MODELING VERTICAL FLOW TREATMENT WETLAND HYDRAULICS TO OPTIMIZE TREATMENT EFFICIENCY

THESIS

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Abstract

An upward Vertical Flow Treatment Wetland (uVFTW) has been designed to use anaerobic and aerobic microbial processes to bioremediate groundwater contaminated with chlorinated hydrocarbons. Hydraulic short-circuiting has been a problem with uVFTWs. Corbin (2008) estimated that for a uVFTW constructed at Wright Patterson AFB to treat contaminated groundwater, groundwater flowed through less than 50% of the wetland's volume, and that the actual mean residence time (1.38 days) was significantly less than the 8.75 days that would be achievable with uniform flow through the wetland cell.

The objective of this research is to investigate how the hydraulics of uVFTWs affects treatment efficiency. A sub-objective is to propose uVFTW design strategies that can be used to maximize treatment efficiency. To accomplish this, a model of a three-layer uVFTW that couples hydraulics and degradation kinetics was built using the MODFLOW-based Groundwater Modeling Software. The model was applied, using data collected by Corbin (2008) and literature values for degradation rate constants, to estimate the effectiveness of various engineering solutions aimed at improving overall treatment efficiency.

The results indicate that, compared to a baseline model, which was constructed to approximate the existing Wright Patterson AFB uVFTW and had a mean residence time (tau) of 6.19 days, all of the proposed engineering solutions would be effective in increasing the mean residence time. Based on the actual flow through the wetland, and

assuming the entire wetland volume was used (*i.e.*, no hydraulic short-circuiting) the nominal hydraulic residence time of the wetland cell would be 9.50 days. Using model simulations to assess the impact of various designs aimed at improving hydraulic performance, the mean residence time increased 10% (tau = 6.89 days) to 180% (tau = 17.5 days) from the base line tau of 6.19 days.

The effect on treatment efficiency, however, was less clear. While there was a significant improvement in treatment efficiency when comparing the proposed engineering solutions and the baseline model, almost the entire improvement occurred with a very small increase in mean hydraulic residence time, from 6.19 days to 6.89 days. Treatment efficiency was essentially unchanged as mean hydraulic residence time increased from 6.89 days through 17.45 days. This is due to the relation between the degradation time constant, which is determined by the degradation rate, and the hydraulic residence time, tau. For the baseline conditions, the first-order degradation rate constant for the influent contaminant, tetrachloroethylene (PCE), was 0.4 d^{-1}. This corresponds to a half-life (*i.e.*, the degradation time constant) of PCE of 1.7 days. Since the degradation time constant is comparable, but smaller than, the baseline tau of 6.19 days, an increase in tau leads to improved destruction efficiency. However, when tau is sufficiently large compared to the degradation half-life, increases in tau have negligible impact on efficiency.

This study demonstrates that a quantitative understanding of contaminant degradation kinetics is important in making decisions regarding constructed uVFTW hydraulics. Hopefully, this study will serve to guide designs of future uVFTWs.

To my wife

Acknowledgments

I would first like to acknowledge Dr. Mark Goltz, my thesis advisor, for originally sparking an interest in groundwater hydrology and biochemistry, and for never accepting the "I'm just a dumb Marine" excuse. I would also like to thank my thesis committee members; Dr. Michael Shelley, for his invaluable insights into past research of the treatment wetland at Wright Patterson AFB; and Dr. Robert Ritzi, for his patient explanations and guidance through the modeling process. I would also like to acknowledge Ms. Erica Becvar, from the Air Force Center for Engineering and the Environment, for sponsoring and supporting my research.

There are three "unsung heroes," whose help during the last 18 months has been invaluable. The first two are 2ndLt Erich Lichtfuss and 2ndLt Stephen Sutara, whose computer expertise, patience, and willingness to spend time helping a "wingman" saved me from numerous computer-related catastrophes. The third is Mrs. Phyllis Poteate. Through the years as a military spouse, mom to six, and barber-extraordinaire, she has earned the wisdom that most of us only think we possess. If I can presume to consider her a friend, her friendship reminds me that you meet great people in every walk of life.

Lastly and most importantly, I want to express my gratitude and love to my family for enduring the ordeal of the past 18 months. To my children, for the joy of seeing a beaming smile and hearing "hi Daddy!" when I come home; and to my wife, for never letting me forget that building a snow man, attending tea parties, and dinner as a family are more important than understanding the equations of groundwater flow.

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MODELING VERTICAL FLOW TREATMENT WETLAND HYDRAULICS TO OPTIMIZE TREATMENT EFFICIENCY

I. Introduction

1.1 Background

An upward Vertical Flow Treatment Wetland (uVFTW) has been designed to use anaerobic and aerobic microbial processes to bioremediate groundwater contaminated with chlorinated hydrocarbons (Amon et al., 2007). In the design that has been used at Wright Patterson AFB (Amon et al., 2007) the tetrachloroethylene- (PCE-) contaminated groundwater is pumped into the bottom gravel layer of the wetland cell. The water then flows upward through three different cell layers, where bacteria biodegrade the contaminants. Treated water then exits over a weir at one end of the rectangular cell. The design objective is to maximize treatment efficiency.

Hydraulic short-circuiting has been a problem with uVFTWs. Corbin (2008) estimated that for the uVFTW at Wright Patterson AFB, groundwater flowed through less than 50% of the wetland's volume. Corbin (2008) also calculated that the actual mean residence time (1.38 days) was significantly less than the 8.75 days that would be achievable with uniform flow through the cell.

The understanding of the hydraulics of constructed wetlands and the processes whereby contaminants are degraded has improved dramatically in the last decade. Initial models of constructed wetlands were little more than "black boxes," giving little understanding of the biological and chemical processes occurring (Langergraber et al., 2009). Recent mechanistic models, although quite complex, are capable of simulating multiple biological and chemical processes (Langergraber et al., 2009). Few of the numerical models currently in use deal with subsurface flow in constructed wetlands, and most of those simulate horizontal flow, rather than vertical flow (Langergraber, 2008). Upward vertical flow treatment wetlands are an even smaller subset of vertical flow wetlands, and there have been very few studies modeling their hydraulics.

1.2 Research Objective

The objective of this research is to investigate how the hydraulics of uVFTWs affects treatment efficiency. A sub-objective is to propose uVFTW design strategies that can be used to maximize treatment efficiency.

1.3 Specific Research Question

1) What design parameters have the greatest impact on treatment efficiency? Would altering the ratio of cell length to width to depth, relative layer thickness, or influent piping configuration improve treatment efficiency?

2) Based on the answer to question 1, what design changes can be implemented to maximize treatment efficiency? How much of an effect on treatment efficiency would these design changes have?

1.4 Research Approach

1) Conduct a literature review. In addition to seeking information on whether this has been tried or modeled before (*i.e.*, how have models been applied to predict treatment efficiency as a function of hydraulics and degradation kinetics in constructed wetlands?), the literature review will be used to determine typical values for environmental and design parameters, as well as typical treatment efficiencies. The literature review will also include case studies, where the impact of hydraulics and degradation kinetics of constructed wetlands (and particularly uVFTWs) on overall treatment efficiency has been assessed.

2) Build a generic model of a three-layer uVFTW that couples hydraulics and degradation kinetics. For simplicity, biodegradation will be described using first-order kinetics, although the first-order rate constant can be different in the different layers. The validity of the first-order model will be assessed in the literature review.

3) Use the model to conduct sensitivity analyses to see how varying design parameters (location of influent piping, baffle placement, cell dimensions, etc.) as well as environmental parameters (degradation rates, existence of high conductivity flow paths that may cause short circuiting), affect treatment efficiency.

4) Apply the model, using data collected by Corbin (2008) and literature values for degradation rate constants for the uVFTW located at Wright-Patterson AFB, to estimate the effectiveness of various engineering solutions at improving overall treatment efficiency.

1.5 Scope and Limitations of Research

The most significant limitation of this research is that it is a modeling study, and therefore depends on the applicability of a number of simplifying assumptions, and that the only data that are available come from the single uVFTW being used to treat chlorinated hydrocarbons in existence. Thus, model validation may not be achievable in this study. However, it is hoped that development and application of the model will provide insights into how uVFTWs can be designed to more efficiently treat water contaminated by chlorinated hydrocarbons.

1.6 Definition of Terms

Term	*Definition*
FWSW	Free Water Surface Wetland
HSFW	Horizontal Subsurface Flow Wetland
VFTW	Vertical Flow Treatment Wetland. The suffix "u" or "d" will be used to distinguish between upward flow (uVFTW) and downward flow (dVFTW) treatment wetlands.
CVOC	Chlorinated volatile organic compound. In general, they have high vapor pressures, low-to-medium water solubility, and low molecular weights. CVOCs are ground-water contaminants of concern because of very large environmental releases, human toxicity, and a tendency for some compounds to persist in and migrate with groundwater to drinking water supply wells (U.S.G.S., 2010).
Halorespiration	Process of anaerobic microbial respiration where microbes gain energy through the use of a halogenated compound (compound containing fluorine, chlorine, bromine, or iodine) as a terminal electron acceptor (Lorah et al., 2007).

Term — *Definition*

Redox — Oxidation-Reduction. A general term describing reactions involving the transfer of electrons from the oxidized compound (reductant/electron donor) to the reduced compound (oxidant/electron acceptor).

Methanogenesis — An oxidation-reduction reaction involving the reduction of carbon dioxide to methane. Under sufficiently reducing conditions, methanogenesis is the dominant oxidation-reduction reaction.

Porosity, *n* — Total porosity is defined as the ratio of the volume of void spaces (V_v) to the total volume (V_T) in a porous medium:

$$n = \frac{V_v}{V_T} \tag{1}$$

Effective porosity is the percentage of interconnected pore spaces, and is always less than total porosity (Domenico and Schwartz, 1990).

Retardation Factor — Ratio of the average flow velocity of groundwater due to advection to the flow velocity of a sorbing contaminant (Domenico and Schwartz, 1990):

$$R = 1 + \frac{\rho_b}{n} K_d \tag{2}$$

where,

ρ_b	Soil bulk density [$M\ L^3$]
n	Porosity
K_d	Sorption distribution coefficient [$L^3\ M^{-1}$]

Use of a retardation factor implicitly assumes linear, equilibrium partitioning of the contaminant between the sorbed and dissolved phases, characterized by the distribution coefficient, which is the ratio of equilibrium contaminant concentrations in the sorbed and dissolved phases.

Critical Flow — In a uVFTW, critical flow is the maximum flow that can be applied per acre prior to fluidizing the bed, and has units of [$L^3\ T^{-1}\ L^{-2}$] (Pardue, 2005).

Term	*Definition*
Hydraulic Conductivity	The capacity of a medium to transmit water. Typically determined experimentally using a number of techniques and applying Darcy's Law (Domenico and Schwartz, 1990):

$$Q = KA\nabla h \tag{3}$$

where,

Q	Volumetric flow [L^3 T^{-1}]
A	Cross sectional area perpendicular to the flow direction [L^2]
∇h	Hydraulic gradient [-]
K	Hydraulic conductivity [L T^{-1}]

RTDF	The Residence Time Distribution Function, f(t), describes the probability that water or a conservative tracer will spend a given amount of time in a reactor bed. Typically displayed graphically with RTDF on the y axis (units of inverse time), and time on the x axis (Clark, 2009).
Mean residence time, τ or tau	The mean residence time, or τ (tau), is the first moment of the RTDF, *f(t)*, and is given by (Clark, 2009):

$$\tau = \int_0^\infty f\,(t) \times t\,dt \tag{4}$$

For discrete data, this equation becomes:

$$\tau = \sum_{i=0}^{i_{max}-1} \left[\frac{f(t_i)+f(t_{i+1})}{2}\right] \left[\frac{(t_i+t_{i+1})}{2}\right] (t_{i+1} - t_i) \tag{5}$$

Variance (second moment)	The variance, also known as the second moment about the mean of the RTDF, *f(t)*, describes the spread of the RTDF (Clark, 2009):

$$\sigma^2 = \int_0^\infty (t-\tau)^2 f(t)dt \tag{6}$$

For discrete data:

$$\sigma^2 = \sum_{i=0}^{i_{max}-1} \left[\frac{(t_i - t_{i+1}}{2} - \tau\right]^2 \left[\frac{f(t_i)+f(t_{i+1})}{2}\right] (t_{i+1} - t_i) \tag{7}$$

Term	*Definition*
Dimensionless variance	The dimensionless variance allows an evaluation of how close a residence time distribution is to a perfect mixer or plug-flow reactor: $$\sigma_\tau^2 = \frac{\sigma^2}{\tau^2} \qquad (8)$$ For the perfect mixer $\sigma_\tau^2 = 1$, while for the plug-flow reactor $\sigma_\tau^2 = 0$. For most reactors, σ_τ^2 is bounded between 0 and 1 (Clark, 2009).
t_{bar}	Nominal, or theoretical, mean residence time [T]. Calculated by: $$t_{bar} = \frac{Vn}{Q} \qquad (9)$$ where, V Volume of treatment wetland [L^3]; n Porosity [-]; Q Volumetric flow rate [L^3 T^{-1}]
STELLA	Structural Thinking Experiential Learning Laboratory with Animation. Software tool designed to model complex dynamic systems (isee systems, 2010).

II. Literature Review

2.1 Review of Treatment Wetland Designs and Purposes

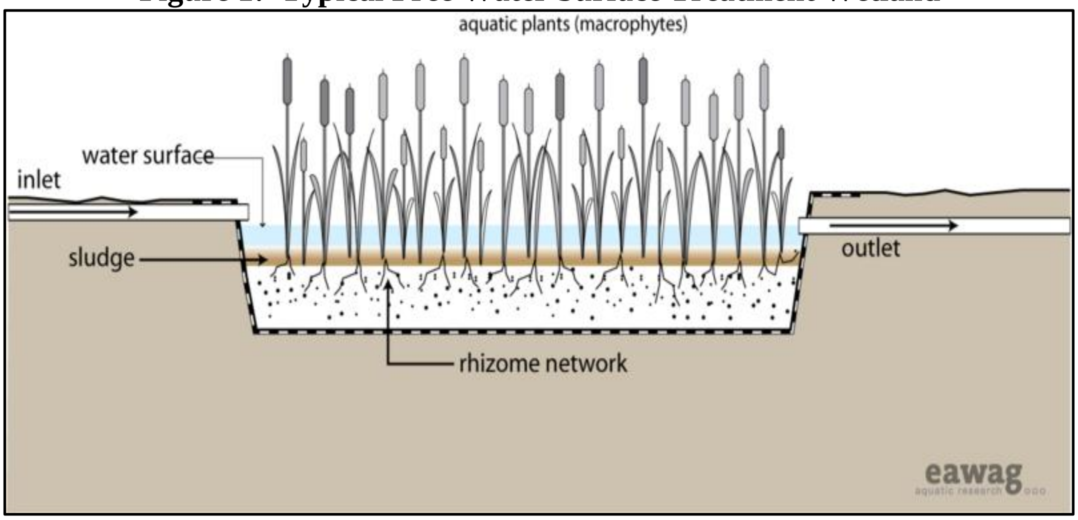
Treatment wetlands have been used for decades to treat a variety of wastewaters, including municipal wastewater, wastewater from mining operations, industrial wastewater, and water contaminated by livestock operations (Cole, 1998). There are several different types of treatment wetlands, each having advantages and disadvantages depending on the type of wastewater to be treated. Treatment wetlands may be divided into two broad categories: surface flow and subsurface flow.

In a Free Water Surface (FWS) treatment wetland, the water is exposed to the atmosphere as it flows horizontally through the cell (Figure 1). Contaminants are treated or removed through sedimentation, filtration, interaction with the aquatic plant root zone, or other processes. FWS treatment wetlands are typically used for storm water runoff or for tertiary treatment of wastewater. Their main advantage is their ability to handle pulse flows and changing water levels. Their main disadvantage is reduced efficiency during sub-freezing weather. An unintended benefit is the creation of wildlife habitat (Kadlec and Wallace, 2009).

FWS treatment wetlands have been used to treat chlorinated hydrocarbons (Kadlec and Wallace, 2009). At a site in Minnesota, contaminated groundwater flowed into a dredged channel which conveyed the water to a lake. The channel was filled and planted, converting it to a treatment wetland. At the Schilling Farm Project in Michigan, a FWS treatment wetland was constructed in the path of a TCE-contaminated groundwater plume (Kadlec and Wallace, 2009).

Keefe et al. (2004) evaluated the fate of volatile organic compounds in a wetland constructed for the treatment of wastewater treatment plant effluent. The wetland is a variation on the FWS system, with flow proceeding alternately through 5 deep zones and 6 shallow zones. Removal efficiencies for the compounds studied ranged from 63% to 87%. The model used was not a mechanistic model, so the specific pathway by which mass was removed was not simulated (though the investigators assumed volatilization was the dominant removal pathway) (Keefe et al., 2004).

Figure 1: Typical Free Water Surface Treatment Wetland

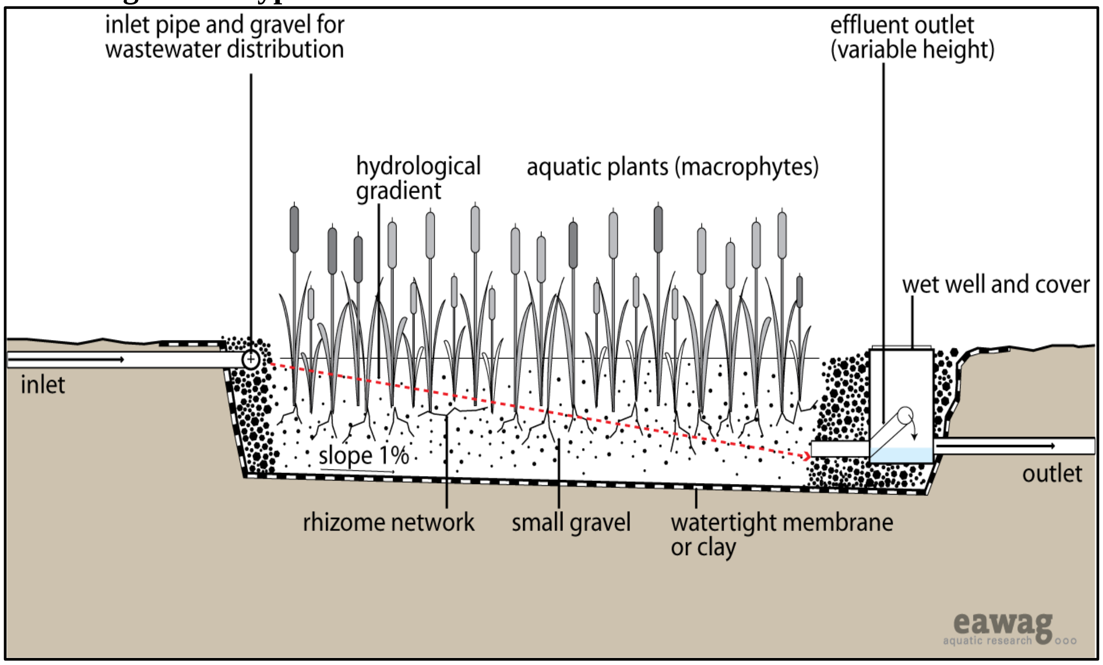


Source: Sandec/Eawag

In a subsurface flow treatment wetland, the water flows entirely beneath the surface and all treatment occurs beneath the surface, as well. Since the water is not exposed to the surface, there is no risk of human contact, and more polluted influent may therefore be treated. These wetlands are commonly used for secondary treatment of residential wastewater, either for individual homes or small communities. Their main advantage is they can operate in freezing conditions. Their main disadvantages are a propensity for clogging of the subsurface media and smaller inlet flow rate (Kadlec and Wallace, 2009).

Subsurface flow treatment wetlands may be further divided into horizontal and vertical flow. A horizontal subsurface flow treatment wetland (HSFW) is built with a sloped bottom to ensure flow in the desired direction (Figure 2). Influent is piped into the cell just below the surface, at the up-gradient end. The contaminated water flows horizontally through a gravel bed, where it is treated through contact with plant roots. The effluent is collected near the bottom of the down-gradient end (Kadlec and Wallace, 2009).

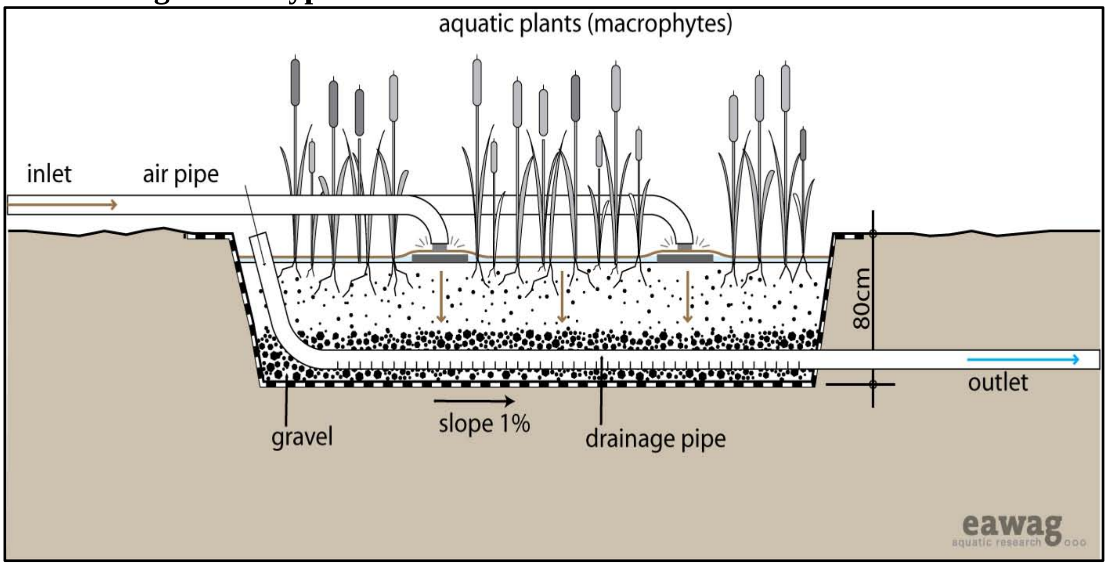
Figure 2: Typical Horizontal Subsurface Flow Treatment Wetland



Source: Sandec/Eawag

A vertical flow treatment wetland is typically understood to mean downward vertical flow (dVFTW). In this type of system, the treatment wetland is "pulse loaded" with a large influx of contaminated water, which is then treated as it moves downward through the cell (Figure 3). This type of system provides a higher level of oxygen than a horizontal subsurface flow system, and is therefore capable of oxidizing ammonia. Downward VFTWs are capable of handling wastewater containing high levels of ammonia, such as landfill leachate and food processing wastes (Kadlec and Wallace, 2009).

Figure 3: Typical Downward Vertical Flow Treatment Wetland



Source: Sandec/Eawag

Upward VFTWs, such as the one constructed at Wright Patterson AFB in 2000, are a more recent design. The impetus for this specific VFTW was the work of Lorah and Olsen (1999), who observed that trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (TeCA) in a plume of contaminated groundwater in a natural wetland underwent anaerobic reductive dechlorination to the daughter products 1,2-dichloroethylene (cDCE), vinyl chloride (VC), 1,1,2-trichloroethane (1,1,2-TCA), and 1,2 dichloroethane (1,2-DCA) as the plume proceeded along an upward flow path from an aerobic sand aquifer through an anaerobic region of a wetland (Lorah and Olsen, 1999). Conditions in the anaerobic region were iron-reducing, sulfate-reducing, and methanogenic. In addition, the organic carbon-rich wetland supplied an abundant quantity of electron donors, eliminating a common limiting factor to the reductive dechlorination pathway (Lorah and Olsen, 1999).

While Lorah and Olsen (1999) recognized how anaerobic processes could naturally biodegrade chlorinated hydrocarbons in a wetland, Amon *et al*. (2007) realized that a combination of anaerobic and aerobic processes in a constructed wetland could be used to biodegrade chlorinated ethenes. Specifically, aerobic microbial populations, using methane as a primary substrate, produce non-specific oxygenases which cometabolically degrade chlorinated ethenes like TCE, cDCE, and vinyl chloride (Bradley, 2003). An upward VFTW, in which the contaminated water flows first through an anaerobic region and then through an aerobic root zone, would allow both anaerobic and aerobic processes to operate with the added benefit that methane produced in the anaerobic region could be used as the primary substrate to support cometabolic degradation of the chlorinated ethenes in the aerobic region.

2.2 Frequency of Use of Upward VFTW

Upward VFTWs are a relatively recent development, and this is reflected in the paucity of information in the literature relative to horizontal flow and downward VFTWs. In 1994, Hans Blix published an excellent survey of the history of the use of treatment wetlands and the (then) current state of technology, covering 104 subsurface flow and 70 FWS treatment wetlands (Blix, 1994). He refers to two pilot scale uVFTWs constructed in Australia for the treatment of municipal wastewater. Both were gravel bed systems in which adsorption and contact with the root zone were the primary mechanisms of contaminant removal (Blix, 1994).

Farahbakhshazad and Morrison (2000) profiled a uVFTW built in 1997 near Piracicaba, Brazil used to remove ammonia, nitrate, and phosphate from the wastewater of a small (1,000 people) community. By obtaining samples from three locations within the cell and two depths per location, the authors found that soil efficiency for the removal of ammonia was not uniform throughout the cell. They speculated this was due to channeling and short circuiting in the subsurface, but since the authors lacked data on hydraulic head and conductivity, they were not able to make a definitive conclusion (Farahbakhshazad and Morrison, 2000).

Kassenga and colleagues conducted bench-scale experiments using an upflow column designed to determine optimum soil composition and conditions for attenuation of chlorinated volatile organic compounds, specifically TCE, cDCE, and 1,2-DCA (Kassenga et al., 2003). The paper, however, does not refer to the Wright Patterson uVFTW, which was still very new at the time of the study. Kassenga et al. (2003) state "it was necessary to conduct bench-scale studies to investigate the feasibility of using constructed wetlands for treatment of VOCs," implying that the existence of a full-scale system was not known. Pardue (2005) published a summary of bench-scale research into using upflow columns to treat VOC-contaminated groundwater. Determinations were made regarding the genetic identification of halorespirers, physical and chemical properties of various soil types, and locations and rates of reactions. The effect on treatment efficiency was evaluated with respect to vegetation type and salinity and inoculation of soil with halorespirers. He refers to three pilot-scale systems currently in different stages of EPA approval: Superfund sites in Connecticut and Massachusetts, and a site along Chesapeake Bay within the Aberdeen Proving Grounds in Maryland (Pardue, 2005).

Wallace and Kadlec (2005) profiled a pilot-scale uVFTW used to degrade BTEX at the site of a former refinery. Contaminated water was introduced in the bottom layer, then flowed vertically through gravel and sand layers. The water then flowed horizontally across the sand layer to the outlet. This flow design was noted as potentially unstable, and short-circuiting was observed. In the full-scale system, the vertical upflow design was abandoned in favor of a center-fed, radial horizontal subsurface flow design.

In a recently published textbook on treatment wetlands (Kadlec and Wallace, 2009), the authors refer to uVFTWs only in passing. They make a general statement that uVFTWs are used to promote anaerobic degradation. In the chapter on organic chemicals the uVFTW at Wright-Patterson AFB is specifically referred to in only two sentences and no information is given as to how the treatment wetland operates. The authors cite two AFIT Master's theses in this passage, although interestingly, the two cited theses (Entingh, 2002; and Blalock, 2003) do not deal with degradation of organic chemicals, but rather with characterizing the hydraulic properties of the treatment wetland cell. In any event, with the exception of the Wright-Patterson AFB uVFTW, Kadlec and Wallace (2009) do not cite any examples of the use of uVFTWs to treat chlorinated hydrocarbons.

The first peer-reviewed article on the Wright Patterson AFB uVFTW was published by Amon *et al*. (2007) of Wright State University. The authors were aware of no other uVFTWs then in existence being used to treat chlorinated organic compounds. See section 2.7 Case Studies for further information on this paper, as well as master's and PhD research involving the uVFTW at WPAFB.

2.3 Typical Values for Environmental and Constructed Wetland Design Parameters

Lorah and Olsen (1999) determined that the wetland sediment thought responsible for the reductive dechlorination of VOCs was 1.8-3.6m thick and comprised of two layers; a lower silty clay layer low in organic carbon (1%), and an upper peat and clay layer high in organic carbon (18%). Average linear groundwater flow velocity in the wetland sediment was estimated at 0.6 m yr^{-1}. The redox conditions in the wetland sediment were extensively characterized, and the authors noted that the reductive dechlorination pathway was most effective under methanogenic conditions. The authors did not evaluate the porosity or hydraulic conductivity of the wetland sediments (Lorah and Olsen, 1999).

In the study of Kassenga et al. (2003) discussed earlier, two soil mixtures were compared: one containing 20% sand and 80% peat, and the other containing 20% sand, 40% peat, and 40% Bion soil, a commercially available product derived from agricultural waste (Kassenga et al., 2003). A summary of soil parameters is presented in Table 1.

Table 1: Soil Parameters from Kassenga et al. (2003)

Parameter	20% sand 80% peat	20% sand 40% peat and 40% Bion soil
Porosity (n)	0.76±0.04	0.72±0.06
Retardation Factor (R)	cDCE 3.51 TCE 2.75 1,1,1-TCA 3.69 VC 1.07	cDCE 7.32 TCE 4.64 1,1,1-TCA 6.56 VC 1.20
Hydraulic conductivity (K)	0.43 m d^{-1}	0.11 m d^{-1}
Critical Flow Total flow for 18m x 36m-cell	0.080 m^3 d^{-1} m^{-2} 51.8 m^3 d^{-1}	0.074 m^3 d^{-1} m^{-2} 48.0 m^3 d^{-1}
Minimum bed depth for effective VC removal	9.00 m	2.10 m

Pardue (2005) did microcosm and mesocosm work similar in nature to Kassenga et al. (2003) (Kassenga did PhD work under Pardue). Pardue (2005) calculated removal rates for 1,1,2,2 tetrachloroacetate, TCE, cDCE, and 1,2 dichloroacetate and determined that most removal occurred in the bottom 10 cm of the column (Pardue, 2005). This was based on a flow of 6.41E-03 gallons per minute per m^2. Applying this value to the 648 m^2 treatment wetland at WPAFB give 4.2 gallons per minute, which is slightly less than the 5.5 gallons per minute reported by Corbin (2008).

The soil type used in the Wright Patterson uVFTW was characterized as Westland soil with silt and clay inclusions, a soil type common to local area fens (Amon et al., 2007). A fen is a peat-forming wetland fed by groundwater rather than precipitation, which results in a generally high nutrient level in the soil (U.S. EPA, 2009). Because the direction of flow is toward the surface in a fen, this type of soil should be well-suited to use in uVFTW (Table 2).

Table 2: Selected Soil Data from Amon et al. (2007)

Effective Porosity	26%
Hydraulic conductivity	0.81 m d^{-1}
Inflow rate	54.7 m^3 d^{-1}
Depth of treatment wetland	1.45 m

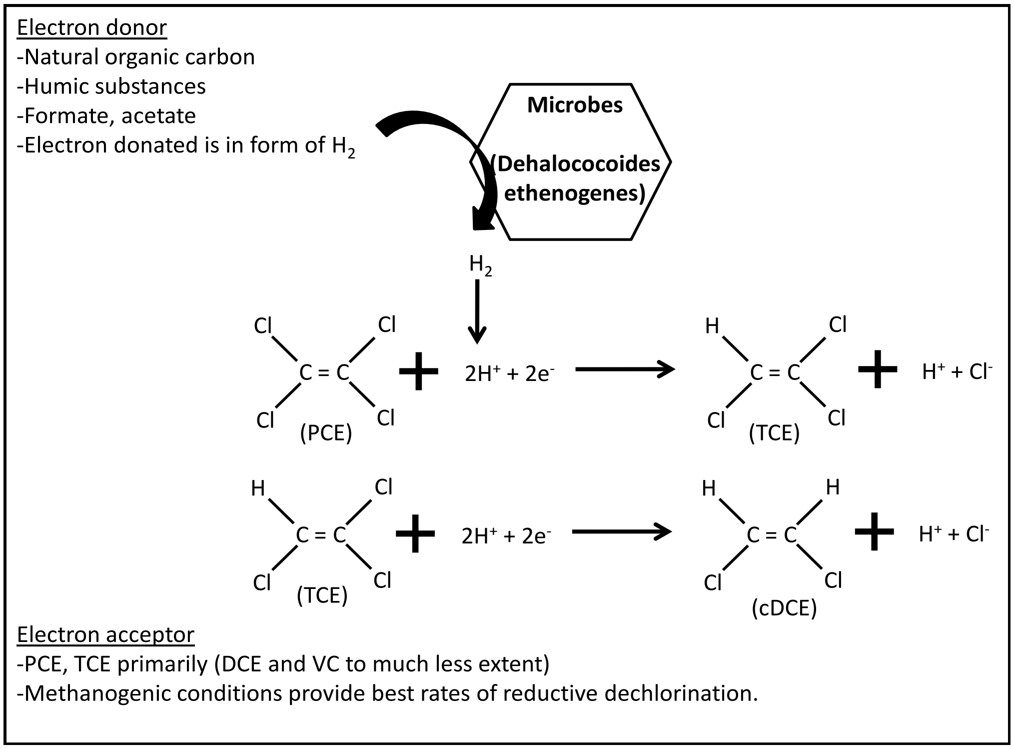
2.4 Modeling Biodegradation Kinetics of Chlorinated Ethenes in Constructed Wetlands

The choice of kinetics used to model biodegradation of chlorinated ethenes in a treatment wetland cannot be made without an understanding of the primary degradation processes occurring in the wetland (Bradley, 2003). The primary processes that occur in a uVFTW are:

1) Anaerobic reductive dechlorination
2) Aerobic cometabolism (methane as primary substrate)

In anaerobic reductive dechlorination, microorganisms use H_2 from fermented organic compounds present in organic rich soil as the electron donor, and PCE or TCE as the terminal electron acceptor (Figure 4). This process, also known as chlororespiration, results in a net energy gain for the microorganisms. Anaerobic reductive dechlorination results in a chlorine ion being stripped off the PCE molecule and replaced with a hydrogen ion.

Figure 4: Anaerobic Reductive Dechlorination of PCE to TCE and TCE to cDCE



Source: material adapted from Vogel et al. (1987)

Anaerobic reductive dechlorination is a stepwise process, meaning PCE is first degraded to TCE, which is then degraded to DCE. Here, the process tends to stall due to the inhibitory effect of increasing concentrations of daughter products, as well as the increasingly reducing conditions required to strip additional chlorine ions. As chlorinated ethenes become reduced, the effectiveness of reducing pathways is less.

Microbes capable of using chlorinated ethenes as electron acceptor must compete for electron donors with other microorganisms and other redox processes. The redox potential governs how successful the process of anaerobic reductive dechlorination will be (Table 3).

Table 3: Gibbs Free Energy Change for Selected Processes

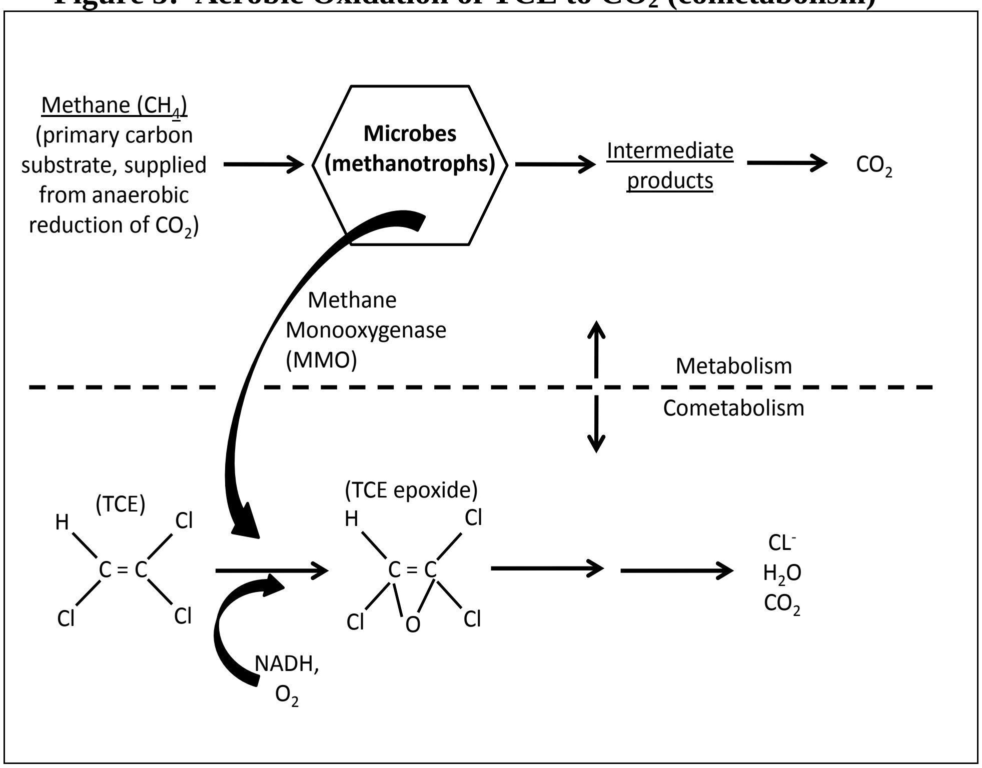
Redox Environment	**Gibbs free energy change**	
Oxygen reducing	-502 kJ/mol	
Nitrate reducing	-477 kJ/mol	
Manganese reducing	-339 kJ/mol	
	-164 kJ/mol	PCE to TCE[1]
	-161 kJ/mol	TCE to cDCE[1]
	-141 kJ/mol	cDCE to VC[1]
	-154 kJ/mol	VC to Ethene[1]
Iron reducing	-117 kJ/mol	
Sulfate reducing	-105 kJ/mol	
CO_2 reducing (methanogenic)	-92 kJ/mol	

Source: (U.S. EPA, 1999),
except for: [1] (He et al., 2002)

Table 3 indicates that anaerobic reductive dechlorination will occur to a much reduced extent under nitrate and manganese reducing conditions as compared to methanogenic conditions. Bradley (2003) noted that PCE will undergo anaerobic reductive dechlorination under all but aerobic conditions, TCE will undergo anaerobic reductive dechlorination under iron reducing, sulfate reducing, or methanogenic conditions, DCE will undergo anaerobic reductive dechlorination under either sulfate reducing or methanogenic conditions, and VC will undergo anaerobic reductive dechlorination only under methanogenic conditions (Bradley, 2003).

A primary substrate to support aerobic cometabolism of chlorinated ethenes (i.e., methane) may be produced from CO_2 and H_2 via anaerobic methanogenesis. This methane is then used by methylotrophs, which produce methane monooxygenase (MMO) enzyme under aerobic conditions to catalyze oxidation of methane to produce CO_2. MMO is a nonspecific enzyme that is also capable of aerobically degrading TCE, DCE, and VC to CO_2, without accumulations of harmful intermediate products. The methylotroph itself oxidizes the primary substrate for growth and energy, but appears to derive no benefit from the cometabolic oxidation of the chlorinated ethene (Figure 5). The extent of cometabolism is typically limited by the availability of the primary substrate, methane (Bradley, 2003).

Figure 5: Aerobic Oxidation of TCE to CO_2 (cometabolism)



Source: Material adapted from McCarty (1997) in Subsurface Restoration, p374

With an understanding of the primary degradation processes that occur in a uVFTW, one can then look at kinetics. Monod kinetics relates the growth rate of a microorganism to the concentration of a limiting substrate, and it has been used to describe the growth rate of microorganisms engaged in anaerobic reductive dechlorination (Suarez and Rifai, 1999).

$$\mu = \mu_{max} \frac{S}{S + K_s} \tag{10}$$

where,

μ:	growth rate of biomass (microorganism) [T^{-1}]
μ_{max}:	max growth rate of biomass (microorganism) [T^{-1}]
S:	growth-limiting substrate concentration [$M\ L^{-3}$]
K_s:	substrate concentration that results in a growth rate, μ, of $\mu_{max}/2$ [$M\ L^{-3}$]

The rate of biomass growth is related to the rate of substrate consumption by equation (11) (Kovarova-Kovar and Egli, 1998).

$$\mu = \frac{Y}{B} \times \frac{dS}{dt} \tag{11}$$

where,

Y:	yield coefficient, mass biomass per mass substrate [$M\ M^{-1}$]
B:	biomass concentration [$M\ L^{-3}$]

Substituting (11) into (10), rearranging the expression, and introducing a negative sign to reflect the fact that substrate is being consumed gives an expression for the rate of change in substrate (chlorinated ethene) concentration.

$$\frac{dS}{dt} = -\frac{\mu_{max}}{Y} B \left(\frac{S}{S + K_s}\right) \quad (12)$$

where,

Y: yield coefficient, mass biomass per mass substrate [M M^{-1}]
B: biomass concentration [M L^{-3}]

From Equation (12), it can be seen that when $S \ll K_s$:

$$\frac{dS}{dt} = -\frac{\mu_{max}}{Y} B \left(\frac{S}{K_s}\right) \quad (13)$$

Rearranging,

$$\frac{dS}{dt} = \left(-\frac{\mu_{max} \times B}{Y \times K_s}\right) S \quad (14)$$

It can be seen from this that when $S \ll K_s$, dS/dt can be approximated by the first order expression:

$$\frac{dS}{dt} = -kS \quad (15)$$

where,

$$k = \left(\frac{\mu_{max} \times B}{Y \times K_s}\right) \tag{16}$$

First-order rate constants that have appeared in the literature are reported in Table 4 and Table 5.

Table 4: First Order Degradation Rate Constants

	PCE to TCE	TCE to cDCE	cDCE to VC	VC to Ethene
Anaerobic reductive dechlorination	Mean: .010 90^{th}%: .022 Range: 0-0.080 (Suarez and Rifai, 1999)	Mean: .003 90^{th}%: .005 Range: 0-0.023 (Suarez and Rifai, 1999)	Mean: .003 90^{th}%: .005 Range: .001-.006 (Suarez and Rifai, 1999)	Mean: .001 90^{th}%: n/a Range: 0-0.007 (Suarez and Rifai, 1999)

All rates listed are in units of [d^{-1}]. Data were taken from Table 7.

Table 5: First Order Degradation Rate Constants, Aerobic Cometabolism

	PCE	TCE	cDCE	VC
Aerobic cometabolism		Mean: .15±.02 (Powell et al., 2010) Mean: .948 90^{th}%: -- Range: .105-1.41 (Suarez and Rifai, 1999)	Mean: .59±.07 (Powell et al., 2010) Mean: .720 90^{th}%: 1.012 Range: .390-1.15 (Suarez and Rifai, 1999)	Mean: 1.730 90^{th}%: -- Range: 1.50-1.96 (Suarez and Rifai, 1999)

All rates listed are in units of [d^{-1}]. Data from Suarez and Rifai (1999) were taken from Table 7. Rates from Powell et al. (2010) are pseudo first-order, and are from lab studies.

2.5 Relationship Between Hydraulic Conductivity, Residence Time, and Treatment Efficiency

The significance of the problem of hydraulic short-circuiting is difficult to determine in the case of uVFTWs due to the fact that uVFTWs are relatively recent innovations and not many are in use. Where they have been used, hydraulic short-circuiting is noted as a potential problem, but the degree to which it is a problem is not quantified (Farahbakhshazad and Morrison, 2000; Wallace and Kadlec, 2005).

Hydraulic short-circuiting has been studied much more in HSFW treatment wetlands and dVFTWs. Araujo et al. (2008) modeled the problem of clogging in HSFW treatment wetlands, noting that dead zones and hydraulic short-circuiting are common ramifications of clogging (Araujo et al., 2008).

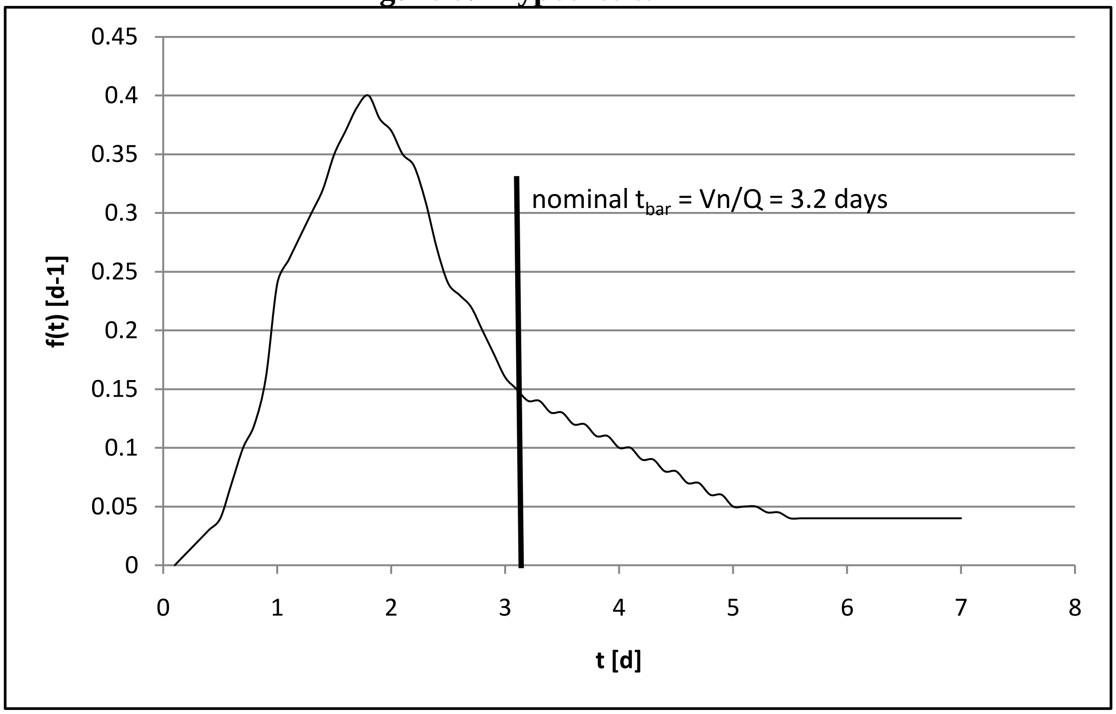
Chazarenc et al. (2003) noted hydraulic short-circuiting and dead zones in conducting pulse tracer experiments to determine hydraulic residence time distributions in a HSFW in France. He attributed this to the structural design of the bed, where influent is injected at one point in the corner of the bed and effluent is removed at the opposite corner, a design which promotes hydraulic short-circuiting (Chazarenc et al., 2003).

Dittrich (2006), in a review of Hungarian usage of HSFWs and dVFTWs, noted that hydraulic short-circuiting was a significant problem in both types due in part to distribution pipe construction deficiencies and the shape of the wetland (Dittrich, 2006). He proposed the use of only gravel as filter media in HSFWs in order to avoid hydraulic short-circuiting, and avoiding the use of gravel as filter media in dVFTWs in order to increase hydraulic residence time (Dittrich, 2006).

Lightbody et al. (2008) observed hydraulic short-circuiting in a three-cell FWS wetland in Georgia. Between three and six fast flow paths were observed which carried water at least 10 times as fast as other areas of the cell, and 20-70% of the flow had a residence time less than the nominal residence time (Lightbody et al., 2008). The authors also note that the wetland was carefully designed to ensure uniform flow, with careful planting of vegetation, multiple inlet and outlet structures, and a flat base to the cell (Lightbody et al., 2008). The fact that short-circuiting still occurred may indicate the difficulty in eliminating this problem by design.

In the examples cited above, hydraulic short-circuiting is determined by calculating the nominal or theoretical residence time by dividing water volume in the cell by the volumetric flow rate. This is then compared to the mean or first moment of the residence time distribution function (RTDF). If the first moment of the RTDF is less than t_{bar}, hydraulic short-circuiting is indicated. Figure 6 illustrates an example where there appears to be short-circuiting, and flow is not going through the entire cell volume.

Figure 6: Hypothetical RTDF

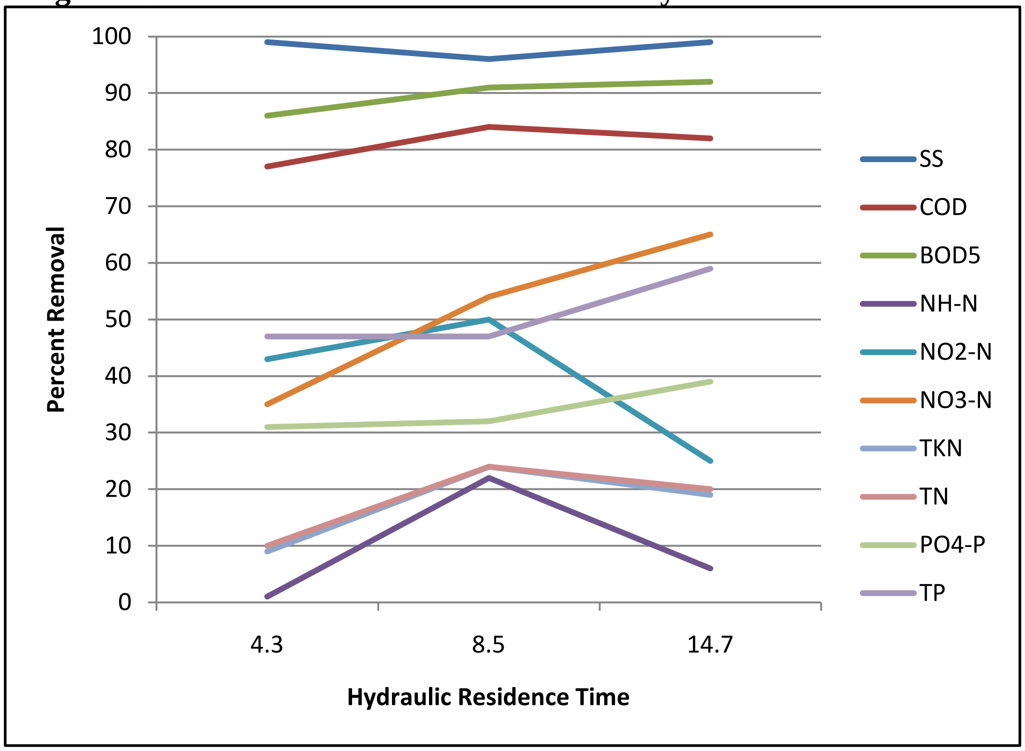


Typical treatment efficiencies vary widely, due to wetland design, type of contaminant, and hydraulic retention time. Farahbakhshazad and Morrison (2000) measured removal rates for nitrate, phosphate, and ammonia for a uVFTW in Brazil. Concentration removal for phosphate was 93%, 78% for nitrate, and 50% for ammonia (Farahbakhshazad and Morrison, 2000). The total depth of the bed was 0.45 m, and the upper 0.25 m was vermiculite with about 35-60% clay content. Sampling was conducted at three sites within the uVFTW, at two depths per site – 0.25 m (bottom of the vermiculite layer) and 0.35 m (bottom gravel layer). The mechanism of removal was adsorption in the bed and precipitation at the surface for phosphate, and plant uptake for nitrate and ammonia (Farahbakhshazad and Morrison, 2000).

Kassenga et al. (2003), in column experiments of cDCE and VC degradation, determined the minimum bed depth to degrade influent concentrations of both contaminants of 13.67 mg/L to below the maximum contaminant levels (MCLs) specified in National Primary Drinking Water Regulations. VC was determined to be the limiting contaminant, requiring the deepest bed depth to degrade the contaminant to below its MCL of 2 µg/L. Based on a first-order rate constant of 0.56 day^{-1}, a bed depth of 2.1m was required (Kassenga et al., 2003).

Lee et al. (2004) evaluated the removal efficiency of a HSFW designed to treat swine waste effluent. Removal efficiency for a variety of effluent constituents was evaluated for three hydraulic residence times: 4.3 days, 8.5 days, and 14.7 days (Figure 7). There was no consistent trend in removal efficiency as a function of hydraulic residence time. Several constituents (NO_3-N, total phosphorus, and PO_4-P) exhibited a positive correlation between removal efficiency and hydraulic residence time, as would be expected, while others (COD, NO_2-N, NH_4-N, and total nitrogen) appeared to have an optimum removal efficiency when the hydraulic residence time was 8.5 days. The authors note that the profiles for nitrate, nitrite, and ammonia may be due to the poor nitrification capability of the treatment wetland (Lee et al., 2004).

Figure 7: Percent Removal as a Function of Hydraulic Residence Time



Source: Adapted from Table 1 and Table 2 of Lee et al. (2004)

Dierberg et al. (2005) conducted a rhodamine dye tracer study on a FWS in south Florida that exhibited significant hydraulic short-circuiting. They determined that a small volume of the wetland conveyed 44% of the volumetric flow, and that this reduced the treatment efficiency for phosphorus in two ways. First, through the shorter residence time; and second, through impaired physical processes such as sedimentation and plant uptake. First-order degradation rate constants for removal of phosphorus in the high residence time zones were twice those of the short-circuit zones (0.50 d^{-1} vs. 0.24 d^{-1}) (Dierberg et al., 2005).

As noted above, although hydraulic short-circuiting of constructed wetlands appears to be a problem, proposed engineering solutions to the problem and attempts to simulate the effects of implementing proposed solutions on wetland performance are only found in the literature infrequently. In one example, Chazarenc et al. (2003) recommended "wide centered injection" at the influent of HSFWs in order to promote mixing and prevent dead zones, but did not offer a more detailed explanation, and made no attempt to model such a design. Lightbody et al. (2009) modeled a short-circuiting FWS treatment wetland using a stream tube model with dispersion and incorporating transverse deep zones as an engineering solution intended to mitigate short-circuiting. The deep zones stretched the entire width of the treatment wetland, transverse to the direction of flow, and were vegetation-free pools from bottom to top. The solution was thought to improve treatment efficiency via two mechanisms. First, the water is rapidly mixed in a lateral direction, which dilutes contaminant concentrations. Second, transverse deep zones disrupt fast flow paths and reduce the likelihood of any one path extending the entire length of the treatment cell (Lightbody et al., 2009). The authors founds that transverse deep zones would increase contaminant removal, provided the zone is long enough (in the direction of flow) to completely dissipate the momentum of incoming fast-path water. Further, contaminant removal increases with the number of deep zones up to a maximum, beyond which wetland area reserved for contaminant treatment drops too low and contaminant removal goes down (Lightbody et al., 2009)

2.6 Use of Models to Predict Treatment Efficiency of Constructed Wetlands

Lightbody et al. (2009) showed how modeling could be useful in predicting efficiency and assisting in wetland design. This section will examine other such uses of modeling. As the understanding of the hydrological, physical, and chemical processes that occur in treatment wetlands has improved, so has the capability to model these systems. Models of treatment wetlands were originally conceived as "black boxes," where concentration in was linked to concentration out by first-order decay coefficients (Langergraber, 2008). Most models in use today are deterministic mathematical models which use numerical methods to arrive at solutions to the equations of flow and transport. These numerical models allow for heterogeneity in space (e.g., spatially varying hydraulic conductivity) and variations in time (e.g., temporally varying influent concentrations) (Konikow et al., 2007).

Langergraber (2008) provides a review of mechanistic models divided into three categories: models of hydraulic behavior and transport only; models of reactive transport under saturated conditions; and models of reactive transport under variably saturated conditions. Of these, the models of reactive transport in saturated conditions are relevant to this research. Using a mixing cell method, a HFTW is divided into numerous equal sized cells, within which degradation occurs by first order decay. This method is a simplification of the advection-dispersion equation, and provides a better fit than plug flow. A mechanistic model using STELLA was also presented. The model incorporates six state variables – carbon cycle, nitrogen cycle, oxygen balance, bacteria growth (heterotrophic and autotrophic), and water budget. It predicted effluent BOD, organic nitrogen, ammonium, and nitrate concentrations well. STELLA was also used in another approach to model nitrogen transformation in HFTWs. Other models use a variety of combinations of continuously stirred tank reactors (CSTRs) and plug flow reactors with the goal of simplifying the model by reducing the number of parameters required (Langergraber, 2008).

Langergraber et al. (2009) demonstrates the multi-component reactive transport module CW2D, designed to model the degradation of municipal wastewater in a HFTW. CW2D is capable of modeling 12 components and 9 processes using Monod kinetics to describe degradation. CW2D is imbedded within the HYDRUS transport program for variably unsaturated flow (Langergraber et al., 2009).

One of the most widely used groundwater modeling software packages is MODFLOW, developed by the U.S. Geological Survey (Konikow et al., 2007). MODFLOW uses the finite difference method to arrive at numerical solutions to the groundwater flow equation (Harbaugh, 2005). MODFLOW is a modular software package which can be coupled with other packages, particularly packages that model transport. RT3D, Reactive Transport in 3 Dimensions, is a separate software package that simulates transport and degradation (Clement, 1997). RT3D uses the output of MODFLOW to determine advective velocities to input into the transport equations. RT3D contains built-in programs to simulate many different fate and transport processes, including a model for both anaerobic and aerobic degradation of PCE and TCE (Clement, 1997). Although MODFLOW and RT3D can be used directly, it is also common to use a more user-friendly interface program such as the Groundwater Modeling System (GMS). GMS is a Windows-based interface to MODFLOW-2005 and RT3D created by the Department of Defense that integrates multiple programs for subsurface flow and contaminant fate and transport (U.S. A.C.E., 2010). This research effort will use MODFLOW-2005 and RT3D within the GMS interface, so further information about them is included in chapter 3.

2.7 Case study: uVFTW at WPAFB

This section will be devoted to summarizing prior research into the hydraulic behavior and degradation characteristics of the uVFTW at WPAFB. The first peer-reviewed article on the Wright Patterson AFB uVFTW was published in 2007 (Amon et al., 2007). Amon et al. (2007) gives a detailed account of construction and operation of the uVFTW, to include inflow rate, physical dimensions of the cell, composition and depths of the different layers of the cell, influent piping, types of vegetation planted, and piezometer layout (Amon et al., 2007). Amon notes that while anaerobic reductive dechlorination of PCE is a major process in the wetland, at shallow depths, due to the availability of methane and root-transported oxygen, oxidative cometabolism is an important degradation process, as well (Amon et al., 2007). Amon et al. (2007) suggest the inclusion of wood chips throughout the cell, as well as filling the cell with dirt as it fills with water (during construction), as means of avoiding uneven compaction and hydraulic short-circuiting (Amon et al., 2007).

Many master's and PhD students at Wright State University and the Air Force Institute of Technology have done research on the uVFTW at WPAFB. Mesocosm studies of the soil type used in the uVFTW include Tritschler (2007), Gruner (2008), and Powell (2011). Studies examining biodegradation characterization of the treatment wetland include Opperman (2002), Clemmer (2003), Kovacic (2003), Sobolewski (2004), Waldron (2007), and Thompson (2008). Research into the hydraulics of the cell includes Entingh (2002), Blalock (2003), and Corbin (2008).

Tritschler et al. (2007) conducted mesocosm experiments to investigate the effects of vegetation and seasonal changes on redox parameters within the mesocosm. She determined that selection of plant species had a large impact on the redox conditions (Tritschler et al., 2007). Therefore, the ability of a treatment wetland to degrade contaminants would be sensitive to selection of plant species (Tritschler et al., 2007). Gruner (2008) conducted mesocosm experiments to characterize bacterial populations of methanogens, methanotrophs, and ammonia oxidizers with respect to planted versus non-planted mesocosms. Powell (2011) conducted field work characterizing contaminant concentrations in the shallow vegetated zone, as well as laboratory microcosm work to determine degradation rates for TCE, cDCE, and 1,1,1-TCA in the presence of methane oxidizers. TCE and cDCE were found to degrade with first-order degradation rates, while 1,1,1-TCA was not found to degrade (Powell et al., 2010).

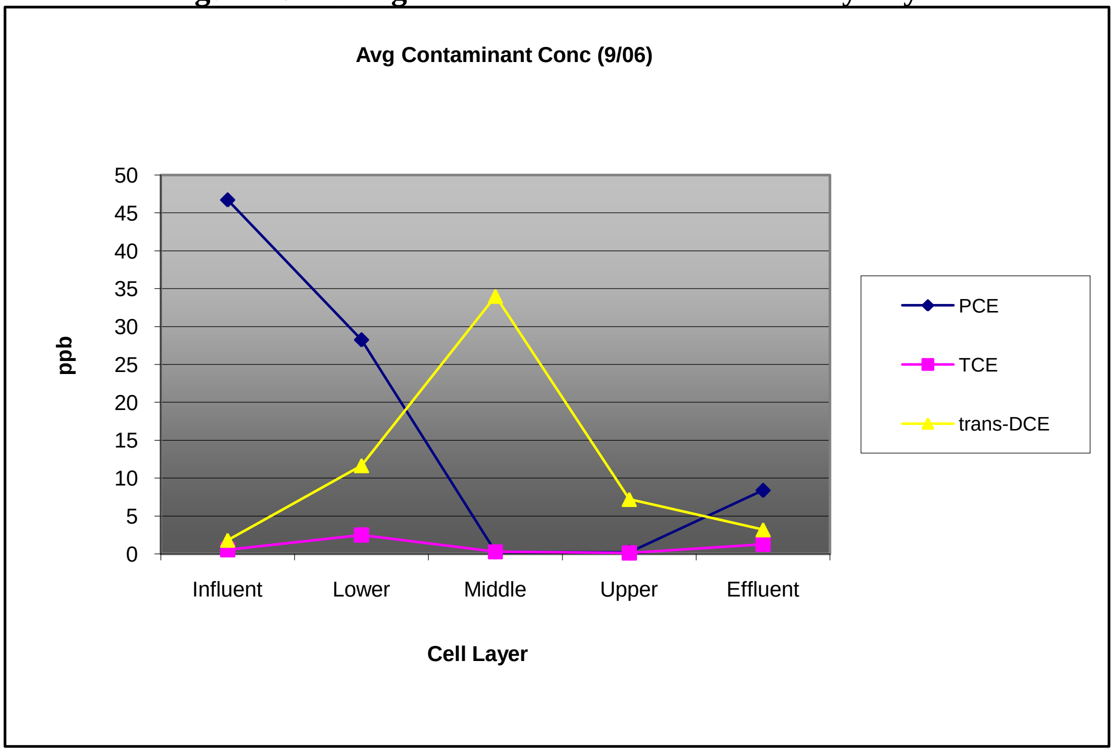
Kovacic (2003) conducted field sampling to characterize organic acid and inorganic anion concentrations in the wetland cell. He found that organic acid concentrations decreased by 93% over the 11 months between December 2002 and January 2003 (Kovacic, 2003). From measurements of dissolved oxygen and oxidative-reductive potential, he determined that the base of the wetland was aerobic, but that quickly changed to anaerobic in the layer immediately above the base. He also found that nitrate and sulfate reducing conditions were correlated with higher concentrations of lactate and formate (Kovacic, 2003).

Waldron (2007) conducted field sampling research to characterize concentration profiles for PCE, TCE, trans-DCE, cDCE, VC, and ethane at each of the three depths of the wetland (Waldron, 2007). This work was a continuation of similar field work done by Sobolewski (2004), Clemmer (2003), and Opperman (2002). Waldron presented summary concentration data for all the sampling – December 2001, January 2003, Fall 2003, September 2006, October 2006, November 2006, and December 2006 (Waldron, 2007). This allowed him to state some observations regarding changes in the uVFTW's treatment efficiency over time:

1) Influent PCE concentration increased by 94% from Fall 2003 to Fall 2006, but treatment efficiency (measured at the top layer, not the effluent weir) held constant at 99%. This has implications for the maximum influent contaminant level the wetland cell can handle without the effluent exceeding maximum contaminant levels (MCLs).
2) Reduction of PCE concentrations was less measured at the effluent weir (85.4%) compared to the top layer of the wetland cell (99%). Waldron concluded from this that some influent water was bypassing treatment and short-circuiting directly to the effluent weir.
3) TCE concentrations in the middle and upper layers declined substantially from Fall 2003 to Fall 2006. Waldron attributes this to continued maturation of the wetland cell.
4) The concentration of trans-DCE increased significantly over the years, becoming the dominant DCE isomer in the wetland cell.
5) The concentration of VC decreased from 2003 to 2006 by approximately an order of magnitude, further indicating maturation of the cell and somewhat allaying concerns about build up of this end product.

Data presented by Waldron show classic reductive dechlorination (Figure 8). As PCE is degraded from the lower to middle layer, concentrations of daughter products increase. These concentrations drop off from middle to upper layers, suggesting either a continuation of sequential anaerobic reductive dechlorination, or that aerobic processes become more prominent in the upper layer (Waldron, 2007). Not shown in Figure 8 due to scale are concentration profiles for VC and Ethane, which show zero concentration at influent, rising to a peak at the middle layer, then falling back to almost zero at effluent.

Figure 8: Average Contaminant Concentration by Layer



Source: Waldron (2007)

Thompson (2008) used STELLA to model the movement of oxygen from roots into the rhizosphere, as well as aerobic cometabolism of TCE (Thompson, 2008). He determined that low organic carbon concentration in the influent, low copper, high oxygen, and high methane concentrations improved destruction of TCE. Treatment efficiency was most affected by hydraulic loading, dropping from 80% to 20% with an increase in loading from 1 L m^{-2} hr^{-1} to 4 L m^{-2} hr^{-1} (Thompson, 2008). The current loading rate for the uVFTW is about 30 m^3 d^{-1}, which is 0.5 L m^{-2} hr^{-1} (Corbin, 2008).

Entingh (2002) was the first to look at the hydraulic behavior of the uVFTW. He describes installation of the grid of 66 piezometer nests, each of which contain 3 piezometers screened in the lower, middle, and upper layers of the wetland cell (Entingh, 2002). Head was measured at all locations, and slug tests were conducted using the Bouwer and Rice (1976) method at all locations in order to calculate values of hydraulic conductivity. Contour plots of head and hydraulic conductivity were constructed, which indicated regions of preferential flow. On-site evaluation confirmed this, as areas of higher head were soft and could not support the weight of foot traffic. One area exhibited fluidization, with significant mounding and water flowing out of the ground.

Because some piezometers were not recovering quickly enough to allow sample collection to test for PCE, these piezometers were developed by pumping water into them. 26 piezometers in the top layer and 10 in the middle layer were initially developed using this technique. This seems to have altered soil properties immediately surrounding the developed piezometers, resulting in changes in calculated hydraulic conductivity values of 1 or 2 orders of magnitude in some cases (Table 6). In order to ensure conditions over the entire wetland were the same, the remaining piezometers in the top and middle layer were subsequently developed (Entingh, 2002).

Table 6: Geometric Means of Hydraulic Conductivity (m d^{-1})

	Top Soil Layer	Middle Soil Layer	Bottom Soil Layer
Before Developing	0.0011	0.0066	14.8
After Developing	0.09	0.06	14.8

Source: Entingh (2002)

Calculated hydraulic residence times provided further evidence of hydraulic short-circuiting. These ranged from 16.5 hours to 15 days (mean 3 days). Approximately 64% of the particles from a MODPATH simulation had residence times less than the mean (Entingh, 2002).

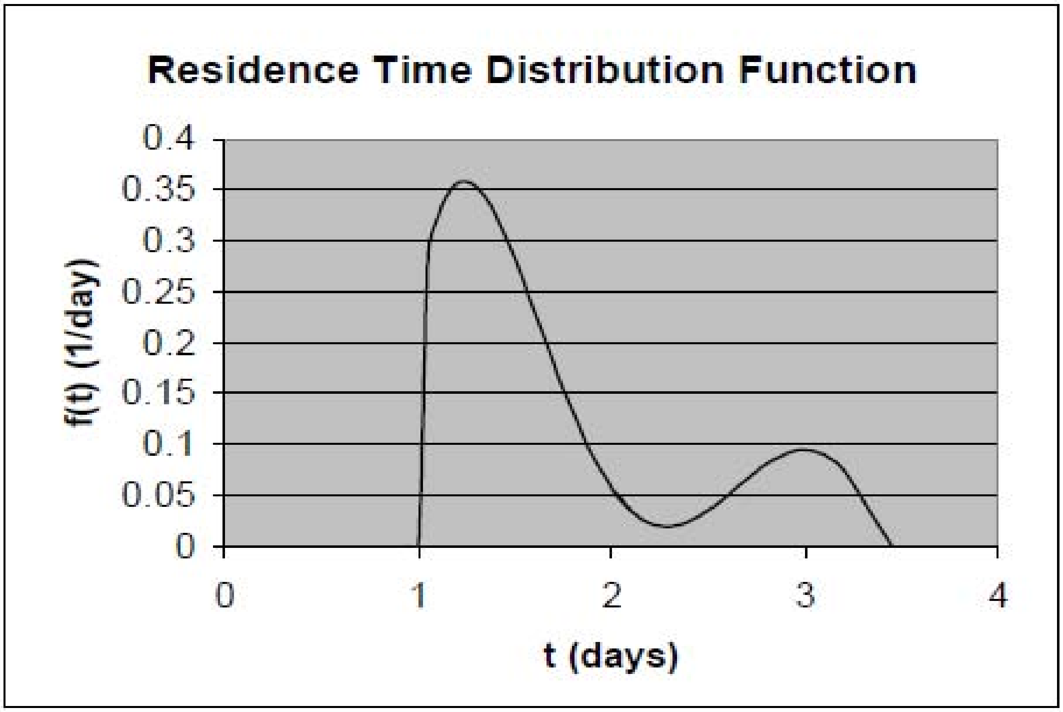
The next year, Blalock (2003) also examined the hydraulic behavior of the uVFTW at WPAFB. Whereas Entingh (2002) used the Bouwer and Rice (1976) method to determine hydraulic conductivity, Blalock (2003) used the Hvorslev method, which was deemed more appropriate (Blalock, 2003; Entingh, 2002)

Blalock (2003) used MODPATH to determine a cumulative residence time distribution function. Fitting a polynomial equation to this distribution, then taking the derivative, gave the residence time distribution function (RTDF). The mean residence time, τ, was then calculated by:

$$\tau = \int_0^\infty f\,(t) \times t\,dt \tag{8}$$

where f(t) is the RTDF. The mean residence time, τ, was then compared to the theoretical mean residence time, t_{bar}=Vn/Q, to determine cell volume utilization (Blalock, 2003). Blalock found that the RTDF was bimodal, with one peak at about 1.25 days and another, much smaller peak at around 3.0 days (Figure 9).

Figure 9: RTDF Calculated by Blalock (2003)



Blalock hypothesized that this pattern could be due to flow leakage or heterogeneous hydraulic conductivities. The mean hydraulic residence time (τ) of the RTDF was calculated to be 1.6 days, which is shorter than the calculated theoretical mean residence time (t_{bar}) of 2.16 days. Blalock concluded that this indicated hydraulic short-circuiting, with areas of stagnant flow contributing to the long tailing of the RTDF.

Corbin (2008) is the most recent study of the hydraulics of the uVFTW at WPAFB. Her work was essentially a replication of and follow-up to the work of Entingh (2002) and Blalock (2003). Field sampling was conducted to determine values of potentiometric head and hydraulic conductivity, and these data were then used in a computer model to provide insight into the hydraulic behavior of the uVFTW and to compare current behavior to prior work (Corbin, 2008).

Corbin (2008) represented the wetland in GMS using a three-dimensional grid of fixed cell length and width, with cell depth varying by layer (Corbin, 2008). The wetland dimensions of 18 m by 36 m were represented by a grid of cells ½ m square, resulting in a 36 x 72 cell matrix. The overall 1.7 m depth of the wetland cell was divided into nine layers. Having nine layers allowed the 1:1 slope of the walls of the cell to be represented, as deeper layers are smaller than shallower ones. Table 7 summarizes the grid construction. Data from Amon et al. (2007) are included for reference.

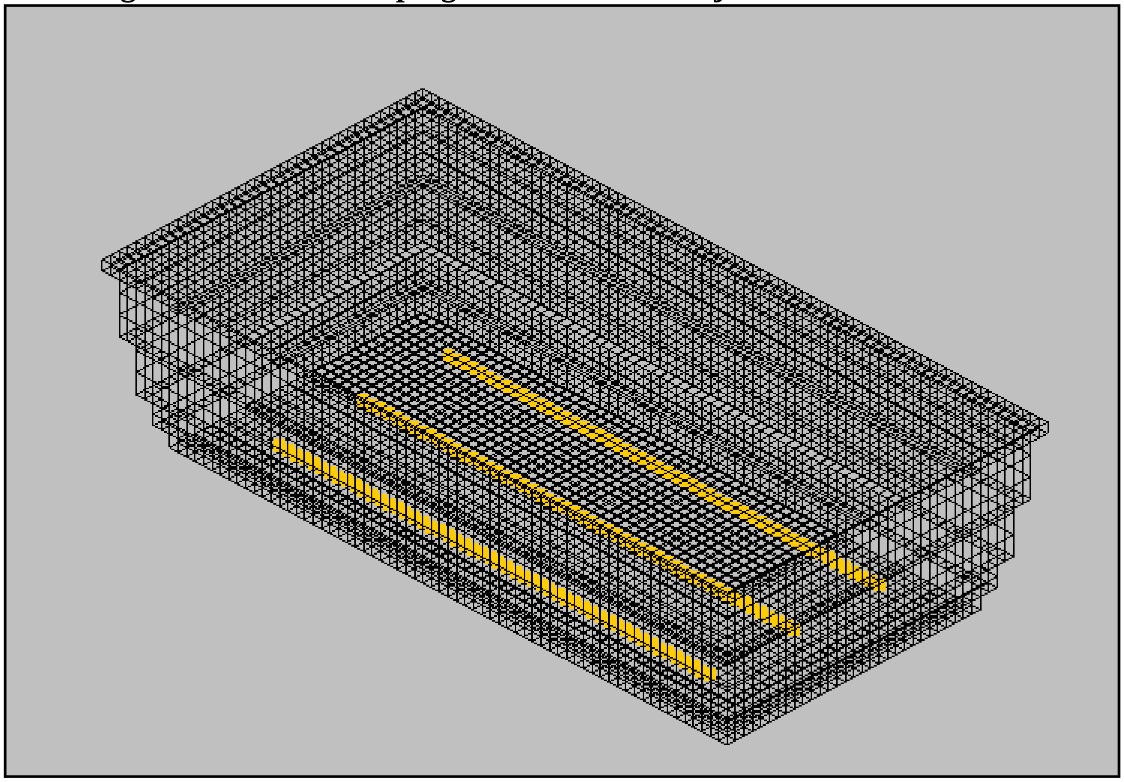
Table 7: Grid Construction, Corbin (2008)

Description	Thickness (m)	Bottom	Top	Width x Length (# cells x # cells)	From Amon et al. (2007)
Open water on surface	0.10	1.60	1.70	36 x 72	
Soil/water interface	0.08	1.52	1.60	36 x 72	
Hydric soil layer 1	0.19	1.33	1.52	36 x 72	0.38 m hydric soil (layer A)
Hydric soil layer 2	0.19	1.14	1.33	34 x 70	
Hydric soil layer 3	0.19	0.95	1.14	34 x 70	0.38 m hydric soil (layer B)
Hydric soil layer 4	0.19	0.76	0.95	34 x 70	
Hydric soil layer 5	0.19	0.57	0.76	32 x 68	0.38 m hydric soil (layer C, 10% wood chips)
Hydric soil layer 6	0.19	0.38	0.57	32 x 68	
Gravel layer	0.23	0.15	0.38	30 x 66	0.23 m limestone gravel (4cm diameter)
Datum	0.00	0.00	0.15	n/a	0.15 m sand

In the flow model, the top layer was represented as a constant head boundary. Corbin (2008) had attempted to represent the top layer as a general head boundary, but determined during model calibration that this resulted in unrealistic head contours a full meter above the wetland surface.

The influent piping was modeled as a series of injection wells that each introduced 0.192 m^3 d^{-1}. The wells are located in cells 15-65, rows 9, 19, and 29 (Figure 10).

Figure 10: Influent Piping Modeled as 153 Injection Wells in 3 Rows



Source: Corbin (2008)

This gives a total of 153 injection wells; and a total flow into the wetland of 0.192 m^3 d^{-1} x 153 = 29.3 m^3 d^{-1}, or 5.38 gpm. This total modeled flow closely matches the measured value of 5.5 gpm (Corbin, 2008), but is well short of the maximum inflow rate of 54.7 m^3 d^{-1} (10.0 gpm) that the pump is capable of supplying to the wetland cell (Amon et al., 2007).

Corbin (2008) used a value of 0.5 for soil porosity for all soil layers, citing Amon et al. (2007). Amon et al. (2007) states that, based on research conducted by others on the type of soil used in the treatment wetland, the soils “might release 50% of their volume as water.” Entingh (2002) also estimated porosity at 0.53 (Entingh, 2002).

Hydraulic conductivity in the horizontal direction was assumed to be isotropic (Corbin, 2008). Corbin (2008) assumed that since the same type of soil was used in each wetland cell layer, that there would be no horizontal anisotropy. Furthermore, the equations used to calculate hydraulic conductivity (Hvorslev, 1951) assume homogeneity and isotropy.

The field measurements to determine hydraulic conductivity were done in a similar manner to prior work, but with a lower pressure flush of the well. This was done in an attempt to avoid the problems of Entingh (2002) who found that hydraulic conductivity changed by 1 or 2 orders of magnitude after the wells were developed. Corbin (2008) found that with the lower pressure development, hydraulic conductivity in two wells increased by an order of magnitude, while in another well it decreased by an order of magnitude, allowing her to conclude that developing the wells produced more accurate values for hydraulic conductivity (Corbin, 2008).

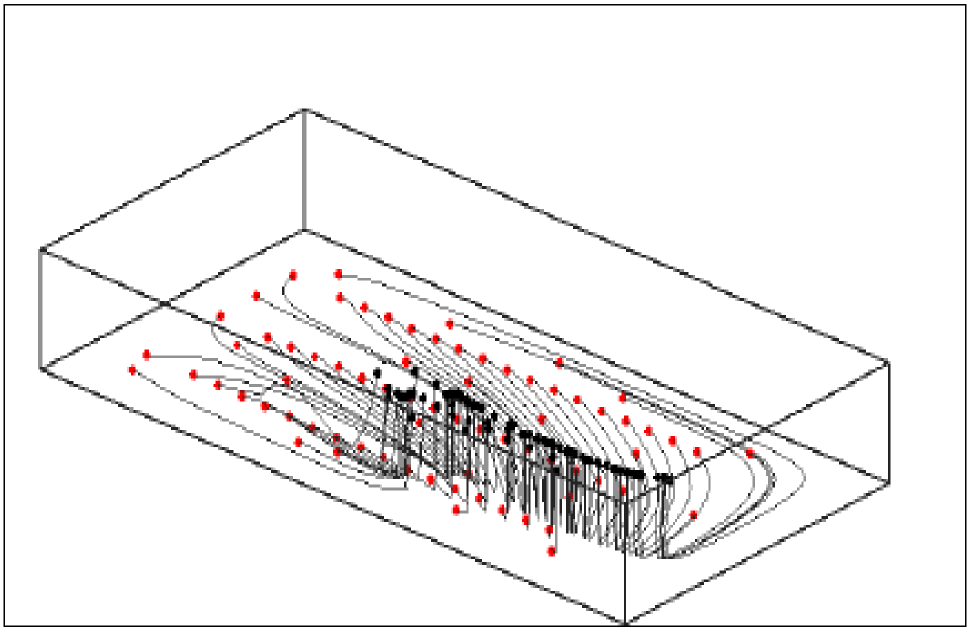
Values for horizontal conductivity were derived from slug test results using the Hvorslev (1951) method and then imported into the model (Corbin, 2008). Values for vertical conductivity (K_v) were not directly measured, but were assumed related to horizontal conductivity (K_h) by the ratio K_h / K_v = 1.5 for all soil layers (1.0 was used for the top open water layer). Corbin (2008) found that the model was not sensitive to the K_h / K_v ratio, as the model returned equivalent outputs for ratio values from 1.0 to 3.0.

Model calibration was conducted by varying the boundary head values while holding other parameters constant until the sum of the residuals between calculated and actual head values was minimized (Corbin, 2008). Corbin (2008) used boundary head settings of 1.7 m at the surface of the water and 2.9 m at the bottom of the model, resulting in a sum of squared weighted residuals (SSWR) of 20.5 m^2. She also found that a SSWR of 12.0 m^2 could be achieved, but the model was then producing unrealistic velocities and water discharge.

Corbin (2008) found that the uVFTW was generally producing upward flow, with piezometers in the bottom layer generally having the highest head readings and piezometers in the top layers having the lowest head values (Corbin, 2008). However, the range of head values within each layer was significant, and there was no pattern to the distribution of head values within each layer. Comparing these data to the Entingh (2002) study, she concluded that the overall variations in head measurements had not changed significantly in the five years between the two studies (Corbin, 2008).

Flow characteristics were similar to those found by Entingh (2002). The water moved horizontally in the gravel layer to the region of highest hydraulic conductivity, then vertically to the surface (Corbin, 2008). In contrast to Entingh, who found that most of the water short-circuited vertically at the north side of the cell, Corbin found that the water was moving to the south side of the cell, then vertically to the surface (Figure 11). She attributed this to a change in the actual behavior of the wetland, as opposed to an error by either herself or Entingh (Corbin, 2008).

Figure 11: MODPATH Water Path-Lines from Bottom Layer (Red Dots) to Top Layer (Black Dots)



Source: Corbin (2008)

MODPATH calculations were done to determine RTDFs. Corbin found that the water spent an average of 0.47 days travelling through the bottom layer, 0.48 days in the middle layer, and 0.43 days in the top layer, for a total of 1.38 days (Corbin, 2008). For areas of the wetland where flow was essentially stagnant, particles of water took >400,000 days to travel from the bottom to the top. Considering the theoretical residence time (t_{bar}) of 8.75 days, water appeared to be flowing through less than half of the volume of the cell (Corbin, 2008). Table 8 summarizes RTDF findings of Entingh (2002), Blalock (2003), and Corbin (2008).

Table 8: Summary of Hydraulic Residence Time Calculations

	Mean hydraulic residence time (τ)	Theoretical hydraulic residence time (t_{bar})
Entingh (2002)	Three days	Not calculated
Blalock (2003)	1.25 days	2.16 days
Corbin (2008)	1.38 days	8.75 days

To determine the theoretical hydraulic residence time, t_{bar}, Blalock (2003) and Corbin (2008) used the same equation:

$$t_{bar} = \frac{Vn}{Q} \tag{9}$$

Blalock (2003) reasoned that since 2/3 of the inflow was assumed to be leaking out the bottom of the wetland and only 1/3 was actually transiting the wetland, V should also be reduced by 2/3. Using a porosity (n) of 0.27, volume (V) of 651 m^3 x 1/3 = 217 m^3, and flow (Q) of 81.8 m^3 d^{-1} x 1/3 = 27.3 m^3 d^{-1}, he arrived at t_{bar} = 2.16 days (Blalock, 2003). Corbin (2008) used porosity of 0.5, volume of 523 m^3, and flow of 30.0 m^3 d^{-1} and arrived at t_{bar} = 8.75 days. Clearly, the reasoning of Blalock (2003) is flawed and the calculation of Corbin (2008) is more accurate.

Although there is significant variation in hydraulic residence time calculations between the three studies, all three came to the conclusion that hydraulic short-circuiting is a problem for the uVFTW at WPAFB. In chapter 3, a baseline model will be constructed similar to Corbin (2008). Various proposed engineering solutions to the problem of hydraulic short-circuiting will be incorporated into the model to determine their effectiveness at improving performance. The ability to evaluate ways of improving the performance of complex systems such as uVFTWs highlights the usefulness of the modeling approach.

III. Methodology

3.1 Overview

The purpose of this chapter is to explain the steps used to evaluate the relationship between uVFTW cell characteristics (hydraulics, layer depths, degradation rates, etc.) and the resulting treatment efficiency of the cell. The first step was to develop a model that simulates uVFTW operation. Model development began by recreating the flow model of Corbin (2008) using the MODFLOW and MODPATH modules of the Groundwater Modeling System (GMS). The flow model was then coupled with a transport code that simulates first-order chlorinated hydrocarbon degradation using first-order degradation rate constants from the literature. After development of the model, the model was used to quantify the sensitivity of simulated treatment efficiency to varying design and environmental parameter values. Finally, model simulations were run to determine the effectiveness of proposed engineering improvements at improving treatment efficiency.

3.2 Model Development

Groundwater Modeling Software (GMS) version 7.1.9 was the software package used for this research effort. It is the current version of the same software used in Corbin (2008). GMS is a user-friendly interface to MODFLOW-2005, a commonly used program used to model groundwater flow in three dimensions. MODFLOW is based upon a finite-differences solution to the following equation for groundwater flow (Harbaugh, 2005):

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right) + W = S_s\frac{\partial h}{\partial t} \qquad (17)$$

where,

K	Hydraulic conductivity along the x, y, and z axes [L T^{-1}]
h	Potentiometric head [L]
W	Source (W>0) or sink (W<0), volume water per unit volume per time [T^{-1}]
S_s	Specific storage of the media [L^{-1}]
t	time [T]

Since it is generally not possible to solve the equation for flow analytically, MODFLOW uses a finite-differences method which is based upon a finite set of discrete points and changes in head values between these points (Harbaugh, 2005). These points represent the center of cells, and the model space is thus represented as a matrix of cells. The equation for groundwater flow, expressed in finite difference form, is the balance of flows into and out of the cell set equal to the change in storage of the cell:

$$\sum Q_i = SS\frac{\Delta \mathrm{h}}{\Delta t}\Delta V \qquad (18)$$

where,

Q_i	Flow rate into the cell [L^3 T^{-1}]
SS	Specific storage [L^{-1}]
ΔV	Volume of the cell [L^3]
Δh	Change in head over time Δt

MODFLOW simulates steady state conditions by setting SS=0. The equation for flow then becomes:

$$\sum Q_i = 0 \tag{19}$$

which simply states that the sum of flows into and out of any cell must equal zero (Harbaugh, 2005). Solving a set of these algebraic equations for all cells in the matrix yields a numerical solution to the equation of flow. Using the finite differences method, flow into and out of cells is calculated according to Darcy's law:

$$q_{i,j-1/2,k} = KR_{i,j-1/2,k}\Delta c_i \Delta v_k \frac{(h_{i,j-1,k} - h_{i,j,k})}{\Delta r_{j-1/2}} \tag{20}$$

where,

$h_{i,j,k}$	head at node (center of cell) i,j,k [L]
$q_{i,j-1/2,k}$	flow rate through the face between cells i,j,k and i,j-1,k [L^3 T^{-1}]
$KR_{i,j-1/2,k}$	hydraulic conductivity along the row between nodes i,j,k and i,j-1,k [LT^{-1}]
$\Delta c_i \Delta v_k$	area of the cell faces normal to the direction of flow [L^2]
$\Delta r_{j-1/2}$	distance between nodes i,j,k and i,j-1,k [L]

The formulation of the subscripts allows similar expressions to characterize the flow through all six faces of each cell.

The design of the uVFTW at WPAFB lends itself to the grid approach to model design in MODFLOW. The model was designed as a grid of 36 cells by 72 cells, each

0.5m square, for a total grid dimension of 18m x 36m. The 1.7m depth of the wetland was structured as 10 layers, with properties outlined in Table 9.

Table 9: Grid Construction, Current Research

Description	Thickness (m)	Bottom	Top	Width x Length	Kh m d^{-1}	Kh/ Kv	Porosity
Layer 1, Const Hd boundary	0.10 (surface at cell center)	1.60	1.80	cells: 36 x 72 meters: 18 x 36	Interpo lated	1.0	0.3
Layer 2, Hydric soil	0.20	1.40	1.60	cells: 36 x 72 meters: 18 x 36	Interpo lated	1.0	0.3
Layer 3, Hydric soil	0.20	1.20	1.40	cells: 34 x 70 meters: 17 x 35	Interpo lated	1.0	0.3
Layer 4, Hydric soil	0.20	1.00	1.20	cells: 34 x 70 meters: 17 x 35	Interpo lated	1.0	0.3
Layer 5, Hydric soil / gravel	0.12	0.90	1.00	cells: 32 x 68 meters: 16 x 34	Interp 250	1.0	0.3
Layer 6, Hydric soil	0.20	.70	.90	cells: 32 x 68 meters: 16 x 34	Interpo lated	1.0	0.3
Layer 7, Hydric soil	0.20	.50	.70	cells: 30 x 66 meters: 15 x 33	Interpo lated	1.0	0.3
Layer 8, Hydric soil	0.18	.30	.50	cells: 30 x 66 meters: 15 x 33	Interpo lated	1.0	0.3
Layer 9, Gravel/soil mix	0.10	.20	.30	cells: 28 x 64 meters: 14 x 32	25	1.0	0.3
Layer 10, Gravel, influent	0.20	0.00	0.20	cells: 28 x 64 meters: 14 x 32	250 2.5e08	Kv= 250.0	0.3
Datum	0.00	0.00	0.00	n/a			

Layer Property Flow was used as the flow package, while the solver used was the Preconditioned Conjugate Gradient Method (PCG2). PCG2 was selected in favor of Strongly Implicit Procedure (SIP1) due to its superiority at handling dry cells (Harbaugh, 2005). For simplicity, precipitation and evapotranspiration were turned off.

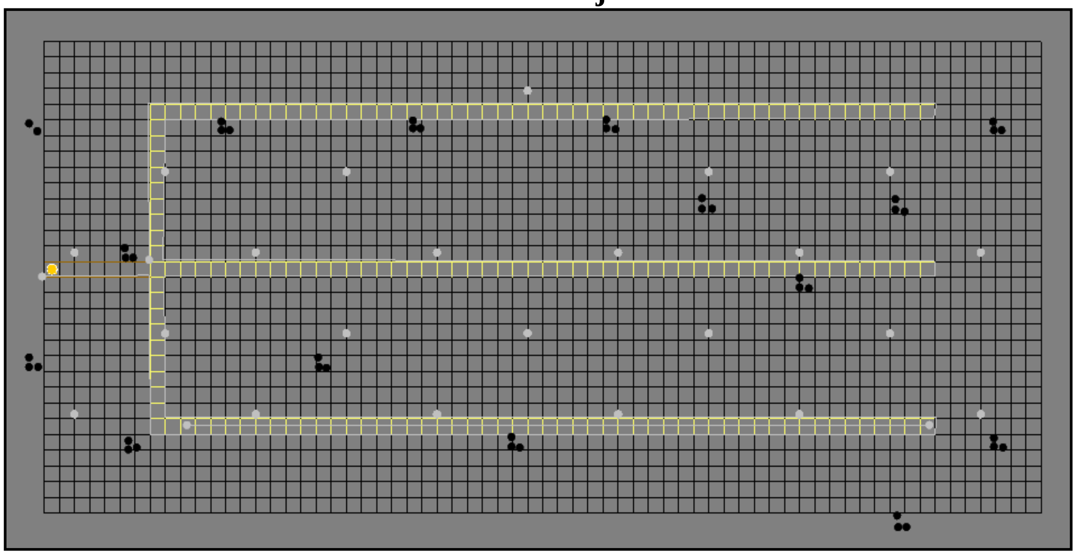
The constant head boundary in layer 1 was used to simulate the effluent weir removing water from the wetland. Head was set to 1.75m in layer 1, which is 0.05m above the center of the cell and represents that depth of standing water on the surface. Water entering layer 1 from below would have the effect of increasing head in the layer. MODFLOW simply removes this amount of water from the wetland model entirely in order to maintain head at the specified level. The drawback to this method is there is no central point from which to measure effluent contaminant concentration. Effluent concentration will be estimated in this research effort by averaging concentration data from the layer 1 cells.

Two other methods of removing water from the wetland were considered and rejected. The first was to model the effluent weir as an extraction well in layer 1. This was rejected due to the artificial effect an extraction well would have on flow. The second was to model the effluent weir as a drain cell. Water would flow out of the wetland if head was above a specified level, but no flow would occur if head was below the specified level. Although this is conceptually a better way to model the effluent weir, in practice the drain cell proved incapable of removing a sufficient quantity of water. Since the drain cell was located in layer 1, which was also the constant head boundary, the constant head boundary always removed more water than the drain cells.

Rather than model the influent piping using 153 injection wells arranged in three rows as was done in Corbin (2008), the influent pipes were modeled as 3 rows of highly permeable cells connected to one cell designated as an injection well (WEL1 package). The injection well was set to 29.3 $m^3 d^{-1}$ to reflect the total inflow (Figure 12).

Horizontal hydraulic conductivity in the influent rows was set to 2.5e08 m d^{-1}, which is six orders of magnitude higher than the surrounding gravel cells (250 m d^{-1}).

Figure 12: Influent Piping Modeled as 3 rows of Highly Permeable Cells Connected to One Injection Well



The purpose for this change to Corbin's (2008) approach was to more accurately model the effect of heterogenous permeability on what is, in effect, a multi-nodal injection well. If, for example, one of the three rows of influent piping was in highly permeable soil, then more of the total flow should flow into that row, and the other two rows would carry substantially less flow. Modeling the influent as separate injection wells does not allow this phenomenon to be simulated.

Another way to model the influent piping would be to use the Multi-Nodal Well package (MNW). This package is designed to simulate wells that are screened in more than one level. Unfortunately, the current package supported by GMS (MNW-1) does not simulate horizontal wells appropriately, and the new package (MNW-2) is not yet supported by GMS (Halford and Hanson, 2002).

The field measurements of head from Corbin (2008) were imported as an Observation Data Set. MODFLOW reported the difference between the calculated head values and the observed head values, within a user-specified standard deviation and confidence interval. This difference between calculated and actual head values, the sum of squared weighted residuals (SSWR), is the objective function MODFLOW uses to measure how close the calculated values are to the measured values. The lower the SSWR, the closer the calculated values are to the measured values.

Corbin (2008) estimated values of hydraulic conductivity from 16 measurements that were based on field slug tests and then calculated using the Hvorslev (1951) method (Table 10).

Table 10: Estimated Hydraulic Conductivity Values from Corbin (2008)

Label	X [m]	Y [m]	Z [m]	K_h [m d^{-1}]
1	5.2	2.8	1.54	.03915
2	4.7	3.2	1.16	.08123
3	4.7	2.8	0.78	51.1997
4	8.3	12.6	1.54	.0494
5	7.9	13.0	1.16	.02025
6	7.9	12.6	0.78	3.15456
7	17.9	10.3	1.53	.01962
8	17.4	10.7	1.16	.43693
9	17.4	10.3	0.78	8.19638
10	21.1	7.6	1.54	.07378
11	20.7	8.0	1.16	.82333
12	27.6	4.8	1.54	.46289
13	27.0	5.8	1.16	.05619
14	27.0	4.8	0.78	51.1997
15	30.2	13.0	1.16	.03187
16	30.2	12.6	0.78	11.1293

For comparison, Table 11 summarizes typical ranges of hydraulic conductivity for different soil types.

Table 11: Typical Values of Hydraulic Conductivity

Soil type	K_h [m d^{-1}], lowest	K_h [m d^{-1}], highest	Source
Silt	0.0001	1.7	(Domenico and Schwartz, 1990)
Clay	0.000001	0.0004	
Sand, fine	0.017	17.3	
Gravel	25.9	2592.0	
Soil	0.004	0.43	(Pardue, 2005)

Considering that the field measurements of Corbin (2008) are all made in the soil layers, it can be seen that the values at the elevation z = 0.78m are much higher than would be expected. When these 16 values are interpolated throughout every cell of the 3D grid, the effect of the large values is magnified, depending on the interpolation technique used (Appendix B).

Interpolation is a technique whereby calculated values are assigned to all cells based upon measured values of specific cells. Three of the more commonly used techniques are Shepard's Method, Gradient Plane Nodal Functions, and Kriging. All use the inverse distance weighting method, which is based on the assumption that cells closest to a measured value should be influenced more by that value than cells farther away (Aquaveo, 2010). They differ in that Shepard's Method constrains the interpolated data set to lie between the minimum and maximum of the measured values, while Gradient Plane Nodal technique produces values that include minima and maxima implied by the measured data. Gradient Plane Nodal should be a better technique than Shepard's Method, unless the measured data include significant outliers. These outliers result in minima and maxima that diverge even farther from actual values. Also, Gradient Plane Nodal will produce negative values, necessitating truncation of the data at a minimum level. Kriging differs from Shepard's Method and Gradient Plane Nodal in that the weights used in inverse distance weighting are a function of the measured values. The variances of the measured values are plotted against distance between the points in what is known as an experimental variogram. The model variogram is a best-fit trend line to the experimental variogram. The equation of the model variogram is used to compute the interpolation weights. Because the interpolation weights are mathematically determined by the spatial relationship of the variance of the measured data, Kriging is considered a more accurate method of interpolation (Aquaveo, 2010). Kriging was the only interpolation method used in this research.

Table 12 illustrates the differences in interpolated hydraulic conductivity data produce by the three techniques.

Table 12: Hydraulic Conductivity Estimates Produced by Three Interpolation Techniques

[m d^{-1}]	Shepard	Gradient	Kriging
Range	0.17 to 49.80	-167.5 to 237.9	-5.66 to 47.0
(truncated)	n/a	0.0001 to 237.9	0.0001 to 47.0
Mean	7.32	10.03	6.32
(truncated)	n/a	22.88	6.35
Median	5.66	1.39	4.83
(truncated)	n/a	1.39	4.83
Std Dev	5.57	50.06	6.37
(truncated)	n/a	38.10	6.34

A problem arose during model construction that necessitated significantly modifying the field data used by Corbin (2008). It was found that the observed head data set and the calculated hydraulic conductivity data set could not both be correct within the context of the uVFTW at WPAFB. Consider Darcy's Law:

$$Q = KA\nabla h \tag{3}$$

where,

Q	Volumetric flow rate [$L^3\ T^{-1}$]
K	Hydraulic conductivity [$L\ T^{-1}$]
A	Cross-sectional area perpendicular to the direction of flow [L^2]
∇h	Head gradient [-]

For the uVFTW at WPAFB, both Q and A are constant. Therefore, if hydraulic conductivity is very large, the head gradient has to be very small. Using values of hydraulic conductivity interpolated from the measured values of Corbin (2008), which the reader will recall were calculated based on slug tests and the Hvorslev (1951) method, and the known values of Q and A, it was possible to estimate a head gradient. The estimated head gradient was 0.006 [m m^{-1}], (1.76m at the bottom and 1.75m at the top of the wetland cell) which was much lower than the measured gradient. Since the head and hydraulic conductivity data were incompatible, and the head data were judged to be more accurate, the observed head data were retained and the hydraulic conductivity data were forced to match by simply dividing the measured values for conductivity by an appropriate constant before interpolating. This was done by trial and error until the summed squared weighted residuals (SSWR) between computed heads and observed heads was minimized. It was found that when the hydraulic conductivity values in layers 2 and 4 were divided by 15, and the hydraulic conductivity values in layer 6 were divided by 45, the SSWR was minimized. Dividing the hydraulic conductivity values by one constant did not produce a realistic head gradient and a single constant chosen to match the calculated and observed head values in the top two layers resulted in a large error in the bottom layer, and vice versa. This necessitated the use of a second constant for the bottom layer values of hydraulic conductivity. Table 13 summarizes the profile of interpolated hydraulic conductivity for the soil layers:

Table 13: Interpolated Hydraulic Conductivity Data

Range	0.0001 – 1.046 m d^{-1}
Mean	0.147 m d^{-1}
Median	0.114 m d^{-1}
Standard Deviation	0.140 m d^{-1}

This had the desired effect of producing a realistic head gradient between the lower level and the upper level while also retaining the hydraulic conductivity heterogeneity.

The interpolated hydraulic conductivity data set was then populated using the Layer Property Flow (LPF) module within MODFLOW. This had the effect of eliminating the gravel layer (Layer 10), as the original scatter data set did not include gravel layer measurements. To simulate a gravel layer, a value of 250.0 m d^{-1} for horizontal hydraulic conductivity was imposed on layer 10 after populating the LPF module with the interpolated data set. Vertical conductivity was estimated by setting the ratio $K_h/K_v = 1.0$ for all layers except layer 10. For layer 10, setting $K_h/K_v = 1.0$ would have resulted in overly high values for K_v for the highly permeable cells. For the gravel scenario, K_v was set directly (not as a ratio) at 250 m d^{-1}. For scenarios with no gravel layer, K_h/K_v was set to 1.0 for the entire layer 10 except the highly permeable influent cells. These were set to $K_h/K_v = 500{,}000{,}000$ so that $K_v = 0.5$ m d^{-1}, which produced $K_h/K_v \approx 1.0$.

Once the flow model was developed, contaminant transport was added to account for degradation. Contaminant transport was incorporated using RT3D, which is a submodule included within MT3DMS, which is itself a module of GMS. RT3D is a multi-species reactive transport model that is designed to simulate natural attenuation and bioremediation (Clement, 1997). RT3D incorporates seven different pre-programmed reaction modules, to simulate the more common contaminants and environmental conditions. The reaction module that will be used in this research effort is the aerobic/anaerobic model for PCE/TCE degradation (Clement, 1997). This module assumes first-order decay for all contaminants, and assumes that all decay happens in the aqueous phase (Clement, 1997). The user must specify first-order anaerobic degradation rate constants for PCE, TCE, DCE, VC, and ethene; as well as first-order aerobic degradation rate constants for TCE, DCE, VC, and ethene. The reaction kinetic equations for aerobic/anaerobic degradation, separated from the transport equations, are summarized as follows (Clement, 1997):

$$\frac{d[PCE]}{dt} = -\frac{K_P[PCE]}{R_P} \tag{21}$$

$$\frac{d[TCE]}{dt} = \frac{Y_{T/P}K_P[PCE] - K_{T1}[TCE] - K_{T2}[TCE]}{R_T} \tag{22}$$

$$\frac{d[DCE]}{dt} = \frac{Y_{D/T}K_{T1}[TCE] - K_{D1}[DCE] - K_{D2}[DCE]}{R_D} \tag{23}$$

$$\frac{d[VC]}{dt} = \frac{Y_{V/D}K_{D1}[DCE] - K_{V1}[VC] - K_{V2}[VC]}{R_V} \tag{24}$$

$$\frac{d[ETH]}{dt} = \frac{Y_{E/V}K_{V1}[VC] - K_{E1}[ETH] - K_{E2}[ETH]}{R_E} \tag{25}$$

$$\frac{d[Cl]}{dt} = \frac{Y1_{C/P}K_P[PCE] + Y1_{C/T}K_{T1}[TCE] + Y1_{C/D}K_{D1}[DCE] + Y1_{C/V}K_{V1}[VC]}{R_C} + \frac{Y2_{C/T}K_{T2}[TCE] + Y2_{C/D}K_{D2}[DCE] + Y2_{C/V}K_{V2}[VC]}{R_C} \qquad (26)$$

where,

[A]	Concentration of species A [mg L^{-1}]
K_1	1st order anaerobic degradation rate constant for species A [T^{-1}]
K_2	1st order aerobic degradation rate constant for species A [T^{-1}]
$Y_{B/A}$	Stoichiometric yield coefficient for the anaerobic reductive dechlorination of A to B, defined as the molecular weight of B divided by the molecular weight of A [-]
Y1, Y2	Stoichiometric yield coefficient for the anaerobic (1) or aerobic (2) production of chloride, defined as the molecular weight of chloride divided by the molecular weight of the species which produces it [-]
R_A	Retardation coefficient for compound A [-]

The user can accept the default K_1 and K_2 values for all layers, in which case both anaerobic and aerobic degradation would occur in all layers. Alternatively, the user can specify different K_1 and K_2 values for each layer. For anaerobic layers, K_2 would be set to zero, while for aerobic layers, K_1 would be set to zero. It can thus be seen from equations (21) to (26) that anaerobic decay is sequential, producing ethane and chloride as final end-products. Aerobic decay produces chloride directly without intermediate products.

In Chapter 2 it was demonstrated that Monod kinetics may be approximated as first-order as long as the concentration of the chlorinated ethene substrate in the influent is at least two orders of magnitude less than the values for K_s. Suarez and Rifai (1999) report the following values for K_s:

PCE:	12.00 mg/L
TCE:	19.00 mg/L
DCE:	28.00 mg/L
VC:	23.00 mg/L

Waldron (2007) reported an average influent concentration for PCE (S in equation 12) of 46.5 µg/L. Since this is less than the reported values of K_s by approximately three orders of magnitude, 1^{st} order degradation is a reasonable approximation. This approximation also assumes that biomass density (B in equation 12) is a constant. In other words, the microbial biomass population must be at steady state. Given that the WPAFB VFTW has been in operation for nine years, this seems reasonable.

In order to keep the model run times within reason, sorption was assumed not to occur, so R=1.0 in the above equations. Influent concentration was set to 1.0 mg L^{-1} for PCE, and 0.0 mg L^{-1} for all other species. Model run times were also limited to 30 days to prevent excessive run times. First order anaerobic degradation rate constants were 0.4 d^{-1} for PCE, 0.014 d^{-1} for TCE, 0.004 d^{-1} for DCE, 0.004 d^{-1} for VC, and , 3.08 d^{-1} for ethene. First order aerobic degradation rate constants were 0.0 d^{-1} for PCE, 0.78 d^{-1} for TCE, 0.90 d^{-1} for DCE, 1.85 d^{-1} for VC, and 0.001 d^{-1} for ethene. All were taken from literature reported values (Powell, 2010 and Suarez and Rifai, 1999). It was assumed that no anaerobic degradation occurred in the top two layers which were assumed to be well oxygenated. It was also assumed that aerobic degradation occurred only in the top two layers. Treatment efficiency was measured by percent reduction in total VOCs from the influent, where concentration was comprised solely of 0.006 mmol L^{-1} of PCE (1.0 mg L^{-1});

to layer 1, where the average molar concentration across the entire layer of PCE, TCE, DCE, and VC constituted a proxy for effluent concentration.

3.3 Sensitivity Analysis

Sensitivity analyses were conducted to see how varying design parameters and environmental parameters affect treatment efficiency. Specifically, baseline values for anisotropy, layer thickness, hydraulic conductivity, and degradation rate constants were varied to determine which parameters have the most effect on overall treatment efficiency. Because of the significant model run times for RT3D, sensitivity analyses were conducted using MODPATH residence times as a proxy for treatment efficiency. The exception to this was sensitivity analyses for degradation rates, which could not be run other than with RT3D.

- The baseline value for vertical anisotropy was $K_h/K_v = 1.0$; and values of 1.5, 2.0, 2.5, and 3.0 were run.
- Layer thickness. The original design called for 114 cm of hydric soil based on the observation cited by Amon et al. (2007) that the root zone of local fens extends down to at least 100 cm. It has since been observed that the root zone in the treatment wetland extends into the bottom layer (personal communication with Dr. Shelley). This may be oxygenating the entire depth of the wetland cell, reducing the anaerobic volume of the bottom layer. Increasing the depth of the treatment wetland may increase the effectiveness of anaerobic processes. Sensitivity analyses were run with wetland depths of 2.0 m and 3.0 m to test this.

- Hydraulic conductivity was varied by running every combination of $K_h = 0.2$ m d^{-1} in layers 1-8, $K_h = 2.0$ m d^{-1} in layers 1-8, $K_h = 25.0$ m d^{-1} in layer 10, $K_h = 250.0$ m d^{-1} in layer 10, and $K_h = 1000.0$ m d^{-1} in layer 10. Layer 9 was held constant at $K_h = 25.0$ m d^{-1}.
- For degradation rates, sensitivity analyses were run using mean values and upper-range values. Minimum values were not used, because these are typically zero (Suarez and Rifai, 1999). Table 14 summarizes values of degradation rate constants that were used.

Table 14: First Order Degradation Rate Constants Used in Sensitivity Analyses

Parameter	Variable	Mean [d^{-1}]	Maximum [d^{-1}]
PCE, anaerobic	K_p	0.01	0.80
TCE, anaerobic	K_{T1}	0.004	0.023
TCE, aerobic	K_{T2}	0.15	1.41
cDCE, anaerobic	K_{D1}	0.003	0.006
cDCE, aerobic	K_{D2}	0.59	1.15
VC, anaerobic	K_{V1}	0.001	0.007
VC, aerobic	K_{V2}	1.73	1.96

3.4 Model Application

The model was then applied to estimate the effectiveness of various engineering solutions at improving overall treatment efficiency.

- Omission of the gravel layer. Corbin (2008) showed most of the water moving laterally in the gravel layer to one area, then up from there (Figure 11). Omission of the gravel layer allowed a test of the hypothesis that lateral hydraulic conductivity would be reduced and flow would be biased upward from the point of injection.

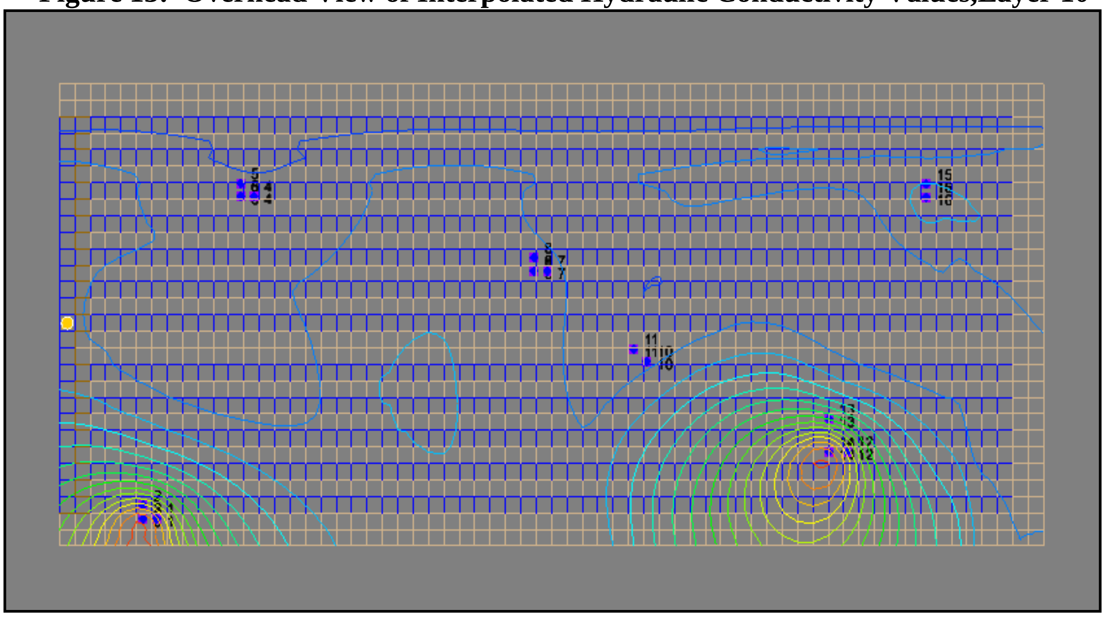
- Configuration of influent piping. With the gravel layer omitted, it may be necessary to inject the water via more than 3 PVC pipes in order to equally disperse the influent across the length and width of the cell bottom. Spacing the pipes 1m apart would allow 13 rows of influent piping to be placed in the bottom layer. Model runs will determine the impact of this design change.
- Mid-layer piping. A lattice network of 3” perforated PVC piping installed midway between the bottom and the top of the cell may “capture” high hydraulic head in one area and re-distribute it laterally throughout the cell. The upward flow may be more evenly distributed from that point. Alternatively, it may exacerbate hydraulic short circuiting by providing a high permeability route to the area of high hydraulic conductivity.
- Division of influent piping network into zones, each one linked to a surface-level shutoff valve. Individual zones could be shut off if it became apparent that hydraulic short-circuiting was occurring in a particular area of the treatment wetland.

IV. Results and Discussion

4.1 Overview

Figure 13 shows the hydraulic conductivity contours in Layer 10 obtained by kriging the 16 modified measured values of conductivity. The figure clearly shows two zones of high conductivity in layer 10. In cross-sectional view A-A, these zones will appear on the left side.

Figure 13: Overhead View of Interpolated Hydraulic Conductivity Values,Layer 10



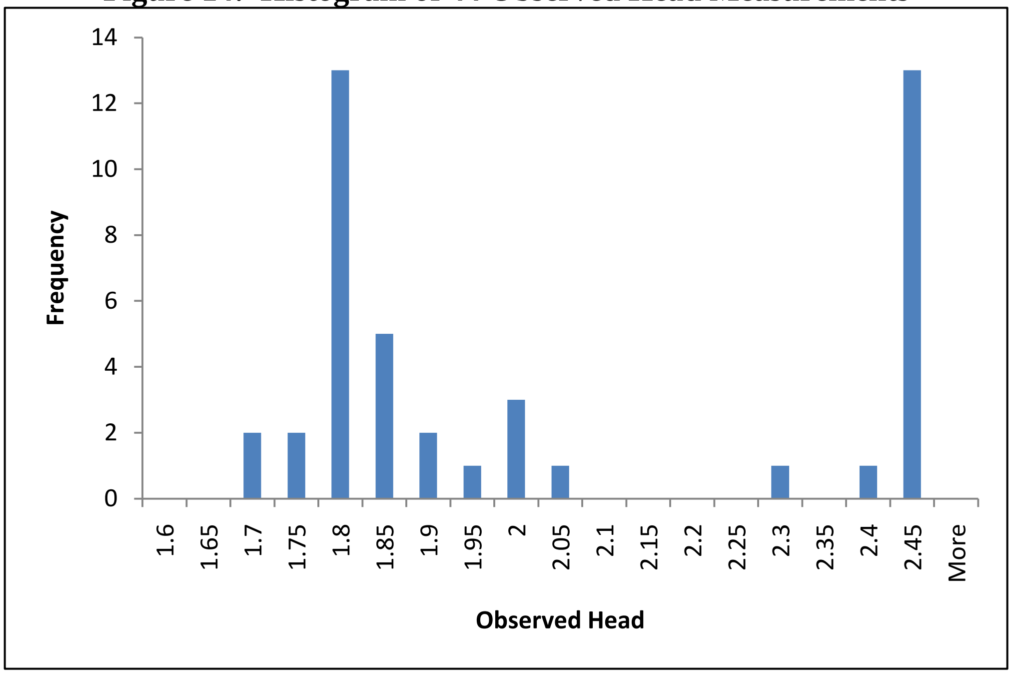
Using these values for hydraulic conductivity, MODFLOW calculated heads that ranged from 1.75m at the surface (the constant head boundary) and 2.40 m at depth, and matched the observed head values with a SSWR of 221 m^2. An additional check on the accuracy of the model was to ensure that the flow budget was accurate. Specifically, the percentage difference between inflows and outflows should be less than 1%. Also, total inflow should equal both the specified flow introduced at the injection well and the calculated outflow at the constant head boundary (Table 15).

Table 15: Baseline Model Flow Budget

	In flows [$m^3 d^{-1}$]	Out flows [$m^3 d^{-1}$]
Constant Heads	0.0	29.3
Wells	29.3	0.0
Totals:	29.3	29.3
Percent Difference:	0.001%	

The SSWR of 221 m^2 is significantly greater than the 20.5 m^2 achieved by Corbin (2008), but this is attributable to a statistical discrepancy between the two research efforts. The data set containing the observed head values requires the user to specify either the standard deviation of the values and the confidence level, or the user must directly specify the confidence interval. The computer then uses this information to decide how close the calculated values are to the observed values. It was discovered during model calibration that the standard deviation used in Corbin (2008) was almost twice the actual standard deviation as calculated directly from the observed head values (0.51 vs. 0.29). Furthermore, closer inspection of the data revealed two distributions (Figure 14). The lower distribution consisted of 29 of the 44 measurements, had a mean of 1.82 m, a standard deviation of 0.09 m, and looked roughly normal. The higher distribution contained the remaining 15 measurements, had a mean of 2.41 m, a standard deviation of 0.05 m, and appeared skewed left.

Figure 14: Histogram of 44 Observed Head Measurements



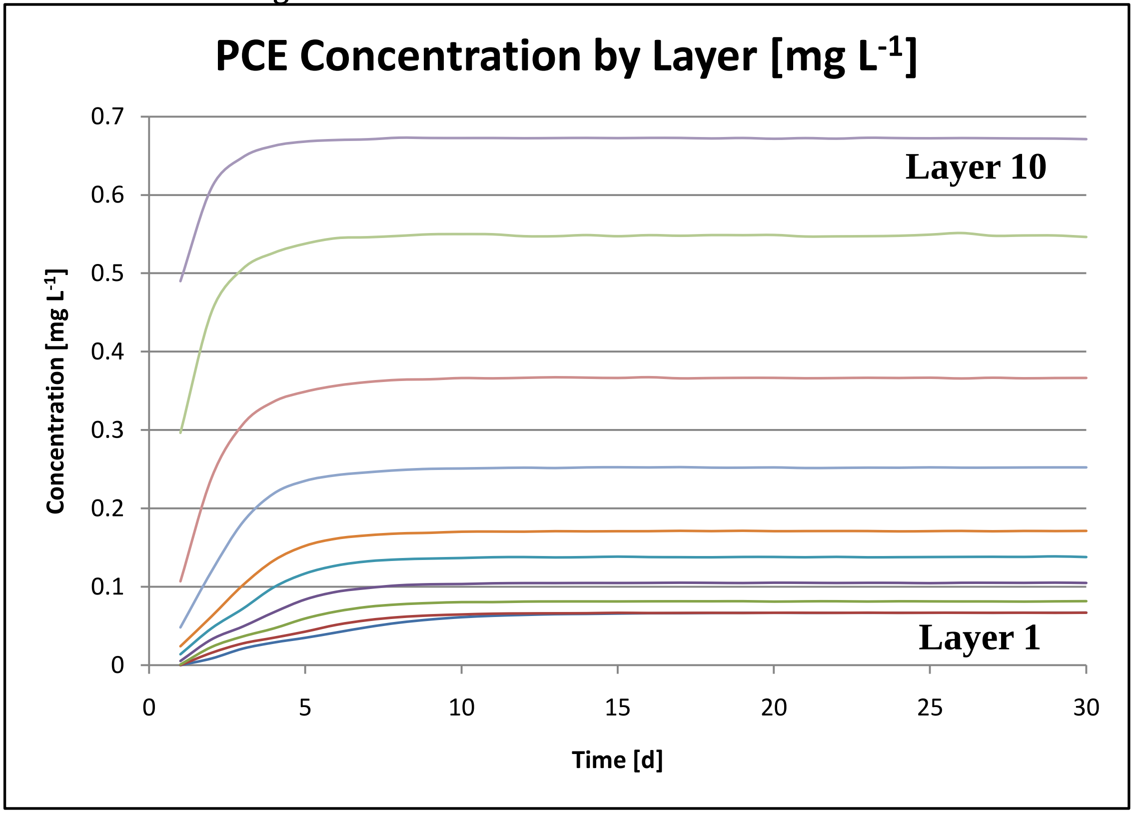
Source: Corbin (2008)

For this research effort, the observed head values for the approximately normally distributed data set were assigned the standard deviation of those data. GMS then calculated an interval of 2xSD, producing a 95% confidence interval. For the second data set, the broader criteria of Chebyshev's theorem were applied. For non-normally distributed data, Chebyshev's theorem states that, for $k>1$, at least $(1 - 1/k^2)$ of the values will fall within k standard deviations away from the mean (McClave et al., 2008). For example, 94% of the values will lie within 4 standard deviations from the mean (1 - 1/16 = 0.94). For the non-normally distributed data, a standard deviation of 0.10 was artificially imposed upon the values in order to produce an interval of 0.20, which is equivalent to 4 standard deviations.

GMS was able to match the n=29 set of observations (which were higher in elevation) within a 95% confidence interval. However, the lower elevation observations could not be matched unless the interval for these observations was directly specified at 0.5, approximately 10 times the standard deviation of the data.

Use of RT3D to evaluate contaminant degradation was severely limited by the computational time required for each model run. Minimum run times for 30 model-days were 12-14 hours, with some runs aborted when it became clear that they would take over 600 hours. Despite these limitations, useful mass and concentration data for models that simulated degradation were acquired. By inspection of Figure 15, it is clear that the model is at steady state, which allows a comparison of percent reduction in total VOCs versus mean hydraulic residence time. Comparing percent reduction in total VOCs for models of proposed design changes with the baseline model allowed an evaluation of the potential benefit of the proposed design change.

Figure 15: PCE Concentration Baseline Model



Initial RT3D runs were conducted with mean values for all degradation rate constants (Table 14). It was determined, based on high concentrations of total VOCs in layer 1 and the lack of correlation between percent removal and mean hydraulic residence time, that mean values were too low for the range of mean hydraulic residence times in the models. Consequently, all RT3D models were re-run using degradation rate constants that were an arithmetic average of the mean and the maximum values (Table 14).

Sensitivity analysis was conducted by varying parameters as outlined in chapter 3, and then comparing how either mean hydraulic residence time or contaminant mass destroyed was affected. Specifically, the percent change in the output parameter (the hydraulic residence time or mass destroyed) was divided by the percent change in the input parameter. The absolute value of the resultant number indicates insensitivity if close to zero, and sensitivity if greater than 1 (Table 16).

Table 16: Sensitivity Analyses Results

Input parameter	% change in mean HRT / % change in input parameter
Anisotropy	0.004 to 0.062
Layer thickness	0.978 to 1.094
Hydraulic conductivity	0.029 to 0.033
PCE rate constant	0.148
TCE rate constant	0.413
DCE rate constant	0.006
VC rate constant	1.379

The model is insensitive to changes in anisotropy and hydraulic conductivity, but sensitive to changes in layer thickness. The model is insensitive to degradation rate constants, with the exception of the rate constant for VC.

4.3 Model Outcomes of Proposed Design Changes

The baseline model, while based upon the uVFTW at WPAFB, is not intended to quantitatively simulate its hydraulic behavior or performance as a treatment reactor. A key aspect of this study is to demonstrate how modeling may be applied to investigate the potential impact of design changes on performance.

Of the seven different models that were evaluated, the baseline was the worst in terms of hydraulic performance. At 6.19 days, the mean hydraulic residence time was the lowest, which also produced the lowest cell volume utilization rate at 65.2% (Table 23). In a MODPATH release of approximately 1,000 particles, 88.9% of them had hydraulic residence times less than the nominal hydraulic residence time of 9.50 days (calculated based on flow of 29.3 m^3 d^{-1}, porosity of 0.30, and wetland volume of 928 m^3). The residence time distribution function (Figure 16) shows characteristic short-circuiting (RTDFs for the remaining models appear in Appendix A). Degradation results for the Baseline Model are summarized in Table 17.

Figure 16: RTDF for Baseline Model

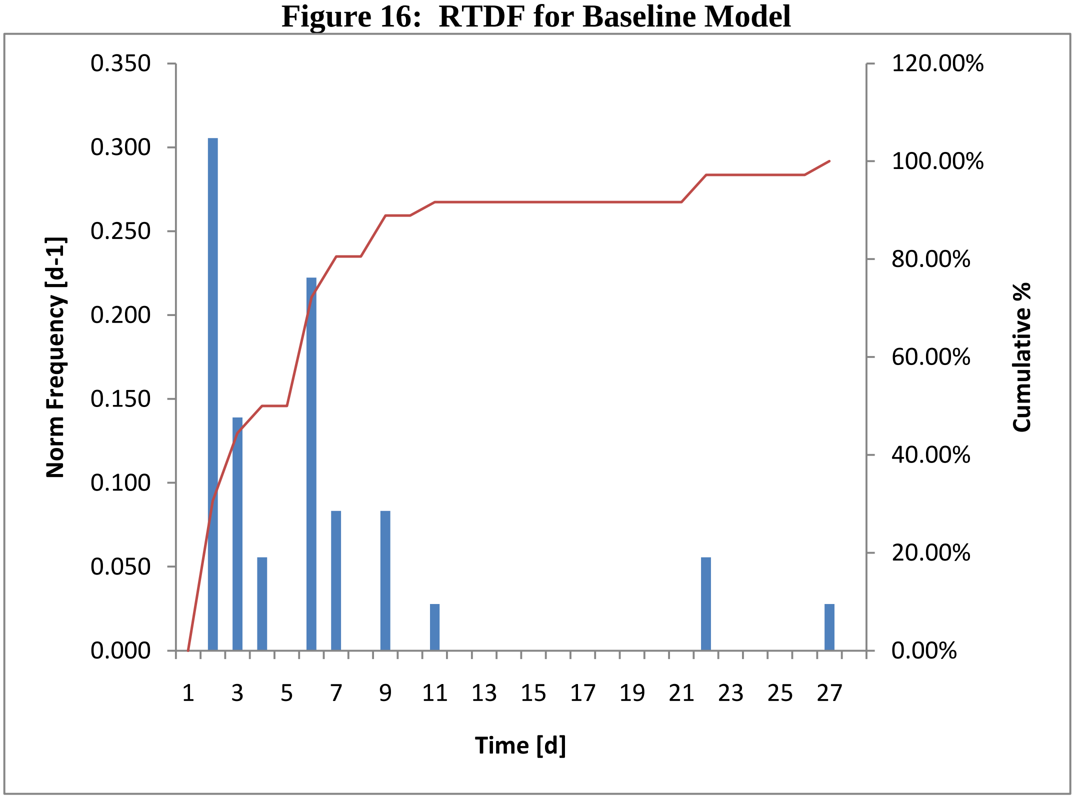


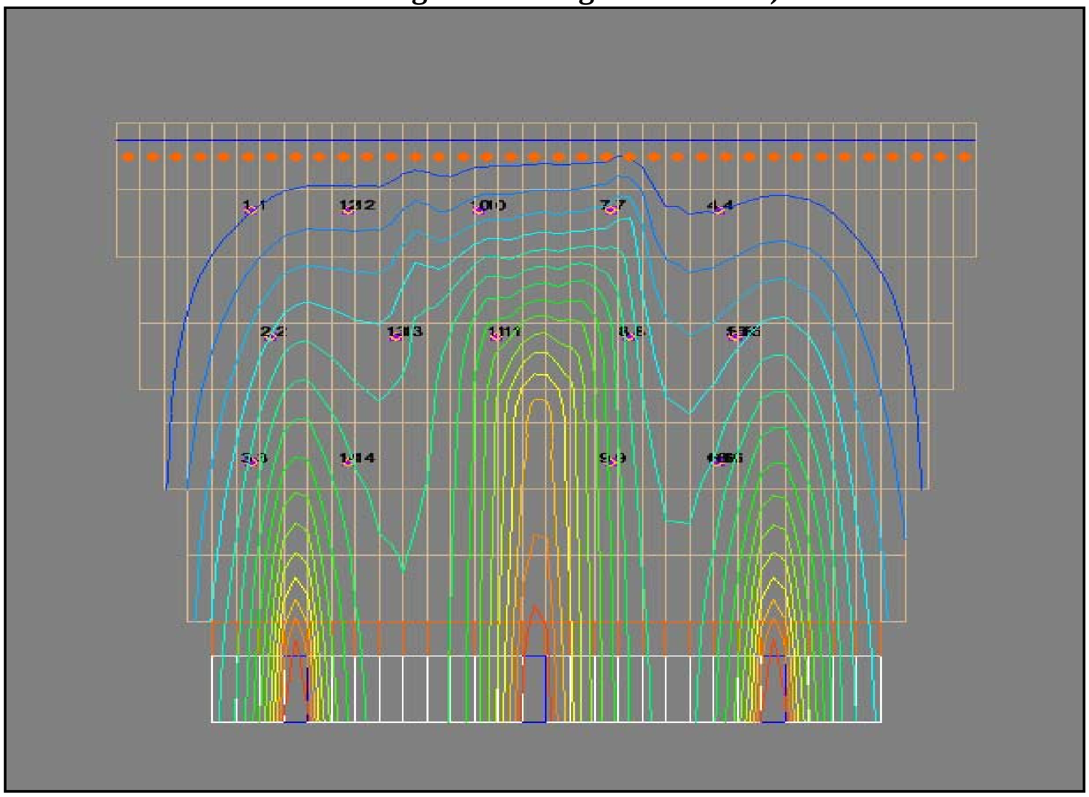
Table 17: Baseline Model Degradation Results

	PCE	TCE	DCE	VC	% Reduction Total VOCs
Baseline [mg L^{-1}]	0.067	0.086	0.004	1.42E-05	81.7%

These destruction efficiencies will serve as the basis for evaluating the effectiveness of subsequent models.

Omission of the gravel in layer 10 (No Gravel, 3 Pipes model) had a slight improvement on hydraulic performance. The mean hydraulic residence time increased to 6.89 days, while cell volume utilization increased to 72.5%. Removing the gravel, but leaving in place the three influent pipes seems to have had the effect of “focusing” the head on three narrow bands of soil centered directly above each influent pipe, decreasing mean hydraulic residence time (Figure 17). Omitting the gravel in layer 10 does seem to have reduced the impact of the zone of high hydraulic conductivity, which is centered above the left-hand influent pipe in Figure 17. All three of the spike-shaped head profiles demonstrate a bias toward upward flow. It should be noted that this model was tested only to evaluate the impact of changing this one design parameter, and was never recommended as a design improvement.

Figure 17: Head Profiles from No Gravel, 3 Pipes Model (Section View A-A: Looking Down Longitudinal Axis)



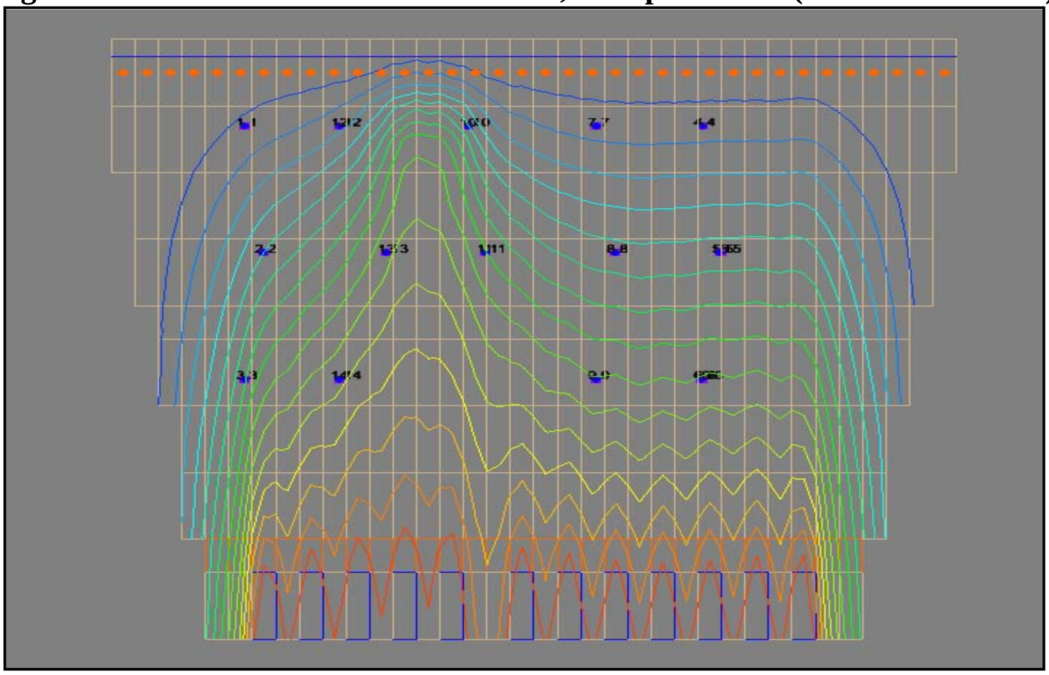
Degradation data for the No Gravel, 3 Pipes model were improved over baseline. Layer 1 concentration was lower than the baseline concentrations for all species, and the reduction in total VOCs was improved from 81.7% to 89.6% (Table 18).

Table 18: Degradation Data for the No Gravel, 3 Pipes Model

	PCE	TCE	DCE	VC	% Reduction Total VOCs
Baseline [mg L^{-1}]	0.067	0.086	0.004	1.42E-05	81.7%
No Gravel 3 Pipes [mg L^{-1}]	0.044	0.044	0.002	0.94E-05	89.6%

The next model, No Gravel 12 Pipes, differs from the prior model in that 12 influent pipes are used instead of 3. The improvement in the hydraulic performance was dramatic, with mean hydraulic residence time increasing 50% to 9.40 days, just slightly below the nominal hydraulic residence time of 9.50 days. Cell volume utilization increased to 99.0%. Instead of the three spike-shaped head profiles seen in the No Gravel 3 Pipes model, a much more evenly distributed head profile is demonstrated (Figure 18). The effects of the zone of high hydraulic conductivity can be seen slightly to the left of center in the figure.

Figure 18: Head Profiles from No Gravel, 12 Pipes Model (Section View A-A)



Despite the improvement in hydraulic residence time, the reduction in total VOCs was not significantly better than the No Gravel 3 Pipes model (compare Table 19).

Table 19: Degradation Data for the No Gravel, 12 Pipes Model

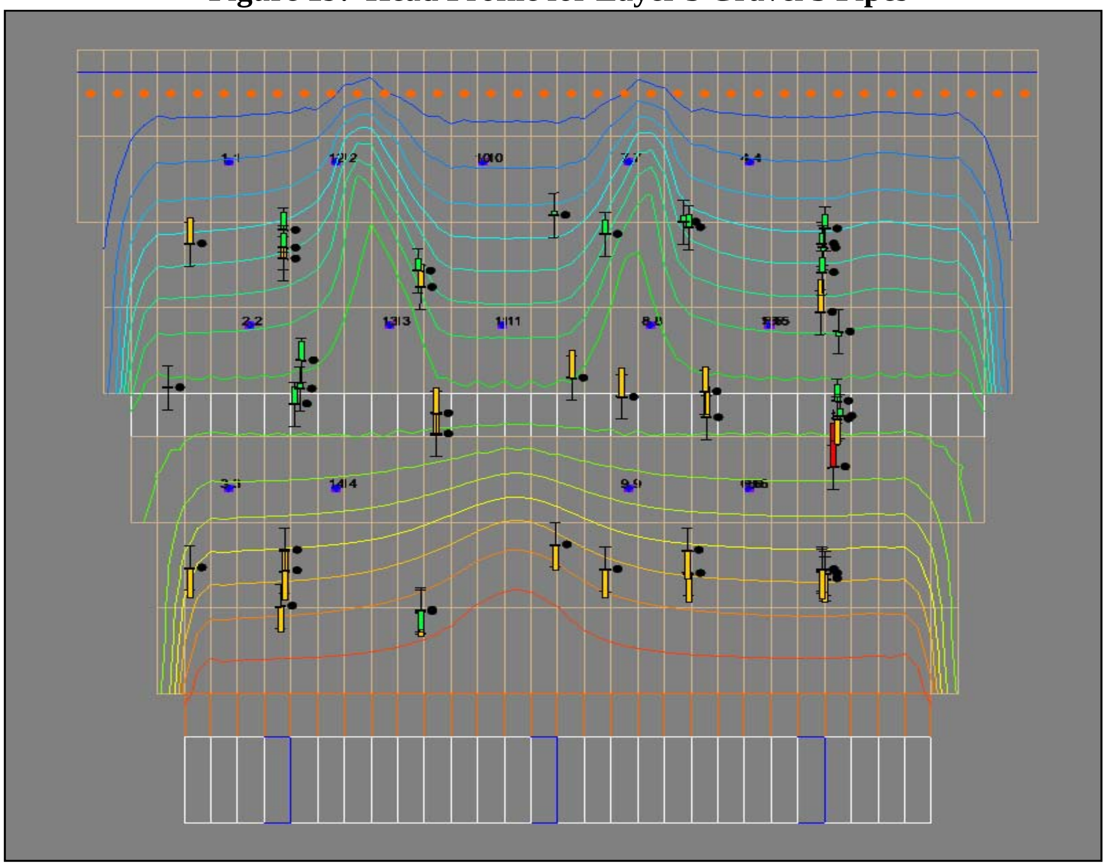
	PCE	TCE	DCE	VC	% Reduction Total VOCs
Baseline [mg L^{-1}]	0.067	0.086	0.004	1.42E-05	81.7%
No Gravel 12 Pipes [mg L^{-1}]	0.028	0.052	0.003	1.32E-05	90.2%

The second proposed design change was to incorporate a layer of gravel or perforated PVC pipes midway between the top and bottom of the wetland. Such a design would create a zone of very high horizontal hydraulic conductivity and would possibly serve to redistribute differences in head from areas of high head to low head. In the Layer 5 Gravel model, horizontal hydraulic conductivity in layer 5 was set to 250,000,000 m d^{-1}, a value high enough to reflect a layer of perforated PVC pipes laid side-by-side in gravel. Layer 10 was gravel, and three influent pipes were used.

The improvement in hydraulic performance was similar to the No Gravel 12 Pipes model. Mean hydraulic residence time increased to 9.44 days and cell volume utilization increased to 99.4%. Some of the improvement in hydraulic residence time was probably attributable to significant tailing in the RTDF, which appears heavy enough to pull the mean to the right. This is supported by the observation that the percentage of MODPATH particles with hydraulic residence time less than the nominal hydraulic residence time was greater in the Layer 5 Gravel model compared to the No Gravel 12 Pipes model, even though mean hydraulic residence time was greater in the Layer 5 Gravel model.

Qualitatively, introducing gravel for Layer 5 did produce a significant change in the head profile (Figure 19). It was anticipated that the Layer 5 Gravel could produce this change in head profile while also decreasing the hydraulic performance of the model, which appears to have happened for this model. The inclusion of gravel in an actual wetland would have required different soil placement techniques than were used in the construction of the uVFTW at WPAFB. This would probably have produced different distributions of hydraulic conductivity in the soil on top of the gravel layer compared to the soil below the gravel layer, and would have produced different results than those predicted by the model, which assumed the hydraulic conductivity of all layers, except for Layer 5, was unchanged.

Figure 19: Head Profile for Layer 5 Gravel 3 Pipes



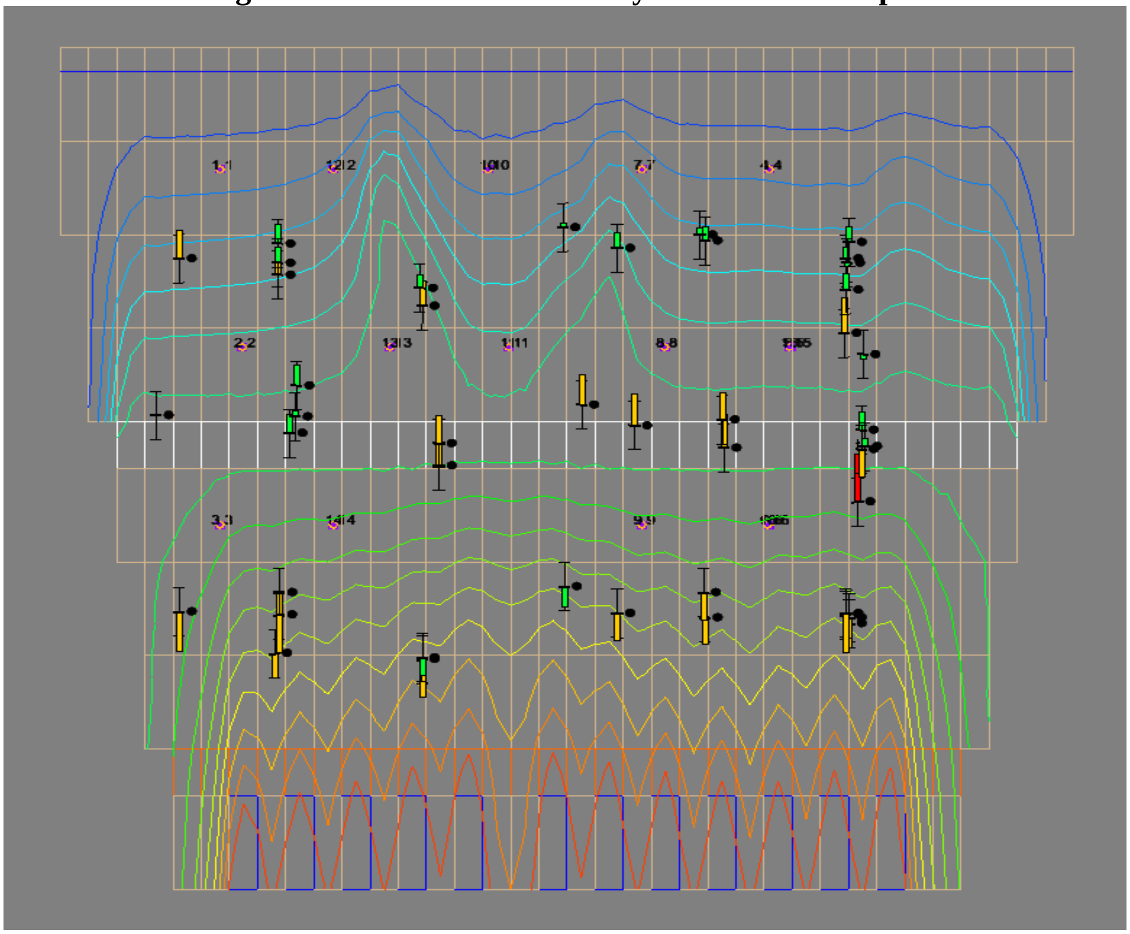
Degradation data for the Layer 5 Gravel model are listed in Table 20. Degradation was better for all species except VC, and % reduction in total VOCs was comparable to the No Gravel 12 Pipes model.

Table 20: Degradation Data for the Layer 5 Gravel Model

	PCE	TCE	DCE	VC	% Reduction Total VOCs
Baseline [mg L^{-1}]	0.067	0.086	0.004	1.42E-05	81.7%
Layer 5 Gravel 3 Pipes [mg L^{-1}]	0.027	0.051	0.003	1.62E-05	90.2%

The next model, Layer 5 Gravel 12 Pipes, combined what seemed to work so well in the prior two models. Layer 10 gravel was removed, 12 influent pipes were used instead of 3, and the Layer 5 high hydraulic conductivity zone was incorporated. While the improvement in hydraulic performance was still significant, the model did not perform as well as either No Gravel 12 Pipes or Layer 5 Gravel. Mean hydraulic residence time was 9.16 days, and cell volume utilization was 96.4%. Notably, however, the percentage of MODPATH particles with hydraulic residence time less than the nominal hydraulic residence time was the second lowest of all the models, indicating that the relatively low mean hydraulic residence time is probably due to a few MODPATH particles with very low hydraulic residence times rather than an overall leftward shift in the RTDF. This is supported qualitatively by the appearance of the RTDF (Appendix A). The effect of the layer 5 gravel is still observed in the head profile (Figure 20).

Figure 20: Head Profile for Layer 5 Gravel 12 Pipes



Degradation data were better than the Baseline model and similar to the other two models examined so far. The concentration of VC went down in this model, whereas it went up in the prior model (compare Table 21).

Table 21: Degradation Data for the Layer 5 Gravel 12 Pipes Model

	PCE	TCE	DCE	VC	% Reduction Total VOCs
Baseline [mg L^{-1}]	0.067	0.086	0.004	1.42E-05	81.7%
Layer 5 Gravel 12 Pipes [mg L^{-1}]	0.027	0.053	0.003	1.01E-05	90.0%

The final proposed design change was to incorporate shutoff valves within each row. If zones of hydraulic short-circuiting were identified during system operation, the influent pipes under those zones could be shut off, redirecting the flow to the remaining open influent pipes. The models that evaluate this proposed design change, 1 Pipe Shutoff and 4 Pipes Shutoff, were constructed so that an entire row (oriented along the longitudinal axis of the wetland), would have to be shut off. However, it is easy to imagine any number of configurations, similar to in-ground sprinkler system designs, which would allow small regions of the wetland to be shut off.

Shutting off entire rows was a good test design given the nature of the hydraulic conductivity heterogeneity (Figure 13). The hydraulic conductivity values showed two zones of high hydraulic conductivity – one centered above row 30, and the other centered above rows 24-30. The 1 Pipe Shutoff model shut off the influent pipe in row 30, while the 4 Pipes Shutoff model shut off the influent pipes in rows 24-30.

1 Pipe Shutoff performed better than baseline, with a mean hydraulic residence time of 8.62 days and percent cell volume utilization of 90.7%. 4 Pipes Shutoff produced a mean hydraulic residence time of 17.45 days, and a cell volume utilization rate of 183.7%. This high value however, was attributable to significant tailing. A few

MODPATH particles had residence times of 130-277 days. This indicates that the high mean hydraulic residence time was due to stagnant or cycling flow. Despite this, the 4 Pipes Shutoff model was the best performer in terms of the percentage of MODPATH particles with hydraulic residence time greater than the nominal hydraulic residence time, at 36.7%.

Degradation performance of the two models was better than the Baseline model for all species and for % reduction in total VOCs. However, the 4 Pipes Shutoff model performed slightly worse than all the other designs as measured by % reduction in total VOCs (Table 22).

Table 22: Degradation Data for the Pipes Shutoff Models

	PCE	TCE	DCE	VC	% Reduction Total VOCs
Baseline [mg L^{-1}]	0.067	0.086	0.004	1.42E-05	81.7%
1 Pipe Shutoff [mg L^{-1}]	0.027	0.053	0.003	1.36E-05	90.1%
4 Pipes Shutoff [mg L^{-1}]	0.033	0.058	0.003	1.02E-05	88.8%

A summary of hydraulic performance and degradation performance data for all models is shown below (Table 23).

Table 23: Summary of Hydraulic and Degradation Data for All Models

	Base-line	No Gravel, 3 Pipes	No Gravel, 12 Pipes	Layer 5 Gravel, 3 Pipes	Layer 5 Gravel, 12 Pipes	1 Pipe Shutoff, 12 Pipes	4 Pipes Shutoff, 12 Pipes
nominal hydraulic residence time [d]	9.50						
tau [d]	6.19	6.89	9.40	9.44	9.16	8.62	17.45
variance [d^2]	34.6	41.6	56.5	103.6	35.2	30.0	514.1
dimensionless variance [-]	0.90	0.88	0.64	1.16	0.42	0.40	1.69
% actual HRT < nominal HRT	88.9%	83.3%	72.2%	77.8%	68.3%	75.3%	63.3%
% volume utilization	65.2%	72.5%	99.0%	99.4%	96.4%	90.7%	183.7%
Average time layer 1-4 [d]	2.12	2.72	2.98	3.39	3.95	3.01	4.66
Average time layer 5 [d]	0.35	0.46	0.47	1.70	0.75	0.47	0.86
Average time layer 6-9 [d]	2.25	3.10	3.07	3.64	3.97	3.13	4.85
Average time layer 10 [d]	0.57	0.71	0.78	0.91	0.96	0.72	1.38
Total [d]	5.28	7.00	7.30	9.64	9.63	7.33	11.75
% Reduction Total VOCs	81.7%	89.6%	90.2%	90.3%	90.0%	88.8%	95.6%
Layer 1 Concentration PCE [$mg\ L^{-1}$]	0.067	0.044	0.028	0.027	0.027	0.027	0.033
Layer 1 Concentration TCE [$mg\ L^{-1}$]	0.086	0.044	0.052	0.051	0.053	0.053	0.058
Layer 1 Concentration DCE [$mg\ L^{-1}$]	0.004	0.002	0.003	0.003	0.003	0.003	0.003
Layer 1 Concentration VC [$mg\ L^{-1}$]	1.42E-05	0.94E-05	1.32E-05	1.62E-05	1.01E-05	1.36E-05	1.02E-05
Note: "% actual HRT < nominal HRT" is the percentage of MODPATH water particles in a release of a total of 1,000 particles that had a residence time less than the nominal hydraulic residence time. The measure is useful in determining if a RTDF with a high tau due to significant tailing actually represents an improvement over baseline.							

The MODPATH average time by layer data show that the water spent an average of 1.70 days in layer 5 in the Layer 5 Gravel model (Table 23). This is almost five times the 0.35 days spent in layer 5 for the baseline model, and exceeds every other model.

Comparing Figure 19 and Figure 17, it appears that the layer 5 gravel is having the intended effect of capturing and redistributing the three spike-shaped head profiles observed in the No Gravel 3 Pipes model. Furthermore, the effect occurs well below layer 5.

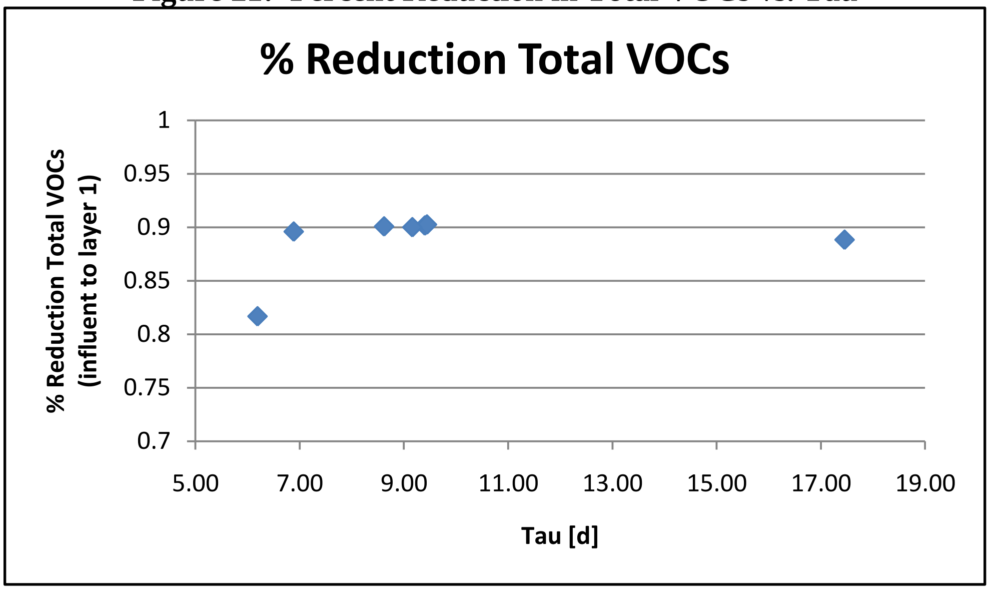
The average time spent in layer 5 in the Layer 5 Gravel 12 Pipes model was anticipated to be close to the 1.70 days observed in the Layer 5 Gravel 3 Pipes model, but the value was only 0.75 days. While this is greater than the values for the other models, with the exception of the 4 Pipes Shutoff model, it is less than half the value for the Layer 5 Gravel model. This is due to the much more evenly distributed head profile observed in the Layer 5 Gravel model with 12 influent pipes compared to the 3 influent pipes model (the orange contour line in Figure 20 barely extends into layer 8, while the same contour line in Figure 19 extends well into layer 8). The high value for the Layer 5 Gravel 3 Pipes model was caused by the time required by the layer 5 gravel to laterally dissipate this differential head, while the relatively low value observed in the Layer 5 Gravel 12 Pipes model is due to the lower head differential.

All models achieved significant improvements over baseline with respect to hydraulic performance. Mean hydraulic residence time increased significantly (between 8.62 to 9.44 days, compared to 6.19 days under the Baseline Model), and the percentage of MODPATH water particles with hydraulic residence time less than the nominal hydraulic residence time also decreased (between 68.3% to 77.8%, compared to 88.9% under the Baseline Model).

With the exception of degradation of VC in the Layer 5 Gravel 3 Pipes, all models performed better than baseline with respect to treatment efficiency, as measured by layer

1 contaminant concentration. Figure 21 is a graph of percent reduction in total VOCs vs. mean residence time.

Figure 21: Percent Reduction in Total VOCs vs. Tau



Although the expected jump in % reduction in total VOCs is seen, almost the entire increase in treatment efficiency occurs over a very small increase in mean hydraulic residence time, from 6.19 days to 6.89 days. Between 6.89 days and 17.45 days, treatment efficiency is essentially unchanged.

To examine this, we make use of Equation (27), which can be used to predict the course of any first-order irreversible reaction, given only the residence time distribution function and the reaction rate constant (Clark, 2009).

$$1-\frac{C_{out}}{C_{in}}=1-\int_0^{\infty}\exp(-kt)\,f(t)\,dt \qquad (27)$$

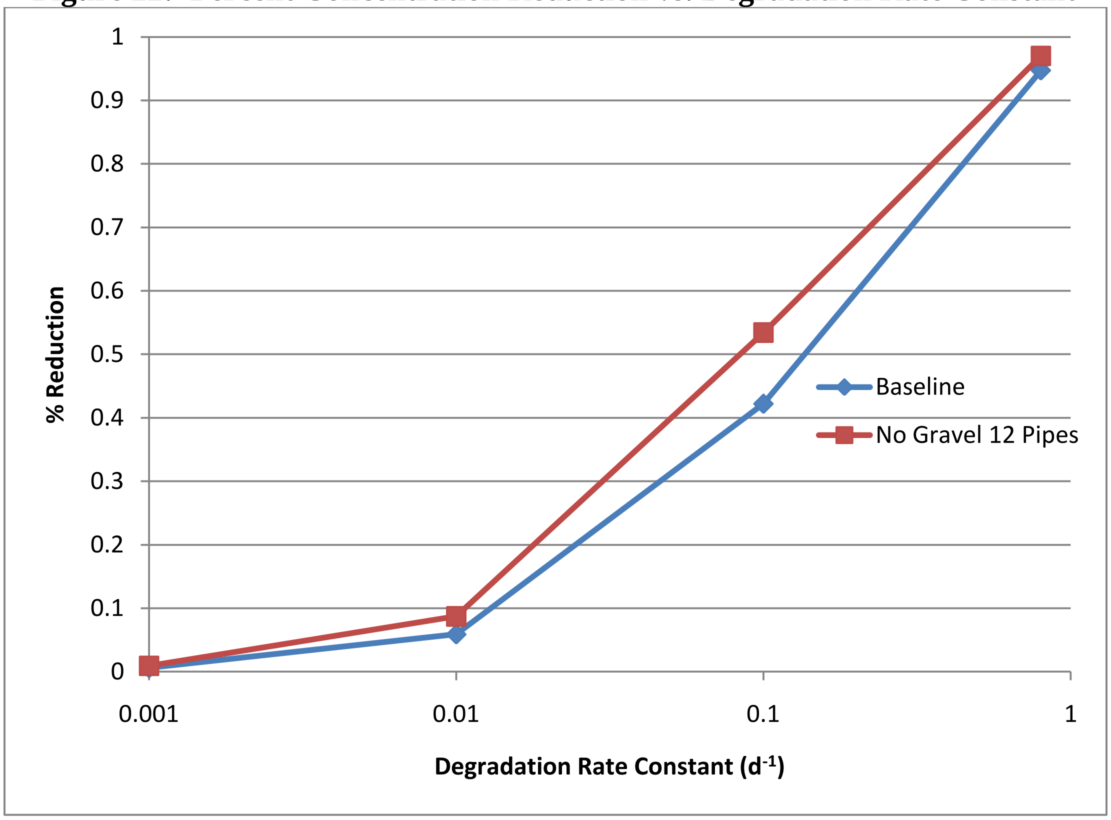
where,

$1-\frac{C_{out}}{C_{in}}$:	Reduction in contaminant concentration C [-]
k:	Degradation rate constant [d^{-1}]
f(t):	Residence Time Distribution Function [T^{-1}]

Equation (27) assumes only one contaminant with only one degradation rate constant, which doesn't apply to the current case, where sequential decay and multiple degradation rate constants are modeled. However, for purposes of illustration, Equation (27) was applied to the Residence Time Distribution Functions for both the Baseline model (tau = 6.19 days) and the No Gravel 12 Pipes model (tau = 9.40 days) with four degradation rate constants (0.001, 0.01, 0.1, and 0.8 d^{-1}) which roughly correspond to the range of degradation rate constants for anaerobic decay of PCE (Suarez and Rifai, 1999). Figure 22 displays the results. At very low values for k, there is no appreciable difference between the two models (0.006% for the Baseline model, 0.009% for the No Gravel 12 Pipes model). This is because for the values of tau used in the two models, the degradation time scale, as approximated by the reciprocal of the rate constant, is too large to show any difference between the models. At very high values for k, there is also no appreciable difference between the two models (94.7% for the Baseline model, 97.0% for the No Gravel 12 Pipes model). This is because the degradation time scale is much smaller than tau. It is only when the values of tau (6.19 and 9.40 days) and the degradation time constant (10 days) are similar that there is a noticeable difference in performance predicted by the two models (42.2% for the Baseline model, 53.4% for the No Gravel 12 Pipes model).

The behavior of Figure 21 is now understood in terms of the relationship between tau, which ranges from 6.19 days to 17.45 days; and the degradation constant, which can be approximated by the value used for anaerobic decay of PCE in the model, 0.40 d^{-1}. The time constant for this value is approximately 2.5 days, so an increase in tau from 6.19 to 6.89 is significant, while an increase from 9.40 to 17.45 is not.

Figure 22: Percent Concentration Reduction vs. Degradation Rate Constant



V. Conclusions and Recommendations

5.1 Summary

The goal of this research effort was to investigate how the hydraulics of uVFTWs affects treatment efficiency. Specifically, the impact of hydraulic short-circuiting upon treatment efficiency was examined. Several engineering design changes were also evaluated with respect to their impact on the hydraulic behavior of the uVFTW and their impact on treatment efficiency. This study confirms the existence of hydraulic short-circuiting determined by prior research by Entingh (2002), Blalock (2003), and Corbin (2008). Furthermore, this study suggests that some simple design changes, such as omitting the bottom layer gravel and introducing the influent via 12 influent pipes instead of 3, would significantly improve the hydraulic performance of the uVFTW. The impact on treatment efficiency of the improvement in hydraulic performance is significant, but occurs over a very small increase in mean hydraulic residence time, from 6.19 days to 6.89 days. Further increases in mean hydraulic residence time, even approaching the nominal hydraulic residence time, result in minimal increases in treatment efficiency.

The key insight of this research is that, during the design or pilot-scale stage of uVFTW development, studies must be conducted to quantify contaminant degradation kinetics to determine an appropriate range of hydraulic residence time to ensure that the uVFTW operates at an optimum level. It should be noted that improving the mean hydraulic residence time into the range where further increases in treatment efficiency do not appear is not necessarily undesirable. However, when the design changes necessary to bring about such hydraulic improvements are costly, they should be avoided.

5.2 Study Strengths, Weaknesses, and Limitations

The main strength of this study was its use of state-of-the-art modeling techniques to simulate the potential impact of alternative uVFTW designs on performance. The wetland model enabled us to evaluate how design changes resulted in changes in hydraulic performance, and how hydraulic performance impacted overall treatment efficiency. These results should therefore be helpful in guiding designs of future uVFTWs.

The main limitation of this study was that, as a modeling study, there is no assurance that the model reflects reality. The uVFTW at WPAFB and the prior research conducted into the degradation and hydraulics inspired the current research, but there was no quantitative match to either the hydraulic performance or the degradation profile of the wetland. Furthermore, all models have built-in assumptions which may lead to invalid results. Assumptions such as isotropy may need to be examined more carefully in conjunction with a careful analysis of the construction techniques used in building the wetland.

5.3 Recommendations for Future Study

The proposed engineering solutions suggested in this study required only imagination to develop. Presumably there are many other possible solutions, and these could be tested in future studies using the same approach taken in this study. One idea to test is to lay down sheets of impermeable geomembrane within the wetland, with layers of dirt separating them. With the proper design, water should be forced to flow in a serpentine manner back and forth as it moves upward through the wetland (think waiting in line at Disneyland). This should increase hydraulic residence time.

Studies could be conducted focusing on RT3D to model degradation. RT3D allows incorporation of factors such as substrate limitations, rhizosome oxygenation, and oxidation-reduction conditions. This would require significantly more computational power than a typical desktop has, as well as specific programming of RT3D.

For any research effort involving the use of modeling software, the student should seek out training in the use of that software as early as possible. If GMS is used, training should be sought out for MODFLOW and GMS, including appropriate sub-modules of both MODFLOW and GMS.

5.4 Conclusion

This study has demonstrated that some proposed engineering solutions to the problem of hydraulic short-circuiting could be effective at mitigating the problem, while also improving treatment efficiency. The conclusion that can be drawn from this is that some of the proposed engineering solutions should be incorporated into future uVFTW designs. Omitting the bottom gravel layer and introducing the influent via many tightly spaced pipes rather than a few pipes with more space between them; and incorporating shutoff valves so that small sections of the influent piping can be shut down if hydraulic short-circuiting is later discovered in a particular area of the wetland; are two specific design changes that are general enough to be included in future wetland designs.

Given that the proposed engineering solutions are inexpensive and easy to incorporate into future designs, there is value in conducting model studies of the effectiveness of such proposed solutions, regardless whether the outcome is positive or negative. Also, degradation kinetics need to be quantitatively understood in order to determine an optimum range for hydraulic residence time, and to ensure that resources are not wasted in an attempt to improve hydraulic performance where no improvement in degradation performance will be achieved. Hopefully, this study will serve to guide designs of future uVFTWs.

Appendix A: Residence Time Distribution Functions

Figure 23: RTDF No Gravel 3 Pipes Model

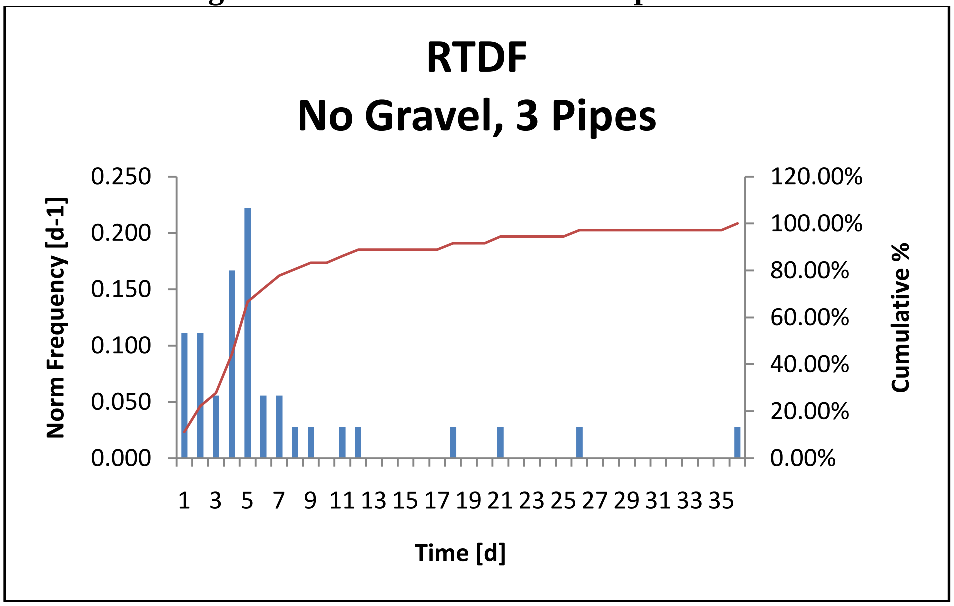


Figure 24: RTDF No Gravel 12 Pipes Model

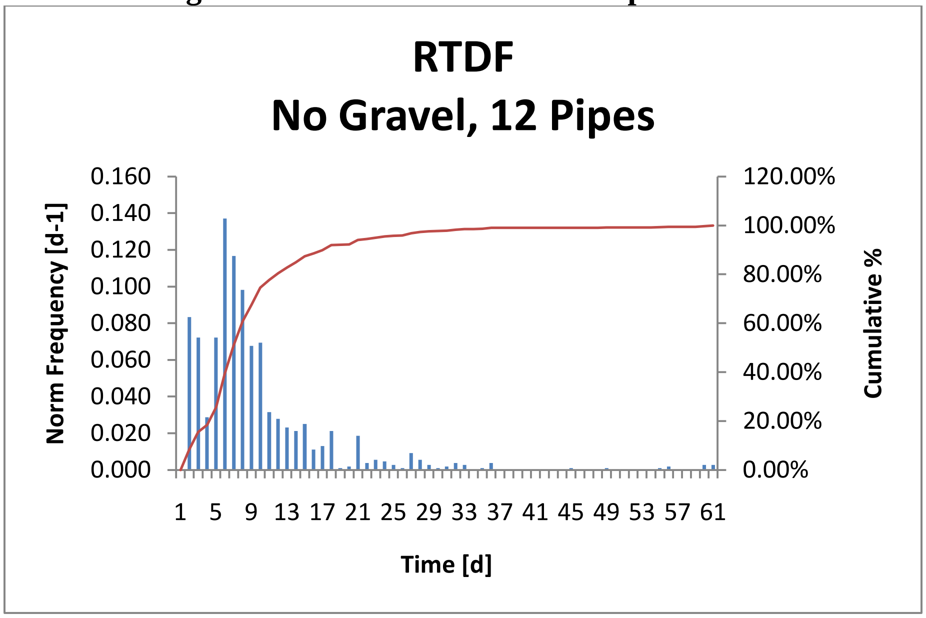


Figure 25: RTDF Layer 5 Gravel Model

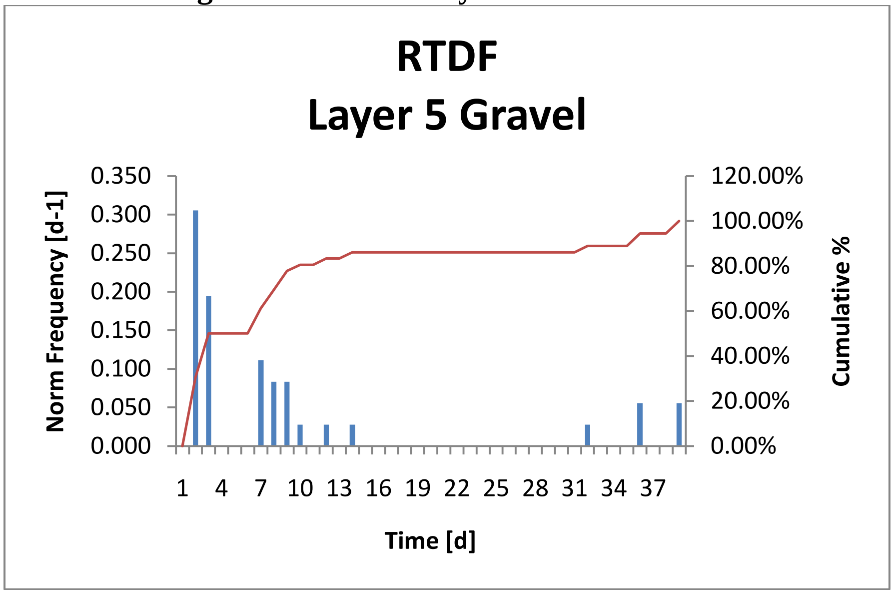


Figure 26: RTDF Layer 5 Gravel 12 Pipes Model

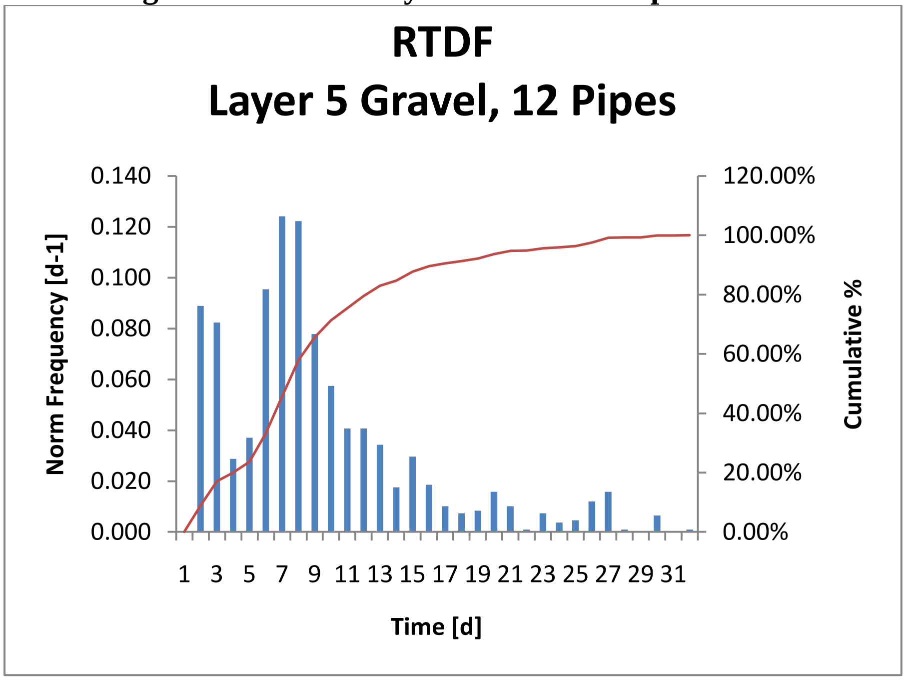


Figure 27: RTDF Row 30 Shutoff Model

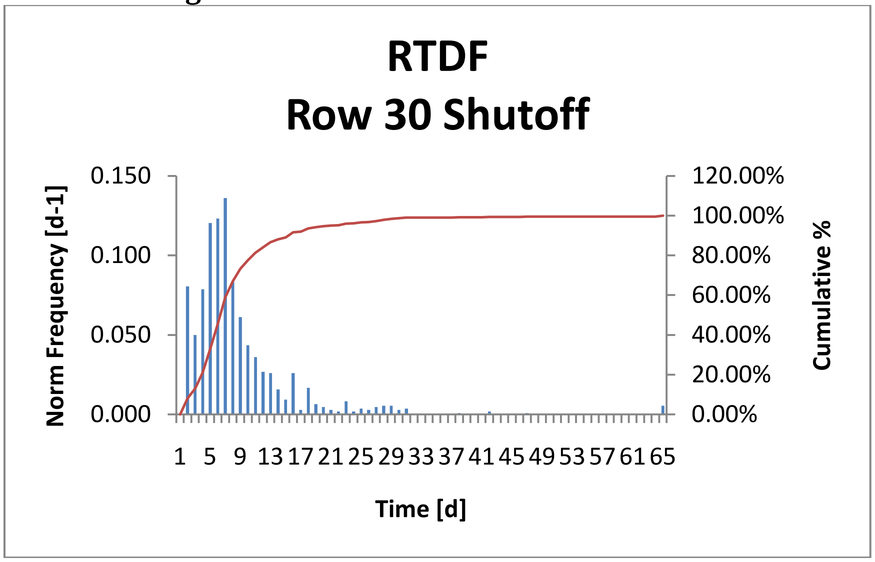
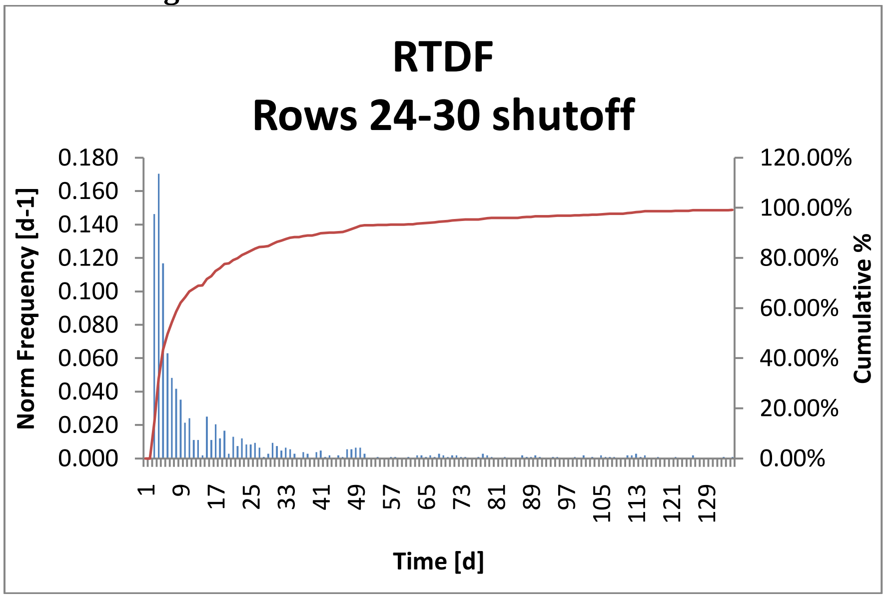


Figure 28: RTDF Rows 24-30 Shutoff Model



Appendix B: Interpolated Hydraulic Conductivity Contour Plots

Figure 29: Interpolated Hydraulic Conductivity Contours (Kriging)

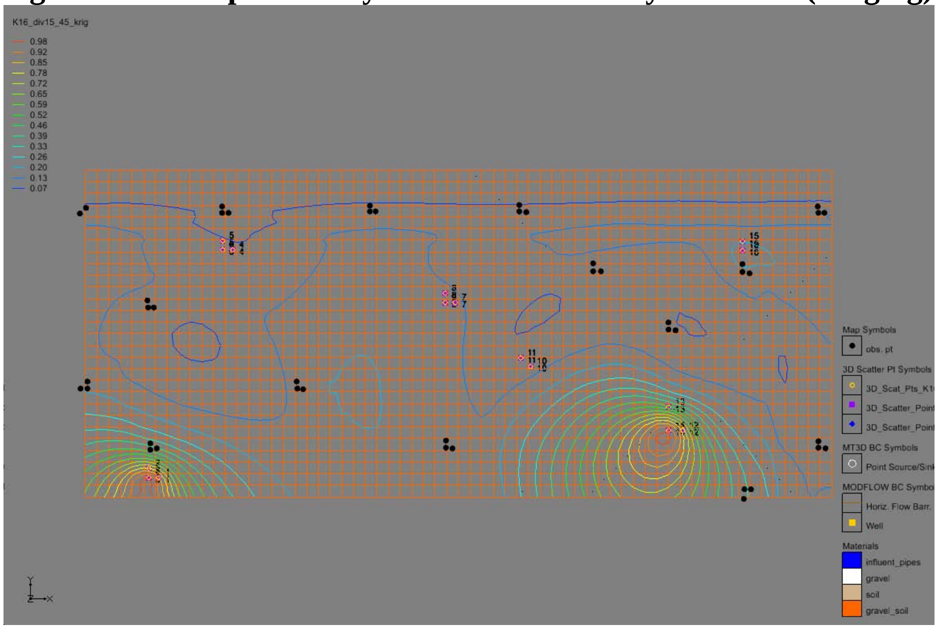


Figure 30: Interpolated Hydraulic Conductivity Contours (Inverse Distance Weighted)

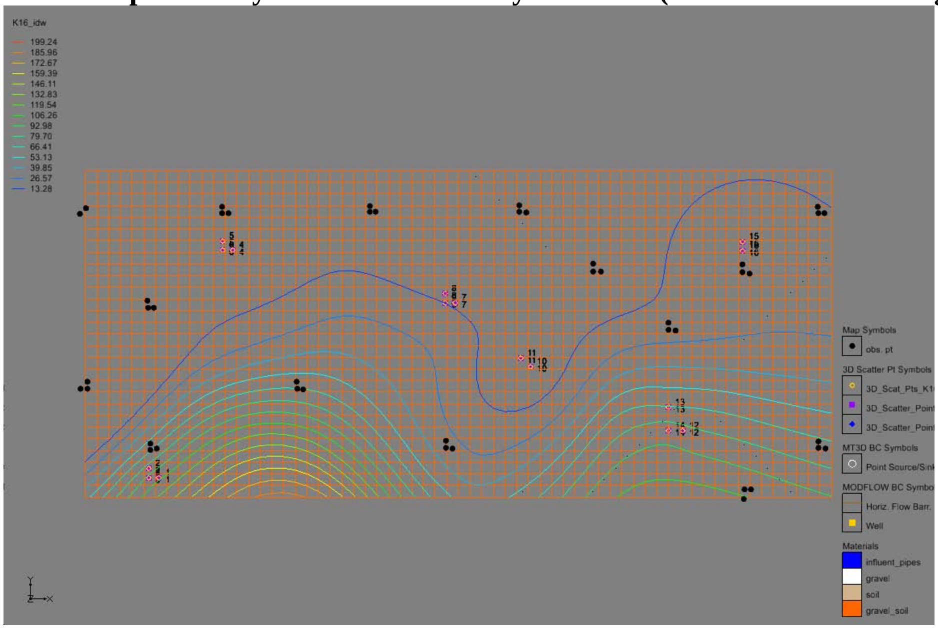
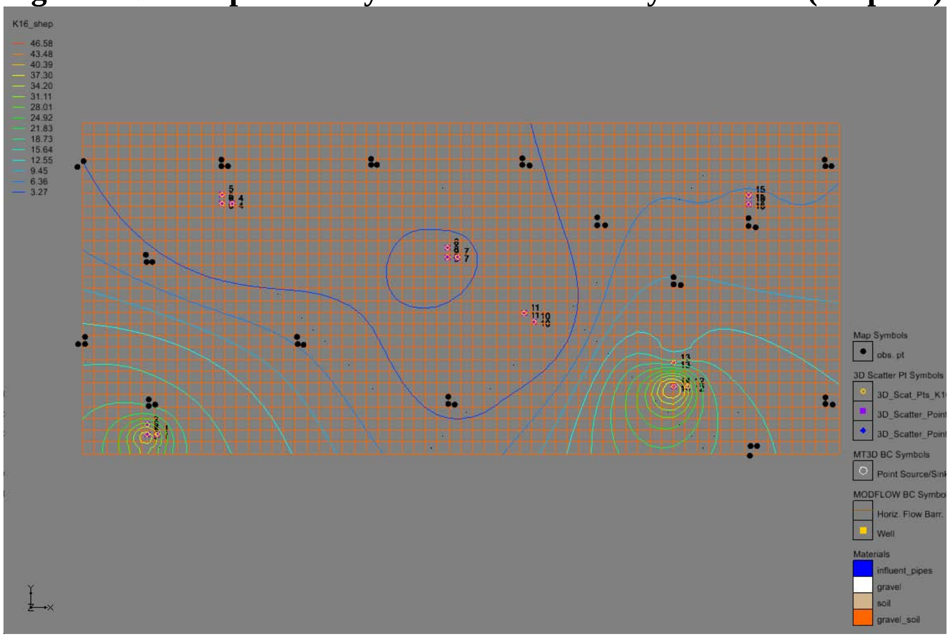


Figure 31: Interpolated Hydraulic Conductivity Contours (Shepard)



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14. ABSTRACT
An upward Vertical Flow Treatment Wetland (uVFTW) at Wright Patterson AFB designed to bioremediate contaminated groundwater exhibits hydraulic short-circuiting. Prior studies estimated that groundwater flowed through less than 50% of the wetland's volume, and that the mean residence time was significantly less than the nominal residence time, which was calculated assuming flow through the entire wetland volume. The objective of this research was to investigate how uVFTW hydraulics affects treatment efficiency, and to propose design strategies to maximize treatment efficiency. A groundwater flow and contaminant transport model of a uVFTW that couples hydraulics and degradation kinetics was built and applied to estimate the effectiveness of engineering solutions aimed at improving treatment efficiency. Model simulations indicate that the engineering solutions improve hydraulic residence times, volumetric utilization, and treatment efficiency over the existing wetland, but also that increasing hydraulic residence time only has a significant impact on treatment efficiency when the time scale for the biodegradation process is similar to the wetland residence time. Degradation kinetics must be quantitatively understood to determine an optimum range for hydraulic residence time, and to ensure that resources are not wasted in an attempt to improve hydraulic performance where no improvement in degradation performance is possible.

15. SUBJECT TERMS
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