MODELING CHLORINATED ETHENE
REMOVAL IN CONSTRUCTED WETLANDS: A
SYSTEM DYNAMICS APPROACH

THESIS

Colby D. Hoefar, Captain, USAF

AFIT/GEE/ENV/00M-09

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

Wright-Patterson Air Force Base, Ohio

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

MODELING CHLORINATED ETHENE REMOVAL IN CONSTRUCTED
WETLANDS: A SYSTEM DYNAMICS APPROACH

THESIS

Presented to the Faculty of the Graduate School of Engineering and Management of the

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the Degree of Master of Science in

Engineering and Environmental Management
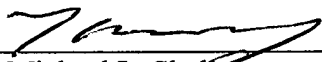
Colby D. Hoefar, B.S.
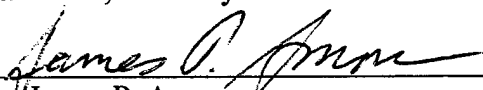
Captain, USAF

March 2000

MODELING CHLORINATED ETHENE REMOVAL IN CONSTRUCTED WETLANDS: A SYSTEM DYNAMICS APPROACH
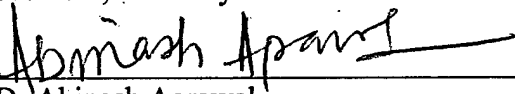
Colby D. Hoefar, B.S.
Captain, USAF

Approved:

Dr. Michael L. Shelley
Chairman, Advisory Committee

7 Mar 00
date

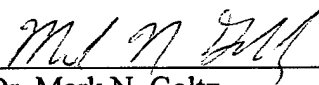Dr. James P. Amon
Member, Advisory Committee

8 Mar 00
date

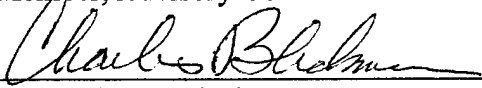Dr Abinash Agrawal
Member, Advisory Committee

8 Mar 00
date

Dr. Mark N. Goltz
Member, Advisory Committee

7 Mar 00
date

Dr Charles A. Bleckmann
Member, Advisory Committee

7 Mar 00
date

Acknowledgements

I would like to express my sincere gratitude to my advisory committee members, Dr. James Amon, Dr. Abinash Agrawal, Dr. Mark Goltz, and Dr. Charles Bleckmann, for their guidance and support throughout the course of this thesis effort. Your insight and experience were greatly appreciated.

I am most indebted to my advisor and advisory committee chairman, Dr. Michael Shelley. Thank you for your patience, insight, support and confidence. This endeavor would not have been possible without it.

Lastly, I would like to thank both my family and close friends, for your unfailing support and love that helped me through this effort. You are the foundation for my success.

Colby D. Hoefar

Table of Contents

List of Figures

List of Tables

Abstract

The purpose of this study is to gain understanding of the dynamics of the processes that degrade Perchloroethene (PCE) to ethylene, or carbon dioxide (CO_2), within the confines of a constructed wetland. A system dynamics approach will be used. This model is focused on identifying and optimizing the naturally occurring processes in stratified wetland sediment that reduce mass, toxicity, mobility, volume or concentration of contaminants in groundwater.

Contaminant fate and transport within a wetland system is an extremely complex and dynamic process. The entities and mechanisms that drive wetland behavior are dynamic. The system dynamics process is favored over other modeling processes for this study as it develops insight into the behavior of the system as a whole versus one influential mechanism in the system.

Confidence in the model was built through verification and testing. Reasonable behavior resulted from a reasonable range of parameter values. The structure of the model represents the mechanisms and their interactions of an actual wetland system. This study provides a fundamental understanding of contaminant fate and transport in a constructed wetland and gives some insight for implementation. Testing identified specific parameters of typical wetland plant species, which could be optimized to have the most effect on contaminant fate. These parameters were the radius of aerobic influence and the number of roots per square meter. A remediation manager can use this model to explore system behavior by controlling or optimizing specific parameters to better manage contaminant fate and transport in a constructed wetland, saving time and resources.

MODELING CHLORINATED ETHENE REMOVAL IN CONSTRUCTED WETLANDS: A SYSTEM DYNAMICS APPROACH

I. Introduction

The purpose of this study is to gain understanding of the dynamics of the processes that degrade Perchloroethene (PCE) to ethylene, or carbon dioxide (CO_2), within the confines of a constructed wetland. A system dynamics approach will be used. This model is focused on identifying and optimizing the naturally occurring processes in stratified wetland sediment that reduce mass, toxicity, mobility, volume or concentration of contaminants in groundwater. These processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants (Lee et al., 1998). This model will specifically concentrate on the removal of Perchloroethene and its daughter products Trichloroethene, isomers of dichloroethene and vinyl chloride, via biotic and abiotic processes within the sediment of a constructed wetland.

A number of groundwater plumes of chlorinated solvents were discovered beneath Air Force bases in the late 1970's. Intense research into these situations discovered this problem is endemic across the Air Force and the Department of Defense. The National Research Council (1994) estimated 7,300 sites at 1,800 locations, owned by DOD, are contaminated (National Research Council, 1994) with chlorinated solvents. Costs of cleanups are staggering. The Office of Management and Budget estimates the cost of remediation at contaminated sites owned by Departments of Defense, Energy, Interior, and Agriculture and the National Aeronautics and Space Administration will total between $234 and $389 billion over the next 75 years (Federal Facilities Policy

Group, 1995). However, use of solvents and degreasers is not declining. Global use of chlorinated solvents trichloroethene (TCE), Perchloroethene (PCE), and 1, 1, 1-trichloroethane (1,1,1-TCA) in 1994 totaled 900,000 metric tons, with the U.S. use accounting for 40 percent of the total (Leder and Yoshida, 1995). Lower molecular weight chlorinated hydrocarbons, particularly TCE, were used as solvents in routine maintenance or cleaning of everything from electronic parts to jet engines, weapon system components, and septic tanks. Chlorinated solvents were also used as intermediates in chemical manufacturing and as carrier solvents for pesticides and herbicides. Typically, they were stored in bulk, usually in large underground storage tanks. As a result of their widespread use in industry, agriculture, commercial business, and homes, chlorinated solvents are among the most common groundwater contaminant. Nine of the 20 most common chemicals found in groundwater at Superfund sites are chlorinated solvents (National Research Council, 1997). TCE is the contaminant most commonly detected in groundwater (National Research Council, 1994), thereby, posing a threat to public health, ecosystem viability, and funds associated with environmental protection and preservation due to the long persistence of the contaminant.

TCE is denser than water, is relatively insoluble, and will tend to migrate toward the bottom of the groundwater aquifer where it will sorb and desorb onto the soil as it is slowly carried by the groundwater flow. TCE is a suspected carcinogen, is very volatile, and is readily removed by air stripping (Masters, 1997). Biodegradation is very slow and will only occur if the conditions are conducive. The degradation pathway for TCE, under anaerobic conditions, is to isomers of dichloroethene (DCE), 1,1 DCE, *cis* 1,2 DCE, or *trans* 1,2 DCE. DCE has been used as a metal degreaser and in the manufacture of a

2

number of products, including vinyl chloride, fumigants, varnish removers, and soap compounds. Although it is not a known carcinogen, exposure to high levels of DCE can cause injury to the central nervous system, liver and kidneys (Masters, 1997). DCE is slightly more water-soluble than TCE and is difficult to volatize. Further reduction of DCE will commonly result in vinyl chloride. Vinyl chloride was once a household cleaning agent, now more commonly used as grain fumigant, fire extinguisher, and solvent. It is very toxic if ingested; only a few milliliters can produce death. It is very persistent and is relatively insoluble in water. It is listed as a probable human carcinogen under the National Drinking Water Standards of 1987. The goal of bioremediation is to biologically breakdown a hazardous contaminant to an innocuous end product. Vinyl chloride can be converted to ethylene, carbon dioxide, or water, under the proper environmental conditions.

Remediation can be divided into three general categories: 1) technologies for solidification, stabilization, and containment; 2) technologies using biological and/ or chemical reactions to destroy or transform the contaminant; 3) technologies which separate the contaminant from the contaminated media, mobilize the contaminant and extract it from the subsurface (National Research Council, 1997).

Solidification and stabilization focus on decreasing the mobility and/ or toxicity of the contaminant by reducing the solubility, volatility, or medium permeability. Generally, these processes are appropriate for shallow contamination and are for soil treatment. Some of the technologies are: asphalt batching, biostabilization, passive-reactive barriers, enhanced sorption, in situ soil mixing, and lime addition (National Research Council, 1997). Containment technologies are designed to prevent contaminant

3

movement away from the zone of contamination through incorporation of physical or hydraulic barriers. Technologies include pump and treat systems, and low permeability barriers utilizing slurry walls, sheet pile walls, and grout walls.

Biological and chemical processes transform the contaminant into a less harmful product. Biological processes (bioremediation) rely on microorganisms to transform the contaminant through varying reactions resulting in a degraded compound. Reactions may be aerobic or anaerobic and can be direct or cometabolic. Environmental conditions impact microbial metabolism and the addition of nutrients, enzymes, or substrates may be necessary to optimize conditions for degradation. Chemical processes transform the compound through chemical reactions; these processes are used less than biological treatment. Biological and chemical processes are the only methods that can completely destroy an organic contaminant. Some biological treatment technologies are biopiles, bioventing and biosparging, composting, engineered in situ bioremediation, and intrinsic bioremediation (natural attenuation). Chemical processes include oxidation, incineration, substitution and zero-valent ion barriers.

Separation, mobilization, and extraction processes separate the contaminant from the soil particles, immobilize it into the aqueous phase or airspace in the soil voids and extract the contaminant to the surface for treatment. These processes can use heat, chemicals, vacuums or electrical current to separate the contaminant from the soil and move it to an extraction zone (National Research Council, 1997).

If the chlorinated ethene contaminated groundwater is in contact with an anaerobic environment (oxygen depleted zone), the contaminant can be degraded through microbial degradation (Sims et al., 1991). This process is called reductive

dehalogenation, and through this process, TCE can degrade into ethylene (Sims et al., 1991). However, attaining the proper conditions for reductive dehalogenation is often very difficult in aquifers due to their typical structure and dynamic nature. Microbial populations are constantly changing as a result of their consumption of organic matter and respiration. One species' waste may be another's food source. Groundwater within the aquifer may be aerobic or anaerobic, possibly occurring in microzones in close proximity to one another. Oxygen levels are very crucial in determining the type of microbial population and the type of degradation that can occur. Aquifers that are very shallow or are dependent on seasonal recharge may fluctuate many times over the year. This fluctuation may create dormant periods for microbial populations, precluding establishment of the stable population required for reductive dehalogenation. Often, remediation methods in this situation concentrate on costly pump and treat containment, soil vapor extraction, air sparging, or dual phase vacuum extraction. Although these methods are generally effective, they are very expensive to install and maintain over the course of many years required for treating the plume. The following table relates costs of available treatment options at several remediation sites.

Table 1 Site Remediation Cost Comparison

Metric	IBR/NA	ISB Recirculating	ISB Barrier	PRB	P & T
$/ 1000 liters treated	.32	.48	1.10	1.40	2.35
$/ kg PCE removed	330	480	1,100	1,400	3,500

Adopted from Quinton et al. IBR/ NA, intrinsic bioremediation/ natural attenuation; ISB, in situ bioremediation with recirculation; ISB Barrier, in situ bioremediation with downgradient biobarrier; PRB, permeable reactive barrier; P&T, pump and treat.

Quinton et al developed a present-value model to provide a consistent basis for cost and performance comparisons. The method is based on a template site with a perchloroethene (PCE) plume 300m long by 120m wide. The model allows varying depths of the water table, (up to 27m) and input variables including remediation duration, estimated engineering and flow/transport modeling cost, equipment costs, operations and maintenance costs, and monitoring costs. Lee, Odom and Buchanan applied the model comparing four primary technologies for remediating the plume. The technologies were, in situ bioremediation (ISB) involving substrate-enhanced anaerobic bioremediation (utilizing source area recirculation system and downgradient biobarrier), intrinsic bioremediation/ natural attenuation (IBR/ NA), in situ permeable reactive barrier (PRB; zero valent iron wall technology), and simple pump and treat system (P&T) (Lee et al., 1998). They calculated total system cost, cost per unit of contaminant removed and cost per unit volume of groundwater treated over a period of 30 years. Results of their analysis are reproduced in Table 1. Intrinsic bioremediation/ natural attenuation is the least cost method and pump and treat is the most expensive. The use of constructed wetlands to intrinsically bioremediate chlorinated solvents would also be less expensive than traditional pump and treat and would fall under t IBR/NA category in the Lee, Odom and Buchanan model.

Natural treatment systems are similar to conventional treatment systems in that both require energy to operate. However, energy for conventional treatment systems is typically of a nonrenewable fossil fuel. Natural treatment systems require the same amount energy input for every kilogram of pollutant degraded as conventional systems, but the source for energy is the sun, wind, rain, soil and biomass (Kadlec, 1996). The

6

driving cost for a natural treatment system is the amount of land required, whereas the driving cost of a conventional treatment system is the amount of energy required. Kadlec and Knight illustrate this point with a simplified example: A conventional treatment system requires about 2 ha of land, $427/d of high quality labor, energy, and chemical input, for a capital cost of about $4,112,000. In contrast, a natural system requires 36 ha of land, $123/d of high quality energies, and solar and wind energies which come with the land for a capital cost of $3,664,000. Contaminant treatment through the use of natural systems, like a constructed wetland, is a viable treatment option.

Wetlands are unique ecosystems whether they are constructed by man or Mother Nature. Typically they are very diverse and rich with flora and fauna exclusively found within a wetland environment. Wetlands have been used as water treatment systems for many decades. Recently, natural wetlands have been observed to remove contaminants from groundwater (Lorah and Olsen, 1999). Some contaminated groundwater plumes are shallow and intersect wetland ecosystems on the surface in accordance with natural groundwater flow. Wetlands formed with groundwater flow are called fens. The fens create a very unique environment. The soils are very hydric and contain significant amounts of organic matter. In many cases, fens receive vertical groundwater flow from an underlying aquifer. In these cases, the groundwater saturates the soil and if the groundwater is anaerobic, creates anaerobic conditions.

Typically only the top six inches or less of sediment are aerobic, resulting from the root zone of the hydrophytic plants indigenous to wetlands. Oxygen drives reactions and microbial processes within this region. Cometabolic degradation, with enzymes produced from the microbes, is the primary pathway for degradation within this zone.

Methane monoxygenase is an enzyme produced by methanotrophs that live within the oxic/ anoxic interface (Lontoh, 1998).

Within the anaerobic region there are various levels of reduction potential, typically a function of depth. Various microbes thrive under the particular condition and can degrade compounds accordingly. Methanogenesis is the most reductive condition where microbes called methanogens degrade organic matter utilizing CO_2 as an electron acceptor. Under these conditions, dehalogenating bacteria can degrade PCE and TCE to ethene or ethane (Sims et al, 1991; Vogel et al, 1987). Aberdeen Proving Grounds have a similar situation and have shown remarkable results indicating TCE has been degraded to non-detectable levels by natural attenuation without engineering enhancement (Lorah, 1999). In situations where contaminated groundwater is not near the surface and is not intercepted by a natural wetland, a constructed wetland can be very effective. The groundwater can be pumped into a constructed wetland, treated and introduced back into the aquifer. In this study, this type of solution is investigated. System dynamics modeling will serve to blueprint the chemical, biological and transport processes degrading TCE within the wetland sediment in order to better understand the behavior of the system and determine optimizing criteria for design.

Problem Statement

In summary, the United States is faced with cleaning up contaminated groundwater resulting from ignorance and poor management practices of the past. Although there are many viable remediation technologies and each contaminated site is unique and many times requires a unique solution, the use of a constructed wetland to remove contaminants, particularly PCE, is a less costly, beneficial, efficient process that

decision makers should recognize as an alternative. In order to help better understand this process and its viability; it is necessary to understand the dynamic degradation processes associated with the operation of a constructed wetland, both in space and time.

The purpose of this thesis is to determine and explore the fundamental processes within the wetland sediment responsible for the degradation of trichloroethylene and its daughter products. This effort would serve as a foundation for a model, which eventually would be utilized in the application of a constructed wetland for PCE removal, allowing remediation managers to predict the performance over time and optimize controllable parameters for degradation. Such a model would be useful to decision-makers when discerning viable alternatives in groundwater remediation.

Research Questions

1. Can a system dynamics model be developed which can reasonably describe contaminant fate and transport in a constructed wetland?

2. What processes within a constructed wetland are most significant in controlling contaminant fate?

3. What combination of controllable parameters gives optimum treatment results?

4. What parameters serve as limitations to the system over time and how can the limitations be avoided?

Scope/ Limitations

This study will focus on the conditions necessary for dechlorination of PCE within the sediment of the wetland. Dechlorination depends on the concentration of contaminant, the microbial consortia present (methanogens, halorespirers, sulfate reducing bacteria, etc.), and ability of the dechlorinating bacteria to compete for the

available hydrogen for dechlorination over microbes utilizing hydrogen in other electron-acceptor reactions (Lee et al, 1998). Complete dechlorination will occur under methanogenic conditions when competing electron-acceptors such as oxygen, nitrate, nitrite, and sulfate are depleted (McCarty, 1996). The dynamic presence of these compounds is very complex; therefore, this study will assume these substances have been depleted within the sediment of the wetland. Controllable parameters within a constructed wetland are dependent upon the phase of operation. In the construction phase, influent flow rate, depth, organic content, soil porosity, and size will determine retention time and therefore dechlorination potential. The flow characteristics will be based on a uniform vertical flow, without boundaries in horizontal directions.

II. Literature Review

Microbial remediation of chlorinated solvents can be accomplished using two different approaches, engineered bioremediation or natural attenuation. Engineered approaches generally focus on a single mechanism, aerobic or anaerobic biodegradation (Lee et al, 1998). Natural attenuation is defined by the United States Environmental Protection Agency as:

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

Conditions for natural attenuation are dependent on solvent concentration, the presence of dechlorinating bacteria, and the absence of impacted receptors. This study looks at a combination of engineered bioremediation and natural attenuation. Although the focus is on using a constructed wetland to treat groundwater contaminated with PCE, once the contaminated water is introduced into the wetland, human intervention ceases and the dechlorination process should occur as if the wetland was fed naturally from an underlying aquifer.

High costs of using other methods of remediation spurred investigation of microbial degradation of organochlorines. Within the last 15 years, studies have shown that aerobic and anaerobic bacteria can use carbon and energy from chlorinated compounds (Lee et al, 1998). Dechlorination as a result of abiotic processes is not

possible within the one to two decade time span of concern in remediation (McCarty, 1997; Vogel and McCarty, 1987; Vogel et al, 1987). Furthermore, 1,1,1-trichloroethane and carbon tetrachloride are the only major chlorinated solvents that can be transformed abiotically in groundwater under likely conditions, while many bacteria can cause the release of chloride from aliphatic and aromatic organochlorines to produce nontoxic metabolites.

Microbial Processes

Dehalogenation of chlorinated solvents can be classified into four broad areas: energy-yielding solvent oxidations, co-metabolic oxidations, energy-yielding reductions, and co-metabolic reductions (Lee et al, 1998).

Energy-yielding Solvent Oxidations

Energy-yielding solvent oxidations enhance microbial growth as the chlorinated solvent acts as the sole source of carbon and energy. Generally these processes occur under aerobic conditions. Vinyl Chloride, a daughter product of DCE and TCE, can be mineralized to CO_2 by *Mycobacterium* sp., *Rhodococcus* sp., *Actinomycetales* sp., or *Nitrosomonas* sp. (Lee et al, 1998). In most conditions however, increasing the number of the halogen substituents relatively oxidizes halogenated aliphatic compounds. The more halogen substituents, the more oxidized the compound and therefore the more susceptible the compound is to reduction (Vogel et al, 1987). This explains the resistance of TCE to degrade in aerobic conditions, the compound is highly oxidized already and there is little energy to gain by further oxidation. Interestingly, the more chlorinated ethenes are dehalogenated faster than the less halogenated ones (Haston and McCarty, 1999).

Co-metabolic Oxidations

Co-metabolic oxidations generally occur under aerobic conditions as well. Typically, these processes are the result of enzymatic action that is intended for other processes. For instance, TCE can be degraded via the activity of the methane monooxygenase (MMO) system of methanotrophic bacteria (Chapelle, 1993). This is an enzyme system that catalyzes the incorporation of molecular oxygen into methane to produce methanol. Two types of MMO have been identified, membrane soluble and membrane insoluble. Both forms can degrade TCE (Chapelle, 1993). Unfortunately, the degradation process is not completely understood. Methanotrophs partially oxidize methane, using NADH as an electron carrier and the enzyme MMO. MMO incorporates oxygen and acts as the catalyst to produce methanol. NADH acts as the reducing power. Following this step, methanol is converted to formaldehyde by methanol dehydrogenase, which is then converted to formate by formaldehyde dehydrogenase. The last step is the oxidation of formate by formate dehydrogenase, with NAD^+ acting as the electron carrier. The NAD^+ picks up hydrogen in the reaction and recycles NADH, to form methanol, yielding a continuous cycle in the presence of methane. However, in the degradation of TCE, the NADH is not regenerated, and the process becomes self-limiting (Chapelle, 1993). This can be overcome by limiting the amount of methane (Lanzarone and McCarty, 1991) or by pulse feeding of methane (Semprini et al, 1990). Feeding the microbes builds up the intracellular NADH levels and MMO activity. During the pulse feeding, TCE is fortuitously degraded.

Energy-yielding Reductions

Energy-yielding reductive bacteria (halorespirers) are distinct from the anaerobic, co-metabolic dechlorinators found among the sulfate reducers and methanogens. Some of the known species are *Desulfomonile tiedjei, Dehalococcides ethenogenes, Deusulfitobacterium resrictus, and Dehalospirillum multivorans* (Lee et al, 1998). In dehalorespiration, bacteria gain energy by reductive dechlorination (using the chlorinated compound as an electron acceptor). The anaerobic process yields chloride, ethene, ethane and carbon dioxide as sole degradation products. Discovery of halorespiring bacteria should be no surprise. Bacteria have been inhabitants of the earth since geologic time began. Many chlorinated compounds result from natural processes; TCE and PCE are emitted during volcanic eruptions (Hoekstra and DeLeer, 1995). Therefore microbial dehalogenation should appear as another microbial adaptation to an available carbon and energy source. Depending on the species, some of these bacteria may produce cis-DCE as a final end product or may completely dechlorinate to ethene. These microbial processes show that oxygen is not required to effect complete dehalogenation and that because the microbes can gain energy from the solvents, contaminated groundwater plumes may be self-enriching for the bacteria.

Co-metabolic Reductions

Co-metabolic reductive dehalogenation is performed by many types of anaerobic bacteria, including certain species of methanogens, sulfate-reducing bacteria, and novel bacteria that don't fall into either category, that are able to reductively dehalogenate PCE and TCE (Bagley and Gossett, 1989). PCE is fully chlorinated and therefore cannot serve as an electron donor for any aerobic or anaerobic bacteria (Lee et al, 1998). TCE is able

14

to give up one electron and can be reduced by microbes in anaerobic conditions, especially methanogens and sulfate reducing bacteria. This process is co-metabolic and is not energy yielding because only a small fraction of the total reducing equivalents derived from the oxidation of electron donors is used to reduce the solvent (Bagley and Gossett, 1989). These co-metabolic reactions are thought to be side reactions, not really affecting the original process. However, in extremely reducing environments, such as a wetland or landfills (high methanogenisis and/or sulfate reducing rates), the co-metabolic reactions can be significant (Lee et al, 1998).

Optimizing conditions may be achieved by incorporating a combination of
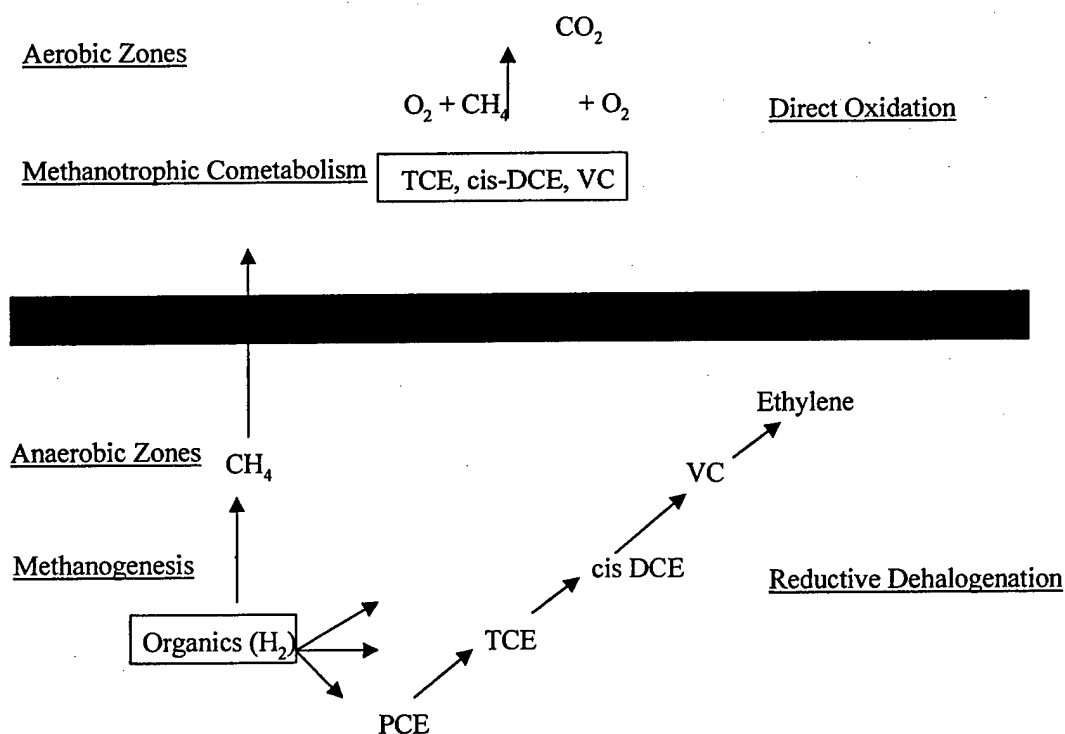
Figure 1 The interplay between different biochemical mechanisms operating within a continuum of aquifer conditions from aerobic to strictly anaerobic. Where oxygen is present, current data suggest that vinyl chloride and perhaps dichloroethene can be oxidized directly to carbon dioxide and chloride. Alternatively, at the interface between aerobic and anaerobic micro-environments where methane and oxygen are co-incident, co-metabolic oxidations convert chlorinated ethenes to carbon dioxide and chloride. Within strictly anaerobic environments where organic electron donors or hydrogen are present, reductive dehalogenation is the predominant mechanism yielding ethene and chloride. Adapted from Lee, Odom and Buchanan (1998).

15

aerobic and anaerobic processes to complement each other in order to accomplish complete degradation. PCE and TCE are highly chlorinated. The molecules are very stable and are not willing to donate electrons in an aerobic environment. However, as discussed above, these compounds can be dechlorinated under highly anaerobic conditions. Complete dechlorination will occur in methanogenic conditions only when competing electron acceptors such as oxygen, nitrate, nitrite, and sulfate have been depleted (Lee et al, 1998). Under these conditions, PCE and TCE can degrade to ethene and ethane. New studies indicate that CH_4 can also be a significant end product (Bradley and Chapelle, 1999). A diagram from Lee, Odom and Buchanan illustrates this concept in Figure 1.

The availability of different electron acceptors can have a positive or negative impact on chlorinated solvent degradation. Often the amount of electron donors is insufficient to fully degrade PCE or TCE. Studies have shown that many different electron donors can sustain reductive dehalogenation in anaerobic environments (Smatlak, 1996, McCarty, 1997b). Nonchlorinated aromatic hydrocarbons can act as electron donors and microbe substrates. Research has shown that microbially catalyzed transformation reactions can occur which couple the oxidation of petroleum hydrocarbons to reduction of chlorinated solvents (Liang and Gribic-Galic, 1993). Additionally, hydrogen is produced by the breakdown of complex materials and intermediates (acetogenic processes and fermentation) and is used by the microorganisms in the reductive dechlorination process.

There is evidence that hydrogen is a key electron donor in the dehalogenation of *cis*-DCE and VC to ethylene (Yang and McCarty, 1998). The dehalogenating organisms

compete for the electrons in hydrogen with organisms using other electron acceptors, such as hydrogen-utilizing methanogens, homoacetogens, and sulfidogens (McCarty, 1997b). Smatlak et al. reports that the dehalogenators compete intensively with methanogens for hydrogen. The dehalogenating bacteria have the ability to use H_2 at lower levels where methanogenesis ceased. However, at higher levels of H_2, the methanogens out-compete the dehalogenators for the hydrogen and dechlorination stagnates (Smatlak, 1996). They found that deliberately choosing an electron donor whose fermentation results in a slow, steady, low-level release of hydrogen favored dechlorination.

In some instances facultative organisms may be grown aerobically and then will degrade solvents anaerobically. The more highly chlorinated compounds are more energetically favorable electron acceptors than are nitrate, sulfate, or carbon dioxide (Vogel et al., 1987). Methane generation in anaerobic zones can provide the carbon and energy source for dehalogenation of TCE, DCE and VC in subsequent aerobic zones. Direct oxidation of VC or DCE with molecular oxygen or ferric iron can also occur in zones with higher redox potential. Therefore, reduction of highly chlorinated compounds such as TCE is a dynamic multi-mechanism process where ethene, ethane, carbon dioxide, and methane can be a significant product of chloroethene degradation as a result of methanogenic activity in sediment (Bradley and Chapelle, 1999).

Iron Reduction

Iron reduction of polychlorinated ethenes has recently been proven as an additional degradation pathway under anaerobic and in some instances, aerobic conditions (Bradley and Chapelle, 1996, 1997). Unfortunately, when PCE is the primary

contaminant, the only daughter products which can be degraded, are DCE and VC (TCE may degrade under these conditions, but there is little evidence to support it). Iron reduction is an oxidation/reduction process; microorganisms can reduce available $Fe(III)$ while oxidizing chlorinated ethenes (Lovely, 1991). In contaminated anaerobic groundwater environments, $Fe(II)$ is the most abundant potential electron acceptor for organic matter decomposition (Lovely, 1991). $Fe(III)$ reduction can cause inhibition in sulfate reduction and methane production zones. This is a result in the decrease in the amount of available electron donors for the sulfate reducers and the methanogens. Depending on the type of soil and the form of available $Fe(II)$, inhibition can vary from 50-100% (Lovely, 1991).

Generally, groundwater contamination with chlorinated ethenes will develop an anaerobic condition. If the conditions are reducing enough to generate methane, chlorinated ethene reduction can occur. As stated previously, compounds with all sites filled with chlorines require increasing reducing conditions, PCE, the most chlorinated, requires the most reducing condition to degrade. Conversely, as the ethenes become less chlorinated, they are more susceptible to oxidation. It is this facet that allows the degradation of DCE and VC via the $Fe(III)$ reduction pathway. Bradley and Chapelle (1996) provide the first evidence that vinyl chloride can be oxidized under anaerobic, Fe (III) reducing conditions. The same authors published kinetic information for DCE and VC mineralization and found that the processes differed in that DCE mineralization followed first order degradation kinetics while VC followed Michaelis-Menton degradation kinetics (Bradley and Chapelle, 1997).

Microbial bioremediation is not the panacea of treatments, but has significant advantages if the concentration of contaminant is not toxic, microbial consortia are present, and there is limited competition among the microbial consortia and other electron acceptors.

Microbial Kinetics

Classical kinetic modeling techniques for biological degradation follow the Michaelis-Menton model for non-elementary reactions. Food utilization by the microbes requires the use of an enzyme, resulting in the following stoichiometry:

$$E + S \rightarrow E + P$$
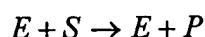
Where E is the enzyme, S the substrate, and P is the product. The enzyme is not consumed but lowers the activation energy or facilitates another reaction. This instance may create a temporary, intermediate enzyme-substrate complex [ES].

$$E + S \underset{k_2}{\overset{k_1}{\Leftrightarrow}} ES \overset{k_3}{\rightarrow} E + P$$

A mathematically derived kinetic law for the above equation yields:

$$\frac{d[S]}{dt} = -\frac{k_1 k_2 [S][E]_0}{k_1 [S] + k_m}$$

This equation is known as the Michaelis-Menton equation (Clark, 1996). k_m is given by

$$k_m = \frac{k_2 + k_3}{k_1}$$

The Michaelis-Menton equation has some unique mathematical characteristics that can be used to help determine the values of the kinetic constants. If there is a large amount of substrate present, the denominator is approximated by $k_1[S]$, which will cancel with $k_1[S]$ in the numerator. This creates a zero-order rate expression in which d[S]/dt is

proportional to $k_2[E]_0$. If the amount of substrate is very small, [S] becomes negligible compared to k_m in the denominator, leading to a first order rate expression, where

$$\frac{d[S]}{dt} = \frac{k_1 k_2 [E]_0}{k_m} [S]$$

This may be the case most likely encountered in this study, as the concentrations of dissolved chlorinated contaminants in the environment are relatively small.

The maximum dechlorination rate (kX) is dependent on the concentration of the organisms performing the degradation. Haston and McCarty (1999) reported higher maximum dechlorination rates in their batch studies than in batch studies by others, comparable rates with column results of other authors, and lower rates than the expanded-bed reactor studies of additional authors. However, all the studies had varying concentrations of dehalogenating organisms. Although Haston and McCarty's half-velocity values varied from other authors, they were within reason and were comparable to specific organism dehalogenation studies. Table 2 shows the half-velocity coefficients (K_s) and the maximum dechlorination rates (kX) for some chlorinated ethenes.

Table 2 Half-Velocity Coefficients (K_s) and Maximum Aqueous Dechlorination Rates (kX) with their 95% Confidence Intervals for Each of the Chlorinated Ethenes with 38 mg/L VSS

Contaminant	kX (μM/day)	k_{app} (μmol (mg of VSS)$^{-1}$d^{-1})	K_s (μM)
PCE	77 $\pm$ 5	2.0 $\pm$ 0.1	0.11 $\pm$ 0.04
TCE	59 $\pm$ 11	1.6 $\pm$ 0.3	1.4 $\pm$ 0.9
cDCE	14 $\pm$ 3	0.37 $\pm$ 0.08	3.3 $\pm$ 2.2
VC	13 $\pm$ 3	0.34 $\pm$ 0.08	2.6 $\pm$ 1.9

Source: adopted from Haston and McCarty, 1999

Contaminant Sorption

Sorption is a significant removal pathway for chlorinated ethenes in sediment. Organic soils are good sorbents for organic contaminants. Adsorption at the solid-liquid interface can be modeled via adsorption isotherms. The Freundlich isotherm is frequently used to empirically fit sorption data rather at the soil-water interface (Clark, 1996). The model takes the following form:

$$q_e = K_f C_e^{1/n}$$

Where K_f is an empirical constant related to the capacity of the adsorbent material to adsorb the adsorbate (the higher the K_f value, the more adsorbate potentially stored) and n is a constant related to the affinity of the adsorbate for the surface. C_e is the equilibrium solute concentration and q_e is the mass of adsorbate per unit mass of adsorbent.

Schwarzenbach and Westall (1981) report for low concentrations, sorption equilibria can be described by the equation:

$$q_e = K_p C_e$$

Where q_e = concentration in the solid phase
K_p = a liquid-solid partition coefficient
C = Concentration in the liquid phase

The partition coefficient of a particular sorbent can be estimated from its 1-octonal/water partition coefficient, K_{OW}, and from the organic content, f_{OC} (fraction organic carbon), of the sorbents if the f_{OC} is greater than 0.0001 (Schwarzenbach and Westall, 1981):

$$\log K_p = 0.72 \log K_{OW} + \log f_{OC}(s) + 0.49$$

21

Table 3. Sorption of Nonpolar Organic Compounds on Natural Aquifer Material

Compound	Ce, ug/L	Log K_{ow}	K_p
Toluene	20	2.69	0.37
1, 4-dimethylbenzene	20	3.15	0.5
1,3,5-trimethylbenzene	20	3.6	1
1,2,3-trimethylbenzene	20	3.6	0.95
1,2,4,5-trimethylbenzene	20	4.05	1.96
n-butylbenzene	20	4.13	3.69
tetrachloroethylene	100	2.6	0.56
chlorobenzene	20	2.71	0.39
1,4-dichlorobenzene	20	3.38	1.1
1,2,4-trichlorobenzene	40	4.05	3.52
1,2,3-trichlorobenzene	40	4.05	3.97
1,2,4,5-tetrachlorobenzene	40	4.72	12.74
1,2,3,4-tetrachlorobenzene	40	4.72	10.48

Source: Adapted from Schwarzenbach and Westall, 1981.

Adopted partition coefficients and octonal-water coefficients for various

compounds from Schwarzenbach and Westall are found in table 3.

Constructed Wetlands

Constructed wetlands have the ability to provide the conditions necessary for

microbial dehalogenation. Constructed wetlands are of two categories, surface flow (SF)

or subsurface flow (SSF).

In surface flow wetlands, the water primarily flows above the ground surface, as

shallow sheet flow, through the dense growth of emergent wetland vegetation (Kadlec

and Knight, 1996). Design components include an input device, the wetland basin, the

wetland plants, and an outlet device. Basin size, shape and number are a function of the

realistic reaction kinetics required to achieve compliance with regulatory discharge

permits. The number of basins is dependent on the flowrate, land constraints and

operational redundancy requirements. The wetland plants allow mineral cycling and

provide a place for microbial populations to attach (essential for water quality

improvement). Plants are selected for their hardiness under the expected conditions,

contaminant uptake abilities if any, cost and availability, importance as wildlife cover and

food source. The outlet device recollects the surface water and sends it to another wetland cell or to the final discharge point such as a stream, river, lake, or groundwater recharge area.

Subsurface flow wetlands use horizontal or vertical flow through sediment or constructed media of the wetland. Microbes can attach themselves to the media or on the roots of wetland plants. Generally, SSF wetlands have no standing water at the surface, although the sediment is saturated completely to the surface. Design components include an input device, the wetland basin, media (to include sediment), wetland plants, and an output device. For optimal performance, these systems must initiate and maintain a consistent flow through a permeable media. The cross-sectional area required to initiate flow into the inlet zone is dependent on the permeability of the media. Plant selection is nearly the same as that for SF wetlands. Outflow devices generally collect .3 to .6m below the surface of the wetland (Kadlec and Knight, 1996).

Water quantity and quality define the extent and species composition of a natural wetland (Mitsch and Gosselink, 1993). The hydrologic conditions influence the soil and available nutrients, which affect the character of the microbes. Water enters natural wetlands via streamflow, runoff, groundwater discharge, and precipitation (Kadlec and Knight, 1996). Water entering a constructed wetland is controlled via an input device. Water exits a wetland via streamflow, groundwater recharge, and evapotranspiration (Kadlec and Knight, 1996). Water exits a constructed wetland via an output device and evapotranspiration. Natural wetlands may have the ability to store large amounts of water or very little amounts of water. Seasonal changes in water depth may affect species composition and sediment biota. Varying terrain underlying the structure of the wetland

may create variable zones within the wetland, some of which may suffer from dryout. The point of this discussion is that natural wetlands and constructed wetlands are similar yet different. Much of the variability as far as changing water depth or outflow has been virtually eliminated from a constructed wetland. As a result, controlled, steady water levels create uniform hydrologic conditions and an absence of pattern effects (Kadlec and Knight, 1996). Pattern effects interact with water flows within the wetland, carrying a disproportionate amount of water in less vegetative channels, causing an imbalance in the treatment of water through the wetland. The important features of wetland hydrology from the standpoint of treatment efficiency are those which determine the duration of water-biota interactions and the proximity of waterborne substances to the sites of biological and physical activity (Kadlec and Knight, 1996).

Wetland Definitions

Hydraulic Loading Rate Hydraulic loading rate is the rainfall equivalent of whatever flow is under consideration. It is not the physical distribution of water uniformly over the wetland surface. The hydraulic loading rate is generally referred as the contaminant or wastewater additional flow to the wetland inlet. It is defined as:

$$q = Q/A$$

where q is in units of m/d,
A = wetland area (wetted land area), m^2
Q = water flow rate, m^3/d

Vertical flow wetlands are often operated with intermittent feed and under these circumstances, the hydraulic loading rate refers to the time average flow rate. The loading rate during a feed portion of a cycle is the instantaneous hydraulic loading rate or hydraulic application rate (Kadlec and Knight, 1996).

24

Mean Water Depth Mean water depth is the average depth throughout the entire wetland and is defined by the following:

$$\tilde{h} = \int_0^L \int_0^W h(x,y)\,dy\,dx$$

where x = longitudinal distance, m
   y = transverse distance, m
   L = wetland length, m
   W = wetland width, m
   h = water depth at coordinates (x, y), m
Units for mean water depth are typically in meters or centimeters.

Wetland Water Volume The wetland water volume for a subsurface flow wetland is primarily dependent on the porosity of the media. However, values for this parameter are often very difficult to ascertain. Constructed wetlands using a clean sand or gravel generally have a porosity in the range of 0.30 to 0.45 (Kadlec and Knight, 1996). However, roots, mineralization, and decayed organic matter contribute to decreased porosity. Lateral pattern effects are minimal but gradients in both vertical and flow directions may be present (Kadlec and Knight, 1996). The equation for wetland water volume is defined as:

$$V = \int_0^L \int_0^W \int_0^h e(x,y,z)\,dx\,dy\,dz = \tilde{\varepsilon} V_T = \tilde{\varepsilon} A \tilde{h}$$

where ϵ = water volume fraction in the water column, m^3/m^3
   V_T = total volume between water and ground surfaces, m^3
   z = vertical distance coordinate, m
   L = wetland length, m
   W = wetland width, m
   h = water depth at coordinates (x, y), m

Nominal Retention Time is defined as:

$$\tau_n = \frac{V}{Q} = \frac{\tilde{\varepsilon} A \tilde{h}}{Q}$$

Units are in days. The flow in this case is generally defined as the average flow (inlet plus outlet divided by 2), however, without an outflow, the inlet flow is used (Kadlec and Knight, 1996). If variations are present in the total flow and water volume, correct calculation will involve integration.

Nominal retention times are not consistent with actual retention times. Actual times are usually smaller. Nominal times assume that the entire volume of water is involved in the flow. Kadlec and Knight report estimates for the Boggy Gut treatment wetland yielded nominal retention time of 19 days where the actual measured retention time was 2 days. It is important to note that the hydraulic loading rate is inversely proportional to the nominal detention time for a given depth. Therefore the hydraulic loading rate embodies the notion of contact duration, just as nominal detention time does (Kadlec and Knight, 1996).

Actual Velocity This is the velocity that would be obtained if measured:

$$v = \frac{Q}{(\varepsilon A)_c}$$

where $(\varepsilon A)_c$ = open area perpendicular to flow, m^2.

Superficial Velocity This is also known as the cross-sectional hydraulic loading rate. For a vertical flow it is defined as:

$$u = \frac{Q}{A_c}$$

where A_c = area perpendicular to flow, m^2. The cross-sectional area is the width times the length.

$$A_c = WL$$

where h_c = mean depth perpendicular to flow, m. The relationship between superficial and actual velocities is porosity.

<u>Hydroperiod</u> This term is used to designate the number of days in a year that there is surface water in a given wetland location. If a wetland were dry for 10 percent of the year, the corresponding hydroperiod would be 328 days. Continuous source treatment wetlands typically have a hydroperiod of 365 days.

<u>Water Mass Balance</u> Water mass balance for a constructed wetland can be separated into two forms, global and internal. Global water mass balance is a determination of the water mass balance within the confines of the wetland boundary. Internal water mass balance is used when focusing on a narrow internal element or subdivision of the water body. The water budget is very dynamic for a constructed wetland. Gains to the system are generally from influent, precipitation, runoff, infiltration, and snowmelt. Losses to the system are from effluent, evapotranspiration, bank loss, and infiltration to groundwater. The following equation can be used to represent these dynamics:

$$\frac{dV}{dt} = Q_i - Q_o + Q_c - Q_b - Q_{gw} + Q_{sm} + PA - ETA$$

where A = wetland top surface area, m^2
    ET   = evapotranspiration rate, m/d
    P   = precipitation rate, m/d
    Q_b = bank loss rate, m^3/d
    Q_c = catchment runoff rate, m^3/d
    Q_{gw} = infiltration to groundwater, m^3/d
    Q_I = influent rate, m^3/d
    Q_o = effluent rate, m^3/d
    t   = time, d
    V   = water storage in wetland, m^3

Inflows and outflows are controllable in a constructed wetland and are a function of treatment requirements and design. The evapotranspiration rate and precipitation rate

is most variable and unknown. Estimates based on region and climate, as well as historical information, are useful starting points. The bank loss rate and groundwater infiltration rate can be controlled to some degree. Use of impermeable membranes or clay layers in construction should limit water losses or gains. Wetlands are generally found as transition areas between terrestrial ecosystems and aquatic ecosystems. Therefore, runoff is a natural input, however, in constructed wetland systems, runoff may depend on site layout and construction of berms and roads surrounding the wetland. Snowmelt will depend on wetland location. All of these factors could have an influence on the treatment of contaminant. Excess water loss could result in non-treatment and a possible permit violation, and excess water gain may overload the system, cause dilution or affect the behavior of the wetland.

Background Concentrations within a Wetland Wetlands have an abundance of activity occurring within their boundaries. As a result, water chemistries may vary, ranging from nutrient rich to nutrient poor. Table 4 depicts some water chemistries of various wetlands found in the literature per Kadlec and Knight.

Table 4 Water Chemistry of Some Typical Natural Wetlands

Chemical Parameter	Units	Theresa Marsh, WI	Porter Ranch Peatland, MI	Portage Fen, MI	Seminole Ranch, FL	Ombrotrophic Bog, Newfoundland	Cypress Dome, FL
Nitrate + nitrite	mg/L	0.1-1.7	0.04±0.02	0.1	0.1		0.08
Ammonium	mg/L	0.1-1.6	0.73±0.81	0.09	0.15		0.14
Organic N	mg/L	0.7-4.8		0.2	0.75		1.2
Total N	mg/L	1.5-6.8		0.4	1		1.6
Dissolved P	mg/L	0.1-0.5	0.02±0.01		0.04		0.07
Total P	mg/L	0.1-0.7	0.04±0.01	0.05	0.07		0.18
Na	mg/L	5-24		3.5		3.9	5
K	mg/L	0.9-9.1	0.7±0.6			0.1	0.34
Ca	mg/L	56-168	19±11	22		0.25	2.9
Mg	mg/L	23-73	4±2	22		0.46	1.4
Fe	mg/L		0.5±1.6				
Chloride	mg/L	17-54	28±25	9			
Sulfate	mg/L	15-99					2.6
pH		7.4-8.2	6.0-7.5	7.7	6.9		4.5
Conductivity	umho/cm	520-940	150-350	520	390		60
Alkanlinity (CaCO$_3$)	mg/L	270-420		182			1.8

Source: Adapted from Kadlec and Knight, 1996.

Phosphorus is generally very low in wetland systems. Typically the total phosphorus is less than 0.1 mg/L and it is often below 0.05 mg/L (Kadlec and Knight, 1996). Increases of total phosphorus of up to one magnitude can occur in agrarian areas as a result of point and non-point source pollution. Rainfall can decrease the total phosphorus if it is a significant source in the water budget.

Organic nitrogen is a product of biomass decomposition. As the proteins are degraded to smaller organic species such as amines, the amines then degrade to ammonium nitrogen. Therefore, low levels of 1 to 2 mg/L of organic nitrogen are present in wetlands.

Ammonium nitrogen provides nutrients for plant growth. In the presence of dissolved oxygen, microbes will convert ammonium to nitrate, making it available to the plants. The ammonium concentration will increase during the winter as plant growth and

microbial processes slow down. Buildup of ammonium may actually occur. Concentrations are generally very low during the growing season, as plants use their stored nitrogen for growth and microbes convert ammonium to nitrate. All of the ammonium resulting from decomposition is consumed and plants will continue to grow until their full growth potential is realized, resulting in low ammonium concentrations on the order of 0.05 to 0.1 mg/L.

Nitrate and nitrite nitrogen are generally below detectable limits. Denitrification is efficient because the necessary carbon source is present with the anoxic conditions required to use nitrate as an electron acceptor.

Carbon sources are very prevalent in wetland systems. Carbon is a source of plant growth and humic substances result from the growth-death decomposition cycle. Total organic carbon (TOC) represents the amount of carbon in the water. Much of the humic material is not a suitable food source for bacteria, therefore, the chemical oxygen demand (COD) is higher than the biochemical oxygen demand (BOD). The orders of magnitude for a natural wetland are TOC ~ 40 mg/L, COD ~ 100 mg/L, and BOD ~ 5mg/L (Kadlec and Knight, 1996).

Metals present in wetlands are generally a reflection of the water source or sediment present. Ca, Mg, Na, and K are most common. Concentrations of 0 to 5 mg/L are typical (Kadlec and Knight, 1996).

pH is a result of the hydrogen ion concentration. Marshes and swamps vary from 6 to 8 while bogs are more acidic and range from 3 to 5. Algal blooms can cause a significant increase in the pH as a result of decreasing the carbon dioxide concentration.

Dissolved oxygen (DO) and redox potential (Eh) are measures of the oxidation

potential of the wetland. DO can vary widely depending on the biological and chemical

processes taking place. Oxygen depletion usually occurs in the +320- +340 mV range.

Generally, there is a vertical DO gradient, with DO decreasing with depth. High DO will

be present at the air-water surface and DO will decrease to zero with depth assuming

there are no additional oxygen inputs with increasing depth. Aerobic degradation by

microbes consumes the available oxygen very quickly. Therefore, DO concentrations of

less than 2 mg/L are not uncommon. As the DO content decreases with depth, other

electron acceptors become prominent. Nitrate reduction may begin before complete

oxygen removal and is complete at +220mV. Manganese reduction (from Mn^{+4} to Mn^{+2})

occurs within the nitrate reduction region and is complete by +220 mV. Ferric iron (Fe^{+3})

is reduced to ferrous iron (Fe^{+2}) by +120 mV and Sulfate (SO_4^{-2}) is reduced to sulfide
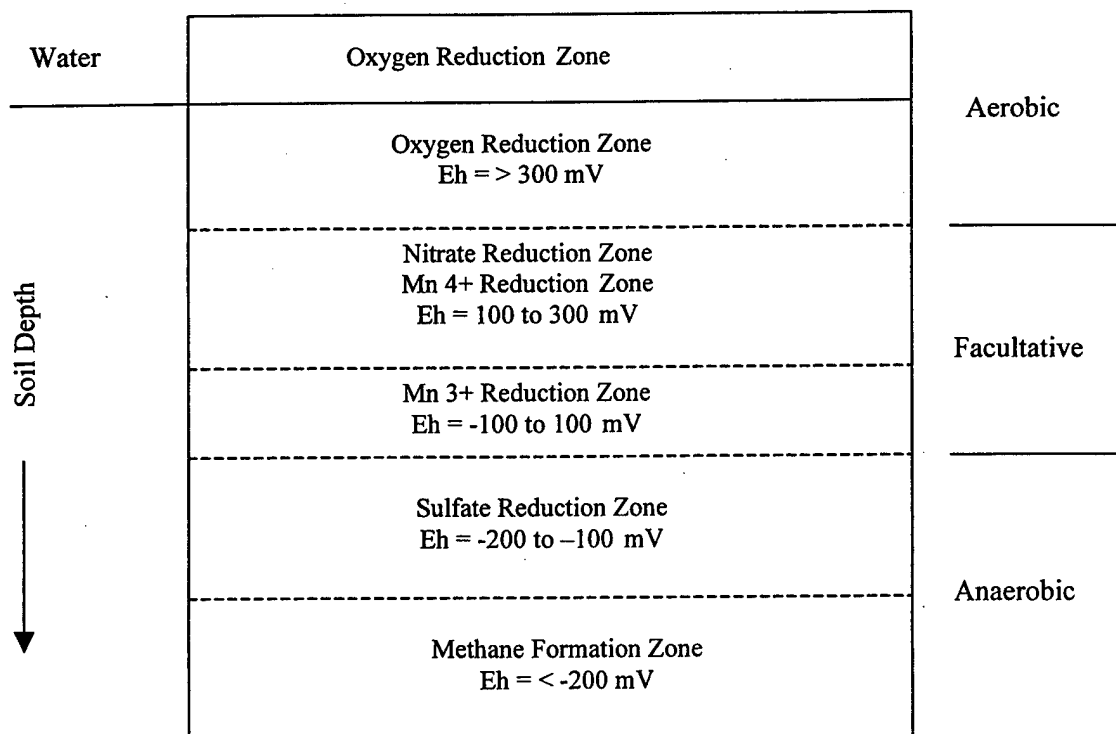

Figure 2 A typical wetland profile for oxidation reduction reactions and redox potential
in a lightly loaded wetland. (Adapted from Kadlec and Knight, 1996)

(SO_2) by $-150mV$. Carbon dioxide (CO_2) is reduced to methane (CH_4) in the -250 to -350 mV range (Kadlec and Knight, 1996). Figure 2 gives a graphical representation of the reduction zones within a wetland.

Wetland Hydrology

Flow through porous media has been a long-standing design problem. The case for a wetland is no different. In subsurface wetland hydrology, flow is fully saturated with an unconfined top interface with air, in or above the bed. Full saturation eliminates capillary fringe (a condition where air and water occupy the voids between particles). Wetland flows, however, are generally very low, change gradually, and are based on very tame slopes. Kadlec and Knight simplify the hydrology by using one-dimensional flow and assuming that, although wetlands are rarely in true steady flow, over a long averaging period, evapotranspiration and rain events can be replaced by their time averages. Therefore these events are not described, but the time average depths and flows are modeled correctly. These flows assume isometric media although plant roots and other particulates may later accumulate. Variability in lateral and transverse flow is accounted for by averaging, and variability in longitudinal flow will increase over time. This equation simplifies the water budget, showing that precipitation increases water flow and evaportranspiration decreases it:

$$Q = Q_i + P - ET$$

where Q = volumetric flowrate, m^3/d,
$\quad Q_i$ = influent volumetric flowrate, m^3/d,
$\quad P$ = precipitation rate, m^3/d, and
$\quad ET$ = evapotranspiration rate, m^3/d.

Water elevation is the water depth plus the bed bottom elevation profile

$$H = B + h$$

where B = the elevation of the bottom of the bed from the datum.

The elevation of the top surface of the media is:

$$G = B + \delta$$

where G = elevation of the bed top above datum, m

δ = thickness of the bed media, m

The majority of the equations previously discussed concern the movement of water in the horizontal plane of a wetland and are mostly design criteria for a constructed wetland. Modeling the flow of water and a contaminant is available through a variety of available models. Kadlec and Knight (1996) discuss a plethora of mathematical models such as residence time distribution functions, plug flow reactors, continuously stirred tank reactors, tanks in series, tanks in series with delay, plug flow with dispersion, etc. All of these models are valid for constructed wetland treatment. The type of model best suited for a particular design is dependent on the wetland and contaminant conditions and characteristics.

Wetland Modeling and Case Studies

Wetland modeling is as dynamic as the wetlands themselves. Each situation is unique and there appears to be no cookie cutter approach in the literature. Generally, the models can be grouped by the wetland type they represent; however, model structure and rate constants tend to be site specific. However, there are some trends in the literature that seem to be present in all wetland models.

The hydrochemical complexities of wetlands are the physical factors that control the wetland and are perhaps the most important and complex (Mitsch et al, 1988). The chemical and biological activities within a wetland are closely related to the hydrology. Good field and laboratory studies are required for accurate model application. A good

understanding of the hydrologic budget will provide better insight to the chemical and biological processes of the wetland.

As most ecological systems, wetlands are constantly changing. Hydrologic changes and organic changes resulting from microbial activity keep the wetland moving along its successional path. Flooding and drought have significant impact as well. Over long periods of time, as this model intends to portray, vegetation succession could play an important role in wetland function.

Wetland interfaces are another area of complexity that is difficult to model. The soil-water interchange consisting of chemical and biological interactions are complex and not fully understood. Interchange between the soil-water and vegetation and the soil-water and air are also very complex chemical and biological interactions. Sediment interactions and processes such as sorption, cation exchange, denitrification, and methanogenesis are all important facets of a wetland and can be significant in a wetland model.

Finally, wetlands are closely knit ecosystems that are in balance with those ecosystems that surround them. Exchanges occur between these adjacent ecosystems and require spatial modeling to accurately represent these relationships.

In the process of reviewing the available literature for contaminant remediation within the sediment of a constructed wetland, no literature was found to directly support contaminant removal through a constructed wetland with vertical flow. Many studies are beginning as the use of wetlands as remediation sites has been proven. However, the majority of these studies involve natural systems. Lorah and Olsen (1999) proved degradation of tetrachloroethane (PCA), DCE and VC within a naturally occurring

freshwater tidal wetland fed by contaminated groundwater. The wetland sediment was comprised of two distinct layers, approximately 1.8 m thick. The lower layer was a silty to sandy clay and the upper layer was primarily peat with varying mixtures of clay and silt. Groundwater flow was generally in the vertical direction at approximately 0.6 m/yr. Identifiable zones of methanogenesis, sulfate reducing and iron reducing zones were present within the wetland. Field results indicated that the contaminant degraded vertically as it entered increasingly reducing conditions. The aquifer was determined aerobic, which fed into an iron reducing zone, followed by a sulfate reducing zone which ultimately led to the methanogenic zone, present in the 0-0.9m peat layer of the wetland. Contaminants were degraded via abiotic dehydrochlorination, dechloroelimination, and hydrogenolysis. All contaminants were degraded to non-detectable levels within the wetland and within 34 days during the microcosm studies. These results demonstrate the feasibility of wetland use in dechlorination of contaminated groundwater.

Bankston and Dwyer (1999) conducted microcosm studies utilizing soil, water and plant material from a freshwater wetland in New Brighton, Michigan. They studied the removal of radio-labeled TCE in three different microcosms: 1) soil and water from the wetland, 2) soil, water and plant species (either a broad leafed cattail, or eastern cottonwood), and 3) autoclaved soil and water from the wetland. The study was designed to imitate the aerobic conditions present within the rhizosphere of the plants. TCE was oxidized to CO_2 in the cattail microcosm and the half-life was determined as 23 days. Cottonwood microcosms achieved faster TCE removal, with a half-life of 16 days. Plant uptake was found responsible for a portion of the removal in both the cattail and cottonwood microcosms.

Zachritz et al. (1996) propose the possibility of using subsurface constructed wetlands in degrading various waste streams of complex halogenated and nonhalogenated compounds based on a small pilot study removing benzoic acid. They chose to use benzoic acid because it degrades aerobically and anaerobically and the pathways are well understood. Additionally, the coenzyme A thioester form is an intermediate in the degradation of aromatic compounds such as phenol, p-cresol, and aromatic acids. The study explored shallow and deep reactors, planted and unplanted, as well as single and double stage. Degradation of at least 80% was achieved in all systems, with the double-stage planted faring the best. The shallow, single-stage planted reactor was reported as very robust and indicated strong performance within design limits. Microbial populations flourished under the conditions with no noticeable difference between planted and unplanted reactors. Conclusions of their study indicate staging of treatment components may be advantageous in certain treatment schemes involving chlorinated organics, suggesting reaeration control of substrates and mediating anoxic, aerobic and anaerobic environments.

Although there was no direct evidence found of TCE removal in a constructed wetland, substantial evidence was found that indicate TCE degradation to ethene, ethane, CO_2, or CH_4 could occur under the correct conditions. Additionally, the absence of previous models indicates this study may be forging new ground.

III. Methodology

The design of a constructed, subsurface flow wetland for the removal of highly chlorinated aliphatic compounds such as PCE or TCE is on the cutting edge of remediation technology. The wetland system and the biodegradation process are very complex and involve countless interactions among various entities and parameters. Systems thinking in conjunction with a requisite mechanistic model enable system behavior assessment over time. System dynamics captures the feedback loops, multiple interactions, time sensitive behavior, non-linear interaction, and changes in the system over time associated with extremely complex systems such as a constructed wetland.

System dynamics reproduces system behavior mechanistically by identifying and simulating the underlying fundamental process driving basic system behavior in contrast to other modeling approaches such as empirically based modeling which ignore the underlying processes (Moorehead et al, 1996). Additionally, since system dynamics allows simulation, it facilitates the study of internal interactions of complex systems such as wetlands, explores the system behavior beyond the range of observed system behavior, and provides insight into the ramifications of various parameters on the dynamic system.

The methodology of this study will follow system thinking and the modeling process. The basic steps of the system dynamics modeling process can be divided into four distinct phases: conceptualization, formulation, testing, and implementation (Colburn, 1997). The system dynamics process is an iterative one, and, as a result, processes may have to be repeated or reformulated in order to provide a true mechanistic representation of the biodegradation process within a wetland.

37

Conceptualization

This model is based on a pilot concept, under consideration and design by the Air Force Institute of Technology, Wright-Patterson AFB OH. The project will serve as the physical representation of this model. Therefore, the structural framework of the model is depicted as a cross-section of the constructed wetland. The uniqueness of this project is the influent configuration for the wetland. This wetland will be a subsurface flow wetland. Contaminated groundwater (PCE or TCE) will be introduced, by uniform distribution, through a piping network installed at the bottom of the wetland. The water distribution system will cover the entire area of the wetland. The purpose of this design is to create a uniform, vertical flow, through the wetland sediment. Total water depth will be controlled via an outlet control device (weir or orifice), ensuring complete saturation of the entire sediment of the wetland. Endemic wetland soil will serve as the media for the constructed wetland. The soil will be engineered for three phases of remediation design, deemed a "safety net" approach. The underlying soil layer will consist of endemic wetland soil, rich in organic material. Preliminary observations have determined an organic carbon content of 62%. This zone will be considered completely anaerobic, as the groundwater will enter as oxygen depleted and will completely saturate this zone. Methanogenic conditions will provide the necessary environment for dechlorinating bacteria to be the primary reductive force within this layer. Anaerobic conditions and the absence of other electron acceptors, such as sulfate, nitrate, and manganese will ensure methanogenic conditions. In place above the methanogenic zone, will be a thin iron-rich soil layer, 6 to 8 inches deep. This zone will also be anaerobic,

and should serve as the first safety net by further degrading DCE and VC, developed in the methanogenic zone, via iron-reduction.

The last sediment layer will consist of the thin root zone and sediment/water/air interface. This layer will be both aerobic and anaerobic. The aerobic zone will consist of the small radius of soil around each root fiber that has been oxygenated by the respiration of the plant. The remaining soil outside the oxygenated zone of influence will be considered anaerobic. This zone will serve as the final safety net in hopes that methane produced from the underlying methanogenic zone will induce methanotrophs to produce methane monooxygenase, which will fortuitously degrade any remaining TCE or TCE daughter products. Terminal degradation products will be ethene, ethane, CO_2, or CH_4.

The reference mode is a description of the time development of interest, defining the time horizon and range of time constraints in the model. It represents the hypothetical behavior of the system based on a vague mental notion of the influences within the system and is focused on the research question. As stated in Chapter 1, the primary research question is to develop a system dynamics model to assess groundwater treatment in wetland sediment and evaluate performance of designed treatment zones and the interactions with adjacent zones and the entire system. This question is very broad, and a comprehensive reference mode would be difficult to develop. However, it may be possible to infer how well the system is performing by observing the behavior of a simple parameter, contaminant concentration in the root zone, over a lengthy period of time (e.g. 2000 days). The observation of the behavior of this parameter over the 2000-day period of simulation would infer the overall ability of the system. Figure 3 shows the hypothesized reference mode for the system. The reference mode is a hypothetical

outcome of the system based on the interactions among mechanisms within the system. The perceived behavior is qualitative in that the outcomes from each of the mechanisms given a constant input are known, however the interactions among the mechanisms and their effects on the behavior of the system are not known. The reference mode for this model is based on a known concentration of contaminant entering an uncontaminated wetland, becoming well mixed, and undergoing microbial degradation over time, and is the predicted behavior resulting from the interactions of the microbial processes, sorption, and transport.
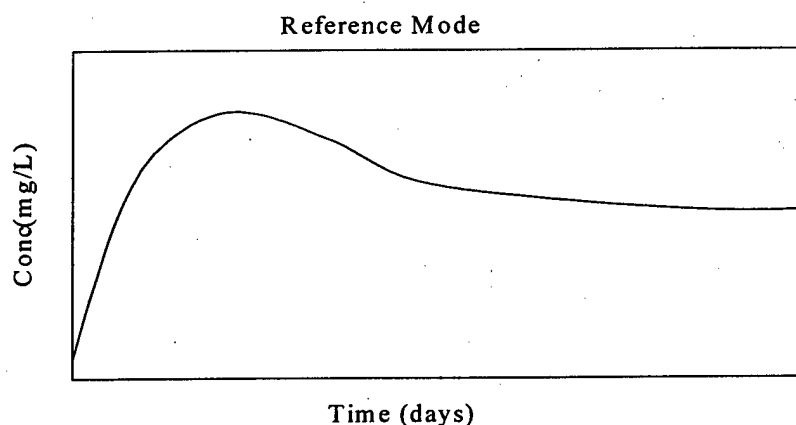
Figure 3 Reference Mode. Hypothetical behavior of system based on a qualitative mental notion of the influences within the system, indicating contaminant concentration in the root zone will increase, and then decline to a steady-state, over 2000 day time horizon.

The influence diagram represents the cause and effect relationships between entities within the system, which most influence the degradation process. The influences between entities and their relationships with one another, when coupled with the reference mode provide the feedback loops and the basic mechanisms responsible for behavior of the system and degradation of contaminant. The influence diagram develops organizing concepts and describes the basic mechanisms in causal form. Figure 4 shows

an atypical system dynamics influence diagram. This format was chosen to help the reader develop a clear picture of the processes occurring in the wetland. This diagram is intended to provide the necessary influences and causal relationships among mechanisms and provide a one-dimensional image to develop the conceptual processes of the wetland and the model.
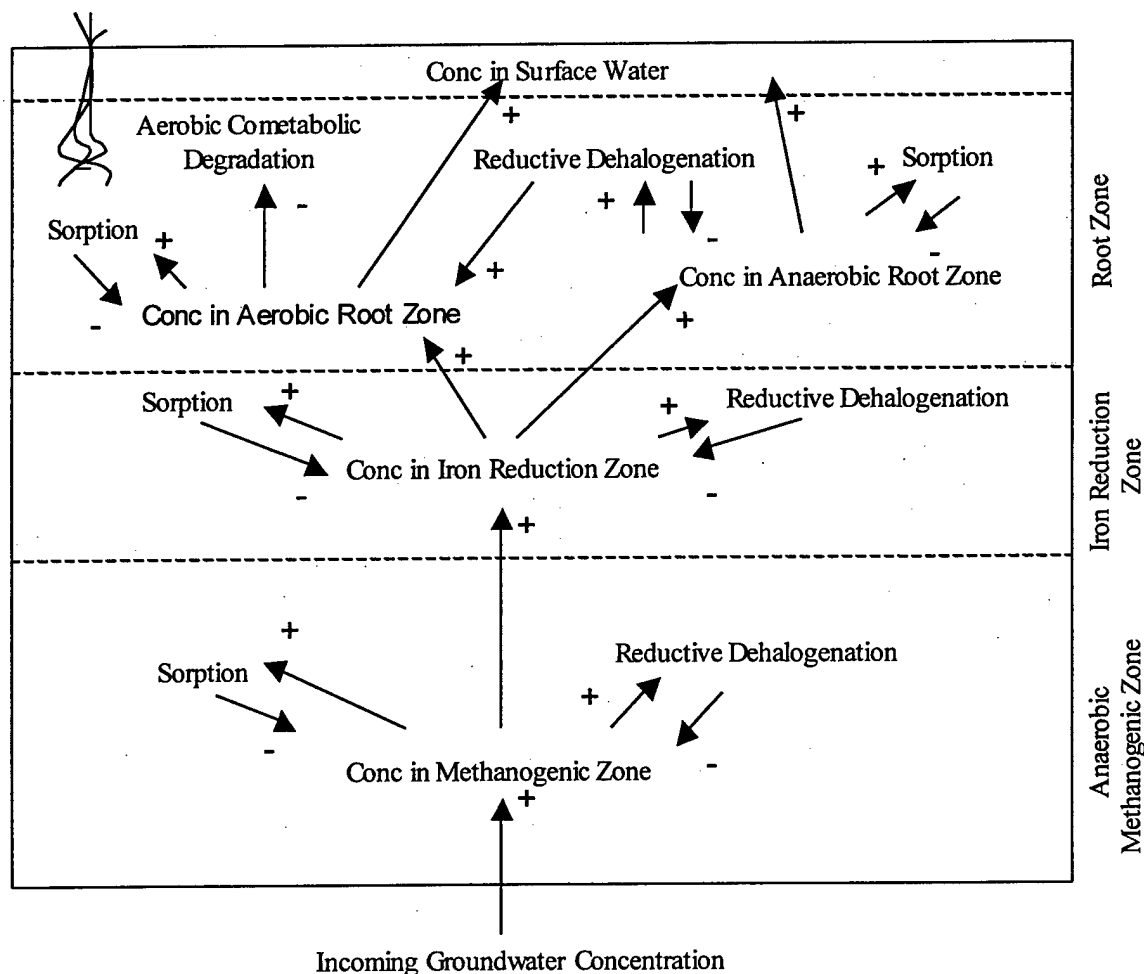
Figure 4 Influence diagram of constructed wetland system.

Formulation

The software package, STELLA 5.1 Research, from High Performance Systems, will be the tool used to implement the model. The principal building blocks of the model are stocks or accumulations and flows or rates of movement to and from a stock.

Developing the model from the conceptual design of the constructed wetland requires knowledge of the processes that are occurring within the wetland and on what level they are occurring. For the most part, this model has been built using a mass balance approach, making the necessary assumptions where appropriate.

The model has been developed so that it represents the processes which are occurring in two dimensions based on a vertical cross-section of the constructed wetland. Wetland physical parameters generally remain constant, although water volumes may change slightly. Hydrologic conditions are primarily dependent on the incoming groundwater flow as well as evaporation and precipitation. In efforts to maintain simplicity in the model and for the reader, the constructed wetland has been developed into three separate zones: the anaerobic methanogenic zone, the anaerobic iron reduction zone, and the root zone. The anaerobic methanogenic zone is the deepest zone, consists of endemic wetland soil, and is highly organic. It is roughly 18" thick and will be the first zone to come in contact with the contaminated groundwater. As a result of the vertical flow of the groundwater, the anaerobic methanogenic zone directly feeds the anaerobic iron reduction zone. This zone is approximately 18" thick and consists of Fe (III) rich soil. Flow in this zone will feed the root zone, which is the approximately 12" or so of soil occupied by the roots of the hydrophytic plants.

The primary processes considered within each zone are advection, sorption, and degradation. The anaerobic methanogenic zone models the production of methane, as its production is necessary for other processes in the aerobic zone. The goal of this project is to try to find optimal conditions for the chlorinated ethene degradation. This will

involve parameter variation and significance testing, among many other simulation tests. The outcomes of these tests will be presented in the next chapter.

Constructed Wetland Physical Parameters

The model has been constructed so that design parameters such as length, width, sediment depth, iron layer depth, sediment porosity, plant porosity, and plant size can be manipulated to adjust for field conditions or testing remediation management scenarios. Appendix D contains the initial or baseline constructed wetland physical parameters utilized in this model.

System Hydrology

The fundamentals of wetland hydrology have been discussed in Chapter 2. To remain consistent with the literature and practices within the field, substances in water will be expressed as concentrations, or mass per unit volume of water. Therefore, knowing the volume of water at any given time will be very important. The volume of water within a wetland is dependent on the hydrologic processes of the wetland. Each wetland may have different sources, outputs, or rates of evapotranspiration and precipitation. The model is constructed using a mass balance equation (MBE):

$$\frac{dV}{dt} = Q_i - Q_o + P - ET$$

where Q_i = groundwater flow (volume/time)

Q_o = constructed wetland outflow (volume/time)
P = precipitation rate (volume/time) and
ET = evapotranspiration rate (volume/time)

Constructed Wetland. The surface area and the depth of the wetland determine the initial water volume for the constructed wetland. These parameters are controlled by the design width, length and overall depth desired for the wetland. The overall depth is a

composite of the various layers previously described for this application, 18" anaerobic

methanogenic zone, 18" anaerobic iron reduction zone, and a 12" root zone. These

parameters as well as varying soil porosity's, plant density, plant porosity and surface

water depth, can all be managed in the Wetland Physical Parameters sector of the model.

The initial water volume for the constructed wetland will assume full saturation

over the entire surface area of the wetland, excluding any surface water. However, over

time, the volume of the wetland is dynamic as precipitation and evapotranspiration can

cause gains and losses, respectively. The model is designed to accommodate up to an

additional six inches of surface water, allowing alternative wetland management

scenarios ranging from fen (little surface water) to marsh (up to six inches of surface

water). This model assumes that each of the vertical zones will be completely saturated.

The water volumes of these zones can be calculated as the area of the zone, times the

depth of the zone, times the porosity of the sediment within the zone. Typical porosities

for wetlands with mineral soils are 50% total pore space (Mitsch and Gosselink, 1993).

The total water volume of the constructed wetland can be calculated at any given

time based on the surface water volume and the total sediment water volume (the sum of

the water volumes of the three zones, methanogenic, iron-reduction, and root). The

influent rate of the wetland is directly related to the incoming groundwater flow.

Precipitation and evapotranspiration can cause a positive or negative change in water

volume, depending on the controlling event. Precipitation is based on storm intensity and

is modeled as rain that falls directly into the wetland. The model is designed to

accommodate single or multiple storm events with varying intensities. For the purposes

of this study, evaluations of the effects of precipitation will be reserved for follow-on

research. Evapotranspiration rate for a wetland is represented by 0.8 times the Class A pan evaporation from an adjacent open site.; The Class A pan evaporation is assumed 8mm/day (Mudgett, 1995). Both the precipitation and evapotranspiration rates are a function of the wetland surface area.

The effluent rate of the constructed wetland is based on an outlet weir, which maintains a relatively constant water volume in the wetland. The influent rate is assumed constant and effects to the influent rate as a result of precipitation (decreasing or possibly negative influent rate as a result of heavy precipitation) are neglected. However, there are losses due to evapotranspiration. Assuming that the wetland water volume is relatively constant ($\frac{dV}{dt} = 0$), the MBE can be arranged so that

$$Q_o = Q_i + P - ET \cdot$$

Hydraulic retention time (HRT): The hydraulic retention time is also calculated within the Hydrology sector. It is the time in days that a volume of water remains in the wetland before it exits with the effluent. It is determined by:

$$HRT = \frac{V_T}{Q_i}$$

where V_T is the total water volume of the wetland.

Vegetation volume and surface area: The vegetation volume is the volume of plants within the free standing surface water. It is dependent on the volume of the surface water and the plant porosity: $V_p = \frac{V_{sw}}{n_p} - V_{sw} \cdot$

Plant porosity is based on a conservative assumption that 75% of the surface area of the wetland consists of plant biomass. Plant surface area is based on the total plant

volume, the surface water depth, and assumed plant stalk diameter = .14 cm (Mudgett, 1995). The plant volume and surface area play definitive roles in the support of microbial populations and developing biofilms. Further development on the role of this type of biota in this system is left to future research.

   Zone development Three zones are presented as a one-dimensional cross-section of the wetland and are separated by the definitive process that is modeled for each layer. Flow in each zone is characterized by bulk transport, simply the concentration of the contaminant times the flowrate. Sorption is modeled as rate-limited, simply applying a transfer coefficient representing the rate of phase change and a partition coefficient, which resembles the affinity of the contaminant to sorb. The partition coefficients and transfer coefficients, K_d and K_r, respectively, are determined for each contaminant. For the model, the concept is conveyed through the development of a concentration gradient between the aqueous and solid phase, adjusted by the partition coefficient and multiplied by the transfer coefficient. Due to the high organic nature of the sediment comprising the sediment of the wetland, the sorption behavior is expected to resemble that of linear or equilibrium sorption. The following equation depicts the sorption for each zone:

$$\frac{dS}{dt} = K_r(K_d C - S)$$

Contaminant degradation is modeled in each zone as well, although degradation rates may differ between zones. Degradation in the anaerobic methanogenic zone is modeled as reductive dehalogenation. As discussed in Chapter 2, if methane is being produced within this zone then conditions for reductive dehalogenation exist. The model, therefore, is designed to degrade incoming contaminants within the anaerobic zone only if methane is being produced within the zone. Degradation is based on Michaelis-

Menton kinetics (see Chapter 2), with initial values from Tandol et al (Tandol et al, 1994). Parameter values are based on a saturable process inherent of the wetland. Contaminant concentrations used to derive these parameters are consistent with previous studies and reflect concentrations expected in the wetland project.

Contaminants in the iron-reduction zone were degraded according to Michaelis-Menton kinetics as well. PCE is not degraded in this zone, as the conditions are not reducing enough. Only trans-DCE, cis-DCE, 1,1 DCE and VC were degraded within this zone. Although there has been some speculation TCE may be able to undergo iron reduction, it is not well established in the literature. Kinetic values for DCE and VC are based on reports from Bradley and Chapelle (1997).

The root zone is the apex of the model so to speak. Aerobic and anaerobic activities, as well as sorption and methane consumption occur in this zone. The zone is distinguished by an aerobic fraction and an anaerobic fraction. The aerobic fraction is based on a key parameter, radius of aerobic influence, which is the average radial distance extending from the individual root where the surrounding soil is considered aerobic. The aerobic fraction is determined by manipulating the three controllable factors unique to the root zone: the number of roots per square meter, the root diameter, and the average root length for specific wetland plant species. Controllable in this case means that the remediation manager or wetland designer has control over the species of wetland plants that will be represented in the wetland. Of these plants, these parameters could be calculated. The root is represented as a cylinder of equal diameter for the entire root length. The radius of aerobic influence is a cylindrical sheath of constant thickness that covers the root for its entire length. The aerobic area per root is calculated by the

47

difference in area between the radius of aerobic influence and the area of the root itself. This provides the aerobic area per root.

$$\text{Aerobic area per root} = \pi \left[\frac{(D+2L)}{2} \right] - \pi \left(\frac{D}{2} \right)^2$$

Where D = root diameter, in meters
L = radius of aerobic influence measured from the root surface, in meters

Therefore, the total aerobic area is the aerobic area per root times the number of roots per sq meter, times the surface area of the wetland:

$$\text{total aerobic area} = N \times CW_L \times CW_W \times \text{Aerobic area per root}$$

where N = number of roots per square meter
CW_L = Constructed wetland length, in meters, and
CW_W = Constructed wetland width, in meters.

The total active area is the total non-biomass area in the root zone (i.e., sediment only, no root biomass):

$$\text{total active area} = CW_L CW_W \left(N \times \pi \left(\frac{D}{2} \right)^2 - 1 \right)$$

The aerobic fraction is given by dividing the total aerobic area by the total active area. This value represents the aerobic portion of the root zone, regardless of its proximity to anaerobic areas within the same zone. The anaerobic fraction is the fraction of sediment, which is not aerobic, and is the complementary fraction of the aerobic fraction. Although this approach may seem oversimplified, it satisfies the needs of the system dynamics model where understanding the behavior of the system and its interactions is the objective.

Contaminant degradation within this zone is modeled as aerobic and anaerobic. Anaerobic degradation is modeled the same as in the anaerobic methanogenic layer.

Aerobic degradation is based on co-metabolism. The system produces methane in the anaerobic methanogenic layer. The methane produced in that zone is transported by the flow into the primarily aerobic root zone where methanotrophs are available to degrade the methane. As a result, the enzyme, methane monooxygenase (MMO), as discussed in Chapter 2, fortuitously degrades all of the chlorinated ethenes with the exception of PCE. This process has been modeled after efforts by Semprini and McCarty (1992), based on their study of co-metabolic transformations of chlorinated aliphatics in the field and the laboratory. The equation, describing the aerobic co-metabolic degradation accounts for the competitive inhibition of methane by $\dfrac{K_m C_{CH_4}}{K_{CH_4}}$ in the denominator, and is slightly modified from Semprini and McCarty (1992):

where C = concentration of the contaminant,
V_{max}, = maximum utilization rate of co-metabolism,
K_m, = half saturation constant for the contaminant,
C_{CH4}= concentration of available methane,

$$\frac{dC}{dt} = [\frac{V_{max}C}{K_m + C + \dfrac{K_m C_{CH_4}}{K_{CH_4}}}]$$

K_{ch4}= the half saturation constants for methane.

Based on this equation, increases in methane concentration should result in decreases in transformation rates due to competitive inhibition (Semprini and McCarty, 1992). The products of aerobic co-metabolism are CO_2, H_2O, and a chloride ion.

Testing

Testing the Dynamic Hypothesis. Initial model runs will be conducted to determine whether the basic mechanisms, and interrelationships of the mechanisms, are sufficient and produce the appropriate behavior, reflecting the reference mode. If

49

behavior does not follow the reference mode, review of the mechanism and the interrelations is required to determine whether those relationships are accurately represented. If the relationships among the mechanisms are reasonable and accurate, the reference mode may need adjustment to reflect the appropriate behavior. The process of testing a model does not prove correctness it merely instills confidence. Parameters that are both within and outside the boundaries of the system will be tested.

Structure Verification Test. The structure verification test compares the structure of the model to the structure of the system it represents. Verification is through someone knowledgeable in the field of the system model or through comparisons of these systems as found in the literature. Passing this test requires no contradictions with the structure of the real system, although levels of detail may be omitted providing the model sufficiently represents the actual system.

Parameter Verification Test. Model parameters should be compared to real observations when possible to ensure conceptual and numerical adherence. Behavioral testing can help determine the validity of parameter values by recognizing unreasonable behavior for the system when certain values are utilized by the model.

Extreme Conditions Test. The model should be explored using extreme conditions to verify behavior will remain reasonable in accordance with the extreme conditions. This test is implored mostly on rate equations within the model, inducing an abnormal condition to produce a predictable response, such as setting influent concentration to zero, the output concentration should also be zero.

Boundary-Adequacy Test. This test determines whether the model includes all relevant structure given the model's purpose. Is the model's level of aggregation

appropriate? To conduct the test, a hypothesis that addresses a change to the model structure is developed and then incorporated to resolve the importance of the hypothesized structure change. If there is no significant change in the resultant behavior, then the basic model structure does not need to add the hypothesized structure. This test also includes testing by analyzing the behavior without adding structure.

Behavior-Reproduction Test. This test is to determine how well the behavior of the model simulates behavior of the real system. Creating the exact numbers is not desired since creating the same behavior patterns is the goal. Of particular importance is comparing the timing sequence of the relative variables of the natural or realistic system to that of the model. The model should follow the same timing sequence of the real system. Inputs from outside the model boundary should not drive the pattern of behavior.

Sensitivity Testing. This type of testing evaluates model output to changing parameter values, which may offer insight to processes or mechanisms which are most sensitive to perturbations or manipulations of the model. By changing the parameter values, the associated behavior can be analyzed to determine the impact of those parameters on behavior.

Implementation

The results from the model runs will be presented and discussed in the following chapter. Testing and verification procedures build confidence in the model and in the system dynamics approach. Once confidence is achieved, the model can be used to explore design criteria and operation parameters which optimize contaminant destruction. Sensitivity analysis can be used to determine specific parameters that have the most

impact on the system. With this information, the model can be used as a management tool to assess various scenarios and optimize treatment conditions.

IV. Results and Discussion

The results of the testing and validation procedures, as described in Chapter 3, are evaluated here to provide confidence in the model and in the system dynamics modeling process. The behavior of the constructed wetland system as a whole and in part, will be discussed to provide a better understanding of the dynamic nature of contaminant removal within a constructed wetland, in hopes that its success will prove a viable alternative in groundwater remediation. This chapter will also serve to answer the research questions for which this study was intended.

As discussed in Chapter 3, the reference mode introduced the hypothetical behavior of the wetland system over the time horizon. Developing the framework required several iterations to ensure the resulting framework was essential and represented the actual structure of a constructed wetland. However, the resulting
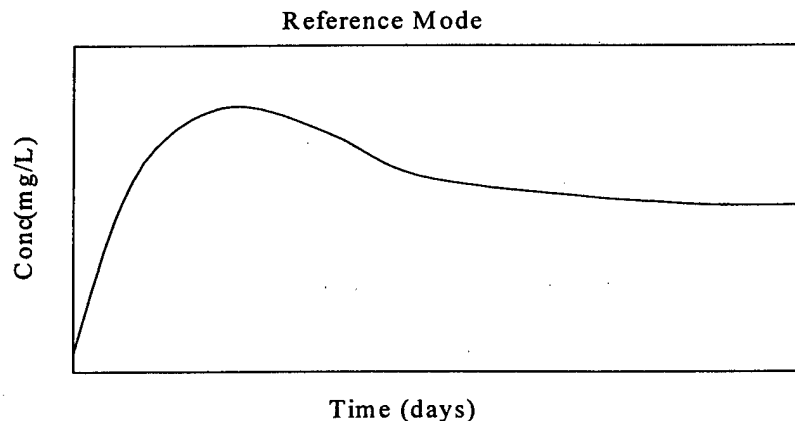
Figure 5 Reference Mode. Hypothetical behavior of system based on a vague mental notion of the influences within the system, indicating contaminant concentration in the root zone will increase, and then decline to a steady-state, over 2000 day time horizon.

behavior was not the same as that predicted by the reference mode. The difference in the behavior predicted by the reference mode and the actual behavior of the model lies in the conceptual formulation of the reference mode. The reference mode was based on the

perceived notion that as contaminant enters the wetland sediment, microorganisms will

reductively dehalogenate the contaminant (assuming methanogenic conditions). Figure 5

indicates that contaminant concentration increases at a very high rate because there is

initially a low population of microorganisms. As the contaminant reaches the saturation

concentration of the zone, (assuming continuously stirred reactor), the microorganisms

flourish on the available substrate, increasing their population. The concentration of the

contaminant continues to climb to a maximum. At this point, the degradation of the

contaminant is faster than the incoming concentration, resulting in a decline in the

concentration as well as the microbial population as there is less substrate to sustain the
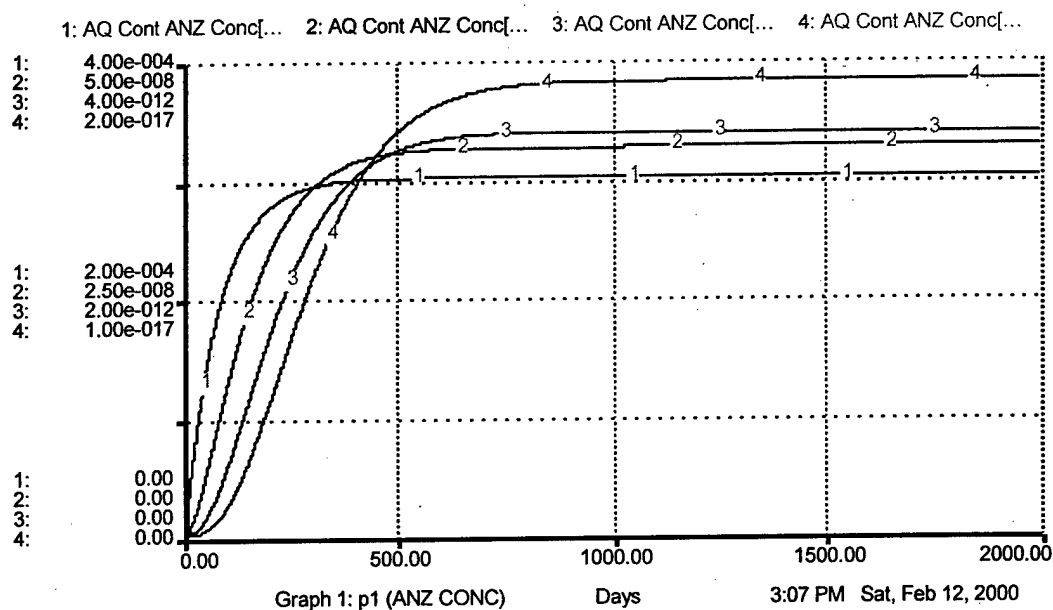
Figure 6 Concentration of contaminants within the anaerobic methanogenic zone
under initial conditions.

earlier population. The decline will continue until steady state is achieved where the degradation of the contaminant is equal to the incoming concentration of the contaminant. However, the behavior of the model did not reflect the behavior of the reference mode. Figure 6 depicts the behavior of the model. It is representative of contaminant concentration, in the root zone, as a result of the degradation and production of contaminants by the microorganisms. As a result of the model structure, incoming contaminant is degraded in the methanogenic zone according to Michaelis-Menton kinetics, and daughter products are formed. Therefore, the aqueous concentration of contaminant present in each zone is actually the net result of degradation and formation for each contaminant, as well as losses due to sorption. As in the reference mode, the model assumes zero concentration at time equal zero. The concentration of the contaminant increases until the zone is saturated, and the concentration reaches a steady state because the rates of sorption and degradation equal the rate of influent. This is where the model and the perceived reference mode differ: the microbial population is assumed to be uninhibited in the model, allowing the degradation rate to become equivalent to the influent rate, resulting in a steady state condition as soon as the zone becomes saturated. The plots in figure 6 represent this concept and form a new reference mode. Note that the scale is unique to each contaminant. This presentation aids in behavior assessment within the zone, at the present conditions, by fully presenting the shape of the plot.

Understanding the system and interactions between mechanisms is the key to developing confidence in the model; good structure and the appropriate level of detail help build confidence. The structure verification test compares the structure of the model

to the structure of the system it represents, in this case, the constructed wetland. The model structure is presented in Appendix A. The structure of the model is built as previously described in Chapter 3, closely following the design of the actual proposed constructed wetland project. In a wetland, there are distinct zones that develop and are distinguishable from others, although the line of delineation is often blurred. For example, a soil core taken from an active wetland would produce a cross-section of many closely related zones. GC analysis could determine the zones as methanogenic, sulfur reducing, nitrate reducing, etc. However, comparing multiple core samples would probably result in the same zones, but at varying depths. As a result, this model is developed after three distinct zones, each defined by the type of degradation expected for that zone as dictated by the type of soil layered in that zone. These zones, in the model, are homogeneous and well mixed. These assumptions eliminate several orders of detail in the real system but are hypothesized to provide behavior consistent with the natural system. This development provides a sufficient level of detail for the model, yet remains general enough to gain an overall understanding of the behavior of the wetland.

The depth of each zone is a controllable parameter in the model. The depth of the root zone is assumed to be 12", approximately the maximum root depth of the hydrophytic plants inherent to the wetland. The iron reduction zone depth is 18". This depth is arbitrarily set to ensure a hydraulic retention time to achieve contaminant removal via iron reduction. The methanogenic zone also has a depth of 18", and is 30" below the surface of the wetland. The depths of these zones and the overall depth of the wetland are parameters that are difficult to validate. There is really no discernable depth at which methanogenisis will occur. Under certain conditions, it may occur a few

56

millimeters below the surface, or several meters below the surface. This variance is

dependent on the presence of oxygen and the available electron acceptors at that depth.

This model assumes that the incoming groundwater is oxygen depleted and that the

conditions are necessary for methanogenisis to occur without bound or competition.

Varying the depth of the zones caused no decrease in the contaminant

Graph 7: p2 (PCE Depth ANZ)   Days   4:19 PM Sat, Feb 12, 2000
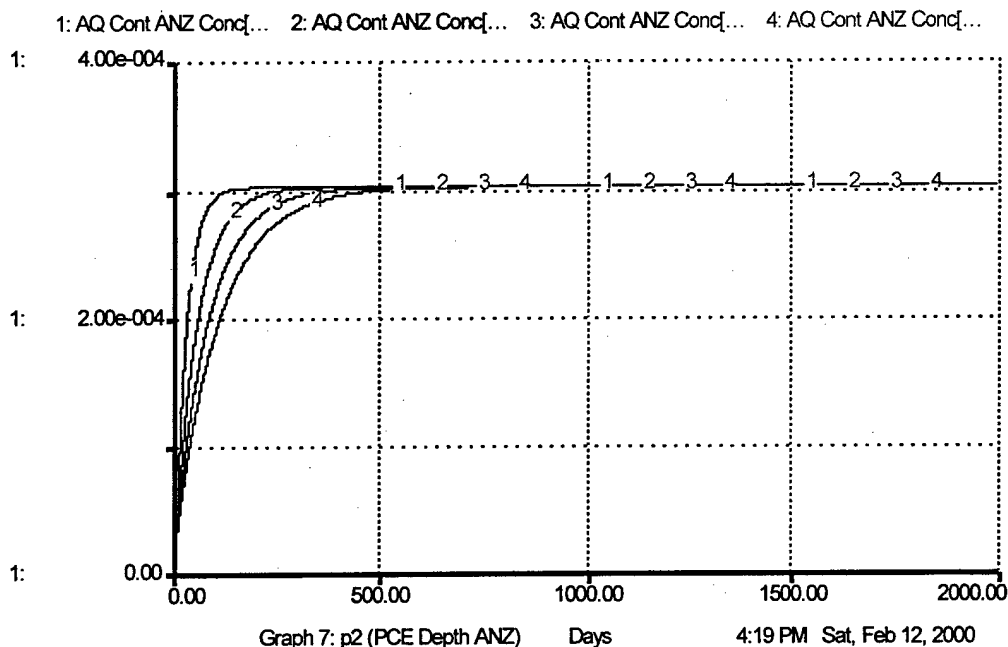
Figure 7 Vinyl chloride concentrations in the anaerobic methanogenic zone while varying depth in that zone. The concentrations are depicted for simulations of 6", 12" 18", and 24".

concentration within the zone, figure 7. Increasing the depth of the zone increases the

volume of a zone, which will increase the amount of time for that zone to reach steady

state, thereby smoothing the curve of the saturable process being modeled. Although

increasing the depth of the zone also increases the reductive dehalogenation ability of the

zone, it does so proportionately, resulting in a non-changing steady state.

Sorption is a very important process within a wetland. The high organic nature of

a wetland can sorb the majority of a contaminant, resulting in initial efficient removal.

However, this could create a false sense of security as sorbed contaminant may desorb over a period of time, reintroducing the contaminant to the wetland and possibly the effluent. Each contaminant may sorb or desorb at different rates, depending on the sorption characteristics of that contaminant. Sorption is simulated assuming rate-limitation. The partition coefficient (K_d) for each contaminant is dependent on the octonal-water coefficient and the fraction of organic carbon (Schwarzenbach and Westfall, 1981). The amount of organic carbon can be relatively controlled in a constructed wetland by adding or limiting organic rich sediment in the construction
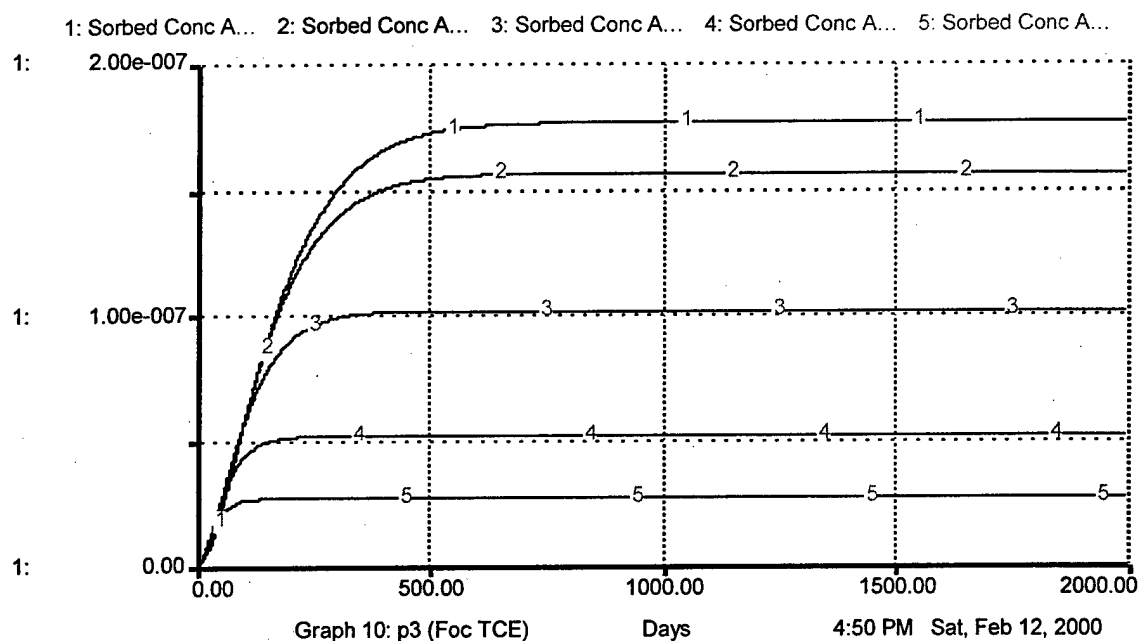
Figure 8 Sorbed concentration of TCE in the anaerobic methanogenic zone while varying the fraction of organic carbon from 0.70, 0.62, 0.40, 0.20, and 0.10. Typical foc values for wetlands range from 20-35% in wetlands with mineral soil to greater than 35% in wetlands with organic soil (Mitsch and Gosselink, 1993).

phase. Organic carbon will accumulate over time, due to the nature of a wetland, but initial conditions can be moderately controlled. Varying the organic content of the wetland in the model results in significant changes in the sorbed concentration as shown

58

in figure 8. The use of a mineral soil or an organic soil could change the sorption properties of the wetland.

Although the organic content may be able to be initially controlled in the construction phase of a wetland, controlling the transfer coefficient (K_r), is difficult if not impossible. Varying the transfer coefficient varied the amount of time the contaminant remained in the sorbed phase.
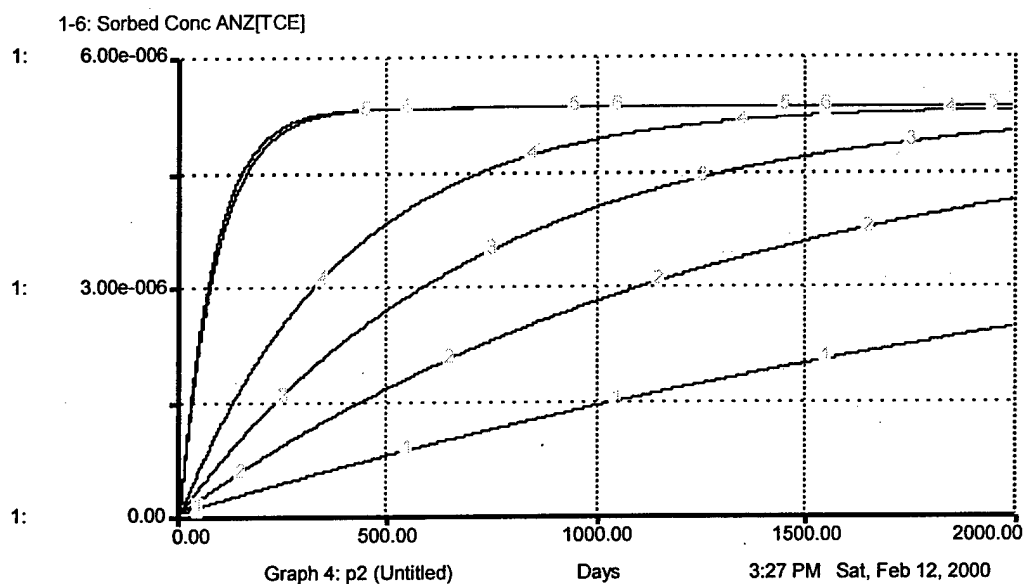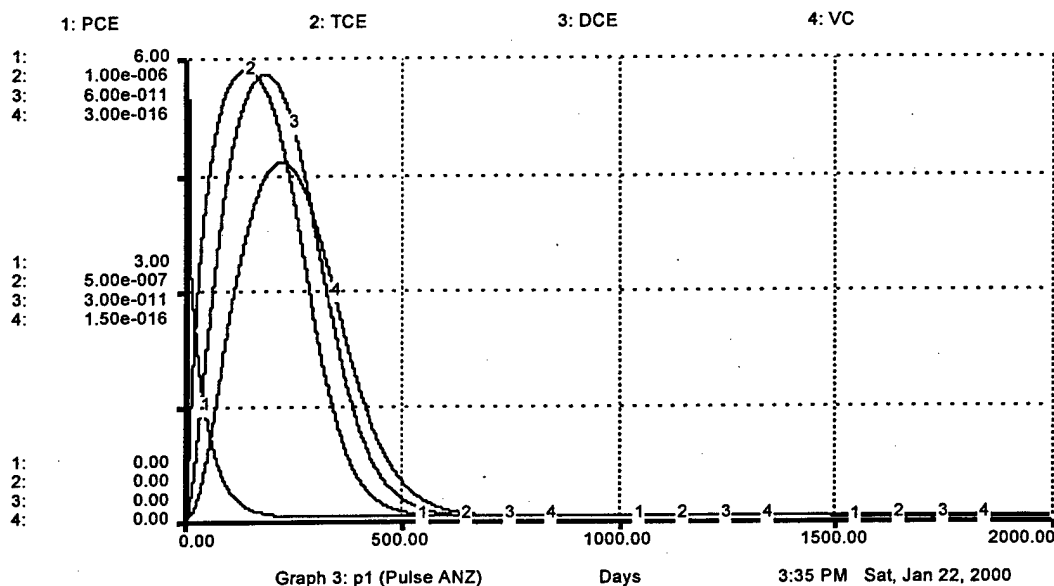

Figure 9 Sorbed concentration of TCE in the anaerobic methanogenic zone while varying the transfer coefficient, K_r, from 0.1, 0.25, 0.5, 1, 25, 50 uM/Lday.

Figure 9 compares the sorbed phase concentrations of TCE as the transfer coefficient is varied. The curves represent the amount of time it takes for the contaminant to reach equilibrium between the solid/liquid phase. Note that the flattest curve corresponds to the lowest $K_r = 0.1$ and the steepest and most drastic curve to the highest $K_r = 50$. When K_r was greater than 25, sorption behaves similar to equilibrium sorption conditions. This area requires laboratory study to determine sorption rates of contaminants in wetland sediment and whether or not they perform according to linear

rate-limited sorption. Although solubility of PCE is only 110 mg/L, unrealistic

concentrations (5000 mg/L) were used to further validate the model and build confidence

through acceptable behavior. Increasing the influent concentration of PCE resulted in

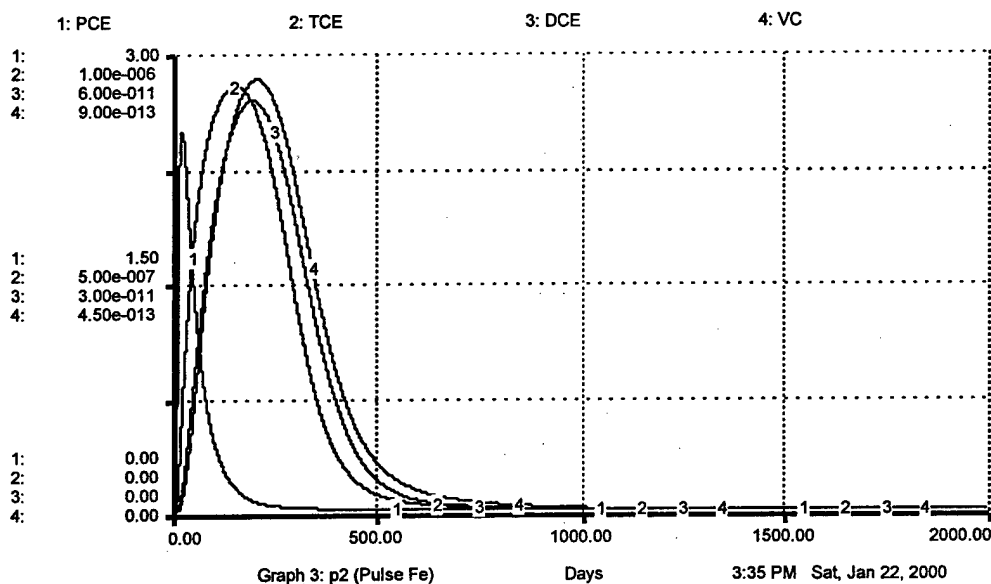higher concentrations of daughter products in other zones within the system, allowing

Figure 10 Concentration of PCE and resulting daughter products (TCE, DCE, and VC) in the anaerobic methanogenic zone undergoing reductive dehalogenation. PCE introduced to zone at 5000 mg/L for 5 days.

behavior analysis and comparison with other zones.

The effects of degradation within the system and within the various zones, were

the most anticipated results of this study. Three zones were constructed to provide three

types of degradation, reductive dehalogenation, iron-reduction, and aerobic co-

metabolism. Degradation in each zone was modeled using Michaelis-Menton kinetics as

discussed in previous chapters. Degradation in the methanogenic zone will not occur if

methanogenic conditions are not present. The results of a step simulation are shown in

figure 10. PCE was introduced to the methanogenic zone at 5000 mg/L for a period of 5

days. This graph verifies that the model is correctly structured, as this is the type of reasonable behavior generally experienced in batch laboratory experiments. The PCE spike is a result of PCE being the only contaminant to enter the wetland at time = 0. However, as soon as it enters the wetland, reductive dehalogenation begins and daughter products are formed. As each daughter product is formed, the same daughter product can start degrading. This explains the slight shift of each daughter product to the right of its parent product. Note the slight difference in the shape of the curves as each contaminant enters and is degraded in the iron reduction zone, figure 10, and then the root zone,

Figure 11 Concentration of PCE and resulting daughter products (TCE, DCE, and VC) in the iron-reduction zone undergoing iron-reduction. PCE introduced to methanogenic zone at 5000 mg/L for 5 days.

figures 11 and 12.

In each case, the plots have a tendency to spread, or widen at the base. This is a result of the bulk flow transport carrying contaminant concentration to each respective zone. Initial concentrations in each zone are a reflection of the concentration of the preceding zone prior to transport.

61
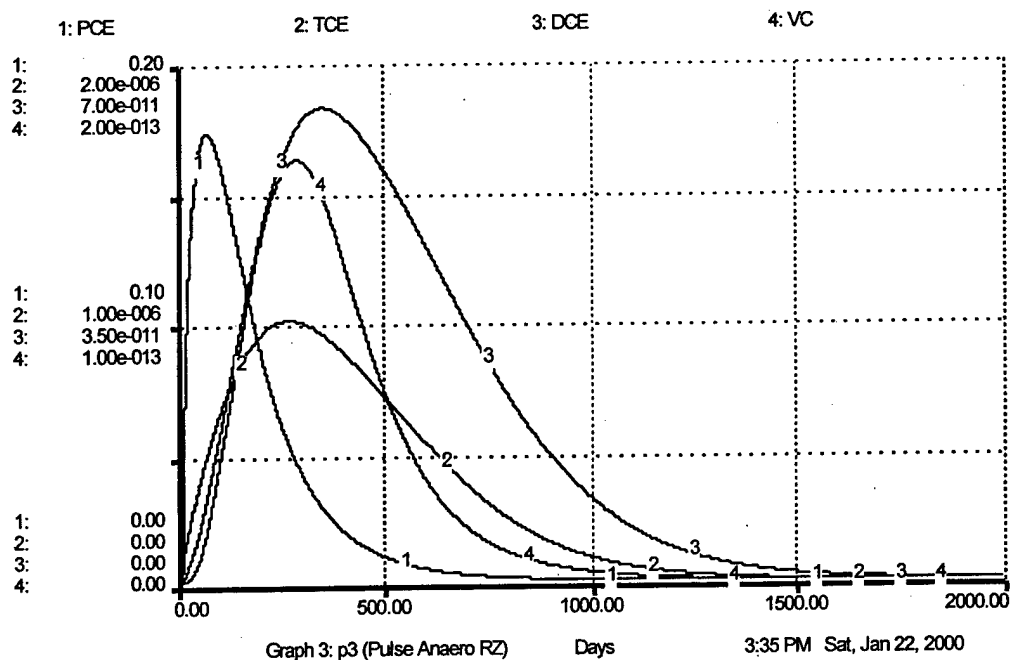
Figure 12 Concentration of PCE and resulting daughter products (TCE, DCE, and VC) in the anaerobic root zone undergoing reductive dehalogenation. PCE introduced to methanogenic zone at 5000 mg/L for 5 days.
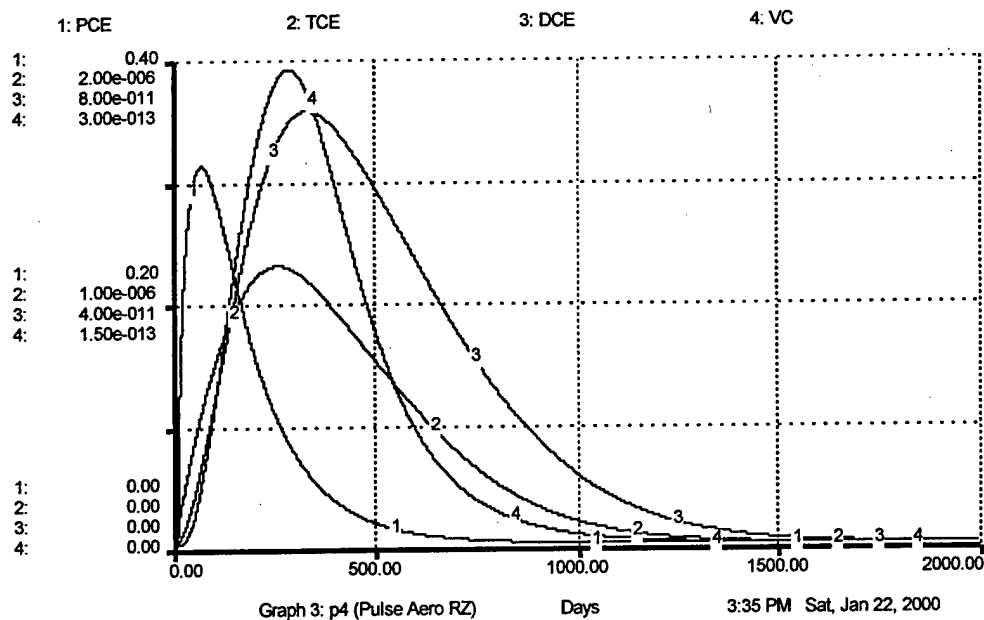

Figure 13 Concentration of PCE and resulting daughter products (TCE, DCE, and VC) in the aerobic root zone undergoing aerobic co-metabolic dehalogenation. PCE introduced to methanogenic zone at 5000 mg/L for 5 days.

The root zone is separated into two compartments, the aerobic root zone and the anaerobic root zone. The anaerobic root zone is the soil area within the root zone that has

no contact with any aerobic influence of the root. The parameters within the aerobic zone

are root diameter, the number of roots per square meter, and the average root length
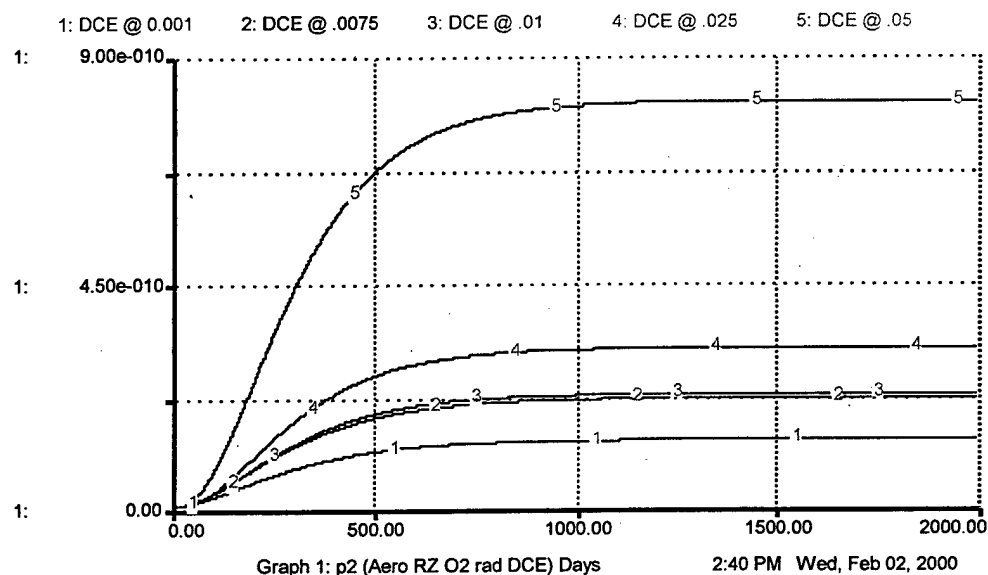
Figure 14 Sensitivity analysis of radius of aerobic influence on DCE concentration in
the aerobic root zone. Parameter was varied from 0.001m to .05m, plots 1-5,
respectively.

(maximum depth). Based on these parameters, the root surface area could be calculated

and a radius of aerobic influence applied. This parameter suggests that each root has a

"sheath" of aerobic activity along its entire length. Although this is a very broad

assumption, it provides a method to determine the aerobic fraction of the root zone. The

remaining fraction of flow is considered anaerobic and degrades the contaminants in

similar fashion to the anaerobic methanogenic zone. Methanogenic conditions are

assumed to dominate this zone and reductive dehalogenation degrades the contaminants.

The aerobic root zone degrades the contaminant through co-metabolism.

Degradation here often continues through to mineralization, as discussed in chapter 2.

The rate of degradation is much faster than the anaerobic root zone. The concentrations

in this zone are primarily a function of the radius of aerobic influence parameter. This

parameter directly affects the aerobic fraction. If the aerobic fraction is much larger than the anaerobic fraction, the majority of the flow from the iron reduction zone is directed to the aerobic root zone. This structure conceptually divides the aerobic and anaerobic portions of the root zone, although they still occur simultaneously. This modeling strategy significantly affects the overall degradation of the contaminant, as co-metabolism is the preferred degradation mechanism for contaminants like DCE and VC, which are slow to degrade under anaerobic conditions. Figure 14 shows a sensitivity analysis of the radius of aerobic influence and its effect on contaminant concentration in the aerobic root zone. Notice the how concentration increases as the radius of aerobic influence is increased. This parameter could be important in optimizing contaminant removal within the wetland by identifying plant species that have very aerobic root systems in a saturated environment.

Increasing the number of roots per square meter also had a positive effect on
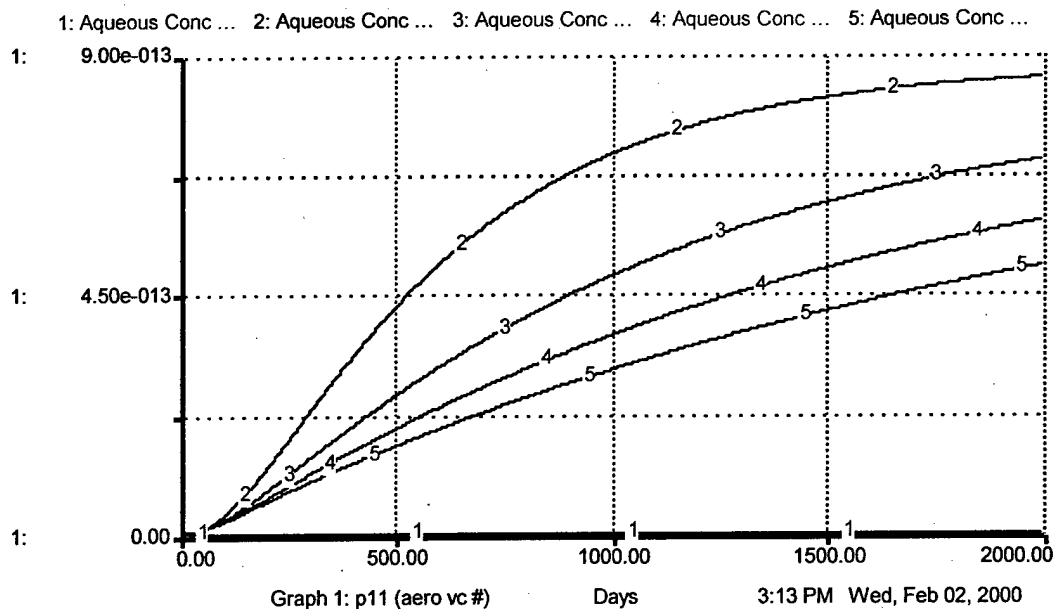
Figure 15 Concentration of VC in the aerobic compartment of the root zone; varying the number of roots per sq meter

64

contaminant degradation in the root zone as shown in figure 15. This parameter is

another optimization parameter for the remediation manager that could possibly provide

guidance to plant specie selection.

The development of the root zone and the parameters within this zone overlook a

significant amount of detail that would be found in the real system. However, including
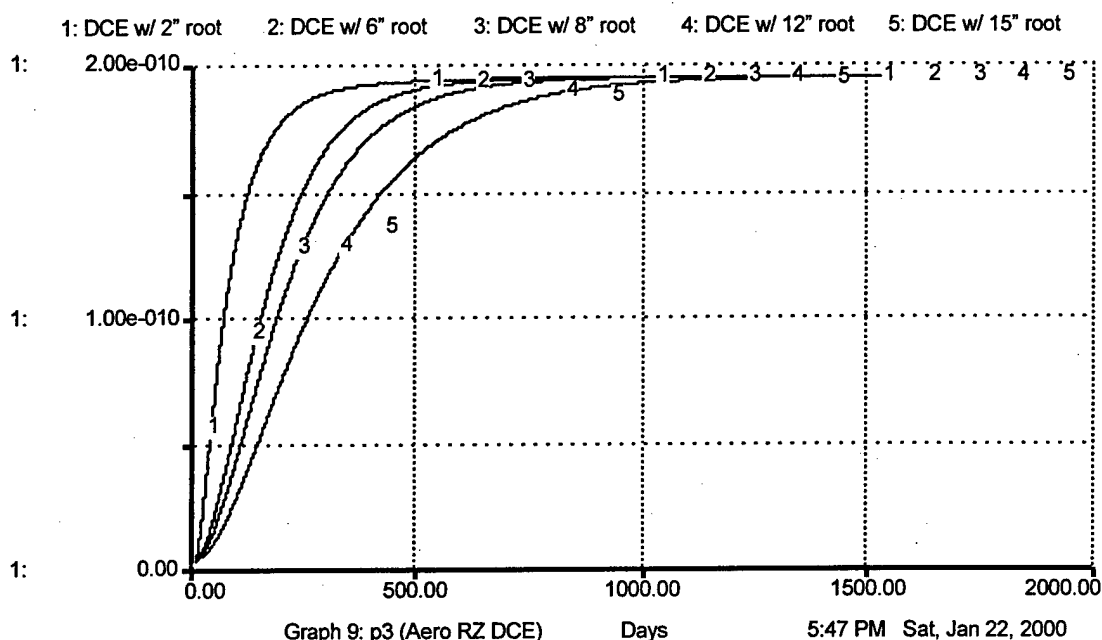
Figure 16 Concentration of DCE in the aerobic fraction of the root zone while varying the length of the root from 2", 6", 8", 12", and 15".

such detail in the model would add unnecessary complexity. Although parameters such

as root diameter, and radius of aerobic influence are based on assumptions, they help

provide the necessary interactions within the system to achieve reasonable behavior for

the zone. Figure 16 shows a simulation varying the root length within the aerobic portion

of the root zone. Increasing the root length increases the volume of the zone. The result,

as shown in figure 16, is a delay in the ability of the zone to achieve steady state. This is

due to the saturable processes being modeled and the assumption that the zone is well

mixed. This concept introduces opportunity for further study relating the oxygen

65

concentration to the aerobic fraction of the root zone. Doing so would create a method to account for the amount of oxygen within the zone, which would have a direct effect on the aerobic degradation of contaminants. Increasing the oxygen content has a direct effect on the rate of cometabolic degradation (Semprini and McCarty, 1991).

Parameter verification is primarily based on the literature review and previous work by Mudgett (1995) and Colburn (1997). The physical parameters of the wetland are based on the wetland pilot project collaboration among the Air Force Institute of Technology, Wright State University, and the Air Force Research Laboratory. Degradation and sorption parameters are from the literature. These values are for various systems and, although they are matched very closely to the conditions within a wetland, are not derived from wetland studies and therefore may not accurately represent the behavior of the degradation and sorption processes within the wetland. Sorption values were based on sediment from a highly eutrophic lake (Schwarzenbach and Westall, 1981), which would be very near if not identical to wetland conditions. Anaerobic degradation parameters were based on studies conducted under methanogenic conditions (Tandol et al, 1994; Liang and Grbic-Galic, 1993; Freedman and Gossett, 1989). Parameters for iron reduction follow studies by Paul M. Bradley and Francis H. Chapelle (1996, 1997) concerning the kinetics of DCE and VC degradation in iron reducing conditions. Aerobic co-metabolism parameters are based on work by Semprini and McCarty (1991; 1992). Empirical information from laboratory studies using wetland soil and groundwater from the project would produce results specific to the project. However, based on the above studies, the values used here are sufficient to provide reasonable behavior of the fate and transport of chlorinated ethenes in the wetland.

Throughout the course of verification and testing, the model was subject to a variety of extreme conditions, testing model structure and verifying model behavior, such as turning the iron reduction zone "off", by setting its depth equal to zero, yielding zero contaminant in the zone, yet allowing the contaminant to degrade in the root zone, as expected. A zero concentration of contaminant entering the wetland yielded a zero output. Additionally, if there is no concentration of methane present in the anaerobic or aerobic zone, none of the contaminant will be degraded. This type of structure was necessary for the model in order to maintain its simplicity and the appropriate level of detail. Although reductive dehalogenation is not dependent on the presence of methane, it does require the same conditions in which methane is produced. Therefore, for purposes of this model, if methane were not present within the anaerobic zone, then reductive dehalogenation would not occur. Additionally, as the structure of the model was developed, it was constantly evaluated against the system boundary to ensure adequate representation. The boundary in this case is the simplified structure of the wetland system as portrayed by the model. The boundary sets the appropriate level of detail for the model to accurately represent the real system. This caused several iterations and significant revision of the model and the conceptual thinking to achieve the structure that most accurately described the real system and produced the most reasonable behavior.

The behavior reproduction test is very difficult to apply to this model, as there is not very much empirical data available on contaminant removal by a constructed wetland. It is important to note here that system dynamics is not based on empirical or heuristic data. The goal is not necessarily to have the numbers be accurate; rather, the

desirable outcome is for reasonable behavior, meaning conceptually and intuitively, the behavior produced resembles behavior of the system being modeled. Heuristic and empirical data can be utilized by the modeler to verify structure and build confidence, but are not required for reasonable behavior. Although historical or empirical data on contaminant removal in constructed wetlands are not readily available, there are some studies that have found natural wetlands that are degrading contaminated groundwater (Lorah and Olsen, 1999b). Comparing this model to the behavior of a similar natural system leads to greater confidence that the model accurately represents the relationships and parameters of the mechanisms in the real system.

This model has similar structure to the natural wetland. The natural wetland had developed into distinct zones of varying depth, with varying functions. Lorah and Olsen (1999a, b) found degradation occurring in zones of methanogenic, iron reduction, and sulfate reducing activity. The majority of these zones were in the top 1m of the wetland. The greater part of degradation occurred in the methanogenic zone and total concentrations of parent and daughter products decreased along the upward flow path. The majority of these attributes are represented in this model, supporting its structure and building confidence that the relationships of the mechanisms in the system are representative.

Sensitivity testing was the most important aspect of the implementation process. This involved changing various parameters to determine the effects on the model and which of those parameters may provide managerial opportunities leading to optimization. Some of these processes have already been discussed. As a result, only parameters that can be engineered were tested. These included physical parameters such as constructed

wetland design length and width, zone depth, sediment porosity, flowrate, soil organic content, soil iron reduction capacity, and root length. The majority of these analyses are volumetric exercises where the volume of the zone in question is altered by a certain parameter. This change in volume causes an increase in the amount of time for the system to become well mixed and therefore achieve steady state. However, as shown earlier with the radius of aerobic influence parameter and the number of roots per square meter parameter in the root zone, significant changes can occur within the system when these parameters are changed. These parameters may be plant species specific, resulting in a design control. Soil organic content has a significant effect on sorption as mentioned earlier. If the iron rich soil comprising the iron reduction zone was not included in the wetland, it would effect the overall contaminant removal in the wetland. With the exception of these parameters, the remaining parameters under human control are nothing more than volume manipulators. The concentration will reach steady state as soon as the volume of the zone is saturated with the contaminant. Under these conditions, the only means of improving degradation conditions are by affecting the degradation rates through engineered techniques, or determining ways to optimize microbial population dynamics.

Engineering conditions within the various zones in order to increase the ability for the available microbial consortia to degrade contaminants at higher rates of utilization would have a significant impact on the concentration of contaminant in a zone. A surfacial analysis varying the rate of utilization of PCE in the anaerobic methanogenic zone, increased degradation of PCE within the zone, but had a synergistic effect on the contaminant concentrations in subsequent zones (figure 17 and 18).
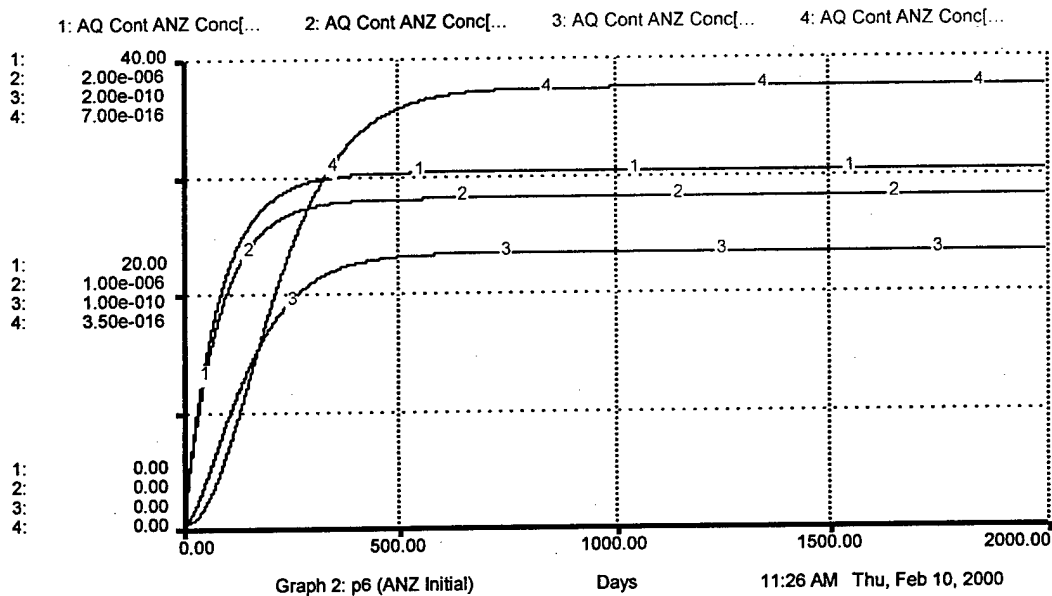
Figure 17 Concentration of PCE and resulting daughter products in the aqueous phase in the anaerobic methanogenic zone under initial conditions.
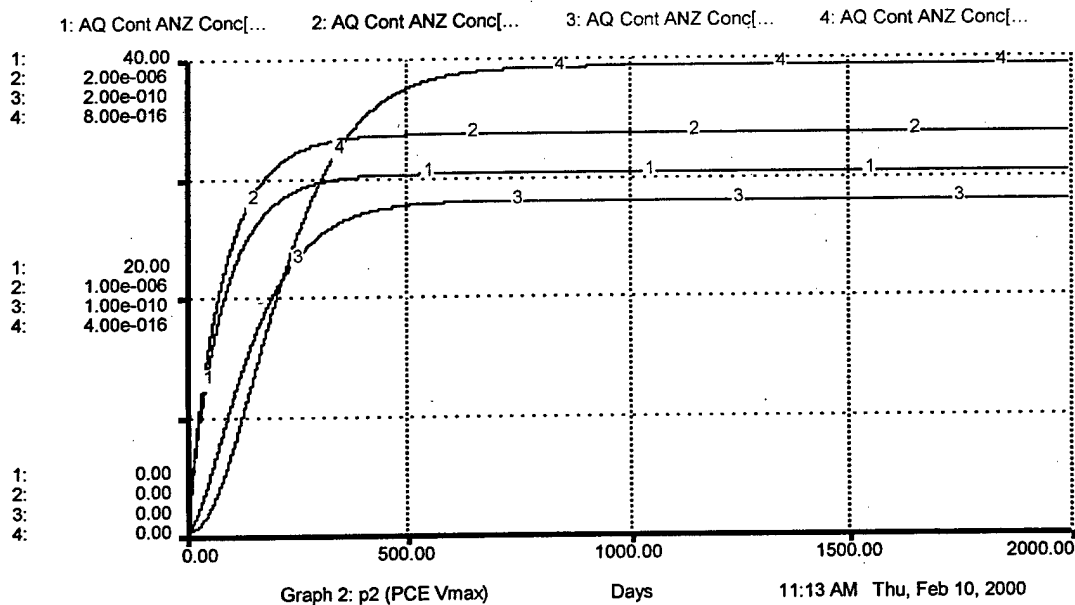
Figure 18 Concentration of PCE and resulting daughter products in the anaerobic methanogenic zone when increasing the V_{max} for PCE.

Notice that each contaminant is on a different scale. PCE is 1, TCE is 2, DCE is

3, and VC is 4. Comparing the concentrations under initial conditions (figure 17) with

contaminant concentrations when PCE V_{max} is increased, slightly raises the concentration

of the daughter products, indicating increased degradation. This analysis requires further

70

research to ensure this behavior is feasible. However, if the conditions in the zones could be manipulated to favor microbes with faster rates of utilization, this would be another optimization capability for the remediation manager.

V. Conclusions and Recommendations for Further Study

The purpose of this study was to develop a system dynamics model to reasonably describe contaminant fate and transport within a constructed wetland. This included determining the processes within the wetland that are most important in controlling contaminant fate, and the combination of parameters that optimize or limit the system.

Wetlands are dynamic, complex systems. Modeling a wetland for contaminant removal, proved a challenging task. Confidence in the model was built through verification and testing. Reasonable behavior resulted from a reasonable range of parameters. The structure of the model adequately represents the mechanisms and their interactions of the actual wetland system. Based on the level of detail presented, this study provides a baseline understanding of the wetland and gives some insight for implementation. Sensitivity testing identified the radius of aerobic influence and the number of roots per square meter, as having the most effect on contaminant fate.

The radius of aerobic influence had a significant impact on contaminant concentrations in the entire root zone. An increase in this parameter will result in an increase in the aerobic fraction of the root zone, which will have a direct effect on the amount of contaminant in the root zone that is degraded aerobically or anaerobically. The number of roots per square meter has an effect on the contaminant concentration as more roots mean greater aerobic capacity in the root zone, which increases the aerobic co-metabolic degradation. These parameters are useful optimization tools for the remediation manager. Choosing plant species that drive more oxygen into the root zone and grow in close proximity to one another will result in a greater amount of aerobic activity within the zone and consequently, increased contaminant degradation.

The fraction of organic carbon affects the partition coefficient for each contaminant. The higher the organic content, the longer the contaminant will stay in the sorbed phase. The goal is to degrade the contaminant rather than contain it. This poses a problem for any remediation project as it transfers the contaminant from one media to another. This should be of little concern, as the inherently long time horizon of a wetland will insure conditions for degradation will still be in place when the contaminant finally desorbs. Additionally, the sediment compositions of wetlands typically have high organic contents, and may tend to increase with time due to the cyclical state of biomass growth and death.

Model Strengths

Given the model's purpose of simulating the fundamental processes of contaminant degradation within a constructed wetland, the model succeeds in encapsulating the sequential degradation of PCE via microbial processes, while establishing the appropriate level of detail required for this study to model contaminant fate and transport within a wetland system. Additionally, the model captures the necessary interactions and feedback loops between mechanisms of the system. The model closely portrays the structure of a natural system and produces behavior that is comparable to the natural system. The model provides a means to develop a fundamental understanding of a wetland system and the mechanisms involved. The model can also be implemented for a variety of conditions for the remediation of contaminated groundwater in a constructed wetland.

Model Limitations

Optimization of the degradation processes, at the current level of detail in the model, is limited to altering the plant species and therefore the radius of aerobic influence within the root, or the number of roots per square meter, thereby increasing the aerobic fraction of the root zone and degrading more contaminant because aerobic degradation is faster than anaerobic degradation. Increasing the organic content of the sediment can increase contaminant removal via sorption. However, there is little that can be done to increase the rate of degradation of the microbes. Adding a level of complexity, that details the interactions of the microbes and specific conditions they thrive in, may derive additional controllable parameters that could be altered to optimize contaminant degradation. The controllable parameters of length, width, zone depth, and root length, have an effect on the overall fate and transport of the contaminant, but are merely exercises in volume manipulation to increase retention time within the zone of interest.

Including further insight into methane generation and consumption, as well as oxygen concentration levels may improve understanding. The degradation of PCE is dependent on methanogenic conditions and not methane itself. It may be important to further define the anaerobic methanogenic zone by adding hydrogen dependence and competition between the methanogens and halorespirers as evidence in the literature suggests (Yang and McCarty, 1998). Additionally, concentration levels of oxygen in the root zone have a direct effect on co-metabolism. This study basically recognized an aerobic portion of the root zone, and did not attempt to calculate an oxygen concentration. Doing so will provide a more accurate representation of co-metabolic degradation and be more accurate with the literature (Semprini and McCarty, 1992). This

model presented a general, fundamental view of the wetland system, which produces reasonable behavior on chlorinated ethene fate and transport. The next step for this model is to add detail in one of the following areas in order to gain a better understanding of the system.

Recommendations for Further Study

Some hints of future research are discussed above. However, this model could benefit from additional study in the following areas:

- Build more definition into the root zone. This area was very difficult to model, as there are so many complex interactions within this zone. Further insight may be gained by better defining the aerobic and anaerobic compartments within this zone as well as the mechanism for oxygen transport in the root system. Determination of the oxygen concentration will have a direct impact on aerobic co-metabolic degradation, and the oxidation of DCE and VC could be modeled, further affecting the contaminant concentrations in the root zone. The aerobic compartment of the root zone has a vital role in contaminant fate.

- Further develop microbial interaction. Methane generation was very basic in this model; further complexity may provide better insight. Methane was modeled as the result of methanogens consuming a very large amount of substrate. Michaelis-Menton kinetics determined substrate consumption. The amount of substrate was large enough so that the methanogens would always be operating at their Vmax. Methane production was a stoichiometric byproduct of the substrate consumption. Methane and methanogenic conditions are keystones to the degradation process. Competitive inhibition with other electron acceptors

could enhance the understanding of degradation in the wetland. This may require delineation of each zone into smaller zones to account for interactions that are occurring on smaller levels.

- Further Develop the Interaction between the Fe Zone and the Methanogenic Zone. Interactions such as competitive inhibition and zone mixing may need to be addressed as there was evidence in the literature that the microbial reduction of ferric iron ($Fe(III)$) to ferrous iron ($Fe(II)$) can inhibit methane production in sediments (Lovely and Phillips, 1986). The inhibition occurs because the ferric iron is a more effective electron acceptor for the metabolism of acetate, which is often a substrate for methanogens. This is important because mixing between the iron zone and the methanogenic zone could occur and iron reduction could outcompete methanogenic food chains for organic matter. The absence of methane would limit co-metabolism in the aerobic zone, thereby affecting degradation in the root zone.

- Develop the Surface Water Zone. The surface water zone is the zone from the sediment/ water interface to the atmosphere/ water interface. It includes the submerged plant stalks and biota within this zone. This zone is really not developed in this model. It acts as the reunion for the outflows of the aerobic root zone compartment and the anaerobic root zone compartment. Biofilm development and contaminant removal within the biofilm could be an additional development of the model. Contaminant volatilization may be another avenue to explore within this zone.

This study provided an initial model of the wetland system at its most basic and general level. The next step in the system dynamics process would be to research some of the areas discussed above and develop the necessary relationships, at the appropriate level of detail, to provide an increased understanding of the wetland system and to provide a better tool for a remediation manager.
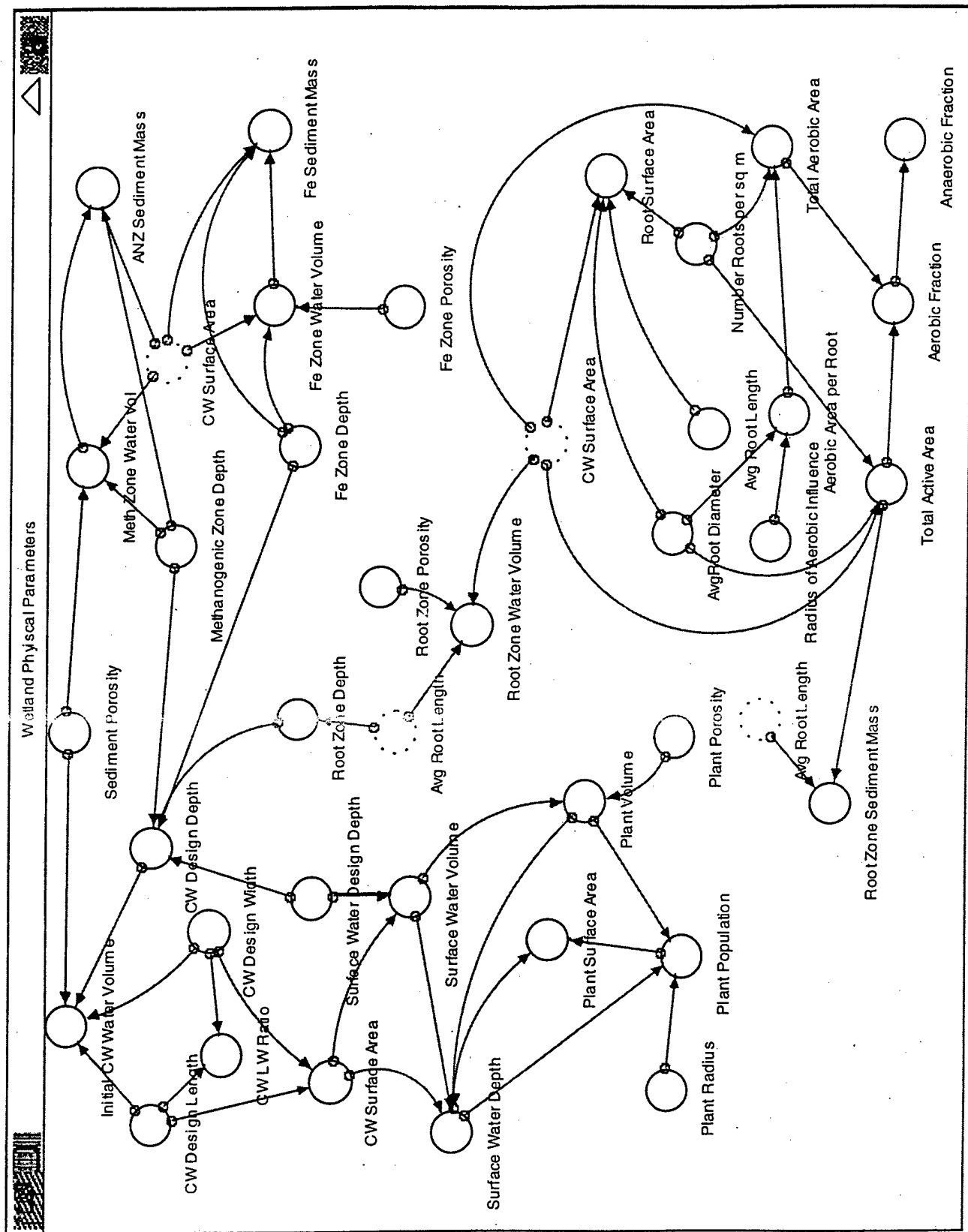
Final Assessment of the Thesis Effort

Contaminant fate and transport within a wetland system is an extremely complex and dynamic process. The entities and mechanisms that drive wetland behavior are dynamic. Understanding the system through the use of a model is an ideal approach. The system dynamics paradigm lends itself nicely to such a challenging system, as it yields insight into the behavior of the overall system. By constructing the model and performing simulations with the model, one learns and begins to understand the complexity of the system, the interactions, interdependencies, and feedback loops and how they are all tied together to comprise the system.

The system dynamics process is favored over other modeling processes for this study as it develops insight to the behavior of the system as a whole versus one influential mechanism in the system. As a result, a remediation manager can use this model to explore system behavior by controlling or optimizing specific parameters to better manage contaminant fate and transport in a constructed wetland, saving time and resources.
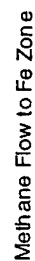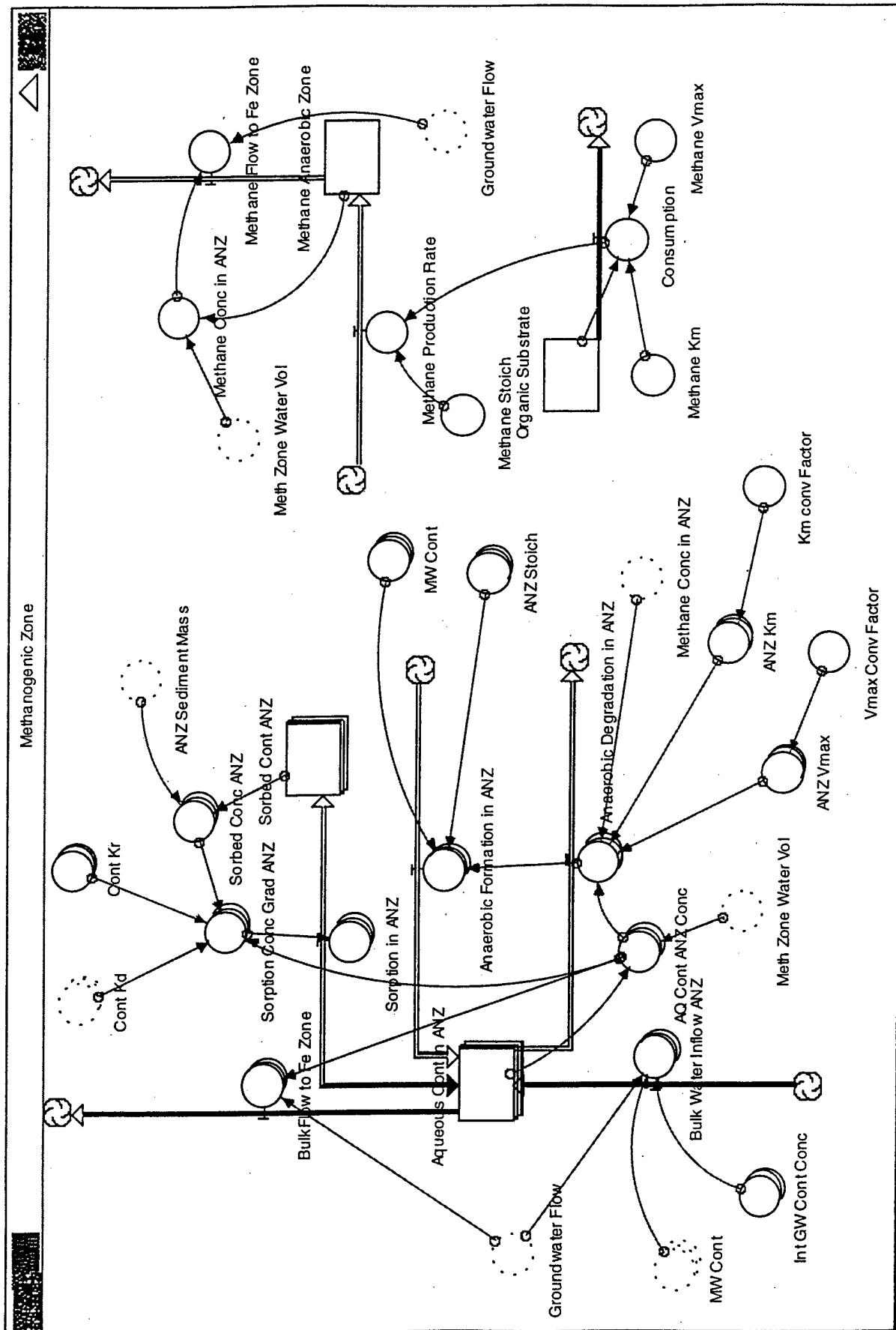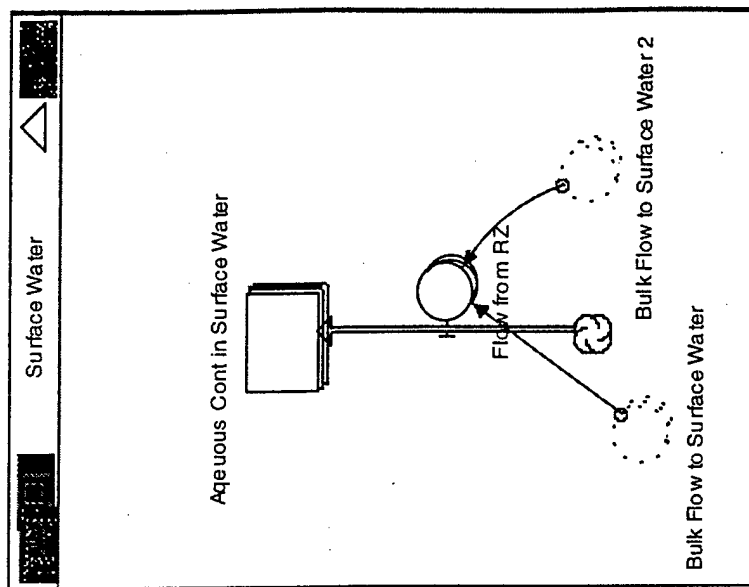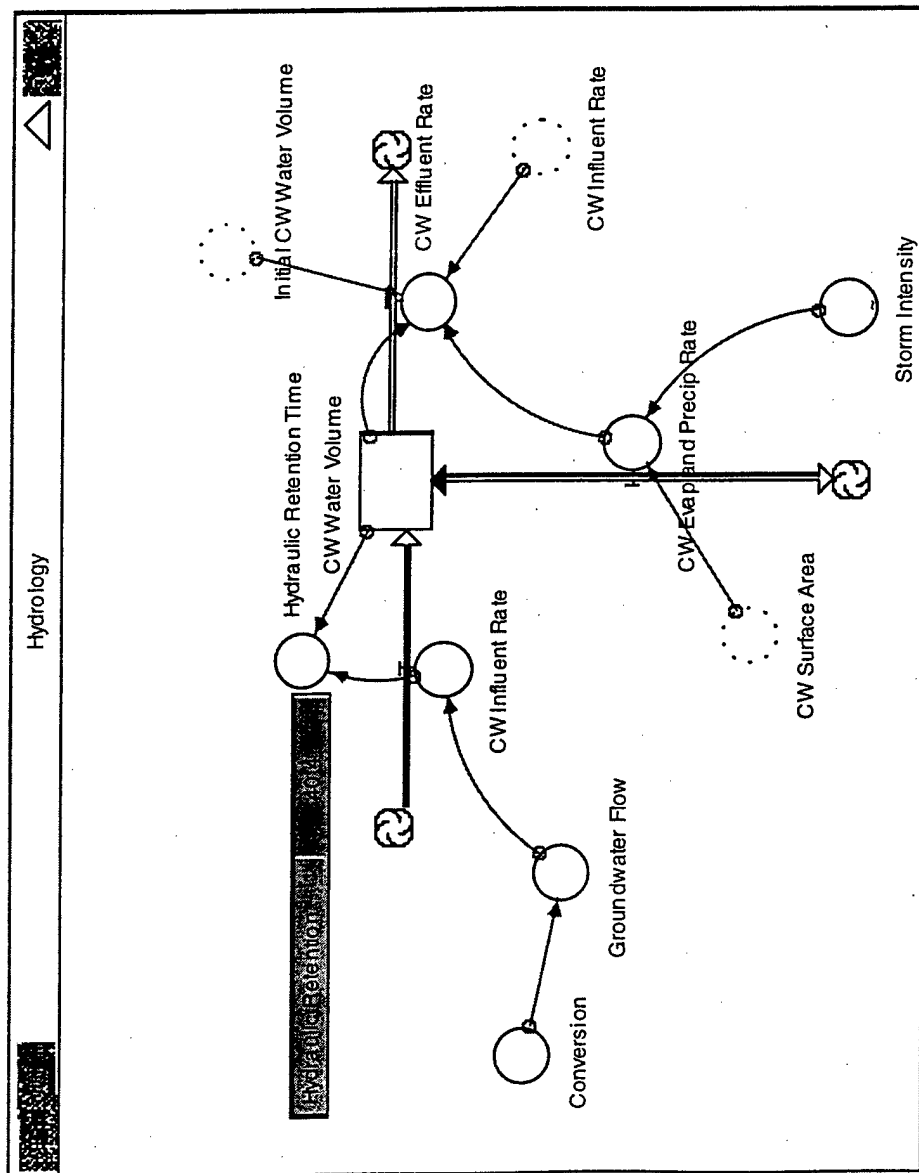
Appendix A

Model Structure

Wetland Physical Parameters

Root Zone Aerobic Sector

Iron Reduction in Anaerobic Zone

81

Methanogenic Zone

Surface Water

Aqueous Cont in Surface Water

Flow from RZ

Bulk Flow to Surface Water 2

Bulk Flow to Surface Water

Hydrology

Initial CW Water Volume

CW Effluent Rate

CW Influent Rate

Hydraulic Retention Time

CW Water Volume

CW Evap and Precip Rate

Storm Intensity

CW Influent Rate

CW Surface Area

Groundwater Flow

Conversion

Root Zone Anaerobic Sector

RZ Stoich 2

MW Cont

Cont Formation in RZ

Groundwater Flow

Anaerobic Deg in RZ 2

Anaero RZ Methane Conc

ANZ Vmax

ANZ Km

Aqueous Conc RZ 2

Bulk Flow to Surface Water 2

Aqueous Cont Root Zone 2

Root Zone Water Volume

Flow from Fe Zone

Bulk Flow from Fe Zone

Anaerobic Fraction

Root Zone Sediment Mass

Sorbed Conc RZ 2

RZ Conc Grad 2

Cont Kd

Sorption Rate 2

Cont Kr

Sorbed Phase RZ 2

Sorbed Cont RZ Methane Conc

Methane Stoich 2

Organic Substrate in RZ

ConsumptionRZ

Methane Km

Methane Vmax

Methane Formation in RZ

Root Zone Water Volume

Anaero RZ Methane Conc

Methane in Anaero RZ

Methane Flow from Fe Zone 2

Methane Flow to Anaero RZ

84

Cont Kd Fe Zone

Fraction OC in Fe Zone

Cont Kow

Fraction OC

Cont Kd

Appendix B

Model Equations

Hydrology

CW_Water_Volume(t) = CW_Water_Volume(t - dt) + (CW_Influent_Rate - CW_Effluent_Rate - CW_Evap_and_Precip_Rate) * dt

INIT CW_Water_Volume = 688
DOCUMENT: Initial value is based on fully saturated wetland at time equal zero, with no surface water present
INFLOWS:
CW_Influent_Rate = Groundwater_Flow

OUTFLOWS:
CW_Effluent_Rate = IF((CW_Influent_Rate-CW_Evap_and_Precip_Rate>=0)
AND(CW_Water_Volume>Initial_CW_Water_Volume)) THEN(CW_Influent_Rate-CW_Evap_and_Precip_Rate) ELSE(0)
CW_Evap_and_Precip_Rate = (8*.8*.001-(Storm_Intensity*.001))*CW_Surface_Area
DOCUMENT: The evaporation an precipitation rates for a wetland is represented by .8 times the Class A pan evaporation from an adjacent open site plus the rainfall that falls directly on the wetland. The Class A pan evaporation rate of 8mm/day is assumed. The quantity is converted to meters cubed per day based on the surface of the wetland (Mudgett, 1995).

Conversion = 6.3090E-5*3600
Groundwater_Flow = 75*Conversion
DOCUMENT: Expressed in meters cubed per day, based on 75 gallon per minute flowrate.

Hydraulic_Retention_Time = CW_Water_Volume/CW_Influent_Rate
Storm_Intensity = GRAPH(PULSE(TIME))
(0.00, 0.00), (10.0, 0.00), (20.0, 0.00), (30.0, 0.00), (40.0, 0.00), (50.0, 0.00), (60.0, 0.00), (70.0, 0.00), (80.0, 0.00), (90.0, 0.00), (100, 0.00)
DOCUMENT: The purpose of this graph is to allow variable or constant input of precipitation to the system. For this study, rainfall will not be considered.

Iron Reduction in Anaerobic Zone

AQ_Cont_in_Fe_Zone[Contaminant](t) = AQ_Cont_in_Fe_Zone[Contaminant](t - dt) + (Cont_Flow_to_Fe_Zone[Contaminant] + Cont_Formation_in_Fe_Zone[Contaminant] - Cont_Flow_to_RZ[Contaminant] - Fe_Reduction[Contaminant] - Sorption_in_Fe_Zone[Contaminant]) * dt

INIT AQ_Cont_in_Fe_Zone[Contaminant] = 0

INFLOWS:

Cont_Flow_to_Fe_Zone[Contaminant] =
IF(Fe_Zone_Water_Volume>0)THEN(BulkFlow_to_Fe_Zone[Contaminant])ELSE(0)
Cont_Formation_in_Fe_Zone[PCE] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Reduction[PCE]*MW_Cont[PCE]/MW_Cont[
PCE]*Fe_Stoich[PCE])
Cont_Formation_in_Fe_Zone[TCE] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Reduction[PCE]*MW_Cont[TCE]/MW_Cont[
PCE]*Fe_Stoich[TCE])
Cont_Formation_in_Fe_Zone[DCE] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Reduction[TCE]*MW_Cont[DCE]/MW_Cont[
TCE]*Fe_Stoich[DCE])
Cont_Formation_in_Fe_Zone[VC] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Reduction[DCE]*MW_Cont[VC]/MW_Cont[
DCE]*Fe_Stoich[VC])

OUTFLOWS:
Cont_Flow_to_RZ[Contaminant] = AQ_Cont_Conc_Fe[Contaminant]*Groundwater_Flow
Fe_Reduction[PCE] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Vmax[PCE]*AQ_Cont_Conc_Fe[PCE]/(Fe_K
m[PCE]+AQ_Cont_Conc_Fe[PCE]))
Fe_Reduction[TCE] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Vmax[TCE]*AQ_Cont_Conc_Fe[TCE]/(Fe_K
m[TCE]+AQ_Cont_Conc_Fe[TCE]))
Fe_Reduction[DCE] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Vmax[DCE]/Fe_Km[DCE]*AQ_Cont_Conc_
Fe[DCE])
Fe_Reduction[VC] =
IF(Fe_Zone_Water_Volume=0)THEN(0)ELSE(Fe_Vmax[VC]*AQ_Cont_Conc_Fe[VC]/(Fe_Km[
VC]+AQ_Cont_Conc_Fe[VC]))
Sorption_in_Fe_Zone[Contaminant] = IF(Fe_Zone_Water_Volume=0) THEN(0)
ELSE(Fe_Zone_Conc_Grad[Contaminant])
Methane_in_Fe_Zone(t) = Methane_in_Fe_Zone(t - dt) + (Methane_Flow_from_ANZ -
Methane_Flow_to_Aero_RZ - Methane_Flow_to_Anaero_RZ) * dt

INIT Methane_in_Fe_Zone = 0

INFLOWS:
Methane_Flow_from_ANZ = Methane_Flow_to_Fe_Zone

OUTFLOWS:
Methane_Flow_to_Aero_RZ = Groundwater_Flow*Methane_Conc_in_Fe_Zone
Methane_Flow_to_Anaero_RZ = Groundwater_Flow*Methane_Conc_in_Fe_Zone
Sorbed_Cont_in_Fe_Zone[Contaminant](t) = Sorbed_Cont_in_Fe_Zone[Contaminant](t - dt) +
(Sorption_in_Fe_Zone[Contaminant]) * dt

INIT Sorbed_Cont_in_Fe_Zone[Contaminant] = 0

INFLOWS:

Sorption_in_Fe_Zone[Contaminant] = IF(Fe_Zone_Water_Volume=0) THEN(0)
ELSE(Fe_Zone_Conc_Grad[Contaminant])
AQ_Cont_Conc_Fe[Contaminant] =
IF(Fe_Zone_Water_Volume>0)THEN(AQ_Cont_in_Fe_Zone[Contaminant]/Fe_Zone_Water_Vol
ume)ELSE(0)
Conc_Sorbed_Cont_in_Fe_Zone[Contaminant] =
IF(Fe_Sediment_Mass>0)THEN(Sorbed_Cont_in_Fe_Zone[Contaminant]/Fe_Sediment_Mass)EL
SE(0)
Cont_Kr_Fe_Zone[Contaminant] = 1
Fe_Conv_Factor = 10^(-6)
DOCUMENT: Converts Fe Vmax and Fe Km from umol/Lday to mol/Lday

Fe_Km[PCE] = 1*Fe_Conv_Factor
Fe_Km[TCE] = 1*Fe_Conv_Factor
Fe_Km[DCE] = 1*Fe_Conv_Factor
Fe_Km[VC] = 1.3*Fe_Conv_Factor
DOCUMENT: Values from Bradley and Chapelle, 1997

Fe_Stoich[PCE] = 0
Fe_Stoich[TCE] = 0
Fe_Stoich[DCE] = 0
Fe_Stoich[VC] = 1
Fe_Vmax[PCE] = 0*Fe_Conv_Factor
Fe_Vmax[TCE] = 0*Fe_Conv_Factor
Fe_Vmax[DCE] = .6*Fe_Conv_Factor
Fe_Vmax[VC] = .76*Fe_Conv_Factor
DOCUMENT: Values from Bradley and Chapelle, 1997, expressed in umol/Ldays

Fe_Zone_Conc_Grad[Contaminant] =
Cont_Kr_Fe_Zone[Contaminant]*(Cont_Kd_Fe_Zone[Contaminant]*AQ_Cont_Conc_Fe[Contam
inant]-Conc_Sorbed_Cont_in_Fe_Zone[Contaminant])
Methane_Conc_in_Fe_Zone =
if(Fe_Zone_Water_Volume=0)then(0)else(Methane_in_Fe_Zone/Fe_Zone_Water_Volume)

Methanogenic Zone

Aqueous_Cont_in_ANZ[Contaminant](t) = Aqueous_Cont_in_ANZ[Contaminant](t - dt) +
(Bulk_Water_Inflow_ANZ[Contaminant] + Anaerobic_Formation_in_ANZ[Contaminant] -
Sorption_in_ANZ[Contaminant] - Anaerobic_Degradation_in_ANZ[Contaminant] -
BulkFlow_to_Fe_Zone[Contaminant]) * dt

INIT Aqueous_Cont_in_ANZ[Contaminant] = 0

INFLOWS:

Bulk_Water_Inflow_ANZ[Contaminant] =
Groundwater_Flow*(Int_GW_Cont_Conc[Contaminant]/MW_Cont[Contaminant])
Anaerobic_Formation_in_ANZ[PCE] =
0*Anaerobic_Degradation_in_ANZ[PCE]*MW_Cont[PCE]/MW_Cont[PCE]*ANZ_Stoich[PCE]
Anaerobic_Formation_in_ANZ[TCE] =
Anaerobic_Degradation_in_ANZ[PCE]*MW_Cont[TCE]/MW_Cont[PCE]*ANZ_Stoich[TCE]
Anaerobic_Formation_in_ANZ[DCE] =
Anaerobic_Degradation_in_ANZ[TCE]*MW_Cont[DCE]/MW_Cont[TCE]*ANZ_Stoich[DCE]
Anaerobic_Formation_in_ANZ[VC] =
Anaerobic_Degradation_in_ANZ[DCE]*MW_Cont[VC]/MW_Cont[DCE]*ANZ_Stoich[VC]

OUTFLOWS:
Sorption_in_ANZ[Contaminant] = Sorption_Conc_Grad_ANZ[Contaminant]
Anaerobic_Degradation_in_ANZ[PCE] =
IF(Methane_Conc_in_ANZ>0)THEN(ANZ_Vmax[PCE]*AQ_Cont_ANZ_Conc[PCE]/(ANZ_Km
[PCE]+AQ_Cont_ANZ_Conc[PCE]))ELSE(0)
DOCUMENT: Calculates the degradation of each incoming contaminant. Process will only occur
if methane is being produced in the anaerobic zone, indicating that the conditions are present which
reductive dehalogenation can occur.

Anaerobic_Degradation_in_ANZ[TCE] =
IF(Methane_Conc_in_ANZ>0)THEN(ANZ_Vmax[TCE]*AQ_Cont_ANZ_Conc[TCE]/(ANZ_Km
[TCE]+AQ_Cont_ANZ_Conc[TCE]))ELSE(0)
Anaerobic_Degradation_in_ANZ[DCE] =
IF(Methane_Conc_in_ANZ>0)THEN(ANZ_Vmax[DCE]*AQ_Cont_ANZ_Conc[DCE]/(ANZ_K
m[DCE]+AQ_Cont_ANZ_Conc[DCE]))ELSE(0)
Anaerobic_Degradation_in_ANZ[VC] = IF(Methane_Conc_in_ANZ>0)
THEN((ANZ_Vmax[VC]*AQ_Cont_ANZ_Conc[VC])/(ANZ_Km[VC]+AQ_Cont_ANZ_Conc[V
C]))
ELSE(0)
BulkFlow_to_Fe_Zone[Contaminant] = Groundwater_Flow*AQ_Cont_ANZ_Conc[Contaminant]
Methane_Anaerobic_Zone(t) = Methane_Anaerobic_Zone(t - dt) + (Methane_Production_Rate -
Methane_Flow_to_Fe_Zone) * dt

INIT Methane_Anaerobic_Zone = 0

INFLOWS:
Methane_Production_Rate = Methane_Stoich*Consumption

OUTFLOWS:
Methane_Flow_to_Fe_Zone = Groundwater_Flow*Methane_Conc_in_ANZ
Organic_Substrate(t) = Organic_Substrate(t - dt) + (- Consumption) * dt

INIT Organic_Substrate = 10^12

OUTFLOWS:

Consumption = Methane_Vmax*Organic_Substrate/(Methane_Km+Organic_Substrate)
Sorbed_Cont_ANZ[Contaminant](t) = Sorbed_Cont_ANZ[Contaminant](t - dt) +
(Sorption_in_ANZ[Contaminant]) * dt

INIT Sorbed_Cont_ANZ[Contaminant] = 0

INFLOWS:
Sorption_in_ANZ[Contaminant] = Sorption_Conc_Grad_ANZ[Contaminant]
ANZ_Km[PCE] = 1*Km_conv_Factor
ANZ_Km[TCE] = 5*Km_conv_Factor
ANZ_Km[DCE] = 40*Km_conv_Factor
ANZ_Km[VC] = 40*Km_conv_Factor
DOCUMENT: Values from Tandol et al, 1994, expressed in umol/100mL

ANZ_Stoich[PCE] = 1
ANZ_Stoich[TCE] = 1
ANZ_Stoich[DCE] = 1
ANZ_Stoich[VC] = 1
ANZ_Vmax[PCE] = 1.25*Vmax_Conv_Factor
ANZ_Vmax[TCE] = 4*Vmax_Conv_Factor
ANZ_Vmax[DCE] = 2.5*Vmax_Conv_Factor
ANZ_Vmax[VC] = 4.5*Vmax_Conv_Factor
DOCUMENT: Values from Tandol et al, 1994, expressed in umol/h

AQ_Cont_ANZ_Conc[Contaminant] =
Aqueous_Cont_in_ANZ[Contaminant]/Meth_Zone_Water_Vol
Cont_Kr[Contaminant] = 50
Int_GW_Cont_Conc[PCE] = .05
DOCUMENT: Groundwater concentration of contaminant converted to mg/L

Int_GW_Cont_Conc[TCE] = 0
Int_GW_Cont_Conc[DCE] = 0
Int_GW_Cont_Conc[VC] = 0
Km_conv_Factor = 10^(-2)
DOCUMENT: Converts Km to mol/l to be consistent with incoming concentration units.

Methane_Conc_in_ANZ = Methane_Anaerobic_Zone/Meth_Zone_Water_Vol
Methane_Km = .25
DOCUMENT: Values based on literature from Semprini and McCarty, 1991

Methane_Stoich = 1
Methane_Vmax = 500
DOCUMENT: Values from Semprini and McCarty, 1991.

MW_Cont[PCE] = 165.8
DOCUMENT: Molecular weights of all contaminants expressed in mg/mol

MW_Cont[TCE] = 131.5
MW_Cont[DCE] = 97
MW_Cont[VC] = 62
Sorbed_Conc_ANZ[Contaminant] = Sorbed_Cont_ANZ[Contaminant]/ANZ_Sediment_Mass
Sorption_Conc_Grad_ANZ[Contaminant] =
Cont_Kr[Contaminant]*(Cont_Kd[Contaminant]*AQ_Cont_ANZ_Conc[Contaminant]-
Sorbed_Conc_ANZ[Contaminant])
Vmax_Conv_Factor = 24*10^(-6)
DOCUMENT: Converts units of Vmax to mol/d to be consistent with incoming concentration.

Root Zone Aerobic Sector

Aqueous_Cont_Root_Zone[Contaminant](t) = Aqueous_Cont_Root_Zone[Contaminant](t - dt) +
(Bulk_Flow_from_Fe_Zone[Contaminant] +
Contaminant_Formation_in_RZ_Anaero[Contaminant] -
Bulk_Flow_to_Surface_Water[Contaminant] - Sorption_Rate[Contaminant] -
Aerobic_Deg_in_RZ[Contaminant]) * dt

INIT Aqueous_Cont_Root_Zone[Contaminant] = 0

INFLOWS:
Bulk_Flow_from_Fe_Zone[Contaminant] =
IF(Fe_Zone_Water_Volume>0)THEN(Aerobic_Fraction*Cont_Flow_to_RZ[Contaminant])ELSE(
Aerobic_Fraction*BulkFlow_to_Fe_Zone[Contaminant])
Contaminant_Formation_in_RZ_Anaero[PCE] =
Anaerobic_Deg_in_RZ[PCE]*MW_Cont[PCE]/MW_Cont[PCE]*RZ_Stoich[PCE]*Aerobic_Fract
ion
Contaminant_Formation_in_RZ_Anaero[TCE] =
Anaerobic_Deg_in_RZ[PCE]*MW_Cont[TCE]/MW_Cont[PCE]*RZ_Stoich[TCE]*Aerobic_Fract
ion
Contaminant_Formation_in_RZ_Anaero[DCE] =
Anaerobic_Deg_in_RZ[TCE]*MW_Cont[DCE]/MW_Cont[TCE]*RZ_Stoich[DCE]*Aerobic_Frac
tion
Contaminant_Formation_in_RZ_Anaero[VC] =
Anaerobic_Deg_in_RZ[DCE]*MW_Cont[VC]/MW_Cont[DCE]*RZ_Stoich[VC]*Aerobic_Fracti
on

OUTFLOWS:

Bulk_Flow_to_Surface_Water[Contaminant] =
Aqueous_Conc_RZ[Contaminant]*Groundwater_Flow
Sorption_Rate[Contaminant] = RZ_Conc_Grad[Contaminant]
Aerobic_Deg_in_RZ[Contaminant] =
(Aerobic_Vmax[Contaminant]*Aqueous_Conc_RZ[Contaminant]/(Aerobic_Km[Contaminant]+A

queous_Conc_RZ[Contaminant]+Aerobic_Km[Contaminant]*Aero_RZ_Methane_Conc/Methane_Km))

DOCUMENT: Represents co-metabolic transformation under aerobic conditions. Methane is the primary substrate and in the process of degrading methane, the enzyme MMO is produced. MMO can fortuitously transform chlorinated alkenes with no benefit to the organisms. Methane can be a competitive inhibitor in this process as it's concentration increases the rate of degradation of the contaminant will decrease. (Semprini and McCarty, 1992)

Methane_in_Aero_RZ(t) = Methane_in_Aero_RZ(t - dt) + (Methane_Flow_from_Fe_Zone) * dt

INIT Methane_in_Aero_RZ = 0

INFLOWS:

Methane_Flow_from_Fe_Zone = Methane_Flow_to_Aero_RZ

Sorbed_Phase_RZ[Contaminant](t) = Sorbed_Phase_RZ[Contaminant](t - dt) + (Sorption_Rate[Contaminant]) * dt

INIT Sorbed_Phase_RZ[Contaminant] = 0

INFLOWS:

Sorption_Rate[Contaminant] = RZ_Conc_Grad[Contaminant]
Aerobic_Conv_Factor = 10^(-6)
DOCUMENT: Converts Aerobic Vmax and Km to mol/Lday

Aerobic_Km[PCE] = 1*Aerobic_Conv_Factor
Aerobic_Km[TCE] = 1*Aerobic_Conv_Factor
Aerobic_Km[DCE] = 12.1*Aerobic_Conv_Factor
Aerobic_Km[VC] = 12.8*Aerobic_Conv_Factor
DOCUMENT: Values from Bradley and Chapelle, 1998, expressed in umol/Lday.

Aerobic_Vmax[PCE] = 0*Aerobic_Conv_Factor
Aerobic_Vmax[TCE] = .995*Aerobic_Conv_Factor
DOCUMENT: Values from Lontoh and Semrau, 1998, expressed in umol/Lday.

Aerobic_Vmax[DCE] = 5.1*Aerobic_Conv_Factor
Aerobic_Vmax[VC] = 12.4*Aerobic_Conv_Factor
DOCUMENT: Values from Bradley and Chapelle, 1998, expressed in umol/Lday.

Aero_RZ_Methane_Conc = Methane_in_Aero_RZ/Root_Zone_Water_Volume
Aqueous_Conc_RZ[Contaminant] =
(Aqueous_Cont_Root_Zone[Contaminant]/Root_Zone_Water_Volume)

RZ_Conc_Grad[Contaminant] =
Cont_Kr[Contaminant]*(Cont_Kd[Contaminant]*Aqueous_Conc_RZ[Contaminant]-
Sorbed_Conc_RZ[Contaminant])

Sorbed_Conc_RZ[Contaminant] = Sorbed_Phase_RZ[Contaminant]/Root_Zone_Sediment_Mass

Root Zone Anaerobic Sector

Aqueous_Cont_Root_Zone_2[Contaminant](t) = Aqueous_Cont_Root_Zone_2[Contaminant](t -
dt) + (Cont_Formation_in_RZ[Contaminant] + Flow_from_Fe_Zone[Contaminant] -
Bulk_Flow_to_Surface_Water_2[Contaminant] - Sorption_Rate_2[Contaminant] -
Anaerobic_Deg_in_RZ[Contaminant]) * dt

INIT Aqueous_Cont_Root_Zone_2[Contaminant] = 0

INFLOWS:
Cont_Formation_in_RZ[PCE] =
Anaerobic_Deg_in_RZ[PCE]*MW_Cont[PCE]/MW_Cont[PCE]*RZ_Stoich[PCE]*Anaerobic_Fr
action

Cont_Formation_in_RZ[TCE] =
Anaerobic_Deg_in_RZ[PCE]*MW_Cont[TCE]/MW_Cont[PCE]*RZ_Stoich[TCE]*Anaerobic_Fr
action

Cont_Formation_in_RZ[DCE] =
Anaerobic_Deg_in_RZ[TCE]*MW_Cont[DCE]/MW_Cont[TCE]*RZ_Stoich[DCE]*Anaerobic_F
raction

Cont_Formation_in_RZ[VC] =
Anaerobic_Deg_in_RZ[DCE]*MW_Cont[DCE]/MW_Cont[VC]*RZ_Stoich[VC]*Anaerobic_Frac
tion

Flow_from_Fe_Zone[Contaminant] =
Anaerobic_Fraction*Bulk_Flow_from_Fe_Zone[Contaminant]

OUTFLOWS:
Bulk_Flow_to_Surface_Water_2[Contaminant] =
Aqueous_Conc_RZ_2[Contaminant]*Groundwater_Flow

Sorption_Rate_2[Contaminant] = RZ_Conc_Grad_2[Contaminant]

Anaerobic_Deg_in_RZ[PCE] =
IF(Anaero_RZ_Methane_Conc>0)THEN((ANZ_Vmax[PCE]*Aqueous_Conc_RZ_2[PCE]/(ANZ_
Km[PCE]+Aqueous_Conc_RZ_2[PCE])))ELSE(0)

Anaerobic_Deg_in_RZ[TCE] =
IF(Anaero_RZ_Methane_Conc>0)THEN((ANZ_Vmax[TCE]*Aqueous_Conc_RZ_2[TCE]/(ANZ_Km[TCE]+Aqueous_Conc_RZ_2[TCE])))ELSE(0)

Anaerobic_Deg_in_RZ[DCE] =
IF(Anaero_RZ_Methane_Conc>0)THEN((ANZ_Vmax[DCE]*Aqueous_Conc_RZ_2[DCE]/(ANZ_Km[DCE]+Aqueous_Conc_RZ_2[DCE])))ELSE(0)

Anaerobic_Deg_in_RZ[VC] =
IF(Anaero_RZ_Methane_Conc>0)THEN((ANZ_Vmax[VC]*Aqueous_Conc_RZ_2[VC]/(ANZ_Km[VC]+Aqueous_Conc_RZ_2[VC])))ELSE(0)

Methane_in_Anaero_RZ(t) = Methane_in_Anaero_RZ(t - dt) + (Methane_Flow_from_Fe_Zone_2 + Methane_Formation_in_RZ) * dt

INIT Methane_in_Anaero_RZ = 0

INFLOWS:
Methane_Flow_from_Fe_Zone_2 = Methane_Flow_to_Anaero_RZ

Methane_Formation_in_RZ = ConsumptionRZ*Methane_Stoich_2

Organic_Substrate_in_RZ(t) = Organic_Substrate_in_RZ(t - dt) + (- ConsumptionRZ - Methane_Formation_in_RZ) * dt

INIT Organic_Substrate_in_RZ = 10^12

OUTFLOWS:
ConsumptionRZ =
Methane_Vmax*Organic_Substrate_in_RZ/(Methane_Km+Organic_Substrate_in_RZ)

Methane_Formation_in_RZ = ConsumptionRZ*Methane_Stoich_2

Sorbed_Phase_RZ_2[Contaminant](t) = Sorbed_Phase_RZ_2[Contaminant](t - dt) + (Sorption_Rate_2[Contaminant]) * dt

INIT Sorbed_Phase_RZ_2[Contaminant] = 0

INFLOWS:
Sorption_Rate_2[Contaminant] = RZ_Conc_Grad_2[Contaminant]

Anaero_RZ_Methane_Conc = (Methane_in_Anaero_RZ/Root_Zone_Water_Volume)

Aqueous_Conc_RZ_2[Contaminant] =
(Aqueous_Cont_Root_Zone_2[Contaminant]/Root_Zone_Water_Volume)

Methane_Stoich_2 = 1

RZ_Conc_Grad_2[Contaminant] =
Cont_Kr[Contaminant]*(Cont_Kd[Contaminant]*Aqueous_Conc_RZ_2[Contaminant]-
Sorbed_Conc_RZ_2[Contaminant])

RZ_Stoich[PCE] = 1
RZ_Stoich[TCE] = 1
RZ_Stoich[DCE] = 1
RZ_Stoich[VC] = 1

Sorbed_Conc_RZ_2[Contaminant] =
Sorbed_Phase_RZ_2[Contaminant]/Root_Zone_Sediment_Mass

Sorption

Cont_Kd[Contaminant] = 10^(.72*LOG10(Cont_Kow[Contaminant])+LOG10(Fraction_OC)+.49)
DOCUMENT: Calculation for sorption partition coefficient in sediment with the exception of the
iron reduction layer. Based on similar studies by Schwarzenbach and Westall, 1981

Cont_Kd_Fe_Zone[Contaminant] =
10^(.72*LOG10(Cont_Kow[Contaminant])+LOG10(Fraction_OC_in_Fe_Zone)+.49)
DOCUMENT: Calculation for sorption partition coefficient in iron reduction layer. Based on
similar studies by Schwarzenbach and Westall, 1981.

Cont_Kow[Contaminant] = 2.6
DOCUMENT: Octanol/ water coefficients for each contaminant.

Fraction_OC = .62
DOCUMENT: Organic carbon fraction in soil based on laboratory analysis.

Fraction_OC_in_Fe_Zone = .3
DOCUMENT: Organic carbon fraction of iron reducing layer based on laboratory analysis.

Surface Water

Aqeuous_Cont_in_Surface_Water[Contaminant](t) =
Aqeuous_Cont_in_Surface_Water[Contaminant](t - dt) + (Flow_from_RZ[Contaminant]) * dt

INIT Aqeuous_Cont_in_Surface_Water[Contaminant] = 0

INFLOWS:
Flow_from_RZ[Contaminant] =
Bulk_Flow_to_Surface_Water[Contaminant]+Bulk_Flow_to_Surface_Water_2[Contaminant]

Wetland Physical Parameters

Aerobic_Area_per_Root = PI*((AvgRoot_Diameter+2*Radius_of_Aerobic_Influence)/2)^2-
PI*(AvgRoot_Diameter/2)^2

Aerobic_Fraction = Total_Aerobic_Area/Total_Active_Area

Anaerobic_Fraction = 1-Aerobic_Fraction

ANZ_Sediment_Mass = CW_Surface_Area*Methanogenic_Zone_Depth-Meth_Zone_Water_Vol
DOCUMENT: Volume of sediment in the anaerobic methanogenic zone

AvgRoot_Diameter = .0672
DOCUMENT: This parameter represents the entire root ball as a single root. All of the plants are
assumed to be homogeneous and share the same conditions throughout the wetland. Assumed to be
3". Units in meters.

Avg_Root_Length = .3048
DOCUMENT: The average maximum depth for each root. Assumed to be 12". Units in meters.

CW_Design_Depth =
Root_Zone_Depth+Fe_Zone_Depth+Methanogenic_Zone_Depth+Surface_Water_Design_Depth
DOCUMENT: Constructed wetland depth is the total water depth of the wetland. It includes the
depth of the water in the sediment and the depth of the surface water. The depth of the sediment is
constant and the depth of the surface water is also constant as it is controlled by the outflow weir in
the actual constructed wetland. Units are in meters.

CW_Design_Length = 42.672
DOCUMENT: Length of the constructed wetland, expressed in meters, equivlent to 180'.

CW_Design_Width = 18.288
DOCUMENT: The design width of the constructed wetland, expressed in meters, equivalent to 60'.

CW_LW_Ratio = CW_Design_Length/CW_Design_Width

CW_Surface_Area = CW_Design_Length*CW_Design_Width

Fe_Sediment_Mass = CW_Surface_Area*Fe_Zone_Depth-Fe_Zone_Water_Volume
DOCUMENT: Volume of sediment in the iron zone

Fe_Zone_Depth = .4572
DOCUMENT: The iron reducing layer is initially set at 18", and is converted to meters.

Fe_Zone_Porosity = .5
DOCUMENT: Porosity of the iron reducing layer.

Fe_Zone_Water_Volume = CW_Surface_Area*Fe_Zone_Depth*Fe_Zone_Porosity

Initial_CW_Water_Volume =
CW_Design_Depth*CW_Design_Length*CW_Design_Width*Sediment_Porosity

Methanogenic_Zone_Depth = .4572
DOCUMENT: Sediment depth is the depth of soil in the constructed wetland. It is the overall depth of the sediment, including the iron reducing layer. Initial conditions are for 12" of hydric soil, followed by 18" of Fe rich soil, followed by an additional 18" of hydric soil. Units are converted to meters.

Meth_Zone_Water_Vol = CW_Surface_Area*Methanogenic_Zone_Depth*Sediment_Porosity

Number_Roots_per_sq_m = 1000

Plant_Population = Plant_Volume/(PI*(Plant_Radius^2)*Surface_Water_Depth)
DOCUMENT: Estimates the number of plant stalks based on volume of surface water and porosity due to vegetation. This values allows us to estimate the available surface area for microbial population associated with the vegetation. Units are in meters squared.

Plant_Porosity = .75
DOCUMENT: The ratio of the volume of surface water to the total water volume including the vegetation within the surface water. Range 0.30 - 0.95, (Shelley and Mudgett, 1999). Unitless.

Plant_Radius = .007
DOCUMENT: Average radius of plant stalks.

Plant_Surface_Area = 2*PI*.007*Surface_Water_Depth*Plant_Population
DOCUMENT: The plant surface area will change with changing surface water volume and depth. It is based on the average plant stalk diameter of .014 meters. Units are in meters squared.

Plant_Volume = Surface_Water_Volume-Plant_Porosity*Surface_Water_Volume
DOCUMENT: The volume of plants taking up space within the surface water volume. It is dependent on the plant porosity and the surface water volume. Units are meters cubed.

Radius_of_Aerobic_Influence = .005
DOCUMENT: Radius from root with aerobic influence.

Root_Surface_Area =
PI*(AvgRoot_Diameter/2)^2*Avg_Root_Length*Number_Roots_per_sq_m*CW_Surface_Area

Root_Zone_Depth = Avg_Root_Length

Root_Zone_Porosity = .65

Root_Zone_Sediment_Mass = Total_Active_Area*Avg_Root_Length

Root_Zone_Water_Volume = Avg_Root_Length*CW_Surface_Area*Root_Zone_Porosity
DOCUMENT: Volume of water in root zone including root biomass.

Sediment_Porosity = .5
DOCUMENT: Mineral soils generally range from 45% to 55% total pore space (Mitsch and Gosselink, 1993)

Surface_Water_Depth = (Surface_Water_Volume+Plant_Volume)/CW_Surface_Area

Surface_Water_Design_Depth = .0254
DOCUMENT: This is a management parameter which has been designed into the constructed wetland, outflow can be controlled to achieve the desired surface water depth. The maximum desired depth of the surface water, .1524 meters (6").

Surface_Water_Volume = CW_Surface_Area*Surface_Water_Design_Depth

Total_Active_Area = Number_Roots_per_sq_m*CW_Surface_Area*PI*(AvgRoot_Diameter/2)^2-CW_Surface_Area

Total_Aerobic_Area = Aerobic_Area_per_Root*CW_Surface_Area*Number_Roots_per_sq_m

Not in a sector

Bibliography

Air Force Institute of Technology and Wright State University, "Abiotic and Biochemical Contaminant Fate and Remediation (ML-01). Joint AFRL/DAGSI Research Proposal. February 1999.

Bagley, D.M., J.M. Gossett. Tetrachlorethene Transformation To Trichloroethene And Cis-1,2-Dichloroethene By Sulfate Reducing Enrichment Culture. Applied Environmental Microbiology 56(8): 2511-16.

Bankston, Jamie L. and Daryl F. Dwyer. 1999. Natural Attenuation of Trichloroethene by Indigenous Wetland Bacteria and Plants. Industrial Waste Technical Conference. Indianapolis, IN. Water Environment Federation.

Bradley, Paul M. and Francis H. Chapelle. 1996. Anaerobic Mineralization of Vinyl Chloride in Fe(III)-Reducing Aquifer Sediments. Environmental Science & Technology 30: 2084-2086.

Bradley, Paul M. and Francis H. Chapelle. 1997. Kinetics of DCE and VC Mineralization under Methanogenic and Fe(III)-Reducing Conditions. Environmental Science & Technology 31: 2692-2696.

Bradley, Paul M. and Francis H. Chapelle. 1998. Effect of Contaminant Concentration on Aerobic Microbial Mineralization of DCE and VC in Stream-Bed Sediments. Environmental Science & Technology 32 (5): 553-557.

Bradley, Paul M. and Francis H. Chapelle. 1999. Methane as a Product of Chloroethene Biodegradation under Methanogenic Conditions. Environmental Science & Technology 33(4): 653-656.

Chapelle, Francis H. Ground Water Microbiology and Geochemistry. New York: John Wiley & Sons Inc. 1993.

Clark, Mark M. Transport Modeling for Environmental Engineers and Scientists. John Wiley & Sons, New York. 1996.

Colburn, Philip A. Investigation of Biodegradation Processes in Solid Waste Landfills. MS Thesis, AFIT/GEE/ENV/97D-04. School of Engineering, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, December 1997

Federal Facilities Policy Group. 1995. Improving Federal Facilities Cleanup. Washington D.C.: Council on Environmental Quality, Office of Management and Budget.

Freedman, David L. and James M. Gossett. 1989. Biological Reductive Dechlorination of Tetrachlorethylene and Trichloroethene to Ethylene under Methanogenic Conditions. Applied and Environmental Microbiology. Sept. 2144-2151.

Haston, Zachary C. and Perry L. McCarty. 1999. Chlorinated Ethene Half-Velocity Coefficients (K_s) for Reductive Dehalogenation. Environmental Science & Technology 33 (2): 223-226.

Hoekstra, EJ, De Leer EWB. Organohalogens: the Natural Alternatives. Chem. Britain. February, 1995: 127-31.

Kadlec, Robert H. and Robert L. Knight. Treatment Wetlands. New York: CRC Press, Inc., 1996

Lanzarone, N.A., and P.L. McCarty. Column Studies on Methanotrophic Degradation of Trichloroethene and 1, 2-Dichloroethane. 1991. Groundwater 28 (6): 910-919.

Leder, A., and Y. Yoshida. 1995. C_2 Chlorinated Solvents (www-cmrc.sru.com/CIN/mar-apr95/article10.html). Menlo Park CA: SRI International.

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

Liang, Li-Nuo, and Dunja Gribic-Galic. 1993. Biotransformation of Chlorinated Aliphatic Solvents in the presence of Aromatic Compounds Under Methanogenic Conditions. Environmental Toxicology and Chemistry 12: 1377-1393.

Lontoh, Sonny and Jeremy D. Semrau. 1998. Methane and Trichloroethylene Degradation by *Methylosinus trichosporium* OB3b Expressing Particulate Methane Monooxygenase. Applied and Environmental Microbiology. 64, No. 3: 1106-1113.

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

Lorah, Michelle M. and Lisa D. Olsen. 1999b. Natural Attenuation of Chlorinated Volatile Organic compounds in a Freshwater Tidal Wetland: Field Evidence of Anaerobic Degradation. Water Resources Research 35 (12): 3811-3827.

Lovely, Derek A. 1991. Dissimilatory Fe(III) and Mn(IV) Reduction. Microbiological Review 55: 260-287.

Lovely, Derek A. and Elizabeth J. P. Phillips. 1986. Organic Matter Mineralization with Reduction of Ferric Iron in Anaerobic Sediments. Applied and Environmental Microbiology 51(4): 683-689.

Masters, Gilbert M. Introduction to Environmental Engineering and Science. (Second Edition). New Jersey: Prentice-Hall, Inc., 1997.

McCarty, P. L. 1996. Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water. Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, Dallas, TX. EPA/540/R-96/509.Washington D.C.: USEPA Office.

McCarty, P. L. 1997. Science 276: 1521-1522.

McCarty, Perry L. 1997b. Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water. Proceedings of the symposium on Natural Attenuation of Chlorinated Organics in Ground Water. EPA/540/R-97/504. Washington D.C.: Office of Research and Development.

Mitsch, William J. and James G. Gosselink. Wetlands (Second Edition). New York: John Wiley & Sons, Inc. 1993.

Mitsch, W.J., M. Straskarba, and S.E. Jorgensen. Wetland Modeling. Amsterdam, Elsevier Science Publishers B.V. 1988.

Moorehead, Daryl L., Robert L. Sinsabaugh, A.E. Linkins, and James F. Reynolds. 1996. "Decomposition Processes: Modeling Approaches and Applications" The Science of the Total Environment 183: 137-149.

Mudgett, Leslie A. A System Dynamics Approach to Modelling the Degradation of Biochemical Oxygen Demand in a Constructed Wetland Receiving Stormwater Runoff. MS Thesis, AFIT/GEE/ENV/95D-12. School of Engineering, Air Force Institute of Technology (AU), Wright-Patterson AFB OH. 1995. ADA305612.

National Research Council, 1994. Alternatives for Ground Water Cleanup. Washington D.C.: National Academy Press.

National Research Council, 1997. Innovations in Ground Water and Soil Cleanup. Washington D.C.: National Academy Press.

Quinton, GE, RJ Buchanan Jr., DE Ellis, and SH Shoemaker. A Method to Compare Ground Water Cleanup Technologies. Remediation. Autumn: 7-16.

Schwarzenbach, Rene P. and John Westall. 1981. Transport of Nonpolar Organic Compounds from Surface Water to Groundwater. Laboratory Sorption Studies. Environmental Science & Technology. 1360-1367.

Semprini, Lewis and Perry L. McCarty. 1991. Comparison Between Model Simulations and Field Results for In-situ Biorestoration of Chlorinated Aliphatics: Part 1. Biostimulation of Methanotrophic Bacteria. Ground Water 29 (3): 365-374.

Semprini, Lewis and Perry L. McCarty. 1992. . Comparison Between Model Simulations and Field Results for In-situ Biorestoration of Chlorinated Aliphatics: Part 2: Cometabolic Transformations. Ground Water 30 (1): 37-44.

Semprini, L., P.V. Roberts, G.D. Hopkins, and P.L. McCarty. 1990. A Field Evaluation of In-situ Biodegradation of Chlorinated Ethenes: Part 2, Results of Biostimulation and Biotransformation Experiments. Groundwater 28 (5): 715-727.

Shelley, Michael L. and Leslie A. Mudgett. 1999. A Mechanistic Simulation Model of a Constructed Wetland Designed to Remove Organic Matter from a Stormwater Runoff. Journal of Environmental Systems 27 (1): 33-54.

Sims, Judith L., Joseph M. Sulflita, and Hugh H. Russell. "Reductive Dehalogenation of Organic Contaminants in Soils and Ground Water". EPA Ground Water Issue. January 1991. pp 1-12.

Smatlak, C., J.M. Gossett, and S.H. Zinder. 1996. Comparative Kinetics of Hydrogen Utilization for Reductive Dechlorination of Tetrachloroethene and Methanogenesis in an Anaerobic Enrichment Culture. Environmental Science & Technology 30 (9): 2850-2858.

Tandol, Valter, Thomas D. DiStefano, Patrick A. Browser, James M. Gossett, and Stephen H. Zindler. 1994. Reductive Dahalogentation of Chlorinataed Ethenes and Halogenated Ethanes by a High Rate Anaerobic Enrichment Culture. Environmental Science & Technology 28 (5): 973-979.

USEPA. 1997. Memorandum: Draft Interim Final OSWER Monitored Natural Attenuation Policy (OSWER directive 9200.4-17), p. 2. Washington D.C.: USEPA, Office of Solid Waste and Emergency Response.

Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformation of Halogenated Aliphatic Compounds. Environmental Science & Technology 21 (8): 722-36.

Vogel, Timothy M. and Perry L. McCarty. 1987. Abiotic and Biotic Transformations of 1, 1, 1-Trichloroethane under Methanogenic Conditions. Environmental Science & Technology 21 (12): 1208-1213.

Yang, Yanru and Perry L. McCarty. 1998. Competition for Hydrogen within a Chlorinated Solvent Dehalogenating Anaerobic Mixed Culture. Environmental Science & Technology 32(22): 3591-97.

Zachritz, Walter H., Leon L. Lundie and Harry Wang. 1996. Benzoic Acid Degradation by Small, Pilot Scale Artificial Wetlands Filter (AWF) Systems. Ecological Engineering 7: 105-116.

Vita

Captain Colby D. Hoefar was born in Oklahoma City, Oklahoma on 23 September 1971. He graduated from Southlake Carroll High School in Southlake, Texas, in 1990. He entered undergraduate studies at the United States Air Force Academy in Colorado Springs, Colorado, where he graduated with a Bachelor of Science Degree in Civil and Environmental Engineering in August 1995. He was commissioned on the same date and received a regular commission.

His first assignment was at the United States Air Force Academy Preparatory School as professional development instructor in August 1995. While there, he was the defensive coordinator and linebacker coach for the school's football program. In April 1996, he was assigned to the 2nd Civil Engineer Squadron, Barksdale AFB, Louisiana. While stationed at Barksdale, he deployed overseas in September 1997 to Soto Cano AB, Honduras as the design civil engineer. In August 1998 he entered the Graduate Engineering and Environmental Management program, School of Engineering, Air Force Institute of Technology. Upon graduation, he will be assigned to the 65th Civil Engineer Squadron, Lajes Field, Azores.

Permanent Address: 2205 Virginia Ln
Haslet TX 76052

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE March 2000	3. REPORT TYPE AND DATES COVERED Master's Thesis

4. TITLE AND SUBTITLE
MODELING CHLORINATED ETHENE REMOVAL IN CONSTRUCTED WETLANDS: A SYSTEM DYNAMICS APPROACH

5. FUNDING NUMBERS
99-411

6. AUTHOR(S)
Hoefar, Colby D., Captain, USAF

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(S)

Air Force Institute of Technology
Graduate School of Engineering and Management (AFIT/ENV)
2950 P Street, Building 640
WPAFB OH 45433-7765

8. PERFORMING ORGANIZATION REPORT NUMBER

AFIT/GEE/ENV/00M-09

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

AFRL/MLQ	DAGSI
Attn: Dr Dave Burris	Attn: Dr Frank Moore
Tyndall AFB FL 32403-6001	3155 Research Blvd., Ste. 205
DSN 523-6040	Kettering OH 45420-4006 937-781-4000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Dr Michael L. Shelley, ENV, 255-2998, michael.shelley@afit.af.mil

12a. DISTRIBUTION / AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

12b. DISTRIBUTION CODE

ABSTRACT (Maximum 200 Words)
The purpose of this study is to gain understanding of the dynamics of the processes that degrade Perchloroethene (PCE) to ethylene, or carbon dioxide (CO_2), within the confines of a constructed wetland. A system dynamics approach will be used. This model is focused on identifying and optimizing the naturally occurring processes in stratified wetland sediment that reduce mass, toxicity, mobility, volume or concentration of contaminants in groundwater. Contaminant fate and transport within a wetland system is extremely complex and the mechanisms that drive wetland behavior are dynamic.
Confidence in the model was built through verification and testing. Reasonable behavior resulted from a reasonable range of parameter values. The structure of the model represents the mechanisms and their interactions of an actual wetland system. This study provides a fundamental understanding of contaminant fate and transport in a constructed wetland and gives some insight for implementation. Testing identified specific parameters of typical wetland plant species, which could be optimized to have the most effect on contaminant fate. These parameters were the radius of aerobic influence and the number of roots per square meter. A remediation manager can use this model to explore system behavior by controlling or optimizing specific parameters to better manage contaminant fate and transport in a constructed wetland, saving time and resources.

14. SUBJECT TERMS
Reductive Dechlorination, Chlorinated Ethenes, Wetlands, System Dynamics, Iron Reduction, Co-metabolism

15. NUMBER OF PAGES
114

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102