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Characterization of Chlorinated Solvent Degradation in a Constructed Wetland

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CHARACTERIZATION OF CHLORINATED SOLVENT DEGRADATION IN A CONSTRUCTED WETLAND

THESIS

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Abstract

Widespread chlorinated ethene contamination of aquifers coupled with high costs of current treatment technologies demand innovative remediation solutions. Wetlands, maintaining anaerobic and aerobic zones promoting the complete degradation of chlorinated ethenes such as Tetrachloroethylene (PCE), could be the answer.

This thesis characterized the chlorinated solvent contamination levels in three strata of an upward flow constructed wetland. Analysis of samples was accomplished by purge-and-trap gas chromatography. Water quality parameters, Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP), pH, Conductivity, and Temperature, were also measured in monitoring wells with a water monitoring sonde.

After removing data outliers caused by short-circuiting flow, PCE concentrations declined from an average of 32.59 ± 0.699 ppb (± 95% confidence interval) in the inflow stream to an average of 0.171 ± 0.807 ppb in the upper layer (a 99.3% reduction). Concentration trends of PCE degradation products cis-1,1-Dichloroethylene (cis-DCE), Vinyl Chloride (VC), and Trichloroethylene TCE) indicate dechlorination processes are occurring. In addition to PCE, TCE at concentrations below 0.6 ppb was the only other analyte detected in the inflow and outflow. Water quality measurements of DO and ORP decreased from the bottom to the middle layer to a level that supports anaerobic reductive dechlorination but not methanogenesis. The DO increased slightly from the middle to the top layer while ORP continued to decrease. DO is required in the top layer to complete the aerobic degradation of cis-DCE and VC.

CHARACTERIZATION OF CHLORINATED SOLVENT DEGRADATION IN A CONSTRUCTED WETLAND

I. Introduction

The purpose of this study is to determine concentrations of chlorinated solvents and their biodegradation by-products contamination in two upward flow constructed wetland cells at Wright-Patterson Air Force Base (WPAFB), Ohio. Previous efforts in the first constructed wetland cell installed a stratified sampling grid with drive point peizometers and developed a methodology for extracting samples of the contaminated groundwater from the wetland sediment matrix. This research follows up the analysis done by Bryan Opperman (2002) who used a gas chromatograph to detect chlorinated solvents such as perchloroethylene (PCE, a.k.a. tetrachloroethene) and its daughter products in wetland samples. First, this effort will determine the concentrations of chlorinated solvents in various layers of the wetland (strata) nearly a year after the initial sampling was done and two years after the construction of the wetland cells. A second analysis effort will measure water quality parameters in the wetland soil to aid in the characterization of the dominant degradation processes occurring throughout the wetland.

A water monitoring sonde will be used to collect measurements such as Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP), pH, temperature, and conductivity. These parameters add to the *weight of evidence* toward the determination of redox conditions and characterization of dominant transformation processes occurring

throughout the wetland (Chapelle, 1994; Chapelle, 2001; Wiedemeier et al., 1997). Ultimately the data gathered will be used in further studies to develop detailed models enabling improved design and construction of wetlands capable of removing chlorinated solvents from ground water.

Background

The number of groundwater-contaminated sites is estimated to be in the range of 300,000 to 400,000. One early report put the price tag for cleaning up these sites between $480 billion to $1 trillion with an estimate of $750 billion (NRC, 1994). Commercial, industry, and government spending on environmental remediation totaled nine billion dollars in 1996. Of that, the government was responsible for $3.8 billion (42 %) (NRC, 1997). The problems continue today as new sites are being added to the National Priority List (NPL). As of August 2000, 1,234 sites were on the NPL and 217 sites had been removed. An additional 59 sites are proposed for the NPL (EPA, 2001). There is promise in new innovative remediation technologies, but their use is not common. In 1996 the EPA reported that conventional pump-and-treat systems were being used in 93% of all Superfund sites (EPA, 1996). According to 1995 EPA data, only 1% of Superfund sites used in-situ bioremediation technology.

The most common contaminants at hazardous waste sites are volatile organic compounds (VOCs), toxic inorganic compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and phthalates (NRC, 1994). This study focuses on the VOC PCE and its degradation products. PCE and its daughter

products are used as chlorinated solvents in many industries as textile cleaners, degreasers, and primarily solvents for greases, oils, and waxes. Due to their prevalent use in all areas of the country, chlorinated solvents are one of the most common contaminants in groundwater systems.

Chlorinated solvents have a long history of use in the United States and the world. They were first produced in Europe before 1900 with US production starting in 1906. The manufacturing increases during WWII broadened the use of these solvents nationwide. Their employment continued to rise for the next 30 years without environmental regulation until the late 1970's when widespread groundwater contamination became suspected (Cherry and Pankow, 1996) and the harmful effects, including cancer, became known. The Resource Conservation and Recovery Act (RCRA) of 1976 and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund) of 1980 exposed the massive groundwater contamination problem at thousands of sites across the country (NRC, 1999). Before this time it was common practice to dispose of these chemicals on the ground or in gravel pits to volatilize into the atmosphere or by dumping them into landfills, settling ponds and lagoons, or by using injection wells (Cherry and Pankow, 1996).

Alkyl halide chemical properties make them useful in a wide range of industrial applications. They tend to have high vapor pressures and relatively high aqueous solubilities, as well as being excellent solvents for non-polar organic compounds and more dense than water (Table 1 below). Unfortunately, these properties also make them harder to control and remediate once they escape into the environment. The chemical

properties of chlorinated solvents have lead to their wide contamination and difficult remediation of groundwaters.

Table 1. Physical Characteristics of PCE and its Daughter Products (Norris, 1994)

Compound	Density (g/ml)	Solubility (mg/l)	Henry's Constant (atm)	Log K_{ow}
Tetrachloroethylene (PCE)	1.630	200	1100	2.88
Trichloroethylene (TCE)	1.400	1,100	550	2.29
1,1-Dichloroethylene (DCE)*	1.013	250	1,400	0.73
Vinyl Chloride (VC)	Gas	1,100	35,500	0.60

* Primary isomer of DCE in microbial degradation of PCE

The high densities of these dense non-aqueous phase liquids (DNAPLs: primarily PCE and TCE) allow the free product to filter through the unsaturated soil zone and the saturated vadose zone to accumulate on top of the water table forming a lens. As the mass of the collected DNAPL increases, it displaces the water from the soil void spaces and penetrates the water table and sinks until it reaches an aquitard or aquiclude (Domenico and Schwartz, 1998). The resulting lens of DNAPL resting on top of an impenetrable surface presents a reduced surface area to volume ratio to oncoming groundwater flow, thus providing less opportunity for the contaminant to solubilize into the ground water. Subsequently the absolute removal rate of the contaminant is reduced. (Johnson and Pankow, 1992).

The high densities of chlorinated solvents combined with their low viscosities enable a rapid downward movement through the soil matrix (Cherry and Pankow, 1996).

The low *absolute* solubilities of these compounds allow the chemicals to move through the aquifer in the DNAPL phase and stagnate in areas of low flow. Once

stabilized the low solubility allows the contaminant to remain for hundreds of years (Johnson and Pankow, 1992). The relatively high solubilities can cause widespread contaminant concentrations that exceed the Maximum Contaminant Levels (MCLs) that are set to protect human health (Table 2 below). Therefore, dilution cannot be depended on for reduction of contaminants below harmful levels (NRC, 1997).

The relatively low octanol-water partition coefficient means that the chlorinated solvents will not sorb to soils significantly. The lower sorption results in less retardation of the solvent enabling it to move with the groundwater flow to contaminate large areas (Cherry and Pankow, 1996).

Halogenated organic compounds (alkyl halides) have become some of the most useful chemicals in industry and agriculture. A subclass of these compounds, chlorinated aliphatic hydrocarbons (CAHs), have been employed in industry as degreasing agents for aircraft and automobile parts, electronic components, and dry cleaning (McCarty, 1997). The Halogenated Solvents Industry estimates that in 1986 PCE production was 560,000 fifty-five gallon drums and TCE production was 260,000 drums (Pankow and Cherry 1996). A more recent evaluation of PCE and TCE uses shows that, besides their use as chemical intermediates, dry cleaning and metal degreasing top the lists (Table 2 below).

Table 2. Uses of the Primary Chlorinated Solvents

Perchloroethylene (1998)		**Trichloroethylene (1999)**	
Chemical intermediate	50%	Chemical intermediate	54%
Dry cleaning/textile processing	25%	Metal cleaning/degreasing	42%
Automotive aerosols	10%	Miscellaneous	4%
Metal cleaning/degreasing	10%		
Miscellaneous	5%		

Source: Halogenated Solvents Industry Alliance

Chlorinated ethenes have become ubiquitous in the environment through their wide spread use. Trichloroethene (TCE) is first on the list of most frequently detected groundwater contaminants at hazardous waste sites followed by PCE at number three. TCE is a daughter product of PCE, which further degrades to the two prevalent dichloroethene (DCE) isomers at numbers 13 and 17 on the list, which in turn degrade to vinyl chloride (VC) at number 18 (NRC, 1994). These chlorinated aliphatic compounds, in addition to trichloroethane (TCA), are among the most commonly observed contaminants found in shallow ground-water systems (Chapelle, 1994). In fact, 10 of the 25 most frequently detected groundwater contaminants at hazardous waste sites are chlorinated hydrocarbons (NRC, 1994).

There are many environmental regulations that now control the use and disposal of chlorinated solvents. The water quality standards used to determine MCLs are contained in the Safe Drinking Water Act. The EPA has established national drinking water regulations setting MCLs for organic chemicals such as TCE and its daughter products (Table 3 below). A Maximum Contaminant Level Goal (MCLG) of zero does not imply that harm will occur at a level above zero, but rather that zero is an aspirational goal. Various states may also have drinking water regulations that apply to these chemicals.

The Clean Water Act (CWA) is the primary document that drives the federal government's regulation of water pollution in the United States. The United States Environmental Protection Agency (EPA), in partnership with other federal, state, and local agencies, administers all programs that are generated from this act (Sullivan, 2001).

Table 3. EPA National Primary Drinking Water Maximum Contaminant Levels (Adapted from EPA Drinking Water Standards, 2002 and CFR Ch. 1 Part 141.12, 2000)

Organic Chemical	**MCLG (mg/L)**	**MCL (mg/L)**	**Potential Health Effects**
Tetrachloroethylene (PCE)	zero	0.005	Liver problems; increased risk of cancer
Trichloroethylene (TCE)	zero	0.005	Liver problems; increased risk of cancer
1,1-Dichloroethylene (1,1-DCE)	0.007	0.007	Liver problems
cis-1,2-Dichloroethylene (cis-DCE)*	0.070	0.070	Liver problems
trans-1,2-Dichloroethylene (trans-DCE)	0.100	0.100	Liver problems
Vinyl chloride (VC)	zero	0.002	Increased risk of cancer

* Primary isomer of DCE during reductive dechlorination

PCE is also one of nearly 200 substances listed as hazardous air pollutants and regulated under the federal Clean Air Act.

The reportable quantity (RQ) for releases of PCE and TCE under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund) is 100 pounds. Releases in excess of this amount must be reported to the National Response Center, the local emergency planning commission, and the state emergency response commission. Some states have lower thresholds that trigger their notification requirements. In addition, PCE and TCE are two of several hundred chemicals subject to material safety data sheet (MSDS), inventory, and release reporting under the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986).

Current Treatment Technologies

The EPA compiled many of the treatment technologies available in the Treatment Technologies for Site Cleanup: Annual Status Report (2001). These technologies can be broken down into source control treatment technologies, in situ groundwater treatment technologies, and in situ groundwater containment technologies. The main interest here is in the two treatment technologies.

Source control treatment technologies include methods such as soil vapor extraction, soil solidification/stabilization, and vitrification. In Situ Groundwater Treatment Technologies include air sparging and permeable reactive barriers among others.

The treatment methods mentioned have many drawbacks in their use such as high expense, increased risk to surrounding environment, small effective scale, small range in types of contaminants able to be treated, and the inability to meet maximum contaminant levels. With the apparent expense and ineffectiveness of traditional pump-and-treat remediation methods that have been employed over the last 30 years, the cost savings and reduced risk of natural attenuation make it worthy of development for remediation of halogenated organics in ground water. Now it is thought that constructed treatment wetlands could be combined with the pumping technology of the traditional pump-and-treat systems to gain the treatment benefits of natural attenuation.

Wetlands

Wetlands possess intrinsic processes that can naturally eliminate chemicals from the groundwater such as phytoremediation and biodegradation. Phytoremediation is a process that uses plants to remove, transfer, stabilize, or destroy contaminants in soil, sediment, and groundwater. The mechanisms of phytoremediation include enhanced rhizosphere biodegradation, phytoextraction, phytodegradation, and phytostabilization. Plants can be used in site remediation, both through the mineralization of toxic organic compounds and through the accumulation and concentration of heavy metals and other inorganic compounds from soil into aboveground shoots (EPA Treatment Technologies for Site Cleanup, 2001). Figure 1, below, summarizes plant processes that play a part in phytoremediation.

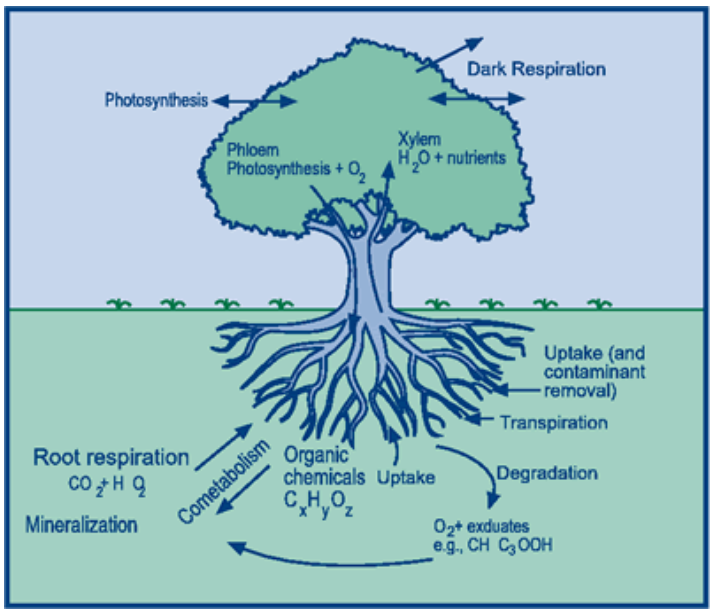


Figure 1. Processes in Phytoremediation (EPA Treatment Technologies for Site Cleanup, 2001)

In the past bioremediation was done by taking the contaminant out of the ground and treating it in an energy intensive process or by augmenting the subsurface environment to promote biodegradation. Ex situ bioremediation includes slurry-phase bioremediation, and solid-phase bioremediation. Land farming, bio-piles, and composting are examples of solid-phase bioremediation. In situ techniques stimulate and create a favorable environment for microorganisms to grow and use contaminants as an energy source. Usually the provision of oxygen, nutrients, and moisture, and controlling the temperature and pH is done for in situ techniques. Microorganisms that are able to degrade certain contaminants may be added to enhance the removal efficiency. Bioventing uses wells to circulate air through the ground to stimulate microbial growth and possibly to remove volatile contaminants (EPA Treatment Technologies for Site Cleanup, 2001).

Just as monitored natural attenuation of contaminants has been observed in the field, so too have the beneficial affects of natural wetlands on waterborne contaminants. Natural attenuation of chlorinated compounds in an aquifer is often slow, which leads to long contaminant plumes that can reach discharge points such as natural wetlands (Lorah and Olsen, 1999).

The unique properties of wetland soils have been shown to degrade manmade chemical contaminants to innocuous products and moreover, these capabilities can be exploited to facilitate engineered bioremediation. Recent studies have detailed the effect that a freshwater tidal wetland had on an aquifer contaminated by PCE at Aberdeen Proving Ground in Maryland (Lorah and Olsen, 1999).

Microbial reductive dehalogenation results in the sequential reduction of PCE to TCE and TCE to DCE where the primary isomer is *cis*-1,2-DCE (trans-1,2-DCE and 1,1-DCE have also been observed in low concentrations) (Song et al., 2002). DCE can further be reduced to VC, and finally VC to ethane (Figure 2 below). The anaerobic biotransformation of these chemical species has been observed in continuous-flow fixed film reactors, in soil, sediment, aquifer microcosms, and to some extent in pure cultures (Freedman and Gossett, 1989).

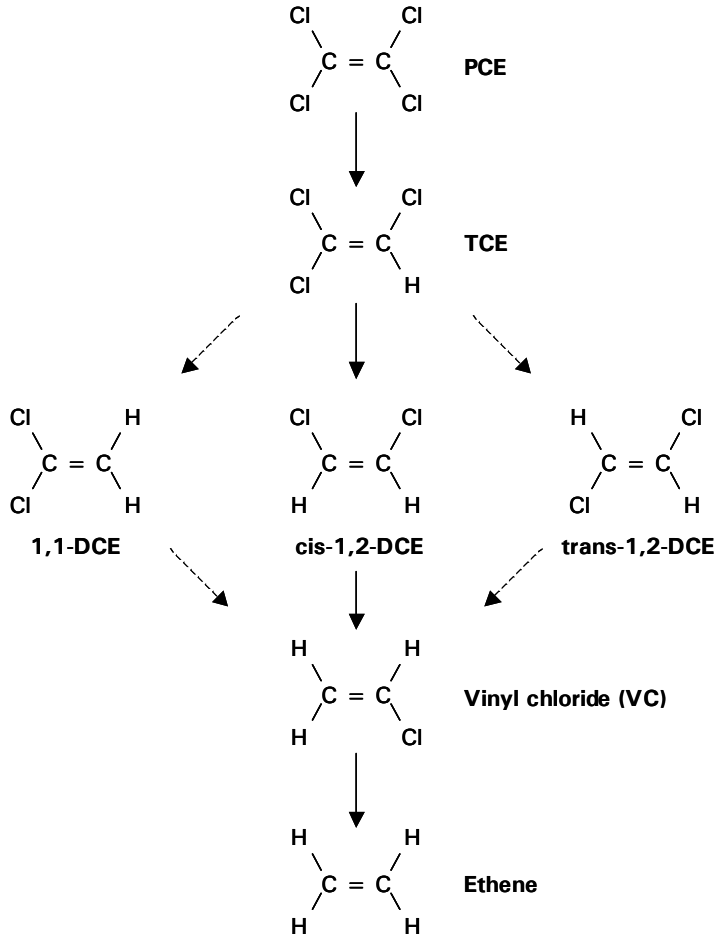


Figure 2. Degradation Pathway for PCE (Adapted from Hageman et al., 2001) Typically seen under anaerobic conditions supporting reductive dechlorination.

These reductive dechlorinating processes have been shown to exist in the reduced anoxic sediments of wetlands. The proof of this degradation and characterization of these redox reactions are shown best by a weight of evidence analysis as described by Wiedemeier et al. (1997). The understanding of the dominant redox reactions is essential for assessing the efficiency of natural attenuation in groundwater (Sewell, 1998). Three things must be demonstrated: first, is a disappearance of electron acceptors along the flow path; second, is the appearance of end products; and third, is to verify the redox zonation. The redox zonation can be determined with direct electro-potential measurements such as Eh. Redox zonation can be more accurately determined with hydrogen concentration measurements. Molecular hydrogen concentrations in groundwater vary depending on the dominant Terminal Electron Accepting Process (TEAP) in that area. This is due to the different efficiencies microbes have to use hydrogen as an electron donor progressing from anoxic methanogenic conditions with the highest hydrogen content to nitrate reduction to sulfate reduction to iron reduction and finally to oxic oxygen reduction.

The purpose of this study is to determine if contaminant degradation to innocuous products is occurring in the wetland. Water samples and water quality measurements will be taken to help determine the predominant TEAP in each of the three wetland strata. To accomplish this, first the concentrations of the contaminants and their degradation products must be determined for each layer. Second, other parameters will be examined to verify the performance of the wetland. Dissolved oxygen concentrations will help identify which areas of the wetland are aerobic and anaerobic. Oxidation Reduction Potential (ORP) measurements can help determine where the strongest reducing conditions are. Conductivity measurements can verify that the water is coming from the

same source and that the water contains minimal suspended solids. The temperature can indicate possible seasonal effects on microbial efficiencies. And lastly, pH can be used to characterize the behavior of many compounds in the wetland and to determine how hospitable the environment is for the microbes. A third parameter, hydrogen concentration, should be measured in the future to further delineate the TEAP.

Research Objectives

The goal of this thesis is to follow up research done a year ago determining the level of chlorinated solvent removal in each of the constructed wetland strata. The previously developed methodology will be used in sampling the same constructed wetland cell number one at WPAFB. The concentrations of PCE and its daughter products will be determined via gas chromatography. Additional data gathered with a water monitoring sonde will aid in characterizing the mechanisms present in the degradation of the chlorinated solvent.

Specific Research Questions

1. Do the concentrations of PCE and its daughter products in three layers of a constructed wetland give evidence of biodegradation?

2. Can pH, conductivity, temperature, oxidation-reduction potential, and dissolved oxygen be measured in a constructed wetland?

3. Do measurements of oxidation-reduction potential and dissolved oxygen indicate that conditions exist for the dechlorination of PCE and subsequent byproducts?

Scope/Limitations

This thesis effort will use the established sampling and analytical methodology to determine the level of contaminants in the wetland. This effort was limited in that only one complete sampling pass through the wetland was possible due to cold weather and equipment difficulties. The previous sampling effort by Opperman in 2001 used the average of three passes for each piezometer that were taken over four weeks. Also, time constraints are imposed by the amount of time it takes to sample and analyze the data without allowing the samples to degrade in storage.

Additionally, the information gathered from the sampling horizons are limited by the piezometer placement and their ability to sample from a thin horizontal layer. First, sampling from piezometers placed in just three strata reduces the resolution needed to characterize what horizontal plane the reactions are occurring. Second, the relatively large screened area of the piezometer (3.5 inches vertically) captures samples that could be influenced by different processes in thin horizontal layers, especially for fast reactions.

This study will also devise, test, and execute a methodology for gathering five additional water-quality parameters of the wetland with a water monitoring sonde. The small number of wells that were installed in the wetland limits this data collection and analysis. There were 6 well nests (18 wells, 3 in each nest) to take sonde readings of the three layers as compared to the 66 piezometer nests. The number of wells could be

increased in the future to show additional trends and to facilitate better comparison of these parameters to contaminant concentrations.

II. Literature Review

Since their recognition as hazardous, difficult to remediate chemicals over the last 30 years, chlorinated solvents such as PCE and TCE have been remediated from groundwater by several methods. The most popular method has been traditional pump-and-treat operations where the contaminated water is pumped to the surface and treated in a variety of ways including air stripping, decomposition beds, concentration and treatment as a hazardous waste, and thermal destruction. These pump-and-treat technologies are extremely expensive to install and operate and most only transfer the contaminant to a different phase for further processing (NRC, 1994).

Natural attenuation of chlorinated solvents at many contaminated sites has shown that a risk management approach such as monitored natural attenuation can be an alternative or cooperative approach to traditional remediation. The United States Environmental Protection Agency (USEPA) has defined natural attenuation as naturally occurring in-situ processes that reduce the mass, toxicity, mobility, volume, or concentration of contaminants. Attenuation processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants (USEPA, 1997). The economic control and destruction of these contaminants in a timely manner is most desired and has spurred research in biodegradation, most recently, constructed wetlands.

Some 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 hydrogeologic 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).

Chemical reactions caused by microorganisms can directly or indirectly decrease the concentrations of contaminants (NRC, 2000) and are often the basis for natural attenuation approaches to contaminant remediation. The transfer of electrons, mostly through redox reactions, allows microorganisms to generate energy for growth, maintenance, and reproduction (Chapelle, 2001). Characterization of the dominant redox reactions can provide valuable insight into the dynamics of the system.

Microbial Growth

Chemical reactions to produce cellular components are made possible by enzymes that bring the chemicals together in a specific way so that they can react quickly. These reactions require energy in the form of Adenosine Triphosphate (ATP). ATP is generated by catalyzing redox reactions where electrons are transferred from an electron-donor substrate to an electron-acceptor substrate. The movement of electrons through a cell is accomplished by electron carriers for the main purpose of generating ATP through

respiration. Microorganisms have become specialized at using certain electron-donor and acceptor pairs that generate specific energy yields (NRC, 2000).

Electron donors are readily available in the environment as both inorganic and organic chemicals. Electron acceptors are more limited and define the redox process they are involved in. Common electron acceptors in the order of their preferred use are O_2, NO_3^-, Mn^{2+}, Fe(III), SO_4^{2-}, and CO_2.

The electron flow through a microorganism starts with an electron donor as seen below in Figure 3. The electron carrier shown here as reduced nicotinamide adenine dinucleotide ($NADH_2$) captures the electron and transports it to where it can be used for respiration, cell synthesis, or maintenance. Respiration generates energy through redox reactions which is captured in high-energy phosphate bonds combining adenosine diphosphate (ADP) and inorganic phosphorous into adenosine triphosphate (ATP). The last molecule to receive the electrons is called the *terminal electron acceptor*.

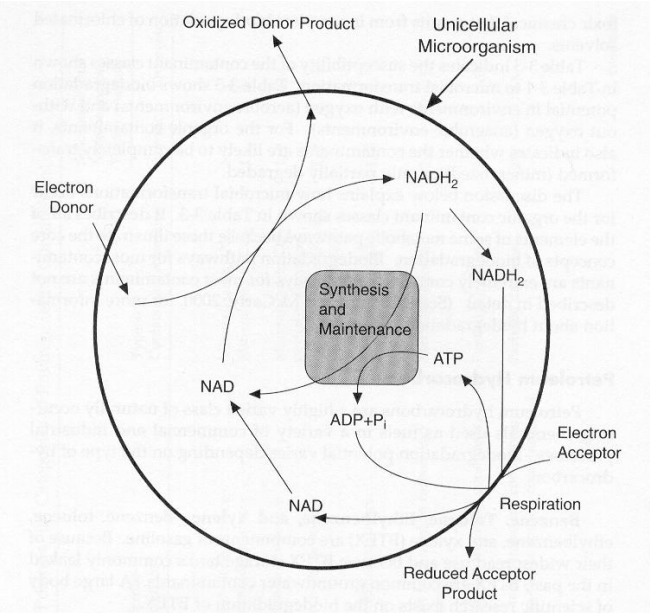


Figure 3. Flow of Electrons Through a Microorganism for Energy

Microbial growth in groundwater makes natural attenuation of contaminants possible. Much research has been done on these microbial processes. Current understanding of these biotransformations of ethenes is summarized below in Table 4.

Table 4. Known Biotransformation Reactions for Ethenes in Groundwater

	Primary Substrate			Co-metabolism	
	Aerobic Donor	Anaerobic Donor	Anaerobic Acceptor	Aerobic	Anaerobic
Tetrachloroethene			X		X
Trichloroethene			X	X	X
Cis-1,2-Dichloroethene*	?	X	X	X	X
Trans-1,2-Dichloroethene	?	X		X	X
1,1-Dichloroethene	?			X	X
Vinyl Chloride	X	X	X	X	X

* Primary TCE dechlorinated product
Note: Biotransformation reactions are indicated with an X; ? indicates uncertainty over whether these reactions occur; a blank space indicates that the reaction is not known to occur. (Adapted from NRC, 2000)

Reductive Dechlorination

This flow of electrons and gain of useful energy for the microbes drives the process of reductive dechlorination shown below in Figure 4. Microbes do exist (*D. ethanogenes*) that can fully dechlorinate chlorinated ethenes, but often two or more populations are required for the sequential dechlorination of PCE to ethene (Flynn et al., 2000). At each step the chlorine atom is cleaved off as a chloride ion (Cl^-) in favor of a hydrogen ion (H^+) and two donated electrons ($2e^-$).

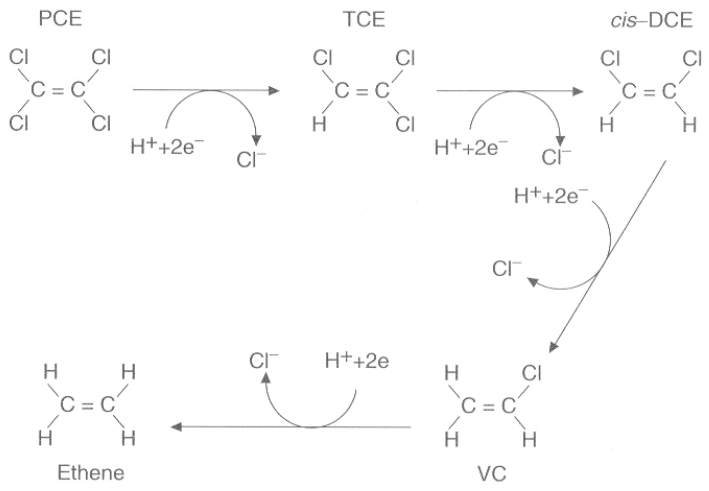


Figure 4. Reductive Dechlorination of PCE (NRC, 2000)

The process of dechlorination has been demonstrated in lab microcosms and column experiments under extremely reducing conditions yielding the innocuous products ethane (which can be converted to methane), carbon dioxide, and hydrogen chloride (Flynn et al., 2000). Unfortunately, theses reactions often do not proceed to completion leaving the more harmful degradation products. The reduction process is initiated by microorganisms that hydrolyze organic material producing organic monomers (sugars, amino acids, and organic acids). The entire reduction process is outlined in Figure 5 below.

Next, fermentation microbes use the organic monomers as the terminal electron acceptor to break down the complex organic sugars forming low-molecular-weight acids, alcohols, and CO_2. Two examples of fermentation reactions are demonstrated in equations 1 and 2 below.

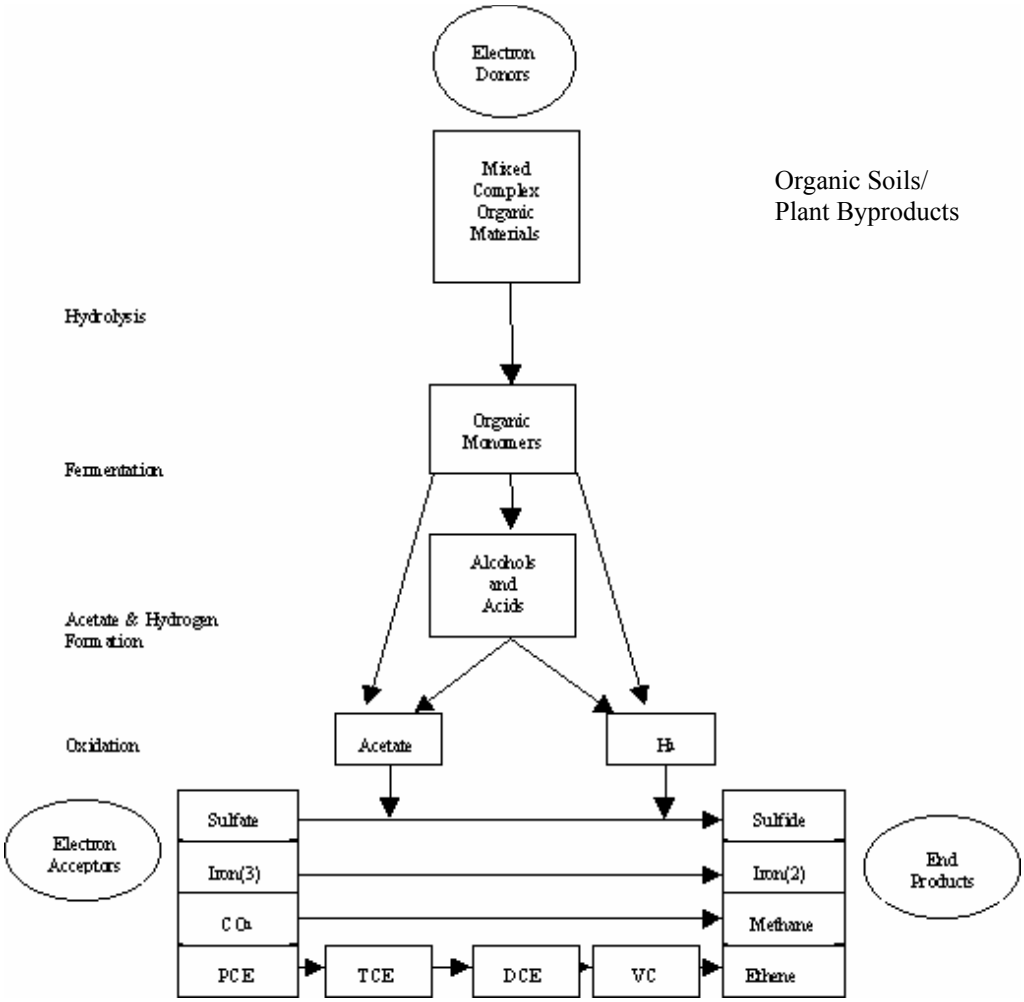


Figure 5. Process Leading to the Reductive Dechlorination of PCE. Process starts with organic matter donating electrons. Microorganisms that can use chlorinated compounds as electron acceptors in halorespiration (bottom row) compete for the electrons in the acetate and hydrogen intermediates with microorganisms that can use sulfate, iron (III), and CO_2 as electron acceptors (McCarty, 1997).

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OCOOH \quad (1)$$
(lactic acid)

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \quad (2)$$
(ethanol)

The fermentation process is thought to be important in breaking down high-molecular-weight hydrocarbons into low-molecular-weight organic compounds in solution making them bioavailable for microbes to use as an energy source (Chapelle, 2001). With the fermented low-molecular-weight organic compounds available to microorganisms, other microbial populations initiate a series of reduction reactions. One microbial population uses the alcohols and organic acids as electron donors to produce acetate and molecular hydrogen. Next, sulfate-reducing microorganisms use the acetate and hydrogen as electron donors for their metabolic processes. When sulfate concentrations are reduced low enough, iron-reducing microorganisms compete with the sulfate-reducers for acetate and hydrogen electrons. Similarly, when iron concentrations are diminished, methanogens compete with the sulfate- and iron-reducers for acetate and hydrogen electrons. Finally, when sulfate and iron are left in very low concentrations, halorespirators successfully compete for acetate and hydrogen electrons to be used in metabolic processes. Conditions will now support the complete degradation of chlorinated ethenes; in particular, the first step in PCE reduction is possible.

Within this series of reactions there are known side reactions that affect the dehalogenation of chemicals. A syntrophic relationship between sulfate-reducing and dehalorespiring bacteria has been demonstrated to actually enhance the performance of the dehalorespirers when there are low concentrations of sulfate or no sulfate present. This is accomplished through interspecies hydrogen transfer where the sulfate reducer gains energy by fermenting lactate (Equation 3 below) and using the dehalogenating bacterium as a biological electron acceptor. Sulphate-reducing bacteria fortuitously

stimulate the dehalogenation processes with the release of hydrogen subsequently used by dehalorespiring bacteria (Drzyzga, 2001).

Sulfate-reducing bacteria ferment lactate to acetate in the absence of sulfate:

$$CH_3\text{-}COH\text{-}COOH + H_2O \rightarrow CH_3\text{-}COOH + CO_2 + H_2 \qquad (3)$$

The extreme reducing conditions required to remove the first chlorine atom from PCE is crucial. The removal of the first chlorine atom from PCE has only been demonstrated when PCE is used as a primary substrate accepting an electron under extremely reducing conditions or when it is co-metabolized under anaerobic methane reducing conditions.

The process of reductive dechlorination is limited in pristine aquifers where there is limited organic material available to donate electrons. Also, pristine aquifers are often aerobic because the addition of oxygen from the percolating recharge water usually exceeds the influx of organic material. Pristine water table aquifers are then more carbon-limited than oxygen-limited (Chapelle, 2001). As demonstrated above, the contaminant must compete for the organic electron donors with the more energetic electron acceptors (Yang and McCarty, 1998). Fortunately, wetlands possess an abundance of natural organic matter (NOM) that can rapidly reduce any sulfate, manganese (IV), iron (III), and carbon dioxide that is present in the contaminated aquifer. In effect the NOM reverses the aerobic conditions found in the aquifer as the oxygen is consumed to deficit levels without resupply and an excess of organic electron donors are available for anaerobic reactions. In the case of constructed remediation wetlands where

the inflow of contaminated water is controlled, design of highly organic sediments and injection of organic matter can ensure reductive dechlorination occurs in the earliest stage of wetland flow. It is important that the dissolved oxygen in the aquifer water is consumed quickly, allowing highly reduced conditions to prevail.

The specific order of this reduction process is driven by the efficiency of different microorganisms to use electron donors at decreasing concentrations. The characteristic potential standard free energy developed from each of the redox reactions results in competitive exclusion of microbes that cannot efficiently function in the prevalent redox conditions (Table 5 below). The universal electron donor, molecular hydrogen, is preferred by each of the above microorganism mediated reduction reactions. Hydrogen concentrations in ground water can subsequently be used to characterize the reducing conditions (redox zonation) in the soil water, indicating which biological process is dominating (Sewell, 1998; Yang and McCarty, 1998; Chapelle, 2001).

Table 5. Potential Energy Yield and Steady State Hydrogen Concentrations Characteristic of Different Anaerobic Oxidation Processes (Chapelle, 2001)

Oxidation/Reduction Reaction	Potential Standard-Free Energy (kJ per H_2)	Characteristic Hydrogen Concentration (nM)
$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$	224	0.01–0.05
$MnO_2 + H_2 \rightarrow Mn(OH)_2$	163	0.1–0.3
$2Fe(OH)_3 \rightarrow 2Fe(OH)_2 + 2H_2O$	50	0.2–0.8
$SO_4^{2-} + 4H_2 + H+ \rightarrow HS^- + 4H_2O$	38	1.0–4.0
$HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O$	34	5.0–15.0

Along with the H_2 concentration, there are two other indicators of what Terminal Electron Acceptor Process (TEAP) is dominating. First, is the transformation of electron acceptors (O_2, NO^{3-}, and SO_4^{2-}) to their reduced form and second is the production of reduced products (NO^{2-}, Fe(II), H_2S, and CH_4) seen in Table 5 above. The measurement of these two concentrations in combination with the hydrogen concentration allows the use of the *weight of evidence* approach to determine the dominating TEAP (Wiedemeier, 1997; Chapelle, 2001). One caution is that some chemical components such as CH4 and H2S are stable under anaerobic conditions; therefore increasing concentrations along a flow path will confirm the dominant TEAP (Chapelle, 2001). This flow path determination is difficult in a heterogeneous aquifer but should be made easier in a carefully constructed upward flow wetland.

There are factors that make flow path determination difficult in a constructed wetland. In the case of an upward flow constructed wetland, the vertical zonation distance can be small when conditions are ideal for the transformation reactions to occur quickly. These thin vertical zones limit the ability of sampling piezometers to capture the indicators of reactions that are dominating the strata of interest. Also, sample points can exist within microenvironments containing different levels of analytes than the majority of the strata. Samples from these areas will miss the more pervasive conditions present.

Redox Potential

The redox potential is a measure of a system's tendency to donate or accept electrons. The traditional method for determining redox potential is with a standard

hydrogen electrode. This method is an equilibrium approach using two half-cells connected by a salt bridge and a conductive wire diagrammed in Figure 6 below. In cell two (standard hydrogen electrode), hydrogen gas is pumped over a catalytic surface allowing the hydrogen species (H_2, H^+, and H_2O) to maintain equilibrium and generate a standard free energy. The potential difference (Eh) between the standard solution (cell two) and the solution being measured (cell one) is measured as voltage on an arbitrary scale.

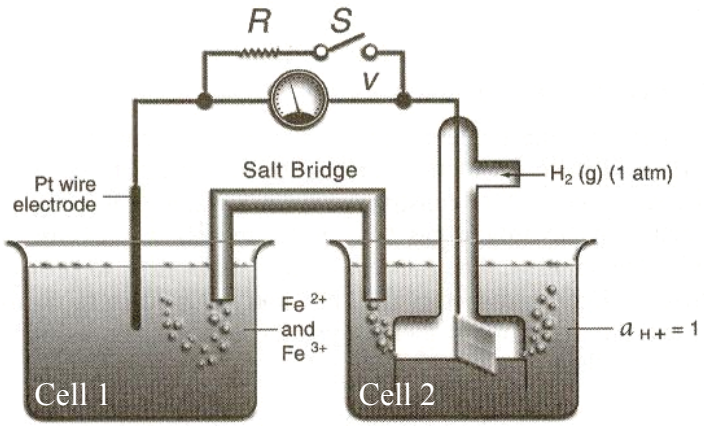


Figure 6. Standard Hydrogen Electrode Measuring Equilibrium Redox Potential (Chapelle, 2001)

In this example an iron solution is being measured. The reaction equation for cell one is:

$$Fe^{3+} + \tfrac{1}{2}H_2 \longleftrightarrow Fe^{2+} + H^+$$

The Nernst equation is used to determine *Eh* from measured species concentrations:

$$Eh = E^0 + \frac{2.303RT}{nF}\log\frac{nFe^{3+}}{nFe^{2+}}$$

The redox potential is often expressed as *pe* analogous to pH:

$$pe = \frac{F}{2.303RT} \cdot Eh$$

Microorganisms require particular electrokinetic conditions to utilize electron transfer for energy. The microbes in turn affect those conditions and dynamically change the conditions in their own sphere of influence. The dynamics of a natural living system dictate that there is no equilibrium in the small environments that microbes live in and have influence over; therefore, there can be no unique description of redox conditions on a macro scale. As a result, measured Eh is a poor indicator of redox conditions. Eh is not a quantitative indicator of redox conditions; redox indicators are needed that can be measured to determine ambient microbial processes. An experiment carried out by Lindberg and Runnels (1984) to evaluate the effectiveness of Eh measurements to determine redox potential in groundwater demonstrated that more information is required to determine the processes that are dominating the given situation. Figure 7 below compares field measurements and computed redox potentials showing that the field measurements do not accurately represent the prevalent redox conditions.

This research shows that redox probes alone cannot accurately characterize the prevailing redox potential in a dynamic (non-equilibrium) system. A broad approach should be taken using weight-of-evidence from three indicators to determine the dominant TEAP. The three indicators that help prove that degradation of chlorinated ethenes are being degraded as mention previously are the consumption of electron acceptors, the production of reduced products, and H_2 concentration.

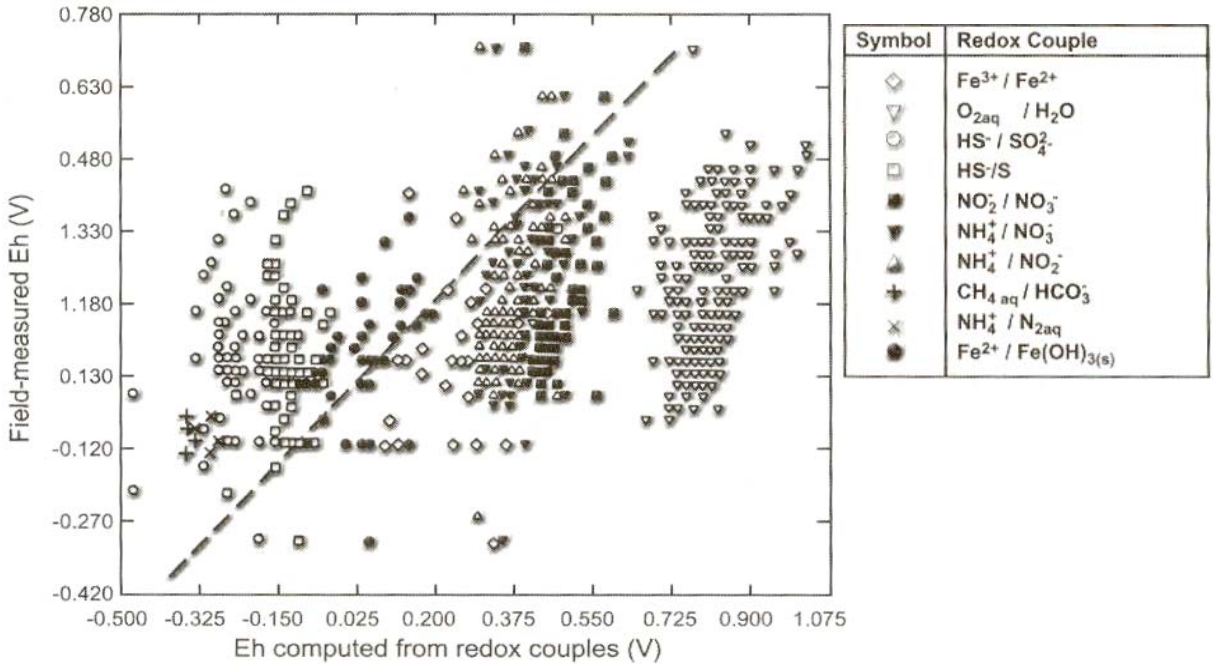


Figure 7. Comparison of Field Measured and Computed Redox Potentials. The dotted line represents the equality relation that would be expected if the measurements were equal. (Lindberg and Runnels, 1984)

Methanogenesis

Under reducing conditions, microbes called methanogens use CO_2 as an electron acceptor for the production of methane. The simplified formula:

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O \quad (3)$$

More applicable to wetland environments is the use of a low-mol-wt organic compound that has been produced by fermentation (equations 1 and 2):

$$CH_3COO + 4H_2 \rightarrow 2\,CH_4 + 2H_2O \quad (4)$$

This reaction requires extremely low redox potential below -200mV. And as mentioned before, all other terminal electron acceptors (O_2, NO_3, SO_4^{2-}) must have

been reduced previously. Methanogenic rates vary and have seasonal patterns based on the preference for water temperatures to be above 25º C (Agnihotri et al., 1999). Freshwater wetlands tend to have a higher rate of methane production than saline wetlands, due to lower sulfate competition for the oxidizable substrate (Chapelle, 2001).

One serious issue associated with the use of anaerobic reductive dechlorination of PCE is that the process does not always continue dechlorinating to ethene. This can lead to accumulation of DCE and VC in groundwater systems if the reducing potential is not high enough or when the reducing potential decreases as the contaminant moves with the groundwater. This is of great concern because both are hazardous compounds and VC is a known human carcinogen (NRC, 1994). This incomplete dechlorination is commonly observed at field sites where reductive dechlorination of TCE is taking place (McCarty, 1997).

As mentioned before, cis-DCE is the predominant DCE isomer produced by anaerobic reductive dechlorination of PCE and TCE. In recent field and microcosm studies, it has been observed that as the daughter products (cis-DCE and VC) migrate to more aerobic conditions they disappear (Edwards and Cox, 1997; Bradley and Chapelle, 1998; Davis and Carpenter, 1990). This disappearance can be explained by several mechanisms. First, anaerobically generated methane (from methanogenesis) can travel up the wetland with the daughter products and be used as a primary substrate for cometabolism of VC and cis-DCE under aerobic conditions. VC and cis-DCE are preferentially consumed by methanotrophs (Anderson and McCarty, 1997). Second, reductive dechlorination of VC in the anaerobic layer produces ethane that can be used as primary substrates for cometabolism of cis-DCE (Koziollek and Bryniok, 1999) and VC

(Koziollek and Bryniok, 1999; Verce et al., 2001) under aerobic conditions. Third, VC can be degraded by aerobes that use it as a growth substrate (Hartmans and de Bont, 1992; Verse et al., 2000; Verse et al., 2001). The rapid degradation of VC under aerobic conditions without an adaptation period or the addition of nutrients was first demonstrated by Davis and Carpenter (1990). Each of these mechanisms for TCE daughter product destruction is provided in an upward flow treatment wetland.

The complete degradation of PCE and TCE to innocuous ethene is difficult to prove. The extent of reductive dechlorination cannot be conclusively determined by measuring the concentration of ethene alone. In a recent field study, lactate was added to a contaminant source area accelerating the natural process of reductive dechlorination that was already occurring. Fluctuations in the concentrations of ethenes during the experiment made it impossible to use ethene concentration data to determine the extent of dechlorination. Carbon isotope data, however, clearly show that all of the TCE that was removed was fully dechlorinated to ethene (Song et al., 2002). This shows that the complete reduction of TCE is possible if there is an adequate supply of active electron acceptors and the retention time is long enough. Additional experiments using carbon isotopes to track carbon transformations in systems similar to constructed wetlands will lend credibility to their ability to completely degrade chlorinated solvents.

Contrary to previous thought, there is increasing evidence that cis-DCE can be aerobically degraded as a sole source of carbon and energy (Bradley, 2000) in addition to its degradation by cometabolism. It is known that microorganisms aerobically grown on VC as a primary substrate can cometabolize cis-DCE, and to a lesser extent, trans-DCE and 1,1-DCE. Even though microorganisms grown on VC can cometabolize DCE, when

VC and cis-DCE are present together, cis-DCE decreases the rate of VC use. This could result in the accumulation of VC in a groundwater system. In addition to the aerobic use of VC as a primary substrate, VC can be cometabolized by microorganisms using an alkene monooxygenase (Verce, M. F. et al., 2000; Freedman and Danko, 2001).

The value of sequential anaerobic and aerobic conditions in treatment scenarios has been demonstrated by the inability of VC-grown organisms to degrade TCE (Bradley and Chapelle, 1996, 1997, and 1998). It has also been shown that high levels of ethane can inhibit methanogenesis. The natural zonation of an upward flow treatment wetland provides the necessary conditions for each stage of the dechlorination process.

When designing natural attenuation treatment systems it is important to also consider any natural sources that might contribute to the presence of chemicals that are being treated. Until recently, it was thought that the presence of VC in the environment resulted from only anthropogenic sources such as the manufacture of polyvinyl chloride (PVC) or from the degradation of PCE and TCE. Thus, an indigenous biological consortium that could efficiently degrade these chemicals for energy was considered unlikely. Now, evidence points to the fact that VC can be produced during soil processes, sometimes exceeding anthropogenic emissions (Keppler et al., 2002). One abiotic source of destruction is initiated by Fe(III) in the presence of chloride and organic matter (Keppler et al., 2002).

Some recent research has shown that humic-metal complexes may act as electron transport mediators in redox reactions in natural environments. The use of Ni and Cu in addition to DOC showed a >95% reduction of TCE in less than six hours (O'Loughlin and Burris, 1999). Further research suggests that small reductions in TCE concentrations

in natural systems without Ni or Cu additions are the result of native DOC-metal complexes or other mediators (O'Loughlin et al., 1999).

III. Methodology

Introduction

Interest in natural remediation processes in wetlands was sparked by the discovery that there were biochemical processes occurring in natural wetlands reducing contaminant concentrations of manmade water inflows (Lorah and Olsen, 1999). Past research has been limited to examining natural wetlands, modeling processes, and conducting laboratory column experiments with wetland sediments. This thesis is a second in a series of efforts to sample and monitor a constructed wetland specifically designed to treat water pumped from a contaminated groundwater aquifer.

This research effort follows up research done by Opperman in 2003 studying a constructed upward-flow treatment wetland at WPAFB, Ohio. The methodology of determining the contaminant and daughter product concentrations in this study follows the methodology used last year very closely allowing results comparisons. In this way the maturation of the wetland can be tracked over time in regard to its ability to degrade chlorinated solvent contaminants in ground water pumped from an aquifer. In addition, other parameters such as dissolved oxygen, oxidation-reduction potential, pH, temperature, and conductivity were investigated with the installation of a second set of monitoring wells.

Last year's research efforts running parallel with Oppermann included determining the levels of several different organic acids and inorganic ions throughout the wetland (Bugg, 2002) as well as determining the flow regime throughout the entire

wetland (Entingh, 2002). This year's efforts in cell 1, in addition to this thesis, included Kovacic (2003) again researching the organic acids and Blalock (2003) researching the flow regime in cell 2 which was subsequently shut down do to the compromise of the liner.

Experimental Constructed Wetland Cells

Two experimental wetland cells were built and completed in August of 2000 in Area A at WPAFB to study the biochemical transformation of chlorinated solvents to their innocuous daughter products. The wetlands were constructed from wetland soil relocated from a drained wetland area on WPAFB and positioned over a contaminated aquifer that provides a source of water to be pumped into the wetlands. The wetlands were designed as upward flow treatment wetlands approximately 120 feet long by 60 feet wide and 72 inches deep from the soil surface to the liner.

Three six-inch parallel-perforated PVC supply lines run along the bottom of the cell encased in a nine-inch bed of gravel. A geo-membrane isolates the system from the surrounding birmed soil. The nine-inch layer of crushed gravel allows an evenly distributed water flow into the first layer of wetland soil. Fifty-four inches of wetland soil was then placed and lightly compacted on top of the gravel layer. The bottom 18-inch layer of wetland soil was amended with 10% wood chips (compost).

An exit weir was constructed at the opposite end of the wetland from the water inlet pipe. The weir level could be adjusted to control the depth of water on the surface. The water exiting the wetland through the weir was then directed to the local sanitary

sewer. A three dimensional drawing of the wetland cell can be seen in Figure 8 depicting the flow of water. In reality, the walls of the wetland cell are angled out at a 1:1 slope to avoid collapse.

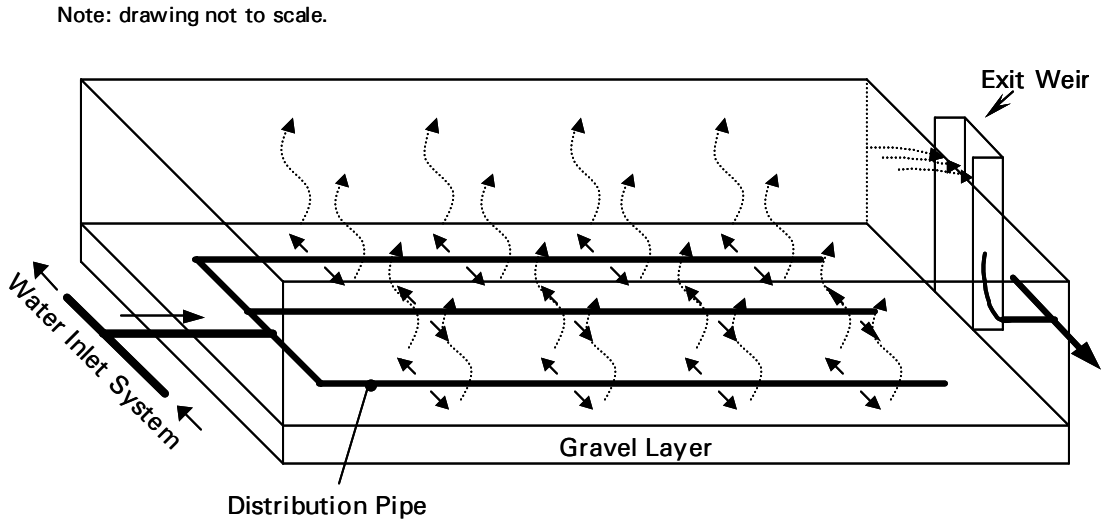


Figure 8. Water Flow Through Constructed Wetland (Enting, 2002)

For sampling purposes the wetland was divided into three horizontal layers, or strata, with the bottom layer being amended with 10% wood chips by volume. The wood chips were added to provide an initial source of organic carbon for the naturally occurring microbes to use for energy yielding reactions (Weidemeier, 1997, Chapelle, 2001). Typical wetland vegetation was planted on the surface in separate plots. Speciallized plant root system tissues transport air (oxygen) to the rhizospere enabling aerobic reactions to occur in smaller microenvironments (Mitsch and Gosselink, 2000). The original assumption made in this effort was that the roots of the plants would only penetrate down to the middle layer supplying oxygen to the root zone. Greenhouse experiments conducted by Dr. Amon at Wright State University have shown that the

roots will penetrate deeper than five feet. Although oxygen is likely to be transported to the lower layer by these deep root systems, it is not known how much oxygen is being transported and how the oxygen affects the microbial degradation occurring in the generally anaerobic environment. A cross-sectional diagram of the first cell depicting the three soil layers and plant roots is shown in Figure 9 below.

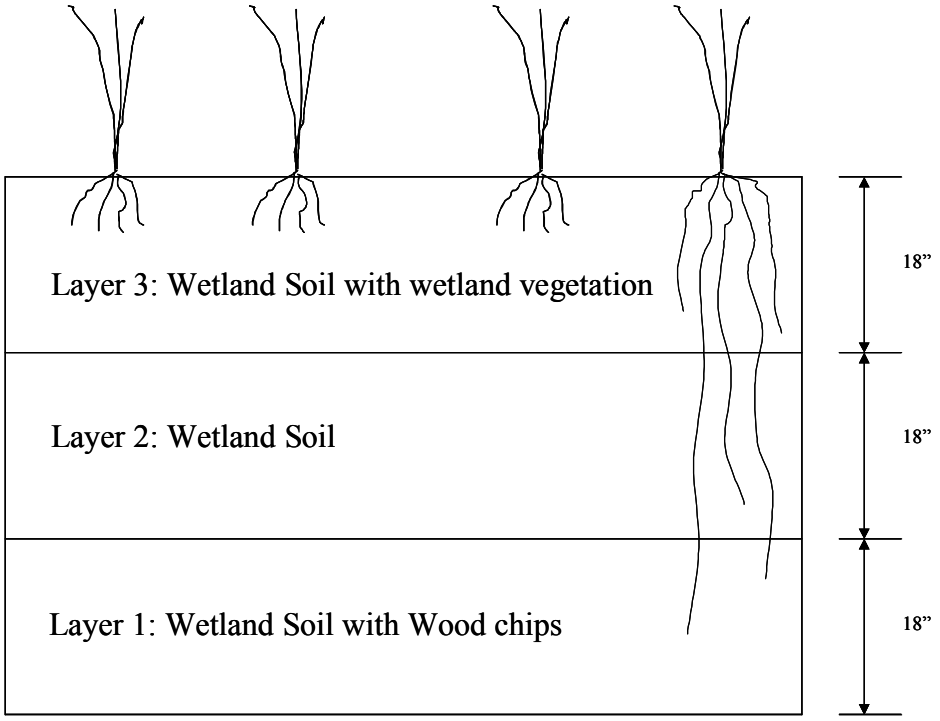


Figure 9. Constructed Wetland Cross Section, Cell 1
(Updated from Opperman, 02)

It was determined that 66 piezometers per layer installed in a regular grid would give adequate coverage for water sampling, water flow analysis, and soil property measurements. The piezometers were installed in the summer of 2001. In order to attain other water parameters with a water monitoring sonde, an additional six nests of wells

were installed. These wells were designed to allow a sonde to be lowered below the water level to take water quality measurements as close to the soil matrix as possible. These locations are represented in Figure 10 below. The small circles represent the piezometer nest locations and the large circles represent the well nest locations.

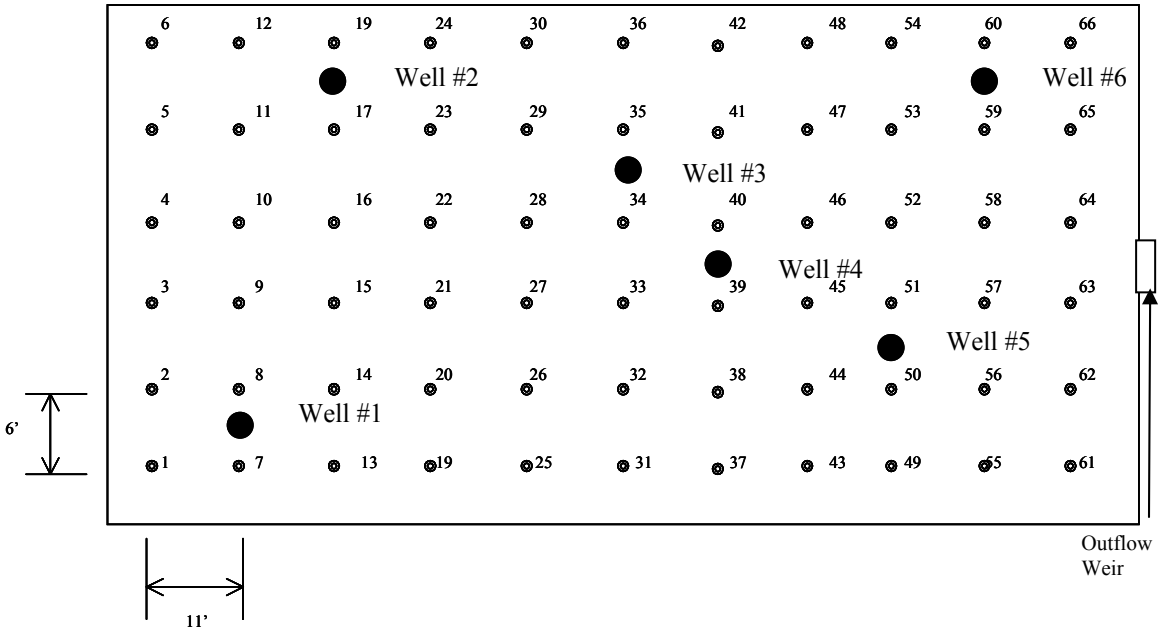


Figure 10. Plan View of Piezometer and Well Locations

A local contractor installed the wells in September 2002. The wells are constructed of 2 ¼ inch internal diameter PVC pipe with four sets of 1/16 inch horizontal slits cut into the pipe to allow water into the well (see Figure 11b and c below). The method used to install the wells was different than that used for the installation of the piezometers. First, a steel pipe with a sacrificial tip was driven into the soil (see Figure 11 b below) to a predetermined depth. Second, the PVC pipe was lowered to the proper depth and the steel pipe was pulled out until the screened area was cleared. The tip of the steel pipe remained in the ground below the PVC pipe. Third, a grout mixture was

poured between the steel pipe and PVC well casing as the steel pipe was pulled out to within six inches of the surface. Fourth, the three pipes in the nest were capped and tied together with clamps and 1 ½ inch metal angle iron. Since the wells were grouted in place they acted as piezometers. Permeable membrane bailers were also provided for sample extraction.

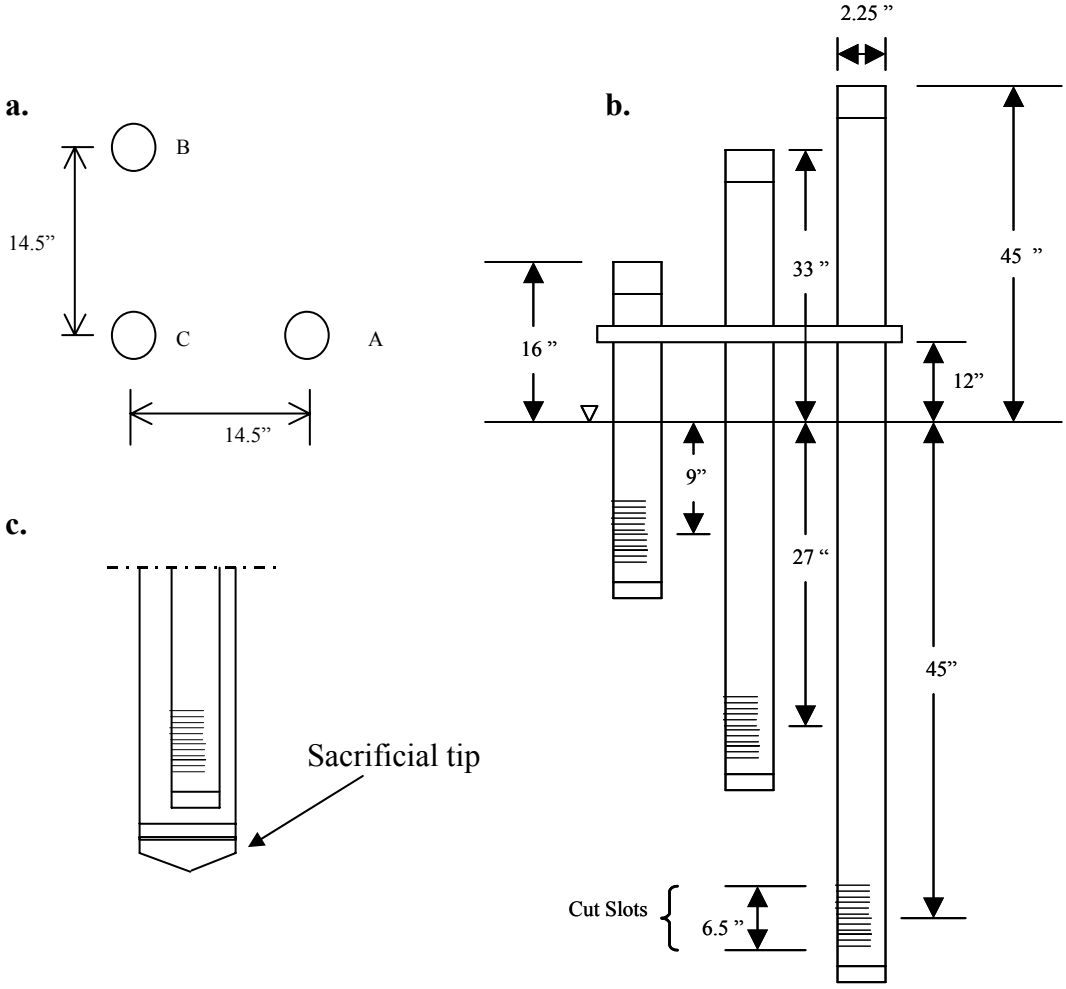


Figure 11. Diagrams of Water Monitoring Wells. **a.** Plan view of well placement, **b.** Elevation of sample wells, and **c.** Pipe used to install wells (Not drawn to scale)

Sampling Procedure

The sampling method developed in 2002 by Opperman and Bugg (Opperaman 2002, Bugg 2002) was used in this sampling effort with some minor refinements. Notes will be made in this chapter indicating the differences between this effort's procedures and last year's procedures. The two efforts gave comparable and similar results, as will be shown in subsequent chapters.

Before taking samples in the field the piezometers were purged to remove the stagnant water and to allow fresh water from the soil matrix to fill the well casing. The purging was completed with a peristaltic pump fitted with Teflon® tubing identical to the sampling apparatus. In the top two layers it was possible to completely drain the piezometers. The bottom layer piezometers had significantly more flow into them not allowing complete evacuation of the water. For these piezometers the purge tubing was slowly lowered down the piezometer as the pump was pumping until it reached the bottom of the screened area. This ensured that the stagnant water was removed from the top and it was not allowed to mix with the fresh water coming in through the screens. The water level in the top layer piezometers was allowed to recover for approximately 24 hours before any sampling was done. The middle and bottom layer piezometers could be sampled the same day do to their faster recharge rates.

After the piezometers recovered from purging, the actual sampling was conducted with a 100 mL glass syringe joined to Teflon® tubing with a three-way cock-stop connector. All sample vials were labeled before sampling. The vials were capped and placed in a box to be transported to the site.

The sampling procedure started with inserting the sampling tube down the piezometer to the middle of the screened area. Next, approximately 20 mL of wetland water was pulled into the syringe to prime the sampling tube. The cockstop valve was then turned and the water and any air in the syringe were ejected from the syringe. This reduced the effects of any residual de-ionized water left in the apparatus after its last rinse. Then approximately 60 mL of wetland water was slowly pulled into the syringe, avoiding the introduction of air bubbles. The cockstop valve was then turned again, allowing the sample to be ejected into a 40 mL sample vial. Care was taken to pour the water down the side of the bottle with as little turbulence as possible. The water was poured until the vial overflowed, leaving a meniscus of water above the vial. The vial was quickly capped with the screw top PTFE septum cap, minimizing the sample's exposure to the atmosphere and ensuring that there were no bubbles or headspace in the vial. After the sample was taken the syringe was rinsed with de-ionized water before moving to the next piezometer for the next sample.

The samples were taken to the lab and immediately analyzed to minimize the loss of analyte and avoid any need for sample preservation procedures. One note is that each sample took over thirty minutes to run in the GC, which meant that the last sample might have remained at room temperature for up to 20 hours before it was sampled. This was a concern and the effects were examined during a standard run of seven vials of 1.018 ppb mix standard solution (see Chapter 4, Method Detection Limit).

Although some of the wells were developed last year before the first sampling effort, it was necessary to develop the wells again for this sample run to attain the

necessary volume and recovery times. The decision was made to develop all the wells in the top two layers to ensure samples could be taken successfully from every well.

Each piezometer was sampled a minimum of two times throughout the effort, but do to the length of time between the two sampling runs (three weeks) causing variations in analyte concentrations, only one data set was used in this analysis. Replicate samples were not taken in the field for this analysis. Replicate aliquots of each sample vial were not analyzed do to the introduction of headspace after the first 5 mL sample was taken by the autosampler. In the field, 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 below an overlying stratum. 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 due to the upward flow path of the water. All piezometers in a layer were sampled before moving on to subsequent layers.

Sampling procedures for the inflow and outflow were different. The inflow was sampled in the pump house through a valve in the pipe feeding cell 1. The valve was turned open and the stream was allowed to flow for about10 seconds before the sample was taken. The outflow was sampled in the pool of water just before the water spilled over the weir. The sampling bottle, with the cap on, was lowered below the surface of the water. The cap was then screwed off allowing the water to completely fill the bottle without the introduction of soil or debris. Nine inflow and eleven outflow samples were taken between 7 Dec 02 and 9 Jan 03. The samples used in this study from one pass of the wetland strata were taken between 4 and 9 Jan 03. An additional 36 samples (12 from

each layer) were taken from cell 2 on 11 Dec 02 before the cell was shut down. The results of this sampling effort in cell 2 are shown in Appendix L.

After all the samples were taken and analyzed in the GC, response data was compiled and entered into spreadsheets to facilitate data analysis. Four analytes (PCE, TCE, cis-DCE, and VC) were found in various concentrations throughout the wetland using the method specified in Chapter 3. Raw sample data is found in Appendix A. Last year, only PCE and TCE were present in high enough concentrations to be detected. With both sets of data, it was possible to graph concentration trends, to find correlations in concentration, and to calculate average concentration levels.

Preparation of Standards

Standard solutions for each analyte were prepared from a custom stock containing 200 mg/L each of PCE, TCE, three isomers of DCE (1,1, trans-, and cis-), and vinyl chloride in a methanol solution. The custom stock solution was supplied by SUPELCO analytical supplies of Bellefonte, PA and was used in place of the EPA standard VOC mix 5.14 that was used last year. Standard solutions for ethene, ethane, and methane were not made for this effort due to lack of time. On inspection of the FID output chromatograms, it seems that there was virtually no appearance of these lighter compounds. Standards could be made and run through the current GC setup to determine if there are concentrations of these lighter components high enough to quantify.

All stocks and standards were made in EPA 40 mL bottles with de-ionized water and capped with a Teflon-lined septum and plastic screw top. Excess pressure was

released from the bottle by inserting a fresh needle through the septum. Gas-tight syringes (10 µL and a 50 µL) were used to transfer the standard solution into the vial. The standard vials were placed in a rotator for 24 hours to equilibrate.

A simple concentration to volume ratio (equation 1) was used to determine what volume of the custom standard solution was needed to make a desired concentration. The concentration was calculated using the following equation:

$$C_1 \times V_1 = C_2 \times V_2 \qquad (1)$$

where: C_1 = concentration of stock solution
V_1 = volume of stock solution transferred
C_2 = concentration of desired standard
V_2 = volume of 40 mL EPA vial (actually 44 mL)

Using this procedure volumes of 10, 5, and 1 µL of the custom standard solution were injected into 40 mL EPA VOC vials (44 mL actual volume) of de-ionized water making standards of concentration 45.4545, 22.7273, and 4.5455 ppb respectively. A second dilution using the 22.7273 ppb stock solution was used to make standard solutions of 0.54095 and 1.0819 ppb. After some analysis of samples it was deemed necessary to make a standard solution of greater than 120 ppb. This was done by injecting 30 µL of the custom standard into a 40 mL vial resulting in a standard concentration of 136.3635 ppb. These standards were run once to formulate the calibration curve. A 10 µL gastight syringe (GLENCO – Houston, TX) was used for each of the transfers. The syringe was rinsed 10 times with methanol and dried between each use. Calibration curves were then created with the ChemStation software after running each of these standard

concentrations through the GC (see Appendix B). The curves were forced through zero resulting in improved R-squared values for each of the analytes of over 0.999.

Purge-and-Trap Methodology

All analysis of the standard solutions used for calibration and of the wetland samples was done by purge and trap gas chromatography. EPA Methods 5030 and 8260B were modified to accommodate the analytical equipment and analytes of interest and are outlined below. An Archon AutoSampler (Varian Analytical Instruments) held the sample vials and robotically sent 5 mL of the samples to an Encon Purge-and-Trap concentrator. EPA 40 mL glass VOA sample vials were used to analyze both standard solutions and wetland samples. The vials were topped with a PTFE septum and capped with a plastic open top screw-on cap. The AutoSampler started the process by sending the sample in line to the purge-and-trap, which in turn passed the concentrated gaseous sample on to the gas chromatograph. The AutoSampler routine included one flush of the syringe and tubing with 1 mL of deionized water and Helium between each sample run. One aliquot was taken for analysis of each sample.

The theory of purge and trap operation used in this study can be found in Opperman's 2002 thesis. The operating parameters for the Encon purge-and-trap system were identical to what Operman used and are listed in Table 6 below.

After about 200 wetland samples, a reddish brown residue built up on the inside of the purge and trap glass purge vessel. To eliminate this residue, the purge vessel was removed and a 50% Nitric Acid solution was poured into the vessel and allowed to sit for

Table 6. Operating Parameters for the Encon Purge-and-Trap

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

one minute. The purge vessel was then triple rinsed with de-ionized water and reinstalled. To ensure a clean baseline chromatogram before the next sample run was started the entire analytical procedure was run with two blank samples. As a secondary operational check, a de-ionized water blank sample was run before the start of every sample cycle to ensure a clean baseline.

The purge-and-trap concentrator was the limiting factor in how many samples could be processed in one day. Each sample cycle took about 25 minutes to complete, and the AutoSampler would not take the next sample until the purge-and-trap had reset to the beginning of the program. The entire analytical process from AutoSampler activation from one sample to the next took 32.5 minutes.

Gas Chromatograph Methodology

An Agilent 6890 Series Gas Chromatograph (GC) was used to analyze the components of each sample. A detailed theory behind the operation of the GC can be

found in Opperman's 2002 thesis. A split column configuration was used to send the sample to two columns after a single injection. The two columns had different lengths and diameters, which caused the flows to be different under the same pressure. A 30m Restek RTX-VRX (Model 49314) column was connected to the micro-Electron Capture Detector (μECD). The μECD was used to detect the heavier chlorinated compounds as listed in Chapter 4, Table 9. A 20m J&W 113-4332 GS-GASPRO column was connected to the Flame Ionization Detector (FID) to detect the lighter non-chlorinated analytes. The GC analytical operating parameters were very similar to what Opperman used and are listed below in Table 7.

The ChemStation software package version 4.1 was used on a desktop computer to run the analytical sequence for the AutoSampler, the Encon purge-and-trap, and the GC. The software plotted the chromatogram, integrated the chromatogram peaks, and determined the concentration of each analyte using the area under the curve based on standard calibration curves that were run. The integration events for the auto-integration were set to optimize peak identification of the desired analytes. This was necessary because the auto integration function did not identify small peaks on the chromatogram. Using individual standard runs the integration events were adjusted to recognize peaks with smaller widths, heights, and areas within certain integration windows. This was required for VC, cis-DCE and trans-DCE that had the smallest responses to low concentrations. The integration events used for the μECD signal are listed below in Table 8.

Table 7. Gas Chromatograph Operating Parameters

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)	1.0 * (Previous effort 0)
Post Temp (deg C)	50
Total Run Time (min)	19.5 * (Previous effort 18.5)

Front Inlet (Split/Splitless)

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)	27.6 * (Previous effort 27.8)
Gas Saver:	On
Saver Flow (mL/min)	20.0
Saver Time (min)	2.00
Gas Type:	Helium

Back Inlet

Inactivated with the temperature and pressure turned off.

Column 1 (Restek 49314 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	Ambient

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	Ambient

Front Detector (µECD)

Temp (deg C)	250
Mode	Constant makeup flow
Combined Flow (mL/min)	45
Makeup Flow (mL/min)	25.0
Makeup Gas Type	Nitrogen
Electrometer	On

Back Detector (FID)

Temp	250
Hydrogen Flow (ml/min)	40.0
Air Flow (mL/min)	400.0
Mode	Constant Makeup Flow
Makeup Flow (mL/min)	45.0
Makeup Gas Type	Nitrogen
Flame & Electrometer	On
Lit Offset	2.0

Table 8. Integration Events for the μECD (Peak identification)

Integration Parameters	**Value**
Initial Slope Sensitivity	500.000
Initial Peak Width	0.030
Initial Area Reject	10.000
Initial Height Reject	2.000

Integration Event	**Time**	**Analyte Identified**
Integration off	0.000	
Integration on	2.650	VC
Integration off	3.000	
Integration on	3.170	Cis-DCE
Integration off	3.400	
Integration on	3.710	Trans-DCE
Integration off	3.920	
Integration on	5.300	TCE
Integration off	5.800	
Integration on	7.750	PCE
Integration off	8.300	

IV. Results and Discussion

The results of the laboratory and field analyses laid out in Chapter 2 are discussed here in detail. Where it is possible, the results from this effort and last year's effort will be compared to shed light on how the wetland might be maturing in its degradation characteristics. The results should enable an improved characterization of the processes that are occurring and provide additional weight of evidence that the contaminants are being degraded to innocuous chemicals. Answering the research questions and evaluating the data should give clues on how to better design a treatment wetland in the future.

The first step in the analytical procedure of the GC was to identify the characteristic retention times for each of the analytes to be measured. Maintenance on the GC between last year's and this year's analysis required cutting off a length of each column. The affect was to decrease the retention times for each of the analytes. Table 9 lists the retention times for the desired analytes for both efforts.

Table 9. Characteristic Retention Times for All Analytes

	Current Effort		**Previous Effort**
Analyte	**Retention Time (min, detector)**		**Retention Time (min, detector)**
PCE	7.920 (μECD)		9.010 (μECD)
TCE	5.509 (μECD)		6.402 (μECD)
cis-DCE	3.818 (μECD)		4.496 (μECD)
trans-DCE	3.238 (μECD)		3.856 (μECD)
1,1 DCE	2.830 (μECD)		3.228 (μECD)
Vinyl Chloride	2.750 (μECD)		6.709 (FID)
Ethene	N/A		2.175 (FID
Ethane	N/A		1.893 (FID)
Methane	N/A		1.359 (FID)

In this study VC was analyzed with the μECD instead of the FID. The GC response for VC with the setup as outlined in Chapter 3 gave a stronger signal on the μECD. The GC FID was set up to detect Ethene, Ethane, and Methane. It was decided that analysis for these analytes was not practical, because 1) in the previous effort the calibration curves proved inaccurate or impossible to create at low concentrations, 2) this year there were no responses on the FID that would indicate the presence of these analytes in a high enough concentration to quantify, and 3) there was not enough time to complete the analysis. Standards for these lighter components could be run in the future with the same GC setup to determine the concentration of these lighter components.

After the characteristic retention times for each chemical were determined, standard solutions were prepared with the custom VOC mix as outlined in Chapter 3. Calibration curves for PCE, TCE, trans-DCE, cis-DCE, and VC were generated by the ChemStation software and are found in Appendix B. The peak for 1,1-DCE was inconsistent and overlapped the VC peak, which made it hard to analyze. This coupled with the fact that 1,1-DCE is the least likely of the DCE isomers to be created during the dechlorination of TCE (Lorah and Olsen, 1999) drove the decision to not include 1,1-DCE in the analysis. It is suggested that 1,1-DCE not be included in future custom mix standards. Nothing lighter than TCE was detected in the previous sampling effort. Last year's effort could not generate calibration curves for methane or VC using the FID. This time a calibration curve was successfully developed for VC using the μECD.

The original goal of the sampling was to take three passes of the wetland in quick succession to allow the calculation of average concentrations for each of the piezometers. During the sampling effort weather and equipment difficulties did not allow samples to

be taken successively in a timely manner. Two passes were made but a large portion of the data had to be thrown out because some of the piezometers did not have adequate water volume to be sampled and the sample runs had almost three weeks between them decreasing their correlation.

Concentrations of PCE, TCE, cis-DCE and VC were found throughout the wetland. This data was compiled in spreadsheet form to allow quick statistical calculations in Excel and Jump software packages. Complete sample data sets are located in Appendix A.

The average concentrations and their respective 95% confidence intervals were the first calculations done. The 95% confidence intervals were calculated in Excel using the average, variance, and the number of the sampled population (66). Below in Table 10 are the values for both efforts. The data sets include all values without censoring. Scanning the data in Table 10 from bottom to top follows the flow of water upward through the wetland. The larger confidence intervals showed that there was an increase in the variability of PCE and TCE concentrations this year except for the concentration of TCE in the top layer. This increased variability could be a result of taking one sampling pass of the wetland this year while last year's data was an average of three passes which would tend to lessen the effects of one-time extreme measurements.

Unlike the sample data from December 2001 the data gathered this year showed the presence of cis-DCE and VC along with the PCE and TCE that was seen before. The presence of cis-DCE and VC were not detected in the inflow or outflow on either occasion. The largest decrease in PCE concentration occurred between the middle of the bottom layer and the middle of the middle layer where the concentration drops by 94% as

Table 10. Analyte Average Concentrations (Outliers not removed and zero response by GC is included in the calculations as zero)

a. Data from Jan 2003

	Average Concentration (ppb ± 95% Confidence Interval)			
Location	**PCE**	**TCE**	**cis-DCE**	**VC**
Outflow	8.637 ± 0.807	0.509 ± 0.041	ND	ND
A	1.178 ± 0.938	0.381 ± 0.192	1.105 ± 0.585	0.256 ± 0.130
B	1.492 ± 0.743	0.721 ± 0.270	1.770 ± 0.724	8.701 ± 6.691
C	25.533 ± 1.726	0.754 ± 0.194	0.311 ± 0.275	0.021 ± 0.023
Inflow	32.59 ± 0.699	0.170 ± 0.011	ND	ND

ND – None Detected

Averages and confidence intervals were computed with 9 samples for the inflow, 11 samples for the outflow, and 66 samples for each layer sampling each piezometer once.

b. Data from Dec 2001

	Average Concentration (ppb ± 95% Confidence Interval)			
Location	**PCE**	**TCE**	**cis-DCE**	**VC**
Outflow	5.593 ± 0.615	2.138 ± 2.117	ND	ND
A	2.422 ± 0.557	0.342 ± 0.343	ND	ND
B	1.797 ± 0.165	0.349 ± 0.031	ND	ND
C	26.821 ± 0.383	0.806 ± 0.034	ND	ND
Inflow	33.97 ± 0.920	0.627 ± 0.194	ND	ND

ND – None Detected

Averages and confidence intervals were computed with 12 samples for the inflow and 4 samples for the outflow. Each piezometer was sampled three times and averaged. The piezometer averages in the three layers were then averaged to arrive at the average concentration for the entire layer.

compared to only a 21% reduction between the inflow and the middle of the bottom layer. The average PCE concentration decreased slightly between the middle and top layers but can be considered almost indistinguishable with their overlapping 95% confidence intervals. Overall the PCE reduction from the inflow to the top layer was 96.4%.

There was a 73.5% removal of PCE from the inflow to the outflow. The increased concentration of PCE in the outflow was mainly a result of the area in the

wetland where the water was bypassing all three treatment layers and flowing directly to the outflow weir.

In Dec 01 there was an increase in the average concentration of PCE from the middle to the top layer. In Jan 03 there was a decrease in average PCE concentration moving from the middle to the top layer. It is hypothesized that this difference is the result of the flow bypass area shrinking and migrating to an area between top layer piezometers, reducing the number of sample points that were affected. This year's samples did not capture as much of the bypassing flow that would have increased the average concentration in the top layer similar to last year.

The increased concentration of PCE in the outflow from Dec 01 to Jan 03 indicates that the volume of water bypassing the layers is greater this year. It is theorized that an increased flow into the wetland would cause the bypass situation to worsen as will be explained here. The increased flow would increase the pressure in the bottom layer. This increase in pressure could subsequently exceed the soil bearing capacity in the weakest area, allowing the water to develop a path of least resistance to the surface. This bypassing flow reduces the pressure in the bottom layer to a steady state point where the vertical flow is balanced.

There is a possible explanation for an increase in flow in wetland cell 1. The original flow meters that were installed in the pump house did not give accurate readings and were replaced this summer. Before they were replaced in Sep 02, a flow measurement was taken at the exit weir and found to be roughly seven gallons per minute (gpm). After the new meters were calibrated and set to 10 gpm, a flow measurement at the exit weir showed 10.8 gpm on 15 November 2002. Even though the measurements

made at the exit weir can only give a rough estimate of the inflow, this three-gpm difference strongly suggests that the inflow had increased. The effect of this increased inflow was an increase in bypass flow and increased concentrations of PCE and TCE in the outflow.

The average TCE concentration in each layer never rose above one ppb. If reductive dechlorination is occurring, the TCE that is generated from PCE dechlorination must be quickly transformed into the lower daughter products at a faster rate. The change in average TCE concentrations as the water moves up the wetland does support the claim that reductive dechlorination is occurring. The 78% increase in TCE concentration from the inflow to the bottom and middle layers indicates that TCE is being generated. The decrease in TCE concentration between the middle and top layers correlates with the PCE concentration remaining somewhat constant. When the PCE is expended the TCE degradation rate exceeds the TCE formation rate, therefore causing a decreasing concentration. Moving to the outflow from the top layer, the TCE concentration increases slightly. Similar to the increase in PCE concentration between the top layer and the outflow, the increased TCE concentration is most likely caused by the flow bypassing the soil layers and not allowing the TCE to degrade. The slight increase in TCE concentration is most likely the result of limited PCE degradation into TCE in the first part of the bottom layer.

PCE and TCE were detected in nearly all of the piezometers in every layer of the wetland. Cis-DCE and VC on the other hand were detected in fewer piezometers. Table 11 below shows the frequency of occurrence and the average concentration of each analyte for all piezometers the analyte was detected.

Table 11. Frequency of Analyte Detection and Average Concentrations Calculated with Non-zero Measurements Only (Outliers not removed)

	Number of Piezometers Analyte was Detected (Ave Conc. ppb ± 95% CI)			
Layer	**PCE**	**TCE**	**Cis-DCE**	**VC**
A	65 (1.20 ± 0.94)	41 (0.61 ± 0.30)	13 (5.61 ± 1.15)	26 (0.65 ± 0.27)
B	66 (1.49 ± 0.74)	46 (1.04 ± 0.35)	20 (5.84 ± 1.05)	43 (13.36 ± 10.03)
C	66 (25.53 ± 1.73)	65 (0.75 ± 0.20)	5 (4.05 ± 1.08)	3 (0.45 ± 0.08)

Note: The bottom layer had 7 piezometers with higher concentrations of TCE than the inflow TCE concentration, the middle layer had 7, and the top layer had 5. There were only 2 piezometers with higher PCE concentrations, both located in the bottom layer.

Comparing these frequencies of occurrence of cis-DCE and VC to their average concentrations in each layer, a correlation can be seen between the layers. As cis-DCE and VC average concentrations increase so does their frequency of occurrence. Also, the concentration ranges for cis-DCE and VC behave differently than the PCE and TCE ranges. For piezometers where cis-DCE is detected, the average concentrations range between 2 and 12 ppb. There does not seem to be any extreme low or high measurements for cis-DCE.

The range of concentration for VC in the middle layer was very large. There were 8 piezometers with VC concentrations over 26 ppb and one reading of over 158 ppb. After eliminating these 8 extreme values the average concentration for the remaining 35 piezometers that VC was detected in is a much lower 0.82 ppb.

The concentrations of cis-DCE and VC in the top and bottom layers were extremely variable, and their frequency of occurrence was small as compared to PCE and TCE. The researcher speculates that this variability of frequency of detection and concentration is a result of shorter reaction times for the degradation of cis-DCE and VC as compared to PCE and TCE. Another explanation might be that the wetland is

continuing to develop the microbial consortia to degrade the cis-DCE and TCE and has not reached a uniform distribution of microbes.

After observing concentration values in a few of the piezometers that were not representative of what was seen throughout the majority of the wetland, it was decided that it would be beneficial to eliminate these outliers to examine how an *ideal* treatment wetland would perform. One obvious reason for the majority of the outliers was the flow that was observed flowing directly to the surface between piezometers 9, 10, 15, and 16. Other outliers are less obvious to explain but were eliminated regardless of their cause in an effort to reduce the affects of extreme values. The data was analyzed with the software statistical package JUMP 5.0. Any value that was more than two standard deviations away from the mean was eliminated. This data analysis can be found in Appendix E. The remaining data was analyzed arriving at a censored mean and 95% confidence interval. The data for both sampling efforts is listed in Table 12 below.

This process worked best for PCE and TCE concentration data manipulation. Their concentrations were less variable and they were detected in the majority of all wells. Most of the outliers that were identified for PCE and TCE concentrations are associated with areas of the wetland that are known not to be performing ideally. The data for cis-DCE and VC concentrations was not as convenient to remove outliers. As mentioned before when cis-DCE was detected the concentration variance was very small without any high or low values. Unfortunately it was only detected in 38 of 200 sampling locations. This made it difficult to quantify what the average concentrations are throughout the three layers of the wetland. All of the cis-DCE concentrations in the bottom and top layers were considered outliers.

Table 12. Analyte Average Concentrations (Outliers removed and zero response by GC is included in the calculations as zero)

a. Data from Jan 2003
(Outliers for layers A, B, and C removed [± 2 standard deviations])

	Average Concentration (ppb ± 95% Confidence Interval)			
Location	**PCE**	**TCE**	**cis-DCE**	**VC**
Outflow	8.637 ± 0.807	0.509 ± 0.041	ND	ND
A	0.171 ± 0.079	0.095 ± 0.042	0	0.113 ± 0.046
B	0.319 ± 0.139	0.439 ± 0.167	1.346 ± 0.573	0.495 ± 0.171
C	26.266 ± 0.872	0.536 ± 0.091	0	0.021 ± 0.023
Inflow	32.59 ± 0.699	0.170 ± 0.011	ND	ND

ND – None Detected
Note: A "0" indicates that all positive readings were eliminated as outliers.
Averages and confidence intervals were computed with 9 samples for the inflow and 11 samples for the outflow. 66 samples were taken for each layer sampling each piezometer once. Number of outliers removed: PCE in A-7, PCE in B-11, PCE in C-4, TCE in A-10, TCE in B-6, TCE in C-6, cis-DCE in A-13, cis-DCE in B-3, cis-DCE in C-5, VC in A-6, VC in B-8, and VC in C-3.

b. Data from Dec 2001
(Outliers for layers A, B, and C removed [± 2 standard deviations])

	Average Concentration (ppb ± 95% Confidence Interval)			
Location	**PCE**	**TCE**	**cis-DCE**	**VC**
Outflow	5.593 ± 0.615	2.138 ± 2.117	ND	ND
A	0.813 ± 0.083	0.173 ± 0.030	ND	ND
B	1.145 ± 0.105	0.172 ± 0.029	ND	ND
C	27.431 ± 1.358	0.706 ± 0.044	ND	ND
Inflow	33.97 ± 0.920	0.627 ± 0.194	ND	ND

ND – None Detected
Averages and confidence intervals were computed with 12 samples for the inflow and 4 samples for the outflow. Each piezometer was sampled three times and averaged. The piezometer averages in the three layers were then averaged to arrive at the average concentration for the entire layer. Number of outliers removed: PCE in A-10, PCE in B-7, PCE in C-2, TCE in A-9, TCE in B-9, and TCE in C-6.

The removal of VC concentration outliers was even more difficult. The removal of the extremely high VC concentration measurements would be easily justified if there were not eight of them (each greater than 26 ppb concentration). This many high concentration readings along with their close proximity to lower concentration readings

makes them less likely to be outliers. This can be seen in the surface plots for VC in Appendix C.

Overall, the removal of outliers for the calculation of cis-DCE and VC concentration averages was not an effective way to gain insight into an ideally performing remediation wetland. There are too few piezometers registering positive readings and the variability in some cases (particularly VC in the middle layer) makes it difficult to determine the efficiency of the system. Perhaps the wetland remains in a maturation stage where the bacteria degrading TCE, cis-DCE, and VC are still approaching a steady state causing their concentrations to fluctuate.

Trends in Contaminant Concentration

To get an idea of how the concentration of the contaminants changed as they passed through the wetland a series of plots were done to examine any trends or relationships. A plot of the concentration data for each of the analytes from the inflow, the three wetland layers, and the outflow is presented below in Figure 12. The error bars represent the 95% confidence intervals for each sample point. All sample data is included in this analysis.

The inflow concentration of TCE decreased significantly from 0.627 ± 0.194 last year to 0.170 ± 0.011 this year (69% decrease). This could be the result of changes in the contaminant plume that is supplying the water. The TCE concentrations remained below one ppb throughout the wetland again this year. The outflow average last year was greater than two ppb, but this number is questionable because only four samples were

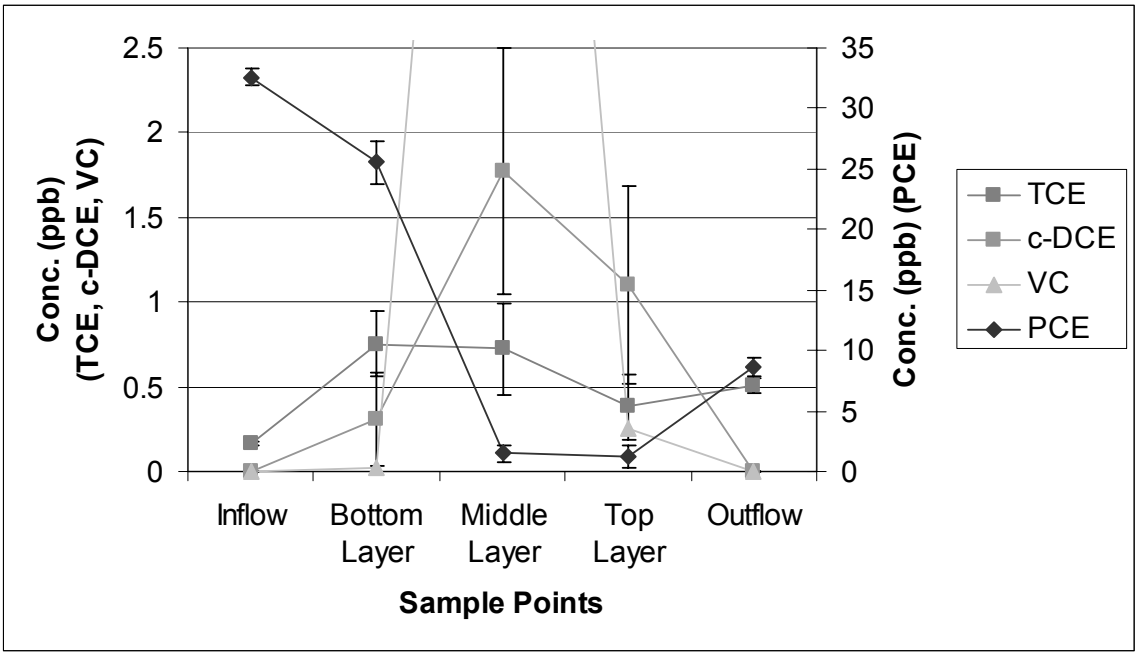


Figure 12. Plot of Average Contaminant Concentration Trends (with 95% CIs; including outliers)

contaminant plume that is supplying the water. The TCE concentrations remained below one ppb throughout the wetland again this year. The outflow average last year was greater than two ppb, but this number is questionable because only four samples were taken and the 95% confidence interval was greater than two.

As the water moves from the inflow into the first layer this difference in the TCE concentrations between the two years is diminished as the concentrations rise to 0.806 ± 0.034 and 0.754 ± 0.194 ppb respectively. This increased TCE in the bottom layer indicates that there is dechlorination of PCE occurring.

Moving to the middle layer, last year the TCE concentration dropped below 0.4 ppb and remained there. This year the concentration stayed above 0.7 ppb in the middle layer and didn't drop to below 0.4 until the top layer. The TCE concentration in the

outflow increased similar to the PCE concentration although not as drastically. The reason for the increase is again most likely due to the bypassing flow. The percentage increase of TCE in the outflow is much less than the PCE. This could be due to the fact that TCE has a higher vapor pressure than PCE and will more readily volatilize into the atmosphere as it moves across the surface of the wetland toward the outflow.

A second plot was done after removing the outliers beyond two standard deviations of the mean. This plot can be seen below in Figure 13. Removing the outliers had the desired affect of decreasing the confidence intervals, but it also reduced the concentration of cis-DCE in the top and bottom layers to zero and VC to near zero.

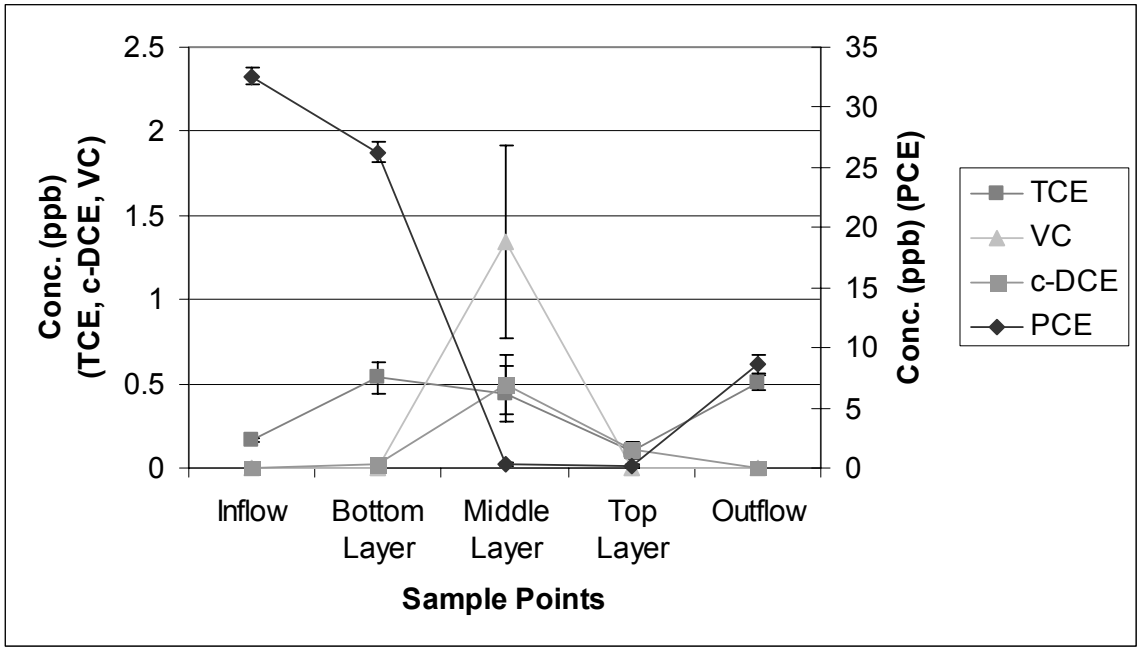


Figure 13. Plot of Contaminant Concentration Trends (with 95% CIs; Outliers Removed)

Moving from left to right in these graphs the interplay of PCE and its degradation products can be seen. The inflow concentration of PCE is slightly reduced by the time it reaches the middle of the bottom layer. This slight reduction is mirrored by an increase

in TCE concentration. Cis-DCE also begins to appear in the bottom layer as the TCE starts to degrade.

Moving to the middle layer there is a sharp drop off of PCE concentration while the cis-DCE and VC concentrations increase to their highest level. The TCE concentration drops slightly as it is being reduced more actively. This indicates that the conditions in the zone starting just below the center of the bottom layer and moving to the center of the middle layer are most favorable for PCE dechlorination.

As the flow of water moves into the top layer, TCE, cis-DCE and VC concentrations are being reduced to very low levels while PCE remains at a relatively low concentration. This indicates that the conditions between the middle and top layers are conducive for the removal of Chlorine atoms from TCE, cis-DCE and VC while the conditions favorable for PCE dechlorination no longer exist.

At the outflow the PCE and TCE concentrations spike higher while cis-DCE and VC concentrations fall to zero. Both PCE and TCE concentrations are a significant fraction of their values observed in the bottom layer. This gives evidence that there is a significant amount of flow that is passing directly from the bottom layer to the surface of the wetland. Since the upwelling flow has been witnessed to occur between nests of piezometers it is assumed that the majority of the middle and top layer piezometers are not collecting the bypassing water. This observation also indicates that the entire flow bypass is not created or perpetuated by the installation of the drive-point piezometers. Rather, weak or liquefied areas of the wetland soil are allowing the pressurized water to find a path of least resistance to the surface.

Both cis-DCE and VC concentrations drop to very low levels in the aerobic top layer. This degradation could theoretically continue as the water moves through the last six inches of the wetland resulting in the non-detectable levels at the outflow. Another possibility is that the cis-DCE and the VC are still present as they reach the surface and merely evaporate into the atmosphere as can be expected with their relatively high vapor pressures. The mechanism behind their total disappearance cannot be determined with the data presented here.

A second series of graphs show the trends of inflow and outflow concentrations. Only PCE and TCE were detected in the inflows and outflows of the wetland. Below Figures 14 and 15 depict the trend of chemical concentrations in the inflow and outflow.

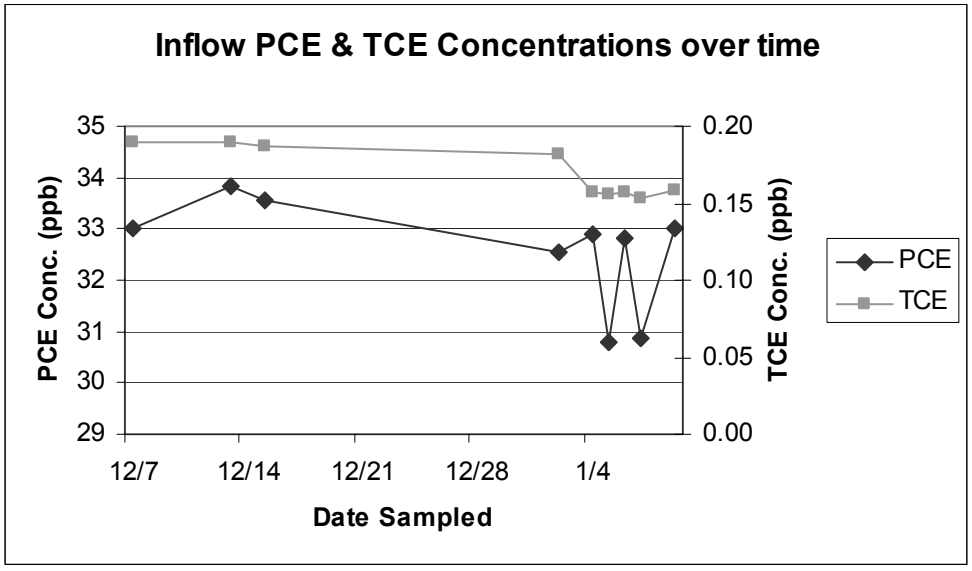


Figure 14. Plot of Inflow Concentrations Over Time

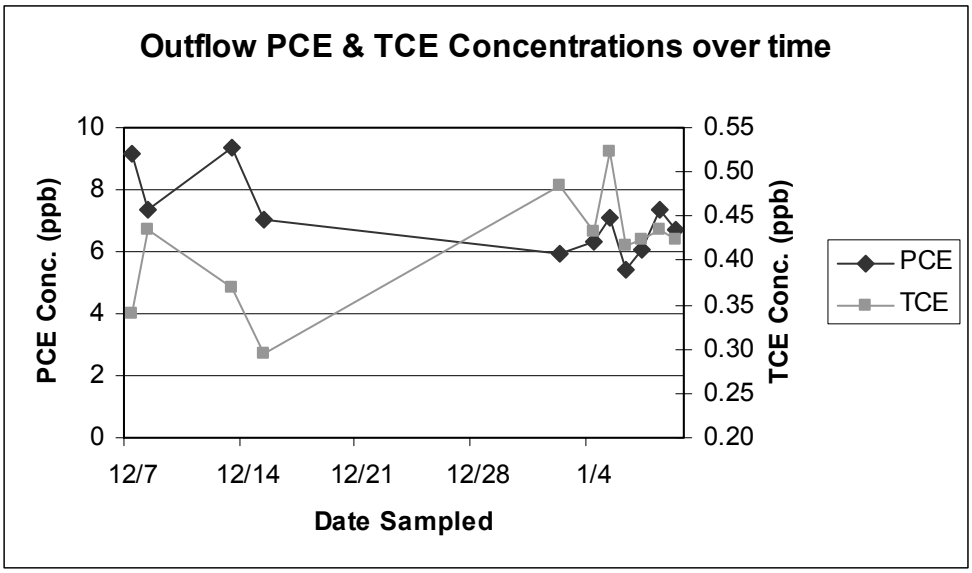


Figure 15. Plot of Outflow Concentrations Over Time

Two additional graphs were made to examine any possible correlations between the inflow and outflow concentrations of each of the chemicals. Figures 16 and 17 are seen below.

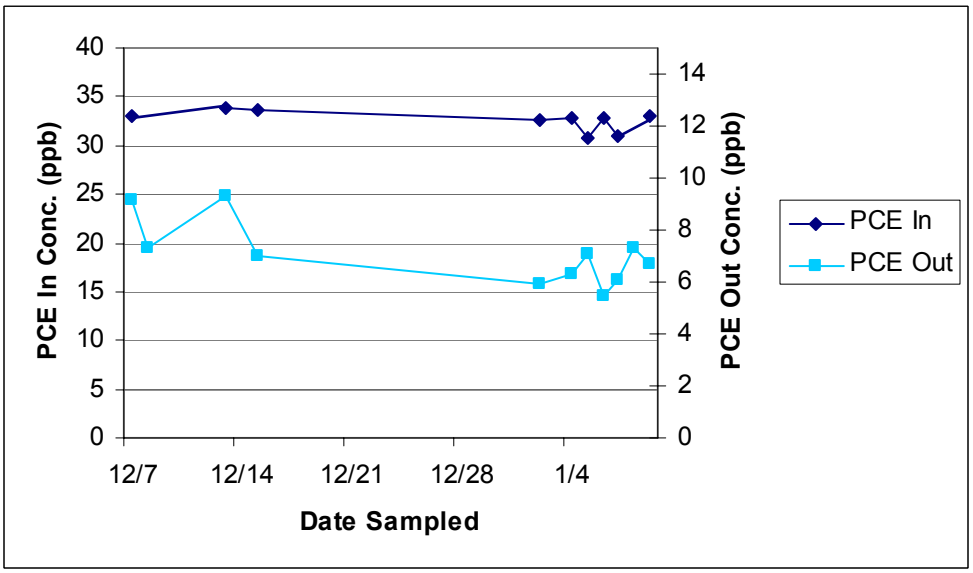


Figure 16. Plot of PCE Inflow and Outflow Concentrations Over Time

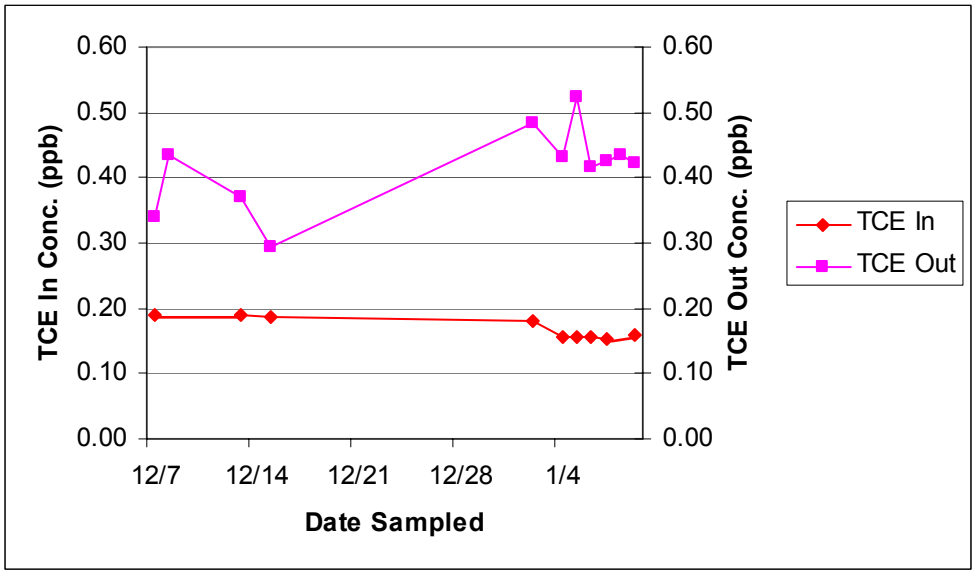


Figure 17. Plot of TCE Inflow and Outflow Concentrations Over Time

Overall there were no strong trends or correlations between the inflow and outflow concentrations to and from the wetland over this short time period. A longer time period of regular sampling might uncover seasonal trends.

Correlations in Contaminant Concentrations

The data was analyzed with a statistical software package JUMP 5.0 for any correlations that might indicate degradation of the contaminants was occurring. The first step was to do a bivariate plot of all the average concentrations measured in the wetland strata. All twelve data sets (four contaminants in three layers) were entered and the resulting plot can be seen in Appendix H-I. A few observations were made and will be discussed below.

The first observation from the multivariate matrix plot was that there were some data sets with strong correlations. The most obvious observation was the inverse correlation between the PCE and TCE concentrations in the bottom layer as seen in Figure 18 below. The plot shows that when PCE concentrations are high the TCE concentrations tend to be low and visa versa.

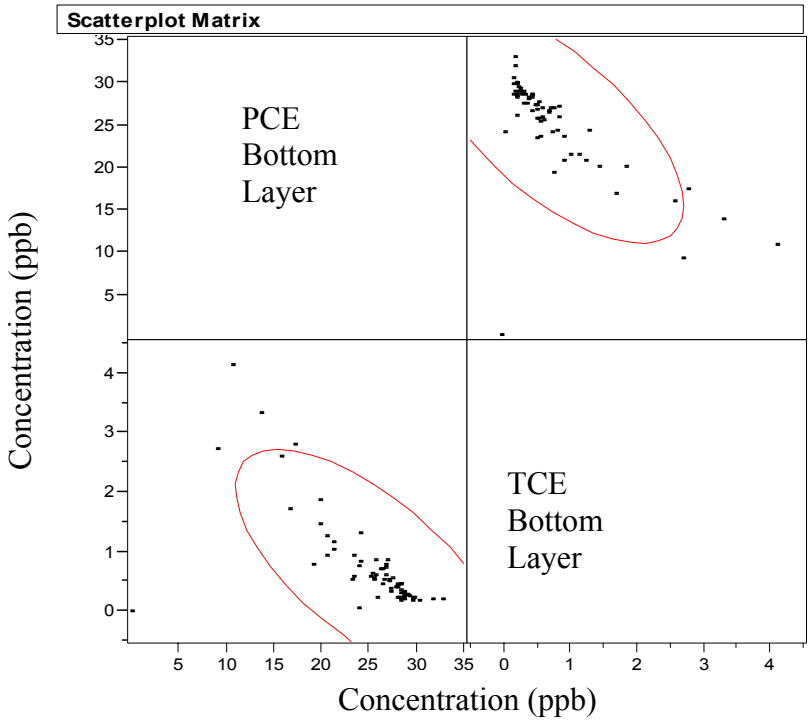


Figure 18. Multivariate Plot of PCE vs TCE Concentration in Bottom Layer Demonstrates the inverse corelation between PCE and TCE concentrations. Gives evidence that PCE is degrading into TCE.

This inverse correlation was expected, as TCE is the first degradation product of PCE. Also, the limited appearance of TCE's daughter products at low concentrations in the bottom layer gave evidence that TCE was not being degraded, strengthening the inverse correlation between PCE and TCE concentrations. It was not expected that such low concentrations of TCE would correlate with PCE concentrations this strongly. A

stepwise regression analysis was done with JUMP 5.0 to examine the strength of correlation and whether cis-DCE and VC concentrations in the bottom layer would add to the explanatory power of the model. Using just the PCE and TCE concentrations in the bottom layer the regression gave an R-squared value of 0.8139. Including the few cis-DCE concentrations in the model the R-squared value increased to 0.8256. Adding VC concentrations to the model further increased the R-squared value to 0.8286. The increase in the R-squared value attributed to the addition of cis-DCE and VC is small, but it does support the inverse relationship between the concentration of PCE and its daughter products. A printout of the stepwise regression analysis can be seen in Appendix H-VI.

The second observation from the multivariate matrix plot was that VC never appeared in a sample with concentrations of cis-DCE in the top layer and VC only appeared in conjunction with cis-DCE 12 times in the middle layer. Additionally, VC was rarely observed in samples with high concentrations of TCE or PCE. Two subplots from the complete multivariate plot for the top and middle layers are shown below in Figures 19 and 20. The bottom layer did not contain enough VC to warrant examination. The cause of this phenomenon is unknown.

A tabular correlation analysis was done in JUMP 5.0 using Spearman's Rho. Spearman's Rho is an estimate of the association between paired data sets. The measure of association ranges from -1 to 1 with 0 indicating no association. The stronger the positive correlation between two sets of data the closer Spearman's Rho gets to one. The stronger the inverse correlation between two data sets the closer Spearman's Rho gets to negative one. An analysis was first done on PCE and TCE concentration data from

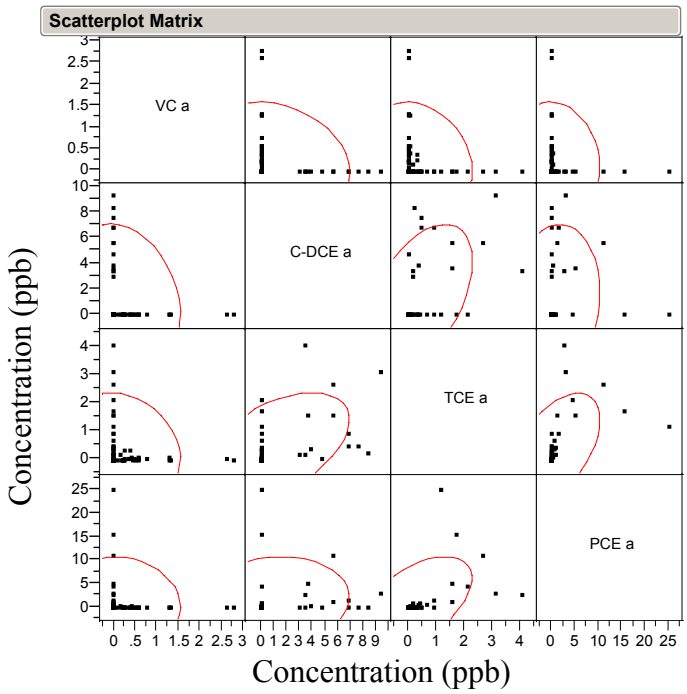


Figure 19. Multivariate Plot of Analyte Concentrations in Top Layer
Notice that VC does not appear when cis-DCE is present and appears infrequently when TCE and PCE are present.

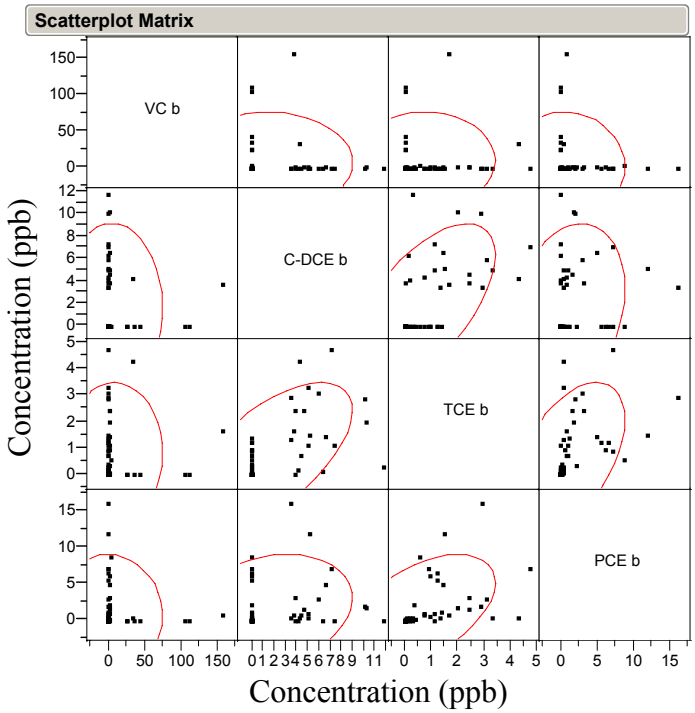


Figure 20. Multivariate Plot of Analyte Concentrations in Middle Layer
Notice that VC does not appear when cis-DCE is present and appears infrequently when TCE and PCE are present.

Dec 01 and Jan 03 and is found in Appendix H-III. A second analysis was done on PCE, TCE, c-DCE, and VC concentration data from Jan 03 and is found in Appendix H-IV.

Throughout both sets of data there are positive correlations between concentrations of PCE and TCE in the top two layers. It has been shown that the majority of PCE degradation occurs between the bottom and middle layers. Once PCE and TCE make it to the middle layer their concentration seems to stay relatively constant through to the top layer. This strong positive correlation could be the result of the fact that once the PCE and TCE move from a highly reducing environment to a more aerobic environment they are no longer being degraded leaving the concentrations constant. This correlation could also be strengthened by flow bypassing the top two layers. In these bypass areas both the PCE and TCE concentrations are elevated in the middle and top layers causing a stronger positive correlation.

Using Spearman's Rho, similar distribution patterns of PCE and TCE are shown between last year's data and this year's data. The strongest pattern of similarities between the two years is in the bottom layer. The areas where PCE and TCE were observed at higher concentrations last year are the same areas they were seen this year. The same holds true for the inverse correlations between the concentrations of TCE and PCE in the bottom layer from last year to this year. The strength of the correlation between the two years decreases progressing vertically through the wetland as the concentration distributions in the top two layers have changed more than in the bottom layer. This relationship will become more obvious in the next section with the presentation of concentration contour plots.

These tabular correlations can be used to help identify patterns in analyte concentrations within each layer and between layers. These relationships can then be used to identify patterns in contour plots.

Surface Plot Analysis

The data generated from the VOC analysis was plotted using Surfer 8.0. One surface plot was completed for each analyte in each layer. These plots enabled quick comparison of concentration patterns that developed between each layer with different analytes and concentration patterns that change over time. The Spearman's Rho analysis from above helped identify correlations that were not recognized at first sight. It also helped quantify which relationships were stronger than others.

As discussed in Chapter 3, the constructed wetland is fed water contaminated with PCE and small amounts of TCE. PCE is the only chemical in this system that is not a daughter product of another chemical. Therefore, the change in PCE concentration between the sampling horizons demonstrates where reductive dechlorination is occurring. The daughter products of PCE degradation are quickly transformed into their subsequent daughter products making it harder to determine where the transformations are occurring and how efficient the reactions are.

PCE and Degradation Product Analysis

In Dec 01 the average PCE concentration dropped 92.9% (33.97 ± 0.92 to 2.42 ± 0.56 ppb) from the inflow to the top layer. This year the average reduction of PCE from the inflow to the top layer was 96.4% (32.59 ± 0.699 to 1.178 ± 0.955 ppb). This

increase in PCE removal does not mean that the system's performance is improving. In fact, the average PCE in the outflow increased significantly from 5.59 ± 0.62 to 8.64 ± 0.81 ppb (54.4%) over the year, while the inflow PCE concentration stayed fairly constant (33.97 ± 0.92 and 32.59 ± 0.70 respectively). This increase in PCE concentration in the outflow, and other anomalies, can be explained by a portion of the vertical flow short-circuiting the treatment layers of the wetland. This short-circuiting flow allows the contaminants to rise to the surface without experiencing the required retention time and contact with microorganisms or enzymes to promote chemical degradation.

Looking at the concentrations of PCE in each of the three layers depicted below in Figure 21 there are obvious conclusions to be made. First, by comparing the concentration of PCE in the bottom layer to the top layer you can see that there are substantial reductions in the PCE concentration throughout the entire wetland. The majority of the PCE is degraded between the middle of the bottom layer and the middle of the middle layer.

Since PCE requires highly reducing conditions to remove the first chlorine atom, the conclusion can be made that the conditions are not sufficiently reduced until the water passes the middle of the first layer. Although inflow oxygen concentrations were not taken, the trend of decreasing concentration from the bottom to middle layer (1.68 to 0.2 mg/L) indicates that the water entering the bottom layer has a high oxygen content, greater than 1.68 mg/L, that must be reduced before dehalogenation of PCE can occur.

The reduction of PCE concentration is limited in the top layer around three wells (10, 16, and 22) marked with a solid rectangle below in Figure 21. This area of the

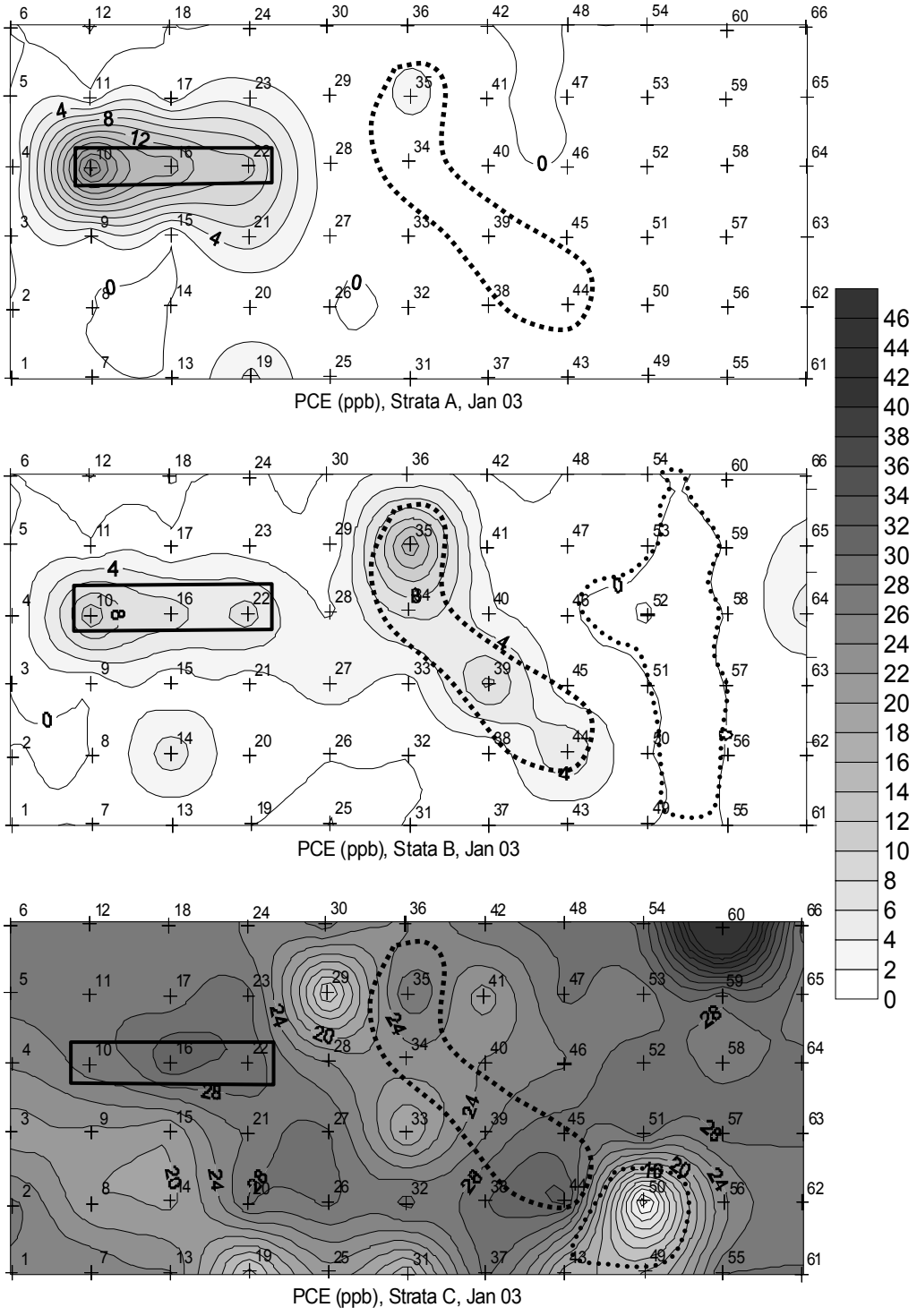


Figure 21. Contour Plots Showing Trends of PCE Concentration
The solid rectangles and square dotted outlines highlight correlations of higher concentrations in each layer. The round dotted outlines highlight an area of expanding low concentration as the water moves from the bottom layer to the top layer.

wetland reflects higher concentrations of PCE in each of the layers, apparently not supporting the complete destruction of the PCE. There are three reasons why this might be occurring: 1) the required microbes are not present in great enough numbers for efficient degradation, 2) this area is lacking some nutrient required for the degradation, or 3) the retention time is not long enough to complete the degradation. By looking at the other areas of the wetland where degradation is occurring at a higher rate, one can assume that the microbes are present and the nutrients should be uniformly present throughout the wetland to support microbe growth. This leaves the lack of retention time as a possible reason for not seeing more degradation of PCE in this area.

Observations made before, during, and after the sampling effort indicate that the lack of retention time is the reason for the increased PCE concentrations observed in this area. The first observation was an upwelling flow of water to the surface from small ¾ inch holes in the wetland soil. This phenomenon was witnessed in the area between piezometers 9, 10, 15, and 16. Attempts were made to plug the holes with bentonite clay but were unsuccessful. To help determine where this water was originating, a sample was taken directly from the flow emerging in this area and analyzed in the GC. The concentrations for PCE and TCE in this sample were 30.997 ppb and 0.391 ppb respectively. The concentrations of PCE and TCE in the inflow on that day were 33.554 ppb and 0.187 ppb respectively. The small reduction in PCE concentration and increase in TCE concentration gives certain evidence that the retention time for the column of water leading to the surface was insufficient to fully degrade the PCE to TCE. A measure of the flow coming to the surface was not made, but, by observation, the total flow of all the leaks could be as much as 2 to 3 gpm.

The second observation was that when the atmospheric temperature dropped below freezing for extended periods the surface around this leaking area never froze and left an opening in the ice with a stream of open water running toward the weir. This shows that the warmer than ambient ground water was escaping to the surface in this area faster than the other areas, halting the formation of ice. This bypassing flow could explain the high concentration of PCE in the outflow (8.64 ppb) when the average PCE concentration in the top layer was much lower (1.18 ppb).

The third observation made was that the vegetation in the area of bypassing flow was not as dense as the remainder of the wetland. There were no root systems holding the soil in place, this allowed the soil to further liquefy and permitted the pressurized water from the bottom layer to follow the path of least resistance to the surface. On a few occasions the researchers stepped off the board path in this area and sunk knee deep in the liquefied soil. This same phenomenon was experienced the year before between piezometers 18 and 24. This year that area had firmed up with additional plant growth that now supported the researchers' weight.

Another PCE concentration pattern can be observed in the middle layer marked in Figure 21 by a square dashed outline in the center of the wetland. Piezometers 34, 35, 39, and 44 in the middle layer all have PCE concentrations above average ranging from 5 to 15 ppb. Comparing this to the bottom layer, where the wells' concentrations range from 23 to 33 ppb PCE, it can be demonstrated that patterns develop along flow lines. Moving up to the top layer nearly all the PCE has been degraded indicating that there is degradation along a flow line if one assumes that vertical flow lines correlate with the location of the piezometers.

One last concentration pattern demonstrated by PCE can be seen starting in the bottom layer around piezometers 43, 49, and 50, demarcated in Figure 21 by a round dotted outline on the right side of the wetland. Around these wells the PCE concentration is less than the layer average. As you move up to the PCE concentration in the middle and top layers the area of lower concentration (less than 2 ppb) spreads out, eventually covering the majority of the wetland other than the area identified as a region of bypassing flow. This trend of decreasing PCE concentrations gives evidence that PCE is being degraded.

In Jan 03 the average concentrations of PCE in the top and middle layers were nearly identical. Last year an increase in the concentration from the middle to the top layer was seen. After examining the PCE contour plots for the two periods, it is apparent that this difference in average concentration in the top layer results from a more extensive flow bypass area last year influencing more top layer piezometers than this year (see Appendix B for contour plots). Last year seven piezometers experienced significantly higher PCE concentrations in areas where bypassing flow was suspected. This year only three piezometers showed increased concentrations, keeping the average concentration of the top layer at a lower level.

There is also evidence that the PCE is being degraded to TCE in the bottom layer. Regions of low PCE concentration correlate with regions of high TCE concentration as demonstrated in the contour plots below in Figure 22a. The thick contour line was drawn on the TCE concentration contour map demarking where higher concentrations of TCE were occurring. This contour was then transposed onto the PCE concentration contour map. This is a visual demonstration suggesting that PCE is being degraded to TCE.

An additional observation is that the TCE concentration in the bottom left corner of the contour plot in Figure 22a, outlined in a dashed line, does not reach as high a concentration as the other hot spots in the bottom layer. One reason for this could be that the TCE is actively transforming into cis-DCE in this area. Evidence of this transformation is seen below in Figure 22b, where cis-DCE concentrations are above

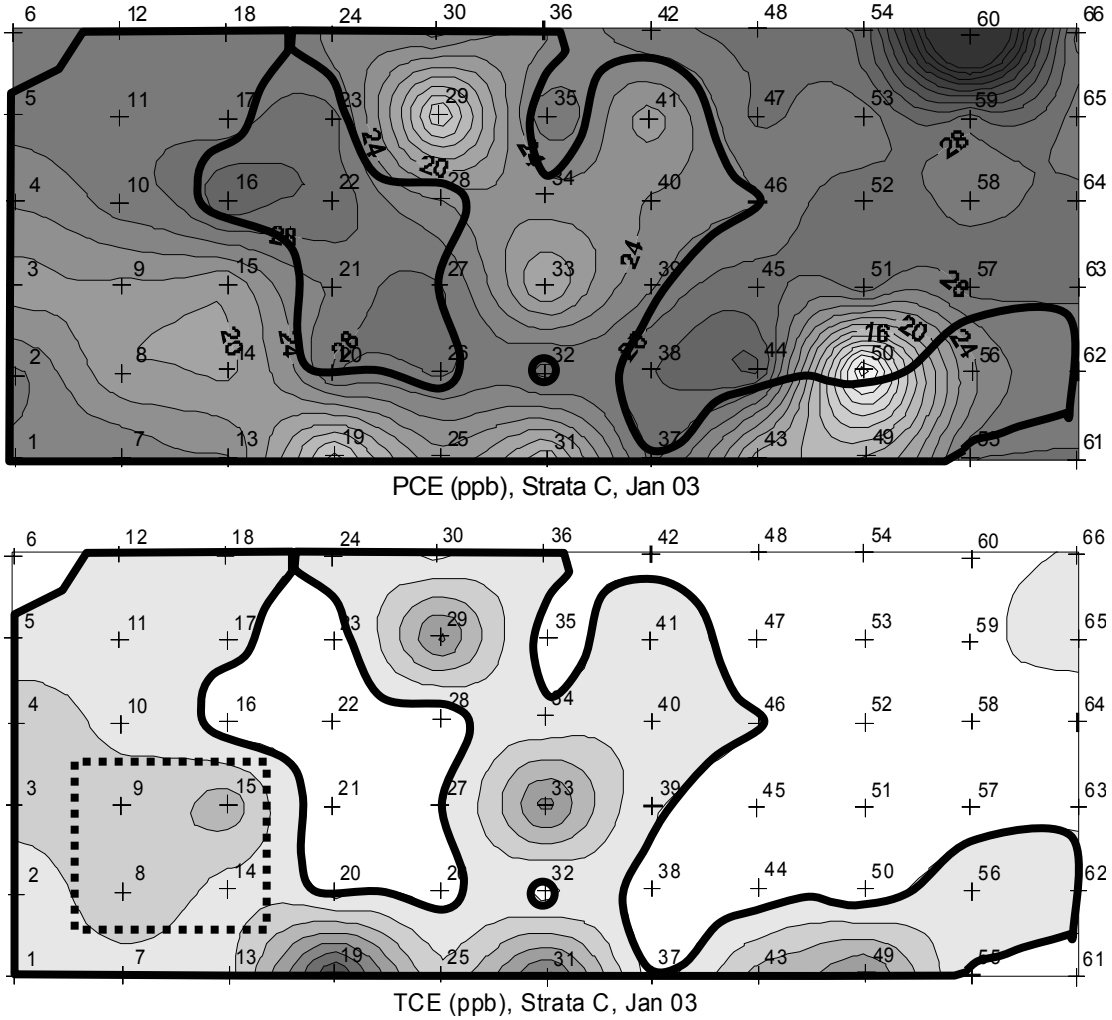


Figure 22a. Contour Plots of PCE and TCE Concentration Trends in Bottom Layer
The solid contour line depicts an area of increased TCE concentration in the bottom layer, which is transposed up to the PCE concentration plot to show an inverse correlation. The small dashed outline depicts an area of moderate TCE concentration.

average in this area. Another correlation is the large area on the right of the TCE contour plot above, where there are no high concentrations of TCE. This section of the thick outline above has been transferred onto the cis-DCE contour plot in Figure 22b below with a thick dashed line to show the correlation between low concentrations of TCE in the bottom layer and raised concentrations of cis-DCE.

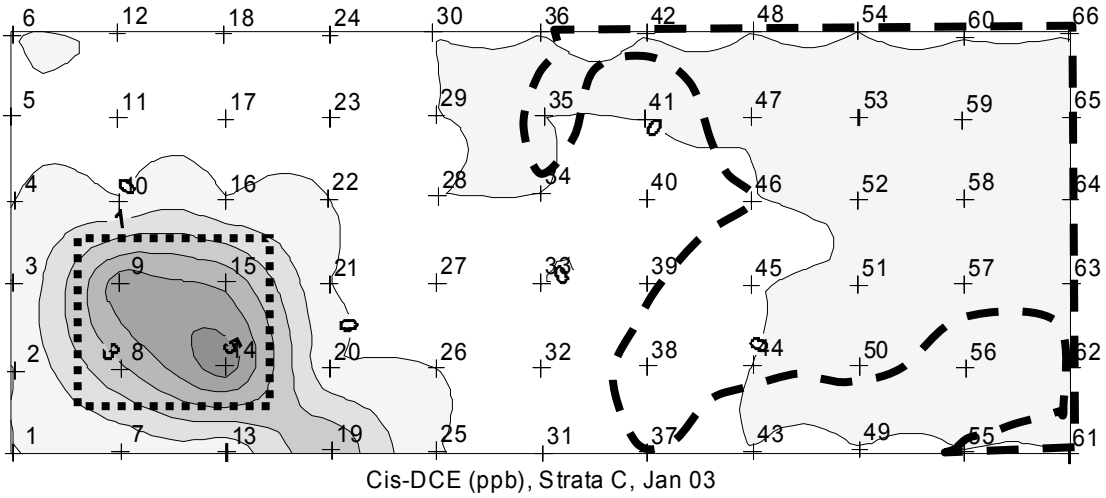
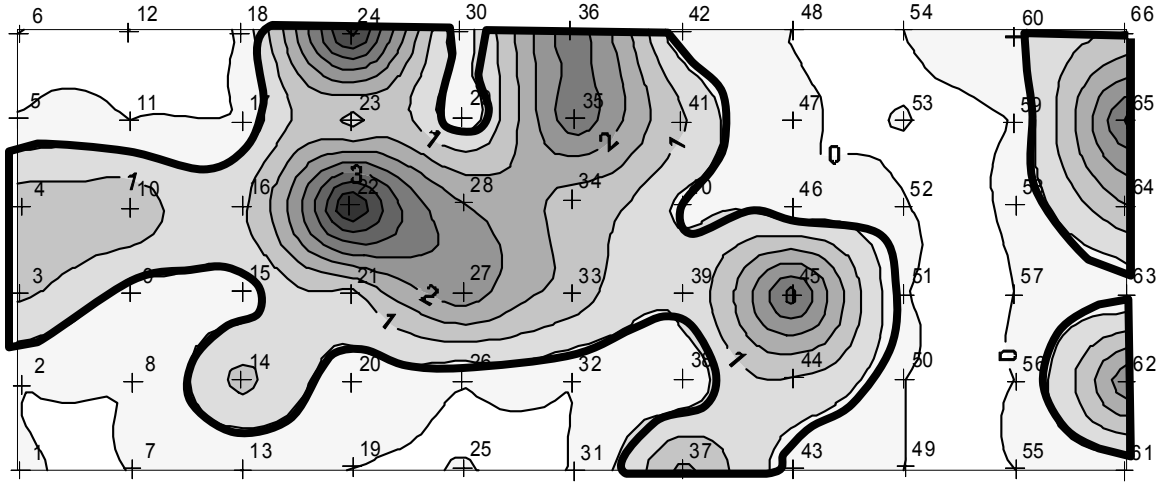


Figure 22b. Contour Plot of cis-DCE Concentration Compared to TCE in Bottom Layer. The small dashed outline depicts an area of high cis-DCE concentration that is transposed back to Figure 22 as a comparison to the TCE concentration plot. The large dashed line depicts an area of no TCE concentration in the bottom layer.

The contour maps of TCE and cis-DCE in the middle and top layers demonstrate a strong positive correlation. This relationship is unexpected as one would reason that a high concentration of cis-DCE would result from TCE degrading to a lower concentration such as the inverse relationship demonstrated between PCE and TCE. The correlation between TCE and cis-DCE is outlined in Figure 23 below.



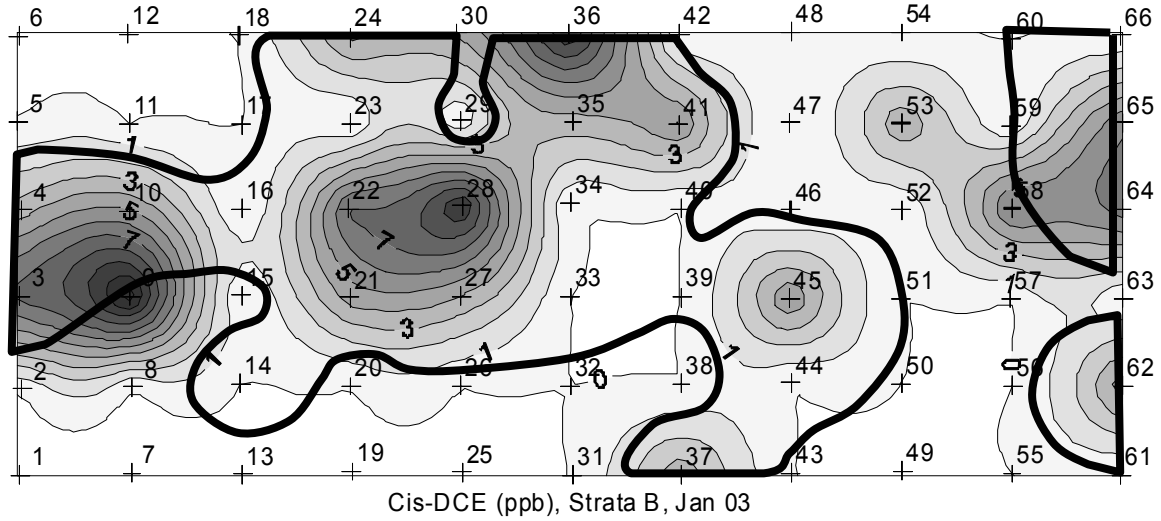


Figure 23. Contour Plots of TCE and cis-DCE Concentration in Middle Layer. Thick line outlines increased TCE concentrations in the middle layer and is transposed down to the cis-DCE plot for comparison of trends.

Water Quality Parameter Analysis

In addition to the relationships between the concentrations of the analytes in the wetland strata, other parameters such as temperature, Oxidation Reduction Potential (ORP), Dissolved Oxygen (DO), specific conductivity, and pH can give additional evidence as to what processes might be occurring. The data gathered from the YSI water

monitoring sonde was compiled and is presented in contour plots. The data from the two sample runs completed consecutively on the 8th and 9th of January 2003 correlate very well and show repeatability. Although the measurements correlate the variation within each layer and between the layers was high in some cases. A third run completed in December 2002 had less of a correlation with the two runs in January. The six wells provided evidence of dominating conditions, but additional wells are required to get an accurate picture of conditions in each layer as they correlate to the sampling piezometers. The data collected on 9 Jan 03 is used in the following discussions as a starting point for further research (See Appendix J for raw data and see Appendix K for contour plots).

The first parameter examined was ORP. The ORP seems to increase from the bottom layer to the top, mirroring the decrease in dissolved oxygen. The ORP measurements show that the bottom layer's ORP averages –19 ± 33 mV ranging from –72 to +30 mV while the middle layer ORP averages –90 ± 28 mV ranging from –118 to –22 mV with 5 of the 6 sample locations reading below –90 mV (see Figure 24 below). The ORP continues to drop moving to the top layer with an average ORP of –100 ± 12.

The next parameter examined was DO. When oxygen is present in ground water aerobic microorganisms dominate the system under less reduced conditions. The first step in the reduction of PCE will not be initiated until all of the oxygen is taken out of the system. The relatively high concentrations of PCE found in the bottom layer indicate that highly reducing conditions have not been achieved. The development of increased reducing conditions between the bottom and middle layers correlates with observed decreasing DO concentrations seen below in Figure 25 contour plots. The average DO concentration in the middle of the bottom layer was 1.68 mg/L with a wide range

between 0.08 and 4.07 mg/L. Moving to the middle layer, the average DO concentration drops to 0.20 mg/L with a much tighter range between 0.08 and 0.52 mg/L. The wide range of DO concentrations in the bottom layer is the result of wells 3 and 4 registering

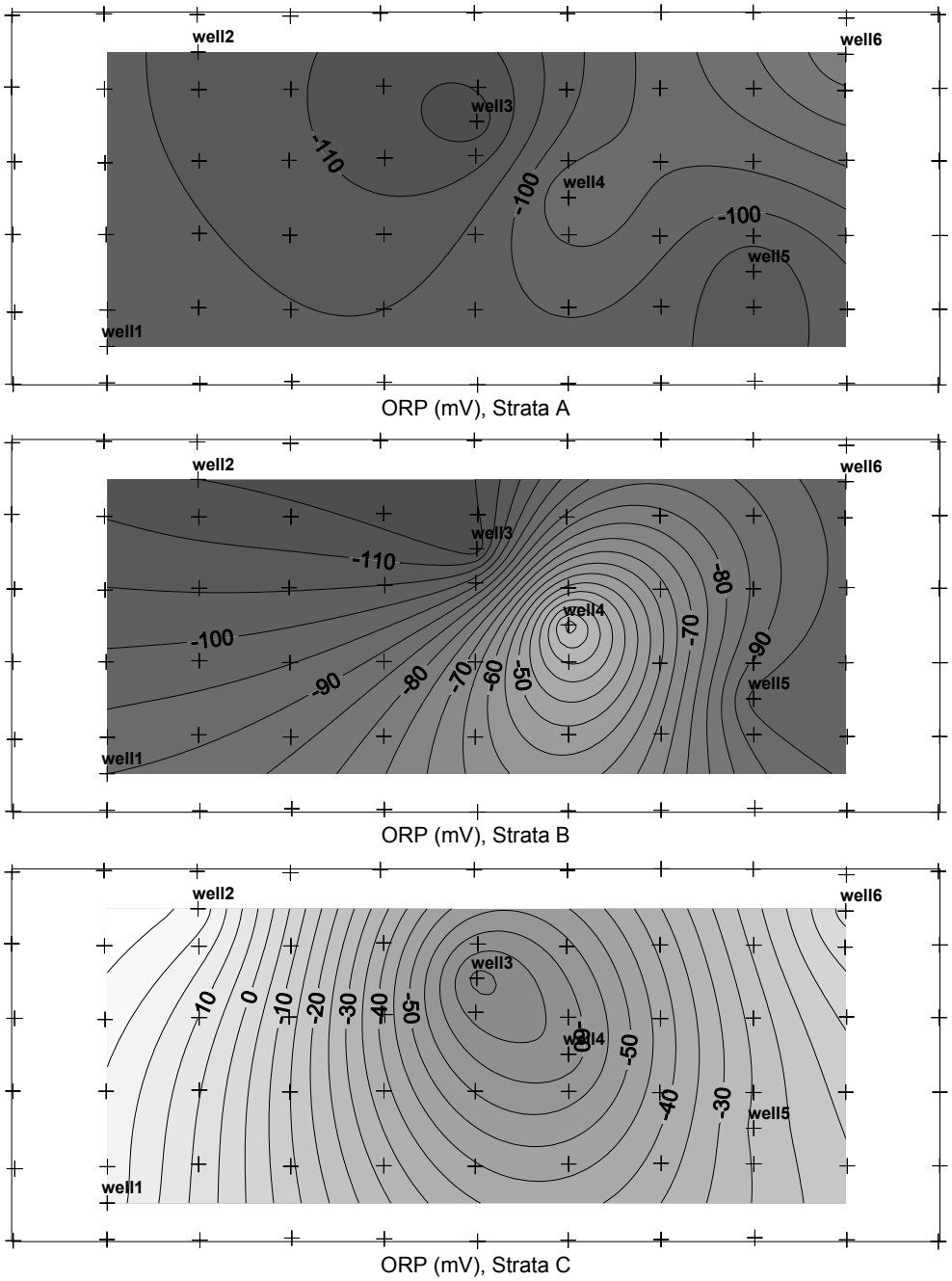


Figure 24. Contour Plots of Oxidation Reduction Potential (9 Jan 03)

below 0.15 mg/L in the center of the wetland. The reduction of PCE seems to be occurring in this same location as witnessed before in the PCE concentration contours

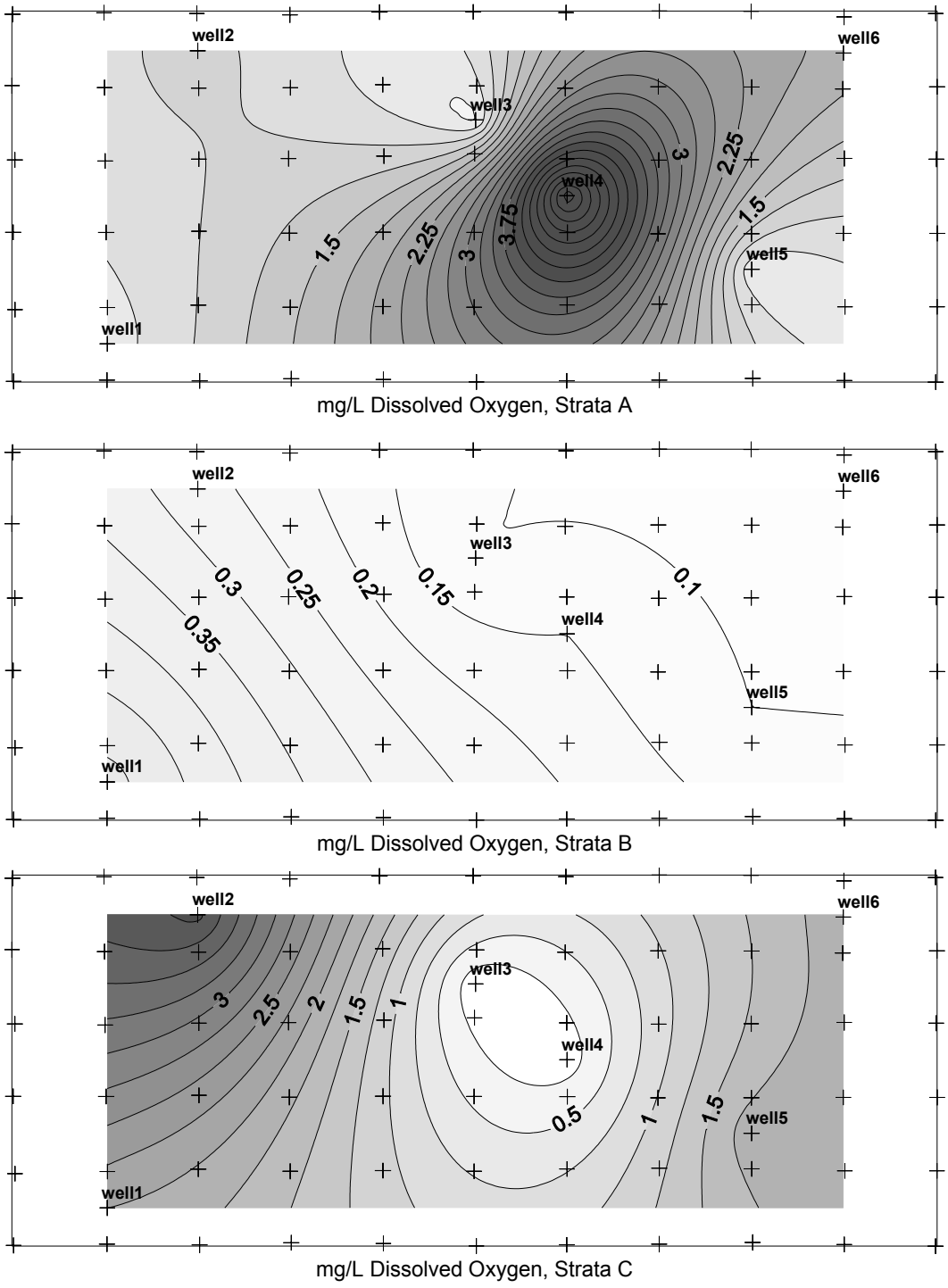


Figure 25. Contour Plots of DO Concentration (9 Jan 03)

(see Appendix C-I for PCE concentration contours). Although inflow DO concentrations were not taken, it is believed that the inflow DO concentration is much higher than the average in the bottom layer. The trend of decreasing DO concentration and the rapid degradation of PCE support the ORP measurements indicating increasingly reductive conditions exist as the water moves from the bottom to the middle layer. With these trends it is then logical to assume that the water being pumped into the wetland is from an oxygen rich aquifer devoid of natural organic matter.

The data collected in this study is proving some previous assumptions wrong. During the design of the wetland, it was assumed that the available oxidizing agents (O_2, NO_3^-, and SO_4^{2-}) would be rapidly reduced in the first portion of the bottom layer before the water reached the middle of the bottom layer. Thus, a strongly reduced (<-200 mV ORP) environment would be established supporting methanogenesis and the subsequent cometabolic destruction of PCE. The evidence laid out here indicates that this is not the case. The presence of increased oxygen concentrations in the bottom layer and an ORP higher than what is required for methanogenesis, as well as the highest concentrations of NO_3^- and SO_4^{2-} in the bottom layer (Kovacic, 2003) indicate that methanogenesis is not occurring in the bottom layer. An analysis of methane and hydrogen concentrations would add additional weight of evidence as to whether methanogenesis is occurring. The evidence also suggests that if methanogenesis is occurring, it would most likely happen between the middle of the bottom layer and the middle of the middle layer. But again, the ORP measurements at this point do not support methanogenic activity dominating any portion of the wetland. Reductive dechlorination, then, could be the dominating

mechanism causing the reduction of PCE concentrations between the bottom and middle layers.

The appearance and subsequent disappearance of cis-DCE and VC as the water moves through the wetland falls in line with what is expected in reductive dechlorination of PCE as discussed with Figures 12 and 13 above (see Appendix C-III and –IV concentration plots). These chemicals are biologically degraded fastest under aerobic conditions, VC being degraded the fastest. The average concentrations of both chemicals increase dramatically from the bottom layer to the middle layer supporting the theory that TCE is being degraded. Then the cis-DCE and VC average concentrations decrease moving into the top layer to a concentration comparable to the bottom layer. The most reducing conditions seen were in the top layer, while the DO concentration increased slightly from the middle to the top layer, giving mixed indications that an aerobic environment was responsible for the degradation of the less chlorinated degradation products. Between the middle of the top layer and the outflow weir, the concentrations of these chemicals were reduced to below the detection limits of the methodology, indicating that they were possibly oxidized in the top six inches of the wetland. This is supported by the fact that highly organic wetland soils tend to be anaerobic except for the top few inches. The plant root systems also transport oxygen into the wetland soils through their root rhizomes where the chemicals can be degraded in small microenvironments. Another possibility is that the cis-DCE and PCE did make it to the surface in low concentrations and were evaporated into the atmosphere. Additional research is needed to characterize the mechanisms responsible for the loss of the less chlorinated degradation products.

As a note, 36 samples were taken from the damaged cell number 2 and analyzed in the GC. This data can be found in Appendix M. The samples were taken on 11 December 2002 from the 18 newly installed wells and 18 piezometers (6 nests each). Even though there were leaks in the liner with a loss of up to 1/3 of the flow out the bottom (Blalock, 2003), the concentration data shows that the levels of PCE were being reduced as the water passed to the top layer. This data could be useful if the wetland is recommissioned for further study.

Error Analysis

A preliminary error analysis was done to examine the method error and provide a level of confidence in the concentration data that was generated. To data for this error analysis was gathered from duplicate samples of the inflow and outflow taken on four separated days. Since only PCE and TCE were found in these samples, this analysis can only be applied to each of them and not to Cis-DCE or VC.

These error values were calculated by first taking the difference in concentration of each of the duplicate sample sets. Next, the four differences were averaged. Lastly, the standard deviation and 95% confidence intervals were calculated to examine the error in the method of analysis. As a note, error from the calibration curve is not included here. The data and results of the calculations can be found in Appendix E. Summary of the resulting data can be found below in Table 13.

This error analysis shows that, on the whole, the method error in calculating the PCE concentration in a sample is higher than the method error of TCE. This is mainly

Table 13. Method Error Analysis for PCE and TCE

	Inflow		Outflow	
Average Conc.	32.59 ± 0.011	0.170 ± 0.699	8.637 ± 0.807	0.509 ± 0.041
	PCE Conc. (ppb)	**TCE Conc. (ppb)**	**PCE Conc. (ppb)**	**TCE Conc. (ppb)**
Average of Differences	0.35592	0.00368	0.16422	0.00167
Standard Deviation	0.16898	0.00492	0.14845	0.00094
95% Confidence Interval	0.16560	0.00482	0.14548	0.00092

due to the fact that the chromatogram peak for PCE had to be manually integrated by drawing a baseline with the ChemStation software. A hump in the baseline on the GC chromatogram did not allow the auto integration function to identify a consistent peak. The subsequent manual integration by the operator brought additional variability into the process, which is demonstrated by the higher average differences and higher 95% confidence intervals for PCE. Manual integration for VC was also required about 40% of the time to avoid the affect of an unidentified overlapping peak. Cis-DCE and TCE never required manual integration at concentrations over about 0.4 ppb concentration. Below 0.4 ppb the peaks had to be manually integrated, but this error in such small concentrations does little to affect the overall average concentrations for an entire wetland layer. Examples of chromatograms that required manual integration can be seen in Appendix L.

An estimate of the total method error can be gained from this information by adding the value of the 95% confidence interval to the average difference between two replicates. From this simple analysis, it is assumed that the method error for PCE is less than ± 0.52 ppb for concentrations in the 30 ppb range and less than ± 0.31 ppb for

concentrations in the 8 ppb range. The method error for TCE using the same reasoning is assumed to be less than ± 0.01 ppb for the low concentrations at which it was observed. The method errors for the other three analytes probably fall in this range. The error in determining the VC and Cis-DCE concentrations is probably less than the PCE concentration errors due to the fact that they were successfully integrated by the auto-integration function eliminating human error of manually drawing the baseline. The error in determining the VC and Cis-DCE concentrations is probably greater than the VC concentration errors due to the fact that their chromatogram peaks were smaller.

Method Detection Limit

A Method Detection Limit (MDL) is used to quantify the minimum concentration of an analyte that can be measured and reported with a desired level of confidence that the analyte concentration is greater than zero (USEPA, 1992). This concept is critically important when monitoring hazardous waste sites where detection of a contaminant gives evidence that down gradient water quality is contaminated. The smallest inaccuracy of measurement could deem the offending facility in the area in or out-of-compliance (Maillard and Williams, 2003). The MDL is less critical for this research effort as there are no regulatory requirements to be met and low concentrations below 1 ppb have little impact on the analysis being done. The MDL is a statistical estimate of the true population determined from a specific set of data. The MDL helps determine the lowest concentration of a compound (analyte signal) that can be distinguished from noise. The

USEPA recommends a single concentration design at a minimum, which was completed for this effort using a 99% confidence level (USEPA, 1992).

A minimum analysis of seven replicate standard solutions is required to determine the MDL with a 95% confidence level. The concentration range for this analysis is generally 1 to 5 times the expected MDL. These standards are then run through the identical analytical procedure used to analyze field samples. The MDL is then calculated using the following formula (USEPA, 1992):

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

where: s = standard deviation of measured concentrations of n samples
n = number of replicate standard determinations
t = Student's t value (t = 3.14 with n-1 degrees of freedom at 1% confidence level when n = 7)
α = Confidence level (1% for this analysis)

The expected MDL for each of the analytes is probably different. For this study, an adequate MDL for all the analytes would be less than 0.5 ppb. A standard solution of 1.0198 ppb was deemed to be sufficient for determining the MDL and was made using the custom mix solution containing all six analytes purchased from SUPELCO, Bellefonte, PA. The same procedure for preparing standard solutions was used in preparing the solutions for the MDL calculations. One stock solution of 22.72 ppb VOC mix was prepared and subsequently used to make the individual 1.0819 ppb standard solutions for the analysis. The data table for the MDL calculations is shown in Appendix E. The Limit of Detection (LOD) and the Limit of Quantitation (LOQ) can also be determined from these samples by taking the standard deviation of the seven samples and

multiplying it by 3 for the LOD and multiplying it by 10 for the LOQ (Christian, 1994). The results are listed below in Table 14.

Using this procedure the highest MDL for an analyte that was detected in the samples was 0.17 ppb for PCE. Although concentrations observed below the MDL are questionable, the researcher opted to include these values to indicate where trace amounts of the substances were seen. The affect of including these small amounts on the statistics is minimal. Overall the MDLs and the LODs calculated were in close agreement as expected.

Table 14. Method Detection Limits (MDLs), Limits of Detection (LOD), and Limits of Quantitation (LOQ) for All Analytes

Analyte:	VC	T-DCE *	C-DCE	TCE	PCE
MDL:	0.1577	0.1968	0.0874	0.0908	0.1692
LOD:	0.1506	0.1880	0.0835	0.0868	0.1617
LOQ:	0.5021	0.6267	0.2782	0.2893	0.5390

* Not detected in any sample.

A few secondary observations can be made from the data generated for the MDL calculations. The first observation is that the concentrations of the analytes seemed to decrease over the time that they were analyzed in the GC. Each sample run lasted approximately 32 minutes giving a time span of 3.7 hours between the analysis of the first sample and the last. In this short time the VC concentration dropped by more than 11% and the PCE concentration dropped by more than 18%. This trend is graphed below in Figure 26. The apparent decrease in concentrations over time could be examined further to determine how this affects concentrations in both the standard preparations and the sample matrix itself.

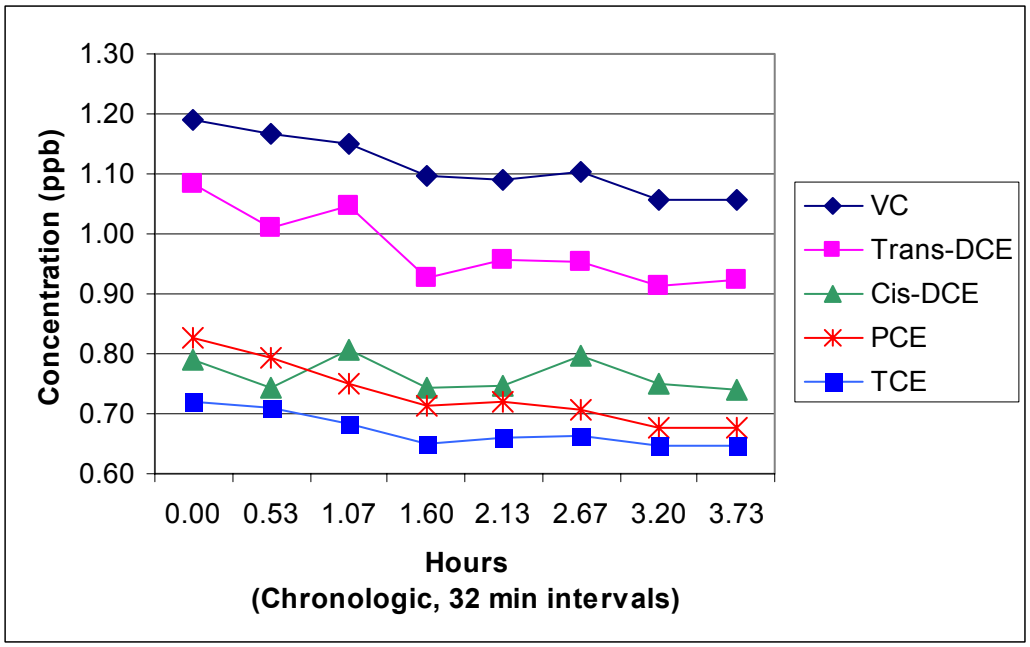


Figure 26. Concentrations of Eight 1.0819 ppb Standard Solutions Graphed Over Time Shows decreasing concentrations over time possibly do to degradation as well as varying starting concentrations for each of the analytes in the custom mix solution.

The second observation was that the concentrations of the analytes in the custom mix used for the MDL calculations varied by as much as 40%. The concentrations in the first vial ranged from a high of 1.19 ppb for VC to a low of 0.72 ppb for TCE. This could have been the result of poor quality control in the preparation of the custom mixes.

Separate ampules of standard mix were used to first, generate the calibration curve and second, to analyze the MDLs. One ampule of standard mix solution was used for each operation. The concentrations in the two separate ampules could have been slightly different causing the analysis of concentrations to be off.

This difference in concentrations could also be caused by different degradation rates between the chemicals. The preparation of the standards required them to be rotated for 24 hours to completely dissolve the chemicals. This time, along with the analysis

time, could allow the chemicals to degrade. The VC and Trans-DCE concentrations were nearer to the 1.0198 ppb standard concentration while the other analyte concentrations were about 30% lower.

V. Conclusions and Recommendations

The purpose of this thesis was to study a constructed wetland to determine and characterize the degradation of chlorinated solvents and provide additional weight of evidence that the wetland is degrading PCE to innocuous products. This study is a follow-up to the initial effort (Opperman, 2002) concluded one year ago, that included the installation of sampling piezometers, development of a sampling methodology, and contaminant concentration determination with a purge-and-trap gas chromatograph (GC). This research employed a similar methodology as before for determining the levels of PCE and its biodegradation byproducts throughout the three horizontal sampling strata in the wetland, as well as the inflow and outflow to and from the wetland. Additionally, 6 nests of 3-2 ¼ inch diameter piezometers were installed for the use of a water monitoring sonde to collect other water quality parameters such as Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP), temperature, conductivity, and pH. Both data collection efforts were successful, providing insights into what processes are occurring and how efficiently the wetland is performing.

This effort's data fell in line with the data generated last year with a few exceptions. The most notable difference was the detection of cis-DCE and VC this year that was not seen last year.

Answers to Specific Research Questions

1. *Do the concentrations of PCE and its daughter products in three layers of a constructed wetland give evidence of biodegradation?*

Yes, the concentrations of PCE and its daughter products do indicate that PCE is being degraded. The detection of PCE and TCE degradation products is the strongest proof to date that PCE is being degraded.

The average PCE and TCE concentrations were similar to those witnessed in Dec 01, showing the same concentration trends as the water moved through the wetland. In Jan 03 the reduction of PCE from the inflow to the top layer was 96.4%, which is greater than the 92.9% reduction in Dec 01. The average PCE concentrations in the top layers were 2.422 ± 0.557 ppb in Dec 01 and 1.178 ± 0.938 ppb in Jan 03. After removing the outliers, the concentrations were 0.813 ± 0.083 ppb and 0.171 ± 0.079 ppb respectively in the top layer, resulting in an improved reduction in PCE concentration from Dec 01 to Jan 03 of 97.0% to 99.3%.

The largest decrease in PCE concentration was observed between the middle of the bottom layer and the middle of the middle layer where the concentration drops by 94% as compared to only a 21% reduction between the inflow and the middle of the bottom layer. Although the removal rate of PCE increased in Jan 03 between the inflow and the top layer, the average PCE concentration in the outflow was elevated 35% higher than Dec 01 at 8.637 ± 0.807. This increase in PCE concentration in the outflow was

presumably due to the increase in bypassing flow caused by an increase in the pumping rate into the wetland.

The TCE concentrations remained below one ppb throughout the wetland again in Jan 03. As expected the TCE concentration changes lagged behind the PCE concentrations as the water moved vertically through the wetland. The TCE concentration increased in the bottom layer from 0.170 ± 0.011 ppb at the inflow to 0.771 ± 0.202 ppb in the center of the bottom layer and then decreased through the middle and top layers to 0.381 ± 0.195 ppb in the middle of the top layer. The average outflow concentration remained elevated at 0.509 ± 0.041 ppb for TCE presumably due to the bypassing flow.

The appearance of cis-DCE and VC lagged behind TCE as expected. As the average TCE concentrations in the middle layer decreased, the concentrations of cis-DCE and VC increased to their highest levels. The concentrations of cis-DCE and VC then fell in the top layer and were not detected in the outflow. This gives evidence that TCE is degrading into its daughter products. The absence of cis-DCE and VC in the outflow further proves that constructed wetlands can be used to completely degrade PCE without the accumulation of the more harmful degradation products such as VC.

This pattern of concentrations through the wetland (Figures 12 and 13) follows what would be expected for the biodegradation of PCE. Even though the concentrations of the contaminants are being reduced, the Minimum Contaminant Level (MCL) for PCE of 5 ppb is not being met in the outflow. It is believed that if the bypassing flow can be reduced, the concentration of PCE in the outflow will be greatly reduced. The other three contaminants do meet their MCL concentrations, but it is still not known how much of

the TCE, cis-DCE, and VC are being volatilized into the atmosphere vs being completely degraded in the top layer.

2. *Can pH, conductivity, temperature, oxidation-reduction potential, and dissolved oxygen be measured in a constructed wetland?*

As demonstrated in Chapters 3 and 4, with the installation of larger diameter piezometers, these water quality parameters can be measured, in place, with a YSI water monitoring sonde. The data gathered gave further insight into what conditions were dominating in each layer of the wetland. The observations indicated what processes were reducing the contaminant concentrations. Replicate measurements need to be done and additional monitoring wells need to be installed to increase the confidence in the data and value of the data when using it in conjunction with concentration measurements.

3. *Do measurements of oxidation-reduction potential and dissolved oxygen indicate that conditions exist for the complete dechlorination of PCE?*

The results of this study are inconclusive at this point, but some trends were observed that can guide future research designs in the wetland. The development of increasingly reduced conditions between the bottom and middle layers correlates with observed decreasing DO concentrations (see Appendix K for DO and ORP contour plots). Supporting evidence of reductive dechlorination was gained from the sonde measurements of ORP and DO.

The results of the water quality measurements do not support the original assumption that extremely reducing conditions supporting methanogenic activity and the cometabolic degradation of PCE are established in the bottom layer. However, the redox measurements between -200 mV and 0 mV do indicated that reductive dechlorination could be the dominant process. The decreasing concentration of dissolved oxygen (DO) paralleled with the decreasing Oxidation Reduction Potential (ORP) between the bottom and middle layers indicate that the water entering the wetland is oxygenated and that the most reduced conditions are occurring toward the top of the wetland. Further analysis of methane, ethene, ethane, and hydrogen concentrations are required to further characterize the prevailing conditions and reactions occurring throughout the wetland.

This thesis effort showed that useful information for characterizing the processes in a constructed wetland could be gathered through water sampling for purge-and-trap and gas chromatograph analysis and the use of a water monitoring sonde. Unlike the previous effort this study used data from one pass of the entire wetland, which proved to be adequate in characterizing the analyte concentrations.

Effort Strengths

This thesis effort was able to validate the sampling method and analytical procedure that was used in the previous effort. The results very closely paralleled those from samples taken in Dec 01, allowing the comparison of analyte concentration similarities and differences on a qualitative as well as quantitative level. The detection of

cis-DCE and VC in Jan 03 using the same equipment and a similar method helps prove that it was not present in the Dec 01 samples. This work has shown that VC can be identified and measured with the gas chromatograph's μECD.

A methodology for use of the YSI water monitoring sonde has been developed and employed successfully. The additional information from the data gathered from the sonde adds to the weight of evidence for the degradation of PCE to innocuous products.

The study characterized the level of PCE, TCE, cis-DCE, and VC throughout all layers of the wetland as well as the inflow and outflow of the wetland. It was shown that PCE is being degraded to three of its daughter products. It also indicated where these degradations are most likely occurring. The relationships between this degradation and other water qualities such as oxygen content and redox potential was also demonstrated adding weight of evidence to the characterization of the Terminal Electron Accepting Processes that are dominating the wetland layers.

Effort Limitations

Limits in this effort are that the lighter daughter products of PCE degradation (ethane, methane, and ethylene) were not examined. This limits the full characterization of the processes occurring in the wetland and does not allow the use of mass balances for further efficiency calculations. It is not know whether these lighter components are detectable in low concentrations with the current GC FID setup.

The measurement of hydrogen concentrations were not done in this effort. These measurements would add evidence toward what terminal electron accepting process was dominating.

Another limitation in this effort is that it was not determined whether the cis-DCE and VC present in the top layer was degraded before it reached the surface or whether it was volatilized into the atmosphere. It will be important to understand what mechanism is reducing these compound's concentrations for the design of future wetlands.

Besides concentration data and water quality measurements, no other data was gathered to help describe the fate of the PCE and the daughter products. There was no attempt at determining what microorganisms are present in the system possibly degrading the contaminants. It is still unknown what the effect of adsorption of the analytes onto the organic wetland soil has on the concentrations of those analytes.

It was discovered that the analytes of interest degrade substantially during the analytical process. There was no effort to determine how much the analytes will degrade in a wetland sample in order to come up with an adjustment factor.

Recommendations for Further Study

1. Complete sampling passes through the wetland at different times during the growing season such as early spring and summer. One complete pass through the wetland for VOC and water quality analysis for each season should give enough data to compare and contrast the results gathered thus far.

2. Analyze inflow and outflow samples on a weekly basis throughout the year to identify any seasonal trends. The data gathered over one month this year showed that there could be some variation in concentrations.
3. Run a more complete error analysis to determine the method error for each analyte and for the sonde measurements.
4. Confirm or disprove the high concentrations of VC seen in the middle layer in this study. The accumulation of the carcinogenic VC at such high levels would have to be addressed in future designs if the condition persists.
5. Find a way to determine if the cis-DCE and VC concentrations observed in the top layer are degraded before they reach the surface or if they are simply volatilizing into the atmosphere.
6. Acquire better redox condition information with multiple readings with the sonde over a longer period of time. This effort could be enhanced with the employment of buried redox probes that could remain in place without disturbance of the soil water.
7. Take samples to be analyzed for Hydrogen concentration. Hydrogen concentration is the most definitive way to substantiate which terminal electron accepting process is occurring.

Appendix A: Chemical Concentration Raw Data

I. GC signal and Calculated Concentrations for the Top Layer

Layer a	Top Layer								
Date		GC Signal (Aea Under the Curve)				Concentration (ppb)			
Collected	Well	VC	C-DCE	TCE	PCE	VC	C-DCE	TCE	PCE
4-Jan-03	1 a	30.74	0	687.8	2983	0.151	0	0.187	0.204
4-Jan-03	2 a	79.69	0	57.1	2120	0.393	0	0.016	0.145
4-Jan-03	3 a	259.39	0	228.2	1771	1.278	0	0.062	0.121
4-Jan-03	4 a	52.91	0	62.7	1324	0.261	0	0.017	0.091
4-Jan-03	5 a	44.23	0	0	1094	0.218	0	0	0.075
4-Jan-03	6 a	0	0	0	1009	0	0	0	0.069
4-Jan-03	7 a	116.77	0	295.2	2452	0.575	0	0.080	0.168
4-Jan-03	8 a	567.16	0	0	892	2.794	0	0	0.061
4-Jan-03	9 a	0	101.91	3469.8	22029	0	6.88	0.945	1.508
4-Jan-03	10 a	0	0	4242.4	368425	0	0	1.155	25.218
4-Jan-03	11 a	0	0	79.6	2919	0	0	0.022	0.200
4-Jan-03	12 a	0	0	0	1367	0	0	0	0.094
4-Jan-03	13 a	535.84	0	90.0	1261	2.640	0	0.024	0.086
4-Jan-03	14 a	97.32	0	39.7	876	0.480	0	0.011	0.060
4-Jan-03	15 a	49.27	0	0	712	0.243	0	0	0.049
4-Jan-03	16 a	0	0	6250.2	226681	0	0	1.702	15.516
4-Jan-03	17 a	0	0	2564.0	11194	0	0	0.698	0.766
4-Jan-03	18 a	115.32	0	36.2	1045	0.568	0	0.010	0.072
4-Jan-03	19 a	0	0	7752.1	67514	0	0	2.111	4.621
4-Jan-03	20 a	0	44.400	582.4	1326	0	2.9975	0.159	0.091
4-Jan-03	21 a	0	55.026	5798.3	77168	0	3.7149	1.579	5.282
4-Jan-03	22 a	0	84.041	9762.1	161819	0	5.6737	2.658	11.076
4-Jan-03	23 a	0	139.40	11447	45123	0	9.411	3.117	3.089
4-Jan-03	24 a	75.15	0	1119.9	2305	0.370	0	0.305	0.158
5-Jan-03	25 a	0	0	0	1076	0	0	0.000	0.074
5-Jan-03	26 a	102.82	0	0	430	0.507	0	0	0.029
5-Jan-03	27 a	54.22	0	1262.8	2454.0	0.267	0	0.344	0.168
5-Jan-03	28 a	0	0	1394.7	9218	0	0	0.380	0.631
5-Jan-03	29 a	0	124.90	778.6	758	0	8.432	0.212	0.052
5-Jan-03	30 a	0	113.29	1834.9	2156	0	7.6482	0.500	0.148
5-Jan-03	31 a	0	0	728.1	13544	0	0	0.198	0.927
5-Jan-03	32 a	0	0	0	397	0	0	0	0.027
5-Jan-03	33 a	0	0	1505.1	13188	0	0	0.410	0.903
5-Jan-03	34 a	0	58.24	1426.3	7240	0	3.9318	0.388	0.496
5-Jan-03	35 a	0	50.955	14889	41107	0	3.4401	4.054	2.814
5-Jan-03	36 a	0	84.358	5868.6	18458	0	5.6951	1.598	1.263
5-Jan-03	37 a	0	0	3391.7	962	0	0	0.924	0.066
5-Jan-03	38 a	16.01	0	0	313	0.079	0	0.000	0.021
5-Jan-03	39 a	86.28	0	184.7	4663	0.425	0	0.050	0.319
5-Jan-03	40 a	0	0	0	1051	0	0	0.000	0.072
5-Jan-03	41 a	0	0	1114.3	1584	0	0	0.303	0.108
5-Jan-03	42 a	0	0	83.0	265	0	0	0.023	0.018
5-Jan-03	43 a	0	0	0	446	0	0	0	0.030
5-Jan-03	44 a	38.28	0	0	1604	0.189	0	0	0.110
5-Jan-03	45 a	0	0	0	224	0	0	0	0.015
5-Jan-03	46 a	266.64	0	0	149	1.314	0	0	0.010
5-Jan-03	47 a	263.30	0	0	334	1.297	0	0	0.023
5-Jan-03	48 a	89.79	0	0	194	0.442	0	0	0.013
5-Jan-03	49 a	0	0	0	122	0	0	0	0.008
5-Jan-03	50 a	47.29	0	0	0	0.233	0	0	0
5-Jan-03	51 a	74.12	0	124.8	0	0.365	0	0.034	0.000
5-Jan-03	52 a	0	0	52.4	656	0	0	0.014	0.045
5-Jan-03	53 a	0	71.090	42.6	265	0	4.7994	0.012	0.018
5-Jan-03	54 a	45.05	0	0	196	0.222	0	0	0.013
5-Jan-03	55 a	0	0	0	432	0	0	0	0.030
5-Jan-03	56 a	45.93	0	0	1029	0.226	0	0	0.070
5-Jan-03	57 a	0	0	0	343	0	0	0	0.023
5-Jan-03	58 a	0	0	0	331	0	0	0	0.023
5-Jan-03	59 a	118.80	0	0	250	0.585	0	0	0.017
5-Jan-03	60 a	0	0	732.7	1321	0	0	0.200	0.090
5-Jan-03	61 a	156.00	0	104.3	419	0.769	0	0.028	0.029
5-Jan-03	62 a	0	0	0	163	0	0	0	0.011
5-Jan-03	63 a	0	0	0	229	0	0	0	0.016
5-Jan-03	64 a	0	50.486	589.4	1454	0	3.4084	0.161	0.100
5-Jan-03	65 a	0	102.12	1667.3	988	0	6.8943	0.454	0.068
5-Jan-03	66 a	0	0	0	166	0	0	0	0.011

II. GC signal and Calculated Concentrations for the Middle Layer

Layer B	Middle Layer								
Date		GC Signal (Aea Under the Curve)				Concentration (ppb)			
Collected	Well	VC	C-DCE	TCE	PCE	VC	C-DCE	TCE	PCE
6-Jan-03	1 b	49.50	0	173.1	3087	0.244	0	0.047	0.211
6-Jan-03	2 b	37.76	0	0	1346	0.186	0	0	0.092
6-Jan-03	3 b	0	109.09	4096.1	1214	0	7.365	1.115	0.083
6-Jan-03	4 b	0	51.731	4976.8	5089	0	3.4924	1.355	0.348
6-Jan-03	5 b	0	0	0	674	0	0	0	0.046
6-Jan-03	6 b	0	0	0	526	0	0	0	0.036
6-Jan-03	7 b	7450.36	0	43.4	952	36.707	0	0.012	0.065
6-Jan-03	8 b	0	0	0	502	0	0	0	0.034
6-Jan-03	9 b	0	174.17	992.0	575	0	11.759	0.270	0.039
6-Jan-03	10 b	0	76.531	5606.1	174716	0	5.1668	1.527	11.959
6-Jan-03	11 b	0	0	0	1157	0	0	0	0.079
6-Jan-03	12 b	0	0	0	630	0	0	0	0.043
6-Jan-03	13 b	0	0	0	507	0	0	0	0.035
6-Jan-03	14 b	0	0	4509.8	82463	0	0	1.228	5.644
6-Jan-03	15 b	0	0	765.2	3451	0	0	0.208	0.236
6-Jan-03	16 b	0	0	3261.9	105484	0	0	0.888	7.220
6-Jan-03	17 b	111.76	0	100.0	1714	0.551	0	0.027	0.117
6-Jan-03	18 b	0	0	0	603	0	0	0	0.041
6-Jan-03	19 b	0	0	0	441	0	0	0	0.030
6-Jan-03	20 b	0	0	1054.5	6732	0	0	0.287	0.461
6-Jan-03	21 b	0	65.674	2751.1	10667	0	4.4337	0.749	0.730
6-Jan-03	22 b	0	106.31	17448.9	104160	0	7.1768	4.751	7.130
6-Jan-03	23 b	57.63	0	2736	14109	0.284	0	0.745	0.966
6-Jan-03	24 b	7051.00	64.000	15859.0	4468	34.740	4.3208	4.318	0.306
6-Jan-03	25 b	244.53	0.000	119.4	464	1.205	0	0.033	0.032
6-Jan-03	26 b	22722.6	0	0	359	111.95	0	0	0.025
6-Jan-03	27 b	221.00	57.714	8898.9	46316.4	1.089	3.8964	2.423	3.170
6-Jan-03	28 b	208.71	151.22	7330.7	24895	1.028	10.209	1.996	1.704
6-Jan-03	29 b	0	0	0	295	0.000	0	0	0.020
6-Jan-03	30 b	127.73	60.72	677.9	984	0.629	4.0992	0.185	0.067
6-Jan-03	31 b	124.95	0	77.9	815	0.616	0	0.021	0.056
6-Jan-03	32 b	126.38	0	0	290	0.623	0	0	0.020
6-Jan-03	33 b	120.40	0	5035.6	18459	0.593	0	1.371	1.263
6-Jan-03	34 b	170.42	0	4526.0	97312	0.840	0	1.232	6.661
6-Jan-03	35 b	0	52.208	10838	235722	0.000	3.5247	2.951	16.135
6-Jan-03	36 b	89.82	149.68	10509.7	28222	0.443	10.105	2.862	1.932
6-Jan-03	37 b	32157.6	55.890	6217.3	12240	158.44	3.7732	1.693	0.838
6-Jan-03	38 b	5331.72	0	79.3	605	26.269	0	0.022	0.041
6-Jan-03	39 b	726.98	0	2086.6	129049	3.582	0	0.568	8.833
6-Jan-03	40 b	282.94	0	1250.0	32940	1.394	0	0.340	2.255
6-Jan-03	41 b	292.89	75.656	4061.7	13542	1.443	5.1077	1.106	0.927
6-Jan-03	42 b	21707.5	0	0	591	106.95	0	0	0.040
9-Jan-03	43 b	70.99	0	669.4	5852	0.350	0	0.182	0.401
9-Jan-03	44 b	227.73	0	3485.6	89647	1.122	0	0.949	6.136
9-Jan-03	45 b	50.69	75.113	12186.9	6410	0.250	5.071	3.318	0.439
9-Jan-03	46 b	8892.12	0	147.8	1260	43.811	0	0.040	0.086
9-Jan-03	47 b	124.21	0	297.9	6807	0.612	0	0.081	0.466
9-Jan-03	48 b	101.51	0	0	738	0.500	0	0	0.050
9-Jan-03	49 b	107.04	0	0	635	0.527	0	0	0.043
9-Jan-03	50 b	172.71	0	0	514	0.851	0	0	0.035
9-Jan-03	51 b	115.56	0	53.6	488	0.569	0	0.015	0.033
9-Jan-03	52 b	67.68	0	81.3	633	0.333	0	0.022	0.043
9-Jan-03	53 b	125.55	57.614	74.2	635	0.619	3.8896	0.020	0.043
9-Jan-03	54 b	0	0	0	430	0.000	0	0	0.029
9-Jan-03	55 b	60.50	0	0	418	0.298	0	0	0.029
9-Jan-03	56 b	180.97	0	40.7	329	0.892	0	0.011	0.023
9-Jan-03	57 b	94.68	0	0	336	0.466	0	0	0.023
9-Jan-03	58 b	0	93.474	415.8	375	0.000	6.3106	0.113	0.026
9-Jan-03	59 b	5417.25	0	0	322	26.690	0	0	0.022
9-Jan-03	60 b	98.52	0	1574.9	2959	0.485	0	0.429	0.203
9-Jan-03	61 b	240.18	0	248.7	1517	1.183	0	0.068	0.104
9-Jan-03	62 b	409.82	69.529	9066.8	23740	2.019	4.694	2.469	1.625
9-Jan-03	63 b	75.13	0	72.8	694	0.370	0	0.020	0.048
9-Jan-03	64 b	462.46	97.045	5416.3	73390	2.278	6.5517	1.475	5.023
9-Jan-03	65 b	51.96	87.35	11395.0	44131	0.256	5.897	3.103	3.021
9-Jan-03	66 b	0	0	3566.5	7858	0.000	0	0.971	0.538

III. GC signal and Calculated Concentrations for the Bottom Layer

Layer c	Bottom Layer								
Date		GC Signal (Aea Under the Curve)				Concentration (ppb)			
Collected	Well	VC	C-DCE	TCE	PCE	VC	C-DCE	TCE	PCE
8-Jan-03	1 c	0	0	2307.2	373744	0	0	0.628	25.582
8-Jan-03	2 c	0	0	1961.8	389980	0	0	0.534	26.694
8-Jan-03	3 c	101.40	0	4612.4	303260	0.500	0	1.256	20.758
8-Jan-03	4 c	0	0	4815.4	354659	0	0	1.311	24.276
8-Jan-03	5 c	0	0	2551.6	389948	0	0	0.695	26.691
8-Jan-03	6 c	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
8-Jan-03	7 c	0	0	3127.3	378837	0	0	0.852	25.931
8-Jan-03	8 c	0	42.157	5373.8	293198	0	2.8461	1.463	20.069
8-Jan-03	9 c	0	69.75	4240.5	314420	0	4.7088	1.155	21.522
8-Jan-03	10 c	0	0	3121.9	396867	0	0	0.850	27.165
8-Jan-03	11 c	94.47	0	2857.6	394909	0.465	0	0.778	27.031
8-Jan-03	12 c	0	0	2668.8	392659	0	0	0.727	26.877
8-Jan-03	13 c	0	0	3008.3	355097	0	0	0.819	24.306
8-Jan-03	14 c	75.58	86.354	2883.2	283373	0.372	5.8299	0.785	19.396
8-Jan-03	15 c	0	56.063	6877.2	294301	0	3.7849	1.873	20.144
8-Jan-03	16 c	0	0	737.9	467046	0	0	0.201	31.969
8-Jan-03	17 c	0	0	2582.0	387286	0	0	0.703	26.509
8-Jan-03	18 c	0	0	2043.7	402910	0	0	0.556	27.579
2-Jan-02	19 c	0	45.339	15145.5	158058	0	3.0609	4.124	10.819
2-Jan-02	20 c	0	0	805.8	414853	0	0	0.219	28.396
2-Jan-02	21 c	0	0	807.9	380876	0	0	0.220	26.070
2-Jan-02	22 c	0	0	603.2	435697	0	0	0.164	29.823
2-Jan-02	23 c	0	0	701	423255	0	0	0.191	28.971
2-Jan-02	24 c	0	0	2124.5	371855	0	0	0.578	25.453
2-Jan-02	25 c	0	0	3748.7	313628	0	0	1.021	21.467
2-Jan-02	26 c	0	0	1051.9	417136	0	0	0.286	28.552
2-Jan-02	27 c	0	0	1659.4	412721.0	0	0	0.452	28.250
2-Jan-02	28 c	0	0	199.4	352014	0	0	0.054	24.095
2-Jan-02	29 c	0	0	9989.2	134762	0	0	2.720	9.224
2-Jan-02	30 c	0	0	1190.0	400424	0	0	0.324	27.408
2-Jan-02	31 c	0	0	12218.1	203650	0	0	3.327	13.940
2-Jan-02	32 c	0	0	914.9	422997	0	0	0.249	28.954
2-Jan-02	33 c	0	0	10231.5	253145	0	0	2.786	17.327
2-Jan-02	34 c	0	0	1904.9	342428	0	0	0.519	23.439
2-Jan-02	35 c	0	0	817	413020	0	0	0.223	28.271
2-Jan-02	36 c	0	0	2119.5	345788	0	0	0.577	23.669
2-Jan-02	37 c	0	0	801.7	417922	0	0	0.218	28.606
2-Jan-02	38 c	0	0	844.6	437567	0	0	0.230	29.951
2-Jan-02	39 c	0	0	2034.1	376017	0	0	0.554	25.738
2-Jan-02	40 c	0	0	2721.4	353374	0	0	0.741	24.188
2-Jan-02	41 c	0	0	3398.7	302716	0	0	0.925	20.720
2-Jan-02	42 c	0	0	1375.3	402426	0	0	0.374	27.545
2-Jan-02	43 c	0	0	6289.2	247193	0	0	1.713	16.920
2-Jan-02	44 c	0	0	677.7	480363	0	0	0.185	32.880
2-Jan-02	45 c	0	0	1218.7	422368	0	0	0.332	28.910
2-Jan-02	46 c	0	0	1925.0	376855	0	0	0.524	25.795
2-Jan-02	47 c	0	0	645.7	417084	0	0	0.176	28.549
2-Jan-02	48 c	0	0	1033.0	426845	0	0	0.281	29.217
2-Jan-02	49 c	0	0	9515.8	234354	0	0	2.591	16.041
2-Jan-02	50 c	0	0	0	2902	0	0	0	0.199
2-Jan-02	51 c	0	0	800.0	434414	0	0	0.218	29.735
2-Jan-02	52 c	0	0	869.5	429751	0	0	0.237	29.416
2-Jan-02	53 c	0	0	1628.2	388545	0	0	0.443	26.595
2-Jan-02	54 c	0	0	585.6	444449	0	0	0.159	30.422
2-Jan-02	55 c	0	0	1490.9	409747	0	0	0.406	28.047
2-Jan-02	56 c	0	0	3412.9	345070	0	0	0.929	23.620
2-Jan-02	57 c	0	0	983.7	422152	0	0	0.268	28.896
2-Jan-02	58 c	0	0	1787.3	397710	0	0	0.487	27.223
2-Jan-02	59 c	0	0	1685.7	416955	0	0	0.459	28.540
2-Jan-02	60 c	0	0	1566.5	872455	0	0	0.427	59.718
2-Jan-02	61 c	0	0	1494.8	412706	0	0	0.407	28.249
2-Jan-02	62 c	0	0	2213.1	378731	0	0	0.603	25.924
2-Jan-02	63 c	0	0	1675.0	416034	0	0	0.456	28.477
2-Jan-02	64 c	0	0	1260.7	418206	0	0	0.343	28.626
2-Jan-02	65 c	0	0	2190.1	394771	0	0	0.596	27.022
2-Jan-02	66 c	0	0	1885.9	398219	0	0	0.514	27.258

IV. GC signal and Calculated Concentrations for the Inflow and Outflow

Inflow Concentrations

Date	GC Signal		Conc (ppb)	
Collected	TCE	PCE	TCE	PCE
7-Dec-02	695	482467	0.189	33.024
8-Dec-02	N/A	N/A		
13-Dec-02	697	494232	0.190	33.829
15-Dec-02	686	490203	0.187	33.554
2-Jan-03	666.513	475342	0.181	32.536
4-Jan-03	575	480741	0.157	32.906
5-Jan-03	571.578	449778	0.156	30.787
6-Jan-03	577.920	479250	0.157	32.804
7-Jan-03	561.492	451157	0.153	30.881
8-Jan-03	N/A	N/A		
9-Jan-03	582.314	482293	0.159	33.012

Min	0.153	30.787
Max	0.190	33.829
Median	0.159	32.906
Sum	1.528	293.33
Average	0.170	32.593
Std Dev	0.016	1.070
95% CI	0.011	0.699

Outflow Concentrations

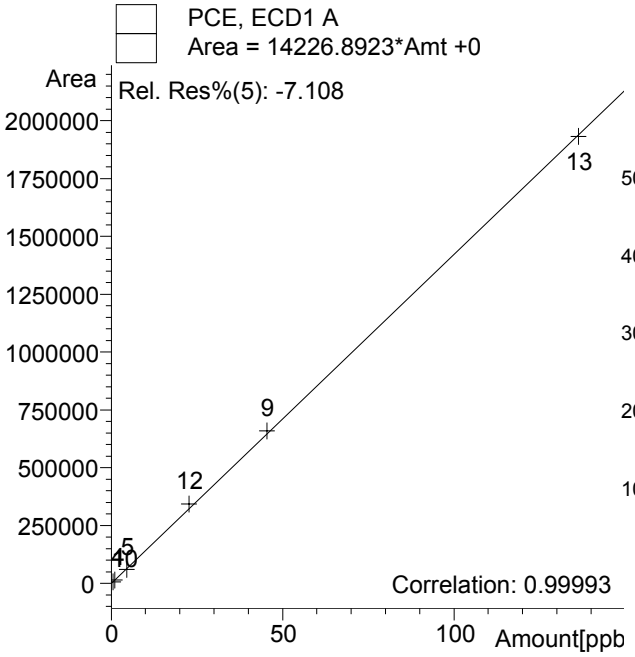
Date	GC Signal		Conc (ppb)	
Collected	TCE	PCE	TCE	PCE
7-Dec-02	1250.10	133666	0.340	9.149
8-Dec-02	1598.55	107111	0.435	7.332
13-Dec-02	1359.44	136319	0.370	9.331
15-Dec-02	1079.91	102827	0.294	7.038
2-Jan-03	1781.87	86511	0.485	5.922
4-Jan-03	1585.59	92540	0.432	6.334
5-Jan-03	1920.90	103763	0.523	7.102
6-Jan-03	1532.12	79497	0.417	5.441
7-Jan-03	1557.73	88307	0.424	6.044
8-Jan-03	1598.55	107111	0.435	7.332
9-Jan-03	1554.62	98031	0.423	6.710

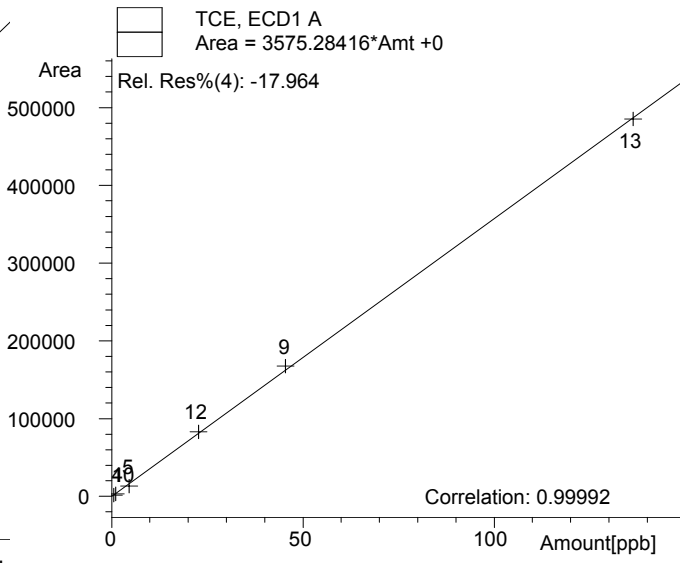
Min	0.294	5.441
Max	0.523	9.331
Median	0.424	7.038
Sum	4.580	77.74
Average	0.509	8.637
Std Dev	0.063	1.236
95% CI	0.041	0.807

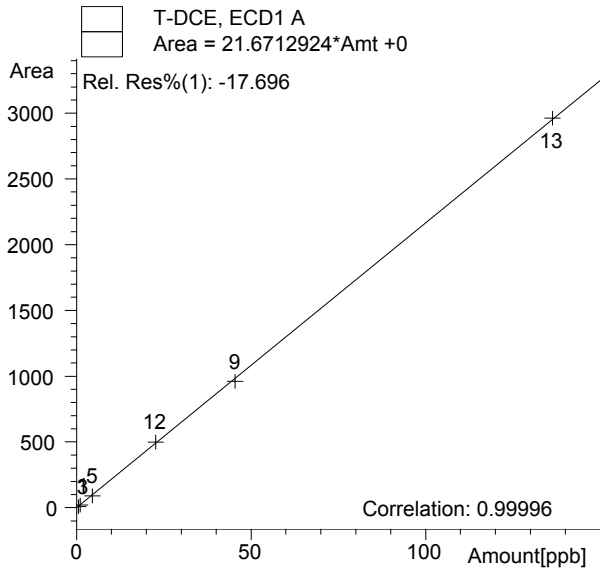
Appendix B: Calibration curves for PCE, TCE, Cis-DCE, Trans-DCE, and VC

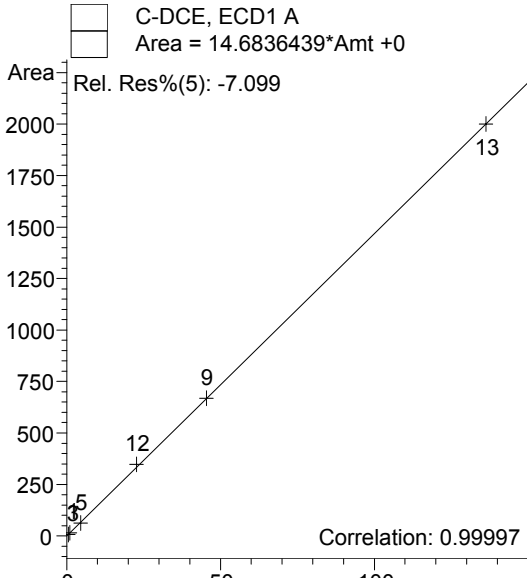
These calibration curves were prepared in the ChemStation software program. Each curve was generated from six concentrations of a standard solution (0.54095, 1.0820, 4.5454, 22.720, 45.4545, and 136.35 ppb). Each curve was forced through zero, which improved the R-squared value to over 0.999 for each of the analytes. The numbers on the regression line represent the standard run that was used.

I. Calibration curves for PCE, TCE, Cis-DCE, and Trans-DCE

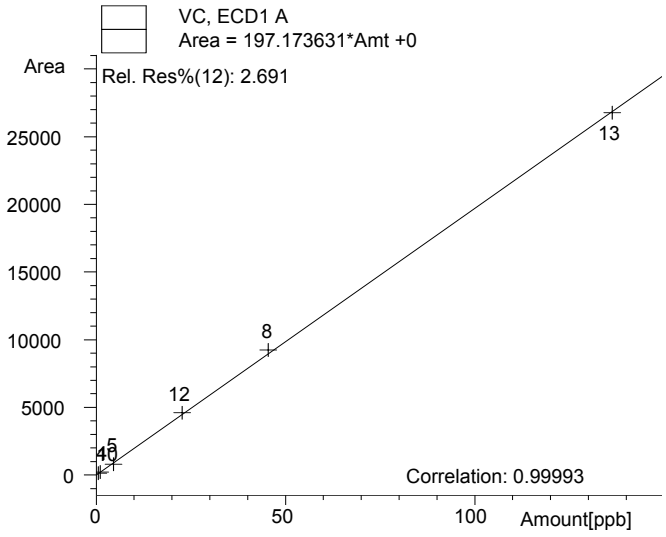






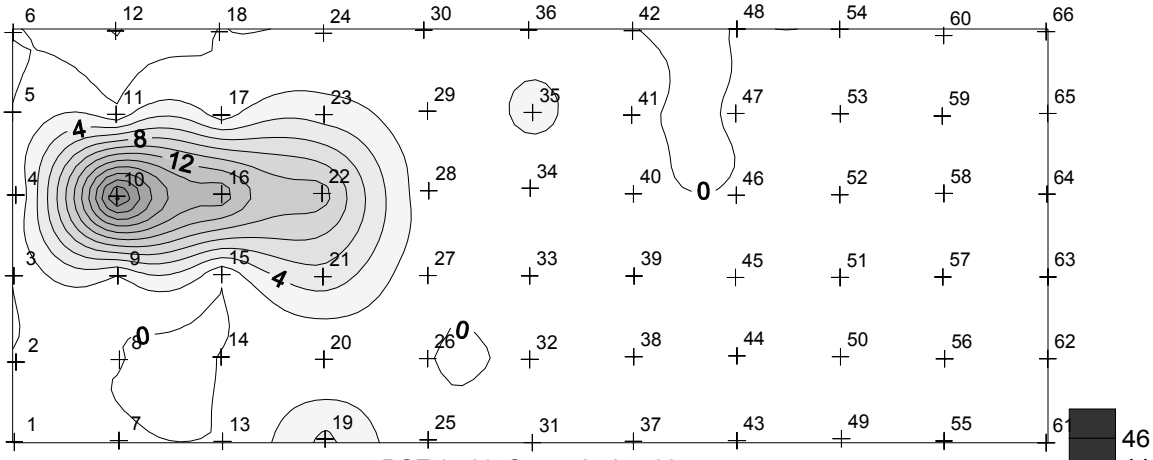


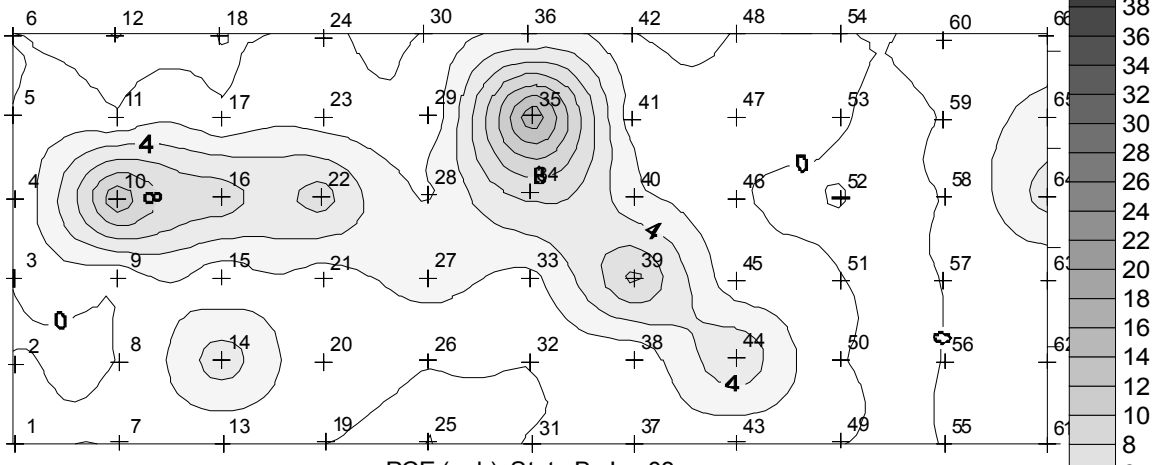
II. Calibration curve for VC

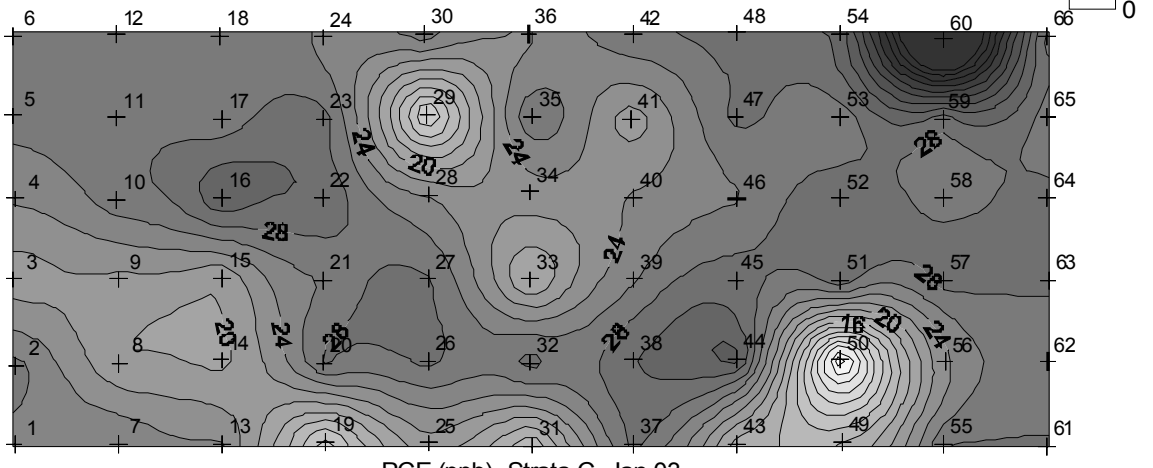


Appendix C: Chemical Concentration Contour Plots (Samples taken Jan 03)

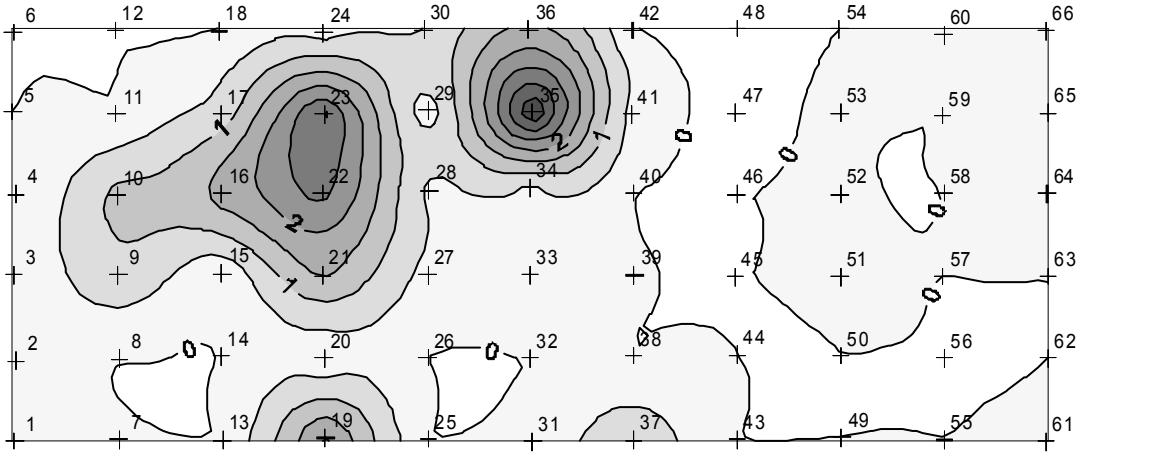
I. PCE concentrations (Jan 03)

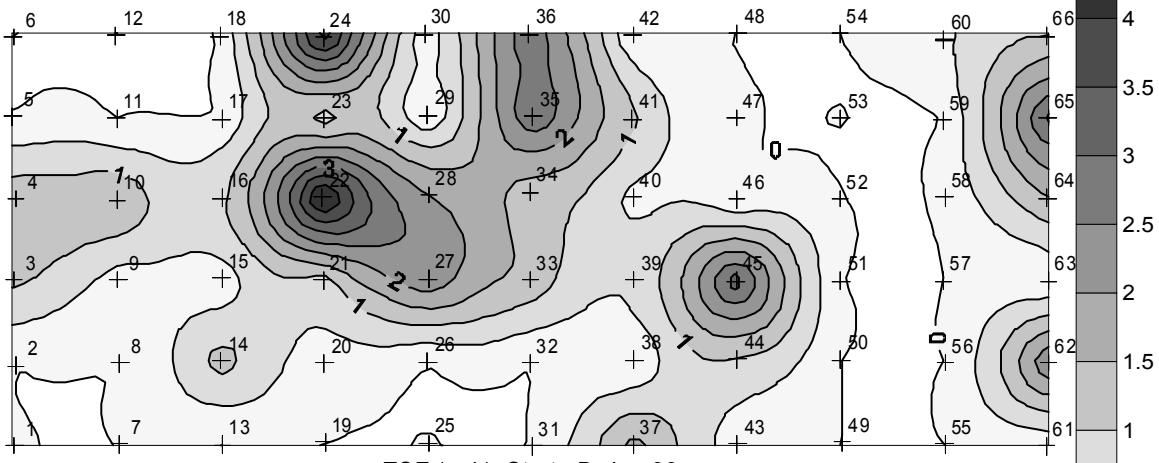


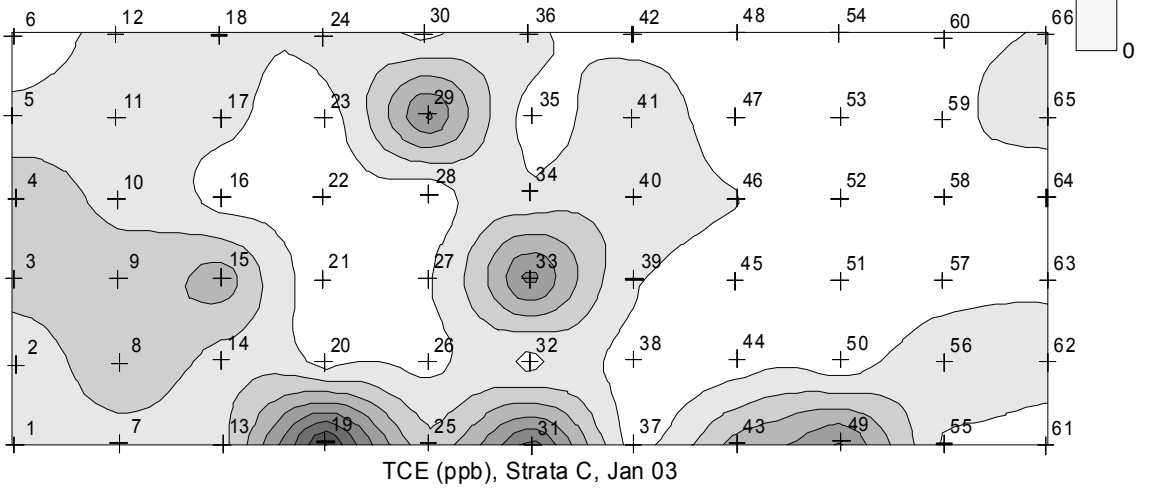




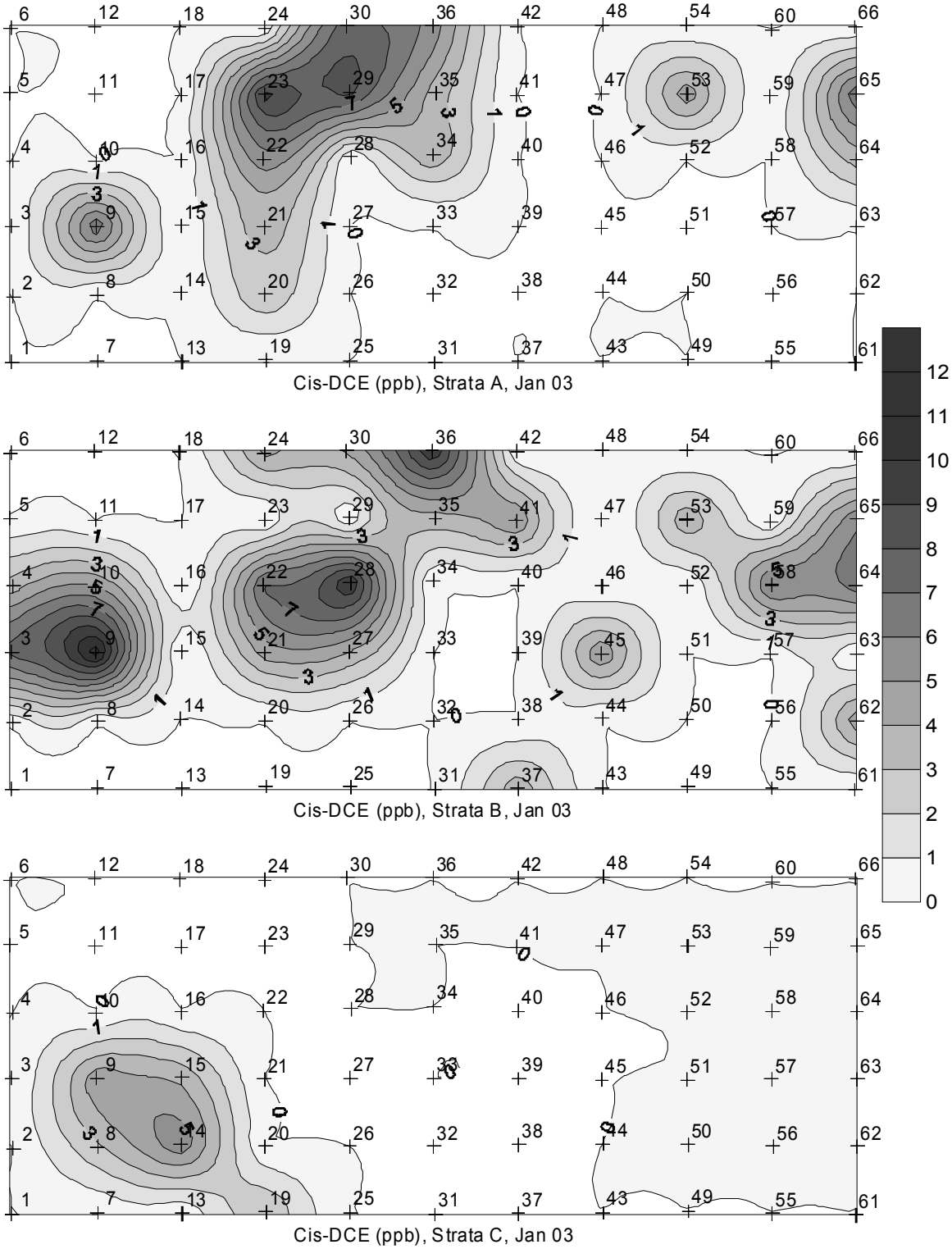
II. TCE concentrations (Jan 03)



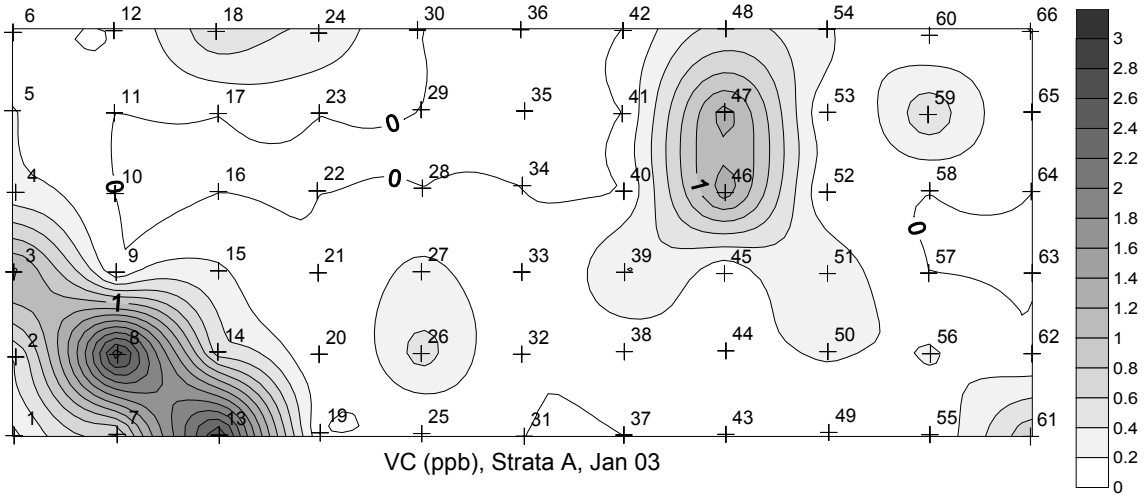




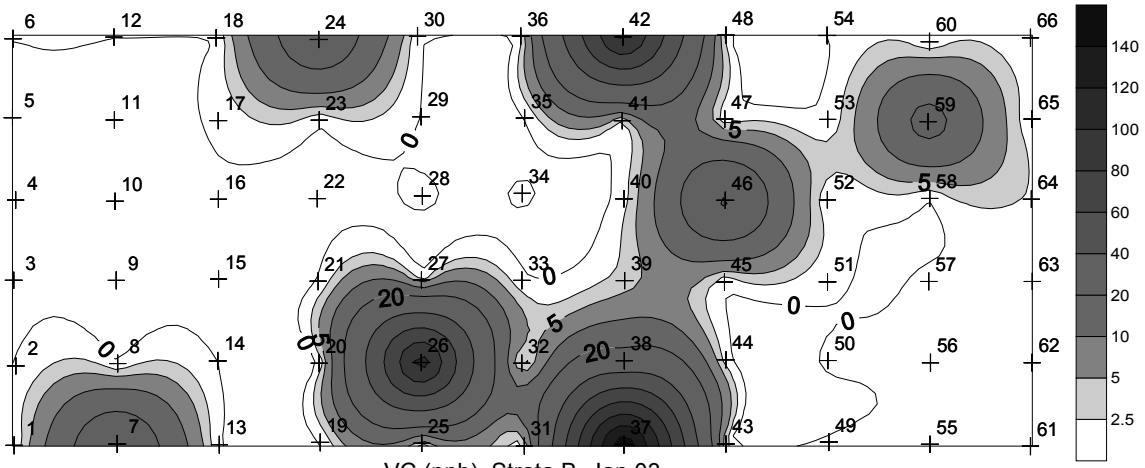
III. Cis-DCE concentrations (Jan 03)



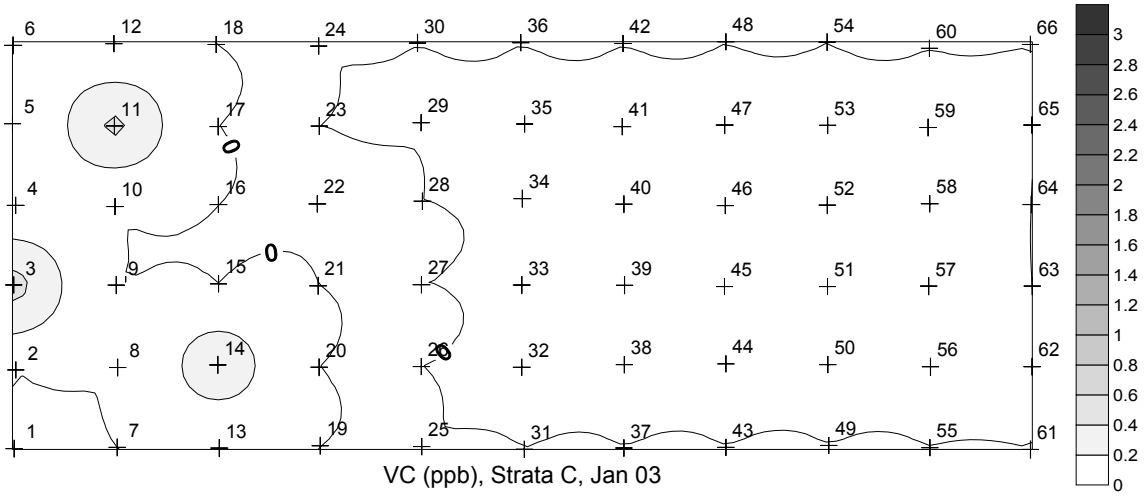
IV. VC concentrations (Jan 03)



VC (ppb), Strata A, Jan 03



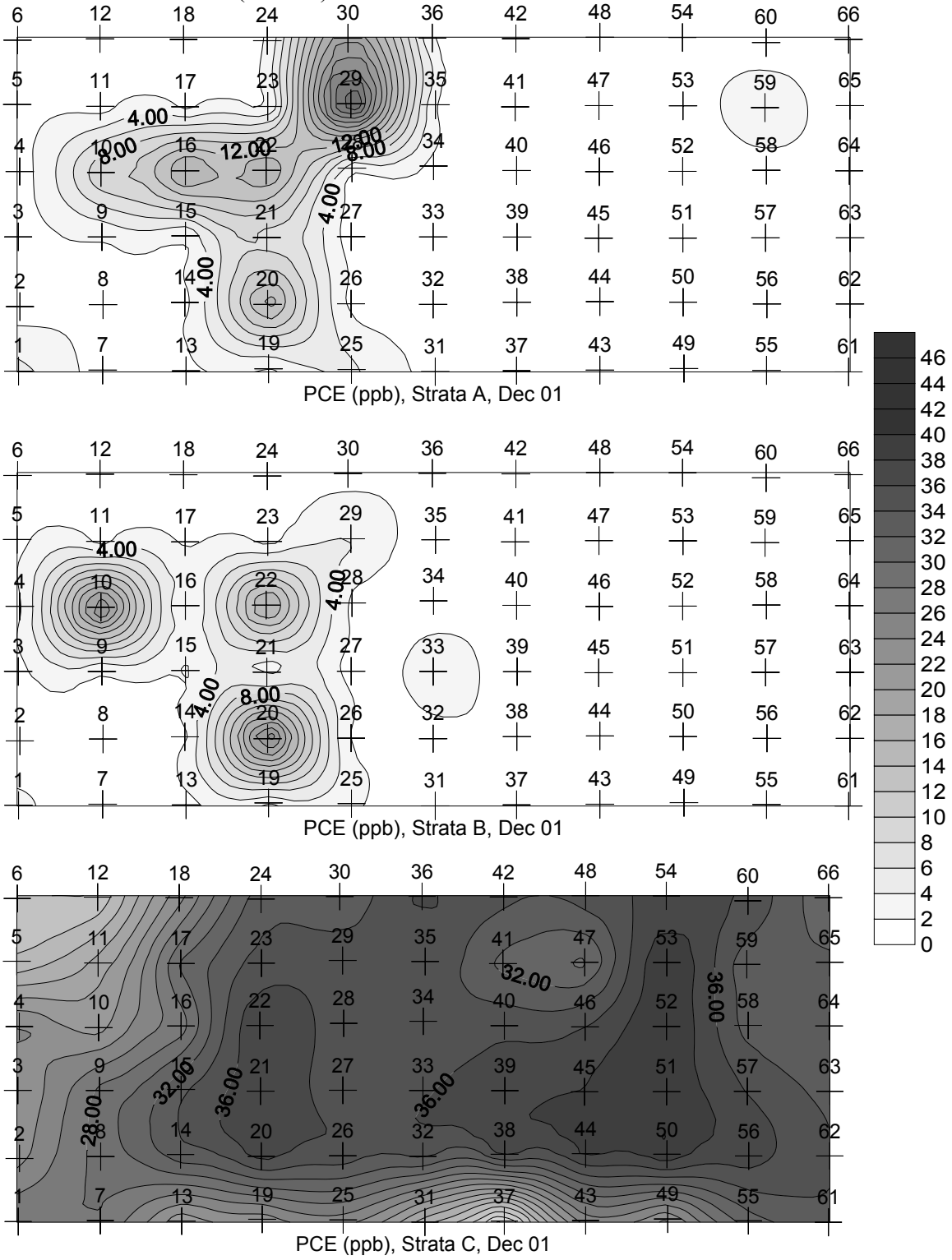
VC (ppb), Strata B, Jan 03



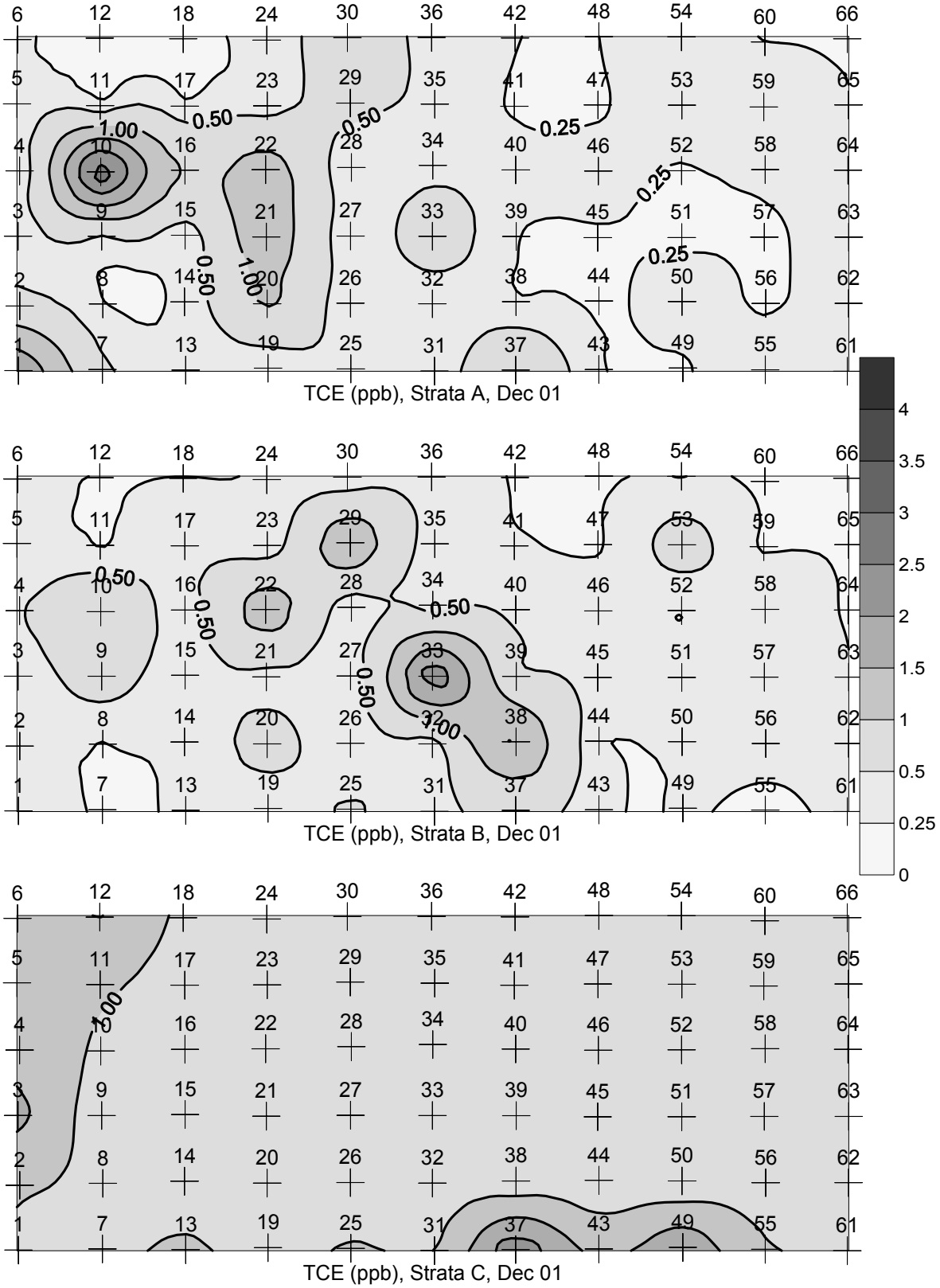
VC (ppb), Strata C, Jan 03

Appendix D: Chemical Concentration Contour Plots (Samples taken Dec 01)
Previous Effort

I. PCE concentrations (Dec 01)

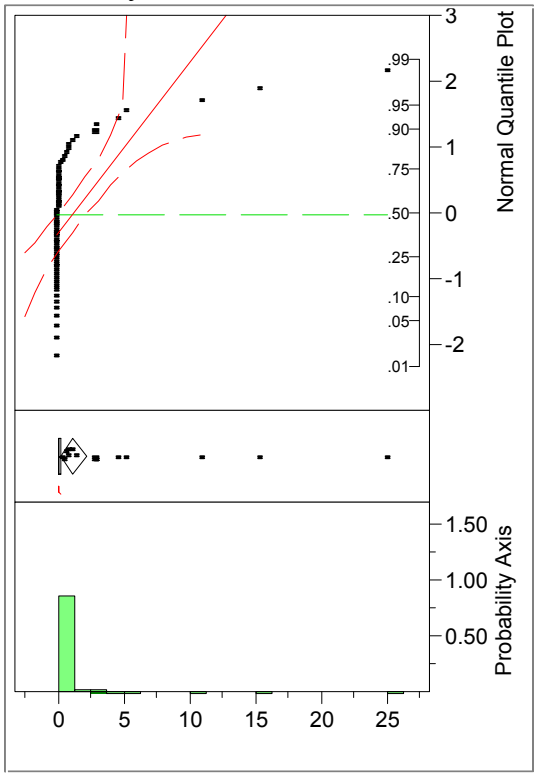


II. TCE concentrations (Dec 01)



Appendix E: Distributions for Outlier Analysis and Confidence Intervals

I. PCE Layer a



Quantiles

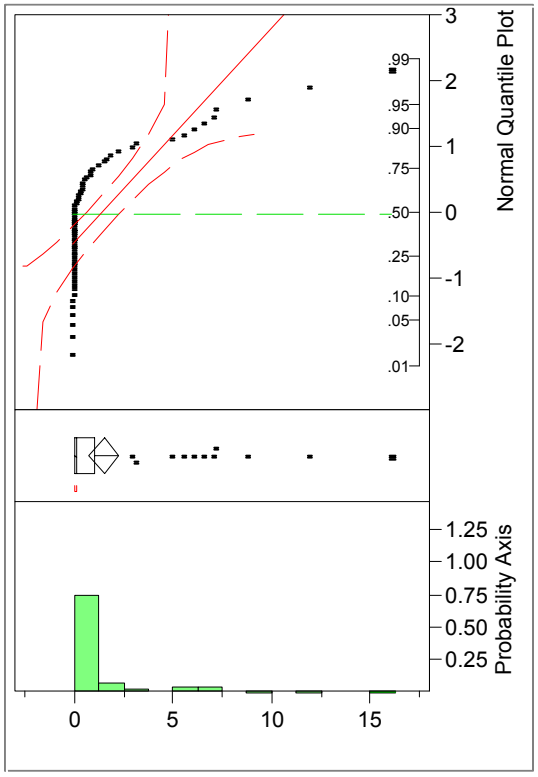
100.0%	maximum	25.218
99.5%		25.218
97.5%		18.669
90.0%		2.896
75.0%	quartile	0.201
50.0%	median	0.073
25.0%	quartile	0.023
10.0%		0.013
2.5%		0.000
0.5%		0.000
0.0%	minimum	0.000

Moments

Mean	1.1777173
Std Dev	3.886446
Std Err Mean	0.4783884
upper 95% Mean	2.133125
lower 95% Mean	0.2223096
N	66
Sum Wgts	66
Sum	77.729342
Variance	15.104462
Skewness	4.8272379
Kurtosis	25.433788
CV	329.9982

Piezometers considered outliers:
10, 16, 19, 21, 22, 23, 35

II. PCE Layer b



Quantiles

100.0%	maximum	16.135
99.5%		16.135
97.5%		13.316
90.0%		6.294
75.0%	quartile	1.040
50.0%	median	0.089
25.0%	quartile	0.039
10.0%		0.025
2.5%		0.020
0.5%		0.020
0.0%	minimum	0.020

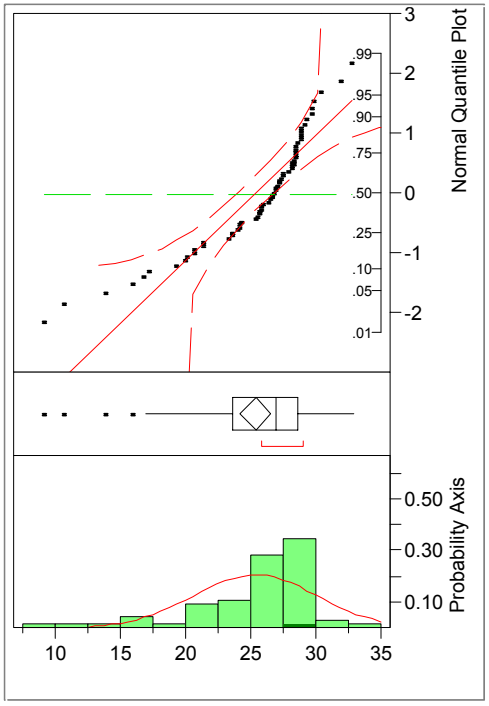
Moments

Mean	1.4918531
Std Dev	3.0790883
Std Err Mean	0.3790096
upper 95% Mean	2.2487875
lower 95% Mean	0.7349187
N	66
Sum Wgts	66
Sum	98.462303
Variance	9.480785
Skewness	2.8736218
Kurtosis	9.0186699
CV	206.39354

Piezometers considered outliers:

10, 14, 16, 22, 27, 34, 35, 39, 44, 64, 65

III. PCE Layer c



Normal(25.3927,4.77622)

Quantiles

100.0%	maximum	32.880
99.5%		32.880
97.5%		32.333
90.0%		29.607
75.0%	quartile	28.549
50.0%	median	26.877
25.0%	quartile	23.669
10.0%		18.155
2.5%		10.181
0.5%		9.224
0.0%	minimum	9.224

Moments

Mean	25.392651
Std Dev	4.7762198
Std Err Mean	0.6017471
upper 95% Mean	26.595526
lower 95% Mean	24.189775
N	63
Sum Wgts	63
Sum	1599.737
Variance	22.812275
Skewness	-1.508027
Kurtosis	2.3454982
CV	18.809457

Fitted Normal

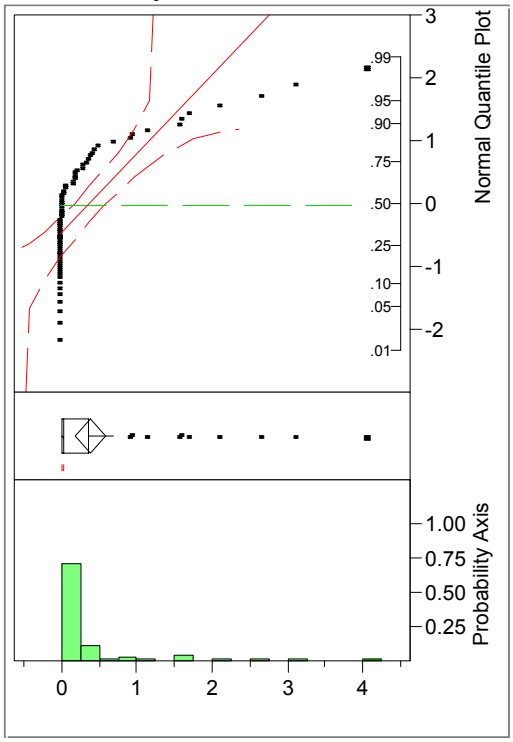
Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	Mu	25.39265	24.18978	26.59553
Dispersion	Sigma	4.77622	4.06356	5.79435

Piezometers considered outliers:

19, 29, 31, 49

IV. TCE Layer a



Quantiles

100.0%	maximum	4.0543
99.5%		4.0543
97.5%		3.4216
90.0%		1.5846
75.0%	quartile	0.3528
50.0%	median	0.0194
25.0%	quartile	0.0000
10.0%		0.0000
2.5%		0.0000
0.5%		0.0000
0.0%	minimum	0.0000

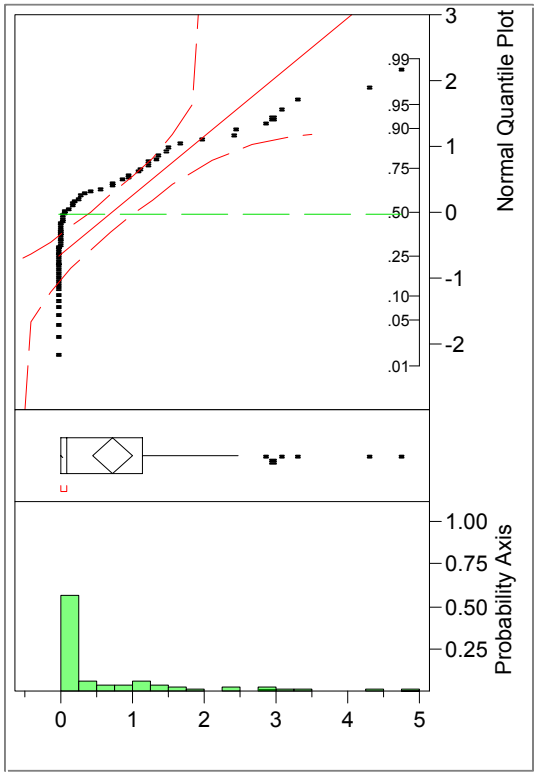
Moments

Mean	0.3809699
Std Dev	0.7947476
Std Err Mean	0.0978267
upper 95% Mean	0.5763433
lower 95% Mean	0.1855966
N	66
Sum Wgts	66
Sum	25.144014
Variance	0.6316238
Skewness	2.8931275
Kurtosis	8.8087231
CV	208.61166

Piezometers considered outliers:

9, 10, 16, 19, 21, 22, 23, 35, 36, 37

V. TCE Layer b



Quantiles

100.0%	maximum	4.7513
99.5%		4.7513
97.5%		4.4591
90.0%		2.5867
75.0%	quartile	1.1435
50.0%	median	0.0744
25.0%	quartile	0.0000
10.0%		0.0000
2.5%		0.0000
0.5%		0.0000
0.0%	minimum	0.0000

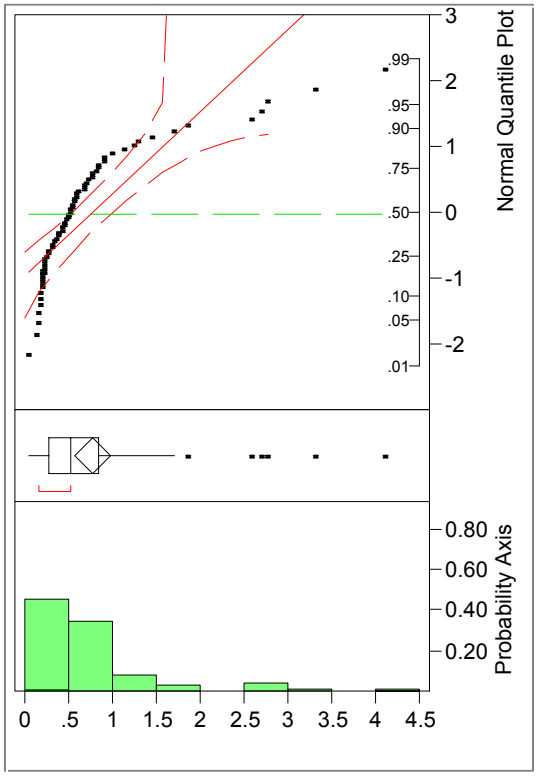
Moments

Mean	0.7214991
Std Dev	1.1205059
Std Err Mean	0.1379247
upper 95% Mean	0.9969539
lower 95% Mean	0.4460444
N	66
Sum Wgts	66
Sum	47.618943
Variance	1.2555335
Skewness	1.8717043
Kurtosis	3.1290983
CV	155.30246

Piezometers considered outliers:

22, 24, 35, 36, 45, 65

VI. TCE Layer c



Quantiles

100.0%	maximum	4.1240
99.5%		4.1240
97.5%		3.6458
90.0%		1.8090
75.0%	quartile	0.8500
50.0%	median	0.5240
25.0%	quartile	0.2680
10.0%		0.1950
2.5%		0.1170
0.5%		0.0540
0.0%	minimum	0.0540

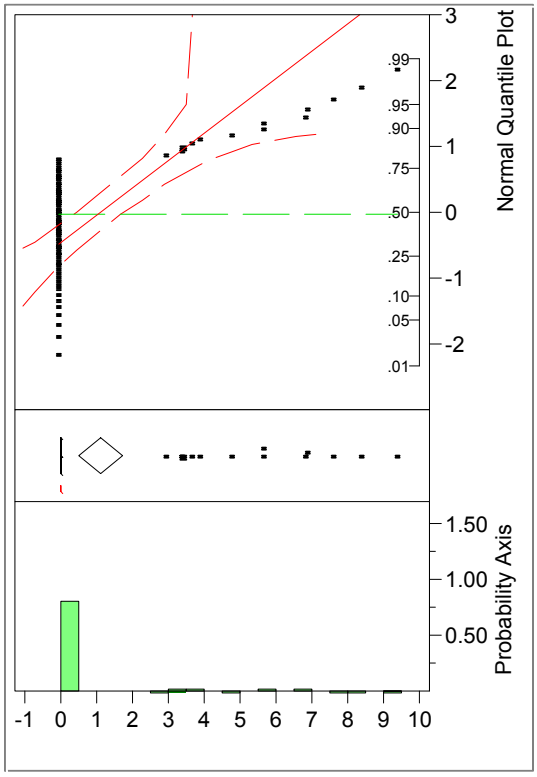
Moments

Mean	0.771254
Std Dev	0.8035824
Std Err Mean	0.1012419
upper 95% Mean	0.9736336
lower 95% Mean	0.5688744
N	63
Sum Wgts	63
Sum	48.589
Variance	0.6457447
Skewness	2.4043652
Kurtosis	6.039335
CV	104.19168

Piezometers considered outliers:

15, 19, 29, 31, 33, 49

VII. Cis-DCE Layer a



Quantiles

100.0%	maximum	9.4110
99.5%		9.4110
97.5%		8.7502
90.0%		5.6801
75.0%	quartile	0.0000
50.0%	median	0.0000
25.0%	quartile	0.0000
10.0%		0.0000
2.5%		0.0000
0.5%		0.0000
0.0%	minimum	0.0000

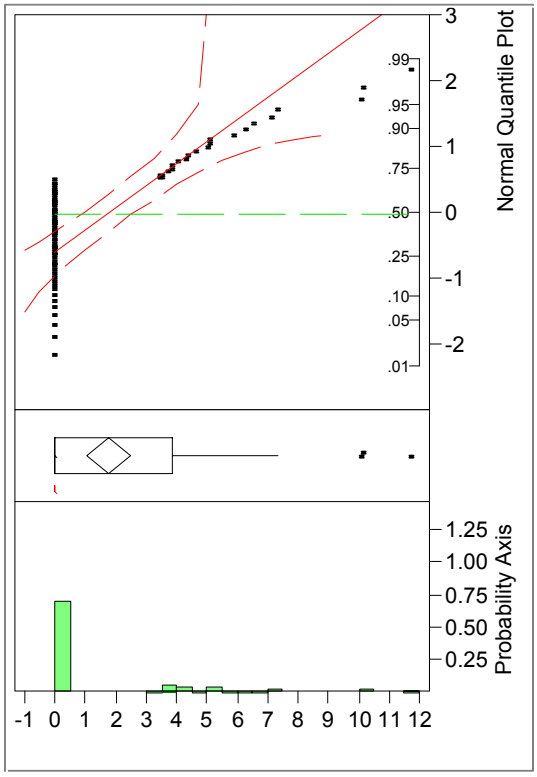
Moments

Mean	1.1049455
Std Dev	2.4236113
Std Err Mean	0.2983259
upper 95% Mean	1.7007435
lower 95% Mean	0.5091475
N	66
Sum Wgts	66
Sum	72.926404
Variance	5.8738919
Skewness	2.0910582
Kurtosis	3.2316682
CV	219.34216

Piezometers considered outliers:

9, 20, 21, 22, 23, 29, 30, 34, 35, 36, 53, 64, 65

VIII. Cis-DCE Layer b



Quantiles

100.0%	maximum	11.759
99.5%		11.759
97.5%		10.713
90.0%		6.383
75.0%	quartile	3.891
50.0%	median	0.000
25.0%	quartile	0.000
10.0%		0.000
2.5%		0.000
0.5%		0.000
0.0%	minimum	0.000

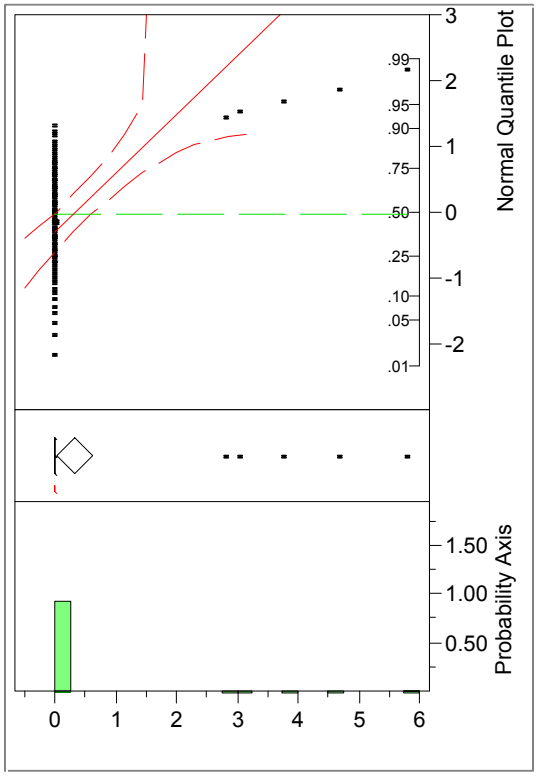
Moments

Mean	1.770349
Std Dev	3.0021768
Std Err Mean	0.3695424
upper 95% Mean	2.5083761
lower 95% Mean	1.0323218
N	66
Sum Wgts	66
Sum	116.84303
Variance	9.0130658
Skewness	1.6127248
Kurtosis	1.8451907
CV	169.58108

Piezometers considered outliers:

9, 28, 36

IX. Cis-DCE Layer c



Quantiles

100.0%	maximum	5.8299
99.5%		5.8299
97.5%		5.1292
90.0%		0.0000
75.0%	quartile	0.0000
50.0%	median	0.0000
25.0%	quartile	0.0000
10.0%		0.0000
2.5%		0.0000
0.5%		0.0000
0.0%	minimum	0.0000

Moments

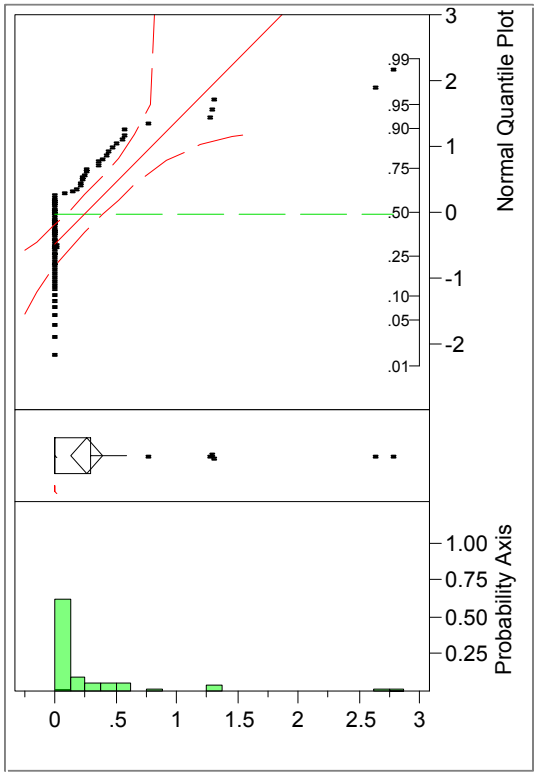
Mean	0.3161013
Std Dev	1.1378047
Std Err Mean	0.1422256
upper 95% Mean	0.6003165
lower 95% Mean	0.0318861
N	64
Sum Wgts	64
Sum	20.230483
Variance	1.2945996
Skewness	3.6611794
Kurtosis	12.891421
CV	359.94941

Piezometers considered outliers:

8, 9, 14, 15, 19

Note: These five piezometers were the only ones greater than zero

X. VC Layer a



Quantiles

100.0%	maximum	2.7943
99.5%		2.7943
97.5%		2.6902
90.0%		0.6403
75.0%	quartile	0.2917
50.0%	median	0.0000
25.0%	quartile	0.0000
10.0%		0.0000
2.5%		0.0000
0.5%		0.0000
0.0%	minimum	0.0000

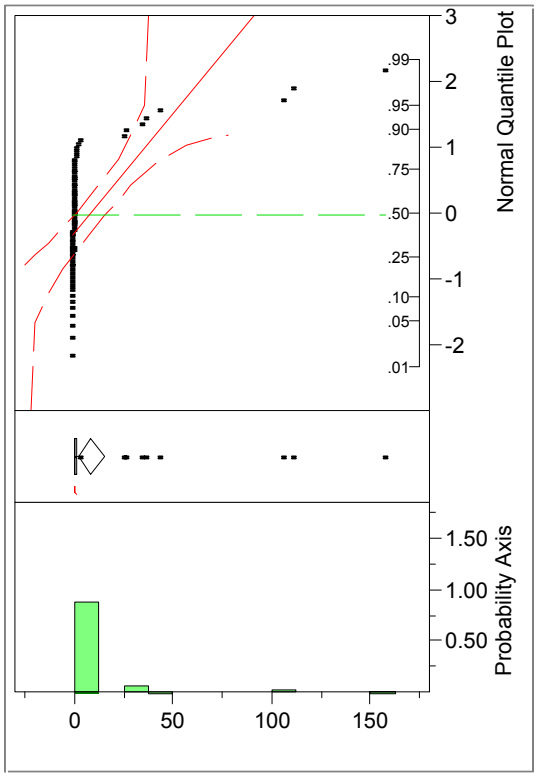
Moments

Mean	0.2559235
Std Dev	0.538333
Std Err Mean	0.0662642
upper 95% Mean	0.3882623
lower 95% Mean	0.1235847
N	66
Sum Wgts	66
Sum	16.890949
Variance	0.2898025
Skewness	3.3444778
Kurtosis	12.451964
CV	210.34922

Piezometers considered outliers:

3, 8, 13, 46, 47, 61

XI. VC Layer b



Quantiles

100.0%	maximum	158.44
99.5%		158.44
97.5%		127.06
90.0%		29.11
75.0%	quartile	1.10
50.0%	median	0.45
25.0%	quartile	0.00
10.0%		0.00
2.5%		0.00
0.5%		0.00
0.0%	minimum	0.00

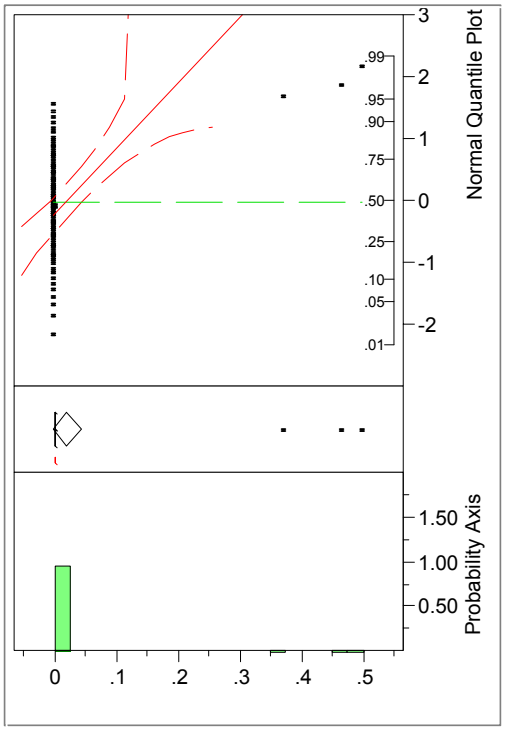
Moments

Mean	8.7013406
Std Dev	27.733053
Std Err Mean	3.4137028
upper 95% Mean	15.518976
lower 95% Mean	1.8837053
N	66
Sum Wgts	66
Sum	574.28848
Variance	769.12222
Skewness	4.0670308
Kurtosis	17.181861
CV	318.72161

Piezometers considered outliers:

7, 24, 26, 37, 48, 42, 46, 59

XII. VC Layer c



Quantiles

100.0%	maximum	0.49960
99.5%		0.49960
97.5%		0.47740
90.0%		0.00000
75.0%	quartile	0.00000
50.0%	median	0.00000
25.0%	quartile	0.00000
10.0%		0.00000
2.5%		0.00000
0.5%		0.00000
0.0%	minimum	0.00000

Moments

Mean	0.0205756
Std Dev	0.0949817
Std Err Mean	0.011781
upper 95% Mean	0.0441109
lower 95% Mean	-0.00296
N	65
Sum Wgts	65
Sum	1.3374112
Variance	0.0090215
Skewness	4.5333094
Kurtosis	19.446886
CV	461.62391

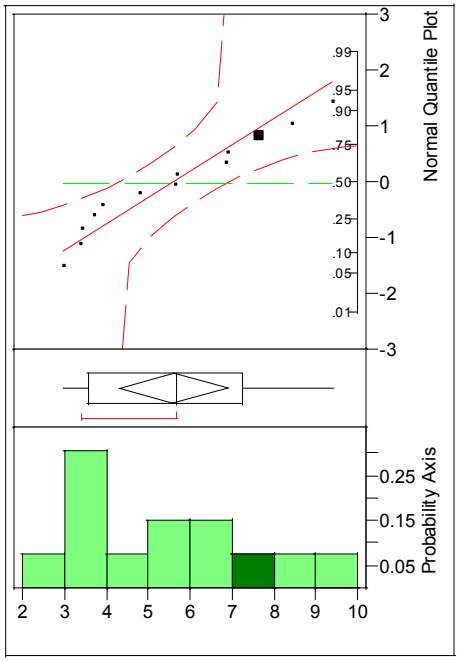
Piezometers considered outliers:

3, 11, 14

Appendix F: Distributions for Cis-DCE and VC not including Piezometers with Concentration Measurements of Zero

I.

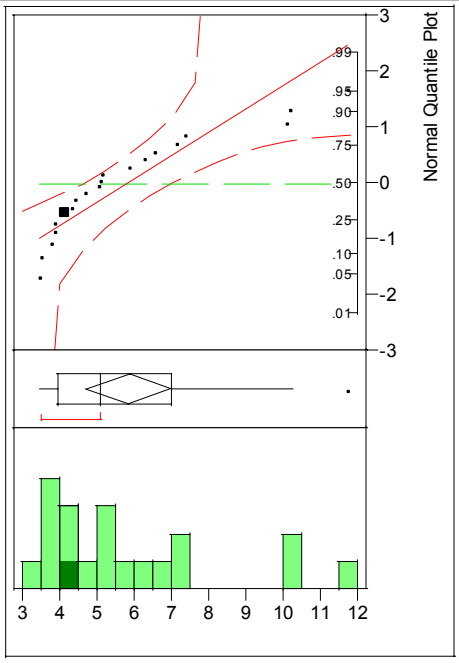
C-DCE a



Quantiles			Moments	
100.0%	maximum	9.4110	Mean	5.6097234
99.5%		9.4110	Std Dev	2.1072438
97.5%		9.4110	Std Err Mean	0.5844443
90.0%		9.0194	upper 95% Mean	6.8831181
75.0%	quartile	7.2713	lower 95% Mean	4.3363287
50.0%	median	5.6737	N	13
25.0%	quartile	3.5775		
10.0%		3.1618		
2.5%		2.9975		
0.5%		2.9975		
0.0%	minimum	2.9975		

II.

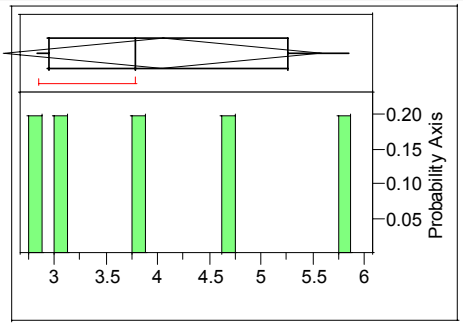
C-DCE b



Quantiles			Moments	
100.0%	maximum	11.759	Mean	5.8421516
99.5%		11.759	Std Dev	2.4070895
97.5%		11.759	Std Err Mean	0.5382416
90.0%		10.198	upper 95% Mean	6.9687041
75.0%	quartile	7.021	lower 95% Mean	4.715599
50.0%	median	5.089	N	20
25.0%	quartile	3.947		
10.0%		3.550		
2.5%		3.492		
0.5%		3.492		
0.0%	minimum	3.492		

III.

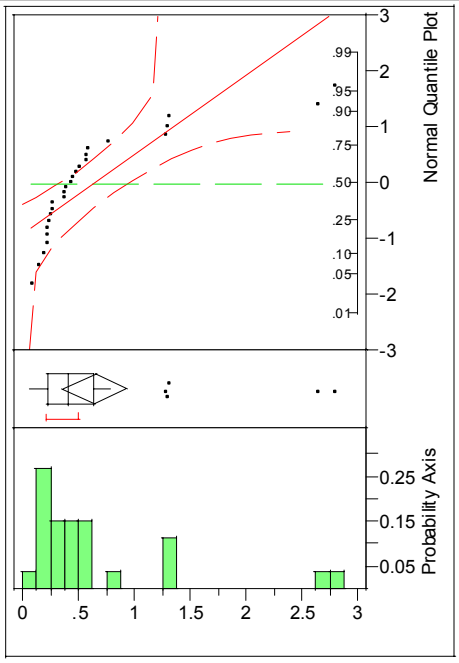
C-DCEC



Quantiles			Moments	
100.0%	maximum	5.8299	Mean	4.0460965
99.5%		5.8299	Std Dev	1.2349261
97.5%		5.8299	Std Err Mean	0.5522757
90.0%		5.8299	upper 95% Mean	5.5794598
75.0%	quartile	5.2693	lower 95% Mean	2.5127332
50.0%	median	3.7849	N	5
25.0%	quartile	2.9535		
10.0%		2.8461		
2.5%		2.8461		
0.5%		2.8461		
0.0%	minimum	2.8461		

IV.

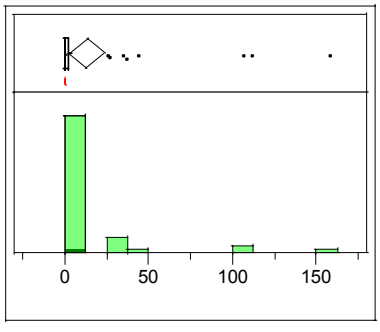
VC a



Quantiles			Moments	
100.0%	maximum	2.7943	Mean	0.6496519
99.5%		2.7943	Std Dev	0.6981895
97.5%		2.7943	Std Err Mean	0.1369262
90.0%		1.7116	upper 95% Mean	0.9316567
75.0%	quartile	0.6311	lower 95% Mean	0.3676471
50.0%	median	0.4089	N	26
25.0%	quartile	0.2313		
10.0%		0.1774		
2.5%		0.0789		
0.5%		0.0789		
0.0%	minimum	0.0789		

V.

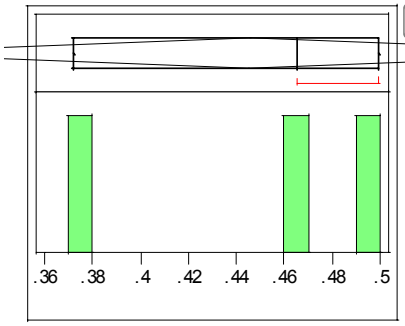
VC b



Quantiles			Moments	
100.0%	maximum	158.44	Mean	13.355546
99.5%		158.44	Std Dev	33.565887
97.5%		153.79	Std Err Mean	5.1187498
90.0%		40.97	upper 95% Mean	23.685601
75.0%	quartile	2.02	lower 95% Mean	3.0254908
50.0%	median	0.63	N	43
25.0%	quartile	0.47		
10.0%		0.27		
2.5%		0.19		
0.5%		0.19		
0.0%	minimum	0.19		

VI.

VC C



Quantiles

100.0%	maximum	0.49960
99.5%		0.49960
97.5%		0.49960
90.0%		0.49960
75.0%	quartile	0.49960
50.0%	median	0.46544
25.0%	quartile	0.37237
10.0%		0.37237
2.5%		0.37237
0.5%		0.37237
0.0%	minimum	0.37237

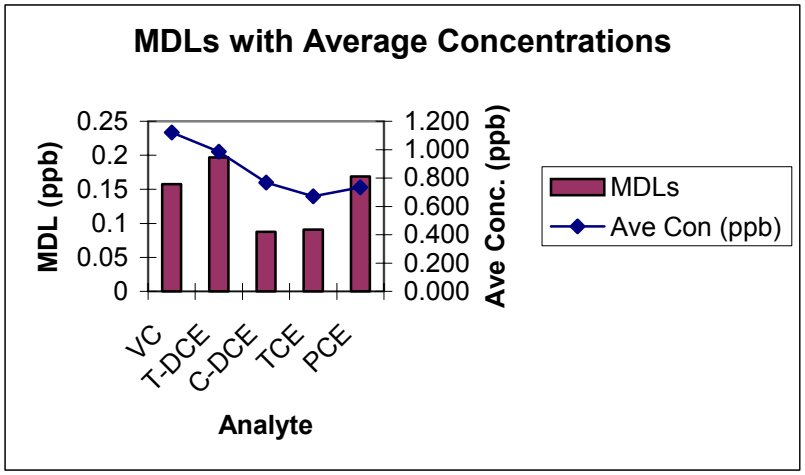
Moments

Mean	0.4458037
Std Dev	0.06585
Std Err Mean	0.0380185
upper 95% Mean	0.6093842
lower 95% Mean	0.2822233
N	3

Appendix G: Method Detection Limit (MDL) Calculations for All Analytes

One stock solution of 22.72 ppb VOC mix was prepared to make the individual 1.0819 ppb standard solutions for analysis.

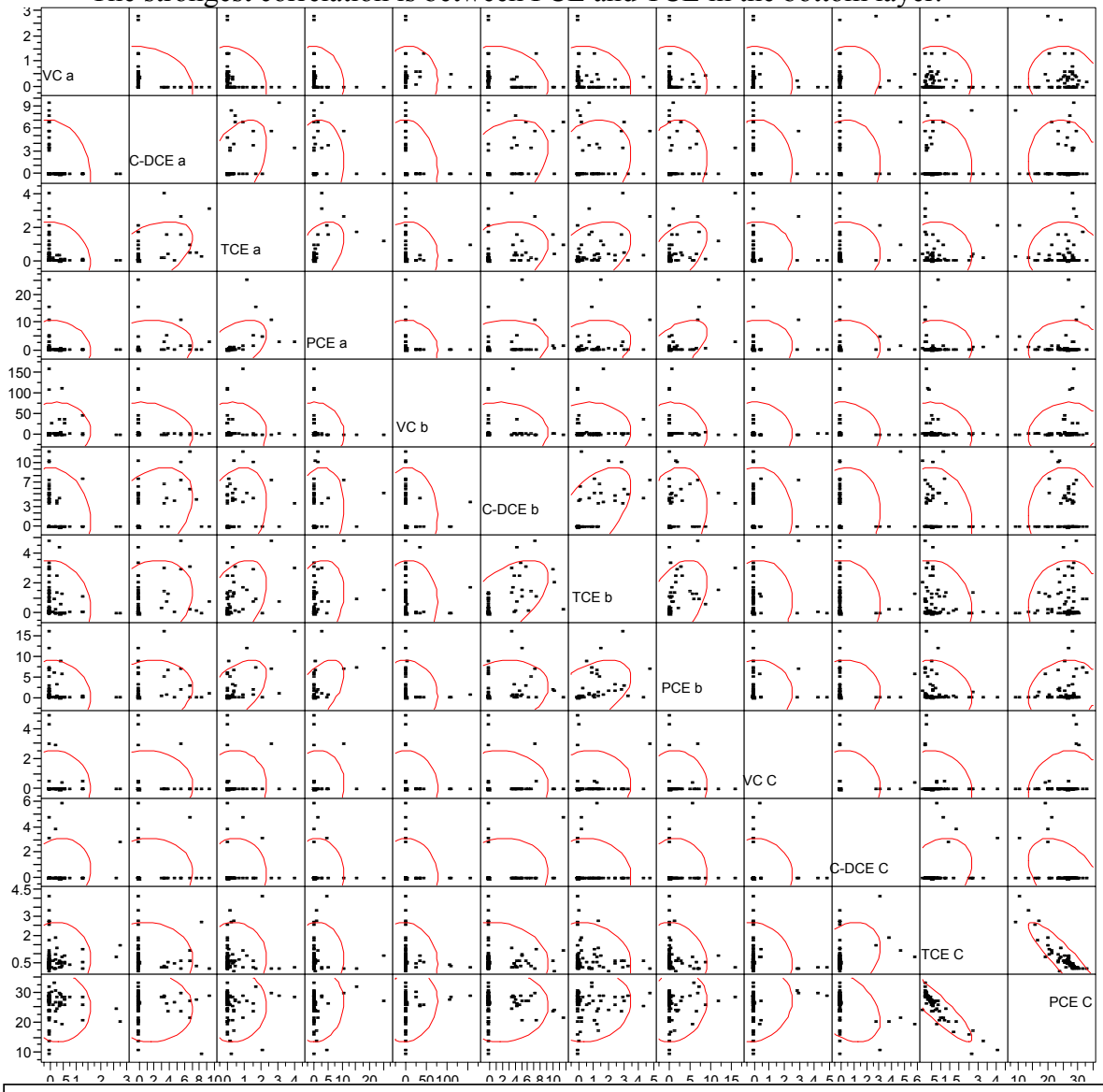
Date		Signal (Area Under the Curve)					Concentration (ppb)				
Run	Vial	VC	T-DCE	C-DCE	TCE	PCE	VC	T-DCE	C-DCE	TCE	PCE
6-Dec-03	1	241.758	23.05	11.68	2641.312	12089.1	1.19112	1.08238	0.78839	0.71923	0.82748
6-Dec-03	2	236.892	21.53	11.02	2604.189	11610.5	1.16715	1.01066	0.74372	0.70912	0.79472
6-Dec-03	3	233.166	22.3016	11.9275	2514.4751	10961.8	1.14879	1.04708	0.80524	0.68469	0.75032
6-Dec-03	4	222.555	19.7386	11.0265	2392.9899	10428.8	1.09651	0.92675	0.74442	0.65161	0.71384
6-Dec-03	5	221.058	20.3716	11.0353	2424.7317	10542.8	1.08913	0.95647	0.74501	0.66025	0.72164
6-Dec-03	6	223.921	20.2796	11.811	2432.936	10345.1	1.10324	0.95215	0.79738	0.66249	0.70811
6-Dec-03	7	214.609	19.4741	11.1072	2368.8843	9908.251	1.05736	0.91433	0.74986	0.64504	0.67821
6-Dec-03	8	214.233	19.6709	10.9377	2369.3543	9883.857	1.05551	0.92357	0.73842	0.64517	0.67654
						Range:	0.13376	0.16806	0.06153	0.07418	0.14928
						Average:	1.122	0.984	0.768	0.672	0.734
						Std Dev:	0.05021	0.06267	0.02782	0.02893	0.05390
						Var:	**0.00252**	**0.00393**	**0.00077**	**0.00084**	**0.00291**
						MDL:	**0.157674**	**0.1967969**	**0.0873704**	**0.0908462**	**0.1692485**



Appendix H: Scatterplot Matrix and Correlation/Regression Analysis

I. Jan 03 data for four analytes in three layers (a, b, and c)

The strongest correlation is between PCE and TCE in the bottom layer.

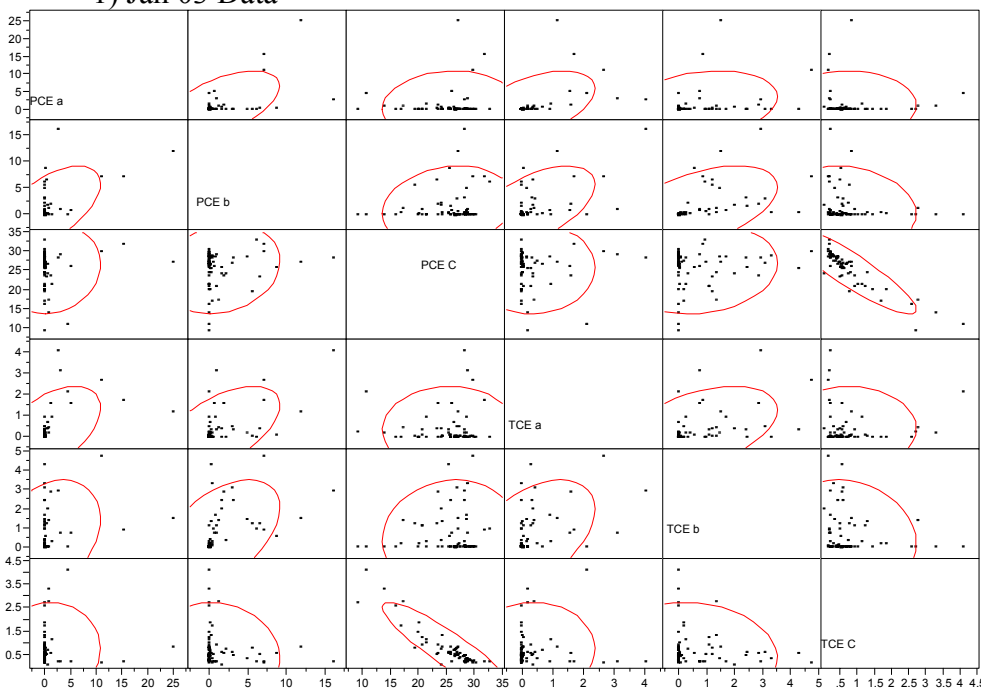


Correlations

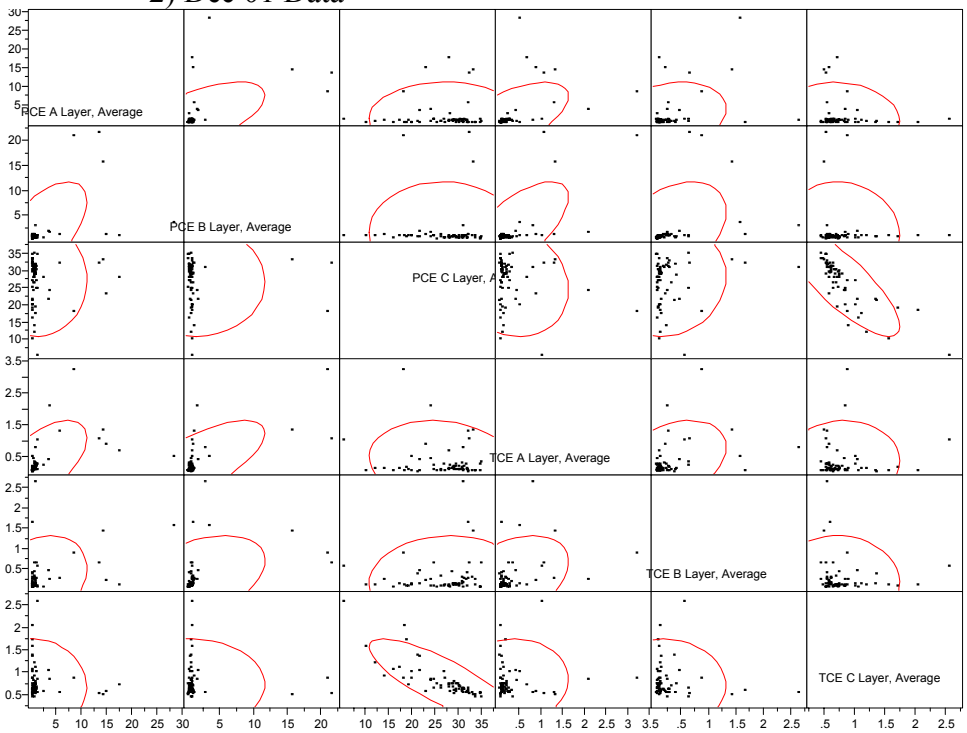
	VC a	C-DCE a	TCE a	PCE a	VC b	C-DCE b	TCE b	PCE b	VC C	C-DCE C	TCE C	PCE C
VC a	1.0000	-0.2294	-0.2209	-0.1425	0.0196	-0.1728	-0.1846	-0.1491	-0.0889	0.1619	0.0058	-0.0540
C-DCE a	-0.2294	1.0000	0.5022	0.0883	-0.1470	0.3976	0.2528	0.1495	-0.0141	0.0512	-0.0422	-0.0777
TCE a	-0.2209	0.5022	1.0000	0.4951	-0.0419	0.2954	0.4424	0.5576	0.0325	0.0514	-0.0019	0.0320
PCE a	-0.1425	0.0883	0.4951	1.0000	-0.0961	0.1886	0.2533	0.5670	0.0573	-0.0105	-0.0036	0.1066
VC b	0.0196	-0.1470	-0.0419	-0.0961	1.0000	-0.0478	0.0077	-0.1202	-0.0872	-0.0914	-0.1589	0.1599
C-DCE b	-0.1728	0.3976	0.2954	0.1886	-0.0478	1.0000	0.6117	0.1905	-0.0295	0.0824	-0.1501	0.0168
TCE b	-0.1846	0.2528	0.4424	0.2533	0.0077	0.6117	1.0000	0.4804	0.0450	-0.0733	-0.1795	0.1287
PCE b	-0.1491	0.1495	0.5576	0.5670	-0.1202	0.1905	0.4804	1.0000	-0.0092	0.0119	-0.1782	0.1767
VC C	-0.0889	-0.0141	0.0325	0.0573	-0.0872	-0.0295	0.0450	-0.0092	1.0000	-0.0457	-0.1709	0.2076
C-DCE C	0.1619	0.0512	0.0514	-0.0105	-0.0914	0.0824	-0.0733	0.0119	-0.0457	1.0000	0.3202	-0.3913
TCE C	0.0058	-0.0422	-0.0019	-0.0036	-0.1589	-0.1501	-0.1795	-0.1782	-0.1709	0.3202	1.0000	-0.9022
PCE C	-0.0540	-0.0777	0.0320	0.1066	0.1599	0.0168	0.1287	0.1767	0.2076	-0.3913	-0.9022	1.0000

II. Scatterplot Matrices for PCE and TCE in three layers (a - Top, b - Middle, and c - Bottom) – Notice similar distribution patterns between the two years.

1) Jan 03 Data



2) Dec 01 Data



III. Correlation analysis for PCE and TCE concentrations in each layer including sample runs in Dec 01 (Analyte, layer, Opp) and Jan 03 (Analyte, layer). A box highlights strong correlations.

Nonparametric: Spearman's Rho

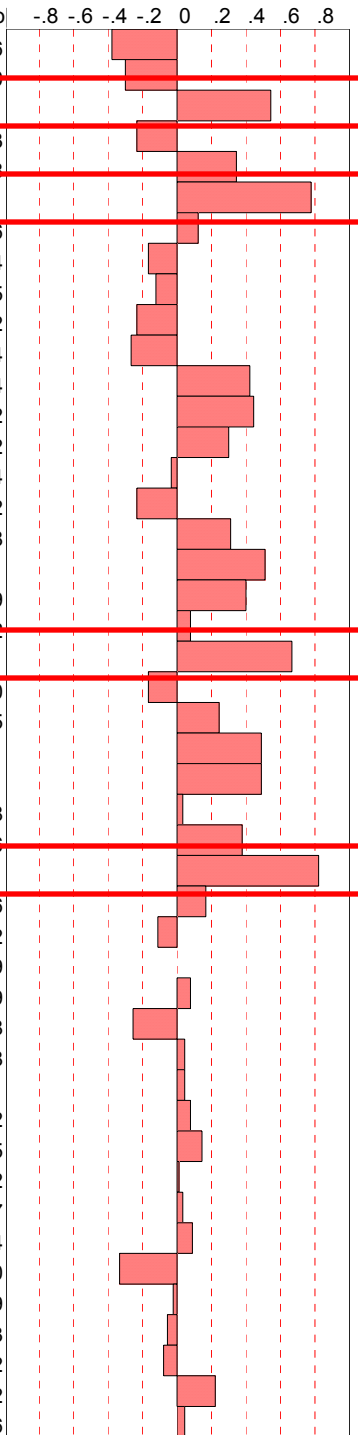
Variable	by Variable	Spearman Rho	Prob>|Rho|
PCE a Opp	PCE a	0.1860	0.1349
PCE b	PCE a	0.4875	<.0001
PCE b	PCE a Opp	0.0395	0.7527
PCE b Opp	PCE a	0.2378	0.0584
PCE b Opp	PCE a Opp	0.4485	0.0002
PCE b Opp	PCE b	-0.0614	0.6296
PCE c	PCE a	-0.2268	0.0739
PCE c	PCE a Opp	-0.1136	0.3753
PCE c	PCE b	0.0138	0.9147
PCE c	PCE b Opp	-0.2741	0.0326
PCE c Opp	PCE a	-0.2371	0.0592
PCE c Opp	PCE a Opp	-0.0628	0.6222
PCE c Opp	PCE b	0.0665	0.6014
PCE c Opp	PCE b Opp	-0.1714	0.1829
PCE c Opp	PCE c	0.3819	0.0022
TCE a	PCE a	0.7819	<.0001
TCE a	PCE a Opp	0.3102	0.0112
TCE a	PCE b	0.4912	<.0001
TCE a	PCE b Opp	0.1716	0.1752
TCE a	PCE c	-0.1054	0.4108
TCE a	PCE c Opp	-0.0851	0.5038
TCE a Opp	PCE a	0.3442	0.0047
TCE a Opp	PCE a Opp	0.8050	<.0001
TCE a Opp	PCE b	0.1874	0.1318
TCE a Opp	PCE b Opp	0.4373	0.0003
TCE a Opp	PCE c	-0.0768	0.5496
TCE a Opp	PCE c Opp	-0.0353	0.7821
TCE a Opp	TCE a	0.4324	0.0003
TCE b	PCE a	0.4008	0.0009
TCE b	PCE a Opp	0.0980	0.4338
TCE b	PCE b	0.8314	<.0001
TCE b	PCE b Opp	-0.0308	0.8093
TCE b	PCE c	-0.0222	0.8628
TCE b	PCE c Opp	0.1676	0.1857
TCE b	TCE a	0.5108	<.0001
TCE b	TCE a Opp	0.1954	0.1159
TCE b Opp	PCE a	0.2142	0.0892
TCE b Opp	PCE a Opp	0.2978	0.0169
TCE b Opp	PCE b	0.1448	0.2537
TCE b Opp	PCE b Opp	0.6935	<.0001
TCE b Opp	PCE c	-0.1572	0.2263
TCE b Opp	PCE c Opp	0.1409	0.2747
TCE b Opp	TCE a	0.2241	0.0750
TCE b Opp	TCE a Opp	0.3511	0.0045
TCE b Opp	TCE b	0.2596	0.0383
TCE c	PCE a	0.1323	0.3013
TCE c	PCE a Opp	0.0323	0.8018
TCE c	PCE b	-0.1584	0.2150
TCE c	PCE b Opp	0.2894	0.0237
TCE c	PCE c	-0.8557	<.0001
TCE c	PCE c Opp	-0.5372	<.0001
TCE c	TCE a	-0.0411	0.7488
TCE c	TCE a Opp	-0.0378	0.7689
TCE c	TCE b	-0.1385	0.2789
TCE c	TCE b Opp	0.1089	0.4035
TCE c Opp	PCE a	0.0668	0.6001
TCE c Opp	PCE a Opp	-0.0705	0.5798
TCE c Opp	PCE b	-0.1648	0.1932
TCE c Opp	PCE b Opp	0.0123	0.9246
TCE c Opp	PCE c	-0.3661	0.0034
TCE c Opp	PCE c Opp	-0.8660	<.0001
TCE c Opp	TCE a	-0.0599	0.6384
TCE c Opp	TCE a Opp	-0.0882	0.4881
TCE c Opp	TCE b	-0.2022	0.1092
TCE c Opp	TCE b Opp	0.1746	0.1747
TCE c Opp	TCE c	0.4923	<.0001

IV. Correlation analysis for PCE, TCE, c-DCE, and VC concentrations in each layer

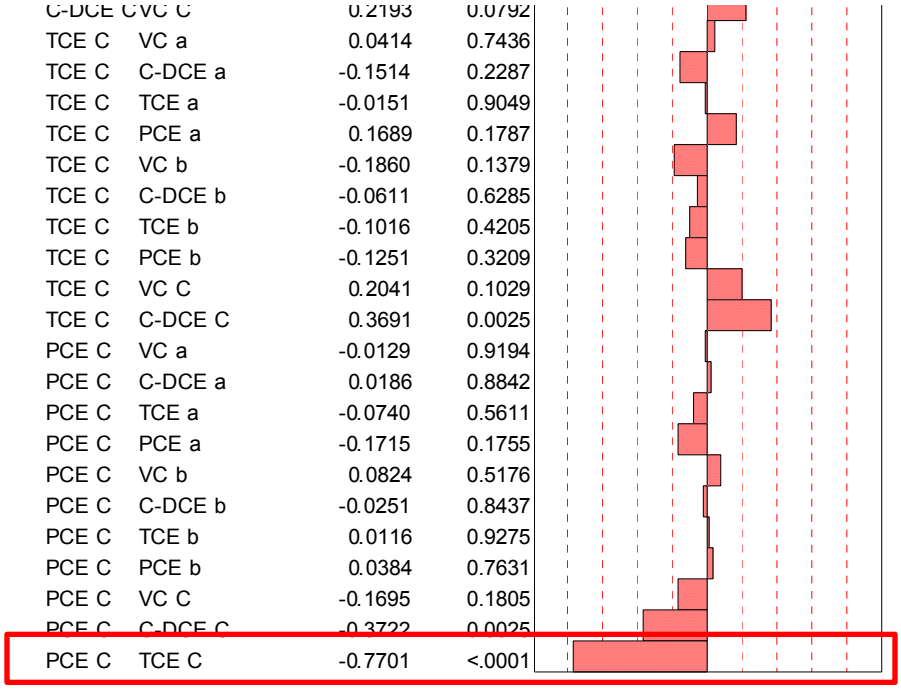
Sample runs in Jan 03 (Analyte, layer). A box highlights strong correlations.

Nonparametric: Spearman's Rho

Variable	by Variable	Spearman Rho	Prob>|Rho|
C-DCE a	VC a	-0.3803	0.0016
TCE a	VC a	-0.3612	0.0140
TCE a	C-DCE a	0.5462	<.0001
PCE a	VC a	-0.2352	0.0573
PCE a	C-DCE a	0.3433	0.0048
PCE a	TCE a	0.7819	<.0001
VC b	VC a	0.1254	0.3156
VC b	C-DCE a	-0.1731	0.1644
VC b	TCE a	-0.1177	0.3465
VC b	PCE a	-0.2300	0.0632
C-DCE b	VC a	-0.2637	0.0324
C-DCE b	C-DCE a	0.4214	0.0004
C-DCE b	TCE a	0.4481	0.0002
C-DCE b	PCE a	0.2977	0.0152
C-DCE b	VC b	-0.0353	0.7784
TCE b	VC a	-0.2371	0.0552
TCE b	C-DCE a	0.3157	0.0098
TCE b	TCE a	0.5108	<.0001
TCE b	PCE a	0.4008	0.0009
TCE b	VC b	0.0769	0.5392
TCE b	C-DCE b	0.6720	<.0001
PCE b	VC a	-0.1686	0.1760
PCE b	C-DCE a	0.2417	0.0505
PCE b	TCE a	0.4912	<.0001
PCE b	PCE a	0.4875	<.0001
PCE b	VC b	0.0304	0.8088
PCE b	C-DCE b	0.3818	0.0016
PCE b	TCE b	0.8314	<.0001
VC C	VC a	0.1641	0.1916
VC C	C-DCE a	-0.1090	0.3872
VC C	TCE a	0.0054	0.9659
VC C	PCE a	0.0763	0.5459
VC C	VC b	-0.2570	0.0388
VC C	C-DCE b	0.0487	0.6998
VC C	TCE b	0.0394	0.7551
VC C	PCE b	0.0749	0.5532
C-DCE C	VC a	0.1437	0.2535
C-DCE C	C-DCE a	0.0135	0.9152
C-DCE C	TCE a	0.0309	0.8067
C-DCE C	PCE a	0.0948	0.4524
C-DCE C	VC b	-0.3371	0.0060
C-DCE C	C-DCE b	-0.0252	0.8419
C-DCE C	TCE b	-0.0519	0.6813
C-DCE C	PCE b	-0.0831	0.5102
C-DCE C	VC C	0.2193	0.0792
TCE C	VC a	0.0414	0.7436

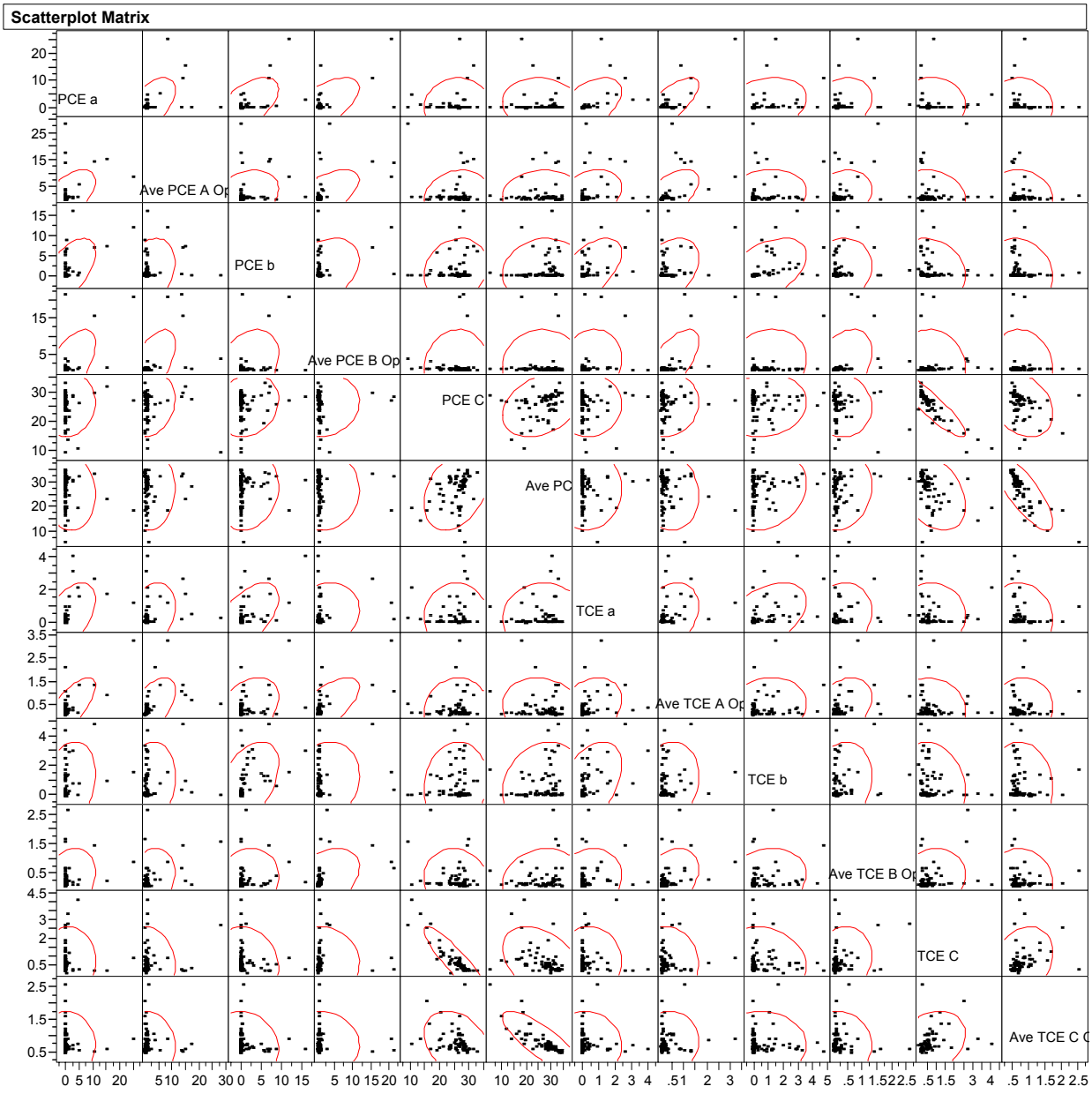


IV. Correlation analysis Continued



C-DCE C	VC C	0.2193	0.0792
TCE C	VC a	0.0414	0.7436
TCE C	C-DCE a	-0.1514	0.2287
TCE C	TCE a	-0.0151	0.9049
TCE C	PCE a	0.1689	0.1787
TCE C	VC b	-0.1860	0.1379
TCE C	C-DCE b	-0.0611	0.6285
TCE C	TCE b	-0.1016	0.4205
TCE C	PCE b	-0.1251	0.3209
TCE C	VC C	0.2041	0.1029
TCE C	C-DCE C	0.3691	0.0025
PCE C	VC a	-0.0129	0.9194
PCE C	C-DCE a	0.0186	0.8842
PCE C	TCE a	-0.0740	0.5611
PCE C	PCE a	-0.1715	0.1755
PCE C	VC b	0.0824	0.5176
PCE C	C-DCE b	-0.0251	0.8437
PCE C	TCE b	0.0116	0.9275
PCE C	PCE b	0.0384	0.7631
PCE C	VC C	-0.1695	0.1805
PCE C	C-DCE C	-0.3722	0.0025
PCE C	TCE C	-0.7701	<.0001

V. Multivariate Scatterplot Matrix of TCE and PCE concentrations for Nov 01 (Analyte, layer) vs Jan 03 (Ave Analyte, layer)



VI. Regression analysis for PCE concentration in Layer C (bottom layer) in relation to daughter products in Layer C. Analysis done in JUMP 5.0.

Stepwise Fit

Response: PCE C

Stepwise Regression Control

Prob to Enter	0.250
Prob to Leave	0.100
Direction	Forward

3 rows not used due to missing values.

Current Estimates

SSE	DFE	MSE	RSquare	RSquare Adj	Cp	AIC
242.37626	59	4.108072	0.8286	0.8199	4	92.88346

Lock	Entered	Parameter	Estimate	nDF	SS	"F Ratio"	"Prob>F"
☑	☑	Intercept	29.3959391	1	0	0.000	1.0000
☐	☑	TCE C	-5.0869872	1	904.4238	220.158	0.0000
☐	☑	C-DCE C	-0.4776524	1	16.67735	4.060	0.0485
☐	☑	VC C	0.28347305	1	4.319006	1.051	0.3094

Step History

Step	Parameter	Action	"Sig Prob"	Seq SS	RSquare	Cp	p
1	TCE C	Entered	0.0000	1151.15	0.8139	5.0716	2
2	C-DCE C	Entered	0.0496	16.51544	0.8256	3.0513	3
3	VC C	Entered	0.3094	4.319006	0.8286	4	4

Appendix I: Method Error Analysis for PCE and TCE

Calculations done in Excel.

Inflow Conc (Signal/AUC)

Duplicate samples taken and analyzed to examine method error

Date	GC Signal		Conc (ppb)		TCE	PCE
Collected	TCE	PCE	TCE	PCE	Difference	Difference
7-Dec-02	675.412	479956	0.184	32.852		
7-Dec-02	715.438	484978	0.195	33.196	0.01090	0.34375
13-Dec-02	702.020	497871	0.191	34.079		
13-Dec-02	692.021	490593	0.188	33.580	0.00272	0.49817
15-Dec-02	684.901	491096	0.186	33.615		
15-Dec-02	686.460	489309	0.187	33.493	0.00042	0.12232
4-Jan-03	576.035	484097	0.157	33.136		
4-Jan-03	573.535	477385	0.156	32.676	0.00068	0.45943
				Average:	**0.00368**	**0.35592**
				Std Dev:	**0.00492**	**0.16898**
				95% CI:	**0.00482**	**0.16560**

Outflow Conc (Signal/AUC)

Duplicate samples taken and analyzed to examine method error

Date	GC Signal		Conc (ppb)		TCE	PCE
Collected	TCE	PCE	TCE	PCE	Difference	Difference
7-Dec-02	1252.94	136465	0.341	9.341		
7-Dec-02	1247.26	130867	0.340	8.958	0.00155	0.38318
13-Dec-02	1356.58	137028	0.369	9.379		
13-Dec-02	1362.30	135610	0.371	9.282	0.00156	0.09706
15-Dec-02	1078.74	103233	0.294	7.066		
15-Dec-02	1081.09	102421	0.294	7.011	0.00064	0.05558
4-Jan-03	1580.24	93424	0.430	6.395		
4-Jan-03	1590.95	91655	0.433	6.274	0.00292	0.12107
				Average:	**0.00167**	**0.16422**
				Std Dev:	**0.00094**	**0.14845**
				95% CI:	**0.00092**	**0.14548**

Appendix J: Data from Water Monitoring Sonde

Data collected with a YSI water monitoring sonde on 9 Jan 03.

TOP LAYER

		Measurement	DateTime	Temp	SpCond	DO Conc	pH	pH	ORP	BP
X Coord	Y Coord	Location	M/D/Y	C	mS/cm	mg/L		mV	mV	psi
26.53409	14.259515	well1	1/9/03 16:31	8.330	0.923	0.620	7.070	-13.200	-100.000	14.010
36.80304	47.311685	well2	1/9/03 16:53	8.890	1.790	1.100	6.880	-2.200	-106.000	13.990
68.33517	39.52486	well3	1/9/03 17:16	8.810	1.155	0.440	7.120	-15.800	-118.000	13.990
78.71099	30.96738	well4	1/9/03 17:31	7.040	0.007	5.930	7.240	-22.100	-90.000	13.990
99.653	22.664735	well5	1/9/03 17:49	6.530	2.257	0.550	6.830	0.300	-109.000	13.990
110.0626	47.064895	well6	1/9/03 18:02	6.830	2.342	1.920	6.810	1.500	-76.000	13.990
			Average	**7.738**	**1.412**	**1.760**	**6.992**	**-8.583**	**-99.833**	**13.993**
			Std Dev	**1.058**	**0.895**	**2.115**	**0.177**	**9.772**	**14.945**	**0.008**
			95% CI	**0.847**	**0.716**	**1.692**	**0.141**	**7.819**	**11.959**	**0.007**

MIDDLE LAYER

		Measurement	DateTime	Temp	SpCond	DO Conc	pH	pH	ORP	BP
X Coord	Y Coord	Location	M/D/Y	C	mS/cm	mg/L		mV	mV	psi
26.53409	14.259515	well1	1/9/03 16:35	9.920	1.121	0.520	6.930	-4.800	-90.000	14.010
36.80304	47.311685	well2	1/9/03 17:02	9.880	2.339	0.270	6.790	2.800	-115.000	13.990
68.33517	39.52486	well3	1/9/03 17:20	10.160	0.945	0.100	7.240	-22.500	-118.000	13.990
78.71099	30.96738	well4	1/9/03 17:37	8.010	0.836	0.150	7.010	-9.700	-22.000	13.990
99.653	22.664735	well5	1/9/03 17:52	8.580	1.824	0.100	6.950	-6.300	-97.000	13.990
110.0626	47.064895	well6	1/9/03 18:06	7.540	2.347	0.080	6.890	-3.000	-98.000	13.990
			Average	**9.015**	**1.569**	**0.203**	**6.968**	**-7.250**	**-90.000**	**13.993**
			Std Dev	**1.118**	**0.691**	**0.170**	**0.152**	**8.539**	**35.060**	**0.008**
			95% CI	**0.895**	**0.553**	**0.136**	**0.121**	**6.832**	**28.053**	**0.007**

BOTTOM LAYER

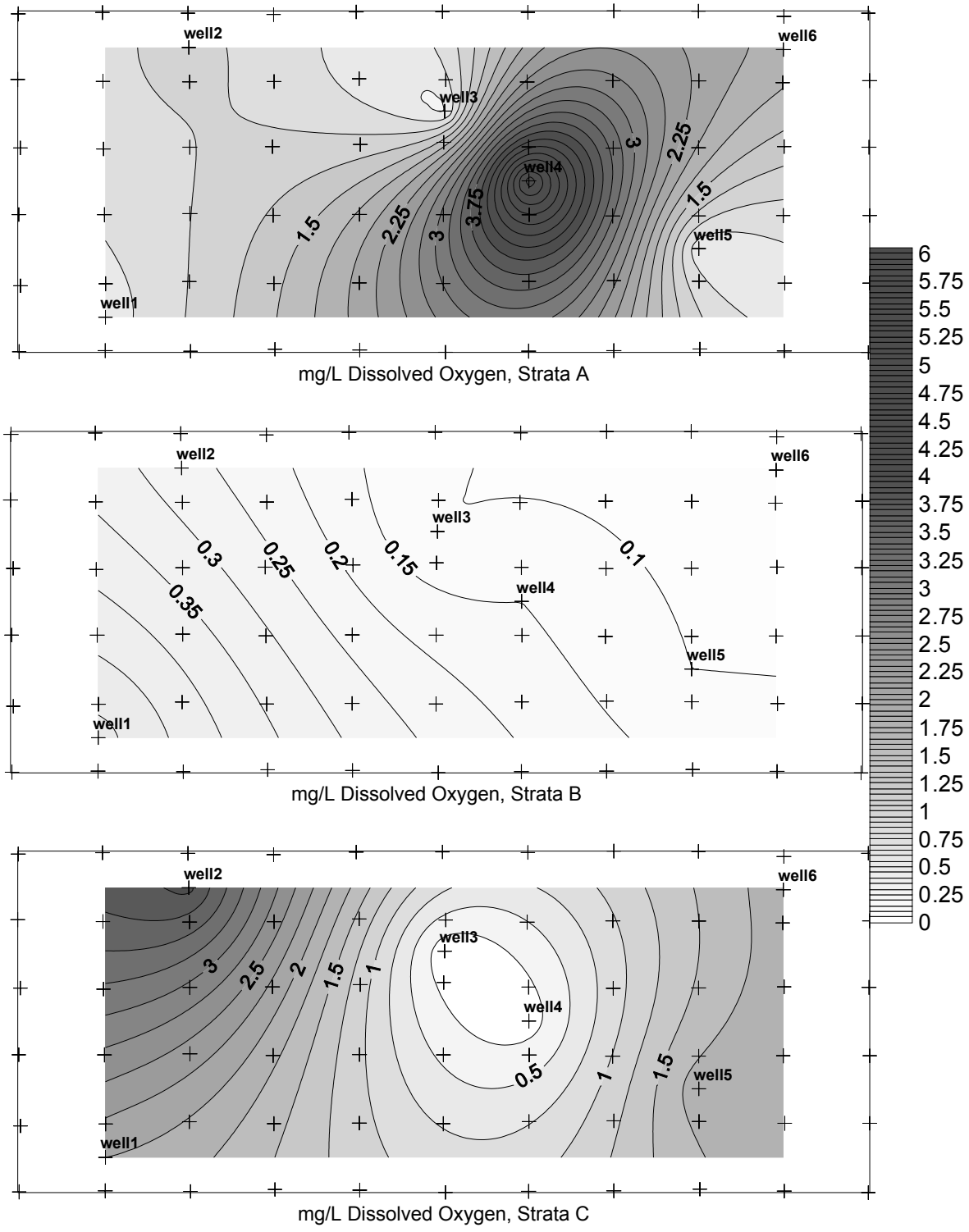
		Measurement	DateTime	Temp	SpCond	DO Conc	pH	pH	ORP	BP
X Coord	Y Coord	Location	M/D/Y	C	mS/cm	mg/L		mV	mV	psi
26.53409	14.259515	well1	1/9/03 16:44	11.770	0.872	2.000	7.060	-12.600	18.000	13.990
36.80304	47.311685	well2	1/9/03 17:10	11.670	0.873	4.070	7.100	-14.600	24.000	14.000
68.33517	39.52486	well3	1/9/03 17:24	10.200	0.865	0.080	7.090	-14.200	-72.000	13.990
78.71099	30.96738	well4	1/9/03 17:44	9.670	0.813	0.130	7.120	-15.900	-63.000	13.990
99.653	22.664735	well5	1/9/03 17:57	11.570	0.860	1.900	7.120	-15.900	-24.000	13.990
110.0626	47.064895	well6	1/9/03 18:15	10.190	0.849	1.890	7.080	-13.400	2.000	13.990
			Average	**10.845**	**0.855**	**1.678**	**7.095**	**-14.433**	**-19.167**	**13.992**
			Std Dev	**0.926**	**0.023**	**1.474**	**0.023**	**1.328**	**41.058**	**0.004**
			95% CI	**0.741**	**0.018**	**1.180**	**0.019**	**1.062**	**32.853**	**0.003**

SpCond = Specific Conductivity
DO = Dissolved Oxygen
ORP = Oxidation Reduction Potential
BP = Atmosphereic Barametric Pressure at time of measurement

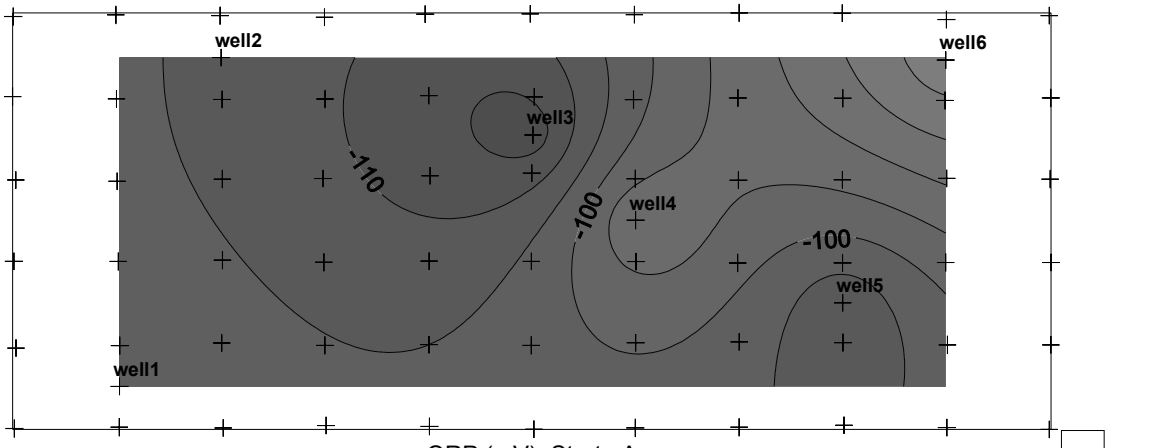
Note: The XY coordinates represent the center of the nests of the three wells. The X and Y coordinates were calculated by computing the midpoint between the two adjacent piezometers that were previously surveyed.

Appendix K: Contour Plots of Water Monitoring Sonde Data (9 Jan 03)

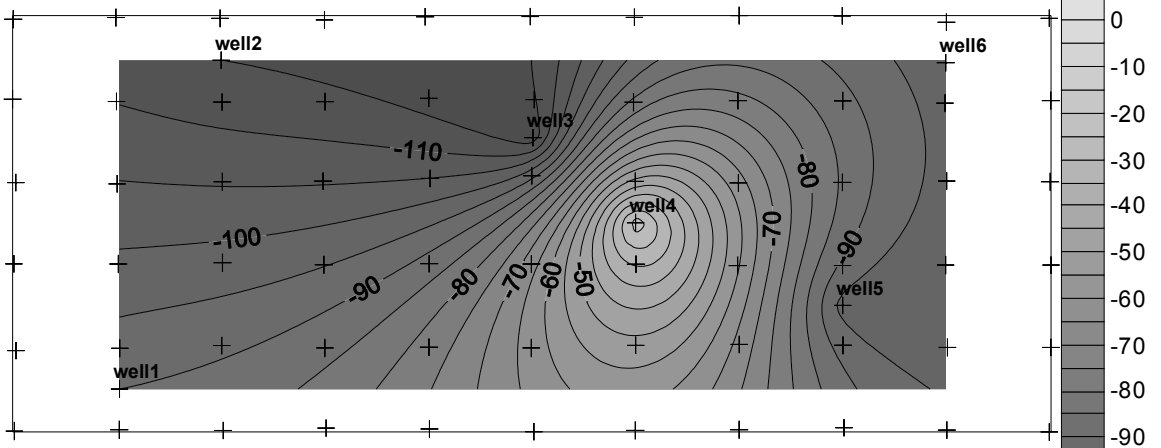
I. Dissolved Oxygen (mg/L)



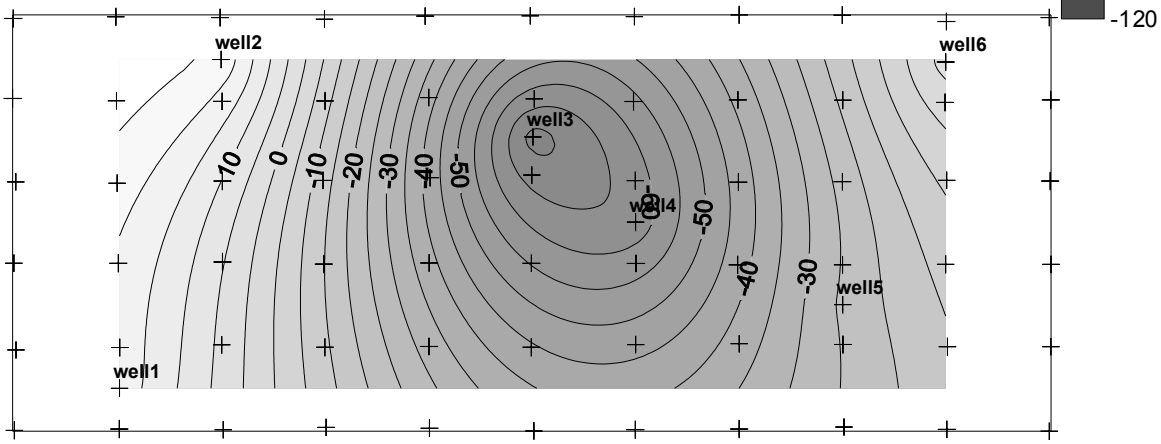
II. Oxidation Reduction Potential (Milivolts)



ORP (mV), Strata A

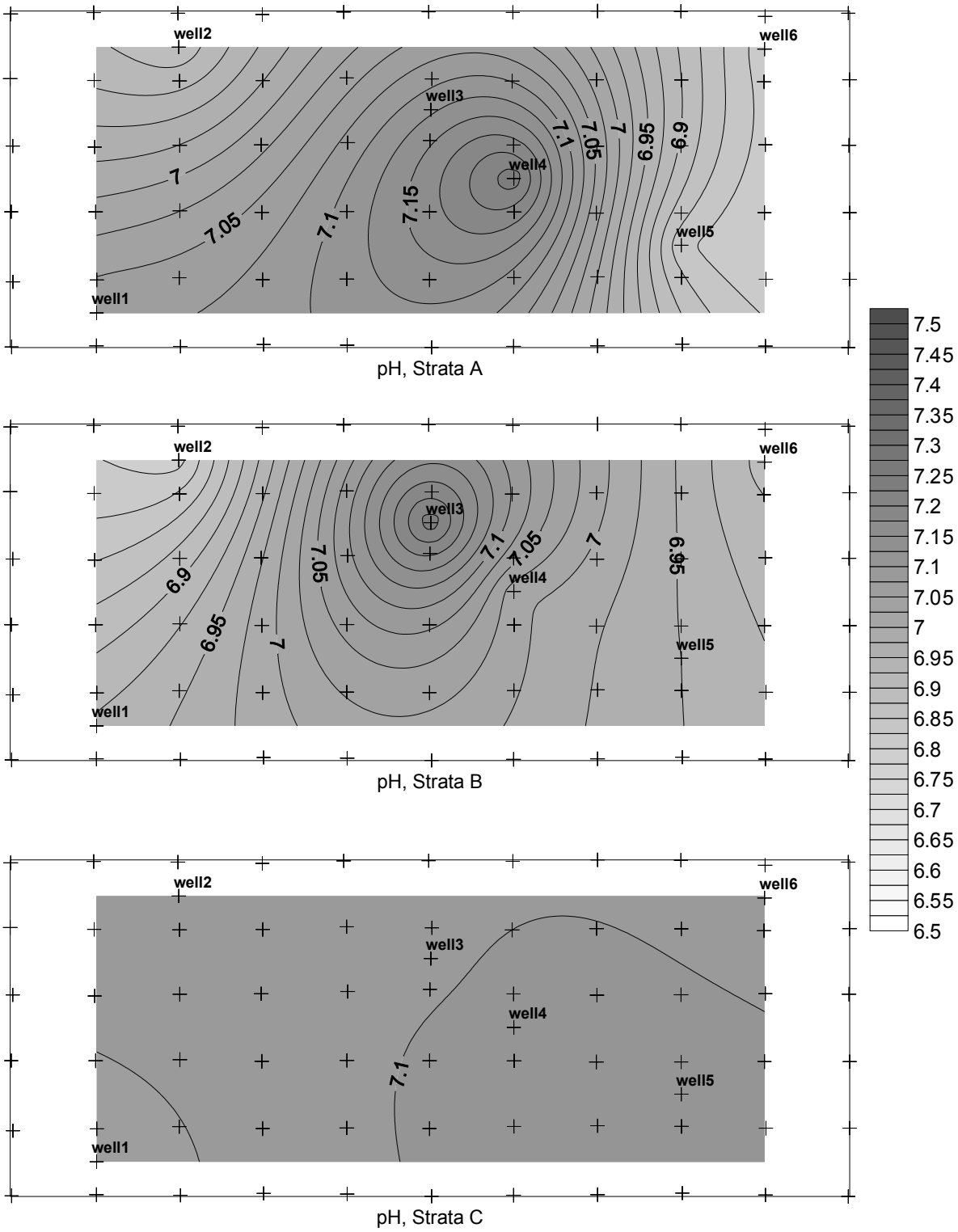


ORP (mV), Strata B

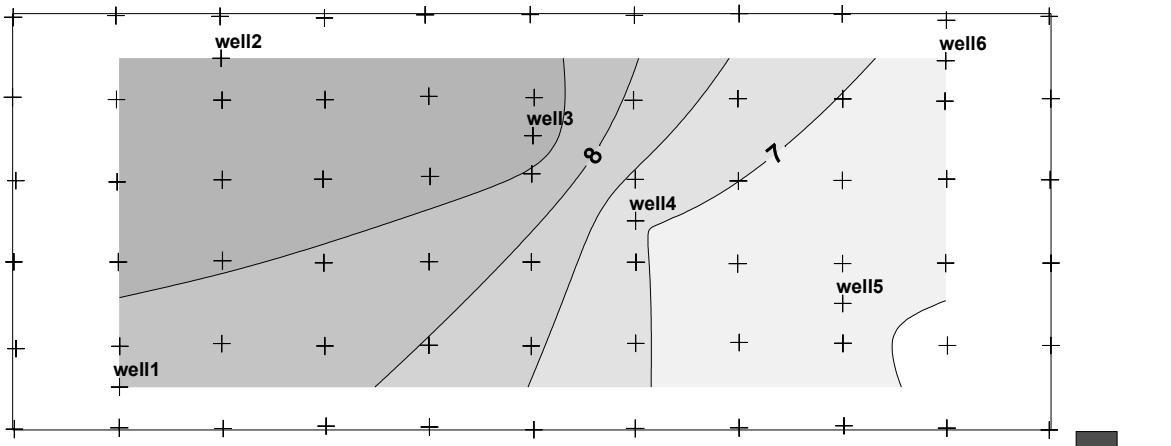


ORP (mV), Strata C

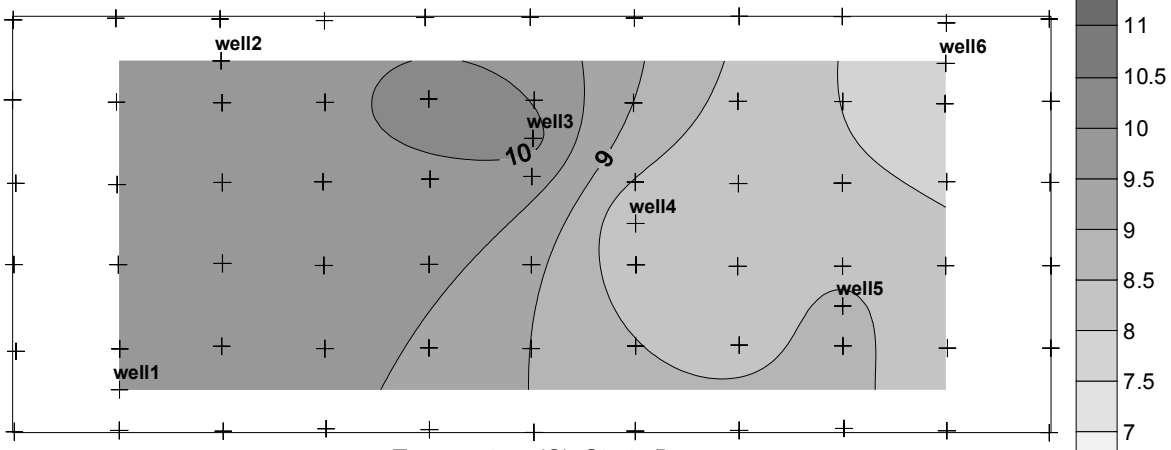
III. pH


well2
well6
well3
well4
well5
well1
7
7.05
7.1
7.15
6.9
6.95
pH, Strata A
pH, Strata B
pH, Strata C
7.5
7.45
7.4
7.35
7.3
7.25
7.2
7.15
7.1
7.05
7
6.95
6.9
6.85
6.8
6.75
6.7
6.65
6.6
6.55
6.5

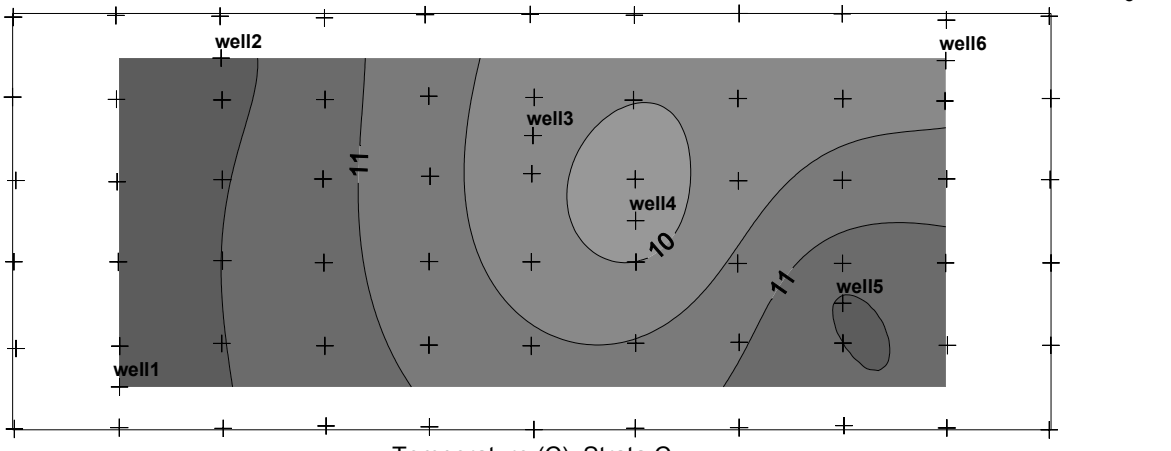
IV. Water Temperature (Degrees Celsius)



Temperature (C), Strata A



Temperature (C), Strata B

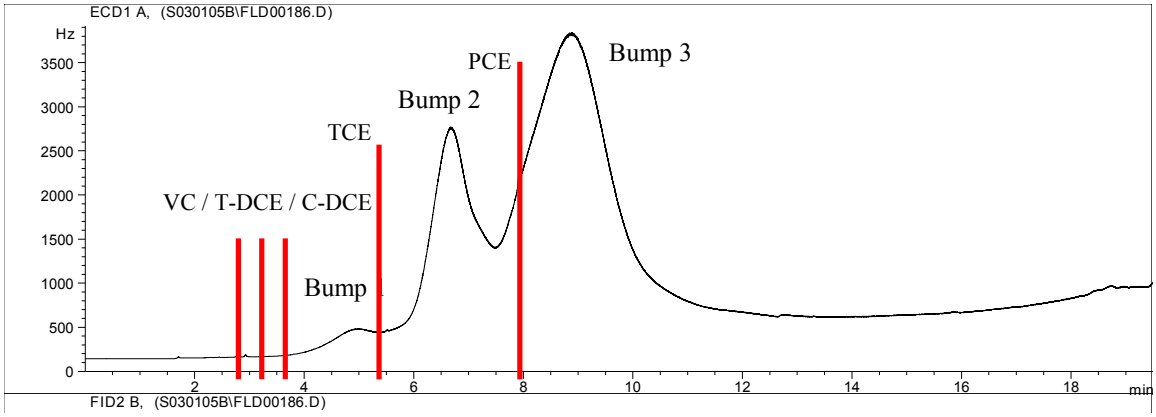


Temperature (C), Strata C

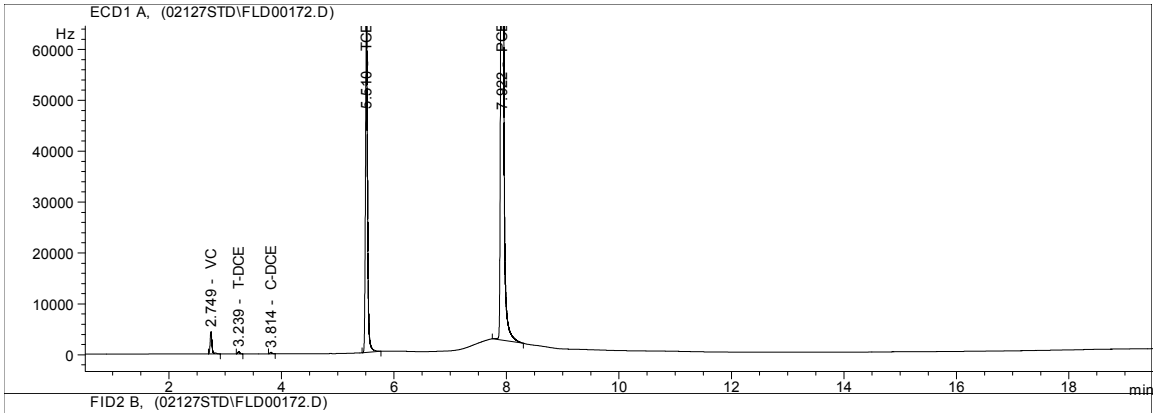
Appendix L: Examples of Output Chromatograms

I. Chromatograms below were generated with ChemStation software in conjunction with an Agilent 6890 Gas Chromatograph.

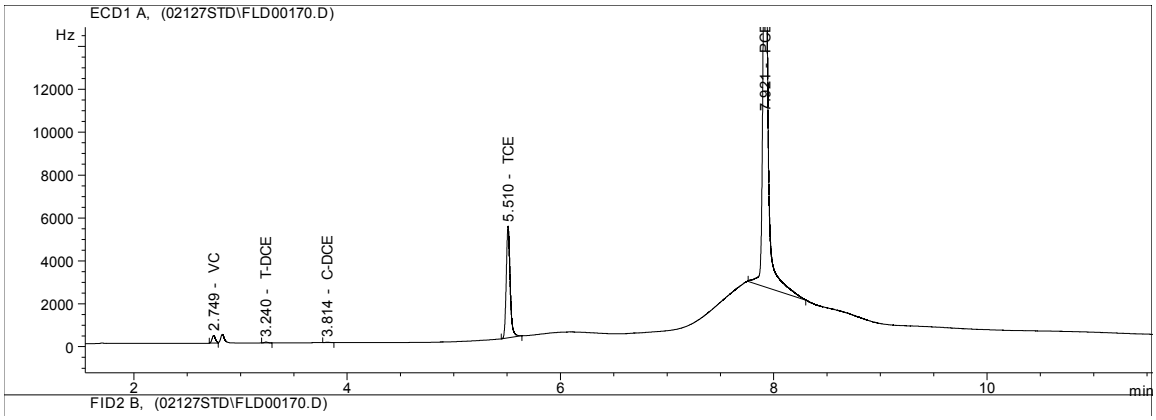
Below is a chromatogram generated from the uECD with a blank de-ionized water sample. Notice the three arbitrary "bumps" in the baseline with respect to the retention times for the five analytes. Retention times marked with a thick vertical line.



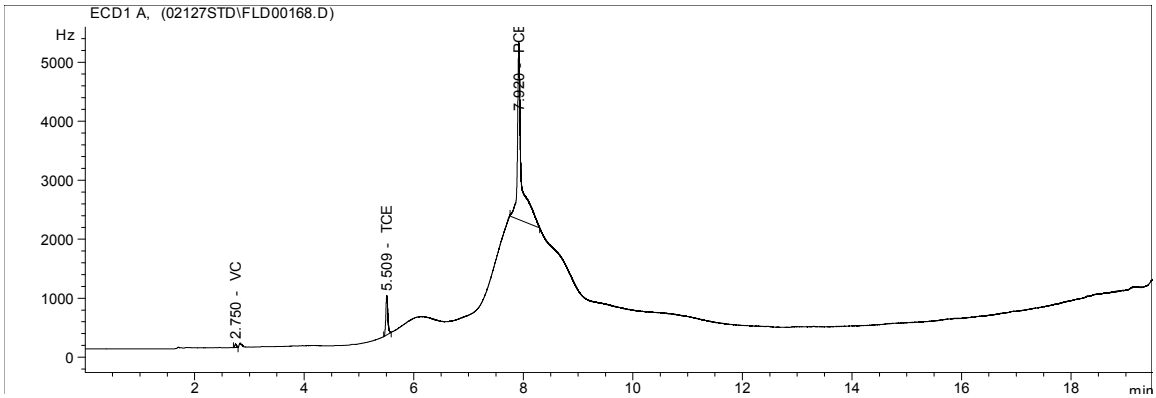
Below is a typical chromatogram output for a **45.45 ppb standard mix solution** from the ChemStation software run with an Agilent 6890 Gas Chromatograph. The high concentration of the analytes minimizes the interference of the "bumps".



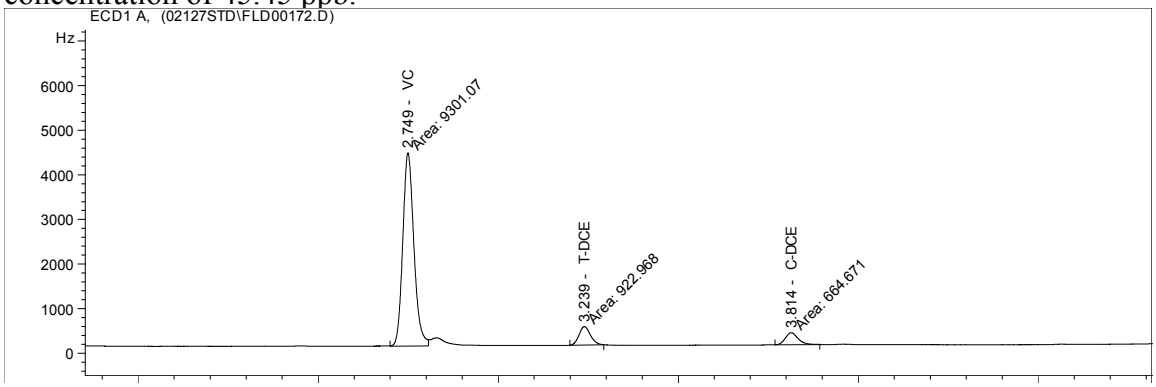
II. Below is a typical chromatogram output for a **4.54 ppb standard mix solution** from the ChemStation software run with an Agilent 6890 Gas Chromatograph. Note that the "humps" in the baseline start to interfere with the autointegration function drawing the baseline for PCE incorrectly.



Below is a typical chromatogram output for a **0.54095 ppb standard mix solution** from the ChemStation software run with an Agilent 6890 Gas Chromatograph. Note that the "humps" in the baseline interfere with the auto-integration function drawing the baseline for PCE incorrectly.



Below is a blow-up of the chromatogram depicting the 3 lightest analytes at a concentration of 45.45 ppb.



Appendix M: VOC Sample Data Taken from Cell 2

Results of Samples Taken From Cell 2 Before it was Shut Down

Date Collected	Location			GC Signal (Aea Under the Curve)				Concentration (ppb)			
				VC	C-DCE	TCE	PCE	VC	C-DCE	TCE	PCE
11-Dec-02	Inflow			0.00	0.00	590.74	507071.00	0.00	0.00	0.16	34.71
11-Dec-02	Outflow			0.00	0.00	1992.59	171011.00	0.00	0.00	0.54	11.71
11-Dec-02	5	a	Piez	0.00	42.05	8707.25	194868.00	0.00	2.84	2.37	13.34
11-Dec-02	21	a	Piez	0.00	73.07	4513.67	128766.00	0.00	4.93	1.23	8.81
11-Dec-02	30	a	Piez	0.00	0.00	766.05	7568.01	0.00	0.00	0.21	0.52
11-Dec-02	43	a	Piez	0.00	77.70	439.83	7623.92	0.00	5.25	0.12	0.52
11-Dec-02	58	a	Piez	37.84	0.00	100.24	6786.28	0.19	0.00	0.03	0.46
11-Dec-02	62	a	Piez	0.00	83.75	16918.80	27728.10	0.00	5.65	4.61	1.90
11-Dec-02	1	a	Well	Empty Well							
11-Dec-02	2	a	Well	0.00	36.29	2794.32	56548.60	0.00	2.45	0.76	3.87
11-Dec-02	3	a	Well	0.00	49.22	601.21	1916.82	0.00	3.32	0.16	0.13
11-Dec-02	4	a	Well	0.00	0.00	1920.11	53115.90	0.00	0.00	0.52	3.64
11-Dec-02	5	a	Well	0.00	0.00	2325.92	73414.30	0.00	0.00	0.63	5.03
11-Dec-02	6	a	Well	0.00	0.00	2005.90	202728.00	0.00	0.00	0.55	13.88
11-Dec-02	5	b	Piez	0.00	0.00	1414.58	410078.00	0.00	0.00	0.39	28.07
11-Dec-02	21	b	Piez	0.00	0.00	1083.59	431168.00	0.00	0.00	0.30	29.51
11-Dec-02	30	b	Piez	0.00	0.00	2684.03	355906.00	0.00	0.00	0.73	24.36
11-Dec-02	43	b	Piez	0.00	0.00	6263.13	203147.00	0.00	0.00	1.71	13.91
11-Dec-02	58	b	Piez	103.66	0.00	69.24	2179.15	0.51	0.00	0.02	0.15
11-Dec-02	62	b	Piez	0.00	38.76	839.14	2098.58	0.00	2.62	0.23	0.14
11-Dec-02	1	b	Well	0.00	0.00	699.04	46115.60	0.00	0.00	0.19	3.16
11-Dec-02	2	b	Well	0.00	0.00	971.45	459755.00	0.00	0.00	0.26	31.47
11-Dec-02	3	b	Well	0.00	0.00	2050.17	327869.00	0.00	0.00	0.56	22.44
11-Dec-02	4	b	Well	0.00	0.00	10131.40	4506.82	0.00	0.00	2.76	0.31
11-Dec-02	5	b	Well	0.00	0.00	1044.51	452642.00	0.00	0.00	0.28	30.98
11-Dec-02	6	b	Well	0.00	0.00	734.70	460126.00	0.00	0.00	0.20	31.49
11-Dec-02	5	c	Piez	0.00	0.00	1243.57	360838.00	0.00	0.00	0.34	24.70
11-Dec-02	21	c	Piez	0.00	0.00	1029.42	420104.00	0.00	0.00	0.28	28.76
11-Dec-02	30	c	Piez	0.00	0.00	2755.21	298757.00	0.00	0.00	0.75	20.45
11-Dec-02	43	c	Piez	0.00	0.00	894.60	426065.00	0.00	0.00	0.24	29.16
11-Dec-02	58	c	Piez	0.00	0.00	2520.11	156089.00	0.00	0.00	0.69	10.68
11-Dec-02	62	c	Piez	0.00	0.00	1385.73	395822.00	0.00	0.00	0.38	27.09
11-Dec-02	1	c	Well	0.00	0.00	4632.14	321159.00	0.00	0.00	1.26	21.98
11-Dec-02	2	c	Well	0.00	0.00	1362.21	212628.00	0.00	0.00	0.37	14.55
11-Dec-02	3	c	Well	0.00	0.00	1905.87	383585.00	0.00	0.00	0.52	26.26
11-Dec-02	4	c	Well	0.00	0.00	1186.18	443517.00	0.00	0.00	0.32	30.36
11-Dec-02	5	c	Well	0.00	0.00	765.38	402334.00	0.00	0.00	0.21	27.54
11-Dec-02	6	c	Well	0.00	0.00	6024.37	31625.30	0.00	0.00	1.64	2.16

a = Top layer
b = Middle layer
c = Bottom layer

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Vita

Captain Nathan D. Clemmer graduated from Oswayo Valley High School in Shinglehouse, Pennsylvania. He then entered undergraduate studies at The Pennsylvania State University, State College, Pennsylvania where he earned his Bachelor of Science degree in Civil Engineering with minors in Environmental Engineering and Military Studies. He was commissioned through the Detachment 720 AFROTC unit in 1996 as a Distinguished Graduate.

Captain Clemmer's first assignment was as a student in Specialized Undergraduate Pilot Training at the 42nd Flight Training Wing, Laughlin Air Force Base, TX, from January 1997 to January 1998. He was then assigned overseas as the Deputy Flight Chief of the Resources Flight, 48th Civil Engineering Squadron, RAF Lakenheath, UK. In January 1999 he moved to the Engineering Flight where he served as a NATO/MILCON program manager until July 2001. While stationed at RAF Lakenheath, he deployed to the 363rd Expeditionary Civil Engineer Squadron, Prince Sultan Air Base, Saudi Arabia from December 2000 until March 2001 as the pavements engineer. In August 2001, he entered the Graduate School of Engineering and Management, Air Force Institute of Technology. Upon graduation, he will be assigned to 375th Civil Engineering Squadron, Scott Air Force Base as the Chief of Maintenance Engineering.

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14. ABSTRACT

Widespread chlorinated ethene contamination of aquifers coupled with high costs of current treatment technologies demand innovative remediation solutions. Sequential anaerobic and aerobic zones of wetland sediments allow complete biodegradation of chlorinated ethenes such as Tetrachloroethylene (PCE).

This thesis characterized the chlorinated solvent contamination levels in three strata of an upward flow constructed wetland. Analysis of samples was accomplished by purge-and-trap gas chromatography. Water quality parameters (Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP), pH, Conductivity, and Temperature) were measured in monitoring wells with a water monitoring sonde.

After removing data outliers caused by short-circuiting flow, PCE concentrations declined from an average of 32.59 ± 0.699 ppb (± 95% CI) in the inflow stream to an average of 0.171 ± 0.079 ppb in the upper layer (99.3% reduction). Concentration trends of the degradation products cis-1,1-Dichloroethylene (cis-DCE), Vinyl Chloride (VC), and Trichloroethylene (TCE) indicate dechlorination processes are occurring. TCE at concentrations below 0.6 ppb and PCE were the only analytes detected in the inflow or outflow. Water quality measurements (DO and ORP) decreased from the bottom to the middle layer to a level that supports anaerobic reductive dechlorination but not methanogenesis. The DO increased slightly from the middle to the top layer while ORP continued to decrease.

15. SUBJECT TERMS

Constructed Wetlands, Chlorinated Ethenes, Reductive Dechlorination, Purge-and-Trap Gas Chromatography

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