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# Influence of temperature on the performance of wetlands treating chlorinated volatile organic compounds

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# INFLUENCE OF TEMPERATURE ON THE PERFORMANCE OF WETLANDS TREATING CHLORINATED VOLATILE ORGANIC COMPOUNDS

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## ABSTRACT

Although various studies have presented models to predict the performance of constructed wetlands at different temperatures, they have focused on the removal of conventional pollutants, and horizontal flows constructed wetlands. On the other hand, investigations on the effect of temperature on the performance of constructed wetlands treating chlorinated volatile organic compounds (VOCs) are limited to microcosm studies.

This study was meant to come up with kinetic and energy balance input data for mathematical models that can be used to predict the performance of upflow constructed wetlands treating chlorinated VOCs at different ambient temperatures. Bench scale continuous upflow wetlands were conducted to investigate the effect of temperature on the performance of upflow wetlands treating chlorinated VOCs. Wetland A was packed with a mixture of row crop compost, soil builder compost, and sand, and Wetland B with Bion Soil®, Latimer peat, and sand. Both wetlands were operated under a controlled environment to simulate field conditions at four phases of temperature (30ºC, 20ºC, 10ºC, and 5ºC). Thermal conductivity coefficients were determined for various wetland bed materials of interest.

The results from this study corroborate the view that temperature affects the performance of wetlands. A reduction in temperature from the highest value of 30°C through the lowest value of 5°C resulted in: (1) a reduction in the degradation rate of TCE by a factor of 4.39 for Wetland A (from $0.0659 \text{cm}^{-1}$ to $0.015 \text{ cm}^{-1}$) and by a factor of 27 (from $0.0802$ to $0.0029 \text{ cm}^{-1}$) for Wetland B, (2) an increase in the extents of breakthrough of TCE, and (3) a reduction in the overall performance efficiencies of the wetlands. The average efficiency of TCE removal in Wetland A was 89.6% at 30°C, and 52 % at 5°C, whereas it was 99.1% at 30°C and 20.1% at

5°C for Wetland B.  Thermal conductivity coefficients of the wetland bed materials were found to be 0.6100 Wm$^{-1}$K$^{-1}$ and 0.3881 Wm$^{-1}$K$^{-1}$ for the compost based mixture and Latimer peat and Bion Soil® based mixture.

# CHAPTER 1. INTRODUCTION

## 1.1 Background and Rationale of the Study

Chlorinated volatile organic compounds (VOCs) such as tetrachloroethene (PCE) and trichloroethylene (TCE) are common contaminants in municipal, industrial, and agricultural effluents largely due to their extensive use as solvents, pesticides, refrigerants, and other industrial chemicals (U.S. EPA, 1997). In addition to chlorinated compounds casually released into the environmental and widespread occurrence, the Environmental Protection Agency (EPA) has identified 1,430 National Priority List hazardous waste sites as the most serious in the nation, where trichloroethylene has been found in at least 852 (60%) of this sites, further targeted for long-term federal clean-up (U.S. EPA, 1997).

Trichloroethylene per se is not carcinogenic; it is thought to become a human health hazard only after processing in the human liver, and result in potential effects on the nervous system, the kidneys, and lungs (U.S. EPA, 2001$a$). The maximum contaminant level (MCL) of trichloroethylene for protection of human health and the environment is 0.005 mg/L, whereas that of vinyl chloride (VC) is 0.002 mg/L (U.S. EPA, 2001$b$). Once TCE enters the environment, its natural degradation by reductive dechlorination through natural or induced mechanisms might result in production of daughter organic compounds such as vinyl chloride, which, in contrast to TCE, is a known carcinogen (U.S. EPA, 2001$a$). As a result, TCE contamination and its potential effect on human health has aroused a considerable amount of research focused on the development of methods for removal of chlorinated ethenes (U.S. EPA, 1997).

Many remediation technologies have been evaluated for effective removal of common contaminants from groundwater; however, natural treatment systems utilizing treatment wetlands have provided the most cost-effective alternative for contaminated groundwater (Kadlec and

Knight, 1996). Conventional remediation technologies for TCE in groundwater target chemical and physical properties for its removal, pumping the contaminated groundwater to the surface and passing it through a treatment system, which either degrades the contaminants or transfers it to another medium (Nyer et al., 2000).

There are a variety of physical and chemical treatment approaches such as soil vapor extraction, chemical treatment, thermal desorption, air sparging, air stripping, pump and treatment, and passive and reactive treatment walls targeting chemical and physical properties of TCE for its successful removal. Most conventional remediation systems pump the contaminated groundwater to the surface passing it through a treatment system, which either degrades the contaminant or transfer it to another medium; however the pump-and treat groundwater remediation methods have proven to be expensive and in many cases ineffective at achieving the proposed level of cleanup especially for chlorinated solvents. Moreover, conventional systems require high maintenance costs and energy from nonrenewable fossil fuel (Nyer et al., 2000; FRTR, 2007; U.S. EPA, 2001*b*).

An alternative to groundwater remediation is the use of biological remediation treatment systems such as permeable barriers, phytoremediation, and natural attenuation (FRTR, 2006). Natural treatment systems used for environmental cleanup have attracted considerable interest due to their potentially lower cost and suitability for applications that require longevity, control and low maintenance (U.S.EPA, 2001). Therefore, promising cost effective remediation systems for chlorinated ethenes are natural and constructed treatment wetlands that operate either by intercepting groundwater plumes or by serving as treatment for pumped groundwater (Lorah et al., 1999; Pardue et al., 2000; Kassenga et al., 2003).

Natural treatment systems require the same amount of energy input for every kilogram of pollutant degraded as conventional systems, but the source for energy is the sun, wind, rain, soil and biomass (Kadlec and Knight, 1996). The driving cost of a conventional treatment system is the amount of land required instead of the amount of energy required (Knight and Kadlec, 1996). Attenuation of TCE and 1,1,2,2,-tetrachloroethane has been observed with high efficiency in wetlands where important fate mechanisms were sorption of VOCs onto peat, their reductive dechlorination by anaerobic organisms in the anaerobic portion of the marsh and cometabolism of chlorinated VOCs by methanotrophic bacteria in the aerobic portions of the marsh. This suggests that upflow treatment wetlands could be designed to mimic the behavior of natural systems (Lorah et al., 1999; Pardue, 2000; Kassenga, 2003).

Removal of VOCs has shown to be significantly prompt in natural peat wetlands bordering the Aberdeen Proving Grounds (Lorah et al., 1997; Lorah and Olsen, 1999a; Lorah and Olsen, 1999b). A natural attenuation approach for treatment of volatile organic compounds (VOCs) has been proposed by Pardue et al. (2000), where an upflow constructed treatment wetland is designed to reductively dechlorinate chlorinated VOCs to lower chlorinated daughter products. Microbial processes based on the metabolic activities of anaerobic bacteria are especially attractive since reductive dechlorination can significantly reduce the toxicity of contaminated groundwater (Haggblom et al., 2000). Biotransformation of chlorinated ethenes can occur via reductive dechlorination, a series of reactions that can convert TCE to dichloroethene (1,2-*cis*-DCE), vinyl chloride (VC) and finally ethene or ethane. A group of anaerobic consortia have been previously described that are capable of sequential replacement of one or more chlorine atoms with hydrogen atoms through metabolic and cometabolic processes (McCarty et al., 2004; Hunkeler et al., 2005).

According to Vogel et al. (1987*a*), under anaerobic conditions, reductive dechlorination is accelerated by carbon availability to produce lower chlorinated daughter products. The higher chlorinated ethenes are degraded via chlorine removal, thus consuming valence electrons from the hydrogen that serves as an electron donor to yield less-halogenated VOCs (Vogel et al., 1987*a*). In addition to dechlorination, methanotrophic bacteria are abundant at the rhizosphere of the wetland plants and can metabolically degrade many of these VOCs (Kassenga, 2003; Pardue et al., 2000).

The U.S. EPA conducted a subsurface flow wetland (SSF) technology assessment, and identified high priority research topics, including the temperature and seasonal effect on wastewater treatment (U.S. EPA, 1993). In view of this, the understanding of temperature effects on the performance of constructed wetlands is a key factor in design and optimization of constructed treatment wetlands for VOCs removal.

In a study by Chunming et al. (1999) on the kinetics of TCE reduction by zerovalent iron and tin oxidation has demonstrated that temperature is important in affecting the rates of the dechlorination reaction; for example, diffusion-controlled reactions in solution have rather low activation energies ($E_a < 21$ KJ mol$^{-1}$) whereas surface-controlled dissolution reactions of most silicate minerals have activation energy values in the range of 42-84 KJ mol$^{-1}$. The reduction of chlorinated ethenes by commercial metals at 10 to 34 ℃ temperature has values of 15-18 KJ mol$^{-1}$, indicative of diffusion-limited reduction rates. Therefore, chemical processes tend to exhibit larger temperature dependence than do physical processes (Chunming et al., 1999).

Physical wetland models such as mesocosms or pilot-scale systems have effectively established design parameters and predicted performance for constructed wetland systems receiving a variety of point and non-point source wastewaters, including petroleum refinery

effluents (Hawkins et al., 1997; Gillespie et al., 1999; Huddleston et al., 2000), agricultural runoff (Moore et al., 2000), and pulp and paper waste streams (Thut, 1993). Other researchers such as Wood et al. (1999), Hill and Payton (1998), and Lionberger and Lincoln (1999) have evaluated the influence of temperature on treatment efficiency of constructed wetlands but assessed horizontal flow wetlands focused on the removal of ammonia, phosphorous, nitrogen, biological oxygen demand and chemical oxygen demand, and potassium.

In a study of treatment of VOCs in upflow wetland mesocosms, Kassenga et al. (2003) determined the degradation rates of target contaminants within the bed of constructed wetlands treating VOCs. This study included field degradation rates, and seasonal and spatial variability of degradation processes due to weather changes (such as temperature and precipitation) (Kassenga et al., 2003). Based on this, it might be assumed that the prediction of the performance of upflow treatment wetlands at different temperatures is of paramount importance in the design of constructed wetlands.

Based on the concept of upflow treatment wetland proposed by Pardue et al. (2000), several questions need to be addressed before embarking on a full-scale upflow constructed treatment wetland. Many parameters are taken into consideration during the design of a wetland such as the most effective type of wetland bed material, the target contaminant characteristics and dispersion profile, the calculation of the effective wetland surface area, the depth and volume, the hydraulic characteristics, and the parameters related to the site. In some cases, the design of a full-scale wetland raises questions on seasonal and temperature conditions that would influence or interfere with the performance of the treatment wetland. Specifically, questions on how the temperature would affect the performance of the constructed wetland treating chlorinated ethenes, and how effective the performance of the constructed wetland for treatment of volatile organic compounds would be at very warm or very cold sites. In view of this, this

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study addresses the need for kinetic and energy balance input data for mathematical models that can be used to predict the performance of upflow wetlands treating chlorinated ethenes and ethanes at different ambient temperatures.

## 1.2 Objectives and Scope of the Study

The main objective of this study was to develop kinetic and energy balance input data for mathematical models that can be used to predict the performance of upflow constructed treatment wetlands treating chlorinated ethenes and ethanes at different ambient temperatures. The specific objectives are as follows:

i)    To assess the variation of performance of the wetlands with temperature, including coming up with mathematical expressions for predicting the corresponding kinetic rate constants.

ii)   To develop a mathematical expression for predicting design temperatures of upflow wetlands packed with different bed materials given ambient temperature data.

iii)  To determine thermal conductivity coefficients of different wetland bed materials of interest so as to be able to quantify heat transfer in the wetlands.

This study is limited to the experimentation of mesocosm-scale upflow constructed wetlands. The study on the effect of temperature on the removal of chlorinated VOCs was simulated in laboratory scale upflow constructed wetlands instead of full-scale upflow wetlands. In addition, this study bases the effects of temperature in the performance of wetlands treating CVOCs using trichloroethylene (TCE) as a representative pollutant for chlorinated volatile organic compounds.

With respect to the organization of this thesis, Chapter 1 presents background information and rationale for this study. It also highlights fundamentals and previous studies on upflow wetlands treating VOCs, the effect of temperature on biodegradation kinetics, and heat transfer on constructed wetland soils. Chapter 2 introduces the conceptual and mathematical description for the prediction of the performance of constructed wetlands treating VOCS. It also covers the conceptual and mathematical expressions for modeling of other experimental data, including those for TCE degradation and calculation of heat transfer coefficients for potential wetland bed materials. The materials and methodology used for the study of the thermal conductivity of wetland soils, and wetland performances at different temperatures constitute Chapter 3. Chapter 4 presents the results and discussion of thermal conductivity coefficients and wetland performances at different temperatures derived from the experiments carried out in chapter tree. Chapter 5 sums up the thesis by presenting the conclusions drawn from this study and making recommendation on future work in this area.

**CHAPTER 2. LITERATURE REVIEW**

**2.1 Upflow Constructed Wetlands Treating Volatile Organic Compounds**

There are several aerial-based design approaches available for constructed wetlands (Kadlec and Knight, 1996). Three configurations of wetlands constitute the variety of treatment wetland technology, based on different characteristic of vegetated ecosystems. Shallow vegetated ecosystems, such as free water surface and subsurface flow, are used for water quality treatment. Free water surface treatment wetlands mimic the hydrologic regime of natural wetlands. In these wetlands, water flows over the soil surface from an inlet point to an outlet point or, in few cases, is totally lost to evapotranspiration and infiltration within the wetland (Knight et al., 1999). In subsurface flow wetlands, the wastewater flows through a constructed media bed planted with wetland plants (U.S. EPA, 1993). For attenuation with higher standards such as complete degradation of contaminants, there is an option of designing vertical wetlands. Downflow or upflow vertical wetlands provide longer detention time of the contaminants in the wetland sediments (Pardue et al., 2000; Kassenga et al., 2003), and minimize volatilization.

Attenuation of high concentration of trichloroethylene (TCE) and 1,1,2,2-tetrachloroethene (1,1,2,2-TeCA) has been observed as groundwater flows through the base of marshes and then upward to their surface (Lorah et al., 1999a; Lorah et al., 1999b). A combination of natural attenuation processes is involved in the reduction of VOC concentrations, mobility, or toxicity in wetlands. Natural attenuation processes include biodegradation, abiotic chemical transformation, volatilization, sorption, dispersion, plant uptake and metabolism (Kassenga, 2003).

A simplified conceptual model for upflow wetland such as the upflow wetland design proposed by Pardue et al. (2000) delivers VOC contaminated water to the subsurface of the

wetland via a subsurface injection system or a buried slotted pipe covered with a geotextile. The treatment occurs as the water is passing through the root bed of the wetlands plants, slowly percolating to the surface. Anaerobic conditions contribute to methanogenic bacteria survival and reductive dechlorination (Pardue et al., 2000). Thus, higher chlorinated ethene serve as electron acceptors during microbial metabolism (Pardue et al., 2000). The major fate mechanisms needed in the design approach are sorption and biodegradation via reductive and oxidative processes (Pardue et al., 2000). The organic sediments would retard the movement of the contaminants relative to groundwater flow, resulting in a longer detention time of the contaminants in the wetland sediments. (Pardue et al., 2000). Previous studies made by Kassenga (2003) presented hydrological and geotechnical characteristics for constructed treatment wetlands treating chlorinated ethenes. The anaerobic transformation of chlorinated ethenes and ethanes have been extensively studied (Ferguson and Pietari, 2000; McCarty et al., 2004; Häggblom et al., 2000; Yang et al., 2005).

Field and laboratory evidence of TCE dechlorination in the absence of oxygen has also been extensively reported (Lorah et al., 1997; McCarty, 1997; McCarty et al., 2004). Several pure cultures of halorespiring bacteria have been identified that are capable of generating energy using TCE as a terminal electron acceptor to produce chlorinated ethene end products. A known pure culture capable of dechlorinating all the way to ethene are strains of the genus *Dehalococcoides*, bacteria that utilize $H_2$ as a sole electron donor, grow slowly in pure culture and requires comprehensive medium for growth (Fennel et al., 2004). If suitable electron donors and corresponding fermenting and dechlorinating organisms are present within a consortium, reductive dechlorination through halorespiration processes can occur at rates that are orders of magnitude faster than cometabolic processes (Fennel et al., 2004; Alvarez-Cohen et al., 2002). Maymó-Gattel at al. (2000) described this microorganism by isolating it in pure culture that

dechlorinated TCE to less chlorinated compounds, *cis*-1,2-dichloroethene (*cis*-1,2-DCE), vinyl chloride (VC) and finally ethene. As pointed out earlier, VC is a known carcinogen that could generate health risks, and for that reason, its reduction is carefully studied.

## 2.2 Effects of Temperature on the Performance of Treatment Wetlands

Studies on temperature effect on wetlands performance have been reported by a number of researchers including Kadlec et al. (2000), Wallace et al. (2000) and Kadlec (2001). However these studies focused on conventional constructed wetlands such as subsurface and surface wetland, for wastewater treatment targeting the removal of biological oxygen demand, nitrogen, and phosphorous. Kadlec and Reddy (2000) studied the temperature dependence of many individual wetland processes and wetland removal of contaminants in surface flow wetland. They concluded that microbial mediated reactions are affected by temperature; the treatment response was much greater to changes at the lower end of the temperature scale (<15ºC) than at the optimal range (20 to 35 ºC). Furthermore they observed that the processes regulating organic matter decomposition were affected by temperature and so were all the nitrogen cycling reactions (mineralization, nitrification and dinitrification). Nonetheless, physical processes involved in the removal of particulate carbon, nitrogen and phosphorous were not much affected by temperature. In colder climates the overall treatment efficiency might decrease. (Kadlec and Reddy, 2000).

Various studies have considered the evaluation of the treatment efficiency of constructed wetlands as a function of temperature depending on components such as substrate composition, degree of plant growth, seasonal changes in evapotranspiration rates, and microbial activities (Winthrop et al., 2002; Chunming et al., 1999; Werth and Reinhard, 1997). For example, Rosso et al. (1995) demonstrated the effects of temperature and pH on microbial growth.

In a recent report of data and models for temperatures and energy flows based on a study of water temperatures and evapotranspiration in surface flow wetlands in hot arid climate, Kadlec et al. (2006) pointed out three reasons for the importance of water temperature in treatment wetlands: (1) temperature modifies the rates of several key biological processes, (2) temperature is sometimes a regulated water quality parameter, and (3) water temperature is a prime determinant of evaporative water loss processes. Several biogeochemical processes that regulate the removal of nutrients in wetlands are affected by temperature, thus influencing the overall treatment efficiency (Kadlec and Reddy, 2000). The temperature conditions in a wetland affect both the physical and the biological activities in the system. The biological reactions responsible for BOD removal, nitrification, and denitrification are known to be temperature dependent (Reed et al., 1995). In light of the studies highlighted above, it is reasonable to expect temperature to be significant in wetlands treating VOCs.

In order to demonstrate that the dechlorination rate is temperature dependent, Zhuang et al. (1999) studied pH, temperature, and electron donor concentration effects on the microbial reductive dechlorination process of tetrachloroethylene and its transformation products. The optimum conditions for reductive dechlorination were achieved at pH and temperature levels of around neutrality, and 35 ℃ respectively. While concentration of TCE (2.1 to 8.4 mg/L) adversely affected the methane production rate, they did not significantly affect the rate of TCE dechlorination. The availability of the electron donor had the greatest impact on the dechlorination process. Zhuang et al. (1999) inferred from their study that microbial reductive dechlorination requires not only a relatively high biomass concentration, but an ample supply of electron donor(s) to provide a steady flow of reducing power for microorganisms.

Dechlorination at different temperatures was studied by Heimann and Jakobsen (2006) with respect to the hydrogen concentration during reductive dechlorination of *cis*-1,2-DCE and

VC. Variations in the temperature between 10 and 30ºC did not affect the hydrogen concentration, and $H_2$ levels at constant ionic strength were independent of the chloride concentration. For that reason, these findings demonstrated that hydrogen concentrations during reductive dechlorination of *cis*-1,2-DCE and VC were apparently not controlled by a constant free energy yield, where both dechlorination at different temperatures and at different chloride levels did not display the characteristic relationship between $H_2$ factors that enter the Gibbs free energy expression (Heimann et al., 2006).

In spite of the above discussion, there are few studies that have focused on the effect of temperature on the performance of constructed wetlands treating VOCs. In a study by Chunming et al. (1999), the degradation of TCE by zero valent iron and tin, kinetics of TCE was considered at different temperatures (10, 25, and 40 ºC). To investigate the temperature effect on TCE reduction rates, Chunming et al. (1999) used activation energy calculations to quantify the energy required to complete the reduction of TCE and oxidation of the other metals present (zero valent iron or tin). This measurements yield sufficient information to suggest that the processes of TCE reduction and oxidation of other metals were temperature dependent.

Another study by Werth and Reinhard (1997) considered the effects of temperature on TCE desorption from silica gel and natural sediments and kinetics. It concluded that the micropore diffusion was characterized by high activation energy values, and thus it was sensitive to temperature. It observed that elevated temperatures speed the release of TCE from slow desorbing sites much more than from fast desorbing site (Werth and Reinhard, 1997).

Additional studies on the influence of temperature on the dechlorination rates of chlorinated ethenes and ethanes have been carried out by our research group, but these studies

were limited to microcosm-scale experiments. Nonetheless, the studies demonstrated the temperature dependence of dechlorination processes.

## 2.3 Heat Transfer in Constructed Wetland Soils

Treatment wetlands are solar powered ecosystems, resulting in annual cyclic temperatures, where an energy balance is dominated by radiation, heat transfer, heat gains or losses, heat conduction and convection among the ground, the atmosphere and the wastewater (Reed et al., 1995). A change in surface water temperature reflects a change in stored heat energy (Edinger et al., 1968; Bogan et al., 2003). Surface water is the primary medium for energy storage, largely because of its relatively high capacity, which is about double of the heat capacity of vegetation, soil minerals, and soil organic matter (Brutsaert et al., 1982). However, wetland vegetation is not dense enough to create a large equivalent surface water reservoir for energy, therefore changes in heat energy stored in wetland vegetation likely can be ignored (Shoemaker et al., 2005). This suggested that the thermal conductivity on wetland bed materials used for constructed wetlands is of interest when determining the surface water temperature of wetlands.

Heat flow in wetland soils may be determined from knowledge of the thermal conductivity and temperature gradient; thermal properties can be determined indirectly by measuring the rise or fall of temperature in response to a constant heat input (Abu-Hamdeh et al., 2000). The thermal conductivity of a soil depends on several factors: properties inherent to the soil itself such as texture, and mineralogical composition (Abu-Hamdeh et al., 2000); as well as peat content that reduces the thermal conductivity of the soil (Ekwue et al., 2006). The incorporation of organic materials into soils to improve soil physical and hydraulic properties is a common practice; however organic materials incorporated into soil reduce bulk density, and furthermore diminishing the thermal conductivity (Ekwue et al., 2006).

Soils such as Bion Soil ®, a product derived from agricultural wastes, and commercially available peat such as Latimer are two of the soils used for wetland bed materials for the bench scale biodegradation wetlands. In a study conducted by Kassenga et al., (2003) Bion soil® and Latimer peat were selected from ten possible mixtures and Bion Soil® was found to be superior to other mixtures. It was inferred that the utilization of Bion Soil® as wetland bed material stimulated the degradation and enhanced sorptive capacity for chlorinated organics (Kassenga et al., 2003). These results also indicated that organic carbon composition was an important factor in selecting bed materials for treatment wetlands for chlorinated organics. Since peat materials are rich in organic carbon and also supply nutrients necessary for microbial growth, they are the most promising candidates for construction of treatment wetlands (Kassenga et al., 2003).

**CHAPTER 3. MATERIALS AND METHODS**

**3.1 Determination of Thermal Conductivity Coefficients of Wetland Soils**

**3.1.1 Wetland Soils Sources and Preparation**

The experiments for the determination of thermal conductivity coefficients of the wetland soils of interest were done to provide input data for equations described later. The soils whose thermal conductivity coefficients were determined were based on the wetland bed material utilized for the laboratory scale upflow wetlands for study. These soils were: Latimer peat, Bion Soil®, sand, row crop compost, and soil builder compost. Mixture of Bion Soil®/Latimer peat/Sand (37.5:37.5:25 w/w), and row crop compost/soil builder compost/ sand (37.5:37.5:25 w/w) were blended. This ratio was adopted based on previous studies reported by Kassenga et al. (2003). Bion Soil® is a product derived from agricultural waste (Dream Maker Diary, Cowlesville, NY), and Latimer is a common commercial peat (Latimer's Peat Moss Farm, West Liberty, OH). Fine to medium sand was used for preparing the wetland soils mixtures. Water was used to calibrate the improvised apparatus (described in the next subsection) used for the determination of thermal conductivity coefficients of the wetland soils of interest.

**3.1.2 Experimental Setups and Procedures**

The determination of thermal conductivity coefficients for various wetland soils was executed using an improvised apparatus with a constant source of heat (as illustrated in Figure 3.1). The apparatus consisted of an aluminum vessel, an insulation material, a temperature measurement device, and a heater plate. The apparatus was mainly an aluminum vessel whose internal walls were covered with an insulation material; in order to avoid contact with the

aluminum walls to the wetland material in study. In view of this, it was considered that no source of heat at the lateral walls of the apparatus was dissipated to the wetland soils.
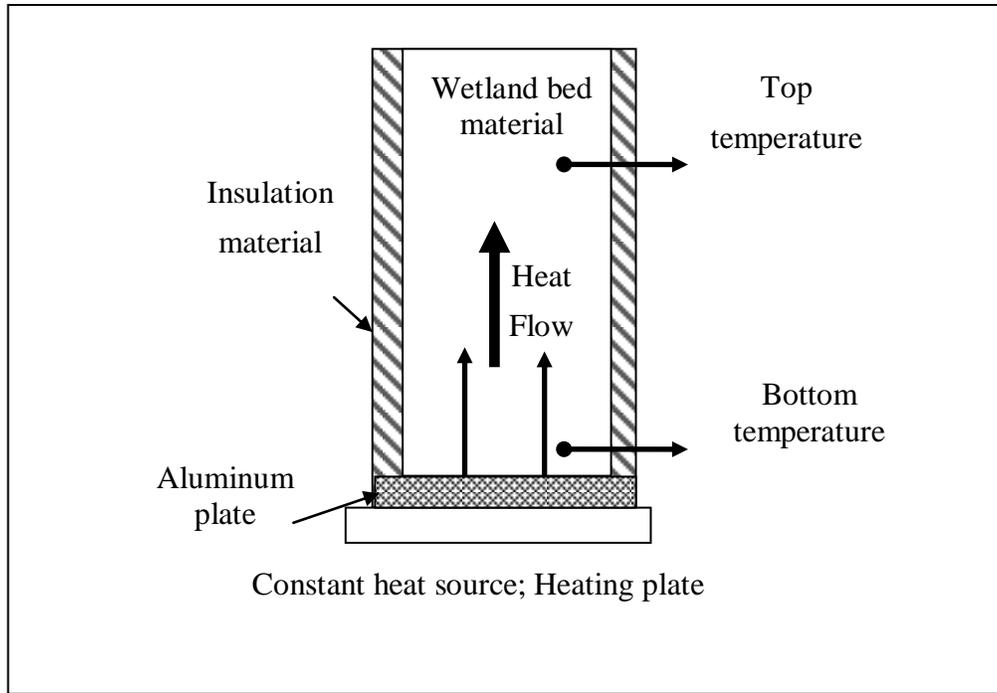


**Figure 3.1** Schematic diagram of the apparatus used to measure heat conductivity coefficients of wetland soils

The bottom of the aluminum vessel was in contact with a constant source of heat (ranging from 30-45°C). The wetland bed materials tested were previously saturated with water. Individual wetland soil materials were tested separately for temperature measurement followed by the mixtures of soils (row crop compost/soil builder compost/sand and Bion Soil®/ Latimer peat/sand).

The temperature was measured by reading the temperatures at a thermometer located at axial position, at different levels of the apparatus (0cm, 7.18cm, 14.37cm, and 21.56cm). Temperature was measured at the bottom level, low and high middle level, and top level along the apparatus. The continuous source of heat (30 to 45°C) would generate heat that traveled

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through the saturated wetland soil. This would result in different temperatures along the apparatus that would range from 30-40°C decreasing to the ambient temperature.

Special care was taken to insure that the saturated wetland soil was well compressed to avoid bulk air space. Repetitive measurements of temperature for each wetland bed materials were taken, until no significant changes were observed in the temperatures measured at each level of the apparatus. The amount of heat that was flowing from the bottom to the top of the apparatus through the wetland soils required a significant time of stabilization of an average of 10 hours.

### 3.1.3 Thermal Conductivity Data Modeling

Thermal properties can be determined indirectly by measuring the rise or fall of temperature in response to a constant heat input (Abu-Hamdeh et al., 2000). Accordingly, in this study, heat transfer quantification was done based on the Fourier equation of heat transfer. Conduction is the energy transferred by greater motion of molecules at higher temperature levels to lower motion molecules (Welty, 2000).

For the improvised experimental system shown in Figure 3.1, the energy balance for the calibration material can be can be represented by the Fourier Equation in the form of Equation 3.1:

$$Q = k_{cm} \cdot \left( -\frac{dT}{dh} \right)_{cm} + \Delta Q_L \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.1)}$$

where:

$Q$ is the source of emission rate of heat transfer rate, $W.h^{-1}$;

$k_{cm}$ is the thermal conductivity of the calibration material, $W/m^{-1}K^{-1}$;

*(dT/dh)* $_{cm}$ is the temperature gradient in direction $h$ for the calibration material, K; and

$\Delta Q_L$ is the heat loss from the source to the surroundings.

For the wetland soil of interest, the Fourier Equation can be written as shown in the Equation 3.2;

$$Q = k_{ws} \cdot \left( -\frac{dT}{dh} \right)_{ws} + \Delta QL \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.2)}$$

where:

$k_{ws}$ is the thermal conductivity for the wetlands soil in study, $W/m^{-1}K^{-1}$: and

*(dT/dh)* $_{ws}$ is the temperature gradient in direction $h$ for the wetland soil in study, K.

Since the quantity of heat from the source is constant, Equations 3.1 and 3.2 can be equated. Upon rearrangement, the resulting equation is Equation 3.3 which can be used to calculate the coefficients of heat conductivity of various wetland soils based on a material with a known heat conductivity coefficient.

$$k_{ws} = k_{cm} \cdot \left( \frac{dT}{dh} \right)_{cm} / \left( \frac{dT}{dh} \right)_{ws} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.3)}$$

With respect to the use of Equation 3.3, the term $k_{cm}$ was obtained from the literature (Beaumont and Keen, 1990) whereas the heat gradient terms *(dT/dh)* $_{cm}$ and *(dT/dh)* $_{ws}$ were obtained from the experiments described in subsection 3.1.2.

## 3.2 Wetlands Performance at Different Temperatures

### 3.2.1 Experimental Setup and Procedure; Constructed Upflow Wetlands

The model proposed by Pardue (2000) for upflow constructed wetlands was used as a basis for building the two laboratory scale upflow wetlands, whereas geotechnical considerations

relied on results presented by Kassenga (2003). The wetlands were accommodated in 60 cm long and 15 cm diameter glass columns, with sampling ports equipped with Mininert Valves (VICI Precision Sampling, Baton Rouge, Louisiana) along the glass wetland columns. The apparatus and accessories on the columns were made from Viton, Teflon, stainless steel, and glass to avoid adsorption of VOCs. The experimental set-up including the feed solution reservoir pumping system and the mesocosm is illustrated in Figure 3.2.

To compare the two types of wetland soil mixtures as well as investigate the influence of temperature on the performance of wetlands, two treatments were adopted with respect to the wetland bed materials. The first treatment, which was used in the wetland referred to here as Wetland A, was a mixture of row crop compost/soil builder compost and sand at a ratio of 37.5:37.5:25 (w/w). The second treatment, which was used in the wetland referred to here as Wetland B, was blended using Bion Soil®, Latimer peat, and sand at a ratio 37.5:37.5:25 (w/w). As suggested in the work presented by Kassenga (2003), the mesocosms were glass cores packed to a uniform bulk density. Wetland and flow characteristics are shown in Table 3.1. The sides of the wetland column were wrapped with aluminum foil to keep off light for minimization of growth of photosynthetic organisms (Kassenga,2003).

The wetlands were fully saturated and flooded to a depth of 10 cm above the level of the packing media. Both wetlands were vegetated with *Typha latifolia*, which previous studies in our research group had shown to be suitable as a wetland plant for systems treating various pollutants. For example, *Typha latifolia* has been used with positive outcomes for enhancement of recalcitrant chlorobenzene biodegradation (Lin, 2003; Alvarez, 2006).

To insure that the wetland performance could be monitored for the effect of temperature with the other major influencing factors held constant, the wetlands were run in a controlled

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environment chamber (Plants Growth Chamber, CONVIRON Manufacturer). Physical conditions such as radiation, humidity, temperature, air flow, and light were adapted to a real cycle of greenhouse conditions. Humidity was set to 80% relative humidity (RH) throughout the study. The lighting was programmed to follow a 24 hours profile of day bright light and dark night cycle (7am-10am: medium lights; 10am-2pm: bright lights; 2pm-7pm: low lights, 7pm-4am: no lights; and from 4am-7am: low lights). Standard visibility lighting was provided by fluorescent lamps.  To complete all the runs for this study, the wetlands were operated under four phases of temperature: 30°C, 20°C, 10°C, and 5°C, in that order.

The feed solution containing TCE as the representative chlorinated VOC was pumped through each wetland at a constant flow rate. Except for very brief breaks (lasting less than one hour) for monitoring or repairing the experimental setup components, the wetlands were operated continuously for a period of 515 days. The feed solution reservoirs were replenished regularly to insure that the reservoirs were at least half full throughout the study. To minimize loss of the feed solution chemical through volatilization, a floating lid was used to eliminate head space above the solution in the reservoirs. The feed solution was stored at a temperature of 4°C insulated enclosures. The feed solution was prepared using neat trichloroethylene (TCE) from Aldrich (Aldrich Chemical Company, Inc.).

Flow rates of the feed solution through each wetland were quantified on a continuous basis by keeping track of quantities of feed solution used and accounting for all losses. During each temperature phase, sampling was done only after the wetland system performance had stabilized, indicating quasi-steady state conditions. To check for these conditions, test samples were taken at a suitable interval. Once that no significant changes in the performances of the wetlands (based on the removal rate constants obtained) were observed, it was considered that

the wetlands were stable at the respective temperature. Thereafter, samples for use in the study were taken.
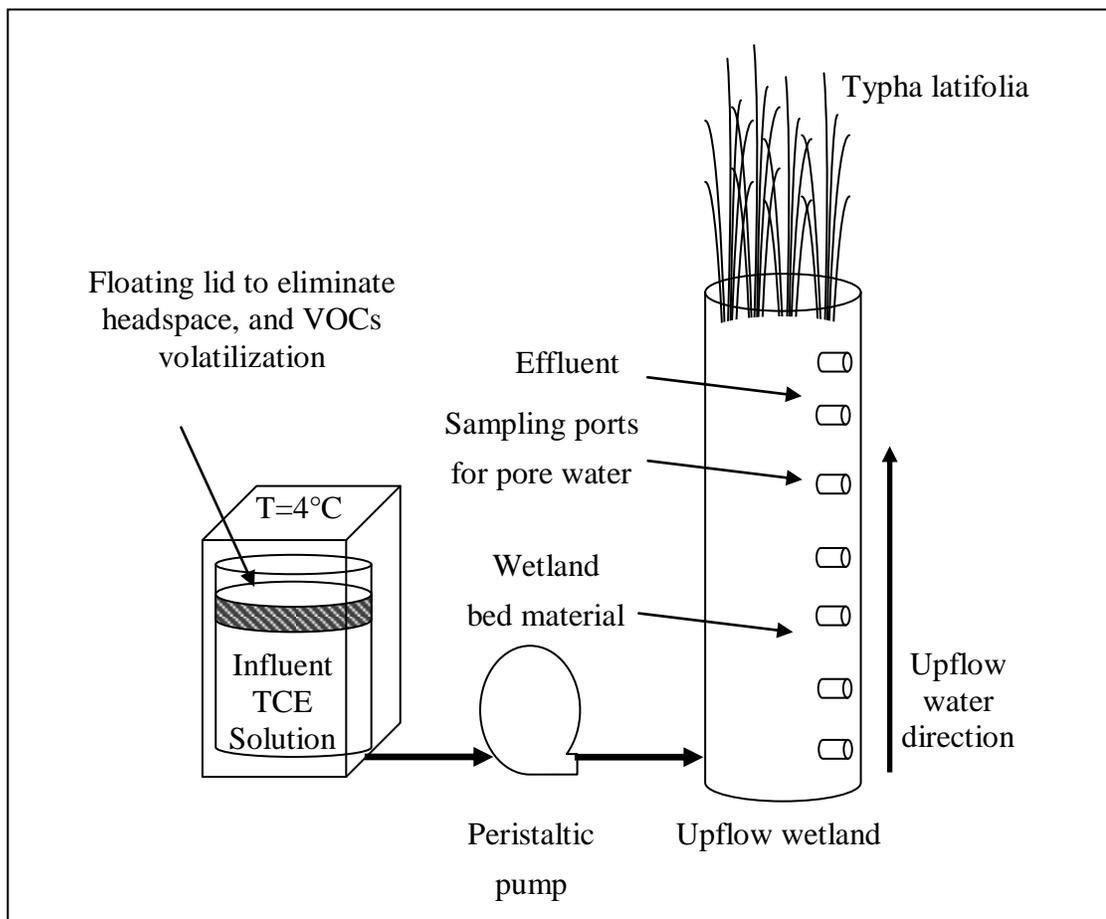


**Figure 3.2** Experimental set-up for evaluating the effect of temperature on the performance of wetlands treating chlorinated VOCs (The set-up was operated in a controlled environment chamber).

Both upflow wetlands were monitored every three hours during the day, but less frequently during the night. Samples for analysis of chlorinated VOCs were collected by withdrawing porewater from the axial center of the wetlands in accordance with the procedure reported by Kassenga (2003).

Sampling for both wetland types was done at the same time, alternating between wetlands for each sampling port level, beginning with the top sampling ports. During each sampling session, seven samples were taken from each wetland. They were collected in clean glass vials

provided with air tight lids. All the samples were analyzed immediately after collection without storage or preservation.

**Table 3.1** Physical Characteristics of the Upflow Wetlands and Flow Data

| Characteristics/ Parameters | Wetland Bed Materials | |
| --- | --- | --- |
| | Wetland A | Wetland B |
| | Packed with a Mixture of BionSoil®/Latimer peat/Sand | Packed with a Mixture of Row crop compost/ soil builder compost/Sand |
| Length, cm | 45 | 53 |
| Diameter, i.d., cm | 15 | 15 |
| Total Volume, cm$^3$ | 7,952 | 9,366 |
| Bulk Density, g/ cm$^3$ | 1.2 | 1.2 |
| Pore Volume, cm$^3$ | 4,374 | 5,151 |
| Hydraulic Residence Time, day | 1.25 | 1.47 |
| Measured Flow Rate, L/day | 3.5 | 3.5 |

### 3.2.2 Analytical procedures

TCE and its dechlorination products, *cis*-1,2-DCE and VC in samples of pore water from the wetlands were analyzed using the U.S. EPA Method 8260B. The gas chromatograph–mass spectrometer (Agilent 6890-5972A) was equipped with a 30 m x 0.25 mm x 0.25 mm film thickness of Agilent-5MS (5% phenyl methyl siloxane capillary column) (Agilent, Palo Alto, CA). Daily blanks, calibration checks and surrogates were run to ensure that the analytical method was stable.

### 3.2.3 Data Modeling

### 3.2.3.1 Wetlands Performance Data Modeling

The model proposed by Pardue (2000) for upflow wetlands treating VOCs is based on first order kinetics. The validity of this choice of model is reinforced by studies reported on

degradation of several chlorinated VOCs including TCE (Kassenga et al., 2003; Kassenga, 2003). For this reason and the fact that the data from this study were found to fit the model well, a first order kinetic model (Equation 3.4) was adopted.

$$C = C_o e^{-kx}$$ ……………………………………………………………....(Eq. 3.4)

where;

    $x$ is the distance along the height of the wetland, cm;

    $C$ is the concentration of TCE at a height x along the height of the wetland, mg/L;

    $C_o$ is the concentration of TCE in the influent feed solution, mg/L; and

    $k$ is the pseudo first order rate constant with respect to distance, cm$^{-1}$.

The experimental data for all the phases of monitoring the wetlands for TCE removal were fitted to Equation 3.4, using spreadsheet techniques.

The Arrhenius Equation for the temperature dependence of the rate constant, Equation 3.5 whose modified form was discussed by Kadlec and Reddy (2000), was used to process the TCE removal rate constant data.

$$k_T = k_R \theta^{T-T_R}$$ …………………………………………………………....(Eq. 3.5)

where:

    $k_T$ is the rate constant at the ambient temperature of operation of the wetland, cm$^{-1}$;

    $k_R$ is the rate constant at the reference temperature, cm$^{-1}$,which in this study was 30°C;

    $\Theta$ is the temperature correction coefficient, dimensionless;

    $T$ is the temperature at which the wetlands are operated, °C; and

    $T_R$ is the reference temperature at which the reference rate was obtained, °C

Equation 3.5 can be changed into the form shown as Equation 3.6 for easier processing of the removal rate constant data.

$$ln\left(\frac{k}{k_R}\right) = (T - T_R)ln\theta \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(Eq. 3.6)$$

To obtain the temperature correction factor $\Theta$, $ln$ $(k/k_R)$ was plotted against (T-$T_R$) using the removal rate constant and temperature data for the four temperature phases of the study.

**3.2.3.2 Energy Balance for Wetland Water Temperature**

A wetland energy balance is a proper framework to interpret and predict not only evaporative processes but also wetland water temperatures (Kadlec et al., 1996). There are many approaches for energy balances such as the ones presented by Priestley and Taylor (1972), Montieth et al (1981), Shuttleworth and Wallace (1985), and Walter et al. (2000). However, these energy balance models were meant for subsurface and surface flow horizontal wetlands. Even the energy balance model put forward by Kadlec et al. (1996) was not devised for upflow wetlands.

The energy flows that determine wetland water temperature and the associated evaporative losses are shown in Figure 3.3. Many things are taken into consideration when applying an energy balance to upflow wetlands. For horizontal flow wetlands, it is assumed that the heat flow in the vertical direction is negligible due to the direction of the flow. Energy sources included in the energy balance to the system are: solar radiation, evapotranspiration, sensible and latent heat, and conductive heat transfer. All these energy forms are exhibited from both within and outside the wetland.

In order to compute the water temperature of an upflow wetland using the following energy balance model, a series of meteorological condition data should be available as inputs

into the model. The mean air temperature is a fair predictor of wetland water temperature for unfrozen conditions (Kadlec and Knight, 1999; Shoemaker et al., 2003). Therefore, throughout the calculation of the upflow wetland water temperature, the temperature of the water at the top of the wetland $T_w$ could be estimated as the air temperature $T_a$. This is for the scenario where the ambient temperatures are in the range of 20-30°C.
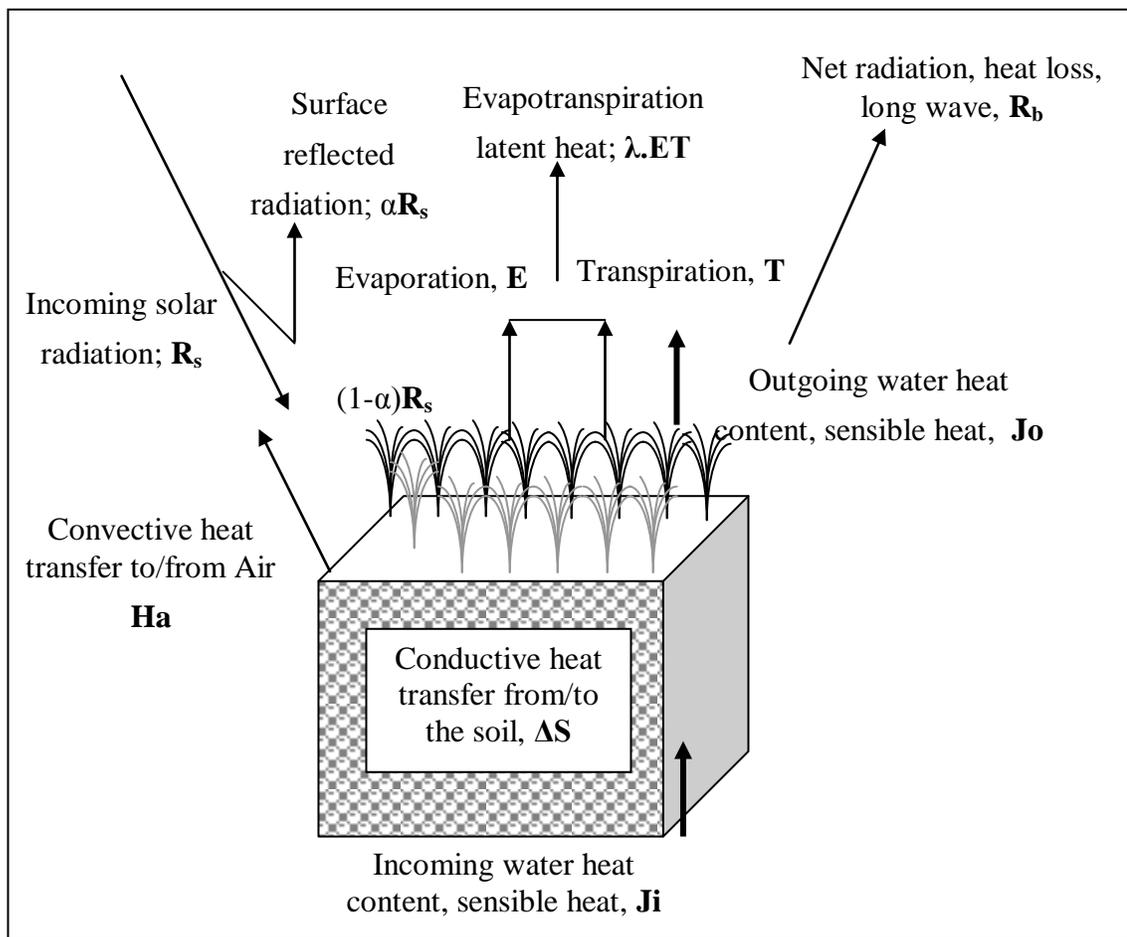


**Figure 3.3** Components of the Wetland energy Balance Model for an Upflow Wetland

This model is used for two different case scenarios. The first scenario is when air temperatures are between 20-30°C. The second scenario requires more consideration when the air temperature at which the wetlands could be operating varies from 20°C to 5°C.

$$T_w = T_a - k_{ws}^{-1}(\Delta h)[Rn - (H_a + \lambda ET + (Jo - Ji))] \dots\dots\dots\dots\dots\dots\dots\dots(\text{Eq. 3.7})$$

where:

$R_n$ is the net radiation absorbed by the wetland, MJ.m$^{-2}$d$^{-1}$;

H$_a$ is the heat transfer to and from the air, MJ.m$^{-2}$d$^{-1}$;

$\lambda ET$ is the heat lost from water loss due to evapotranspiration, m.d$^{-1}$;

$J_e$ is the effluent water heat content, MJ.m$^{-2}$d$^{-1}$;

$J_i$ is the influent water heat content, MJ.m$^{-2}$d$^{-1}$;

k$_{ws}$ is the thermal conductivity of the wetland soil, MJ.m$^{-1}$d$^{-1}$°C$^{-1}$;

T$_a$ is the air temperature, °C;

T$_w$ is the temperature at the top of the wetland, °C; and

$\Delta h$ is the height of the wetland, m.

The net radiation reaching the surface of the upflow wetland is calculated through various steps that estimate the absorptive and reflective losses from incoming extraterrestrial radiation Ra. A fraction α of this radiation is reflected by the wetland, a value of 0.23 is commonly used for vegetated systems (ASCE,1990).

The amount of radiation through the outer atmosphere is solar radiation calculated using Equation 3.8:

$$(1-\alpha)R_s = \left[ 0.25 + 0.5\left(\frac{S}{100}\right) \cdot R_a \right] \quad\text{.................................................(Eq. 3.8)}$$

where:

$R_s$ is the solar radiation, MJ.m$^{-2}$d$^{-1}$;

α is the surface reflected radiation coefficient, 0.23;

$R_a$ is the extraterrestrial radiation, MJ.m$^{-2}$d$^{-1}$; and

*S* is the percent daily sunshine.

The net outgoing long wave (heat) radiation is calculated based on atmospheric characteristics of cloud cover, absolute temperature, and moisture content conditions in the engineering wetlands using the Equation 3.9:

$$R_b = \left[0.1 + 0.9\left(\frac{S}{100}\right)\right]\left[0.34 - 0.139\sqrt{P_{satw(T_{dp})}}\right]\sigma(T + 273)^4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.9)}$$

where:

$R_b$ is the outgoing long wave radiation, MJ.m$^{-2}$d$^{-1}$;

$P_{satw\,(Tdp)}$ is the water vapor pressure at dew point, KPa;

*T* is the temperature of the air, °C; and

$\sigma$ is the Boltzman's constant, 4.903.10$^{-9}$ MJ.m$^{-2}$ K$^{-4}$d$^{-1}$.

The saturation water vapor pressure was computed using Equation 3.10;

$$ln\left[P_{satw(T)}\right] = 19.0971 - \frac{5349.93}{T + 273.16} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.10)}$$

where:

$P_{satw(T)}$ is the saturation water vapor pressure at temperature *T*,

kPa; and *T* is the temperature of the air, °C.

$$P_{wa} = RH \cdot P_{satw}(T) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.11)}$$

where:

$P_{wa}$ is the ambient water vapor pressure, kPa;

*RH* is the relative humidity fraction; and

$P_{satw}(T)$ is the saturation water vapor pressure at the ambient air temperature, kPa.

The total net radiation is given by Equation 3.12;

$$R_n = 0.77 \cdot R_s - R_b \ \text{.................................................................(Eq. 3.12)}$$

where:

$R_n$ is the net radiation absorbed by the wetland, $\text{MJ.m}^{-2}\text{d}^{-1}$;

$R_s$ is the solar radiation, $\text{MJ.m}^{-2}\text{d}^{-1}$; and

$R_b$ is the outgoing long wave radiation, $\text{MJ.m}^{-2}\text{d}^{-1}$.

The evapotranspiration and volumetric latent heat of water is calculated using Eq. 3.13:

$$\lambda ET = \lambda_m \rho ET = \lambda_m \rho K_e \cdot \left[ P_{satw}(T_w) - P_{wa} \right] \ \text{.................................(Eq. 3.13)}$$

where:

$ET$ is the water loss due to Evapotranspiration, $\text{m.d}^{-1}$;

$P_{satw}(T_w)$ is the saturation water vapor pressure at $T_w$, kPa;

$T_w$ is the wetland water temperature, °C;

$K_e$ is the water vapor mass transfer coefficient, $\text{m.d}^{-1}\text{kPa}^{-1}$ ,

$\lambda_m$ is the latent heat of vaporization of water, $2.453 \ \text{MJ.kg}^{-1}$,

$\rho$ is the density of wetland water, $\text{kg.m}^{-3}$; and

$\lambda$ is the volumetric latent heat of water, $\text{MJ.m}^{-2}$.

The water vapor mass transfer coefficient can be computed based on the Equation 3.14;

$$Ke = (0.0001)(1.965 + 2.60 \cdot u) \ \text{.................................................(Eq. 3.14)}$$

where:

$u$ is the wind speed, m/s.

The relationship between heat and mass transfer in the air-water system is based on heat and mass transfer coefficients (ASCE, 1990). Convective heat transfer to and from the air is calculated using Equation 3.15;

$$Ha = h(T_{Tw} - T_a) \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.15)}$$

where:

$H_a$ is the convective heat transfer to, and from the air, MJ.m$^{-2}$d$^{-1}$;

$h$ is the heat transfer coefficient, MJ.m$^{-2}$d$^{-1}$°C$^{-1}$;

$T_{Tw}$, is the temperature of the wetland water at the top of the wetland, °C; and

$T_a$ is the ambient temperature, °C.

The heat transfer coefficient can be calculated using Equation 3.16;

$$h = \gamma\lambda K_e = \frac{c_p P}{0.62\lambda} = 0.0666 \cdot 2453 \cdot Ke = 163.3Ke = 0.321 + 0.425u \quad\ldots\ldots\ldots\text{(Eq. 3.16)}$$

where:

$u$ is the wind speed, m/s;

$\gamma$ is the psychometric constant, kPa.°C$^{-1}$,

$c_p$ is the heat capacity of air, MJ.kg$^{-1}$°C$^{-1}$; and

$P$ is the ambient air pressure, kPa.

The sensible heat from the inlet and outlet water through the wetland is given by Equation 3.17;

$$(J_e - J_i) = \rho \cdot c_p (q_e T_e - q_i T_i) \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(Eq. 3.17)}$$

where:

$c_p$ is the heat capacity of the water, MJ.kg$^{-1}$°C$^{-1}$;

$q_i$ is the influent hydraulic loading rate, m.d$^{-1}$;

$q_e$ is the effluent hydraulic loading rate, m.d$^{-1}$;

$T_i$ is the temperature of the influent wetland water, ℃; and

$T_e$ is the temperature of the effluent wetland water, ℃.

## CHAPTER 4. RESULTS AND DISCUSSION

### 4.1 Thermal Conductivity Coefficients

Results of the experiments carried out for the determination of thermal conductivity coefficients of different wetland bed materials of interest in study are presented in Table 4.1.

**Table 4.1** Thermal Conductivity Coefficients for Different Wetland Bed Materials under Saturated Conditions.

| Wetland bed material in study | Thermal conductivity coefficient, $Wm^{-1}K^{-1}$ |
| --- | --- |
| Soil builder compost | 0.31 |
| Row crop compost | 0.43 |
| Sand | 0.42 |
| Bion Soil® | 0.43 |
| Latimer peat | 0.53 |
| Mixture of Bion Soil®/Latimer peat/sand | 0.39 |
| Mixture of Row crop compost/soil builder compost/sand | 0.61 |

It can be observed from Table 4.1 that, among the individual wetland bed material constituents, soil builder compost had the lowest thermal conductivity coefficient while Latimer peat had the highest. The differences in thermal conductivity coefficients justify the need to mix different constituents to obtain wetland bed materials with the desired thermal and geotechnical characteristics. It is noteworthy that the thermal conductivity coefficient of water is $0.61 \ Wm^{-1}K^{-1}$, which is far higher than those of the wetland bed material components tested. Therefore, the fact that the mixture of row crop compost and soil builder compost plus sand had a thermal conductivity coefficient as high as that of water, suggest that heat conductivity in the mixture was heavily influenced by water.

The relatively low thermal conductivity coefficients of compost materials and Bion Soil® are understandable given their high organic contents. The relatively higher thermal conductivity of Latimer peat, which also has a high organic content, suggests that it must have been influenced more by its geotechnical properties than its organic content. The lower thermal conductivity coefficient of the mixture of Bion Soil®, Latimer peat, and sand than any of its constituents suggests that the constituents exhibited different geotechnical properties upon being mixed. Such phenomena as consolidation, expansion, and segregation of soil constituents can results in the aforementioned changes (Das, 2002)

The results reported here are comparable to those reported in the literature. A study on some compacted Trinidadian Soils showed that as the peat content of the soil increased, the thermal conductivity would decrease (Ekwue et al., 2006). For example, thermal conductivity values for three type of soils (Piarco, Maracas, and Talparo) ranged between 0.4 and 0.8 $W.m^{-1}K^{-1}$ for soils with peat content greater than 12% (Ekwue et al., 2006). Other studies by Ohu et al. (1985) and De-Kimpe et al. (1982) demonstrate that thermal conductivity and bulk density declined with increasing peat contents. The decline of bulk density was attributed to the greater pore space normally obtained when soils are amended with organic matter (De-Kimpe et al., 1982)

A study by Abu-Hamdeh and Reeder (2000) demonstrated that the thermal conductivity of soil decreases as the percentage (on weight basis) of organic matter increases in the soil samples. The thermal conductivity of clay loam soil was 0.17 $W.m^{-1}K^{-1}$ at 30% organic matter content. However, it is widely understood that thermal conductivity varies not only with organic matter content but also with soil texture, water content, salt concentration, bulk density, and peat content (Abu-Hamdeh and Reeder, 2000; Goldsmid et al., 1981; Ekwue et al., 2006). Since organic matter content reduces the thermal conductivity of a material, its incorporation in

wetland beds is expected to be more beneficial during the winter than during the summer period (Ekwue et al., 2006).

The thermal conductivity of saturated sand obtained in this research is similar to the results obtained by Goldsmid et al. (1981) which measured values of thermal conductivity from about 0.3 $W.m^{-1}K^{-1}$ to about 1.6 $W.m^{-1}K^{-1}$ as the specific water content ranging from about 0.005 to 0.05 kg/kg. Notably, within that range, the thermal contact resistance between the sand particles is very sensitive to the amount of water that is present (Goldsmid et al., 1981).

The relatively low heat conductivity of the wetland bed materials tested in this study implies that, the wetlands would cool more slowly during the winter, which is a good thing. On the other hand, the wetlands would also warm up slowly during the summer, which may not be the best thing. On the whole, the low rate of heat transfer within the wetland and to and from its surroundings is favorable, because it insures that the wetlands will be able to operate under fairly steady temperatures.

**4.2 Wetlands Performance at Different Temperatures**

Profiles representing the performance of the wetlands monitored in this study during the four phases of temperature are presented in Figures 4.1 to 4.32. Phase 1 (30°C) is represented by Figures 4.1-4.8, and Phase 2 (20°C) is covered by Figures 4.9 to 4.16. Phase 3 (10°C) is represented by Figures 4.17 to 4.24 while Phase 4 (5°C) is covered by Figures 4.25 to 4.32. TCE removal kinetic rate data based on regression analysis of the data for Figures 4.1 to 4.32 are summarized in Table 4.2.
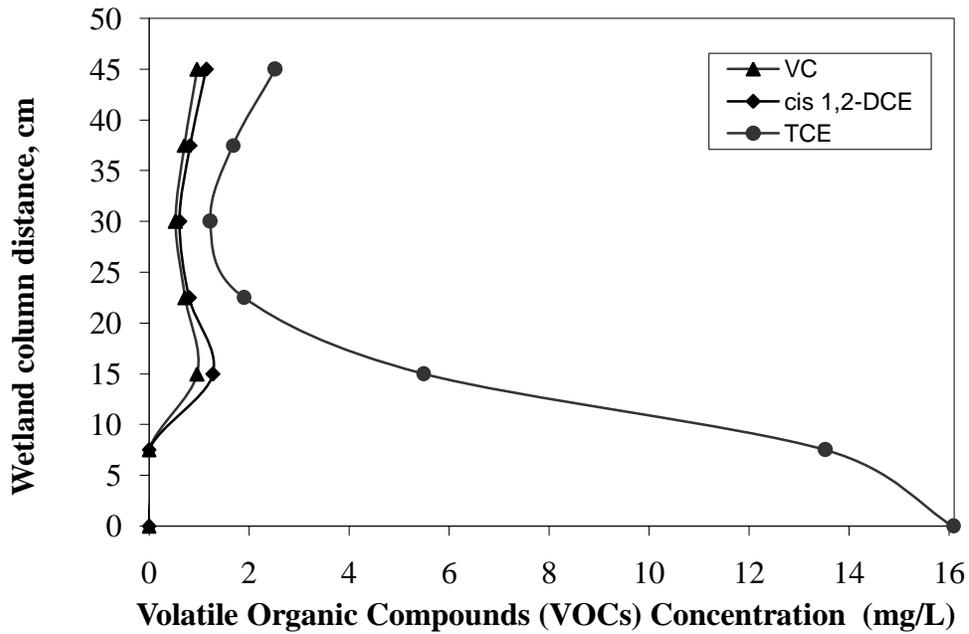
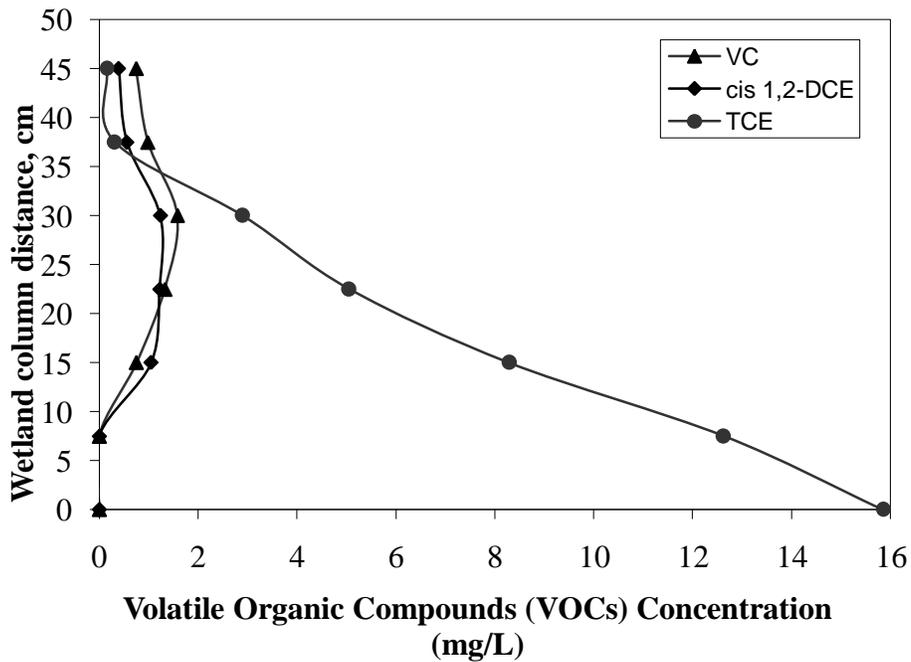**Figure 4.1** Removal of TCE in Wetland A (packed with Compost/Sand) at 30°C, day 385



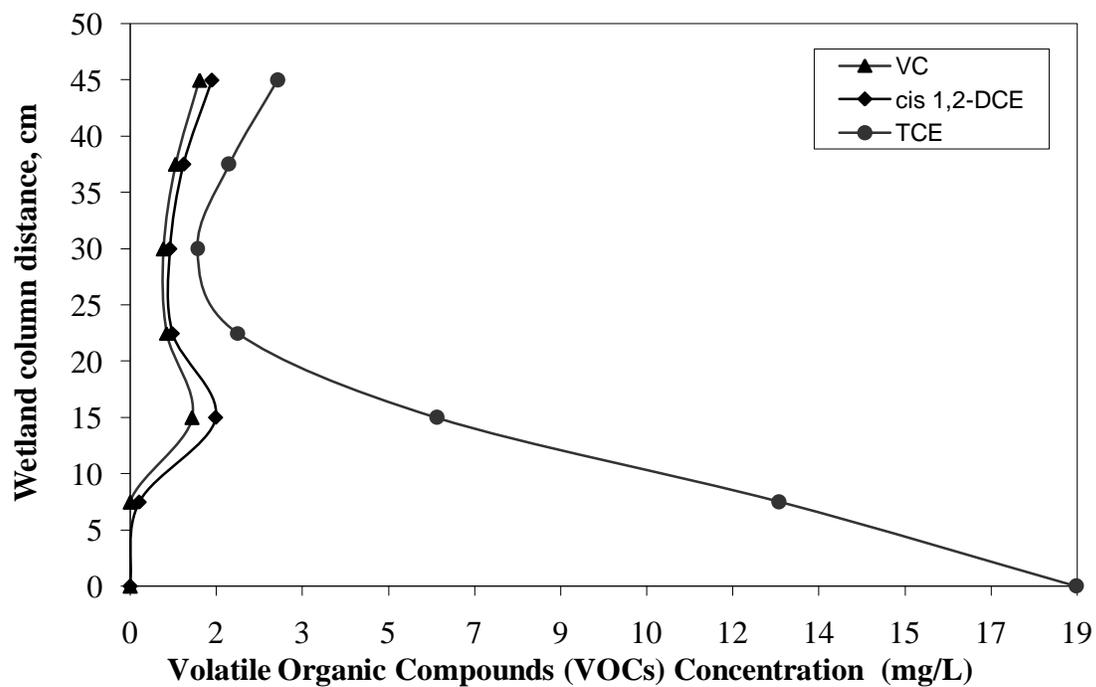**Figure 4.2** Removal of TCE in Wetland B ( with BionSoil®/Latimer/Sand) at 30°C, day 385

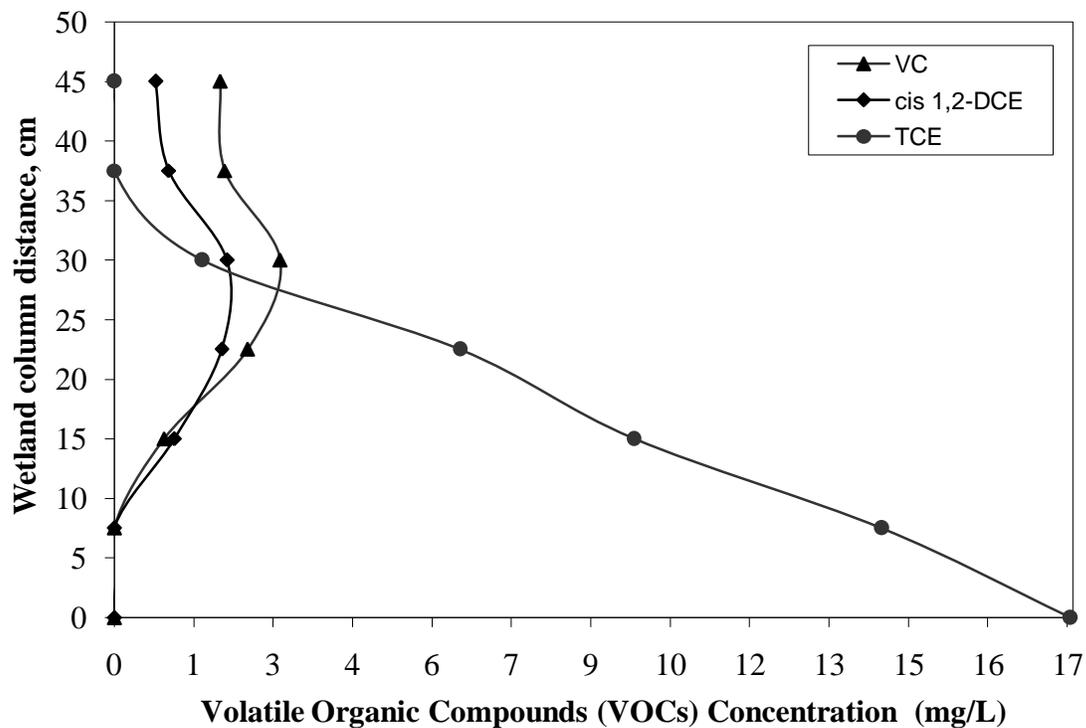**Figure 4.3** Removal of TCE in the Wetland A (packed with Compost/Sand) at 30°C, day 392



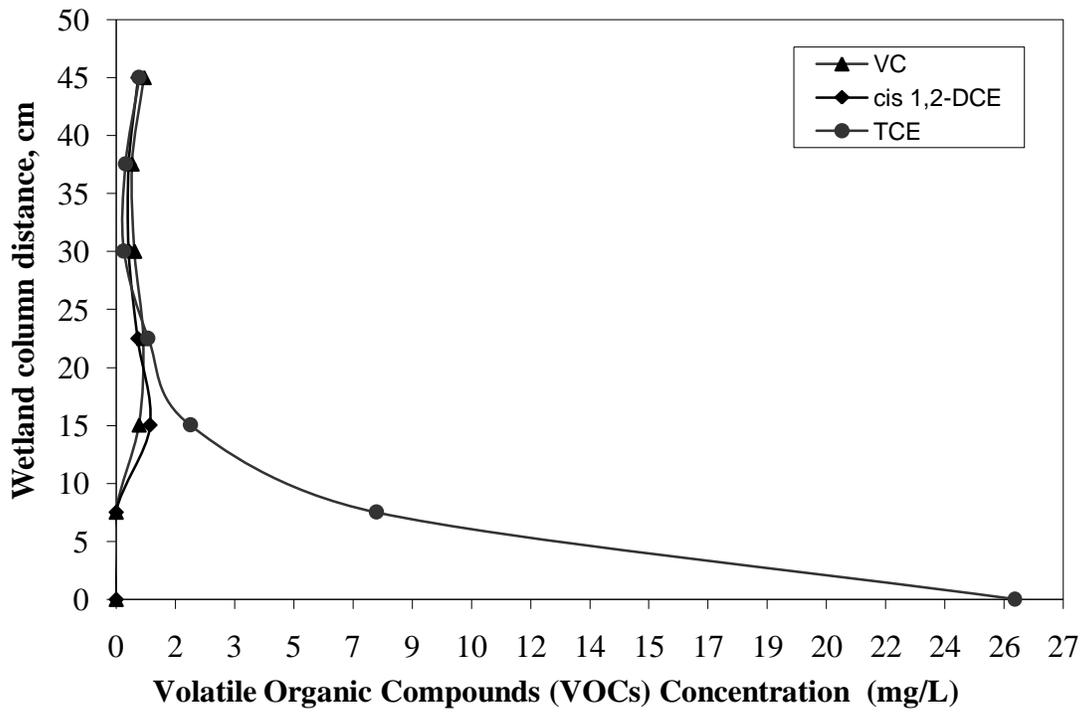**Figure 4.4** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 30°C, day 392

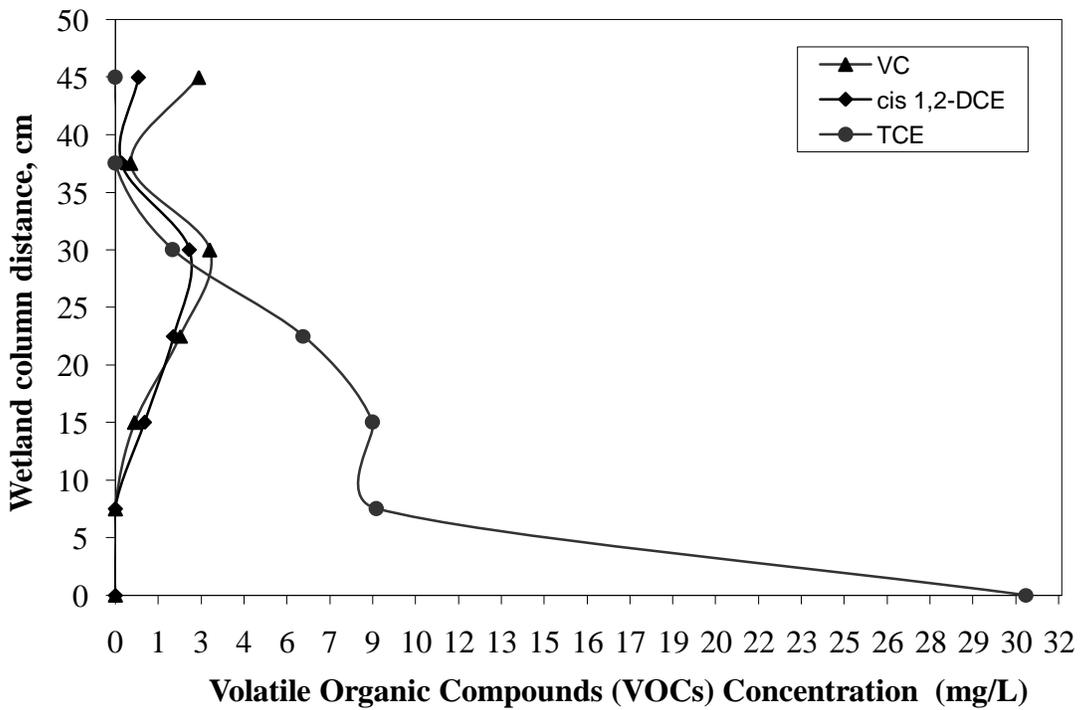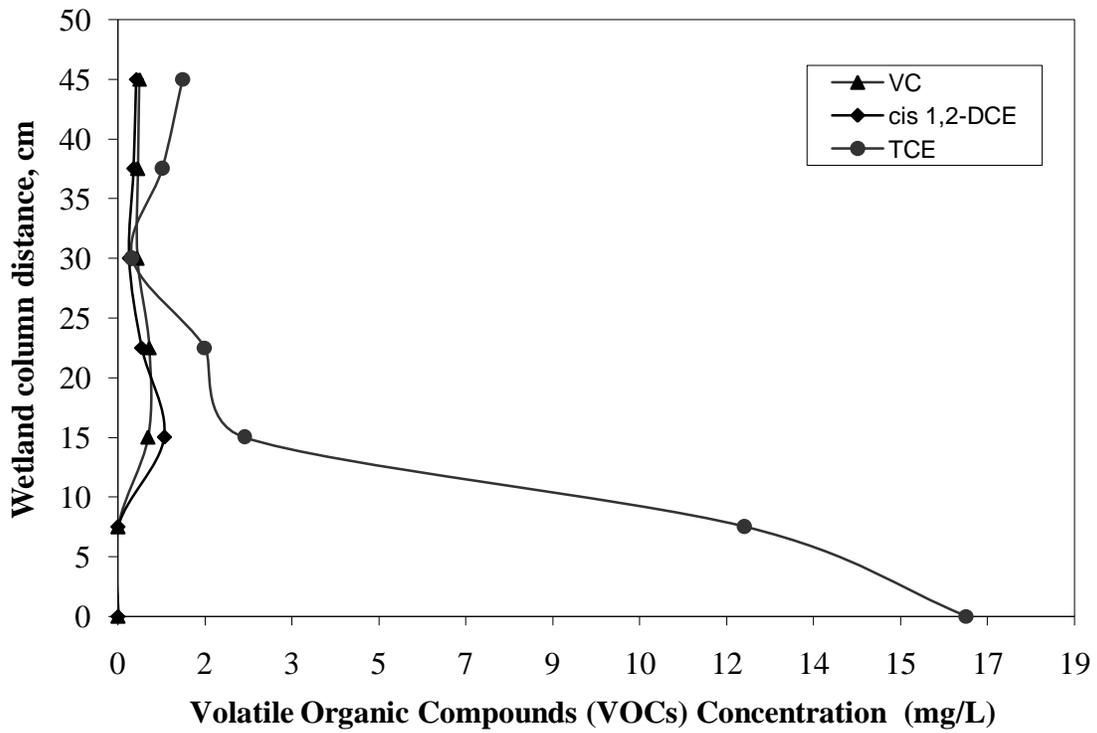**Figure 4.5** Removal of TCE in Wetland A (packed with Compost/Sand) at 30°C, day 399



**Figure 4.6** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 30°C, day 399

**Figure 4.7** Removal of TCE in Wetland A (packed with Compost/Sand) at 30°C, day 406
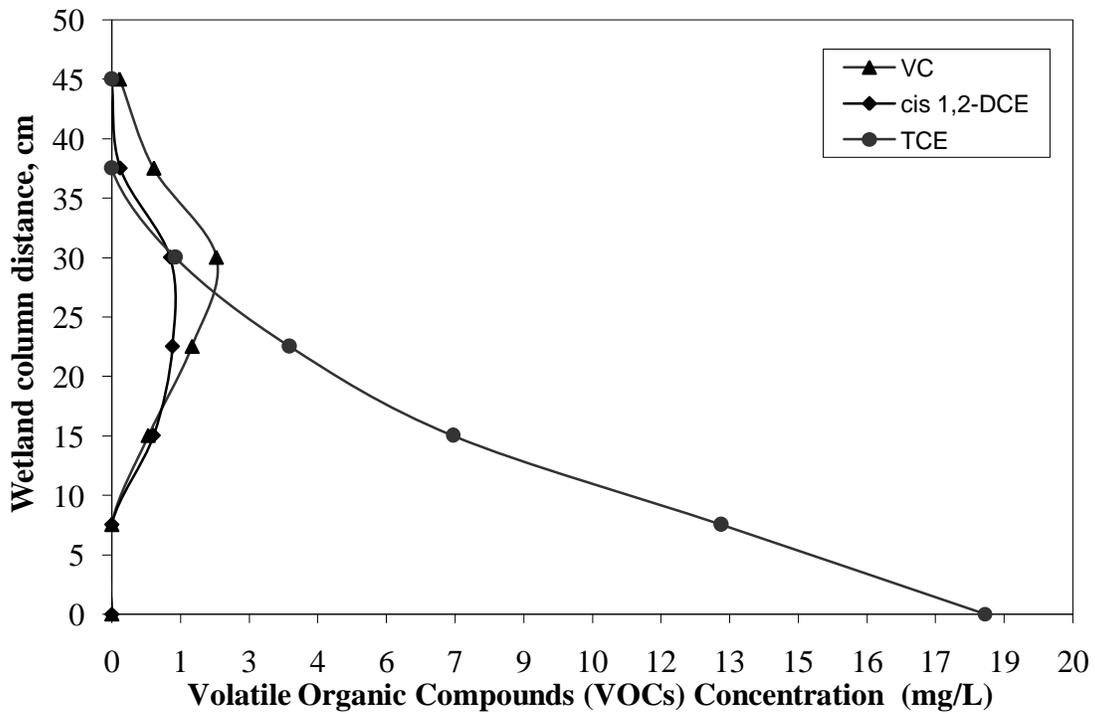


**Figure 4.8** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 30°C, day 406
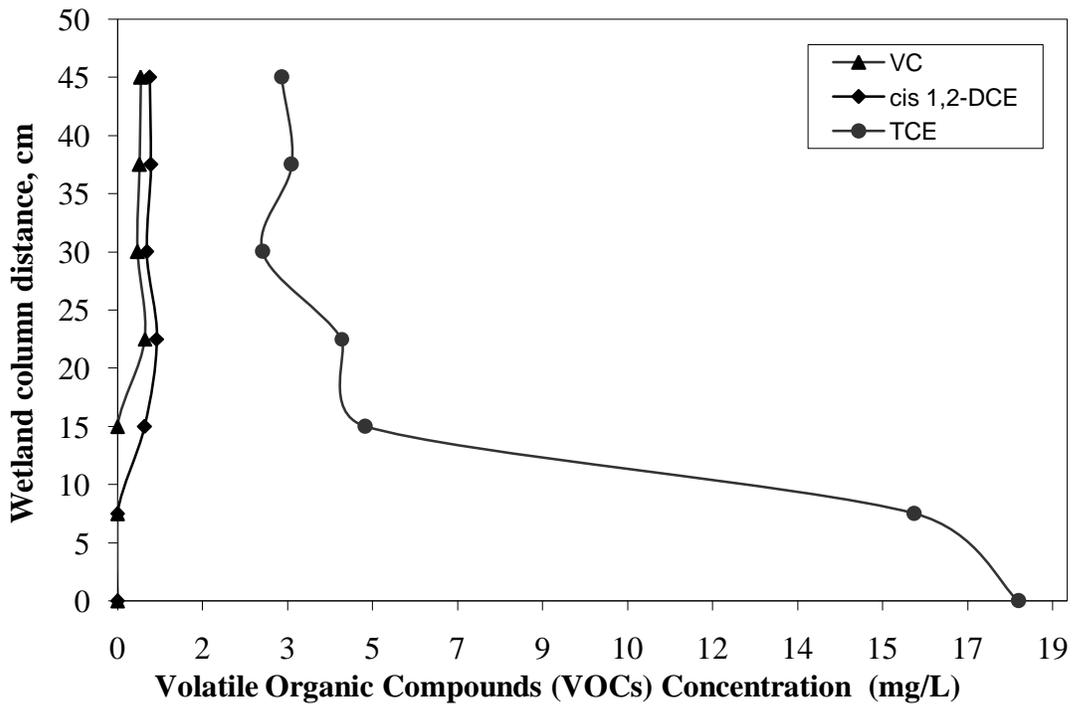
**Figure 4.9** Removal of TCE in Wetland A (packed with Compost/Sand) at 20°C, day 429
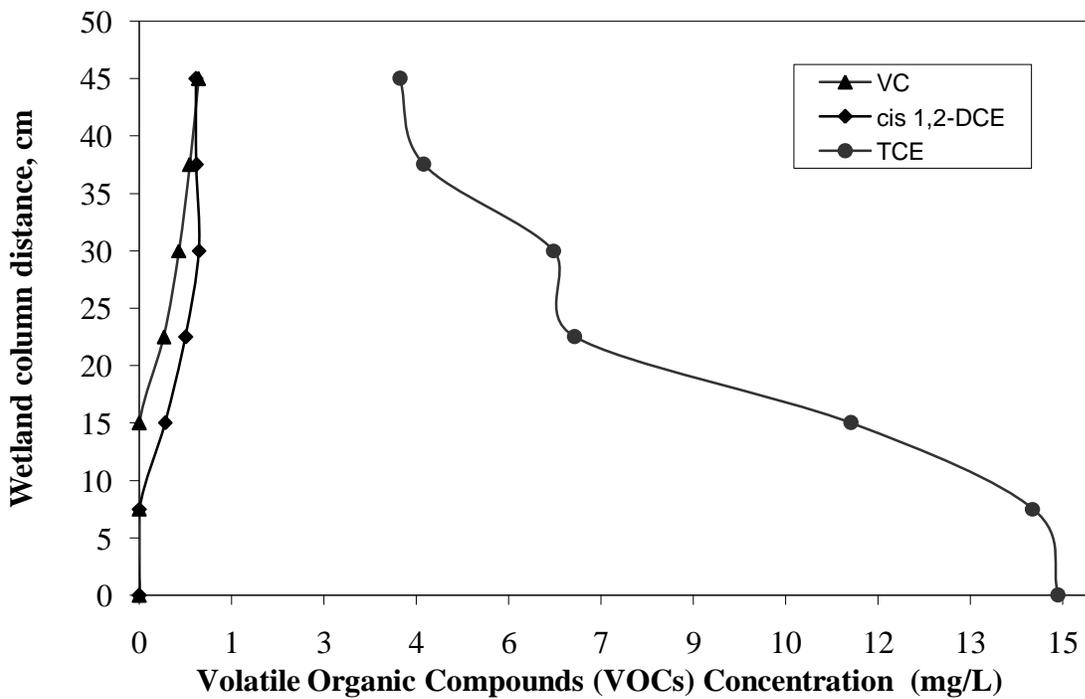


**Figure 4.10** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 20°C, day 429

**Figure 4.11** Removal of TCE in Wetland A (packed with Compost/Sand) at 20°C, day 434



**Figure 4.12** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 20°C, day 434

**Figure 4.13** Removal of TCE in Wetland A (packed with Compost/Sand) at 20°C, day 439



**Figure 4.14** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 20°C, day 439
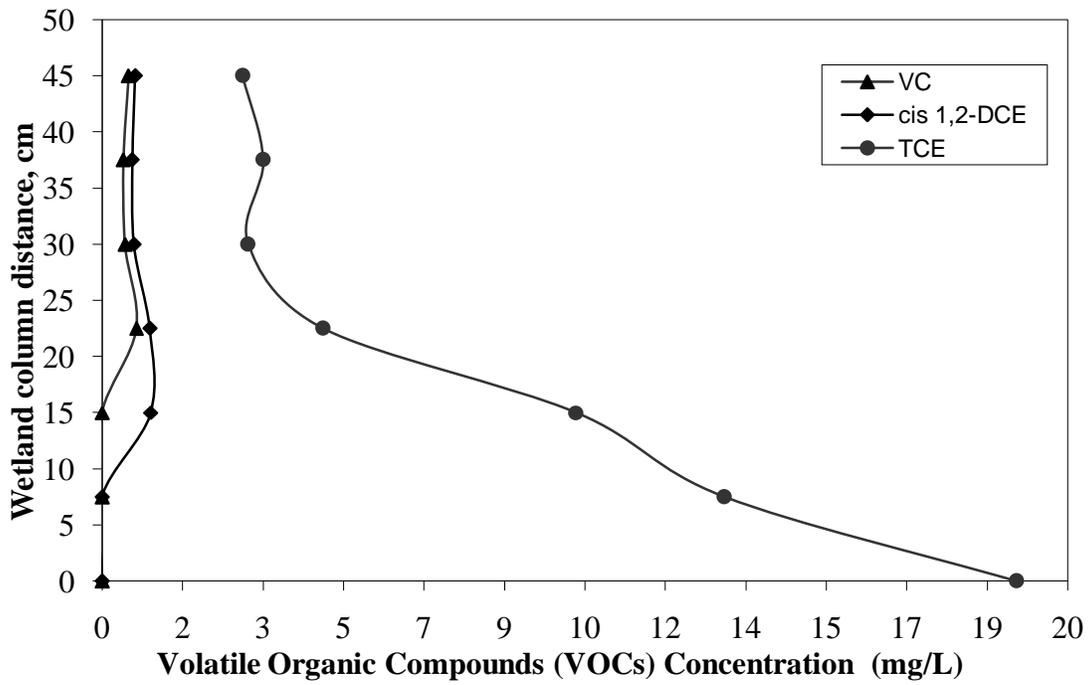
40

**Figure 4.15** Removal of TCE in Wetland A (packed with Compost/Sand) at 20°C, day 445
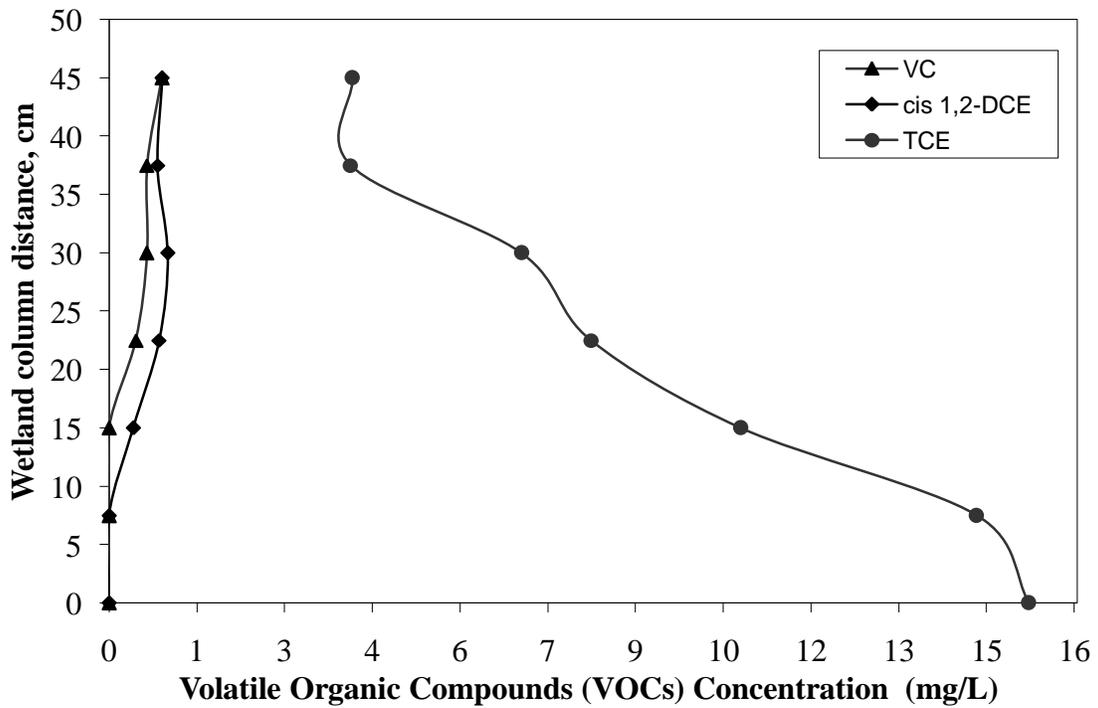


**Figure 4.16** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 20°C, day 445

**Figure 4.17** Removal of TCE in Wetland A (packed with Compost/Sand) at 10°C, day 452
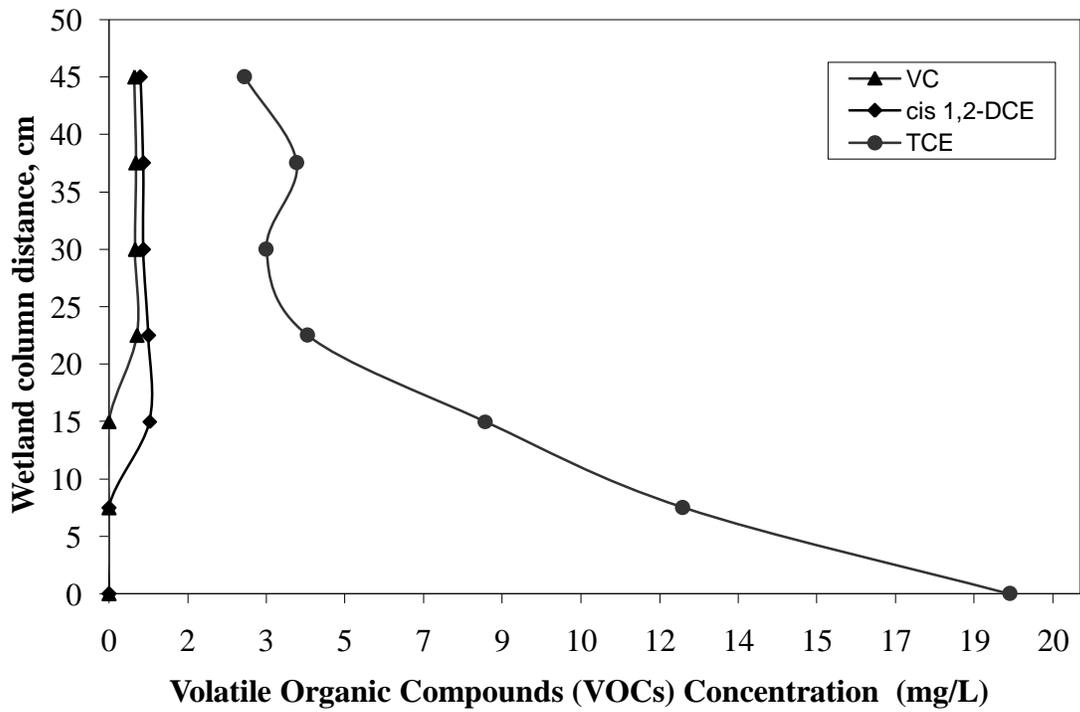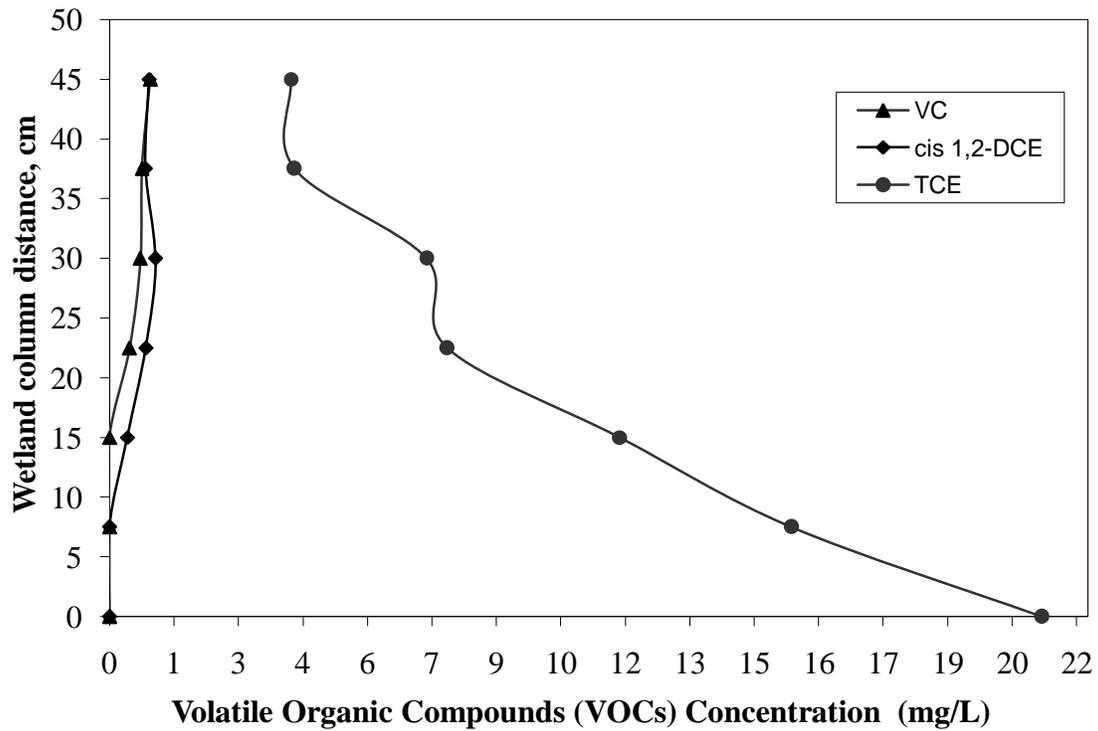


**Figure 4.18** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 10°C, day 452
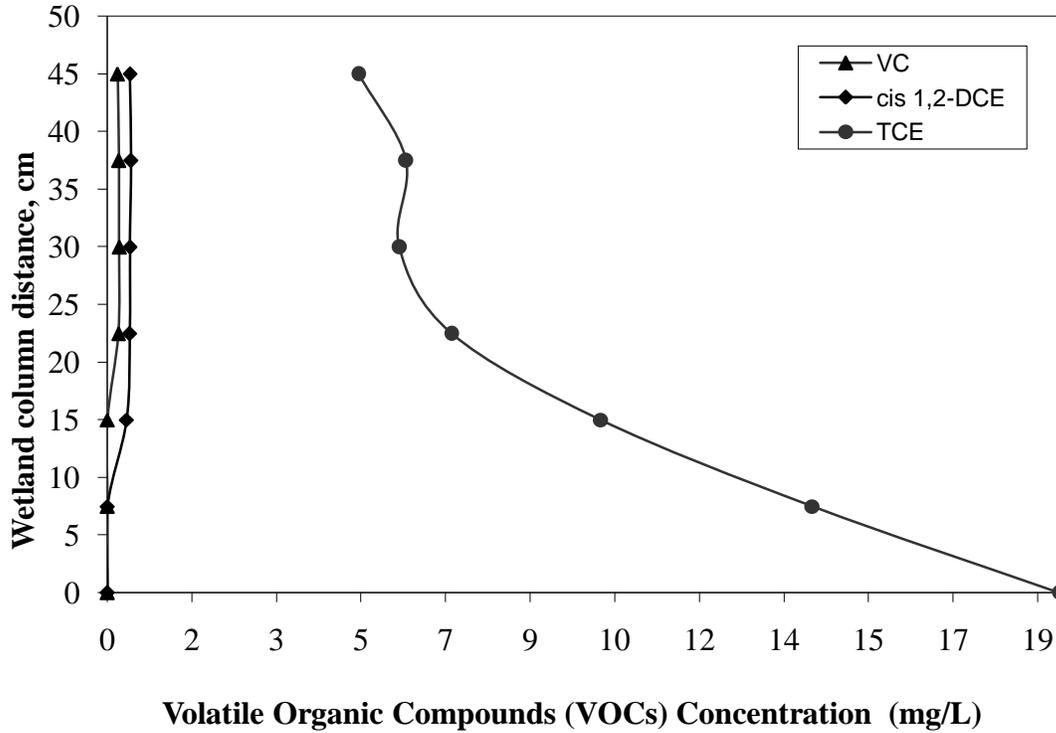
**Figure 4.19** Removal of TCE in Wetland A (packed with Compost/Sand) at 10°C, day 459
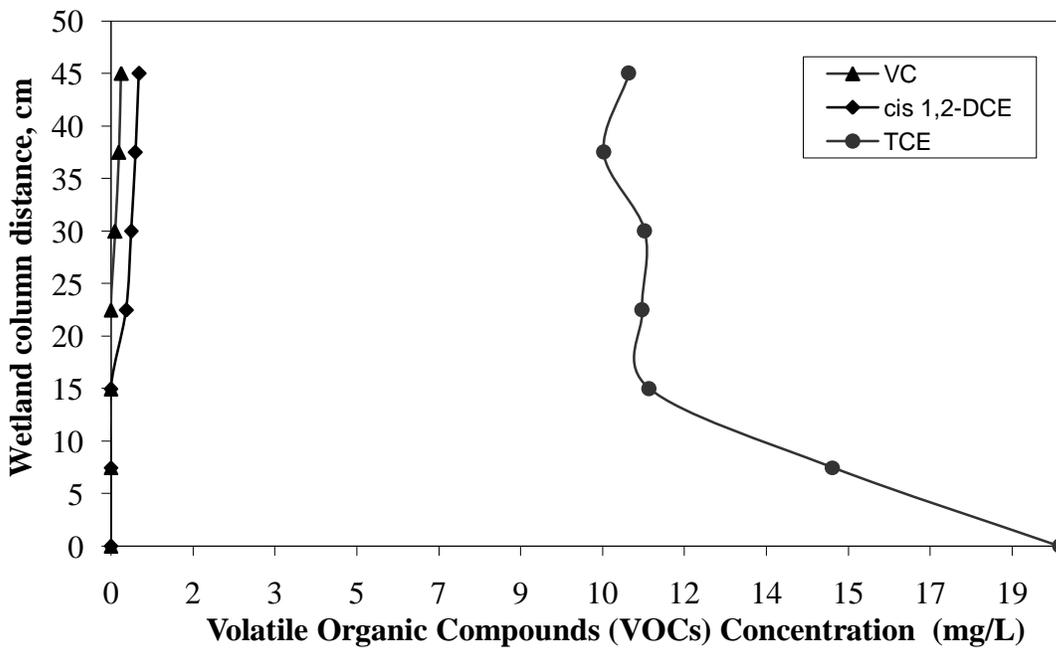


**Figure 4.20** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 10°C, day 459
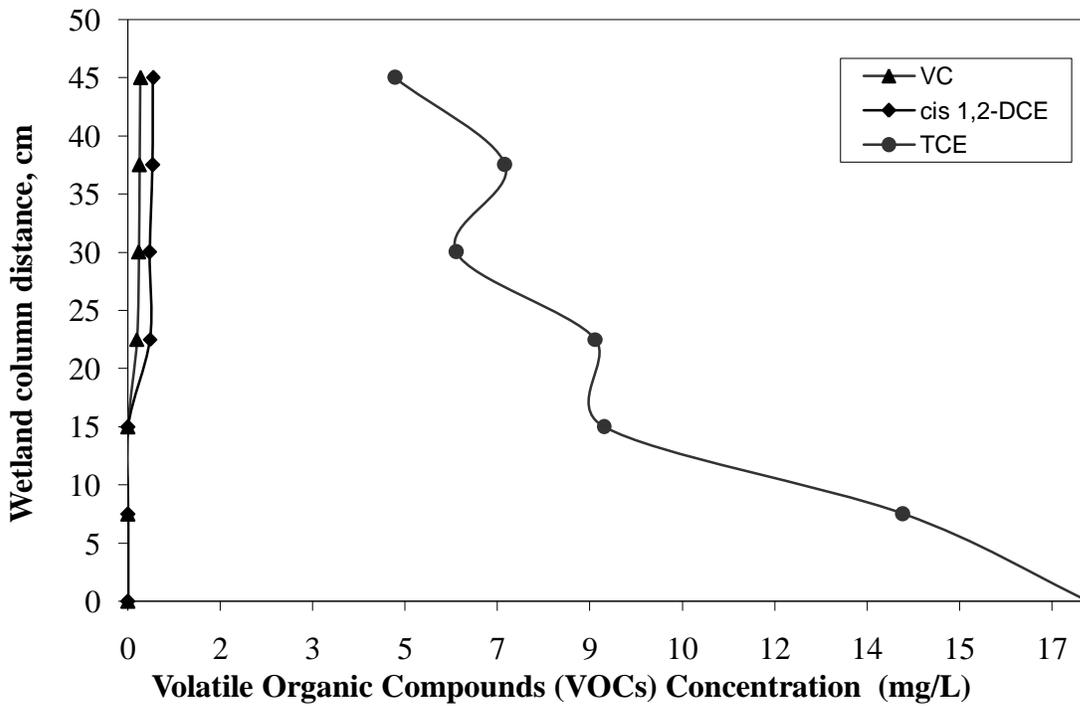
**Figure 4.21** Removal of TCE in Wetland A (packed with Compost/Sand) at 10°C, day 466
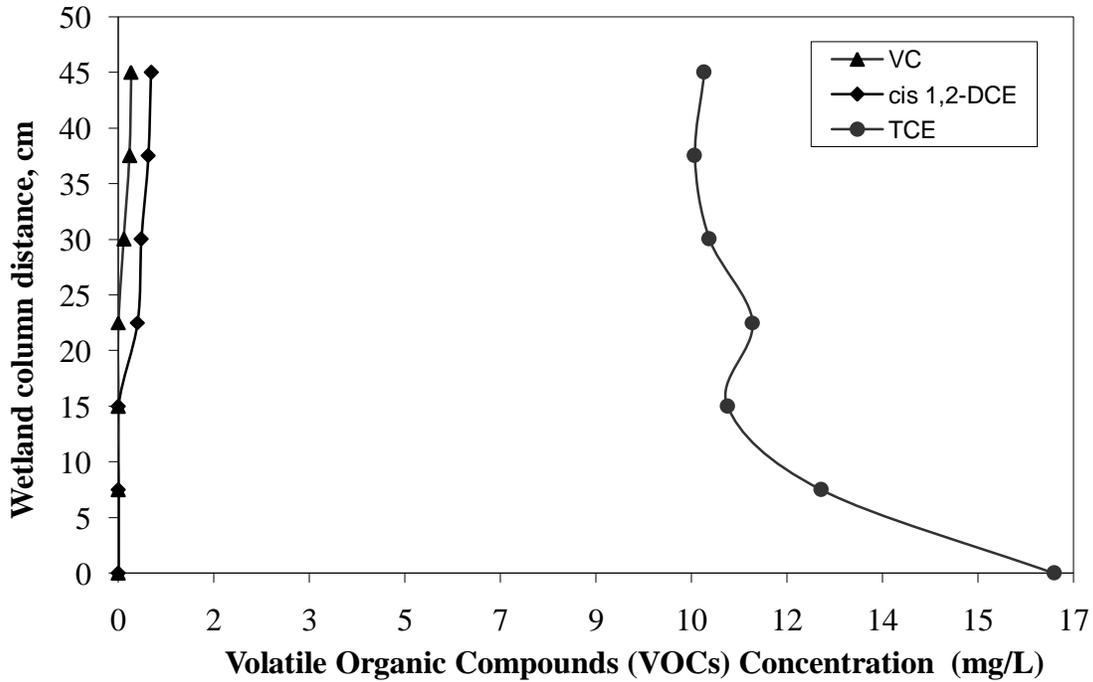


**Figure 4.22** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 10°C, day 466
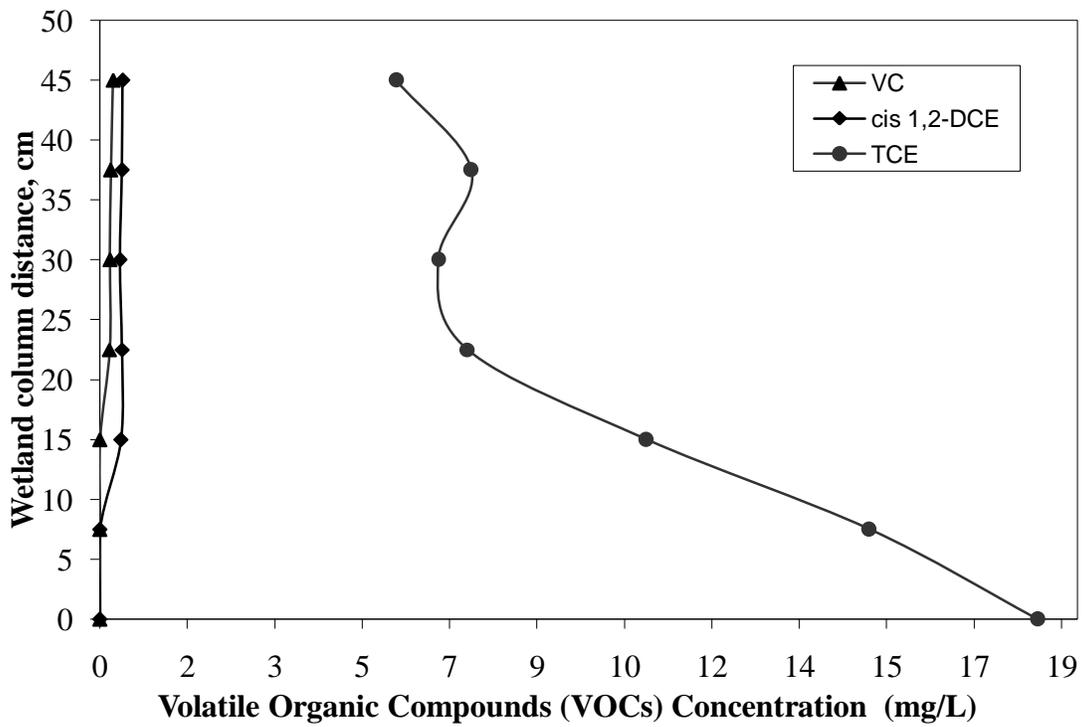
**Figure 4.23** Removal of TCE the Wetland A (packed with Compost/Sand) at 10°C, day 475
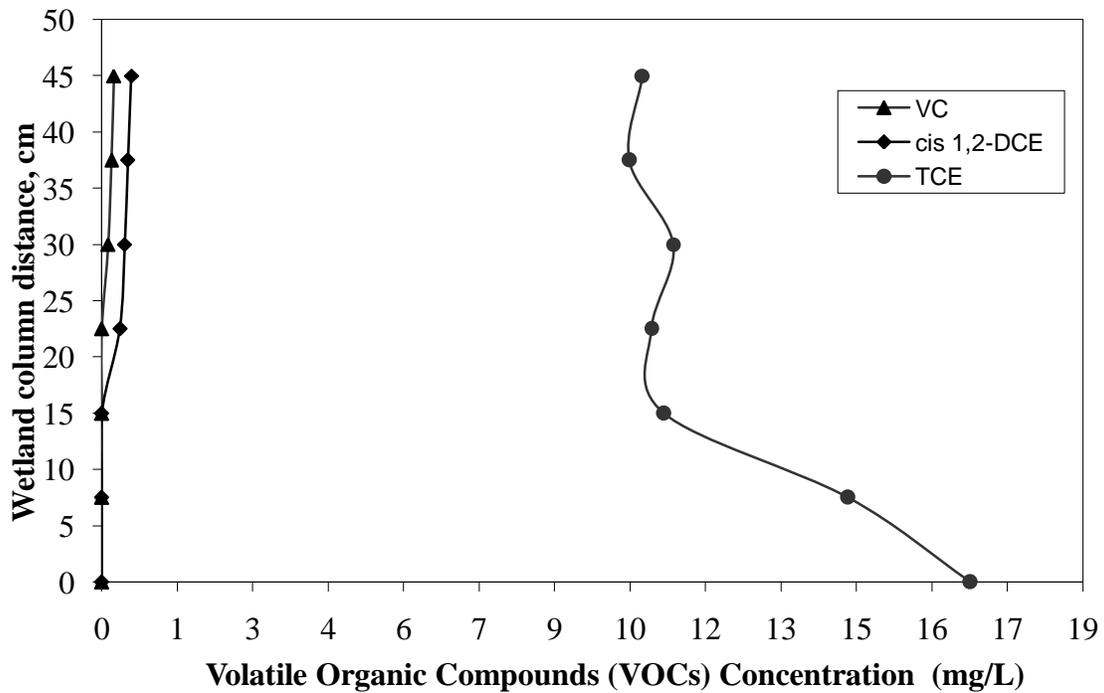


**Figure 4.24** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 10°C, day 475
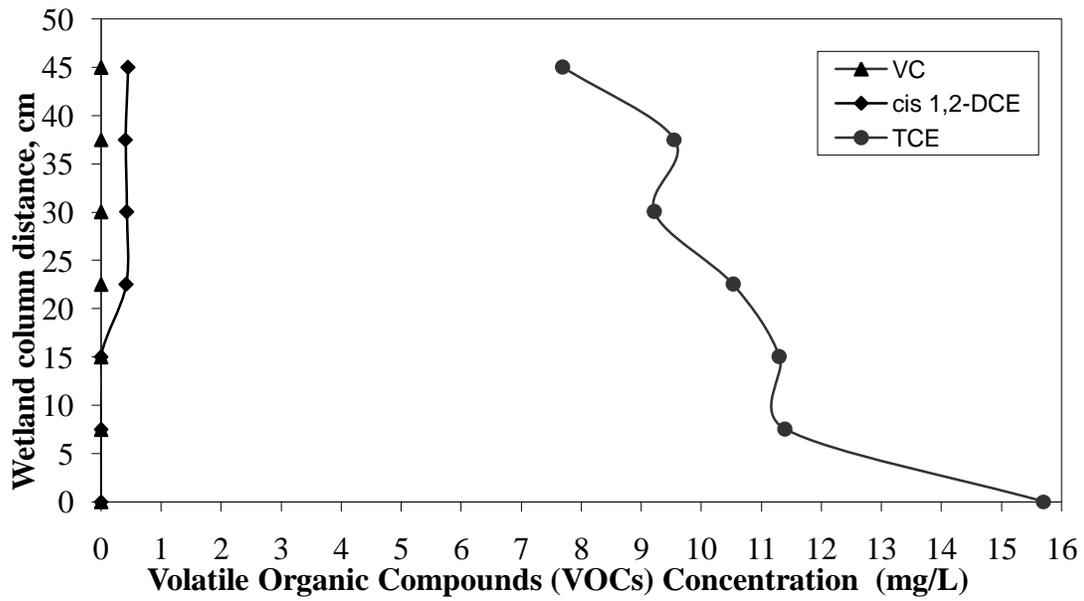
**Figure 4.25** Removal of TCE in Wetland A (packed with Compost/Sand) at 5°C, day 489
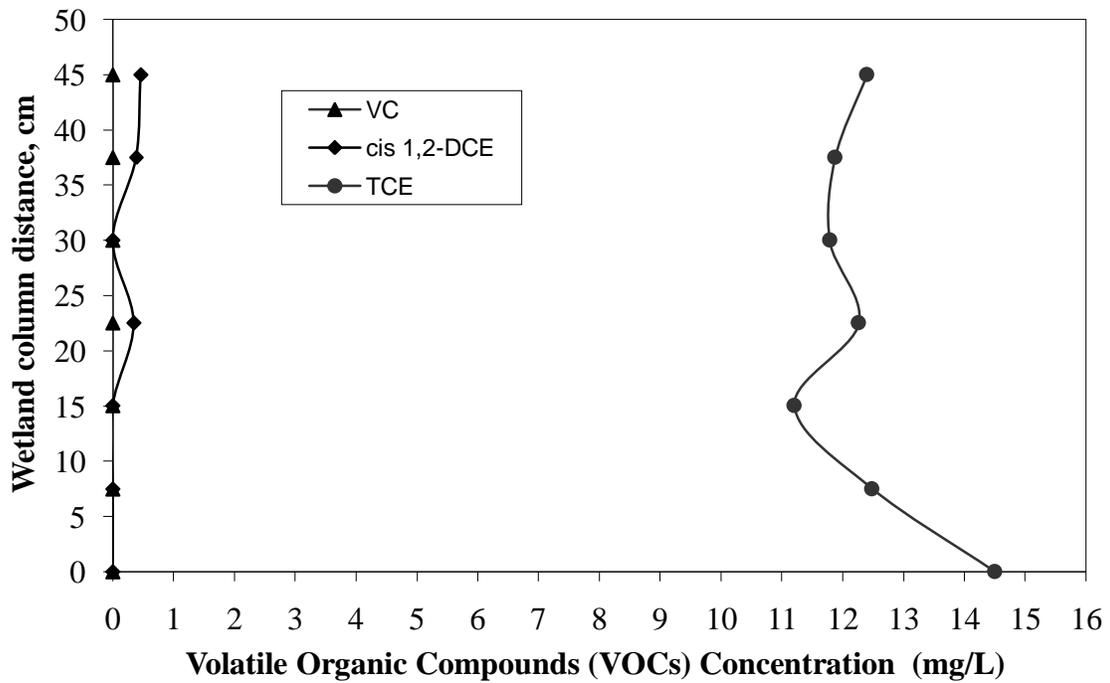


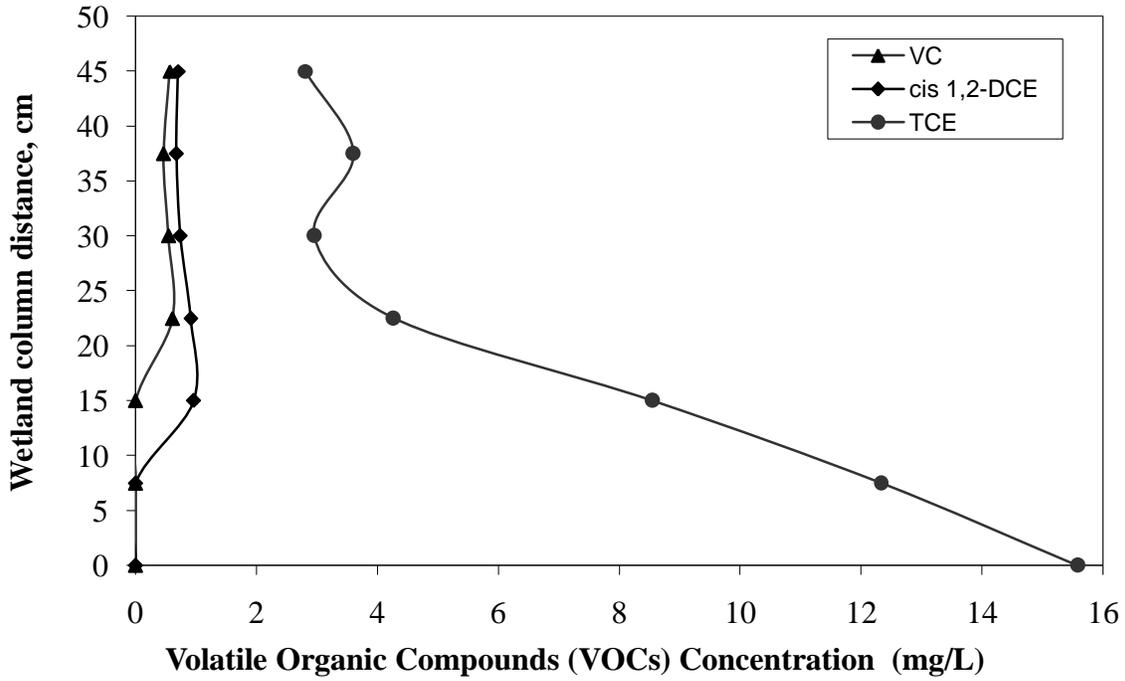**Figure 4.26** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand)  at 5°C, day 489

**Figure 4.27** Removal of TCE in Wetland A (packed with Compost/Sand) at 5°C, day 496
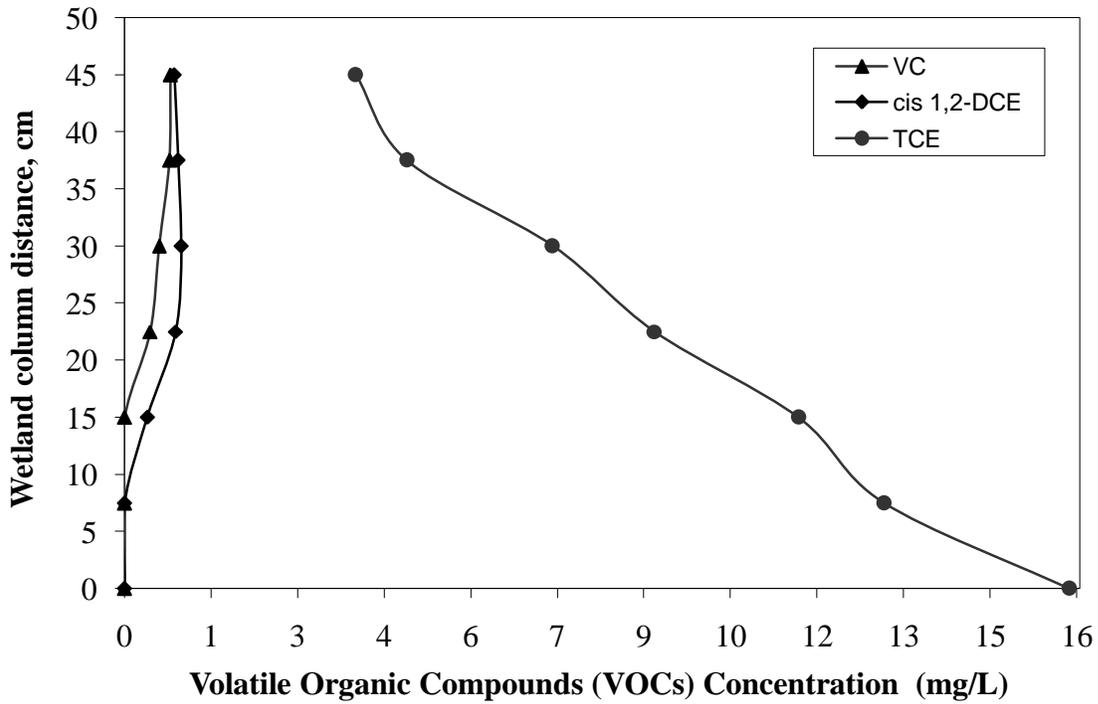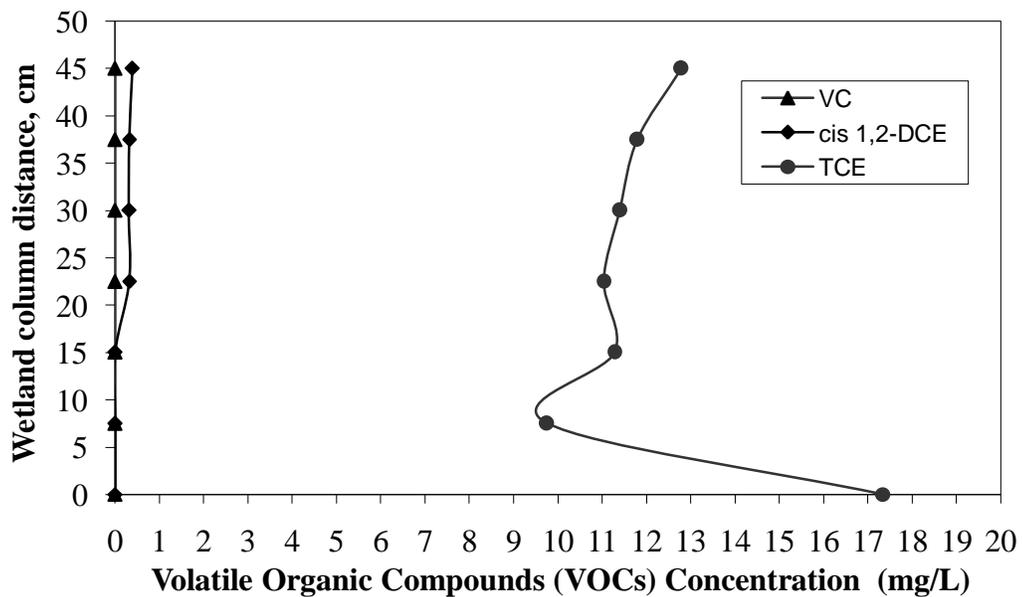


**Figure 4.28** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 5°C, day 496
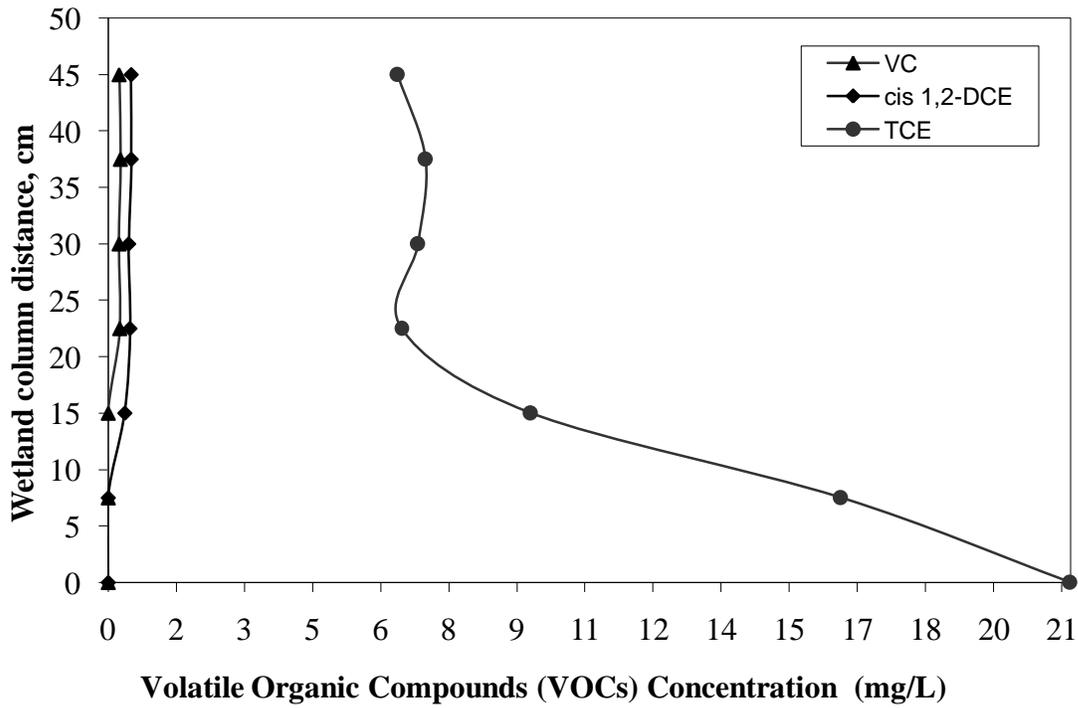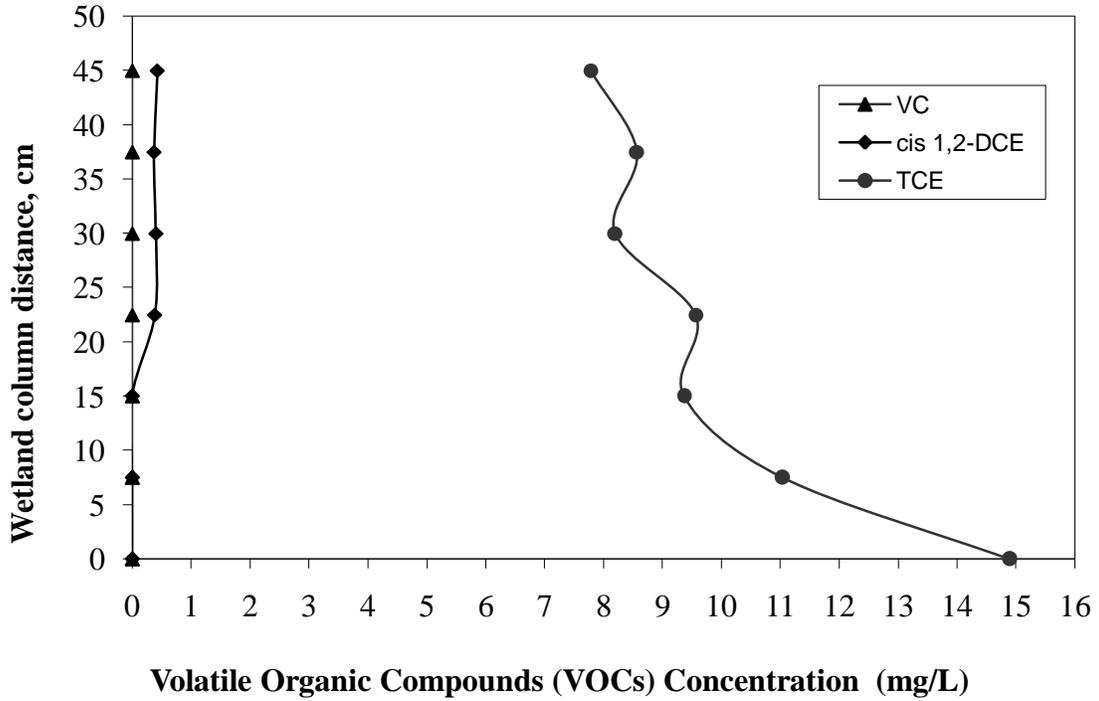
**Figure 4.29** Removal of TCE in Wetland A (packed with Compost/Sand) at 5°C, day 503
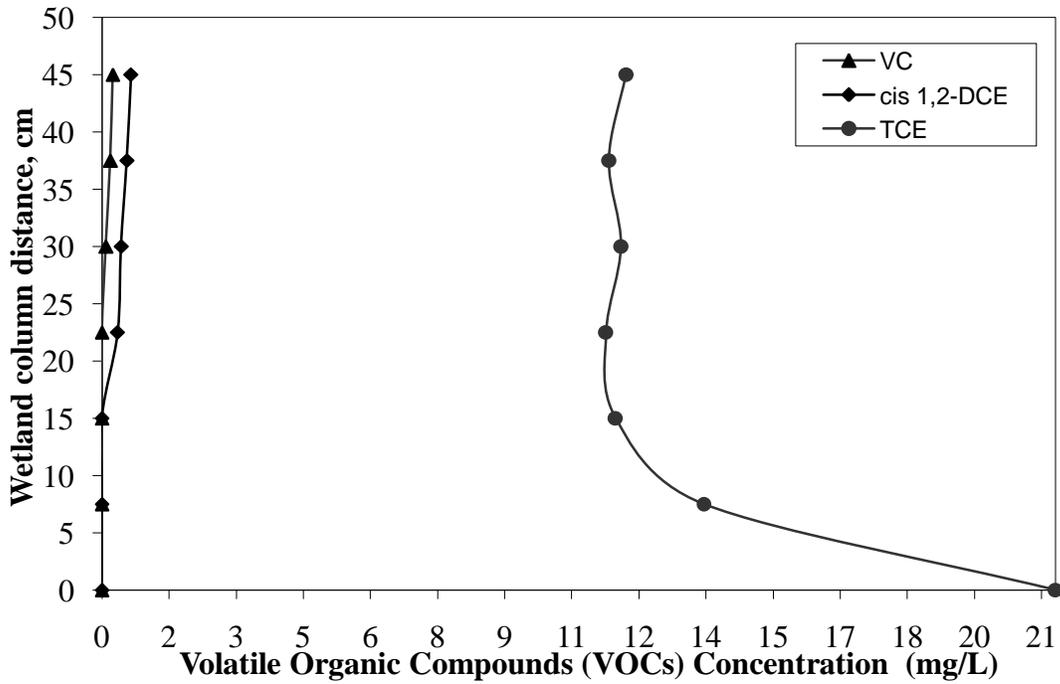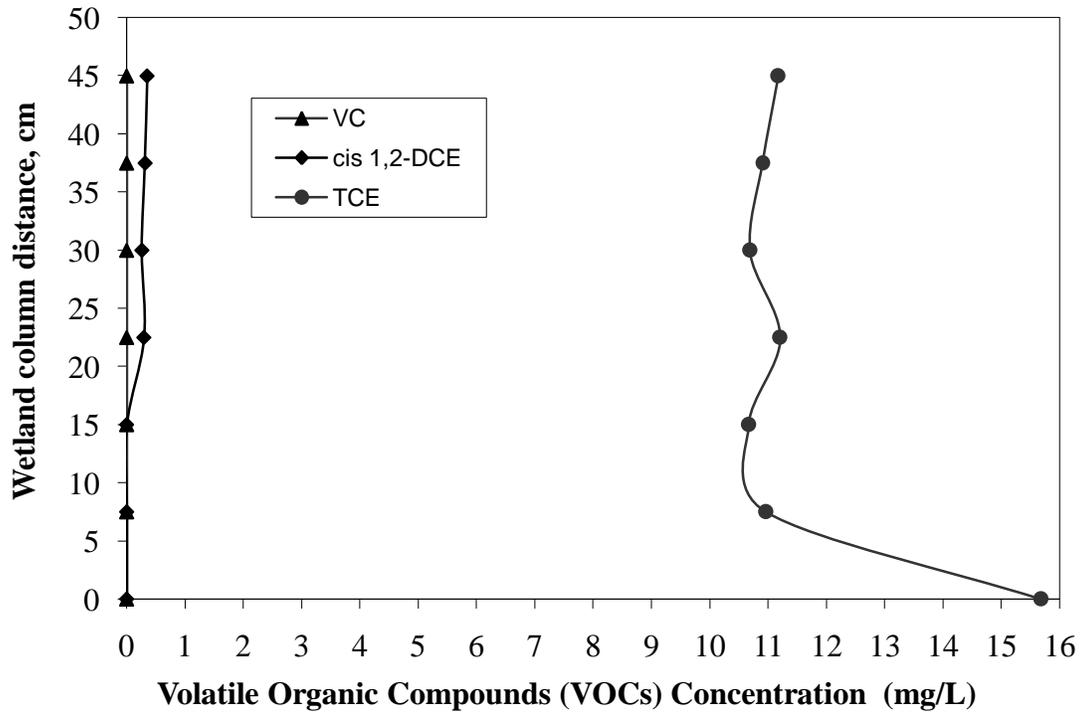


**Figure 4.30** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 5°C, day 503

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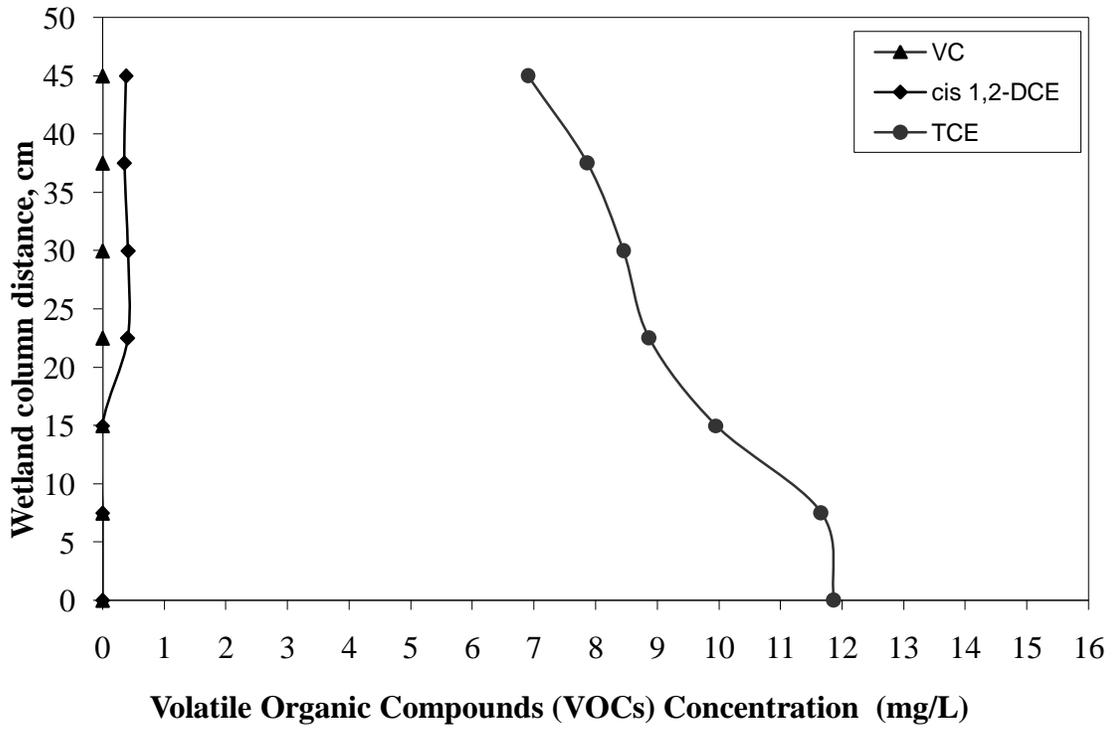
**Figure 4.31** Removal of TCE in Wetland A at (packed with Compost/Sand) 5°C, day 515
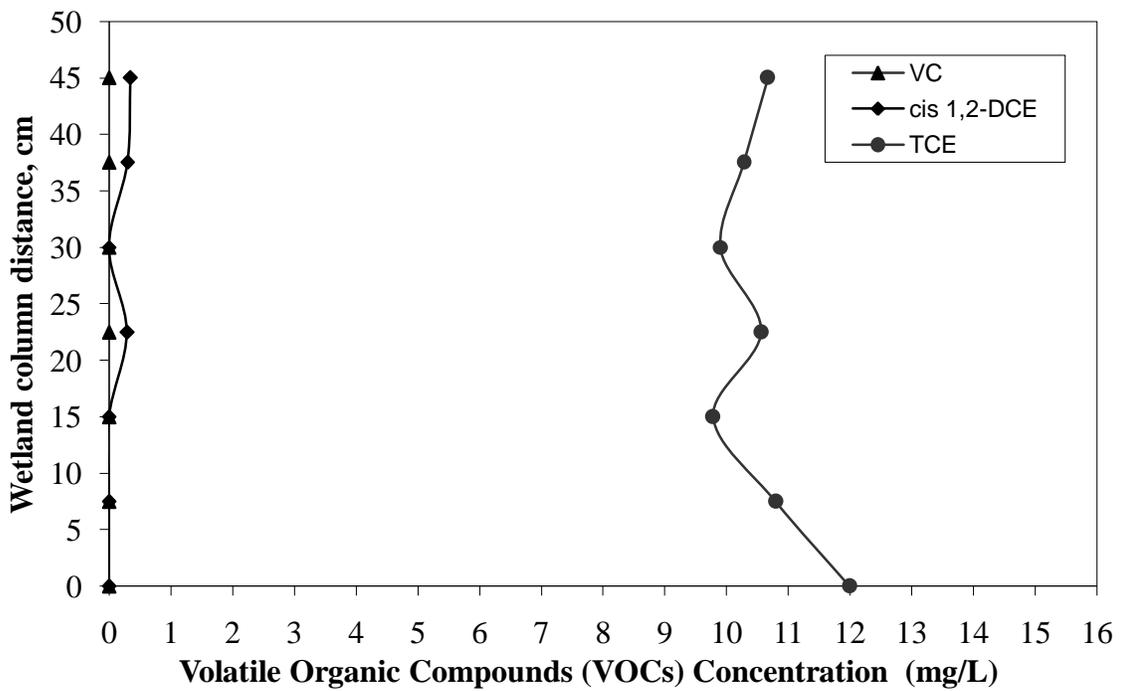


**Figure 4.32** Removal of TCE in Wetland B (with BionSoil®/Latimer/Sand) at 5°C, day 515
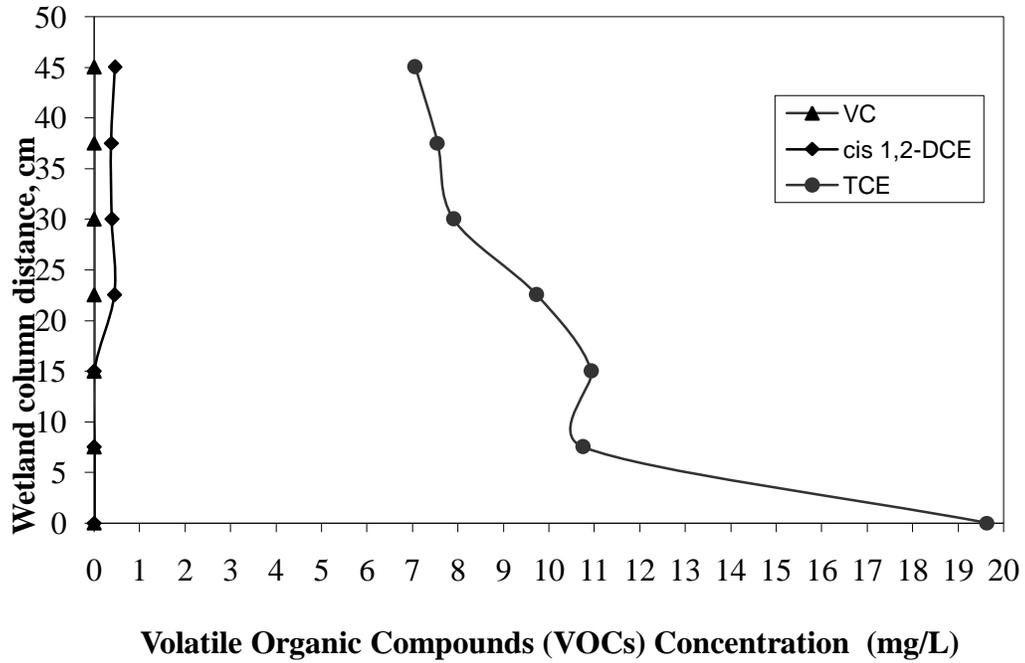
It can be observed that TCE concentrations decreased from the influent to the effluent along the height of both Wetlands. Simultaneously, *cis*-1,2-DCE increased in concentration as the TCE concentration was reduced. VC concentration was consistent during the four phases of temperature, increasing at the same time as the concentration of TCE was decreasing along the height of the wetlands. Overall, the wetlands did not exhibit a significant build up of the TCE degradation products even at the higher temperatures of 20°C and 30°C. Considering that one of the products of  TCE dechlorination, VC is a confirmed carcinogen (U.S. EPA, 2001*a*), the apparently fast degradation of the daughter products is a favorable condition.

It is apparent that at the higher temperatures of 30°C and 20°C, the largest proportion of TCE removal took  place within the first 20-25 cm. A similar observation has been reported by Kassenga (2003) and Kassenga et al. (2003).

The upward decrease in concentration of TCE and the simultaneous formation of *cis*-1,2-DCE indicates that biodegradation was indeed occurring as the TCE solution was flowing upward through the wetland soils. These results are similar to findings by many other researchers where attenuation of TCE has been detected (Lorah et al., 1999; Kassenga et al., 2000, Kassenga, 2003).

Figures such as 4.1 and 4.3 suggest an increase in concentration of TCE with height of the wetland, which is contrary to the expected trend. This trend can be attributed to occasional occurrences of preferential flow, for example, through spaces previously occupied by decaying roots. The cessation of the flows could have resulted from consolidation of the bed material as well as from growth of roots through the previously empty spaces.

The complete degradation of TCE into *cis*-1,2-DCE, and then into VC and finally into ethene suggests the presence of  *Dehalococcoides* sp., a bacterium capable of degrading TCE

completely to ethene via *cis*-1,2-DCE and VC (Wiedemeier et al., 1996; Maymo-Gatell et al., 2000). *Dehalococcoides ethenogenes* strain 195, which was discovered by Maymo-Gattel et al. (1997) is able to dechlorinate TCE completely to ethene, in contrast to other known microorganisms such as *Dehalobacter restrictus* (Fennell and Gossett, 1997), and *Desulfitobacterium frapperi* (Maymo-Gatell et al., 2001) which cannot degrade TCE further than *cis*-1,2-DCE.

Even though the pattern of TCE degradation followed the same trend at the different temperatures in the wetlands, the rate of degradation of TCE was greater at higher temperatures (30°C and 20°C) than at the lower temperatures (10°C and 5°C), the concentration of TCE decreased slowly. Other researchers have demonstrated that reductive dechlorination is temperature dependent (Zhuang et al., 1995). The optimum temperature for the performance of conventional treatment wetlands is 25°C (Kadlec and Knight, 1996). Other researchers have reported that the temperature range for maximum dechlorination rates is from 25 to 35°C for TCE (Holliger et al., 1993). Although these results are mostly based on microcosm studies, there is agreement between them and the results obtained in this study. In terms of microbial activity, it has been documented that the optimum temperature for methanogenesis is at 25°C where the microbial activity is high (Boon and Mitchell, 1995; Sorrell et al., 1997).

It is well known that *Dehalococcoides ethenogenes* strain 195 uses TCE as an electron acceptor in anaerobic respiration and requires $H_2$ as its sole electron donor, and that it grows slowly in pure culture (Richardson et al., 2002). Also, it is well understood that the increasing temperatures might stimulate hydrogen production from the organic substrate to a larger degree relative to hydrogen consumption by dechlorinators (potentially resulting in compensation concentrations that increase with temperature) (Hiennman et al., 2006). Reductive dechlorination of chlorinated solvents such as TCE, and  *cis*-1,2-DCE  are commonly linked to the utilization of

$H_2$ as an electron donor (Fennel and Gossett, 1998; Maymo-Gattel et al., 1999; 2001, Kassenga et al., 2004).

Heinman et al. (2006) observed that the re-addition of TCE resulted in complete, sequential dechlorination of TCE via *cis*-1,2-DCE and VC to ethene, which was accompanied by a decrease in $H_2$. After complete dechlorination of all chlorinated compounds they observed a characteristic rise of hydrogen concentrations back to approximately the initial levels. This observation is consistent with findings of others (Yang et al., 1998; He et al., 2002; Kassenga et al., 2006) and demonstrates the presence of hydrogen producing substrates throughout the experimental period.

Another noteworthy feature of the performance results during the 5 and 10°C temperature phase, is the incomplete removal of the parent chemical TCE throughout the wetland. Figures 4.1-4.32 indicate that TCE and its daughter products broke through during all the four temperature phases of this study, which might be interpreted to mean that the wetlands were not completely effective in removing TCE and its daughter products. This view is not correct because the breakthrough of TCE and its daughter products can be attributed to high hydraulic and pollutant loading rates. The hydraulic loading rate adopted in this study was 19.8 cm $d^{-1}$ whereas Kassenga (2003) adopted a rate of about 4.9 cm $d^{-1}$ for similar wetlands. Kassenga (2003) treated chlorinated VOCs with concentrations less than 6 mg/L whereas in this study, TCE concentration was higher than 15 mg/L. The high hydraulic and pollutant loading rates were adopted to ensure enough data points for computing TCE removal rates. It is noteworthy that at lower hydraulic loading rates (for example, 11.3 cm $d^{-1}$, complete removal of TCE and its daughter products was achieved.

Although at 5°C no significant degradation is expected to occur (Mander and Jenssen, 2003), it is evident from Figures 4.26-4.32 that a significant removal of TCE occurred in Wetland A. Although much lower than for Wetland A, an appreciable degree of removal of TCE also occurred in Wetland B. It is noteworthy that the TCE removal rate at 5°C is more than five (5) times higher for Wetland A than for Wetland B. The unexpected relatively better performance of the wetlands at 5°C can be attributed to the insulating property of the wetland bed material, which minimizes heat loss from the wetland. However, this argument presupposes that processes within the wetland generates a significant amount of heat or the feed water had a higher temperature. Temperature within the wetlands was not monitored, and as such the above arguments can not be confirmed or discredited.

A number of noteworthy observations can be made with respect to Table 4.2 and Figure 4.33. The TCE removal rate constants show a significant decrease with temperature for both wetlands. This observation is consistent with results from microcosm studies for chlorinated VOCs (Lorah et al., 1999; Lorah et al., 1997; Kassenga et al., 2003, Kassenga, 2003) and pilot scale as well as full-scale wetlands treating conventional pollutants (Kadlec and Reddy, 2000; Zhuang et al., 1995).

**Table 4.2** Summary of TCE Removal Rate Constant Data for the Upflow Wetlands for Different Temperatures

| Temperature, °C and Kinetics, $cm^{-1}$ | Wetland A | Wetland B |
|---|---|---|
| 30 | $0.0680 \pm 0.0200$ | $0.0829 \pm 0.0156$ |
| 20 | $0.0424 \pm 0.0020$ | $0.0336 \pm 0.0031$ |
| 10 | $0.0268 \pm 0.0020$ | $0.0101 \pm 0.0018$ |
| 5 | $0.0138 \pm 0.0039$ | $0.0031 \pm 0.0012$ |
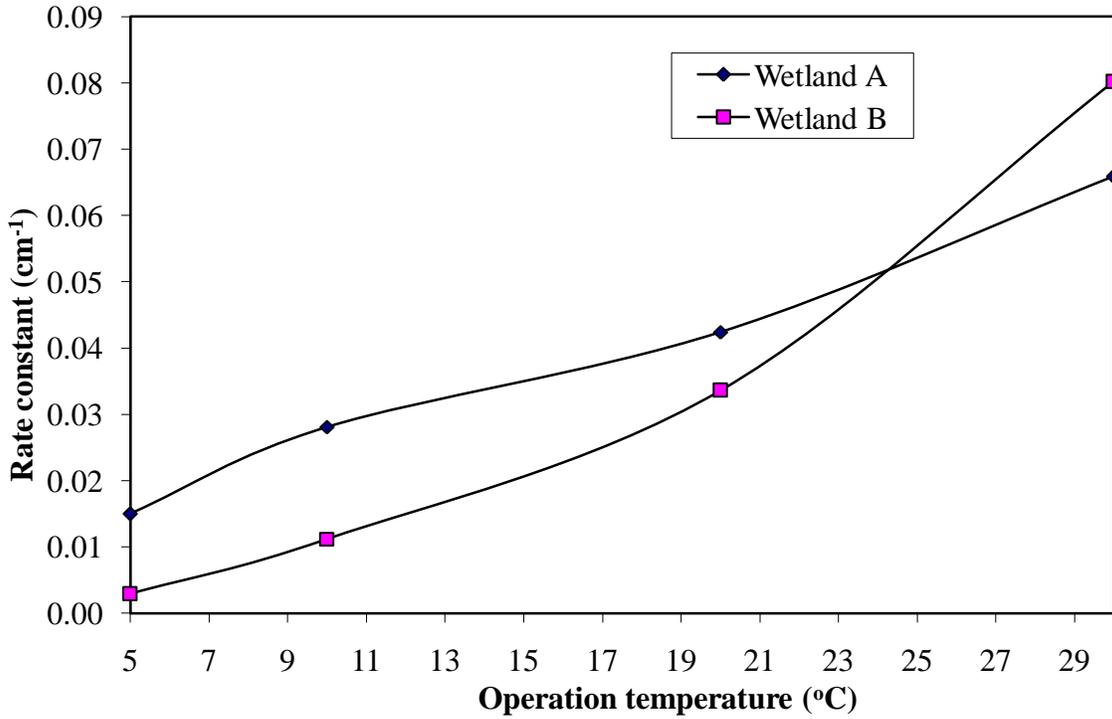
**Figure 4.33** Variation of TCE Removal Rate Constant Values with Temperature

The decrease in the TCE removal rates is steeper for Wetland B than for Wetland A. The TCE removal rate constant of Wetland A decreased by a factor of 4.4 due to the decrease in temperature from 30°C to 5°C. On the other hand, the TCE removal rate constant of Wetland B decreased by a factor of 27.8. Wetland A performed worse than Wetland B at the higher temperature of 30°C, but performed significantly better at all other temperatures. Overall, Wetland A performed better than Wetland B by and average factor of 2.43. Wetland A outperformed Wetland B by a factor of 5.13 during the 10°C temperature phase.

No direct comparisons can be made between the TCE removal rate constants determined in this study and most studies reported in the literature such as Lorah et al., (1997); and Lorah et al., (1999) which are temporal rather than spatial like the ones from this study. Neglecting the effects of sorption, dispersion, and advection on TCE removal, some comparison can be done between this study and other studies reported in the literature. The temporal TCE removal rate

constants corresponding to the rate constants given in Table 4.2 range between 0.54 d$^{-1}$ and 2.37 d$^{-1}$ for Wetland A, and between 2.89 d$^{-1}$ and 0.106 d$^{-1}$ for Wetland B. Kassenga et al. (2003) have reported temporal removal rates of 0.37 to 0.84 d$^{-1}$ for *cis*-1,2-DCE and 0.42 to 6.52 d$^{-1}$ for 1,1,1-TCA at around 25°C for similar wetlands. Lorah et al. (1997) have reported TCE removal rates of between 0.1 and 0.3 d$^{-1}$ for microcosm experiments at room temperature based on sediments from Aberdeen Proving Grounds. The spatial removal rates of 0.09 to 0.41 cm$^{-1}$ for *cis*-1, 2-DCE and 0.42 to 2.8 cm$^{-1}$ for 1,1,1-TCA reported by Kassenga et al., (2003) are lower than the ones from this study.

Comparing further the reductions in TCE removal rate constants, ratios of the rate constants for different temperatures are $k_{(30°C)}/k_{(20°C)} = 1.55$; $k_{(20°C)}/k_{(10°C)} = 1.51$, and $k_{(10°C)}/k_{(5°C)}$ =1.90 for Wetland A. Corresponding figures for Wetland B are $k_{(30°C)}/k_{(20°C)} = 2.39$; $k_{(20°C)}/k_{(10°C)} = 3.00$, and $k_{(10°C)}/k_{(5°C)}$ =3.82. Evidently, the ratios for Wetland B are consistently higher than those for Wetland A (by a factor of close to 2).

Comparing these results to a laboratory scale wetland treating wastewater nitrate removal in laboratory scale construction wetlands (Wood et. al, 1999); the removal rate obtained was around 0.062 to 0.077 h$^{-1}$ between 18°C to 23°C degrees and at 30°C was 0.184 h$^{-1}$. This yields a $k_{(30°C)}/k_{(20°C)}$ of 2.64. Another study by Kadlec and Reddy (2000) reported ratios for rate of removal from detrital plant tissue in Lake Apopka marsh. Those wetlands were used for the treatment of eutrophic water with *Typha* species for decomposition, nitrogen release and phosphorus release. The ratios of removal rate constants for decomposition was $k_{(30°C)}/k_{(20°C)} = 1.7$, $k_{(30°C)} k_{(20°C)} = 1.4$ for the nitrogen release, and $k_{(30°C)}/k_{(20°C)} = 4.5$ for a phosphorus release.

The data given in Table 4.2 and presented in Figure 4.33 can be used to derive temperature correction factors for Wetland A and B using Equation 3.5 as discussed earlier.

Considering that Figure 4.33 indicates an uncharacteristic change in the rate of decrease of TCE removal rate with temperature between 10°C and 5°C for Wetland A, calculations for the temperature correction factor can be done with both the inclusion and exclusion of the data for the 5°C phase for comparison purposes. The Arrhenius equation can be written as Equations 3.18 and 3.19 for Wetlands A and B, respectively when the data for the 5°C temperature phase are excluded.

$$k_T = k_{30}(1.047)^{T-30} \ (R^2 = 1.000) \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(Eq. 3.18)}$$

$$k_T = k_{30}(1.111)^{T-30} \ (R^2 = 0.995) \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(Eq. 3.19)}$$

When the data for the 5°C temperature phase are included in the regression analysis, the expressions corresponding to Equations 3.18 for Wetland A and Equation 3.19 for Wetland B are Equations 3.20 and 3.21, respectively:

$$k_T = k_{30}(1.061)^{T-30} \ (R^2 = 0.952)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(Eq. 3.20)}$$

$$k_T = k_{30}(1.134)^{T-30} \ (R^2 = 0.926)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{(Eq. 3.21)}$$

The temperature correction factors given above are higher compared to the design temperature correction factors suggested by the U.S. EPA (1983) that are 1.085 and 1.090 for subsurface and surface flow wetlands treating conventional pollutants. For biological oxygen demand the values were of 1.08 to 1.00 (Metcalf and Eddy, 1991). Values of correction factors range from 1.11 to 1.37 at less than 10°C, 1.07 to 1.16 at 10 to 15°C, and 1.06 to 1.12 at 15-20°C for nitrification reactions (Stanford et al., 1973; Marion and Black, 1987). Temperature coefficients for nitrification reaction in two mineral soils were 1.52-1.61 (5-10°C); 1.14-1.16 for (10-15°C); 1.07-1.08 for (15-25°C); and 1.06-1.07 for (25-35°C) (Stanford et al., 1975). Phosphorus was shown to increase rapidly with temperature, with temperature correction factors of 1.048 (10 to 20°C) and 1.077(20 to 30°C) (Kadleck and Reddy,2000).

Overall, a reduction in temperature from the highest value of 30°C through the lowest value of 5°C resulted in: (1) a reduction in the degradation rate of TCE by a factor of 4.39 for Wetland A (wetlands packed with Bion Soil®/Latimer peat/sand) (from 0.0680 cm$^{-1}$ to 0.0138 cm$^{-1}$) and by a factor of 27 (from 0.0829 to 0.0031 cm$^{-1}$) for Wetland B (row crop compost/soil builder compost/sand), (2) an increase in the extent of breakthrough of TCE, and (3) a reduction in the overall performance efficiencies of the wetlands. The average efficiency of TCE removal in Wetland A was 89.6% at 30°C, and 52% at 5°C. Corresponding figures for Wetland B are 99.1% at 30°C and 20.1% at 5°C.

**4.3 Application of the Wetlands Performance and Energy Balance Results.**

The wetland energy balance analysis results pertinent to Equation 3.7 can provide temperature data needed to use Equations 4.18 to 4.21. Equations 4.18 to 4.21 give the removal rate data, which are needed as inputs into Equation 3.5. Equation 3.5 can be used to size the wetlands of interest.

The design has to be done in an iterative manner because, the wetland bed depth which is the goal of the design, is also an input into the energy balance equation used to predict the temperature in the wetland, The wetland temperature is needed to determine the pollutant (TCE) removal rate constant, which is used to compute the wetland depth. In view of the above, the design procedure has to start with an assumption of a wetland bed depth based on experience.

**CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS**

This study was carried out with the objective to develop kinetic and energy balance input data for mathematical models that can be used to predict the performance of upflow constructed wetlands treating chlorinated ethenes and ethanes at different ambient temperatures. The results obtained from this study have corroborated the notion that temperature affects the performance of upflow wetlands: the higher the ambient temperature, the more effective the performance of the wetland.

A reduction in temperature from the highest value of 30°C through the lowest value of 5°C resulted in: (1) a reduction in the degradation rate of TCE by a factor of 4.39 for Wetland A (wetlands packed with Bion Soil®/Latimer peat/sand) (from 0.0680 cm$^{-1}$ to 0.0138 cm$^{-1}$) and by a factor of 27 (from 0.0829 to 0.0031 cm$^{-1}$) for Wetland B (row crop compost/soil builder compost/sand), (2) an increase in the extent of breakthrough of TCE, and (3) a reduction in the overall performance efficiencies of the wetlands. The average efficiency of TCE removal in Wetland A was 89.6% at 30°C, and 52% at 5°C. Corresponding figures for Wetland B are 99.1% at 30°C and 20.1% at 5°C.

It is noteworthy that at 5°C Wetland A outperformed Wetland B by a factor of more than 2.5. This implies that a wetland system using a bed material blended using compost materials and sand is likely to perform significantly better at low temperatures than the one using a mixture of peat Bion Soil® and sand, or that it cools slower than the other material.

Thermal conductivity coefficients of the wetland bed materials of interest were found to be 0.61 Wm$^{-1}$K$^{-1}$ for the compost based material and 0.39 Wm$^{-1}$K$^{-1}$ for the Latimer peat and Bion Soil® based material. The thermal conductivity of the compost based wetland bed material was found to be heavily influenced by water.

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A mathematical expression for predicting the design temperature of upflow wetlands was derived based on existing models. Temperature correction factors using the outputs of the temperature prediction were also developed for use in the Arrhenius equation.

The temperature correction factor for the compost based wetland bed material was higher than that for the peat and Bion Soil® based material, signifying that the TCE removal rate constant decreases with temperature more slowly in this material than in the peat and Bion Soil® based material.

In the absence of better options, the mathematical expression and corresponding input data presented in this study can be used to design upflow wetlands for treating TCE given different climatic and meteorological conditions using either of the two types of wetland bed materials studied. It is also possible to extrapolate the mathematical expressions and input data so that they can be used for wetlands treating other chlorinated VOCs. This can be done by comparing and contrasting results from this study and microcosm studies for TCE with those of other compounds of interest. However, the resulting design output will be less reliable. Ideally, experiments similar to the ones reported in this study need to be done for other compounds of interest. As such, this is an interesting and potentially productive area for future research.

It is known that effects of temperature on the performance of wetlands results from the changes in both the chemistry and microbial activity in the wetlands. As such, future studies in this area can focus on the changes in the chemistry of the wetland and microbial community structure with temperature to complement the results from this study.

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**APPENDIX**

Data for Determination of Temperature Correction Factors at 30°C Reference Temperature
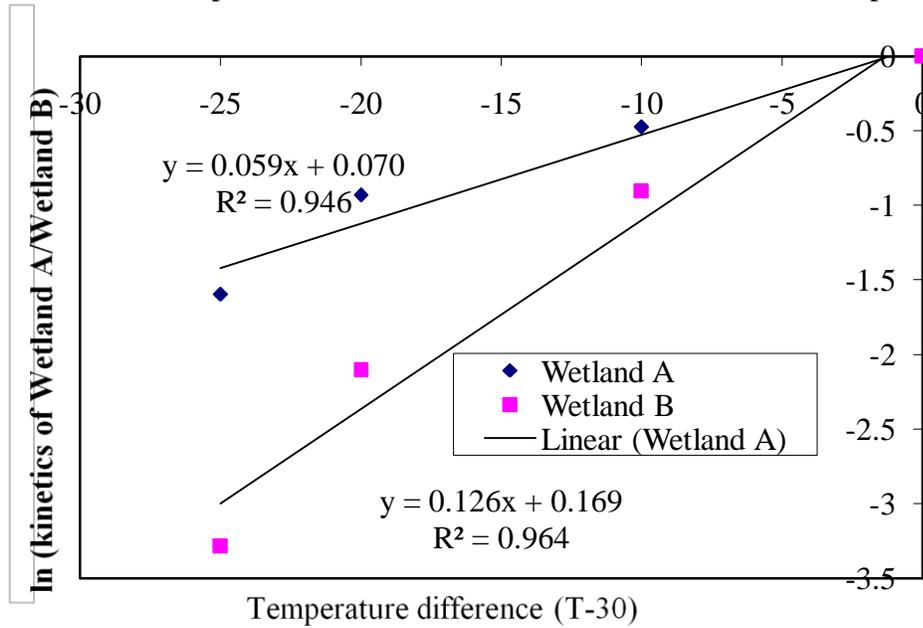


**Figure 1.** Relationship of Removal Rate Constants and Temperature for Wetland A, and Wetland B Using 30°C as a Temperature Reference for Temperatures 30,20,10 and 5°C
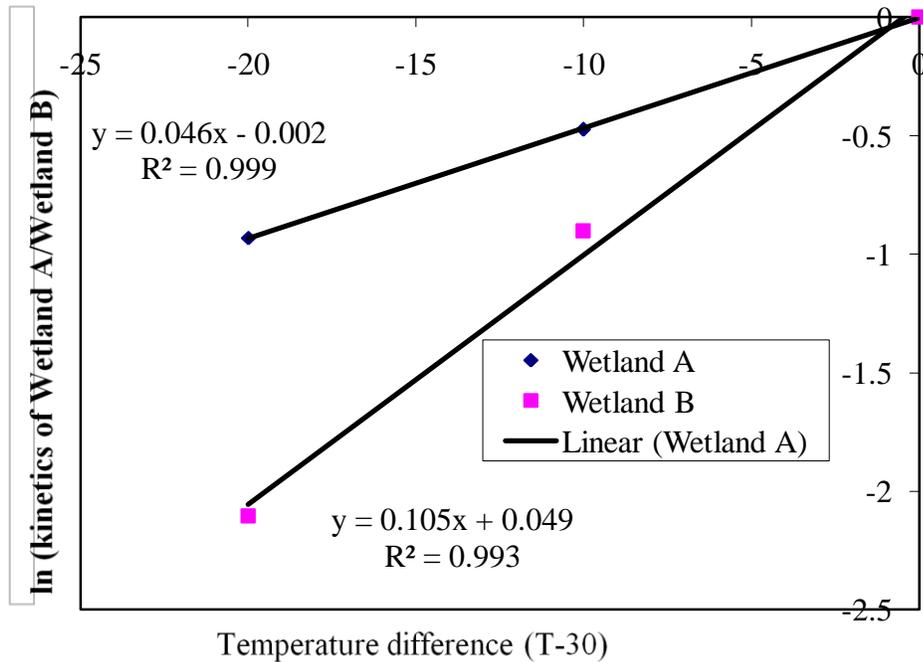


**Figure 2.** Relationship of Removal Rate Constants and Temperature for Wetland A, and Wetland B Using 30°C as a Temperature Reference for Temperatures 30,20, and 10°C

**VITA**

Maria Gabriela "MG" Murillo was born in 1980, in Valencia, Venezuela. She attended high school in Venezuela and part in Montreal-Canada. She graduated with a Chemical Engineering bachelor's degree from the University of Carabobo in Venezuela. After graduation she was accepted for graduate studies at Louisiana State University (LSU) in Baton Rouge, Louisiana. She is pursuing the degree of Master of Science in civil engineering from the department of civil and environmental engineering. She will enroll as a process engineer in a consulting engineering firm in Baton Rouge, Louisiana.