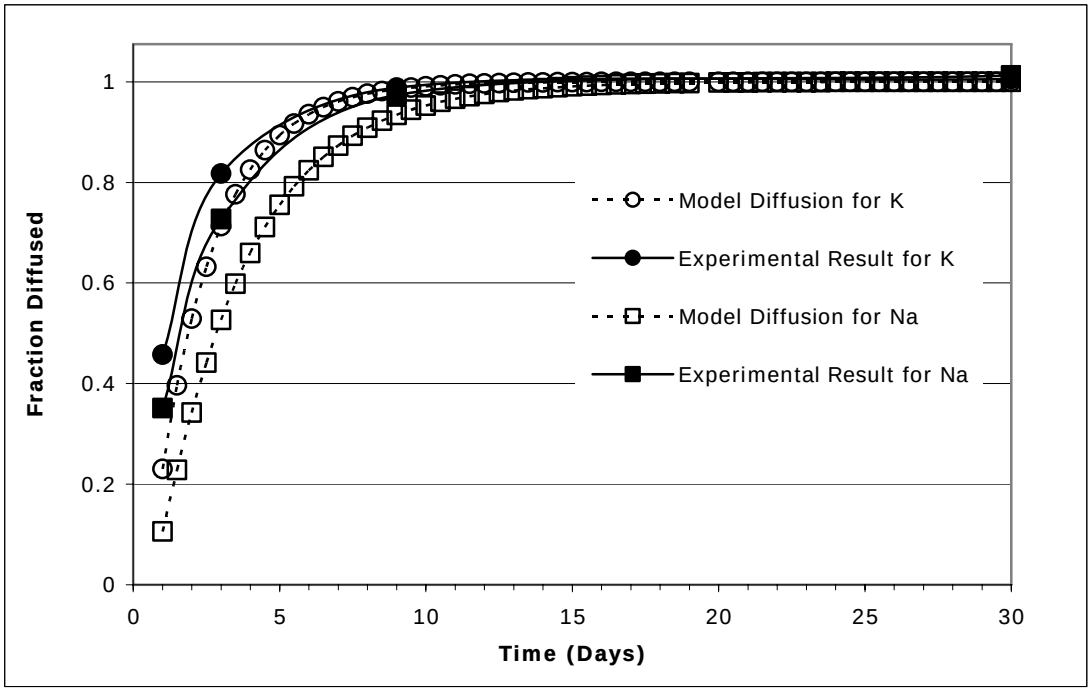


Figure 20. Analytical and Laboratory Diffusion Curves for K^+ and Na^+

Field Testing

The field implementation of the pore-water sampler provided limited data on the overall performance of the samplers in regards to obtaining accurate measurements of the targeted chlorinated ethene compounds within the wetland cell. However, useful knowledge on the physical operations of deploying the pore-water sampler in the field was obtained. As mentioned in Chapter 3, two connected pore-water samplers were placed in a middle layer 2 ¼" monitoring well (MW4) at the wetland cell and retrieved 20 days later. Water samples were also obtained from the subject monitoring well prior

to deploying the samplers and after they were removed. Table 11 shows the concentrations of the targeted compounds detected in both the pore-water samplers (PW Bottom and PW Top, denoting the pore-water (PW) sampler that was on bottom and the one that was on top) and the grab samples taken from the well (Grab 12/15 and Grab 1/4).

From the limited analytical data collected, there is not an observable correlation between the results obtained via the pore-water samplers and the results obtained through the direct sampling of the well. For some of the analytes, such as PCE, the amount detected in the pore-water samplers was significantly less than that detected in the grab samples. For other analytes, the amount detected in the pore-water samplers was significantly more than that detected in the grab samples (e.g., cis-DCE). In addition, Table 11 also includes the December 2006 analytical results obtained from the middle layer piezometer closest to MW4, piezometer 40M. From this limited available data, no correlation can be made between the results from piezometer 40M, the pore-water samplers, or the grad samples taken from the monitoring well. One possible explanation for the discrepancy is that, due to the continuous flow of water around the pore-water samples and the heterogeneity experience in the field, the samplers may need to remain in the well for a longer time than what was expected from the laboratory test. Also, since the PVC pore-water sampler is organic material, the chlorinated ethenes may be absorbing to the plastic sampler and not diffusing into the sample cavity. Finally, as mentioned in Chapter 3, only half of the sampling cavity of the top pore-water sampler was within the screened interval of the well and therefore results obtained from this pore-water sampler (i.e., PW Top) are suspect.

Table 11. Results from Field Implementation of Pore-Water Samplers

	Grab 12/15	PW BOTTOM	PW TOP	Grab 1/4	Piez 40M
PCE (μg/L)	21.20	12.49	2.35	25.31	10.87
TCE (μg/L)	2.25	7.34	0.75	1.83	1.91
trans-DCE (μg/L)	153.94	20.14	2.03	109.25	58.95
cis-DCE (μg/L)	0.00	2.48	1.41	0.00	0.00
VC (μg/L)	0.09	0.17	0.00	0.04	0.28
Ethane (μg/L)	0.0009	0.00	0.0001	0.0002	0.0009

Of greater value than the analytical results of the field implementation of the pore-water samplers, was the experience of physically deploying the samplers in the field for the first time. From this experience in-sights into a full scale deployment of these pore-water samplers can be made. The requirement to transport the pore-water samplers in water to prevent the introduction of air into the pores of the permeable plate would make the transporting of bulk number of samplers difficult. An on-site vacuum chamber where the samplers could be evacuated of air immediately prior to installing the samplers could relieve the need for transporting the samplers in water.

Even with two pore-water samplers deployed to only a total depth of 33 inches bgs, the suction pressure created by the viton washers rubbing against the inside of the well casing made removing the samplers a challenge. The two samplers were able to be removed by hand, but with anticipated chains of upwards to 15 samplers with 15 viton washers, a jack recovery system will need to be developed. Employing such a jack

recovery system could potentially impact the integrity of the well casing (i.e., displace the whole well casing).

Finally, the pore-water samplers are quite time consuming to assemble and to prepare for deployment. Inserting the septa material and washer to effectively cover the sampling ports can be difficult, since they are so small. The overall number of parts involved is cumbersome. These issues could limit the full scale implementation of these pore-water samplers.

V. Conclusions and Recommendations

The purpose of this thesis was to characterize the concentration of chlorinated ethenes within a vertical flow constructed wetland in order to evaluate the effectiveness of a constructed wetland as a viable treatment technology for chlorinated solvent contaminated groundwater. Through the characterization of the chlorinated ethene concentrations within the wetland cell insight was gained on the degradation processes taking place within the wetland. A constructed wetland cell located at WPAFB was used as the basis of this research effort. The WPAFB wetland cell has been a source of research for evaluating the remediation of chlorinated ethene contaminated groundwater since its construction in September 2000. This research effort was a follow up to the research performed by Bryan Opperman (2002), Nathan Clemmer (2003) and Teresa Sobolewski (2004).

This research employed a similar methodology as before for determining the levels of PCE and its degradation byproducts within the lower, middle, and upper layers of the wetland cell, as well as the inflow and outflow to and from the wetland. In addition, in order to obtain a more detailed contaminant profile within the wetland cell, a sampling method enabling the collection of a closely-spaced vertical sampling interval using pore-water samplers was introduced in this research effort.

The results of this research will spur more focused evaluation of the effectiveness of constructed vertical flow wetlands as a viable remediation technology. Through this and future research an understanding of the degradation of chlorinated solvent contamination within a constructed wetland cell will aid in the validation and development of this alternative remediation technology.

Answers to Specific Research Questions

1. *Do the vertical profile concentrations of PCE and its degradation products within the wetland cell provide further evidence of the biodegradation potential of an engineered wetland?*

Consistent with the results of the previous researchers, the data collected from September through December 2006 provided strong evidence supporting the effectiveness of a constructed wetland for the treatment of PCE contaminated groundwater. For the data collected from September through December 2006, the concentration of PCE monitored at the effluent represented an 85.4% reduction in concentration as compared to the influent PCE concentrations. Comparing the PCE concentrations of the upper layer of the wetland cell with the influent concentrations, a higher, 98.9%, reduction was observed. These higher PCE concentrations in the effluent, as compared to the upper layer, provide evidence that a portion of the contaminated groundwater being injected into the wetland cell is not being treated. Contaminated water must be by-passing or short circuiting the wetland system.

The contaminant concentration profiles of PCE and its daughter products found throughout the wetland cell provides insight into the biodegradation processes taking place. The sequential accumulation of PCE daughter products within the layers of the wetland cell is evident of anaerobic reductive dechlorination. The rapid reduction of PCE concentrations and increase in TCE concentrations at the bottom of the cell followed by an increase in DCE, VC, and ethane concentrations along with a decrease in TCE concentration in the middle part of the cell, supports the hypothesis that the wetland cell

offers favorable anaerobic environmental conditions for the complete step wise reductive dechlorination of PCE to ethane. In addition, between the middle and upper layer of the wetland cell TCE, DCE, VC, and ethane concentrations all decrease, supporting degradation processes other than anaerobic reductive dechlorination. Due to the proximity to the surface and influx of oxygen through the rhizospheres of the plant material, aerobic oxidation of the less chlorinated ethenes may be taking place in the upper layer. Other possible degradation pathways within the upper part of the wetland cell include anaerobic oxidation, cometabolism, and direct volatization.

2. *As the WPAFB wetland cell has matured, is there evidence to support an increase or decrease in the wetland cells capability to degrade the contaminants?*

From the data collected for this research effort, the WPAFB wetland cell is continuing to mature since its initial operation in 2000. Although the influent PCE concentration has increased by 94.3%, as compared to the Fall 2003 data, the percentage of PCE destroyed measured in the upper layer of the wetland has remained virtually unchanged. Comparing the influent and upper layer PCE concentration, the Fall 2003 data showed a 98.8% reduction and the September-December 2006 data showed a 98.9% reduction. The 98.9% reduction in PCE concentrations from the September-December 2006 data, is also greater than the reductions measured in December 2001 and January 2003, 92.9% and 96.4% respectively. As the wetland cell is now over 5 years old and has experienced several seasonal changes involving the growth and senescence of wetland vegetation, its overall effectiveness in degrading the parent PCE is increasing. The annual loading of decayed vegetation matter within the wetland can provide a continuous

source of organic carbon to act as an electron donor, and also provides an additional source to which the chlorinated ethenes could absorb to.

Also of note is the rate of degradation and where the degradation is taking place within the wetland cell over the lifespan of the cell. The September-December 2006 data shows the TCE concentration rapidly increasing between the influent and lower layer and then rapidly decreasing between the lower and middle layers. Whereas, for the Fall 2003 data, the TCE concentrations also rapidly increase between the influent and lower layer, but then more slowly, gradually declines through the middle and upper layers. This suggest that the environmental conditions within the bottom of the cell are ideal for the anaerobic dechlorination of the PCE to TCE, for both time periods, but that conditions have changed in the September-December 2006 period to allow the rapid decrease in the TCE concentrations between the lower and middle layers. Perhaps, the conditions have become more reducing, favoring the rapid destruction of the TCE, or other TCE degradation pathways have developed.

Another item of interest in the aging of the wetland cell is the significant increase in trans-DCE measured during September-December 2006 as compared to earlier sampling sets. After previously not being detected anywhere in the wetland cell in December 2001 and January 2003, and then at relatively low levels in the Fall 2003 (maximum average concentration of 4.5 μg/L in the middle layer), trans-DCE concentrations increased significantly during this research effort. For the September-December 2006 data set, the trans-DCE concentrations increase through the lower layer and reached a maximum average concentration in the middle layer (28.4 μg/L). The concentration of trans-DCE is significantly greater than the concentration of cis-DCE

observed in the September-December 2006 data, and is thus contrary to published research which shows that cis-DCE is the dominant DCE isomer resulting from the reduction of TCE. It is unclear what may have caused this increase in trans-DCE concentrations; perhaps a microbial consortium, favoring the reduction of trans-DCE was lost. Additional research will need to be performed to study this increase in trans-DCE.

A final observation in the maturation of the wetland cell is in regards to the observed VC concentrations. The VC concentrations were significantly less in the September-December 2006 data set as compared to the January 2003 and Fall 2003 data sets. The maximum average concentration for the September-December 2006 data was 0.2 μg/L (middle layer) as compared to 8.7 μg/L (middle layer) and 10.0 μg/L (upper layer), for the January 2003 and Fall 2003 data respectively. This change in VC concentration supports a change in the underlying degradation process of the wetland. The accumulation of VC is often a concern in the remediation of PCE contaminated groundwater, and therefore not experiencing a substantial accumulation of VC during this research effort is a significant highlight in the maturation of the wetland cell. Between the Fall 2003 and September-December 2006 sampling events, highly reducing conditions may have developed resulting in the rapid anaerobic reductive dechlorination of the VC, or perhaps favorable aerobic or anaerobic oxidation conditions developed resulting in the oxidation of the DCE precluding the generation of VC.

3. *Are the analytical results obtained from the pore-water sampling methodology consistent with previous analytical results?*

Limited analytical data from the use of the pore-water samplers was generated during this research effort. Due the amount of time needed to produce the pore-water sampler prototype and the lack of a suitable monitoring well at the wetland cell, only one field test of the pore-water sampler prototype was completed. This limited field test involved only two of the pore-water samplers chained together and inserted into an existing 2 ¼- inch monitoring wells at the wetland cell. As presented in Chapter IV, there was not an observable correlation between the results obtained via the pore-water samplers and the results obtained through the direct sampling of the well, both prior to the installation of the pore-water samplers and after they were removed. Nor was there a correlation between the results obtained from the pore-water samplers and the standard piezometer data. Future testing and field experiments will need to be performed in order to accurately evaluate the effectiveness of the pore-water sampler prototypes.

However, the experience of deploying the pore-water samplers in the field provided valuable information. Issues including effectively evacuating the air from the porous plates, transporting the samplers in water, the difficulty in extracting the samplers from the monitoring well, and the overall cumbersome nature of the prototype create challenges that will need to be addressed prior to a full scale implementation of these pore-water samplers. The information to be gained through the implementation of a pore-water sampling device is extremely valuable for this research project, and therefore, the development of the prototype designed and built for this research effort needs to continue.

Recommendations for Further Study

1. Continue the research and development for an effective pore-water sampler to be implemented at the WPAFB wetland test cell. The biogeochemical conditions within a wetland can change drastically over small intervals, and therefore, the knowledge to be gained from a closely-spaced vertical sampling interval using pore-water samplers will be invaluable. The pore-water sampler will allow a more detailed characterization profile and a better understand of the degradation pathways taking place within the wetland. The following are specific recommendations regarding the development of the existing pore-water sampler prototype:

a. Install monitoring wells in the WPAFB wetland test cell which are screened the entire depth of the wetland. This will allow multiple pore-water sampler chambers to be deployed in a single monitoring well to gain the desired detailed profile.

b. Instead of using a screw to connect each of the pore-water sampler chambers, consider a threaded connection installed directly on each end of the PVC sampler. This will eliminate the need for the screw and simplify the assembly/installation process.

c. Develop a sampling methodology of the wetland cell that can be used to validate the data obtained from the pore-water samplers. An accurate direct sampling method needs to be implemented to confirm the results from the pore-water samplers.

d. Modify the existing pore-water sampler design for the pore-water sampler chamber which sits at the bottom of the monitoring well. Since the bottom pore-water sampler chamber will only have another chamber installed on top of it and in order to allow the bottom pore-water sampler's cavity to rest as close to the bottom of the well as

possible, eliminate the unneeded portion of the bottom chamber, thus producing a shorter chamber.

e. Enlarge the sampling port holes which allow access to the sampling chamber's cavities. The larger holes will make it easier to retrieve the samples.

2. Establish and implement a year round sampling plan for the wetland test cell. A year round sampling plan will help evaluate the wetland cell's effectiveness due to seasonal changes.

3. As during past research efforts, collect complimentary inorganic data (nitrate/nitrite, Fe(III)/Fe(II), sulfate/sulfite, and Cl^-) to help gain information on the underlying degradation processes.

4. Establish and implement an effective methodology to obtain dissolved oxygen (DO) concentrations throughout the wetland system. Knowledge of the DO concentrations would be invaluable in identifying the transition zones between anaerobic and aerobic zones.

5. Evaluate the water flow pattern through the wetland test cell. Knowledge of the water flow pattern can help eliminate bypass, evaluate retention times, and understand the distribution of the contaminated water throughout the wetland test cell.

6. Collect and analyze core samples from the wetland test cell. Core samples will help evaluate the amount of contaminants being absorbed to the soil matrix.

7. Establish a sampling and analytical methodology to effectively evaluate abiotic degradation processes.

Appendix A. Raw Analytical Chemical Data

September 2006

			0.0004		0.00185		0.1433		0.021		0.4639		0.0032
Date	**Piez #**	**PCE Area**	**PCE (ppb)**	**TCE Area**	**TCE (ppb)**	**trans-DCE Area**	**trans-DCE (ppb)**	**cis-DCE Area**	**cis-DCE (ppb)**	**VC Area**	**VC (ppb)**	**Ethane Area**	**Ethane (ppb)**
9/15/2006	INF1	109585	47.012	425.458	0.7871	1.31373	0.18825751	0	0		0	0	0
	INF2	107557	46.142	163.003	0.30156	1.24762	0.17878395	0	0		0	0	0
	2M	4172.6	1.79	1580.94	2.92474	60.83125	8.71711813	0	0	0.159	0.0737	0.16739	0.00054
	2L	41111	17.637	2488.8	4.60429	390.54742	55.9654453	0	0	0.126	0.0583	0	0
	4L	38406	16.476	3023.77	5.59397	133.638	19.1503254	0	0		0	0	0
	4M	311.04	0.1334	111.126	0.20558	126.286	18.0967838	1.10725	0.023252	0.754	0.3499	0.67825	0.00217
	4U	243.35	0.1044	87.6296	0.16211	9.69446	1.38921612	0	0	0.935	0.4338	0.33354	0.00107
	14L	10182	4.3681	1823.05	3.37264	205.434	29.4386922	0	0	0.467	0.2164	0.10779	0.00034
	14M	199.69	0.0857	44.0138	0.08143	199.221	28.5483693	0.57697	0.012116	0.952	0.4414	0.54931	0.00176
	14U	222.04	0.0953	36.8695	0.06821	182.803	26.1956699	0.78169	0.016415	0.217	0.1005	0.3443	0.0011
	16L	95012	40.76	1255.12	2.32197	26.1471	3.74687943	0	0		0	0.04358	0.00014
	16M	521.16	0.2236	56.9154	0.10529	81.8795	11.7333324	0.59409	0.012476	0.128	0.0593	0.44277	0.00142
	16U	791.18	0.3394	103.733	0.19191	21.6761	3.10618513	0	0	0.059	0.0275	0.46332	0.00148
	26L	96016	41.191	529.308	0.97922	16.1386	2.31266138	0	0	0.116	0.0539	0	0
	26M	467.31	0.2005	26.8459	0.04966	5.70838	0.81801085	0	0	0.009	0.0043	0.17462	0.00056
	28L	38376	16.463	1758.88	3.25393	75.6284	10.8375497	0	0	0.482	0.2236	0.73642	0.00236
9/20/2006	INF1	111911	48.01	202.774	0.37513	0	0	0	0		0	0	0
	INF2	111928	48.017	524.39	0.97012	51.55893	7.38839467	0	0		0	0	0
	9L	12121	5.2001	1997.68	3.6957	396.2995	56.7897184	0	0	1.512	0.7012	0.5213	0.00167
	9M	248.13	0.1064	49.798	0.09213	215.31314	30.854373	0	0	0.295	0.1367	0.95955	0.00307
	9U	670.35	0.2876	43.8442	0.08111	78.0892	11.1901824	0	0	0.16	0.0742	0.21899	0.0007
	11L	176.5	0.0757	105.462	0.1951	32.4436	4.64916788	0	0	1.598	0.7414	1.22115	0.00391
	11M	184.57	0.0792	23.501	0.04348	7.78847	1.11608775	0	0		0	0.12308	0.00039
	28L	38235	16.403	2041.77	3.77727	106.28284	15.230331	0	0	0.562	0.2607	0.73761	0.00236
	28M	146.5	0.0628	49.0256	0.0907	267.496	38.3321768	0	0	0.245	0.1136	0.39208	0.00125

Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	28U	1066.6	0.4576	212.754	0.39359	8.00745	1.14746759	0	0	0.185	0.0858	0.21366	0.00068
	38L	86719	37.202	1720.36	3.18267	0	0	0	0		0	0	0
	38M	380.71	0.1633	54.229	0.10032	367.108	52.6065764	1.62653	0.034157	0.14	0.0649	0.2175	0.0007
	38U	252.24	0.1082	28.7708	0.05323	48.5758	6.96091214	0	0		0	0.20489	0.00066
	40L	96353	41.335	618.717	1.14463	0	0	0	0		0	0	0
	40M	195.81	0.084	44.7163	0.08273	99.0667	14.1962581	0	0	0.663	0.3075	0.27618	0.00088
	40U	303.9	0.1304	34.5101	0.06384	8.84732	1.26782096	0	0	0.171	0.0792	0.22539	0.00072
	50L	98448	42.234	777.195	1.43781	0	0	0	0		0	0	0
	50M	665.38	0.2854	23.0296	0.0426	6.19754	0.88810748	0	0		0	0.13801	0.00044
	50U	364.29	0.1563	17.8812	0.03308	17.6931	2.53542123	0	0		0	0.11466	0.00037
	52L	90315	38.745	682.587	1.26279	59.1329	8.47374457	0	0	0.11	0.051	0.03718	0.00012
	52M	516.4	0.2215	23.5763	0.04362	46.2894	6.63327102	0	0	0.335	0.1554	0.36605	0.00117
	52U	251.59	0.1079	15.3886	0.02847	10.0862	1.44535246	0	0	0.525	0.2437	0.32694	0.00105
	62L	41937	17.991	1974.52	3.65286	73.168	10.4849744	0	0	0.196	0.0911	0.03608	0.00012
	62M	530.8	0.2277	265.787	0.49171	276.408	39.6092664	0	0	1.456	0.6756	0.68936	0.00221
	62U	227.39	0.0976	22.4328	0.0415	5.8882	0.84377906	0	0	0.58	0.269	0.27671	0.00089
	64L	81617	35.014	1243.4	2.30029	18.8368	2.69931344	0	0	0.043	0.0199	0	0
	64M	348.56	0.1495	191.223	0.35376	353.02	50.587766	0	0	0.79	0.3666	1.74798	0.00559
	64U	377.63	0.162	59.6141	0.11029	48.9839	7.01939287	0	0	0.663	0.3074	0.46834	0.0015
	EFF1	24011	10.301	766.462	1.41795	19.0529	2.73028057	0	0	0.026	0.0119	0.04148	0.00013
	EFF2	20061	8.606	683.507	1.26449	19.7069	2.82399877	0	0		0	0	0
9/26/2006	INF1	102779	44.092	297.564	0.55049	21.8664	3.13345512	0	0	0.123	0.0571	0	0
	INF2	109570	47.006	191.377	0.35405	0	0	0	0		0	0	0
	59L	92484	39.676	567.722	1.05029	16.7587	2.40152171	0	0		0	0	0
	59M	309.38	0.1327	38.6505	0.0715	243.499	34.8934067	1.27058	0.026682	0.127	0.059	0.19114	0.00061
	59U	512.19	0.2197	27.4227	0.05073	91.4556	13.1055875	0	0	0.064	0.0298	0.21458	0.00069
	57L	83341	35.753	791.765	1.46477	29.00775	4.15681058	0	0	0.134	0.062	0	0
	57M	216.67	0.093	69.1351	0.1279	1683.36	241.225488	0	0	0.385	0.1788	0.21365	0.00068
	57U	308.55	0.1324	47.0719	0.08708	130.905	18.7586865	0.46886	0.009846	0.256	0.1187	0.15586	0.0005
	47L	20126	8.634	2934.92	5.4296	127.116	18.2157228	0	0	0.772	0.3581	0.10888	0.00035

Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	47M	353.38	0.1516	79.8303	0.14769	257.83414	36.9476323	0.79493	0.016693	0.121	0.0562	0.17002	0.00054
	47U	550.64	0.2362	16.0717	0.02973	7.5752	1.08552616	0	0		0	0.10758	0.00034
	45L	99184	42.55	463.178	0.85688	10.956	1.5699948	0	0		0	0	0
	45M	246.6	0.1058	37.8491	0.07002	635.128	91.0138424	0	0	0.57	0.2645	0.31512	0.00101
	45U	427.91	0.1836	29.6187	0.05479	57.1144	8.18449352	0	0	0.078	0.0361	0.15056	0.00048
	36L	105271	45.161	794.307	1.46947	0	0	0	0		0	0	0
	36M	721.89	0.3097	84.6955	0.15669	105.606	15.1333398	0	0	0.164	0.076	1.19072	0.00381
	36U	561.01	0.2407	48.6955	0.09009	25.9213	3.71452229	0	0	0.077	0.0356	0.76076	0.00243
	33L	16118	6.9146	2173.4	4.02079	137.324	19.6785292	0	0	0.907	0.4209	0.15911	0.00051
	33M	336.91	0.1445	131.052	0.24245	4.32775	0.62016658	0.86426	0.018149	0.209	0.0968	0.24697	0.00079
	33U	529.87	0.2273	107.726	0.19929	154.268	22.1066044	0	0	0.598	0.2773	0.46175	0.00148
	23L	101071	43.359	253.622	0.4692	0	0	0	0		0	0	0
	23M	318.99	0.1368	41.5537	0.07687	39.92532	5.72129836	0.92891	0.019507	0.37	0.1718	1.47578	0.00472
	23U	631.28	0.2708	25.8026	0.04773	13.6339	1.95373787	0	0		0	0.19064	0.00061
	21L	104639	44.89	1181.61	2.18598	11.6233	1.66561889	0	0		0	0	0
	21M	551.53	0.2366	230.648	0.4267	140.683	20.1598739	1.27104	0.026692	0.715	0.3317	0.70947	0.00227
	21U	1218.1	0.5226	213.5	0.39498	33.67083	4.82502994	1.65687	0.034794	0.544	0.2525	0.55248	0.00177
	EFF1	14498	6.2197	617.069	1.14158	36.8136	5.27538888	0	0		0	0	0
	EFF2	19654	8.4317	667.293	1.23449	13.5328	1.93925024		0		0	0	0
October 2006													
			0.0004		0.00185		0.1433		0.021		0.4639		0.0032
Date	**Piez #**	**PCE Area**	**PCE (ppb)**	**TCE Area**	**TCE (ppb)**	**trans-DCE Area**	**trans-DCE (ppb)**	**cis-DCE Area**	**cis-DCE (ppb)**	**VC Area**	**VC (ppb)**	**Ethane Area**	**Ethane (ppb)**
10/11/2006	INF1	107574	46.149	172.286	0.31873	1.53971	0.22064044	0	0	0	0	0	0
	INF2	108414	46.51	191.213	0.35374	0	0	0	0	0	0	0	0
	2L	31542	13.532	2503.17	4.63086	262.302	37.5878766	1.1223	0.023568	0.079	0.0366	0	0
	2M	2418.9	1.0377	939.178	1.73748	88.3034	12.6538772	0	0	0.131	0.0608	0.20493	0.00066
	2U	249.95	0.1072	50.9454	0.09425	10.8264	1.55142312	0	0	0	0	0.25492	0.00082
	4L	38919	16.696	2866.62	5.30325	48.5851	6.96224483	0	0	0.015	0.0069	0.05182	0.00017
	4M	220.42	0.0946	130.72	0.24183	54.7784	7.84974472	1.24178	0.026077	1.022	0.4741	0.81419	0.00261
	4U	240.09	0.103	303.27	0.56105	56.4053	8.08287949	0	0	1.032	0.4785	0.38637	0.00124

Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	14L	8896.4	3.8166	1702.7	3.15	164.287	23.5423271	0	0	0.491	0.2276	0.04089	0.00013
	14M	112.79	0.0484	32.4952	0.06012	44.3543	6.35597119	0.78343	0.016452	1.404	0.6511	0.81878	0.00262
	14U	153.19	0.0657	25.7335	0.04761	77.2675	11.0724328	0	0	0.248	0.1151	0.3304	0.00106
	16L	93484	40.105	862.52	1.59566	4.10307	0.58796993		0		0	0	0
	16M	421.8	0.181	54.3403	0.10053	52.81777	7.56878644	0.84068	0.017654	0.129	0.0599	0.34226	0.0011
	16U	512.68	0.2199	71.3681	0.13203	14.4652	2.07286316	0	0	0.087	0.0405	0.53701	0.00172
	26L	86922	37.289	503.896	0.93221	30.2028	4.32806124	0	0	0.168	0.0779		0
	26M	330.71	0.1419	30.5173	0.05646	6.37049	0.91289122	0	0	0.035	0.0163	0.13389	0.00043
	26U	372.92	0.16	37.9041	0.07012	8.52939	1.22226159	0	0	0	0	0.15517	0.0005
	28L	32338	13.873	1731.96	3.20413	244.667	35.0607811	0	0	0.604	0.2802	0.59749	0.00191
	28M	347.15	0.1489	63.9454	0.1183	842.349	120.708612	0.78938	0.016577	0.206	0.0956	0.37303	0.00119
	28U	971.8	0.4169	151.76	0.28076	8.24394	1.1813566	0	0	0.189	0.0876	0.25902	0.00083
	38L	91258	39.15	1388.38	2.5685	14.1061	2.02140413	0	0	0	0		0
	38M	344.47	0.1478	51.1009	0.09454	457.175	65.5131775	0.93433	0.019621	0.135	0.0628	0.18546	0.00059
	38U	210.61	0.0904	18.7091	0.03461	14.68324	2.10410829	0.36218	0.007606	0	0	0.21705	0.00069
	40L	96332	41.326	566	1.0471	2.60502	0.37329937	0	0	0	0		0
	40M	552.52	0.237	624.546	1.15541	279.683	40.0785739	1.14569	0.024059	0.674	0.3126	0.23304	0.00075
	40U	372.22	0.1597	33.4824	0.06194	3.18448	0.45633598	0.46724	0.009812	0.199	0.0922	0.21555	0.00069
	50L	96284	41.306	566.783	1.04855	7.33401	1.05096363	0	0	0	0		0
	50M	505.83	0.217	20.5981	0.03811	5.69299	0.81580547	0	0	0	0	0.09782	0.00031
	50U	319.64	0.1371	18.0147	0.03333	27.1068	3.88440444	0	0	0	0	0.06951	0.00022
	52L	87093	37.363	684.65	1.2666	32.9702	4.72462966	0	0	0.073	0.0341	0	0
	52M	495.35	0.2125	18.917	0.035	25.3212	3.62852796	0	0	0.296	0.1374	0.31603	0.00101
	52U	402.42	0.1726	19.1637	0.03545	6.36076	0.91149691	0	0	0.423	0.1962	0.10711	0.00034
	62L	37389	16.04	2353.66	4.35427	81.0105	11.6088047	0	0	0.124	0.0575	0	0
	62M	739.31	0.3172	202.53	0.37468	293.217	42.0179961	0	0	1.549	0.7186	0.73842	0.00236
	62U	258.04	0.1107	24.8816	0.04603	7.21425	1.03380203	0	0	0.52	0.241	0.26827	0.00086
	EFF1	15377	6.5966	687.18	1.27128	21.5938	3.09439154	0	0	0	0		0
	EFF2	19447	8.3428	755.068	1.39688	18.1625	2.60268625	0	0	0	0		0

November 2006

			0.0004		0.00185		0.1433		0.021		0.4639		0.0032
Date	**Piez #**	**PCE Area**	**PCE (ppb)**	**TCE Area**	**TCE (ppb)**	**trans-DCE Area**	**trans-DCE (ppb)**	**cis-DCE Area**	**cis-DCE (ppb)**	**VC Area**	**VC (ppb)**	**Ethane Area**	**Ethane (ppb)**
11/10/2006	INF1	106848	45.838	173.412	0.32081	0	0	0	0	0	0	0	0
	INF2	106382	45.638	179.639	0.33233	0	0	0	0	0	0	0	0
	9L	21051	9.031	2156.3	3.98916	422.075	60.4833475	0	0	0.848	0.3933	0.35033	0.00112
	9M	78.28	0.0336	581.145	1.07512	281.529	40.3431057	0	0	0.458	0.2122	0.8028	0.00257
	9U	585.19	0.251	101.559	0.18788	114.677	16.4332141	0	0	0.226	0.105	0	0
	11L	98.203	0.0421	493.344	0.91269	217.478	31.1645974	2.19008	0.045992	1.234	0.5723	1.08425	0.00347
	11M	50.525	0.0217	14.3658	0.02658	9.74411	1.39633096	0	0	0	0	0.16161	0.00052
	11U	352.86	0.1514	26.8039	0.04959	7.27556	1.04258775	0	0	0	0	0.23728	0.00076
	21L	97589	41.866	669.18	1.23798	4.08831	0.58585482	0	0	0	0	0	0
	21M	326.71	0.1402	238.388	0.44102	66.0185	9.46045105	1.50988	0.031707	0.394	0.1828	0.53518	0.00171
	21U	451.95	0.1939	108.264	0.20029	46.74763	6.69893538	0.76691	0.016105	0.347	0.1609	0.84376	0.0027
	23L	99191	42.553	246.242	0.45555	0	0	0	0	0	0	0	0
	23M	231	0.0991	310.636	0.57468	9.25917	1.32683906	0	0	0.548	0.254	1.28998	0.00413
	23U	440.36	0.1889	20.8984	0.03866	4.6558	0.66717614	0	0	0.078	0.0361	0.34353	0.0011
	33L	37727	16.185	2426.36	4.48877	36.0175	5.16130775	0	0	0.109	0.0504	0.02333	7.5E-05
	33M	314.48	0.1349	79.612	0.14728	3.6872	0.52837576	0	0	0.228	0.1059	0.26479	0.00085
	33U	580.51	0.249	98.2118	0.18169	2.64755	0.37939392	0	0	0.785	0.3643	0.6601	0.00211
	36L	99000	42.471	984.517	1.82136	3.18072	0.45579718	0	0	0	0	0	0
	36M	305.3	0.131	83.9294	0.15527	202.988	29.0881804	0.7951	0.016697	0.133	0.0615	0.86694	0.00277
	36U	1054.8	0.4525	52.1348	0.09645	6.29462	0.90201905	0	0	0.094	0.0435	0.53398	0.00171
	45L	93524	40.122	471.507	0.87229	0	0	0	0	0	0	0	0
	45M	223.04	0.0957	46.4672	0.08596	448.377	64.2524241	0	0	0.297	0.1379	0.24112	0.00077
	45U	479.42	0.2057	38.5503	0.07132	40.3497	5.78211201	0	0	0.055	0.0256	0.18259	0.00058
	47L	34610	14.848	2785.87	5.15386	91.5766	13.1229268	0	0	0.291	0.1348	0.03826	0.00012
	47M	249.38	0.107	35.9255	0.06646	31.10594	4.4574812	0.82737	0.017375	0.11	0.051	0.14476	0.00046
	47U	558.09	0.2394	16.6005	0.03071	3.67951	0.52727378	0	0	0	0	0.15157	0.00049
	57L	81194	34.832	939.474	1.73803	32.97519	4.72534473	0	0	0.042	0.0194	0	0
	57M	181.53	0.0779	24.5635	0.04544	106.674	15.2863842	0	0	0.464	0.2154	0.1942	0.00062

Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	57U	300.08	0.1287	37.5168	0.06941	65.4377	9.37722241	0	0	0.417	0.1933	0.19762	0.00063
	59L	88689	38.048	500.128	0.92524	7.88722	1.13023863	0	0	0	0	0	0
	59M	200.47	0.086	26.5315	0.04908	102.96	14.754168	0	0	0.084	0.0389	0.15369	0.00049
	59U	551.02	0.2364	31.1381	0.05761	122.783	17.5948039	0	0	0.045	0.0207	0.24068	0.00077
	64L	87902	37.71	575.297	1.0643	0	0	0	0	0	0	0	0
	64M	337.13	0.1446	332.683	0.61546	130.76	18.737908	0	0	1.016	0.4712	0.83292	0.00267
	64U	603.81	0.259	266.223	0.49251	42.7989	6.13308237	0	0	0.542	0.2517	0.48078	0.00154
	EFF1	18435	7.9084	385.034	0.71231	18.0087	2.58064671	0	0	0	0	0	0
	EFF2	17718	7.6011	409.387	0.75737	34.4667	4.93907811	0	0	0	0	0	0
11/18/2006	INF1	109622	47.028	266.534	0.49309	0	0	0	0	0	0	0	0
	INF2	109963	47.174	186.719	0.34543	0	0	0	0	0	0	0	0
	2L	27378	11.745	1897.67	3.51069	245.519	35.1828727	0	0	0.142	0.0657	0	0
	2M	1194	0.5122	635.977	1.17656	257.622	36.9172326	0	0	0.115	0.0532	0.09256	0.0003
	2U	244.34	0.1048	39.2943	0.07269	18.0559	2.58741047	0	0	0	0	0.17148	0.00055
	4L	45931	19.704	3033.46	5.6119	31.448	4.5064984	0	0	0	0	0	0
	4M	297.24	0.1275	156.51	0.28954	33.09314	4.74224696	1.18359	0.024855	0.697	0.3232	0.7011	0.00224
	4U	234.93	0.1008	363.606	0.67267	11.21679	1.60736601	0.96178	0.020197	0.641	0.2972	0.18224	0.00058
	14L	10794	4.6307	1856.23	3.43403	157.244	22.5330652	0	0	0.281	0.1306	0	0
	14M	149.59	0.0642	34.1308	0.06314	67.6904	9.70003432	0	0	1.653	0.767	0.72342	0.00231
	14U	246.75	0.1059	37.4691	0.06932	121.373	17.3927509	0.6699	0.014068	0.252	0.1169	0.19319	0.00062
	16L	99788	42.809	728.141	1.34706	0	0	0	0	0	0	0	0
	16M	429.62	0.1843	49.3906	0.09137	55.82743	8.00007072	0.83169	0.017466	0.074	0.0344	0.42261	0.00135
	16U	268.7	0.1153	64.638	0.11958	29.7145	4.25808785	0	0	0.044	0.0204	0.47824	0.00153
	26L	85105	36.51	325.121	0.60147	25.3981	3.63954773	0	0	0	0	0	0
	26M	319.19	0.1369	17.9753	0.03325	12.2138	1.75023754	0	0	0	0	0.2421	0.00077
	26U	486.15	0.2086	37.084	0.06861	19.8782	2.84854606	0	0	0	0	0.12564	0.0004
	28L	36182	15.522	1187.15	2.19623	183.213	26.2544229	0	0	0.503	0.2334	0.37374	0.0012
	28M	280.61	0.1204	45.0618	0.08336	243.876	34.9474308	0.85352	0.017924	0.158	0.0731	0.45171	0.00145
	28U	763.67	0.3276	104.369	0.19308	12.2786	1.75952338	0	0	0.108	0.0502	0.21249	0.00068
	38L	89913	38.573	1058.28	1.95782	13.019	1.8656227	0	0	0	0	0	0

Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	38M	346.33	0.1486	49.7429	0.09202	824.035	118.084216	0	0	0.09	0.0418	0.20558	0.00066
	38U	505.83	0.217	30.9946	0.05734	24.2577	3.47612841	0	0	0	0	0.16911	0.00054
	40L	99438	42.659	386.279	0.71462	0	0	0	0	0	0	0	0
	40M	1259.8	0.5404	1508.02	2.78984	227.281	32.5693673	0	0	0.568	0.2634	0.27969	0.00089
	40U	399.04	0.1712	33.0635	0.06117	8.82618	1.26479159	0	0	0.27	0.1251	0.3437	0.0011
	50L	90154	38.676	942.174	1.74302	19.1961	2.75080113	0	0	0	0	0	0
	50M	517.58	0.222	14.3264	0.0265	10.3724	1.48636492	0	0	0	0	0.13026	0.00042
	50U	293.56	0.1259	12.0203	0.02224	24.7307	3.54390931	0	0	0	0	0.07488	0.00024
	52L	81731	35.063	565.721	1.04658	21.8555	3.13189315	0	0	0.05	0.0233	0	0
	52M	506.55	0.2173	22.5277	0.04168	129.513	18.5592129	0	0	0.353	0.1638	0.36549	0.00117
	52U	383.81	0.1647	18.3535	0.03395	28.9483	4.14829139	0	0	0.271	0.1259	0.086	0.00028
	62L	63488	27.236	1837.97	3.40024	62.2503	8.92046799	0	0	0	0	0	0
	62M	530.84	0.2277	269.614	0.49879	267.915	38.3922195	0	0	1.493	0.6924	0.25372	0.00081
	62U	428.53	0.1838	23.093	0.04272	16.8616	2.41626728	0	0	0.22	0.1019	0.23646	0.00076
	EFF1	7604.3	3.2622	356.513	0.65955	98.8206	14.160992	0	0	0	0	0.04389	0.00014
	EFF2	7410.8	3.1792	392.732	0.72655	86.1218	12.3412539	0	0	0	0	0	0
December 2006													
			0.0004		0.00185		0.1433		0.021		0.4639		0.0032
Date	**Piez #**	**PCE Area**	**PCE (ppb)**	**TCE Area**	**TCE (ppb)**	**trans-DCE Area**	**trans-DCE (ppb)**	**cis-DCE Area**	**cis-DCE (ppb)**	**VC Area**	**VC (ppb)**	**Ethane Area**	**Ethane (ppb)**
12/12/2006	INF1	108119	46.383	268.981	0.49761	0	0	0	0	0.019	0.0086	0	0
	INF2	107777	46.236	177.915	0.32914	0	0	0	0	0	0	0	0
	L2	42996	18.445	1579.17	2.92146	73.4409	10.524081	0	0	0	0	0	0
	M2	1234	0.5294	384.614	0.71154	589.882	84.5300906	0	0	0.238	0.1104	0.34115	0.00109
	U2	411.8	0.1767	48.917	0.0905	6.98761	1.00132451	0.54674	0.011481	0	0	0.22263	0.00071
	L4	51575	22.126	2488.53	4.60378	20.0058	2.86683114	0	0	0	0	0.03623	0.00012
	M4	362.9	0.1557	128.131	0.23704	30.636	4.3901388	1.06818	0.022432	0.831	0.3854	0.83433	0.00267
	U4	202.28	0.0868	239.218	0.44255	28.00388	4.012956	0.76915	0.016152	0.849	0.394	0.35855	0.00115
	L9	15434	6.6212	1654.72	3.06123	434.85	62.314005	0	0	0.899	0.4172	0.38619	0.00124
	M9	326.65	0.1401	1318.64	2.43948	697.527	99.9556191	0	0	0.565	0.262	0.99555	0.00319
	U9	349.03	0.1497	51.2068	0.09473	279.017	39.9831361	0	0	0.066	0.0306	0.25296	0.00081

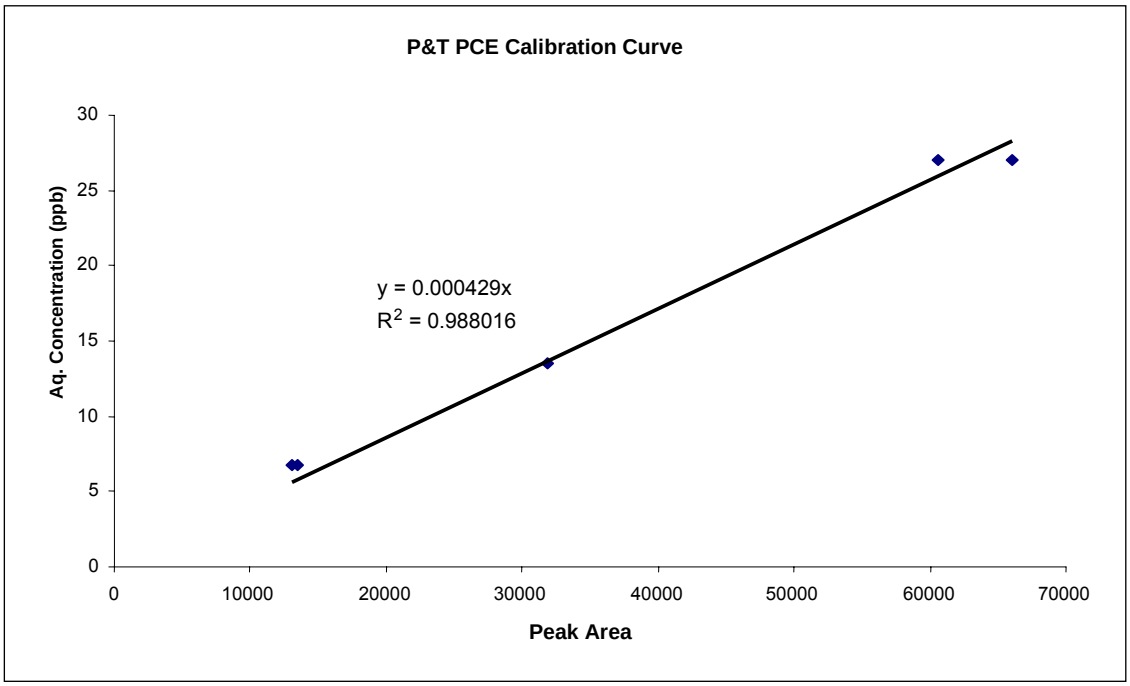
Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	L11	158.41	0.068	80.8578	0.14959	270.053	38.6985949	0.95405	0.020035	1.384	0.6419	1.75782	0.00563
	M11	164.43	0.0705	15.3876	0.02847	11.0997	1.59058701	0	0	0	0	0.13415	0.00043
	U11	254.83	0.1093	25.8724	0.04786	10.5873	1.51716009	0	0	0	0	0.20427	0.00065
	L14	10804	4.635	2229.92	4.12535	235.5742	33.7577829	0	0	0.31	0.144	0.04577	0.00015
	M14	150.19	0.0644	93.2871	0.17258	264.187	37.8579971	0	0	1.39	0.645	0.39035	0.00125
	U14	150.31	0.0645	19.8173	0.03666	139.518	19.9929294	0	0	0.341	0.1581	0.32112	0.00103
	L16	101629	43.599	281.361	0.52052	5.56229	0.79707616	0	0	0	0	0.02077	6.6E-05
	M16	498.79	0.214	55.5037	0.10268	66.2607	9.49515831	0.66104	0.013882	0.067	0.0313	0.31901	0.00102
	U16	255.81	0.1097	43.6995	0.08084	60.8939	8.72609587	0	0	0.119	0.0553	0.69197	0.00221
	L21	100771	43.231	375.481	0.69464	3.31858	0.47555251	0	0	0	0	0	0
	M21	2933.5	1.2585	814.235	1.50633	575.851	82.5194483	0	0	0.353	0.1638	0.42939	0.00137
	U21	1102.4	0.4729	281.858	0.52144	146.726	21.0258358	0	0	0.287	0.133	0.7855	0.00251
	Eff1	13007	5.58	472.607	0.87432	40.3944	5.78851752	0	0	0	0	0.04477	0.00014
	Eff2	12739	5.4649	480.369	0.88868	36.5722	5.24079626	0	0	0	0	0.0284	9.1E-05
12/14/2006	L23	96352	41.335	299.016	0.55318	8.17157	1.17098598	9.55219	0.200596	0	0	0	0
	M23	523.5	0.2246	259.31	0.47972	39.2468	5.62406644	0	0	0.73	0.3385	1.47689	0.00473
	U23	433.96	0.1862	45.8232	0.08477	19.5743	2.80499719	0	0	0.2	0.093	0.94569	0.00303
	L26	66989	28.738	521.054	0.96395	168.919	24.2060927	0	0	0.392	0.1821	0.09554	0.00031
	M26	418.61	0.1796	32.5703	0.06026	13.5213	1.93760229	0	0	0	0	0.16274	0.00052
	U26	319.64	0.1371	33.9233	0.06276	10.2191	1.46439703	0	0	0	0	0.10193	0.00033
	L28	27210	11.673	1032.08	1.90935	124.676	17.8660708	0	0	0.543	0.2519	0.33403	0.00107
	M28	311.22	0.1335	47.7657	0.08837	361.271	51.7701343	0	0	0.166	0.0771	0.5209	0.00167
	U28	14772	6.3372	61.4651	0.11371	24.4753	3.50731049	0	0	0.11	0.051	0.26147	0.00084
	L33	43298	18.575	1683.62	3.1147	43.2351	6.19558983	0	0	0.09	0.0415	0.20511	0.00066
	M33	343.68	0.1474	74.5622	0.13794	29.86862	4.28017325	0	0	0.216	0.1004	0.25396	0.00081
	U33	13067	5.6059	241.893	0.4475	95.7336	13.7186249	0	0	0.813	0.3772	0.80667	0.00258
	L36	98112	42.09	431.301	0.79791	4.02642	0.57698599	0	0	0	0	0	0
	M36	33325	14.296	138.98	0.25711	93.7737	13.4377712	0	0	0.107	0.0496	0.91589	0.00293
	U36	723.01	0.3102	75.7202	0.14008	11.55	1.655115	0.52776	0.011083	0.078	0.0362	0.29418	0.00094
	L38	92764	39.796	873.339	1.61568	19.1732	2.74751956	0	0	0	0	0	0

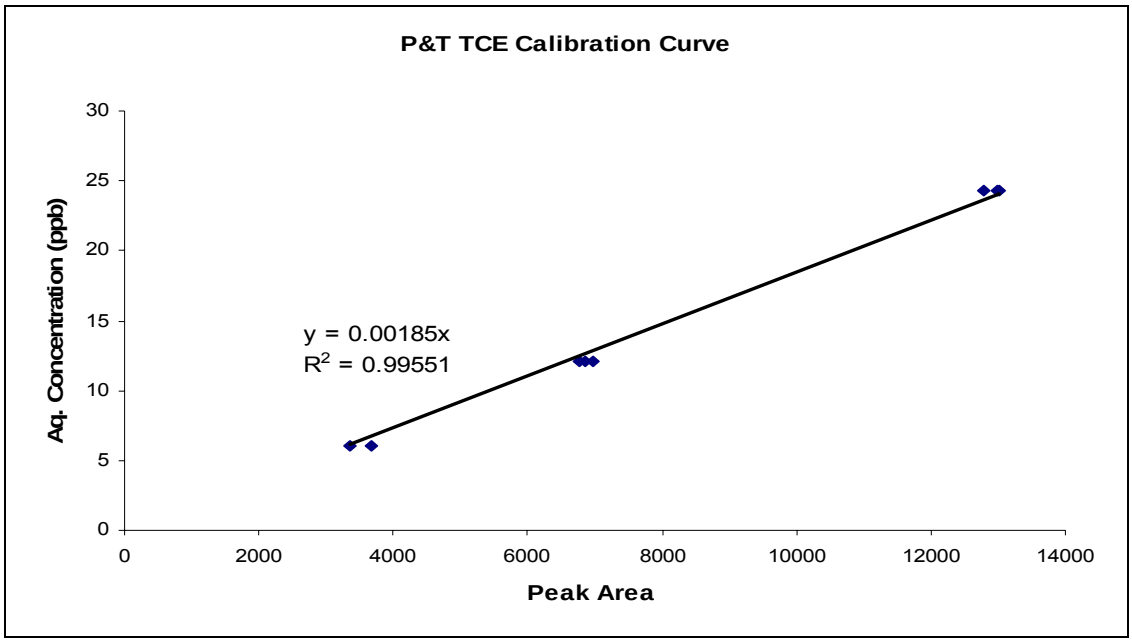
Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	M38	530.98	0.2278	31.4203	0.05813	406.527	58.2553191	0.63943	0.013428	0.162	0.0753	0.21684	0.00069
	U38	496.43	0.213	21.3169	0.03944	15.1166	2.16620878	0	0	0.052	0.0243	0.19521	0.00062
	L40	95248	40.861	345.351	0.6389	4.10094	0.5876647	0	0	0	0	0	0
	M40	25329	10.866	1029.86	1.90524	411.392	58.9524736	0	0	0.599	0.2778	0.27569	0.00088
	U40	21830	9.3652	613.807	1.13554	595.878	85.3893174	0	0	0.22	0.1021	0.37335	0.00119
	L45	93510	40.116	437.878	0.81007	15.9762	2.28938946	0	0	0	0	0	0
	M45	543.18	0.233	26.5897	0.04919	193.537	27.7338521	0	0	0.396	0.1835	0.32329	0.00103
	U45	474.65	0.2036	43.7356	0.08091	43.8588	6.28496604	0	0	0.138	0.0642	0.31208	0.001
12/15/2006	INF1	108375	46.493	177.633	0.32862	5.49186	0.78698354	0	0	0	0	0	0
	INF2	109267	46.876	181.769	0.33627	0	0	0	0	0	0	0	0
	L47	47303	20.293	1965.47	3.63612	56.5765	8.10741245	0	0	0.095	0.0441	0	0
	M47	259.29	0.1112	39.8712	0.07376	65.1138	9.33080754	0	0	0.09	0.0416	0.22347	0.00072
	U47	191.53	0.0822	14.2722	0.0264	3.80566	0.54535108	0	0	0	0	0.24815	0.00079
	L50	91926	39.436	691.99	1.28018	21.9233	3.14160889	0	0	0	0	0.02481	7.9E-05
	M50	356.17	0.1528	17.8409	0.03301	18.7349	2.68471117	0	0	0	0	0.2786	0.00089
	U50	163.2	0.07	12.6762	0.02345	9.09762	1.30368895	0	0	0	0	0.1378	0.00044
	L52	89884	38.56	608.221	1.12521	24.0795	3.45059235	0	0	0.034	0.0159	0	0
	M52	415.62	0.1783	18.6347	0.03447	55.01981	7.88433877	0	0	0.272	0.1264	0.34648	0.00111
	U52	377.26	0.1618	20.6252	0.03816	26.654	3.8195182	0	0	0.398	0.1849	0.19008	0.00061
	L57	79179	33.968	965.64	1.78643	27.4602	3.93504666	0	0	0.055	0.0254	0	0
	M57	545.47	0.234	19.5645	0.03619	157.34	22.546822	0	0	0.563	0.2613	0.29531	0.00095
	U57	210.02	0.0901	81.3328	0.15047	89.1232	12.7713546	0	0	0.576	0.2671	0.30232	0.00097
	L59	90709	38.914	465.936	0.86198	8.93338	1.28015335	0	0	0	0	0	0
	M59	467.55	0.2006	20.1138	0.03721	67.7765	9.71237245	0	0	0.107	0.0496	0.25124	0.0008
	U59	441.96	0.1896	23.6119	0.04368	185.01	26.511933	0	0	0.082	0.0378	0.25705	0.00082
	L62	71491	30.67	1359.09	2.51432	47.9781	6.87526173	0	0	0	0	0	0
	M62	506.17	0.2171	275.852	0.51033	163.018	23.3604794	0	0	1.239	0.5748	0.20351	0.00065
	U62	401.52	0.1722	21.2461	0.03931	7.76443	1.11264282	0	0	0.223	0.1035	0.30819	0.00099
	L64	92474	39.671	485.062	0.89736	6.42201	0.92027403	0	0	0	0	0	0
	M64	794.34	0.3408	512.184	0.94754	66.0772	9.46886276	0	0	0.857	0.3974	0.56201	0.0018

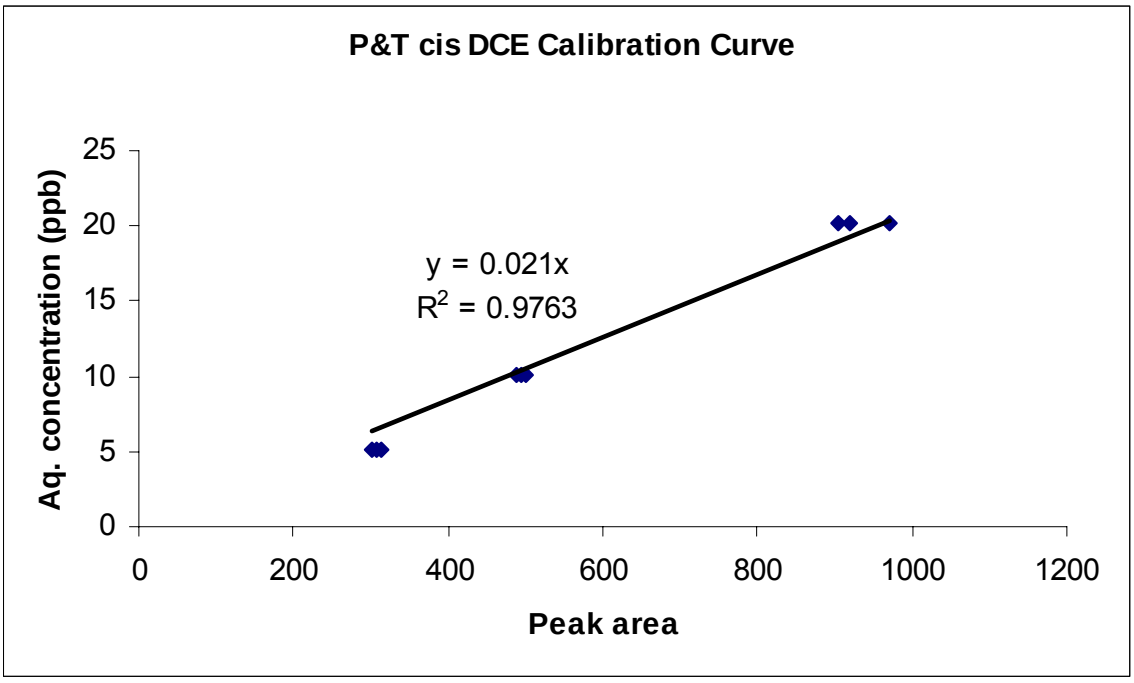
Date	Piez #	PCE Area	PCE (ppb)	TCE Area	TCE (ppb)	trans-DCE Area	trans-DCE (ppb)	cis-DCE Area	cis-DCE (ppb)	VC Area	VC (ppb)	Ethane Area	Ethane (ppb)
	U64	15837	6.7942	91.0487	0.16844	167.081	23.9427073	0	0	0.734	0.3405	0.71672	0.00229
	EFF1	15388	6.6013	478.843	0.88586	16.2121	2.32319393	0	0	0	0	0	0
	EFF2	15047	6.4553	459.161	0.84945	19.9231	2.85498023	0	0	0	0	0.02759	8.8E-05

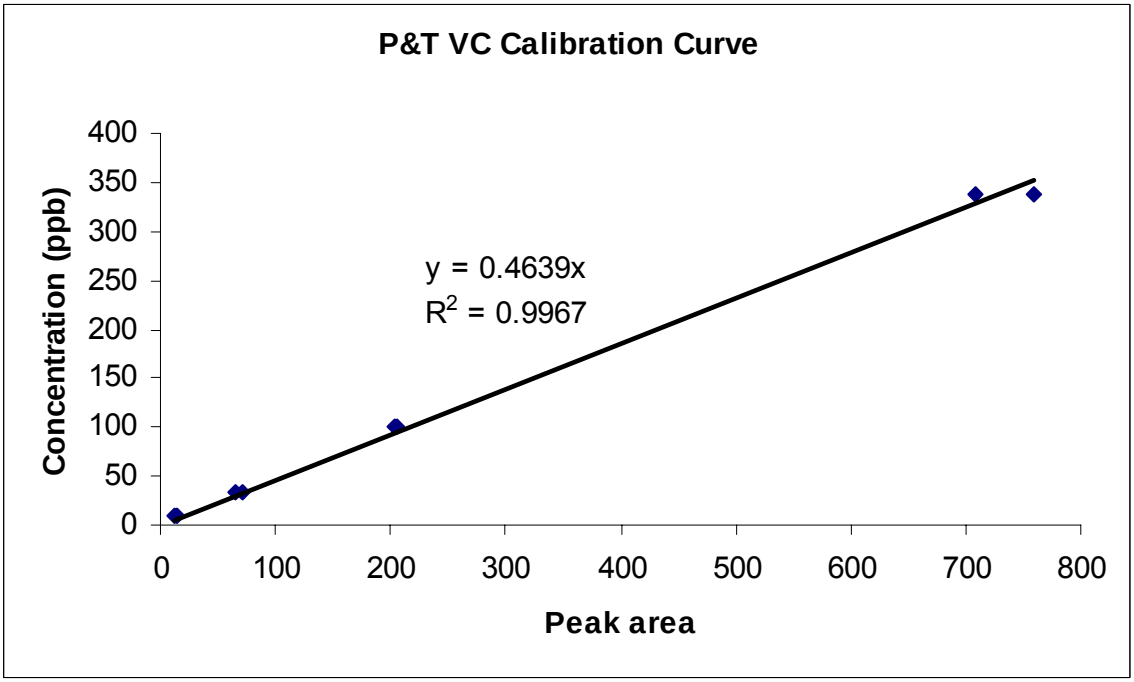
Appendix B

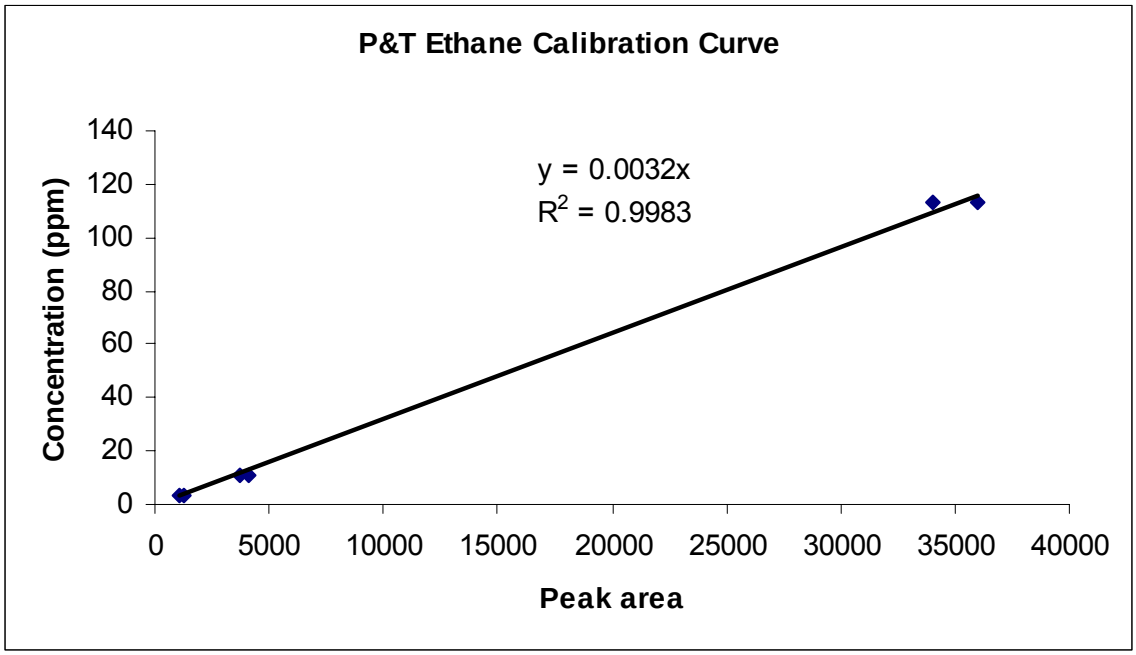
Calibration Curves

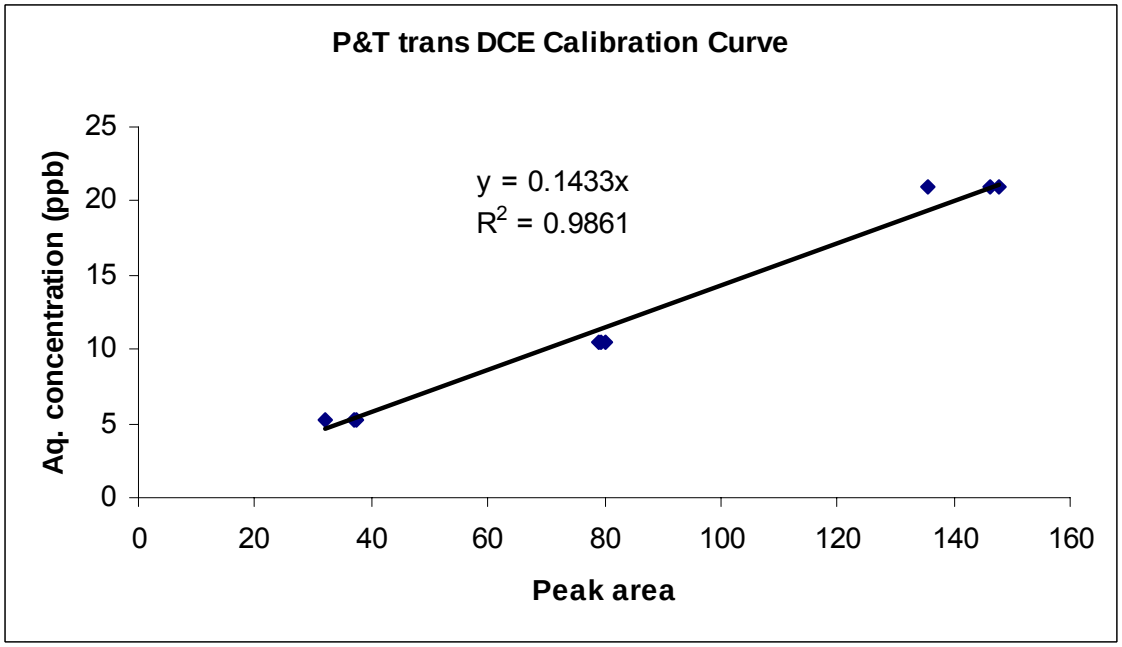





P&T cis DCE Calibration Curve
Aq. concentration (ppb)
25
20
15
10
5
0
y = 0.021x
R2 = 0.9763
0
200
400
600
800
1000
1200
Peak area


P&T VC Calibration Curve
Concentration (ppb)
400
350
300
250
200
150
100
50
0
y = 0.4639x
R2 = 0.9967
0
100
200
300
400
500
600
700
800
Peak area


P&T Ethane Calibration Curve
y = 0.0032x
R2 = 0.9983
Concentration (ppm)
Peak area
0
20
40
60
80
100
120
140
0
5000
10000
15000
20000
25000
30000
35000
40000


P&T trans DCE Calibration Curve
y = 0.1433x
R2 = 0.9861
Aq. concentration (ppb)
Peak area
0
5
10
15
20
25
0
20
40
60
80
100
120
140
160

Appendix C

Field Parameters

Date	Piez #	T (°C)	pH	Cond (µS)
9/14/2006	2L	21.3	6.85	194.9
	2M	23.6	6.75	325
	2U	24.7	7.07	387
	4L	21.2	6.82	188.9
	4M	22.8	6.81	194.8
	4U	27.3	6.85	312
	14L	20.9	6.88	191.6
	14M	23.7	6.75	340
	14U	26	6.89	320
	16L	23.9	7	290
	16M	25	6.65	357
	16U	26.9	6.74	324
	26L	21.5	7	195.7
	26M	24.2	6.93	388
	26U			
	28L	21.4	7	189.1
	28M	23.2	6.85	321
	28U	22.9	6.9	343
	Inf	18.1	7.14	311
	Eff	22	7.1	277
9/19/2006	28L	16.9	6.92	148.7
	28M	17.7	6.71	171.3
	28U	17.6	6.85	168.4
	38L	17	7.04	152.4
	38M	17.6	6.8	191.8
	38U	17.4	7.14	162.4
	40L	17.7	7.1	155.1
	40M	18.3	7.06	168.6
	40U	17.9	7.1	174
	50L	17.4	7.05	157.1
	50M		6.86	
	50U	18.6	6.99	197
	52L	17.7	7.05	155
	52M	18.6	6.98	289
	52U	18.5	7.04	168.5
	62L	18.3	7.03	163
	62M	18.7	7.1	166.2
	62U	18.4	7.18	356
	64L	18.5	7.17	162.7

Date	Piez #	T (°C)	pH	Cond (µS)
	64M	20.1	7.22	173.5
	64U	19.5	7.24	180.6
	9L	18.1	6.97	167.5
	9M	18.8	6.96	166.2
	9U	19.7	6.96	192.9
	11L	18.8	6.88	167.1
	11M	20	6.93	192.2
	11U	19.9	7.04	195
	Inf	15.7	7.08	153.1
	Eff	18.2	7.02	161.9
9/25/2006	21L	16.6	6.87	379
	21M	16.9	6.66	668
	21U	16.5	6.9	657
	23L	16.2	6.84	361
	23M	16.7	6.8	374
	23U	16.2	6.85	547
	33L	16.3	6.88	353
	33M	16.1	6.96	378
	33U	15.6	6.9	366
	36L	16.3	6.97	333
	36M	16.4	6.92	338
	36U	16.1	6.91	514
	45L	16	6.96	338
	45M	16.1	6.86	402
	45U	15.2	7.04	369
	47L	16.1	7.02	333
	47M	16.2	6.95	434
	47U	15.6	7	709
	57L	16.2	7.03	332
	57M	16.1	6.95	373
	57U	15.7	7.1	384
	59L	16.5	7.04	326
	59M	16	7.07	370
	59U	15.8	7.17	398
	Inf	15.2	7.11	307
	Eff	15.8	7.17	317

September Averages	
T (°C) L-Layer	18.59907
pH L-Layer	6.966528
Cond (µS) L-Layer	237.1583
T (°C) M-Layer	19.59583
ph M-Layer	6.881343
Cond (µS) M-Layer	309.3139
T (°C) U-Layer	20.00287
ph U-Layer	6.977917
Cond (µS) U-Layer	343.2074
T (°C) Inf	16.33333
pH Inf	7.11
Cond (µS) Inf	257.0333
T (°C) Eff	18.66667
pH Eff	7.096667
Cond (µS) Eff	251.9667

Date	Piez #	T (°C)	pH	Cond (µS)
10/9/2006	2L	19	6.8	245
	2M	19.6	6.7	422
	2U	19.1	6.85	220
	4L	18.8	6.8	245
	4M	18.9	6.72	239
	4U	19.5	6.85	236
	14L	19.5	6.92	256
	14M	20.6	6.79	294
	14U	20.5	6.85	299
	16L	20.2	6.99	271
	16M	21.5	6.7	330
	16U	21.2	6.82	285
	26L	20.4	7	262
	26M	21.6	6.85	332
	26U	21	7.02	309
	28L	20.2	6.97	267
	28M	20.9	6.82	301
	28U	21	6.89	296
	38L	21	7.04	284
	38M	21.6	6.87	330
	38U	22.7	7.05	318
	40L	21.7	7.15	283
	40M	23	7.03	341
	40U	22.4	7.08	333
	50L	21.5	7.05	279
	50M	23.7	6.85	357
	50U	22.8	6.95	335
	52L	22.5	7.07	260
	52M	22.5	6.99	315
	52U	24.4	7.19	305
	62L	22.2	7.07	270

Date	Piez #	T (°C)	pH	Cond (µS)
	62M	24.5	7.07	294
	62U	24.4	7.26	340
	Inf	17.7	7.21	200
	Eff	23	7.27	275
	64L	18.5	7.17	162.7
	64M	20.1	7.22	173.5
	64U	19.5	7.24	180.6
	9L	18.1	6.97	167.5
	9M	18.8	6.96	166.2
	9U	19.7	6.96	192.9
	11L	18.8	6.88	167.1
	11M	20	6.93	192.2
	11U	19.9	7.04	195
	21L	16.6	6.87	379
	21M	16.9	6.66	668
	21U	16.5	6.9	657
	23L	16.2	6.84	361
	23M	16.7	6.8	374
	23U	16.2	6.85	547
	33L	16.3	6.88	353
	33M	16.1	6.96	378
	33U	15.6	6.9	366
	36L	16.3	6.97	333
	36M	16.4	6.92	338
	36U	16.1	6.91	514
	45L	16	6.96	338
	45M	16.1	6.86	402
	45U	15.2	7.04	369
	47L	16.1	7.02	333
	47M	16.2	6.95	434
	47U	15.6	7	709
	57L	16.2	7.03	332
	57M	16.1	6.95	373
	57U	15.7	7.1	384
	59L	16.5	7.04	326
	59M	16	7.07	370
	59U	15.8	7.17	398
	Inf	15.2	7.11	307
	Eff	15.8	7.17	317

October Averages	
T (°C) L-Layer	18.45568
pH L-Layer	6.969261
Cond (µS) L-Layer	305.0057
T (°C) M-Layer	18.99261
ph M-Layer	6.874943
Cond (µS) M-Layer	370.1534
T (°C) U-Layer	18.78239
ph U-Layer	6.983239
Cond (µS) U-Layer	395.4091
T (°C) Inf	16.45
pH Inf	7.16
Cond (µS) Inf	253.5

T (°C) Eff	19.4
pH Eff	7.22
Cond (µS) Eff	296

Date	Piez #	T (°C)	pH	Cond (µS)
11/9/2006	64L	16.5	6.5	422
	64M	16.4	6.55	256
	64U	16.6	6.7	283
	9L	15.4	6.6	272
	9M	14.7	6.63	423
	9U	14.3	6.69	310
	11L	14.8	6.63	269
	11M	14.2	6.5	295
	11U	14.2	6.67	302
	21L	15.5	6.67	271
	21M	14.7	6.4	519
	21U	14.7	6.6	285
	23L	17	6.7	277
	23M	16.1	6.52	275
	23U	15.9	6.52	273
	33L	16.8	6.6	273
	33M	16.8	6.53	476
	33U	15.9	6.6	274
	36L	18.1	6.7	279
	36M	18	6.6	278
	36U	17.8	6.7	255
	45L	16.6	6.65	278
	45M	16.1	6.45	321
	45U	16.4	6.75	306
	47L	17.8	6.57	296

Date	Piez #	T (°C)	pH	Cond (µS)
	47M	17.4	6.47	375
	47U	17.2	6.6	369
	57L	17	6.53	284
	57M	16.9	6.35	336
	57U	16.3	6.7	317
	59L	16.7	6.65	280
	59M	16	6.65	310
	59U	16.4	6.8	334
	Inf	15.5	6.63	480
	Eff	17.2	6.6	285
11/17/2006	2L	11.7	7.08	201
	2M	10.2	7.05	209
	2U	9.7	7.38	210
	4L	12.6	6.95	194
	4M	11.1	6.9	189
	4U	10.2	7.01	188.2
	14L	12.6	6.86	205
	14M	11.2	6.72	209
	14U	10.5	6.8	230
	16L	13.7	6.98	218
	16M	11.8	6.7	250
	16U		6.8	
	26L	13.5	6.98	233
	26M	11.7	6.92	283
	26U	11.5	7.07	265
	28L	14.2	6.97	232
	28M	13	6.8	255
	28U	13.7	7.11	272
	38L	13.7	6.96	229
	38M	11.6	6.7	278
	38U	11.1	7.05	261
	40L	13.4	6.95	235
	40M	12.7	6.85	238
	40U	12.4	7	258
	50L	13.1	6.9	220
	50M	11.6	6.8	240
	50U	11.3	7	245
	52L	13.3	7	230
	52M	12	6.7	255
	52U	11	6.8	255
	62L	12.9	6.8	218
	62M	11.5	6.9	263

Date	Piez #	T (°C)	pH	Cond (µS)
	62U	11.4	6.8	235
	Inf	13.5	7.59	205
	Eff	11.1	6.75	260

November Averages

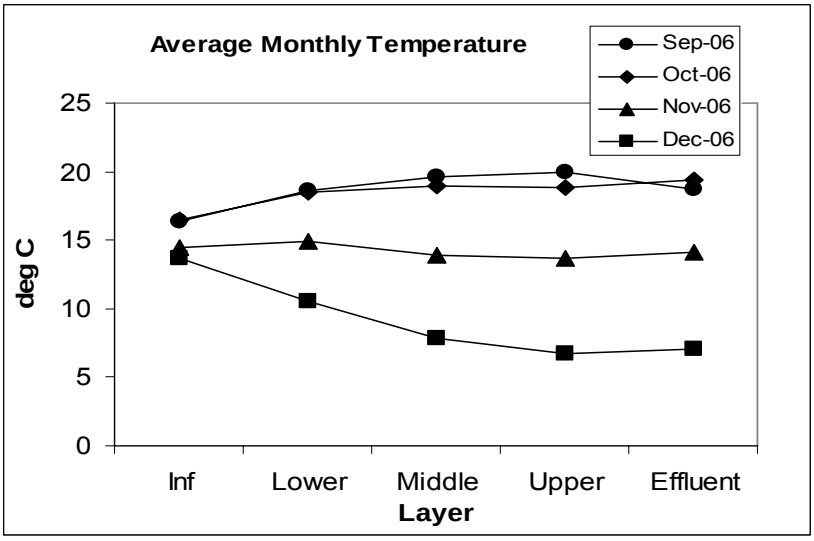
T (°C) L-Layer	14.85909
pH L-Layer	6.783182
Cond (µS) L-Layer	255.2727
T (°C) M-Layer	13.89545
ph M-Layer	6.667727
Cond (µS) M-Layer	296.9545
T (°C) U-Layer	13.62636
ph U-Layer	6.825
Cond (µS) U-Layer	271.3236
T (°C) Inf	14.5
pH Inf	7.11
Cond (µS) Inf	342.5
T (°C) Eff	14.15
pH Eff	6.675
Cond (µS) Eff	272.5

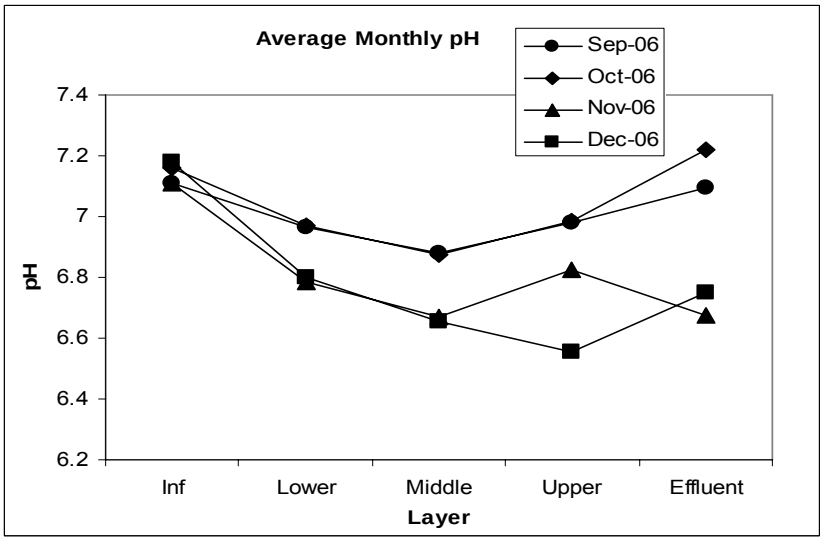
Date	Piez #	T (°C)	pH	Cond (µS)
12/11/2006	L2	10	6.97	146
	M2	7.2	6.6	150
	U2	frozen		
	L4	10	6.82	159
	M4	7.7	6.74	150
	U4	6.4	6.5	153
	L9	10.4	6.92	165
	M9	9.1	6.93	165
	U9	7.5	6.77	180
	L11	9.8	6.8	165
	M11	7	6.78	178
	U11	5.7	7	185
	L14	10.5	6.79	175
	M14	7.8	6.75	164
	U14	6.2	6.63	180
	L16	10.2	6.6	178

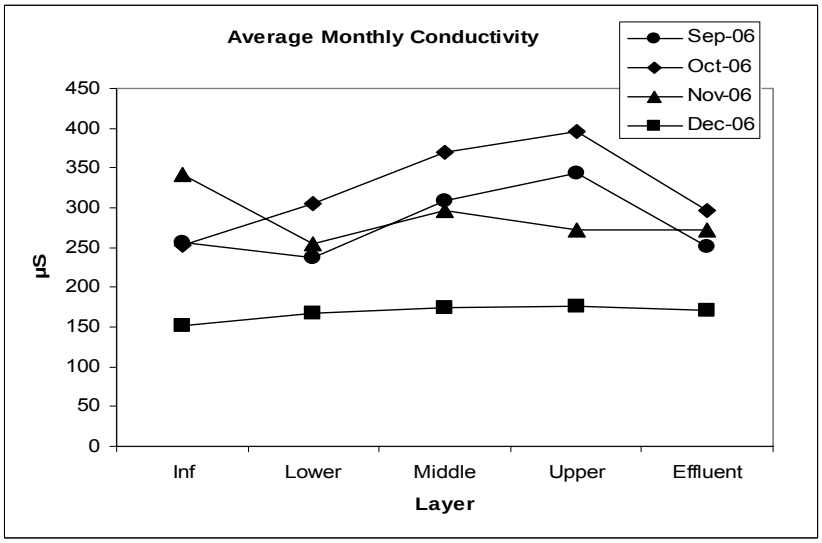
Date	Piez #	T (°C)	pH	Cond (µS)
	M16	7.2	6.3	192
	U16	6.8	5.5	171.1
	L21	10.5	6.7	175
	M21	8.2	6.35	204
	U21	7.2	5.8	190
	INF	13.5	7.26	153
	EFF	7.4	6.8	171
12/13/2006	L23	10.7	6.82	158
	M23	7.9	6.74	162
	U23	6.8	6.5	173
	L26	10.6	6.92	161
	M26	8	6.93	165
	U26	6.9	6.77	155
	L28	10.5	6.8	165
	M28	7.8	6.78	165
	U28	7	7	180
	L33	10.8	6.79	165
	M33	7.9	6.75	178
	U33	6.6	6.63	185
	L36	10.9	6.6	175
	M36	8.1	6.3	164
	U36	6.6	6.6	180
	L38	10.6	6.7	178
	M38	8	6.35	192
	U38	6.7	6.4	175
	L40	10.7	6.8	175
	M40	7.8	6.7	206
	U40	6.8	6.6	191
	L45	10.2	7	162
	M45	7.7	6.7	187
	U45	6.9	6.5	165
12/14/2006	L47	10.9	6.8	160
	M47	8	6.7	163
	U47	6.8	6.54	174
	L50	10.8	6.89	164
	M50	8.1	6.95	160
	U50	7.1	6.74	152
	L52	10.5	6.82	164
	M52	8	6.81	165
	U52	7.2	7	178
	L57	11	6.78	164
	M57	7.9	6.68	181

Date	Piez #	T (°C)	pH	Cond (µS)
	U57	6.7	6.64	185
	L59	11.2	6.68	170
	M59	8.3	6.4	165
	U59	6.8	6.65	181
	L62	10.6	6.77	177
	M62	8.1	6.38	187
	U62	6.9	6.45	173
	L64	10.8	6.87	172
	M64	7.9	6.75	187
	U64	6.9	6.65	190
	INF	13.8	7.1	152
	EFF	6.8	6.7	170

December Averages	
T (°C) L-Layer	10.55119
pH L-Layer	6.801726
Cond (µS) L-Layer	166.9345
T (°C) M-Layer	7.895238
ph M-Layer	6.653036
Cond (µS) M-Layer	173.9345
T (°C) U-Layer	6.778373
ph U-Layer	6.552937
Cond (µS) U-Layer	176.0532
T (°C) Inf	13.65
pH Inf	7.18
Cond (µS) Inf	152.5
T (°C) Eff	7.1
pH Eff	6.75
Cond (µS) Eff	170.5


Average Monthly Temperature
Sep-06
Oct-06
Nov-06
Dec-06
25
20
15
10
5
0
deg C
Inf
Lower
Middle
Upper
Effluent
Layer


Average Monthly pH
Sep-06
Oct-06
Nov-06
Dec-06
7.4
7.2
7
6.8
6.6
6.4
6.2
pH
Inf
Lower
Middle
Upper
Effluent
Layer


Average Monthly Conductivity
Sep-06
Oct-06
Nov-06
Dec-06
450
400
350
300
250
200
150
100
50
0
µS
Inf
Lower
Middle
Upper
Effluent
Layer

Bibliography

Agency for Toxic Substances and Disease Registry (ATSDR). 1997. *ToxFAQs for Tetrachloroethylene*. http://www.atsdr.cdc.gov/tfacts18.html.

Agency for Toxic Substances and Disease Registry (ATSDR). 2003. *ToxFAQs for Trichloroethylene*. http://www.atsdr.cdc.gov/tfacts19.html.

Anderson, T.A., E.A. Guthrie, and B.T. Walton (1993). "Bioremediation." *Environmental Science and Technology*. 27(13): 2630-2636.

Bouwer, E.J. 1994. "Bioremediation of chlorinated solvents using alternate electron acceptors." *Handbook of Bioremediation*, edited by R.D. Norris et al. pp. 149-175, A.F. Lewis, New York.

Bradley, P.M., and F.H. Chapelle. 1996. "Anaerobic mineralization of vinyl chloride in Fe(III)-reducing, aquifer sediments." *Environmental Science and Technology*, 30:2084-2086.

Bradley, P.M. 2000. "Microbial Degradation of Chloroethenes in Groundwater Systems." *Hydrogeology Journal*, Vol. 8:104-111.

Bradley, P.M., and F.H. Chapelle. 1997. "Kinetics of DCE and VC mineralization under methanogenic and Fe(III)-reducing conditions." *Environmental Science and Technology*, 31:2692-2696.

Bugg, Bradley M. *An Anion Characterization of a Constructed Wetland Used For Chlorinated Ethene Remediation.* MS Thesis, AFIT/GEE/ENV/02M-01. Graduate School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson Air Force Base OH, March 2002.

Chapelle, Francis H. *Ground-Water Microbiology and Geochemistry.* New York: John Wiley and Sons, Inc., 2001.

Clemmer, Nathan D. *Characterization of Chlorinated Solvent Degradation in a Constructed Wetland*. MS Thesis, AFIT/GEE/ENV/03-3. Graduate School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson Air Force Base OH, March 2003.

Crank, John. *The Mathematics of Diffusion, Second Edition.* Oxford University Press, New York, 1975.

Davis, L., S. Vanderhoof, J. Dana, K. Selk, K. Smith, G. Gophen, and L. Erickson (1998)

"Movement of Chlorinated Solvents and Other Volatile Organics through Plants Monitored by Fourier Transform Infrared (FT-IR) Spectrometry," *Journal of Hazardous Substances Research.* 1(4): 1-26.

DiStefano, Thomas D., James M. Gossett, and Stephen H. Zinder. 1991. "Reductive Dechlorination of High Concentrations of Tetrachloroethene to Ethene by an Anaerobic Enrichment Culture in the Absence of Methanogenesis." *Applied and Environmental Microbiology,* 57(8): 2287-2292.

Entingh, Andrew C. *Groundwater Flow Through a Constructed Treatment Wetland*. MS Thesis, AFIT/GEE/ENV/02M-3. Graduate School of Engineering and Management, Air Force Institute of Technology, Wright-Patterson AFB OH, March 2002.

Flynn, Shannon J., Frank E. Löffler, and James M. Tiedje. 2000. "Microbial Community Changes Associated with a Shift from Reductive Dechlorination of PCE to Reductive Dechlorination of cis-DCE and VC." *Environmental Science and Technology,* 34: 1056-1061.

Halogenated Solvents Industry Alliance (HSIA). 2001. Trichloroethylene White Paper. Washington, DC. (http://www.hsia.org/white_papers/tri%20wp.htm).

Halogenated Solvents Industry Alliance (HSIA). 2005. Perchloroethylene White Paper. Arlington, VA. (http://www.hsia.org/white_papers/tri%20wp.htm).

Helfferich, F. 1966. *Ion Exchange, A Series of Advances.* Marcel Dekker, New York.

Hesslein, R. H. 1976. "An in situ sampler for close interval pore water studies." *Limnology and Oceanography*, 21:912-914.

Huling, Scott G. and James W. Weaver. *Ground Water Issue Dense Nonaqueous PhaseLiquids.* EPA/540/4-91-002. U.S. Environmental Protection Agency, Washington, D. C., 1991.

Interstate Technology and Regulatory Council (ITRC). "DNAPL Source Reduction: Facing the Challenge." April 2002.

Interstate Technology and Regulatory Council (ITRC). "Overview of In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones." October 2005.

Kassenga, Gabriel, John H. Pardue, William M. Moe, and Kimberly S. Bowman. 2004. "Hydrogen Thresholds as Indicators of Dehalorespiration in Constructed Treatment Wetlands." *Environmental Science and Technology*, 38:1024-1030.

LaForce, Matthew J., Collen M. Hansel, and Scott Fendorf. "Constructing Simple Wetland Sampling Devices." *Soil Science of America Journal,* 64: 809-811 (2000).

Laor, Yael, Daniel Ronen, and Ellen R. Graber. "Using a Pasive Multilayer Sampler for Measuring Detailed Profiles of Gas-Phase VOCs in the Unsaturated Zone." *Environmental Science and Technology.* 37, 352-360.

Lee, M.D., J.M. Odom, and R.J. Buchanan Jr. "New Perspectives on Microbial Dehalogenation of Chlorinated Solvents: Insights from the Field." *Annual Review of Microbiology*, 52: 423-451 (1998).

Li, Y.H., and S. Gregory (1974). "Diffusion of ions in sea water and in deep-sea sediments." *Geochimica et Cosmochimica Acta*, 38, 703-714.

Lorah, Michelle M., and Lisa D. Olsen (1999a). "Natural Attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland: Field evidence of anaerobic biodegradation." *Water Resources Research*, 35 (12), 3811-3827.

Lorah, Michelle M., and Lisa D. Olsen (1999b). "Degradation of 1,1,2,2-Tetrachloroethane in a Freshwater Tidal Wetland: Field and Laboratory Evidence." *Environmental Science and Technology.* 33(2), 227-234.

Lorah, Michelle M., David R. Burris, Linda Jo Dyer, and Christopher P. Antworth. *Natural Attenuation of Chlorinated Solvent Ground-Water Plumes Discharging into Wetlands.* U.S. Geological Survey and Air Force Research Laboratory. September 2003.

Maymo-Gatell, Xavier, Y.T. Chen, James M. Gossett, and Stephen H. Zinder. 1997. "Isolation of a Bacterium that Reductively Dechlorinates Tetrachloroethene to Ethene." *Science*, 276:1568-1571.

Maymo-Gatell, X., Gossett, J.M., and Zinder, S.H. 1997a. "*Dehalococcus Ethenogenes* Strain 195: *Ethene Production from Halogenated* Aliphatics." *In Situ and On-Site Bioremediation,* Vol. 3. p. 23. Alleman, B.C. and A. Leeson (Eds.). Battelle Press, Columbus, OH.

Maymo-Gatell, Xavier, Timothy Anguish, and Stephen H. Zinder. 1999. "Reductive Dechlorination of Chlorinated Ethenes and 1,2 Dichloroethane by "*Dehalococcoides ethenogenes"* 195." *Applied and Environmental Microbiology, 65(7):3108-3113.*

McCarty, P.L., and L. Semprini. "Ground-water treatment for chlorinated solvents." *Handbook of Bioremediation.* E.d. R.D. Norris et al., pp. 87-116. A.F. Lewis, New York, 1994.

McCutcheon, S. and J. Schnoor (eds.) (2003). *Phytoremediation Transformation and Control of Contaminants.* John Wiley & Sons, Inc., Hoboken, New Jersey.

Moore, James A. 1993. "Using Constructed Wetlands to Improve Water Quality." *Oregon State University Extension Service.* EC1408. Agricultural Communications, Oregon State University, Corvallis, OR. http://extension.oregonstate.edu/catalog/html/ec/ec1408/.

Narayanan, M., N. Russell, L. Davis, and L. Erickson (1999). "Fate and Transport of Trichloroethylene in a Chamber with Alfalfa Plants," *International Journal of Phytoremediation.* 1: 387-411.

Office of the Deputy Under Secretary of Defense (Installations and Environment) (DoD). 2005. *Defense Environmental Programs Fiscal Year 2005, Annual Report to Congress.*

Opperman, Bryan C. Determination of Chlorinated Solvent Contamination in an Upward Flow Constructed Wetland. MS Thesis, AFIT/GEE/ENV/02M-07. Graduate School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson Air Force Base OH, March 2002.

Pankow, James F. and John A. Cherry. *Dense Chlorinated Solvent and Other DNAPLs in Groundwater.* Portland, OR: Waterloo Press, 1996.

Parsons Corporation. 2004. "Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents." Prepared for Air Force Center of Environmental Excellence, Naval Facilities Engineering Service Center, and Environmental Security Technology Certification Program.

Pivetz, Bruce, *Phytoremediation of Contaminated Soil and Ground Water at Hazardous Waste Sites*, EPA/540/S-01/500, U.S. Environmental Protection Agency, Washington, D.C., 2001.

Ramsar Convention on Wetlands. 2005. *World Wetland Day – 2005.* March 18, 2005. http://www.ramsar.org/wwd/5/wwd2005_rpt_canada3.htm.

Remediation Technologies Development Forum (RTDF) Phytoremediation of Organics Action Team, Chlorinated Solvents Workgroup. "Evaluation of Phytoremediation for Management of Chlorinated Solvents In Soil and Groundwater." January 2005.

Sobolewski, Teresa T. *Characterization of Chlorinated Solvent Degradation Profiles Due to Microbial and Chemical Processes in a Constructed Wetland.* MS Thesis, AFIT/GEM/ENV/04M-17. Graduate School of Engineering and Management,

Air Force Institute of Technology (AU), Wright-Patterson Air Force Base OH, March 2004.

Sullivan, Thomas F.P., Ed. *Environmental Law Handbook* 8th ed. Lanham, MD: Government Institutes, 2005.

United States Environmental Protection Agency (EPA). 2006a. "Consumer Factsheet on: Tetrachloroethylene." http://www.epa.gov/safewater/dwh/c-voc/tetrachl.html.

United States Environmental Protection Agency (EPA). 2006b. "Consumer Factsheet on: Trichloroethylene." http://www.epa.gov/safewater/dwh/c-voc/trichlor.html.

United States Environmental Protection Agency (EPA). 2006c. *Superfund Information System, CERCLIS Database.* http://www.epa.gov/superfund/sites/cursites/.

United States Environmental Protection Agency (EPA). 2006d. *Toxic Release Inventory (TRI) Program, OSHA Carcinogens.* http://www.epa.gov/tri/chemical/oshacarc.htm.

United States Environmental Protection Agency (EPA). 2006e. *Drinking Water Contaminants, List of Contaminants and their MCLs.* http://www.epa.gov/safewater/contaminants/index.html.

United States Environmental Protection Agency (EPA). "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites." OSWER Directive 9200.4-17P, 1999.

Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. "Transformation of halogenated aliphatic compounds." *Environmental Science and Technology* 21:722-736.

Walton, Barbara T., Todd A. Anderson. 1990. "Microbial Degradation of Trichloroethylene in the Rhizosphere: Potential Application to Biological Remediation of Waste Sites." *Applied and Environmental Microbiology,* 56(4): 1012-1016.

Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, J.E. Hansen, P. Haas, and F.H. Chapelle. *Technical Protocol for evaluating natural attenuation of chlorinated solvents in ground water*, EPA/600/R-98/128, U.S. Environmental Protection Agency, Washington, D. C., 1998.

Whitkamp, M., and M. L. Frank. 1969. "Evolution of carbon dioxide from litter, humus and subsoil of a pine stand." *Pedobiologia* 9:358-365.

Yang, Yanru and Perry L. McCarty. "Competition for Hydrogen within a Chlorinated Solvent Dehalogenating Anaerobic Mixed Culture." *Environmental Science and Technology*, 32:3591-3597 (1998).

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From – To)*
23-06-2007	**Master's Thesis**	August 2005 – March 2007

4. TITLE AND SUBTITLE

Characterization of Chlorinated Ethene Degradation in a Vertical Flow Constructed Wetland

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Waldron, James M., Civ, USAF

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S)
Air Force Institute of Technology
Graduate School of Engineering and Management (AFIT/EN)
2950 Hobson Way
WPAFB OH 45433-7765

8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEM/ENV/07-M17

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

N/A

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Chlorinated solvents, including perchloroethene (PCE) and trichlorethene (TCE), are among the most common groundwater contaminants found in the United States. The use of constructed wetlands has shown promise as an effective and less costly alternative for the treatment of chlorinated solvent contaminated groundwater.

This study characterized and evaluated the concentration of chlorinated ethenes within a vertical flow constructed wetland, fed with PCE contaminated groundwater, at Wright-Patterson Air Force Base (WPAFB), Ohio. Chlorinated ethene concentrations were characterized within three distinct layers of the wetland cell, as well as within the influent, and effluent. In addition, a pore-water sampler prototype was designed and developed for this research effort in order to obtain a more detailed contaminant profile.

PCE concentrations declined from an average of 46.5 μg/L in the influent to an average of 0.5 μg/L in the upper layer, a 98.9% decrease. The chlorinated ethene concentration profiles indicate that the lower half of the wetland provides favorable conditions for the complete anaerobic reductive dechlorination of the PCE. Within the upper half of the wetland, contaminant profiles indicate dominant degradation processes other than anaerobic reductive dechlorination, possibly including aerobic or anaerobic oxidation or direct volatization.

15. SUBJECT TERMS

Chlorinated Ethenes, Constructed Wetlands, Anaerobic Reductive Dechlorination, Remediation

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
REPORT	ABSTRACT	c. THIS PAGE			Charles A. Bleckmann, Civ, USAF (ENV)
U	U	U	UU	132	19b. TELEPHONE NUMBER *(Include area code)* (937) 255-3636, ext 4721; e-mail: charles.bleckmann@afit.edu