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**DETERMINATION OF CHLORINATED SOLVENT
CONTAMINATION IN AN UPWARD FLOW
CONSTRUCTED WETLAND**

THESIS

Bryan C. Opperman, Captain, USAF

AFIT/GEE/ENV/02M-07

**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY**

Wright-Patterson Air Force Base, Ohio

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AFIT/GEE/ENV/02M-07

DETERMINATION OF CHLORINATED SOLVENT CONTAMINATION IN AN
UPWARD FLOW CONSTRUCTED WETLAND

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Presented to the Faculty

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In Partial Fulfillment of the Requirements for the

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Bryan C. Opperman, B.S.

Captain, USAF

March 2002

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UPWARD FLOW CONSTRUCTED WETLAND

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Bryan C. Opperman

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Abstract

The purpose of this study is to determine chlorinated solvent contamination levels in an upward flow constructed wetland at Wright-Patterson Air Force Base (WPAFB), Ohio. A stratified grid sampling methodology will be used in sampling the contaminated groundwater. Analysis will be accomplished by means of purge-and-trap gas chromatography. The contaminant concentration levels will be used to enhance the design and construction of man-made wetlands used to remove chlorinated solvents from aquifers.

PCE levels declined from an average of 33.97 ppb in the inflow stream to an average of 3.65 ppb in the upper layer, a 91% reduction. High concentrations occurred in areas where high hydraulic pressure gradients and hydraulic conductivities combined to allow contaminated water to migrate to the upper layers of the wetland with minimal contact time for reduction. Removing these areas from the data set increased the PCE reduction efficiency to nearly 98% with an upper level concentration average of 0.84 ppb. Trichloroethene (TCE) inflow rates averaged 0.63 ppb while TCE concentrations in the upper layer averaged 0.175 ppb. TCE concentrations peaked in the middle layer of the wetland suggesting that reduction of PCE was occurring there and in the bottom layer.

DETERMINATION OF CHLORINATED SOLVENT CONTAMINATION IN AN UPWARD FLOW CONSTRUCTED WETLAND

I. Introduction

The purpose of this study is to determine the levels of chlorinated solvent contamination in an upward flow constructed wetland at Wright Patterson Air Force Base (WPAFB), Ohio. A stratified grid sampling methodology will be used in obtaining samples of the contaminated groundwater from the wetland sediment. Analysis will be accomplished by means of a gas chromatograph programmed to specifically detect chlorinated solvents such as tetrachloroethene (PCE) and its daughter products. The effort will concentrate on determining the concentrations of chlorinated solvents at various layers of the wetland as the contaminated groundwater is pumped through the wetland sediment. These concentration levels will then be used to develop detailed models that allow for the accurate design and construction of man-made wetlands specifically designed to remove chlorinated solvents from subsurface waters.

Chlorinated solvents have a long history of use in the United States and the world. Chlorinated aliphatic compounds such as trichloroethene (TCE), trichloroethane (TCA), and tetrachloroethene (PCE), dichloroethene (DCE) and their degradation products are among the most commonly observed contaminants found in shallow ground-water systems (Chapelle, 1993). In California, for example, a water-quality survey of 7,167 water supply wells revealed that 812, or about 11%, contained measurable concentrations of organic contaminants. By far the most common contaminants found were TCE and TCA (Chapelle, 1993).

It is not surprising that widespread groundwater contamination by chlorinated solvents has occurred throughout the world. The United States (US) first began to produce the chlorinated solvent carbon tetrachloride in 1906 with PCE and TCE production beginning in 1923. Health concerns were first raised in the 1970s and have since caused a decline in the production of TCE and PCE in the US. However, the US still manufactures chlorinated solvents in large quantities. In 1986, it was estimated that PCE production was 560,000 fifty-five gallon drums while TCE production totaled 260,000 drums (Pankow and Cherry, 1996). Worldwide, the use of the chlorinated solvents TCE, PCE, and 1,1,1-trichloroethane (1,1,1-TCA) in 1994 totaled 900,000 metric tons (Leder and Yoshida, 1995). Chlorinated solvents comprise nine of the 20 most common chemicals found in Superfund sites throughout the country (National Research Council, 1997). Chlorinated solvents, and their natural transformation products represent the most prevalent organic groundwater contaminants in the country. These solvents, consisting primarily of chlorinated aliphatic hydrocarbons (CAHs), have been used widely for degreasing of aircraft engines, automobile parts, electronic components, and clothing (McCarty, 1997). Because of the heavy industrial nature of the operations occurring with typical flight line operations on Air Force bases worldwide, contamination of groundwater aquifers occurred on a widespread basis. It is estimated that over 7300 sites at over 1800 different locations owned by the Department of Defense (DoD) have groundwater that contains some type of contamination (National Research Council, 1994). The costs to clean up these contaminated aquifers is very high. It is estimated that it could take upwards of \$389 billion to remediate the contaminated groundwater and soil at DoD and several other government agencies over the next 75 years. Cost

estimates for the cleanup of all public and privately owned sites go as high as one trillion dollars (National Research Council, 1997).

PCE is used as a solvent, as a heat transfer medium, and in the manufacture of chlorofluorocarbons. It has caused cancerous tumors in laboratory animals and is a suspected human carcinogen (Masters, 1997). TCE is the most common organic water contaminant and is classified as a possible human carcinogen (Hageman et al, 2001). It has been commonly used to clean everything from electronic parts to jet engines and septic tanks. It is among the most frequently found contaminants in groundwater (Masters, 1997). 1,2-Dichloroethane is a metal degreaser used in the manufacture of a number of products including fumigants, varnish removers, and soap compounds. Although not a known carcinogen, high exposure levels can cause liver, kidney, and central nervous system damage (Masters, 1997). Vinyl Chloride (VC) is the most toxic of the chlorinated solvents. And only a few milliliters can cause death in humans. It is also a known human carcinogen and is used primarily in the production of polyvinyl chloride resins such as PVC piping (Masters, 1997). VC has been widely distributed in the environment as an original component of numerous chlorinated solvent contaminant plumes or as a significant intermediate product of reductive dehalogenation of polychlorinated ethenes under anaerobic conditions (Bradley and Chapelle, 1996).

Chlorinated solvents are released into the environment under two scenarios: 1) as relatively pure solvent mixtures that are more dense than water, or 2) as mixtures of fuel hydrocarbons and chlorinated aliphatic hydrocarbons that may or may not be more dense than water. These products are commonly referred to as non-aqueous phase liquids (NAPLs). If the NAPL is denser than water, it is referred to as a dense non-aqueous

phase liquid. IF the NAPL is less dense than water, it is referred to as a light non-aqueous phase liquid. As groundwater moves through or past the NAPL source areas, soluble constituents partition into the groundwater and create the contaminant plume (Wiedemeier et al, 1997).

Because chlorinated solvents are relatively soluble and highly volatile, the processes of dissolution, dispersion, and volatilization are significant transport mechanisms (National Research Council, 1997). The table below provides the solubilities and vapor pressures for a number of chlorinated solvents (Cohen and Mercer, 1993).

Table 1. Solubilities and Vapor Pressures of Chlorinated Solvents

Compound	Solubility (mg/L)	Vapor Pressure (mm Hg)
Methylene Chloride	20,000	349
Chloroform	8,200	160
Carbon tetrachloride	800	900
1,1-Dichloroethylene	400	495
Trans-1,2-Dichloroethylene	600	265
1,1-Dichloroethane	5,500	182
1,2-Dichloroethane	8,700	64.0
Trichloroethene	1,100	57.8
Tetrachloroethene	150	140
1,1,1-Trichloroethane	1,360	100

These solubilities are several orders of magnitude greater than current drinking water standards, thereby preventing dilution by hydrodynamic dispersion from being a viable mechanism for managing contaminated sites (National Research Council, 1997).

The National Research Council has stated that remediation can be divided into three different categories. First, technologies are available that can contain, solidify, or

stabilize the contaminant. Examples of these technologies include vitrification, in situ soil mixing, and passive-reactive barriers. These technologies are directed at decreasing the mobility and/or toxicity of the contaminant. Reducing contaminant solubility or volatility and subsurface permeability does this. Second, there are technologies that remove the contaminant from the groundwater, mobilize the contaminant and ultimately extract it from the subsurface. Examples of these technologies include air sparging, pump-and-treat systems, and soil vapor extraction. These technologies are designed to separate contaminants from geologic materials in the subsurface, mobilize them into the groundwater or air in soil pores, and extract them from the subsurface. Finally, biological and chemical reactions can be used to destroy or transform the contaminant. These biological processes are generally known as bioremediation. The goal of bioremediation is to biologically convert a hazardous contaminant such as PCE, TCE, or VC to an innocuous end product. For example, VC can be converted into ethylene, carbon dioxide and water under the proper environmental and biological conditions (Bradley and Chapelle, 1996). Both aerobic and anaerobic microorganisms are capable of using contaminants as sources of carbon and energy for growth. Examples of biological reaction technologies include biostabilization, composting, and engineered in situ bioremediation.

Using a constructed wetland to remove contaminants is a relatively new technology. The term “constructed” wetland is used to define those wetlands that are built expressly for the purposes of water quality treatment. Constructed wetlands differ from “created” wetlands in the respect that created wetlands are built primarily for habitat replacement and mitigation of destroyed wetlands. In 1973, the first intentionally

engineered, constructed wetland treatment systems in North America were constructed to remove contaminants from storm runoff and municipal runoff. Since then, wetlands have also been designed and constructed to treat process waters from industry (Kadlec and Knight, 1996).

Wetlands are defined by three primary factors. The first of these is the presence of water, either at the surface or within the root zone of the wetland plants. Another distinguishing feature of a wetland, whether natural or man-made is that the vegetation is adapted to the wet conditions (hydrophytes) and, conversely, are characterized by an absence of flooding-tolerant vegetation (Mitsch and Gosselink, 2000). The final characteristic of wetlands is the presence of hydric soil. Hydric soils are generally characterized by a lack of oxygen induced by regular and seasonal flooding. The resulting lower dissolved oxygen level results in the accumulation of organic matter in wetland soils because of a reduced level of microbial activity and organic decomposition which requires oxygen (Kadlec and Knight, 1996).

Two wetlands were constructed at WPAFB for the purpose of studying the removal of chlorinated solvent contamination from groundwater via biochemical processes. They were designed to pump the contaminated groundwater upwards into the sediment of the wetland. Two different wetland cells have been constructed to date. The first was constructed using three layers of traditional wetland-soils from areas on WPAFB. Each layer is approximately 18 inches thick. The lower layer was mixed with wood chips to provide an initial source of available organic carbon for the microorganisms in the soil. This organic carbon facilitates microbial growth (Weidemeier, 1997). The top two layers were unaltered except for the introduction of

traditional wetland vegetation in the top layer. The vegetation introduces oxygen into the root zone enabling aerobic reactions to occur. A cross-sectional diagram of the first cell is shown in Figure 1.

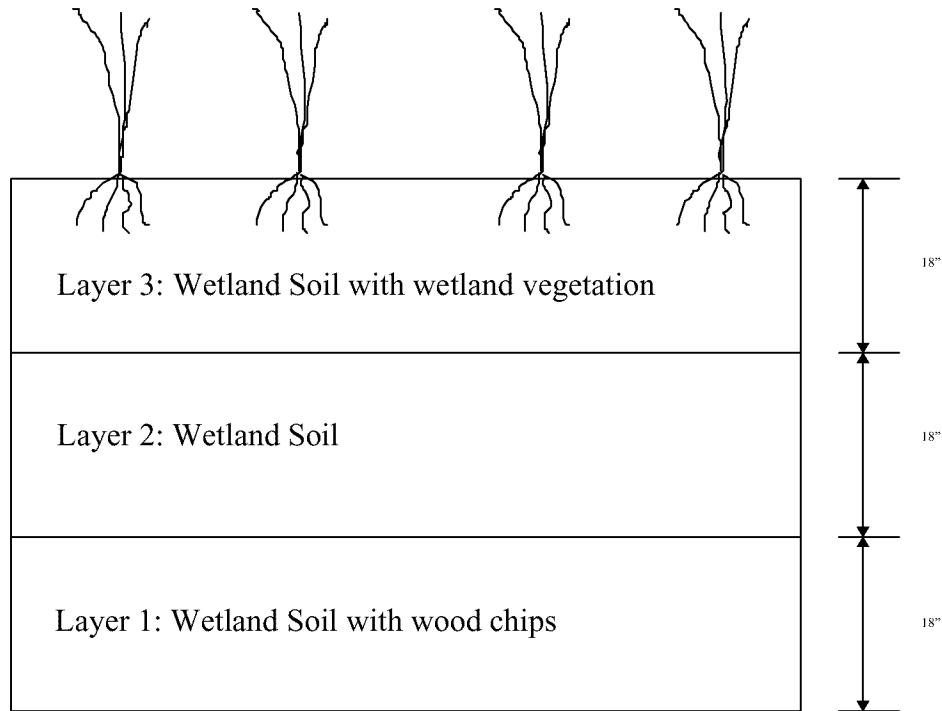


Figure 1. WPAFB Constructed Wetland Cross Section, Cell 1

The second of the two cells constructed include a layer of iron-rich soil. Iron has been shown to facilitate the mineralization of certain chlorinated solvents (Chapelle, 1996). A layer of iron-rich soil was placed in the second cell for the purposes of investigating the reactions and processes leading to further degradation of chlorinated solvents. A cross-section of the second cell is shown in Figure 2.

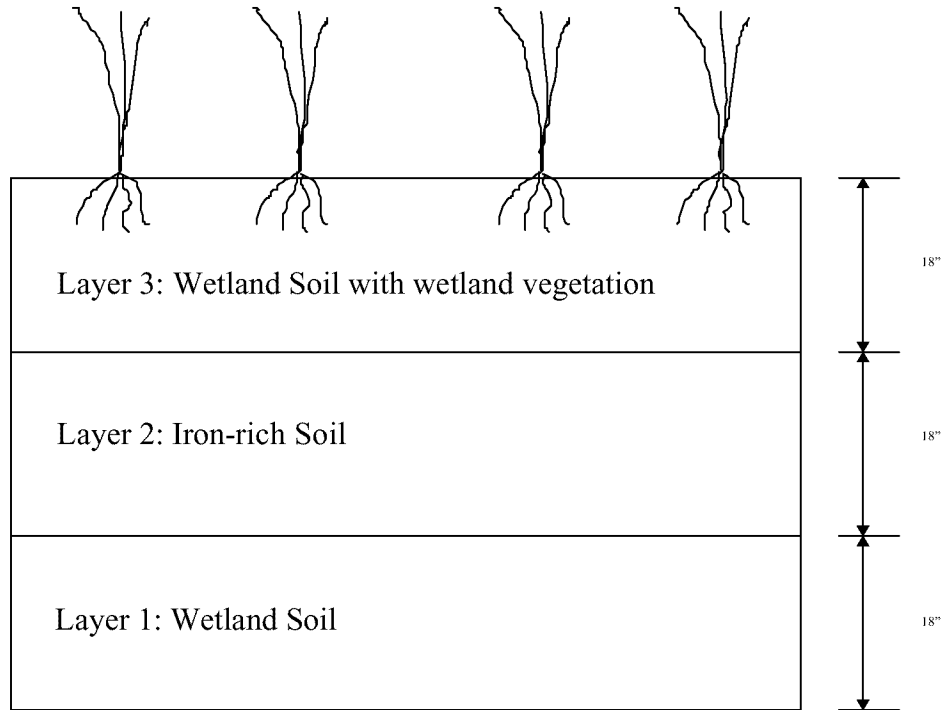


Figure 2: WPAFB Constructed Wetland Cross-Section, Cell 2

The first purpose of this thesis is to develop a protocol for sampling the groundwater at several different levels (strata) of constructed wetlands at WPAFB. The second purpose is to analyze the sampled groundwater to determine the level of chlorinated solvent removal in each of the wetland strata and associated vegetation plots. The concentrations of PCE and its daughter products will be determined via gas chromatography.

Research Questions

1. What are the concentrations of the chlorinated solvent PCE and its daughter products in the various levels of a constructed wetland?

2. What is the optimal sampling and analytical methodology required to accurately sample the water present throughout the sediment layers of an upward flow constructed wetland?
3. How effective is an upward flow constructed treatment wetland in removing PCE and its daughter products from water pumped from a contaminated aquifer?

Scope/Limitations

This study will focus primarily on the development of a sound sampling and analysis protocol designed to determine contaminant levels in the constructed wetland. A concurrent study will be conducted to determine the water pressure contour lines in the constructed wetland. That study will require the development and installation of a grid of sampling points. This grid will serve as the basis from which samples for this study will be taken. A total of three samples will be taken from each sampling point in each stratum. Another limitation to the scope of this study includes the limited number of sampling points (piezometers) available for the collection of samples. A sampling protocol will be developed to both statistically and practically optimize their use. Finally, sampling and analysis time constraints will force the number of samples that can be analyzed via gas chromatography (GC) to be smaller than may be desired statistically.

II. Literature Review

Background

Chlorinated solvents such as PCE and TCE can be removed from groundwater by several methods. Among these methods are the demonstrated technologies associated with traditional pump-and-treat operations. Although these pump-and-treat technologies have been proven to be effective in removing contaminants from groundwater, they are also extremely expensive to install and operate. Recent research efforts have discovered that remediation of chlorinated solvents can also be accomplished by natural attenuation. The United States Environmental Protection Agency defines natural attenuation as:

Naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants (USEPA, 1997).

In practice, natural attenuation has several other names, such as intrinsic remediation, intrinsic bioremediation, or passive bioremediation. This natural attenuation can often be the dominant factor in the fate and transport of contaminants such as PCE and TCE. Advantages of natural attenuation include: 1) contaminants are ultimately transformed into relatively innocuous byproducts such as carbon dioxide, ethane, and water, 2) natural attenuation is non-intrusive and allows for continued use of land and local facilities during remediation, and 3) natural attenuation is less costly than currently available remediation technologies such as pump-and-treat. Disadvantages of natural

attenuation include: 1) natural attenuation is subject to natural and manmade changes in local hydro geologic conditions that may affect contaminant removal, 2) time frames for complete remediation may be relatively long, and 3) intermediate products of bioremediation (e.g. vinyl chloride) may be more toxic than the original contaminant (Wiedemeier et al, 1997).

Microbial Processes

Microbial bioremediation is the process of allowing certain populations of microorganisms to act upon chlorinated solvents in groundwater in order to remove them from the environment. Microbial metabolism and bioremediation of these chlorinated solvents can be separated into four different areas. These are co-metabolic oxidation reactions, co-metabolic reduction reactions, energy-yielding solvent oxidation reactions, and energy-yielding reduction reactions. (Lee et al, 1998).

Co-metabolic Oxidations

Co-metabolic oxidation reactions are usually the result of activities that are intended for other processes. When a chlorinated aliphatic hydrocarbon is biodegraded via co-metabolism, the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the microorganisms for other purposes. The organism receives no known benefit from the degradation of the chlorinated aliphatic hydrocarbon; in fact, the co-metabolic degradation of the chlorinated aliphatic hydrocarbon may be harmful to the microorganism responsible for the production of the enzyme or cofactor (Wiedemeier et al, 1997). For example, TCE can be degraded to its daughter products by certain methanotropic bacteria. These bacteria produce an enzyme known as methane

monooxygenase (MMO) that can produce methanol from methane and oxygen (Chapelle, 1993). The bacteria can oxidize methane into methanol using MMO and NADH as an electron donor. The MMO acts as the catalyst for the oxidation reaction. The methanol is then converted into formaldehyde by the enzyme methanol dehydrogenase. Finally, the formaldehyde is converted into formate by the enzyme formaldehyde dehydrogenase. In this final step, the reaction involves using the NAD^+ ion as an electron acceptor. The NAD^+ receives hydrogen in the reaction and returns to NADH and is therefore recycled throughout the process. This entire process will continue to occur as long as methane is present and can easily occur in the sediment of a wetland where production of methane occurs readily due to the decomposition of organic matter. When TCE is present in the groundwater, the NAD^+ does not receive any hydrogen and therefore no NADH is generated. By limiting the amount of methane present or by feeding the microbes to build up NADH, the TCE can be degraded (Chapelle, 1993). When the amount of methane is limited, there is little competition between methane and TCE for MMO. When methane is abundant, it competes with TCE for MMO and TCE is unable to be degraded. Additionally, once the high levels of methane are consumed, not enough dissolved oxygen remains in the system for TCE degradation to occur (Semprini et al, 1991). Because the co-metabolic oxidation reaction described above involves the use of oxygen, it typically occurs in the upper layers of wetland sediment where plant roots supply oxygen to the system. However, the use of oxygen is not characteristic of all co-metabolic reactions.

Co-metabolic Reductions

Co-metabolic reduction reactions that degrade chlorinated solvents occur in anaerobic conditions. In these anaerobic conditions, certain bacteria such as methanogens and sulfate-reducers are able to reduce PCE and TCE (Bagley and Gosset, 1989). The reactions undertaken by these types of bacteria is considered to be co-metabolic rather than energy-yielding because only a fraction of the total reducing equivalents derived from the oxidation of electron donors is used to reduce the solvent (Bagley and Gosset, 1989). Reduction of chlorinated solvents appears to be a minor by-product in these cases. However, in situations where high organic levels and high methanogenic respiration are found, such as wetland sediments, the partial co-metabolic dechlorination of solvents can be significant (Lee et al, 1998).

Co-metabolic dechlorinations such as those described above undoubtedly are responsible for the incomplete, relatively slow transformations of chloroethenes observed at many field sites. The organisms that can mediate such processes are ubiquitous, but the process is sufficiently slow and incomplete that a successful natural attenuation strategy cannot completely rely upon it (Gosset and Zinder, 1997).

Energy-yielding Oxidations

Energy-yielding solvent oxidation reactions occur in situations where microbes use the chlorinated solvent as the sole source of carbon and energy. As the name suggests, these reactions may take place in areas where oxygen is readily available, such as the root zone of wetland sediment. However, research has shown that these reactions may occur in anaerobic conditions as well. Under aerobic and some anaerobic

conditions, the less-oxidized chlorinated aliphatic hydrocarbons (VC, DCE) can be used as the substrate (electron donor) in biologically mediated redox reactions (Weidemeier et al, 1997). This process is probably restricted to the fringe of contaminant plumes because readily oxidizable substrates and oxygen rarely co-occur within the core of mature contaminant plumes. An example of this reaction is the conversion of 1,2-DCE to carbon dioxide by certain aerobic bacteria in streambed sediments. Experiments showed that the microorganism community in the sediment was able to fully eliminate 1,2-DCE when no other sources of carbon were present. Although no microbial growth was observed during the experiment, studies suggest that growth would occur in the presence of greater contaminant concentrations. This suggests that DCE can be degraded as the primary substrate in microbial metabolism and that this process may contribute to the natural attenuation of DCE even under circumstances where aerobic cometabolism is not favored (Bradley and Chapelle, 2000).

Energy-yielding Reductions

Energy-yielding reduction reactions or dehalorespiration is the process by which microorganisms are capable of using PCE, TCE, or chlorobenzoates as electron acceptors for biologically useful energy generation. These microorganisms are distinct from the co-metabolic reactions found among the methanogens and sulfate-reducers. Depending on the species of microbes present, these bacteria may produce cis-DCE as a final end product or may carry out complete dechlorination to ethane (Lee et al, 1997). These microbial processes show that oxygen need not be present for complete mineralization of chlorinated solvents. They further suggest that because of the energy yielding nature of

the reactions, chlorinated solvent plumes may be self-enriching for dehalogenating bacteria. That is, the contaminant plume continues to supply the electron acceptors necessary for microbial growth (Lee et al, 1997). Hydrogen and simple organic compounds are typically seen as the electron donors in these reactions.

The four biodegradation pathways described above have been well studied and proven to provide the necessary reactions and conditions necessary to remove and/or transform chlorinated solvents from groundwater. The interplay between the reactions is shown in Figure 3. In aerobic conditions, VC can be oxidized directly to carbon dioxide and chloride. At the interface between aerobic and anaerobic microenvironments, where methane and oxygen are both available, cometabolic oxidations can convert chlorinated ethenes to carbon dioxide and chloride. In anaerobic environments where electron donors such as organic carbon or hydrogen are present, reductive dehalogenation is the predominant mechanism (Lee et al, 1997).

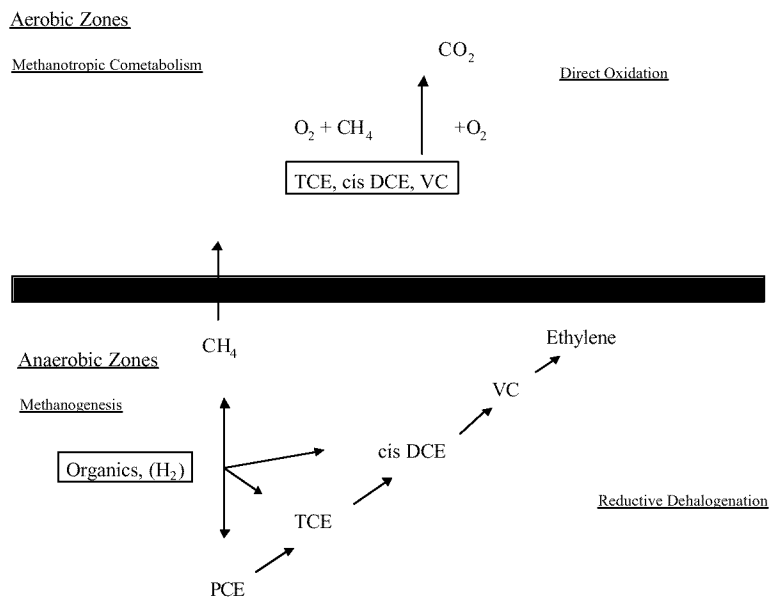


Figure 3. Interplay Between Different Biological Mechanisms Within a Wetland Aquifer with Both Aerobic and Anaerobic Conditions.

Rapid microbial mineralization of VC has been observed in laboratory cultures and aquifer samples under aerobic conditions and in systems enriched with methane and oxygen. Because of this, it has been suggested that sequential anaerobic/aerobic biodegradation by indigenous microorganisms may be an effective means of bioremediating aquifers contaminated with chlorinated ethenes (Vogel, 1994). However, the addition of oxygen to groundwater to stimulate biodegradation is expensive and in many cases impractical (Bradley and Chapelle, 1996).

In contrast to reactions in which the chlorinated hydrocarbon is used as an electron acceptor (see energy-yielding reduction reactions above), only the least oxidized chlorinated aliphatic hydrocarbons (VC and DCE) can be used as electron donors in biologically mediated redox reactions. For example, PCE is fully chlorinated and does not serve as an electron donor for aerobic or anaerobic microbial consortia (Lee et al,

1997). TCE, however, is able to give up one electron and is able to be reductively dechlorinated. This reaction is described above as a co-metabolic reduction. McCarty and Semprini (1994) describe investigations in which VC and 1,2-dichloroethane were shown to serve as primary substrates under aerobic conditions. In addition, Bradley and Chapelle (1996) show evidence of mineralization of VC under iron reducing conditions so long as there is sufficient bio-available Fe(III) (Wiedemeier et al, 1997).

Constructed Wetlands

Wetlands hold properties that make them unique among major ecosystem groups on the earth. They have a higher rate of biological activity than most other ecosystems. Because of this, they are able to transform many of the common pollutants that occur in conventional wastewater (or groundwater) into harmless byproducts or essential nutrients that can be used for additional biological productivity (Kadlec and Knight, 1996). This capacity for transforming contaminants has led to research into using constructed wetlands as a means of removing contaminants from both surface wastewater and subsurface groundwater flows. Natural attenuation of chlorinated solvents within subsurface groundwater is very slow. It is often so slow that long plumes of contaminant are generated that can reach surface discharge sites such as wetlands (O'Loughlin and Burris, 1999). Recent studies have detailed the effect that a freshwater tidal wetland had on an aquifer contaminated by PCE at Aberdeen Proving Ground in Maryland at the head of Chesapeake Bay (Lorah and Olsen, 1999). Results at Aberdeen indicate that natural attenuation processes increase dramatically as contaminated groundwater passes through the root zone of a wetland system. Rate constants of 30-40 year⁻¹ have been observed for

dechlorination of TCE in wetlands as opposed to $1-4 \text{ year}^{-1}$ that is typically found in non-wetland contaminated aquifers (Pardue et al, 2000).

One of the first demonstrations of using wetland sediments to remove chlorinated solvents via reductive dechlorination was performed using sediment from the Everglades in south Florida (Parsons and Lage, 1985). The studies identified the dechlorination kinetics of PCE, TCE, and other chlorinated solvents. The conclusions of these studies are that wetlands are ideal environments for reductive dechlorination processes (Pardue et al, 2000). Additional research of the root zone associated with wetland plants demonstrated that the biodegradation of chlorinated organics in the region directly adjacent to plant roots can be dramatically higher than in bulk soil (Anderson and Walton, 1995). A key mechanism in this degradation is the co-metabolism of chlorinated solvents and daughter products by methanotropic organisms that function under aerobic conditions using methane as an electron donor (Pardue et al, 2000). This process was described in detail earlier in this chapter. The process was confirmed by laboratory work performed by Lorah and Olsen in 1999.

Sorption of Contaminants

Another aspect of wetlands that enable them to remove and/or transform chlorinated solvents via natural attenuation is the sorption of the contaminants to suspended solids and sediments. Sorption of organic contaminants in wetlands is often greater than other ecosystems because the high biological productivity of the wetland system result in suspended solid and sediments that are dominated by organic matter. That is, the wetland sediment has a high organic fraction or f_{oc} . For example, the f_{oc} of

the peat soils found in a marsh environment can exceed 0.5 as compared to 0.05 for an average mineral soil or 0.0001 for an aquifer. This sorption, or retardation, of the contaminant is believed to provide sufficient contact time for microbial activity to reduce the chlorinated solvent (Pardue et al, 2000).

Purge-and-Trap Technique

Analysis of volatile organic compounds from water samples can be accomplished by either analyzing the static headspace above the sample or by the active removal of the compound from the sample via a purge and trap technique. To analyze the static headspace, a sample is placed in a closed container, such as a 40 mL EPA Volatile Organic Analysis (VOA) vial, where a portion of the compound is allowed to migrate from the aqueous phase into the gaseous phase. Once equilibrium is reached, a volume of the headspace above the water sample is removed and injected into a gas chromatograph for analysis. The purge and trap technique is a dynamic technique used to remove the compound from the water sample before analysis. Water samples that contain volatile organic compounds are placed in a purge vessel and a flow of some inert gas (commonly Helium) is passed through the water at a constant flow rate for a predetermined amount of time. The figure below shows the purge flow path during a typical purging sequence.

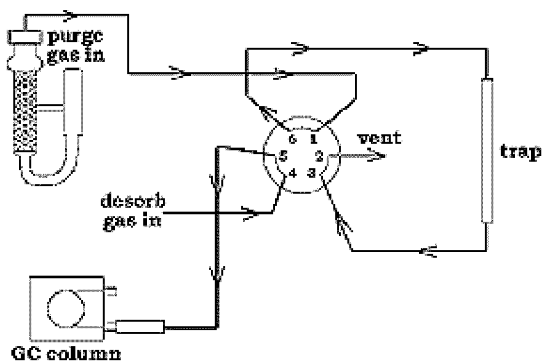


Figure 4. Valve Position During Purging Sequence.

The volatile organic compounds are carried out of the water matrix and are carried to an absorbent trap where the compounds are concentrated. After the purging process is completed, the trap is rapidly heated. This rapid heating, called the desorb phase, coupled with a back flushed flow of a carrier gas, transports the compounds to the gas chromatograph for analysis. The figure below shows the flows of purge and carrier gasses during the desorb phase.

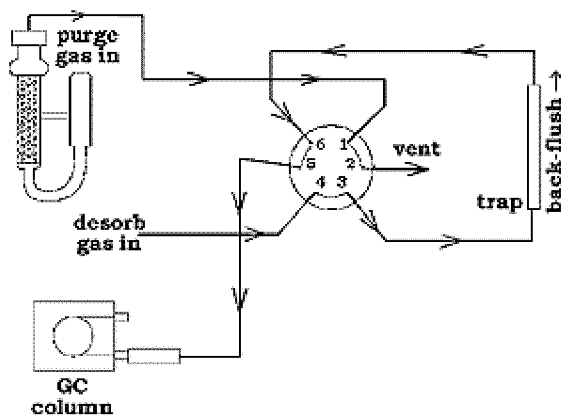


Figure 5. Valve Position During Desorb Sequence

Gas Chromatography Technique

Gas chromatography is one of the established, highly sophisticated methods for analyzing volatile organic compounds such as PCE and TCE in ground water. The principle of GC involves a mobile phase (carrier gas) and a stationary phase (column packing or capillary column coating). Carrier gasses are usually nitrogen, argon-methane, helium, or hydrogen. Packed columns usually contain a stationary phase that is a liquid that has been coated on an inert granular solid (APHA, 1998). Components of a sample containing a volatile organic compound are injected into the column along with the carrier gas (Wilson, 1995). The column is installed in an oven with the inlet attached to the injection port and the outlet attached to a detector. Temperature control of the entire system is precisely maintained. When the sample is injected into the column, the organic compounds are vaporized and moved through the column by the carrier gas. The compounds travel at different rates; governed by the partition coefficients between the mobile and stationary phases (APHA, 1998). The compounds are moved through the column until the detector is reached. Various types of detectors can then be used depending on the analyte in question. These detectors include the electrolytic conductivity detector, the electron capture detector, and the flame ionization detector. A simplified diagram of a gas chromatography device is shown in Figure 6.

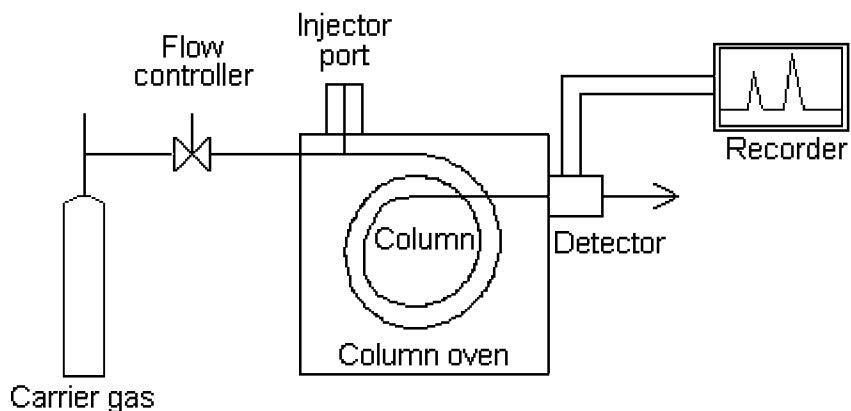


Figure 6. Simple Gas Chromatograph Diagram

The time that the compound remains in the column (both in the mobile and stationary phases) is called the retention time, t_r . The dead time is the time a non-retained compound spends in the mobile phase, which is also the amount of time the non-retained compound spends in the column. Dead time is also generally reported in minutes. The adjusted retention time is the time a compound spends in the stationary phase. The adjusted retention time, t'_r , is the difference between the dead time and the retention time for a compound.

$$t'_r = t_r - t_m \quad (1)$$

The capacity factor, k , is the ratio of the mass of the compound in the stationary phase relative to the mass of the compound in the mobile phase. The capacity factor is a unitless measure of the column's retention of a compound.

$$k = \frac{t_r - t_m}{t_m} \quad (2)$$

The phase ratio, β , relates the column diameter and film thickness of the stationary phase. The phase ratio is unitless and constant for a particular column and represents the volume ratio.

$$\beta = \frac{r}{d_f} \quad (3)$$

The distribution constant, K_d , is a ratio of the concentration of a compound in the stationary phase relative to the concentration of the compound in the mobile phase. The distribution constant is constant for a certain compound, stationary phase, and column temperature.

$$K_D = k \times \beta \quad (4)$$

The selectivity, α , is a ratio of the capacity factors of two peaks. The selectivity is always equal to or greater than one. If the selectivity equals one the two compounds cannot be separated. The higher the selectivity, the more separation between two compounds or peaks.

$$\alpha = \frac{k_A}{k_B} \quad (5)$$

The linear velocity, u , is the speed at which the carrier gas or mobile phase travels through the column. The linear velocity is generally expressed in centimeters per second.

$$u = \frac{L}{t_m} \quad (6)$$

where L is the length of the column.

The efficiency is related to the number of compounds that can be separated by the column. The efficiency is expressed as the number of theoretical plates (N , unitless). It

reflects the number of times a solute partitions between the two phases during its passage through the column (Willard et al, 1988). Theoretical plates is a concept and a column does not contain anything resembling physical distillation plates or any other similar feature. Theoretical plates numbers are an indirect measure of peak width for a peak at a specific retention time. Columns with high plate numbers are considered to be more efficient (i.e., higher column efficiency) than columns with lower plate numbers. A column with a high number of plates will have a narrower peak at a given retention time than a column with a lower number of plates. The efficiency increases as the height equivalent to a theoretical plate decreases, thus the column can separate more compounds. The efficiency increases as the number of theoretical plates increases, thus the column's ability to separate two closely eluting peaks increases (Agilent Technologies, 2002). Theoretical plates can be calculated using:

$$N = 5.545 \times \left(\frac{t_r}{W_h} \right)^2 \quad (7)$$

where t_r is the adjusted retention time and W_h is the peak width at the base (units of time). The larger the calculated value for N , the greater the efficiency of the column.

III. Methodology

Introduction

This thesis effort was centered on the study of an upward-flow constructed wetland at WPAFB, Ohio. The wetland was designed and constructed with the purpose of treating an aquifer contaminated with the industrial chemical, PCE. The design of the wetland is intended to allow the chemical to be reductively dechlorinated using biochemical means. The study of the use of constructed wetlands as means of removing contaminants from groundwater aquifers is relatively new. Up to now, research efforts in this field have involved modeling efforts (Hoefar, 2000), laboratory efforts involving wetland sediments and column studies (Lanzarone and McCarty, 1991), and investigation of processes underway in natural wetlands experiencing contaminated water inflows (Lorah and Olsen, 1999). This thesis is part of the first research effort involving a wetland specifically designed with the purpose of treating a contaminated groundwater aquifer.

Background of Wetland Construction

The wetlands at WPAFB were designed and constructed using knowledge already obtained by previous research involving natural wetlands and laboratory column studies. As described earlier the wetland was constructed in three 18" layers. The top two layers, hereafter labeled layers A and B, were composed of traditional wetland soils obtained from a geographically separated area on WPAFB. The third layer, labeled C, was composed of the same wetland soils. However, layer C was mixed with wood chips intended to provide an initial source of organic carbon for the wetland sediment

organisms. A cross-sectional representation of the wetland design is shown in Figure 7. The wetland was planted with various types of vegetation that occur naturally in wetland environments.

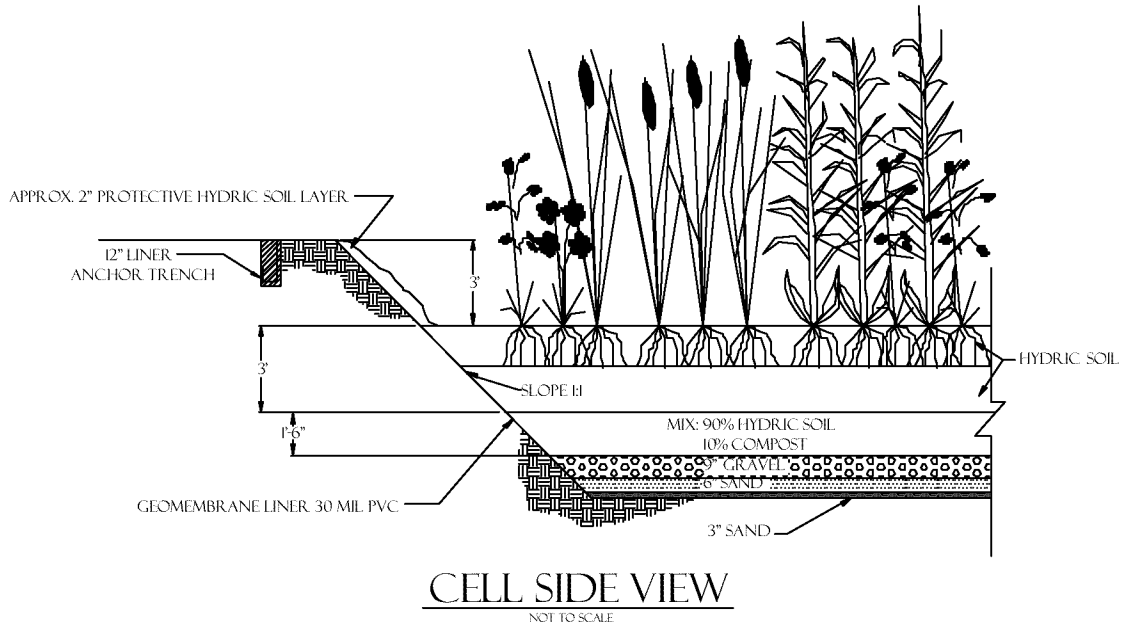


Figure 7. Cross-sectional Design of Constructed Wetland at WPAFB.

The gravel layer contains three PVC pipes that run the length of the wetland. These pipes are designed to evenly distribute the contaminated water throughout the wetland footprint. Typical wetland vegetation was planted either via seeding or plugs in September 2000. The vegetation was planted in a manner that addressed the number of available plants and the expected size of the mature plants. An overhead view of the wetland and the various vegetative plots can be found in Figure 8. Table 2 gives a description of the types of vegetation found in each subplot.

Because different kinds of vegetation have different biological makeups, it was decided to plant several different types of vegetation. Differences in root mass and

penetration depth along with variations in active and dormant phases are two examples of how wetland plants create a unique microcosm. The microcosms that these vegetative subplots create may have an effect on the efficiency of the wetland to remove the chlorinated ethenes (Amon, 2002).

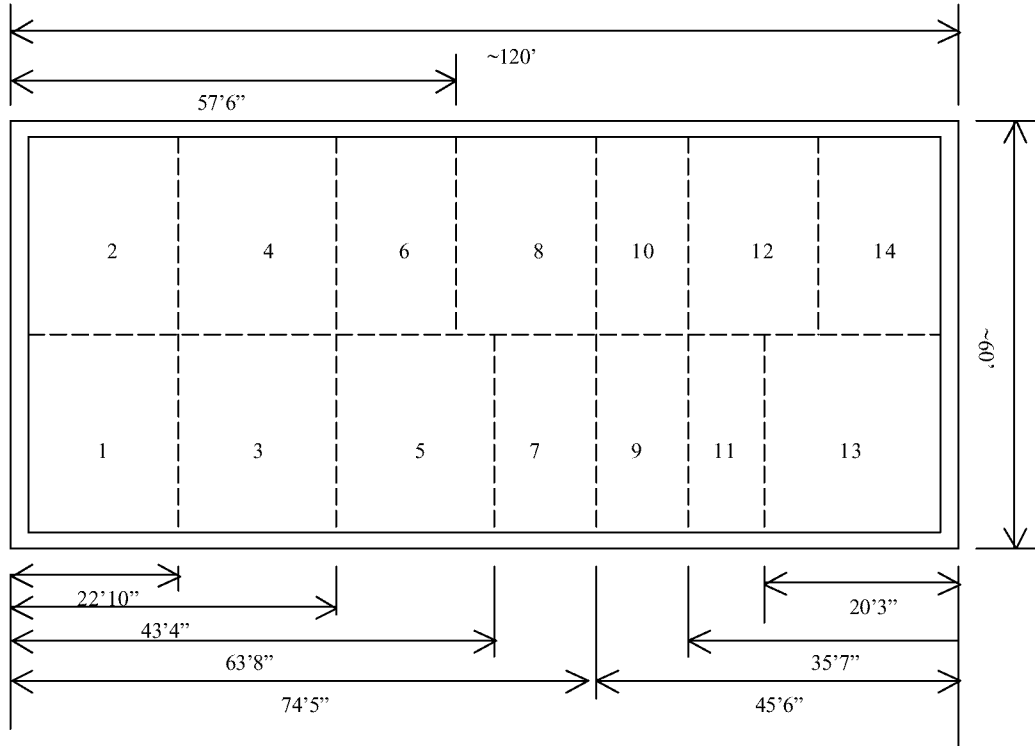


Figure 8. Overhead Representation of Vegetative Plots in WPAFB Constructed Treatment Wetland.

Table 2. Wetland Vegetation by Subplot

Subplot	Piezometers included	Vegetation	Subplot	Piezometers included	Vegetation
1	1, 2, 3, 7, 8, 9	<i>Carex Hystercina</i>	8	34, 35, 36, 40, 41, 42	<i>Juncus Effusus</i> <i>Scirpus Validus</i>
2	4, 5, 6, 10, 11, 12	<i>Scirpus Atrovirens</i>	9	43, 44, 45	<i>Carex Vulpinoidea</i>
3	13, 14, 15, 19, 20, 21	<i>Eleocharis Erythropodo</i>	10	46, 47, 48	<i>Juncus Torreyi</i> <i>Juncus Dudleyi</i> <i>Carex Lupiformis</i>
4	16, 17, 18, 22, 23, 24	<i>Carex Comosa</i>	11	49, 50, 51	Mix
5	25, 26, 27, 31, 32, 33	<i>Acorus Calamus</i>	12	52, 53, 54, 58, 59, 60	Blank
6	28, 29, 30	<i>Scirpus Atrovirens</i>	13	55, 56, 57, 61, 62, 63	<i>Carex Hystercina</i> <i>Mimulus Ringens</i> <i>Penthorum Sedoides</i> <i>Ascepias Incarnata</i>
7	37, 38, 39	<i>Eleocharis acicularis</i> <i>Carex Cristatella</i>	14	64, 65, 66	<i>Carex Cristatella</i> <i>Carex Vulipinoidea</i> <i>Penthorum Sedoides</i> <i>Mimulus Ringens</i> <i>Asclepias Incarnata</i>

Delineation of study area

This thesis is only one part of an ongoing joint research effort between the Air Force Institute of Technology, the Air Force Research Laboratory, and Wright State University in the field of contaminant bioremediation using constructed wetland technologies. To date, the efforts included laboratory column studies and modeling research. While these efforts are ongoing, this study and others are beginning to investigate the processes occurring in the WPAFB constructed wetland. Other concurrent field research efforts include determining the levels of several different organic acids throughout the various layers of the wetland (Bugg, 2002) as well as determining the flow regime throughout the entire wetland (Entingh, 2002). The organic acid research effort is similar to this thesis in preparation and sampling alone. Laboratory procedures

for the two efforts vary greatly. The study of the hydraulic flows in the wetland involved the placement of a three-dimensional grid of sampling locations within the study area. Measurements of well drawdown and recovery, porosity, hydraulic conductivity, and head pressures were desired. These measurements were then analyzed using a computer program. Operational requirements of the computer program required a three-dimensional grid to create nodes for the creation of contours. This grid also served as the sampling grid for this effort.

The “usable” surface area of the wetland was determined by measurement and review of the design drawings. It was determined that a grid of sixty-six sampling locations per layer could be placed in the wetland and that this grid would satisfy all three research efforts. The sixty-six locations consisted of 6 rows of 11 piezometers. This grid was employed in all three layers. An overhead view of the sampling grid overlaid with vegetative plots is shown in Figure 9.

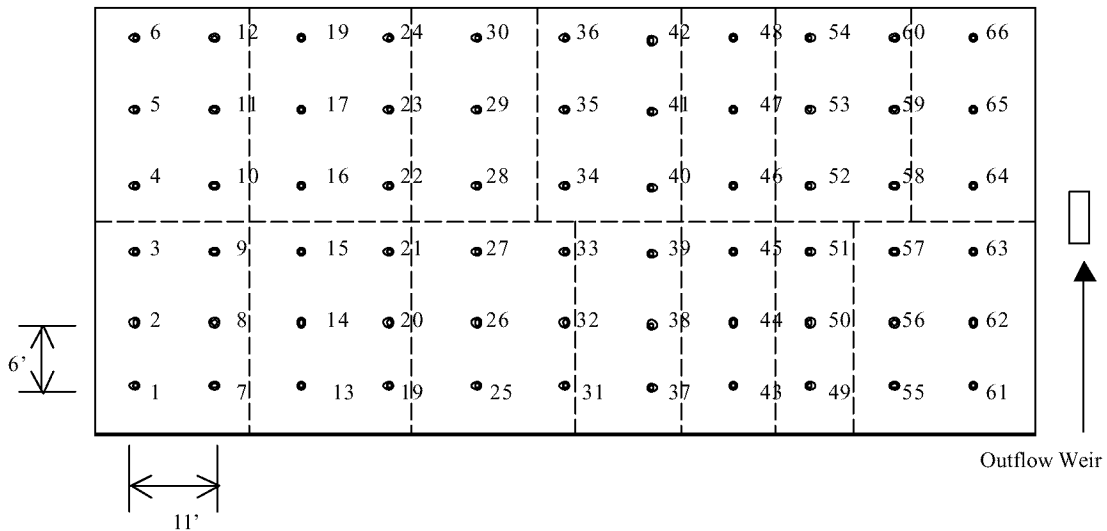


Figure 9. Overhead View of Sampling Point Locations

A team of surveyors professionally laid out the grid with the location of each sampling point determined to within six inches. Each sampling location contained three piezometers placed in the center of each layer. An overhead representation is shown below.

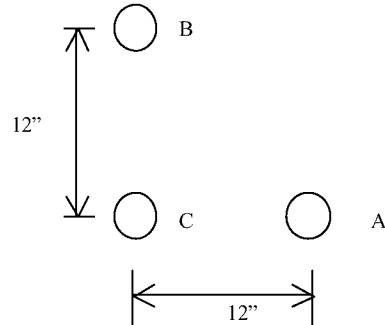


Figure 10. Layout of a Typical Sampling “nest”

Installation of Piezometers

Upon completion of the grid placement, it was necessary to determine the depths at which the piezometers would be placed for each layer. As the effort centers on determining the contaminant levels resident in each wetland sediment layer, it was decided that the screened areas of the piezometers would be placed in the exact center of the layer. As is shown in Figure 11, the depths for the piezometers in layers A, B, and C were 9, 27, and 45 inches respectively.

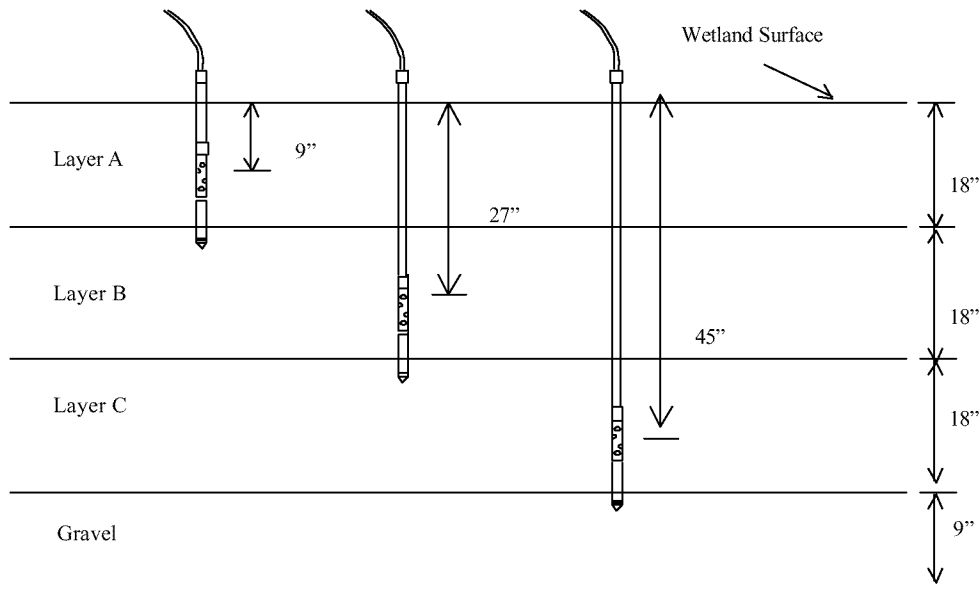


Figure 11. Side Representation of Piezometer Depths.

The screened area of the piezometers is designed to allow groundwater to flow into the piezometer where it can then be sampled. In order to protect these screens from damage and possible clogging during placement, they were delivered with a protective shield. This shield was pointed in order to facilitate the driving of the piezometers.

Earlier researchers had placed piezometers in each layer of the wetland sediment in order to evaluate pressure head and provide temporary sampling points. Investigation of these existing piezometers revealed that water levels (piezometric heads) in the layer C piezometers were approximately 2.5 feet above the surface. Water levels in layers B and A were approximately 1.5 and 0.5 feet, respectively. This information was used to determine the length of tubing attached to each piezometer. This tubing and the addition of associated stainless-steel piping resulted in total apparatus lengths of 30, 54, and 90

inches for layers A, B, and C respectively. These lengths were necessary to ensure that water was unable to escape the piezometer tubing due to piezometric head alone.

Assembly of each piezometer apparatus involved attaching Teflon-lined tubing to the hose-barb fitting on the piezometer. Appropriate lengths of stainless-steel piping were then connected to the piezometer and secured with stainless-steel pipe connectors. Installation of each piezometer was then accomplished by means of a 25-pound slide hammer used to drive each one to its predetermined depth. Piezometers were Solinst Model 615 Stainless Steel Drive Point piezometers and were installed per manufacturer's recommendations.

Well Development Procedures

During installation of the 198 sampling points it was noted that some piezometers showed water levels in the Teflon tubing nearly instantly while others showed water only after several days or not at all. This led to concerns as to whether sufficient water was present in each sampling point to allow for proper analysis. All piezometers in layer C showed high water levels in the tubing. This was expected as they were driven to a depth where higher hydrostatic water pressures were present. Layers B and A showed several points that appeared to have extremely low water recharge rates. The sampling and analytical procedures that were used in this study required that a minimum of 60 mL of water be present in the screen portion of the piezometer. This amount consisted of the 40 mL required to fill the sample vial plus at 20 mL required to flush the sampling instrument. In order to determine what locations would not provide adequate amounts of water for proper analysis, all piezometers in layers A and B were purged until they were completely dry. Purging was accomplished by means of a 60 mL plastic syringe and $\frac{1}{4}$

inch Teflon tubing. Times of purging were noted and tabulated. Approximately 2 hours after the initial purging, all piezometers were again purged and the quantity of water removed was measured in a graduated cylinder. Recovered volumes and times of second purging were noted. Approximately 24 hours after the initial purges took place, a third purge was performed. Again, volumes of water removed and times were noted. This information was used to determine short term and long term recharge rates for all piezometers in layers A and B. The tabulated recovery data can be found in Appendix A.

As previously stated, analytical procedures required that at least 60 mL of water be in the piezometer at the time of sampling. Those piezometers that had recovered volumes of 60 mL or less after either the short or long-term purge were identified and deemed as candidates for well development procedures. Those wells are indicated in the figures below as larger black circles.

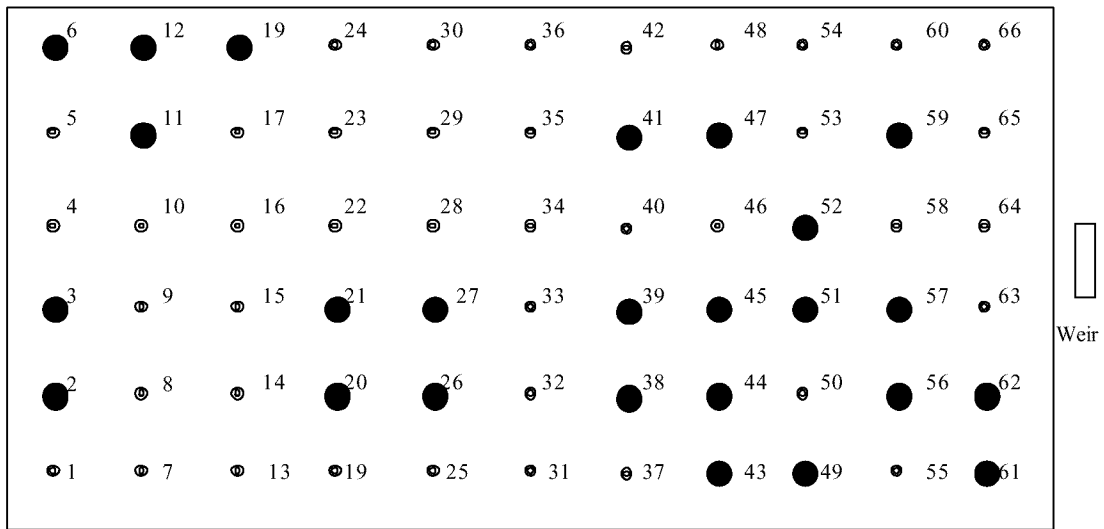


Figure 12. Piezometers in Layer A Requiring Well Development Efforts.

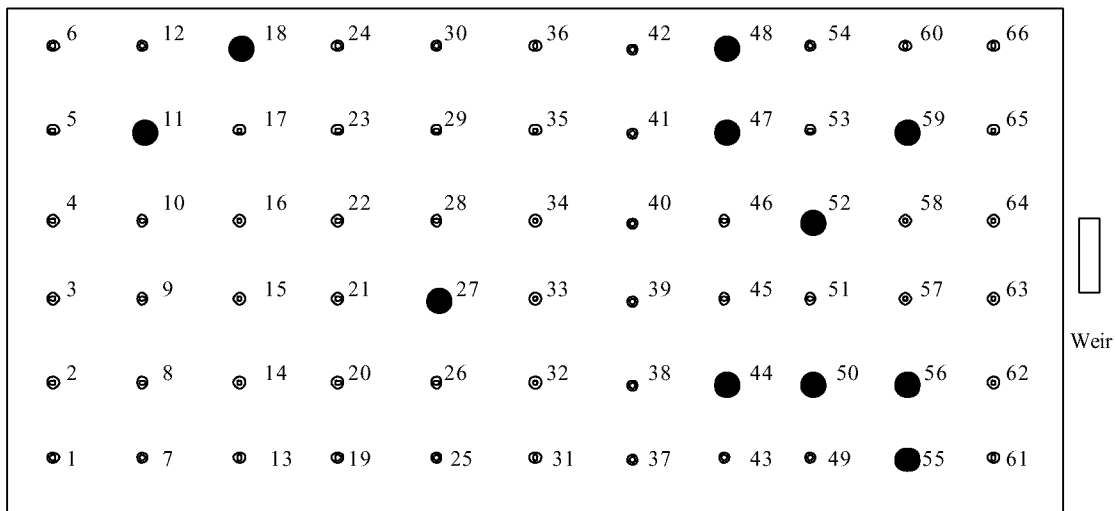


Figure 13. Piezometers in Layer B that Requiring Well Development Efforts.

A monitoring well should be a “transparent” window into the groundwater from which samples can be collected that are considered to be indicative of the water present in the surrounding soil matrix (Aller, et al, 1989). Monitoring well development is an attempt to remove particulate matter from the well intake thereby facilitating the movement of water into and out of the piezometer. One option for well development involves pumping, overpumping and backwashing. In this procedure, water is initially pumped from the well before the pump is reversed and water is pushed into the well. This outward surge of water flows into the surrounding soil formation and tends to loosen any particulate matter that may be clogging the well screen. The sequence is repeated until sufficient development has occurred. Well development procedures involved pumping water from the surface of the wetland into the piezometer using a peristaltic pump (Solinst model 410) for approximately 20 seconds. The pump was then reversed and the well was purged dry using the pump. This procedure was repeated two more

times. Upon completion of this development procedure, the developed wells were again tested for recovery rates in the same manner as described above. Review of the data showed that nearly all developed wells showed increased recovery rates sufficient to provide greater than 60 mL of water after 24 hours or earlier. Recovery rates for the developed sampling points can be found in Appendix B. Two locations continued to show low recovery rates and were deemed to be invalid sampling locations. These locations were at piezometers 48 and 56 in layer B.

It was decided that each usable sampling point would be sampled 3 times. Three analyses allows for the calculation of a mean concentration and standard deviation. Analyzing each point eliminated the possibility of introducing statistical bias into the results. Additionally, by sampling all available locations, a better characterization of the entire wetland, layer by layer, could be realized.

Options for Taking Samples

Upon completion of piezometer installation and development of poorly recharging locations, it was necessary to determine the procedures by which the actual water samples would be taken. Initially, two possible sampling procedures were available for evaluation. The first involved the use of an ISCO VOC sampler. This device enables the user to take up to 24 samples from one sampling location. After an initial purging procedure in which 3 total piezometer volumes are removed, 40 mL sampling vials are filled and capped with a stopcock type cap. Each vial is flushed with 3 volumes of sample and is capped in a manner that avoids exposing the sample to the atmosphere and possible volatilization. This method was deemed inadequate mainly because of the relatively low water recovery rates present in the upper layers of the

wetland. There simply wasn't a high enough recharge rate to allow the VOC sampler to execute the purge procedure and fill the vial. Additionally, the use of the stopcock cap was incompatible for use in a gas chromatograph auto sampler. The stopcock cap would have to be removed and replaced with a cap and septa and would allow the sample to be exposed to air, thereby eliminating the benefit of taking the sample without exposure to the atmosphere. EPA methods allow for the changing of vial caps to allow an autosampler to be used, however, the ISCO sampling method was eliminated due to the low volumes of water present in many piezometers.

The second sampling method involved the use of a peristaltic pump to extract water from the piezometer and fill the 40 mL VOA vials. This method was also deemed inappropriate because of the high pumping and purging rates of the pump. Water recovery rates weren't sufficient to provide enough water to take an adequate sample.

The final method investigated and the one eventually chosen involved a simple combination of a 100 mL glass syringe joined to Teflon tubing and fittings. This syringe and tubing combination was able to reach the screened area of the piezometer and extract the required amount of water necessary to fill the vial. The tubing was disconnected and the vial was filled and immediately capped minimizing the amount of exposure to the atmosphere. None of the three proposed sampling methods allowed for a sample to be taken without exposure to the atmosphere but the glass syringe method was chosen as the best choice. This method was chosen because it required less water to be present in the piezometer at the time of sampling. It was also less cumbersome to handle in the field.

Sampling procedure

The first step in taking of a sample in the upper layers (A and B) was to purge the piezometer until completely dry (or no more water could be extracted). Purging was accomplished using the syringe and tubing system described above. The piezometer was allowed to recover water for approximately 24 hours before actual sampling took place. At that time, the tubing was placed directly to the bottom of the piezometer and approximately 20 – 30 mL of water were extracted to rinse the tubing and syringe apparatus. Then approximately 50 – 60 mL were taken and used to fill the 40 mL sample vials. Remaining water extracted was disposed of into the surface water of the wetland. Vials were immediately capped with no air space to minimize atmospheric exposure and sample data was noted and labeled. This sampling method enabled water to be sampled that had recently been directly exposed to the soil matrix and its associated redox conditions. Since samples were taken from the bottom of the screened area, there was no influence from the water at the top of the water column that was exposed to air for nearly 24 hours. This was a concern because it was expected that the water at the top of the column would have a lower concentration due to the volatilization of the contaminants. If enough water wasn't present in the piezometer at the time of sampling, it is possible that the water at the top of the column could be drawn into the syringe and conceivably affect the concentrations of the contaminants present in the sample. At no time during the actual taking of the sample was all the water present in the piezometer completely removed. If this had been the case, the water at the top of the piezometer water column could have affected the sample concentration. Therefore, it was determined that this “water cap” remained in the piezometer during sampling. Additionally, approximately

15 mL of water remained in the tubing connected to the syringe after the sample was extracted. This 15 mL of water provided a “safety cushion” to ensure that the water cap wasn’t sampled and did not affect the concentrations present in the actual sample.

For layer C, the procedure was altered slightly. Approximately 75 percent of the sampling locations in layer C had sufficient pressure head to allow water to directly flow from the Teflon-lined tubing if the tubing was bent over towards the wetland surface. Water from these points was sampled directly from the flow after approximately 10 seconds. This time enabled all water in the flow to be directly from the surrounding soil matrix. Those points in layer C that did not have sufficiently high pressures and flows were sampled in a manner similar to that of layers A and B. The only difference is that the piezometer could not be completely purged due to the moderately high recovery rates. Approximately 300 mL of water was removed from the screened area before the sample was taken. This enabled the sample to come directly from the soil matrix. Samples were taken from the wetland and placed on ice during transport to the environmental laboratory. The samples were then immediately analyzed to avoid any need for sample preservation procedures.

Techniques for preparation of stocks and standards

In order to accurately quantify contaminant concentrations present in the wetland samples, it was necessary to construct stock solutions and standard solutions for each analyte of interest. Those analytes were PCE, TCE, three isomers of DCE (1,1, trans-, and cis-), vinyl chloride, ethene, ethane, and methane. Of these analytes only the last three were gaseous and required special preparation techniques.

Preparation of stocks and standards for the liquid analytes began with acquiring appropriately sized serum bottles, syringes, and chemicals in pure form. The first step in creation of a stock solution is to fill a 60 mL serum bottle with de-ionized water and cap with a gray-butyl Teflon-lined stopper with an aluminum crimp. Excess pressure was removed from the bottle by inserting a fresh needle through the stopper. A 10uL gas-tight syringe was then used to extract a predetermined amount of chemical and inject it into the serum bottle. The fresh needle was left in place to allow displaced water to escape during the injection. The serum bottle was then placed in a rotator for a minimum of 24 hours to allow the chemical to completely dissolve. The amount of chemical injected into the serum bottle depended on the final desired concentration of the stock solution. For example, 10 uL of TCE was injected into the serum bottle to create a stock solution with a concentration of 202.5 mg/L. The concentration was calculated using the following equation:

$$Conc = \frac{Mass}{Vol} \quad (8)$$

where: Conc = concentration of stock solution
Mass = mass of TCE injected
Vol = volume of serum bottle (actually 72 mL)

The mass of TCE injected was determined using the following equation:

$$Mass = Vol_{inj} \times Dens \quad (9)$$

where: Vol_{inj} = volume of TCE injected into serum bottle (10uL)
Dens = Density of TCE (1.458 gm/mL)

Therefore, the mass of TCE injected was 14.58 mg. Substituting this mass into Equation 1 gives the stock solution concentration of 202.5 mg/L or ppm. This TCE was allowed to

completely dissolve into the water for at least 24 hours in a rotator. The procedure was repeated for the remaining non-gaseous phase chemicals.

Gaseous phase chemical stock solution construction was performed in a slightly different manner. A 60 mL serum bottle was connected to a cylinder and completely filled with the gas. A fresh needle was placed into the stopper during filling to allow the air in the bottle to be purged and replaced with the gas. This bottle was filled for a minimum of 5 minutes to ensure no ambient air remained and the bottle was filled completely with pure gas. A measured volume of gas was then extracted using a gas-tight syringe and injected into a 40 mL sample vial that contained 30 mL of de-ionized water. For example, 1 cc of ethane was extracted from the 60 mL serum bottle and injected into the headspace of the 40 mL (actually holds 44 mL) sample vial. The sample vial was placed in a rotator for a minimum of 24 hours. It was first necessary to determine the amount of ethane that dissolved into the water. This was accomplished using the equation:

$$f_w = \frac{1}{\left[1 + \frac{K_H}{RT} \times \frac{V_a}{V_w}\right]} \quad (10)$$

where: f_w = fraction of ethane dissolved in water

V_a = Volume of air in sample vial (14 mL)

V_w = Volume of water in sample vial (30 mL)

K_H = Henry's Law Constant for ethane at 25°C (489.78 L-atm/mol)

R = Ideal gas constant (.0821 L-atm/molK)

T = Temperature in degrees Kelvin (298.15)

Therefore, the fraction of ethane dissolved into the water in the sample vial was calculated to be 0.09669. The number of moles of ethane in the 1 cc injection was determined using the ideal gas law:

$$n = \frac{PV}{RT} \quad (11)$$

where: n = moles of gas injected
 V = volume of gas injected

The 1 cc injected was determined to contain 4.0056×10^{-5} moles of ethene. The mass of this ethene was calculated by multiplying the number of moles injected by the molecular weight of ethene (30.07 g/mol). The mass of ethene injected was determined to be 1.2048 mg. Multiplying the mass of ethene injected by f_w and using appropriate unit factors gave the concentration of ethene in water to be 3.882 mg/L (ppm). Additional standards were created for ethane and the other gaseous chemicals by injecting various amount of gas stock into the sample vials. The range of concentrations for the standards was designed to encompass the expected concentrations in the wetland water samples.

Purge and trap methodology

Standard solutions and wetland water samples were analyzed by purge and trap gas chromatography. The specific methods were adapted EPA Methods 5030 and 8260B. The 40 mL VOA sample vials containing either standard solutions or actual wetland samples were placed in an Archon AutoSampler system built by Varian Analytical Instruments. The Archon AutoSampler was used in concert with an Encon Purge and Trap sample concentrator. The theory behind purge and trap methodology is described in detail in Chapter 2. Specific operating parameters of the instrument are shown below.

Sample Volume (mL)	5
Purge Gas	Helium
Purge Gas flow Rate (ml/min)	40
Purge time (min)	11
Purge Temp (deg C)	Ambient
Dry Purge time (min)	2
Desorb preheat (deg C)	245

Desorb Temp (deg C)	250
Desorb time (min)	2
Bake time (min)	10
Bake temp (deg C)	250
Moisture Reduction Bake (deg C)	260 (used to remove moisture from the trap after run)

The Archon AutoSampler is an automated device designed to work in conjunction with an Agilent 6890 Series Gas Chromatograph. It is designed to automate the tedious sample handling procedures associated with purge and trap analysis for VOCs under current USEPA guidance. A number of vials are placed in the sample holding tray inside of the Archon. A robotic arm transfers each vial in succession to a water probe, which extracts water from the sample vial and transfers it to an Encon Purge-and-Trap sample concentrator and is placed in a purge vessel. Helium gas is then purged through the sample before being vented from the system. Organic volatiles present in the water sample are retained on the absorbent trap. After purging, the trap is rapidly heated and the VOCs are desorbed to the GC. The vial is then returned to the tray and the instruments are automatically prepared for the next sample.

Gas Chromatograph methodology

After the sample is desorbed from the Encon Purge and Trap it is sent to the GC. The theory behind the operation of the GC is found in Chapter 2. The GC used in this effort was set up using a split column configuration. In this configuration, a splitter was used to send the sample into two columns and two detectors after injection into a single inlet. The front column was a Restek RTX-VRX and was connected to the micro-Electron Capture Detector (μ ECD). The back column was a J&W 113-4332 GS-

GASPRO and was connected to the flame ionization detector (FID). GC program

parameters were:

Oven

Initial Temp (deg C)	50
Initial Time (min)	1.50
Ramp (deg C/min)	10.00
Final Temp (deg C)	220
Hold Time at final Temp (min)	0
Post Temp (deg C)	50
Total Run Time (min)	18.50

Front Inlet

Mode:	Split
Initial Temp (deg C)	200
Pressure (psi)	15.00
Split Ratio:	5:1
Split Flow (mL/min)	20.6
Total Flow (mL/min)	27.8
Gas Saver:	On
Saver Flow (mL/min)	20.0
Saver Time (min)	2.00
Gas Type:	Helium

Back Inlet (not used)

Column 1 (Restek RTX-VRX)

Max Temp (deg C)	260
Nominal Length (m)	20
Nominal Diameter (µm)	180
Nominal Film Thickness (µm)	1.00
Mode	Const Press
Pressure (psi)	15.00
Nominal Init Flow (mL/min)	0.5
Average Velocity (cm/sec)	24
Inlet	Front
Outlet	Front
Outlet Pressure	Amb

Column 2 (J&W 113-4332 GS-GASPRO)

Max Temp (deg C)	260
Nominal Length (m)	30
Nominal Diameter (µm)	320
Nominal Film Thickness (µm)	n/a
Mode	Const Press
Pressure (psi)	15.00
Nominal Init Flow (mL/min)	3.6
Average Velocity (cm/sec)	52
Inlet	Front
Outlet	Back
Outlet Pressure	Amb

Front Detector (µECD)

Temp (deg C)	250
Mode: Constant Column+makeup flow	
Combined Flow (mL/min)	45
Makeup Flow:	On
Makeup Gas Type:	Nitrogen

Back Detector (FID)

Temp	250
Hydrogen Flow (ml/min)	40.0
Air Flow (mL/min)	400.0
Mode: Const Column+Makeup Flow	
Combined Flow (mL/min)	20.0

Electrometer: On

Makeup Flow: On
Makeup Gas Type: Nitrogen
Flame: On
Electrometer: On
Lit Offset: 2.0

IV. Results and Discussion

The results of the sampling and analytical laboratory procedures, as described in Chapter 3, are provided here in order to present a detailed characterization of the chlorinated solvent contamination levels in the various strata of the upward flow constructed wetland. These results are intended to provide an indication of the ability of the wetland to remove chlorinated solvents from groundwater inflow. It is hoped that the results will provide a starting point from which to design future upward flow wetlands designed to remediate contaminated groundwater. This chapter will also attempt to answer the research questions posed earlier in Chapter 1.

The first observations made during this effort were made during the piezometer installation phase. Some areas of the wetland exhibited soil characteristics that enabled the piezometers to be rather easily installed. Other areas of the wetland proved quite difficult in installing piezometers. Piezometer nests 1 – 30 proved much easier to install than nests 31 – 66. During construction of the wetland, the soil in the area of piezometers 31 – 66 appeared to be compacted more than the remainder of the wetland. The heavy equipment used during construction was staged in that area. This suggests that the repeated passes of the equipment over these strata possibly resulted in the increased soil compaction and in the difficulties encountered during the installation of the piezometers.

This effort revolved around the sampling of water in a constructed wetland and using gas chromatographic techniques for analysis. The first step in this effort involved determining the characteristic GC column retention times for the analytes of interest. A rather large amount of a chemical was injected into a 40 mL vial to create a solution of approximately 50 – 100 ppm. It was not necessary to determine the exact concentration

of these solutions as determining the retention time was the item of interest. Using concentrations in the parts per million range ensured that peaks could easily be identified. Solutions were created for all analytes and analyzed using the methods detailed in Chapter 3. Table 3 shows the characteristic retention times of each analyte and the detector that showed the greatest response to the spiked sample.

Table 3. Characteristic Retention Times for All Analytes

Analyte	Retention Time (min, detector)
PCE	9.010 (μ ECD)
TCE	6.402 (μ ECD)
cis-DCE	4.496 (μ ECD)
trans-DCE	3.856 (μ ECD)
1,1 DCE	3.228 (μ ECD)
Vinyl Chloride	6.709 (FID)
Ethane	1.893 (FID)
Ethene	2.175 (FID)
Methane	1.359 (FID)

The next step in this process involved the creation of calibration curves for the analytes of interest. Stock solutions for both gaseous and liquid analytes were prepared and then diluted as described earlier in order to provide standard solutions encompassing the range of expected concentrations. Calibration curves were developed for PCE, TCE, trans-DCE, cis-DCE, ethene, and ethane and are found in Appendix C. An attempt was made to create a calibration curve for 1,1 DCE in the manner detailed in Chapter 3. Approximately 5 μ L of 1,1 DCE was injected into a 40 mL VOA vial filled with de-ionized water. The calculated concentration of this “spiked” sample was 137.8 ppm. This solution was allowed to dissolve for 24 hours and then placed into the purge and trap for analysis. A large peak occurred on the μ ECD at 3.228 minutes as shown in the table above. However, when standard solutions were prepared in the <50 ppb range, no

response was registered by either of the detectors. It was determined that the method utilized for this effort was unable to detect 1,1 DCE in such low concentrations. Of the three possible isomers of DCE that are possible products of the reductive dechlorination, several studies have indicated that cis-DCE dominates over trans-DCE and that 1,1-DCE is the least significant daughter product (Lorah and Olsen, 1999). Because of this, the inability of the instrument to detect 1,1-DCE at low concentrations was considered to be of no consequence. Additionally, stock solutions of methane and vinyl chloride were created at concentrations of 1.464 ppm and 57.57 ppm respectively. Retention times for both analytes were identified on the FID but no response was observed when calibration curves were attempted.

Each viable sampling point was sampled three times throughout the effort. Samples were first taken in the top strata followed by the middle and bottom strata. This was intended to eliminate any adverse affects caused by sampling on overlying strata. That is, if a piezometer in the bottom layer was purged and sampled, there may have been an unwanted effect on those piezometers located in the same nest in overlying layers. Therefore, the sequence for sampling a particular piezometer nest was A, B, and C. All piezometers in a layer were sampled before moving on to subsequent layers. All samples were taken between 29 Nov and 19 Dec 01.

After all piezometers in a layer were sampled and analyzed 3 times, response data was compiled and placed in a spreadsheet to facilitate data analysis. Each sample output was examined to determine what contaminants were present. Only PCE and TCE were present in high enough concentrations to provide adequate instrument response. All other analytes were non-detectable using the method specified in Chapter 3. From this data, it

was possible to calculate average concentration levels. Raw sample data is found in Appendix D.

The top layer was the first layer to be sampled the required 3 times. As described earlier, sampling occurred in a “top-to-bottom” manner. A sampling “pass” involved sampling of all piezometers in the top layer, followed by the middle and bottom layers. This process was repeated two more times to get the requisite 3 samples from each piezometer. The contour plot below shows the average concentrations of PCE in the top layer for the three sample runs.

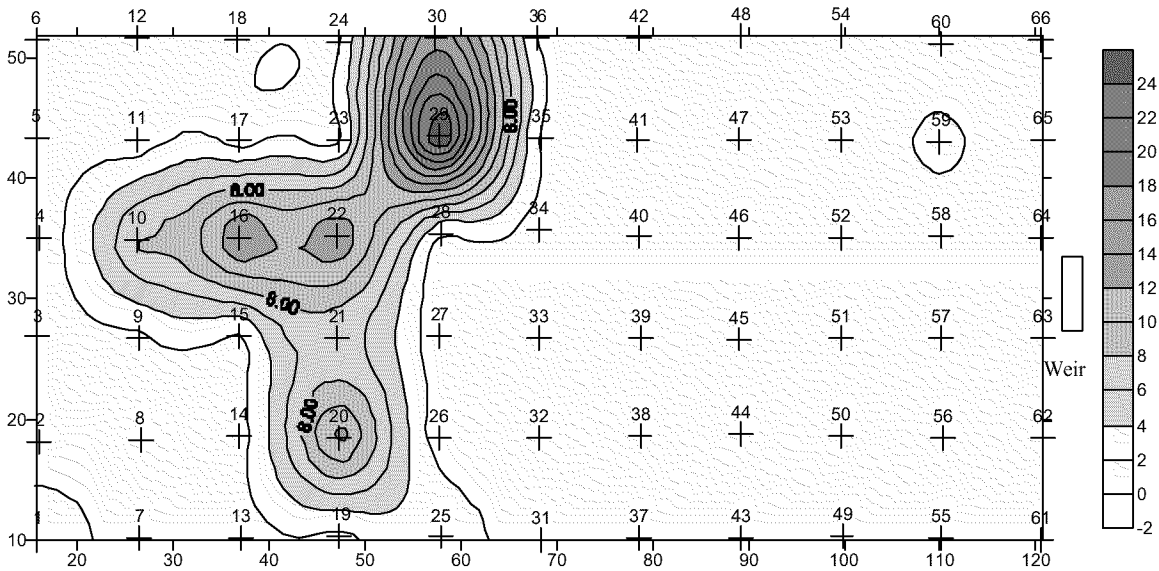


Figure 14. Average PCE Concentration (in ppb) in Top Layer

The average concentration of PCE in the top layer during the three runs was 3.6537 ppb with a maximum concentration of 31.22 ppb at piezometer 29A during the second sample pass. This average concentration was determined using BestFit which is a probability distributing fitting program. The software examines input data and determines what continuous distribution most likely produced the data. Population parameters can then be

determined from this best fit distribution. The BestFit software determined that the input data for PCE concentration in the top layer closely resembles a two-parameter lognormal distribution. The BestFit fit results and statistics are shown in Appendix E.

Large concentrations of PCE were discovered adjacent to piezometers 10A, 16A, 20A, 22A, and 29 A. These high concentrations were expected because of observations made in the field. When all of the piezometers were tested to determine volume of water recovered after purging, it was determined that piezometer 22A had a recovered volume of 100 mL two hours after being completely purged. Similarly, 10A had a recovered volume of 123 ml after two hours. Additionally, all of these piezometers were located in a portion of the wetland where the installation of the piezometers was relatively easy. Another research effort underway at the time of sampling was designed to obtain hydraulic conductivity values for each layer of the wetland (Entingh, 2002). This effort also involved documenting the level to which water rose in each piezometer tube due to water pressure gradients. Figure 15 shows the water levels present in each piezometer in the top layer. Values are for the top layer only and are measured in feet above a datum point at the bottom of the wetland. Hydraulic head elevations were measured on 1 Nov 01 before any sampling efforts took place.

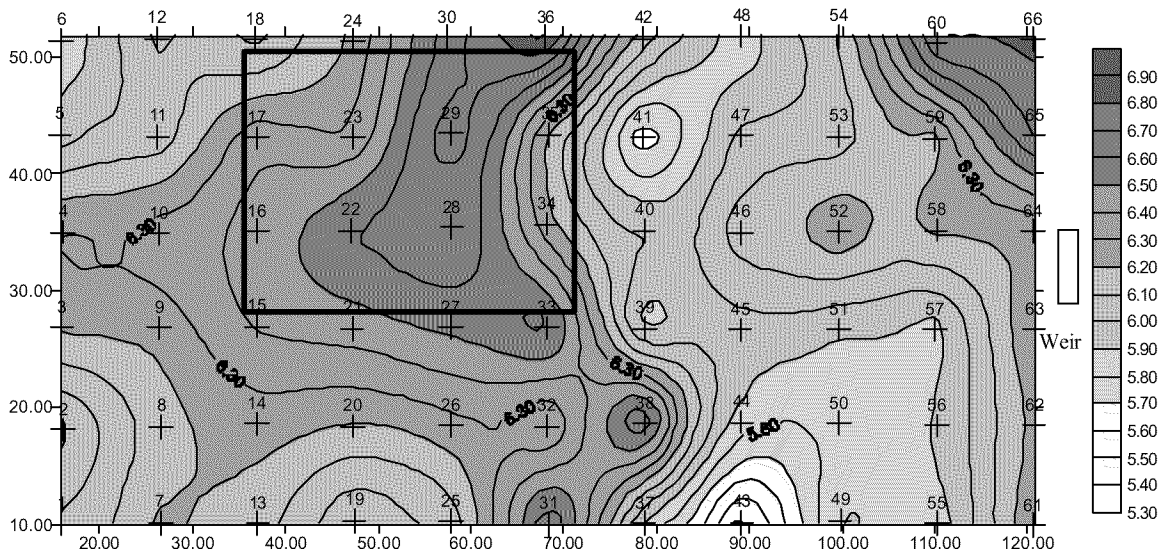


Figure 15. Water Potential Levels in Top Layer Piezometers.

The contour plot shows higher hydraulic head readings as darker shades. High hydraulic head readings were found to have occurred within the boxed area of Figure 15. These same areas also showed elevated PCE levels as shown in Figure 14.

Hydraulic conductivity is defined as the rate at which water can move through a permeable medium (USEPA, 2002). Figure 16 shows the hydraulic conductivities discovered during this concurrent research.

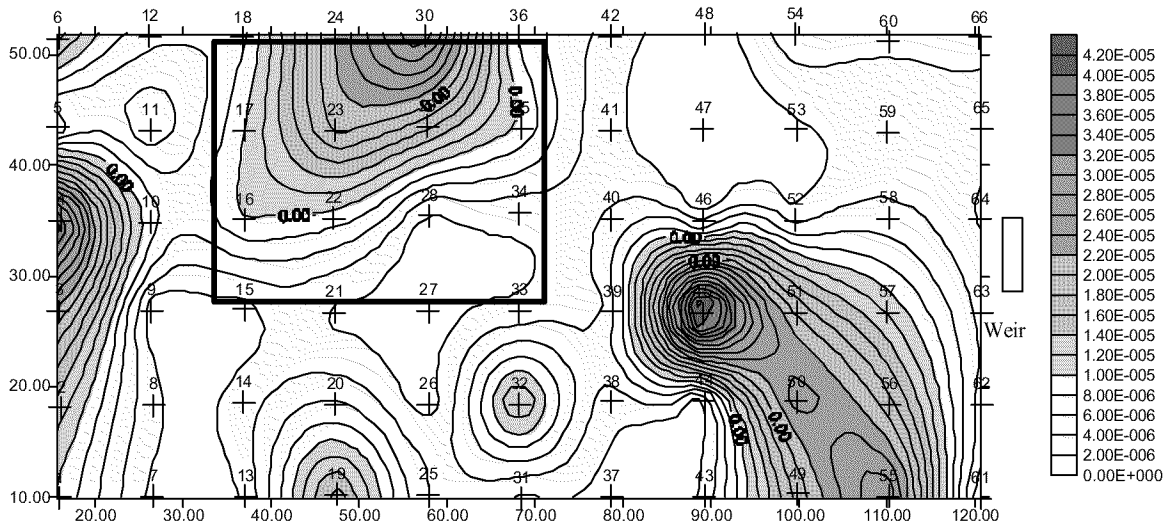


Figure 16. Hydraulic Conductivities (ft/sec) in the Top Layer.

Elevated hydraulic conductivity readings occur in three main areas of the top layer of the wetland cell. The darker shadings of the contour plot indicate these areas. As was the case with hydraulic head readings and PCE levels, the area enclosed by the box shows the elevated reading area. Hydraulic conductivity and water level readings for the top layer are found in Appendix F.

Interesting correlations became evident when comparing hydraulic conductivities, piezometer water levels, and contaminant concentrations. High levels of all three were observed the same area. The high volumes recovered during testing, coupled with the ease of the installation of the piezometers in the boxed area led to a hypothesis that there was significantly higher upward water flow to those piezometers. The combined effects of this appeared to result in water that would contain high contaminant levels being able to migrate rapidly to the upper layers. This hypothesis was bolstered by the findings of elevated levels of PCE found at those points. Combining the findings of elevated PCE levels with the data from the concurrent research showing elevated hydraulic

conductivities and head in the same areas as the elevated contaminant levels leads to the conclusion that PCE-laden water is, in fact, rapidly flowing to the upper layer of the wetland. It is interesting to note that elevated PCE levels appear only in those areas that contain both high hydraulic conductivities and high hydraulic head readings. For example, piezometer 45A showed elevated hydraulic conductivities (Figure 16) but a lower water level (Figure 15). Piezometer 45A did not have elevated PCE concentrations (Figure 14).

Figure 14 shows several piezometers that have higher than average PCE concentrations. Piezometer 20A had an initial recovered volume of only 2 mL two hours after being completely purged. Well development efforts resulted in a recovered volume of 400 mL after two hours. This increased recovered volume, coupled with elevated hydraulic conductivities and water levels at that point suggest that higher concentrations of PCE were reaching the upper layer in the vicinity of this piezometer during sampling. Piezometer 16A was not subjected to well development efforts in this study. However, a concurrent study effort did develop the well before samples were taken. These well development efforts are suspected of creating voids and channels in the sediment layers that allowed for PCE-laden water to rapidly migrate to upper layers of the wetland in a manner similar to piezometer 20A. Piezometer 29A was located in an area of the wetland that became virtually fluidized during the study. Shortly after the installation of the piezometers, the inflow rate was increased in an attempt to completely saturate all portions of the wetland. This was combined with the raising of the surface water level by approximately 2 inches. Because some areas of the wetland initially had no standing water and the surface soil was completely dry, slats were placed in the outflow weir in an

attempt to raise the level of the surface water and completely saturate all portions of the wetland. After these efforts, the soil near 29A began to become increasingly spongy. Eventually, the area deteriorated to a point at which the soil could not support the weight of the researchers. Extreme care had to be taken to avoid stepping into the fluidized area. On several occasions, this occurred and the researchers sank over 2.5 feet into the sediment. This was a significant change from the original soil conditions that permitted the researcher to freely stand in the area. The soil conditions deteriorated so much that water was ultimately observed to be flowing directly from the soil in this area. During recovered volume tests, 29A showed values that exceeded the ability of the purging instrument to completely purge the piezometer. These observations, along with hydraulic conductivities and water levels, and the significantly higher levels of PCE seem to suggest that the water being pumped into the bottom of the wetland was able to migrate to the upper layers, and ultimately the surface, extremely fast, thereby minimizing the contact time with the desired reducing conditions. Higher concentrations of PCE were also found in the piezometers surrounding 10A, 16A, 20A, and 22A as described above. As stated earlier, it was observed throughout the sampling effort that groundwater freely flowed from the sediment in the vicinity of piezometer 29A. This would suggest that the sediment in that area was so completely deteriorated that groundwater was able to flow to the top layer and the surface rapidly with minimal exposure to the subsurface reducing conditions.

Gilbert (1987) describes the method used to calculate a 95% confidence interval about the mean for a non-normal distribution. The formula used for the upper and lower limits are:

$$UL = \bar{x} + Z \times \left(\frac{s}{\sqrt{n}} \right) \quad (12) \quad LL = \bar{x} + Z \times \left(\frac{s}{\sqrt{n}} \right) \quad (13)$$

where: \bar{x} = mean value of the non-normal distribution
 Z = value of the standard normal variable that cuts off 2.5% of the distribution tail (1.96 for the upper limit, -1.96 for the lower limit)
 s = standard deviation of the non-normal distribution
 n = number of samples taken.

It was determined that a 95% confidence interval would be calculated for the data once outliers were removed in order to eliminate any adverse influences on the data. It was desired that an average concentration and a 95% confidence interval be obtained to better characterize the contaminant levels in an “undamaged” constructed wetland. The resulting data set was analyzed using BestFit and is shown in Appendix H. The program determined that a four-parameter Beta General distribution provided the best fit to the data once outliers were removed. The BestFit analysis provided a mean value of the distribution of 0.83885 ppb and a standard deviation of 0.43924 ppb. Using the formulas for upper and lower bounds, average concentration of PCE in the upper layer of the wetland was calculated to be 0.83885 ± 0.114 ppb.

The average TCE concentration contour for the top layer is shown below in Figure 17.

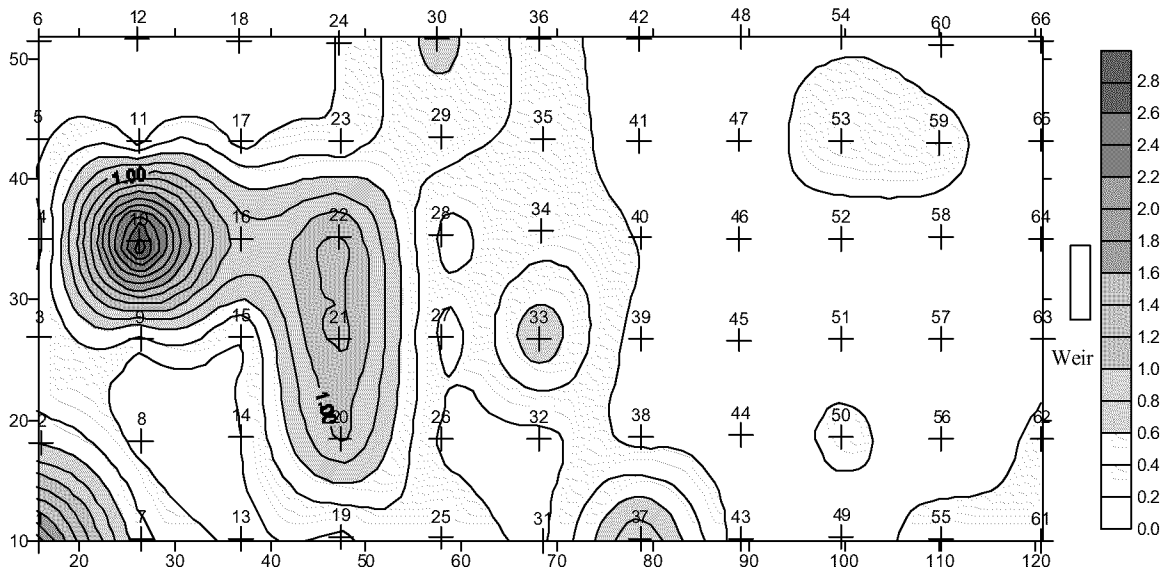


Figure 17. Average TCE Concentration in ppb in Top Layer

The average TCE concentration in the top layer over the course of the three sample runs was 0.34198 ppb with a maximum concentration of 3.76 ppb at piezometer 10A in the third and final sample taken at that piezometer. BestFit was again used to analyze the sample data with an inverse Gaussian distribution providing the best fit. BestFit results are shown in Appendix E. Outliers were removed from the data and a 95% confidence interval for the mean concentration of TCE in the upper layer was calculated using the method prescribed earlier. The resulting data set most closely resembled an inverse Gaussian distribution as shown in Appendix H. The resulting average concentration of TCE in the upper layer of the wetland was calculated to be 0.17582 ± 0.034 ppb.

Similarities appear when comparing the contour plots of PCE and TCE concentrations in the top layer. Piezometer 10A shows the highest level of TCE in the layer with a concentration of 3.76 ppb found in the third sample taken from the

piezometer. This was expected as the high PCE concentrations were also found there. TCE levels in piezometer 29A were not as elevated as those found in piezometer 10A even though PCE levels were higher than those found in 10A. Average PCE concentrations at piezometer 10A were 10.19 ppb. Average TCE concentrations at 10A were 2.96 ppb. Average PCE concentrations at piezometer 29A were much higher with an average value of 32.79 ppb while TCE levels averaged only 0.604 ppb. This suggests that the upward flow of the water was so great at piezometer 29A that very little reduction to TCE was able to take place while a slower upward flow of water at piezometer 10A allowed for some reduction to TCE to occur. The areas around piezometers 10A, 16A, 20A, 21A, 22A also show increased TCE levels for this layer and, again, higher than normal upward flows in those areas are suspected of causing the elevated rates.

The contour plot below shows the PCE concentrations found in the middle layer.

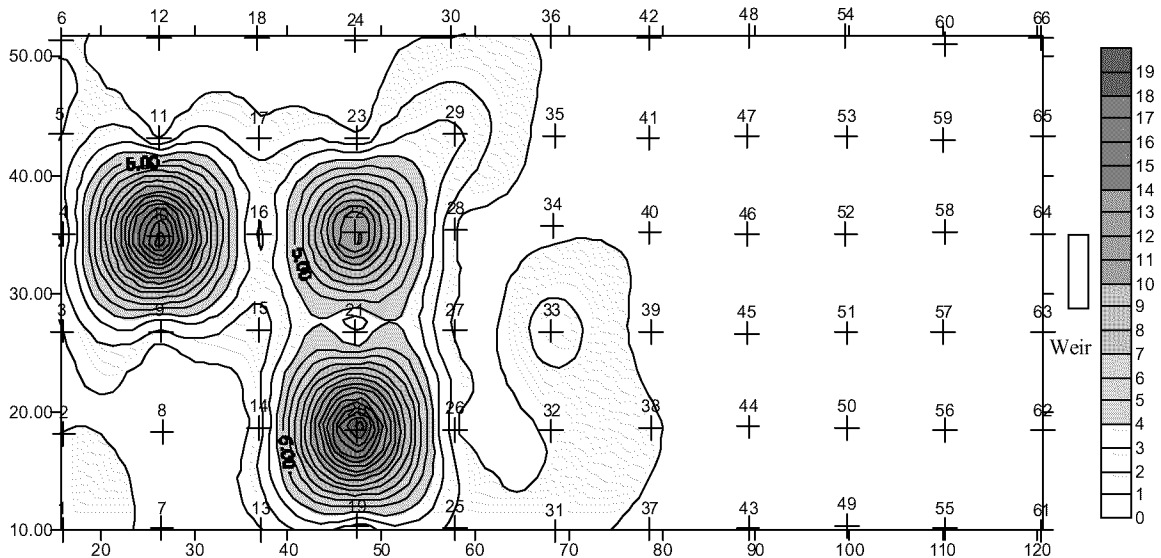


Figure 18. Average PCE Concentration in ppb in Middle Layer

The average concentration of PCE in ppb throughout the middle layer during the three runs was 1.38945 ppb with a maximum concentration of 26.47 ppb found at piezometer 10B during the third sample taken at the point. A lognormal distribution provided the best fit of the input data. BestFit results are shown in Appendix E. Once outliers were removed, a logistic distribution provided the best fit of the data. Average concentration of PCE in the middle layer of the wetland was calculated to be $0.83969 \pm .068$ ppb.

The average TCE concentration contour in the middle layer is shown in Figure 19.

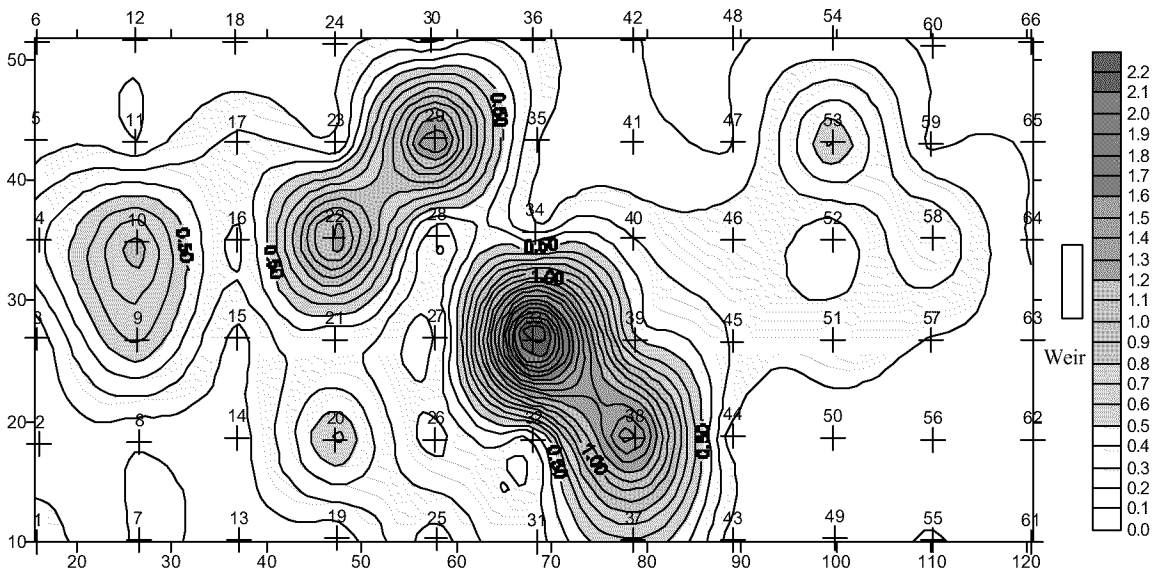


Figure 19. Average TCE Concentration in ppb in Middle Layer

The average TCE concentration in the middle layer over the course of the three sample runs was 2.099 ppb with a maximum concentration found at piezometer 33B of 2.92 ppb during the second sample taken. A Pearson5 distribution provided the best fit to the input data. BestFit results are shown in Appendix E. Once outliers were removed, an inverse Gaussian distribution provided the best fit of the data. Average concentrations of TCE in the middle layer of the wetland were then calculated to be 0.16665 ± 0.028 ppb.

There appears to be a correlation between elevated PCE and TCE levels in the middle layer. Piezometers 10B, 20B, 22B, and 29B all showed higher than average PCE levels in the middle layer. These piezometers also show higher than average TCE levels. This suggests that the increased upward water flow at these piezometers results in elevated contaminant levels. This also seems to indicate that the flow regime in those areas is such that it allows sufficient contact time for some, but not all, PCE to be reduced to TCE.

Figure 20 shows the water levels present in each piezometer in the middle layer (Entingh, 2002). The area enclosed by the box shows where PCE concentrations were greatest. This area shows somewhat higher water levels when compared to other piezometers in the layer, although the levels were not the highest found. The highest water levels were recorded at piezometer 33B.

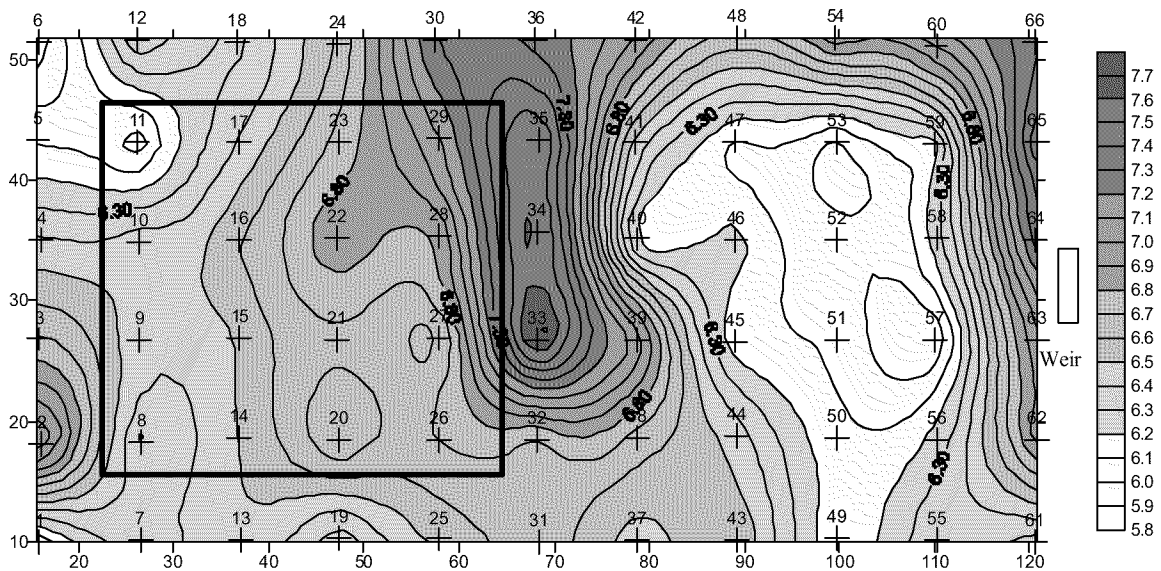


Figure 20. Water Potential Levels in Middle Layer Piezometers.

Figure 21 shows the hydraulic conductivities found in the middle layer (Entingh, 2002). The area enclosed by the box shows where hydraulic conductivities were the highest in the middle layer.

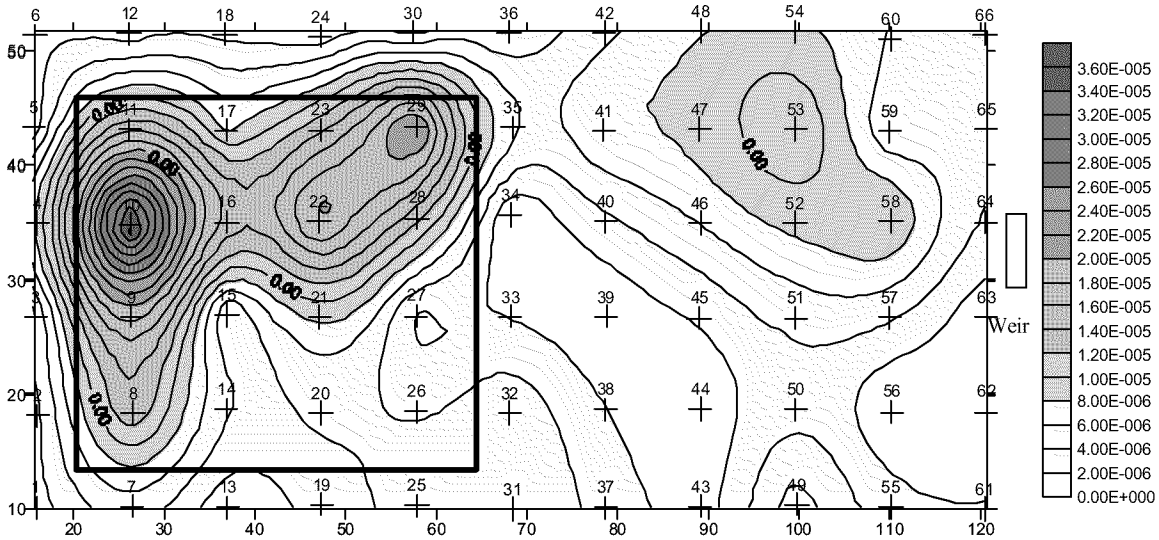


Figure 21. Hydraulic Conductivities (ft/sec) in the Middle Layer.

As was the case with the top layer, a combination of high hydraulic conductivities and water levels resulted in the elevated PCE levels detected at certain piezometers. Hydraulic conductivity and water level data for the middle layer can be found in Appendix F.

Figure 22 shows the average PCE concentrations found in the lower layer. Piezometer 29C could not be driven to its predetermined depth. Samples taken from this piezometer showed concentrations of 1.706, 1.104 and 1.16 ppb for the three samples. Significantly lower concentrations of PCE were detected in piezometer 37C. PCE concentrations for the three samples were found to be 5.736, 7.329, and 6.883 ppb.

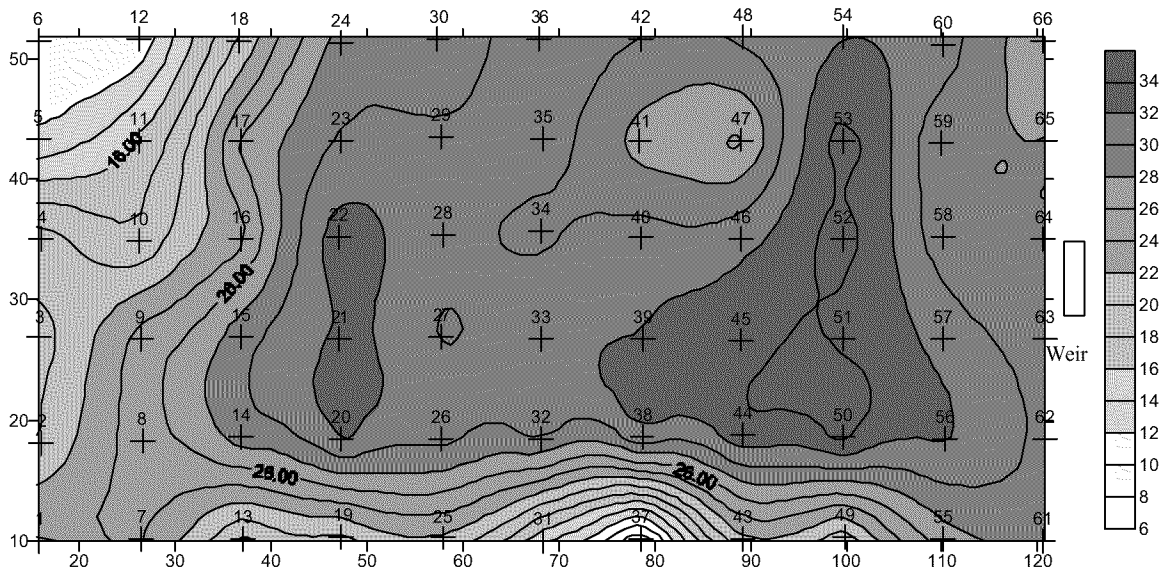


Figure 22. Average PCE Concentration in ppb in Bottom Layer

The average concentration of PCE in the bottom layer during the three sample runs was 26.839 ppb with a maximum concentration of 42.03 ppb found at piezometer 44C during the third sample taken at that point. A four-parameter Beta General distribution provided the best fit to the input data. BestFit results are found in Appendix E. Once outliers were removed, a triangular distribution provided the best fit of the data. Average concentration of PCE in the middle layer of the wetland was calculated to be 26.96 ± 1.41 ppb.

During the purging and sampling of piezometer 37C it was discovered that it was possible to completely remove all of the water from the screened portion. This low recovered volume rate appears to have just the opposite affect that large recovered volumes have on the level of contaminant present. The soil conditions in this area appear to have allowed the contaminated groundwater to remain in the soil matrix and be exposed to reducing conditions much longer than elsewhere in the layer. This would

result in the significantly lowered concentrations of PCE discovered. A second area of low PCE concentration is found in the area around piezometer 6C. This piezometer was not sampled during this effort because it did not correctly deploy during installation as described earlier. It was omitted from the data for the contour plot and may have contributed to the lowered concentrations shown in the contour plot. However, those piezometers located around it, 5C and 12C, also showed decreased levels of PCE that would indicate slower upward flow and recovery rates. These slower flows would then allow for longer contact times that resulted in the lower PCE concentrations.

The average TCE concentration contour in the bottom layer is shown below in Figure 23.

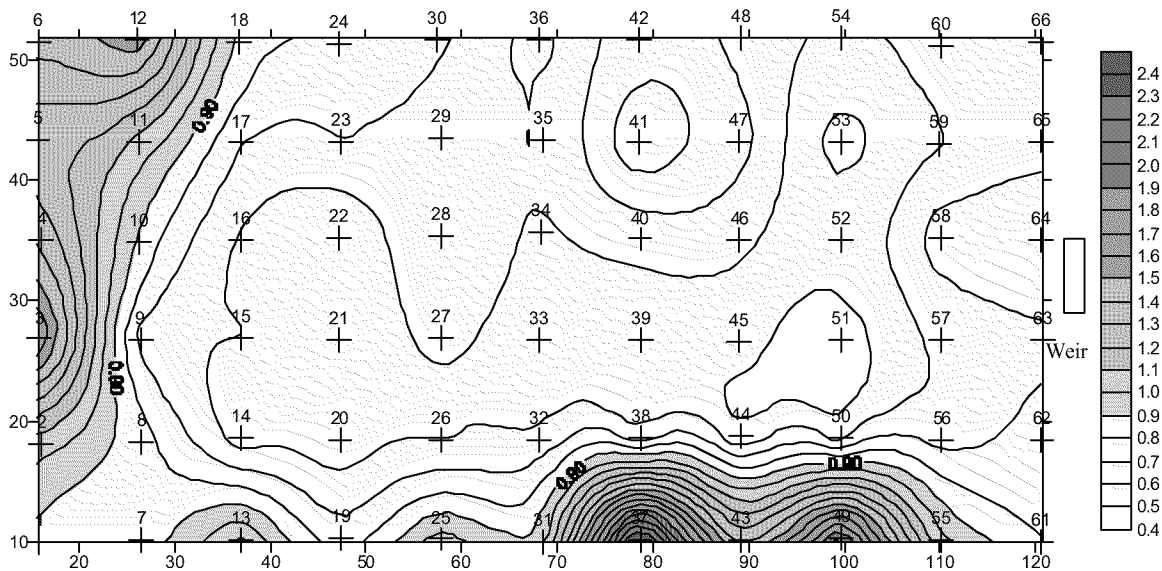


Figure 23. Average TCE Concentration in ppb in Bottom Layer

The average TCE concentration in the bottom layer was 0.81043 ppb with a maximum value of 2.79 ppb at piezometer 37C on the third sample run. A LogLogistic distribution provided the best fit of the input data. BestFit results are shown in Appendix E. Once

outliers were removed, a Weibull distribution provided the best fit of the data. Average concentration of TCE in the bottom layer of the wetland was calculated 0.70578 ± 0.044 ppb.

When comparing the average PCE and TCE concentrations in the bottom layer, a distinct correlation becomes evident. PCE concentrations in the bottom layer are the lowest in the areas surrounding piezometers 37C and 49C. There is also a low concentration region at the beginning of the cell (piezometers 1 – 6). When compared to the TCE concentration contour of the bottom layer, the same areas show elevated levels of TCE compared to the remainder of the layer. This seems to suggest that soil conditions in these areas are such that PCE is very effectively reduced to TCE. Flow regimes, soil conditions, and microbial community composition in those areas may all collaborate to create these unique conditions in the cell.

Samples of the inflow stream were taken throughout the sampling effort from a tap in the source well line as it surfaced in the adjacent pump house. These inflow samples were analyzed using the same methodology applied to the wetland samples. Samples were also taken from the area directly adjacent to the outflow weir. These grab samples were taken directly from the surface water before it flowed out of the wetland and entered the sanitary sewer system. The concentrations of PCE and TCE in both the inflow and outflow stream are found in Table 4.

Table 4. Inflow and Outflow PCE and TCE Concentrations

Sample Date	Inflow PCE Concentration	Inflow TCE Concentration	Outflow PCE Concentration	Outflow TCE Concentration
29 Nov 01	31.43 ppb	0.47 ppb	Not Sampled	Not Sampled
30 Nov 01	32.77 ppb	0.50 ppb	Not Sampled	Not Sampled
1 Dec 01	33.70 ppb	0.52 ppb	Not Sampled	Not Sampled
4 Dec 01	33.56 ppb	0.61 ppb	Not Sampled	Not Sampled
6 Dec 01	33.52 ppb	0.51 ppb	Not Sampled	Not Sampled
9 Dec 01	33.65 ppb	0.48 ppb	Not Sampled	Not Sampled
11 Dec 01	34.66 ppb	0.49 ppb	Not Sampled	Not Sampled
13 Dec 01	32.87 ppb	0.69 ppb	Not Sampled	Not Sampled
14 Dec 01	35.71 ppb	0.51 ppb	5.25 ppb	0.59 ppb
15 Dec 01	36.57 ppb	1.70 ppb	5.01 ppb	5.22 ppb
16 Dec 01	32.54 ppb	0.51 ppb	6.44 ppb	0.69 ppb
18 Dec 01	36.64 ppb	0.53 ppb	5.67 ppb	2.05 ppb
Averages	33.97 ppb	0.63 ppb	5.76 ppb	2.42 ppb

A comparison of average concentrations of PCE for all layers, inflows, and outflows is shown in Table 5. The effect of all piezometers is taken into account. None are omitted from the table.

Table 5. Summary of Average PCE Concentrations in ppb

Sample Type	Avg PCE Conc (ppb)
Inflow	33.97
Bottom Layer	26.839
Middle Layer	1.38945
Top Layer	3.6537
Outflow	5.758

It is easily seen from the above table how the overall concentrations decrease as the water travels upward through the wetland sediment. The effects of the top layer and surface water being directly fed from the inflow are seen in the elevated average

concentrations found in the upper layer and the outflow. At several times throughout the sampling and analysis effort, water was also observed to be flowing directly from the berm surrounding the wetland cell above the water level. This water, bypassing the reductive conditions of the wetland, along with the PCE-laden water flowing from areas surrounding nests 10, 16, 20, 22, and 29 is believed to be a primary cause of the higher PCE concentrations in the outflow stream.

It is interesting to note that the average concentration of PCE in the middle layer was lower than the average concentration found in the upper layer. It is believed that the higher top layer concentrations were a result of the soil conditions in the vicinity of piezometer nests 10, 16, 20, 22, and 29. As stated earlier, the high water flows in these areas enabled groundwater to reach the surface with minimal contact time with reducing conditions. The PCE concentration data was analyzed using JUMP 4.0 in order to determine what readings could be considered outliers for the two layers. Box and whisker plots were generated for all PCE data. Those data points that fell outside of the area of the whiskers were considered to be outliers. Removing the impact of these significantly higher concentrations in both the top and middle layers results in an average top layer PCE concentration of 0.83885 ppb and an average middle layer PCE concentration of 0.83969 ppb. This suggests that nearly all reduction of PCE occurs in the bottom layer of the wetland with minimal degradation occurring in the middle and top layers. Table 6 shows the average PCE concentrations in the wetland once outliers were removed from the data.

Table 6. Summary of Average PCE Concentrations with Outliers Removed

Sample Type	Avg PCE Conc (ppb)
Inflow	33.97
Bottom Layer	26.96
Middle Layer	0.839
Top Layer	0.838
Outflow	5.758

In areas located away from the effects of the high flowing piezometers, the reduction of PCE is over one order of magnitude. For example, nest 53 showed PCE concentrations that averaged 34.95 ppb in the bottom layer. The top layer had average PCE concentrations of 0.88 ppb.

A comparison of the average TCE concentrations for all layers, inflows, and outflows is shown in Table 7. As was the case in Table 5, all piezometers are included.

Table 7. Summary of Average TCE Concentrations

Type	Avg TCE Conc (ppb)
Inflow	0.628
Bottom Layer	0.81043
Middle Layer	2.099327
Top Layer	0.34198
Outflow	2.42

As in Table 5, which showed average PCE concentrations throughout the wetland cell, average TCE concentrations decrease as the flow moves upward except for an increase in concentrations in the middle layer. This may suggest that some PCE is being reduced to TCE in the bottom layer with the resulting TCE shown in the middle layer. The outflow concentrations of TCE are the highest found throughout the study. The elevated PCE levels in the surface water are expected to elevate the surface TCE readings

as the PCE degrades at the surface. As was the case with average PCE concentrations in areas less affected by the high flowing piezometers, TCE concentrations were significantly reduced. For example, TCE concentrations at nest 55 declined from an average of 1.02 ppb in the bottom layer to an average of 0.28 in the top layer. Table 8 shows the average TCE concentrations in the wetland once outliers were removed from the data.

Table 8. Summary of Average TCE Concentrations with Outliers Removed

Type	Avg TCE Conc (ppb)
Inflow	0.628
Bottom Layer	0.71
Middle Layer	0.167
Top Layer	0.176
Outflow	2.42

The USEPA method detection limit (MDL) is described as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. The MDL protects against incorrectly reporting the presence of a compound at low concentrations in cases when noise and actual analyte signal may be indistinguishable. The MDL concentration does not imply accuracy or precision of the quantitative measurement (USGS, 2002)

The procedure for determining the method detection limit for a given analyte specifies a minimum of seven replicate spikes prepared at a low concentration (generally 1 to 5 times the expected MDL) and processed through the entire analytical procedure. The MDL is then calculated using the following formula (USEPA, 1992):

$$MDL = s \times t_{(n-1, \alpha=0.99)} \quad (14)$$

where: s = standard deviation of standard measured concentrations of n spiked determinations

n = number of replicate spike determinations at 1 to 5 times the expected MDL

t = Student's t value at $n-1$ degrees of freedom at $1-\alpha$ (99%) confidence level
when $n = 7$ and $\alpha = 1$, $t = 3.14$

α = level of significance

The MDL for PCE was determined by analyzing 7 replicate samples containing 1.53 ppb of PCE. The MDL for PCE was calculated to be 0.417 ppb. The MDL for TCE was determined by analyzing 7 replicate samples containing 1.38 ppb. The MDL for TCE was calculated to be 0.187 ppb.

V. Conclusions and Recommendations for Further Study

The purpose of this study was to develop a sampling and analysis protocol that could be used to determine the levels of PCE and its daughter products as they traversed the layers of an upward flow constructed treatment wetland. This included the development and placement of a three-dimensional sampling grid that would provide a sufficient number of sampling points necessary to accurately characterize the contaminant levels present throughout the wetland cell. It also included creation of a unique sampling and analysis protocol used to analyze over 600 water samples taken from throughout the wetland. Field and laboratory efforts proved to be both slow and physically demanding. Significant effort went into the installation of the sampling grid and the development of the sampling and analysis methodology used.

Contaminant levels throughout the wetland cell were determined by purge-and-trap gas chromatography. Levels of PCE were shown to decline from an average of 33.97 ppb in the inflow stream to an average of 3.6537 ppb in the upper layer. This was nearly a 91% reduction in the amount of PCE present. Several areas of the wetland exhibited abnormally high levels of PCE throughout the layers. These high concentrations occurred in areas where high hydraulic pressure gradients and hydraulic conductivities combined to allow PCE-laden water to migrate to the upper layers of the wetland with minimal contact time for reduction to take place. Removing those points from the data set increased the PCE reduction efficiency to nearly 98% with an upper level concentration average of 0.83885 ppb. TCE inflow rates averaged 0.628 ppb while TCE concentrations in the upper layer averaged 0.175 ppb. TCE concentrations within

the wetland peaked in the middle layer of the wetland suggesting that the additional TCE was resulting from the reduction of PCE there and in the bottom layer.

Several areas of the wetland exhibited abnormal behavior that indicated water from the lower levels was able to reach the top of the wetland before any significant reduction was able to take place. The causes of this rapid migration appear to be two-fold. First, the flow rate from the pump house was increased in the early stages of the study. This increase is suspected of causing the soil to become fluidized in one area of the wetland. Additionally, this effort and a concurrent research project attempted to develop those wells that showed extremely low recovery rates. These development efforts are suspected of causing channelization in the sediment layers. This channelization, combined with the increased inflow rate, allowed for the supply water to reach the upper levels before reduction could take place.

The concentration of PCE entering the wetland via the inflow stream increased during the course of the sampling effort leading to an increase in PCE concentration in the lower layer of the wetland. However, the middle and upper layers of the wetland showed declining contaminant concentrations during the course of the sampling efforts. This suggests that the wetland is an ongoing state of flux. That is, the ability of the wetland to degrade chlorinated solvents appears to be improving over time. Microbial community populations may be increasing as they consume the organic carbon that was placed in the bottom layer during construction. Inflow concentrations and average sample concentrations over time are shown in Appendix D.

Effort Strengths

This study succeeded in its effort to develop a sound sampling methodology for an upward flow constructed treatment wetland. The sampling method developed proved to be successful in being able to extract water samples and prepare them for analytical procedures.

The study succeeded in characterizing the level of PCE and TCE contamination throughout all areas of the wetland. It confirmed that PCE levels are efficiently reduced as the water flows up through the wetland. It showed that a wetland designed specifically for the purpose of removing PCE from an aquifer was a viable method of bioremediation.

Effort Limitations

This effort proved limiting in that it was unable to provide any insight as to the level of any additional PCE daughter products. The three isomers of DCE, VC, ethane, ethylene, and methane were not found at detectable concentrations. The methods used may not have been sensitive enough to accurately detect these compounds at the levels at which they may have occurred.

Further insight to the ultimate fate of PCE in this wetland is needed. This effort was unable to determine exactly what processes were occurring that resulted in the reduction of PCE levels as the water moved through the wetland layers. For example, no effort was made to determine what effects the adsorption of PCE to wetland sediment had on the levels of PCE found in the water.

The next step in this effort should be to determine how much PCE remains in the wetland sorbed to sediment particles. The literature states that additional daughter products of PCE, such as DCE and VC, can be expected to occur in the sediment of a

wetland exposed to chlorinated solvents (Lorah and Olsen, 1999). Additional efforts should be undertaken in an attempt to determine if and at what level the daughter products of PCE not identified in this study are occurring in the sediment layers of the constructed wetland at WPAFB.

Recommendations for Further Study

Some suggestions for future research are hinted above. However, this overall effort could benefit from study in the following areas:

- Determine the amount of dissolved oxygen (DO) present in the water throughout the wetland sediment. Also, quantify the levels of conductivity and pH occurring in the wetland. Further insight to the processes occurring in the wetland may be gained by quantifying these properties of the water as it moves through the layers.
- Repeat this effort in the adjacent cell of the wetland. The second wetland cell was constructed using a layer of iron-rich soil. This iron layer is expected to provide additional pathways for chlorinated solvent destruction. Originally, this effort had planned to compare the reduction efficiency of two differently constructed cells but time constraints prevented any study of the second cell to be completed.
- An attempt should be made to determine the effect that adsorption has on the levels of chlorinated solvent contamination in the wetland. Significant amounts of PCE and other chlorinated solvents may remain in the wetland sorbed to sediment particles. Core samples may be taken and analyzed to determine if any significant sorption of contaminants is taking place.

- A study of the effect of the flow rate through the wetland should be done.

This effort made no attempt at adjusting the inflow rate into the wetland.

Increasing or decreasing the rate at which PCE-laden water enters the wetland sediment should have a large impact on the ability of the wetland to remove the contaminant.

Final Assessment of Thesis Effort

Sampling and analyzing the water in the sediment of a constructed treatment wetland is a time-consuming and physically demanding process. The results of this effort shed light on the efficiency and effectiveness of the processes occurring in the wetland. The discoveries can be used to adjust the design parameters of constructed wetlands such as inflow rates, sediment layer thickness, and wetland surface area. The results can be used to enhance the design of future wetland cells in an attempt to optimize the efficiency of a constructed treatment wetland to remove chlorinated solvents from an aquifer.

Appendix A: Recovery Data Before Development

The following table details the top layer of the wetland, only.

Top Strata	First Purge	Second Purge	Elapsed Time (1 - 2)	Volume (mL)	Recovery Rate (mL/hr)	Third Purge	Elapsed Time (2-3)	Volume (mL)	Recovery Rate (mL/hr)
1	11/3/01 1:50 PM	11/3/01 4:11 PM	2:21	25	10.64	11/4/01 9:19 AM	17:08	100	5.84
2	11/3/01 1:55 PM	11/3/01 4:12 PM	2:17	2	0.88	11/4/01 9:21 AM	17:09	19	1.11**
3	11/3/01 1:58 PM	11/3/01 4:14 PM	2:16	1	0.44	11/4/01 9:22 AM	17:08	25	1.46**
4	11/3/01 2:01 PM	11/3/01 4:15 PM	2:14	13	5.82	11/4/01 9:24 AM	17:09	67	3.91
5	11/3/01 2:04 PM	11/3/01 4:16 PM	2:12	22	10.00	11/4/01 9:26 AM	17:10	96	5.59
6	11/3/01 2:06 PM	11/3/01 4:17 PM	2:11	5	2.29	11/4/01 9:28 AM	17:11	24	1.40**
7	11/3/01 2:23 PM	11/3/01 4:26 PM	2:03	63	30.73	11/4/01 9:39 AM	17:13	108	6.27
8	11/3/01 2:20 PM	11/3/01 4:24 PM	2:04	11	5.32	11/4/01 9:38 AM	17:14	131	7.60
9	11/3/01 2:17 PM	11/3/01 4:23 PM	2:06	14	6.67	11/4/01 9:36 AM	17:13	68	3.95
10	11/3/01 2:15 PM	11/3/01 4:22 PM	2:07	123	58.11	11/4/01 9:35 AM	17:13	127	7.38
11	11/3/01 2:12 PM	11/3/01 4:20 PM	2:08	5.5	2.58	11/4/01 9:33 AM	17:13	21	1.22**
12	11/3/01 2:10 PM	11/3/01 4:19 PM	2:09	6	2.79	11/4/01 9:33 AM	17:14	28	1.62**
13	11/3/01 2:25 PM	11/3/01 4:27 PM	2:02	14	6.89	11/4/01 9:40 AM	17:13	76	4.41
14	11/3/01 2:28 PM	11/3/01 4:28 PM	2:00	10	5.00	11/4/01 9:41 AM	17:13	58	3.37
15	11/3/01 2:30 PM	11/3/01 4:29 PM	1:59	51	25.71	11/4/01 9:42 AM	17:13	139	8.07
16	11/3/01 2:46 PM	11/3/01 4:30 PM	1:44	10	5.77	11/4/01 9:44 AM	17:14	127	7.37
17	11/3/01 2:48 PM	11/3/01 4:31 PM	1:43	29	16.89	11/4/01 9:45 AM	17:14	65	3.77
18	11/3/01 2:50 PM	11/3/01 4:31 PM	1:41	3	1.78	11/4/01 9:46 AM	17:15	20	1.16**
19	11/3/01 2:57 PM	11/3/01 4:43 PM	1:46	79	44.72	11/4/01 9:55 AM	17:12	132	7.67
20	11/3/01 2:58 PM	11/3/01 4:41 PM	1:43	2	1.17	11/4/01 9:53 AM	17:12	9	0.52**
21	11/3/01 3:00 PM	11/3/01 4:40 PM	1:40	8.5	5.10	11/4/01 9:52 AM	17:12	22	1.28**
22	11/3/01 3:02 PM	11/3/01 4:39 PM	1:37	100	61.86	11/4/01 9:50 AM	17:11	145	8.44
23	11/3/01 3:03 PM	11/3/01 4:35 PM	1:32	48	31.30	11/4/01 9:49 AM	17:14	145	8.41
24	11/3/01 3:05 PM	11/3/01 4:34 PM	1:29	36	24.27	11/4/01 9:56 AM	17:22	141	8.12
25	11/3/01 3:16 PM	11/3/01 4:45 PM	1:29	57	38.43	11/4/01 9:56 AM	17:11	63	3.67
26	11/3/01 3:14 PM	11/3/01 4:46 PM	1:32	0	0.00	11/4/01 9:56 AM	17:10	2	0.12**
27	11/3/01 3:13 PM	11/3/01 4:46 PM	1:33	0	0.00	11/4/01 9:57 AM	17:11	2	0.12**
28	11/3/01 3:12 PM	11/3/01 4:47 PM	1:35	9	5.68	11/4/01 9:58 AM	17:11	45	2.62
29	11/3/01 3:11 PM	11/3/01 4:50 PM	1:39	145	87.88	11/4/01 10:07 AM	17:17	145	8.39
30	11/3/01 3:07 PM	11/3/01 4:52 PM	1:45	145	82.86	11/4/01 10:06 AM	17:14	145	8.41
31	11/3/01 3:20 PM	11/3/01 5:01 PM	1:41	55	32.67	11/4/01 10:05 AM	17:04	142	8.32
32	11/3/01 3:21 PM	11/3/01 4:59 PM	1:38	13	7.96	11/4/01 10:04 AM	17:05	85	4.98
33	11/3/01 3:22 PM	11/3/01 4:58 PM	1:36	12	7.50	11/4/01 10:03 AM	17:05	64	3.75
34	11/3/01 3:23 PM	11/3/01 4:58 PM	1:35	28	17.68	11/4/01 10:02 AM	17:04	145	8.50
35	11/3/01 3:25 PM	11/3/01 4:56 PM	1:31	62	40.88	11/4/01 10:09 AM	17:13	124	7.20
36	11/3/01 3:26 PM	11/3/01 4:55 PM	1:29	145	97.75	11/4/01 10:10 AM	17:15	145	8.41
37	11/3/01 3:33 PM	11/3/01 5:02 PM	1:29	14	9.44	11/4/01 10:10 AM	17:08	113	6.60
38	11/3/01 3:32 PM	11/3/01 5:03 PM	1:31	5	3.30	11/4/01 10:11 AM	17:08	30	1.75**
39	11/3/01 3:31 PM	11/3/01 5:04 PM	1:33	0	0.00	11/4/01 10:12 AM	17:08	9	0.53**
40	11/3/01 3:30 PM	11/3/01 5:05 PM	1:35	22	13.89	11/4/01 10:14 AM	17:09	116	6.76
41	11/3/01 3:28 PM	11/3/01 5:05 PM	1:37	3	1.86	11/4/01 10:14 AM	17:09	12	0.70**
42	11/3/01 3:27 PM	11/3/01 5:07 PM	1:40	124	74.40	11/4/01 10:15 AM	17:08	145	8.46
43	11/3/01 3:35 PM	11/3/01 5:13 PM	1:38	1	0.61	11/4/01 10:18 AM	17:05	8	0.47**

44	11/3/01 3:36 PM	11/3/01 5:12 PM	1:36	1	0.63	11/4/01 10:17 AM	17:05	4	0.23	**
45	11/3/01 3:37 PM	11/3/01 5:11 PM	1:34	5	3.19	11/4/01 10:17 AM	17:06	39	2.28	**
46	11/3/01 3:40 PM	11/3/01 5:11 PM	1:31	9	5.93	11/4/01 10:16 AM	17:05	57	3.34	
47	11/3/01 3:42 PM	11/3/01 5:10 PM	1:28	4	2.73	11/4/01 10:15 AM	17:05	19	1.11	**
48	11/3/01 3:42 PM	11/3/01 5:09 PM	1:27	30	20.69	11/4/01 10:14 AM	17:05	57	3.34	
49	11/3/01 3:51 PM	11/3/01 5:14 PM	1:23	3	2.17	11/4/01 10:19 AM	17:05	27	1.58	**
50	11/3/01 3:49 PM	11/3/01 5:17 PM	1:28	145	98.86	11/4/01 10:21 AM	17:04	145	8.50	
51	11/3/01 3:48 PM	11/3/01 5:18 PM	1:30	4	2.67	11/4/01 10:22 AM	17:04	16	0.94	**
52	11/3/01 3:46 PM	11/3/01 5:19 PM	1:33	3	1.94	11/4/01 10:22 AM	17:03	25	1.47	**
53	11/3/01 3:45 PM	11/3/01 5:21 PM	1:36	136	85.00	11/4/01 10:23 AM	17:02	118	6.93	
54	11/3/01 3:44 PM	11/3/01 5:22 PM	1:38	62	37.96	11/4/01 10:25 AM	17:03	144	8.45	
55	11/3/01 3:52 PM	11/3/01 5:28 PM	1:36	70	43.75	11/4/01 10:31 AM	17:03	134	7.86	
56	11/3/01 3:54 PM	11/3/01 5:27 PM	1:33	0	0.00	11/4/01 10:29 AM	17:02	0	0.00	**
57	11/3/01 3:56 PM	11/3/01 5:26 PM	1:30	4	2.67	11/4/01 10:29 AM	17:03	17	1.00	**
58	11/3/01 3:59 PM	11/3/01 5:26 PM	1:27	20	13.79	11/4/01 10:28 AM	17:02	120	7.05	
59	11/3/01 4:01 PM	11/3/01 5:25 PM	1:24	6	4.29	11/4/01 10:27 AM	17:02	27	1.59	**
60	11/3/01 4:02 PM	11/3/01 5:24 PM	1:22	33	24.15	11/4/01 10:26 AM	17:02	129	7.57	
61	11/3/01 4:09 PM	11/3/01 5:29 PM	1:20	8	6.00	11/4/01 10:31 AM	17:02	18	1.06	**
62	11/3/01 4:08 PM	11/3/01 5:30 PM	1:22	0	0.00	11/4/01 10:31 AM	17:01	0	0.00	**
63	11/3/01 4:07 PM	11/3/01 5:31 PM	1:24	9	6.43	11/4/01 10:32 AM	17:01	52	3.06	
64	11/3/01 4:06 PM	11/3/01 5:32 PM	1:26	8	5.58	11/4/01 10:33 AM	17:01	56	3.29	
65	11/3/01 4:05 PM	11/3/01 5:34 PM	1:29	145	97.75	11/4/01 10:35 AM	17:01	145	8.52	
66	11/3/01 4:03 PM	11/3/01 5:36 PM	1:33	145	93.55	11/4/01 10:37 AM	17:01	145	8.52	

** Indicates possible candidate for well development efforts

Bold numbers indicate that well was completely recovered in elapsed time. No numbers higher than 145mL (total volume of well and tube)

Those piezometers that are shaded were deemed as candidates for well development efforts.

The following table details the middle layer of the wetland, only.

Middle Strata	First Purge	Second Purge	Elapsed Time (1 - 2)	Volume (mL)	Recovery Rate (mL/hr)	Third Purge	Elapsed Time (2-3)	Volume (mL)	Recovery Rate (mL/hr)
1	11/4/01 10:59 AM	11/4/01 1:00 PM	2:01	225	111.57	11/5/01 9:49 AM	20:49	185	8.89
2	11/4/01 11:02 AM	11/4/01 1:01 PM	1:59	16	8.07	11/5/01 9:58 AM	20:57	86	4.11
3	11/4/01 11:07 AM	11/4/01 1:03 PM	1:56	137	70.86	11/5/01 10:00 AM	20:57	196	9.36
4	11/4/01 11:09 AM	11/4/01 1:05 PM	1:56	128	66.21	11/5/01 10:03 AM	20:58	162	7.73
5	11/4/01 11:10 AM	11/4/01 1:07 PM	1:57	26	13.33	11/5/01 10:10 AM	21:03	125	5.94
6	11/4/01 11:12 AM	11/4/01 1:08 PM	1:56	43	22.24	11/5/01 10:12 AM	21:04	147	6.98
7	11/4/01 11:22 AM	11/4/01 1:17 PM	1:55	159	82.96	11/5/01 10:20 AM	21:03	153	7.27
8	11/4/01 11:21 AM	11/4/01 1:15 PM	1:54	163	85.79	11/5/01 10:18 AM	21:03	157	7.46
9	11/4/01 11:19 AM	11/4/01 1:13 PM	1:54	15	7.89	11/5/01 10:17 AM	21:04	67	3.18
10	11/4/01 11:17 AM	11/4/01 1:12 PM	1:55	154	80.35	11/5/01 10:16 AM	21:04	165	7.83
11	11/4/01 11:15 AM	11/4/01 1:10 PM	1:55	1	0.52	11/5/01 10:14 AM	21:04	17	0.81
12	11/4/01 11:14 AM	11/4/01 1:09 PM	1:55	20	10.43	11/5/01 10:14 AM	21:05	128	6.07
13	11/4/01 11:24 AM	11/4/01 1:19 PM	1:55	68	35.48	11/5/01 10:21 AM	21:02	154	7.32
14	11/4/01 11:25 AM	11/4/01 1:20 PM	1:55	45	23.48	11/5/01 10:23 AM	21:03	153	7.27
15	11/4/01 11:27 AM	11/4/01 1:21 PM	1:54	66	34.74	11/5/01 10:24 AM	21:03	152	7.22
16	11/4/01 11:28 AM	11/4/01 1:22 PM	1:54	38	20.00	11/5/01 10:25 AM	21:03	140	6.65
17	11/4/01 11:30 AM	11/4/01 1:24 PM	1:54	192	101.05	11/5/01 10:27 AM	21:03	187	8.88
18	11/4/01 11:31 AM	11/4/01 1:25 PM	1:54	64	33.68	11/5/01 10:28 AM	21:03	140	6.65
19	11/4/01 11:42 AM	11/4/01 1:28 PM	1:46	103	58.30	11/5/01 10:38 AM	21:10	147	6.94
20	11/4/01 11:40 AM	11/4/01 1:37 PM	1:57	77	39.49	11/5/01 10:36 AM	20:59	139	6.62
21	11/4/01 11:38 AM	11/4/01 1:31 PM	1:53	191	101.42	11/5/01 10:34 AM	21:03	181	8.60
22	11/4/01 11:37 AM	11/4/01 1:29 PM	1:52	184	98.57	11/5/01 10:33 AM	21:04	170	8.07
23	11/4/01 11:35 AM	11/4/01 1:27 PM	1:52	23	12.32	11/5/01 10:31 AM	21:04	133	6.31
24	11/4/01 11:33 AM	11/4/01 1:26 PM	1:53	14	7.43	11/5/01 10:30 AM	21:04	73	3.47
25	11/4/01 11:43 AM	11/4/01 1:40 PM	1:57	114	58.46	11/5/01 10:39 AM	20:59	160	7.63
26	11/4/01 11:44 AM	11/4/01 1:41 PM	1:57	101	51.79	11/5/01 10:41 AM	21:00	149	7.10
27	11/4/01 11:46 AM	11/4/01 1:43 PM	1:57	4	2.05	11/5/01 10:42 AM	20:59	18	0.86
28	11/4/01 11:48 AM	11/4/01 1:43 PM	1:55	225	117.39	11/5/01 10:44 AM	21:01	225	10.71
29	11/4/01 11:50 AM	11/4/01 1:45 PM	1:55	195	101.74	11/5/01 10:46 AM	21:01	188	8.95
30	11/4/01 11:52 AM	11/4/01 1:46 PM	1:54	48	25.26	11/5/01 10:48 AM	21:02	162	7.70
31	11/4/01 12:06 PM	11/4/01 1:55 PM	1:49	141	77.61	11/5/01 10:57 AM	21:02	182	8.65
32	11/4/01 12:04 PM	11/4/01 1:52 PM	1:48	113	62.78	11/5/01 10:56 AM	21:04	203	9.64
33	11/4/01 12:03 PM	11/4/01 1:51 PM	1:48	225	125.00	11/5/01 10:54 AM	21:03	240	11.40
34	11/4/01 12:00 PM	11/4/01 1:50 PM	1:50	170	92.73	11/5/01 10:52 AM	21:02	225	10.70
35	11/4/01 11:59 AM	11/4/01 1:48 PM	1:49	225	123.85	11/5/01 10:52 AM	21:04	225	10.68
36	11/4/01 11:54 AM	11/4/01 1:48 PM	1:54	225	118.42	11/5/01 10:51 AM	21:03	225	10.69
37	11/4/01 12:08 PM	11/4/01 1:58 PM	1:50	34	18.55	11/5/01 10:59 AM	21:01	149	7.09
38	11/4/01 12:11 PM	11/4/01 2:00 PM	1:49	225	123.85	11/5/01 11:00 AM	21:00	225	10.71
39	11/4/01 12:13 PM	11/4/01 2:03 PM	1:50	225	122.73	11/5/01 11:03 AM	21:00	225	10.71
40	11/4/01 12:14 PM	11/4/01 2:04 PM	1:50	37	20.18	11/5/01 11:05 AM	21:01	131	6.23
41	11/4/01 12:16 PM	11/4/01 2:05 PM	1:49	20	11.01	11/5/01 11:06 AM	21:01	112	5.33
42	11/4/01 12:17 PM	11/4/01 2:06 PM	1:49	22	12.11	11/5/01 11:07 AM	21:01	135	6.42

43	11/4/01 12:26 PM	11/4/01 2:13 PM	1:47	10	5.61	11/5/01 11:13 AM	21:00	66	3.14
44	11/4/01 12:24 PM	11/4/01 2:12 PM	1:48	5	2.78	11/5/01 11:12 AM	21:00	18	0.86**
45	11/4/01 12:22 PM	11/4/01 2:11 PM	1:49	94	51.74	11/5/01 11:11 AM	21:00	145	6.90
46	11/4/01 12:21 PM	11/4/01 2:09 PM	1:48	13	7.22	11/5/01 11:10 AM	21:01	98	4.66
47	11/4/01 12:20 PM	11/4/01 2:08 PM	1:48	12	6.67	11/5/01 11:09 AM	21:01	36	1.71**
48	11/4/01 12:19 PM	11/4/01 2:07 PM	1:48	5	2.78	11/5/01 11:08 AM	21:01	19	0.90**
49	11/4/01 12:28 PM	11/4/01 2:14 PM	1:46	59	33.40	11/5/01 11:14 AM	21:00	117	5.57
50	11/4/01 12:29 PM	11/4/01 2:15 PM	1:46	2	1.13	11/5/01 11:15 AM	21:00	3	0.14**
51	11/4/01 12:30 PM	11/4/01 2:16 PM	1:46	47	26.60	11/5/01 11:16 AM	21:00	137	6.52
52	11/4/01 12:32 PM	11/4/01 2:17 PM	1:45	2	1.14	11/5/01 11:17 AM	21:00	15	0.71**
53	11/4/01 12:33 PM	11/4/01 2:21 PM	1:48	163	90.56	11/5/01 11:18 AM	20:57	150	7.16
54	11/4/01 12:35 PM	11/4/01 2:22 PM	1:47	13	7.29	11/5/01 11:19 AM	20:57	61	2.91
55	11/4/01 12:44 PM	11/4/01 2:28 PM	1:44	4	2.31	11/5/01 11:27 AM	20:59	32	1.53**
56	11/4/01 12:42 PM	11/4/01 2:27 PM	1:45	2	1.14	11/5/01 11:26 AM	20:59	0	0.00**
57	11/4/01 12:42 PM	11/4/01 2:26 PM	1:44	2	1.15	11/5/01 11:25 AM	20:59	138	6.58
58	11/4/01 12:40 PM	11/4/01 2:25 PM	1:45	139	79.43	11/5/01 11:23 AM	20:58	146	6.96
59	11/4/01 12:39 PM	11/4/01 2:24 PM	1:45	2	1.14	11/5/01 11:22 AM	20:58	28	1.34**
60	11/4/01 12:38 PM	11/4/01 2:24 PM	1:46	4	2.26	11/5/01 11:21 AM	20:57	172	8.21
61	11/4/01 12:45 PM	11/4/01 2:30 PM	1:45	86	49.14	11/5/01 11:28 AM	20:58	71	3.39
62	11/4/01 12:47 PM	11/4/01 2:31 PM	1:44	18	10.38	11/5/01 11:29 AM	20:58	90	4.29
63	11/4/01 12:48 PM	11/4/01 2:32 PM	1:44	11	6.35	11/5/01 11:30 AM	20:58	91	4.34
64	11/4/01 12:50 PM	11/4/01 2:33 PM	1:43	74	43.11	11/5/01 11:32 AM	20:59	184	8.77
65	11/4/01 12:52 PM	11/4/01 2:34 PM	1:42	225	132.35	11/5/01 11:32 AM	20:58	225	10.73
66	11/4/01 12:53 PM	11/4/01 2:34 PM	1:41	225	133.66	11/5/01 11:32 AM	20:58	225	10.73

** Indicates possible candidate for well development efforts

Bold numbers indicate that well was completely recovered in elapsed time. No numbers higher than 225mL (total volume of well and tube)

Those piezometers that are shaded were deemed as candidates for well development efforts.

Appendix B: Recovery Data After Well Development Efforts

The following table details the top layer of the wetland, only.

Top Strata	First Purge	Second Purge	Elapsed Time (1-2)	Volume (mL)	Recovery Rate (mL/hr)	Third Purge	Fourth Purge	Elapsed Time (3-4)	Volume (mL)	Recovery Rate (mL/hr)
2	11/8/01 1:09 PM	11/9/01 4:24 PM	27:15:00	193	7.08	11/11/01 9:32 AM	11/11/01 10:32 AM	1:00:00	130	130.00
3	11/8/01 1:07 PM	11/9/01 4:21 PM	27:14:00	144	5.29	11/11/01 9:33 AM	11/11/01 10:34 AM	1:01:00	201	197.70
6	11/8/01 1:00 PM	11/9/01 4:18 PM	27:18:00	127	4.65	11/11/01 9:35 AM	11/11/01 10:36 AM	1:01:00	123	120.98
11	11/8/01 12:55 PM	11/9/01 4:12 PM	27:17:00	125	4.58	11/11/01 9:43 AM	11/11/01 10:38 AM	0:55:00	120	130.91
12	11/8/01 12:48 PM	11/9/01 4:10 PM	27:22:00	154	5.63	11/11/01 9:38 AM	11/11/01 10:41 AM	1:03:00	117	111.43
18	11/8/01 12:40 PM	11/9/01 4:06 PM	27:26:00	136	4.96	11/11/01 9:46 AM	11/11/01 10:43 AM	0:57:00	124	130.53
20	11/8/01 12:35 PM	11/9/01 3:57 PM	27:22:00	400	14.62	11/11/01 9:49 AM	11/11/01 10:44 AM	0:55:00	300	327.27
21	11/8/01 12:31 PM	11/9/01 4:00 PM	27:29:00	231	8.41	11/11/01 9:50 AM	11/11/01 10:46 AM	0:56:00	156	167.14
26	11/8/01 12:40 PM	11/9/01 3:53 PM	27:13:00	123	4.52	11/11/01 9:52 AM	11/11/01 10:48 AM	0:56:00	122	130.71
27	11/8/01 12:20 PM	11/9/01 3:51 PM	27:31:00	133	4.83	11/11/01 9:55 AM	11/11/01 10:49 AM	0:54:00	90	100.00
28	11/8/01 1:30 PM	11/9/01 3:40 PM	26:10:00	156	5.96	11/11/01 9:56 AM	11/11/01 10:52 AM	0:56:00	113	121.07
38	11/8/01 12:12 PM	11/9/01 3:58 PM	27:46:00	149	5.37	11/11/01 9:58 AM	11/11/01 10:54 AM	0:56:00	123	131.79
39	11/8/01 11:10 AM	11/9/01 3:32 PM	28:22:00	135	4.76	11/11/01 9:59 AM	11/11/01 10:56 AM	0:57:00	105	110.53
41	11/8/01 11:02 AM	11/9/01 3:29 PM	28:27:00	174	6.12	11/11/01 10:01 AM	11/11/01 10:58 AM	0:57:00	136	143.16
43	11/8/01 11:02 AM	11/9/01 3:24 PM	28:22:00	134	4.72	11/11/01 10:02 AM	11/11/01 10:59 AM	0:57:00	100	105.26
44	11/8/01 10:41 AM	11/9/01 3:22 PM	28:41:00	136	4.74	11/11/01 10:04 AM	11/11/01 11:00 AM	0:56:00	63	67.50
45	11/8/01 11:05 AM	11/9/01 3:16 PM	28:11:00	257	9.12	11/11/01 10:07 AM	11/11/01 11:05 AM	0:58:00	204	211.03
47	11/8/01 10:48 AM	11/9/01 3:12 PM	28:24:00	123	4.33	11/11/01 10:10 AM	11/11/01 11:06 AM	0:56:00	78	83.57
49	11/8/01 10:15 AM	11/9/01 3:04 PM	28:49:00	110	3.82	11/11/01 10:13 AM	11/11/01 11:10 AM	0:57:00	97	102.11
51	11/8/01 10:11 AM	11/9/01 2:59 PM	28:48:00	125	4.34	11/11/01 10:15 AM	11/11/01 11:13 AM	0:58:00	112	115.86
52	11/8/01 10:09 AM	11/9/01 2:49 PM	28:40:00	187	6.52	11/11/01 10:18 AM	11/11/01 11:15 AM	0:57:00	157	165.26
56	11/8/01 9:44 AM	11/9/01 2:20 PM	28:36:00	146	5.10	11/11/01 10:21 AM	11/11/01 11:21 AM	1:00:00	134	134.00
57	11/8/01 9:49 AM	11/9/01 2:24 PM	28:35:00	90	3.15	11/11/01 10:24 PM	11/11/01 11:27 PM	1:03:00	415	395.24
59	11/8/01 9:18 AM	11/9/01 2:29 PM	29:11:00	133	4.56	11/11/01 10:21 AM	11/11/01 11:21 AM	1:00:00	98	98.00
61	11/8/01 9:05 AM	11/9/01 2:09 PM	29:04:00	126	4.33	11/11/01 10:28 AM	11/11/01 11:31 AM	1:03:00	36	34.29
62	11/8/01 9:12 AM	11/9/01 2:06 PM	28:54:00	126	4.36	11/11/01 10:29 AM	11/11/01 11:32 AM	1:03:00	78	74.29

The following table details the middle layer of the wetland, only.

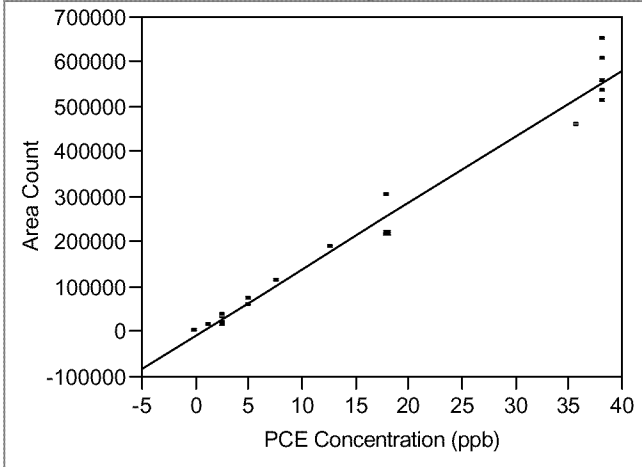
Middle Strata	First Purge	Second Purge	Elapsed Time (1-2)	Volume (mL)	Recovery Rate (mL/hr)	Third Purge	Fourth Purge	Elapsed Time (3-4)	Volume (mL)	Recovery Rate (mL/hr)
11	11/8/01 11:52 AM	11/9/01 4:15 PM	28:23:00	266	9.37	11/11/01 9:41 AM	11/11/01 10:40 AM	0:59:00	176	178.98
27	11/8/01 12:24 PM	11/9/01 3:48 PM	27:24:00	202	7.37	11/11/01 9:53 AM	11/11/01 10:50 AM	0:57:00	154	162.11
44	11/8/01 10:43 AM	11/9/01 3:19 PM	28:36:00	183	6.40	11/11/01 10:05 AM	11/11/01 11:02 AM	0:57:00	105	110.53
47	11/8/01 11:08 AM	11/9/01 3:10 PM	28:02:00	298	10.63	11/11/01 10:09 AM	11/11/01 11:08 AM	0:59:00	204	207.46
48	11/8/01 11:01 AM	11/9/01 3:06 PM	28:05:00	25	0.89	11/11/01 10:11 AM	11/11/01 11:09 AM	0:58:00	0	0.00
50	11/8/01 10:13 AM	11/9/01 3:02 PM	28:49:00	136	4.72	11/11/01 10:14 AM	11/11/01 11:12 AM	0:58:00	31	32.07
52	11/8/01 10:05 AM	11/9/01 2:43 PM	28:38:00	156	5.45	11/11/01 10:17 AM	11/11/01 11:17 AM	1:00:00	192	192.00
55	11/8/01 9:54 AM	11/9/01 2:16 PM	28:22:00	443	15.62	11/11/01 10:20 AM	11/11/01 11:20 AM	1:00:00	283	283.00
56	11/8/01 9:40 AM	11/9/01 2:18 PM	28:38:00	107	3.74	11/11/01 10:22 AM	11/11/01 11:22 AM	1:00:00	8	8.00
59	11/8/01 9:22 AM	11/9/01 2:32 PM	29:10:00	167	5.73	11/11/01 10:27 AM	11/11/01 11:30 AM	1:03:00	176	167.62

Development efforts failed to improve the recovered volumes in piezometers 48B and 56B enough to enable sampling.

Appendix C: Calibration Curves

A. PCE Calibration Curve (output from JUMP 4.0; combination of six different calibrations).

Bivariate Fit of Area Count By PCE Concentration (ppb)



— Linear Fit

Linear Fit

Area Count = -6262.471 + 14748.613 PCE Concentration (ppb)

Summary of Fit

RSquare	0.981471
RSquare Adj	0.980699
Root Mean Square Error	31009.7
Mean of Response	182763.7
Observations (or Sum Wgts)	26

Analysis of Variance

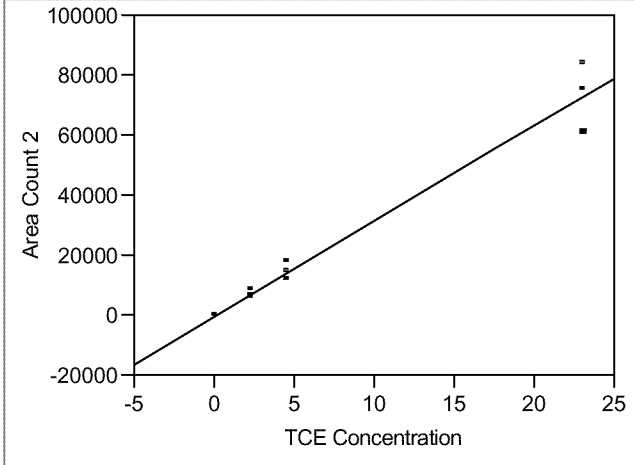
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1.22245e12	1.2225e12	1271.269
Error	24	2.30784e10	961601630	Prob > F
C. Total	25	1.24553e12		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	-6262.471	8067.909	-0.78	0.4452
PCE Concentration (ppb)	14748.613	413.6495	35.65	<.0001

B. TCE Calibration Curve (output from JUMP 4.0; combination of three different calibrations).

Bivariate Fit of Area Count 2 By TCE Concentration



— Linear Fit

Linear Fit

$$\text{Area Count 2} = -203.8138 + 3175.1658 \text{ TCE Concentration}$$

Summary of Fit

RSquare	0.971776
RSquare Adj	0.968953
Root Mean Square Error	5399.96
Mean of Response	23530.55
Observations (or Sum Wgts)	12

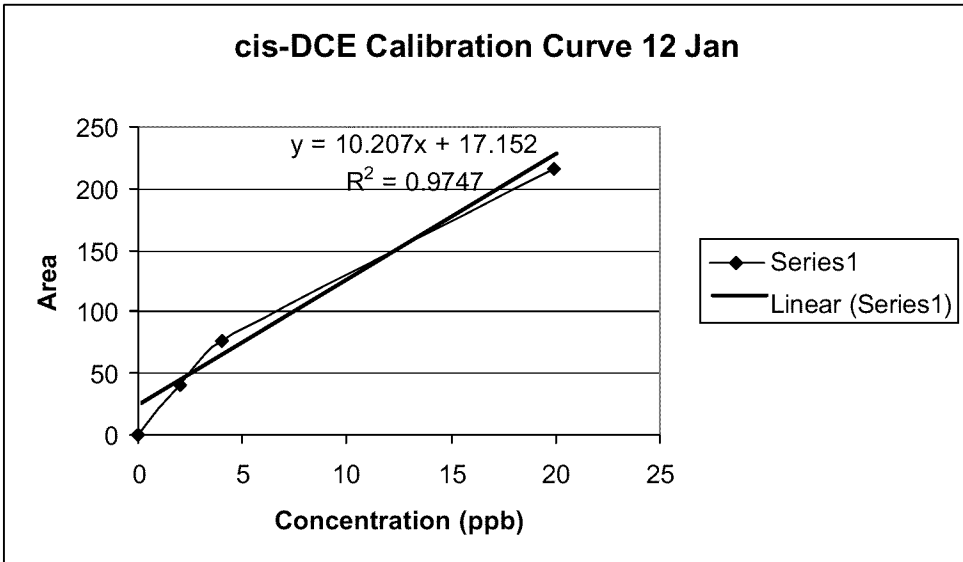
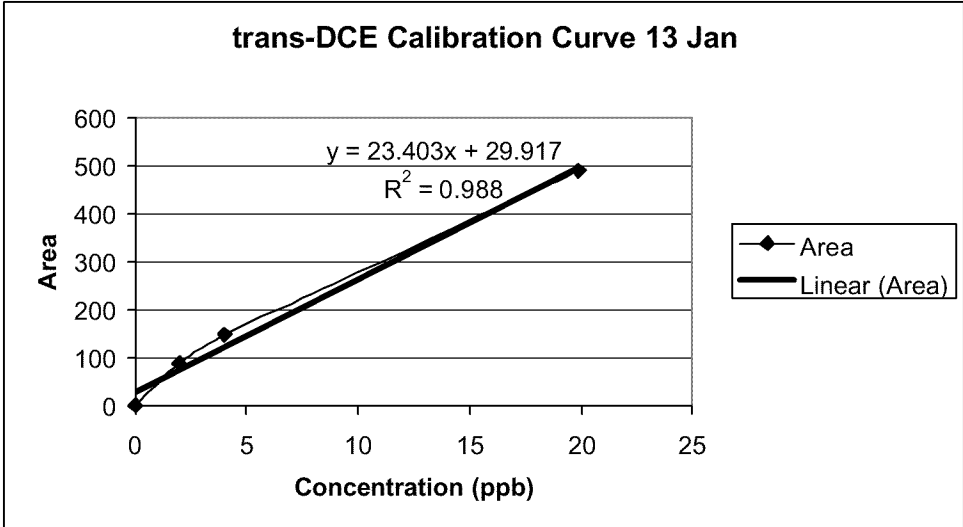
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1.00398e10	1.004e+10	344.3043
Error	10	291595686	29159569	Prob > F
C. Total	11	1.03314e10		<.0001

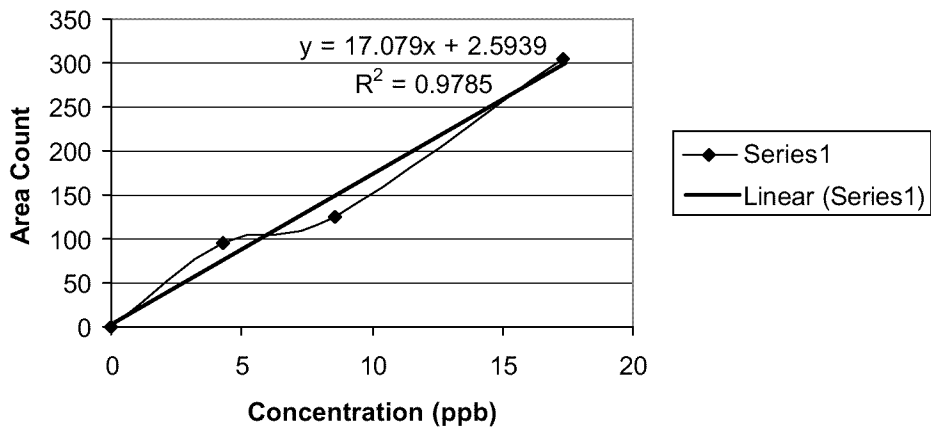
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	-203.8138	2016.451	-0.10	0.9215
TCE Concentration	3175.1658	171.1178	18.56	<.0001

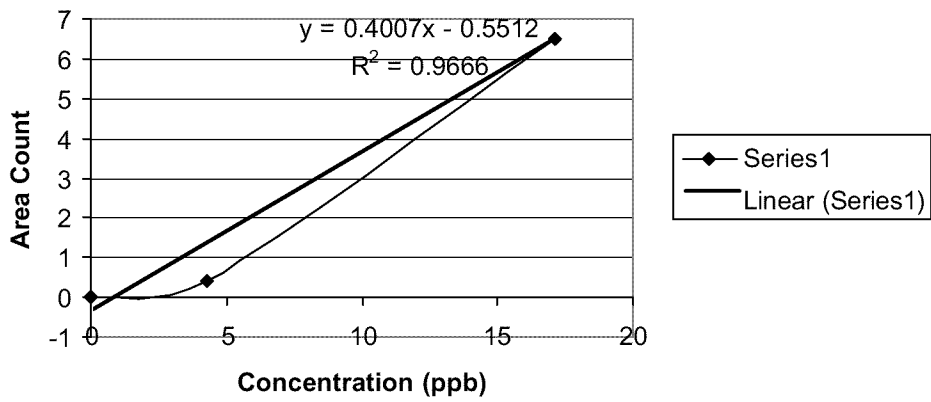
C. Calibration Curves for t-DCE, c-DCE, ethane, and ethene.



Ethane Calibration Curve 25 Jan



Ethene Calibration Curve - 29 Jan



Appendix D: Sample Data

PCE in Top Layer

**Calibration Curve from JUMP
4.0**

Top Layer (A)

14748.61 -6262.47

GC Responses

Sample Concentrations (ppb)

Sample Location	1	2	3	1	2	3
1	62492.7	37741	57409	<i>4.661806</i>	<i>2.983567</i>	<i>4.317116</i>
2	2149.9	720	1120.02	<i>0.570384</i>	<i>0.473432</i>	<i>0.500555</i>
3	1310.49	603	812	<i>0.513469</i>	<i>0.465499</i>	<i>0.47967</i>
4	5549.4	959	806	<i>0.80088</i>	<i>0.489637</i>	<i>0.479263</i>
5	15049	2749	1946	<i>1.444981</i>	<i>0.611005</i>	<i>0.556559</i>
6	1374.4	1017	N/D	<i>0.517803</i>	<i>0.49357</i>	
7	7517.19	1937	1685	<i>0.934302</i>	<i>0.555949</i>	<i>0.538862</i>
8	29877	9135	4815	<i>2.450364</i>	<i>1.043995</i>	<i>0.751086</i>
9	33574	5899	3367	<i>2.701032</i>	<i>0.824584</i>	<i>0.652907</i>
10	171385	141531	51860	<i>12.04503</i>	<i>10.02084</i>	<i>3.940877</i>
11	1197	511	400	<i>0.505774</i>	<i>0.459262</i>	<i>0.451735</i>
12	537	345	318	<i>0.461024</i>	<i>0.448006</i>	<i>0.446176</i>
13	19337	5077	3280	<i>1.735721</i>	<i>0.76885</i>	<i>0.647008</i>
14	18799	4353	2716	<i>1.699243</i>	<i>0.719761</i>	<i>0.608767</i>
15	17445	5494	2937	<i>1.607437</i>	<i>0.797124</i>	<i>0.623752</i>
16	152080	247378	248127	<i>10.73609</i>	<i>17.19758</i>	<i>17.24837</i>
17	15440	3390	840	<i>1.471492</i>	<i>0.654466</i>	<i>0.481569</i>
18	963	601	2700	<i>0.489909</i>	<i>0.465364</i>	<i>0.607682</i>
19	19090	4298	2398	<i>1.718973</i>	<i>0.716031</i>	<i>0.587206</i>
20	201793	190304	193791	<i>14.10678</i>	<i>13.32779</i>	<i>13.56422</i>
21	103939	90527	45835	<i>7.471989</i>	<i>6.562615</i>	<i>3.532364</i>
22	211529	240188	170886	<i>14.76691</i>	<i>16.71008</i>	<i>12.0112</i>
23	3482	2328	830	<i>0.660704</i>	<i>0.58246</i>	<i>0.480891</i>
24	24103	4183	3676	<i>2.05887</i>	<i>0.708234</i>	<i>0.673858</i>
25	49234	53067	42761	<i>3.762826</i>	<i>4.022715</i>	<i>3.323938</i>
26	6310	1095	1304	<i>0.852451</i>	<i>0.498859</i>	<i>0.513029</i>
27	1493	709	757	<i>0.525844</i>	<i>0.472687</i>	<i>0.475941</i>
28	6821.4	399	924	<i>0.887126</i>	<i>0.451668</i>	<i>0.487264</i>
29	382199	454280	405142	<i>26.33885</i>	<i>31.22615</i>	<i>27.89445</i>
30	149011	264506	353012	<i>10.528</i>	<i>18.35891</i>	<i>24.35988</i>
31	15941	6418	2854	<i>1.505462</i>	<i>0.859774</i>	<i>0.618124</i>
32	16039	4133	2554	<i>1.512106</i>	<i>0.704844</i>	<i>0.597783</i>
33	21125	6572	5114	<i>1.856952</i>	<i>0.870215</i>	<i>0.771359</i>
34	16154	3159	1999	<i>1.519904</i>	<i>0.638804</i>	<i>0.560152</i>
35	20604	4044	3506	<i>1.821627</i>	<i>0.69881</i>	<i>0.662332</i>
36	16050	7410	3273	<i>1.512852</i>	<i>0.927034</i>	<i>0.646533</i>
37	25489	10517	8677	<i>2.152845</i>	<i>1.137698</i>	<i>1.012941</i>
38	1001	211	263	<i>0.492485</i>	<i>0.438921</i>	<i>0.442446</i>

39	1271	298	245	0.510792	0.44482	0.441226
40	19381	3792	1878	1.738704	0.681723	0.551948
41	789	330	321	0.478111	0.446989	0.446379
42	14019	5396	2799	1.375144	0.790479	0.614395
43	642	380	382	0.468144	0.450379	0.450515
44	255.3	123	185	0.441924	0.432954	0.437158
45	929	257	235	0.487603	0.44204	0.440548
46	31009	6888	4752	2.527117	0.891641	0.746814
47	936	122	146	0.488078	0.432886	0.434513
48	26407	6913	5546	2.215088	0.893336	0.80065
49	1093	236	190	0.498723	0.440616	0.437497
50	24851	10948	7665	2.109586	1.166921	0.944324
51	279	101	124	0.443531	0.431462	0.433022
52	238	168	153	0.440751	0.436005	0.434988
53	14686	3490	1934	1.420369	0.661247	0.555745
54	14438	5042	5994	1.403554	0.766477	0.831025
55	20975	6434	7792	1.846782	0.860859	0.952935
56	309	158	133	0.445565	0.435327	0.433632
57	600	131	4403	0.465296	0.433496	0.723151
58	16986	4494	2093	1.576316	0.729321	0.566526
59	21416	67884	9057	1.876683	5.027352	1.038706
60	9976	2330	1860	1.101017	0.582595	0.550728
61	20012	5204	2797	1.781488	0.777461	0.614259
62	22954	5794	4480	1.980964	0.817465	0.728372
63	13407	3685	1777	1.333649	0.674468	0.5451
64	16680	4205	4132	1.555568	0.709726	0.704776
65	7460	840	928	0.930425	0.481569	0.487535
66	8435	2075	2554	0.996532	0.565305	0.597783
			Averages	2.641482	2.443814	2.207571

Averages are for each “pass-through” of the wetland.

N/D = non detectable

PCE in Middle Layer

Calibration Curve from JUMP
4.0

Middle Layer (B)

14748.61 -6262.47

GC Responses

Sample Concentrations (ppb)

Sample Location	1	2	3	1	2	3
1	25034	16158	16543	2.121994	1.520175	1.546279
2	18154	5610	2991	1.65551	0.804989	0.627413
3	12763	5389	1548	1.289984	0.790005	0.529573
4	9360	3985	3668	1.05925	0.694809	0.673316
5	12517	5279	2798	1.273304	0.782546	0.614327
6	18330	6627	8063	1.667443	0.873945	0.97131
7	11361	3909	2064	1.194924	0.689656	0.56456
8	13966	3909	2460	1.371551	0.689656	0.59141
9	20657	2844	2460	1.825221	0.617446	0.59141
10	263928	316855	332065	18.31972	21.90833	22.93961
11	1631	508	410	0.535201	0.459058	0.452413
12	15040	5640	3171	1.444371	0.807023	0.639618
13	13909	4318	2395	1.367686	0.717388	0.587002
14	17004	8245	3015	1.577536	0.98365	0.62904
15	18173	8650	2589	1.656798	1.01111	0.600156
16	19998	8103	4563	1.780538	0.974022	0.733999
17	20258	9013	4783	1.798167	1.035723	0.748916
18	15063	5792	3365	1.445931	0.817329	0.652771
19	15927	5990	3378	1.504512	0.830754	0.653653
20	275128	288249	378061	19.07911	19.96876	26.05828
21	22503	7970	4267	1.950385	0.965004	0.71393
22	213943	253172	211644	14.93059	17.59043	14.77471
23	1671	1922	558	0.537913	0.554932	0.462448
24	10090	3304	1532	1.108746	0.648635	0.528488
25	25416	27444	9685	2.147895	2.285399	1.081286
26	13977	3813	1368	1.372297	0.683147	0.517369
27	1369	717	1847	0.517437	0.473229	0.549846
28	8736	331	1156	1.016941	0.447057	0.502994
29	68038	42645	26999	5.037794	3.316073	2.255227
30	14032	4783	2453	1.376026	0.748916	0.590935
31	22140	8421	4645	1.925772	0.995583	0.739559
32	17566	6698	3186	1.615641	0.878759	0.640635
33	47943	51236	10656	3.675293	3.898568	1.147123
34	7651	3916	2090	0.943375	0.690131	0.566322
35	3363	N/D	1339	0.652636		0.515402
36	15901	4285	3943	1.50275	0.71515	0.691961
37	10442	5962	5064	1.132613	0.828856	0.767969
38	13496	9971	7089	1.339683	1.100678	0.90527
39	2715	1711	989	0.608699	0.540625	0.491671
40	12273	6224	3628	1.25676	0.84662	0.670603

41	1427	841	469	0.521369	0.481637	0.456414
42	6328	N/D	1741	0.853672		0.542659
43	7758	4052	2552	0.95063	0.699352	0.597647
44	492	302	207	0.457973	0.445091	0.438649
45	13297	5765	4306	1.326191	0.815498	0.716574
46	14103	6197	4818	1.38084	0.844789	0.751289
47	343	132	125	0.447871	0.433564	0.43309
48	Invalid	Invalid	Invalid			
49	11305	3855	8615	1.191127	0.685995	1.008737
50	188	N/D	1616	0.437361		0.534184
51	11515	2997	6744	1.205366	0.62782	0.881878
52	218	72	145	0.439395	0.429496	0.434446
53	9719	2318	7881	1.083591	0.581782	0.95897
54	3722	898	1256	0.676977	0.485501	0.509775
55	5718	872	2146	0.812312	0.483738	0.570119
56	Invalid	Invalid	Invalid			
57	14779	1354	3268	1.426675	0.516419	0.646194
58	15514	675	3229	1.47651	0.470381	0.64355
59	2580	68	196	0.599546	0.429225	0.437904
60	2022	112	629	0.561712	0.432208	0.467262
61	14409	558	7447	1.401587	0.462448	0.929543
62	12180	259	3717	1.250455	0.442175	0.676638
63	9940	221	3239	1.098576	0.439599	0.644228
64	7564	82	1235	0.937476	0.430174	0.508351
65	11379	72	1974	1.196144	0.429496	0.558457
66	11602	158	3908	1.211264	0.435327	0.689588
			Averages	2.055666	1.748949	1.649296

Averages are for each “pass-through” of the wetland.
N/D = non detectable

PCE in Bottom Layer

Calibration Curve from JUMP
4.0

Bottom Layer (C)

14748.61 -6262.47

GC Responses

Sample Concentrations (ppb)

Sample Location	1	2	3	1	2	3
1	320343	358771	373585	22.14483	24.75036	25.75479
2	269034	312065	288147	18.66592	21.58355	19.96184
3	234999	304141	285222	16.35825	21.04628	19.76352
4	418042	243909	267993	28.76911	16.96237	18.59534
5	153319	207347	159077	10.8201	14.48336	11.21051
6	Invalid	Invalid	Invalid			
7	329434	389756	334831	22.76122	26.85123	23.12716
8	339345	422915	321311	23.43322	29.09951	22.21046
9	327664	425212	323982	22.64121	29.25526	22.39156
10	272194	265244	249819	18.88018	18.40895	17.36309
11	220681	256993	219610	15.38744	17.84951	15.31483
12	132767	175417	127248	9.426613	12.31841	9.052409
13	272001	275997	207684	18.86709	19.13803	14.50621
14	423719	462916	382683	29.15403	31.8117	26.37166
15	396383	459658	419666	27.30057	31.5908	28.87922
16	376253	269959	359877	25.93569	18.72864	24.82535
17	349896	423108	378336	24.14861	29.1126	26.07692
18	345845	256695	266810	23.87394	17.8293	18.51513
19	423244	177258	241994	29.12182	12.44324	16.83253
20	424532	469097	520944	29.20915	32.23079	35.74617
21	446423	467317	487996	30.69343	32.1101	33.5122
22	434339	481139	534603	29.8741	33.04728	36.67229
23	396101	456942	463821	27.28144	31.40665	31.87306
24	319616	458290	483490	22.09553	31.49804	33.20668
25	284292	327237	333314	19.70046	22.61226	23.0243
26	424439	448559	471876	29.20285	30.83825	32.41922
27	365128	441122	482836	25.18138	30.334	33.16234
28	424619	437474	455313	29.21505	30.08666	31.2962
29	Invalid	Invalid	Invalid			
30	231661	477485	510387	16.13192	32.79952	35.03038
31	174596	206246	227717	12.26274	14.40871	15.86451
32	403930	446600	471576	27.81227	30.70543	32.39888
33	453069	441997	460486	31.14405	30.39333	31.64694
34	404080	423981	463190	27.82244	29.17179	31.83028
35	419530	453383	472137	28.87	31.16534	32.43691
36	424700	452982	505228	29.22054	31.13815	34.68058
37	64039	84630	78873	4.76665	6.162781	5.772439
38	452128	451732	501575	31.08024	31.05339	34.4329
39	442788	472453	480684	30.44696	32.45834	33.01642
40	419145	450561	482638	28.8439	30.974	33.14891
41	384028	385686	415505	26.46286	26.57528	28.59709

42	443274	429918	438001	30.47992	29.57434	30.12239
43	314775	309553	323101	21.7673	21.41323	22.33183
44	474139	460737	533251	32.57265	31.66396	36.58062
45	484005	452656	503779	33.2416	31.11604	34.58233
46	435692	459005	475157	29.96583	31.54652	32.64168
47	365518	356434	382731	25.20783	24.5919	26.37492
48	419797	436959	472282	28.8881	30.05174	32.44674
49	277439	255729	270036	19.23581	17.7638	18.73386
50	488391	502675	531012	33.53898	34.50748	36.42881
51	468124	479159	523393	32.16482	32.91303	35.91222
52	493416	503888	520392	33.87969	34.58973	35.70875
53	482638	519305	525919	33.14891	35.63504	36.08349
54	449012	452779	492352	30.86897	31.12438	33.80755
55	388000	378686	410506	26.73217	26.10066	28.25815
56	461693	447368	499984	31.72878	30.7575	34.32502
57	418409	466796	474768	28.79399	32.07478	32.6153
58	346241	436660	465906	23.90079	30.03147	32.01443
59	361992	426767	442335	24.96875	29.36069	30.41625
60	393403	473535	491553	27.09851	32.5317	33.75338
61	387939	417027	464544	26.72804	28.70029	31.92208
62	376714	450234	463469	25.96695	30.95182	31.8492
63	370606	435087	457599	25.55281	29.92481	31.45119
64	349234	422991	453272	24.10372	29.10467	31.15781
65	340764	418730	465000	23.52943	28.81576	31.953
66	332213	389011	429264	22.94965	26.80072	29.53
			Averages	25.34409	27.12624	27.99253

Averages are for each “pass-through” of the wetland.

TCE in Top Layer

Calibration Curve from JUMP
4.0

Top Layer (A)

3175.166 -203.814

GC Responses

Sample Concentrations (ppb)

Sample Location	1	2	3	1	2	3
1	6568	6407	6466	2.132743	2.082037	2.100619
2	2149	1158	1080	0.741005	0.428895	0.40433
3	129	32	1080	0.104818	0.074268	0.40433
4	77	38	N/D	0.088441	0.076158	
5	168	274	261	0.117101	0.150485	0.14639
6	146	105	515	0.110172	0.097259	0.226386
7	974	1535	1227	0.370946	0.547629	0.450626
8	175	171	183	0.119305	0.118045	0.121825
9	861	588	391	0.335357	0.249377	0.187333
10	4879	12321	12974	1.600803	3.944617	4.150276
11	102	55	71	0.096314	0.081512	0.086551
12	93	32	56	0.09348	0.074268	0.081827
13	221	164	458	0.133793	0.115841	0.208434
14	275	391	493	0.1508	0.187333	0.219457
15	244	161	148	0.141036	0.114896	0.110802
16	1931	3100	3020	0.672347	1.040517	1.015321
17	123	58	313	0.102928	0.082457	0.162768
18	111	77	85	0.099149	0.088441	0.09096
19	150	115	291	0.111432	0.100409	0.155839
20	2215	3466	4076	0.761791	1.155787	1.347902
21	2096	4700	5106	0.724313	1.544428	1.672295
22	3591	4500	4072	1.195155	1.481439	1.346643
23	198	1158	236	0.126549	0.428895	0.138517
24	408	523	356	0.192687	0.228906	0.17631
25	566	1416	1472	0.242448	0.510151	0.527788
26	189	91	428	0.123714	0.09285	0.198986
27	111	221	118	0.099149	0.133793	0.101353
28	217	80	91	0.132533	0.089386	0.09285
29	1412	1589	1356	0.508891	0.564636	0.491254
30	1289	2695	1992	0.470153	0.912965	0.691559
31	338	175	228	0.170641	0.119305	0.135997
32	160	104	251	0.114581	0.096944	0.143241
33	2257	2484	2483	0.775019	0.846511	0.846196
34	620	916	654	0.259455	0.352679	0.270163
35	1245	211	1185	0.456295	0.130643	0.437399
36	324	1415	298	0.166232	0.509836	0.158043
37	1650	3552	4142	0.583848	1.182872	1.368689
38	121	108	78	0.102298	0.098204	0.088756
39	106	212	73	0.097574	0.130958	0.087181
40	293	616	327	0.156469	0.258196	0.167177

41	71	66	52	0.086551	0.084976	0.080567
42	173	181	163	0.118675	0.121195	0.115526
43	100	227	21	0.095684	0.135682	0.070804
44	39	31	N/D	0.076473	0.073953	
45	52	167	N/D	0.080567	0.116786	
46	268	534	593	0.148595	0.23237	0.250952
47	28	64	27	0.073008	0.084346	0.072693
48	144	199	134	0.109542	0.126864	0.106392
49	67	46	36	0.085291	0.078677	0.075528
50	500	951	664	0.221662	0.363702	0.273313
51	32	N/D	20	0.074268		0.070489
52	32	N/D	28	0.074268		0.073008
53	1052	1001	731	0.395511	0.379449	0.294414
54	319	252	380	0.164657	0.143556	0.183869
55	502	684	900	0.222292	0.279612	0.34764
56	29	N/D	20	0.073323		0.070489
57	106	79	118	0.097574	0.089071	0.101353
58	316	219	214	0.163712	0.133163	0.131588
59	568	664	595	0.243078	0.273313	0.251582
60	185	116	109	0.122455	0.100723	0.098519
61	563	567	296	0.241504	0.242763	0.157413
62	638	512	432	0.265124	0.225441	0.200246
63	404	310	268	0.191427	0.161823	0.148595
64	409	180	165	0.193002	0.12088	0.116156
65	210	176	121	0.130328	0.11962	0.102298
66	117	97	98	0.101038	0.09474	0.095055

N/D = non detectable

TCE in Middle Layer

**Calibration Curve from JUMP
4.0**

Middle Layer (B)

3175.166 -203.814

GC Responses

Sample Concentrations (ppb)

Sample Location	1	2	3	1	2	3
1	606	632	681	0.255046	0.263235	0.278667
2	325	207	195	0.166547	0.129383	0.125604
3	145	91	153	0.109857	0.09285	0.112376
4	551	933	1618	0.237724	0.358033	0.57377
5	249	191	193	0.142611	0.124344	0.124974
6	442	343	442	0.203395	0.172216	0.203395
7	102	79	57	0.096314	0.089071	0.082142
8	130	63	101	0.105133	0.084031	0.095999
9	1514	2844	1247	0.541015	0.959891	0.456925
10	2429	2665	2848	0.829189	0.903516	0.961151
11	53	46	48	0.080882	0.078677	0.079307
12	112	180	183	0.099464	0.12088	0.121825
13	249	267	272	0.142611	0.14828	0.149855
14	264	275	238	0.147335	0.1508	0.139147
15	240	302	244	0.139777	0.159303	0.141036
16	418	950	238	0.195837	0.363387	0.139147
17	845	871	887	0.330318	0.338506	0.343545
18	180	142	183	0.12088	0.108912	0.121825
19	160	119	87	0.114581	0.101668	0.09159
20	1449	1737	2592	0.520544	0.611248	0.880525
21	746	655	631	0.299138	0.270478	0.26292
22	4241	4257	4557	1.399868	1.404907	1.499391
23	187	158	107	0.123085	0.113951	0.097889
24	520	227	166	0.227961	0.135682	0.116471
25	509	520	2933	0.224497	0.227961	0.987921
26	295	235	169	0.157099	0.138202	0.117416
27	164	158	138	0.115841	0.113951	0.107652
28	249	79	27	0.142611	0.089071	0.072693
29	4399	4620	5418	1.449629	1.519232	1.770558
30	216	169	125	0.132218	0.117416	0.103558
31	707	564	495	0.286856	0.241818	0.220087
32	496	131	101	0.220402	0.105448	0.095999
33	6235	9906	8488	2.027867	3.184027	2.737436
34	275	280	216	0.1508	0.152374	0.132218
35	270	886	166	0.149225	0.343231	0.116471
36	778	625	427	0.309217	0.26103	0.198671
37	4011	499	330	1.327431	0.221347	0.168122
38	3203	9971	2107	1.072956	3.204498	0.727777
39	3079	163	150	1.033903	0.115526	0.111432
40	845	781	660	0.330318	0.310161	0.272053

41	217	308	136	0.132533	0.161193	0.107022
42	171	165	101	0.118045	0.116156	0.095999
43	241	394	212	0.140092	0.188278	0.130958
44	170	207	178	0.11773	0.129383	0.12025
45	768	828	627	0.306067	0.324964	0.26166
46	632	681	708	0.263235	0.278667	0.28717
47	36	35	17	0.075528	0.075213	0.069544
48	Invalid	Invalid	Invalid			
49	195	180	246	0.125604	0.12088	0.141666
50	N/D	N/D	N/D			
51	698	534	697	0.284021	0.23237	0.283706
52	N/D	47	N/D		0.078992	
53	2208	2318	1032	0.759587	0.794231	0.389212
54	158	79	114	0.113951	0.089071	0.100094
55	75	85	126	0.087811	0.09096	0.103873
56	Invalid	Invalid	Invalid			
57	519	163	485	0.227646	0.115526	0.216938
58	741	293	2523	0.297564	0.156469	0.858794
59	51	28	21	0.080252	0.073008	0.070804
60	49	27	69	0.079622	0.072693	0.085921
61	339	37	250	0.170956	0.075843	0.142926
62	308	50	285	0.161193	0.079937	0.153949
63	228	47	227	0.135997	0.078992	0.135682
64	72	51	39	0.086866	0.080252	0.076473
65	174	35	86	0.11899	0.075213	0.091275
66	106	27	73	0.097574	0.072693	0.087181

N/D = non detectable

TCE in Bottom Layer

Calibration Curve from JUMP
4.0

Bottom Layer (C)

3175.166 -203.814

GC Responses

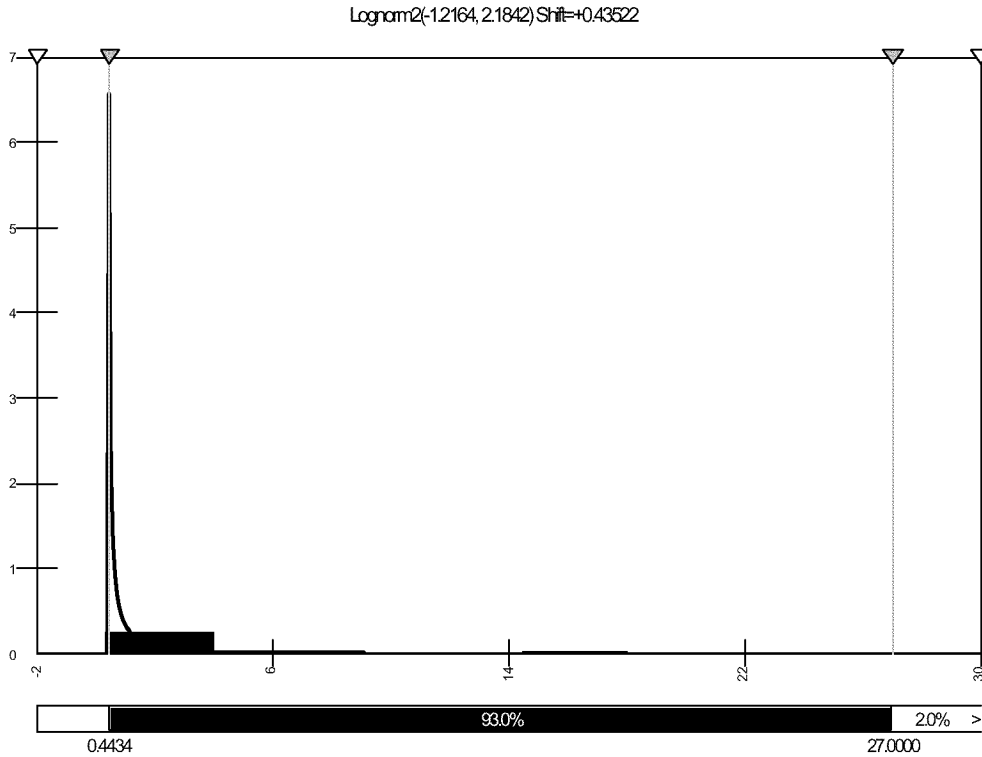
Sample Concentrations (ppb)

Sample Location	1	2	3	1	2	3
1	2456	2520	2595	0.837693	0.857849	0.88147
2	2752	2941	3534	0.930916	0.990441	1.177203
3	4894	4974	5953	1.605527	1.630722	1.939053
4	1915	4732	5868	0.667308	1.554506	1.912282
5	3884	4049	3031	1.287433	1.339399	1.018786
6	Invalid	Invalid	Invalid			
7	2533	2541	2296	0.861944	0.864463	0.787302
8	2595	2384	2520	0.88147	0.815017	0.857849
9	2403	1653	1582	0.821001	0.584793	0.562432
10	2669	2600	2567	0.904776	0.883045	0.872652
11	3435	3130	2995	1.146023	1.049965	1.007448
12	5932	4651	3860	1.932439	1.528995	1.279875
13	3043	3800	3296	1.022565	1.260978	1.102246
14	1811	1514	1230	0.634554	0.541015	0.451571
15	1925	1604	1664	0.670458	0.56936	0.588257
16	1644	1746	1595	0.581958	0.614083	0.566526
17	2381	2044	1691	0.814072	0.707936	0.596761
18	2535	2501	2583	0.862573	0.851865	0.877691
19	1545	3365	1408	0.550779	1.123977	0.507631
20	1364	1523	1630	0.493774	0.54385	0.577549
21	1517	1579	1598	0.54196	0.561487	0.567471
22	1455	1463	1238	0.522434	0.524953	0.454091
23	1986	2229	1876	0.689669	0.766201	0.655025
24	2611	1952	2094	0.886509	0.678961	0.723683
25	2561	3142	3719	0.870762	1.053745	1.235467
26	1529	1690	1775	0.54574	0.596446	0.623216
27	1894	1629	1870	0.660694	0.577234	0.653136
28	1760	2280	1958	0.618492	0.782263	0.680851
29	Invalid	Invalid	Invalid			
30	3087	1829	1362	1.036423	0.640223	0.493144
31	2497	2653	2938	0.850606	0.899737	0.989496
32	1799	1779	1710	0.630775	0.624476	0.602745
33	1557	1629	1587	0.554558	0.577234	0.564006
34	1530	1659	1800	0.546055	0.586682	0.63109
35	1686	1756	1643	0.595186	0.617232	0.581643
36	1477	1687	1606	0.529363	0.595501	0.56999
37	6816	7732	9425	2.21085	2.499338	3.032539
38	1733	1639	1738	0.609988	0.580383	0.611563
39	1589	1689	1474	0.564636	0.596131	0.528418
40	1617	1856	1901	0.573455	0.648726	0.662899

41	2543	2575	2707	0.865093	0.875171	0.916744
42	1984	2003	2624	0.689039	0.695023	0.890604
43	3755	3936	4585	1.246805	1.30381	1.508209
44	1341	1333	1449	0.48653	0.484011	0.520544
45	1504	1536	1683	0.537866	0.547944	0.594241
46	1721	1725	1915	0.606209	0.607469	0.667308
47	2081	2020	2403	0.719589	0.700377	0.821001
48	1822	1858	2062	0.638018	0.649356	0.713605
49	5698	5928	7409	1.858742	1.931179	2.397611
50	1573	1586	1449	0.559597	0.563691	0.520544
51	1340	1388	969	0.486215	0.501332	0.369371
52	1470	1495	1578	0.527158	0.535032	0.561172
53	1351	1479	889	0.48968	0.529992	0.344175
54	1650	1613	1661	0.583848	0.572195	0.587312
55	2867	2906	3367	0.967135	0.979418	1.124607
56	1854	1836	1981	0.648096	0.642427	0.688094
57	1686	1755	1917	0.595186	0.616917	0.667938
58	2823	1863	1919	0.953277	0.650931	0.668568
59	2085	1596	1342	0.720849	0.566841	0.486845
60	2226	1765	1701	0.765256	0.620066	0.59991
61	2571	2155	2324	0.873911	0.742895	0.79612
62	2294	2008	2185	0.786672	0.696598	0.752343
63	2108	1939	1881	0.728092	0.674867	0.6566
64	2156	2275	2151	0.74321	0.780688	0.741635
65	2417	1865	1518	0.82541	0.651561	0.542275
66	2112	1834	1756	0.729352	0.641798	0.617232

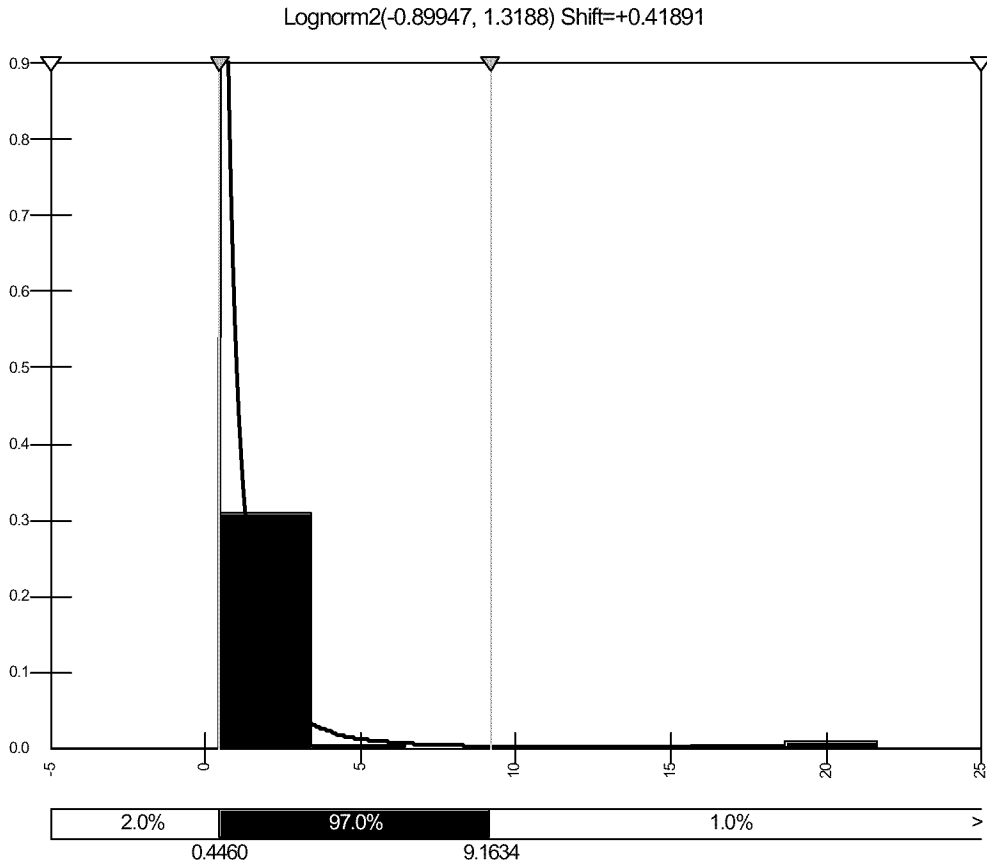
Appendix E: BestFit Analysis of Raw Sample Data

A. BestFit Results for PCE Concentration in Upper Layer



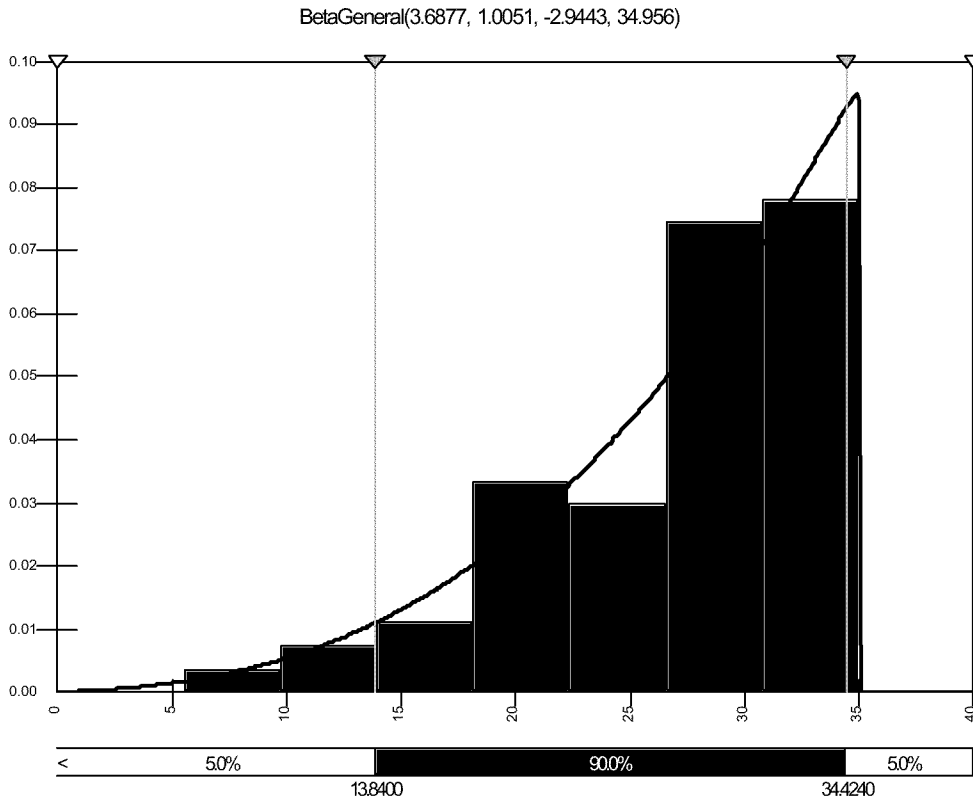
	Fit	Input
Function	RiskLognorm2(-1.2164, 2.1842, RiskShift(0.43522))	N/A
Shift	0.43521893	N/A
μ	-1.216405451	N/A
s	2.184180199	N/A
Left X	0.4386	0.4386
Left P	2.00%	6.06%
Right X	26.7284	26.7284
Right P	98.00%	98.48%
Diff. X	26.2899	26.2899
Diff. P	96.00%	92.42%
Minimum	0.43522	0.43601
Maximum	+ Infinity	28.486
Mean	3.6537	2.4224
Mode	0.43773	0.45675 [est]
Median	0.73151	0.93246
Std. Deviation	34.8127	4.8859
Variance	1211.9239	23.51
Skewness	1297.9184	3.5273
Kurtosis	197173029.6	15.9421

B. BestFit Results for PCE Concentrations in Middle Layer



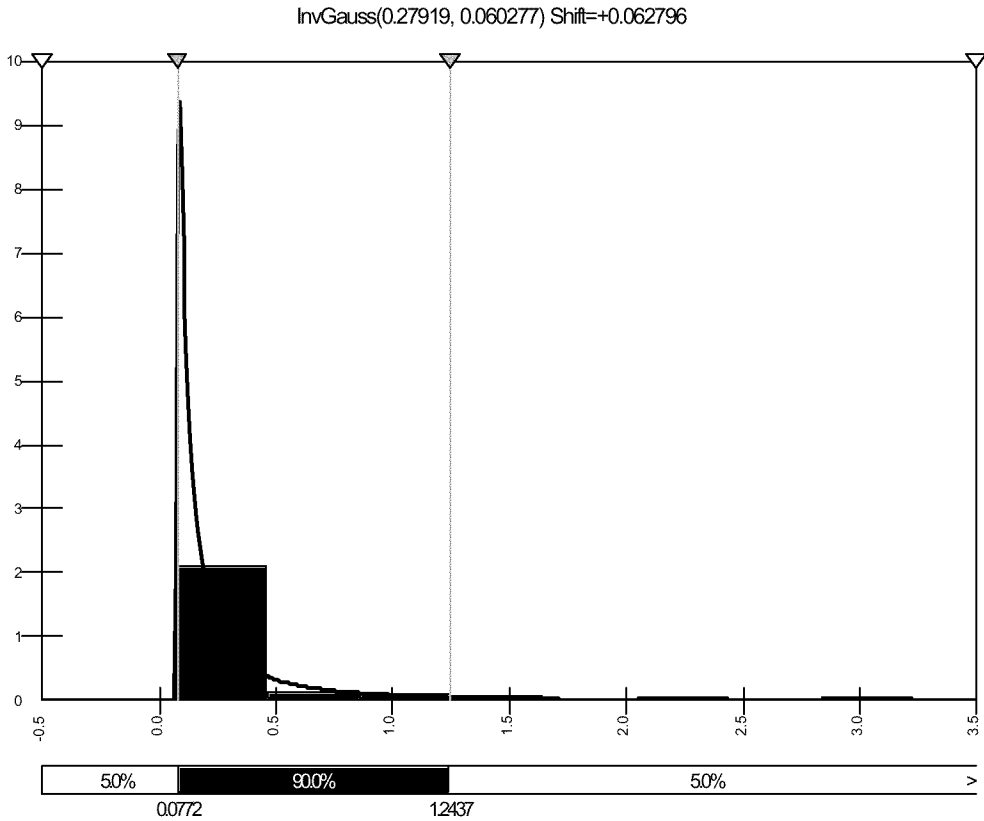
	Fit	Input
Function	RiskLognorm2(-0.89947, 1.3188, RiskShift(0.41891))	N/A
Shift	0.418912238	N/A
μ	-0.899468758	N/A
s	1.318762232	N/A
Left X	0.446	0.446
Left P	2.00%	3.13%
Right X	9.1634	9.1634
Right P	99.00%	95.31%
Diff. X	8.7174	8.7174
Diff. P	97.00%	92.19%
Minimum	0.41891	0.43445
Maximum	+ Infinity	21.702
Mean	1.38945	1.7999
Mode	0.49037	0.48482 [est]
Median	0.8257	0.88713
Std. Deviation	2.10238	4.0314
Variance	4.42001	15.998
Skewness	16.6633	4.32
Kurtosis	1513.1085	20.2993

C. BestFit Results for PCE Concentrations in the Bottom Layer



	Fit	Input
Function	RiskBetaGeneral(3.6877, 1.0051, -2.9443, 34.956)	N/A
Shift	N/A	N/A
a1	3.687733345	N/A
a2	1.005110068	N/A
min	-2.944253111	N/A
max	34.95644919	N/A
Left X	13.84	13.84
Left P	5.00%	4.69%
Right X	34.424	34.424
Right P	95.00%	95.31%
Diff. X	20.584	20.584
Diff. P	90.00%	90.63%
Minimum	-2.9443	5.5673
Maximum	34.956	34.956
Mean	26.839	26.821
Mode	34.885	30.231 [est]
Median	28.424	29.044
Std. Deviation	6.5168	6.3805
Variance	42.468	40.075
Skewness	-0.9935	-1.228
Kurtosis	3.5081	4.1135

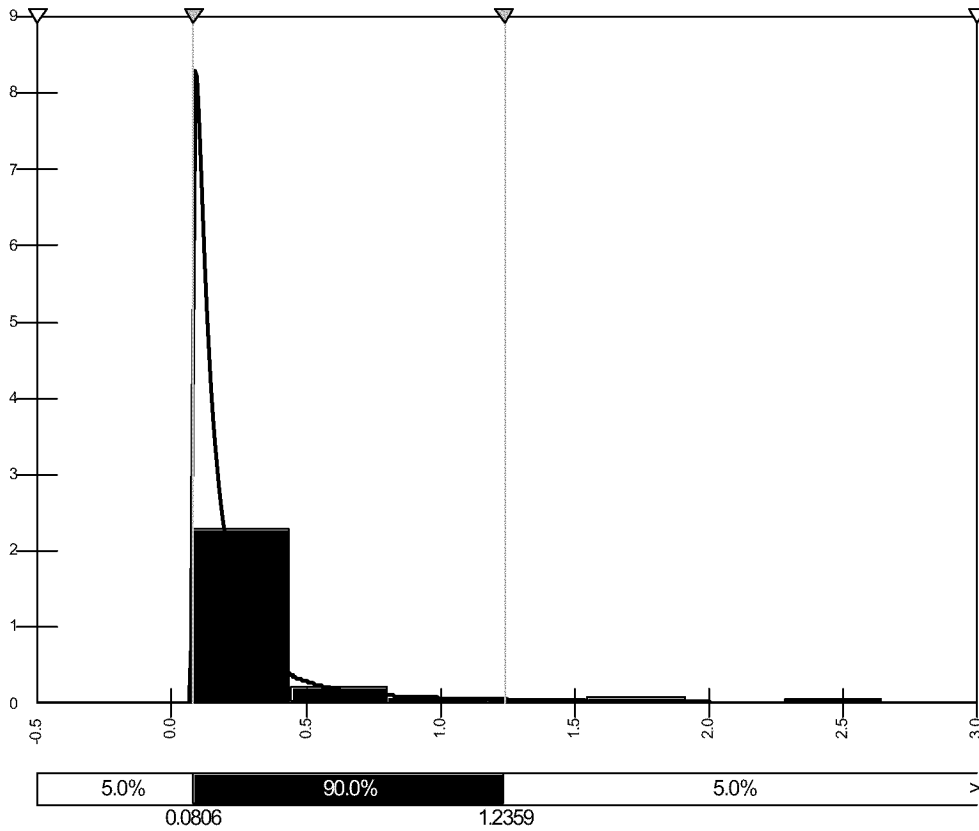
D. BestFit Results for TCE Concentrations in Top Layer



	Fit	Input
Function	RiskInvGauss(0.27919, 0.060277, RiskShift(0.062796))	N/A
Shift	6.28E-02	N/A
μ	0.279187789	N/A
?	6.03E-02	N/A
Left X	0.0772	0.0772
Left P	5.00%	7.58%
Right X	1.2437	1.2437
Right P	95.00%	93.94%
Diff. X	1.1665	1.1665
Diff. P	90.00%	86.36%
Minimum	0.062796	0.071906
Maximum	+ Infinity	3.2319
Mean	0.34198	0.34198
Mode	0.082786	0.14272 [est]
Median	0.15134	0.14398
Std. Deviation	0.60085	0.51743
Variance	0.361025	0.26367
Skewness	6.4564	3.5973
Kurtosis	72.4761	17.9029

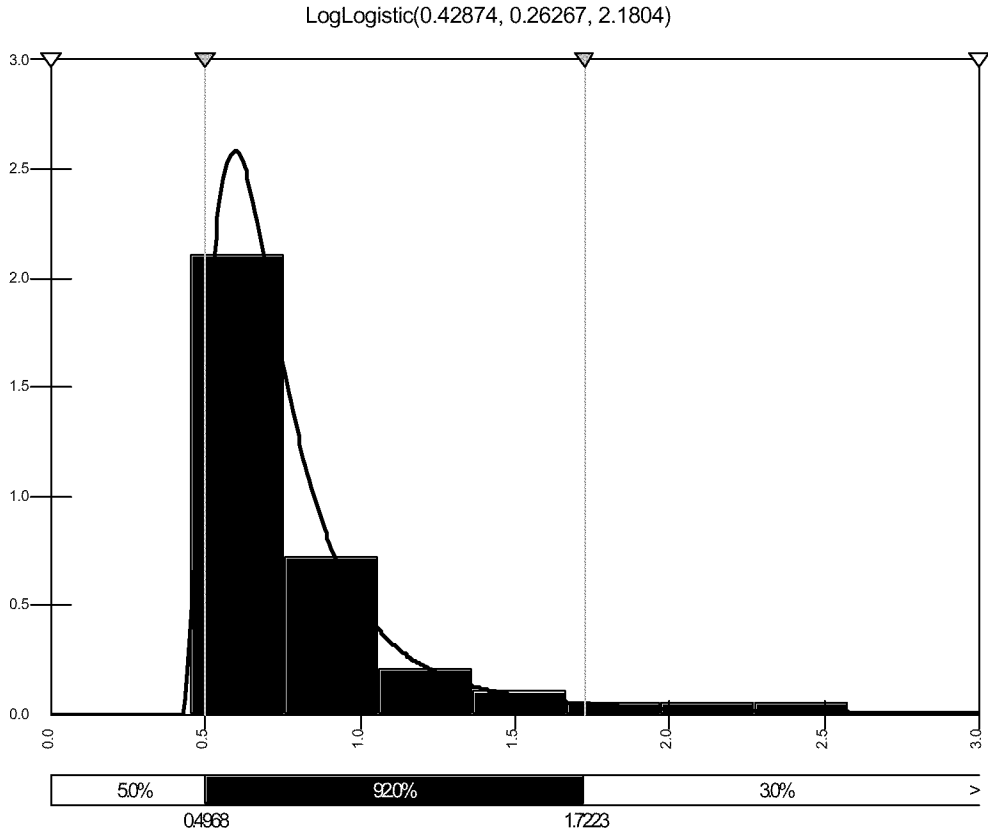
E. BestFit Results for TCE Concentrations in the Middle Layer

Pearson5(1.0331, 0.067583) Shift=+0.058496



	Fit	Input
Function	RiskPearson5(1.0331, 0.067583, RiskShift(0.058496))	N/A
Shift	0.058496052	N/A
a	1.033115594	N/A
b	6.76E-02	N/A
Left X	0.0806	0.0806
Left P	5.00%	7.94%
Right X	1.2359	1.2359
Right P	95.00%	93.65%
Diff. X	1.1553	1.1553
Diff. P	90.00%	85.71%
Minimum	0.058496	0.073428
Maximum	+ Infinity	2.6498
Mean	2.099327	0.31872
Mode	0.091737	0.13075 [est]
Median	0.151683	0.14513
Std. Deviation	+ Infinity	0.44956
Variance	+ Infinity	0.1989
Skewness	7.7179 [est]	3.3136
Kurtosis	67.9195 [est]	14.907

F. BestFit Results for TCE Concentrations in the Bottom Layer



	Fit	Input
Function	RiskLogLogistic(0.42874, 0.26267, 2.1804)	N/A
Shift	N/A	N/A
g	0.428741544	N/A
b	0.26267117	N/A
a	2.180374021	N/A
Left X	0.4968	0.4968
Left P	5.00%	3.13%
Right X	1.7223	1.7223
Right P	97.00%	95.31%
Diff. X	1.2255	1.2255
Diff. P	92.00%	92.19%
Minimum	0.42874	0.45231
Maximum	+ Infinity	2.5809
Mean	0.81043	0.80644
Mode	0.59546	0.66136 [est]
Median	0.69141	0.6798
Std. Deviation	0.79248	0.37943
Variance	0.628029	0.14172
Skewness	3.7618 [est]	2.6043
Kurtosis	22.2511 [est]	10.7628

Appendix F: Hydraulic Conductivities and Water Levels in Top and Middle Layers

A. Water levels observed in upper layer piezometers. Head levels from arbitrary datum point in bottom of wetland.

Piez #	obs head	Piez #	obs head
01A	6.015335	34A	6.227627
02A	5.86496	35A	6.170668
03A	6.231627	36A	6.953793
04A	6.320252	37A	5.871002
05A	5.949877	38A	6.744002
06A	5.821502	39A	5.82821
07A	6.219668	40A	6.012002
08A	6.14246	41A	5.613418
09A	6.235793	42A	6.162835
10A	6.338627	43A	5.34496
11A	6.026835	44A	0
12A	6.12846	45A	5.963002
13A	6.149543	46A	6.162543
14A	6.254043	47A	6.025335
15A	6.412793	48A	5.844168
16A	6.450877	49A	5.929793
17A	6.36896	50A	5.828335
18A	5.963085	51A	5.914418
19A	5.906668	52A	6.289752
20A	0	53A	6.04271
21A	6.443293	54A	6.099127
22A	6.603043	55A	5.835918
23A	6.29846	56A	0
24A	6.212877	57A	5.855335
25A	6.038043	58A	6.233293
26A	0	59A	6.172127
27A	0	60A	6.807793
28A	6.701043	61A	6.286543
29A	6.75946	62A	0
30A	6.633168	63A	6.30821
31A	6.709252	64A	6.226502
32A	6.163043	65A	6.710877
33A	6.663127	66A	6.825002

B. Hydraulic conductivities in upper layer

Piez #	K	Piez #	K
01A	9.61E-06	34A	2.74E-06
02A	1.31E-05	35A	0.00001
03A		36A	7.08E-06
04A	3.66E-05	37A	
05A	1.5E-06	38A	2.83E-06
06A	1.53E-05	39A	4.07E-06
07A	1.47E-06	40A	
08A		41A	2.62E-06
09A	3.45E-07	42A	
10A		43A	2.28E-06
11A	2.28E-06	44A	5.68E-08
12A		45A	4.92E-05
13A	1.9E-06	46A	1.24E-06
14A	3.32E-06	47A	1.16E-06
15A	1.09E-06	48A	2.03E-07
16A	1.06E-05	49A	
17A		50A	2.49E-05
18A	6.92E-06	51A	
19A	1.77E-05	52A	2.42E-06
20A		53A	
21A	1.6E-06	54A	5.58E-06
22A		55A	2.84E-05
23A	2.08E-05	56A	
24A		57A	1.18E-05
25A	3.59E-06	58A	
26A	7.28E-07	59A	2.63E-06
27A	8.56E-07	60A	
28A	1.15E-06	61A	1.88E-07
29A		62A	3.14E-06
30A	3.27E-05	63A	
31A	1.33E-06	64A	1.8E-06
32A	1.55E-05	65A	
33A	2.3E-06	66A	4.9E-06

C. Water levels observed in middle layer piezometers. Head levels from arbitrary datum point in bottom of wetland.

Piez #	obs head	Piez #	obs head
01B	6.005502	34B	7.659543
02B	7.242377	35B	7.633127
03B	6.704793	36B	7.256252
04B	6.418668	37B	6.447627
05B	6.086752	38B	6.652293
06B	5.829627	39B	7.098752
07B	6.38321	40B	6.095335
08B	6.272543	41B	6.456543
09B	6.431127	42B	7.005335
10B	6.473752	43B	6.596543
11B	5.935627	44B	6.461918
12B	6.501335	45B	6.11971
13B	6.503127	46B	6.25971
14B	6.502127	47B	6.084293
15B	6.50471	48B	6.664668
16B	6.596835	49B	6.111127
17B	6.40771	50B	0
18B	6.26696	51B	6.088127
19B	6.228252	52B	6.04571
20B	6.822043	53B	5.97371
21B	6.677293	54B	6.976002
22B	6.900002	55B	6.397043
23B	6.730418	56B	0
24B	6.600377	57B	5.879168
25B	6.527752	58B	6.247043
26B	6.707918	59B	6.159668
27B	6.542418	60B	7.02721
28B	6.79796	61B	6.24071
29B	7.080293	62B	6.93696
30B	7.316002	63B	6.97471
31B	6.690335	64B	7.359627
32B	6.643752	65B	7.57271
33B	7.803877	66B	7.375585

B. Hydraulic conductivities in middle layer

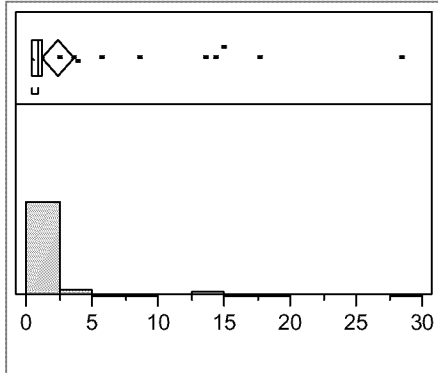
Piez #	K	Piez #	K
01B		34B	1.70E-07
02B	1.48E-06	35B	
03B	1.08E-06	36B	2.04E-06
04B	7.89E-06	37B	3.71E-06
05B	4.83E-07	38B	
06B	1.51E-06	39B	6.15E-07
07B		40B	
08B	1.39E-05	41B	8.02E-06
09B		42B	
10B	3.89E-05	43B	8.13E-07
11B		44B	3.57E-07
12B	5.83E-07	45B	2.16E-06
13B	4.30E-07	46B	
14B		47B	
15B	1.31E-06	48B	
16B		49B	7.07E-06
17B	7.64E-06	50B	
18B		51B	4.57E-06
19B		52B	
20B	4.75E-06	53B	1.22E-05
21B		54B	
22B	2.12E-05	55B	
23B		56B	3.48E-08
24B	1.75E-07	57B	
25B	5.02E-06	58B	1.05E-05
26B		59B	4.18E-06
27B	1.28E-06	60B	
28B		61B	2.10E-06
29B	2.37E-05	62B	
30B	5.73E-07	63B	4.55E-07
31B		64B	
32B	5.94E-06	65B	
33B		66B	5.42E-06

Appendix G: Outlier Analysis

A. Box and whisker plot from JUMP that shows what sample points were considered outliers for PCE in the upper layer. Those points that fell outside of the whiskers were considered outliers.

Distributions

PCE A Layer, Average



Quantiles

100.0%	maximum	28.486
99.5%		28.486
97.5%		21.239
90.0%		6.700
75.0%	quartile	1.241
50.0%	median	0.932
25.0%	quartile	0.513
10.0%		0.455
2.5%		0.437
0.5%		0.436
0.0%	minimum	0.436

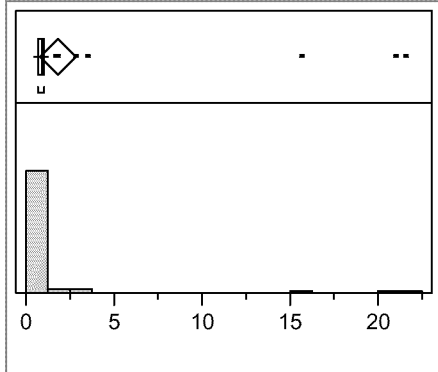
Moments

Mean	2.422360
Std Dev	4.885858
Std Err Mean	0.601408
upper 95% Mean	3.623455
lower 95% Mean	1.221265
N	66.000000

Piezometers 1, 10, 16, 20, 21, 22, 29 and 30A were considered outliers.

B. Box and whisker plot from JUMP that shows what sample points were considered outliers for PCE in the middle layer. Those points that fell outside of the whiskers were considered outliers.

Distributions
PCE B Layer, Average



Quantiles

100.0%	maximum	21.702
99.5%		21.702
97.5%		21.298
90.0%		1.784
75.0%	quartile	1.041
50.0%	median	0.887
25.0%	quartile	0.633
10.0%		0.487
2.5%		0.437
0.5%		0.434
0.0%	minimum	0.434

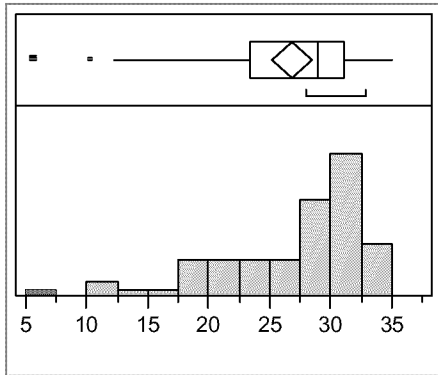
Moments

Mean	1.797278
Std Dev	4.032143
Std Err Mean	0.504018
upper 95% Mean	2.804478
lower 95% Mean	0.790077
N	64.000000

Piezometers 1, 10, 20, 22, 25, 29, and 33B were considered outliers

C. Box and whisker plot from JUMP that shows what sample points were considered outliers for PCE in the bottom layer. Those points that fell outside of the whiskers were considered outliers.

Distributions
PCE C Layer, Average



Quantiles

100.0%	maximum	34.956
99.5%		34.956
97.5%		34.874
90.0%		33.089
75.0%	quartile	31.153
50.0%	median	29.044
25.0%	quartile	23.427
10.0%		17.861
2.5%		8.504
0.5%		5.567
0.0%	minimum	5.567

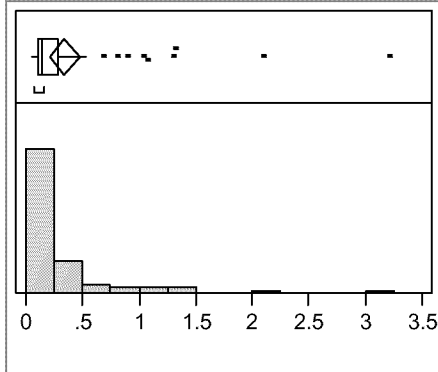
Moments

Mean	26.82095
Std Dev	6.38054
Std Err Mean	0.79757
upper 95% Mean	28.41477
lower 95% Mean	25.22714
N	64.00000

Piezometers 12 and 37C were considered outliers.

D. Box and whisker plot from JUMP that shows what sample points were considered outliers for TCE in the top layer. Those points that fell outside of the whiskers were considered outliers.

Distributions
TCE A Layer, Average



Quantiles

100.0%	maximum	3.2319
99.5%		3.2319
97.5%		2.4713
90.0%		0.9501
75.0%	quartile	0.2882
50.0%	median	0.1440
25.0%	quartile	0.1039
10.0%		0.0789
2.5%		0.0526
0.5%		0.0479
0.0%	minimum	0.0479

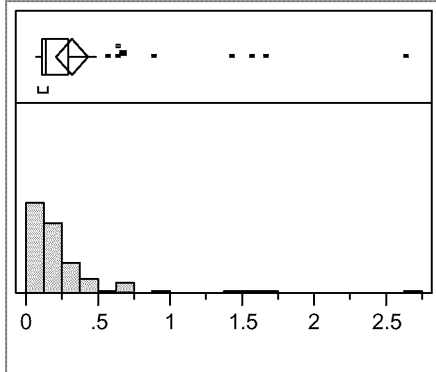
Moments

Mean	0.3412054
Std Dev	0.5178488
Std Err Mean	0.0637428
upper 95% Mean	0.4685087
lower 95% Mean	0.2139022
N	66

Piezometers 1, 10, 20, 21, 22, 30, 33, and 37A were considered outliers.

E. Box and whisker plot from JUMP that shows what sample points were considered outliers for TCE in the middle layer. Those points that fell outside of the whiskers were considered outliers.

Distributions
TCE B Layer, Average



Quantiles

100.0%	maximum	2.6498
99.5%		2.6498
97.5%		2.0364
90.0%		0.6617
75.0%	quartile	0.2926
50.0%	median	0.1429
25.0%	quartile	0.1063
10.0%		0.0804
2.5%		0.0700
0.5%		0.0642
0.0%	minimum	0.0642

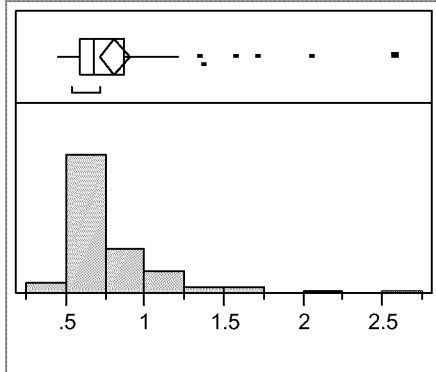
Moments

Mean	0.3147478
Std Dev	0.4471144
Std Err Mean	0.0558893
upper 95% Mean	0.4264337
lower 95% Mean	0.2030618
N	64

Piezometers 9, 10, 20, 22, 29, 33, 37, 38, and 53B were considered outliers.

F. Box and whisker plot from JUMP that shows what sample points were considered outliers for TCE in the bottom layer. Those points that fell outside of the whiskers were considered outliers.

Distributions
TCE C Layer, Average



Quantiles

100.0%	maximum	2.5809
99.5%		2.5809
97.5%		2.2569
90.0%		1.2841
75.0%	quartile	0.8628
50.0%	median	0.6798
25.0%	quartile	0.5881
10.0%		0.5418
2.5%		0.4537
0.5%		0.4523
0.0%	minimum	0.4523

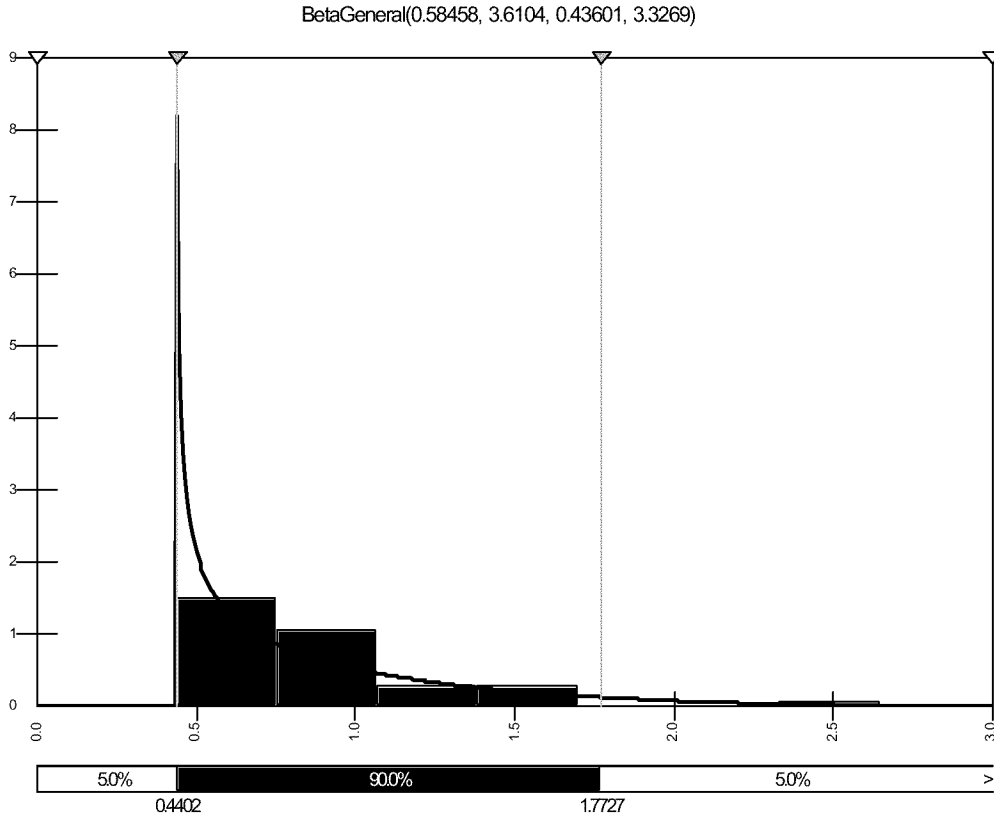
Moments

Mean	0.8064412
Std Dev	0.3794322
Std Err Mean	0.0474290
upper 95% Mean	0.9012207
lower 95% Mean	0.7116618
N	64

Piezometers 3, 4, 12, 37, 43, and 49 were considered outliers.

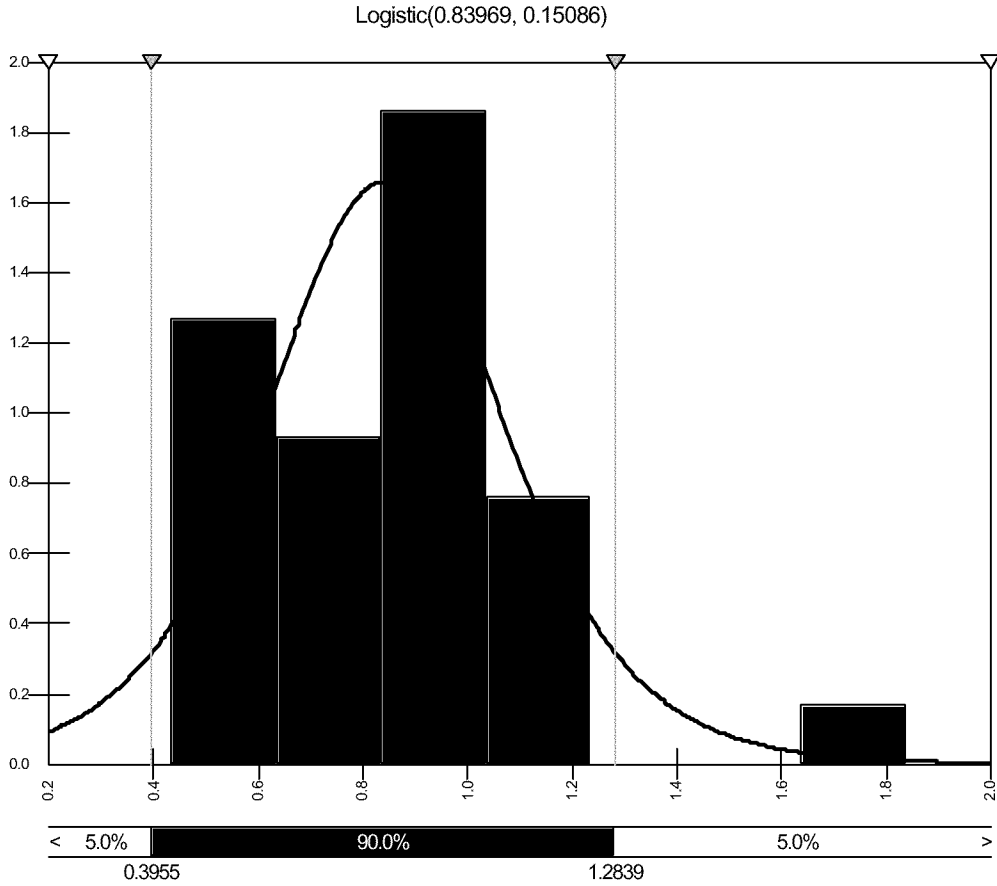
Appendix H: BestFit Analysis of Outlier Data

A. BestFit Results for PCE Concentrations in Upper Layer with outliers removed.



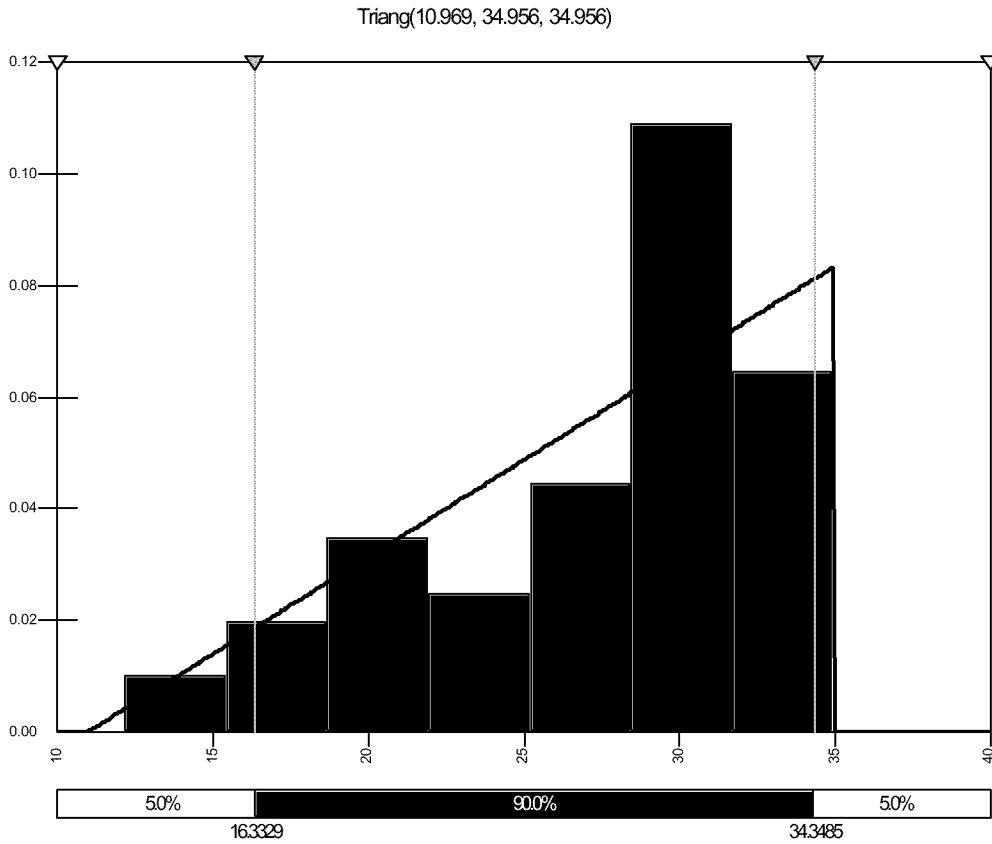
	Fit	Input
Function	RiskBetaGeneral(0.58458, 3.6104, 0.43601, 3.3269)	N/A
a1	0.584582481	N/A
a2	3.610440099	N/A
min	0.436005135	N/A
max	3.326868096	N/A
Left X	0.4402	0.4402
Left P	5.00%	7.02%
Right X	1.7727	1.7727
Right P	95.00%	98.25%
Diff. X	1.3326	1.3326
Diff. P	90.00%	91.23%
Minimum	0.43601	0.43601
Maximum	3.3269	2.6476
Mean	0.83885	0.84565
Mode	0.43601	0.45675 [est]
Median	0.68073	0.86918
Std. Deviation	0.43924	0.39833
Variance	0.19293	0.15589
Skewness	1.5326	1.6949
Kurtosis	5.1997	8.345

B. BestFit Results for PCE Concentrations in Middle Layer with outliers removed.



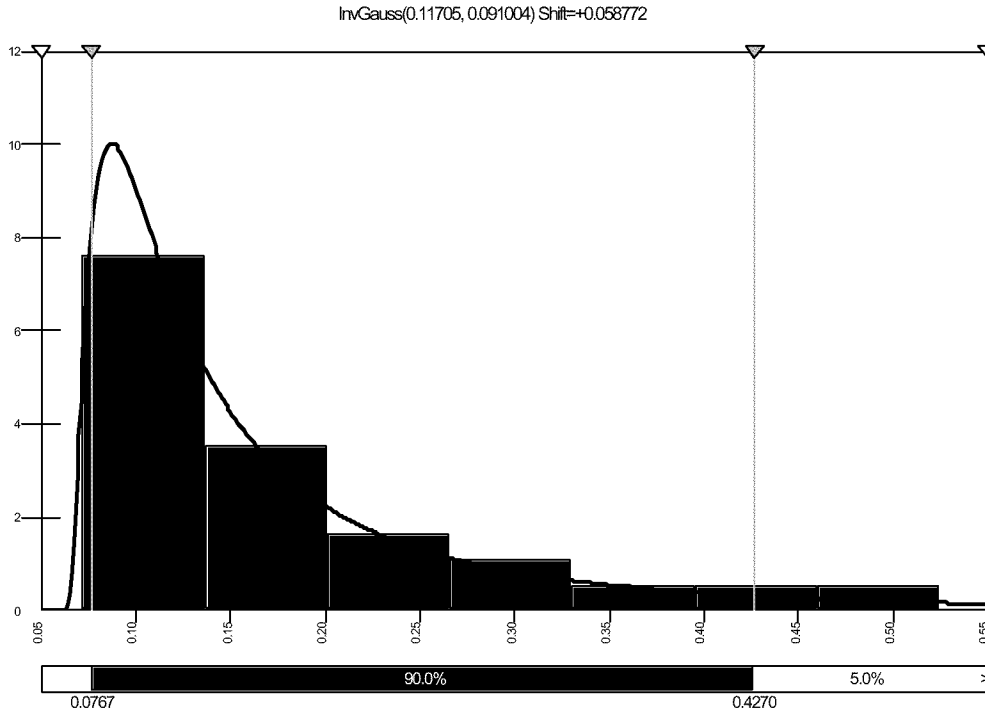
	Fit	Input
Function	RiskLogistic(0.83969, 0.15086)	N/A
Shift	N/A	N/A
a	0.839693614	N/A
β	0.150860081	N/A
Left X	0.3955	0.3955
Left P	5.00%	0.00%
Right X	1.2839	1.2839
Right P	95.00%	96.61%
Diff. X	0.8884	0.8884
Diff. P	90.00%	96.61%
Minimum	- Infinity	0.43445
Maximum	+ Infinity	1.8382
Mean	0.83969	0.85125
Mode	0.83969	0.48482 [est]
Median	0.83969	0.86985
Std. Deviation	0.27363	0.28205
Variance	0.074873	0.078205
Skewness	0	0.9831
Kurtosis	4.2	5.146

C. BestFit Results for PCE Concentration in Bottom Layer with outliers removed.



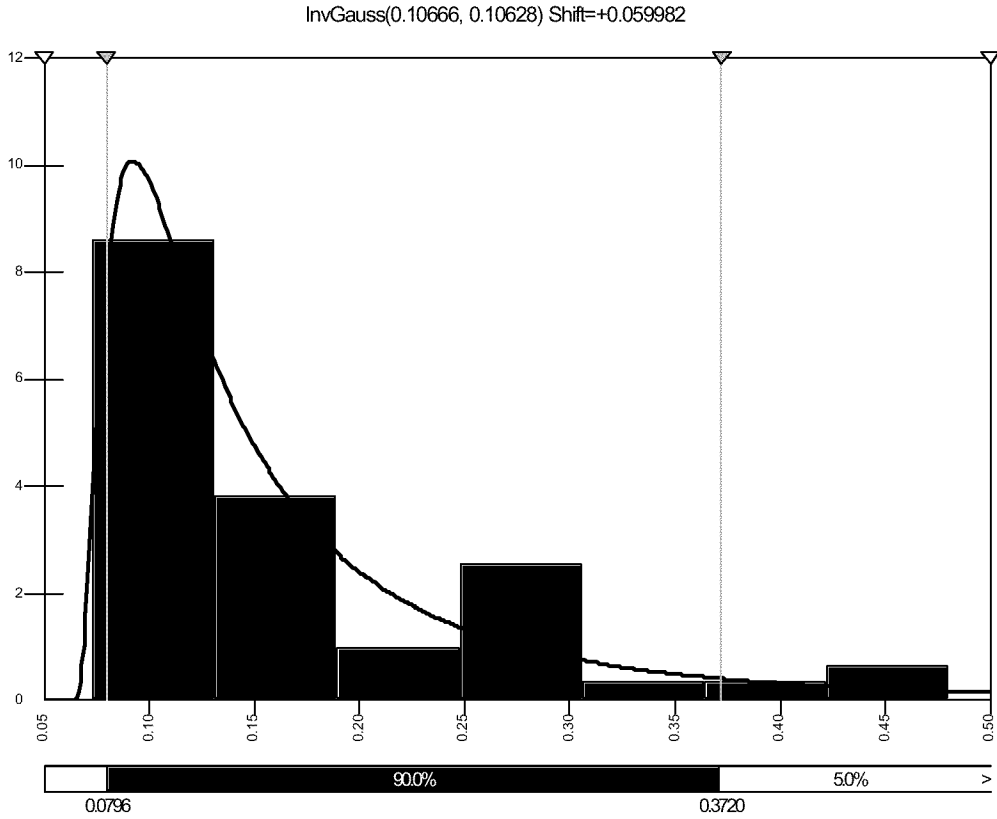
	Fit	Input
Function	RiskTriang(10.969, 34.956, 34.956)	N/A
Shift	N/A	N/A
min	10.96943038	N/A
m. likely	34.9581614	N/A
max	34.9581614	N/A
Left X	16.3329	16.3329
Left P	5.00%	4.84%
Right X	34.3485	34.3485
Right P	95.00%	95.16%
Diff. X	18.0155	18.0155
Diff. P	90.00%	90.32%
Minimum	10.969	12.171
Maximum	34.956	34.956
Mean	26.96	27.431
Mode	34.956	30.231 [est]
Median	27.93	29.115
Std. Deviation	5.6536	5.4562
Variance	31.964	29.29
Skewness	-0.5657	-0.9297
Kurtosis	2.4	3.0433

D. BestFit Results for TCE Concentration in Top Layer with outliers removed.



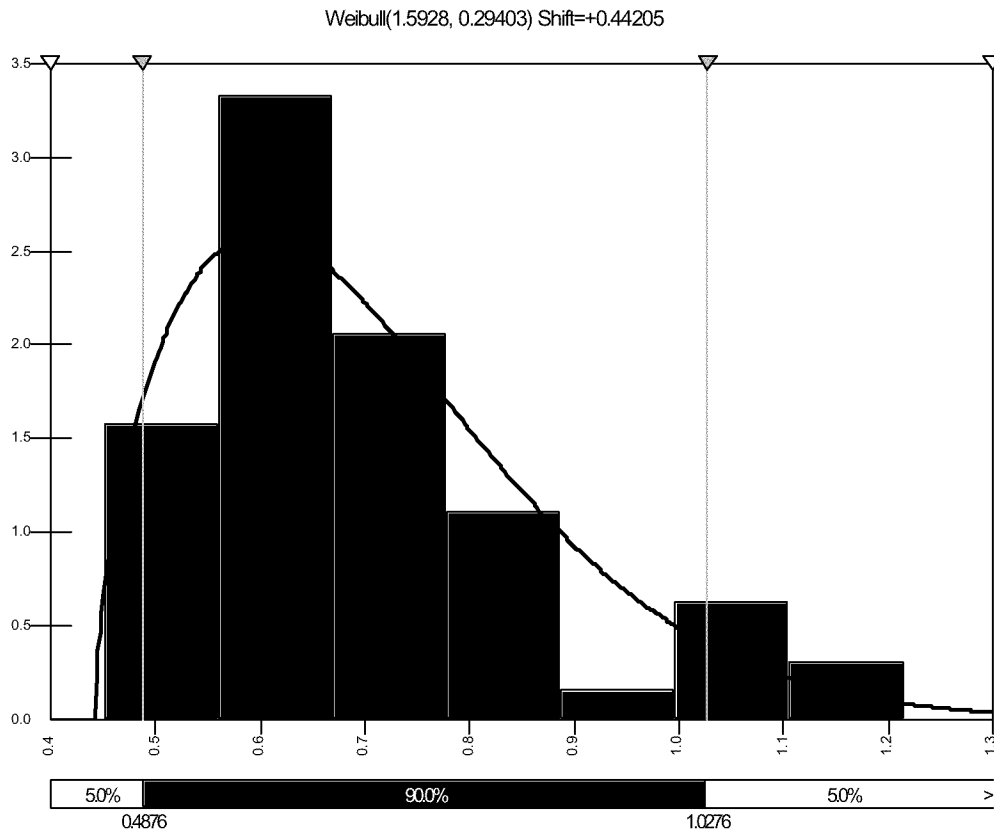
	Fit	Input
Function	RiskInvGauss(0.11705, 0.091004, RiskShift(0.058772))	N/A
Shift	5.88E-02	N/A
μ	0.117052302	N/A
σ	0.091003886	N/A
N/A	N/A	N/A
N/A	N/A	N/A
N/A	N/A	N/A
Left X	0.0767	0.0767
Left P	5.00%	7.02%
Right X	0.427	0.427
Right P	95.00%	94.74%
Diff. X	0.3504	0.3504
Diff. P	90.00%	87.72%
Minimum	0.058772	0.071906
Maximum	+ Infinity	0.52474
Mean	0.17582	0.17582
Mode	0.087305	0.14272 [est]
Median	0.13132	0.13799
Std. Deviation	0.13275	0.11174
Variance	0.017623	0.012266
Skewness	3.4024	1.5976
Kurtosis	22.2935	5.027

E. BestFit Results for TCE Concentration in the middle layer with outliers removed.



	Fit	Input
Function	RiskInvGauss(0.11705, 0.091004, RiskShift(0.058772))	N/A
Shift	5.88E-02	N/A
μ	0.117052302	N/A
σ	0.091003886	N/A
Left X	0.0767	0.0767
Left P	5.00%	7.02%
Right X	0.427	0.427
Right P	95.00%	94.74%
Diff. X	0.3504	0.3504
Diff. P	90.00%	87.72%
Minimum	0.058772	0.071906
Maximum	+ Infinity	0.52474
Mean	0.17582	0.17582
Mode	0.087305	0.14272 [est]
Median	0.13132	0.13799
Std. Deviation	0.13275	0.11174
Variance	0.017623	0.012266
Skewness	3.4024	1.5976
Kurtosis	22.2935	5.027

F. BestFit Results for TCE Concentrations in the bottom layer with outliers removed.



Fit	Input
Function	RiskWeibull(1.5928, 0.29403, RiskShift(0.44205))
Shift	0.442050029
a	1.592847939
β	0.294027645
Left X	0.4876
Left P	5.00%
Right X	1.0276
Right P	95.00%
Diff. X	0.54
Diff. P	90.00%
Minimum	0.44205
Maximum	+ Infinity
Mean	0.70578
Mode	0.60014
Median	0.67564
Std. Deviation	0.16945
Variance	0.028715
Skewness	0.8973 [est]
Kurtosis	3.6209 [est]

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Vita

Captain Bryan C. Opperman was born in Waverly, Iowa. He graduated from Waynesville High School in Waynesville, Missouri, in 1989. He entered undergraduate studies at the University of Missouri-Rolla in Rolla, Missouri, where he graduated with a Bachelor of Science Degree in Electrical Engineering in on 14 May 1994. He was commissioned on the same date and received a reserve commission.

His first assignment was at Ellsworth Air Force Base, South Dakota in September 1994. While stationed at Ellsworth, he was the Chief of Maintenance Engineering and Commander of the Readiness Flight. During his tenure at Ellsworth, he deployed overseas in 1996 to Haiti as a project engineer for United States Support Group-Haiti. He also deployed to the Kingdom of Saudi Arabia in June 1997 as a design engineer for the 4404th Civil Engineering Squadron at Prince Sultan Air Base. In November 1997, he was assigned to the 823rd RED HORSE Squadron at Hurlburt Field, Florida as an electrical project engineer. While assigned to RED HORSE, he executed numerous projects at locations around the world. In August 2000 he entered the Graduate School of Engineering and Management, Air Force Institute of Technology. Upon graduation, he will be assigned to Headquarters, 7th Air Force at Osan Air Base, South Korea.

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