REMEDIATION OF DDT IN SOIL

REMEDIATION OF DDT CONTAMINATED SOIL: A FIELD STUDY

By

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A Thesis

Submitted to the School of Graduate Studies

In Partial Fulfillment of the Requirements

For the Degree

Master of Science

McMaster University

MASTER OF SCIENCE (2003) **McMaster University**
(Environmental Science) **Hamilton, Ontario**

TITLE: Remediation of DDT Contaminated Soil: A Field Study

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SUPERVISOR: Professor James E. Smith

NUMBER OF PAGES: xiii, 252

Abstract

Point Pelee National Park in Leamington, Ontario, Canada contained a large component of private farming and recreation until the 1960's. DDT was applied at the park as pest control in the orchards and recreational areas between 1948 and 1960. Recent studies have shown that the compounds DDT, DDE and DDD are highly persistent in the shallow soils of Point Pelee National Park. A laboratory treatability experiment has been effective in the removal of DDT, DDE and DDD from columns packed with soil collected from Point Pelee National Park, using hydroxypropyl-β-cyclodextrin. Cyclodextrins are microbially produced cyclic oligosaccharides which have a unique hydrophilic shell and a hydrophobic cavity. They are able to form inclusion complexes and aid in the transport of relatively insoluble compounds. A pilot-scale field remediation experiment involving the application of hydroxypropyl-β-cyclodextrin to a Random Latin-Squares design was completed at Point Pelee National Park over the course of five months. Systematic soil sampling and analyses provided DDT, DDE and DDD concentrations throughout the remediation experiment in order to assess the removal efficiency of hydroxypropyl-β-cyclodextrin. *In-Situ* volumetric moisture content was monitored throughout the study with a TDR based system. Systematic soil sampling and analyses at the conclusion of the study provided water content, organic matter content, bulk density, porosity, hydraulic conductivity as well as sampling with depth. The application of a hydroxypropyl-β-cyclodextrin solution did result in a substantial decrease of the concentrations of DDT, DDE and DDD from the surface soil at Point Pelee National Park. By the end of the experiment, the concentration of DDD was consistently below the regulatory limits set by the Ontario Ministry of Environment and Energy for Parkland/Recreational Land-Use. In addition to the observed decrease in concentration, there was a decrease in the degree of variation between the measured concentrations, transport of the mass of DDT, DDE and DDD to depth and an observed tailing effect at late-times. There were also fundamental changes to the system due to the application of the cyclodextrin (HPCD) solution including an increase in moisture content and organic matter, a decrease in infiltration and a corresponding decrease in field saturated hydraulic conductivity. There was no appreciable benefit of the application of a high concentration solution over a low concentration solution due to an observed "clogging"-effect. The results of this study indicates that further research is necessary to determine the extent of vertical mobilization of DDT, DDE and DDD to groundwater and the role of biological matter in the observed fundamental changes responsible for the "clogging"-effect.

Acknowledgements

This thesis is dedicated to everyone in my life who has encouraged me to reach for the stars and helped me to believe in myself and my capabilities. To my parents, Harold and Nalini Badley, a very special thank you for fostering my love of learning from an early age. Thank you for all your love and support throughout the years. To my brother, Roger Badley, for providing a constant source of friendly competition...thanks for keeping me on my toes. All my love goes out to Shawn Hanneson. You have been my friend, my confidant, my shoulder to cry on...my rock.

Thank you to my advisor, Dr. James Smith for making me prove my capabilities and helping me to find some much needed confidence in the process. I am especially appreciative to Marina Laferova for her counsel, her assistance and for being a part of my most memorable field trip. A special thanks for the guidance provided by Nadia Marenco and Bradley Markham. To Dr. Alan Crowe, Shelley Spencer and Viktor Terlaky for your advice, useful feedback and valuable assistance in the field.

Funding for this research was provided in part by CRESTech (Centre for Research in Earth and Space Technology).

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Chapter 1: Introduction and Background

1.1 Scope

Point Pelee National Park (PPNP) in Leamington, Ontario, Canada contained a large component of private farming and recreation between 1920 and 1960. Between 1948 and 1960, DDT (1,1,1-trichloro-2,2-bis(ρ-chlorophenyl)ethane) was widely used to control the mosquito population in recreational areas, and as pest control in the orchards (Crowe, 1999). In the former Camp Henry area, concentrations of DDT in surficial soils consistently surpassed ministry guidelines (Crowe, 1999). That DDT concentrations dramatically decreased with depth would be expected since DDT is typically bound to the upper soil layers. Nadia Marenco (2002), has further identified that soil conditions at Point Pelee National Park do influence the half-life of DDT. In her study it was identified that sandy aerobic soils within the former orchard contained the highest levels of DDT exceeding 80μg/g in some instances.

Cyclodextrins are naturally produced cyclic oligosaccharides that are formed by the enzymatic degradation of starch by bacteria. Chemically modified cyclodextrins can facilitate the transport of low-polarity and relatively insoluble organic molecules and have been widely used in the pharmaceutical industry for over thirty years. They are commonly used to enhance drug solubility and bioavailability, reduce the instability of certain drugs and increase drug effectiveness (Cerestar website, February 13, 2002). The

potential for these compounds to be used to enhance the solubility of persistent organic contaminants has only begun to be explored within the last decade.

A series of experiments conducted by Mark L. Brusseau and colleagues (Wang and Brusseau, 1993; Brusseau et al., 1994; Wang and Brusseau, 1995; McCray and Brusseau, 1998; etc.) has provided evidence that forms of cyclodextrin can indeed be used to complex with organic contaminants, such as DDT and metals. Experiments carried out by Kyle Schepanow (2002), at the National Water Research Institute in Burlington, Ontario provided laboratory column data on the effectiveness of hydroxypropyl-β-cyclodextrin to enhance the solubility of DDT and its derivatives. Soil samples collected from PPNP were used in column flushing experiments that resulted in the removal of approximately 80% of the initial DDT mass. The results of these previous studies suggest that cyclodextrin may be an effective agent for remediating DDT contaminated soils in the field.

This study hypothesizes that:

1. The application of hydroxypropyl-β-cyclodextrin will effectively result in a significant and substantial decrease of the concentration of DDT and its derivatives within the upper 15cm of the soil profile at PPNP.
2. The decrease in DDT concentration will be proportional to the amount and concentration of the hydroxypropyl-β-cyclodextrin applied.

The specific objectives of this research were:

1. To apply 20 pore volumes of differing concentrations of hydroxypropyl-β-cyclodextrin to a randomized Latin Squares design in the former orchard area.

2. To determine the fundamental soil properties of each application plot in order to determine if a correlation exists between the effectiveness of DDT removal and the following parameters: DDT, DDE (1,1-dichloro-2,2-bis(ρ-chlorophenyl) ethylene), and DDD (1,1,-dichloro-2,2-bis(ρ-chlorophenyl)ethane) concentration; soil organic content; bulk density; porosity; soil moisture content and; hydraulic conductivity.
3. To determine the required concentration and volume of hydroxypropyl-β-cyclodextrin solution that will reduce present levels of DDT, DDE and DDD to levels which comply with the Ministry of Environment guidelines of 1.6μg/g for Recreational/Parkland land-use.
4. To determine whether a decrease in DDT, DDE and DDD concentration at the surface is due to an increase in degradation and/or mobility.
5. To estimate the half-life of DDT, DDE and DDD within the augmented system.

1.2 Point Pelee National Park

Point Pelee is located in Southwestern Ontario, approximately ten kilometers south of Leamington (Figure 1.1). It is the southernmost part of Canada, as it lies at the 42nd parallel; the same latitude as Northern California. Point Pelee is a sandy peninsula composed of Eastport sand which extends into Lake Erie (Stewart, 1977). As glaciers receded from the area approximately 10,000 years ago, their waters picked up sand and dropped it in a ridge extending across the bottom of Lake Erie (Stewart, 1977). The land is continually changing due to natural processes and human intervention. The vegetation

in the area plays a vital role as it effectively acts as a sand binder, holding the complex land together (Stewart, 1977). The Devonian Limestone bedrock of the area is generally not visible as it is buried deep beneath the sand.

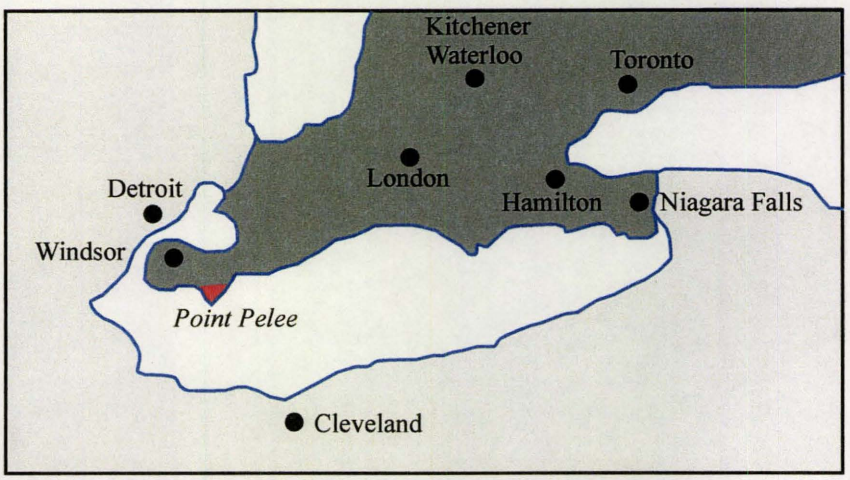

Figure 1.1: Location of Point Pelee National Park within Southern Ontario

The fifteen kilometer sand spit was established as a National Park in 1918, in order to protect and preserve the ecologically unique land and species. The northern boundary of the park is formed by a clay dyke that crosses the peninsula approximately ten kilometers inland from the point (Stewart, 1977). The majority of the 4000 acre park consists of a 2700 acre freshwater marsh (Point Pelee National Park, 1982). The marsh level continually fluctuates in response to annual precipitation and Lake Erie levels.

The location of Point Pelee, the latitude and the surrounding lake, results in a distinct climate and an unusual mixture of flora and fauna (Point Pelee National Park, 1982). The vegetation and wildlife found in the park is more characteristic of Southern United States, than the rest of Canada. Its location on one of the major bird migration routes has made it an exceptional bird watching location.

In the early nineteenth century Point Pelee experienced major alterations to its landscape when humans permanently settled here. The DeLauriers, who were involved in farming, were among the first settlers, in 1832 (Stewart, 1977). By the end of the century farming had intensified. In order to increase yields dunes were leveled, land was cleared and wet areas were drained. Extensive orchards of peaches and apples were also planted as the settlers turned to cash crops (Point Pelee National Park, 1982). During the early years of the Park's operation, the private land activities were permitted to continue, and agriculture continued right through to the 1960's. The lingering agriculture resulted in the introduction of the renowned pesticide, DDT, to the unique and fragile landscape.

1.3 The History of DDT

The creation of DDT was first reported in 1874 by Othmen Zeidler, a German graduate student (Friedman, 1992). Paul Hermann Müller, a Swiss citizen, was awarded the Nobel Prize in Medicine and Physiology in 1948 for discovering the insecticidal qualities of DDT. The pesticide was first used during World War II, in order to protect the soldiers from vector-borne diseases. Worldwide use for agricultural purposes as well as the continued control of vector-borne diseases began shortly after the war. Within a few years the production of DDT was far above that of any pre-existing pesticide (Dunlap, 1981). In the beginning DDT was hailed as the best insecticide of its time, until the deleterious effect of its use began to be observed. The 1962 release of Rachel Carson's phenomenal book, *Silent Spring* spurred the public outcry and the political debate over the use of DDT. In 1972, the U.S. EPA, banned DDT from being used (Dini, 1999a). In Canada, all uses of DDT were discontinued in 1985 (Crowe, 1999). The Ontario Ministry of Environment now has a standard limit of 1.6μg/g for soil concentrations of DDT in Recreation/Parkland areas. Despite its ban in the developed countries, DDT is still widely used in developing countries in order to keep insect-borne diseases, such as malaria under control (Coulston, 1989; Boyce, 1998).

1.4 DDT and its Derivatives

DDT generally refers to the isomer ρ,ρ'-DDT, 1,1,1-trichloro-2,2-bis(ρ-chlorophenyl)ethane. The second isomer, o,ρ'DDT (1,1,1-trichloro-2-(o-chlorophenyl)-2-(ρ-chlorophenyl)ethane), however was present in the technical grade of DDT (up to

30%) that was manufactured for application, as it also had insecticidal properties (Boul, 1994). DDT has a molecular weight of 354.4, a melting point of 108^0C, and a vapor pressure of $1.9x10^{-7}$mm at 20^0C (Howard and Meylan, 1997). DDT has a weak dipole due to the slight electronegativity of the three chlorine atoms on the β-carbon atom (Champion and Olsen, 1971). It has a relatively low water solubility of 3μg/L at 25^0C. DDT is a hydrophobic and lipophilic compound (Howard and Meylan, 1997).

The primary residues of DDT are DDE (1,1-dichloro-2,2-bis(ρ-chlorophenyl)ethylene), and DDD (1,1,-dichloro-2,2-bis(ρ-chlorophenyl)ethane). DDE is generally formed through photochemical reactions in the presence of sunlight or through dehydrochlorination of DDT, while reductive dechlorination of DDT will produce DDD (Aislabie et al, 1997, Crowe, 1999). In comparison to DDT, DDE has a solubility of 40μg/L at 24^0C, and DDD has a solubility of 160μg/L at 24^0C. The further degradation pathway of DDT is outlined in Figure 1.2.

The inherent chemical stability of this compound is attributed to the fact that its molecular structure contains chlorinated aliphatic and aromatic structures, making it a persistent pollutant (Corona-Cruz et al., 1999). Chlorinated hydrocarbons do not naturally occur in the environment, which may contribute to its persistence as it has limited natural degradation processes. This chemical stability and persistence was initially attractive as it eliminated the need for reapplication, but now it is the source of environmental concern for scientists and researchers.

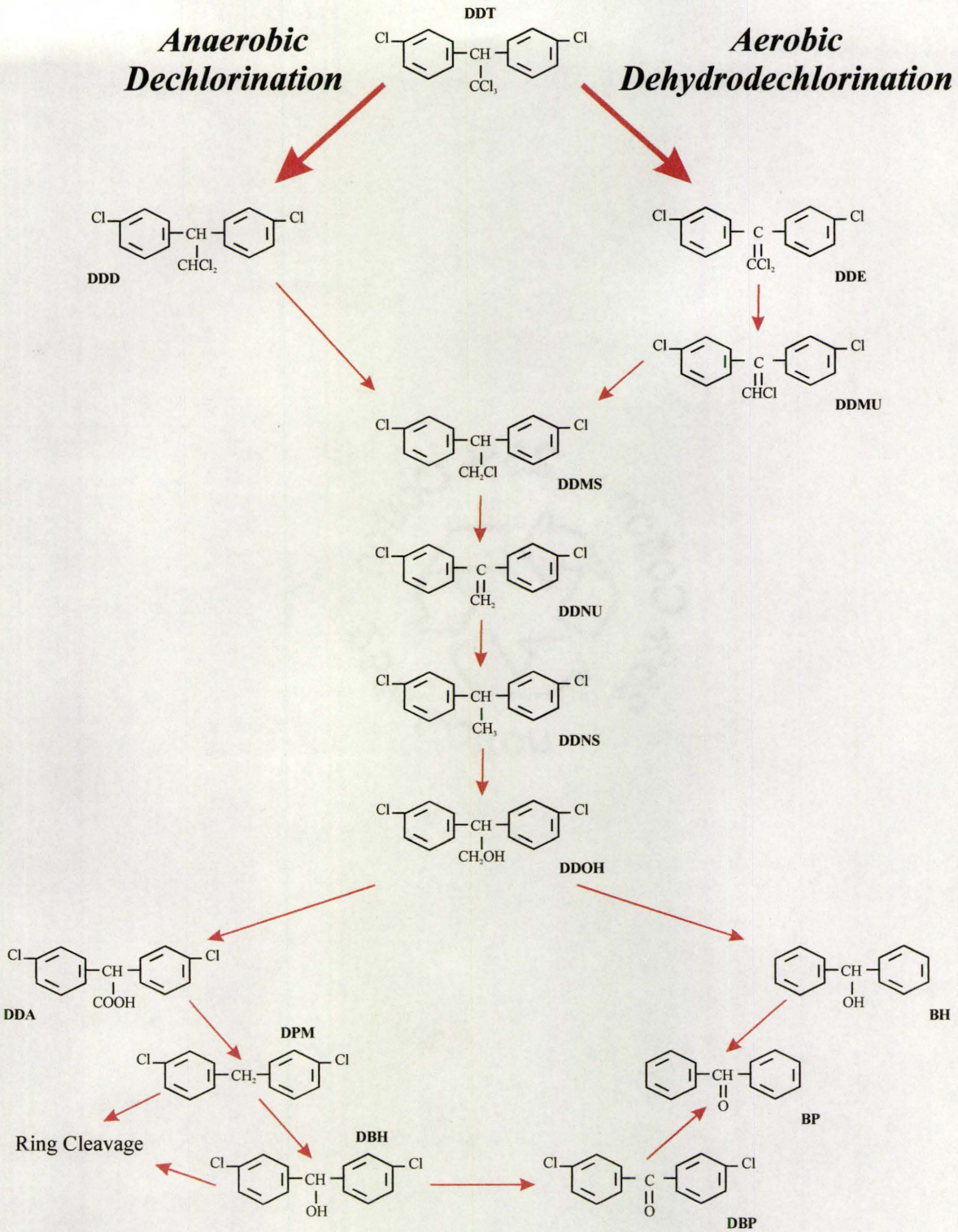

Figure 1.2: Aerobic and Anaerobic Degradation of DDT (modified from Aislabie et al., 1997)

1.5 Anaerobic and Aerobic Degradation

As mentioned previously there are two primary residues which are formed by the two principal routes of DDT degradation. Under anaerobic or reducing conditions, DDD is formed as DDT undergoes reductive dechlorination. Under aerobic conditions, DDE is the predominant degradation product (Corona-Cruz et. al, 1999). DDT is significantly more stable under aerobic conditions and will not undergo an appreciable degradation, however in anaerobic conditions DDT is readily degraded to DDD (Guenzi and Beard, 1968).

Microbial dechlorination of both isomers of DDT results in DDD production in anaerobic conditions. The addition of a microbial energy source increases the rate of DDT degradation, which indicates that the process of dechlorination is co-metabolic (Aislabie, 1997, and Guenzi and Beard, 1968). The degradation rate of DDT in anaerobic soils is dependent on, and directly proportional to, the quantity of microbes (Guenzi and Beard, 1968). Some researchers suggest that this apparent link could simply be the production of anaerobic conditions due to the enhanced microbial growth with the addition of an energy source (Aislabie et al., 1997). Under these anaerobic conditions, DDD is able to undergo further degradation, producing DDMU, DDNU, DDOH, DDA, and DBP (Refer to Figure 1.2) (Aislabie et al., 1997).

The dehydrochlorination of DDT, in the presence of oxygen or aerobic conditions, will produce DDE. This derivative of DDT is the main residue found in drier soils. Utilizing sterile and non-sterile treatments, Guenzi and Beard (1976), showed that the formation of DDE under aerobic conditions is mainly a chemical process with some

microbial input. The chemical conversion of DDT to DDE is also enhanced with increased water content and temperature (Guenzi and Beard, 1976). As DDT is degraded and DDE becomes the primary residue in the soil it is expected that the degradation rate will slow even further as DDE is not readily degraded (Boul et al., 1994).

Corona-Cruz et al. (1999) found that the best DDT degradation results, 84.4% mass reduction, were achieved in a sequential anaerobic-aerobic fermentation system using *P. chrysosporium*. This system also resulted in a higher amount of DDE degradation, than an exclusively aerobic system.

1.6 DDT in Soil

Orchard soils typically contain higher levels of residues than other soils, due to management practices (Edwards, 1973). Routinely, the trees were sprayed as many as six times during the growing season. Tree spacing and falling leaf decay also resulted in more through fall. The application of DDT in granular form rather than in a spray may also have increased the persistence as it concentrates the compound (Boul, 1994).

Bound residues generally refer to compounds which are not extractable with an organic solvent in the laboratory. In the case of DDT, it is considered to be a weakly bound substance in soil (Boul, 1994). The general trend in soils is that there is a decrease in DDT concentration with increasing depth, with the majority of DDT being seen in the surface soils (Boul et al, 1994). The extent of downward movement of DDT is within the

uppermost organic layer, with the fall of uncontaminated litter onto the surface (Dimond and Owen, 1996).

Khan (1982) has shown that bound pesticides tend to be less toxic to insects, limiting their bioavailability. Dimond and Owen (1996), however, present several examples of high levels of DDT in wildlife, suggesting that even after thirty years there is continued activity of the compound.

The persistence of DDT in contaminated soil is due to both chemical and physical binding that occurs between the pesticide and the soil organic fraction (Khan, 1982). The major binding mechanism is hydrophobic bonding, as the non-polar DDT is associated with the relatively non-polar organic matter of the soil (Boul, 1994).

The conditions and properties of the DDT contaminated soil will affect the degradation of DDT and its residues. The degradation of ρ,ρ′-DDT to ρ,ρ′-DDE was observed to be extremely slow in soils with low levels of several metals (Al, Ba, Cd, Co, Cr, Fe and K) (Hitch and Day, 1992). As soil moisture increases, the degradation of DDT will also increase. This increase may be related to the introduction of anaerobic conditions that promote the degradation of DDT to form DDD, or it may be related to the increased volatilization discussed below. Organic content can also affect the persistence of this pollutant, as it increases the binding capacity.

Technical grade DDT has a relatively low vapor pressure and it is not readily volatilized. The addition of even a small amount of water, however, will greatly increase the volatilization flux of DDT and its residues from soil (Spencer et al., 1996). This can cause a substantial increase in atmospheric DDT in tropical areas after rain or in irrigated

fields. Spencer et al. (1996) also showed that DDT may be more persistent in deeply plowed agricultural fields where the contaminated soil has been redistributed lower into the subsurface, away from surface volatilization and prevalent microbial degradation.

DDT degradation in soils is relatively low, with a half life in temperate environments, anywhere between two and upwards of thirty years (Dimond and Owen, 1996). The half-life in tropical climates is much smaller, which can most likely be attributed to the increase in temperature which in turn may increase the microbial activity and the volatilization (Boul, 1994). Dimond and Owen (1996) found that the DDT residue in a Maine forest soil, showed little decrease in the two decades after application, but showed a noticeable decrease in the third decade.

1.7 DDT and Point Pelee National Park

Farming and private recreation was a large component of the park until the 1960's. Between 1948 and 1960, DDT was widely used to control the mosquito population in recreational areas, and as pest control in the orchards (Crowe, 1999). The pesticide was generally applied in granular form, as a particulate spray, or as "toss bombs" for extreme trouble spots. There is no appreciable amount of DDT or its residues in the groundwater at Point Pelee (Crowe et al., 2002). In the former Camp Henry area, concentrations of DDT in surficial soils consistently surpassed ministry guidelines (Crowe, 1999). This was mainly confined to the area north of the campground (former orchard area), or in the immediate vicinity of the camp buildings. The DDT

concentrations dramatically decrease with depth as is expected since DDT is typically bound to the upper soil layers.

The studies performed by Marenco (2002) and Crowe et al. (2002), examined the relationship between soil conditions, former land-use at Point Pelee National Park and the concentration of DDT and its derivatives. In both investigations, it was clear that the concentration of DDT within natural areas is relatively low and is within ministry guidelines. The highest concentration of DDT and its derivatives was found in the former orchard areas. This is to be expected as the management practice of orchards includes spraying the fruit trees several times each season. The two studies (Marenco, 2002 and Crowe et al. 2002) also investigated the presence of preferential pathways of degradation within microenvironments in the park. It was discovered that in areas close to the marsh, which were lower in elevation, there was the potential for an increase in water table levels during certain times of the year. In these areas, the soil would become much wetter and intermittently anaerobic, providing an oscillating aerobic/anaerobic environment that preferentially yields the degradation of DDT to DDD. Conversely, areas of higher elevation had a continually drier aerobic environment where DDT is preferentially degraded to DDE.

1.8 Cyclodextrin

Cyclodextrins are microbially produced cyclic oligosaccharides that are formed by the action of amylase of *Bacillus macerans* on starch and related compounds (Bender and Komiyama, 1978). These compounds are unique as they have a hydrophilic, polar

shell and a hydrophobic, nonpolar cavity. Cyclodextrins are able to form water soluble inclusion complexes in its nonpolar cavity, facilitating the transport of low-polarity and relatively insoluble organic contaminants. The formation of these water-soluble inclusion complexes is described by:

$$S + CD \leftrightarrow CD\text{-}S, \qquad (1)$$

where, S is the concentration of uncomplexed dissolved compound, CD is the concentration of uncomplexed cyclodextrin, and CD-S is the concentration of complexed solutes (Wang and Brusseau, 1993). The enhanced solubility and associated transport effect was found to be the greatest for the most hydrophobic compounds (Brusseau et al., 1994).

There are three isomers of cyclodextrin; ά, β, and γ. The β-cyclodextrin homologue is the least expensive isomer; however it has limited water solubility. In order to overcome this deficiency, the β-cyclodextrin isomer is typically chemically modified in order to augment its solubility (Wang and Brusseau, 1993). The two most commonly used cyclodextrin compounds in the current environmental literature are hydroxypropyl-β-cyclodextrin (HPCD) and carboxymethyl-β-cyclodextrin (CMCD).

Hydroxypropyl-β-cyclodextrin (HPCD) (Figure 1.3), the form of cyclodextrin used in this study, is one of the modified compounds that have been used to examine the enhanced solubility of chlorinated hydrocarbons as it has been found to be very water soluble. Its molecular weight is 1500g/mol (Wang and Brusseau, 1993). Due primarily to the nonpolar cavity of cyclodextrin, the HPCD derivative was observed to have a decreased surface tension with increasing concentrations from approximately

72.5dynes/cm to 62.5dynes/cm (Wang and Brusseau, 1993). The magnitude in decrease, however, was much less than is generally seen with micelle-forming surfactants.

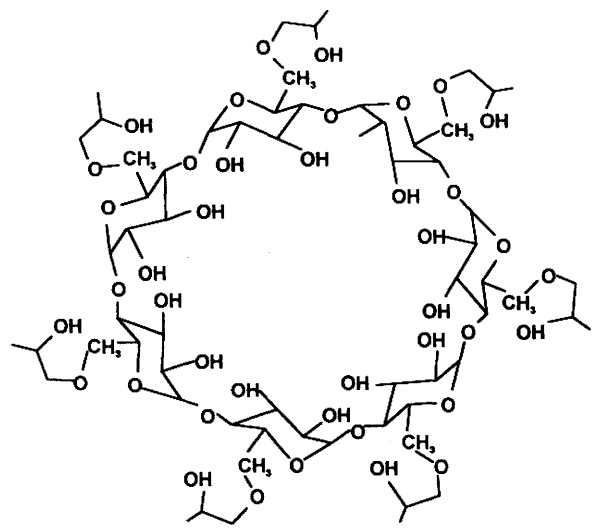

Figure 1.3: Structure of Hydroxypropyl-β-cyclodextrin (Reproduced from Wang and Brusseau, 1993)

Carboxymethyl-β-cyclodextrin (CMCD) is another derivate which has been utilized for the combined transport of organic compounds and heavy metals (Wang and Brusseau, 1995 and Brusseau et al., 1997). CMCD has an average molecular weight of 1375g/mol and a pH of 6.8 in a 1% solution (Wang and Brusseau, 1995). CMCD is capable of simultaneously complexing organic compounds and metals as they are complexed at different locations on the cyclodextrin molecule. It is speculated that metal is complexed outside the cavity due to interactions with the acidic functional groups, whereas organic compounds are involved with inclusion complexes inside the hydrophobic cavity (Wang and Brusseau, 1995).

The first field scale experiment involving cyclodextrin as a flushing agent was performed by McCray and Brusseau (1998) for NAPL mixtures at Operable Unit One at

Hill Air Force Base in Layton, Utah. In accordance to previous laboratory findings by Brusseau et al. (1994), the cyclodextrin was not measurably retarded however there was a slight tailing effect. The tailing observed in the field is most likely due to hydraulic or porous media heterogeneity (McCray and Brusseau, 1998).

Cyclodextrins are nontoxic and biodegradable, thus making it a good choice for aquifer remediation. In addition, extracted chlorinated solvents can be separated from the solution without degradation of the cyclodextrin, allowing for possible reuse. In the field application of cyclodextrin performed by Blanford et al. (2000), the recovered solution was airstripped and 98% of the TCE was recovered from the 10% HPCD solution.

1.8.1 Theoretical Relationships

The enhanced solubility of compounds by cyclodextrin is essentially due to the partitioning of solutes from water into the cyclodextrin cavity (Wang and Brusseau, 1993). A linear partition model can be used to represent the solubilization of organic compounds by cyclodextrin:

$$C = C_d(1 + K_{cw}X_{CD}), \qquad (2)$$

where, C is the total aqueous-phase concentration, C_d is the aqueous solubility of the compound, K_{cw} is the partition coefficient of the organic compound between cyclodextrin and water, and X_{CD} is the concentration of cyclodextrin (kg/L). Wang and Brusseau (1993), found that experimental data fit the linear partition model extremely well for all

of the compounds tested which included; trichloroethene, chlorobenzene, naphthalene, anthracene, and ρ,ρ′-DDT (Figure 1.4).

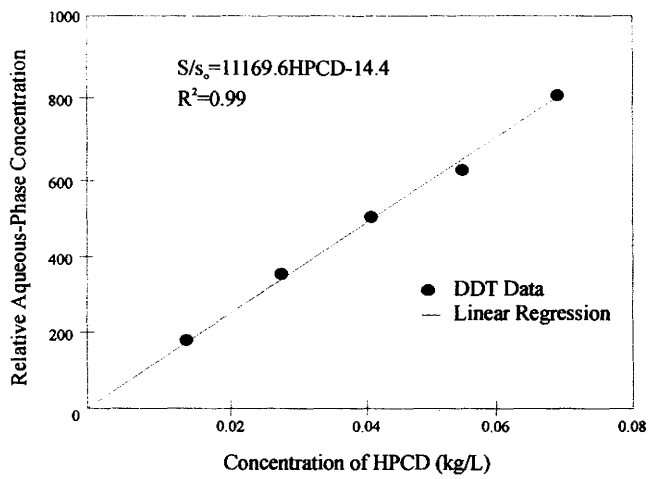

Figure 1.4: Relative Aqueous-Phase Concentration vs. HPCD Concentration for DDT - Experimental Data and Calculated Linear Regression with the Partitioning Model (Reproduced from Wang and Brusseau, 1993)

A modified sorption equation can be obtained by substituting equation 2 into the linear isotherm equation, $S = K_d C_d$ (Brusseau et al., 1994):

$$S = \frac{K_d C}{1 + XK_c}, \qquad (3)$$

Under the influence of cyclodextrin a modified retardation factor for organic compounds can then be derived if it is assumed that the cyclodextrin complex is not sorbed by the soil matrix (Brusseau et al., 1994):

$$R = 1 + \frac{\rho}{n} \frac{K_d}{1 + XK_c}, \qquad (4)$$

This modified retardation factor can be used to predict the enhanced transport of the organic contaminants. Predicted and measured retardation factors were generated in

Brusseau et al. (1994), and with the exception of two of the compounds, the values were within 10% of each other (Table 1.1).

Compound	R^m, with HPCD	R^p, with HPCD
TCE	1.0	1.0
Naphthalene	0.9	1.0
Biphenyl	1.1	1.1
Trichlorobenzene	1.1	1.1
2-chlorobiphenyl	1.1	1.1
Anthracene	1.1	1.9
Pyrene	2.4	2.6
2,4,4'-trichlorobiphenyl	1.6	2.6

Table 1.1: Measured (R^m) and Predicted (R^p) Retardation Factors with the use of HPCD for Organic Compounds in an experimental column study (Adapted from Brusseau et al. 1994.).

A predicted enhancement-removal factor can also be calculated for metals. The removal factor is based on the molar complexation ratio (M^R) between the metal and cyclodextrin, using (Brusseau et al., 1997);

$$\frac{C_m}{C_o} = 1 + M^R \frac{M^x}{M_0^C} \qquad (X)$$

where, C_m is measured maximum solute concentration in the effluent (mg/L), C_o is the initial aqueous concentration of the contaminant (mg/L), M^x is the aqueous concentration of CMCD (mol/L) and $M^C{}_0$ is the initial aqueous concentration of the metal (mol/L).

1.8.2 Pore Exclusion and Sorption

Brusseau et al. (1994), found that in a sandy subsoil collected from the Canadian Air Force base in Borden, Ontario, and a surface soil collected from a site near Tucson, Arizona, the optimized retardation factor was 1.0 for HPCD and the tracer pentafluorobenzoate (PFBA). These results indicate that there is no measurable sorption or "pore exclusion" of HPCD, that is, it acts conservatively. Surfactants, on the other hand, may be significantly retarded by interactions with the soil matrix, reducing their effectiveness. According to these findings, cyclodextrin can achieve maximum effectiveness as it does not undergo any reactions (Brusseau et al., 1994). The effectiveness of cyclodextrin was, however, slightly diminished in a porous media with a larger organic carbon content (12.6%) than the Borden soil, but not to a significant extent (Brusseau et al., 1994).

1.8.3 Stereoselective Interaction

In Wang and Brusseau (1993), hydroxypropyl-β-cyclodextrin was used to examine the enhanced solubility of trichloroethene, chlorobenzene, naphthalene, anthracene and DDT. In this instance, it was observed that the DDT had a relatively smaller solubility enhancement as compared to the other compounds, and due to the differences seen in the calculated log K_{cw} and log K_{ow} values it was postulated that DDT may be undergoing a different form of incorporation. It was found that for trichloroethene, chlorobenzene, naphthalene, and anthracene the log K_{cw} of 1.71, 1.92, 2.72 and 3.47, respectively, was approximately one order of magnitude smaller than their

corresponding log K_{ow} values. DDT, however, had a log K_{cw} of 4.05 that was approximately two orders of magnitude smaller than its log K_{ow} value of 6.36. These fundamental property differences and the observed decrease in solubility enhancement of DDT indicated that stereoselective interaction may be occurring. In order for complete inclusion of a solute in the cyclodextrin cavity, the molecular volume must be smaller than the cavity volume ($0.346nm^3$), as the process is diffusion controlled (Wang and Brusseau, 1993). The molecular volume (nm^3) of a compound may be predicted by the ratio of the diffusion volume (cm^3/mol) to Avogadro's number. DDT has a molecular volume of $0.508nm^3$, restricting it to partial entry into the HPCD cavity.

Wang and Brusseau (1995), found that carboxymethyl-β-cyclodextrin (CMCD), did not exhibit stereoselective interaction with organic compounds, and that the solution actually enhanced the extremely low solubility of DDT, more so than the other compounds (anthracene, trichlorobenzene, and biphenyl).

Cations such as Ca^+ or Na^+ may interact with functional groups of polyelectrolytic molecules, affecting their solubility and complexation capacity. Wang and Brusseau (1995), observed that despite the addition of $CaCl_2$, the CMCD only weakly interacted with the Ca^{2+} molecules as it selectively complexed the metal ion (Cd^{2+}).

A 50:50 mixture of CMCD and HPCD was used in an attempt to further enhance the removal of organic compounds (Brusseau et al., 1997). The mixed solution increased the removal of phenanthrene by approximately 20%, compared to CMCD alone. The lower solubilization power of CMCD, compared to HPCD is due to the presence of carboxyl groups near the end of the cavity which alter its polarity.

The solubilization ability of a KNO_3 solution vs. the 50:50 mixture was evaluated using both freshly incorporated and aged phenanthrene and to determine whether the observed enhancement was restricted by age of incorporation (Brusseau et al., 1997). The system flushed with the KNO_3 experienced significant tailing for the aged system. This tailing effect was not present in the system flushed with cyclodextrin, illustrating that removal by solubilization enhancement due to cyclodextrin is not age restricted for the organic contaminant, phenanthrene (Brusseau et al., 1997).

1.8.4 Solubilization versus Mobilization

The majority of previous research involving the use of cyclodextrins to remediate the subsurface has targeted NAPLs. When dealing with the remediation of NAPLs it is necessary to know whether the increase in aqueous concentration is due to mobilization/emulsification or solubilization of the contaminant. This is especially important when working in the field due to the possible ramifications that may result from the transport of free phase NAPL.

Generally, an interfacial tension of approximately less than 0.1 dynes/cm is necessary to attain the formation of macroemulsions, which can then be mobilized (McCray and Brusseau, 1998). In the field study conducted by McCray and Brusseau (1998), the NAPL-water interfacial tension only experienced a reduction from 37dynes/cm to 15dynes/cm in the presence of a 10% HPCD solution. This relatively small decrease in interfacial tension (relative to surfactants) and the absence of macroemulsion droplets in the collected effluent lead to the conclusion that solubilization

rather than mobilization was responsible for the enhanced apparent aqueous concentrations. Consistently, in the column experiments performed by Boving et al. (1999), there was also no mobilization of free-phase NAPL by the HPCD. However, mobilization of the free phase NAPL was seen in all the experiments done with methyl-β-cyclodextrin (MCD). The NAPL-water interfacial tension once again exhibited a reduction from approximately 40dynes/cm to 20dynes/cm in the presence of HPCD. In the presence of MCD there was a slightly larger reduction in the interfacial tension from approximately 40dynes/cm to 10dynes/cm. Although there is a larger reduction in the interfacial tension with MCD, the resulting interfacial tension is still much larger than the generalized limit of 0.1dynes/cm that is necessary for the formation of macroemulsions (McCray and Brusseau, 1998).

MCD is less polar and had a greater effect on interfacial tension than HPCD, thereby producing higher apparent solubilization rates. The increased reduction of interfacial tension with MCD resulted in the additive behavior of buoyant and viscous forces to cause the mobilization of free phase NAPL.

Chapter 2: Experimental Design

2.1 Site Selection

Between September 2000 and June 2002, a quantitative study on the DDT concentrations within Point Pelee at three separate locations was carried out by Nadia Marenco (2002), as part of her Masters of Science thesis research at McMaster University. Among these three locations, the study determined that the highest concentrations of DDT were found in the sandy, aerobic conditions of the former orchard area (Figure 2.1). The former orchard area located east of the park road, and north of Old Camp Henry had a unique environment with a combination of characteristics that resisted DDT degradation. This previously investigated grid (Marenco, 2002) encompassed an area of 20m x 20m and each corner was marked with wooden posts. Ten 1m x 1m plots were randomly chosen throughout the grid and the DDT concentration was quantified through extensive sampling. This location is well characterized and known to have relatively high concentrations of DDT, DDE and DDD in the soil.

Consequently, in consultation with Parks Canada and Environment Canada personnel, this location was selected for the pilot-scale field remediation study. An area in the southwest corner of the site investigated by Marenco (2002) was chosen as the location for the remediation experiment. The selected area was undisturbed during the previous study (Figure 2.2).

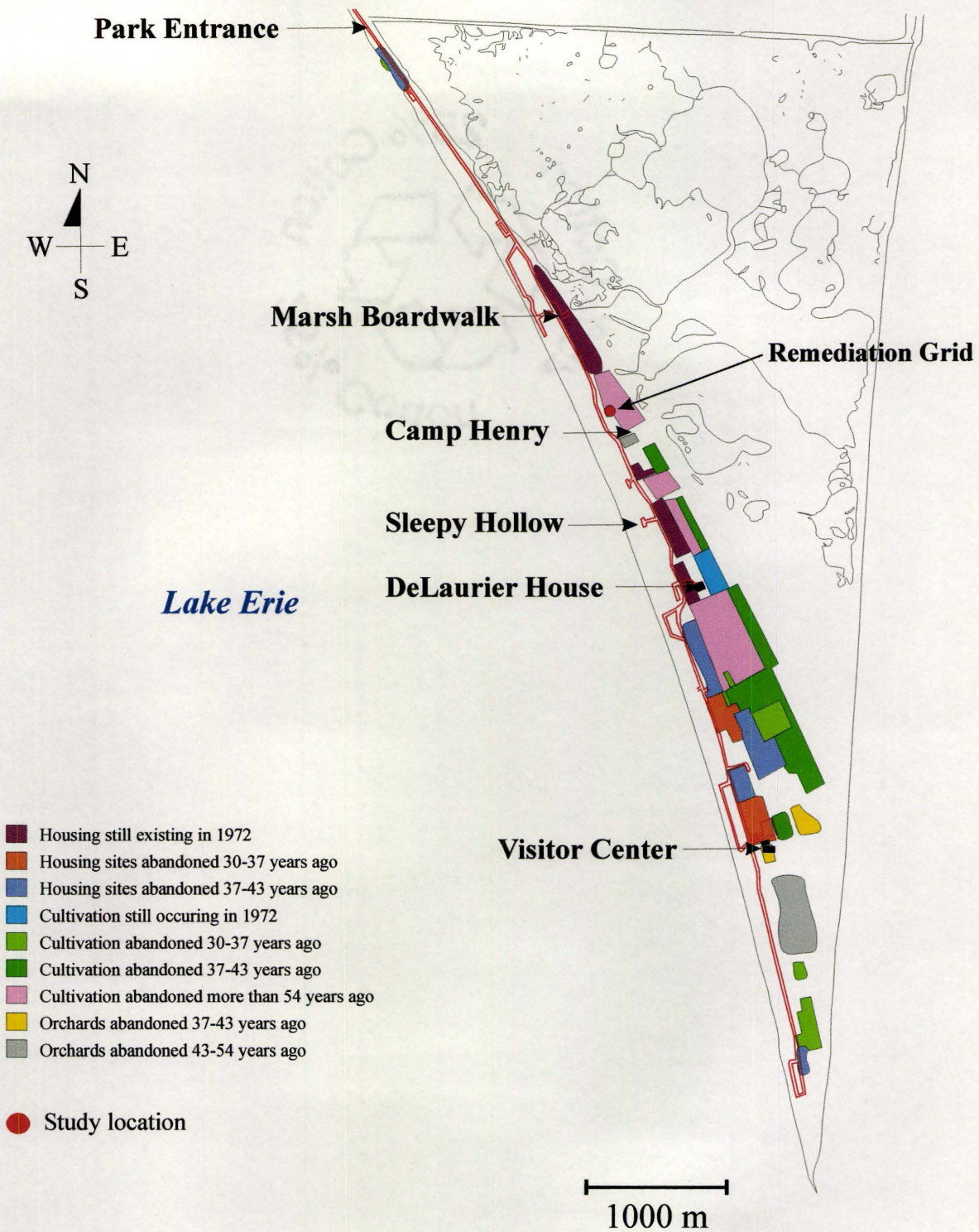

Figure 2.1: Historical Landuse at Point Pelee National Park and Remediaiton Grid location (Adapted from Marenco, 2002)

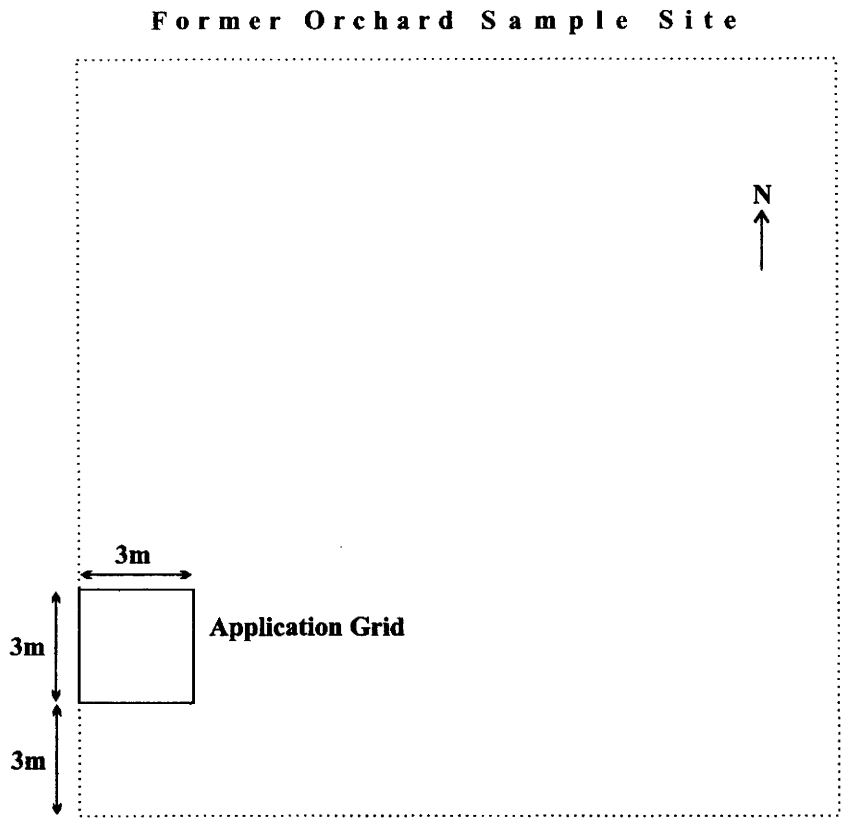

Figure 2.2: Location of the Remediation Grid within the Former Orchard Sampling Site used by Marenco (2002)

2.2 Laboratory Column Experiments

Previous laboratory work was completed at the Canadian Centre for Inland Waters by Kyle Schepanow (2002), as part of his undergraduate senior thesis at McMaster University. During the summer of 2001, soil was collected from the upper 30cm at the Sleepy Hollow site in Point Pelee for use in bench-scale laboratory column experiments. Sleepy Hollow is a sandy dune site located on the west side of the main park road (See Figure 2.1). Samples of approximately 60g were packed in glass columns and flushed at a variety of rates in both a continuous flow and pulse fashion with differing concentrations of cyclodextrin (HPCD) and a control (water).

In the laboratory, flushing the columns with eighteen pore volumes of a 20% cyclodextrin solution removed approximately 80% of the initial DDT mass. Both a 10% and 5% solution were found to remove approximately 40% of initial DDT mass with the application of eighteen pore volumes. There was no significant difference between the continuous and pulse experiments with regards to the effectiveness of DDT removal. In addition, water had no measurable effect on the removal of DDT mass. The results of Schepanow (2002) were the basis for the selected cyclodextrin (HPCD) solution concentrations and application rates.

2.3 Experimental Design

A pore volume (V_ρ) is the measure of void space within a specific volume of soil as described by the following equation:

$$V_\rho = \eta V_s \qquad (x)$$

Where V_ρ is the pore volume, η is the porosity of the soil and V_s is the volume of the soil considered.

As the surface soil (A horizon) is where the highest concentrations of DDT were found, this depth interval was the focus of this remediation study. An average pore volume for the former orchard area was calculated by multiplying the area of the application plots ($0.49m^2$) by the targeted depth (0.15m) and the average porosity value (0.45), previously determined by Marenco (2002). Based on these values one pore volume was approximately thirty-three liters. A value of 33.3L was selected as one pore volume to facilitate solution preparation in the field within a 100L container.

$$V_\rho = Area \times depth \times porosity$$
$$V_\rho = (0.49m^2)(0.15m)(0.45)$$
$$V_\rho = 0.033075m^3 \times 1000\,{}^{L}\!/_{m^3}$$
$$V_\rho = 33L$$

Three different treatments were used throughout this experiment: 1) a 20% by wt. cyclodextrin solution, 2) a 10% by wt. cyclodextrin solution, and 3) a control (nothing). The remediation grid was comprised of nine individual application plots in order to allow for each treatment to be completed in triplicate. To minimize any edge effects during application, the actual application area was surrounded by a buffer area. Each treatment was applied to an area of $0.49m^2$ (70cm x 70cm) that was at the center of a larger area of $1m^2$. As a result the entire remediation grid, including application area and buffer area was $9m^2$ (Figure 2.3).

A Latin squares design was used to provide two attempts at control of the natural variation in experimental material (Ashton and McMillian, 1981). The location of each treatment within the Latin squares design was determined using the random number generator in Microsoft® Excel 2000. Each square in the grid was numbered from one to nine, starting in the upper left hand corner and moving across the grid horizontally (Figure 2.4). Three numbers between 1 and 9 were generated for each treatment by using the "RANDBETWEEN" function. These generated numbers corresponded to one of the numbered application plots, thereby randomly determining the location of each treatment replication within the remediation grid (Figure 2.5).

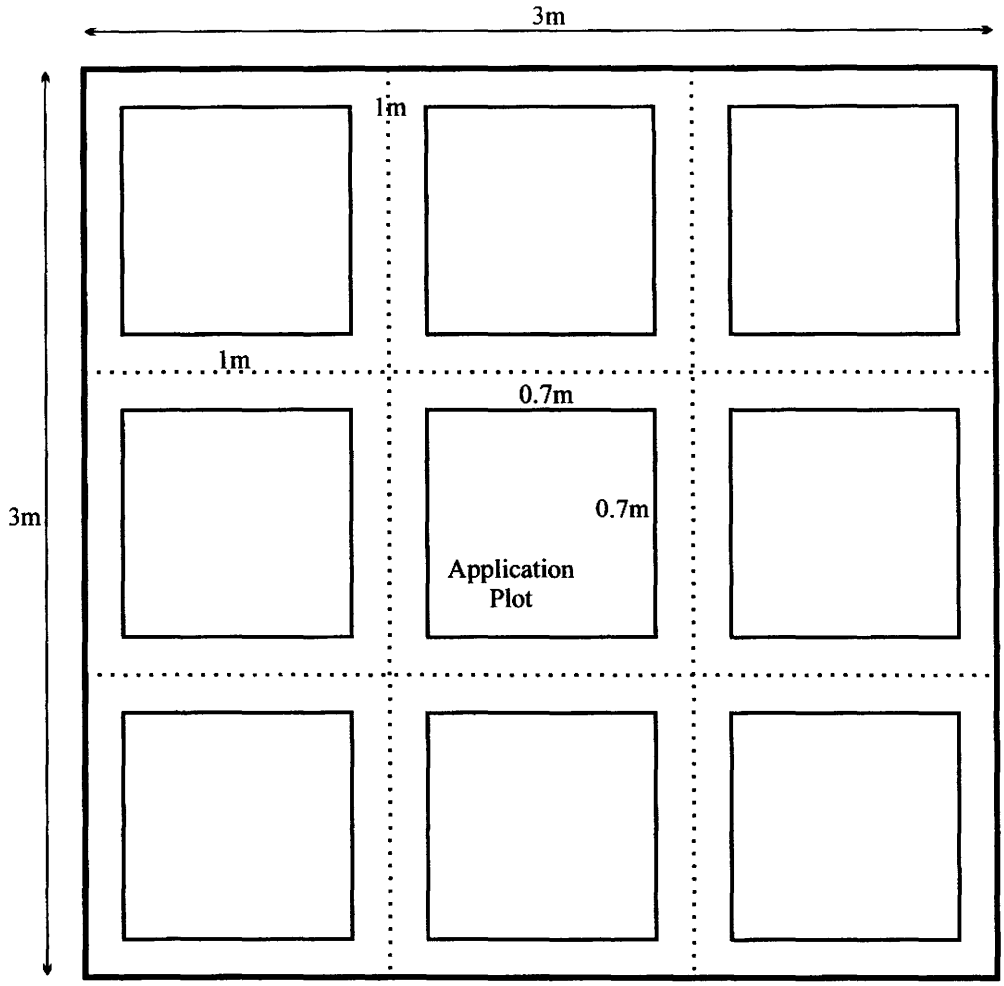

Figure 2.3: Layout of the Remediation Grid

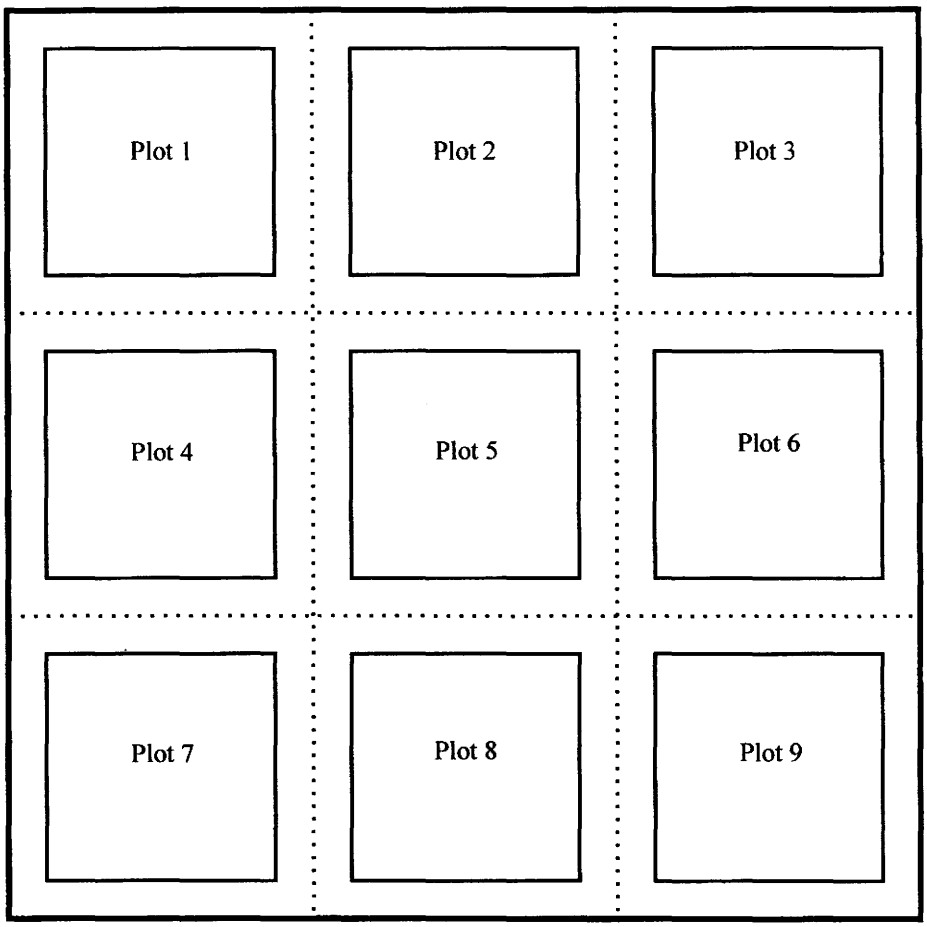

Figure 2.4: Remediation Grid with the Numbering of each Application Plot

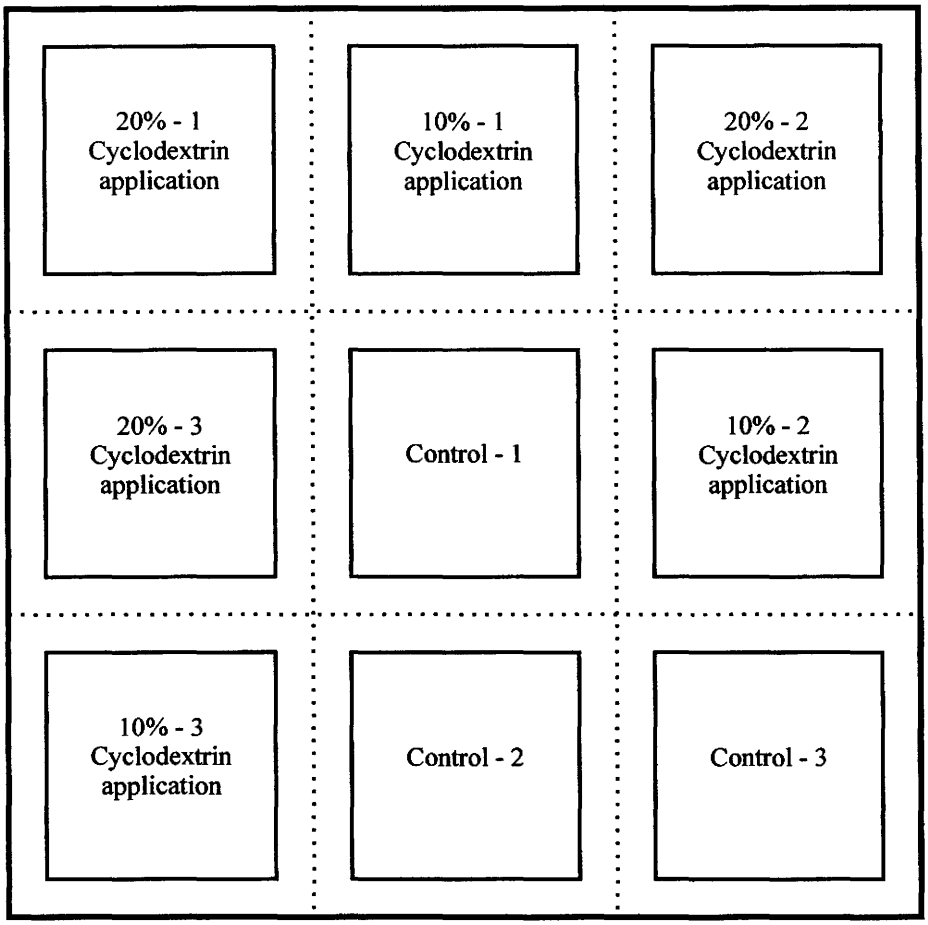

Figure 2.5: Location of Each Treatment within the Remediation Grid

Chapter 3: Experimental Methods

3.1 Design of the Remediation Grid

In the field the southwest stake marking the former orchard area of Marenco's study (2002), at the UTM coordinates of 0373428, 4646532, was located. Secondly, the northwest stake located at the UTM coordinates of 0373418, 4646551, was also found. In order to determine the precise western boundary of that sampling grid a thirty meter measuring tape was held between the southwestern and northwestern stake. Three meters north of the southwestern stake marked the southwest corner of the remediation grid located at 0373422, 4646539 (Refer to Figure 2.2). The UTM coordinates of this southwest corner were determined using an average of three hundred and thirty-seven readings from a Garmin GPS 5. At this location a metal stake, 1/2 inches wide and one meter long, was inserted halfway into the ground using a rubber mallet. The metal stake marking the northwest corner of the remediation grid was inserted three meters north of the southwest stake along the western boundary of the historic site. The locations of the two remaining corners were determined by measuring three meters east from the two previously inserted stakes. Pythagorean Theorem was used to verify that the four stakes formed a perfect square.

Inside the remediation grid the location for the one meter grids was determined relative to the corners using a measuring tape. At the center of the $1m^2$ grids, $0.49m^2$ application plots were positioned using a measuring tape. Along the boundary of each

application plot hedge clippers were inserted into the ground vertically and used to cut the grass and roots that were located along this line. This facilitated the insertion of black plastic garden edging which would enclose each application plot. Thick yellow rope, 1inch in diameter, was used to fence-off the entire remediation grid (Figure 3.1).

Figure 3.1: The Remediation Grid after Initial Sampling on June 11, 2002 (facing North)

3.2 Cyclodextrin Solution

A dry powder form of cyclodextrin was obtained from Cerestar Incorporated. C*Cavitron 82006 is their technical grade of hydroxypropyl-β-cyclodextrin which is produced through the substitution of hydroxypropyl groups onto the hydroxyl groups of the cyclodextrin (Cerestar website, 2002). Some properties of this particular form of hydroxypropyl β-cyclodextrin are listed in Table 3.1.

Dry Substance (%)	95
Degree of Substitution	6.5
Ash (%)	5.0
Propylene glycol (%)	6.0
pH (1% sol.)	7.5
Solubility (water 25°C)	>50%

Table 3.1: C*Cavitron 82006 Properties (provided on Cerestar Website, 2002.)

In the laboratory prior to field visits, the dry cyclodextrin powder was pre-measured and secured in industrial buckets to ensure secure transport. Each bucket was placed on a Sartorius BP 34000-P scale, the scale tared and subsequently filled with 5kg of cyclodextrin powder. They were then immediately covered with heavy plastic, which was secured with twine, to ensure that the powder did not become damp from the moisture in the air.

In the field, three pore volumes of cyclodextrin solution for each treatment was made simultaneously in one tank (3 x 33.3L), to ensure the three replicates received the same concentration. The 10% and 20% solutions were each mixed in separate, dedicated 115L capacity Nalgene tanks with spigots. These Nalgene tanks were set-up on a table approximately 3 meters away from the remediation grid in order to prevent contamination in the event of an accidental spill (Figure 3.2).

Carboys, with a capacity of 20L, were used to transport tap water filled at a nearby park building. The source of tap water at Point Pelee National Park is groundwater from within the park. Two of the pre-measured cyclodextrin buckets were slowly poured into one of the Nalgene tanks to make the 10% solution (10kg/100L). Four of the pre-measured cyclodextrin buckets were used to make the 20% solution (20kg/100L). The powder form of cyclodextrin is very light and fluffy therefore, water was first added slowly with watering cans against the side of the tank to minimize generating air-borne cyclodextrin "dust". Dedicated plastic dingy paddles were used to stir each solution. Once the cyclodextrin solution reached a thick paste consistency, water was added directly from the top of the carboys, until they were almost full. Using a watering can the tanks were precisely filled to the final volume of 100L. Finally, the solution was thoroughly stirred and left to sit overnight before application.

Figure 3.2: Location of Cyclodextrin Mixing Station with respect to the Remediation Grid (facing a north-east direction)

3.3 Cyclodextrin Application

A pore volume (33.3L) of cyclodextrin solution was applied to all treatment plots weekly beginning the week of June 18, 2002. Following the application of the 13th pore volume the 20% solution was no longer used due to reduced rates of infiltration and the potential horizontal movement of the solution (See Section 4.4 for further details). The schedule was amended a second time following the application of the 15th pore volume. Two pore volumes a week were then carried out biweekly until a total of 19 pore volumes of solution had been applied to the 10% sites (See Appendix B for the complete cyclodextrin application schedule).

In the lab, prior to the field season, the two Nalgene tanks were calibrated to a volume of 100L with gradations marked every 2L. A volumetric flask was used to precisely measure 2L of water, which was then poured into the tank. The level of water was then marked on labeling tape that lined two sides of the tank. This process was repeated for both tanks until a total volume of 100L was marked on each of their sides. In addition to the marked 2L gradations, additional gradations were made to denote the 33.3L, 66.6L and 99.9L levels of water to aid in application. A 20cm piece of polypropylene tubing was attached to the spigot to facilitate the transfer of solution between the tanks and watering cans.

The watering cans were used to apply the solution to the application plots. Each treatment had several dedicated watering cans. Prior to the field season, the two outer rings of holes in the watering can spout were filled with a waterproof adhesive to achieve a narrower flow area while maintaining a fast flow rate. In addition, silicone sealant was

used to seal the joint between the spout and the neck of the watering can. The silicone sealant was re-applied several times during the field season to continually ensure an impermeable seal.

For the application of the first seven pore volumes, the watering cans were filled directly from the tank. A watering can was used to apply the entire pore volume to a specific plot, before beginning the application on the additional replicates. The previously applied gradations on the tank were used to verify that a total of 33.3L of solution was applied to each plot.

For the remaining twelve pore volumes, the cyclodextrin solution was divided up into three equal volumes amongst the carboys prior to application. This allowed the application of all three replicates to occur simultaneously. In order to prevent any mix-ups the carboys and watering cans were marked with identical numbers that corresponded to the application plot replicate. To prevent residual cross-contamination the carboys were rinsed with Liquinox, a biodegradable laboratory detergent, and water after applications. In addition, carboys which housed the 20% solution were used only to fill the 20% tank and correspondingly for the 10% solution, in order to systematically maintain consistency.

3.4 Soil Sampling for DDT Analyses

A 50:50 rinse comprised of n-hexane and spectrophotometric grade acetone was used to rinse all tools and containers prior to each soil sampling for DDT analysis. The n-hexane serves as a binder and neutralizer of any DDT that may be lingering on the

equipment and the acetone evaporates any remaining moisture. The rinse was mixed in the laboratory prior to field visits, by combining equal parts of n-hexane and spectrophotometric grade acetone in a Teflon squirt bottle. Amber 120ml straight-sided, pre-cleaned, wide mouth jars were obtained from VWR Canlab. These sample containers were rinsed in the laboratory and a blank strip of labeling tape was used to differentiate these pre-rinsed containers.

DDT soil sampling locations within the application grid were randomly chosen by the random number generator in Microsoft Excel 2000. The 70cm by 70cm application plot was divided into 49 sections that measured 10cm by 10cm. Once again to eliminate edge effects, the outer edge of the grid was not used for sampling, leaving a total of 25 possible sampling locations. Locations were numbered 1 to 25 starting in the upper left (north-west) hand corner, as was done with the remediation grid (Figure 3.3). Using the "RANDBETWEEN" function, numbers between 1 and 25 were randomly generated to determine the weekly sampling locations. See Appendix A for soil sampling locations used for the analyses of DDT, DDE and DDD concentrations.

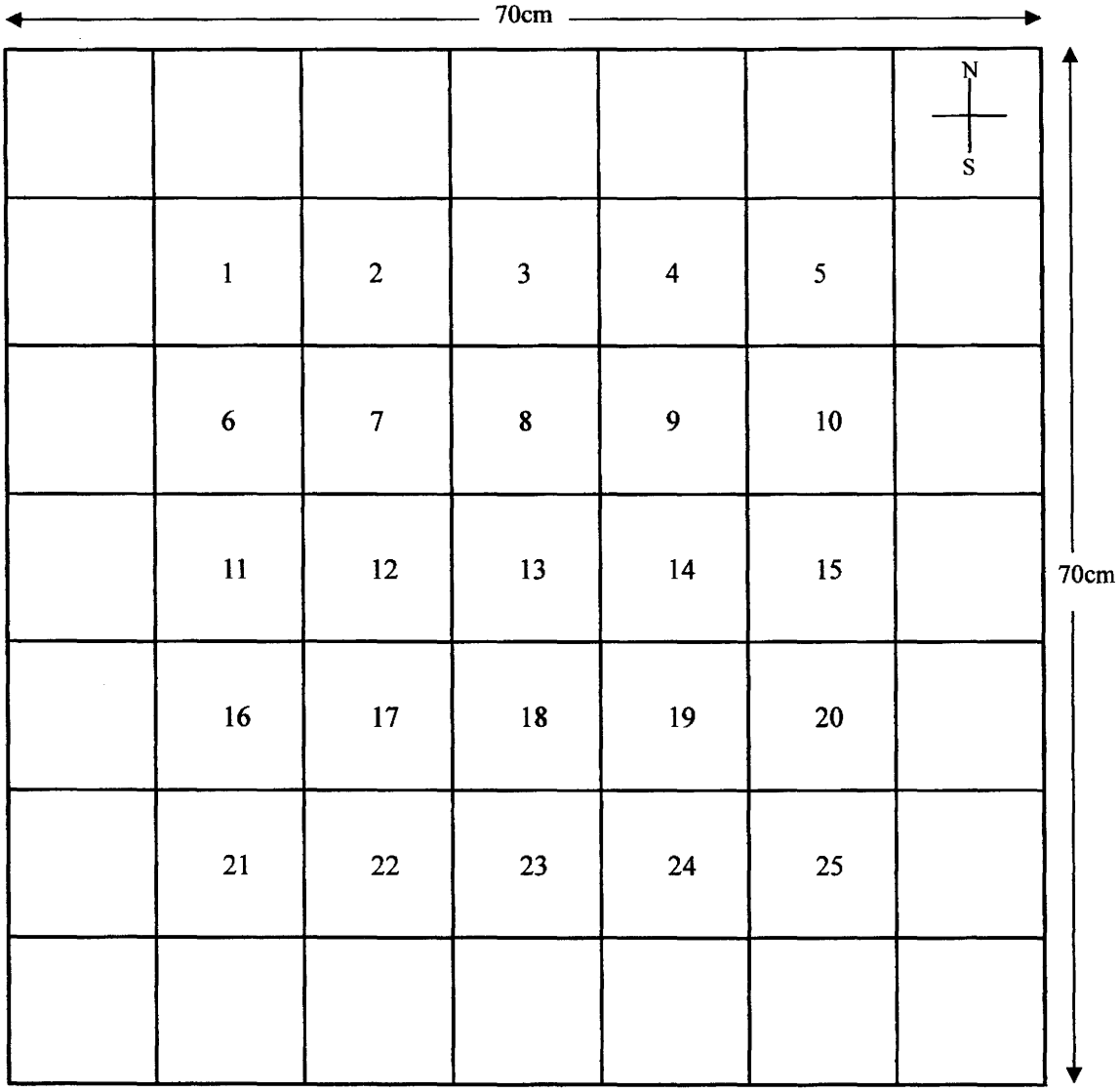

Figure 3.3: Soil Sampling Locations within Individual Treatment Plots for DDT Analysis

In the field a sample processing area was assembled approximately a meter away from the remediation grid. One individual was solely responsible for rinsing the sampling equipment with the 50/50 mixture at the processing area. A second individual was solely responsible for the actual sampling done within the application grid. These roles were retained for the duration of the experiment to ensure consistency. Disposable latex gloves were worn by both individuals, at all times during sampling. All sampling tools were first wiped with a kim-wipe and then pre-rinsed with the 50/50 mixture at the processing area. The pre-determined, random sampling location was marked with a stainless steel wire flag after finding the midpoint of this location with the tape measure. A utility knife was used to cut out a circle approximately 5-6cm in diameter, around the flagged midpoint. Using the knife the upper 2-3cm of thatch was removed to facilitate sampling of the looser soil material below. A stainless steel trowel was used to remove soil from the hole and place it in the pre-labelled sampling container. The jar was completely filled to minimize head space and possible volatilization of the DDT in the sample. On average the sampling hole was approximately 6.5 to 7.5cm deep. Once filled, the sampling jar was first covered with aluminum foil and then the lid to both protect and preserve the sample. Samples were stored on ice in a cooler until they could be transferred to a refrigerator (constant temperature of 4°C) pending analysis at the National Laboratory of Environmental Testing in the National Water Research Institute of Environment Canada.

Soil sampling for the analyses of DDT, DDE and DDD concentrations was performed initially on all application plots following the set-up of the grid on June 11,

2002. Final soil sampling for the analysis of DDT, DDE and DDD concentrations was also performed on all the application plots on November 4, 2002. Throughout the cyclodextrin application period soil samples were only taken from the treatment plots after the application of every two pore volumes of cyclodextrin (HPCD) solution for the analyses of DDT, DDE and DDD concentrations. The soil samples were collected just prior to the application of the next cyclodextrin solution application. That is, there was a time period of one or two weeks between the application of cyclodextrin solution and the next soil sampling. The control plots were only sampled during initial and final sampling for DDT analysis. It should be noted that after the application of fifteen pore volumes, the application schedule was amended. As a result, DDT soil sampling was performed at this time despite the application of only one pore volume. Subsequent sampling reverted to the initial schedule and was performed after every two pore volumes (See Appendix A for a complete list of soil sampling dates for the analysis of DDT, DDE and DDD concentrations).

3.5 Soil Moisture Content (θ)

Soil water comes from two principal natural sources: precipitation and groundwater (Ellis, 1995). The nature and density of vegetation cover of an area will dictate the amount of precipitation that reaches the ground. Surfaces that are highly vegetated may receive a smaller quantity of precipitation due to interception, while surfaces that are devoid of vegetation may receive a surplus of precipitation. Soil water content is an important indictor of the amount of plant available water that can be used

for growth. The water content is also needed for the calculation of most soil physical properties (Klute, 1986). In this study, the application of the aqueous solution cyclodextrin was an additional source of soil water.

$$Depth\ of\ solution\ applied\ to\ each\ plot(d_a) = \frac{33L/PV}{4900cm^3}$$

$$d_a = \frac{33000cm^3/PV}{4900cm^2}$$

$$d_a = 6.735cm = 67.35mm/PV$$

The total volume of water applied to the 10% treatment plots was approximately 1.5 times the annual precipitation of approximately 880.3mm (Crowe et al., 2002) at Point Pelee National Park.

$$Total\ 10\%\ solution\ applied = \frac{(67.35mm/PV)(19PV)}{880.3mm}$$

$$Total\ 10\%\ solution\ applied = 1.45$$

The 20% plots received approximately the same volume of water as the average annual precipitation.

$$Total\ 10\%\ solution\ applied = \frac{(67.35mm/PV)(13PV)}{880.3mm}$$

$$Total\ 10\%\ solution\ applied = 0.99$$

In-Situ Moisture Content (θ_{in})

Moisture content was measured in the field each week prior to the cyclodextrin application. Therefore, a period of one or two weeks had elapsed since the last application of cyclodextrin solution. Throughout the remediation experiment moisture content readings were performed in the north-east corner of all the application plots.

A Soil Point Moisture system, which includes an MP-917 instrument and a 20cm single diode rugged probe, was utilized to determine the *in-situ* volumetric moisture content (E.S.I. Environmental Sensors Inc., Victoria, British Columbia). This system utilizes conventional time domain reflectometry (TDR) techniques as its baseline and employs techniques to improve on problems such as signal-to-noise ratio and signal quality validation, that are specific to soil applications of TDR (E.S.I., 1997). The Soil Point Moisture system allows a user to determine soil moisture with minimal disturbance to the surrounding soil.

To begin use, the 20cm rugged single diode probe (probe type twelve), was plugged into to a probe cable connector which is then connected to the MP-917 instrument. The display window is comprised of two sections: 1) the Segment number window on the left and 2) the NANOSEC./%MOISTURE window on the right hand side. Prior to measurement, the probe type must be selected on the MP-917 instrument in order to produce correct readings. To do this, the instrument is placed in Mode select by holding down the MODE button while turning the MP-917 on, then releasing. The MP-917 will display the current mode of operation in the NANOSEC./%MOISTURE window in the leftmost digit. Mode 0 was used in the field as it is the stand alone instrument

operation. If the instrument was not in mode 0, then the MODE button was pressed until 0 was displayed and then MEASURE/DISPLAY was pressed to accept it. The probe type number will then appear in the rightmost digits of the display. If the number 12 was not already shown then the MODE button was used to advance the probe type number until 12 was shown on the display. MESURE/DISPLAY was pressed to accept the probe type and these settings will be maintained until a new probe type is selected. Although there is no need to reset the settings, this procedure was followed each week to ensure that the settings were correct before measurements were taken.

Once the mode settings were verified the MP-917 instrument was turned off. The probe was inserted into the ground in the north-east corner of the application grid, taking care not to insert it into a set of previously used holes. As the MP-917 is turned on the battery voltage is momentarily shown in the NANOSEC./%MOISTURE display window. A battery voltage of 11 or lower indicates that the unit requires charging and, therefore, the unit was not operated if this situation arose as it could result in erroneous readings. After the battery voltage was displayed the unit would be in idle mode signaled by a flashing dash in the NANOSEC./%MOISTURE display window. The MEASURE/DISPLAY button was pressed to begin the measurement and it is signaled by alternating flashing dash lines in both windows. Once the measurement was complete the volumetric percentage of moisture present in the 20cm sampling depth would be displayed in the NANOSEC./%MOISTURE window. By moving the TIME DELAY/MOISTURE switch to the TIME DELAY position (up) the display will show the propagation time in nanoseconds (E.S.I., 1997).

Gravimetric water content (θ_g)

Soil water content is generally expressed as the ratio of the mass of water present to the mass of the sample after drying to a constant weight; the gravimetric water content (Klute, 1986). Gravimetric water content as expressed as a percentage is determined using the following formula:

$$\theta_g = \left(\frac{mass\ of\ water\ in\ soil}{dry\ soil\ mass} \right) \times 100$$

The most common procedure as outlined in Methods of Soil Analysis – Part 1 (Klute, 1986), is intended for use in routine work and provides moderate precision (a precision of ± 0.5% water content). Soil samples collected for bulk density measurements on November 4, 2002 were also used to determine gravimetric soil moisture content. See Section 3.10 for further details. Gravimetric soil moisture contents were determined using the above formula.

Volumetric Water Content (θ_v)

The volumetric water content is the volume of water present in a given volume of soil (Klute, 1986). If a volume basis of water content is required, a known sample volume of soil must be obtained. Coring methods as described in the bulk density section can be used to obtain a sample of known volume. The volumetric water content as expressed as a percentage can be calculated using the following equation:

$$\theta_v = \left(\frac{volume\ of\ water\ in\ soil}{volume\ of\ soil\ sample} \right) \times 100$$

The core samples collected for bulk density measurements were also used to determine volumetric water content. See section 3.9 for further details.

3.6 Soil Sampling Procedures for DAPI Staining

On the morning of October 22, 2002, soil samples were collected to be used to approximately determine the amount of bacteria present within the different application plots using the method of DAPI staining. The location within each plot was randomly determined by the random number generator in Microsoft Excel 2000. Using the "RANDBETWEEN" function, a number between 1 and 25 was randomly generated to determine the sampling locations. The sampling procedure for the bacteria samples was similar to the procedure followed during DDT sampling. See Section 3.4 for further details. Instead of storing samples in a 120 mL straight-sided amber sampling jar, 5-6 gram samples were stored in sterile Petri dishes. The Petri dishes were then covered, labeled and wrapped in parafilm. The samples were then stored on ice in a cooler, until they could be transferred to a refrigerator and kept at $4^{o}C$.

3.7 Soil Profile and Soil Sampling with Depth

During final sampling on November 4, 2002, a two meter by three meter pit that was one and a half meters deep was dug along the eastern edge of the remediation grid. This pit was used to complete soil sampling with depth for DDT, DDE and DDD

analysis, bulk density, porosity, organic content and water content. It also allowed for a closer inspection of the soil profile for soil classification.

As was seen during sampling of the control plots the majority of the soil type in this particular area is a loose sandy material. During sampling of the control plots, it was common to see infilling of the hole. It was a concern that this would be a hindrance during depth sampling and prohibit the digging of a pit. As the outcome of the digging a large pit was unknown, the pit was first started about half a meter east of the remediation grid edge rather than directly adjacent to it. This would provide critical information on the behavior of the sand and whether collapse of the pit would be a problem.

Figure 3.4: Collection of Soil during the Analysis of the Soil Profile

Before any digging began, a tarp was laid on the ground adjacent to the proposed location of the pit. This was done to allow for soil collection and to facilitate the refilling of the hole once sampling was complete (Figure 3.4). Digging began by removing the upper thatch layer in large sections and placing them in order on the tarp. A pit that was one meter by three meters was first dug to a depth of one meter. It was clear that collapse would not be a concern, and that a smooth vertical face could be formed to allow for easy depth sampling. At this time, the pit was widened until its western side was parallel with the eastern border of the remediation grid. Since the pit wall met the eastern border of the remediation grid, it allowed for sampling that could be correlated with the application plots in that location. Specifically, the soil profile and depth sampling was performed on plot three (20%-1), six (10%-2) and nine (control-3).

First DDT soil sampling was completed along the south side of the profile for all three application plots at depths of 15cm and 30cm below the ground surface. Core samples to be used for the determination of bulk density, porosity, water content and organic content were also taken at these depths and at the additional depth of 70cm, along the north side of the soil profile. The Soil Point Moisture Probe System (E.S.I., Victoria, British Columbia) was also used to determine the *in-situ* volumetric moisture content at intervals of 10cm to a depth of 90cm (Refer to Section 3.5 for details on the operation of this system). The 20cm long TDR probe was inserted horizontally at each sample location. See Figure 3.5 for a visual display of sampling locations within the three application plots.

Figure 3.5: The Face of the Sampling Pit on November 4, 2002. DDT sampling was performed on the left, in-situ moisture content in the middle and core samples was performed on the right of each plot face.

Once sampling was complete, the soil collected on the tarp was used to refill the hole. The soil was compacted through stomping at several depths during the infilling. Finally, the thatch was replaced after the hole was filled.

3.8 *In-Situ* Hydraulic Conductivity

During the final sampling which took place on November 4, 2002, a 2800KI Guelph Permeameter manufactured by SOILMOISTURE Equipment Corporation (Santa Barbara, California) was used to determine the field saturated hydraulic conductivity of each application plot. The Guelph Permeameter uses a constant head method to determine the hydraulic conductivity of a soil and operates on the Mariotte siphon principle (SOILMOISTURE, 1986).

The Guelph Permeameter is used to determine the steady-state recharge of water to soil while maintaining a constant level of water in an augured hole. The Guelph Permeameter is packaged in four main components for convenient storage and easy transportation. The four components are; the Tripod Assembly, the Support Tube and Lower Air Tube Fittings, the Reservoir Assembly and the Well Head Scale and Upper Air Tube Fittings. A bulb of field saturated soil is created in the vicinity of the hole and then the steady-state rate of recharge is determined and used to calculate field saturated hydraulic conductivity.

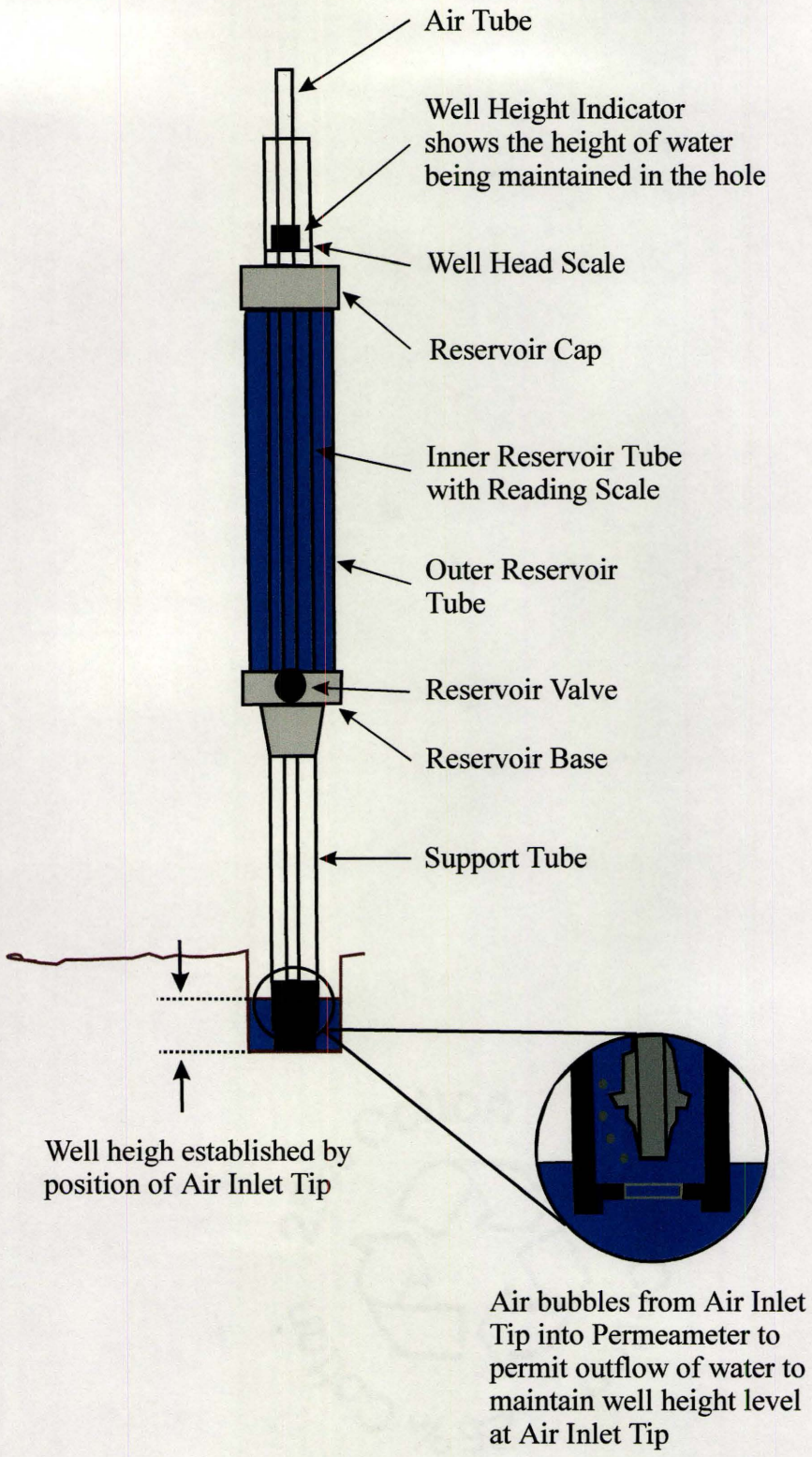

Figure 3.6: Schematic Diagram of the Guelph Permeameter (adapted from the Soil Moisture Equipment Corporation Manual, Model 2800KI, 1986)

Figure 3.6 is a diagram of the Guelph Permeameter and all its components. To begin, the tripod was assembled by fitting the Tripod Legs into the Tripod Base. The Tripod Support Chain was then passed through the hole in the Tripod Legs and secured with the "S" Hook. The Tripod Support Chain can be adjusted to accommodate any angle necessary for the legs. The Tripod Busing with the wide end up was slid onto the Support Tube. The Lower Air Tube that is inside the Support Tube was connected to the Middle Air Tube at the base of the Reservoir. The tube was pushed firmly into the coupling until the ridge on the inside of the coupling snapped into the groove on the end of the Lower Air Tube. The Support Tube was then connected to the Reservoir Assembly by sliding it into the recess on the bottom of the Reservoir Base. It is of utmost importance that this connection is airtight and that the Support Tube is seated completely into the Reservoir Base. The entire assembly was then lowered into the tripod, ensuring that the Tripod Bushing was fully pushed downward into the Tripod Base as this will provide support and stability. Once the permeameter was secure, the Upper Air Tube was connected to the top of the Middle Air Tube (inside the Reservoir Assembly). The entire Air Tube was pressed down to ensure that the Air Inlet Tip at the bottom of the Support Tube was fully seated in the Air Tip Seating Washer. The Well Height Indicator which is attached to the Middle Air Tube should be seated flush against the Reservoir Cap. The Well Head Scale is lowered over the Upper Air Inlet Tube and was seated against the bottom of the recess in the Reservoir Cap. If the Well Head Scale is seated properly the "0" reading will be 5mm below the top of the Reservoir Cap and the bottom of the Well Height Indicator will line up with the 5mm mark.

After the permeameter was assembled it was then filled with water. The Fill Plug in the Reservoir Cap was removed and the supplied tube assembly that was attached to the plastic water container was inserted. The plastic water container was held above the height of the Reservoir Cap to allow the water to fill the Permeameter. This allows water to drain into the Reservoir and fill both the Inner and Outer Reservoirs. The permeameter was not filled while it was positioned in the well hole, because if the Air Inlet Tip is not seated flush against the bottom this will result in water leaking out of the bottom. If the well hole is filled then measurements will have to be postponed until the water has completely percolated from the bottom of the hole. After the Guelph Permeameter is filled, the Fill Plug was replaced in the Reservoir Cap.

Well preparation can be completed before or after the assembly of the Guelph Permeameter. During this investigation, one researcher was responsible for the assembly of the Guelph Permeameter and the other the well preparation of all the wells. The two-piece auger handle can be attached to any of the three auxiliary tools by the quick connect fitting. The main soil auger was used to remove bulk amounts of soil and organic material by rotating the handle while applying a steady firm downward pressure. After a few turns, the auger was lifted out of the hole and inverted to remove the collected sample. The soil auger was used to produce a well 2-3cm smaller than the final desired depth. At this time the sizing auger was used as a finishing tool to produce a 6cm diameter well hole of uniform geometry and to clean debris off the bottom.

The Guelph Permeameter was used to measure the field saturated hydraulic conductivity at both a depth of 15cm and 30cm. Therefore, a representative field

saturated hydraulic conductivity was determined for the overlying Ah horizon as well as the lower Bm horizon. A well hole was first dug to the depth of 15cm for all the plots, measurements taken, and then the hole was extended to a depth of 30cm to allow for deeper measurements.

Once a well hole was prepared the tripod was centered over the hole and the Guelph Permeameter was slowly lowered into the tripod, taking care not to bump or knock the side of the hole. The Tripod Legs were adjusted to the angle of the land for the 15cm wells; however, the tripod was not used for the 30cm wells. Instead the Guelph Permeameter was held in place while the Tripod Bushing was slid down to the top of the well hole to stabilize it.

Prior to beginning measurements it was ensured that the notch on the Reservoir Valve was pointing up and thereby both Reservoirs were connected. The Inner Reservoir can be used by itself when taking measurements in materials with a low rate of infiltration. Work by Marenco (2002), indicated that this site had a relatively high saturated hydraulic conductivity and therefore the combined Reservoirs were used for all measurements. To begin readings, the Air Inlet Tip was slowly raised by using the Upper Air Tube. It is important to slowly raise the Air Inlet Tip to ensure that a large surge of water does not temporarily overfill the well. The Air Inlet Tip was raised until the lower edge of the Well Height Indicator reached 5cm on the Well Head Scale, thereby establishing a 5cm ponded height of water in the well. The rate of water fall in the reservoir indicates the outflow of water from the well into the surrounding soil, while a constant head of 5cm of water is maintained. The level of water in the Reservoir was

noted and recorded over regular time intervals against the scale stamped on the inner reservoir tube. The time interval used between readings will be dependent on the type of material under investigation and therefore was left up to the discretion of the operator. For example, clay soils may require a longer interval, while sandy soil may require a shorter interval. At this particular site all the plots took approximately five minutes to reach steady state (see Appendix H for further details on the Guelph Permeameter data). The difference between consecutive readings divided by the time interval equals the rate of fall of water, R, in the reservoir. The rate of water fall was monitored until the rate did not significantly change over three consecutive time intervals.

The program GP CAL (Zhang and Parkin, 1998), was used to calculate the field saturated hydraulic conductivity with the obtained steady-state measurements. A K_{fs} value can be calculated with the measured steady-state values using a one-ponded height technique or a two-ponded height technique. In this case the one-ponded height technique was employed and the numerical solution is based on the Reynolds et al. (1989) solution of the Laplace equation:

$$K_{fs} = \frac{CQ}{\left(2\pi H^2 + C\pi a^{*2} + 2\pi H/\alpha\right)}$$

where K_{fs} if the field saturated hydraulic conductivity (cm/sec), H is the ponded height of water in the well (cm), a is the well radius (cm), α is determined according to the soil texture, and C is a dimensionless proportionality parameter primarily dependent on the H/a ratio. The accuracy of the calculation of K_{fs} using this equation increases as the

relative importance of the field-saturated component of flow increases over the capillarity component of flow (Reynolds and Elrick, 1987).

Within the GP CAL program the following parameters were changed from the default settings, before solving for K_{fs}:

1. The reservoir constant was input – 35.22cm^2
2. The soil type was changed to medium sand.
3. A value of 0.36cm was automatically input by the program for the α parameter.
4. The well radius was input – 3cm
5. The ponded height of waster in the well (H) was input – 5cm
6. The steady-state rate of fall determined using the Guelph Permeameter was input (R1)

In addition the input units of time and length were changed to minutes and centimeters, respectively. The output units of K_{fs} were set as cm/s.

3.9 Bulk Density (ρ_b)

Bulk density is the ratio of the mass of dry solids to the bulk volume of the soil which includes both the solid and void space (Klute, 1986). It is a widely used value as it provides information about the soil structure and it is needed for calculating porosity. Bulk density will vary with the structural condition of a soil, as it is directly related to the packing. Soil compaction, which can often be a result of machinery, occurs as a mass of soil is compressed into a smaller volume resulting in an elevated bulk density (Ellis,

1995). Bulk densities are generally reported in g/cm^3 and the following equation is used to calculate bulk density:

$$Bulk\ Density = \frac{mass\ of\ oven\ dry\ soil}{sample\ volume}$$

The core sampling method, (Klute, 1986), was used to obtain undisturbed samples in the field during final sampling on November 4, 2002. This method consists of cylindrical 60cm^3 metal cores being pressed down into the soil to a desired depth and then carefully removed in order to sample a known volume of undisturbed soil (Klute, 1986). The metal cylinder (approximately 3.3cm high with an inner diameter of 4.8cm) is initially hand pressed into the soil as far as possible in order to minimize the disturbance of the sample. Then another core is placed on top of the first cylinder and a rubber mallet is used to gently tap the sampling core to the desired depth. Once the core is in place, a small shovel can be used to gently pry it up with care to ensure that no soil falls out of the bottom. A small putty knife is used to trim the soil extending beyond the sides of the core. For the surface samples taken from each plot scissors were used to trim roots and twigs that extended beyond the sides of the metal core. Samples were then placed into a pre-labelled Ziploc baggie, sealed and immediately transferred to a cooler to be kept at 4°C until transfer to a refrigerator was possible.

In the laboratory, samples were transferred into a pre-labelled, pre-weighed aluminum dish and placed in a drying oven at 105°C for twenty-four hours or until a

constant weight was achieved (Klute, 1986). Once dry, the samples were removed from the drying oven and placed in a dessicator for twenty minutes to cool. The dessicator is used to prevent moisture from being absorbed by the sample as it cools to room temperature. Cooled samples are then weighed to determine an oven dry soil weight.

3.10 Porosity (η)

The porosity of a soil is the percentage volume of pore space which can be occupied by either air or water (Ellis, 1995). As with bulk density, porosity will also vary with structural makeup of a soil. As a soil is compacted, large pores will be lost, thereby restricting the flow of air, water and solutes within a soil matrix. Porosity can be generated for a soil of known bulk density (ρ_b), and particle density (ρ_p), and is generally calculated with the following formula:

$$\eta = \left(1 - \left(\frac{\rho_b}{\rho_p}\right)\right) \times 100$$

In this study, values of porosity for the soil cores taken during final sampling on November 4, 2003 were calculated in a different manner in order to take into account both the organic and mineral matter contents. The particle density or the volume of soil solids, of each sample was calculated by first taking into account the proportions of mineral and organic matter. The mass of organic matter within the soil was calculated by multiplying the percentage of organic matter determined through loss on ignition (See Section 3.11), with the mass of oven dried soil. The mineral matter mass was then calculated by subtracting the amount of mass of organic matter from the initial oven dry

soil weight. The volume of solids, was then calculated by dividing the mass of organic matter by the particle density of organic matter (1.1g.cm^3) and likewise, the mass of mineral matter was divided by the particle density of mineral matter (2.65g/cm^3). The two volumes were added together to get a final volume of solids, comprised of an organic and mineral component as follows:

$$v_s = \frac{M_{om}}{\rho_{om}} + \frac{M_{mm}}{\rho_{mm}}$$

where v_s is the volume of the solids, M_{om} is the mass of organic matter in a sample, ρ_{om} is the density of organic matter, M_{mm} is the mass of mineral matter in the sample and ρ_{mm} is the density of mineral matter. The value of volume of solids was divided by the bulk volume in the following equation to determine the porosity of the soil cores:

$$n = \left(\frac{v_b - v_s}{v_b} \right) \times 100$$

where n is the porosity, v_b is the volume of the soil sample (60cm^3) and v_s is the volume of the solids as calculated above.

3.11 Organic Matter

Soil organic matter is derived from four main sources: plant litter, leachates, *in situ* roots and soil organisms (Ellis, 1995). Plant litter is the primary contributor and is composed of a variety of debris including leaves, stems, flowers, twigs and bark. Leachates are composed of organic substances washed into the soil from vegetation. Soil organisms contribute through biochemical decomposition, and incorporation of the soil

organic matter. Soil organic matter has a special chemical composition which consists of predominately carbon, nitrogen, oxygen and hydrogen (Ellis, 1995). Organic compounds vary in shape and size and some are particularly complex structures.

Organic matter is commonly determined in the laboratory by loss on ignition. Organic matter is burned off of soil samples when they are heated to a temperature of 400°C. Oven dried core samples previously used for the determination of bulk density, porosity and moisture content were then used for the determination of organic matter by loss on ignition.

Approximately 5g of the oven dried sample for each plot was weighed and placed into a small aluminum dish. Samples were ignited for a minimum of sixteen hours at a temperature of 400°C in a muffle furnace (Sparks, 1996). Subsequent to ignition the samples were placed in a dessicator to cool for at least thirty minutes. Samples were then weighed and the organic matter content was determined using the following formula:

$$\%\, organic\ matter = \left(\frac{mass\ of\ organic\ matter}{mass\ of\ oven\ dried\ soil} \right) \times 100$$

3.12 DDT Soil Sample Splitting

DDT soil samples were analyzed at the National Laboratory for Environmental Testing (NLET) at the National Water Research Institute, Environment Canada in Burlington, Ontario. Samples collected in the field were mechanically split in the laboratory at McMaster University. The analysis required a minimum of 15g of soil,

however, a minimum of 30g of soil was sent to NLET in order to allow for the completion of quality control samples.

Sample splitting was completed in a fume hood, using the Navigator Portable Balance for weighing. In addition, loose material such as roots, grass, and rocks that could interfere with the analysis of DDT were picked out of samples to be submitted using the following procedure. A watch glass, a set of stainless steel tweezers, a stainless steel scoopula and a stainless steel spatula were rinsed with the 50:50, acetone/n-hexane mixture. 60ml straight-sided amber sample jars were also rinsed with the mixture as they were used to submit the processed proportion of the sample to NLET. The collected sample was retrieved from the refrigerator and the lid and foil was removed. The stainless steel spatula was used to divide the sample in half by slicing directly down the center of the jar. This method produced samples that were representative of all the different depths sampled. One half of the sample was scooped onto the watch glass. The stainless steel tweezers were then used to pick out any visible and discernable twigs, roots etc. These items were then placed on a clean kimwipe and discarded. The 60ml sample jar was placed onto the Navigator Portable Balance and tarred. Once processed the sample was transferred to the 60mL sample jar using the stainless steel scoopula. The soil was weighed to ensure that there was at least 30g of soil. The jar was covered with foil to minimize volatilization and then covered with the lid. Labelling tape was applied to the jar and the sampling label was replicated exactly. In addition, a label that was specifically designed for NLET was also secured to the jar. The remaining sample was

left in the original sample container, re-covered with the foil and lid and stored in a refrigerator.

3.13 DAPI Staining Procedures

Soil samples collected to be analyzed for bacterial numbers using a DAPI stain need to be fixed with a 4% paraformaldehyde (PFA) solution within 24 hours of collection. The 4% PFA solution needs to be used within 72 hours of conception.

4% Paraformaldehyde Solution

To begin 150mL of Milli Q water was placed in a beaker and then heated to a temperature of 60°C on a magnetic stirring hotplate. The beaker was covered with aluminum foil to minimize evaporation during heating which would result in a change of volume. Once the water reached a temperature of 60°C, 10 grams of PFA crystals were added to the water. A magnetic stir bar that had been placed in the beaker before the water was added was then used to stir the solution to assist in dissolution of the crystals. In addition to the stirring, drops of NaOH were added to also assist in the dissolution of the PFA crystals. Once the crystals had dissolved, the solution was left to cool to room temperature. The solution was then placed on a magnetic stir plate and a pH meter was used to monitor the pH. HCL was added in a drop-wise fashion to lower the pH to 7.2 or conversely drops of NaOH were added to raise the pH if necessary. Once the pH was stable (between 7.15 and 7.2), the solution was transferred to a 250mL volumetric flask. Milli Q water was added to the solution to produce a final volume of 250mL. The

solution was inverted several times to mix it and then it was sterilized by filtration. The filtered solution was then covered with aluminum foil and stored in the refrigerator at 4°C.

Sample Fixation

Soil samples taken on October 22, 2002 were fixed the following morning on October 23, 2002. The parafilm around the Petri dishes was removed and 20mL of 4% PFA was added to all the Petri dishes. This is a mix of approximately 1 part soil, 3 parts PFA. Using a disposable pipette, the PFA was well mixed into the soil to ensure the entire sample was fixed. The Petri dishes were then recovered and sealed with parafilm. They were then left to fix overnight in the refrigerator and processed the following day.

DAPI sample preparation

The following day on October 24, 2002, eight of the nine samples were transferred from the Petri dishes to centrifuge tubes. Due to a limited number of centrifuge tubes, one of the control samples (plot 9) was not analyzed. Samples were then centrifuged using a Sorval centrifuge for twenty minutes at a speed of 25000rpm while the temperature was maintained at 4°C. In order to remove the 4% PFA, the supernatant was decanted and discarded.

The samples were then washed with 1xPBS as the centrifuge tubes were filled with the solution and then shaken to distribute it throughout the soil. The samples were

centrifuged again at the same settings for twenty minutes. After centrifuging, the 1xPBS was decanted off and discarded. This procedure was repeated for all the samples.

Finally, 10mL of ethanol-PBS was added to all the tubes. Once again, the tubes were shaken to distribute the ethanol-PBS throughout the soil. The DAPI staining was performed on dilutions of this final solution.

Dilutions were first carried out on two samples to determine the optimum dilution for viewing and final direct enumeration. Plot 4 and 5 were used as the test samples and ten individual dilutions of one-tenth were performed to a final dilution of one in one millionth. Eppendorf containers were used to carry out the dilutions. From the final solution, 20μL was removed using a micro pipette and placed into the container. Added to this was 180μL of the 1xPBS solution and a dilution of one tenth was the result. From this dilution, 20μL was removed using a micro pipette and placed into another container. Added to this was 180μL of the 1xPBS solution producing a dilution of one-one hundredth. This method was used until a final dilution of one in one millionth was mixed.

Two separated slides with ten individual viewing sites was used to view all the dilutions for each of the samples. A micro pipette was used to remove 4μL from each container and place it into an individual viewing well. The pipette tip was then used to spread the solution throughout the circle. The slide was left to dry for thirty minutes before ethanol dehydration was performed. Ethanol dehydration consisted of the slides being placed in solutions of increasingly higher concentrations of ethanol, beginning with a 50% ethanol solution. The slides were left in this solution for three minutes before

being transferred to an 85% ethanol solution with tweezers. After three minutes in that solution the slides were again transferred to a 90% ethanol solution. This was the last solution and then slides were then placed in a container of milli Q water for three minutes. The slides were left to dry in a dark cupboard overnight.

The following day the slides were stained with DAPI in a dark room. The 5µg/mL DAPI stain was thawed as it is stored in the freezer. In a Petri dish a micro-pipette was used to place the DAPI stain over the entire slide. A cover slip was placed on the slide to seal in the DAPI stain. The slide was left for thirty minutes to allow the stain to set. Once set, the cover slip was removed and the slide was rinsed with milli Q water. The slide was left in the fume hood to dry for another thirty minutes. Paramount was applied liberally all over the slide and a cover slip was applied. The cover slip was pressed on firmly to help in the removal of any air bubbles and to spread the paramount over the entire slide. The slide was left to dry overnight before being viewed with a Lecia DMRA microscope.

The Lecia DMRA, an epifluorescence microscope, was equipped with a 10X HC Plan eyepiece. A small drop of immersion oil was used in conjunction with the 100X oil immersion HCX PL Flowtar Objective lens. A UV emission of 470nm was used to see an excitation level of 360/40. A bar counter was used to count the number of cells within a randomly located grid. Fields were randomly changed without observing the change and the DAPI counted until a minimum of 200 cells were counted. The bacterial density in the original sample was calculated by using the following formula (Kepner, and Pratt, 1994):

$$Bacteria\,(cells/mm) = \frac{N \times A_t}{d \times V_f \times G \times A_g}$$

where N is the number of cells counted, A_f is the effective area of the filter (25mm^2), A_g is the area of the counting grid (1mm^2), V_f is the volume of diluted sample filtered (0.004ml), and d is the dilution factor (V_{final}/V_{sample}) (30x for this method), accounting for the addition of preservative and dispersant as well as any dilution prior to addition of sample to the filter funnel. The number of bacteria was then converted to numbers of cells per soil mass.

3.14 National Laboratory for Environmental Testing (NLET) Method for Analysis of DDT, DDE and DDD

According to the schedule of services for the fiscal year of 2002-2003, the NLET analysis for DDT, DDE and DDD is completed using Method 03-3751. Method 03-3751 is completed using the following steps:

1. 20g wet sediment sample is ultrasonically extracted using a 1:1 mixture of acetone and hexane
2. the concentrated extract is partitioned with water and back-extracted with dichloromethane
3. the combined extract is concentrated, cleaned up and fractionated on a 3% (w/w) deactivated silica gel column
4. the combined extract is then reconcentrated to a final volume of 10mL prior to analysis
5. Dual column capillary gas liquid chromatography with electron capture detectors is used to analyze for the organochloride pesticides DDT, DDE and DDD

Chapter 4: Results and Discussion

4.1 Soil Classification

Classification of a soil, to a soil order, reflects the degree of development, or lack there of, of a soil from its parent material. Assessment of the soil profile reveals the presence or absence of diagnostic horizons which will determine the soil order. The classification of a soil allows the comparison and prediction of behavior of similarly classified soils (Brady and Weil, 1999).

A close inspection of the soil profile at the study site was facilitated by the sampling pit that was dug during the final sampling on November 4, 2002 (See Figure 4.1). The top 2.5cm of the soil was a thatch type layer that was primarily comprised of roots. For sampling this layer was always removed to allow sampling of the soil below it. This is classified as an Of horizon, as this organic fibric horizon contains readily identifiable botanical material. The layer from a depth of 2.5 to 20cm of the profile is a dark, organic rich layer that is comprised of roots, decaying organic matter and biological life. The organic carbon content (discussed in section 4.2) is well below 17% which would classify this layer as an Ah horizon (ISSS, 1979). Underlying the Ah horizon is a horizon that has been slightly altered by pedogenic processes, but not to a great extent. The horizon which encompasses a depth of 20-50cm is much lighter than the overlying Ah horizon, however, it does have a darker and deeper brown hue then the soil below it. This Bm horizon also contains less than 2% organic matter. The bottom of the Bm

horizon is not distinct and the soil profile transitions for 20-30cm with a BC horizon above a C horizon at a depth of 80cm. The transition BC horizon has a slightly browner hue than the underlying C horizon which is comprised of white sand. This deep white sand has been essentially unaffected by any pedogenic processes.

The presence of the Bm horizon dictates that this soil belongs to the Brunisolic Soil Order within the Canadian System of Soil Classification (ISSS, 1997). Furthermore, the 20cm thickness of the Ah horizon designates this soil profile within the Great Group, Melanic, making this a Melanic Brunisol.

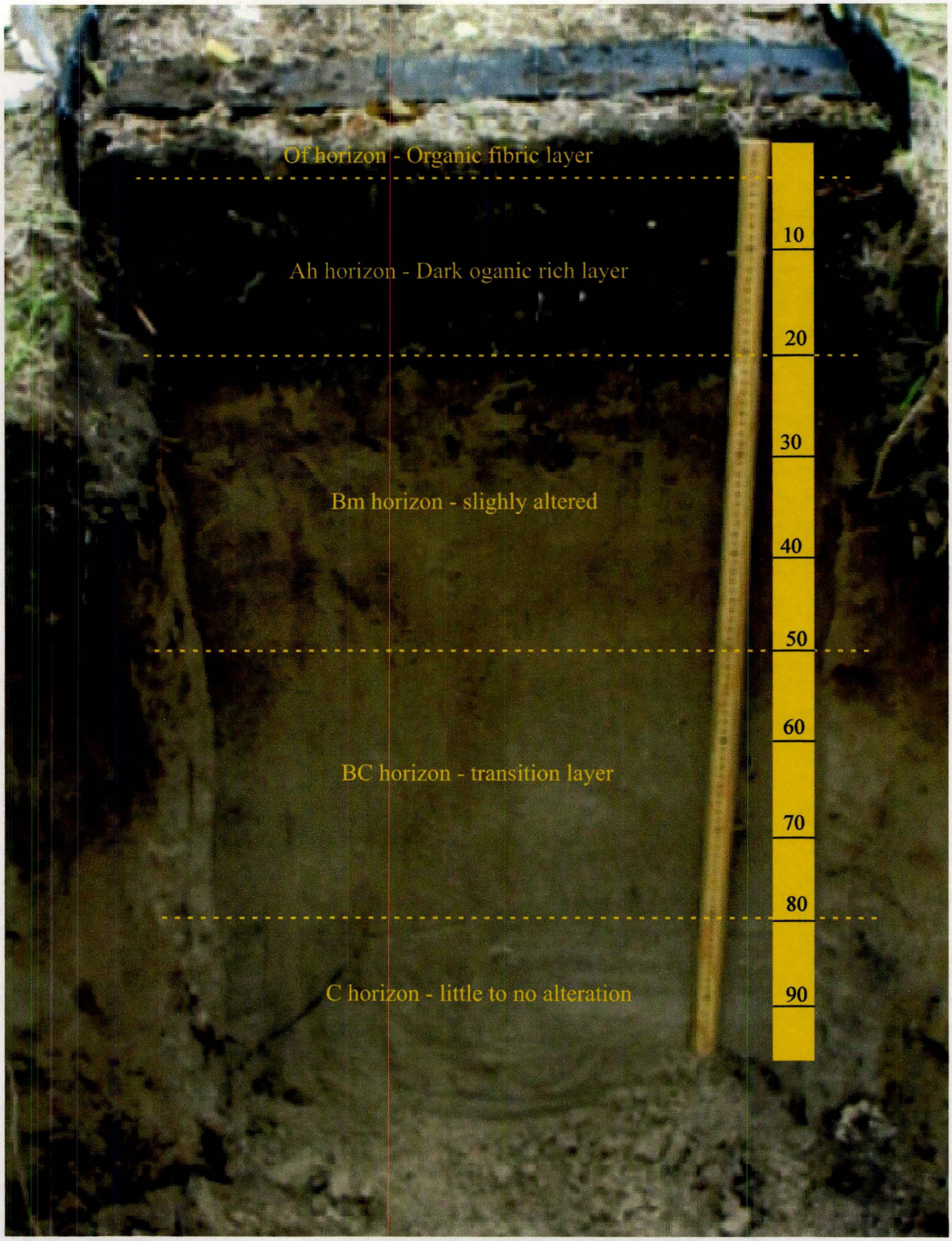

Figure 4.1: Soil Profile of Plot 6:10%-2 during the final sampling on November 4, 2002, illustrating the individual soil horizons

4.2 Physical Soil Properties

Soil texture and structure will fundamentally influence physical properties thereby determining the behavior of a soil such as water-holding capacity, drainage and compactibility. Furthermore, the behavior of organic contaminants within a soil matrix is heavily dependant on the physical and chemical properties of the soil. A high rate of drainage will propagate an aerobic environment and the persistence of organic contaminants such as DDT.

Marenco, 2002, performed extensive grain-size analysis throughout the area of the study site. It was determined in all locations that the mineral soil in this area fell within the sand textural class.

The measured physical properties of the soil in the remediation grid are presented in Table 4.1. The bulk density values determined within the shallow Ah horizon of the plots ranged from approximately 0.5 to 1.6g/cm^3. The average bulk density in the Ah horizon for all the plots is 0.97g/cm^3. The presence of a stone or twig can provide a misrepresentative bulk density measurement and is the main cause of this high degree of variation. The bulk density values determined with depth show little variation and are quite stable with values between 1.30 to 1.50g/cm^3. The average bulk density with depth is 1.47g/cm^3. With the depth soil samples there were no stones or twigs to interfere with the calculation. Cultivated sandy loams and sands generally have bulk densities within the range of 1.2-1.8g/cm^3 (Brady and Weil, 1999). The deeper soil samples exhibit values that are within this range. A visual inspection alone reveals that the surface soil of the plots is quite different from the soil at depth due to the large collection of organic

matter throughfall and it is located in an area surrounded by forests. Therefore the measured values of bulk density do not reveal any substantial differences between treatments.

In the surface soils of the plots the porosity is primarily above 50% and has an average value of 56.5% and a maximum value of 75%. The measured values of porosity are typical for high-organic matter surface soils (Brady and Weil, 1999). The porosity of the soil samples with depth, however, are slightly lower with an average value of 42.3%. This decrease in porosity is not unusual as sub-soils, where increase compaction occurs, generally have lower values than surface soils (Brady and Weil, 1999). As observed with the bulk density there is no change in values between treatments.

Sample Name	Gravimetric Water Content (%)	Volumetric Water Content (%)	Bulk Density (g/cm3)	Organic Matter thru loss on ignition (%)	Porosity (%)
20%-1, Core i	52.4	38.6	0.74	31.9	59.7
20%-1, Core ii	43.2	37.9	0.88	14.9	60.0
20%-2, Core i	38.6	41.2	1.07	14.7	51.4
20%-2, Core ii	68.7	55.9	0.81	20.3	60.5
20%-3, Core i	43.2	42.3	0.98	18.9	53.3
20%-3, Core ii	32.3	31	0.96	18.6	54.2
10%-1, Core i	40.5	30.3	0.75	14.0	66.2
10%-1, Core ii	80.1	37.4	0.47	33.4	74.1
10%-2, Core i	47.5	38.3	0.81	17.7	62.0
10%-2, Core ii	38.6	39	1.01	17.8	52.3
10%-3, Core i	29.0	32.8	1.13	13.0	49.5
10%-3, Core ii	34.2	36.1	1.05	8.6	55.5
Control-1, Core i	6.5	7.8	1.20	4.3	52.1
Control-1, Core ii	5.8	7.8	1.35	2.4	47.2
Control-2, Core i	8.5	8.4	0.99	7.4	58.9
Control-2, Core ii	8.6	8.7	1.01	8.8	57.3
Control-3, Core i	11.0	15.6	1.41	4.9	43.2
Control-3, Core ii	27.4	23.9	0.87	14.5	60.4
20%-2 - Ah horizon	14.5	22.4	1.54	4.1	38.3
20%-2 - Bm horizon	6.6	10.6	1.60	1.9	38.0
20%-2 - BC horizon	6.7	9.4	1.39	2.2	45.8
10%-2 - Ah horizon	16.0	22.4	1.41	8.3	40.7
10%-2 - Bm horizon	6.0	9.1	1.52	1.6	41.4
10%-2 - BC horizon	5.0	7.6	1.53	1.5	40.9
Control-3 - Ah horizon	7.4	9.6	1.30	2.8	49.1
Control-3 - Bm horizon	4.7	6.6	1.42	0.9	45.8
Control-3 - BC horizon	4.4	6.8	1.54	1.4	40.8

Table 4.1: Physical and Chemical Properties of the Soil within the Remediation Grid Measured in the Laboratory from core samples taken during the final sampling on November 4, 2002

4.3 Organic Matter Content

Soil organic matter consists of a wide range of organic substances such as living organisms, remains of organisms and compounds produced as organisms undergo decay (Brady and Weil, 1999). Organic matter in soil can increase the amount of water that a soil can hold, which can have ramifications on the fate of organic contaminants in the soil matrix. High organic matter content will generally result in increase adsorption of an organic contaminant onto the soil matrix.

The calculated values of organic matter content from the soil cores taken during the final sampling on November 4, 2003 are presented in Table 4.1. In contrast to both the bulk density and porosity values there is a detectable difference in organic matter between treatments. Within the surface soil of the control plots the percentage of organic matter ranges between 2.4 and 14.5%. Conversely, the percentage of organic matter ranges from 8% to 33% in the treatment plots. The control plots have an overall average organic matter content of 7.05%, the 10% application plots have an overall average organic matter content of 17.4% and the 20% application plots have an overall average organic matter content of 19.9% (See Table 4.2).

	Organic Matter Content (%) of the Control Plots	Organic Matter Content (%) of the 10% Application Plots	Organic Matter Content (%) of the 20% Application Plots
Average	7.05	17.4	19.9
Standard Deviation	4.3	8.5	6.3
Variation	18.5	72.9	39.8

Table 4.2: Descriptive Statistics of the Organic Matter Content in the Control, 10% and 20% Application Plots as determined by Loss on Ignition.

To determine if the organic matter content values of the control plots and application plots were statistically significantly different a two sample difference of means test was completed (McGrew and Monroe, 1993). The following equations were used to calculate the t value:

$$t = \frac{\overline{X}_1 - \overline{X}_2}{\sigma_{\overline{X}_1 - \overline{X}_2}}$$

$$\sigma_{\overline{X}_1 - \overline{X}_2} = \sqrt{s_1^2/n_1 + s_2^2/n_2}$$

where X_1 is the sample mean of the 10% or 20% plots, X_2 is the sample mean of the control plots, σ_{X1-X2} is the standard error of the difference of means, s_1^2 is the variance of either application plot sample set, s_2^2 is the variance of the control plot sample set, n_1 is the sample size of the application plot values and n_2 is the sample size of the control plot values. For both the application plots and the control plots, the sample size was 6. The degrees of freedom for the two sample difference of means test were calculated as follows:

$$df = n_1 + n_2 - 2$$

The difference between the means of the 10% plots and control plots had a t value of 2.65 and 10 degrees of freedom. The difference between the means of the 20% plots and the control plots had a t value of 4.12 and 10 degrees of freedom. Using the t distribution in McGrew and Monroe (1993), the organic matter content values of the application plots at the end of the remediation experiment were statistically significantly different than the values of the control plots (based on a 95% confidence interval).

The significant difference in organic matter content is primarily contained within the surface soils of the plots, as the values of organic matter content is relatively low with depth. However, there is a slight increase in organic matter content seen within the Ah horizon below the application plots. Therefore, it is clear that the application of cyclodextrin has resulted in an increased content of organic matter in the soil.

4.4 Moisture Content

Soil moisture content is a vital measurement when investigating the behavior of any colloidal matter within the soil matrix. An increase or decrease in the moisture content of a soil can intimately affect the adsorption or desorption of contaminants, biological activity, rates of degradation, redox potential, gas exchange, among others. Both water and DDT constituents are electronegative molecules and as such they compete for absorption sites on soil particles. DDT is weakly electronegative (Champion and Olsen, 1971), while water is a highly electronegative molecule making it the preferentially absorbed molecule under saturated conditions. As moisture content is directly related to the soil structure, the sandy soil within the study site is well drained and supports an aerobic environment. This aerobic environment provides a favorable condition for the persistence of DDT and its constituents.

In-situ moisture content (θ_{in}), revealed an interesting trend over the course of the experiment (See Table 4.3 and Figure 4.2). Throughout the remediation experiment there was a continual increase in the moisture content of the application plots. At the end of the remediation experiment there was double the amount of water retained by the 10%

plots and almost three times as much in the 20% plots relative to the control plots. In Figure 4.2 there is clearly a consistent variation seen in all three of the plots throughout the remediation experiment that is apparently from precipitation. However, there was no local precipitation data available to confirm these conclusions.

It should be noted that all measurements of *in-situ* volumetric moisture content with the TDR system were taken before the application of the next pore volume (33.3L) of cyclodextrin solution. Therefore a time period of at least one week elapsed between the application of cyclodextrin solution and the corresponding measurement of *in-situ* volumetric moisture content.

After the application of just one pore volume of cyclodextrin solution there was a slight increase in the θ_{in} of both the 10% and 20% plots. Two weeks after the application of the second pore volume (July 8, 2002) the average θ_{in} of the 10% and 20% application plots was approximately double that of the control plots. By July 22nd (Julian Day, 203), the fifth pore volume of cyclodextrin solution had been applied to the application plots one week prior and there was not only a difference between the control plots and the application plots, but also a noticeable difference between the two treatments. The average moisture content for the control plots was 11.8%, the average moisture content for the 10% application plots was 17.3%, and the average moisture content for the 20% application plots was 25.6%. On September 16th (Julian Day, 259), one week after the application of the thirteenth pore volume of cyclodextrin solution, the moisture content of the 10% plots was approximately 15% higher than the control sites and the moisture content of the 20% plots was approximately a further 12% greater.

Sampling Date	Julian Day	# of Pore Volume applied	20%-1 (Plot 1)	20%-2 (Plot 3)	20%-3 (Plot 4)	10%-1 (Plot 2)	10%-2 (Plot 6)	10%-3 (Plot 7)	Control-1 (Plot 5)	Control-2 (Plot 8)	Control-3 (Plot 9)
11-Jun-02	162	0	5.6	5.5	5.4	8.6	10.5	6.1	7.7	8.9	9.4
17-Jun-02	168	0	5.5	4.8	4.4	5.6	6.3	4.2	5.5	5.9	5.5
25-Jun-02	176	1	10.0	9.6	9.2	9.7	9.4	10.3	7.7	7.9	9.7
08-Jul-02	189	2	10.5	10.8	11.0	9.6	8.3	10.0	3.5	6.3	5.8
10-Jul-02	191	3	19.9	20.5	19.7	17.6	19.2	18.3	11.9	13.2	15.9
15-Jul-02	196	4	11.9	11.7	15.2	10.8	8.3	11.5	4.8	6.5	4.8
22-Jul-02	203	5	21.1	23.2	32.6	16.1	16.2	19.8	10.7	12.4	12.4
30-Jul-02	211	6	25.5	28.3	34.0	18.4	18.1	20.1	12.6	13.8	15.2
06-Aug-02	218	7	21.5	22.2	28.2	13.5	13.5	15.2	5.2	6.1	5.9
12-Aug-02	224	8	23.7	23.6	27.6	14.2	15.2	17.8	3.5	4.1	3.8
19-Aug-02	231	9	30.7	29.5	37.6	19.5	17.1	21.2	11.5	11.4	10.0
26-Aug-02	238	10	30.3	25.4	33.5	17.3	19.4	18.7	7.3	7.2	6.5
03-Sep-02	246	11	25.7	25.5	27.1	14.5	20.2	17.6	4.7	3.9	3.7
09-Sep-02	252	12	26.8	27.6	24.7	14.6	21.3	19.0	4.1	4.1	2.8
16-Sep-02	259	13	33.1	29.0	31.4	17.4	19.8	20.6	4.8	4.2	4.2
23-Sep-02	266	*13/14	39.4	34.1	39.3	21.9	25.0	25.4	10.5	10.1	12.9
07-Oct-02	280	*13/15	36.9	27.2	33.8	20.5	19.8	23.3	11.4	11.1	11.4
21-Oct-02	294	*13/17	31.2	28.1	30.2	19.5	24.1	21.5	11.4	11.7	11.7
04-Nov-02	308	*13/19	34.7	29.6	29.6	22.7	23.7	21.6	11.2	12.4	12.9

Table 4.3: In-Situ Volumetric Moisture Content of the Remediation Grid measured with a TDR system, expressed as a Percentage of Moisture (* 20% Solution never received more than 13 pore volumes; Control received only precipitation)

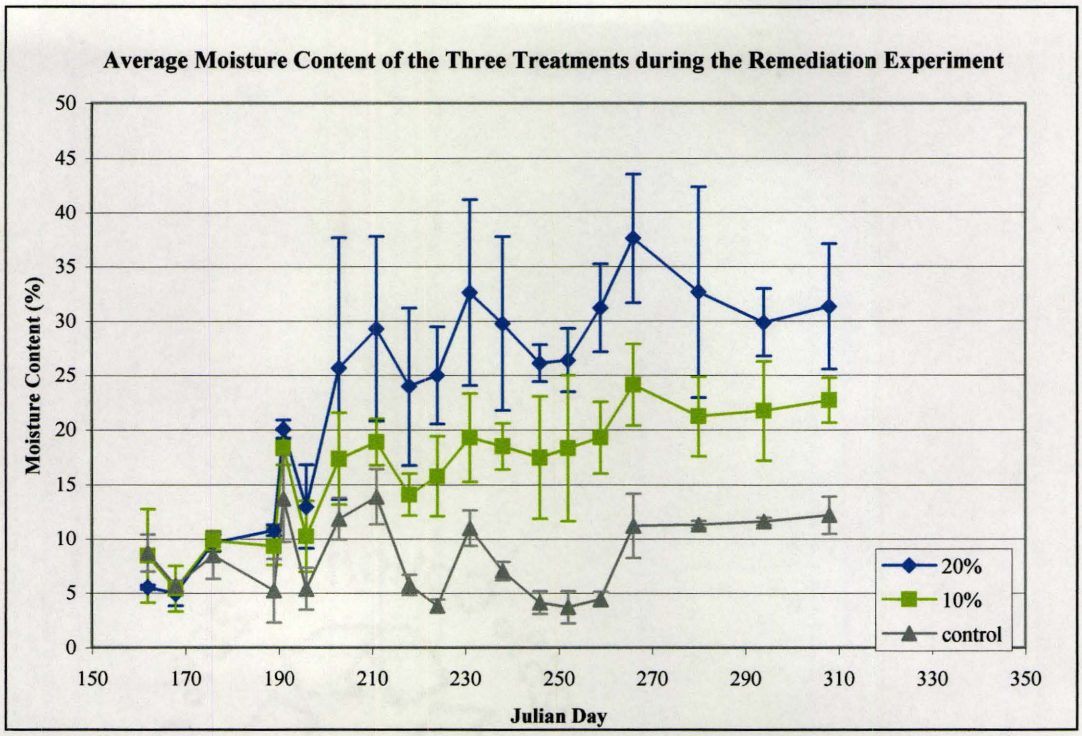

Figure 4.2: The Average *In-Situ* Moisture Content of the Treatments determined by TDR, throughout the Rememdiation Experiement

During the final sampling on November 4, 2002, two weeks after the final application of 10% cyclodextrin solution there was still an approximate 10% difference in θ_{in} between each of the treatments, despite the fact that the 20% solution had not been applied during the previous eight weeks. The average θ_{in} of the control plots was approximately 12%, the average θ_{in} for the 10% application plots was 23% and the 20% application plots had an average of 31% moisture. It is apparent that the plots treated with the cyclodextrin are retaining more moisture in their pores than the control plots. Within the plots receiving the 20% solution the increase in water retained is twice as much as the plots being treated with the 10% solution.

To further assess the data statistical analyses were performed to determine whether the initial *in-situ* moisture content between treatments and the late-time in-situ moisture content between treatments was statistically significantly different. The initial, undisturbed values of *in-situ* moisture content for each of the three treatments taken on both June 11 and June 17, 2003 (Table 4.3) were averaged to determine a mean initial moisture content value. The measured values of *in-situ* moisture content for each of the three treatments taken on October 21 and November 4, 2003 (Table 4.3) were summed and averaged to determine a late-time moisture content value. The values of initial and late-time average, standard deviation and variance are listed in Table 4.4 and Table 4.5 respectively.

	Initial *In-situ* Moisture Content of the 20% Plots (%)	Initial *In-Situ* Moisture Content of the 10% Plots (%)	Initial *In-Situ* Moisture Content of the Control Plots (%)
Average	5.2	6.9	7.15
Standard Deviation	0.5	2.3	1.8
Variance	0.2	5.2	3.1

Table 4.4: Descriptive Statistics of the Initial, Undisturbed *In-Situ* Volumetric Moisture Content Measurements, measured with a TDR

	Late-Time *In-situ* Moisture Content of the 20% Plots (%)	Late-time *In-Situ* Moisture Content of the 10% Plots (%)	Late-time *In-Situ* Moisture Content of the Control Plots (%)
Average	30.6	22.2	11.9
Standard Deviation	2.3	1.7	0.6
Variance	5.1	2.8	0.4

Table 4.5: Descriptive Statistics of the Late-Time *In-Situ* Volumetric Moisture Content Measurements, measured with a TDR

To determine if these values were statistically significantly different a two sample difference of means test was completed (McGrew and Monroe, 1993). The following equations were used to calculate the t value:

$$t = \frac{\overline{X}_1 - \overline{X}_2}{\sigma_{\overline{X}_1 - \overline{X}_2}}$$

$$\sigma_{\overline{X}_1 - \overline{X}_2} = \sqrt{s_1^2/n_1 + s_2^2/n_2}$$

where X_1 is the initial sample mean, X_2 is the late-time sample mean, $\sigma_{X1 - X2}$ is the standard error of the difference of means, s_1^2 is the variance of the initial sample set, s_2^2 is the variance of the late-time sample set, n_1 is the sample size of the initial values and n_2 is the sample size of the late-time values. The degrees of freedom for the two sample difference of means test were calculated as follows:

$$df = n_1 + n_2 - 2$$

A comparison was completed between the 20% and 10% application plots, the 20% and control plots and between the 10% and control plots, with both initial and late-time data. Once the t value was calculated the t distribution in McGrew and Monroe (1993) was used to determine if the *in-situ* moisture contents were statistically significantly different (based on a 95% confidence interval). Table 4.6 and 4.7 illustrate the results of the statistically testing, with "S" signifying a statistically significant difference between the pairs and a "NS" signifying that the pair is not statistically significantly different.

	Initial *in-situ* moisture content in the 20% plots	**Initial *in-situ* moisture content in the 10% plots**	**Initial *in-situ* moisture content in the control plots**
Initial *in-situ* moisture content in the 20% plots	/	NS	S
Initial *in-situ* moisture content in the 10% plots	NS	/	NS
Initial *in-situ* moisture content in the control plots	S	NS	/

Table 4.6: Two Sample Difference of Means Results of the Initial, Undisturbed *In-situ* Moisture Content of Each Treatment (Note: at the 95% confidence level).

	Late-Time *in-situ* moisture content in the 20% plots	**Late-Time *in-situ* moisture content in the 10% plots**	**Late-Time *in-situ* moisture content in the control plots**
Late-Time *in-situ* moisture content in the 20% plots	/	S	S
Late-Time *in-situ* moisture content in the 10% plots	S	/	S
Late-Time *in-situ* moisture content in the control plots	S	S	/

Table 4.7: Two Sample Difference of Means Results of the Late-Time *In-situ* Moisture Content of Each Treatment (Note: at the 95% confidence level).

The statistical analyses show that the initial moisture contents are not statistically significantly different from one other with the exception of the 20% plots versus the control plots. Initially there was a statistical difference between the moisture contents of the 20% and control plots, however in this case it is the control plots that have larger moisture contents. In the late-time data, the moisture contents of all three treatments are statistically significantly different. With the late-time data, it is the application plots (20% and 10% treatments) that have larger moisture contents than the control plots.

The differences in moisture content between treatments that are observed with the *in-situ* TDR measurements are clearly present in the core measurements of volumetric water content (θ_v) (See Table 4.1). The θ_v of the 10% and 20% application plots are not very different as is seen with the *in-situ* moisture content, but the large difference seen between the application plots and the control plots is similar. Overall, the θ_v values are slightly higher than the *in-situ* measurements. The difference between measurements is to be expected though as the TDR system is an *in-situ* measurement. The TDR measurement determines the average moisture content over a length of 20cm within the vicinity of the probe. The core method is an isolated sample that encompasses a total sample volume of $60cm^3$. Therefore, local variations are averaged with the TDR measurement, unlike with the core method.

During the final sampling on November 4, 2002, θ_{in} was taken along the soil profile to determine whether the variation in moisture content was confined to the surface soil, or whether it had had an effect at depth as well. The increase in θ_{in} seen in the

surface soil of the treatment plots was detected at lower depths below the application plots (See Figure 4.3). The difference in soil moisture content between the three treatments is inversely proportional to the depth below the surface. At a depth of 80cm there is no appreciable difference between the θ_{in} of the three profiles.

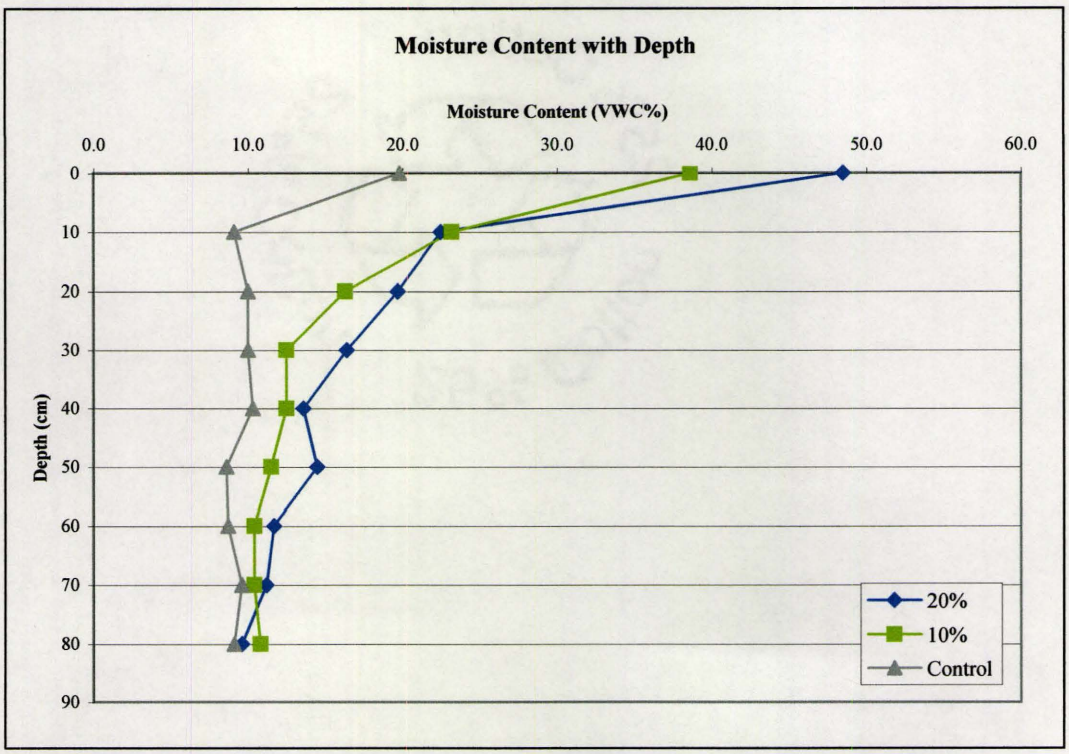

Figure 4.3: Moisture Content with Depth below the Treatments, measured by TDR, on November 4, 2002 (Note: surface reading was determined gravimetrically with a soil core).

It is intuitively obvious that there will be a change in moisture content since each application plot was receiving an additional input of 33.3L for each pore volume, i.e. in addition to the natural precipitation. As mentioned above, however, all the *in-situ* volumetric moisture content measurements were taken at least one week after the application of one pore volume (33.3L) of cyclodextrin solution. At the time of the final sampling, the 20% plots had not received an application of cyclodextrin solution for two months and the 10% plots had received their last application two weeks prior. In the sandy soil that is typical of this area, there is a high rate of drainage and hydraulic conductivity measurements are typically on the order of 10^{-3} cm/s (Marenco, 2002). With these properties it is expected that a significant amount of drainage would have taken place resulting in comparable moisture contents between treatments. The change in retention could be due to a number of factors including, a change in hydraulic conductivity, pore clogging with the cyclodextrin compound or bio-clogging due to an increase in biological activity. These possibilities will be explored further in later sections.

4.5 Infiltration of Cyclodextrin Solution

The rate at which water enters the soil to fill pores and move through the soil is the rate of infiltration. The rate at which water will percolate into the soil will be dependent on several factors such as, structure, porosity and the hydraulic conductivity. Indirectly, the rate of infiltration will play a role in the amount of organic contaminants that persist within a soil matrix. If there is a high rate of infiltration, any water

percolating into the system will quickly be drained. With respect to DDT, this particular scenario results in an aerobic environment in which DDT persists and is eventually degraded preferentially to DDE which is also quite persistent.

The initial application of one pore volume of cyclodextrin (HPCD) was completed in approximately two hours without causing surface ponding. By the application of the sixth pore volume, five weeks later, the time required for the 33.3L of 20% solution to infiltrate had risen to three hours. Despite the increase in required application time, there was also an increase in the amount of ponding. The infiltration time of the 20% solution increased further after each pore volume was applied. During the application of the thirteenth pore volume it was apparent that the infiltration rate of the 20% application plots had been substantially altered. At this date the time required for the infiltration of one pore volume ranged between four and seven hours. In addition to this substantial increase in application time, there was also extensive ponding of the solution not only within the application plot, but also beyond the garden edging which separated each plot (See Figure 4.4). This extensive ponding indicates that the application rate of the cyclodextrin solution had exceeded the maximum infiltration rate without causing ponding. The increase in application time combined with this prevalent ponding prompted the termination of the application of the 20% solution. The increase in both application time and ponding observed in the 20% plots was not experienced within the 10% application plots at any time during the remediation experiment.

Figure 4.4: Excess Ponding of the 20% Cyclodextrin Solution beyond the Garden Edging Surrounding Plot 4:20%-3 during the Application of the Thirteenth Pore Volume

Due to the heterogeneous nature of field experiments there are numerous potential explanations for the observed change in infiltration. Two of the principal reasons postulated are a biotic decrease in pore space due to the development of "bio-films", or an abiotic physical clogging of the pores due to crystallization of the cyclodextrin within the soil matrix. The addition of cyclodextrin (HPCD), a sugary, starch acts as a food source and could potentially stimulate the growth of bacteria within the application plots. This increase in growth could in turn result in a decrease of pore space as bacteria begin to fill pores. This possibility is further explored in Section 4.8.

Cyclodextrin (HPCD), is a sugary solution and it was apparent that the solution was having some effect on the application plots. As the experiment progresses there was little plant growth within the application plots. In addition to this, there was also a noticeable hardening of the soil and grass with each successive application of cyclodextrin solution. The hydroxypropyl-β-cyclodextrin solution would also occasionally attract butterflies that would drink the solution resting on grass and soil (Figure 4.5). Further testing beyond this study would be required to determine whether the precipitation of the cyclodextrin (HPCD) solution within the soil matrix had an affect on the change in infiltration.

Figure 4.5: Butterflies Drinking Cyclodextrin Solution on September 4, 2002

4.6 Hydraulic Conductivity

The hydraulic conductivity, K, expresses the ability of a fluid to move through a porous media due to a given hydraulic gradient. Hydraulic conductivity is a constant of proportionality and is a function of both the soil media and the fluid flowing through it. The proportionality constant, K, is derived from the following components:

$$K = \frac{Cd^2 \rho g}{\mu}$$

where C is another constant of proportionality that is determined by the distribution of the grain sizes, the sphericity and roundness of the grains, and the nature of their packing, d is the average diameter of the grains, ρ is the fluid density, g is the gravitational constant ($9.8 m^2/s$), and μ is the fluid viscosity.

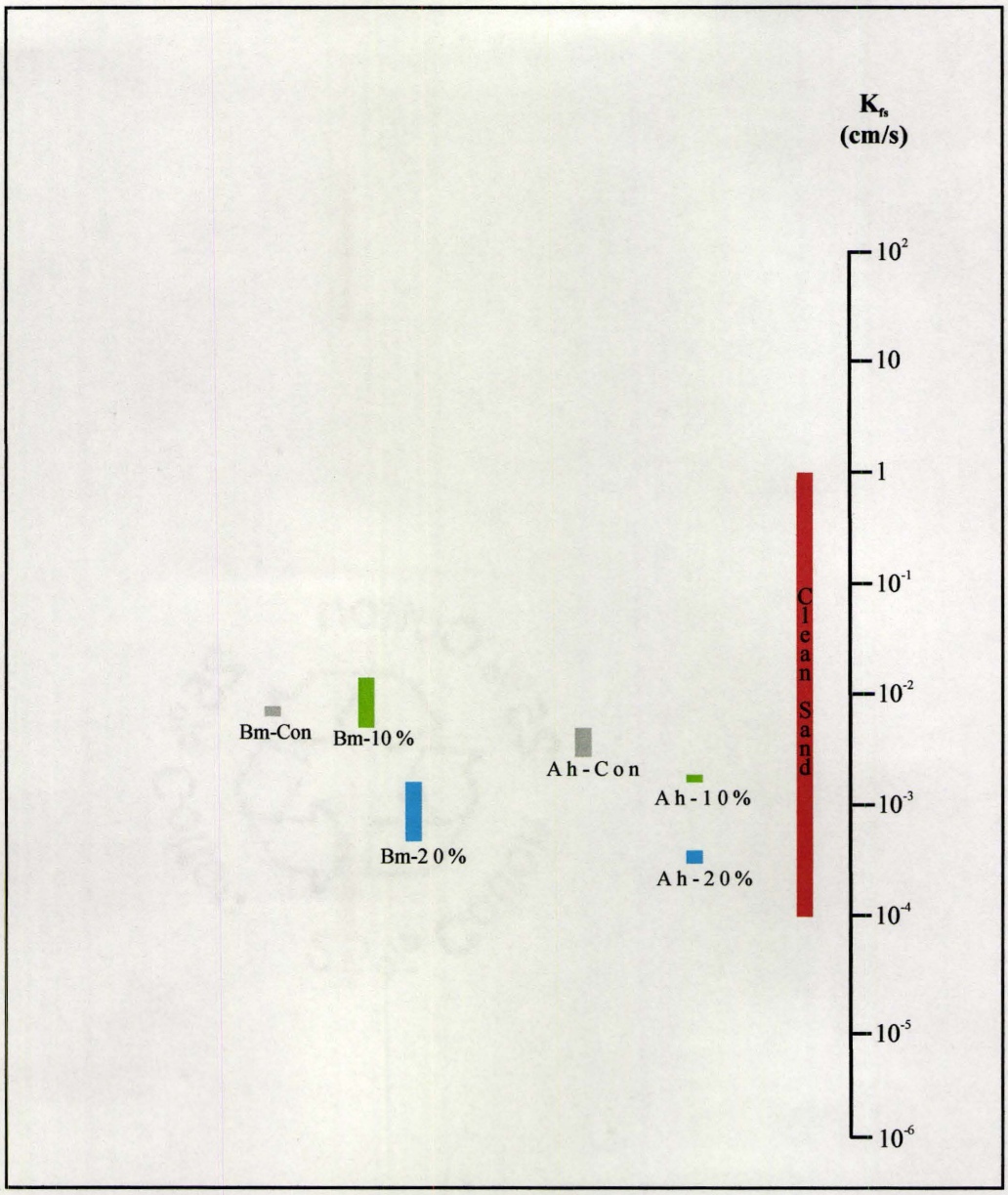

Figure 4.6: Range of Field Saturated Hydraulic Conductivity Values measured with a Guelph Permeameter (SOILMOISTURE Equipment Corporation, Santa Barbara, California), in the Ah and Bm Horizons (Note: log scale)

The increase in both moisture content and infiltration rate of the application plots throughout the remediation experiment indicated a change in the hydraulic properties of the soil. Measurement of field saturated hydraulic conductivity (K_{fs}) with the Guelph permeameter indicated that there was indeed a change in the hydraulic conductivity of the 20% application plots (See Figure 4.6). In the Ah horizon, the K_{fs} of the 20% application plots was one order of magnitude lower than the K_{fs} measured in all the 10% and control plots. At depth, in the Bm horizon, there is a smaller difference in the measure K_{fs}. The K_{fs} of the 10% and control plots ranged from 1.3×10^{-2}cm/s to 7.1×10^{-3}cm/s, while in the 20% plots, it ranged from 1.6×10^{-3}cm/s to 7.1×10^{-4}cm/s. Hydraulic conductivity generally tends to differ by several orders of magnitude even within similar soil types and structures. While the difference between the 20% application plots and the additional plots is only one order of magnitude, there has clearly been a shift in the values as a direct result of the remediation experiment.

This decrease in hydraulic conductivity is sufficient enough to account for the change in the observed infiltration rates. At the beginning of the remediation experiment, the amount of time required for application of one pore volume was calculated assuming a unit vertical gradient, using the lowest K_{fs} value (10^{-3}cm/s) and the average porosity value (0.46) determined by Marenco (2002) in the following calculations:

$$q = \frac{Q}{A}, \text{ rearranges to}$$

$$t = \frac{Vol}{(A)(q)}$$

$$t = \frac{0.0338m^3}{(0.49m^2)(10^{-5}m/s)}$$

$$t = 1.92hrs/PV$$

Therefore, originally, the information results in an estimated application time of approximately two hours for one pore volume. By simply decreasing the value of q by one order of magnitude to coincide with the decrease in K_{fs}, there is a corresponding increase in time by one order of magnitude. See the calculations below:

$$t = \frac{0.0338m^3}{(0.49m^2)(10^{-6}m/s)}$$

$$t = 19.2hrs/PV$$

This is consistent with the observation of substantially longer times required for the infiltration of the 33.3L applied and the observed increase in surface ponding. The application of the thirteenth pore volume of 20% cyclodextrin (HPCD) solution took between four and seven hours to complete and was accompanied with substantial ponding. The above calculations indicate that this application should have been completed in nineteen hours rather than four or seven hours in order to prevent the observed ponding.

4.7 Concentration of DDT and its Derivatives

Soil sample analysis for DDT and its derivatives revealed that both the para-para and ortho-para isomers were present. The individual concentrations of each isomer for all compounds and all samples can be found in Appendix A. Throughout the rest of this thesis only the total concentration, the sum of the two isomers, for each compound will be discussed and henceforth will be referred to as DDT, DDE or DDD. The total concentration of each compound was determined as follows:

$$Total\ DDx = o,p'\ DDx + p,p'\ DDx$$

where x refers to the suffix of the constituent of interest (T,E or D).

Within individual plots the concentrations of DDT, DDE and DDD differed greatly (See Figure 4.7 – 4.12), however the observed trends between treatments and between the different derivates were strikingly similar. The high variation in soil concentration prompted the averaging of all available unaltered values of DDT and its derivatives, including the soil concentrations measured by Marenco (2002), to calculate the initial values of all the plots and final sampling values of the control plots. These values were used and averaged, in order to determine the best representative undisturbed soil average value (See Table 4.8). This calculated undisturbed average concentration was also used in the determination of per cent remaining. Due to the prevalent variation in DDT, DDE and DDD soil concentrations, the change in concentration over the course of the remediation experiment will typically be discussed in terms of the average value (See Table 4.9, and 4.10) of the three plots for each treatment.

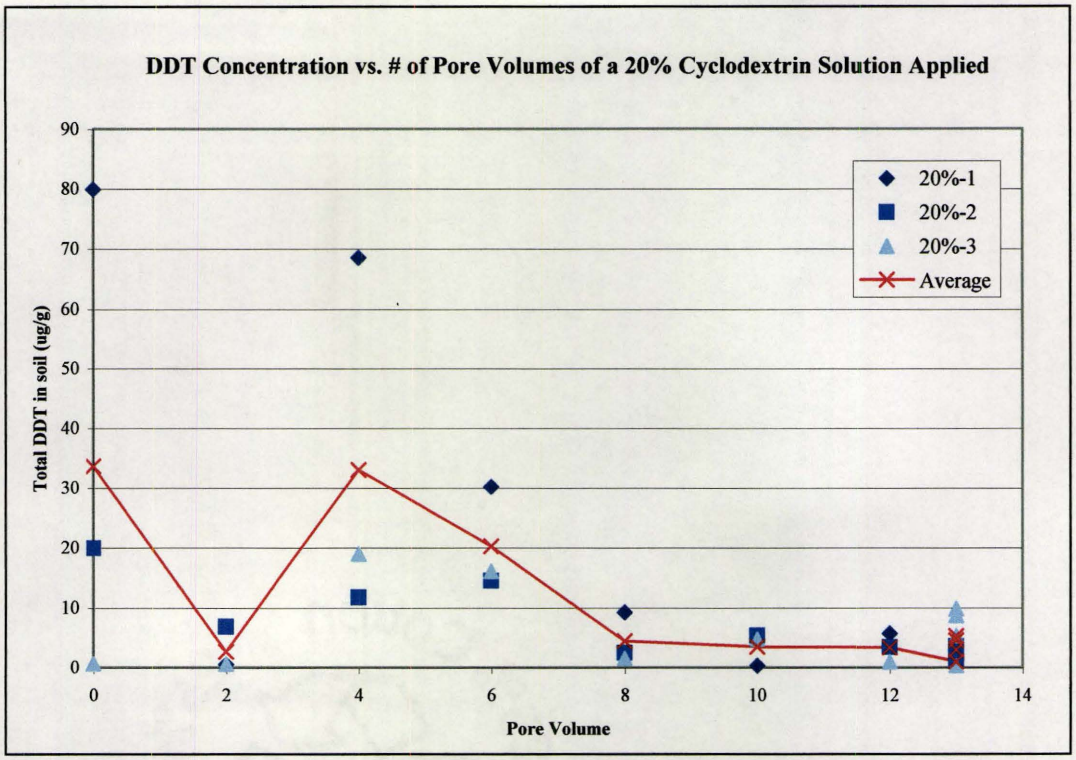

Figure 4.7: The Sample and Average DDT Concentration in Soil of the 20% Application Plots with respect to the number of Pore Volumes of Cyclodextrin Solution Applied.

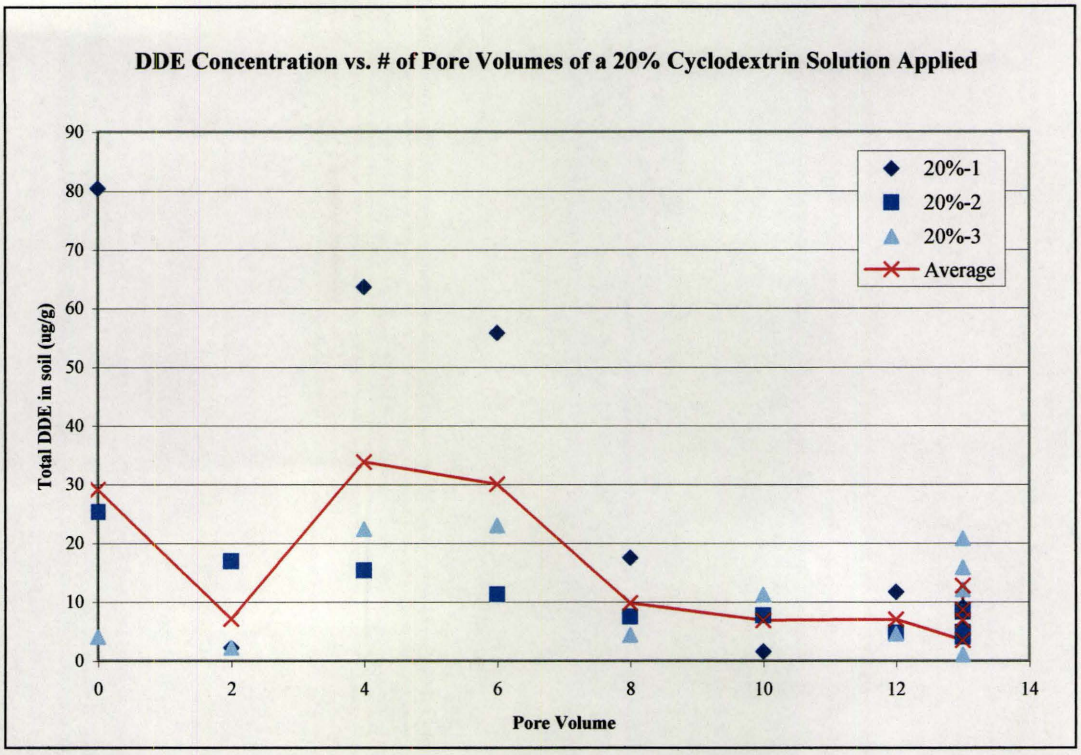

Figure 4.8: The Sample and Average DDE Concentration in Soil of the 20% Application Plots with respect to the number of Pore Volumes of Cyclodextrin Solution Applied

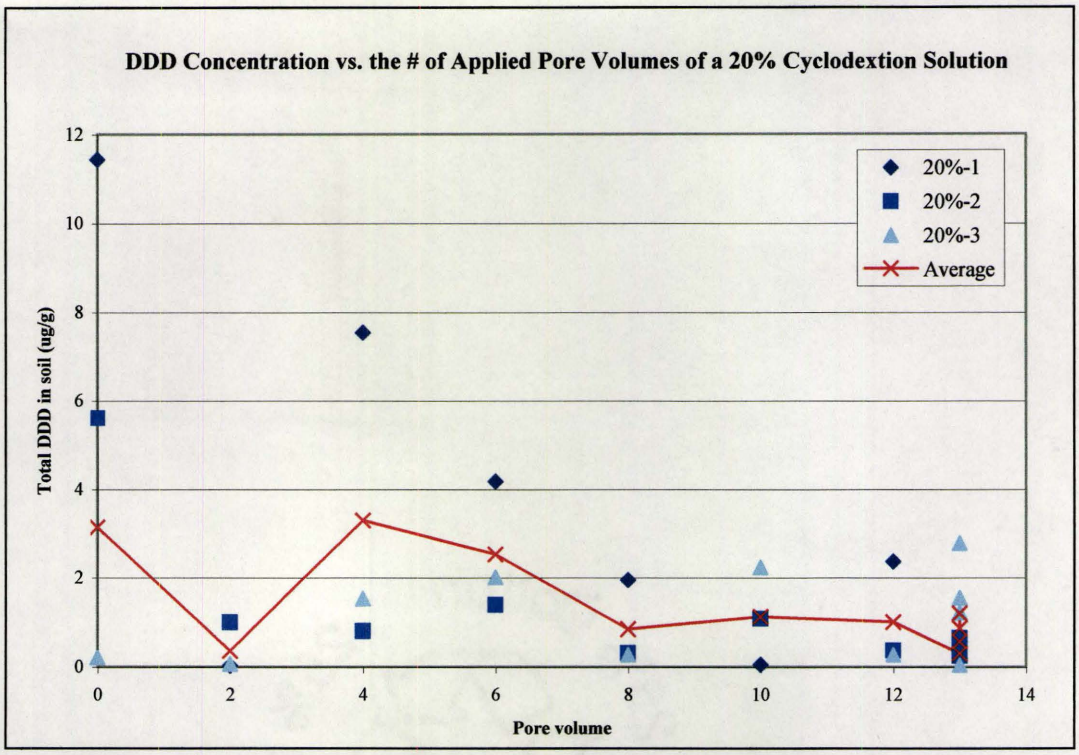

Figure 4.9: The Sample and Average DDD Concentration in Soil of the 20% Application Plots with respect to the number of Pore Volumes of Cyclodextrin Solution Applied

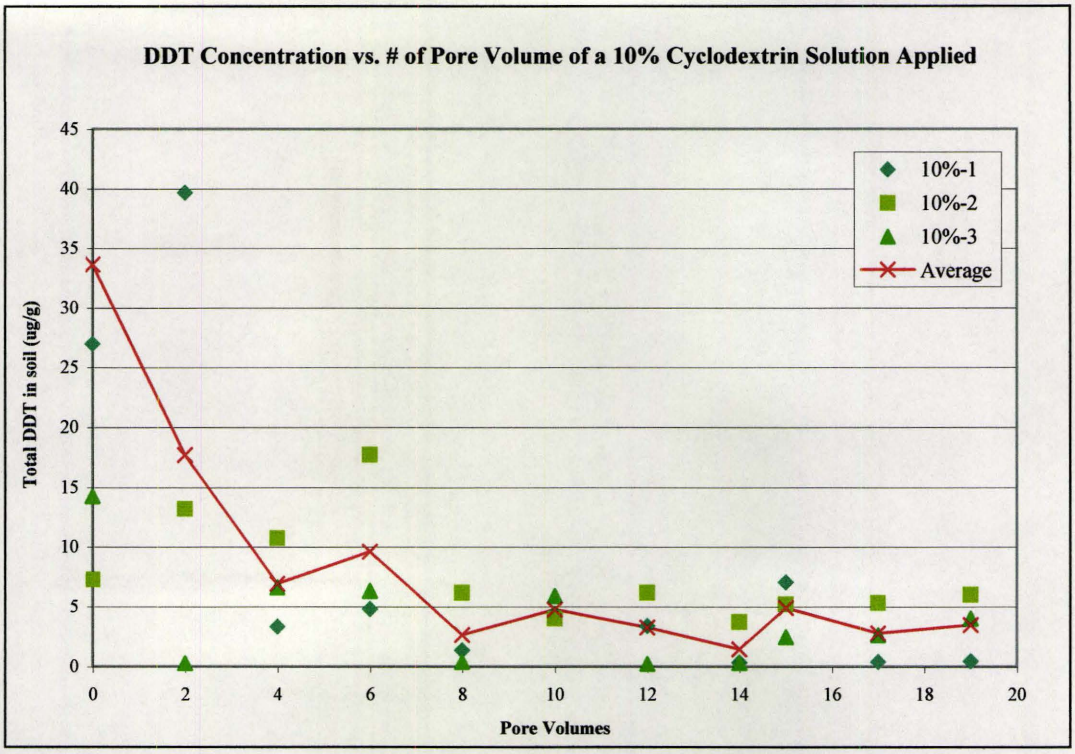

Figure 4.10: The Sample and Average DDT Concentration in Soil of the 10% Application Plots with respect to the number of Pore Volumes of Cyclodextrin Solution Applied

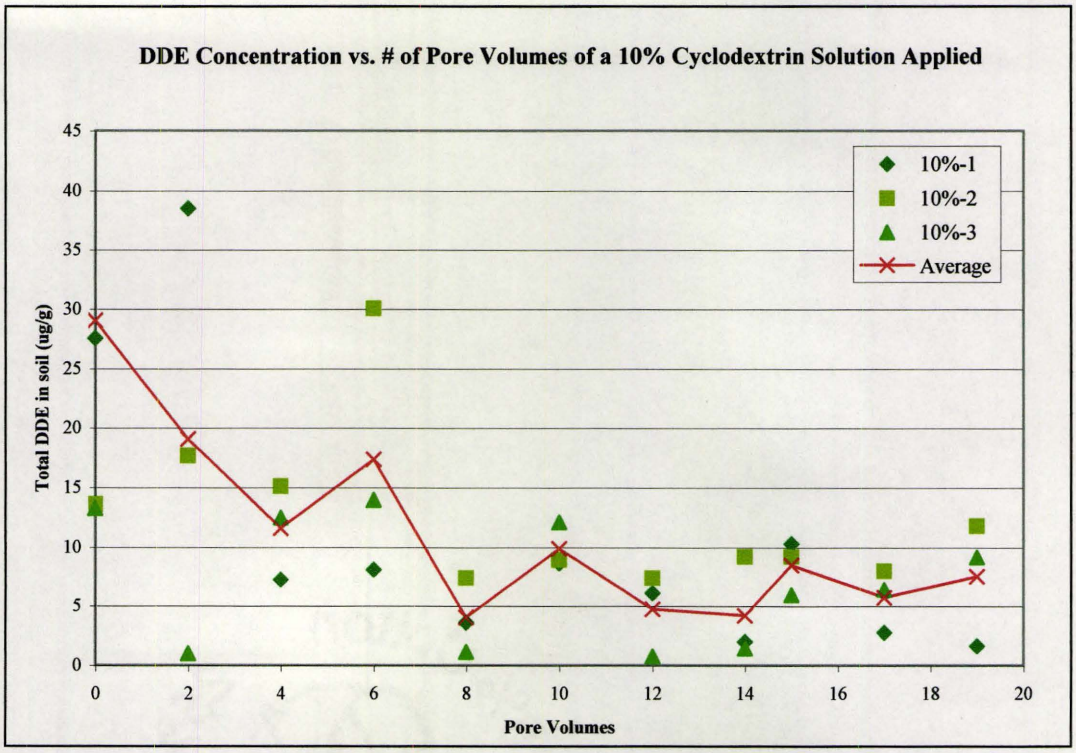

Figure 4.11: The Sample and Average DDE Concentration in Soil of the 10% Application Plots with respect to the number of Pore Volumes of Cyclodextrin Solution Applied

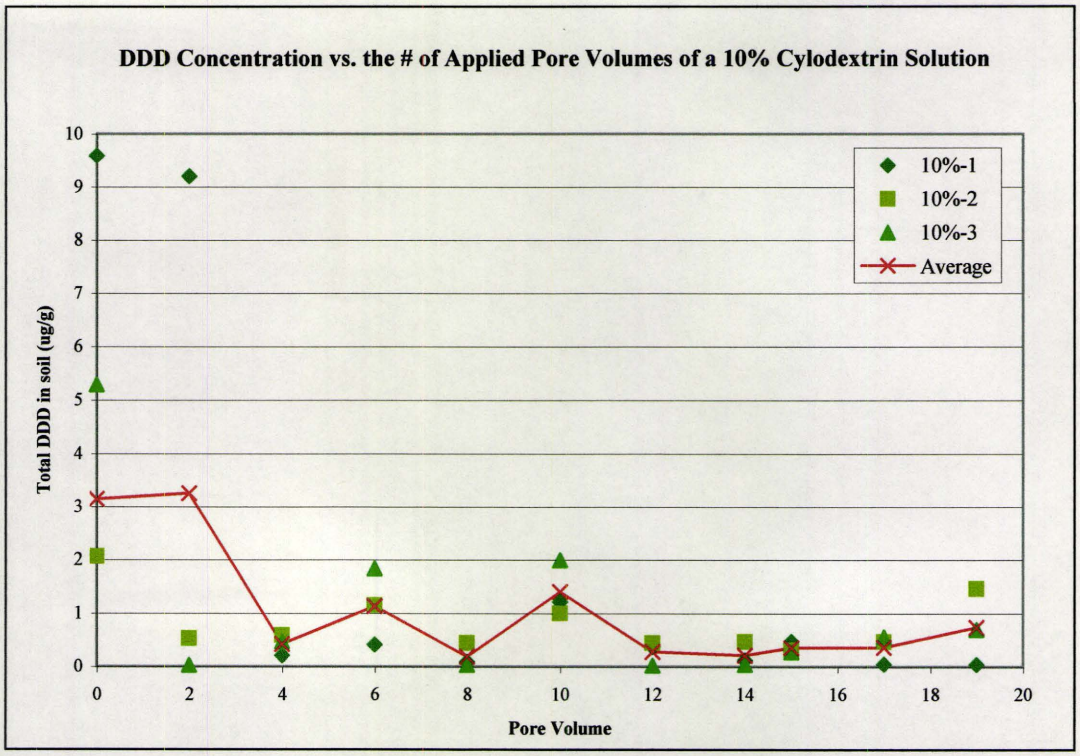

Figure 4.12: The Sample and Average DDD Concentration in Soil of the 10% Application Plots with respect to the number of Pore Volumes of Cyclodextrin Solution Applied

Sample Name	DDT (µg/g)	DDE (µg/g)	DDD (µg/g)
20%-1	79.9	80.4	11.4
10%-2	27.0	27.5	9.59
20%-2	19.9	25.2	5.60
20%-3	0.637	4.03	0.208
10%-2	7.25	13.6	2.06
10%-3	14.3	13.3	5.29
Control-1 (initial)	10.8	21.5	3.95
Control-1(final)	165	16.2	4.93
Control-2 (initial)	0.185	2.43	0.022
Control-2 (final)	2.03	3.45	0.189
Control-3 (initial)	15.0	31.3	3.22
Control-3 (final)	11.7	12.1	2.23
S-1	67.6	56.2	0.991
S-2	43.7	58.3	2.84
S-3	5.05	9.76	0.252
S-4	18.6	30.1	0.500
S-5	24.3	14.0	0.820
S-6	57.4	37.2	4.00
S-7	2.40	6.16	0.084
S-8	154	152	10.4
S-9	8.90	16.1	0.350
S-10	4.09	8.04	0.106
Average	**33.6**	**29.0**	**3.14**
Variance*	**2155**	**1146**	**12**
95% Confidence Interval	**33.6 ± 19.4**	**29.04 ± 14.1**	**3.14 ± 1.47**
Coefficient of Variation	**138%**	**117%**	**100%**

Table 4.8: The Calculated Average Undisturbed Concentration of DDT, DDE and DDD; used as Initial Values for Average DDT, DDE, DDD Concentrations and for the Calculation of Percentage of DDT, DDE, DDD Remaining in Soil (Note: units of variance are $(\mu g/g)^2$)

Sampling Date	# of pore volumes previously applied	DDT (µg/g)	DDE (µg/g)	DDD (µg/g)	DDX (µg/g)
11-Jun-02	0	33.6	29.0	3.14	65.8
08-Jul-02	2	2.66	7.12	0.36	10.1
15-Jul-02	4	33.1	33.8	3.30	70.2
30-Jul-02	6	20.2	30.0	2.52	52.8
12-Aug-02	8	4.42	9.77	0.84	15.0
26-Aug-02	10	3.49	6.83	1.12	11.4
09-Sep-02	12	3.36	7.00	1.01	11.4
24-Sep-02	13	1.00	3.51	0.30	4.81
08-Oct-02	13	4.58	8.64	1.20	14.4
22-Oct-02	13	5.28	12.7	0.87	18.9
04-Nov-02	13	3.01	6.93	0.57	10.5
Average late-time concentration	$pv \geq 10$	3.45	7.61	0.84	11.9

Table 4.9: Average Concentration of DDT, DDE and DDD within the Soil of the 20% Application Plots

Sampling Date	# of pore volumes previously applied	DDT (µg/g)	DDE (µg/g)	DDD (µg/g)	DDX (µg/g)
11-Jun-02	0	33.6	29.0	3.14	65.8
08-Jul-02	2	17.7	19.0	3.25	40.0
15-Jul-02	4	6.89	11.6	0.42	18.9
30-Jul-02	6	9.61	17.4	1.13	28.1
12-Aug-02	8	2.63	4.03	0.19	6.85
26-Aug-02	10	4.77	9.89	1.40	16.1
09-Sep-02	12	3.25	4.74	0.28	8.27
24-Sep-02	14	1.45	4.20	0.21	5.86
08-Oct-02	15	4.90	8.49	0.36	13.7
22-Oct-02	17	2.78	5.73	0.36	8.87
04-Nov-02	19	3.48	7.54	0.73	11.7
Average late-time concentration	$pv \geq 10$	3.44	6.77	0.56	10.8

Table 4.10: Average Concentration of DDT, DDE and DDD within the Soil of the 10% Application Plots

4.7.1 Variance in Concentration of DDT, DDE and DDD

Marenco (2002), identified that there was a high degree of inter and intra-variation in DDT, DDE and DDD within the investigated study sites. The study site in Marenco (2002), in the former orchard area encompassed a total area of 400 m^2 within which the differences were seen in samples over a distance on the order of meters. In this remediation experiment, the entire study site encompassed an area of only $9m^2$, yet a similar degree of variation reported by Marenco (2002), was observed within this small area (See Tables 4.11 thru 4.13). The variance between the initial DDT, DDE and DDD concentrations that were averaged (Table 4.8) illustrates this high degree of variance with values of 2155, 1146 and 12$(\mu g/g)^2$ respectively.

It was postulated that the observed variation was a function of the organic matter content of the soil. Soil samples collected for the analyses of DDT, DDE and DDD concentration were split before submission. The remaining soil that was not submitted for analyses was stored in the refrigerator and in April 2003 they were used for the analyses of organic matter content as outlined in Section 3.11. It should be noted that the samples that were analyzed for organic matter content had been collected at least five months prior and in some cases there was very little sample remaining. The results of the loss on ignition analyses to determine % organic matter are detailed in Appendix E. The concentrations of DDT for each sampling were then converted to a value that was a function of the amount of organic matter present in the sample. Graphs were then plotted of the DDT concentrations as a function of the organic matter versus Julian Day

(Appendix F). There was no apparent change in the degree of variation of DDT concentration.

During the initial phase of set-up, soil samples within the 20% plots had DDT concentrations that ranged from 0.2μg/g to 80μg/g with a variance of approximately 1700$(\mu g/g)^2$, regardless of the fact that these plots are less than 0.5m apart. Variations of this magnitude were also observed within an individual plot that had an area of 0.49m^2. For example, the DDT concentration in Plot 1:20%-1 ranged from 80μg/g to 0.5μg/g and back to 68ug/g by the third sampling when four pore volumes of a 20% cyclodextrin (HPCD) solution had been applied. While this is the most extreme case observed, it illustrates the high degree of variability of the DDT concentration present in the soil at this scale. The variation between the concentrations of DDE is also quite high in the 20% plots with an initial value of 1556$(\mu g/g)^2$. The variance in DDD concentration is much lower compared to that of DDT and DDE with an initial value of 31$(\mu g/g)^2$ in the 20% plots.

Overall, the initial variance in the 10% plots is much lower than is observed in the 20% plots. During the 2nd sampling, however, the variance increases noticeably to 404, 353 and 26$(\mu g/g)^2$ for DDT, DDE and DDD respectively.

As the remediation experiment progressed, one of the noticeable trends is a substantial decrease in variation after ten pore volumes of cyclodextrin (HPCD) solution had been applied. After the application of ten pore volumes, the variance in DDT concentration of the 10% plots was consistently below 10$(\mu g/g)^2$, as was the variance in the 20% plots with the exception of one sampling set. DDE and DDD concentrations

also experienced a decrease in the variance between plots as the remediation experiment progressed. It is interesting to note that at the end of the remediation experiment in both treatments, the DDE concentration has the largest variance. This is in contrast to the initial condition when the DDT concentrations had the largest initial variation. The variance between the DDD concentrations is the smallest of all the constituents with a value of approximately $0.5(\mu g/g)^2$ by the end of the experiment.

To further assess the data statistical analyses were performed to determine whether the initial variance of DDT, DDE and DDD concentration is statistically different than the late-time variance of DDT, DDE and DDD concentration in the 20% and 10% plots. The average and variance values of the initial, undisturbed concentrations are given in Table 4.8. The late-time averages of DDT, DDE and DDD concentrations for both the 20% and 10% application plots are given in Table 4.9 and 4.10. The late-time concentrations of DDT, DDE and DDD in the 20% application plots had variance values of 7.5, 26.1 and 0.72 respectively. In the 10% application plots the late-time concentrations of DDT, DDE and DDD had variance values of 5.33, 13.3 and 0.29 respectively. An analysis of variance or ANOVA F test was performed to compare the initial, undisturbed sample set to the late-time sample set from the 20% and 10% application plots for DDT, DDE and DDD concentration. The equations and calculations of the ANOVA F test can be found in Appendix I. For DDT, DDE and DDD concentration the F test generated a value greater than 1, indicating that the different samples are from separate and distinct populations and that the between-group variance is significantly larger than the within-group variance.

One of the possible causes of the high degree of variation and local "hot spots" seen in Marenco (2002), was the historic use of "DDT toss bombs," where DDT was wrapped in cheesecloth and literally tossed into the orchard. Although this application method could explain a few local "hot spots" that were scattered among an area of $400m^2$, it fails to satisfactorily explain the degree of variability and the presence of such differing concentrations within such a small area, i.e. on the order of tens of centimeters. It can be postulated that in order to see such a degree of variation on the tens of centimeters scale, it would more likely be due to microscale effects that may be occurring within the soil matrix. It may be due to a local difference of hydraulic properties such that water has percolated down preferential areas and exhibited differing retention of water in specific areas. These microscale differences ultimately reduce concentrations in certain areas while other areas receiving much less water, retained more DDT.

A competing postulation is that areas with a higher concentration were more effectively leached. The degree of sorption of organic contaminants onto sediment is generally a function of the fraction of organic carbon as well as the concentration of the solute. Likewise, it can be postulated that desorption of contaminants from the soil matrix will be a function of concentration. Therefore, areas of higher concentration will experience preferentially removal of a contaminant over areas of lower concentration. Further research is needed to provide definitive reasoning for the high degree of observed variance.

Sampling Date	# of Pore Volumes previously applied	Variance of DDT Concentration between plots $(\mu g/g)^2$	Variance of DDE Concentration between plots $(\mu g/g)^2$	Variance of DDD Concentration between plots $(\mu g/g)^2$
11-Jun-02	0	1709	1556	31.6
08-Jul-02	2	13.1	72.1	0.30
15-Jul-02	4	957	682	13.7
30-Jul-02	6	75.3	534	2.15
12-Aug-02	8	17.7	47.2	0.92
26-Aug-02	10	7.53	23.8	1.18
09-Sep-02	12	5.72	16.6	1.40
24-Sep-02	13	0.36	5.09	0.07
08-Oct-02	13	21.0	39.0	1.91
22-Oct-02	13	8.69	49.2	0.35
04-Nov-02	13	4.17	19.9	0.31

Table 4.11: Variance between the DDT, DDE and DDE Concentrations in Soil of the 20% Application Plots during the Remediation Experiment

Sampling Date	# of Pore Volumes previously applied	Variance of DDT Concentration between plots $(\mu g/g)^2$	Variance of DDE Concentration between plots $(\mu g/g)^2$	Variance of DDD Concentration between plots $(\mu g/g)^2$
11-Jun-02	0	100.	66.4	14.2
08-Jul-02	2	404	353	26.6
15-Jul-02	4	13.7	16.0	0.04
30-Jul-02	6	50.0	129	0.51
12-Aug-02	8	9.53	9.91	0.05
26-Aug-02	10	0.96	3.72	0.27
09-Sep-02	12	8.86	12.4	0.05
24-Sep-02	14	3.86	18.8	0.05
08-Oct-02	15	5.32	5.13	0.01
22-Oct-02	17	5.99	7.19	0.07
04-Nov-02	19	7.85	27.9	0.51

Table 4.12: Variance between the DDT, DDE and DDE Concentrations in Soil of the 10% Application Plots during the Remediation Experiment

Sampling Date	# of Pore Volumes previously applied	Variance of DDT Concentration between plots $(\mu g/g)^2$	Variance of DDE Concentration between plots $(\mu g/g)^2$	Variance of DDD Concentration between plots $(\mu g/g)^2$
11-Jun-02	0	58.5	216	4.36
04-Nov-02	0	8398	42.6	5.64

Table 4.13: Variance between the DDT, DDE and DDE Concentrations in Soil of the Control Plots during Initial and Final Sampling

4.7.2 Change in Average Concentration of DDT, DDE and DDD

The average concentration of DDT, DDE and DDD within soil behaves remarkably similarly in both treatments. After the application of approximately ten pore volumes a tailing effect is observed in which the average concentration of DDT, DDE and DDD does not decline significantly (See Figures 4.7 thru 4.12). In order to better quantify the change in concentration of DDT, DDE and DDD an average late-time concentration after the application of ten pore volumes (August 26, 2002 to November 4, 2002) was calculated for the eighteen measured soil concentrations. See Table 4.9 and 4.10.

The initial DDT concentration of 33.64μg/g was reduced to 3.4μg/g in both treatments, after the application of approximately ten pore volumes. The 20% plots had an average tailing concentration of 3.45μg/g and the 10% plots had an average late-time concentration of 3.44μg/g. Therefore there was a measured decrease of approximately 30μg/g in the average DDT concentration in soil as a direct result of the application of the cyclodextrin (HPCD) solutions. This represents a decrease of approximately 90% for both treatments from the initial DDT concentration.

Although the initial average concentration of DDE within the soil was lower than that of DDT, i.e. 29.04μg/g, it also begins to plateau within both treatments after the application of approximately ten pore volumes. The average late-time concentration of DDE was 7.61μg/g for the 20% plots and 6.77μg/g for the 10% plots. This is a 73% decrease in the DDE concentration of the 20% plots and a 77% decrease in the DDE concentration of the 10% plots.

A similar trend was observed in the measurements of DDD concentration. The initial value of 3.14μg/g, decreased to values that were consistently below 1.4μg/g for the remainder of the experiment. The application plots had an average late-time DDD concentration of 0.84μg/g within the 20% plots and 0.56μg/g within the 10% plots. This represents an overall decrease of approximately 2.3μg/g or a decrease of 73% for the 20% plots and 82% for the 10% plots.

To further assess the data statistical analyses were performed to determine whether the initial concentrations of DDT, DDE and DDD are statistically significantly different than the late-time concentrations of DDT, DDE and DDD. The initial, undisturbed concentrations of DDT, DDE and DDD and their descriptive statistics are listed in Table 4.4. Soil samples which had received an application of ten pore volumes or greater were denoted as a late time concentration of DDT, DDE and DDD for both the 20% and 10% application plots. Descriptive statistics of the late-time concentrations of DDT, DDE and DDD for the two treatments are listed in Table 4.14 and 4.15. It is interesting to note the change in the coefficient of variation (CV) in the late-time data as compared to the undisturbed values (Table 4.8). The coefficient of variation is a relative measure of dispersion of a sample set. There is a noticeable decrease in the CV for DDT and DDE, but little to no decrease in the CV of the late-time concentration of DDD. The degree of variation has therefore decreased in the late-time data as compared to the initial, undisturbed values.

	DDT (µg/g)	DDE (µg/g)	DDD (µg/g)
Average	3.45	7.61	0.843
Standard Deviation	2.74	5.11	0.849
Variance*	7.50	26.1	0.720
Coefficient of Variation	79%	67%	101%

Table 4.14: Descriptive Statistics of the Late-Time Concentrations of DDT, DDE and DDD for the 20% Application Plots (* Note variance is in units of $(\mu g/g)^2$)

	DDT (µg/g)	DDE (µg/g)	DDD (µg/g)
Average	3.44	6.77	0.557
Standard Deviation	2.31	3.64	0.543
Variance*	5.33	13.3	0.295
Coefficient of Variation	67%	54%	97%

Table 4.15: Descriptive Statistics of the Late-Time Concentrations of DDT, DDE and DDD for the 10% Application Plots (* Note variance is in units of $(\mu g/g)^2$)

To determine if these values were statistically significantly different a two sample difference of means test was completed (McGrew and Monroe, 1993). The following equations were used to calculate the t value:

$$t = \frac{\overline{X}_1 - \overline{X}_2}{\sigma_{\overline{X}_1 - \overline{X}_2}}$$

$$\sigma_{\overline{X}_1 - \overline{X}_2} = \sqrt{s_1^2/n_1 + s_2^2/n_2}$$

where X_1 is the initial sample mean, X_2 is the final sample mean, σ_{X1-X2} is the standard error of the difference of means, s_1^2 is the variance of the initial sample set, s_2^2 is the variance of the final sample set, n_1 is the sample size of the initial values and n_2 is the sample size of the final values. The degrees of freedom for the two sample difference of means test were calculated as follows:

$$df = n_1 + n_2 - 2$$

The two sample difference of means tests indicated that there are statistically significant differences between the initial and late-time concentrations for all the constituents within both treatments (Table 4.12 and 4.13).

	Initial DDT	Initial DDE	Initial DDD
Late-time DDT	S	/	/
Late-time DDE	/	S	/
Late-time DDD	/	/	S

Table 4.16: Two Sample Difference of Means Results of the Initial and Late-Time Concentrations of DDT, DDE and DDD for the 20% Application Plots (Note: at the 95% confidence level)

	Initial DDT	Initial DDE	Initial DDD
Late-time DDT	S	/	/
Late-time DDE	/	S	/
Late-time DDD	/	/	S

Table 4.17: Two Sample Difference of Means Results of the Initial and Late-Time Concentrations of DDT, DDE and DDD for the 10% Application Plots (Note: at the 95% confidence level)

As discussed above the average late-time concentration of both DDT and DDE have been substantially reduced with the application of a hydroxypropyl-β-cyclodextrin solution. However, both the DDT and DDE concentrations are still above the regulatory limits of 1.6μg/g for Soil Quality of Recreational/Parkland Use in a Potable Groundwater Water Situation set by the Ontario Ministry of the Environment and Energy (Table 4.14). In contrast, the average DDD concentration was consistently below 1.4μg/g by the end of the experiment which is below guidelines for acceptable concentrations in soil.

	OMOEE (1997)[1]	CEQG (2002)[2]
DDT	1.6μg/g	0.70μg/g
DDE	1.6μg/g	---
DDD	2.2μg/g	---

Note: 1. Soil quality for Recreations/Parkland Land-Use in a potable groundwater situation set by the Ontario Ministry of the Environment and Energy
2. Canadian Environmental Quality Guideline for Recreational/Parkland Land-Use set by Environment Canada

Table 4.18: Provincial and Federal Soil Quality Guidelines for DDT in a Recreational/Parkland Land-Use Scenario

Based on the results of Schepanow (2002), it was anticipated that desorption of the DDT, DDE and DDD from the soil matrix with a cyclodextrin (HPCD) solution would follow the kinetics of a first order reaction and illustrate an exponential decay. The negligible change in concentration of these contaminants in the soil after the application of ten pore volumes indicates that there was a significant tailing effect. This tailing effect is exhibited by the non-linearity of logarithmic plots that a first order decay would exhibit. McCray and Brusseau (1998) found that hydroxypropyl-β-cyclodextrin

also exhibited a tailing effect in a field study despite previous laboratory work (Wang and Brusseau, 1993; Brusseau et al., 1994) that indicated a lack of retardation. They postulated that the observed tailing in the field was most likely due to hydraulic or porous media heterogeneity.

4.7.3 Percentage of DDT, DDE and DDD Remaining in Soil

Column-flushing experiments of Schepanow (2002), demonstrated that twenty pore volumes of a 20% hydroxypropyl-β-cyclodextrin solution could potentially achieve 80% mass removal of the initial DDT, DDE and DDD concentrations within a controlled environment. Conversely, Schepanow (2002) observed that twenty pore volumes of a 10% hydroxypropyl-β-solution removed 50% of the initial mass of DDT, DDE and DDD in the column. The column experiments were performed in the laboratory under controlled homogeneous conditions. With field experiments there is limited control over external conditions and the soil is relatively heterogeneous even in seemingly homogenous systems.

As is to be expected there were some unforeseen differences in the extent of mass removal of DDT, DDE and DDD from this system (Table 4.19 and 4.20) as compared to that observed by Schepanow (2002). As previously discussed, there was no appreciable additional change in the average concentration after the application of approximately ten pore volumes despite some small variations. The primary difference seen in the field experiment is the difference in removal efficiency of the individual constituents. Schepanow (2002) observed an insignificant difference in the amount of removal of

DDT, DDE and DDD, while there was a clear difference exhibited in this field experiment.

The 20% cyclodextrin (HPCD) solution removed approximately 90%, 73% and 73% of the mass of DDT, DDE and DDD respectively, initially present in the soil. The 10% cyclodextrin (HPCD) solution removed approximately 90%, 77% and 82% of the initial mass of DDT, DDE and DDD respectively, that was present in the soil. The results observed by Schepanow (2002) showed an increased removal of DDT, DDE and DDD with a 20% cyclodextrin (HPCD) solution compared to the removal by a 10% cyclodextrin (HPCD) solution. In this field study, however, the 10% cyclodextrin (HPCD) solution removed the same percentage of DDT as achieved with the application of a 20% solution. In terms of DDE and DDD concentration, the 10% solution removed a larger percentage of mass than was achieved by a 20% solution. There were six additional pore volumes of 10% cyclodextrin (HPCD) solution applied after the termination of the 20% cyclodextrin (HPCD) solution treatment. Despite this, there was still significantly less mass of cyclodextrin applied to the 10% plots. This will be explored further in Section 4.7.7.

Sampling Date	# of pore volumes previously applied	%DDT remaining	%DDE remaining	%DDD remaining
11-Jun-02	0	100	100	100
08-Jul-02	2	7.90	24.51	11.60
15-Jul-02	4	98.26	116.43	104.94
30-Jul-02	6	60.16	103.34	80.37
12-Aug-02	8	13.13	33.65	26.83
26-Aug-02	10	10.38	23.53	35.66
09-Sep-02	12	9.99	24.11	32.01
24-Sep-02	13	2.96	12.08	9.58
08-Oct-02	13	13.61	29.76	38.08
22-Oct-02	13	15.68	43.81	27.63
04-Nov-02	13	8.95	23.87	18.18
Average late-time concentration	$pv \geq 10$	10.25	26.20	26.75

Table 4.19: Average Concentration of %DDT, %DDE and %DDD Remaining within the Soil of the 20% Application Plots

Sampling Date	# of pore volumes previously applied	%DDT remaining	%DDE remaining	%DDD remaining
11-Jun-02	0	100	100	100
08-Jul-02	2	52.64	65.62	103.55
15-Jul-02	4	20.47	40.01	13.44
30-Jul-02	6	28.57	59.83	36.07
12-Aug-02	8	7.83	13.89	5.95
26-Aug-02	10	14.18	34.07	44.71
09-Sep-02	12	9.66	16.33	8.87
24-Sep-02	14	4.32	14.47	6.63
08-Oct-02	15	14.55	29.25	11.34
22-Oct-02	17	8.25	19.73	11.41
04-Nov-02	19	10.34	25.98	23.39
Average late-time concentration	$pv \geq 10$	10.22	23.31	17.83

Table 4.20: Average Concentration of %DDT, %DDE and %DDD Remaining within the Soil of the 10% Application Plots

4.7.4 Preferential Removal of DDT, DDE and DDD

In certain soil microenvironments, DDT can exhibit preferential degradation towards a particular daughter product. Marenco (2002) and Crowe et al. (2002) identified that at Point Pelee National Park, within soils in the vicinity of the marsh there is an alternating anaerobic/aerobic environment. In these soils the degradation of DDT shows a preferential pathway towards the creation of DDD. In other areas where there is consistently an aerobic environment, such as at the site in this study, the degradation of DDT tends to produce DDE (Aislabie et al., 1997; Guenzi and Beard, 1968).

With the application of a hydroxypropyl-β-cyclodextrin solution there is a possibility that it could result in the preferential removal of DDT, DDE or DDD. There is also a possibility that the amount of liquid being added, or the cyclodextrin molecule itself could potentially change the local soil microenvironment, thereby changing the preferred degradation route. The latter hypothesis, however, is beyond the scope of this investigation and would require further exploration.

In order to determine if the cyclodextrin (HPCD) solution exhibited preferential removal, the percentage of each constituent was calculated with respect to the total mass of DDT and its derivatives. The term DDX was used to denote the total mass of all the derivatives and was calculated as follows:

$$DDX = DDT + DDE + DDD$$

The percentage of each constituent present was then determined using the average values:

$$\%DDT = \left(DDT/_{DDX}\right)\times 100,$$

$$\%DDE = \left(DDE/_{DDX}\right)\times 100,$$

$$\%DDD = \left(DDD/_{DDX}\right)\times 100$$

Figure 4.13 illustrates the relative proportion of each of these constituents. A change in the relative concentrations, an indicator of preferential removal, would be present as a shift in the values within the chart. Although there is some shift in the values along the %DDE axis, the shift along this axis is highly variable. There is no clear systematic trend. This is consistent with the variation seen in the values of DDT, DDE and DDD.

As previously discussed there was a lot of variation observed in the measured soil concentrations of DDT, DDE and DDD. In order to better quantify in the relative proportion of constituents, a second ternary diagram was generated (Figure 4.14). This second diagram contains the initial relative proportion of the DDT, DDE and DDD concentration and the relative proportions of the average late-time concentration (Table 4.9 and 4.10). Figure 4.14 clearly illustrates a shift in the average relative proportions of the constituents. There is a larger proportion of DDE present in soil after treatment with hydroxypropyl-β-cyclodextrin solution. There is a slight increase in the relative proportion of DDD in the late-time data. As discussed in Section 4.7.3, there was an overall decrease in the DDT, DDE and DDD concentration of 90%, 73% and 73%,

respectively with the application of a 20% cyclodextrin solution. The plots that received a 10% cyclodextrin (HPCD) solution had an overall decrease of 90%, 77% and 82% in the concentrations of DDT, DDE and DDD respectively. Figure 4.14 also exhibits that DDT is preferentially removed from soil relative to DDE and DDD with the application of hydroxypropyl-β-cyclodextrin. In addition DDD is slightly preferentially removed over DDE from soil with the application of a 10% cyclodextrin solution. The application of a 20% cyclodextrin (HPCD) solution has removed DDE and DDD in relative proportions.

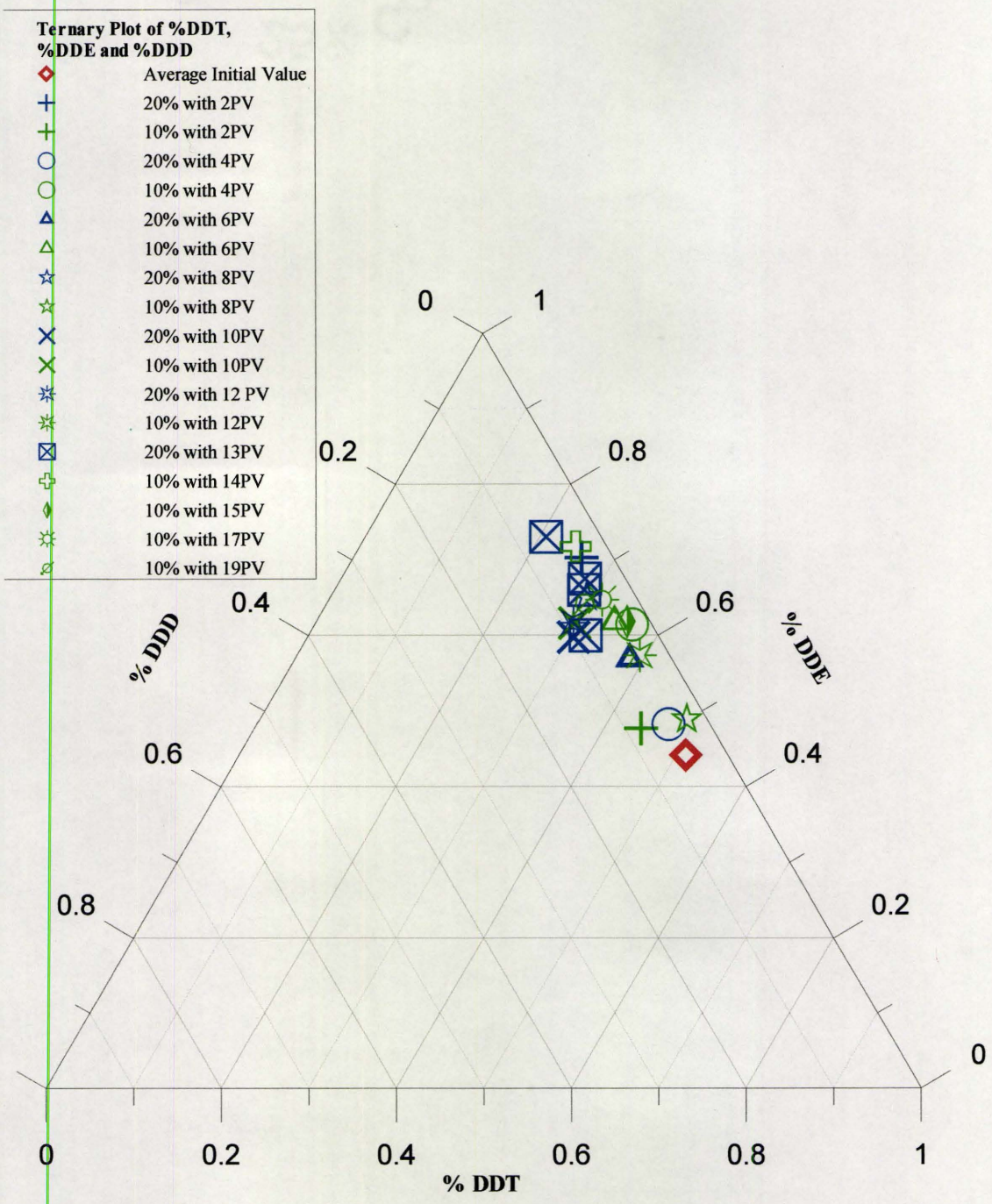

Figure 4.13: Ternary Graph Illustrating %DDT, %DDE and %DDD as a function of DDX throughout the Remediation Experiment

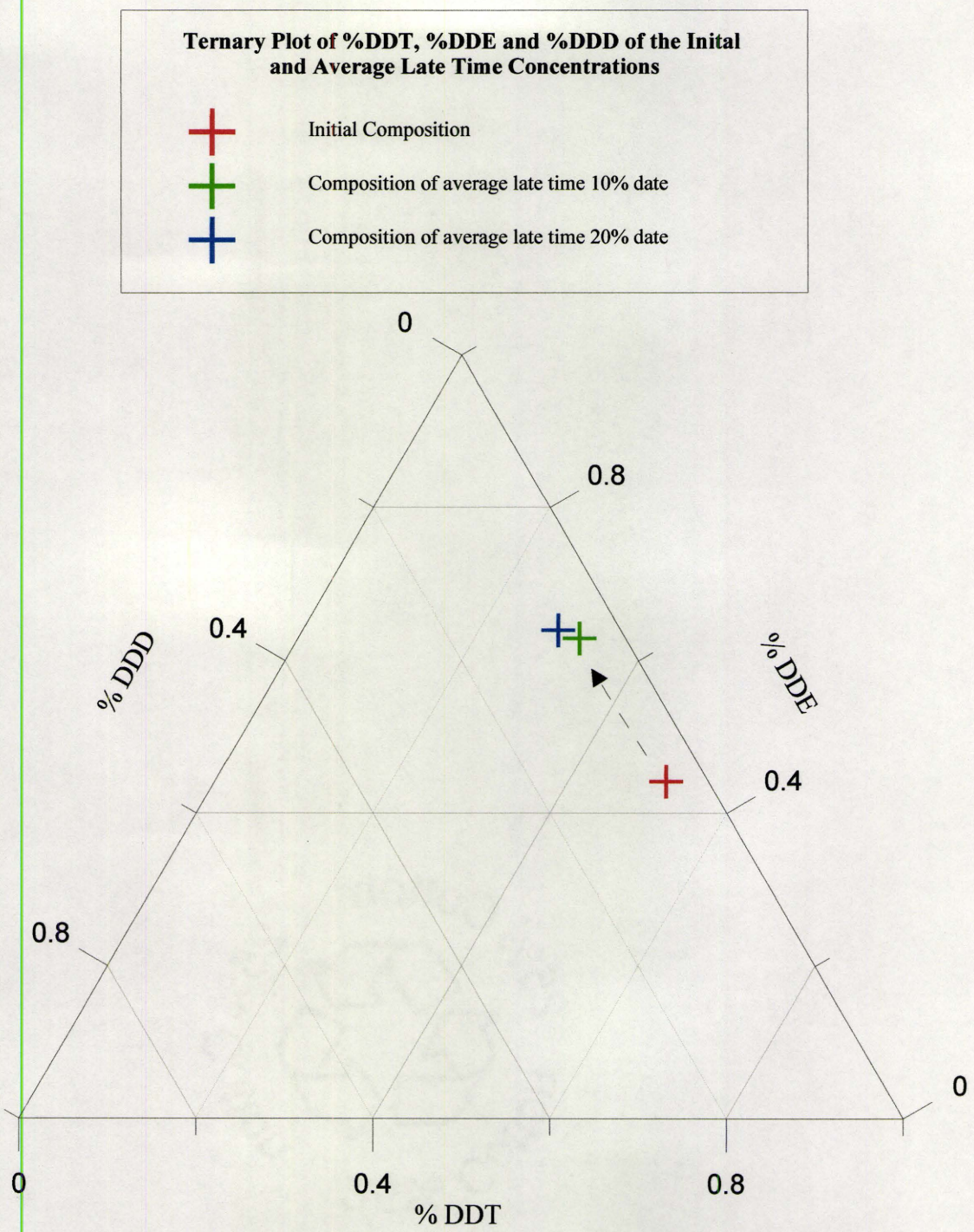

Figure 4.14: Ternary Graph Illustrating %DDT, %DDE and %DDD as a function of DDX for the Average Initial and Late Time Data (average value after the applicaiton of ten pore volumes)

4.7.5 Concentration of DDT and its Derivatives with Depth

In untreated soil at Point Pelee National Park, the soil concentration of DDT, DDE and DDD are relatively small at depth and generally fall below both provincial and federal guidelines (Marenco, 2002 and Crowe et al. 2002). In this study soil samples were collected during final sampling on November 4, 2002 at depths of 11cm and 35cm along the soil profile under Plot 3:20%-2, Plot 6:10%-2 and Plot 9:Control-3. These soil samples were analyzed for DDT, DDE and DDD concentration in order to determine if the decrease in concentration at the surface could be attributed to mobilization to depth.

Figures 4.15 thru 4.17 and Table 4.21 display the data from the soil samples at depth. The data indicates that there is downward mobilization of DDT, DDE and DDD within the soil profile. The increase in concentration of DDT, DDE and DDD under the treatment plots as compared to the soil beneath the control plots was calculated as follows (see Table 4.18):

$$\%Increase = \left(\frac{C_t - C_i}{C_i} \right) \times 100$$

where C_t is the concentration at time, t in µg/g, and C_i is the initial concentration, in µg/g.

There was a substantial increase in the concentration of DDT, DDE and DDD at depth below the application plots as compared to the concentration below the control plots. Although the difference in concentration (Table 4.21) may appear to be small, the percentage increase (Table 4.22) is substantial. The soil samples at depth below the 10% and 20% application plots for all constituents have increased by over 100%. At 11cm

below the surface, the increase in concentration has changed the DDE concentration to be slightly above ministry guidelines, while DDT and DDD are still below guidelines.

Treatment	Depth (cm)	DDT (µg/g)	DDE (µg/g)	DDD (µg/g)
20%	11	1.286	2.451	0.226
10%	11	1.075	2.052	0.139
Control	11	0.098	0.761	0.007
20%	35	0.213	0.206	0.017
10%	35	0.237	0.176	0.020
Control	35	0.005	0.017	0.0006

Table 4.21: Concentration of DDT, DDE and DDD at Depths of 11cm and 35cm (Sampled during final sampling on November 4, 2002)

Treatment	Depth (cm)	% Increase in DDT Concentration	% Increase in DDE Concentration	% Increase in DDD Concentration
20%	11	1212	222	3128
10%	11	997	170	1886
20%	35	4160	1112	2733
10%	35	4640	935	3233

Table 4.22: Increase in DDT, DDE and DDD Concentration at Depth for the application plots compared to the Control Plots; expressed as a percentage (Determined using the Concentration of DDT, DDE and DDD from soil samples taken on November 4, 2002)

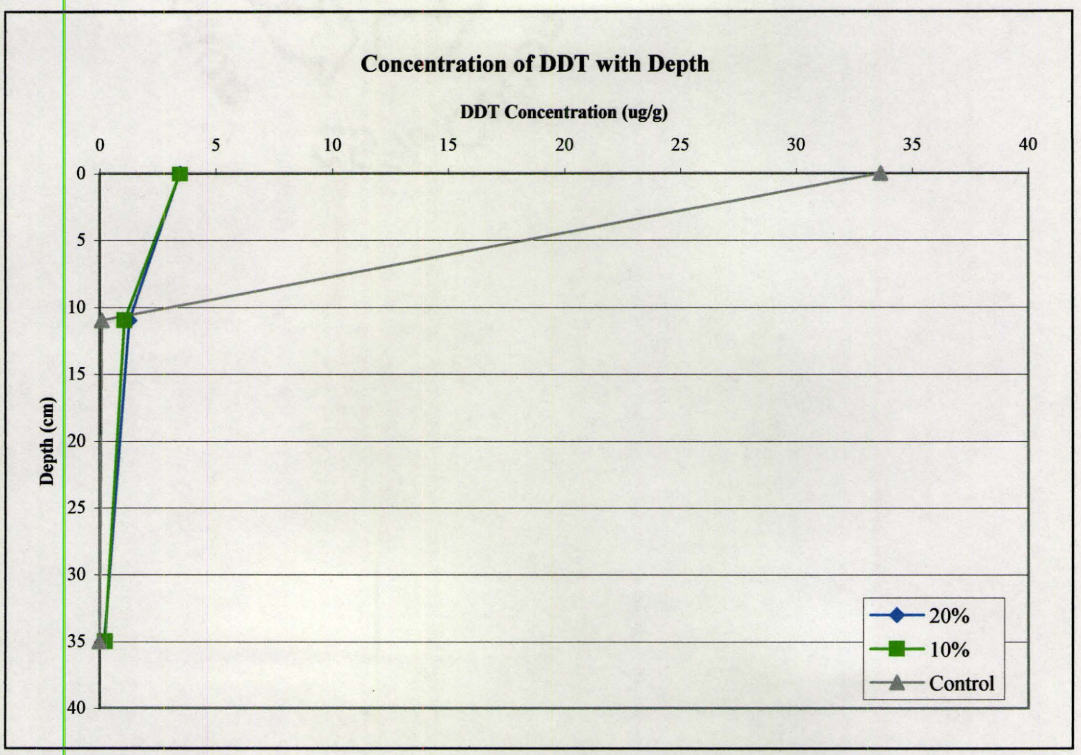

Figure 4.15: DDT Concentration with Depth in the Soil Profile from soil samples taken during the final sampling on November 4, 2002.

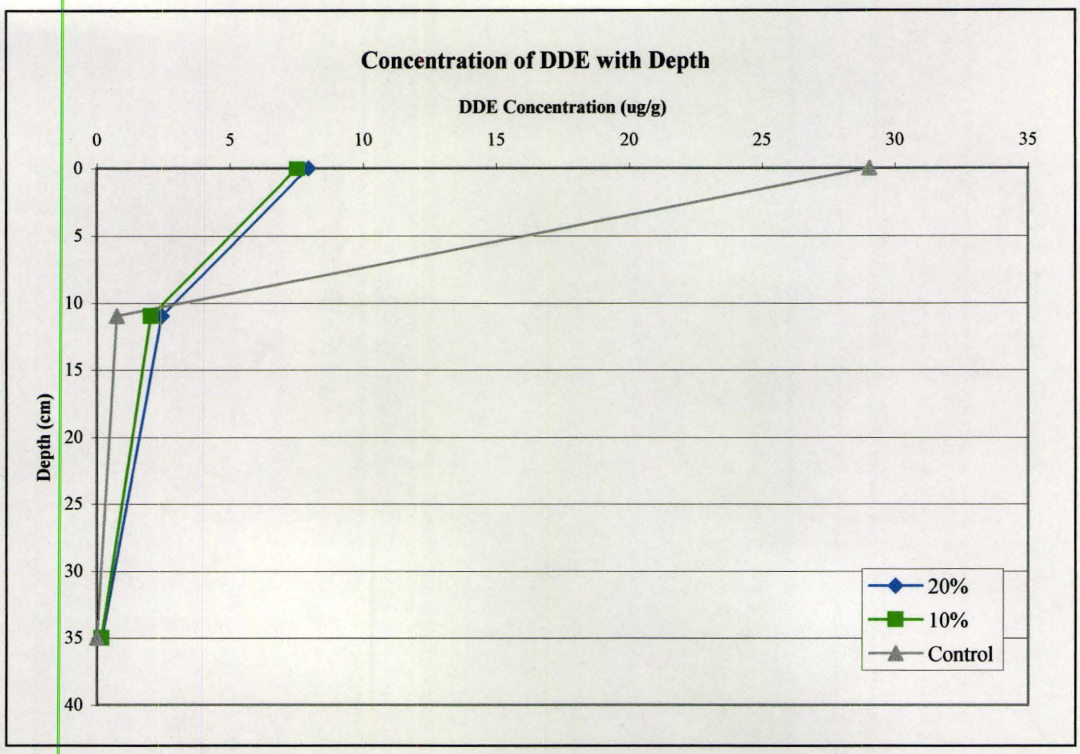

Figure 4.16: Total DDE Concentration with Depth in the Soil Profile from Soil Samples taken during the Final Sampling on November 4, 2002

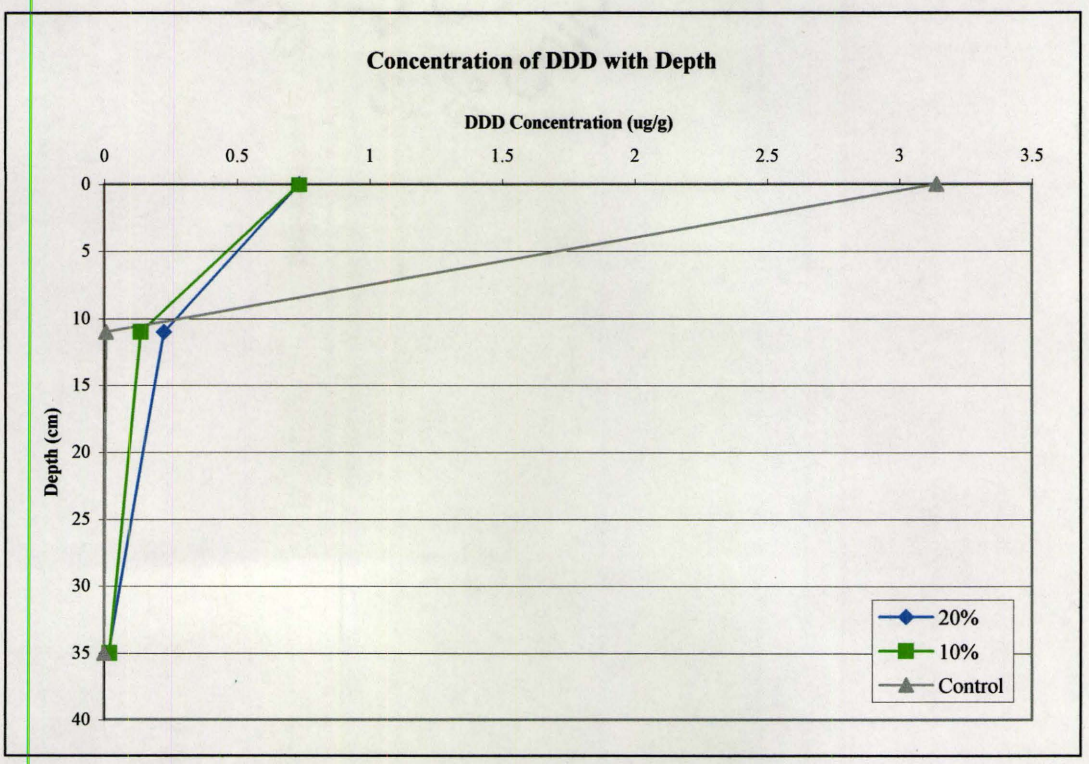

Figure 4.17: Total DDD Concentration with Depth in the Soil Profile from Soil Samples taken during the Final Sampling on November 4, 2002

To determine if the increase in DDT, DDE and DDD concentration at depth could account for the decrease in surface concentration, the estimated total mass of each constituent within the soil profile was calculated. The mass was calculated using the depth profiles and assuming a straight line between data points. The two point form of an equation for a line, given below, was used to derive equations that could be used for the calculation of contaminant concentration at a specified depth within the soil profile:

$$y - y_1 = \frac{y_2 - y_1}{x_2 - x_1}(x - x_1), \quad \text{for a line between } (x_1,y_1) \text{ and } (x_2,y_2)$$

Line equations were calculated for the points shown in Figures 4.15 thru 4.17. These equations were then used to determine the mass of contaminant at a specified depth using the following equation:

$$Mass = Height \times Area \times Bulk\ Density \times Concentration$$

where, the height was 1cm, the area was $1cm^2$ and the bulk density (g/cm^3) was the measured values (see Table 4.23). Complete derivations of slope and calculated concentration with depth can be found in Appendix G. The calculated mass for each constituent within each treatment is given in Tables 4.24 to 4.26.

Depth (cm)	Plot 3: 20%-2	Plot 6: 10%-2	Plot 9: Control-3
0-5	0.95	0.91	1.0
6-20	1.54	1.41	1.3
21-35	1.6	1.52	1.42

Table 4.23: Bulk Density Values (g/cm^3) for each Soil Profile at Different Depths

Depth (cm)	Mass of DDT (µg)	Mass of DDE (µg)	Mass of DDD (µg)
0	33.643	29.038	3.140
1	30.593	26.467	2.855
2	27.543	23.896	2.570
3	24.493	21.325	2.286
4	21.443	18.754	2.001
5	18.393	16.183	1.716
6	19.946	17.696	1.860
7	15.981	14.353	1.490
8	12.016	11.011	1.120
9	8.051	7.669	0.750
10	4.086	4.326	0.380
11	0.127	0.989	0.009
12	0.122	0.949	0.009
13	0.117	0.909	0.008
14	0.112	0.868	0.008
15	0.107	0.828	0.008
16	0.102	0.788	0.007
17	0.097	0.747	0.007
18	0.092	0.707	0.007
19	0.087	0.667	0.006
20	0.082	0.627	0.006
21	0.084	0.640	0.006
22	0.079	0.596	0.006
23	0.073	0.552	0.005
24	0.067	0.508	0.005
25	0.062	0.464	0.005
26	0.056	0.420	0.004
27	0.051	0.376	0.004
28	0.045	0.332	0.003
29	0.040	0.288	0.003
30	0.034	0.244	0.003
31	0.029	0.200	0.002
32	0.023	0.156	0.002
33	0.018	0.112	0.002
34	0.012	0.068	0.001
35	0.007	0.024	0.0008
Total	***217.918***	***203.782***	***20.296***

Table 4.24: Calculated Mass of DDT, DDE and DDD with Depth below Plot 9: Control-3 from Soil Samples taken during Final Sampling on November 4, 2003.

Depth (cm)	Mass of DDT (µg)	Mass of DDE (µg)	Mass of DDD (µg)
0	3.291	7.553	0.697
1	3.103	7.078	0.653
2	2.915	6.603	0.609
3	2.727	6.128	0.566
4	2.539	5.653	0.522
5	2.351	5.178	0.478
6	3.506	7.624	0.704
7	3.200	6.854	0.632
8	2.895	6.084	0.561
9	2.590	5.314	0.490
10	2.285	4.544	0.419
11	1.980	3.774	0.348
12	1.912	3.630	0.335
13	1.843	3.486	0.321
14	1.774	3.342	0.308
15	1.705	3.198	0.294
16	1.636	3.054	0.281
17	1.568	2.910	0.267
18	1.499	2.766	0.254
19	1.430	2.622	0.241
20	1.31	2.478	0.227
21	1.342	2.425	0.222
22	1.271	2.275	0.208
23	1.120	2.125	0.194
24	1.128	1.976	0.180
25	1.056	1.827	0.166
26	0.985	1.676	0.153
27	0.913	1.527	0.139
28	0.842	1.377	0.125
29	0.770	1.227	0.111
30	0.699	1.078	0.097
31	0.627	0.928	0.083
32	0.556	0.778	0.069
33	0.484	0.629	0.055
34	0.412	0.479	0.041
35	0.341	0.330	0.027
Total	*60.740*	*120.54*	*11.081*

Table 4.25: Calculated Mass of DDT, DDE and DDD with Depth below Plot 3: 20%-2 from Soil Samples taken during Final Sampling on November 4, 2003.

Depth (cm)	Mass of DDT (µg)	Mass of DDE (µg)	Mass of DDD (µg)
0	3.166	6.866	0.668
1	2.967	6.411	0.619
2	2.768	5.957	0.570
3	2.569	5.502	0.520
4	2.370	5.048	0.471
5	2.172	4.594	0.422
6	3.057	6.414	0.577
7	2.749	5.709	0.501
8	2.441	5.005	0.425
9	2.133	4.301	0.348
10	1.824	3.597	0.272
11	1.516	2.893	0.196
12	1.466	2.783	0.189
13	1.417	2.673	0.182
14	1.368	2.563	0.175
15	1.319	2.452	0.168
16	1.269	2.342	0.161
17	1.220	2.232	0.154
18	1.171	2.122	0.147
19	1.122	2.011	0.140
20	1.073	1.901	0.133
21	1.103	1.931	0.136
22	1.050	1.812	0.128
23	0.997	1.693	0.121
24	0.944	1.574	0.113
25	0.891	1.455	0.106
26	0.838	1.337	0.098
27	0.785	1.218	0.091
28	0.732	1.099	0.083
29	0.678	0.980	0.076
30	0.625	0.861	0.068
31	0.572	0.743	0.060
32	0.519	0.624	0.053
33	0.466	0.505	0.045
34	0.413	0.386	0.038
35	0.360	0.267	0.030
Total	***52.134***	***99.865***	***8.288***

Table 4.26: Calculated Mass of DDT, DDE and DDD with Depth below Plot 6: 10%-2 from Soil Samples taken during Final Sampling on November 4, 2003.

The total mass of DDT, DDE and DDD contained within the soil profile of the application plots is considerably less than the total mass contained in the profile of the control plot. With regard to mass of DDT, the application plots contain less than 30% of the total mass within the soil profile of the control plot. The total mass of DDE and DDD within the soil profile of the application plots is approximately 60% of the mass in the control plot. Therefore, while the decrease in concentration at the surface is partially accounted for by the vertical mobilization within the soil column, it is not the solitary mechanism occurring.

There are two possible explanations for the mass-loss from the soil profile: 1) actual transport to depth is greater than investigated, 2) Relatively rapid in-situ degradation caused by the presence of a readily available co-metabolite i.e. cyclodextrin. It is possible that the transport of DDT, DDE and DDD to depth was greater than was revealed in the analysis. The depth profile is based on only two different depths beneath one plot of each treatment. In addition, to maintain plot integrity the soil samples were taken on the edge of the plots. It has been shown that there is a high degree of variance in the soil samples analyzed for DDT, DDE and DDD. It is possible that the locations that were sampled underneath the application plots had a lower concentration than the surrounding soil. However, both the 10% plot and 20% plot had a similar concentration and the treatment substantially reduced sample variance within the surface soils. The groundwater beneath the treatment plots was not sampled during this study. Therefore, the possibility that the displaced DDT, DDE and DDD is in the groundwater has not been fully assessed.

A competing postulate is that the plots that were treated with the cyclodextrin solution experienced relatively rapid *in-situ* degradation due to the addition of an energy source. It has been shown in laboratory experiments that DDT can be substantially degraded within approximately 30 days with the addition of an energy source. Aislabie et al. (1997) observed a decrease in the concentration of DDT by approximately 50% using the ligninolytic fungi, *P. Chrysosporium*, and ^{14}C-labelled DDT. Similarly Katayama et al. (1993), observed a drop in the DDT concentration from 90ηg/mL to approximately 20ηg/mL in only 3 days using the soil bacteria *Bacillus* sp. B75. Finally, Guenzi and Beard (1968) observed a DDT concentration of 11μg in an anaerobic culture with an added energy source compared to a value of 80μg in a sterile culture. In this instance the DDT was transformed to DDD, however, it too is readily degraded. Therefore, it is probable that there was enhanced *in-situ* degradation of all the constituents with the addition of the cyclodextrin (HPCD) solution: an energy source for bacteria. However, quantification of that effect would require work beyond that conducted in this study.

4.7.6 Pore Volume Half-Life

Generally the degradation of DDT and its derivatives can be expressed as a first-order kinetic reaction. The natural half-life ($t_{1/2}$) can then be calculated as shown in the following two equations:

$$\frac{C_t}{C_o} = e^{-kt}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

where C_t is the concentration at time t, C_o is the concentration at time zero, k is the decay constant and t is amount of time between measurements. In addition, Schepanow (2002), observed a first-order kinetic relationship between the mass of cyclodextrin applied and desorption of the DDT, DDE and DDD molecules from the soil within laboratory columns. Despite the fact that in this study the observed tailing effect alters this system at late-times from a simple first-order kinetic reaction, the estimate of desorption pore volume half-life ($pv_{1/2}$) was calculated using the first-order equation (see equations below):

$$\frac{C_{pv}}{C_o} = e^{-kpv}$$

$$pv_{1/2} = \frac{\ln 2}{k}$$

where C_{pv} is the concentration after the application of pv number of pore volumes, C_o is the initial concentration before any pore volumes of solution were applied, k is the decay constant and pv is the number of pore volumes applied. The tailing-effect will cause the

calculated $pv_{1/2}$ to be larger than a simple first-order system. However, this approach provides a systematic comparison of the systems. The $pv_{1/2}$ was calculated by least-squares best fit of the equation below to the natural logarithim of C_{pv}/C_o which was plotted against the number of pore volumes applied using the least squares best-fit function within Microsoft Excel ©.

$$\ln \frac{C_{pv}}{C_o} = -k\, pv$$

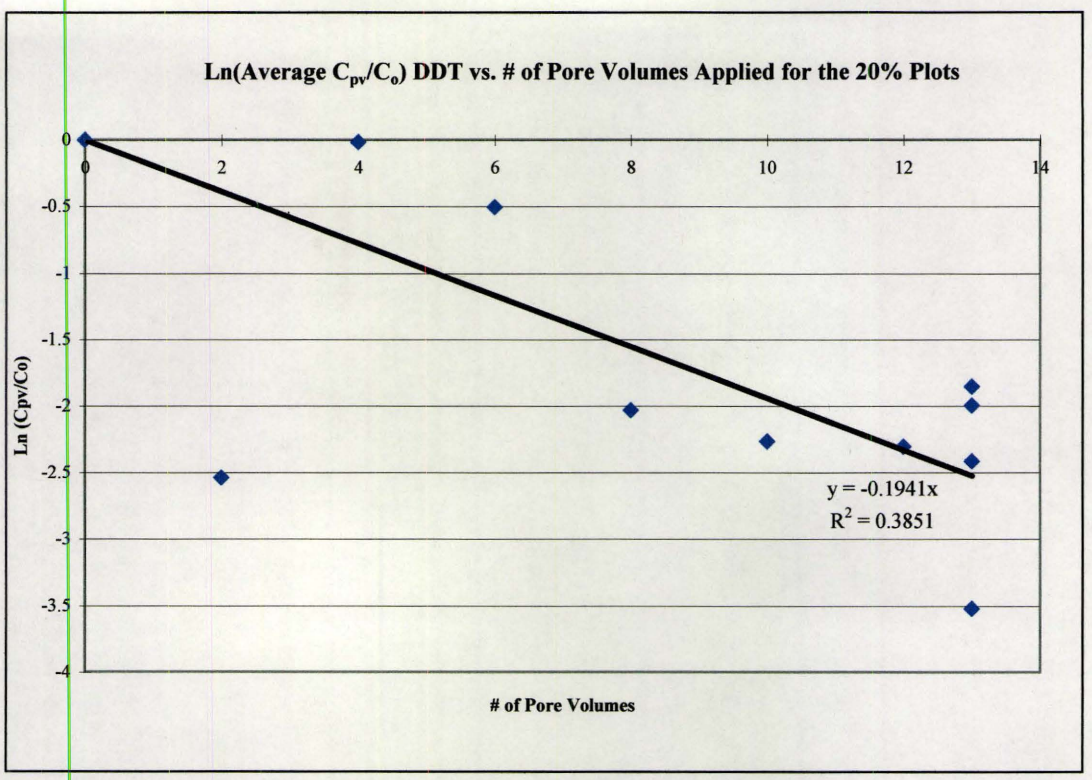

Figure 4.18: Plot of Ln(Average C_{pv}/C_o) of DDT vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 20% Plots that was used for the Determination of $pv_{1/2}$

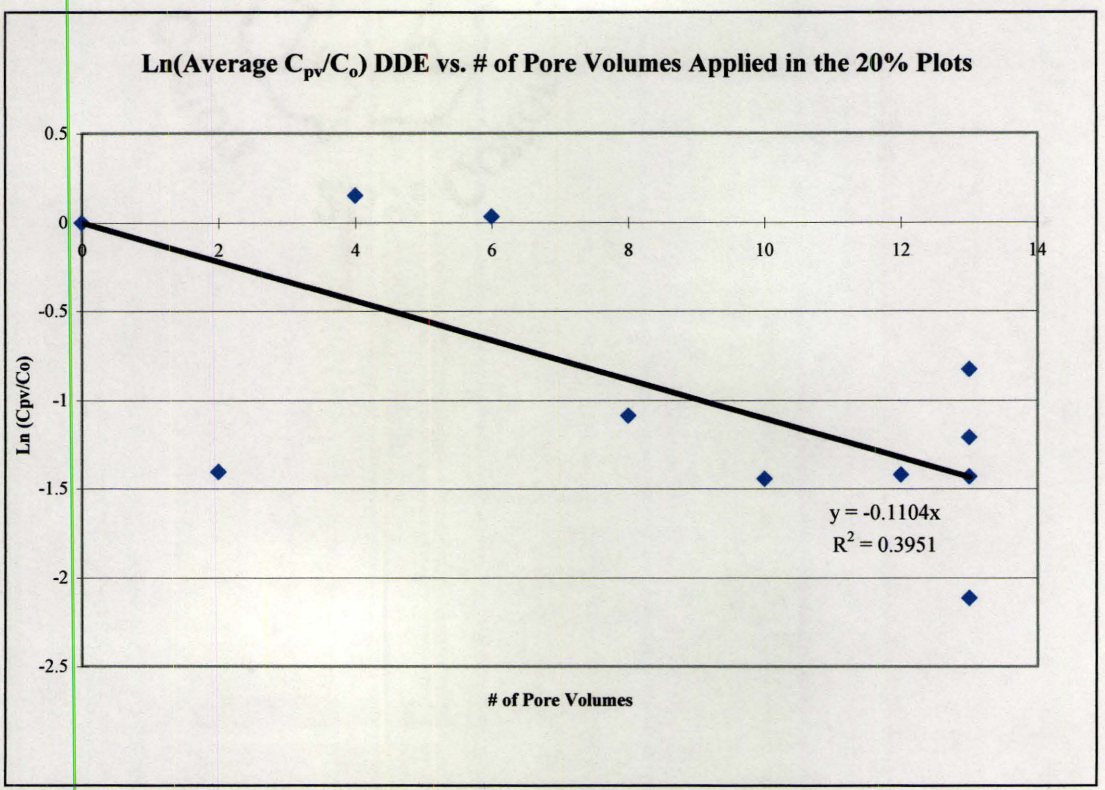

Figure 4.19: Plot of Ln(Average C_{pv}/C_o) of DDE vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 20% Plots that was used for the Determination of $pv_{1/2}$

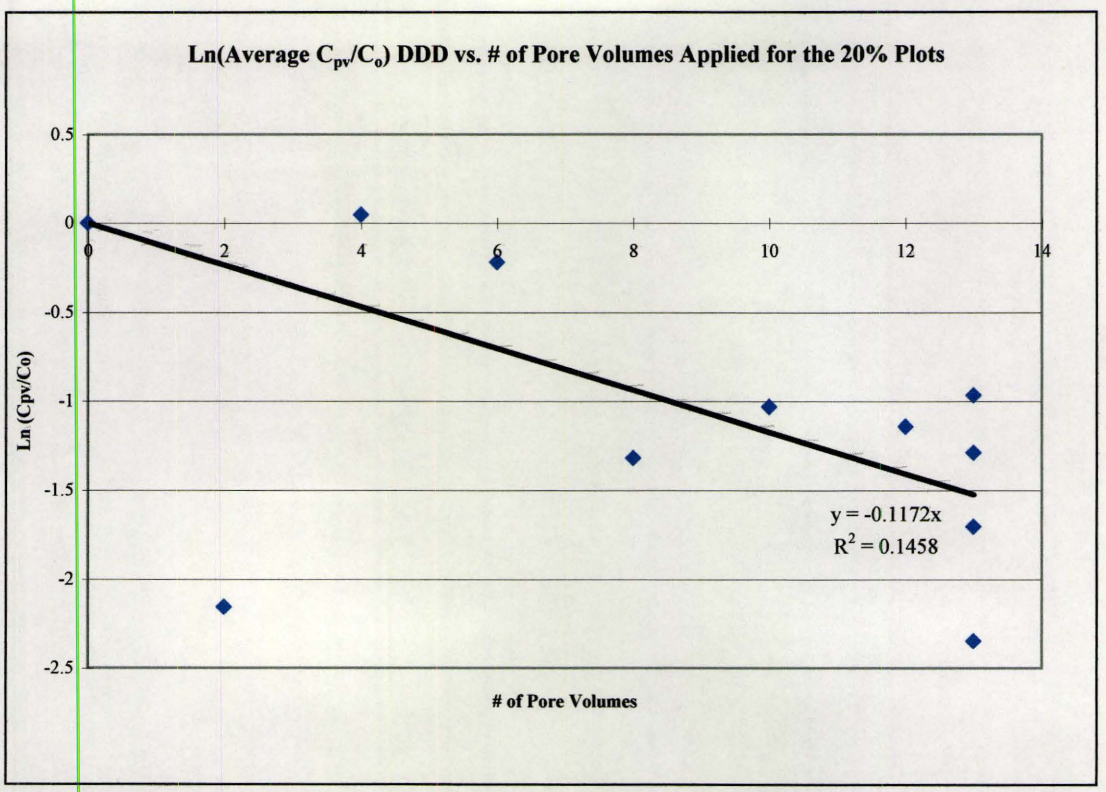

Figure 4.20: Plot of Ln(Average C_{pv}/C_o) of DDD vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 20% Plots that was used for the Determination of $pv_{1/2}$

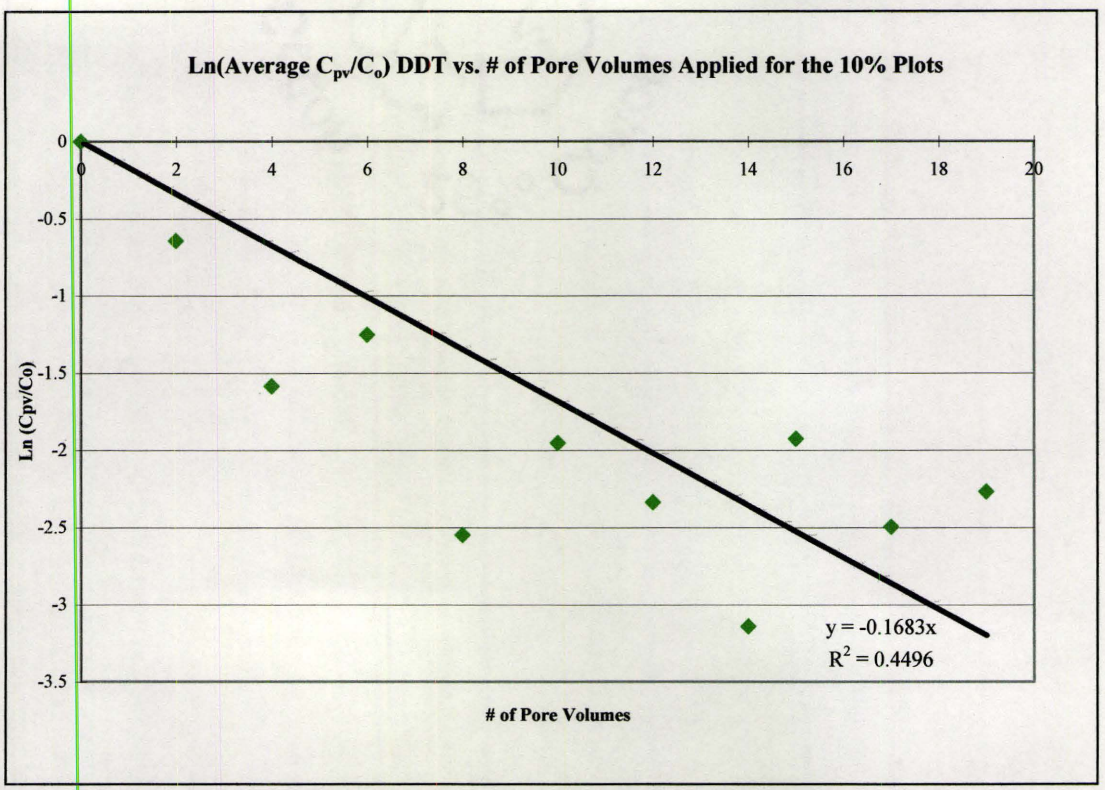

Figure 4.21: Plot of Ln(Average C_{pv}/C_o) of DDT vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 10% Plots that was used for the Determination of $pv_{1/2}$

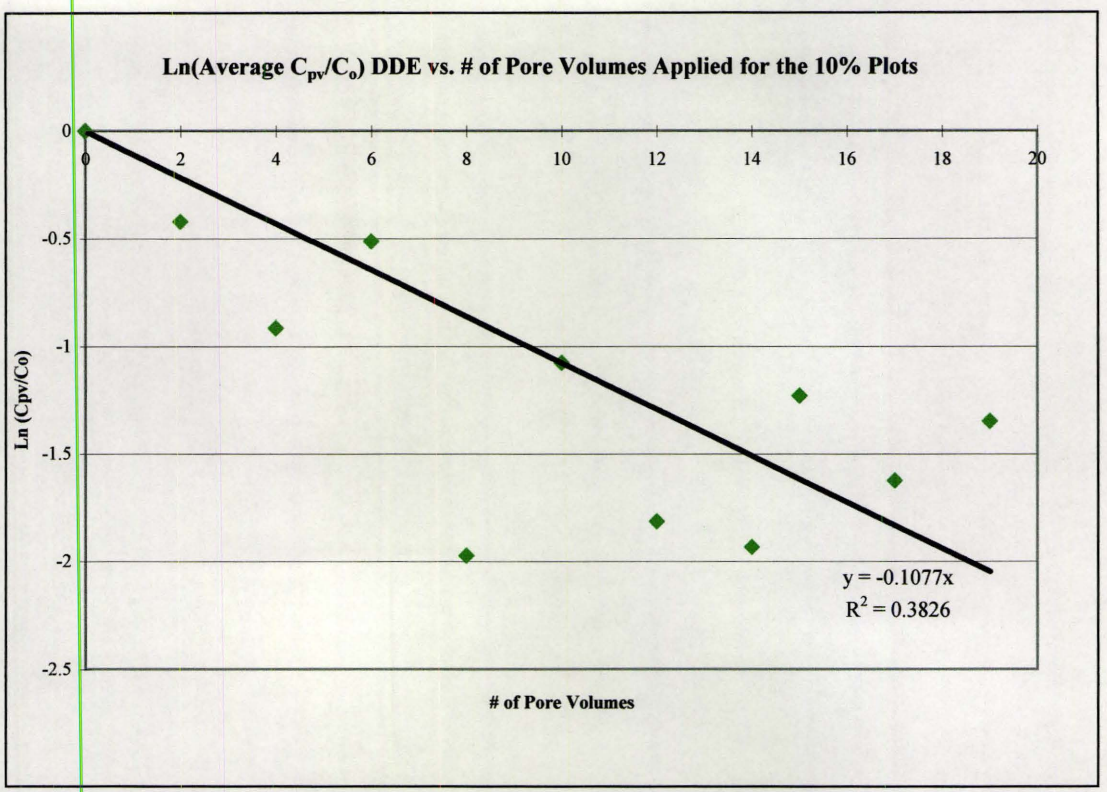

Figure 4.22: Plot of Ln(Average C_{pv}/C_o) of DDE vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 10% Plots that was used for the Determination of $pv_{1/2}$

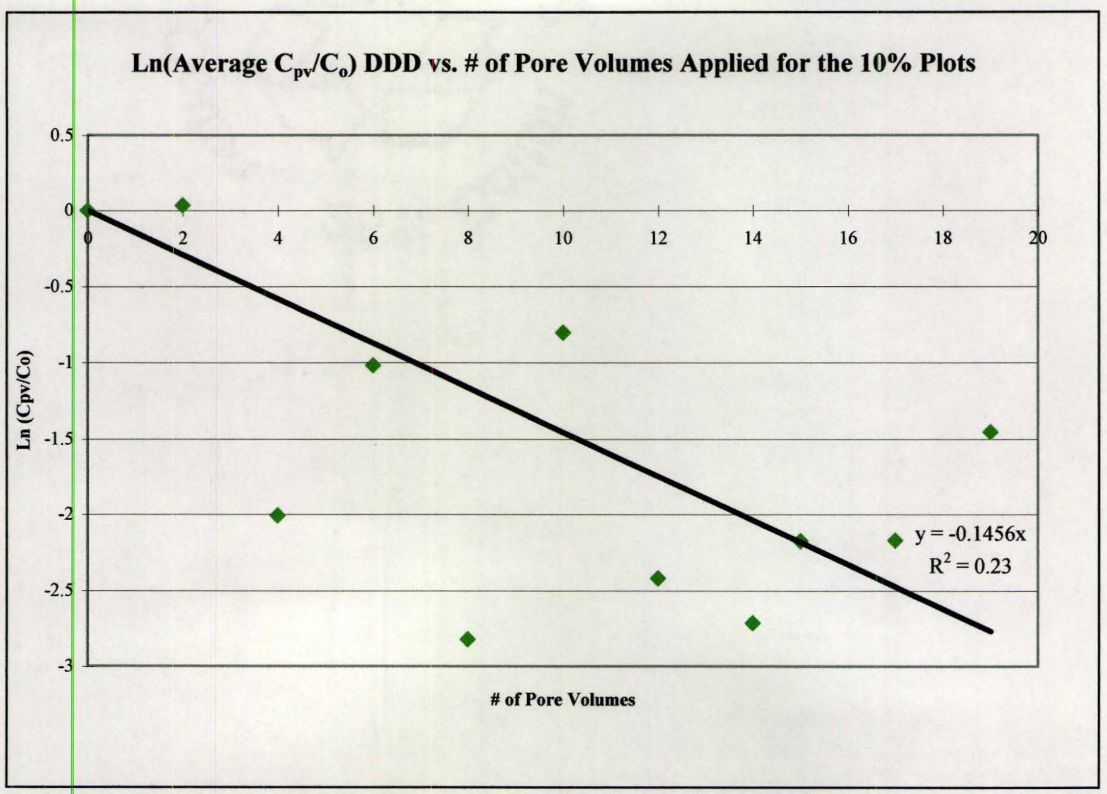

Figure 4.23: Plot of Ln(Average C_{pv}/C_o) of DDD vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 10% Plots that was used for the Determination of $pv_{1/2}$

A trend line was then generated that was forced through the intercept (0,0). The slope of the line was k (Figures 4.18 thru 4.23). The fit values of k were then used to calculate $pv_{1/2}$ using equation shown above. Table 4.27 shows the calculated $pv_{1/2}$ of the two treatments. In addition to the generated line equation an R^2 value was generated. The R^2 values are relatively low due to the high variability of sample concentration discussed previously. The tailing effect causes the slope of the line to be lower and the $pv_{1/2}$ to be longer.

	20% Plots	10% Plots
$pv_{1/2}$ for DDT	3.57	4.12
$pv_{1/2}$ for DDE	6.28	6.43
$pv_{1/2}$ for DDD	5.91	4.76

Table 4.27 Calculated Values of Pore Volume Half-Life

The $pv_{1/2}$ for the two treatments is remarkably similar, despite the difference in cyclodextrin concentration. In this study there was an observed "clogging"-effect due to the application of a 20% hydroxypropyl-β-cyclodextrin. It is anticipated that if this "clogging"-effect had not occurred the 20% solution would have been twice as effective as the 10% solution as observed in Schepanow (2002).

Previously, the value of pore volume half-life was generated using a least-squares best fit function of a plot of Ln(Average Cpv/Co) vs. the number of pore volumes added, in Microsoft Excel ©. When all the measured values of DDT, DDE and DDD are input into this function it skews the calculation of pore volume half-life due to the presence of a

substantial tailing effect after the application of ten pore volumes. The presence of a tailing effect results in the decrease of the slope of a trendline thereby resulting in a conservative (lower) pore volume half-life estimate. A pore volume half-life which is representative of the exponential decay observed in the early-time data can be calculated. If the soil concentrations of DDT, DDE and DDD that have received the application of more than ten pore volumes of cyclodextrin solution (September 9, 2003 to November 4, 2003), are eliminated this provides a trendline that is less affected by the processes that generate the tailing effect. The early-time plots of Ln (Average C_{pv}/C_o) vs. the Number of Pore Volumes of Cyclodextrin Solution Applied are presented in Appendix H. The early-time pore volume half-lives are presented in Table 4.28 thru 4.30.

	All data $pv_{1/2}$	Early time $pv_{1/2}$
20% application plots	3.57	3.24
10% application plots	4.12	2.77

Table 4.28: Comparison of an All Data Pore Volume Half-Life and an Early-Time Pore Volume Half-Life for the Concentration of DDT

	All data $pv_{1/2}$	Early time $pv_{1/2}$
20% application plots	6.28	6.05
10% application plots	6.44	4.47

Table 4.29: Comparison of an All Data Pore Volume Half-Life and an Early-Time Pore Volume Half-Life for the Concentration of DDE

	All data $pv_{1/2}$	Early time $pv_{1/2}$
20% application plots	5.91	5.80
10% application plots	4.76	3.41

Table 4.30: Comparison of an All Data Pore Volume Half-Life and an Early-Time Pore Volume Half-Life for the Concentration of DDD

The elimination of the late-time "tailing" data in the calculation of an early-time pore volume half-life did produce shorter half-life values. Within the 10% application plots the early-time pore volume half-lives are shorter for DDT, DDE and DDD by approximately 30%. The early-time pore volume half-lives of the 20% application plots for DDT, DDE and DDD were shorter than the all data values by approximately 10%, 6% and 2% respectively.

The relatively smaller decrease in the early-time pore volume half-life of DDT, DDE and DDD with the application of the 20% cyclodextrin (HPCD) solution is in keeping with the degree of tailing observed (Figure 4.7 – 4.12). The observed tailing in the decrease of DDT, DDE and DDD concentration within the 20% plots is smaller than is observed within the 10% application plots due to the application of thirteen pore volumes as compared to nineteen pore volumes.

Marenco (2002), estimated a conservative DDT *in-situ* degradation half-live in the former orchard area to be between 25 and 30 years. With the application of four pore volumes which took place over the course of four weeks, the average concentration of DDT was reduced by half. This represents a substantial decrease in the concentration

over a short period of time relative to the natural system. Although half-life estimates vary for soils in different environments, the half-life of DDT and its derivatives within a temperate climate is generally on the order of tens of years. The cyclodextrin treatment achieved that degree of mass removal from the surface soil with the application of approximately four pore volumes applied over a period of weeks. In addition to this, Schepanow (2002), showed that there was no real benefit to waiting between applications as it did not increase the amount of DDT desorbed. Therefore it is possible that the application of four pore volumes could be completed over the course of four days, yet still attaining similar results. It should be noted that further field testing is recommended to confirm these estimates as it is clear that the effectiveness of cyclodextrin in the field can differ from the observed laboratory behavior.

4.7.7 Mass Half-Life

Although the estimated pore volume half-life is similar for both treatments it is important to consider that this represents a fundamental difference in the mass of cyclodextrin applied. One pore volume of hydroxypropyl-β-cyclodextrin for the 20% solution contains twice the mass of cyclodextrin that is contained in one pore volume of 10% solution. Figures 4.24 thru 4.26 illustrates the average %DDT, %DDE and %DDD remaining as a function of mass of cyclodextrin applied to the plots. These graphs clearly illustrate that a larger application of cyclodextrin in the form of a 20% solution is required to achieve similar removal results that the 10% solution achieved with substantially less mass of cyclodextrin.

With regards to the DDT in soil, approximately 33.3kg of cyclodextrin in the form of a 10% solution was required to achieve a mass removal of 90% of the initial DDT within a treatment plot. Approximately 66.6kg of cyclodextrin powder in the form of a 20% solution was required to achieve the same 90% mass removal of DDT from soil in a plot of the same size. Approximately 40kg of cyclodextrin in the form of a 10% solution and approximately 66.6kg of cyclodextrin in the form of a 20% solution is required to achieve a mass removal of 80% of the initial DDE concentration in soil. In order to achieve a mass removal of 90% of the initial DDD concentration in soil, 40kg of cyclodextrin in the form of a 10% solution is required, or 86.6kg of cyclodextrin in the form of a 20% solution is required. With regards to the different constituents, approximately two times the mass of cyclodextrin in the form of 20% solution was required to achieve the results that the 10% solution achieved.

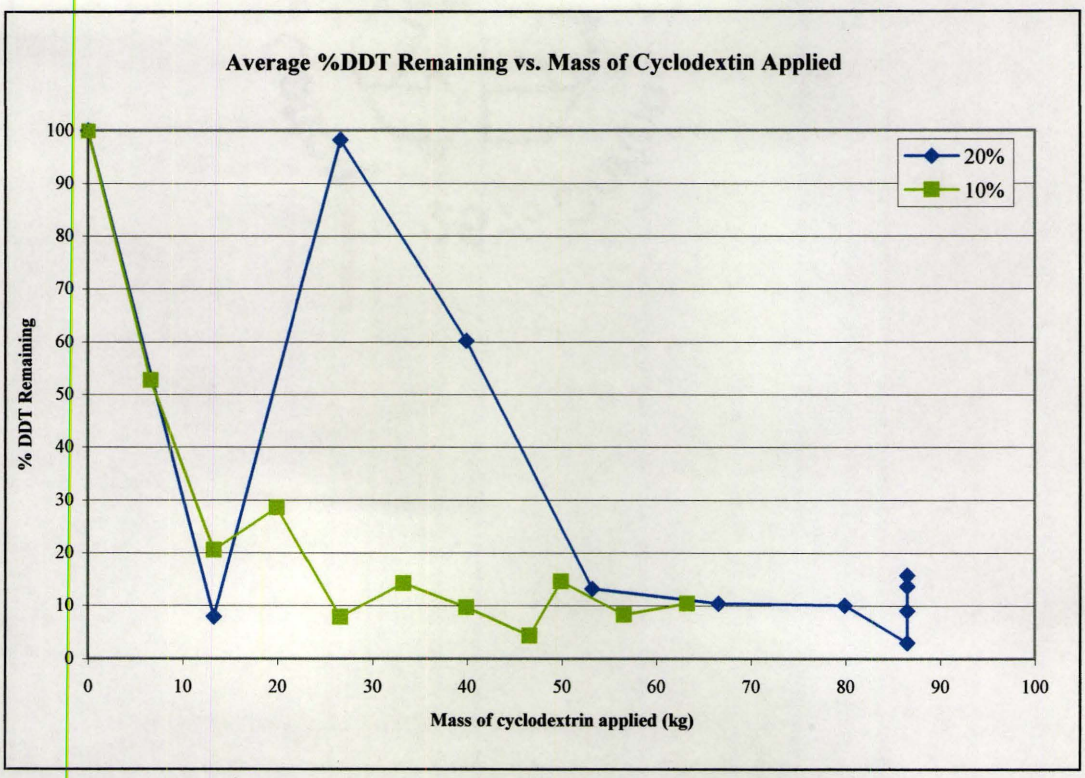

Figure 4.24: Average Percentage of DDT Remaining as a Function of the Mass of Cyclodextrin Applied to a Treatment Plot

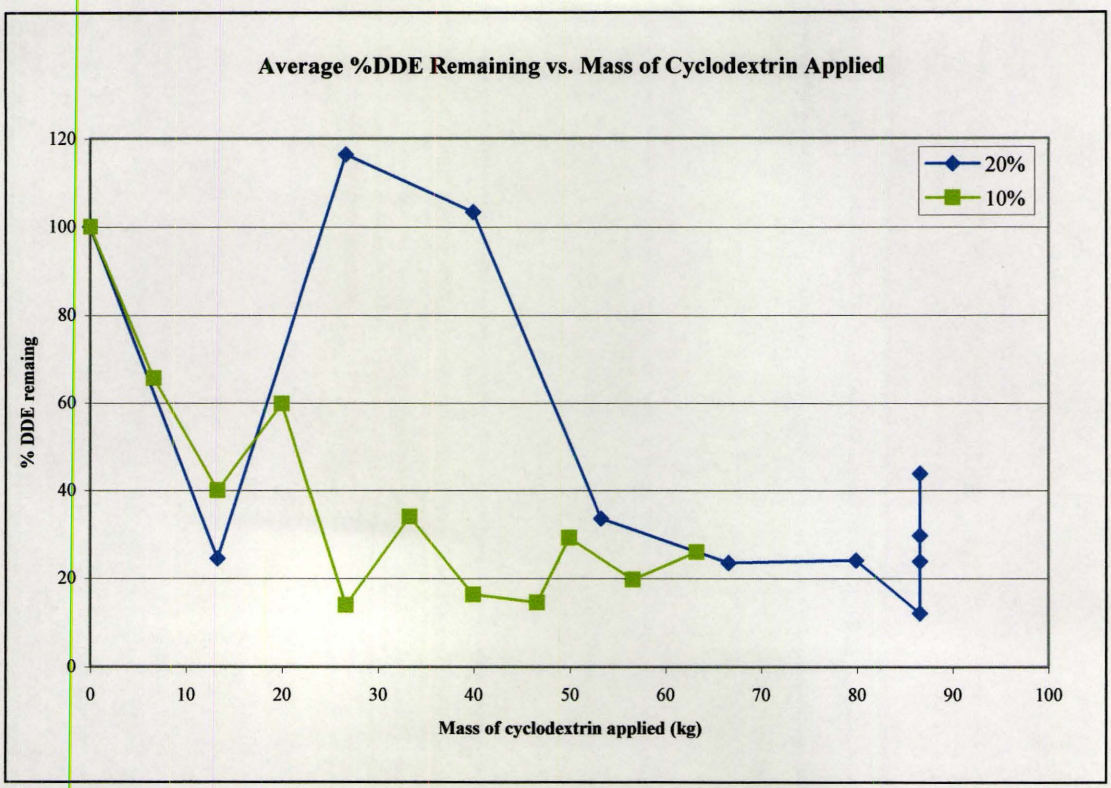

Figure 4.25: Average Percentage of DDE Remaining as a Function of the Mass of Cyclodextrin Applied to a Treatment Plot

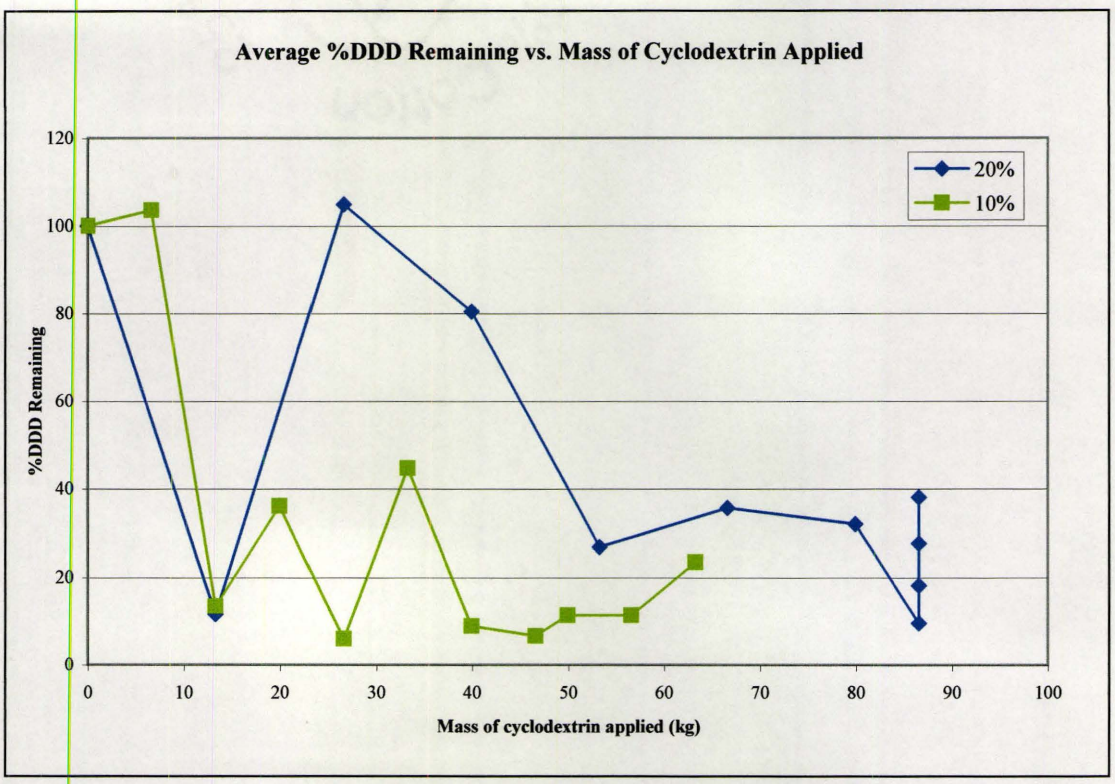

Figure 4.26: Average Percentage of DDD Remaining as a Function of the Mass of Cyclodextrin Applied to a Treatment Plot

In order to better quantify the mass of cyclodextrin required to achieve the removal of DDT and its derivatives, a mass half-life ($kg_{1/2}$) was determined. As with the estimate of pore volume half-life, the first order equations were rearranged to solve for mass half-life (see below):

$$\ln \frac{C_{kg}}{C_o} = -k\, kg_{1/2}$$

$$kg_{1/2} = \frac{\ln 2}{k}$$

where C_{kg} is the concentration after the application of kg amount of cyclodextrin powder, C_o is the initial concentration, k is the decay constant and kg is the mass of cyclodextrin powder applied. The value of the k, was determined in the same manner as with pore volume half-life. The natural logarithmic values of average C_{kg}/C_o were plotted against the mass of cyclodextrin applied in Microsoft Excel ©. The least squares best fit function in Microsoft Excel © was used to fit the data (Figures 4.27 - 4.32). The slope of the line, or k, was then substituted into the second equation above and solved for $kg_{1/2}$. See Table 4.31 for the calculated values of $kg_{1/2}$ for both treatments.

	20% Plots	**10% Plots**
$kg_{1/2}$ for DDT	23.8	13.7
$kg_{1/2}$ for DDE	41.8	21.5
$kg_{1/2}$ for DDD	39.4	15.9

Table 4.31: Calculated Values of Mass Half Life in kg per Treatment Plot

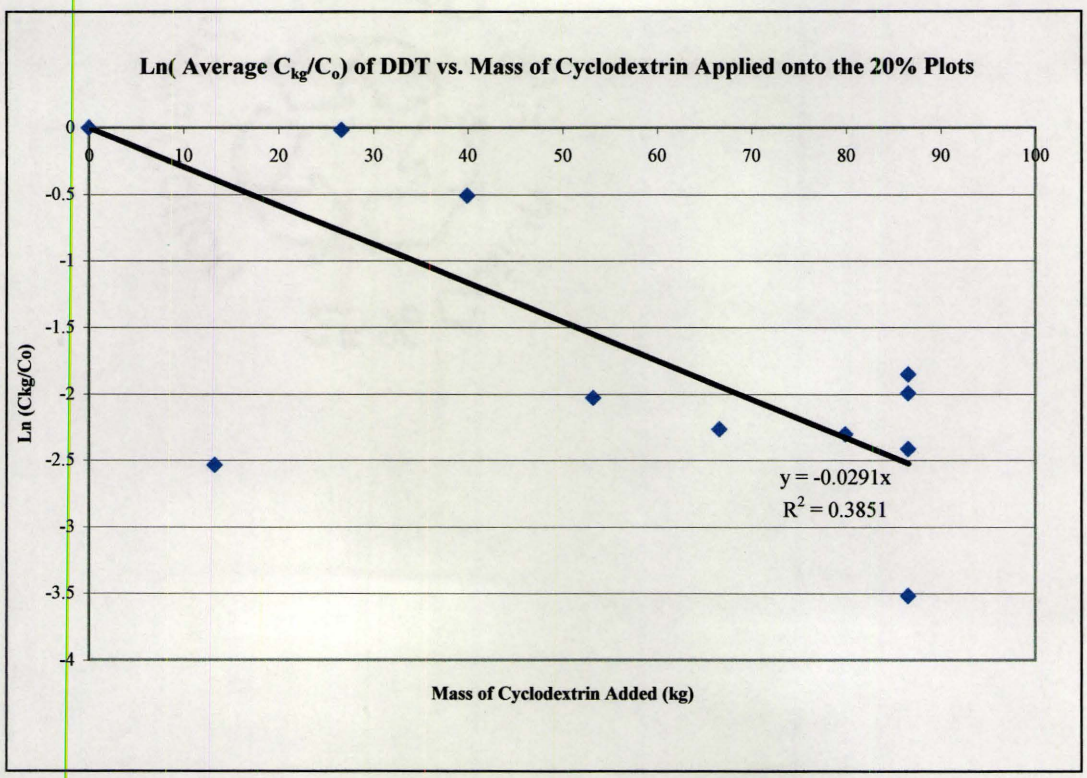

Figure 4.27: Plot of Ln(Average C_{kg}/C_o) of DDT vs. Mass of Cyclodextrin Applied to the 20% Plots that was used for the Determination of $kg_{1/2}$

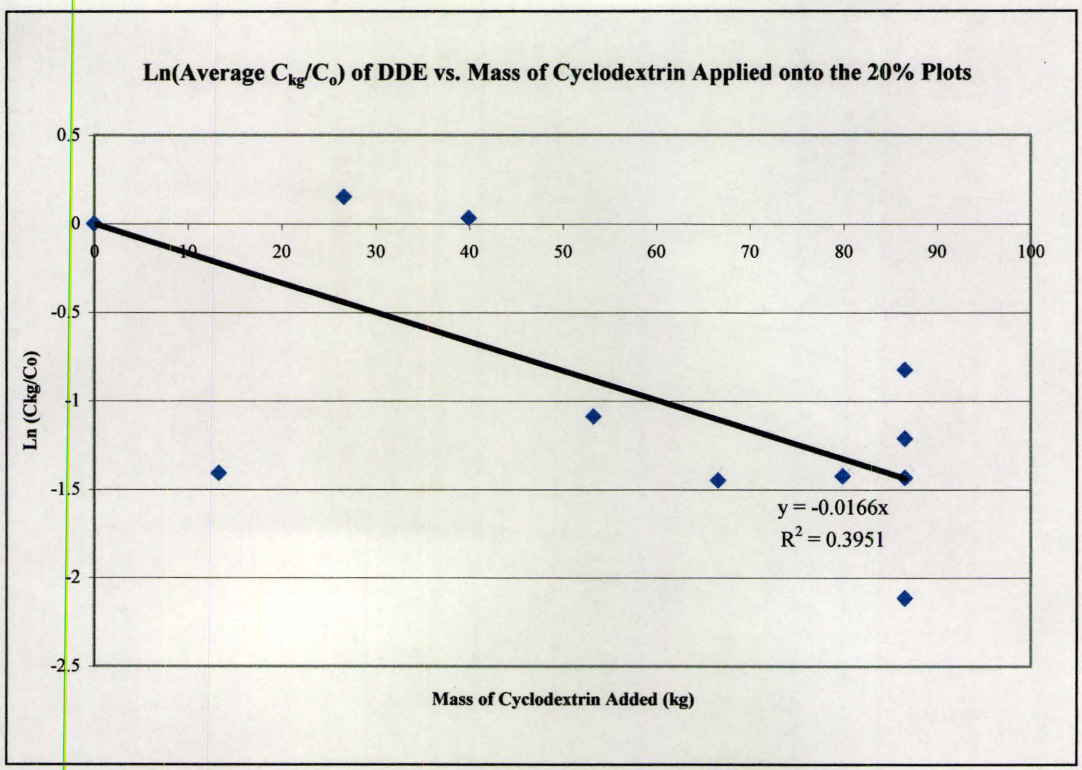

Figure 4.28: Plot of Ln(Average C_{kg}/C_o) of DDE vs. Mass of Cyclodextrin Applied to the 20% Plots that was used for the Determination of $kg_{1/2}$

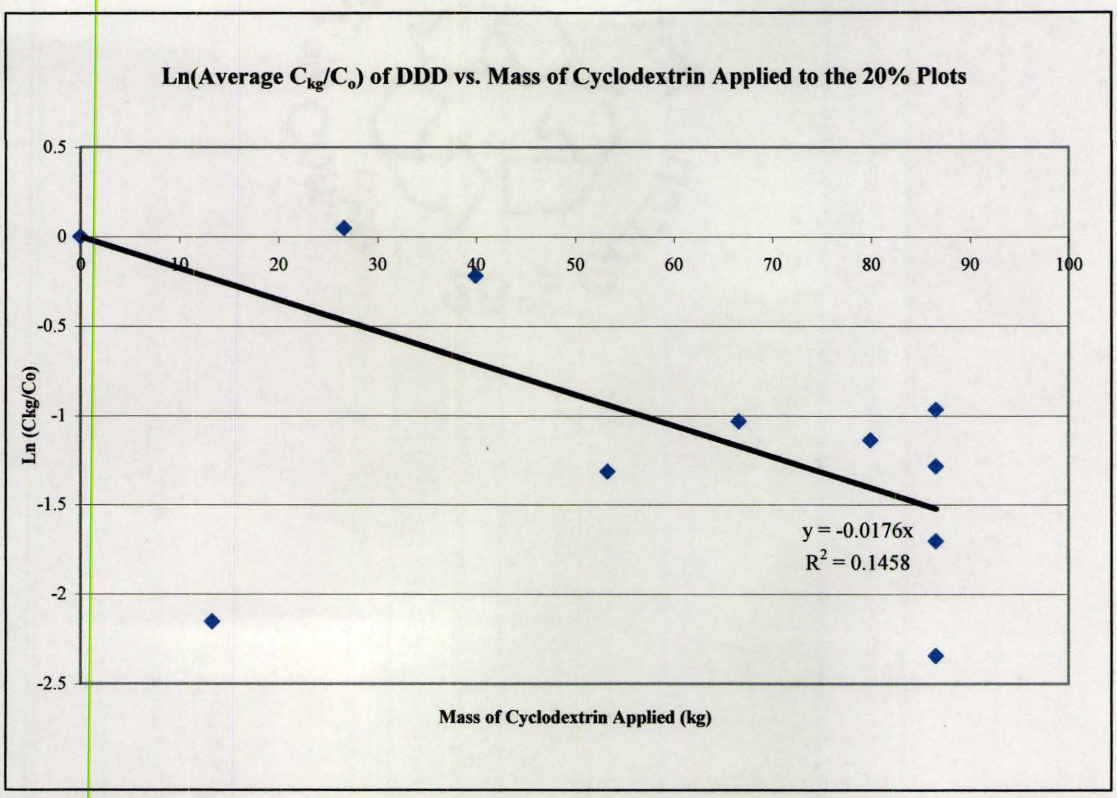

Figure 4.29: Plot of Ln(Average C_{kg}/C_o) of DDD vs. Mass of Cyclodextrin Applied to the 20% Plots that was used for the Determination of $kg_{1/2}$

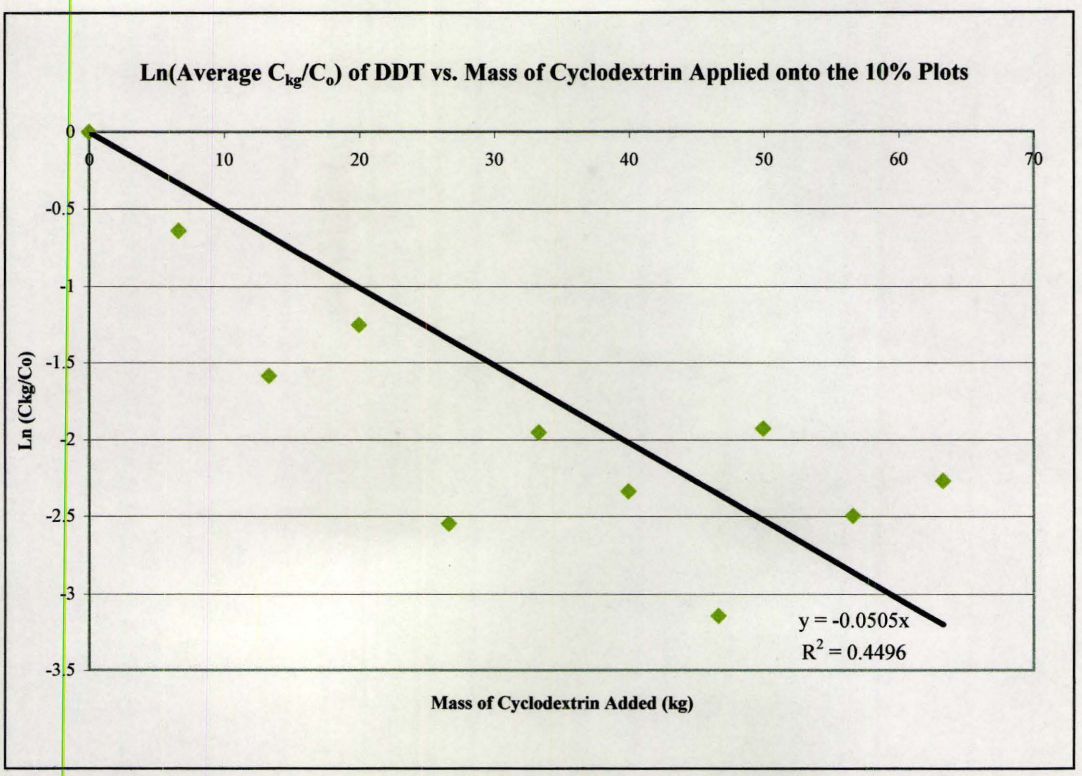

Figure 4.30: Plot of Ln(Average C_{kg}/C_o) of DDT vs. Mass of Cyclodextrin Applied to the 10% Plots that was used for the Determination of $kg_{1/2}$

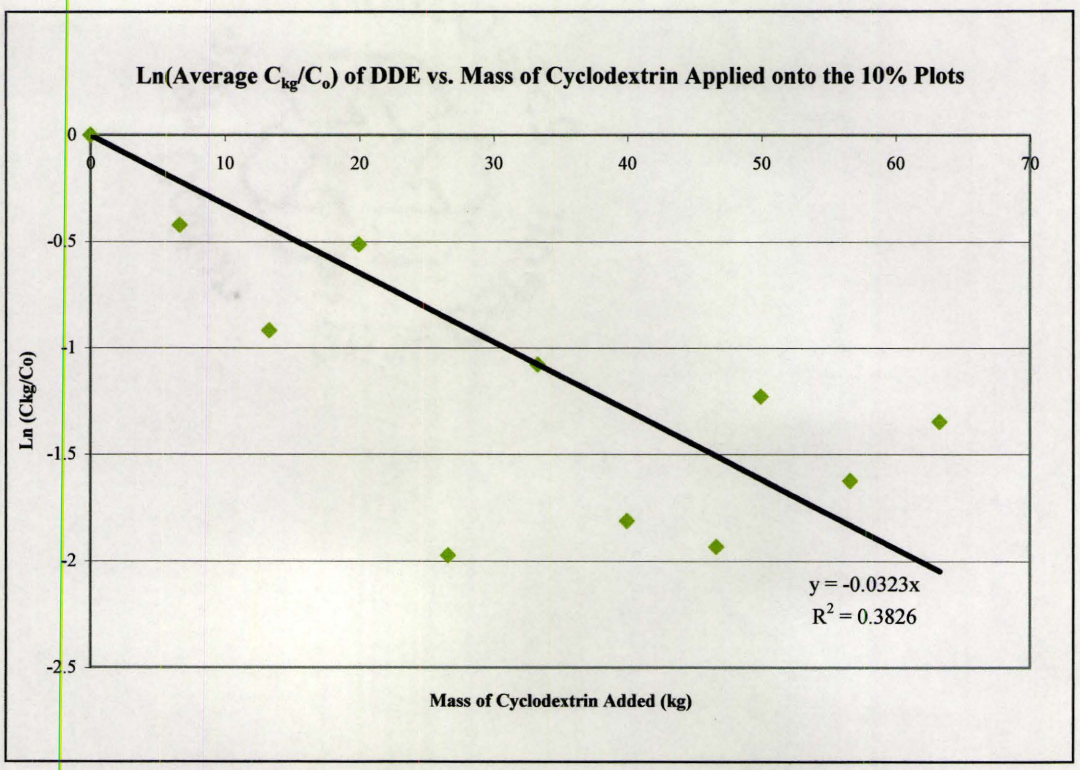

Figure 4.31: Plot of Ln(Average C_{kg}/C_o) of DDE vs. Mass of Cyclodextrin Applied to the 10% Plots that was used for the determination of $kg_{1/2}$

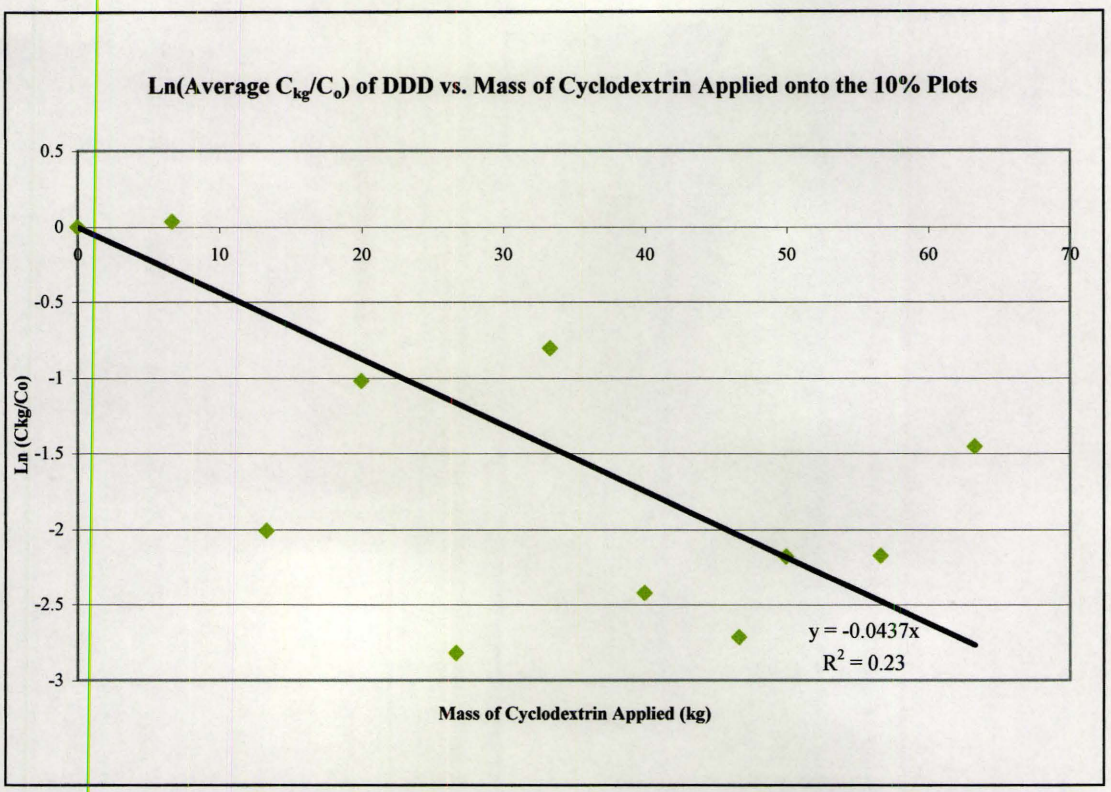

Figure 4.32: Plot of Ln(Average C_{kg}/C_o) of DDD vs. Mass of Cyclodextrin Applied to the 10% Plots that was used for the Determination of $kg_{1/2}$

In the case of DDT, approximately 13.7kg of cyclodextrin powder in the form of a 10% solution is required to decrease the concentration by half. Conversely, approximately 23.8kg in the form of a 20% solution is required for the same proportion of removal of DDT. To achieve a 50% mass removal of DDE the application of 21.5kg of cyclodextrin powder in the form of a 10% solution is required as compared to the application of 41.3kg in the form of a 20% solution. Approximately, 15.9kg of cyclodextrin powder in the form of a 10% solution must be applied to decrease the concentration of DDD in soil by half, while 39.4kg of cyclodextrin in the form of a 20% solution is required to produce the same results.

The values of $kg_{1/2}$ and the trends observed in Figures 4.24 thru 4.26 illustrate that approximately half of the mass of cyclodextrin in the form of a 10% solution achieved the same results as the 20% solution. This is in contrast to the observations of Schepanow (2002). In that laboratory experiment is was determined that less mass of cyclodextrin in the form of a 20% solution was required for the same rate of DDT removal achieved by more mass of cyclodextrin in the form of a 10% solution. As discussed in the pore volume half-life section there was an observed "clogging"-effect with the application of a 20% hydroxypropyl-β-cyclodextrin in this remediation field study. Schepanow (2002), did not have an observed "clogging"-effect which resulted in decreased infiltration rates. It is anticipated that if this "clogging"-effect had not occurred the 20% hydroxypropyl-β-cyclodextrin solution would have been twice as effective as the 10% solution, as observed in Schepanow (2002).

The generated mass half-lives also confirm the postulation of preferential removal which was discussed in Section 4.7.3. A larger mass of cyclodextrin must be applied in the form of either solution (10% or 20%) to achieve a removal of 50% of the mass of DDE. The removal of 50% of the mass of DDT requires the smallest amount of cyclodextrin powder applied in the form of either solution.

The calculated values of mass half-life can be normalized by taking into account the mass of soil targeted. This normalized value provides an application ratio which can be used in future remediation work to calculate the mass of cyclodextrin required. The mass of soil targeted was determined as follows:

$$Mass\ of\ soil = (A)(d_s)(p_b)$$

where A is the area of soil targeted (4900cm^2 for this study), d_s is the depth of soil targeted (15cm for this study) and p_b is the bulk density (0.907g/cm^3 for the 20% plots and 0.87g/cm^3 for the 10% plots). The bulk density values were determined by taking the average of all the measured values for each treatment (Table 4.1). The mass of soil targeted is converted to kg. The values of mass half-life are divided by the mass of soil targeted as follows:

$$Applicaiton\ Mass\ Ratio = \frac{kg_{1/2}}{mass\ of\ soil}$$

The resulting application ratio is dimensionless and has units of kg of cyclodextrin added/kg of soil targeted and are listed in Tables 4.28.

	DDT	DDE	DDD
20% application mass ratio	0.357	0.626	0.591
10% application mass ratio	0.215	0.335	0.248

Table 4.32: Application Mass Ratios for 20% and 10% Cyclodextrin Solutions for the Removal of DDT, DDE and DDD

4.8: Analyses of Biological Activity

Direct enumeration of the bacteria present within the remediation grid can help to provide a clearer picture of the role that bacteria may have played in changing the system and causing the observed change in infiltration. According to Kepner and Pratt (1994), identifying the primary factors responsible for the regulation of bacterial numbers is a major goal of microbiologists. In this scenario, aside from microscale differences, the soil matrix is relatively homogeneous. Measurement of physical and chemical properties indicates that all the control plots tend to be similar, however, there are some natural variations which is to be expected in a field study.

The bacterial counts of the plots are displayed in Table 4.29. The bacterial counts of the plots show variation, even within treatment. However, the average bacterial count in the 20% plots is 633cells/g of soil, in the 10% plots there are 463cells/g of soil and finally within the control plots there is 320cells/g of soil. The amount of bacterial cells contained within the 20% plots is nearly double that of the control plots. Similarly, the 10% plots contain nearly one and a half times the amount of cells in the control plots. The difference between the amounts of bacterial cells in the 20% plots as compared to the

10% is substantial as well. There are nearly one and a half time as many bacterial cells in the 20% as compared to the 10% plots.

	Weight of Soil Sample (g)	Bacterial Count (Cell/g of soil)
20%-1 (Plot 1)	5	760
20%-2 (Plot 3)	5	673
20%-3 (Plot 4)	5	465
10%-1 (Plot 2)	5	463
10%-2 (Plot 6)	5	523
10%-3 (Plot 7)	5	403
Control-1 (Plot 5)	5	282
Control-2 (Plot 8)	5	358

Table 4.33: Bacterial Cell Count Determined by DAPI Staining

This increase in bacterial numbers of the treatment plots is in keeping with the increase seen in organic matter of the treatment plots. The increase in bacterial numbers could account for the change in infiltration that is observed. There are now more bacteria, occupying more space, thereby potentially decreasing the open pore space in the soil matrix. It is also possible that the bio-clogging effect could reduce the "exposure" of the soil surfaces to the cyclodextrin solution and thereby reducing desorption and removal.

It should be noted that there are some limitations with the procedure used for the determination of bacterial numbers. First, Kepner and Pratt (1994) have shown that

DAPI counts under-estimate bacterial counts in the presence of fine sediment. Soil samples that are undergoing direct enumeration should first be sonified to ensure the release of all bacterial cells from the soil matrix. The exclusion of sonification from the counting procedure undoubtedly makes these numbers conservative estimates. Secondly, the count of bacterial numbers is frequently subjected to investigator bias. Individual interpretations of what actually constitutes a countable bacterial cell can result in substantial differences in estimates (Kepner and Pratt, 1994). It may be a better practice to have several investigators perform a count of the bacterial cells and then average the numbers to account for this bias. Regardless of these considerations, these preliminary data are consistent with field observations of reduced infiltration rates and hydraulic conductivity.

Chapter 5: Conclusions and Recommendations

5.1: Conclusions

Recent studies have shown that DDT, DDE and DDD are highly persistent in the shallow soils of Point Pelee National Park. The level of these contaminants are particularly high within the vicinity of the former orchard and are generally well above regulatory limits. Laboratory column experiments have revealed the ability of a hydroxypropyl-β-cyclodextrin solution to aid in the removal of DDT, DDE and DDD from soil columns. It was the expected outcome of this pilot-scale field remediation experiment that the application of a hydroxypropyl-β-cyclodextrin solution to the soils of Point Pelee National Park would result in the substantial decrease of the concentration of DDT and its derivatives.

As anticipated the application of a hydroxypropyl-β-cyclodextrin solution did result in a substantial decrease in the concentration of DDT, DDE and DDD. The application of a 20% cyclodextrin (HPCD) solution resulted in a decrease of 90%, 77% and 82% of the initial DDT, DDE and DDD concentrations in soil. The 10% solution resulted in the decrease of the initial DDT, DDE and DDD concentration of 90%, 74% and 73% respectively. The initial and late-time concentrations of DDT, DDE and DDD are statistically significantly different as a direct result of the application of cyclodextrin solution. Over the course of four months with the application of approximately ten pore volumes, the concentration of DDT, DDE and DDD have declined to concentrations that

based on reported degradation half-lives at Point Pelee National Park would have taken approximately fifty years to reach in the natural system.

The concentration of DDT and DDE are not yet below the regulatory limits of the Ontario Ministry of Environment and Energy or below the Canadian Environmental Quality Guidelines set by Environment Canada. It is anticipated that with the application of additional cyclodextrin, the concentrations of both DDT and DDD would fall within regulatory limits. The concentration of DDD in soil was consistently below regulatory limits by the end of the remediation experiment as a direct result of the application of the hydroxypropyl-β-cyclodextrin solution.

There were however, some unanticipated results and changes in the system due to the application of the cyclodextrin solution. Based on the work of Schepanow (2002), it was anticipated that a 20% hydroxypropyl-β-cyclodextrin solution would result in an increased desorption of DDT, DDE and DDD over a 10% solution from the soil profile. This, however, was not the case in the field experiment. There was no appreciable difference between the amount of removal of DDT, DDE and DDD achieved by a 20% and a 10% cyclodextrin (HPCD) solution. The relative increase in removal of DDT, DDE and DDD by the 10% cyclodextrin (HPCD) solution over the 20% solution is attributed to the observation of changes within the soil matrix and the decrease in infiltration.

In laboratory experiments more mass was required in the form of a 10% solution to achieve the same decrease in concentration as a 20% solution. On the contrary, in this remediation experiment it was estimated that approximately half the mass of

hydroxypropyl-β-cyclodextrin solution in the form of a 10% solution was required to accomplish a similar decrease in contaminant concentration obtained by a 20% solution. This difference relative to laboratory column results is attributed largely to changes in soil physical properties in the presence of the 20% hydroxypropyl-β-cyclodextrin solution.

A tailing effect was observed in this field study that had not been observed in the laboratory column treatability studies performed by Schepanow (2002). Within his column experiments, there was a proportional relationship between the number of pore volumes applied and the decrease in contaminant concentration. The concentration of DDT, DDE and DDD in this field study, however, reached a plateau after the application of approximately ten pore volumes of solution. This tailing effect indicated that the late-time relationship between DDT, DDE and DDD concentration and the amount of hydroxypropyl-β-cyclodextrin solution applied does not follow a simple first order reaction.

Marenco (2002), discovered a high degree of variation in the concentration of DDT and its derivatives within the former orchard area, on the scale of meters. In this study, it was discovered that a high degree of variation was also present on the scale of centimeters within the study site. The application of the hydroxypropyl-β-cyclodextrin solution resulted in a substantial decrease in the degree of variation of the concentration of DDT, DDE and DDD as the experiment progressed. Within both treatments, the variance in the DDT concentration decreased from approximately $1700(\mu g/g)^2$ to $10(\mu g/g)^2$ during the remediation experiment. The variance in the DDE concentration

decreased from approximately $1550(\mu g/g)^2$ to $20(\mu g/g)^2$ and variance in the DDD concentration decreased from $31(\mu g/g)^2$ to less than $1(\mu g/g)^2$. This decrease in variation may potentially be attributed to the lateral migration of DDT and its derivatives within the application plots, however, further testing is required to confirm this postulation. A competing postulate would be that the higher concentration locations were more effectively leached.

Vertical mobilization of the mass of DDT and its derivatives within the soil profile accounted for only a portion of the decrease seen in the surface concentration of these contaminants. Leaching to groundwater is expected to account for a proportion of the mass. Finally, a portion of the decrease in concentration may be due to enhanced *in-situ* biological degradation.

There were some unanticipated fundamental changes in the soil physical properties as a result of the application of the hydroxypropyl-β-cyclodextrin solutions. The weekly recorded *in-situ* moisture content increased with the application of only one pore volume of cyclodextrin (HPCD) solution. The difference between *in-situ* moisture contents of the application plots over the control plots continued to increase as the remediation experiment progressed. This increase in moisture content was still observed at the end of the remediation experiment. The application of the 20% solution had not taken place for approximately two months, yet the plots were still retaining a higher amount of moisture. Statistical testing also revealed that the initial and late-time moisture contents were statistically significantly different due to the application of a cyclodextrin solution.

The increase in moisture content was accompanied by a decrease in the maximum infiltration rate. The observed decrease in infiltration rate was only observed in the 20% application plots and resulted in eventual lateral spreading of the cyclodextrin solution beyond the garden edging. Due to the decrease in infiltration rate the application of the 20% hydroxypropyl-β-cyclodextrin solution was suspended as a precautionary measure to protect the integrity of surrounding plots.

In-situ field saturated hydraulic conductivity (K_{fs}) measurements taken at the end of the treatment period confirmed a decrease in K_{fs} for the 20% plots. The K_{fs} values of the 20% plots were an order of magnitude smaller in both the Ah horizon and the Bm horizon than the K_{fs} values of the 10% and control plots. The decrease in K_{fs} was sufficient to account for the change in infiltration rates and persisted to the end of the study despite the fact that the 20% cyclodextrin solution had not been applied for two months.

Direct enumeration of bacterial cells using DAPI staining techniques has shown that there was an increase in the number of bacterial cells in the application plots. This is consistent with the fact that hydroxypropyl-β-cyclodextrin is an oligosaccharide which may act as a food source for biological matter within the soil matrix. The increase in bacterial cell numbers parallels the increase in the percentage of organic matter seen within the application plots. It follows to reason that the increase in bacterial cells has played some role in the changes seen within the soil matrix of the application plots.

It is unclear whether this is the minimum attainable concentration of DDT, DDE and DDD for this system, or whether the concentration could be further decreased by

reapplication of the cyclodextrin solution. The concentration of DDT, DDE and DDD could potentially decrease over time without the application of additional cyclodextrin solution as the changes in the fundamental properties of the system in the 20% plots lasted for two months after the cyclodextrin application was terminated. Perhaps in an alternate system where the concentrations of DDT, DDE and DDD were initially lower it would be attainable to reach regulatory limits prior to the occurrence of any substantial tailing effect. This information is useful as the observed tailing effect could prove to be a significant challenge if the primary goal of cyclodextrin application is to reduce the concentration of DDT, DDE and DDD to below regulatory limits.

5.2 Recommendations

Within this system there was no apparent benefit to applying more than ten pore volumes as there was no appreciable change in the concentration of DDT and its derivatives after this point. There was also no appreciable benefit to using a 20% solution over a 10% solution. Therefore, it is recommended that a small number of pore volumes of a 10% cyclodextrin solution be used at Point Pelee National Park for any related remediation work. The technical grade of hydroxypropyl-β-cyclodextrin is quite expensive ($7.00USD/kg) so it is also more economical to apply fewer pore volumes of the 10% solution. In addition it is recommended that the 20% hydroxypropyl-β-cyclodextrin solution not be used for further remediation work at Point Pelee National Park as it caused many fundamental changes in the system. Further experimentation is required to determine if these effects are site specific, biological, or only physical.

It is recommended that soil sampling for the analysis of DDT, DDE and DDD concentration be completed again without the application of additional cyclodextrin solution to see if there was a decrease over time. Groundwater sampling of the water below the application plots should be completed in order to fully assess the vertical mobilization of DDT, DDE and DDE due to the application of a hydroxypropyl-β-cyclodextrin solution.

Further research is required to determine the full extent that the biological component plays within this system. Additional enumeration using DAPI staining techniques, and sonification should be completed to provide an accurate count of the bacterial cells in the system. Direct enumeration by multiple investigators would also be prudent to achieve an accurate count.

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Appendix A: Soil Sampling Locations for DDT, DDE and DDD Analysis

Date	Plot 1: 20%-1	Plot 2: 10%-1	Plot 3: 20%-2	Plot 4: 20%-3	Plot 5: Con-1	Plot 6: 10%-2	Plot 7: 10%-3	Plot 8: Con-2	Plot 9: Con-3
11-Jun-02	3	3	1	1	15	18	5	5	20
08-July-02	16	25	4	16	-	9	21	-	-
15-July-02	5	20	13	25	-	24	7	-	-
30-July-02	13	6	11	10	-	21	20	-	-
12-Aug-02	4	23	15	22	-	1	1	-	-
26-Aug-02	6	11	16	19	-	5	3	-	-
09-Sep-02	20	13	21	17	-	3	6	-	-
24-Sep-02	15	9	14	21	-	17	17	-	-
07-Oct-02	10	8	3	18	-	4	2	-	-
22-Oct-02	1	10	25	13	-	11	25	-	-
04-Nov-02	11	14	8	5	17	8	8	20	1

Soil Sampling Locations within the Remediation Grid throughout the Remediation Experiment for the Analysis of DDT, DDE and DDD (Sampling Locations refer to the grid numbers assigned as outlined in Figure 3.3)

Appendix B: Cyclodextrin Application Schedule

Date	20% Application Plots	10% Application Plots	Control Plots
11-June-02	-	-	-
18-June-02	1 pore volume	1 pore volume	-
25-June-02	1 pore volume	1 pore volume	-
09-July-02	1 pore volume	1 pore volume	-
10-July-02	1 pore volume	1 pore volume	-
16-July-02	1 pore volume	1 pore volume	-
23-July-02	1 pore volume	1 pore volume	-
31-July-02	1 pore volume	1 pore volume	-
07-Aug-02	1 pore volume	1 pore volume	-
13-Aug-02	1 pore volume	1 pore volume	-
20-Aug-02	1 pore volume	1 pore volume	-
27-Aug-02	1 pore volume	1 pore volume	-
04-Sep-02	1 pore volume	1 pore volume	-
10-Sep-02	1 pore volume	1 pore volume	-
17-Sep-02	-	1 pore volume	-
24-Sep-02	-	1 pore volume	-
08-Oct-02	-	2 pore volume	-
22-Oct-02	-	2 pore volume	-
04-Nov-02	-	-	-

Schedule for the Application of Hydroxypropyl-β-Cyclodextrin Solution throughout the Remediation Experiment

Appendix C: DDT, DDE and DDD Concentrations Provided by the National Laboratory for Environmental Testing (NLET)

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (μg/g)	ρ,ρ-DDT (μg/g)	o,ρ-DDE (μg/g)	ρ,ρ-DDE (μg/g)	o,ρ-DDD (μg/g)	ρ,ρ-DDD (μg/g)
11-Jun-02	0	11.2	68.7	0.945	79.5	3.08	8.36
08-Jul-02	2	0.0564	0.476	0.0137	2.2	0.0139	0.0178
15-Jul-02	4	6.23	62.3	0.682	63	2.5	5.05
30-Jul-02	6	4.42	25.8	0.336	55.5	1.18	3
12-Aug-02	8	1.12	8.13	0.202	17.3	0.688	1.26
26-Aug-02	10	0.0795	0.262	0.0172	1.56	0.0205	0.0333
09-Sep-02	12	0.536	5.18	0.106	11.6	0.78	1.59
24-Sep-02	13	0.269	0.975	0.0423	5.4	0.171	0.405
08-Oct-02	13	0.141	1.22	0.049	5.16	0.176	0.385
22-Oct-02	13	0.561	2.99	0.11	8.99	0.149	0.271
04-Nov-02	13	0.26	1.09	0.0447	4.29	0.0676	0.135

Concentrations of DDT, DDE and DDD within the soil of Plot 1:20%-1

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	4.89	22.1	0.343	27.2	1.7	7.89
08-Jul-02	2	6.78	32.9	0.404	38.1	2.23	6.97
15-Jul-02	4	0.462	2.87	0.0791	7.17	0.0784	0.131
30-Jul-02	6	0.691	4.11	0.0782	8.02	0.162	0.249
12-Aug-02	8	0.158	1.21	0.0303	3.58	0.0314	0.0571
26-Aug-02	10	0.517	3.9	0.0618	8.59	0.356	0.861
09-Sep-02	12	0.451	2.94	0.0769	6.03	0.13	0.243
24-Sep-02	14	0.045	0.312	0.0399	1.95	0.042	0.08
08-Oct-02	15	1.04	6	0.118	10.2	0.219	0.254
22-Oct-02	17	0.07	0.34	0.03	2.74	0.0173	0.0331
04-Nov-02	19	0.0436	0.408	0.0381	1.6	0.0151	0.0262

Concentrations of DDT, DDE and DDD within the soil of Plot 2:10%-1

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (μg/g)	ρ,ρ-DDT (μg/g)	o,ρ-DDE (μg/g)	ρ,ρ-DDE (μg/g)	o,ρ-DDD (μg/g)	ρ,ρ-DDD (μg/g)
11-Jun-02	0	3.88	16	0.299	25	1.48	4.12
08-Jul-02	2	1.41	5.43	0.125	16.8	0.186	0.81
15-Jul-02	4	1.78	9.93	0.153	15.2	0.381	0.423
30-Jul-02	6	1.87	12.6	0.142	11.1	0.545	0.841
12-Aug-02	8	0.48	1.97	0.0996	7.34	0.14	0.168
26-Aug-02	10	0.707	4.66	0.0849	7.61	0.247	0.83
09-Sep-02	12	0.428	3	0.048	4.7	0.102	0.269
24-Sep-02	13	0.212	1.22	0.0521	4	0.115	0.17
08-Oct-02	13	0.465	2.08	0.047	4.82	0.0922	0.153
22-Oct-02	13	0.608	2.99	0.118	8.14	0.259	0.381
04-Nov-02	13	0.33	2.06	0.0341	4.34	0.106	0.191

Concentrations of DDT, DDE and DDD within the soil of Plot 3:20%-2

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	0.124	0.513	0.0297	4	0.161	0.0466
08-Jul-02	2	0.0815	0.52	0.0131	2.2	0.0185	0.0468
15-Jul-02	4	2.63	16.3	0.188	22.2	0.691	0.84
30-Jul-02	6	1.53	14.5	0.243	22.7	0.845	1.16
12-Aug-02	8	0.224	1.33	0.0482	4.32	0.108	0.163
26-Aug-02	10	0.687	4.08	0.129	11.1	0.638	1.59
09-Sep-02	12	0.136	0.8	0.0405	4.51	0.068	0.206
24-Sep-02	13	0.042	0.272	0.009	1.02	0.011	0.03
08-Oct-02	13	1.22	8.61	0.15	15.7	0.691	2.09
22-Oct-02	13	1.16	7.52	0.207	20.6	0.708	0.835
04-Nov-02	13	0.9	4.39	0.0861	12	0.469	0.744

Concentrations of DDT, DDE and DDD within the soil of Plot 4:20%-3

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	1.34	5.91	0.106	13.5	0.105	1.96
08-Jul-02	2	1.89	11.3	0.161	17.5	0.223	0.305
15-Jul-02	4	1.26	9.46	0.115	15	0.204	0.386
30-Jul-02	6	3.33	14.4	0.153	29.9	0.592	0.561
12-Aug-02	8	0.604	5.55	0.0839	7.29	0.123	0.321
26-Aug-02	10	0.553	3.46	0.0713	8.84	0.108	0.894
09-Sep-02	12	0.604	5.55	0.0839	7.29	0.123	0.321
24-Sep-02	14	0.62	3.1	0.0818	9.12	0.127	0.342
08-Oct-02	15	0.665	4.53	0.0658	9.14	0.108	0.209
22-Oct-02	17	0.667	4.63	0.0891	7.91	0.14	0.327
04-Nov-02	19	0.921	5.06	0.118	11.7	0.274	1.19

Concentrations of DDT, DDE and DDD within the soil of Plot 6:10%-2

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	1.26	13	0.266	13	1.79	3.5
08-Jul-02	2	0.0464	0.216	0.0122	0.985	0.00918	0.0175
15-Jul-02	4	0.842	5.77	0.287	12.2	0.23	0.237
30-Jul-02	6	1.28	5.02	0.166	13.8	0.864	0.97
12-Aug-02	8	0.0365	0.346	0.0098	1.11	0.00933	0.0189
26-Aug-02	10	0.82	5.06	0.115	12	0.673	1.32
09-Sep-02	12	0.018	0.187	0.00713	0.74	0.00517	0.0133
24-Sep-02	14	0.04	0.241	0.027	1.39	0.012	0.022
08-Oct-02	15	0.335	2.12	0.0797	5.88	0.118	0.16
22-Oct-02	17	0.488	2.13	0.0878	6.33	0.286	0.271
04-Nov-02	19	0.593	3.41	0.118	9.06	0.351	0.347

Concentrations of DDT, DDE and DDD within the soil of Plot 7:10%-3

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	2.22	8.54	0.225	21.3	1.09	2.86
04-Nov-02	0	13.4	152	0.14	16.1	4.33	0.596

Concentrations of DDT, DDE and DDD within the soil of Plot 5:Control-1

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	0.0464	0.139	0.0223	2.41	0.00609	0.0157
04-Nov-02	0	0.382	1.65	0.0444	3.41	0.0435	0.146

Concentrations of DDT, DDE and DDD within the soil of Plot 8:Control-2

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
11-Jun-02	0	4.65	10.4	0.404	30.9	0.257	2.96
04-Nov-02	0	1.65	10.1	0.126	12	0.242	1.99

Concentrations of DDT, DDE and DDD within the soil of Plot 9:Control-3

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
Ah horizon – 11cm	13	0.226	1.06	0.031	2.42	0.0597	0.166
Bm horizon – 35cm	13	0.0373	0.176	0.00398	0.202	0.00486	0.0124

Concentrations of DDT, DDE and DDD within the soil profile beneath Plot 3:20%-2

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
Ah horizon – 11cm	19	0.162	0.913	0.032	2.02	0.0351	0.104
Bm horizon – 35cm	19	0.0593	0.178	0.0035	0.172	0.00473	0.0158

Concentrations of DDT, DDE and DDD within the soil profile beneath Plot 6:10%-2

Sampling Date	# of pore volumes previously applied	o,ρ-DDT (µg/g)	ρ,ρ-DDT (µg/g)	o,ρ-DDE (µg/g)	ρ,ρ-DDE (µg/g)	o,ρ-DDD (µg/g)	ρ,ρ-DDD (µg/g)
Ah horizon – 11cm	0	0.0207	0.077	0.00164	0.759	0.00195	0.00557
Bm horizon – 35cm	0	0.000668	0.0045	0.000222	0.0171	0.000134	0.000448

Concentrations of DDT, DDE and DDD within the soil profile beneath Plot 9:Control-3

Appendix D: Soil Sampling Locations of Soil Cores used for the Analyses of Physical and Chemical Soil Properties

Date	Plot 1: 20%-1	Plot 2: 10%-1	Plot 3: 20%-2	Plot 4: 20%-3	Plot 5: Con-1	Plot 6: 10%-2	Plot 7: 10%-3	Plot 8: Con-2	Plot 9: Con-3
Core i	22	7	10	23	3	7	4	4	8
Core ii	12	4	17	6	25	19	10	23	16

Soil Sampling Locations within the Remediation Grid during Final Sampling on November 4, 2002 for the Analysis of Physical and Chemical Properties (Sampling Locations refer to the grid numbers assigned as outlined in Figure 3.3)

Appendix E: Raw Data from the Laboratory Analysis of Physical and Chemical Soil Properties

Plot	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of wet soil (g)	Wt. of oven dried soil (g)	Wt. of water in soil (g)
20%-1 (Core i)	1.30	68.73	45.55	67.43	44.25	23.18
20%-1 (Core ii)	1.25	76.48	53.77	75.23	52.52	22.71
20%-2 (Core i)	1.25	89.96	65.24	88.71	63.99	24.72
20%-2 (Core ii)	1.32	83.69	50.15	82.37	48.83	33.54
20%-3 (Core i)	1.25	85.27	59.92	84.02	58.67	25.35
20%-3 (Core ii)	1.32	77.65	59.03	76.33	57.71	18.62
10%-1 (Core i)	1.26	64.30	46.13	63.04	44.87	18.17
10%-1 (Core ii)	1.32	51.79	29.34	50.47	28.02	22.45
10%-2 (Core i)	1.21	72.62	49.62	71.41	48.41	23.00
10%-2 (Core ii)	1.25	85.25	61.84	84.00	60.59	23.41
10%-3 (Core i)	1.31	88.79	69.14	87.48	67.83	19.65
10%-3 (Core ii)	1.30	86.12	64.49	84.82	63.19	21.63
Con-1 (Core i)	1.81	78.29	73.59	76.48	71.78	4.70
Con-1 (Core ii)	3.08	89.00	84.31	85.92	81.23	4.69
Con-2 (Core i)	1.79	66.10	61.04	64.31	59.25	5.06
Con-2 (Core ii)	1.82	67.46	62.26	65.64	60.44	5.20
Con-3 (Core i)	3.11	97.00	87.66	93.89	84.55	9.34
Con-3 (Core ii)	3.14	69.69	55.37	66.55	52.23	14.32

Raw Laboratory Data Measured from Surface Soil Cores for the Determination of Physical Properties (taken during Final Sampling from all the Application Plots)

Plot	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of wet soil (g)	Wt. of oven dried soil (g)	Wt. of water in soil (g)
20%-2: Ah horizon	1.25	107.35	93.92	106.1	92.67	13.43
20%-2: Bm Horizon	1.83	104.27	97.92	102.44	96.09	6.35
20%-2: BC horizon	1.85	91.02	85.14	89.17	83.56	5.61
10%-2: Ah horizon	1.31	99.12	85.66	97.81	84.35	13.46
10%-2: Bm Horizon	9.65	106.3	100.83	96.65	91.18	5.47
10%-2: BC horizon	9.48	105.96	101.4	96.48	91.92	4.56
Con-3: Ah horizon	1.83	85.4	79.66	83.57	77.83	5.74
Con-3: Bm horizon	9.49	98.48	94.52	88.99	85.03	3.96
Con-3: BC horizon	9.48	106.02	101.92	96.54	92.44	4.1

Raw Laboratory Data Measured from Depth Soil Cores for the Determination of Physical Properties (taken during Final Sampling from all the Application Plots)

Plot	Wt. of dish (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of oven dried soil (g)	Wt. of ignited soil (g)	Wt. of organic matter (g)
20%-1 (Core i)	0.74	5.48	3.97	4.74	3.23	1.51
20%-1 (Core ii)	0.73	6.16	5.35	5.43	4.62	0.81
20%-2 (Core i)	0.74	5.42	4.73	4.68	3.99	0.69
20%-2 (Core ii)	0.74	5.87	4.83	5.13	4.10	1.04
20%-3 (Core i)	0.74	5.28	4.42	4.54	3.69	0.86
20%-3 (Core ii)	0.73	6.00	5.02	5.27	4.29	0.98
10%-1 (Core i)	0.74	5.95	5.22	5.21	4.48	0.73
10%-1 (Core ii)	0.74	5.23	3.73	4.49	2.99	1.50
10%-2 (Core i)	0.74	5.48	4.64	4.74	3.90	0.84
10%-2 (Core ii)	0.73	5.11	4.33	4.38	3.59	0.78
10%-3 (Core i)	0.74	5.42	4.81	4.68	4.07	0.61
10%-3 (Core ii)	0.74	5.30	4.91	4.56	4.17	0.39
Con-1 (Core i)	0.74	5.66	5.45	4.92	4.71	0.21
Con-1 (Core ii)	0.73	6.16	6.03	5.43	5.29	0.13
Con-2 (Core i)	0.73	6.56	6.13	5.83	5.40	0.43
Con-2 (Core ii)	0.74	5.53	5.11	4.79	4.37	0.42
Con-3 (Core i)	0.74	6.29	6.02	5.55	5.28	0.27
Con-3 (Core ii)	0.74	6.67	5.81	5.93	5.07	0.86

Raw Laboratory Data Measured from Surface Soil Cores for the Determination of Chemical Properties (taken during Final Sampling from all the Application Plots)

Plot	Wt. of dish (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of oven dried soil (g)	Wt. of ignited soil (g)	Wt. organic matter (g)
20%-2: Ah horizon	0.74	6.07	5.85	5.33	5.11	0.22
20%-2: Bm Horizon	0.74	6.10	6.00	5.36	5.26	0.10
20%-2: BC horizon	0.73	6.63	6.50	5.90	5.76	0.13
10%-2: Ah horizon	0.74	6.25	5.79	5.51	5.05	0.46
10%-2: Bm Horizon	0.73	6.46	6.37	5.73	5.63	0.09
10%-2: BC horizon	0.74	5.96	5.88	5.22	5.14	0.08
Con-3: Ah horizon	0.74	6.52	6.36	5.78	5.62	0.16
Con-3: Bm horizon	0.74	6.20	6.15	5.46	5.41	0.05
Con-3: BC horizon	0.74	5.90	5.83	5.16	5.09	0.07

Raw Laboratory Data Measured from Depth Soil Cores for the Determination of Chemical Properties (taken during Final Sampling from all the Application Plots)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.31	6.09	5.63	4.73	0.9	20.83
2	1.31	6.63	6.12	5.64	0.48	9.98
4	1.31	5.38	5.01	3.71	1.3	35.14
6	1.25	6.26	4.32	3.65	0.67	21.82
8	1.25	6.45	5.12	4.38	0.74	19.12
10	1.24	6.69	5.64	5.15	0.49	11.14
12	1.26	6.87	5.15	4.27	0.88	22.62
13	1.24	6.22	5.22	4.53	0.69	17.34
13	1.25	7.92	6.74	6.26	0.48	8.74
13	1.25	6.64	5.68	5.02	0.66	14.90
13	1.27	7.34	6.42	5.85	0.57	11.07

Raw Laboratory Data Measured from Surface Soil Samples of Plot 1:20%-1 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.25	6.68	6.3	5.42	0.88	17.43
2	1.25	6.05	5.57	4.54	1.03	23.84
4	1.31	6.01	5.72	5.2	0.52	11.79
6	1.26	6.45	5.66	5.24	0.42	9.55
8	1.25	6.49	5.99	5.45	0.54	11.39
10	1.25	6.63	5.52	4.89	0.63	14.75
12	1.25	6.62	5.49	4.73	0.76	17.92
14	1.24	6.7	5.54	5.15	0.39	9.07
15	1.24	6.2	4.99	4.42	0.57	15.20
17	1.25	6.98	5.01	4.3	0.71	18.88
19	1.25	6.75	5.17	4.77	0.4	10.20

Raw Laboratory Data Measured from Surface Soil Samples of Plot 2:10%-1 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.33	6.76	6.59	6.06	0.53	10.08
2	1.24	6.35	6.19	5.72	0.47	9.49
4	1.29	6.82	5.97	5.07	0.9	19.23
6	1.24	6.32	4.35	3.2	1.15	36.98
8	1.25	6.83	5.92	5.05	0.87	18.63
10	1.24	6.42	5.08	4.12	0.96	25.00
12	1.25	7.09	5.3	4.31	0.99	24.44
13	1.26	6.53	4.97	4.42	0.55	14.82
13	1.25	7.32	5.84	5.25	0.59	12.85
13	1.25	6.31	5.16	4.54	0.62	15.86
13	1.32	6.39	5.32	4.81	0.51	12.75

Raw Laboratory Data Measured from Surface Soil Samples of Plot 3:20%-2 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.28	7.57	7.44	7.06	0.38	6.17
2	1.25	6.23	5.77	5.15	0.62	13.72
4	1.25	6.36	6.09	4.95	1.14	23.55
6	1.25	5.79	3.81	2.82	0.99	38.67
8	1.26	6.78	5.74	5.22	0.52	11.61
10	1.24	6.65	5.59	4.82	0.77	17.70
12	1.24	6.19	5.53	4.98	0.55	12.82
13	1.25	6.3	5.45	4.89	0.56	13.33
13	1.26	6.4	5.25	4.52	0.73	18.30
13	1.31	6.57	5.47	4.81	0.66	15.87
13	1.25	6.64	4.16	3.2	0.96	32.99

Raw Laboratory Data Measured from Surface Soil Samples of Plot 4:20%-3 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.32	5.85	5.54	4.96	0.58	13.74
2	1.28	6.31	6.02	5.35	0.67	14.14
4	1.32	6.12	5.55	4.76	0.79	18.68
6	1.26	6.46	4.38	3.4	0.98	31.41
8	1.26	5.27	4.15	3.58	0.57	19.72
10	1.24	6.76	6.33	5.86	0.47	9.23
12	1.26	6.34	5.27	4.52	0.75	18.70
14	1.24	7.39	4.24	3.35	0.89	29.67
15	1.24	6.78	5.55	5.02	0.53	12.30
17	1.25	6.72	5.47	4.78	0.69	16.35
19	1.25	6.49	4.8	4.1	0.7	19.72

Raw Laboratory Data Measured from Surface Soil Samples of Plot 6:10%-2 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.24	6.33	6.06	5.62	0.44	9.13
2	1.25	6.12	6.03	5.81	0.22	4.60
4	1.25	6.46	5.87	5.26	0.61	13.20
6	1.24	6.33	5.64	5.28	0.36	8.18
8	1.26	7.54	6.48	5.91	0.57	10.92
10	1.26	7	6	5.05	0.95	20.04
12	1.24	6.39	5.32	4.87	0.45	11.03
14	1.26	6.63	5.21	4.9	0.31	7.85
15	1.26	6.37	5.37	4.88	0.49	11.92
17	1.26	6.71	5.5	4.88	0.62	14.62
19	1.25	7.78	7.05	6.69	0.36	6.21

Raw Laboratory Data Measured from Surface Soil Samples of Plot 7:10%-3 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.3	5.29	5.1	4.71	0.39	10.26
0	1.24	6.82	6.23	5.9	0.33	6.61

Raw Laboratory Data Measured from Surface Soil Samples of Plot 5:Control-1 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

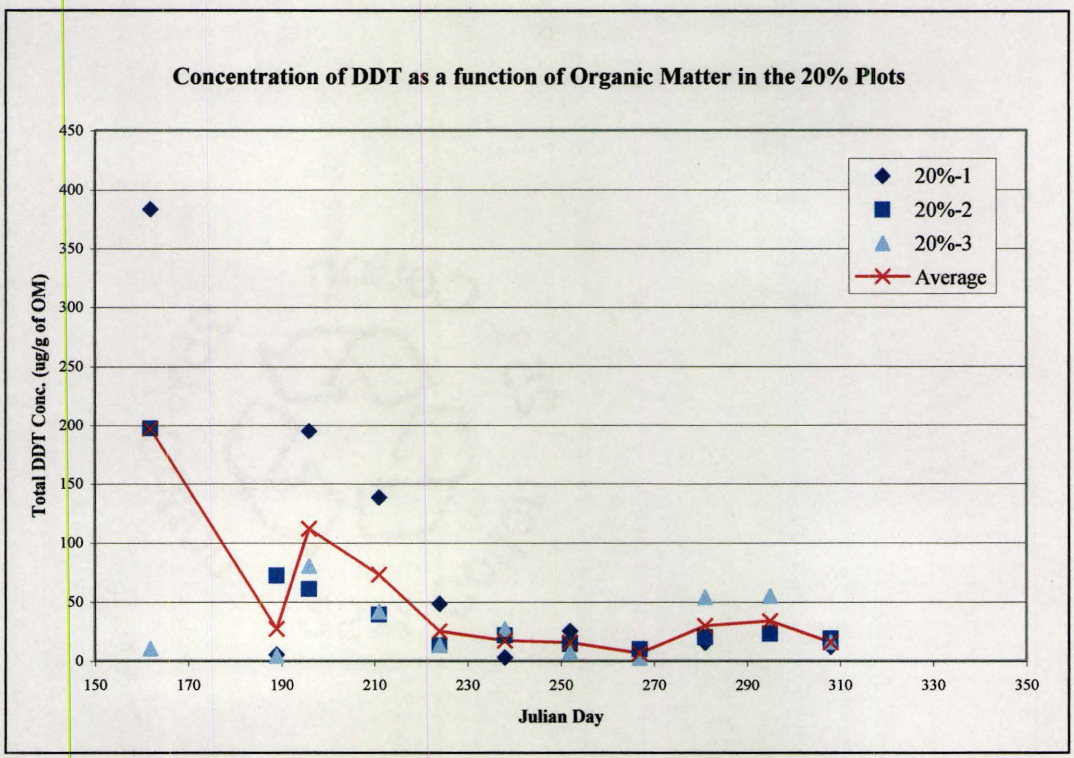
# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.31	6.44	6.24	5.8	0.44	8.92
0	1.25	6.12	5.92	5.35	0.57	12.21

Raw Laboratory Data Measured from Surface Soil Samples of Plot 8:Control-2 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis)

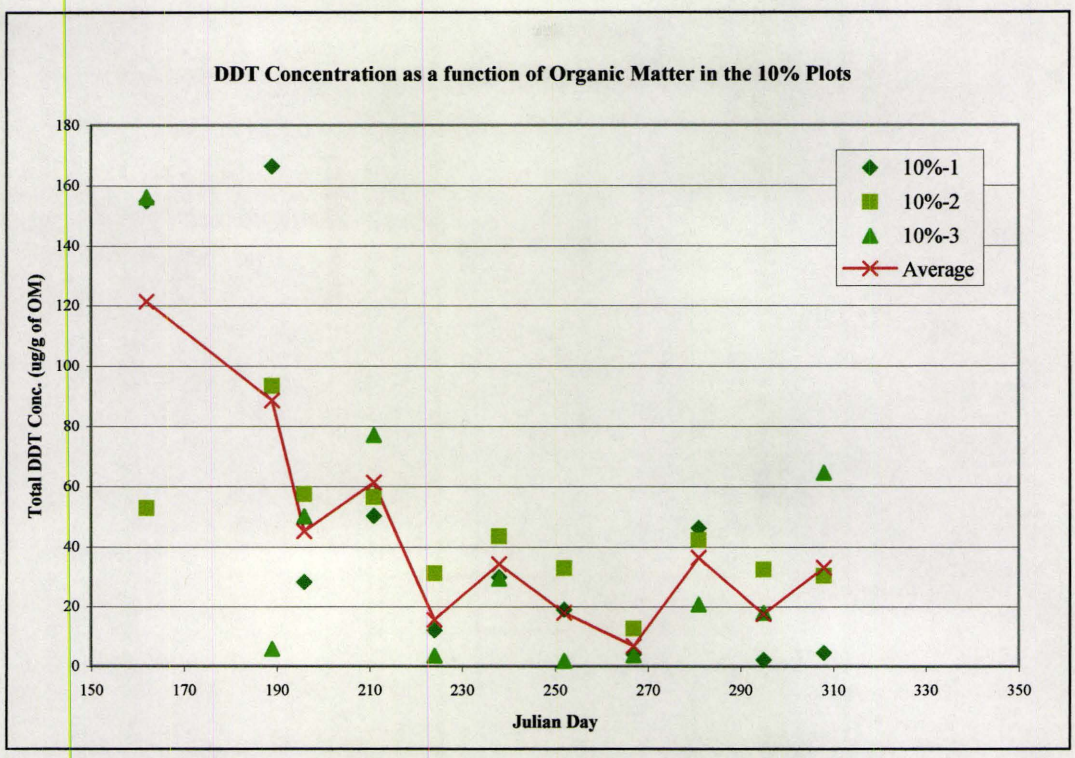
# of Pore Volumes Previously Applied	Wt. of dish (g)	Wt. of dish and wet soil (g)	Wt. of dish and oven dried soil (g)	Wt. of dish and ignited soil (g)	Wt. of Organic Matter (g)	Loss on Ignition (%)
0	1.31	5.99	5.75	5.2	0.55	12.39
0	1.24	4.78	4.53	3.65	0.88	26.75*

Raw Laboratory Data Measured from Surface Soil Samples of Plot 9:Control-3 for the Determination of %Loss on Ignition (Note: Measurements were performed on Remaining Soil Samples from the Analyses of DDT, DDE and DDD in April 2003. Samples were stored in the Refrigerator prior to Analysis (*Last Available Material in Jar Analyzed))

Appendix F: Graphs of DDT Concentration as a Function of Organic Matter versus Julian Day



Concentration of DDT in the 20% Application Plots, expressed as a function of Organic Matter vs. Julian Day.



Concentration of DDT in the 10% Application Plots, expressed as a function of Organic Matter vs. Julian Day.

Appendix G: In-Situ Moisture Content with Depth (measured with TDR system)

Depth (cm)	Plot 3:20%-2	Plot 6:10%-2	Plot 9:Control-3
Surface (VWC-core in lab)	48.5	38.6	19.8
10	22.5	23.2	9.1
20	19.7	16.3	10.0
30	16.4	12.5	10.0
40	13.6	12.5	10.3
50	14.5	11.5	8.6
60	11.7	10.4	8.7
70	11.2	10.4	9.6
80	9.6	10.8	9.1

Moisture Content with Depth Measured with TDR, from the Soil Profile during Final Sampling on November 4, 2002.

Appendix H: Raw Field Saturated Hydraulic Conductivity Data Measured with the Guelph Permeameter

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		20.2		
2	0.5	0.5	20.4	0.2	0.4
3	1.0	0.5	20.9	0.5	1.0
4	2.0	1	21.8	0.9	0.9
5	3.0	1	22.7	0.9	0.9
6	40	1	23.6	0.9	0.9
7	5.0	1	24.5	0.9	0.9
8	6.0	1	25.4	0.9	0.9
9	7.0	1	26.3	0.9	0.9
10	8.0	1	27.2	0.9	0.9

Field Saturated Hydraulic Conductivity Data for Plot 1: 20%-1 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		8.4		
2	0.5	0.5	9.0	0.6	1.2
3	1.0	0.5	9.5	0.5	1.0
4	1.5	0.5	10.4	0.9	1.8
5	2.0	0.5	11.1	0.7	0.7
6	3.0	1	12.2	1.1	1.1
7	40	1	13.3	1.1	1.1
8	5.0	1	14.5	1.2	1.2
9	6.0	1	15.5	1.0	1.0
10	7.0	1	16.6	1.1	1.1
11	8.0	1	17.7	1.1	1.1

Field Saturated Hydraulic Conductivity Data for Plot 2: 10%-1 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		30.0		
2	0.5	0.5	34.4	4.4	8.8
3	1.0	0.5	39.2	4.8	9.6
4	1.5	0.5	43.4	4.2	8.4
5	2.0	0.5	47.6	4.2	8.4
6	2.5	0.5	51.8	4.2	8.4
7	3.0	0.5	55.6	3.8	7.6
8	3.5	0.5	59.4	3.8	7.6

Field Saturated Hydraulic Conductivity Data for Plot 2: 10%-1 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		27.0		
2	1.0	1	22.3	0.3	0.3
3	2.0	1	22.6	0.3	0.3
4	3.0	1	23.0	0.4	0.4
5	40	1	23.4	0.4	0.4
6	5.0	1	23.7	0.3	0.3
7	6.0	1	24.1	0.4	0.4
8	7.0	1	24.4	0.3	0.3
9	8.0	1	24.6	0.2	0.2
10	9.0	1	25.0	0.4	0.4
11	10.0	1	25.3	0.3	0.3

Field Saturated Hydraulic Conductivity Data for Plot 3: 20%-2 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		9.9		
2	0.5	0.5	11.5	1.6	3.2
3	1.0	0.5	11.7	0.2	0.4
4	2.0	1	12.4	0.7	0.7
5	3.0	1	13.0	0.6	0.6
6	40	1	13.5	0.5	0.5
7	5.0	1	14.0	0.5	0.5
8	6.0	1	14.5	0.5	0.5
9	7.0	1	15.0	0.5	0.5
10	8.0	1	15.5	0.5	0.5
11	9.0	1	15.9	0.4	0.4
12	10.0	1	16.4	0.5	0.5

Field Saturated Hydraulic Conductivity Data for Plot 3: 20%-2 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		27.4		
2	0.5	0.5	27.5	0.1	0.2
3	1.0	0.5	27.7	0.2	0.4
4	2.0	1	28.2	0.5	0.5
5	3.0	1	28.6	0.4	0.4
6	40	1	29.0	0.4	0.4
7	5.0	1	29.3	0.3	0.3
8	6.0	1	29.7	0.4	0.4
9	7.0	1	30.1	0.4	0.4
10	8.0	1	30.4	0.3	0.3
11	9.0	1	30.7	0.3	0.3
12	10.0	1	31.1	0.4	0.4

Field Saturated Hydraulic Conductivity Data for Plot 4: 20%-3 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		31.4		
2	0.5	0.5	31.5	0.1	0.2
3	1.0	0.5	31.5	0	0
4	2.0	1	32.0	0.5	0.5
5	3.0	1	32.5	0.5	0.5
6	40	1	33.0	0.5	0.5
7	5.0	1	33.5	0.5	0.5
8	6.0	1	33.7	0.2	0.2
9	7.0	1	34.2	0.5	0.5
10	8.0	1	34.6	0.4	0.4

Field Saturated Hydraulic Conductivity Data for Plot 4: 20%-3 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		7.4		
2	0.5	0.5	8.9	1.5	3.0
3	1.0	0.5	10.3	1.4	2.8
4	1.5	0.5	11.6	1.3	2.6
5	2.0	0.5	12.8	1.2	2.4
6	2.5	0.5	14.0	1.2	2.4
7	3.0	0.5	15.3	1.3	2.6
8	3.5	0.5	16.5	1.2	2.4
9	4.0	0.5	17.8	1.3	2.6
10	4.5	0.5	19.0	1.2	2.4
11	5.0	0.5	20.3	1.3	2.6
12	5.5	0.5	21.6	1.3	2.6
13	6.0	0.5	23.0	1.4	2.8

Field Saturated Hydraulic Conductivity Data for Plot 5: Control-1 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		29.2		
2	0.5	0.5	30.1	0.9	1.8
3	1.0	0.5	31.0	0.9	1.8
4	1.5	0.5	33.1	2.1	4.2
5	2.0	0.5	35.5	2.4	4.8
6	2.5	0.5	37.9	2.4	4.8
7	3.0	0.5	40.3	2.4	4.8
8	3.5	0.5	42.7	2.4	4.8
9	4.0	0.5	45.1	2.4	4.8
10	4.5	0.5	47.6	2.5	5.0
11	5.0	0.5	50.1	2.5	5.0
12	5.5	0.5	52.3	2.2	4.4

Field Saturated Hydraulic Conductivity Data for Plot 5: Control-1 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		30.7		
2	0.5	0.5	31.2	0.5	1.0
3	1.0	0.5	32.1	0.9	1.8
4	1.5	0.5	32.9	0.8	1.6
5	2.0	0.5	33.6	0.7	1.4
6	2.5	0.5	34.3	0.7	1.4
7	3.0	0.5	34.9	0.6	1.2
8	40	1	36.1	1.2	1.2
9	5.0	1	37.3	1.2	1.2
10	6.0	1	38.3	1.0	1.0
11	7.0	1	39.5	1.2	1.2
12	8.0	1	40.6	1.1	1.1
13	9.0	1	41.7	1.1	1.1
14	10.0	1	42.8	1.1	1.1

Field Saturated Hydraulic Conductivity Data for Plot 6:10%-2 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		7.7		
2	0.5	0.5	10.0	2.3	4.6
3	1.0	0.5	12.2	2.2	4.4
4	1.5	0.5	14.5	2.3	4.6
5	2.0	0.5	16.8	2.3	4.6
6	2.5	0.5	19.1	2.3	4.6
7	3.0	0.5	21.4	2.3	4.6
8	3.5	0.5	23.6	2.2	4.4
9	4.0	0.5	25.7	2.1	4.2
10	5.0	1	29.8	4.1	4.1
11	5.5	0.5	31.7	1.9	3.8
12	6.0	0.5	33.8	2.1	4.2

Field Saturated Hydraulic Conductivity Data for Plot 6:10%-2 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		36.4		
2	0.5	0.5	36.7	0.3	0.6
3	1.0	0.5	37.4	0.7	1.4
4	1.5	0.5	38.2	0.8	1.6
5	2.0	0.5	38.8	0.6	1.2
6	3.0	1	40.0	1.2	1.2
7	40	1	41.2	1.2	1.2
8	5.0	1	42.4	1.2	1.2
9	6.0	1	43.6	1.2	1.2
10	7.0	1	44.8	1.2	1.2

Field Saturated Hydraulic Conductivity Data for Plot 7:10%-3 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		38.1		
2	0.5	0.5	40.8	2.7	5.4
3	1.0	0.5	43.5	2.7	5.4
4	1.5	0.5	46.1	2.6	5.2
5	2.0	0.5	48.6	2.5	5.0
6	2.5	0.5	51.1	2.5	5.0
7	3.0	0.5	53.5	2.4	4.8
8	3.5	0.5	55.7	2.2	4.4
9	4.0	0.5	58.0	2.3	4.6
10	4.5	0.5	60.3	2.3	4.6
11	5.0	0.5	62.4	2.1	4.2
12	5.5	0.5	64.7	2.3	4.6

Field Saturated Hydraulic Conductivity Data for Plot 7:10%-3 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		8.2		
2	1.0	1	12.0	3.8	3.8
3	1.5	0.5	14.0	2.0	4.0
4	2.0	0.5	15.8	1.8	3.6
5	2.5	0.5	17.7	1.9	3.8
6	3.0	0.5	19.6	1.9	3.8
7	3.5	0.5	21.5	1.9	3.8
8	4.0	0.5	23.5	2.0	4.0
9	4.5	0.5	25.3	1.8	3.6
10	5.0	0.5	27.1	1.8	3.6
11	5.5	0.5	29.2	2.1	4.2
12	6.0	0.5	31.0	1.8	3.6
13	6.5	0.5	33.0	2.0	4.0

Field Saturated Hydraulic Conductivity Data for Plot 8: Control-2 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		6.1		
2	0.5	0.5	8.9	2.8	5.6
3	1.0	0.5	11.4	2.5	5.0
4	1.5	0.5	13.9	2.5	5.0
5	2.0	0.5	16.4	2.5	5.0
6	2.5	0.5	18.8	2.4	4.8
7	3.0	0.5	21.4	2.6	5.2
8	3.5	0.5	23.9	2.5	5.0
9	4.0	0.5	26.4	2.5	5.0
10	5.0	1	31.5	5.1	5.1

Field Saturated Hydraulic Conductivity Data for Plot 8: Control-2 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		38.5		
2	0.5	0.5	41.0	2.5	5.0
3	1.0	0.5	43.2	2.2	4.4
4	2.0	0.5	47.1	3.9	3.9
5	2.5	0.5	49.0	1.9	3.8
6	3.0	0.5	50.8	1.8	3.6
7	3.5	0.5	53.0	2.2	4.4
8	4.0	0.5	54.7	1.7	3.4
9	4.5	0.5	56.9	2.2	4.4
10	5.0	0.5	58.8	1.9	3.8
11	5.5	0.5	60.6	1.8	3.6
12	6.0	0.5	62.6	2.0	4.0
13	6.5	0.5	64.8	2.2	4.4
14	7.0	0.5	66.4	1.6	3.2
15	7.5	0.5	68.5	2.1	4.2

Field Saturated Hydraulic Conductivity Data for Plot 9: Control-3 at a Depth of 15cm in the Ah horizon, Measured with a Guelph Permeameter on November 5, 2002.

Reading Number	Time	Time Interval (min)	Water Level in Reservoir (cm)	Water Level Change (cm)	Rate of Water Level Change, R_1 (cm/min)
1	0		38.0		
2	0.5	0.5	40.4	2.4	4.8
3	1.0	0.5	42.9	2.5	5.0
4	1.5	0.5	45.5	2.6	5.2
5	2.0	0.5	47.7	2.2	4.4
6	2.5	0.5	50.3	2.6	5.2
7	3.5	1	55.3	5.0	5.0
8	4.0	0.5	57.7	2.4	4.8
9	4.5	0.5	60.1	2.4	4.8

Field Saturated Hydraulic Conductivity Data for Plot 9: Control-3 at a Depth of 30cm in the Bm horizon, Measured with a Guelph Permeameter on November 5, 2002.

Appendix I: Calculations of Analysis of Variance (ANOVA) Test

	DDT Concentration	DDE Concentration	DDD Concentration
Average (μg/g)	33.6	29.0	3.14
Variance $(\mu g/g)^2$	2155	1146	12

Average and Variance Values of the Initial, Undisturbed Concentrations of DDT, DDE and DDD (Note: Taken from Table 4.8)

	DDT Concentration	DDE Concentration	DDD Concentration
Average (μg/g)	3.45	7.61	0.84
Variance $(\mu g/g)^2$	7.5	26	0.72

Average and Variance Values of the Late-Time Concentrations of DDT, DDE and DDD for the 20% Application Plots (Note: Average values taken from Table 4.9)

	DDT Concentration	DDE Concentration	DDD Concentration
Average (μg/g)	3.44	6.77	0.56
Variance $(\mu g/g)^2$	5.3	13.3	0.29

Average and Variance Values of the Late-Time Concentrations of DDT, DDE and DDD for the 10% Application Plots (Note: Average values taken from Table 4.10)

The following equations were taken from Statistical Problem Solving in Geography (McGrew and Monroe, 1993) and used to calculate the ANOVA test statistic (F). An F value that is approximately equal to one indicates that samples are from the same population and the between-group variance is approximately equal to the within-group variance. However, an F value that is greater than one indicates that these samples are from separate and distinct populations and the between-group variance is significantly larger than the within group variance.

$$F = \frac{MS_B}{MS_W}$$

where MS_B is the between-group mean squares and MS_W is the within-group mean squares. To calculate the between-group mean squares, the following three equations are used.

$$\overline{X}_T = \frac{\sum_{i=1}^{k} n_i \overline{X}_i}{N} \qquad (1)$$

where X_i is the mean of sample i, n_i is the number of observations in sample i, k is the number of groups or samples and N is the total number of observations in all samples.

$$SS_B = \sum_{i=1}^{k} n_i \left(\overline{X}_i - \overline{X}_T\right)^2 \qquad (2)$$

where SS_B is the between-group sum of squares, and X_T is the between-group mean squares as calculated in equation 1. The between-group mean squares (MS_B), is than calculated as follows:

$$MS_B = \frac{SS_B}{k-1} \qquad (3)$$

The within-group mean squares were then calculated using the following two equations:

$$SS_W = \sum_{i=1}^{k} (n_i - 1) s_i^2 \quad (4)$$

$$MS_W = \frac{SS_W}{N - k} \quad (5)$$

The calculated values of the F test statistic using the outlined equations 1 thru 5 are listed below. For DDT, DDE and DDD concentration the initial, undisturbed values, the late-time 20% values and the late-time 10% values were compared.

	MS_B	MS_W	F
DDT Concentration	6209	827	7.5
DDE Concentration	3251	450	7.2
DDD Concentration	41	4.9	8.4

Calculated F Test Statistic Values for the Analysis of Variance Test

Appendix J: Calculations for Mass of DDT, DDE and DDD with Depth

Depth Interval (cm)	Line Equation for the Concentration of DDT	Line Equation for the Concentration of DDE	Line Equation for the Concentration of DDD
0-11	$y = \frac{x - 3.465}{-0.1981}$	$y = \frac{x - 7.951}{-0.5}$	$y = \frac{x - 0.734}{-0.04618}$
12-35	$y = \frac{x - 1.778}{-0.04471}$	$y = \frac{x - 3.4799}{-0.09354}$	$y = \frac{x - 0.3218}{-0.008708}$

Line Equations for the Concentration of DDT in the Soil Profile of Plot 3:20%-2

Depth Interval (cm)	Line Equation for the Concentration of DDT	Line Equation for the Concentration of DDE	Line Equation for the Concentration of DDD
0-11	$y = \frac{x - 3.479}{-0.2185}$	$y = \frac{x - 7.5447}{-0.49934}$	$y = \frac{x - 0.7344}{-0.05413}$
12-35	$y = \frac{x - 1.45912}{-0.03492}$	$y = \frac{x - 2.91187}{-0.07817}$	$y = \frac{x - 0.19354}{-0.004958}$

Line Equations for the Concentration of DDT in the Soil Profile of Plot 6:10%-2

Depth Interval (cm)	Line Equation for the Concentration of DDT	Line Equation for the Concentration of DDE	Line Equation for the Concentration of DDD
0-11	$y = \frac{x - 33.643}{-3.05}$	$y = \frac{x - 29.038}{-2.571}$	$y = \frac{x - 3.14}{-0.2848}$
12-35	$y = \frac{x - 0.1406}{-0.003875}$	$y = \frac{x - 1.102}{-0.031}$	$y = \frac{x - 0.0099337}{-0.0002667}$

Line Equations for the Concentration of DDT in the Soil Profile of Plot 9:Control-3

Depth (cm)	Concentration of DDT (µg/g)	Concentration of DDE (µg/g)	Concentration of DDD (µg/g)
0	3.46	7.95	0.734
1	3.27	7.45	0.688
2	3.07	6.95	0.642
3	2.87	6.45	0.595
4	2.67	5.95	0.549
5	2.47	5.45	0.503
6	2.28	4.95	0.457
7	2.08	4.45	0.411
8	1.88	3.95	0.364
9	1.68	3.45	0.318
10	1.48	2.95	0.272
11	1.28	2.45	0.226
12	1.24	2.36	0.217
13	1.20	2.26	0.208
14	1.15	2.17	0.200
15	1.11	2.08	0.191
16	1.06	1.98	0.182
17	1.02	1.89	0.174
18	0.973	1.80	0.165
19	0.928	1.70	0.156
20	0.884	1.61	0.148
21	0.839	1.51	0.139
22	0.794	1.42	0.130
23	0.750	1.33	0.121
24	0.705	1.23	0.113
25	0.660	1.14	0.104
26	0.615	1.05	0.0954
27	0.571	0.954	0.0867
28	0.526	0.861	0.0780
29	0.481	0.767	0.0693
30	0.437	0.674	0.0606
31	0.392	0.580	0.0518
32	0.347	0.487	0.0431
33	0.302	0.393	0.0344
34	0.258	0.299	0.0257
35	0.213	0.206	0.0170

Calculated Concentrations of DDT, DDE and DDD with Depth below Plot 3:20%-2 (Calculated using the Provided Line Equations Above)

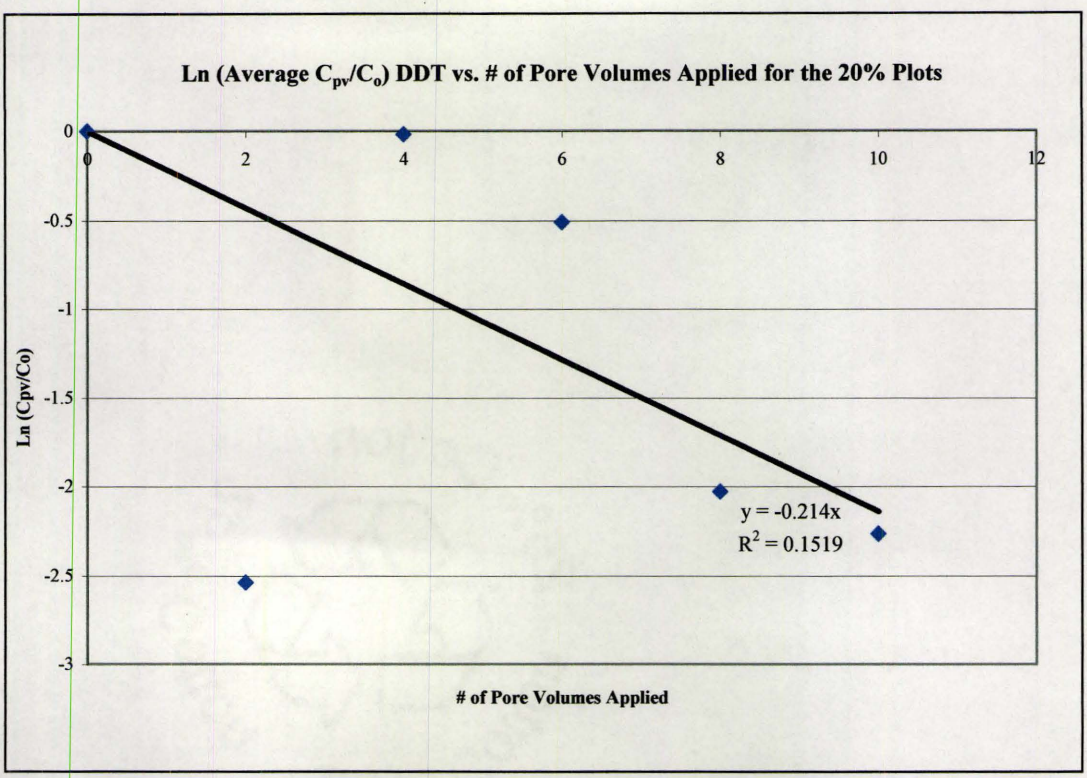
Depth (cm)	Concentration of DDT (µg/g)	Concentration of DDE (µg/g)	Concentration of DDD (µg/g)
0	3.48	7.54	0.734
1	3.26	7.04	0.680
2	3.04	6.55	0.626
3	2.82	6.05	0.572
4	2.60	5.55	0.518
5	2.39	5.05	0.464
6	2.17	4.55	0.410
7	1.95	4.05	0.355
8	1.73	3.55	0.301
9	1.51	3.05	0.247
10	1.29	2.55	0.193
11	1.07	2.05	0.139
12	1.04	1.97	0.134
13	1.00	1.89	0.129
14	0.970	1.82	0.124
15	0.935	1.74	0.119
16	0.900	1.66	0.114
17	0.865	1.58	0.109
18	0.830	1.50	0.104
19	0.796	1.43	0.0993
20	0.761	1.35	0.0944
21	0.726	1.27	0.0894
22	0.691	1.19	0.0845
23	0.656	1.11	0.0795
24	0.621	1.03	0.0745
25	0.586	0.958	0.06959
26	0.551	0.879	0.0646
27	0.516	0.801	0.0597
28	0.481	0.723	0.0547
29	0.446	0.645	0.0497
30	0.411	0.567	0.0448
31	0.377	0.489	0.0398
32	0.342	0.410	0.0349
33	0.307	0.332	0.0299
34	0.272	0.254	0.0250
35	0.237	0.176	0.0200

Calculated Concentrations of DDT, DDE and DDD with Depth below Plot 6:10%-2 (Calculated using the Provided Line Equations Above)

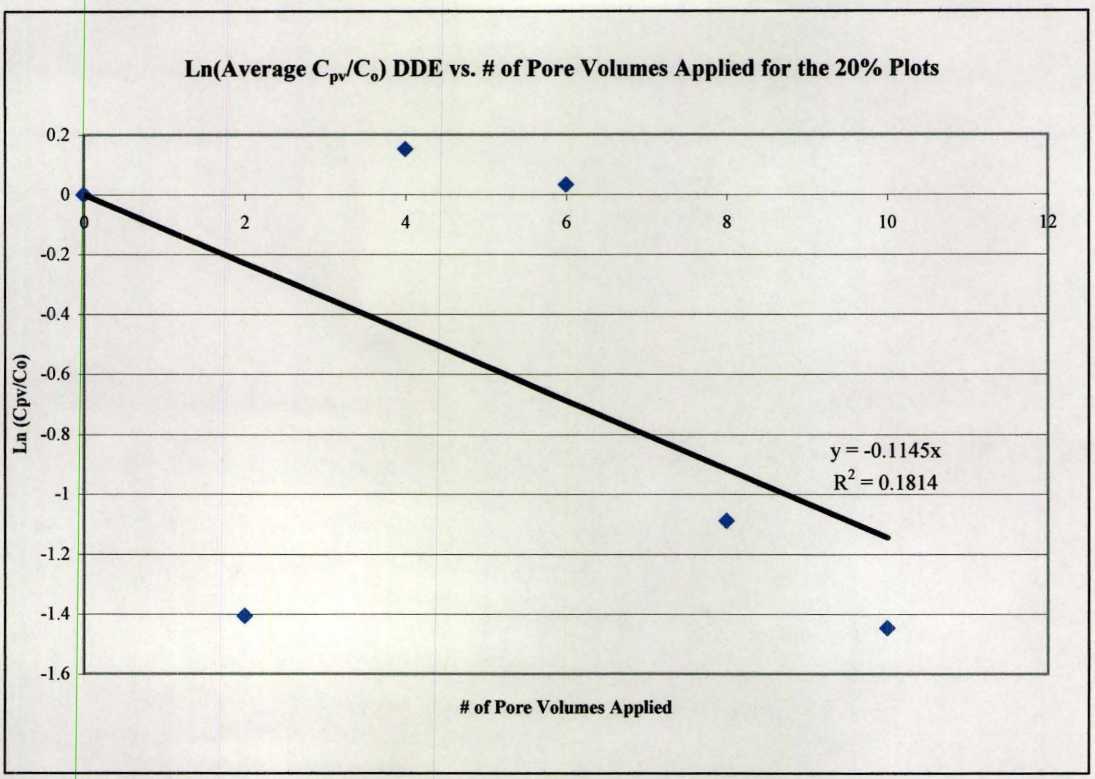
Depth (cm)	Concentration of DDT (µg/g)	Concentration of DDE (µg/g)	Concentration of DDD (µg/g)
0	33.6	29.0	3.14
1	30.6	26.5	2.85
2	27.5	23.9	2.57
3	24.5	21.3	2.28
4	21.4	18.7	2.00
5	18.4	16.2	1.72
6	15.3	13.6	1.43
7	12.3	11.0	1.15
8	9.24	8.47	0.862
9	6.19	5.90	0.577
10	3.14	3.33	0.292
11	0.098	0.761	0.0072
12	0.0941	0.73	0.00673
13	0.0902	0.699	0.00647
14	0.0863	0.668	0.00620
15	0.0825	0.637	0.00593
16	0.0786	0.606	0.00567
17	0.0747	0.575	0.00540
18	0.0708	0.544	0.00513
19	0.0670	0.513	0.00487
20	0.0631	0.482	0.00460
21	0.0592	0.451	0.00433
22	0.0553	0.42	0.00407
23	0.0515	0.389	0.00380
24	0.0476	0.358	0.00353
25	0.0437	0.327	0.00327
26	0.0398	0.296	0.003
27	0.0360	0.265	0.00273
28	0.0321	0.234	0.00247
29	0.0282	0.203	0.00220
30	0.0243	0.172	0.00193
31	0.0205	0.141	0.00167
32	0.0166	0.11	0.00140
33	0.0127	0.079	0.00113
34	0.00885	0.048	0.000866
35	0.00498	0.017	0.000599

Calculated Concentrations of DDT, DDE and DDD with Depth below Plot 9:Control-3 (Calculated using the Provided Line Equations Above)

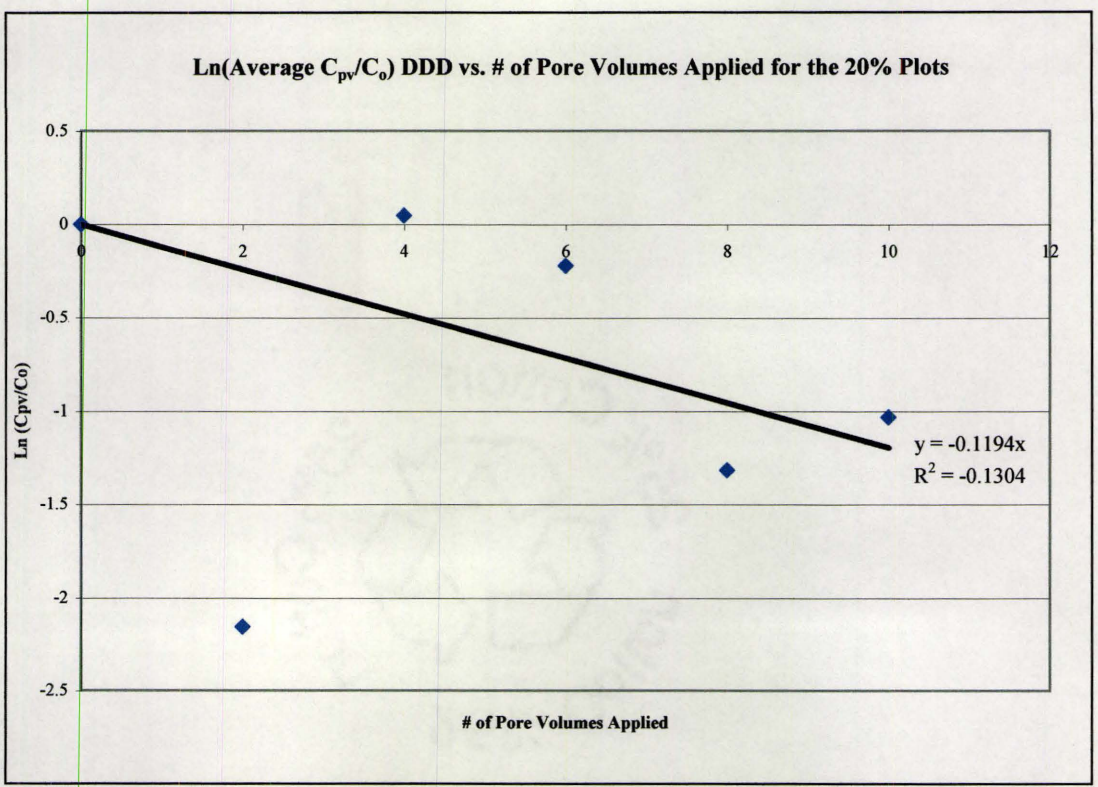
Appendix K: Early-Time Graphs of Ln (Average C_{pv}/C_o) vs. the Number of Pore Volumes of Cyclodextrin Solution Applied



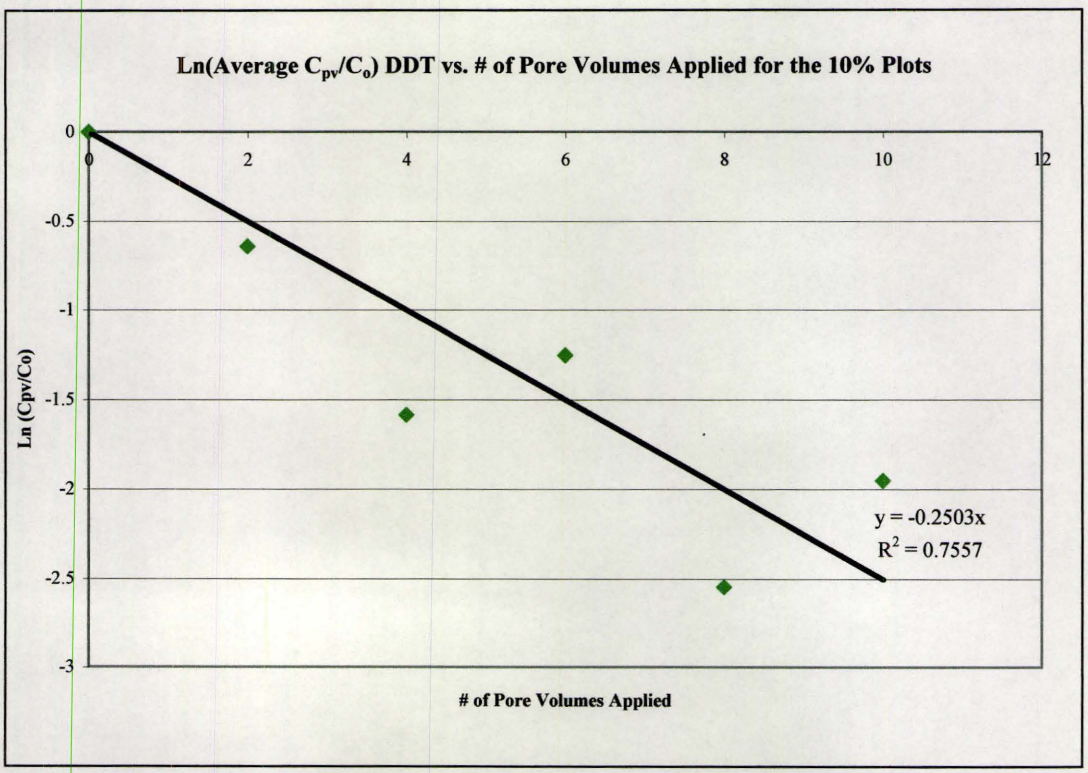
Early-Time Plot of Ln(Average C_{pv}/C_o) of DDT vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 20% Plots that was used for the Determination of an Early-Time $pv_{1/2}$



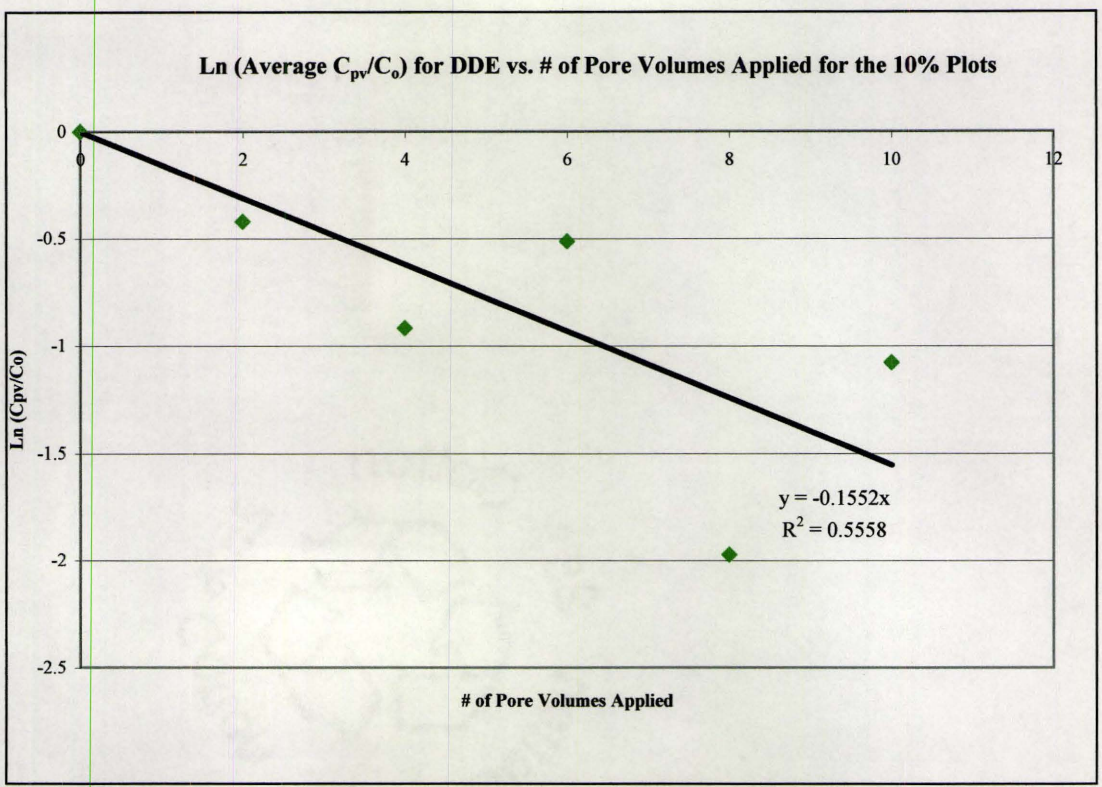
Early-Time Plot of Ln(Average C_{pv}/C_o) of DDE vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 20% Plots that was used for the Determination of an Early-Time $pv_{1/2}$



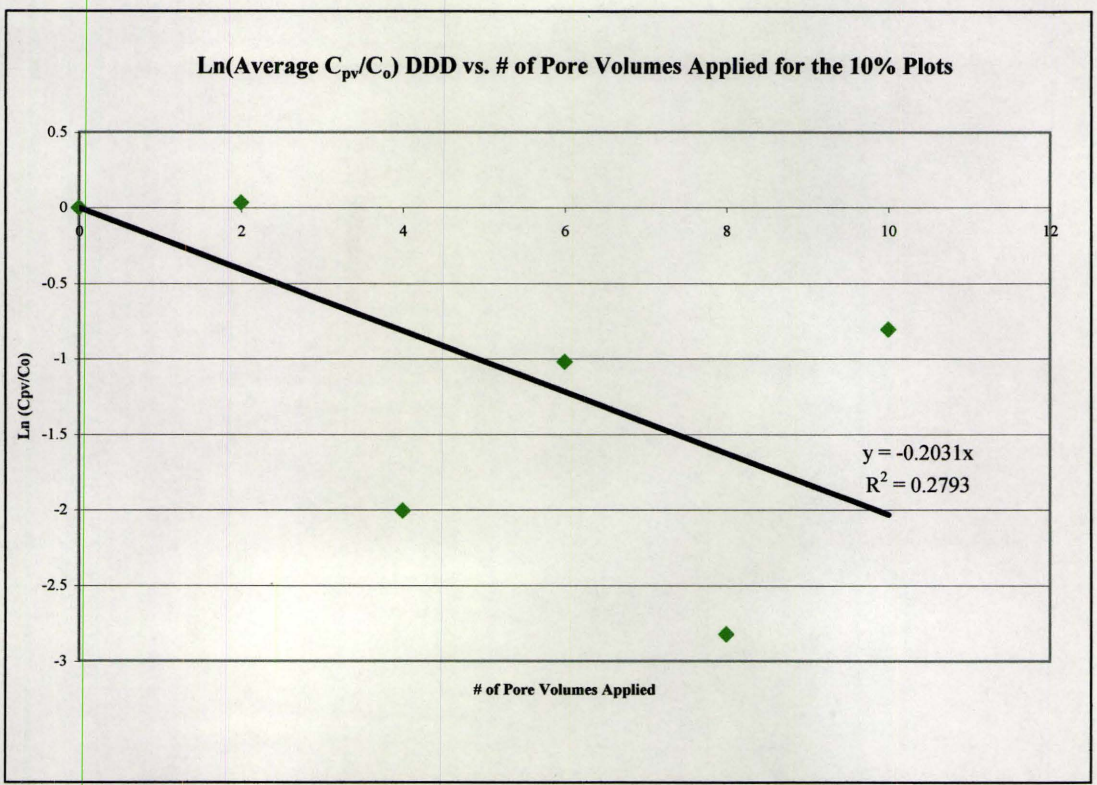
Early-Time Plot of Ln(Average C_{pv}/C_o) of DDD vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 20% Plots that was used for the Determination of an Early-Time $pv_{1/2}$



Early-Time Plot of Ln(Average C_{pv}/C_o) of DDT vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 10% Plots that was used for the Determination of an Early-Time $pv_{1/2}$



Early-Time Plot of Ln (Average C_{pv}/C_o) of DDE vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 10% Plots that was used for the Determination of an Early-Time $pv_{1/2}$



Early-Time Plot of Ln (Average C_{pv}/C_o) of DDD vs. Number of Pore Volumes of Cyclodextrin Solution Applied to the 10% Plots that was used for the Determination of an Early-Time $pv_{1/2}$

Appendix L: Soil Sampling Locations for HACH and DAPI Analyses

Date	Plot 1: 20%-1	Plot 2: 10%-1	Plot 3: 20%-2	Plot 4: 20%-3	Plot 5: Con-1	Plot 6: 10%-2	Plot 7: 10%-3	Plot 8: Con-2	Plot 9: Con-3
09-Sep-02	20	13	21	17	6	3	6	24	7
16-Sep-02	8	24	22	14	8	15	16	19	3
24-Sep-02	9	19	7	12	22	14	22	17	15
22-Oct-02	21	16	6	4	9	13	18	21	11

Soil Sampling Locations within the Remediation Grid for DAPI Staining and for HACH Kit Analysis (Sampling Locations refer to the grid numbers assigned as outlined in Figure 3.3)

Appendix M: HACH Analysis Method and Results

(Note: HACH Methods and Results were not reported due to the presence of suspected interference of colour with the spectophometric readings. It is recommended that methods which are more appropriate for the analysis of soil be used for further work in the determination of the concentration of the major ions in the system.)

Soil Sampling Procedures for HACH Analyses

Soil samples to be used for biological analysis with the HACH kit were taken on September 9, 17, and 24, 2002. Sample locations were randomly determined by the random number generator in Microsoft Excel 2000. Using the "RANDBETWEEN" function numbers between 1 and 25 were randomly generated to determine the sampling locations. The sampling procedure for the biological samples was similar to the procedure followed during DDT sampling. See Section 3.5 for further details. The single difference between the two sampling regimes was the amount of soil sampled. For DDT analysis a 120mL straight-sided amber jar was filled, while for biological sampling 60mL straight-sided amber jars were filled.

Spectrophotometer Analysis

A DR/2010 Spectrophotometer manufactured by the Hach Company was used to provide approximate measurements of the soil concentration of the following compounds: 1) Sulphate, 2) Sulphide, 3) Total Iron, 4) Ferrous Iron, and 5) Colour. This analysis involves the spectrophotometric analysis of water samples that have reagents added to them which react with the compound of interest. Hach methods are based on industry accepted methods (Hach Company, 1996-2003). Correct sampling, storage and preservation of a sample is critical for the accurate determination of a compound concentration.

As previously mentioned, generally the DR/2010 spectrophotometer is used to analyze water samples however in this case it was being used to analyze soil samples. As

such, sample manipulation was required prior to measurement with the unit. With water samples, a sample blank is used to provide a background concentration and then the sample with the added reagents is used for measurement of a compound concentration. The sample blank consisted of the decanted water from a soil sample without the added reagents. The unit has internal calibration curves for each parameter and when a program number is entered that calibration curve is accessed for reference against a measurement.

De-gassed Water

De-gassed water was used for the HACH kit analysis of both ferrous iron and sulphide concentration as it involved measuring the reduced form of the compound. Any oxygen present in the water could react with the compound and oxidize the sample and result in an underestimation of the compound concentration. Milli Q water was brought to a boil in a flask using a standard household-use microwave. Once the water had been boiled it was transferred into a heat resistant glass container that can withstand temperatures up to 140°C. The water was then left to cool for approximately two hours. The lid was removed and the top was covered with parafilm. Nitrogen gas was then bubbled through the water for half an hour in order to de-gas it. De-gassed water was always used within twenty-four hours.

Analysis for Ferrous Iron

Four soil samples of approximately 5grams each were weighed and immediately transferred to labeled centrifuge tubes and stoppered to differentiate between the replicates. 25mL of de-gassed Milli Q water was added to each centrifuge tube. The soil

and water mixture was acidified with 1mL of concentrated nitric acid to facilitate release of the ferrous iron from the soil matrix into the aqueous form. Vigorous shaking was completed for 1 minute to thoroughly mix samples and aid in the release of the compounds. Samples were then centrifuged with a Sorval centrifuge at 25000rpm for ten minutes to reduce the floating particulate matter. The HACH machine was turned on by pressing the ON button. The stored program number, 255, for the ferrous iron (Fe^{2+}) powder pillow was entered. The wavelength dial was then rotated until the display showed 510nm.

Once the samples were centrifuged, the first sample was decanted and placed into a 25mL sample cell. A ferrous iron powder pillow was added, the cell stoppered and then shaken several times. Then the HACH was used to time a three minute reaction period by pressing SHIFT TIMER. While the reaction was taking place, the sample blank was decanted from the centrifuge tube and placed into the second 25mL sample cell. The sides of the sample blank cell were wiped down with a kimwipe in order to remove any smudges or fingerprints which could interfere with the spectrophotometric reading. The cell was then placed into the cell holder and the light shield closed. Once the timer beeped signaling the end of the reaction period ZERO was pressed to zero the HACH with the sample blank. The sample blank was removed and kept for further use. The sides of the sample cell were cleaned with a kimwipe before it was placed into the cell holder. The ferrous iron content in mg/L was measured by pressing READ. Once the sample was measured it was emptied into a chemical waste container and the sample cell was rinsed three times with Milli Q water. The same procedure was used to determine

the ferrous iron content of the two remaining replicates. This procedure was completed for each soil sample collected for biological analyses.

Analysis for Sulfide

Four soil samples of approximately 5grams each were weighed and immediately transferred to labeled centrifuge tubes and stoppered to differentiate between the replicates. 25mL of de-gassed Milli Q water was added to each centrifuge tube. The soil and water mixture was acidified with 1mL of concentrated nitric acid to facilitate release of the sulfide from the soil matrix into the aqueous form. The sulfide reagents were also added to the samples before centrifuging to further facilitate the release of the sulfide from the soil into the water. One milliliter of Sulfide 1 Reagent was added to the three sample tubes in turn. The tubes were all stoppered and shaken for thirty seconds before 1mL of Sulfide 2 Reagent was added. The tubes were once again stoppered and shaken for thirty seconds. Samples were then centrifuged at 2500rpm for five minutes to reduce the floating particulate matter and to allow for the reaction of the Sulfide Reagents. The HACH machine was turned on by pressing the ON button. The stored program number, 690, for sulfide (S^{2-}) was entered. The wavelength dial was then rotated until the display showed 665nm.

Once the samples were centrifuged, the sample blank was decanted and placed into a 25mL sample cell. The sides of the cell were wiped down with a kimwipe in order to remove any smudges or fingerprints which could interfere with the spectrophotometric reading. The cell was then placed into the cell holder and the light shield closed. The

HACH was zeroed with the sample blank by pressing ZERO. The sample blank was removed and kept for further use. The first sample was then decanted and placed into the second 25mL sample cell. The sides of the sample cell were cleaned with a kimwipe before it was placed into the cell holder. The sulfide content in mg/L was measured by pressing READ. Once the sample was measured it was emptied into a chemical waste container and the sample cell was rinsed three times was Milli Q water. The same procedure was used to determine the sulfide content of the two remaining replicates. This procedure was completed for each soil sample collected for biological analyses.

Analysis for Total Iron

Four soil samples of approximately 5grams each were weighed and immediately transferred to labeled centrifuge tubes to differentiate between the replicates. 25mL of Milli Q water was added to each centrifuge tube. The soil and water mixture was acidified with 0.1mL of concentrated nitric acid to facilitate release of the sulfate from the soil matrix into the aqueous form. As this analysis is pH dependent the pH of the solution was monitored using pH paper to ensure that it was between 3 and 5. Vigorous shaking was completed for 1 minute to thoroughly mix samples and aid in the release of the compounds. Samples were then centrifuged at 2500rpm for ten minutes to reduce the floating particulate matter. The HACH machine was turned on by pressing the ON button. The stored program number, 265, for the iron (Fe) Ferro Ver powder pillow was entered. The wavelength dial was then rotated until the display showed 510nm.

Once the samples were centrifuged, the first sample was decanted and placed into a 10mL sample cell. The Cell Riser was inserted that is used with the 10mL sample cells. The contents of a Ferro Ver Iron Reagent Powder Pillow were added, the cell stoppered and then shaken several times. Then the HACH was used to time a three minute reaction period by pressing SHIFT TIMER. While the reaction was taking place, the sample blank was decanted from the centrifuge tube and placed into the second 10mL sample cell. The sides of the sample blank cell were wiped down with a kimwipe in order to remove any smudges or fingerprints which could interfere with the spectrophotometric reading. The cell was then placed into the cell holder and the light shield closed. Once the timer beeped signaling the end of the reaction period ZERO was pressed to zero the HACH with the sample blank. The sample blank was removed and kept for further use. The sides of the sample cell were cleaned with a kimwipe before it was placed into the cell holder. Within thirty minutes after the timer beeped the iron content in mg/L was measured by pressing READ. Once the sample was measured it was emptied into a chemical waste container and the sample cell was rinsed three times with Milli Q water. The same procedure was used to determine the iron content of the two remaining replicates. This procedure was completed for each soil sample collected for biological analyses.

Analysis for Sulfates

Four soil samples of approximately 5grams each were weighed and immediately transferred to labeled centrifuge tubes to differentiate between the replicates. 25mL of

Milli Q water was added to each centrifuge tube. The soil and water mixture was acidified with 1mL of concentrated nitric acid to facilitate release of the sulfate from the soil matrix into the aqueous form. Vigorous shaking was completed for 1 minute to thoroughly mix samples and aid in the release of the compounds. Samples were then centrifuged at 2500rpm for ten minutes to reduce the floating particulate matter. The HACH machine was turned on by pressing the ON button. The stored program number, 680, for the sulfate (SO_4^{2-}) powder pillow was entered. The wavelength dial was then rotated until the display showed 450nm.

Once the samples were centrifuged, the first sample was decanted and placed into a 25mL sample cell. The contents of a Sulfa Ver 4 Sulfate Reagent Powder Pillow were added, the cell stoppered and then shaken several times. Then the HACH was used to time a five minute reaction period by pressing SHIFT TIMER. While the reaction was taking place, the sample blank was decanted from the centrifuge tube and placed into the second 25mL sample cell. The sides of the sample blank cell were wiped down with a kimwipe in order to remove any smudges or fingerprints which could interfere with the spectrophotometric reading. The cell was then placed into the cell holder and the light shield closed. Once the timer beeped signaling the end of the reaction period ZERO was pressed to zero the HACH with the sample blank. The sample blank was removed and kept for further use. The sides of the sample cell were cleaned with a kimwipe before it was placed into the cell holder. Within five minutes after the timer beeped the sulfate content in mg/L was measured by pressing READ. Once the sample was measured it was emptied into a chemical waste container and the sample cell was rinsed three times with

Milli Q water. The same procedure was used to determine the sulfate content of the two remaining replicates. This procedure was completed for each soil sample collected for biological analyses.

Application Plot	Sulfide Conc. (mg/L)	Sulfate Conc. (mg/L)	Ferrous Iron Conc. (mg/L)	Total Iron Conc. (mg/L)
20%-1	0.000	0.00	0.000	0.27
20%-2	0.006	9.33	0.223	0.29
20%-3	0.022	0.33	0.037	0.34
10%-1	0.095	0.33	0.093	0.29
10%-2	0.000	0	0.237	0.34
10%-3	0.052	0	0.10	0.32
Control-1	0.003	2.67	0.010	0.12
Control-2	0.000	0	0.437*	0.25
Control-3	NA	0	NA	0.24

Sulfide, Sulphate, Ferrous Iron and Total Iron Concentrations of the Application Plots (* Note: Suspected Erroneous Value due to Interference of Floating Particulate Matter)