# A FIELD AND MODELING STUDY OF DDT

# A FIELD AND MODELING STUDY OF DDT IN SOIL AND GROUNDWATER FOLLOWING *IN-SITU* SOIL REMEDIATION

By

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# Abstract

The shallow soils of a former orchard area in Point Pelee National Park, near Leamington, Ontario, Canada have elevated concentrations of chlorinated pesticides above the regulatory limits. Previous studies in this area have shown that the DDT, DDE and DDD are highly persistent with an estimated half-life of DDT in the range of 15-30 years. In 2002 a pilot-scale field remediation experiment involving the application of cyclodextrin was conducted. This experiment resulted in substantial decrease of DDT, DDE and DDD concentrations in the upper soil layer within the remediation grid. Soil samples were collected within the treatment plots a year after the cyclodextrin application was completed to assess any further changes in concentrations of DDT, DDE and DDD. Groundwater samples were collected in the vicinity of the soil remediation grid which provided DDT, DDE and DDD concentrations in groundwater to assess the vertical mobilization of the compounds. Mass balance of the "soil – groundwater" system was calculated in order to estimate the degradation rate of DDT within the remediation zone. The 2-D unsaturated/saturated flow and solute transport numerical model "HYDRUS 2-D" was used to gain a better estimation of DDT, DDE and DDD mass and distribution in groundwater. The effectiveness of cyclodextrin application for remediation of DDT contaminated soils was assessed. After remediation treatments had stopped, there was no indication of further degradation of DDT and its metabolites in the upper layer of soil. The groundwater concentration of DDT, DDE and DDD near the remediation grid was 10-100 times higher than background value. This increase in groundwater concentration is a direct indication of DDT, DDE and DDD mobilization by cyclodextrin. The estimates of total mass of DDT in groundwater are less than 1% of mass leached from the soil. It was concluded that the application of cyclodextrin promoted enhanced co-metabolic biodegradation of DDT and it metabolites DDE and DDD. The estimated half-life for the displaced DDT was less than 2 months. This work demonstrates that cyclodextrin can be a highly effective agent for remediation of DDT contaminated soils.

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# 1. Introduction and Background Information

## *1.1 Introduction*

DDT was a miracle insecticide due to its high effectiveness and low cost. It was used worldwide from the 1940's for controlling insect vector-transmitted diseases, and for agricultural purposes. DDT was so effective that even 30 years after it was banned in USA, Canada and other countries, debates about "should it be banned or not?" still arise (Dini, J.W. 1999a; Dini, J.W. 1999b). The scales tipped with an enormous amount of research indicating harmful effects of DDT on living organisms (Carson, 1962; WHO, 1979; CCME, 1999; ATSDR, 2002). Loss of DDT from soil occurs at a very slow rate. Its primary daughter products, DDE and DDD, are also toxic. All three chemicals have low water solubility, persist in the environment and tend to accumulate in the upper soil layer (Howard and Meylan, 1997).

Point Pelee National Park (PPNP) is one of Canada's 18 National Parks. It was established as a Park in 1918 to protect and preserve the unique association of plants and animals, which could not be found anywhere else in Canada (Point Pelee National Park, 1982). Some commercial, agricultural and residential land-use activities continued in the Park until the late 1960's to after 2000. Applications of DDT accompanied agricultural and residential activities until about 1970 (Crowe et al., 2002). Even though there has not been any additional input of DDT to PPNP in the past 35 years, the residues of this pesticide and its metabolites are still found in the soil at levels above the regulatory limits

(Crowe et al.; 2002, Marenco, 2002; Badley, 2003) placing Park staff, visitors and wildlife under potential health risk.

A number of methods of remediation of soils and groundwaters contaminated with DDT and its derivatives have been proposed. Those methods include biodegradation (Aislibie et al., 1997; Corona-Cruz, 1999), creating anaerobic conditions by flooding (Guenzi and Beard, 1968; Guenzi et al., 1971; Spencer et al., 1996; Aislibie et al., 1997; Corona-Cruz, 1999), alternating aerobic and anaerobic conditions (Aislibie et al., 1997), enhanced solubilization/mobilization by surfactants (Kile and Chiou, 1989) and enhanced solubilization by cyclodextrins (Wang and Brusseau, 1993; Brusseau et al., 1994; McCray and Brusseau, 1998).

Cyclodextrins are cyclic oligosaccharides that are produced by enzymatic degradation of starch by bacteria. This compound, when dissolved in water, enhances the solubility of low-polarity, relatively insoluble organic molecules. Thereby, it has the potential to clean up soils and groundwater contaminated with such contaminants as DDT and its metabolites (Wang and Brusseau, 1993; Brusseau et al., 1994; McCray and Brusseau, 1998; etc.).

## *1.2 DDT and its Metabolites*

### 1.2.1 The History of DDT

DDT is an organochlorine insecticide which saved millions lives from fatal diseases such as malaria, typhus etc. It was also used worldwide for agriculture control of unwanted pest.

DDT was synthesized in 1874 in Germany by a graduate student named Othmar Zeidler as a part of his doctoral research (Friedman, 1992). Several decades later in 1938 Paul Müller revealed its insecticidal properties for his discovery in 1948 he received the Nobel Prize (Boul, 1994). In the beginning, DDT was used for the control of insect vector-transmitted diseases, such as malaria and typhus. After World War II, DDT was a prevalent insecticide for agricultural, residential, recreational and public health applications due to its low cost, effectiveness, and persistence in the environment.

DDT was never manufactured in Canada; it was imported from the USA. The production of DDT between 1945 and 1983 was approximately 1.5 million tonnes in North America (CCME, 1999).

DDT was treated as a miracle pesticide until the book "Silent Spring" written by Rachel Carson (1962) changed it to poison. She revealed to the world the harmful effects of DDT on the environment. DDT was closely studied in terms of its toxicity. This pesticide is a killer not only for unwanted insects, but it affects birds, animals and humans in many different ways. It may cause liver cancer, and damage nervous and reproductive systems (WHO, 1979; CCME, 1999; ATSDR, 2002). DDT and its metabolites concentrate in living organisms as a result of adsorption from water, filtering out by algae

containing high amount of these pesticides, or biological magnification, that is, progressive accumulation in different steps of a food chain (WHO, 1979; Harris et al., 2000).

As a result of environmental and human health concerns the United States banned DDT in 1972. In Canada all uses of DDT were suspended in 1985, and existing stocks were permitted to be used until December 31, 1990 (CCME, 1999). Despite the severe restrictions and bans, chemical factories in the US still continued to manufacture and export DDT to Third World countries, because in many tropical countries DDT is the primary tool in the suppression of mosquito-born diseases such as malaria and yellow fever (Boul, 1994; Dini, 1999a; Dini, 1999b).

### 1.2.2 Physical and Chemical Properties of DDT, DDE and DDD

The term DDT (dichlorodiphenyltrichloroethane) is commonly applied to 1,1,1 – trichloto-2,2-bis(*p*-chlorophenyl)ethane - the isomer *p,p'*-DDT, and to its isometric forms, including *o,p'*-DDT and *m,p'*-DDT (CCME, 1999). There are two primary metabolites of DDT: DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane) (Table 1.1). The chemical structures of these compounds are presented in Figure 1.1 (Howard and Meylan, 1997).

DDT is a white crystalline powder that has very low solubility in water (0.025-0.085mg/L [Howard and Meylan, 1997]; 3μg/L [CCME, 1999]), is strongly hydrophobic ($\log K_{ow}$=6.91 [Howard and Meylan, 1997]; $\log K_{ow}$=6.0 [CCME, 1999]), and has high

solubility in organic solvents such as ethanol (20g/L [CCME, 1999]) or acetone (580g/L [CCME. 1999]). DDE and DDD have notably higher water solubilities, 0.12-0.14mg/L (Howard and Meylan, 1997) and 0.09-0.1mg/L (Howard and Meylan, 1997), respectively. The other properties of DDE and DDD are substantially similar to the chemical, and physical properties of DDT.

Depending on soil type, climatic conditions, and soil binding the half-life for DDT varies from several days in flooded soils under anaerobic conditions, to 15 years in dry soils under aerobic conditions (Boyce, 1998; Corona-Cuz, 1999; CCME, 1999). DDT breakdown in the environment follows a near first-order kinetic model, however total loss is more complex with degradation of the daughter products DDE and DDD, and therefore a first-order model can be inappropriate (Boul, 1995).

| Abbrevation | Name | Formula | Full Name |
|---|---|---|---|
| DDT | Dichloro-Diphenyl-Trichloro-Ethane | $C_{14}H_9Cl_5$ | 1,1,1-trichloro-2,2-bis[ρ-chlorophenyl]-ethane |
| DDE | Dichloro-Diphenyl-Dichloro-Ethylene | $C_{14}H_8Cl_4$ | 1,1′-dichloro-2,2-bis[chlorophenyl]-ethylene |
| DDD | Dichloro-Diphenyl-Dichloro-Ethane | $C_{14}H_{10}Cl_4$ | 1,1′-dichloro-2,2-bis[ρ-chlorophenyl]-ethane |

**Table 1.1: Chemical Identity of DDT, DDE and DDD**

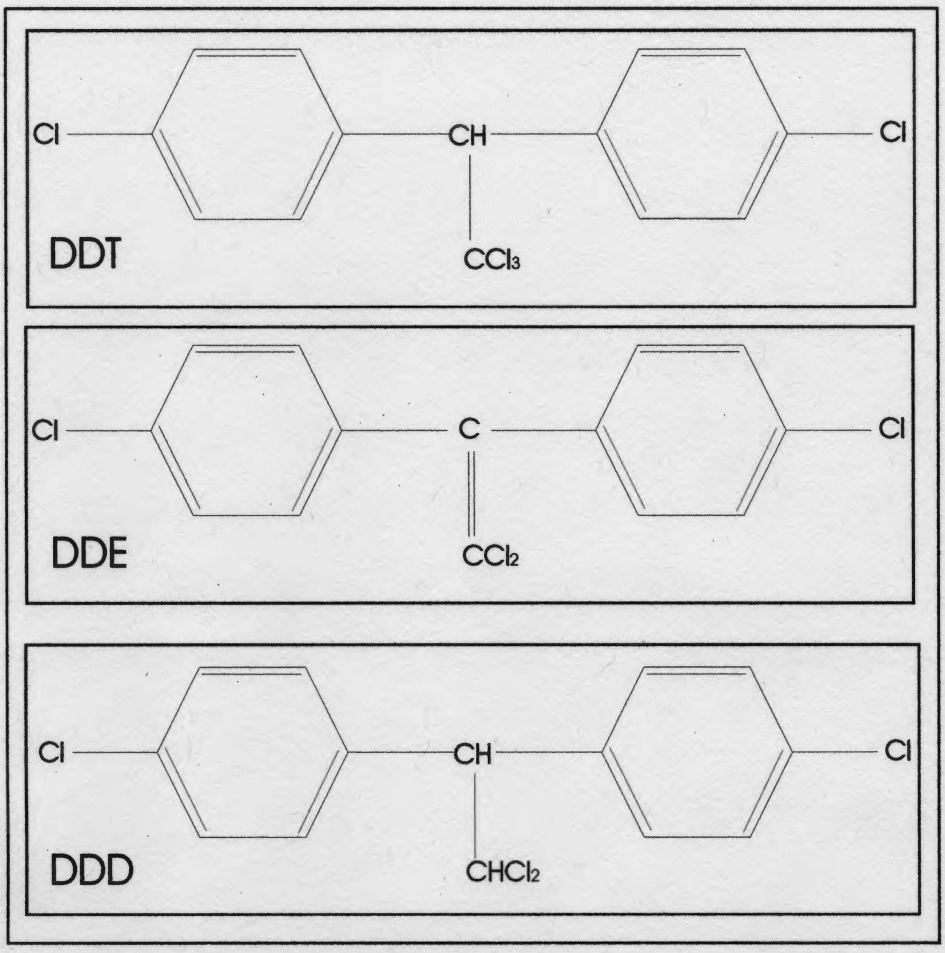


**Figure 1.1: The Chemical Structures of DDT, DDE and DDD**

### 1.2.3 Degradation of DDT in Soils

The loss of DDT residues is very slow. It occurs through different processes including runoff, volatilization, wind erosion, photolysis, chemical aerobic and anaerobic degradation and biodegradation (Boul, 1995; Woodwell et al.1971). Due to extremely low solubility in water, DDT and its primary breakdown products DDE and DDD are highly

persistent in soils. The rate of disappearance becomes even slower as the proportion of DDE in total residues increases (Boul et al., 1994). The degradation of DDT and its metabolites involves both biotic and abiotic factors (Boul, 1995) and it is difficult to separate these two factors.

Mainly DDT degrades by dechlorination to DDE and DDD. There are two primary pathways: DDT → DDE → DDD and DDT → DDD (Corona-Cruz, 1999). The DDT conversion to DDE occurs under aerobic conditions, it is basically a chemical process with some biodegradation (Guenzi and Beard, 1976), also DDE forms through photochemical reactions in the presence of sunlight or through dechlorination in bacteria and animals (Aislabie, 1997). The rate of this process is higher with temperature increase and the presence of water (Guenzi and Beard, 1976).

The formation of DDD occurs by dechlorination under anaerobic conditions through nucleophilic reduction of the trichloromethyl (Guenzi and Beard, 1967; Aislabie et al., 1997). Some research showed that creating anaerobic conditions in soil by flooding allows chemical and microbial degradation of DDT directly to DDD, preventing formation of DDE (Guenzi and Beard, 1968; Spencer et al., 1996; Corona-Cruz et al., 1999). The reduction of DDE and DDD continues during the aerobic phase after anaerobic conditions through ring cleavage reaction, hence the coupled anaerobic-aerobic system can be effective in the degradation of DDT and its primary daughter products (Corona-Cruz et al., 1999).

Binding properties of DDT and metabolites are relatively low (Khan, 1982). Due to their hydrophobic properties, these compounds are more likely to be weakly bound

with soil components (Boul, 1995), therefore they have high extractability from soils. Hydrophobic bonding is the major binding mechanism, where DDT and its metabolites associate with non-polar organic matter, rather than with polar water content of the soil (Boul, 1995). The DDT recovery is higher in moist soils than in dried soils (Boul, 1995).

### 1.2.4 DDT in Groundwater

DDT is highly persistent in soils (Hitch and Day, 1992). It has low water solubility and does not readily leach to groundwater. The commonly observed lower DDT concentrations in the top 5cm of soil are explained as dilution by bioturbation of soil particles from dead plant matter, and wind-blown input rather than leaching (Boul et al., 1994). The main factors affecting pesticide movement are physical properties of the soil, and climatic conditions (Bailey and White, 1970).

There are three main ways pesticides move through the unsaturated zone to groundwater: (1) transport in the dissolved phase; (2) transport in the gaseous phase; and (3) facilitated transport (Yaron, 1989). DDT and its metabolites have low water solubility (Howard and Meylan, 1997, CCME, 1999), therefore the mass transport in the dissolved phase is relatively unimportant. Diffusion of organic molecules is a slow process even with high moisture content (Yaron, 1989), hence it is unlikely that groundwater contamination with DDT will be substantially affected by this process, unless groundwater flow is equal to 0, e.g. clay.

Volatilization of chemicals depends on the vapor pressure which for DDT is relatively low ($1.60\times10^{-7}$mm Hg at 20°C [Howard and Meylan, 1997]). Loss of DDT to the vapor phase in terms of contamination of groundwater is likely to be insignificant. The predominant mechanism of DDT movement to groundwater is transport in the adsorbed phase (facilitated transport). DDT is strongly adsorbed by clay minerals and organic matter that enhances its solubility and hence downward movement (Boul, 1995).

Although these transport mechanisms are relatively slow, due to high persistence in soil over long period of time DDT can reach groundwater and cause contamination of sources of drinking water. U.S. Geological Survey (USGS, online) reviewed 974 studies on pesticides in groundwater on the area of the United States; according to their research concentrations of pesticides are commonly low and seldom exceed water-quality standards. They sampled about 3,000 wells for DDT concentration and DDT was detected in 3% of the wells.

## *1.3 Point Pelee National Park*

### 1.3.1 Geographical and Historical Information about PPNP

Point Pelee is one of Canada's 18 National Parks. It is located in southwestern Ontario about ten kilometers south of Leamington (Figure 1.2) and is the most southerly location of main land Canada. Due to its geographical position and its position within Lake Erie, a unique association of plants and animals has been established within this place which is not found anywhere else in Canada. Point Pelee was established as a Park in 1918 to protect and preserve the unique plants and animals of the area (Point Pelee National Park, 1982). The Park is a V-shaped cuspate of sand (Figure 1.3) which was built 7,000 to 10,000 years ago on top of the Pelee Moraine. Changes in glacial and post-glacial lake levels and subsequent rise in water levels resulted in deposition of sands that formed the barrier bars which are composed of shoreface and aeolian sands (Crowe et al., 2004) The Park is about 16 $km^2$, is the smallest national park of Canada, and the most of the area is covered by wetlands (Point Pelee National Park, 1982). Point Pelee is internationally known for its spring and fall migration of birds. Thousands of visitors come to the Park each year.

After establishing the Park in 1918, some of commercial, agricultural and residential land use continued for several decades: apple orchards and vegetable fields until the late 1960's, houses, summer cottages and campgrounds until today, and trailer parks until the 1960's (Crowe et al., 2002).


**Figure 1.2: Location of Point Pelee National Park** (online source: http://www.pc.gc.ca/pn-np/on/pelee/visit/visit1_E.asp, received May 26, 2004)

**Figure 1.3: Point Pelee Peninsular** (online source: http://www.pc.gc.ca/pn-np/on/pelee/index_e.asp, received May 26, 2004)

### 1.3.2 DDT in PPNP

From 1948 to 1967 DDT was used in Point Pelee National Park for mosquito control in recreational areas and pest-control in the apple orchards and vegetable fields (Crowe et al., 2002). It was applied as a particulate spray or as "toss" bombs (Marenco, 2002). During the mid-1990's researchers from the University of Windsor discovered unexpected high levels of DDT and its metabolites in reptiles and amphibians (Crowe et al., 2002). Further investigations revealed high levels of DDT in several locations within PPNP, some of them far above the soil quality guidelines (Crowe, 1999, Marenco, 2002).

Crowe et al. (2002) compiled results of previous studies done in PPNP, related to DDT contamination. The relation of concentrations of DDT, DDE and DDD to soil types, former land-use and hydrological variation was investigated. The lowest concentration of DDT was found in the saturated marsh sediments, where DDT primary degrades to DDD under anaerobic conditions. The highest concentration of DDT and its metabolites was discovered within former agricultural areas (apple orchards and vegetable fields). These areas have drier soil condition, and DDT primary degrades to DDE under aerobic conditions. Concentration of DDT in the former agricultural areas ranges up to >100μg/g, with numerous locations above the soil quality guidelines (Table 1.2).

During summer 2002 and spring 2003 Mills (2004c) conducted groundwater sampling in the Park. The DDT concentration in a natural area where pesticides were not used extensively was approximately 0.021ηg/L; in the area of former orchards it is up to 4.18ηg/L and in the marsh area it is approximately 0.097ηg/L. Thus the groundwater

concentration of DDT is below groundwater quality guidelines (Table 1.2), with the highest concentration in the area of former orchards.

Marenco (2002) characterized soils in PPNP in terms of their tendency for degrading DDT. The primary product of DDT degradation is DDE at Marenco's (2002) three study sites. Relatively low-elevation areas (<175m amsl) are expected to degrade DDT faster due to anaerobic conditions during flooding by marsh waters in some years. Relatively high-elevation areas (>175m asml) have lower degradation rates, because soils remain aerobic.

| | CCREM (1987) | OMOEE (1997)[a] | CCME (2003)[b] |
|---|---|---|---|
| **Soil** | | | |
| **Total DDT** | | - | 0.70[d] μg/g |
| **DDT** | | 1.6[c] μg/g | - |
| **DDE** | | 1.6[c] μg/g | - |
| **DDD** | | 2.2[c] μg/g | - |
| **Groundwater** | | | |
| **Total DDT** | 30 μg/L | | |
| **DDT** | | 50[e] ηg/L | |

a: Ontario Ministry of Environment and Energy
b: Canadian Council of Ministers of the Environment
c: soil quality guidelines for Recreational/Parkland Land-Use in a portable groundwater situation
d: soil quality guidelines for Recreational/Parkland Land-Use
e: portable groundwater in a course-grained soil texture

**Table 1.2: Soil and Groundwater Quality Guidelines for DDT, DDE and DDD (Crowe et al., 2002)**

## *1.4 Flushing of DDT by Cyclodextrin Solutions*

### 1.4.1 Background Information

Due to high persistence in the environment and high bioaccumulation, remediation of soil contaminated with DDT and its metabolites is desirable. There are several approaches to remediation of pesticide contaminated soils. Those include the approaches discussed below.

DDT and its metabolites are not easily biodegradable in natural systems. The biodegradation is primarily co-metabolic, that is, the microorganisms do not gain nutrients or energy for growth from the DDT and its metabolites, rather they require an alternate carbon source as a growth substrate (Foght et al., 2001, Gaw et al., 2003). Microbial cultures that are not found in a given soil, may be added or the existing microbial community may be stimulated to degrade DDT by adding organic matter and nutrients (Aislibie et al., 1997; Kantachote et al., 2004). This technique is called enhanced bioremediation (Chacko, 1966; Aislibie et al., 1997; Corona-Cruz, 1999). However, high levels of dissolved organic carbon in soil can decrease the bioavailability of DDT due to binding contaminant to dissolved organic carbon and thereby retard degradation (Kantachote et al., 2004). Consequently, enhanced bioremediation of DDT and its metabolites has met with limited success. Gaw et al. (2003) showed a highly significant negative correlation between copper concentration and the ratio DDT:DDE, indicating that elevated copper or other compounds at toxic doses concentrations can reduce the biodegradation of DDT.

Creating anaerobic conditions enhances biodegradation, which promotes the formation of DDD as a degradation product of DDT (Guenzi et al., 1971; Spencer et al., 1996; Aislibie et al., 1997). Anoxic conditions can be achieved by soil flooding. DDD is a less persistent metabolite of DDT than DDE. Therefore, creating anaerobic conditions is a valuable step in a remediation process.

Alternating aerobic and anaerobic conditions (Aislibie et al., 1997) can accelerate bioremediation by exploiting more than one transformation pathway. Anaerobic conditions promote reductive dechlorination of DDT to DDD. Further degradation is through ring cleavage reactions which require oxygen; therefore this step favors aerobic conditions. The reduction percentage of DDT in a sequential anaerobic-aerobic fermentation of different bacterial cultures ranged from 31% to 84% (Corona-Cruz et al., 1999).

The bioremediation techniques described above degrade (transform) the target compounds (DDT and its metabolites). Alternatively, or concurrently, the contaminant can be mobilized and removed from the zone of concern. Flushing with cosolvents (Junasz, A. et al, 2003; Smith et al., 2004), surfactants (Kile and Chiou, 1989; Parfitt et al., 1995; Smith et al., 2004) and cyclodextrins (Brusseau et al., 1994, Smith et al., 2004) serve this purpose. For example, Smith et al. (2004) demonstrated the high ability of cosolvents to remove DDT. Some surfactants are preferred over some cosolvents due to their lower toxicity and availability for biodegradation. However the rate of solubilization of DDT in surfactant solutions is much lower than in cosolvents. DDT removal by solutions of surfactants such as Triton X-100 and polypropylene glycolethoxylate varied

from 25% to 45% depending on the solution concentration (Parfitt et al., 1995). You et al. (1996) demonstrated the ability of selected surfactant to enhance the biotransformation of DDT and its metabolites.

The primary focus of this work is flushing of DDT and its metabolites from soil with cyclodextrins, specifically hydroxypropyl-β-cyclodextrin. This remediation approach combines aspects of mobilization, alternating aerobic/anaerobic conditions, and potentially enhanced bioremedation.

Cyclodextrins (CDs) are a family of cyclic oligosaccharides that are produced by intramolecular transglycosylation reaction from degradation of starch by cyclodextrin glucanotransferase enzyme (Singh et al., 2002). They are naturally occurring water-soluble glucans. There are three types of parent CDs: α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin. The molecule of cyclodextrin is ring-shaped. The interior is relatively apolar compared to water, therefore, the interior cavity is lipophilic (Bender and Komiyama, 1978). The exterior of the molecular is hydrophilic, hence CDs are highly soluble in water. β-cyclodextrin which is the most popular due to its relatively low price, accessibility and effectiveness (Singh et al., 2002), has water solubility of 1.85g/100ml (Bender and Komiyama, 1978); where as hydroxypropyl-β-cyclodextrin, chemically modified β-cyclodextrin, has an aqueous solubility 0.8 kg/L that is greater than 80% by mass (Blanford et al., 2001).

Cyclodextrins have the ability to form solid inclusion complexes with a very wide range of solid, liquid and gaseous compounds by a phenomenon of molecular complexation (Bender and Komiyama, 1978; Singh et al., 2002). Since the interior cavity

is lipophilic CDs easily form complexes with hydrophobic compounds that have low water solubility.

Cyclodextrins are widely used in many industries. In the food industry they are used in taste modification by masking off flavors. In the pharmaceuticals industry they control the release of drugs. In the cosmetics industry they mask unpleasant odors. In the environmental protection industry they enhance the solubility of highly insoluble target compounds (Singh et al., 2002).

As mentioned above CDs have high water solubility and they have the ability to form inclusion complexes with a very wide range of compounds that have relatively low water solubilities (Wang and Brusseau, 1993). They are not sorbed, and therefore not retarded. They do not exhibit pore exclusion under typical aqueous conditions (Brusseau et al., 1994; McCray and Brusseau, 1998), and do not precipitate (Wang and Brusseau, 1995). CDs do not have a critical micelle concentration and therefore they do not form emulsion like surfactants. Also CDs are naturally occurring compounds, hence they are friendly to the environment, easily biodegradable, and by increasing solubility of toxic compounds they enhance the rate of bioavailability (Bardi et al., 2000). This unique combination of properties makes cyclodextrins favorable compounds for soil remediation.

Wang and Brusseau (1993) demonstrated the ability of hydroxypropyl-β-cyclodextrin to enhance solubilization of some low-polarity organic compounds. Relative aqueous-phase concentration increased linearly with increasing concentration of cyclodextrin. Their experiments revealed the relatively smaller solubility enhancement of DDT compared to the other low-polarity organic compounds. This effect was surmised to

be due to large molecular volume of DDT and CD is relatively small cavity (Wang and Brusseau, 1993).

Semple and Doick (2003) reported that the portion of contaminates extracted from the soil by cyclodextrins correlates closely with the portion of contaminant that is available for mineralization in soil. Therefore, this soil extraction technique can be an indicator of the biodegradable fraction of contaminants in soil.

### 1.4.2 Laboratory Treatability Experiment by Schepanow (2002)

Bench-scale laboratory column experiments to assess the potential for cyclodextrin to mobilize and degrate DDT were completed by Schepanow (2002) at the Canadian Centre for Inland Waters, Burlington. Soil contaminated with DDT was collected at the Sleepy Hollow site in Point Pelee National Park. Samples were flushed with MilliQ water and 5%, 10% and 20% solutions of hydroxypropyl-β-cyclodextrin (HPCD) by two methods: Continuous flow and Pulse-Wait. The cyclodextrin removed over two orders of magnitude more pesticide mass than the MilliQ water. The pulse-wait method removed 6-10% more DDT that Continuous Flush. A 20% cyclodextrin solution removed 83% of the initial mass of DDT during Pulse-Wait technique after application of 18 pore volumes. Both 5% and 10% cyclodextrin solutions removed close to 50% of DDT. The results of these bench-scale experiments were the basis for the Pilot-Scale field experiments conducted by Badley (2003).

### 1.4.3 Pilot-Scale Field Experiment by Badley (2003)

To determine the ability of cyclodextrin to remove DDT from soil under field conditions6 a pilot-scale field experiment was conducted by Badley (2003). The location of the remediation grid was chosen within the former orchard sampling site (Figure 1.4) used by Marenco (2002). This area has the highest concentration of DDT and its metabolites among investigated sites within Point Pelee National Park (Marenco, 2002).

The area of the remediation grid was $9m^2$ which included 9 plots of $0.49m^2$ area each and a buffer area to avoid interference among plots (Figure 1.5, Figure 1.6)). Three different treatments were applied to the plots: 1) a 20% by wt. cyclodextrin solution to three plots; 2) a 10% by wt. cyclodextrin solution to three plots; and 3) three control plots with no applications. The application of 19 pore volumes of 10% cyclodextrin solution resulted in the decrease of the initial DDT, DDE and DDD concentrations of 90%, 74% and 73% respectively. After the 13 pore volumes applications of 20% cyclodextrin solution, the initial concentration of DDT, DDE and DDD decreased by 90%, 77% and 82%, respectively. A tailing effect was observed during this field study, in that after approximately 10 pore volumes the concentration of DDT, DDE and DDD reached a plateau.

Some fundamental changes in the soil physical properties were observed during the experiment. First, as a result of the application of the cyclodextrin solution, the moisture content increased gradually with every applied pore volume. After the application of 20% solution was stopped, the plots still maintained a higher moisture content. Second, a decrease in infiltration rates was observed, especially for 20% plots.

The field saturated hydraulic conductivity determined using the Guelph Permeameter was an order of magnitude lower for the 20% plots then for control plots. Third, the number of bacterial cell in the application plots was higher than for controls. This was explained by the fact that hydroxypropyl-β-cyclodextrin is an oligosaccharide which may be a food source for micro fauna.

## 1.5 Problem Description

The work of Badley (2003) was focused on the remediation of DDT contaminated soil. Most sampling was done in the top 15 cm of the profile. The observed loss of DDT and its derivatives during that pilot-scale field experiment, could be attributed to two different mechanisms: mobilization by cyclodextrin and biological degradation.

To some extent DDT, DDE and DDD molecules were captured in the cyclodextrin cavity and traveled as a conservative solution downward through the profile. This mobilization of pesticides was confirmed by sampling the soil profile on November 4$^{th}$, 2002 which was the last day of the field experiment. Compared to control plots the increase in DDT concentration at the 35cm depth was 4600% for both 10% and 20% treatment plots. The increase in DDE concentration at the 35cm depth was 940% and 1100% for 10% and 20% treatment plots respectively. The increase in DDD concentration at the 35cm depth was 3200% and 2700% for 10% and 20% treatment plots respectively (Badley, 2003).

During the cyclodextrin solution application, the top layer of the profile became fully saturated and generated anaerobic conditions (Essa, 2004). As was mentioned above anaerobic conditions promote microbially mediated reductive dechlorination of DDT to DDD. Also between applications as solution drains and percolates downward to the water table, the anaerobic conditions in the soil may change back to aerobic conditions that

promote microbially mediated ring cleavage reactions. Therefore this alteration of aerobic and anaerobic conditions could have stimulated further DDT degradation.

Cyclodextrin, as an oligosaccharide is an additional food source for micro fauna. Hence the addition of cyclodextrin solution into the soil promotes the growth of the microbial population which can lead to cometabolic biodegradation of DDT and its derivatives.

The relative contribution of each of these mechanisms to the loss of DDT and its metabolites from the topsoil (Ah) layer is not known. This study will focus upon the relative fate of DDT, DDE and DDD. That was addressed using groundwater sampling in the area of the remediation grid, additional soil sampling within the treatment plots, and numerical modeling of unsaturated/saturated subsurface flow and transport. The comparison of results of the numerical modeling with groundwater concentrations aided the estimation of the proportion of DDT, DDE and DDD that was mobilized by cyclodextrin versus the proportion that underwent chemical and/or biological degradation. Overall this study will further evaluate the efficiency of soil remediation by cyclodextrin for DDT and its metabolites.

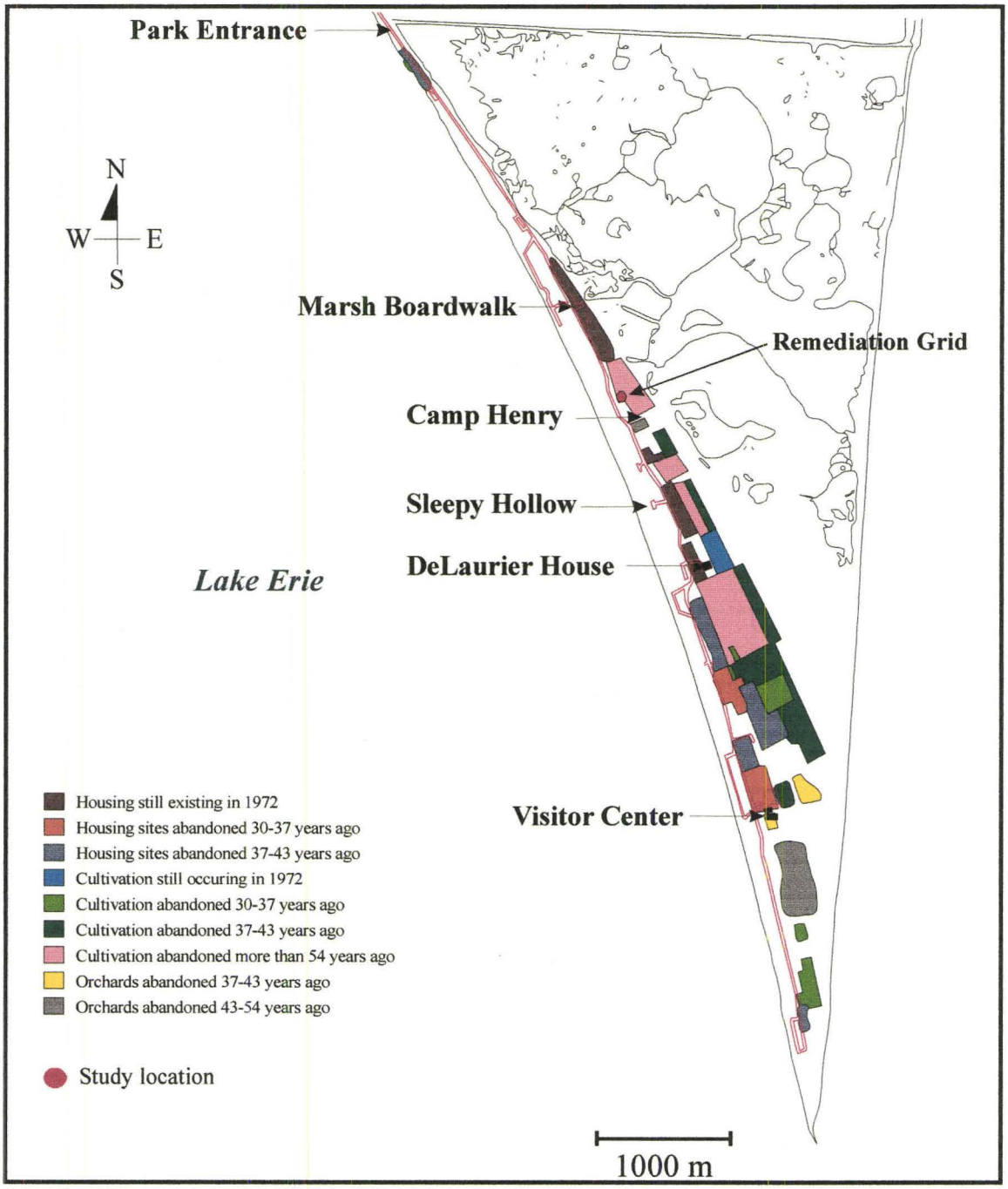


**Figure 1.4: Historical Landuse at Point Pelee National Park and Remediation Grid Location (Adapted from Marenco, 2003)**

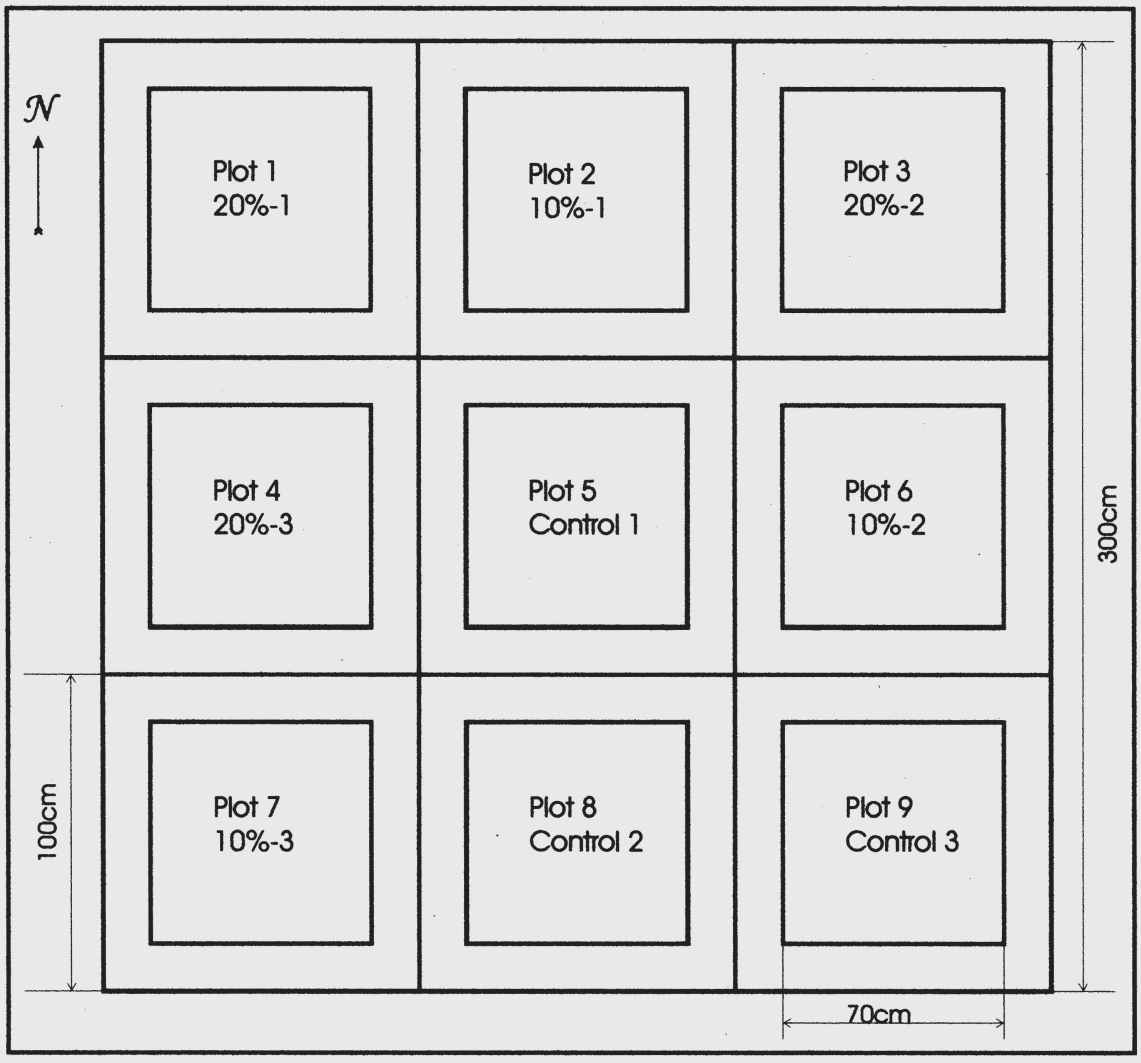


**Figure 1.5: Layout of Remediation Grid with the Numbering of Each Application Plot and Location of Each Treatment (Adapted from Badley, 2003)**


**Figure 1.6: Remediation Grid (Adapted from Badley, 2003)**

## *1.6 Hypothesizes and Objectives*

This study hypothesizes that:

1. Concentration of DDT, DDE and DDD in shallow soil in treatment plots is significantly lower one year after treatments stopped
2. Degradation has caused the mass of DDT in local groundwater to be significantly lower than the mass lost from the soil.

The specific objectives of this research were:

1. To conduct soil sampling of the treatment plots one year after application of cyclodextrin solution to assess any change in concentration of DDT, DDE and DDD.
2. To conduct groundwater sampling under the application grid to assess the vertical mobilization of DDT and its derivatives.
3. To calculate mass balance of the "soil – groundwater" system in order to determine the amount of DDT that was degraded and leached from treatment plots to groundwater using data of 2002, 2003 and 2004. To compare the results of arithmetical average to ln-transformed data.
4. To use the 2-D unsaturated/saturated flow and solute transport numerical model HYDRUS 2-D to simulate the pilot-scale field experiment conducted

by Badley (2003) and the system behavior during 500 days after the application of cyclodextrin.

5. To compare the results of numerical simulations to the results of groundwater sampling to better evaluate the mass of DDT in groundwater.
6. To estimate the proportion of DDT, DDE and DDD that was mobilized by cyclodextrin versus the proportion that underwent degradation.
7. To further assess the effectiveness of cyclodextrin application in removing DDT and its derivatives from sandy soils.
8. Perform numerical simulations using HYDRUS 2D to demonstrate the potential of pump-and-treat to remove DDT, DDE, DDD in cyclodextrin solutions flushed to groundwater.

# 2. Field Investigation

## 2.1 Introduction

A pilot-scaled field experiment conducted by Badley (2003) has demonstrated the ability of a hydroxypropyl-β-cyclodextrin solution to remove DDT and its derivatives from soil. The soil flushing with 10% cyclodextrin solution removed 90%, 74% and 73% of the initial DDT, DDE and DDD concentrations, respectively. The 20% cyclodextrin solution removed 90%, 77% and 82% of the initial DDT, DDE and DDD concentrations respectively (Badley, 2003). The mass balance for this experiment was calculated by using the arithmetical average. However, the concentration of DDT and its derivatives has been shown to have a ln-normal distribution (Marenco, 2002), therefore the mass balance should also be calculated for ln-transformed data.

Some anticipated fundamental changes in the soil physical properties were observed during the field experiment. As a result of the application of the cyclodextrin solution moisture content increased gradually with every applied pore volume. After the application of 20% solution was stopped, the plots still maintained higher moisture content. Also, a decrease in infiltration rates was observed, especially for the 20% plots. The field saturated hydraulic conductivity determined using the Guelph Permeameter was an order of magnitude lower for the 20% plots then for the 10% and control plots (Badley 2003). The number of bacterial cells in the application plots was higher than for the control plots. This was explained by the fact that hydroxypropyl-β-cyclodextrin is an oligosaccharide which can be a food source for micro fauna. Badley (2003) did not include groundwater sampling in her study. She concluded that the mass loss from the

shallow soil could be the result of biodegradation or leaching to groundwater or both. Additional soil sampling could determine if there was an additional decrease in concentration over time due to biological activity or other factors after the treatment stopped. Groundwater sampling under the application grid could assess the vertical mobilization of DDT and its derivatives to groundwater. Comparison of the masses found in groundwater to the masses lost from the soil could provide a relative measure of the magnitude of mass loss by leaching versus biodegradation.

## 2.2 Methods

### 2.2.1 Soil Sampling for DDT, DDE and DDD Analyses

To ensure consistency, the technique of soil sampling for DDT and its derivatives in September 2003 was exactly the same as the technique during the field experiment in 2002 (Badley, 2003).

Sampling locations were randomly chosen from within the treatment grid from locations that were not used for sampling during the field experiment in 2002. Three samples were taken from each of nine plots which included three plots for each treatment. Sampling holes were approximately 6.5-7.5cm deep and 5-6cm in diameter. The upper 2-3cm of thatch was removed. The design of the remediation grid is shown in Figure 1.5. All tools and containers for sampling were rinsed with 50:50 mixture of n-hexane and spectrophotometric grade acetone in the laboratory and also in the field between samplings to avoid cross-contamination among the plots. The n-hexane serves as a binder and neutralizer of any DDT that may be remaining on the equipment and the acetone evaporates any remaining moisture. A total of 27 samples (3 samples × three plots × three treatments) were transferred to the National Laboratory of Environmental Testing (NLET) in the National Water Research Institute of Environmental Canada for DDT, DDE and DDD analyses. The results of DDT, DDE and DDD analyses by NLET are present in Appendix A.

### 2.2.2 Groundwater Sampling for DDT, DDE and DDD

Groundwater sampling was completed in two phases. The first phase was conducted during a 4-day period from October 6$^{th}$-10$^{th}$, 2003. The second phase was conducted during a 3-day period from March 8$^{th}$-10$^{th}$. Both trips are described in two internal reports entitled "Report on Sampling of Groundwater in the Vicinity of the Cyclodextrin Soil Remediation Plot at Point Pelee National Park" (Mills, 2004a) and "Report on Sampling of Groundwater in the Vicinity of the Cyclodextrin Soil Remediation Plot at Point Pelee National Park. Phase II" (Mills, 2004b).

A water table well (1.5-inch PVC) was installed during Phase I. A 3-inch auger was used to excavate the sand. The depth to the bottom of the well was 2.95 metres and the well screen extended from 1.50 metres below ground surface to the bottom of the well. An end cap was installed on the bottom and one section of riser was installed above the screen interval, leaving 30cm of casing exposed above ground surface. Excavated material was backfilled around the well casing leaving a mound around the well.

Sampling locations in Phase I (Figure 2.1) were based on prior knowledge of groundwater flow in PPNP. The study area is close to the flow divide at PPNP. Groundwater flow is from west to east during the summer months and in some years may be from east to west during the winter months. The overall net flow is from west to east, i.e., from ground water divide towards the marsh. The groundwater velocities are estimated to be 0.5–2.0 meters per year (Crowe et al., 2004). Therefore, any contaminants flushed to groundwater would flow from west to east, so more sampling was focused in

this direction relative to the north-south direction. During Phase I, sampling points were installed at two depths: 2.4 and 2.7m below surface, at each of 14 locations to facilitate sampling as close to the water table as possible throughout the year, corresponding to 10cm below high and low water table levels, respectively (Figure 2.2).

The bottom metre of drive pipe and the entire sampling tip was rinsed with 50:50 hexane/acetone to remove any trace contaminants. After the tip was driven to the correct depth, the drive rod was removed, leaving the sampling tips the set depth. The shallow sampling points were rinsed with the 50:50 hexane/acetone solution to remove any trace contaminants and driven to 240cm below ground surface within the drive rod. Clean sand obtained from Ricci Bros. company was used to backfill the hole and the drive rod was then removed. The 1-L groundwater samples were obtained from the deep sampling points (270cm) using a Masterflex peristaltic pump attached to a generator. Each sample consisted of 2-500ml amber bottles that had been approved for organochlorine analysis. After each sample had been obtained, rinsed aluminum foil was placed on the top of each bottle and the cap was secured. The samples were kept cool and delivered to National laboratory for Environmental Testing (NLET) the following day.

Sampling locations in Phase II (Figure 2.3) were based on Phase I results as described below. Analyses of October samples revealed the higher concentrations of DDT and DDE at 100cm west from the west edge of application grid, at the south edge of application grid and at 300cm east from east edge of grid. Therefore sampling locations for Phase II were expanded to the east by two additional meters and additional depths 25, 125 and 200cm below the water table were sampled (Mills, 2004b).

During Phase II the water table was determined to be at 250cm below ground surface. Sampling locations were 2.75cm, 3.75cm and 4.5m below ground surface (Figure 2.4, 2.5 and 2.6). The permanent drive point installation technique only worked at 4 of 8 sampling locations (REM-GW-W100, REM-GW-N100, REM-GW-S100 and REM-GW-E300S). At each of these locations, the soil was excavated to the water table using a 3" Guelph Permeameter auger prior to the insertion of the ½" drive rod, and the bottom metre of drive pipe and the entire sampling tip was rinsed with 50:50 hexane/acetone to remove any trace contaminants. The drive-point sampling tips were initially driven to 25cm below the water table (275cm below surface), where a 4-L groundwater sample was collected. The drive point was removed and rinsed with 50:50 hexane/acetone. Then it was driven to 125cm below the water table (375cm below surface) and a second 4-L sample was extracted. Finally, the drive point was removed, rinsed with 50:50 hexane/acetone and driven to 200cm below water table (450cm below surface) and a final 4-L sample was extracted. The drive tip and tubing were left at 200cm below the water table for future use. The sampling points were made of machined aluminum, these were attached to Teflon tubing that had 24-1/8" diameter holes drilled in it over the 5cm interval (Figure 2.7). These holes were covered with Nitex cloth to prevent clogging.

The second technique employing a stainless steel temporary drive point was used during Phase II, because the ½" drive rod assembly broke and the screen at the tip of the drive rod was clogging. This technique was employed at the following sampling locations: REM-GW-E100, REM-GW-E300, REM-GW-E500 and REM-GW-E300N. The sampling tip was driven to predetermined depth and after sample extraction removed

to be washed with water and rinsed with 50:50 acetone/hexane solution and then driven to the next required depth.

A total of 24-4L groundwater samples were obtained during Phase II. The samples were kept cool and delivered to the National Laboratory for Environmental Testing on March 12, 2004 for subsequent OC1-W analysis. The list of sampling locations is presented in Appendix B.

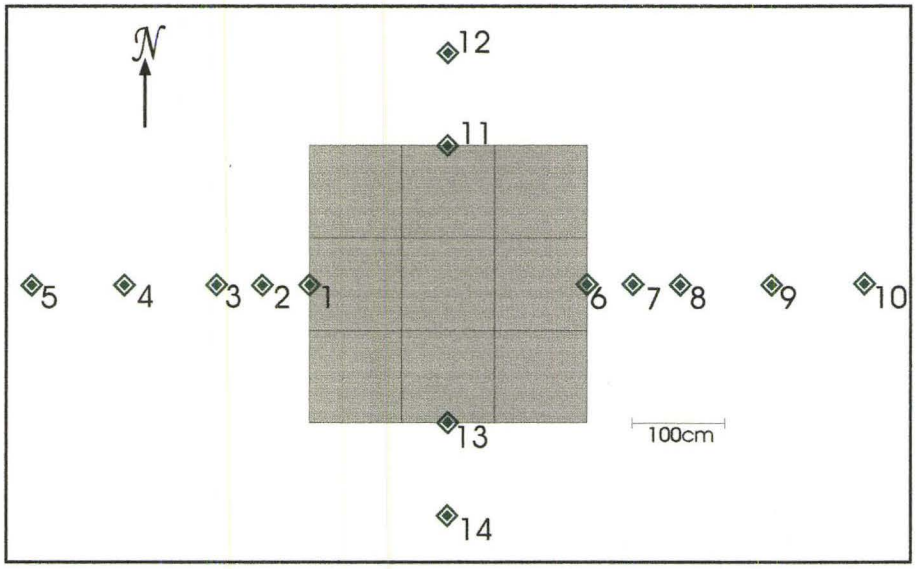


**Figure 2.1: Drive-point Locations of Groundwater Sampling on October 6th-10th**

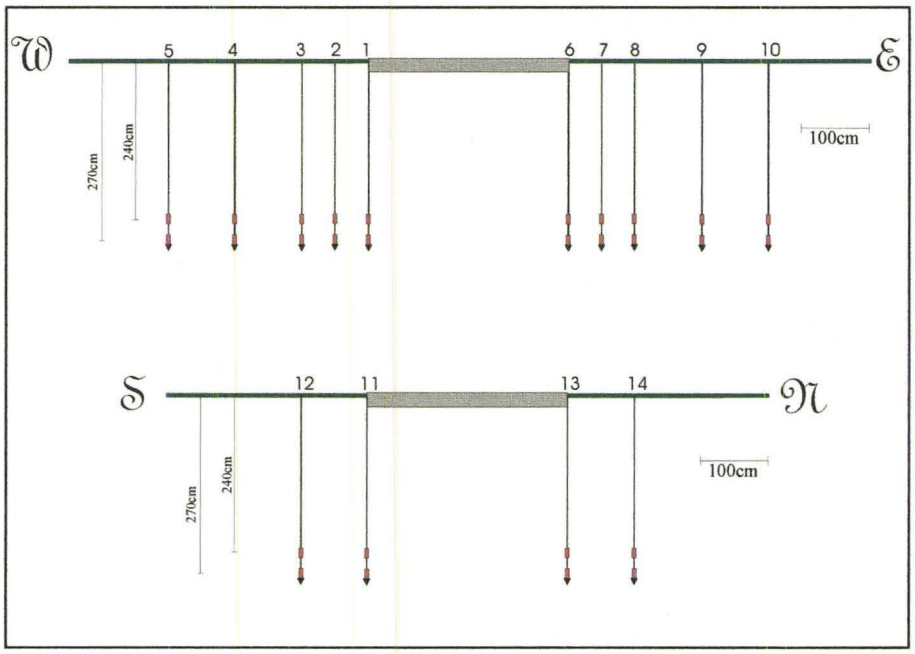


**Figure 2.2: Cross-section from West to East and from South to North Showing Drive-point Sampler Locations on October 6th-10th**

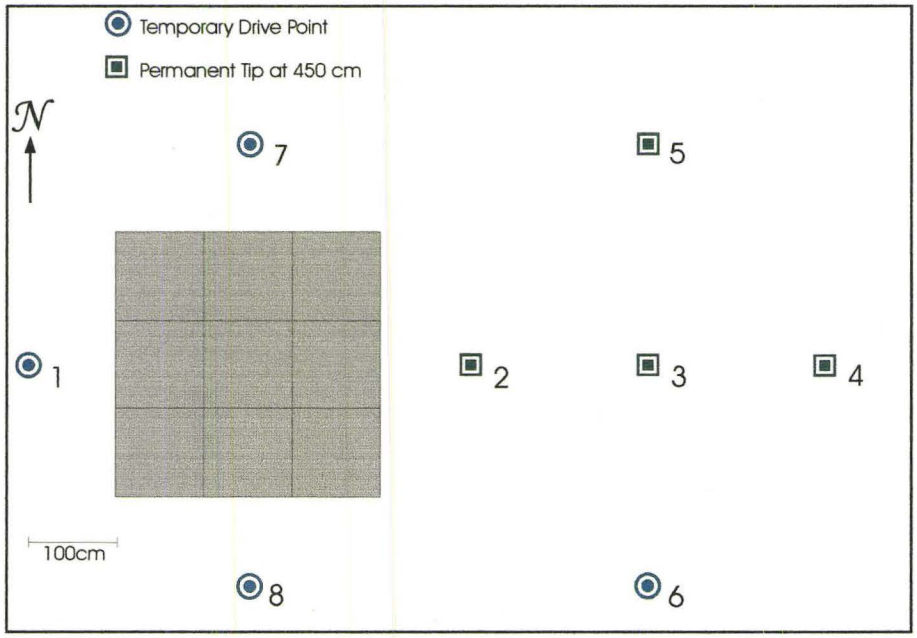


**Figure 2.3: Drive-point Locations of Groundwater Sampling on March 8th-10th**

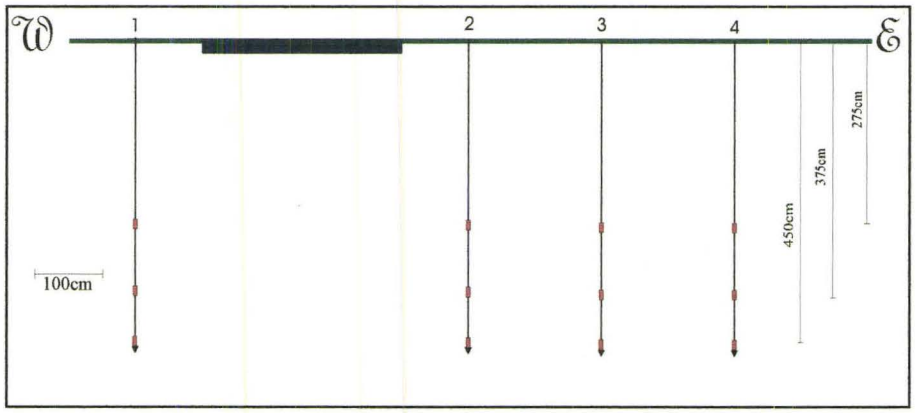


**Figure 2.4: Cross-section from West to East Showing Drive-point Sampler Locations on March 8th-10th**

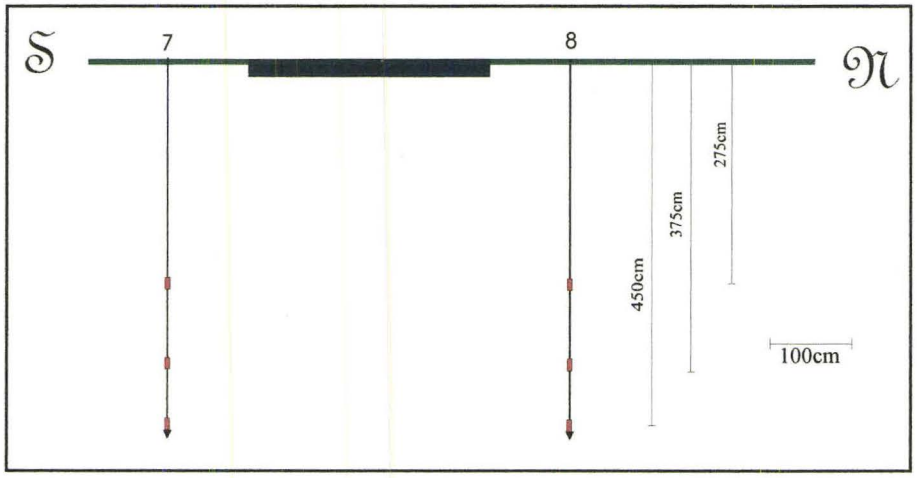


**Figure 2.5: Cross-section from South to North Showing Drive-point Sampler Locations on March 8th-10th**

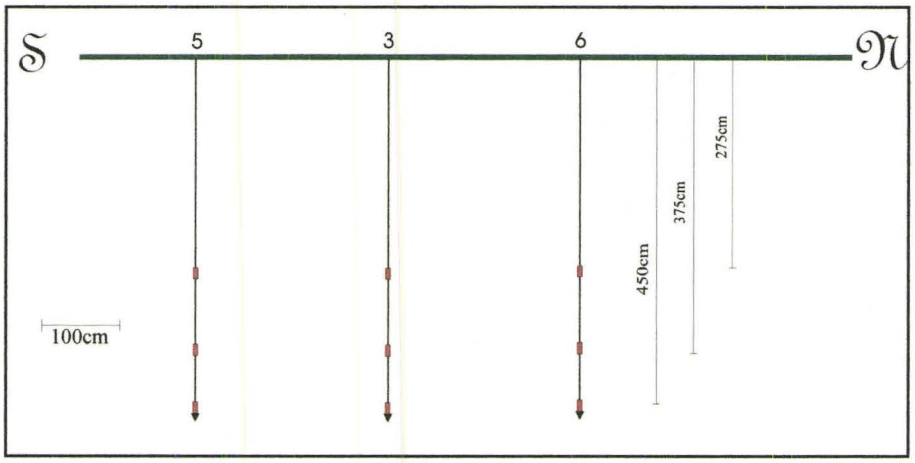


**Figure 2.6: Cross-section from South to North 300cm East from East Edge of Application Grid Showing Drive-point Sampler Locations on March 8th-10th**

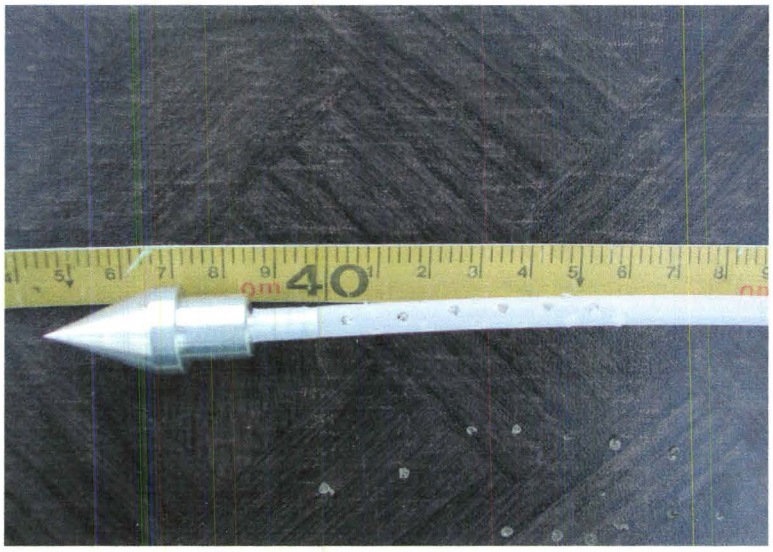

**Figure 2.7: The Sampling Point Used for Groundwater Sampling**

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

The NLET analysis for DDT, DDE and DDD is conducted by using Methods 03-3751 for soil and 03-3251 for groundwater (Schedule of Services, 2003-04). Preferred amount for soil analyses is 20g wet of homogeneous sample. Preferred amount for groundwater analyses is 1000mL. Method 03-3751 includes following steps for organochlorine pesticides in sediments such as DDT, DDE and DDD:

- a 20g wet sediment sample is ultrasonically extracted using a 1:1 mixture of acetone and hexane;

- the concentrated extract is partitioned with water and back extracted with dichloromethane;
- the combined extract is concentrated, cleaned up and fractionated on the 3% (w/w) deactivated silica gel column;
- then it is reconcentrated to a final volume of 10mL;
- dual column capillary gas liquid chromatography with electron capture detectors is used for analysis.

Method 03-3251 includes following steps for organochlorine pesticides in groundwater such as DDT, DDE and DDD:

- a 1 litre water sample is extracted with dichloromethane ($CH_2Cl_2$);
- the extract is dried, concentrated, cleaned up, and fractionated on a 3% (w/w) deactivated silica gel column;
- the it is reconcentrated to a final volume of 1mL prior to analysis;
- dual column capillary gas liquid chromatography with electron capture detectors is used for analysis.

The results were reported within an EXCEL spreadsheet including detection limits.

## 2.3 Results and Discussions

### 2.3.1 Statistical Analyses

Soil sample concentrations of DDT, DDE and DDD measured by Marenco (2002), Badley (2003) and from the sampling in September 2003 in this study, were used for mass balance calculations. Both the para-para and ortho-para isomers were present in soil samples. In this work the sum of these two isomers was used for each compound. According to Marenco (2002) concentrations of DDT and its derivatives in the study area have frequency distributions closer to a ln-normal distribution than to a normal distribution. The sample sizes are not large enough to tell definitely if the data have normal or ln-normal distribution, hence all statistical analyses were presented on both sets of data, i.e., non-transformed and ln-transformed.

#### *2.3.1.1 2002 vs. 2003*

Resampling of the application grid during September 2003 was done in order to see if there were decreases in concentrations of DDT, DDE and DDD due to vertical mobilization by the cyclodextrin solution or/and biodegradation. Table 2.1 presents the comparison of average concentrations for years 2002 and 2003 and Table 2.2 presents the comparison of average concentrations for years 2002 and 2003 for ln-transformed data. For most of data the concentration obtained in 2003 is higher than that obtained in 2002. However, there is no apparent mechanism which could increase the concentration of

DDT. Therefore, the observed increase was attributed to spatial variation and these samples were considered representative of undisturbed soil samples. The pooled data obtained in 2002 and 2003 is taken as the best representation of late-time concentration.

#### *2.3.1.2 Initial concentration*

The best representation for the initial conditions is given by the combination of all undisturbed soil samples taken in 2001, 2002 and 2003 from undisturbed soil in the former orchard area at Camp Henry (Table 2.3). The soil sample concentrations revealed a high degree of variation within a total area of $400m^2$, when distances between samples were on the orders of meters (Marenco, 2002) as well as within the application grid ($9m^2$), when distances between samples were on the orders of tens of centimeters (Badley, 2003). The mean values of DDT, DDE and DDD concentrations are 26.09, 24.45, and 2.33 (μg/g) respectively for arithmetical data and 8.90, 14.45, and 0.72 (μg/g) respectively for the ln-transformed data. These values will be used to calculate the total mass of DDT, DDE and DDD in the initially soil profile. The values of variance for DDT, DDE and DDD are 1659.7, 891.3, and 10.3 $(\mu g/g)^2$ respectively for the arithmetical data, and 3.0, 1.2 and 3.2 $(\mu g/g)^2$ respectively for ln-transformed data.

### *2.3.1.3 Late-time concentration*

Late-time refers to the time in Badley's study after which no further DDT was removed. Badley (2003) showed that after the application of 10 pore volumes of treatment solution the concentrations of DDT, DDE and DDD stayed approximately the same for the rest of the experiment. Resampling of the soil was done in September 2003, to see if there were additional decreases in concentrations of DDT, DDE and DDD due to vertical mobilization by cyclodextrin and/or biodegradation. The best estimate of late-time concentrations was taken as the data from all samples collected after 10 pore volumes (Badley, 2003) combined with data from sampling of the 10% and 20% plots in September 2003 (Table 2.4 and Table 2.5). The degree of variation of late-time concentrations within 10% and 20% plots is not as high as for the initial soil concentrations. The mean values of DDT, DDE and DDD late-time concentrations for the 10% plots are 3.77, 6.85 and 0.49 (μg/g) respectively for arithmetical data and 2.31, 5.09 and 0.28 (μg/g) respectively for ln-transformed data. In the 10% plots the late-time concentrations of DDT, DDE and DDD had variance values of 7.8, 15.6 and 0.2 $(\mu g/g)^2$ respectively for the arithmetical data, and 1.5, 0.9 and 1.5 $(\mu g/g)^2$ respectively for ln-transformed data. The mean values of DDT, DDE and DDD late-time concentrations for the 20% plots are 5.21, 10.30 and 1.00 (μg/g) respectively for arithmetical data and 3.36, 7.96 and 0.59 (μg/g) respectively for ln-transformed data. In the 20% plots the late-time concentrations of DDT, DDE and DDD had variance values of 28.4, 62.5 and 1.4 $(\mu g/g)^2$

respectively for the arithmetical data, and 1.1, 0.6 and 1.2 $(\mu g/g)^2$ respectively for log-transformed data.

### *2.3.1.4 Ln-transformed average*

Marenco (2002) showed that the log-transformed data can be the better representative of the distribution of concentrations, hence the arithmetical average of ln-transformed data was anti-logged in order to determine the average concentration for initial conditions and late-time conditions at the 10% and 20% plots (Table 2.6).

| Year | 10% plots | | | 20% plots | | |
|---|---|---|---|---|---|---|
| | DDT, μg/g | DDE, μg/g | DDD, μg/g | DDT, μg/g | DDE, μg/g | DDD, μg/g |
| 2002 | 3.43 | 6.77 | 0.56 | 3.45 | 7.62 | 0.84 |
| 2003 | 4.43 | 7.02 | 0.37 | 8.72 | 15.65 | 1.33 |

**Table 2.1: Arithmetic Average Late-time Concentrations of DDT, DDE and DDD for Years 2002 and 2003**

| Year | 10% plots | | | 20% plots | | |
|---|---|---|---|---|---|---|
| | anti-lnDDT, μg/g | anti-lnDDE, μg/g | anti-lnDDD, μg/g | anti-lnDDT, μg/g | anti-lnDDE, μg/g | anti-lnDDD, μg/g |
| 2002 | 2.14 | 5.32 | 0.30 | 2.37 | 6.05 | 0.49 |
| 2003 | 2.69 | 4.67 | 0.25 | 6.74 | 13.77 | 0.86 |

**Table 2.2: Average Ln-transformed Late-time Concentrations of DDT, DDE and DDD for Years 2002 and 2003**

| Sample Name | DDT, μg/g | DDE, μg/g | DDD, μg/g | lnDDT | lnDDE | lnDDD |
|---|---|---|---|---|---|---|
| 10%-1 | 27.0 | 27.5 | 9.59 | 3.2958 | 3.3142 | 2.2607 |
| 10%-2 | 7.25 | 13.6 | 2.06 | 1.9810 | 2.6101 | 0.7227 |
| 10%-3 | 14.3 | 13.3 | 5.29 | 2.6603 | 2.5878 | 1.6658 |
| 20%-1 | 79.9 | 80.4 | 11.4 | 4.3808 | 4.3870 | 2.4336 |
| 20%-2 | 19.9 | 25.2 | 5.6 | 2.9907 | 3.2268 | 1.7228 |
| 20%-3 | 0.637 | 4.03 | 0.208 | -0.4510 | 1.3938 | -1.5702 |
| Control 1 - initial | 10.8 | 21.5 | 3.95 | 2.3795 | 3.0681 | 1.3737 |
| Control 2 - initial | 0.185 | 2.43 | 0.022 | -1.6874 | 0.8879 | -3.8167 |
| Control 3 - initial | 15.0 | 31.3 | 3.22 | 2.7081 | 3.4436 | 1.1694 |
| Control 1 - final | 165.0 | 16.2 | 4.93 | 5.1059 | 2.7850 | 1.5953 |
| Control 2 - final | 2.03 | 3.45 | 0.189 | 0.7080 | 1.2384 | -1.6660 |
| Control 3 - final | 11.7 | 12.1 | 2.23 | 2.4596 | 2.4932 | 0.8020 |
| Control 1 2003 | 10.15 | 39.067 | 0.451 | 2.3175 | 3.6653 | -0.7963 |
| Control 1 2003 | 14.82 | 16.758 | 0.325 | 2.6960 | 2.8189 | -1.1239 |
| Control 1 2003 | 9.72 | 11.549 | 0.587 | 2.2742 | 2.4466 | -0.5327 |
| Control 2 2003 | 0.2385 | 2.5683 | 0.0275 | -1.4334 | 0.9432 | -3.5939 |
| Control 2 2003 | 0.2303 | 0.9366 | 0.0194 | -1.4684 | -0.0655 | -3.9415 |
| Control 2 2003 | 5.012 | 12.598 | 0.504 | 1.6118 | 2.5335 | -0.6852 |
| Control 3 2003 | 6.74 | 15.582 | 0.39 | 1.9081 | 2.7461 | -0.9416 |
| Control 3 2003 | 19.28 | 13.21 | 0.567 | 2.9591 | 2.5810 | -0.5674 |
| Control 3 2003 | 2.942 | 6.9462 | 0.2841 | 1.0791 | 1.9382 | -1.2584 |
| S-1 | 67.6 | 56.2 | 0.991 | 4.2136 | 4.0289 | -0.0090 |
| S-2 | 43.7 | 58.3 | 2.84 | 3.7773 | 4.0656 | 1.0438 |
| S-3 | 5.05 | 9.76 | 0.252 | 1.6194 | 2.2783 | -1.3783 |
| S-4 | 18.6 | 30.1 | 0.5 | 2.9232 | 3.4045 | -0.6931 |
| S-5 | 24.3 | 14.0 | 0.82 | 3.1905 | 2.6391 | -0.1985 |
| S-6 | 57.4 | 37.2 | 4.0 | 4.0500 | 3.6163 | 1.3863 |
| S-7 | 2.4 | 6.16 | 0.084 | 0.8755 | 1.8181 | -2.4769 |
| S-8 | 154.0 | 152.0 | 10.4 | 5.0370 | 5.0239 | 2.3418 |
| S-9 | 8.9 | 16.1 | 0.35 | 2.1861 | 2.7788 | -1.0498 |
| S-10 | 4.09 | 8.04 | 0.106 | 1.4085 | 2.0844 | -2.2443 |
| Average | 26.09 | 24.45 | 2.33 | 2.19 | 2.67 | -0.32 |
| Variance $(\mu g/g)^2$ | 1659.7 | 891.3 | 10.3 | 3.0 | 1.2 | 3.2 |
| Standard Deviation | 40.74 | 29.86 | 3.21 | 1.75 | 1.09 | 1.80 |
| 95% Confidence Interval | 26.1±14.3 | 24.5±10.5 | 2.3±1.1 | 2.2±0.6 | 2.7±0.4 | -0.3±0.6 |
| Coefficient of Variance, % | 156 | 122 | 138 | 80 | 41 | -557 |

**Table 2.3: Concentrations of DDT, DDE and DDD, Which Represent the Undisturbed Initial Soil Conditions. The data labeled "S" is from Marenco(2002); labeled "2003" is from this study; the remainder is from Badley (2003)**

| # pore volumes | DDT, μg/g | DDE, μg/g | DDD, μg/g | lnDDT | lnDDE | lnDDD |
|---|---|---|---|---|---|---|
| 2-10 | 4.417 | 8.6518 | 1.217 | 1.4855 | 2.1578 | 0.1964 |
| 2-12 | 3.391 | 6.1069 | 0.373 | 1.2211 | 1.8094 | -0.9862 |
| 2-14 | 0.357 | 1.9899 | 0.122 | -1.0300 | 0.6881 | -2.1037 |
| 2-15 | 7.04 | 10.318 | 0.473 | 1.9516 | 2.3339 | -0.7487 |
| 2-17 | 0.41 | 2.77 | 0.0504 | -0.8916 | 1.0188 | -2.9878 |
| 2-19 | 0.4516 | 1.6381 | 0.0413 | -0.7950 | 0.4935 | -3.1869 |
| 6-10 | 4.013 | 8.9113 | 1.002 | 1.3895 | 2.1873 | 0.0020 |
| 6-12 | 6.154 | 7.3739 | 0.444 | 1.8171 | 1.9979 | -0.8119 |
| 6-14 | 3.72 | 9.2018 | 0.469 | 1.3137 | 2.2194 | -0.7572 |
| 6-15 | 5.195 | 9.2058 | 0.317 | 1.6477 | 2.2198 | -1.1489 |
| 6-17 | 5.297 | 7.9991 | 0.467 | 1.6671 | 2.0793 | -0.7614 |
| 6-19 | 5.981 | 11.818 | 1.464 | 1.7886 | 2.4696 | 0.3812 |
| 7-10 | 5.88 | 12.115 | 1.993 | 1.7716 | 2.4944 | 0.6896 |
| 7-12 | 0.205 | 0.7471 | 0.0185 | -1.5847 | -0.2915 | -3.9916 |
| 7-14 | 0.281 | 1.417 | 0.034 | -1.2694 | 0.3485 | -3.3814 |
| 7-15 | 2.455 | 5.9597 | 0.278 | 0.8981 | 1.7850 | -1.2801 |
| 7-17 | 2.578 | 6.4178 | 0.557 | 0.9470 | 1.8591 | -0.5852 |
| 7-19 | 4.003 | 9.178 | 0.698 | 1.3870 | 2.2168 | -0.3595 |
| 2003 2a | 8.67 | 13.63 | 0.861 | 2.1599 | 2.6123 | -0.1497 |
| 2003 2b | 0.921 | 3.5536 | 0.1135 | -0.0823 | 1.2680 | -2.1760 |
| 2003 2c | 11.31 | 10.807 | 0.897 | 2.4257 | 2.3802 | -0.1087 |
| 2003 6a | 4.317 | 8.5741 | 0.3309 | 1.4626 | 2.1487 | -1.1059 |
| 2003 6b | 3.978 | 9.2321 | 0.308 | 1.3808 | 2.2227 | -1.1777 |
| 2003 6c | 4.305 | 11.311 | 0.345 | 1.4598 | 2.4258 | -1.0642 |
| 2003 7a | 0.1704 | 1.1485 | 0.0324 | -1.7696 | 0.1385 | -3.4296 |
| 2003 7b | 1.339 | 4.5062 | 0.221 | 0.2919 | 1.5055 | -1.5096 |
| 2003 7c | 4.87 | 0.434 | 0.1976 | 1.5831 | -0.8347 | -1.6215 |
| Average | 3.77 | 6.85 | 0.49 | 0.84 | 1.63 | -1.27 |
| Variance $(\mu g/g)^2$ | 7.8 | 15.6 | 0.2 | 1.5 | 0.9 | 1.5 |
| Standard Deviation | 2.79 | 3.95 | 0.48 | 1.24 | 0.94 | 1.24 |
| 95% Confidence Interval | 3.8±1.1 | 6.9±1.5 | 0.5±0.2 | 0.8±0.5 | 1.6±0.4 | -1.3±0.5 |
| Coefficient of Variance, % | 74 | 58 | 97 | 148 | 58 | -98 |

**Table 2.4: Concentrations of DDT, DDE and DDD, Which Represents the Late-time Concentrations for 10% Plots. The data labeled "2003" is from this study; the remainder is from Badley (2003)**

| # pore volumes | DDT, μg/g | DDE, μg/g | DDD, μg/g | lnDDT | lnDDE | lnDDD |
|---|---|---|---|---|---|---|
| 1-10 | 0.3415 | 1.5772 | 0.0538 | -1.0744 | 0.4557 | -2.9225 |
| 1-12 | 5.716 | 11.706 | 2.37 | 1.7433 | 2.4601 | 0.8629 |
| 1-13-14 | 1.244 | 5.4423 | 0.576 | 0.2183 | 1.6942 | -0.5516 |
| 1-13-15 | 1.361 | 5.209 | 0.561 | 0.3082 | 1.6504 | -0.5780 |
| 1-13-17 | 3.5510 | 9.1 | 0.42 | 1.2672 | 2.2083 | -0.8675 |
| 1-13-19 | 1.35 | 4.3347 | 0.2026 | 0.3001 | 1.4667 | -1.5965 |
| 3-10 | 5.367 | 7.9949 | 1.077 | 1.6803 | 2.0788 | 0.0742 |
| 3-12 | 3.428 | 4.748 | 0.371 | 1.2320 | 1.5577 | -0.9916 |
| 3-13-14 | 1.432 | 4.0521 | 0.285 | 0.3591 | 1.3992 | -1.2553 |
| 3-13-15 | 2.545 | 4.867 | 0.2452 | 0.9341 | 1.5825 | -1.4057 |
| 3-13-17 | 3.598 | 8.258 | 0.64 | 1.2804 | 2.1112 | -0.4463 |
| 3-13-19 | 2.39 | 4.3741 | 0.297 | 0.8713 | 1.4757 | -1.2140 |
| 4-10 | 4.767 | 11.229 | 2.228 | 1.5617 | 2.4185 | 0.8011 |
| 4-12 | 0.936 | 4.5505 | 0.274 | -0.0661 | 1.5152 | -1.2946 |
| 4-13-14 | 0.314 | 1.029 | 0.041 | -1.1584 | 0.0286 | -3.1942 |
| 4-13-15 | 9.83 | 15.85 | 2.781 | 2.2854 | 2.7632 | 1.0228 |
| 4-13-17 | 8.68 | 20.807 | 1.543 | 2.1610 | 3.0353 | 0.4337 |
| 4-13-19 | 5.29 | 12.0861 | 1.213 | 1.6658 | 2.4921 | 0.1931 |
| 2003 1a | 2.56 | 9.342 | 0.311 | 0.9416 | 2.2345 | -1.1680 |
| 2003 1b | 2.176 | 8.1354 | 0.35 | 0.7775 | 2.0962 | -1.0498 |
| 2003 1c | 9.26 | 19.303 | 1.498 | 2.2257 | 2.9603 | 0.4041 |
| 2003 3a | 6.798 | 10.2554 | 0.582 | 1.9166 | 2.3278 | -0.5413 |
| 2003 3b | 6.925 | 11.2210 | 0.653 | 1.9351 | 2.4178 | -0.4262 |
| 2003 3c | 5.97 | 12.888 | 0.665 | 1.7867 | 2.5563 | -0.4080 |
| 2003 4a | 11.02 | 18.786 | 1.195 | 2.3997 | 2.9331 | 0.1781 |
| 2003 4b | 27.15 | 40.048 | 5.8 | 3.3014 | 3.6901 | 1.7579 |
| 2003 4c | 6.59 | 10.903 | 0.889 | 1.8856 | 2.3890 | -0.1177 |
| Average | 5.21 | 10.30 | 1.00 | 1.21 | 2.07 | -0.53 |
| Variance $(\mu g/g)^2$ | 28.4 | 62.5 | 1.4 | 1.1 | 0.6 | 1.2 |
| Standard Deviation | 5.33 | 7.90 | 1.20 | 1.03 | 0.78 | 1.11 |
| 95% Confidence Interval | 5.2±2.0 | 10.3±3.0 | 1.0±0.5 | 1.2±0.4 | 2.1±0.3 | -0.53±0.4 |
| Coefficient of Variance, % | 102 | 77 | 119 | 85 | 37 | -210 |

**Table 2.5: Concentrations of DDT, DDE and DDD, Which Represents the Late-time Concentrations for 20% Plots. The data labeled "2003" is from this study; the remainder is from Badley (2003)**

| | anti-lnDDT, µg/g | anti-lnDDE, µg/g | anti-lnDDD, µg/g |
|---|---|---|---|
| **Initial concentration** | 8.90 | 14.45 | 0.72 |
| **Late-time concentration in the 10% plots** | 2.31 | 5.09 | 0.28 |
| **Late-time concentration in the 20% plots** | 3.36 | 7.96 | 0.59 |

**Table 2.6: Ln-transformed Average Concentrations of DDT, DDE and DDD**

#### *2.3.1.5 t'-test*

To determine if the concentration values of DDT and its derivatives within control, 10% and 20% plots were statistically significantly different than each other an analysis of independent samples when variances are not equal was completed (Snedecor and Cochran, 1980), this analysis is also called "*t*-Test: Two-Sample Assuming Unequal Variances". The following equations were used to calculate the $t'$ value:

$$t' = \frac{\overline{X}_1 + \overline{X}_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \qquad (2.1)$$

where $\overline{X}_1$ and $\overline{X}_2$ are means of two independent samples, $s_1^2$ and $s_2^2$ are variances of $\overline{X}_1$ and $\overline{X}_2$ independent samples, $n_1$ and $n_2$ are sample sizes.

The approximate number of degrees of freedom in $t'$ was calculated using:

$$v' = \frac{(\upsilon_1 + \upsilon_2)^2}{\left( \upsilon_1^2 / v_1 + \upsilon_2^2 / v_2 \right)} \tag{2.2}$$

where $\upsilon_1 = s_1^2 / n_1$ and $\upsilon_2 = s_2^2 / n_2$, $v_1 = n_1 - 1$ and $v_2 = n_2 - 1$.

A comparison was completed for each compound between initial conditions (control), late-time concentration within 10% plots and late-time concentration within 20% plots. The *t* distribution in Snedecor and Cochran (1980) was used to determine if the concentrations for DDT, DDE and DDD were statistically significant different at a 95% confidence level between the distinct treatments. The results are shown in Tables 2.7, 2.8 and 2.9, with "S" indicating a statistically significant difference between the pairs and "NS" indicating that pairs were not statistically significant different. The detailed *t*-test calculations can be found in Appendix C.

The statistical analysis shows that the DDT concentrations are significantly different from one another with the exception of 10% plots versus 20% plots at late time. The significant difference of late-time concentrations in the 10% plots from 20% plots will be reached at a 78% confidence level. The DDE and DDD concentrations are statistically significantly different at the 95% confidence level for all plots.

To determine if the ln-transformed concentration values of DDT and its derivatives within control, 10% and 20% plots were statistically significantly different *t*-Test: Two-Sample Assuming Unequal Variances was completed at 95% confidence interval. Equations 2.1 and 2.2 were used to calculate the $t'$ value. The results are shown in Tables 2.10, 2.11 and 2.12, with "S" indicating a statistically significant difference between the pairs and "NS" indicating that pairs are not statistically significant different.

| | Initial concentration | Late-time concentration in the 10% plots | Late-time concentration in the 20% plots |
|---|---|---|---|
| **Initial concentration** | | S | S |
| **Late-time concentration in the 10% plots** | S | | NS |
| **Late-time concentration in the 20% plots** | S | NS | |

**Table 2.7: Statistical Comparison of DDT Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence level)**

| | Initial concentration | Late-time concentration in the 10% plots | Late-time concentration in the 20% plots |
|---|---|---|---|
| **Initial concentration** | | S | S |
| **Late-time concentration in the 10% plots** | S | | S |
| **Late-time concentration in the 20% plots** | S | S | |

**Table 2.8: Statistical Comparison of DDE Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence level)**

| | Initial concentration | Late-time concentration in the 10% plots | Late-time concentration in the 20% plots |
|---|---|---|---|
| **Initial concentration** | | S | S |
| **Late-time concentration in the 10% plots** | S | | S |
| **Late-time concentration in the 20% plots** | S | S | |

**Table 2.9: Statistical Comparison of DDD Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence level)**

| | Ln-transformed initial concentration | Ln-transformed late-time concentration in the 10% plots | Ln-transformed late-time concentration in the 20% plots |
|---|---|---|---|
| **Ln-transformed initial concentration** | | S | S |
| **Ln-transformed late-time concentration in the 10% plots** | S | | NS |
| **Ln-transformed late-time concentration in the 20% plots** | S | NS | |

**Table 2.10: Statistical Comparison of Ln-transformed DDT Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence level)**

| | Ln-transformed initial concentration | Ln-transformed late-time concentration in the 10% plots | Ln-transformed late-time concentration in the 20% plots |
|---|---|---|---|
| **Ln-transformed initial concentration** | | S | S |
| **Ln-transformed late-time concentration in the 10% plots** | S | | NS |
| **Ln-transformed late-time concentration in the 20% plots** | S | NS | |

**Table 2.11: Statistical Comparison of Log-transformed DDE Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence level)**

| | Ln-transformed initial concentration | Ln-transformed late-time concentration in the 10% plots | Ln-transformed late-time concentration in the 20% plots |
|---|---|---|---|
| **Ln-transformed initial concentration** | | S | NS |
| **Ln-transformed late-time concentration in the 10% plots** | S | | S |
| **Ln-transformed late-time concentration in the 20% plots** | NS | S | |

**Table 2.12: Statistical Comparison of Ln-transformed DDD Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence level)**

The statistical analyses show that for the ln-transformed DDT, DDE and DDD concentrations the control plots are significantly different from the 10% plots. This means that at the 95% confidence level late-time concentrations in the 10% plots and initial concentrations are statistically significantly different as a result of cyclodextrin solution application. The ln-transformed concentrations of DDT and DDE in control plots versus 20% are statistically significant different from one other at the 95% confidence level. The ln-transformed concentrations of DDD in control plots versus 20% are not statistically significant different at the 95% confidence level. The ln-transformed concentrations in 10% plots versus 20% are not statistically significant different for DDT and DDE and they are statistically significant different for DDD concentrations at the 95% confidence level.

Overall the statistical analysis showed that concentrations of DDT and DDE within 10% and 20% treatment plots are statistically different from initial concentrations for the arithmetical data and as well as for the ln-transformed data as a direct result of cyclodextrin solution applications. Concentrations of DDD within the 10% plots are statistically different from initial concentrations for the arithmetical data and for the ln-transformed data. The concentrations of DDD within 20% are statistically different from initial concentrations for arithmetical data, but not statistically different for the ln-transformed data. There are a couple of possible explanations for this. First, DDD may not be mobilized as effectively as DDT and DDE. Second, DDD is a primary degradation product of DDT under anaerobic conditions and those conditions were induced within

20% plots. Therefore the concentration of DDD within the 20% plots may include some formation of DDD by degradation of DDT.

### *2.3.1.6 Coefficient of variation*

Direct comparison of averages, standard deviations, and variances of distinct samples can be inappropriate, because they are absolute measures, and their values depend on the size and magnitude of the units from which they are calculated (McGrew & Monroe, 1993). The mean and standard deviation often change together for data from different populations (Snedecor and Cochran, 1980). The coefficient of variation (CV) is used to describe the amount of variation in samples:

$$CV = \frac{s}{\overline{X}} \times 100 \qquad (2.3)$$

where CV is the coefficient of variation, s is standard deviation, and $\overline{X}$ is the mean of sample.

The coefficients of variation for non-transformed and ln-transformed data are presented in Tables 2.13 and 2.14. There is a substantial decrease of the coefficient of variation for the late-time concentrations of DDT, DDE and DDD. However, for the ln-transformed data the coefficient of variation is almost the same for the initial concentration of DDT and the late-time concentration of DDT within 20% plots and significantly higher for the late-time concentration of DDT within 10% plots. There is no large change in the coefficient of variation for ln-transformed concentrations of DDE. There is a substantial decrease of the coefficient of variation for late-time concentrations

of DDD. These trends do not invoke any systematic explanation and reflect the high variability of the system relative to the number of samples taken.

| | DDT | DDE | DDD |
|---|---|---|---|
| **Initial concentration** | 156 | 122 | 138 |
| **Late-time concentration in the 10% plots** | 74 | 58 | 97 |
| **Late-time concentration in the 20% plots** | 102 | 77 | 119 |

**Table 2.13: The Coefficient of Variation (%) for DDT, DDE and DDD Concentration from Initial Conditions and Late-time Conditions within 10% and 20% plots**

| | lnDDT | lnDDE | lnDDD |
|---|---|---|---|
| **Initial concentration** | 80 | 41 | 557 |
| **Late-time concentration in the 10% plots** | 148 | 58 | 98 |
| **Late-time concentration in the 20% plots** | 85 | 37 | 210 |

**Table 2.14: The Coefficient of Variation (%) for ln-transformed DDT, DDE and DDD Concentration from Initial Conditions and Late-time Conditions within 10% and 20% plots**

### 2.3.2 Mass of DDT, DDE and DDD Removed from Soil

Only the top layer of soil has high concentration of DDT and its derivatives, the concentration dramatically drops with depth (Marenco, 2002; Badley, 2003). Hence essentially all the mass of DDT, DDE and DDD that was removed by flushing with cyclodextrin, was from the top 15 centimeters. Therefore, the mass was calculated assuming the mean concentration represents the top 15cm. The following equation was used to determine the mass of contaminant in the soil:

$$Mass = Height \times Area \times BulkDensity \times Concentration \quad (2.4)$$

where, the *Height* was 15cm, the *Area* was 14,700cm$^2$ (3 plots of size 70×70cm) and average *Bulk Density* was 1.26 g/cm$^3$ (Badley, 2003). The mass was calculated for both arithmetical and ln-transformed data (Tables 2.15-2.20).

#### *2.3.2.1 Arithmetical Average*

The concentration data reported by Badley (2003) was combined with the additional samples collected in September 2003. Decreases in concentrations before treatment and after treatment and therefore the mass of DDT, DDE and DDD in the 10% plots were 86%, 72% and 79% respectively (Tables 2.15; 2.16 and 2.17). For 20% plots decreases in concentrations and therefore the mass of DDT, DDE and DDD were 80%, 58% and 57% respectively (Tables 2.15; 2.16 and 2.17). The initial and late-time concentrations of DDT, DDE and DDD are statistically significant different as a result of application of cyclodextrin solutions. Therefore using equation 2.4, the best estimate of

the mass of DDT, DDE and DDD flushed to groundwater is 12.00, 8.82, and 0.88 g respectively for the arithmetical data.

#### *2.3.2.2 Ln-transformed Average*

Decrease in concentrations between pre-treatment and after-treatment and therefore the mass of DDT, DDE and DDD in the 10% plots was 74%, 65% and 61% respectively (Tables 2.18; 2.19 and 2.20). For 20% plots, decrease in concentrations and therefore the mass of DDT, DDE and DDD was 62%, 45% and 18% respectively (Tables 2.18; 2.19 and 2.20). The statistical analysis showed that ln-transformed initial concentrations versus ln-transformed late-time concentrations in the 10% and 20% plots are statistically significant different at the 95% confidence level with an exception of ln-transformed initial concentrations versus ln-transformed late-time concentrations of DDD in the 20% plots. There are several possible explanations why DDD concentration did not decrease as much. DDD might not be removed as effectively as DDT and DDE, or number of samples is too small to make a definite conclusion, or DDT transforms DDD. The last possible explanation is supported by a study conducted by Essa (2004). Her research showed that detectible $SO_4^{2-}$ reduction occurred only in the 20% plots indicating highly anoxic conditions one year after the last application. That can lead to an increase in the concentration of DDD, because it is produced under anaerobic conditions. Therefore, using equation 2.4, the best estimate of the mass of DDT, DDE and DDD flushed to groundwater is 3.37, 4.40 and 0.16 g respectively for the ln-transformed data.

Even with this high percentage mass removal of contaminants the remaining concentration of DDT is still above the current CCME Soil Quality Guidelines for Recreational/Parkland Land use (Table 2.21) which are 0.7 μg/g for total DDT (sum of DDT and its derivatives).

| | Initial | Late-time for 10% plots | Late-time for 20% plots |
|---|---|---|---|
| **Average DDT concentration, μg/g** | 26.09 | 3.77 | 5.21 |
| **Mass of DDT, g** | 7.25 | 1.05 | 1.45 |
| **Removed Mass, g** | | 6.20 | 5.80 |
| **Removed Mass,%** | | 86 | 80 |

**Table 2.15: Calculated Mass of DDT in the Top 15cm of Soil Using the Arithmetical Average of Concentration**

| | Initial | Late-time for 10% plots | Late-time for 20% plots |
|---|---|---|---|
| **Average DDE concentration, μg/g** | 24.45 | 6.85 | 10.30 |
| **Mass of DDE, g** | 6.79 | 1.90 | 2.86 |
| **Removed Mass, g** | | 4.89 | 3.93 |
| **Removed Mass,%** | | 72 | 58 |

**Table 2.16: Calculated Mass of DDE in the Top 15cm of Soil Using the Arithmetical Average of Concentration**

| | Initial | Late-time for 10% plots | Late-time for 20% plots |
|---|---|---|---|
| **Average DDD concentration, μg/g** | 2.33 | 0.49 | 1.00 |
| **Mass of DDD, g** | 0.65 | 0.14 | 0.28 |
| **Removed Mass, g** | | 0.51 | 0.37 |
| **Removed Mass,%** | | 79 | 57 |

**Table 2.17: Calculated Mass of DDD in the Top 15cm of Soil Using the Arithmetical Average of Concentration**

| | Initial | Late-time for 10% plots | Late-time for 20% plots |
|---|---|---|---|
| **Average Ln-transformed DDT concentration, μg/g** | 8.90 | 2.31 | 3.36 |
| **Mass of DDT, g** | 2.47 | 0.64 | 0.93 |
| **Removed Mass, g** | | 1.83 | 1.54 |
| **Removed Mass,%** | | 74 | 62 |

**Table 2.18: Calculated Mass of DDT in the Top 15cm of Soil Using the Ln-transformed Average of Concentration**

| | Initial | Late-time for 10% plots | Late-time for 20% plots |
|---|---|---|---|
| **Average Ln-transformed DDE concentration, μg/g** | 14.45 | 5.09 | 7.96 |
| **Mass of DDE, g** | 4.01 | 1.41 | 2.21 |
| **Removed Mass, g** | | 2.60 | 1.80 |
| **Removed Mass,%** | | 65 | 45 |

**Table 2.19: Calculated Mass of DDE in the Top 15cm of Soil Using the Ln-transformed Average of Concentration**

| | Initial | Late-time for 10% plots | Late-time for 20% plots |
|---|---|---|---|
| **Average Ln-transformed DDD concentration, μg/g** | 0.72 | 0.28 | 0.59 |
| **Mass of DDD, g** | 0.20 | 0.08 | 0.16 |
| **Removed Mass, g** | | 0.12 | 0.04 |
| **Removed Mass,%** | | 61 | 18 |

**Table 2.20: Calculated Mass of DDD in the Top 15cm of Soil Using the Ln-transformed Average of Concentration**

| | | 10% plots | 20% plots |
|---|---|---|---|
| **CCME (2003)*, μg/g** | 0.7 | | |
| **Average Concentration of Total DDT**, μg/g** | | 11.11 | 16.51 |
| **Ln-transformed Average Concentration of Total DDT, μg/g** | | 7.68 | 11.91 |

* - CCME Quality Guideline for Recreational/Parkland-Use set
** - Total DDT is sum of DDT, DDE and DDD

**Table 2.21: Comparison of Soil Quality Guidelines for Total DDT with Total Average Concentration of DDT in Studying Area**

### 2.3.3 Mass of DDT, DDE and DDD in Groundwater

During summer 2002 Mills (2004c) conducted groundwater sampling for DDT in the Point Pelee National Park. The groundwater samples in the area of former orchard revealed low concentrations of DDT (0 - 0.0659ng/L) and DDE (0.0327 - 0.0691ng/L) with concentrations of DDD below detection limits. The average concentration of DDT in the area of Point Pelee National Park is 0.051ng/L and the average concentration of DDE is 0.102ng/L. Canadian Council of Ministers of the Environmental (CCME) does not recommend a water quality guideline for DDT or its derivatives, because it has been recognized that water quality guidelines for highly persistent, bioaccumulative substances such as DDT have a high level of scientific uncertainty and limited practical management value, and therefore, no longer recommended (CCME, 2004). The guideline for total DDT recommended by Canadian Council of Resource and Environment Ministers before the value was withdrawn in 1987 was 30μg/L. The Ontario Ministry of Environment and Energy recommends 0.05μg/L as a guideline for DDT concentration in groundwater. Therefore the groundwater concentration met the requirements.

The first groundwater samples within the immediate area of the remediation grid were obtained in October 2003. Fourteen samples were obtained at the depth of 270cm, which was just below the water table. The results of groundwater sampling are presented in Table 2.22 and Figure 2.8. Samples were analyzed for the following isomers: *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD. In this study DDT concentration is taken as the sum of isomers *o,p'*-DDT and *p,p'*-DDT. The concentration of *p,p'*-DDD in all

samples is below detection limit, which is equal 2.24ng/L. DDD may be present at lower concentrations below detection limit or it may have fully degraded under anaerobic conditions present at the sampling points. DDT was found only at three locations: 1) 1m west from the west edge of the application grid at concentration 6.10ng/L; 2) 3m east from the east edge of the application grid at concentration 1.49ng/L; 3) on the south edge of the application grid at concentration 9.27ng/L (Figure 2.8). At the rest locations DDT concentration is below detection limit, which is 0.75ng/L for *o,p'*-DDT and 1.30ng/L for *p,p'*-DDT. The *p,p'*-DDE was detected in eight of fourteen samples at concentrations from 1.64 to 17.0ng/L. At the rest locations *p,p'*-DDE concentration is below the detection limit, which is 1.28ng/L. The observed DDT and DDE concentrations are 10-100 times above the DDT and DDE concentrations found in the local area of the former orchard before the pilot-scale field experiment (Mills, 2004c). These increases in concentrations of DDT and DDE are attributed to the cyclodextrin applications to the remediation grid.

The highest concentrations of *p,p'*-DDE were found at the same three locations where DDT was detected (Figure 2.8). This concentration distribution may be a result of the nearly exponential decrease in the removal of DDT with subsequent applications of cyclodextrin solution. The first pore volumes removed most of the mass of DDT creating a ring-shaped area of high concentration of DDT and its derivatives. Then this area moved a couple meters to east by net groundwater flow from west to east with an average velocity 0.5-2 m/year.

In the three samples, where concentrations of both DDT and DDE were found, the relative %DDT–%DDE are 26:74; 13:87 and 50:50. The last ratio is consistent with average ratios found in soil samples in the study area (Marenco, 2002; Badley, 2003). However, the first two samples contain lower percentage of DDT, which is indicative of and/or consistent with further degradation of DDT.

The concentrations found in groundwater samples taken in October 2003 were very low and could only account for a very small proportion of the mass removed from the soil during treatment. While promising, these results warranted more extensive groundwater sampling, i.e. over a larger area in the direction of net groundwater flow and over a greater depth interval.

| Sample #* | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Sample Name** | W000-270 | W050-270 | W100-270 | W200-270 | W300-270 | E000-270 | E050-270 |
| *o,p'*-DDT, ng/L | <0.75*** | <0.75 | **2.14** | <0.75 | <0.75 | <0.75 | <0.75 |
| *p,p'*-DDT, ng/L | <1.30*** | <1.30 | **3.96** | <1.30 | <1.30 | <1.30 | <1.30 |
| sumDDT, ng/L | <2.05 | <2.05 | **6.10** | <2.05 | <2.05 | <2.05 | <2.05 |
| *p,p'*-DDE, ng/L | **1.87** | **2.45** | **17.0** | <1.28*** | **1.64** | <1.28 | <1.28 |
| *p,p'*-DDD, ng/L | <2.24*** | <2.24 | <2.24 | <2.24 | <2.24 | <2.24 | <2.24 |

** Sample Number Corresponds to the well number on Figure 2.1*

***Sample Name consists of three parts: letter N, S, E, and W indicates the direction (North, South, East and West) of sampling place relatively to the remediation grid; the first number (000, 050, 100, 200, 300) indicates the distance (cm) of the sampling well from the closest edge of the grid; the second number (270) indicates the sampling depth (cm).*

****Detection Limits:*
*o,p'-DDT=0.75ng/L*
*p,p'-DDT=1.30ng/L*
*p,p'-DDE=1.28ng/L*
*p,p'-DDD=2.24ng/L*

**Table 2.22: The results of Groundwater Analysis, Obtained in October 2003, Provided by the National Laboratory for Environmental Testing (NLET)**

| Sample #* | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|
| Sample Name** | E100-270 | E200-270 | E300-270 | N000-270 | N100-270 | S000-270 | S100-270 |
| *o,p'*-DDT, ng/L | <0.75*** | <0.75 | **1.49** | <0.75 | <0.75 | **1.33** | <0.75 |
| *p,p'*-DDT, ng/L | <1.30*** | <1.30 | <1.30 | <1.30 | <1.30 | **7.94** | <1.30 |
| sumDDT, ng/L | <2.05 | <2.05 | **1.49** | <2.05 | <2.05 | **9.27** | <2.05 |
| *p,p'*-DDE, ng/L | **1.93** | **2.73** | **10.1** | <1.28*** | <1.28 | **9.14** | <1.28 |
| *p,'p*-DDD, ng/L | <2.24*** | <2.24 | <2.24 | <2.24 | <2.24 | <2.24 | <2.24 |

**Table 2.22:** ***Continued***

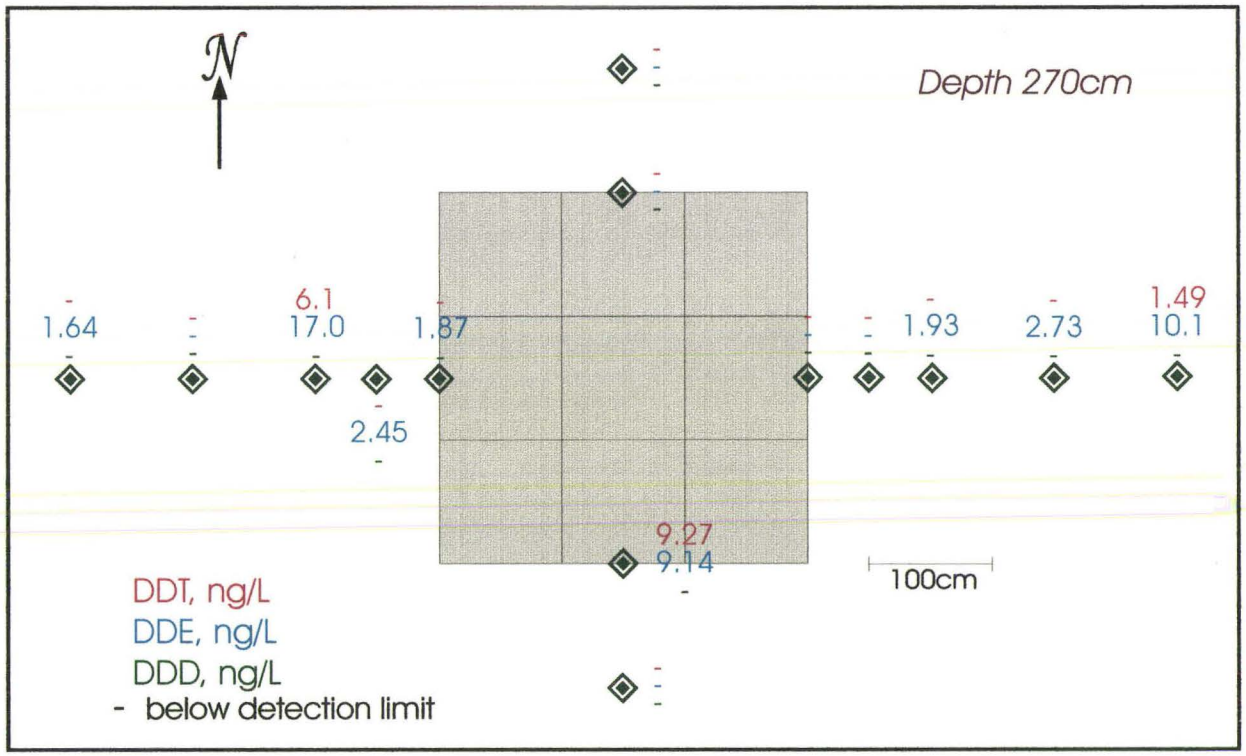


**Figure 2.8: The Results of Groundwater Sampling in October 2003**

The second groundwater sampling was conducted in March 2004 (Mills, 2004b). The 24 samples were taken from 3 depths (275cm, 375cm and 450cm below ground surface) which were 25, 125 and 200cm below the water table at 8 locations. Five wells were located on the east side from the remediation grid because the local net groundwater flow moves from west to east with velocity of 0.5–2m/year. The results of groundwater sampling in March are present in Table 2.23 and Figures 2.9; 2.10; 2.11; 2.12; 2.13 and 2.14. The samples were analyzed for the following compounds: *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD. In this part compound DDT is referred to as sum of *o,p'*-DDT and *p,p'*-DDT, compound DDE is referred to as sum of *o,p'*-DDE and *p,p'*-DDE, and compound DDD is referred to as sum of *o,p'*-DDD and *p,p'*-DDD.

At eight sampling points none of the compounds were detected. Six of those were located at the depth 450cm (Figure 2.11). The other two points at the 450cm depth have low concentrations of DDT and DDE. Therefore, it is reasonable to conclude that the bottom of the plume near the 450cm depth.

The sampling point, with the highest concentration of DDT, DDE and DDD was located 250cm north off the well located 300cm east from the edge of the remediation grid at the depth 275cm, which is 25cm below the water table (Figure 2.9). The concentration of DDT (89ng/L) is two orders of magnitude higher than the rest of samples and the concentration of DDE (35.05ng/L) is 10-50 times higher than any of the other locations. Also, this is the only point where DDD was detected. It had a concentration of 4.70ng/L, whereas at all the other locations DDD is below the detection limits of 0.58ng/L for *o,p'*-DDD and 0.19ng/L for *p,p'*-DDD.

At the rest of the sampling points DDT was found in the range of 2.93ng/L to below detection limits which were 1.21ng/L for *o,p'*-DDT and 0.51ng/L for *p,p'*-DDT. The DDE concentration ranges from 4.03ng/L to below detection limits which were 0.29ng/L for *o,p'*-DDE and 0.56ng/L for *p,p'*-DDE up. All the DDT and DDE concentration values are on the same order of magnitude except for the single sample with the highest values discussed above.

According to spatial distribution concentrations the plume's center of mass was located at 3-5m east from the east edge of the remediation grid, 2.5-3.5m below the ground surface and within about one meter of the water table. This is consistent with the groundwater flow direction and velocity reported by Crowe et al. (2004).

In the samples, where both concentrations of DDT and DDE were found, the ratios %DDT:%DDE vary from 17:83 to 45:55. Most of the samples have higher concentrations of DDE, which may indicate aerobic degradation of DDT. Only the sample with the highest concentrations has a percentage of DDT that is significantly higher than its metabolites, i.e. %DDT:%DDE:%DDD ratio: 69:27:4. In addition to not being consistent with the rest of the samples; this relative proportion of DDT to its metabolites is inconsistent with the relative proportions lost from the soil and inconsistent with reported degradation rates and pathways in the literature. Hence, the data at this location is questionable and warrants further investigation.

| Sample #* | 1A | 1B | 1C | 2A | 2B | 2C |
|---|---|---|---|---|---|---|
| **Sample Name**** | W100-275 | W100-375 | W100-450 | E100-275 | E100-375 | E100-450 |
| ***o,p'*-DDT, ng/L** | –*** | – | – | – | – | – |
| ***p,p'*-DDT, ng/L** | 0.58 | 0.58 | – | – | – | – |
| **sumDDT, ng/L** | 0.58 | 0.58 | – | – | – | – |
| ***o,p'*-DDE, ng/L** | – | – | – | – | – | – |
| ***p,p'*-DDE, ng/L** | 2.77 | 0.80 | – | 0.97 | – | 0.65 |
| **sumDDE, ng/L** | 2.77 | 0.80 | – | 0.97 | – | 0.65 |
| ***o,p'*-DDD, ng/L** | – | – | – | – | – | – |
| ***p,p'*-DDD, ng/L** | – | – | – | – | – | – |
| **sumDDD, ng/L** | – | – | – | – | – | – |

* *Sample Number Corresponds to the well number on Figure 2.3 and a letter corresponds to the sampling depth (cm): A-275, B-375 and C-450*

** *Sample Name consists of four parts: the first letter N, S, E, and W indicates the direction (North, South, East and West) of sampling place relatively to the remediation grid; the first number (100, 300 and 500) indicates the distance (cm) of the sampling well from the closest edge of the grid; if there is a second letter N or Sit indicates one of the two sampling wells located 250cm north or south from the sampling well situated 300cm east from the edge of the grid and the second number (275, 375 or 450) indicates the sampling depth (cm).*

*** *Detection Limits: o,p'-DDT=1.21ng/L; p,p'-DDT=0.51ng/L, o,p'-DDE=0.29ng/L; p,p'-DDE=0.56ng/L, o,p'-DDD=0.58ng/L; p,p'-DDD=0.19ng/L*

**Table 2.23: The results of Groundwater Analysis, Obtained in March 2004, Provided by the National Laboratory for Environmental Testing (NLET)**

| Sample #* | 3A | 3B | 3C | 4A | 4B | 4C |
|---|---|---|---|---|---|---|
| Sample Name** | E300-275 | E300-375 | E300-450 | E500-275 | E500-375 | E500-450 |
| *o,p'*-DDT, ng/L | – | – | – | – | – | – |
| *p,p'*-DDT, ng/L | 1.16 | 2.44 | 1.83 | 0.67 | 1.11 | – |
| sumDDT, ng/L | 1.16 | 2.44 | 1.83 | 0.67 | 1.11 | – |
| *o,p'*-DDE, ng/L | – | – | – | – | – | – |
| *p,p'*-DDE, ng/L | 1.51 | 3.53 | 2.22 | 0.81 | 1.26 | – |
| sumDDE, ng/L | 1.51 | 3.53 | 2.22 | 0.81 | 1.26 | – |
| *o,p'*-DDD, ng/L | – | – | – | – | – | – |
| *p,p'*-DDD, ng/L | – | – | – | – | – | – |
| sumDDD, ng/L | – | – | – | – | – | – |

**Table 2.23**: *Continued*

| Sample #* | 5A | 5B | 5C | 6A | 6B | 6C |
|---|---|---|---|---|---|---|
| Sample Name** | E300N-275 | E300N-375 | E300N-450 | E300S-275 | E300S-375 | E300S-450 |
| *o,p'*-DDT, ng/L | 7.72 | – | – | – | – | – |
| *p,p'*-DDT, ng/L | 81.30 | 1.00 | 0.46 | 2.93 | – | – |
| sumDDT, ng/L | 89.00 | 1.00 | 0.46 | 2.93 | – | – |
| *o,p'*-DDE, ng/L | 0.21 | – | – | – | – | – |
| *p,p'*-DDE, ng/L | 34.80 | – | – | 3.97 | – | – |
| sumDDE, ng/L | 35.05 | – | – | 3.97 | – | – |
| *o,p'*-DDD, ng/L | 1.30 | – | – | – | – | – |
| *p,p'*-DDD, ng/L | 3.39 | – | – | – | – | – |
| sumDDD, ng/L | 4.70 | – | – | – | – | – |

**Table 2.23**: *Continued*

| Sample #* | 7A | 7B | 7C | 8A | 8B | 8C |
|---|---|---|---|---|---|---|
| Sample Name** | N100-275 | N100-375 | N100-450 | S100-275 | S100-375 | S100-450 |
| *o,p'*-DDT, ng/L | – | – | – | – | – | – |
| *p,p'*-DDT, ng/L | – | 2.81 | – | – | 2.60 | – |
| sumDDT, ng/L | – | 2.81 | – | – | 2.60 | – |
| *o,p'*-DDE, ng/L | – | – | – | – | – | – |
| *p,p'*-DDE, ng/L | 0.81 | 4.03 | – | – | 3.11 | – |
| sumDDE, ng/L | 0.81 | 4.03 | – | – | 3.11 | – |
| *o,p'*-DDD, ng/L | – | – | – | – | – | – |
| *p,p'*-DDD, ng/L | – | – | – | – | – | – |
| sumDDD, ng/L | – | – | – | – | – | – |

**Table 2.23**: *Continued*

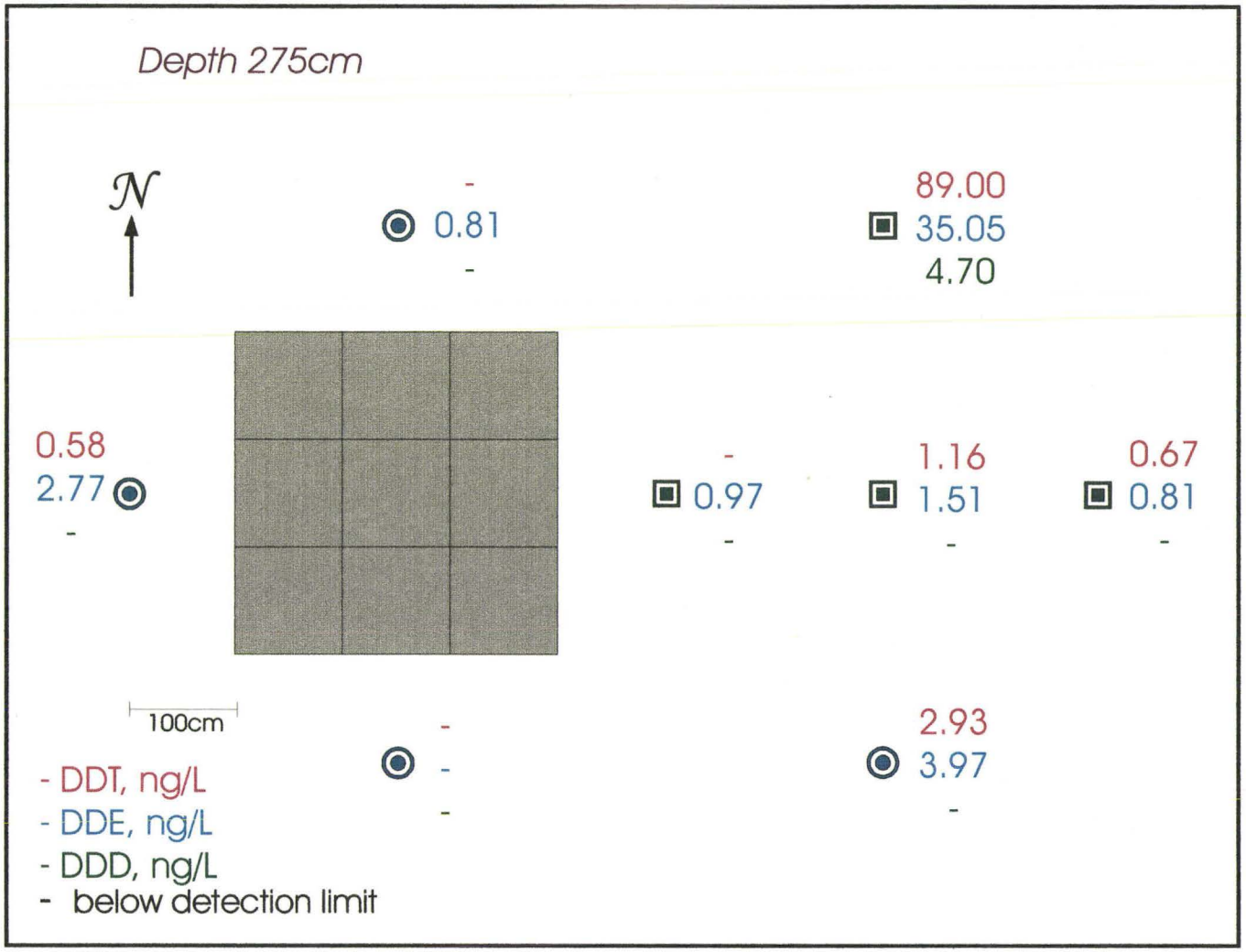


**Figure 2.9: The Results of Groundwater Sampling in March 2004 at depth 275cm**

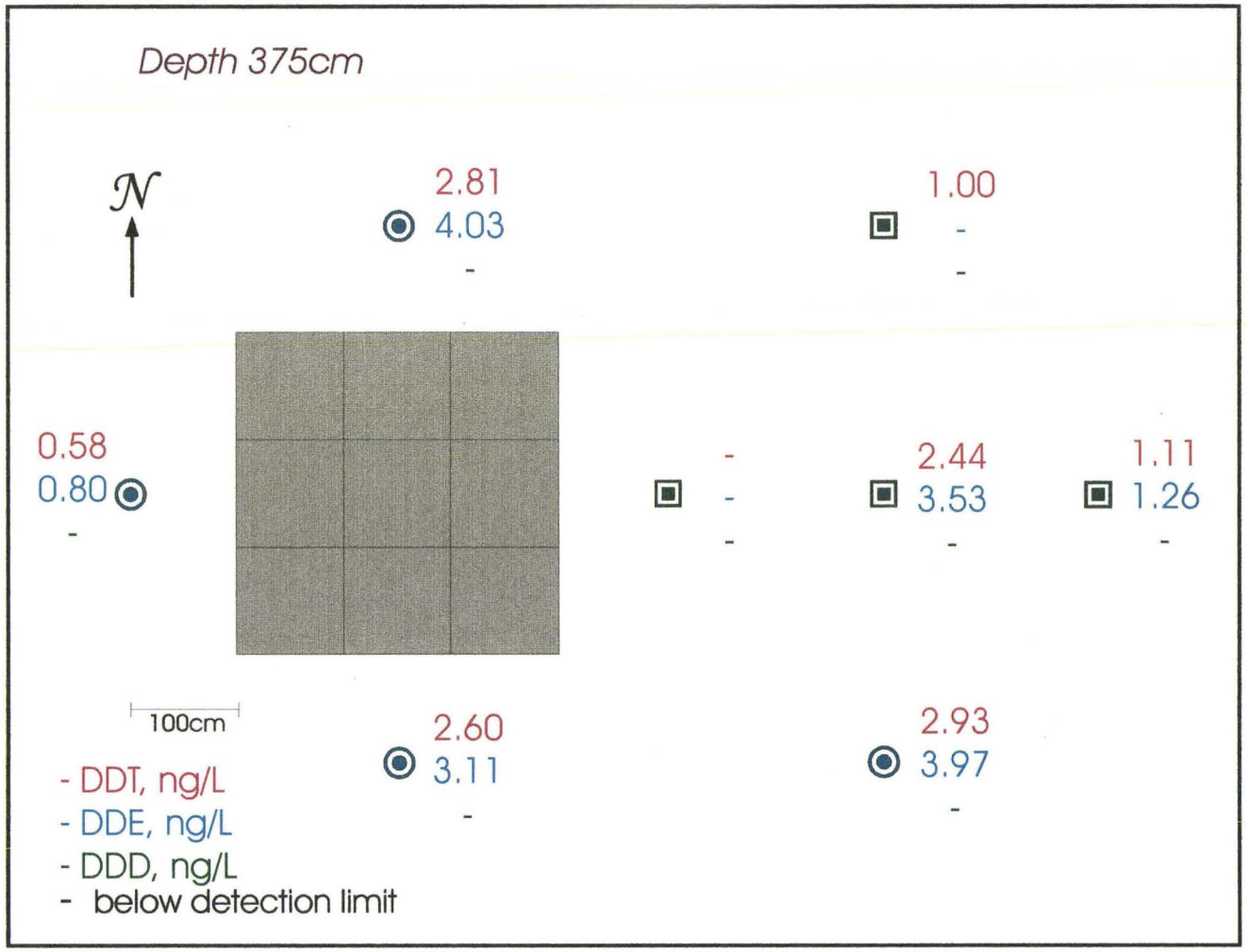


**Figure 2.10: The Results of Groundwater Sampling in March 2004 at depth 375cm**

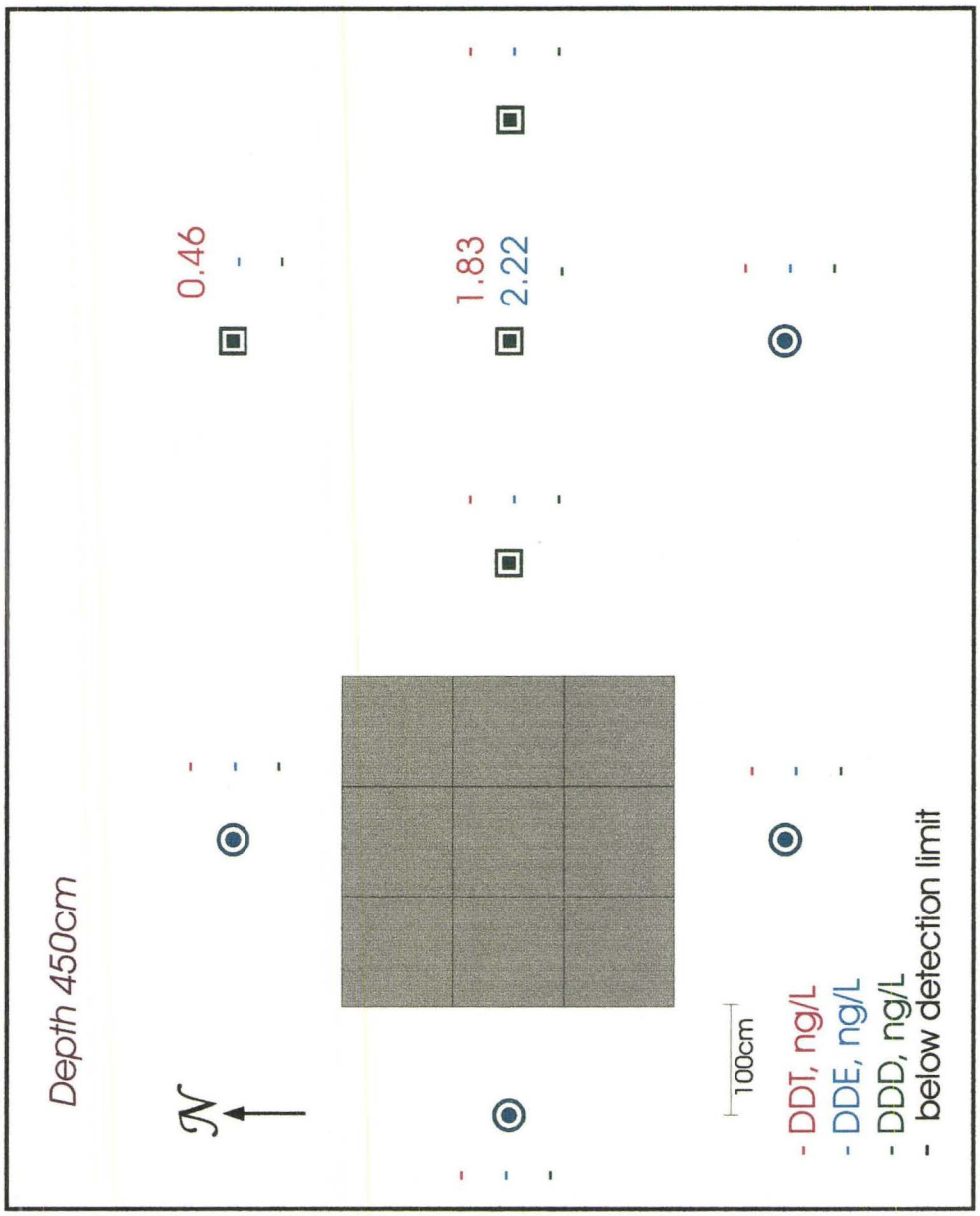


**Figure 2.11: The Results of Groundwater Sampling in March 2004 at depth 450cm**

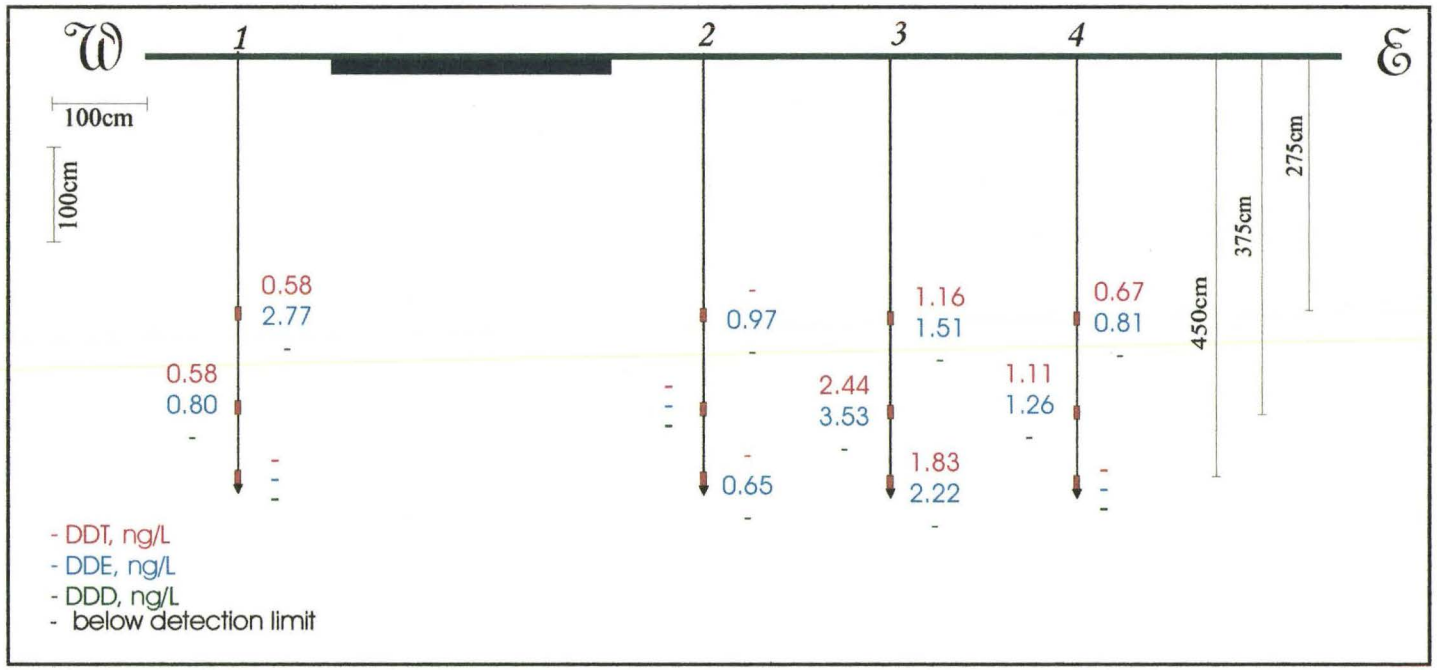


**Figure 2.12: The Results of Groundwater Sampling in March 2004, Cross-section View from West to East through the Middle of the Application Grid**

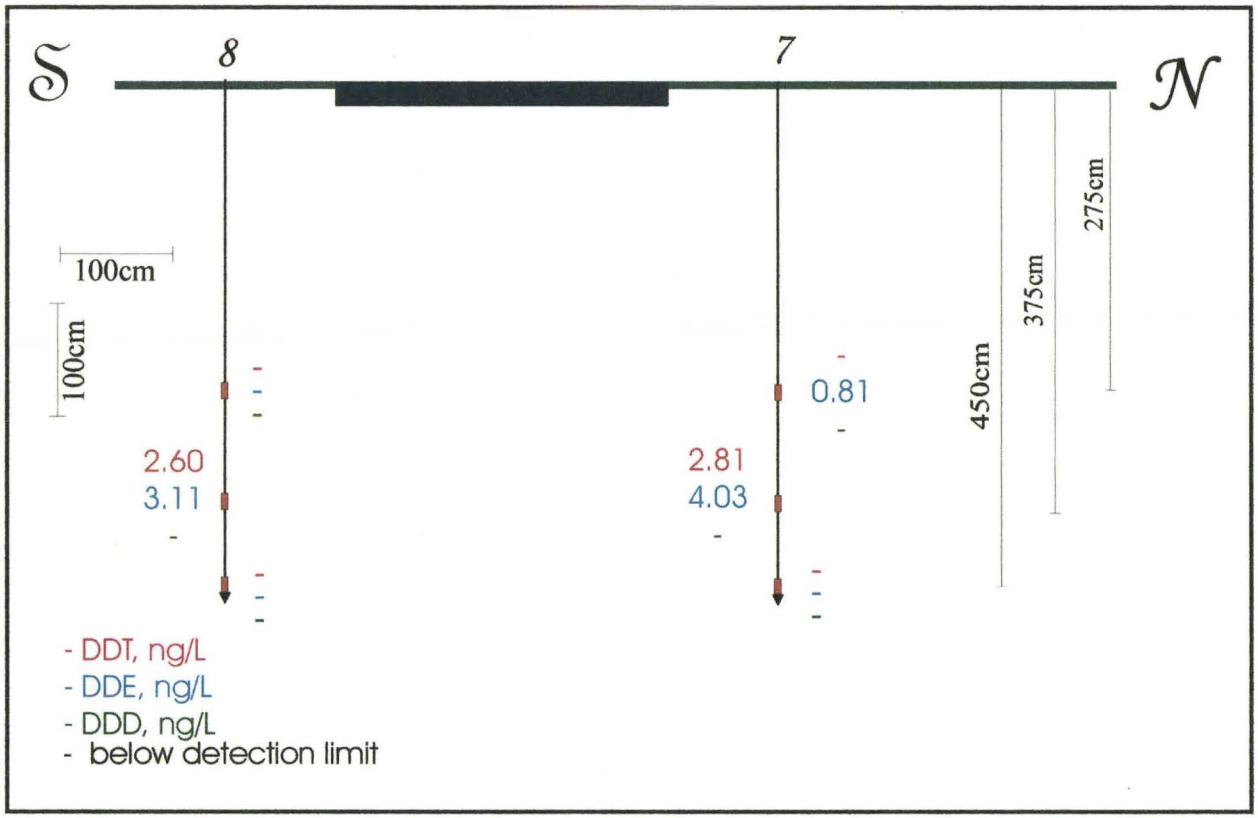


**Figure 2.13: The Results of Groundwater Sampling in March 2004, Cross-section View from North to South through the Middle of the Application Grid**

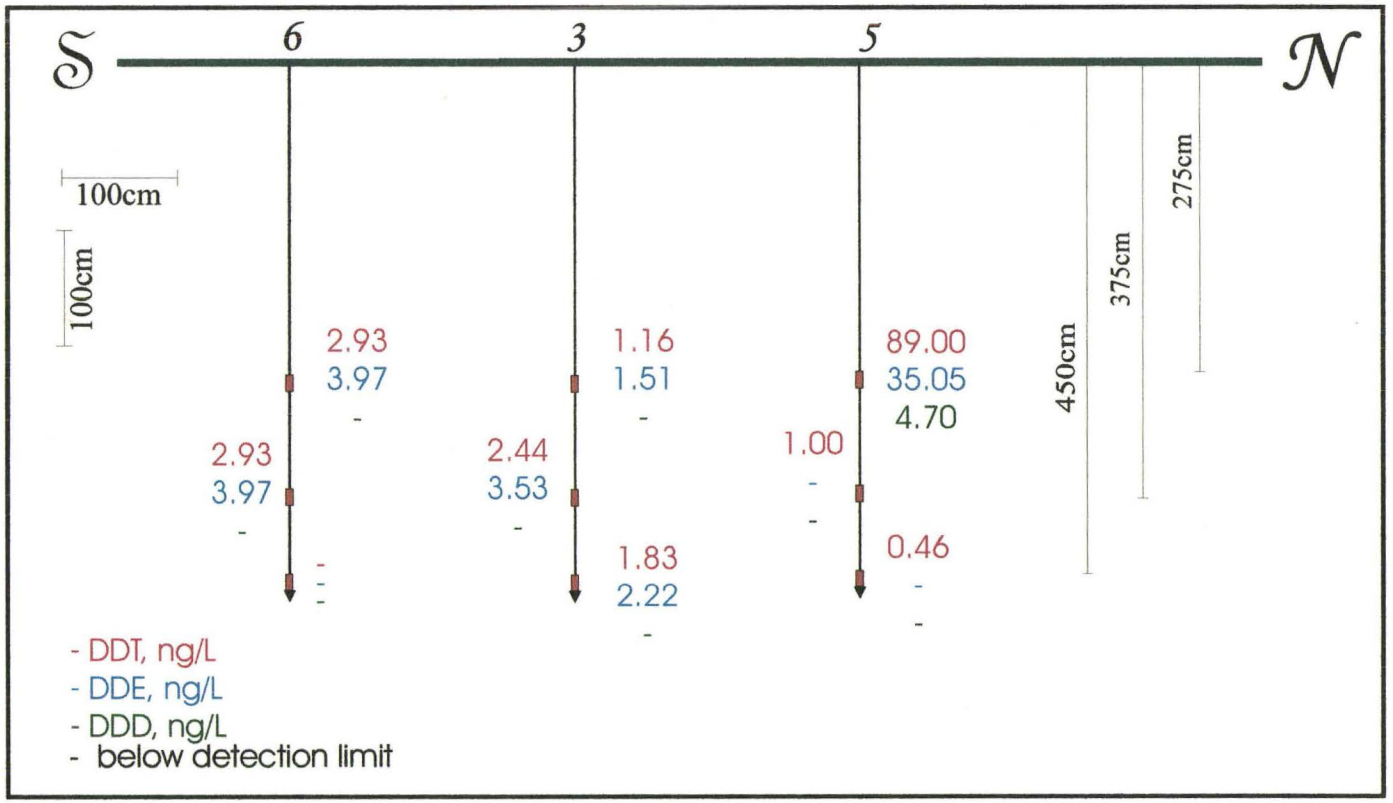


**Figure 2.14: The Results of Groundwater Sampling in March 2004, Cross-section View from North 300cm East from East Edge of Application Grid**

To calculated the mass of DDT and DDE found in groundwater in March 2004 the total sampling area which is 11m×7m was divided into 8 rectangular parts each of them corresponds to a particular sampling well (Figure 2.15). Zero concentration was assigned to the points where concentration is below detection limit. The volumes assigned to each well are not equal. They are based on the spatial distribution wells including sampling depths, and the expected mass distribution due to advection and dispersion. Vertically, the profile was divided into 3 layers, A, B and C, each of them are associated with one of the three sampling depths (275cm, 375cm and 450cm).

The first layer, A, is 80 cm thick, the top boundary is at the depth 245cm below ground surface which is based on the depth of water table at the time of sampling (250cm below ground surface), and the height of the capillary fringe (5cm) (Marenco, 2002). The bottom boundary of the A layer and the top boundary of the B layer are at the depth 325cm below ground surface, which is in the middle between the two sampling depths, 275cm and 375cm below ground surface. The B layer is 95cm thick. The bottom boundary of the B layer and top boundary of the C layer locate at the depth 420cm below ground surface, this boundary is closer to the sampling depth 450cm, assigning a larger area for the B layer to err on the side of overestimation of mass because more samples have detectible values of DDT and DDE. This is further justified by the fact that the source of DDT is from the vadose zone and therefore the shallower samples are expected to have higher concentrations and relatively weak transverse dispersion is the primary mechanism for vertical migration during groundwater flow. While this is not a rigorous assignment of the boundary location, it errs on the side of over estimating the mass in

groundwater, which is preferred over an underestimate since mass loss due to remediation is under consideration. The C layer is 130cm thick with the bottom boundary at 550cm, which is 100cm below the sampling depth of 450cm. Again, this provides a large volume to these samples and reduces the possibility of the underestimation of total mass.

The mass of DDT and DDE present in groundwater was calculated by the following equation:

$$Mass = Area \times Height \times Porosity \times Concentration \quad (2.3)$$

where *Area* is are of the rectangular part from Figure 2.15 [$cm^2$]; *Height* is the thickness of A, B and C layers [cm]; *Porosity* is equal 0.43 for the studied system; *Concentration* is DDT or DDE concentration found at this location [$ng/cm^3$].

The mass of DDT and DDE was calculated separately for each depth location and them summed. The results of DDT and DDE mass calculations are present in Tables 2.24, 2.25, and 2.26. Most of the DDT and DDE mass concentrated in the top part of aquifer. In the A layer the DDT mass is 0.38mg and DDE mass is 0.19mg. In the second layer, B, there is 0.03mg of DDT and 0.04mg of DDE. The third layer, C, has 0.01mg of DDT and 0.01mg of DDE. Therefore the estimate of total mass found in groundwater during the March 2004 sampling is 0.42mg of DDT and 0.24mg of DDE.

It is noteworthy that 85% of DDT mass and 60% of DDE mass was contributed by one sample 5A - E300N-275 (Table 2.23) where the highest concentrations of DDT and DDE were found. That is also the sample with unexpected relative proportions of DDT:DDE:DDD as discussed above. Based upon the groundwater sampling scheme there are not enough data to dismiss this sample or extrapolate further beyond this point.

However, this will be revisited in Chapter 4 relative to numerical modeling simulations with HYDRUS 2D.

For mass calculations the concentration of DDT at locations with non-detected values is equal to 0, but it is more likely that concentration of DDT in these samples is somewhat below detection limits. Therefore the maximum possible mass of DDT in groundwater could be found if the detection limit concentration is assigned to the samples with non-detected values. The detection limit for *o,p*-DDT is 1.21ng/L and detection limit for *p,p*-DDT is 0.51ng/L. The results of maximum possible DDT mass calculations are present in Tables 2.27, 2.28, and 2.29. In the A layer the maximum possible DDT mass is 0.41mg. In the B layer maximum possible DDT mass is 0.07mg. The C layer maximum possible DDT mass is 0.08mg. Therefore the estimate of maximum possible mass of DDT found in groundwater during the March 2004 sampling is 0.55mg. This value is at the same order of magnitude with estimated above value, the difference is only 0.13mg.

To compare mass found during the March 2004 groundwater sampling with the mass found during the October 2003 groundwater sampling, the October sampled area was divided into rectangular parts using the same principle as for March samples. That is larger areas were assigned to the samples with the higher concentrations (Figure 2.17) to reduce the possibility of underestimation of mass in groundwater. Due to insufficient data on DDT concentration, i.e. many non-detects, only the mass of DDE was estimated for the October sampling. The size of the sampled area is 7m by 11m, which is the same with sampling area in March, but the area sampled in March was moved 3m to the east. The estimated height of the sample layer is 80cm, which is consistent with the height of A

layer of the March sampled profile. The calculated DDE mass in the top 80cm of the aquifer found in October 2003 is 0.12mg (Table 2.30). The DDE mass in A layer for March sampling is 0.19mg. Given the estimation method and the sparse data, these numbers are too close to make meaningful comparison or conclusions for flow, transport. and/or reactions between October 2003 to March 2004. They are reported here for completeness and to provide a reference point for the different sampling dates.

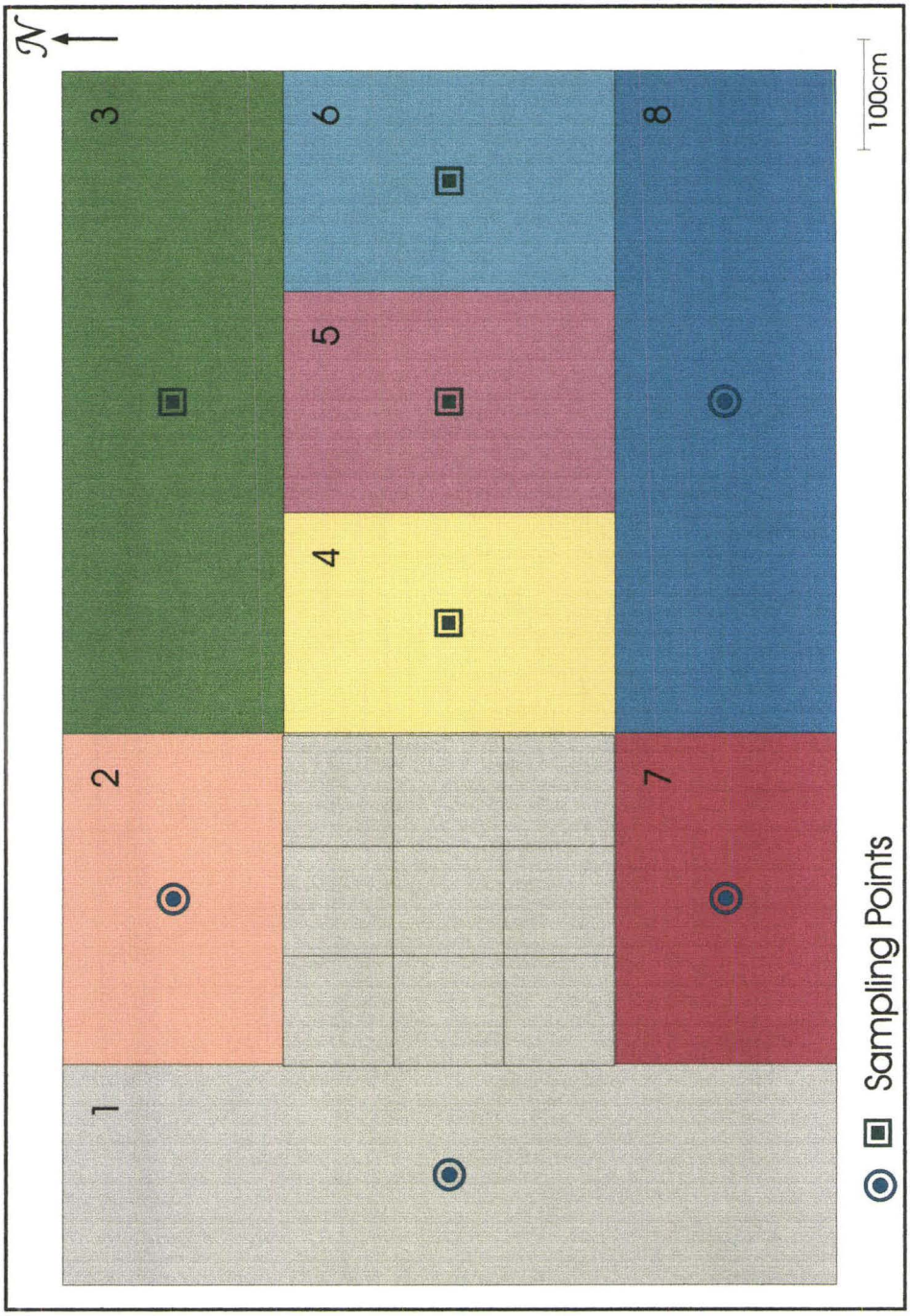


**Figure 2.15: The Division into Rectangular Parts of the Sampling in March 2004 area**

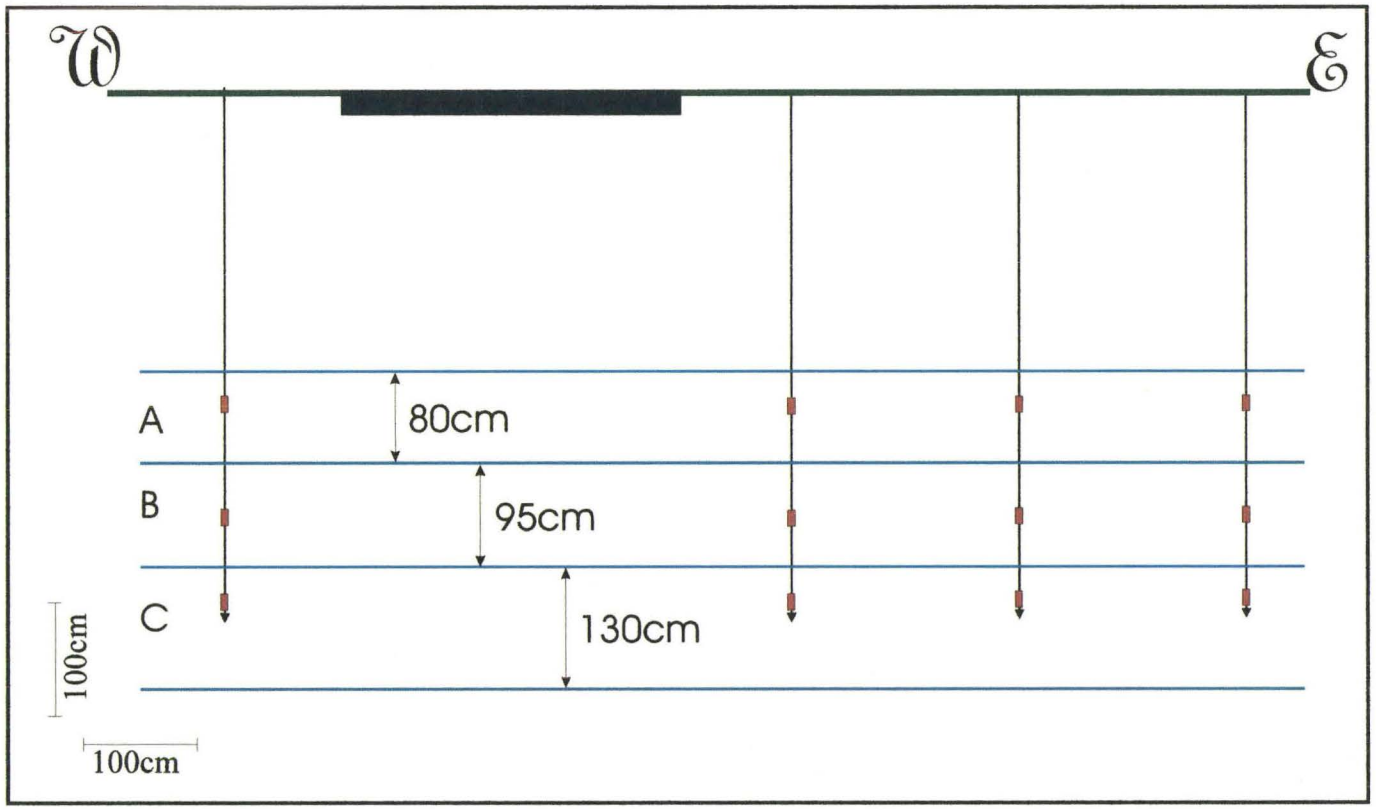


**Figure 2.16: The Division of the Sampling in March 2004 Profile into Three Layers for the Mass Calculations**

| Sample Name | Area, cm2 | Total Volume, cm3 | Volume of Groundwater, cm3 | DDT, ng/L | DDT, ng/cm3 | Mass of DDT, ng | DDE, ng/L | DDE, ng/cm3 | Mass of DDE, ng |
|---|---|---|---|---|---|---|---|---|---|
| 1A | 230000 | 18400000 | 7728000 | 0.58 | 0.00058 | 4482.24 | 2.77 | 0.002770 | 21406.56 |
| 2A | 60000 | 4800000 | 2016000 | ND* | – | – | 0.81 | 0.000810 | 1632.96 |
| 3A | 120000 | 9600000 | 4032000 | 89.00 | 0.08900 | 358848.00 | 35.05 | 0.035050 | 141321.60 |
| 4A | 60000 | 4800000 | 2016000 | ND | – | – | 0.97 | 0.000970 | 1955.52 |
| 5A | 60000 | 4800000 | 2016000 | 1.16 | 0.00116 | 2338.56 | 1.51 | 0.001510 | 3044.16 |
| 6A | 60000 | 4800000 | 2016000 | 0.67 | 0.00067 | 1350.72 | 0.81 | 0.000810 | 1632.96 |
| 7A | 60000 | 4800000 | 2016000 | ND | – | – | ND | – | – |
| 8A | 120000 | 9600000 | 4032000 | 2.93 | 0.00293 | 11813.76 | 3.97 | 0.003970 | 16007.04 |
| | | Total: | 25872000 | | Total: | 378833 | | Total: | 187000 |

* non-detected

**Table 2.24: Calculations of DDT and DDE Mass in the A Layer at the Sampling Depth 275cm for the samples obtained in March 2004**

| Sample Name | Area, cm2 | Total Volume, cm3 | Volume of Groundwater, cm3 | DDT, ng/L | DDT, ng/cm3 | Mass of DDT, ng | DDE, ng/L | DDE, ng/cm3 | Mass of DDE, ng |
|---|---|---|---|---|---|---|---|---|---|
| 1B | 230000 | 21850000 | 9177000 | 0.58 | 0.00058 | 5322.66 | 0.80 | 0.000800 | 7341.60 |
| 2B | 60000 | 5700000 | 2394000 | 2.81 | 0.00281 | 6727.14 | 4.03 | 0.004030 | 9647.82 |
| 3B | 120000 | 11400000 | 4788000 | 1.00 | 0.00100 | 4788.00 | ND | – | – |
| 4B | 60000 | 5700000 | 2394000 | ND* | – | – | ND | – | – |
| 5B | 60000 | 5700000 | 2394000 | 2.44 | 0.00244 | 5841.36 | 3.53 | 0.003530 | 8450.82 |
| 6B | 60000 | 5700000 | 2394000 | 1.11 | 0.00111 | 2657.34 | 1.26 | 0.001260 | 3016.44 |
| 7B | 60000 | 5700000 | 2394000 | 2.60 | 0.00260 | 6224.40 | 3.11 | 0.003110 | 7445.34 |
| 8B | 120000 | 11400000 | 4788000 | ND | – | – | ND | – | – |
| | | Total: | 30723000 | | Total: | 31561 | | Total: | 35902 |

* non-detected

**Table 2.25: Calculations of DDT and DDE Mass in the B Layer at the Sampling Depth 375cm for the samples obtained in March 2004**

| Sample Name | Area, cm2 | Total Volume, cm3 | Volume of Groundwater, cm3 | DDT, ng/L | DDT, ng/cm3 | Mass of DDT, ng | DDE, ng/L | DDE, ng/cm3 | Mass of DDE, ng |
|---|---|---|---|---|---|---|---|---|---|
| 1C | 230000 | 29900000 | 12558000 | ND* | – | – | ND | – | – |
| 2C | 60000 | 7800000 | 3276000 | ND | – | – | ND | – | – |
| 3C | 120000 | 15600000 | 6552000 | 0.46 | 0.00046 | 3013.92 | ND | – | – |
| 4C | 60000 | 7800000 | 3276000 | ND | – | – | 0.65 | 0.000650 | 2129.40 |
| 5C | 60000 | 7800000 | 3276000 | 1.83 | 0.00183 | 5995.08 | 2.22 | 0.002220 | 7272.72 |
| 6C | 60000 | 7800000 | 3276000 | ND | – | – | ND | – | – |
| 7C | 60000 | 7800000 | 3276000 | ND | – | – | ND | – | – |
| 8C | 120000 | 15600000 | 6552000 | ND | – | – | ND | – | – |
| | | Total: | 42042000 | | Total: | 9009 | | Total: | 9402.12 |

* non-detected

**Table 2.26: Calculations of DDT and DDE Mass in the C Layer at the Sampling Depth 450cm for the samples obtained in March 2004**

| Sample Name | Area, $cm^2$ | Total Volume, $cm^3$ | Volume of Groundwater, $cm^3$ | $DDT_{max}$, ng/L | $DDT_{max}$, $ng/cm^3$ | Maximum Mass of DDT, ng |
|---|---|---|---|---|---|---|
| 1A | 230000 | 18400000 | 7728000 | 1.79 | 0.00179 | 13833.12 |
| 2A | 60000 | 4800000 | 2016000 | 1.72 | 0.00172 | 3467.52 |
| 3A | 120000 | 9600000 | 4032000 | 89.00 | 0.08900 | 358848.00 |
| 4A | 60000 | 4800000 | 2016000 | 1.72 | 0.00172 | 3467.52 |
| 5A | 60000 | 4800000 | 2016000 | 2.37 | 0.00237 | 4777.92 |
| 6A | 60000 | 4800000 | 2016000 | 1.88 | 0.00188 | 3790.08 |
| 7A | 60000 | 4800000 | 2016000 | 1.72 | 0.00172 | 3467.52 |
| 8A | 120000 | 9600000 | 4032000 | 4.14 | 0.00414 | 16692.48 |
| | | Total: | 25872000 | | Total: | 408344.16 |

**Table 2.27: Calculations of Maximum Possible DDT Mass in the A Layer at the Sampling Depth 275cm for the samples obtained in March 2004**

| Sample Name | Area, $cm^2$ | Total Volume, $cm^3$ | Volume of Groundwater, $cm^3$ | $DDT_{max}$, ng/L | $DDT_{max}$, $ng/cm^3$ | Maximum Mass of DDT, ng |
|---|---|---|---|---|---|---|
| 1B | 230000 | 21850000 | 9177000 | 1.79 | 0.00179 | 16426.83 |
| 2B | 60000 | 5700000 | 2394000 | 4.02 | 0.00402 | 9623.88 |
| 3B | 120000 | 11400000 | 4788000 | 2.21 | 0.00221 | 10581.48 |
| 4B | 60000 | 5700000 | 2394000 | 1.72 | 0.00172 | 4117.68 |
| 5B | 60000 | 5700000 | 2394000 | 3.65 | 0.00365 | 8738.10 |
| 6B | 60000 | 5700000 | 2394000 | 2.32 | 0.00232 | 5554.08 |
| 7B | 60000 | 5700000 | 2394000 | 2.60 | 0.00260 | 6224.40 |
| 8B | 120000 | 11400000 | 4788000 | 1.72 | 0.00172 | 8235.36 |
| | | Total: | 30723000 | | Total: | 69501.81 |

**Table 2.28: Calculations of Maximum Possible DDT Mass in the B Layer at the Sampling Depth 375cm for the samples obtained in March 2004**

| Sample Name | Area, $cm^2$ | Total Volume, $cm^3$ | Volume of Groundwater, $cm^3$ | $DDT_{max}$, ng/L | $DDT_{max}$, $ng/cm^3$ | Maximum Mass of DDT, ng |
|---|---|---|---|---|---|---|
| 1C | 230000 | 29900000 | 12558000 | 1.72 | 0.00172 | 21599.76 |
| 2C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 3C | 120000 | 15600000 | 6552000 | 1.67 | 0.00167 | 10941.84 |
| 4C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 5C | 60000 | 7800000 | 3276000 | 3.04 | 0.00304 | 9959.04 |
| 6C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 7C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 8C | 120000 | 15600000 | 6552000 | 1.72 | 0.00172 | 11269.44 |
| | | Total: | 42042000 | | Total: | 76308.96 |

**Table 2.29: Calculations of Maximum Possible DDT Mass in the A Layer at the Sampling Depth 450cm for the samples obtained in March 2004**

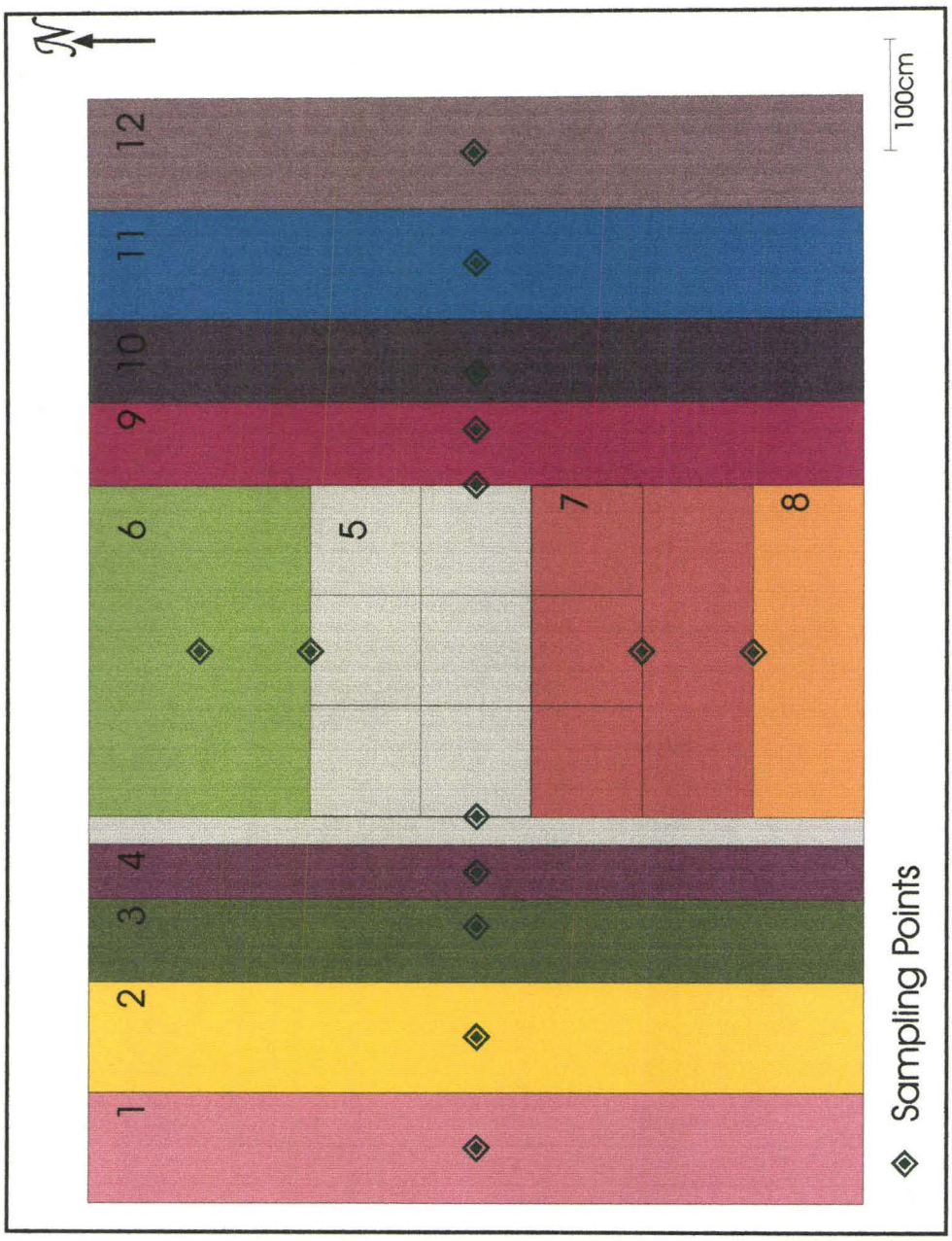


**Figure 2.17: The Division into Rectangular Parts of the Sampling in October 2003 area**

| Sample Name | Area, $cm^2$ | Total Volume, $cm^3$ | Volume of Groundwater, $cm^3$ | $DDT_{max}$, ng/L | $DDT_{max}$, $ng/cm^3$ | Maximum Mass of DDT, ng |
|---|---|---|---|---|---|---|
| 1B | 230000 | 21850000 | 9177000 | 1.79 | 0.00179 | 16426.83 |
| 2B | 60000 | 5700000 | 2394000 | 4.02 | 0.00402 | 9623.88 |
| 3B | 120000 | 11400000 | 4788000 | 2.21 | 0.00221 | 10581.48 |
| 4B | 60000 | 5700000 | 2394000 | 1.72 | 0.00172 | 4117.68 |
| 5B | 60000 | 5700000 | 2394000 | 3.65 | 0.00365 | 8738.10 |
| 6B | 60000 | 5700000 | 2394000 | 2.32 | 0.00232 | 5554.08 |
| 7B | 60000 | 5700000 | 2394000 | 2.60 | 0.00260 | 6224.40 |
| 8B | 120000 | 11400000 | 4788000 | 1.72 | 0.00172 | 8235.36 |
| | | Total: | 30723000 | | Total: | 69501.81 |

**Table 2.28: Calculations of Maximum Possible DDT Mass in the B Layer at the Sampling Depth 375cm for the samples obtained in March 2004**

| Sample Name | Area, $cm^2$ | Total Volume, $cm^3$ | Volume of Groundwater, $cm^3$ | $DDT_{max}$, ng/L | $DDT_{max}$, $ng/cm^3$ | Maximum Mass of DDT, ng |
|---|---|---|---|---|---|---|
| 1C | 230000 | 29900000 | 12558000 | 1.72 | 0.00172 | 21599.76 |
| 2C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 3C | 120000 | 15600000 | 6552000 | 1.67 | 0.00167 | 10941.84 |
| 4C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 5C | 60000 | 7800000 | 3276000 | 3.04 | 0.00304 | 9959.04 |
| 6C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 7C | 60000 | 7800000 | 3276000 | 1.72 | 0.00172 | 5634.72 |
| 8C | 120000 | 15600000 | 6552000 | 1.72 | 0.00172 | 11269.44 |
| | | Total: | 42042000 | | Total: | 76308.96 |

**Table 2.29: Calculations of Maximum Possible DDT Mass in the A Layer at the Sampling Depth 450cm for the samples obtained in March 2004**

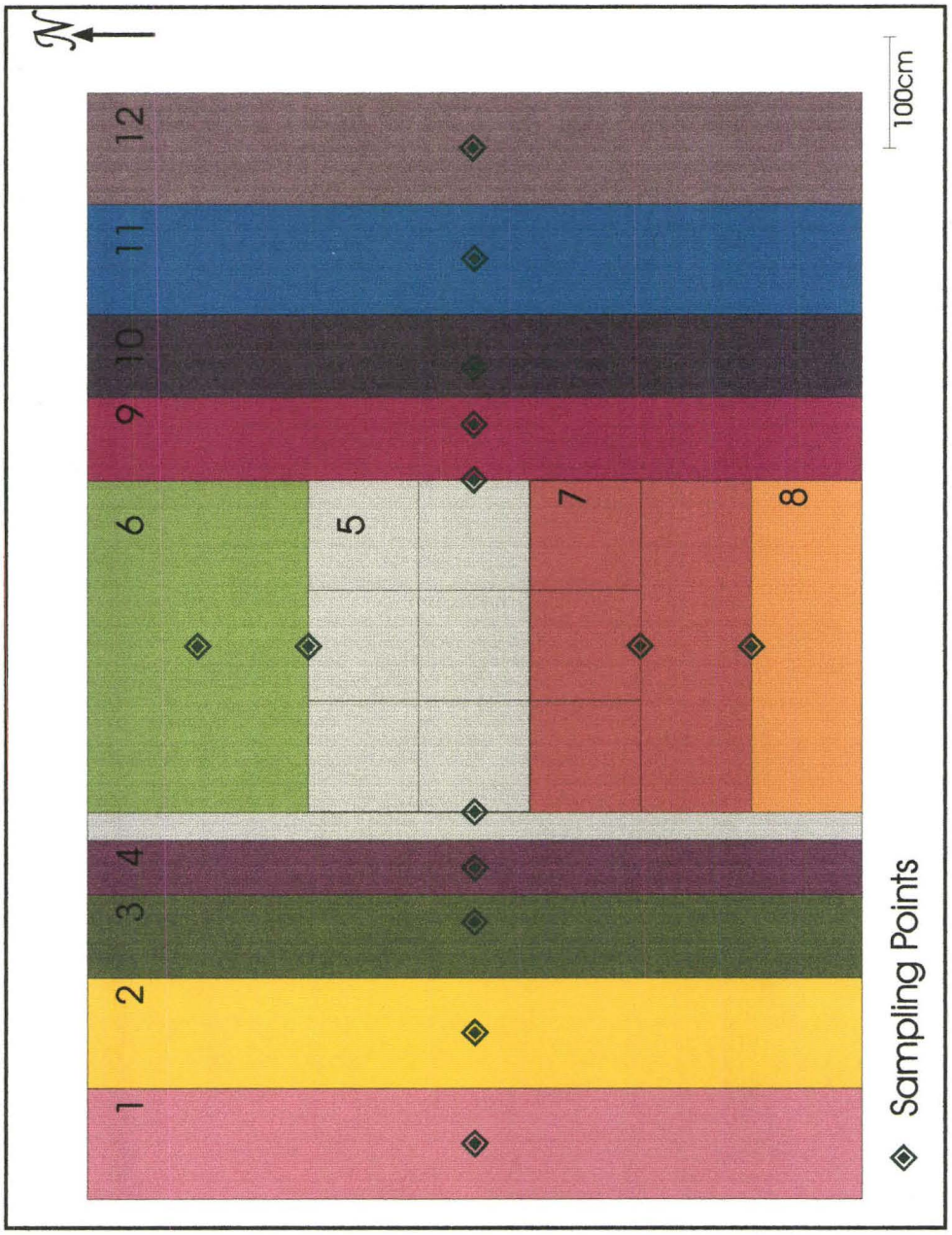


**Figure 2.17: The Division into Rectangular Parts of the Sampling in October 2003 area**

| Sample Name | Area, $cm^2$ | Total Volume, $cm^3$ | Volume of Groundwater, $cm^3$ | DDE, ng/L | DDE, $ng/cm^3$ | Mass of DDE, ng |
|---|---|---|---|---|---|---|
| 1A | 70000 | 5600000 | 2352000 | 1.64 | 0.00164 | 3857.28 |
| 2A | 70000 | 5600000 | 2352000 | ND | – | – |
| 3A | 52500 | 4200000 | 1764000 | 17.00 | 0.01700 | 29988.00 |
| 4A | 35000 | 2800000 | 1176000 | 2.45 | 0.00245 | 2881.20 |
| 5A | 77500 | 6200000 | 2604000 | 1.87 | 0.00187 | 4869.48 |
| 6A | 60000 | 4800000 | 2016000 | ND | – | – |
| 7A | 60000 | 4800000 | 2016000 | 9.14 | 0.00914 | 18426.24 |
| 8A | 30000 | 2400000 | 1008000 | ND | – | – |
| 9A | 52500 | 4200000 | 1764000 | ND | – | – |
| 10A | 52500 | 4200000 | 1764000 | 1.93 | 0.00193 | 3404.52 |
| 11A | 70000 | 5600000 | 2352000 | 2.73 | 0.00273 | 6420.96 |
| 12A | 140000 | 11200000 | 4704000 | 10.10 | 0.01010 | 47510.40 |
| | | Total: | 25872000 | | Total: | 117358 |

**Table 2.30: Calculations of DDE Mass in the Groundwater found in October 2003**

### 2.3.4 Mass Balance Soil versus Groundwater

If there were no DDT degradation in the system, the expected mass of DDT in groundwater would be equal to the total mass of DDT removed from soil, i.e., 12g based on the arithmetical data and 3.37g based on the ln-transformed data. The estimated mass of DDT found during the March 2004 sampling is 0.42mg, which is 3-4 orders of magnitude less than the estimates of the mass removed from soil. The mass of DDT in groundwater is 0.0035% and 0.012% of the mass lost from the soil based upon the arithmetical and the ln-transformed data respectively. Assuming that the groundwater sampling scheme has captured the groundwater plume, this reduction in mass would be attributed to the biological and/or cometabolic degradation as enhanced by the presence of cyclodextrin in solution. Based on these masses estimates of the half-life for DDT in the groundwater can be calculated by the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \qquad 2.4$$

where $t_{1/2}$ is the half-life, $k$ is the decay constant.

The decay constant can be found from the following equation

$$\ln\left(\frac{C_t}{C_o}\right) = -kt \qquad 2.5$$

where $C_t$ is the concentration or mass at time t, $C_0$ is the concentration or mass at time zero, $k$ is the decay constant, and $t$ is the time since the chemical was last applied.

The estimated half-life for DDT in the cyclodextrin plume in the groundwater system is less than two months (43-49days). This estimate treats the DDT degradation as

a first order reaction. While total DDT loss is complicated by other environmental factors such as volatilization, runoff, erosion, leaching (Boul, 1994; Marenco, 2002), half-life estimates are frequently quoted as useful quantification of the persistence of DDT.

The estimated maximum possible mass of DDT found during the March 2004 sampling is 0.55mg, which is still 3-4 orders of magnitude less than the estimates of the mass removed from soil. The maximum possible mass of DDT in groundwater is 0.0046% and 0.016% of the mass lost from the soil based upon the arithmetical and the ln-transformed data respectively. Assuming that the groundwater sampling scheme has captured the groundwater plume, the maximum estimated half-life for DDT in the cyclodextrin plume is less than two months (44-51days).

Given the low concentration, which represents more than 99.9% mass loss, the possibility that the groundwater plume may have moved further east from the remediation plots needs to be more fully evaluated. That is, if the groundwater velocities during the study period were larger than estimated from historic data reported by Crowe et al. (2004) then the center of mass of the plume could be further east and the groundwater sampling scheme used in this study may have only sampled the western trailing portion of the plume. In chapter 3 this possibility will be further addressed and conservative estimates will be provided for expected concentrations for the case of high groundwater velocities using the highest historic local groundwater velocities and the numerical model HYDRUS 2D.

# 3. Numerical Modeling

## *3.1 Introduction*

The unsaturated/saturated numerical model, HYDRUS-2D was used to model the pilot-scale experiment conducted by Badley (2003) to assess the distribution of the mass of DDT and cyclodextrin in the groundwater system including the year and a half following the experiment. The simulations include 19 applications of cyclodextrin, one pore volume to each plot during the first 13 applications and one pore volume to ½ the plots during the last 6 applications, because the application of 20% solution was ceased.

HYDRUS-2D is a modeling environment for analysis of flow and solute transport in variably saturated porous media. It was developed by the U.S. Salinity Laboratory, U.S. Department of Agriculture, Agriculture Research Service (Simunek et al., 1999). This environment has an interactive graphical user interface, which runs under Microsoft Windows. It includes the two-dimensional finite element model SWMS-2D that is used for the analysis of water flow and solute transport in variable saturated porous media. HYDRUS-2D includes a mesh generator for defining unstructured finite element grids, MESHGEN-2D.

HYDRUS-2D has extensive capabilities; it can simulate unsaturated/saturated water flow, heat, and multiple component solute transport in porous media.

The governing equations of this program are the Richards' equation for saturated-unsaturated water flow and convection-dispersion type equations for heat and solute transport. The flow model solved in two dimensions is Richards' equation:

$$\nabla \cdot K(\psi)\nabla H = C(\psi)\frac{\partial \psi}{\partial t} \tag{3.1}$$

where $K(\psi)$ is unsaturated hydraulic conductivity at pressure head $\psi$ ($LT^{-1}$), $C(\psi)$ is specific moisture capacity ($L^{-1}$), $H = \psi + z$ is total head (L), $\psi$ is pressure head (L) and $z$ is elevation (L).

The program can also solve the modified form of Richards' equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i}\left[K\left(K_{ij}{}^{A}\frac{\partial \psi}{\partial x_j} + K_{iz}{}^{A}\right)\right] - S \tag{3.2}$$

where $\theta$ is the volumetric water content [$L^3L^{-3}$], $\psi$ is the pressure head [L], $S$ is a sink term [$T^{-1}$], $x_i$ ($i$=1,2) are the spatial coordinates[L], t is time [T], $K_{ij}{}^{A}$ are components of a dimensionless anisotropy tensor $\mathbf{K^A}$, and $K$ is the unsaturated hydraulic conductivity function [$LT^{-1}$].

## 3.2 Methods

The following section discusses the input data for the HYDRUS-2D simulations. First, the common model parameters will be described, followed by parameters specific to each simulation. All input parameters for all simulations are presented in Table 3.1.

*Soil Profile.* For the modeling purposes the soil profile was divided into two hydrostratigraphic layers: A horizon and B horizon (Figure 3.1). The physical and hydraulic properties are present in Table 3.2. The A horizon includes the Of horizon (0–2.5cm), and Ah horizon (2.5–20.0cm) (Badley, 2003). This zone is distinguished by higher organic content, higher porosity, smaller bulk density and lower saturated hydraulic conductivity (Table 3.2). The B horizon includes the Bm horizon (20–50cm), BC horizon (50–80cm) and C horizon at a depth from 80cm to low permeability clay aquitard at 900cm (Crowe et al., 2004). The B-layer is primarily composed of sand with low organic content (Badley, 2003). This subdivision of the domain was determined by similar hydraulic properties.

*Groundwater level.* According to historical data (Crowe et al., 2002) the depth of water table varies in the range of 50–70cm during a single year. At the time of groundwater sampling in October 2003 and March 2004 the water table was determined at depths 2.7m and 2.5m below ground surface, respectively (Mills, 2003; Mills 2004). The estimated average water table from the period from June 2002 until March 2004 is 2.4m.

**Table 3.1: Summary for Input Data in HYDRUS-2D simulations**

| **Model*** | **1** | **2** | **3** |
|---|---|---|---|
| **Main Processes** | | | |
| ▪ Water Flow | ✓ | ✓ | ✓ |
| ▪ Solute Transport | ✓ | ✓ | ✓ |
| **Geometry Information** | | | |
| ▪ Length Units | cm | cm | cm |
| *Geometry Type* | | | |
| ▪ Rectangular | ✓ | ✓ | ✓ |
| ▪ Type of Flow | vertical | vertical | vertical |
| *Soil Profile* | | | |
| ▪ Number of materials (Heterogeneity) | 2 | 2 | 2 |
| ▪ Number of Layers (Mass Balance) | 2 | 2 | 2 |
| **Time Information** | | | |
| ▪ Time Units | days | days | days |
| *Time Discretization* | | | |
| ▪ Initial Time | 0 | 0 | 0 |
| ▪ Final Time | 7 | 638 | 638 |
| ▪ Initial Time Step | 0.001 | 0.001 | 0.001 |
| ▪ Minimum Time Step | 0.0005 | 0.0001 | 0.0001 |
| ▪ Maximum Time Step | 0.8 | 1 | 1 |
| *Boundary Conditions* | | | |
| ▪ Number of Time-Variable Boundary Records | 3 | 51 | 51 |
| **Print Options** | | | |
| ▪ Number of Print Times | 40 | 72 | 72 |
| **Iteration Criteria** | | | |
| *Iteration Criteria* | | | |
| ▪ Maximum Number of Iterations | 10 | 10 | 10 |
| ▪ Water Content Tolerance | 0.001 | 0.001 | 0.001 |
| ▪ Pressure Head Tolerance | 0.1 | 0.1 | 0.1 |
| *Time Step Control* | | | |
| ▪ Lower Optional Iteration Range | 3 | 3 | 3 |
| ▪ Upper Optional Iteration Range | 7 | 7 | 7 |
| ▪ Lower Time Step Multiplication Factor | 1.5 | 1.5 | 1.5 |
| ▪ Upper Time Step Multiplication Factor | 0.7 | 0.7 | 0.7 |
| *Internal Interpolation Tables* | | | |
| ▪ Lower Limit of the Tension Interval | 0.001 | 0.001 | 0.001 |
| ▪ Upper Limit of the Tension Interval | 250 | 250 | 250 |
| *Initial Conditions* | | | |
| ▪ In the Pressure Head | ✓ | ✓ | ✓ |
| ▪ In theWater Content | | | |
| **Soil Hydraulic Model** | | | |
| ▪ van Genuchtem-Mualem | + | + | + |
| ▪ Hysteresis | No | No | No |

*Table 3.1. Continued*

| **Model*** | **1** | **2** | **3** |
|---|---|---|---|
| **Water Flow Parameters** | | | |
| *A Horizon* | | | |
| ▪ $Q_r$ | 0.0465 | 0.0465 | 0.0465 |
| ▪ $Q_s$ | 0.5656 | 0.5656 | 0.5656 |
| ▪ Alpha | 0.0649 | 0.0649 | 0.0649 |
| ▪ n | 1.9929 | 1.9929 | 1.9929 |
| ▪ $K_s$ | 493.02 | 493.02 | 493.02 |
| ▪ I | 0.5 | 0.5 | 0.5 |
| *B Horizon* | | | |
| ▪ $Q_r$ | 0.0531 | 0.0531 | 0.0531 |
| ▪ $Q_s$ | 0.3933 | 0.3933 | 0.3933 |
| ▪ Alpha | 0.0316 | 0.0316 | 0.0316 |
| ▪ n | 4.3647 | 4.3647 | 4.3647 |
| ▪ $K_s$ | 1369.46 | 1369.46 | 1369.46 |
| ▪ I | 0.5 | 0.5 | 0.5 |
| **Solute Transport – General Information** | | | |
| *Time Weighting Scheme* | | | |
| ▪ Crank-Nicholson Scheme | ✓ | ✓ | ✓ |
| *Space Weighting Scheme* | | | |
| ▪ Galerkin Finite Elements | ✓ | ✓ | ✓ |
| ▪ Mass Units | mg | % | mg |
| ▪ Stability Criteria | 0.2 | 2 | 2 |
| ▪ Use Tortuosity Factor | ✓ | ✓ | ✓ |
| ▪ Number of Solutes | 1 | 1 | 1 |
| ▪ Pulse Duration | 8 | 146 | 146 |
| **Solute Transport Parameters** | | | |
| *A Horizon* | | | |
| ▪ Bulk Density | 0.97 | 0.97 | 0.97 |
| ▪ Longitudinal Dispersivity | 3 | 45 | 45 |
| ▪ Transverse Dispersivity | 0.5 | 4.5 | 4.5 |
| *B Horizon* | | | |
| ▪ Bulk Density | 1.43 | 1.43 | 1.43 |
| ▪ Longitudinal Dispersivity | 3 | 45 | 45 |
| ▪ Transverse Dispersivity | 0.5 | 4.5 | 4.5 |

* 1. Single Application to One Plot
2. Cyclodextrin Applications
3. DDT Mobilization by Cyclodextrin

Since it is not possible in HYDRUS-2D to combine variable groundwater level and horizontal groundwater flow in one simulation, two preliminary simulations were done to determine the effect of variable groundwater levels on the size of the plume. Both of them had no initial groundwater flow. One had constant water table depth at 240cm below ground surface, the other had variable water table depth in the range of 210–280cm below ground surface. The simulations showed that the plumes differ in vertical dimension by only 15%. This relatively small effect of variable water table may be included in the value of transverse dispersivity. Therefore, it was concluded that a constant water table depth simulation with horizontal groundwater flow could capture the primary flow and transport.

*Common parameters*. All simulation included water flow and solute transport. The geometry of each domain is rectangular. Flow and transport occur in the vertical plane. The soil hydraulic functions used in all simulations, are van Genuchten-Mualem functions with no hysteresis. The Crank-Nickolson time weighting scheme and Galerkin finite elements space weighting scheme is used.

| **Property** | **A Horizon** | **B Horizon** |
|---|---|---|
| **Average Bulk Density, g/cm$^3$** | 0.97 | 1.43 |
| **Average Porosity, %** | 56.5 | 42.3 |
| **Average Organic Matter Content, %** | 13.4 | 1.6 |
| **Calculated Residual Soil Water Content, %** | 4.6 | 5.3 |
| **Calculated Saturated Hydraulic Conductivity, cm/day** | 493 | 1370 |

**Table 3.2: Physical, Chemical and Hydraulic Properties of Soil within the Remediation Grid Measured by Badley (2003) and Calculated by HYDRUS-2D Based on Field Data**

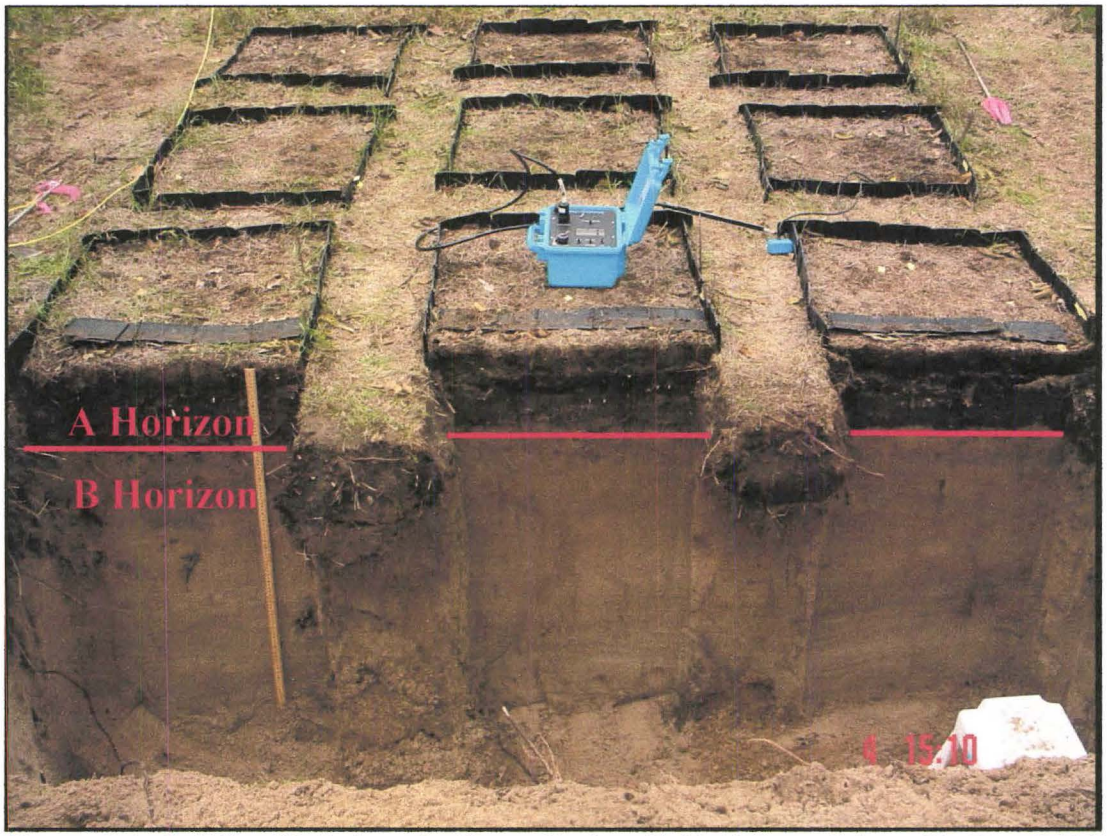


**Figure 3.1: Soil Profile below the Remediation Grid (Adopted from Badley, 2003)**

*List of simulated applications.* A total of three simulations were performed using HYDRUS-2D for simulating system behavior during and after the pilot-scale field experiment conducted by Badley (2003).

1. Single application to one plot - to understand the nature of the treatment and to demonstrate a single infiltration event of the solute.
2. Cyclodextrin applications - to demonstrate the 19 cyclodextrin applications, to determine where the plume of cyclodextrin was at the times of groundwater sampling.
3. DDT mobilization by cyclodextrin - to demonstrate the DDT removal from the top soil layer, to determine the expected DDT concentration and distribution in groundwater.

During the field remediation trials (Badley, 2003) one pore volume (33.3L) was applied to each plot, which was 70cm×70cm. The average duration of each application was 3 hours. That corresponds to a prescribed flux for a variable flux boundary in HYDRUS-2D of 54.4cm/day. This application rate is well below the saturated hydraulic conductivity (Table 3.2).

The initial condition for concentration distribution is $C(x, y, 0) = 0$

The variable-flux boundary was a third-type solute transport boundary condition.

The boundary conditions is described by the following equation:

$$\left(-D\frac{\partial C}{\partial x} + v_x C\right)\Big|_{x=0} = v_x C_0 \qquad (3.1)$$

### 3.2.1 Simulation of Single Application to One Plot

This first simulation was done in a smaller domain compared to the other simulations. It is 190cm in horizontal dimension and 160cm in vertical dimension (Figure 3.2). The distance between nodes is 2cm in both horizontal and vertical dimensions. The domain has two additional zones, which represent the plastic garden edging which enclosed each application plot. Low saturated moisture content (1%) and low saturated hydraulic conductivity (0.001cm/day) were assigned for this layer. This simulation models a single application to one plot during 3 hours and then shows the system behavior during the remaining 7 days period.

The initial water flow conditions were introduced as pressure head values. The pressure head values have linear distribution with depth with the top value equal to -240cm and the bottom value equal to -80cm, because water table depth is 240cm below the surface. The boundary conditions are presented in Figure 3.3. The top boundary has two types of boundary conditions: no flux and variable flux, the latter represents the application plot, the values for this boundary present in Table 3.3. The solution is applied for 3 hours (1.000-1.126 days) at the rate 54.4 cm/day and after the application is ceased the prescribed flux equals to 0. The cyclodextrin concentration value is 15% by wt, which introduces average concentration of cyclodextrin solution. Constant hydraulic head boundary is introduced in constant pressure head values assigned for the left, right and bottom boundaries. For the left and the right boundaries it has linear distribution with depth with the top value equals to -238cm, because the nodes in left and right top corners

belong to the top boundary, and the bottom value equals to -80cm. The pressure head value for the bottom boundary is -80cm.

The dispersivity values are 3cm for longitudinal dispersivity and 0.5cm for transverse dispersivity. These values are relatively small due to smaller scale of the domain.

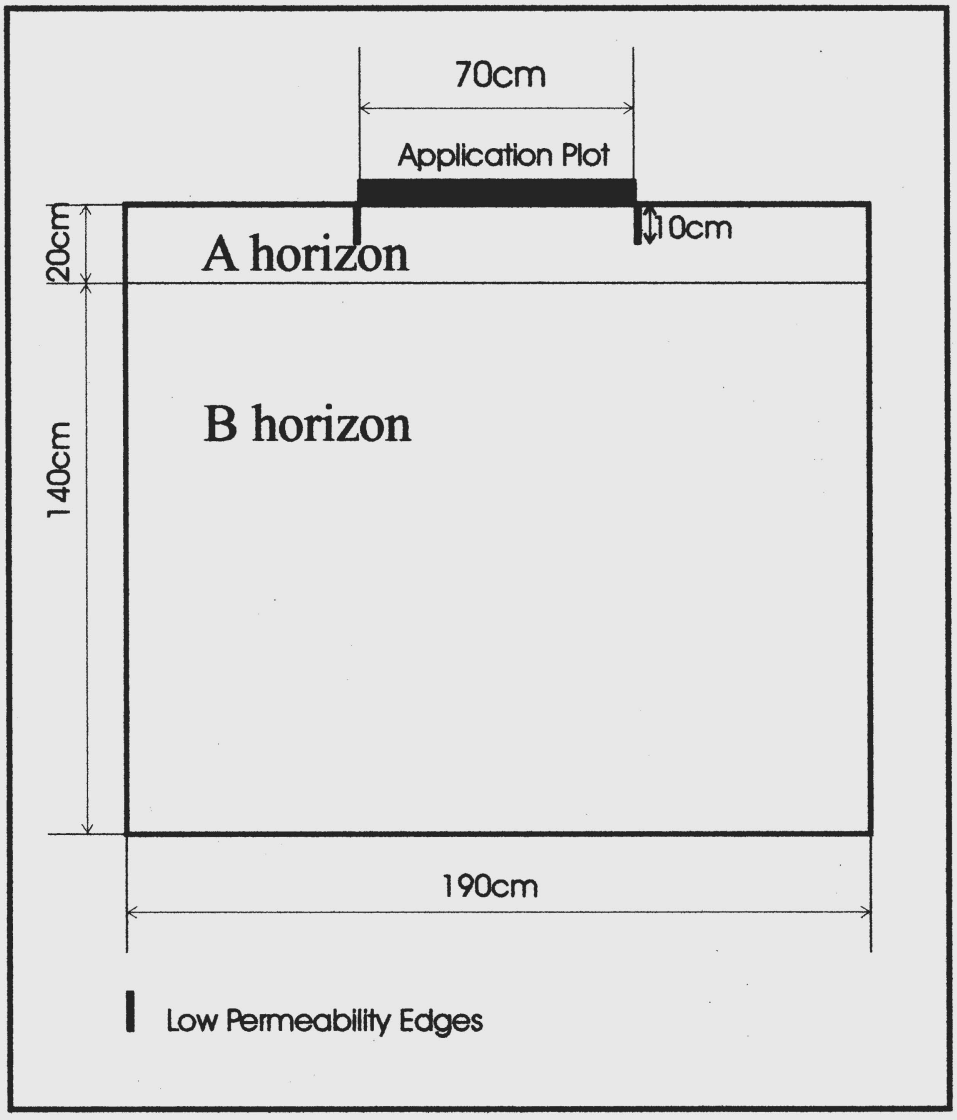


**Figure 3.2: The Layout of the Domain Geometry for a Single Application to One Plot Simulation**

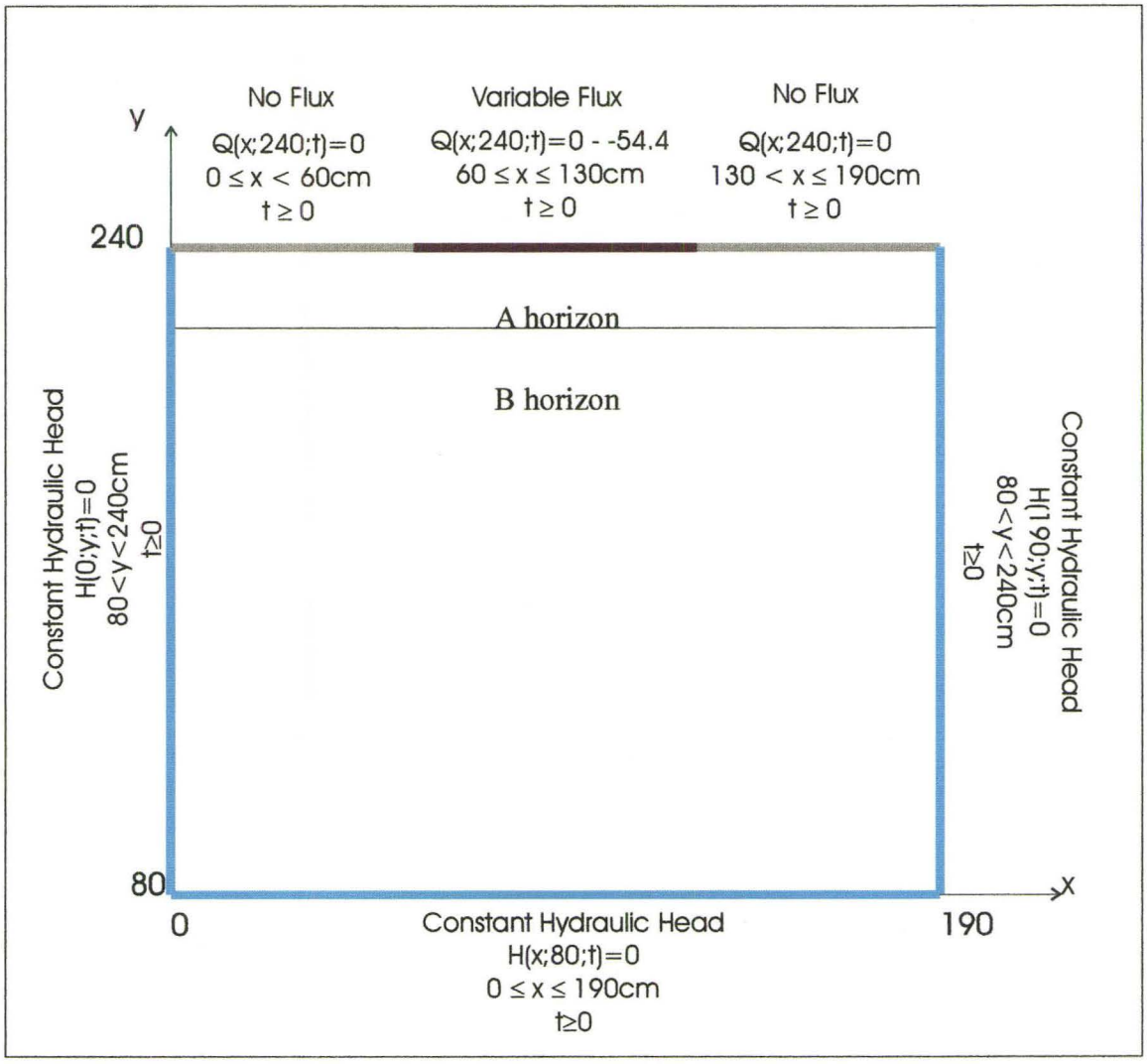


**Figure 3.3: The Layout of the Boundary Conditions for a Single Application to One Plot Simulation**

| Time, days | Precipitation, cm | Prescribed Flux, cm | Concentration Value, % |
|---|---|---|---|
| 1 | 0 | 0 | 0 |
| 1.126 | 0 | -54.4 | 15 |
| 8 | 0 | 0 | 0 |

**Table 3.3: Values for Variable Boundary Conditions for Single Application to One Plot Model**

### 3.2.2 Simulations of Cyclodextrin Applications and DDT Mobilizations

The simulations of cyclodextrin applications and DDT mobilization have the same geometry of the domain, the same initial conditions and boundary conditions, except the variable flux boundary, which differs in the values of prescribed flux and in solute concentration.

#### *3.2.2.1 The geometry of the domain for Cyclodextrin applications and DDT mobilization simulations*

The geometry of the domain is rectangular (Figure 3.4). It is 34.7m in horizontal dimension and 9m in vertical dimension. The vertical dimension is determined by the depth of the aquitard and size of the contaminated plume. The vertical and horizontal distance between nodes is 10cm, therefore it is 348 nodes in horizontal dimension and 91 nodes in vertical dimension. The application plots are located 1600cm from the edges of the domain; hence there is no boundary effect on solute transport.

#### *3.2.2.2 The initial conditions for Cyclodextrin applications and DDT mobilization simulations*

The initial water flow conditions are introduced by assigning the pressure head values linear distribution with depth, the top value is -240cm, the bottom value is 660cm and the slope is given by the tangentum alpha value of -0.0002 that represents the hydraulic gradient corresponding to horizontal groundwater flow with velocity of 1m/year. This value is based on the historical average groundwater flow velocity of 0.5-

2m/year (Crowe et al., 2004) and the apparent center of mass of the contaminated plume, which was determined by groundwater sampling in March 2004. The groundwater movement is from west to east, i.e., from the left to the right of the domain.

#### *3.2.2.3 The Boundary Conditions for Cyclodextrin Applications and DDT Mobilization Simulations*

The boundary conditions are presented in Figure 3.5. The top boundary has two types of boundary conditions: atmospheric and variable flux, the latter represents the three application plots; the values for the top boundary are presented in Table 3.4. The prescribed flux on the application plots equals to 54.4cm/day during the 3 hours of cyclodextrin solution application that represents one pore volume to each plot. Between the applications the prescribed flux equals to net infiltration rate caused by precipitation the same value as for the atmospheric boundary described below.

The precipitation data for the atmospheric boundary were obtained from Climate Normals and Averages for Point Pelee National Park presented on Environmental Canada website (http://climate.weatheroffice.ec.gc.ca/climate_normals/index_e.html, 2004). Monthly averages for total precipitation from January to December are 1.9, 1.9, 2.5, 2.7, 2.6, 2.8, 2.4, 2.9, 3.1, 1.8, 2.8 and 2.3 mm. Because the rate of evatransporation is not known several preliminary simulations were run with different rates of precipitation to match vertical portion of the center of mass of the plume determined using HYDRUS-2D with the center of mass found by groundwater sampling in March 2004. For summer months (April to September) the monthly average data were reduced by 8 times and for

winter months (October to March) - by 4 times, because evatransporation is higher for summer months. The net infiltration values caused by precipitation are presented in Table 3.4, the net infiltration rate varies from 0.03cm/day to 0.0625cm/day that is 10-25% of the precipitation rate.

The bottom boundary is a "No Flux" boundary (Figure 3.5). It represents the boundary between the aquifer and the aquitard. The aquitard consists of clay, therefore it is low permeability layer and solute transport occurs primary by diffusion, hence the flux across this boundary can be neglected for the short time frame of these simulations.

Constant hydraulic head boundary is assigned for the left and right boundaries. It is introduced as constant pressure head values. Constant pressure head values have linear distribution with depth, for the left boundary the top value is -230cm because the nodes in left and right top corners belong to the top boundary and the bottom value is 660cm and for the right boundary the top value is -230.694cm and the bottom value is 659.306cm. The difference between values on left and right boundaries on the same level is 0.694cm, that creates hydraulic gradient, which is equal 0.0002, and associated groundwater velocity is 1m/year.

#### *3.2.2.4 The Dispersivity Values for Cyclodextrin Applications and DDT Mobilization Simulations*

The dispersivity values are 45cm for longitudinal and 4.5 for transverse. The longitudinal dispersivity was set to one tenth of a travel distance (Fetter, 1999). That is, since the plume moved 4.5 meters, the longitudinal dispersivity was set to 45cm. The

ratio of longitudinal to transverse dispersivity is within the commonly reported range of 6 to 20 (Fetter, 1999). The transverse dispersivity was set to 4.5cm.

#### *3.2.2.5 Variable Flux Boundary for Cyclodextrin Applications Simulation*

*Cyclodextrin applications.* The cyclodextrin applications to the three plots model simulates 13 weekly applications of one pore volume (33.3L) of 15% by wt. cyclodextrin solution to each plot for three hours for each application, followed by 2 weekly applications of half pore volume (16.6L) of 10% by wt. cyclodextrin solution to each plot for three hours and 2 bi-weekly applications of half pore volume (16.6L) of 10% by wt. cyclodextrin solution to each plot for six hours. Table 3.5 represents the key dates of the pilot-scale field experiment and soil/groundwater sampling which were used in simulation. The 15% concentration is the average of the 10% and 20% solutions, applied in the field experiment (Badley, 2003). After 13 pore volumes the applications of 20% solution were ceased and 10% solution was applied to 3 of 6 treatment plots. To apply the correct mass in the model half the pore volumes of 10% cyclodextrin solution were applied to each of three plots. The concentration values which were used in the simulation are introduced in Table 3.6. The model simulates system behavior for 638 days from the beginning of the field experiment on June 11$^{th}$, 2002 until March 10$^{th}$, 2004, when the sampling of groundwater was completed (Table 3.5).

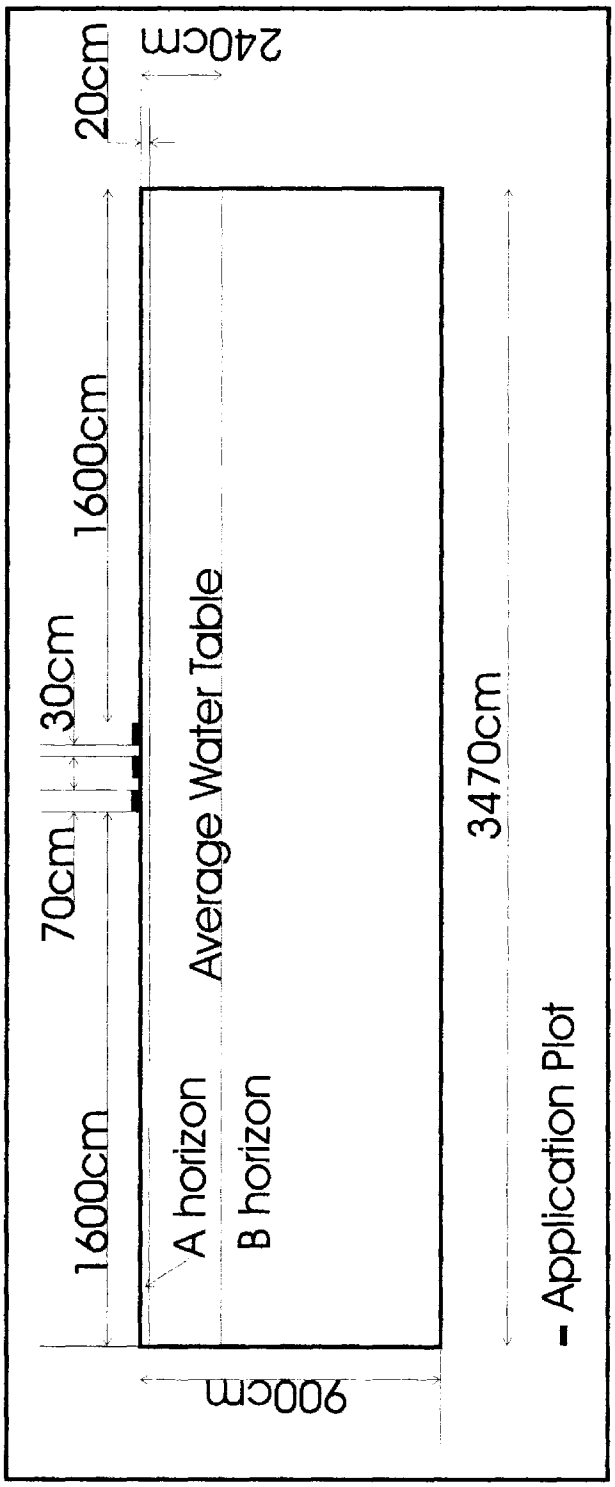


**Figure 3.4: The Layout of the Domain Geometry for the Cyclodextrin Applications Simulation and DDT Mobilization by Cyclodextrin Simulations**

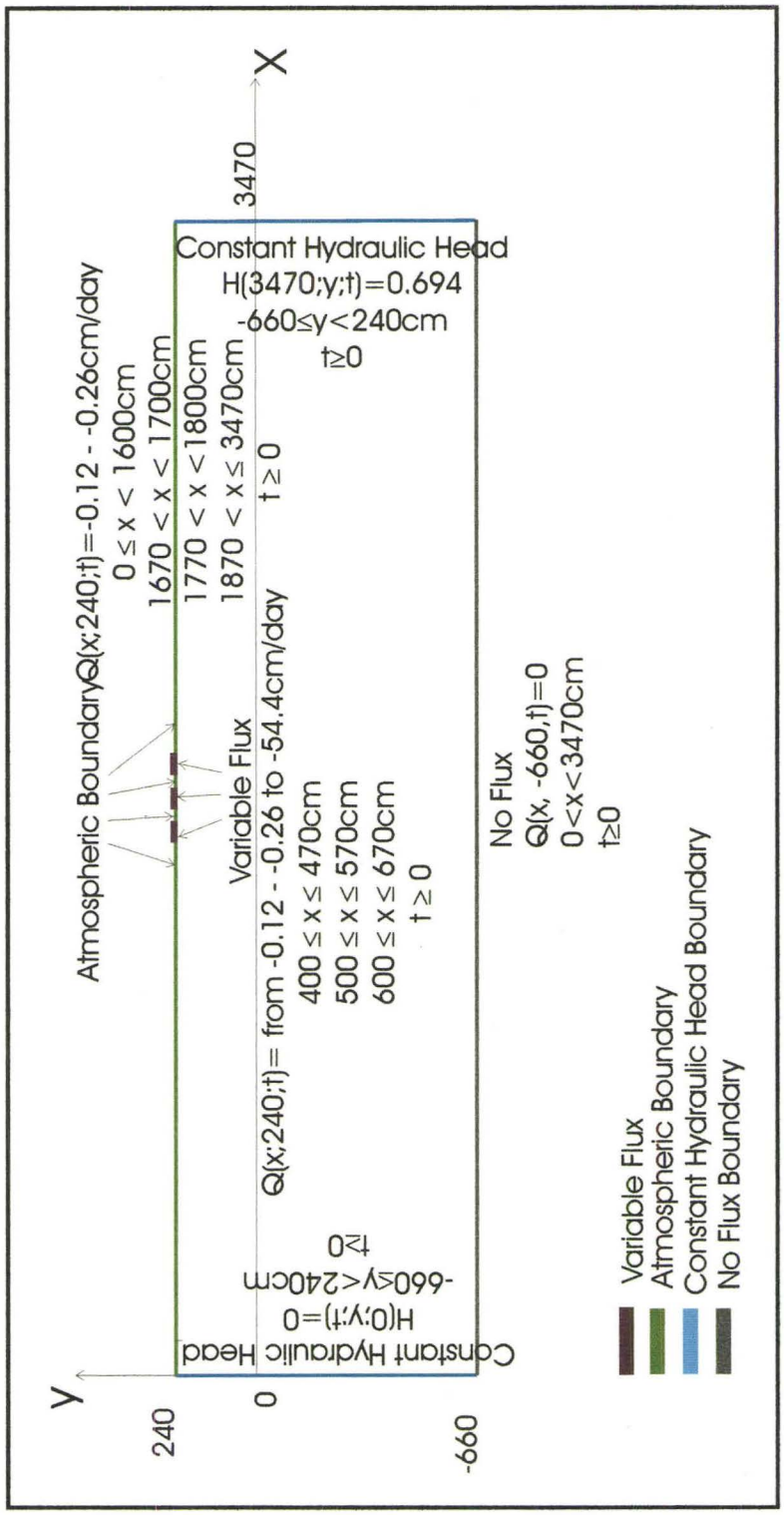


**Figure 3.5: The Layout of the Boundary Conditions for the Cyclodextrin Applications and DDT Mobilization Simulation**

**Table 3.4: Values for Atmospheric and Variable Boundary Conditions for the Cyclodextrin Applications and DDT Mobilization Simulations**

| Time, days | Net Infiltration Caused by precipitation, cm/day | Prescribed Flux, cm/day |
|---|---|---|
| 6 | 0.035 | -0.14 |
| 6.125 | 0.035 | -54.40 |
| 14 | 0.035 | -0.14 |
| 14.125 | 0.035 | -54.40 |
| 27 | 0.03 | -0.12 |
| 27.125 | 0.03 | -54.40 |
| 29 | 0.03 | -0.12 |
| 29.125 | 0.03 | -54.40 |
| 34 | 0.03 | -0.12 |
| 34.125 | 0.03 | -54.40 |
| 41 | 0.03 | -0.12 |
| 41.125 | 0.03 | -54.40 |
| 49 | 0.03 | -0.12 |
| 49.125 | 0.03 | -54.40 |
| 56 | 0.0375 | -0.15 |
| 56.125 | 0.0375 | -54.40 |
| 62 | 0.0375 | -0.15 |
| 62.125 | 0.0375 | -54.40 |
| 69 | 0.0375 | -0.15 |
| 69.125 | 0.0375 | -54.40 |
| 76 | 0.0375 | -0.15 |
| 76.125 | 0.0375 | -54.40 |
| 84 | 0.0375 | -0.15 |
| 84.125 | 0.0375 | -54.40 |
| 90 | 0.0375 | -0.15 |
| 90.125 | 0.0375 | -54.40 |
| 97 | 0.0375 | -0.15 |
| 97.125 | 0.0375 | -27.20 |
| 104 | 0.0375 | -0.15 |
| 104.125 | 0.0375 | -27.20 |
| 118 | 0.05 | -0.20 |
| 118.25 | 0.05 | -54.40 |
| 132 | 0.05 | -0.20 |
| 132.25 | 0.05 | -54.40 |
| 146 | 0.05 | -0.20 |
| 172 | 0.05 | -0.20 |
| 203 | 0.05 | -0.20 |
| 234 | 0.05 | -0.20 |
| 262 | 0.0625 | -0.25 |
| 293 | 0.065 | -0.26 |
| 323 | 0.0325 | -0.13 |

*Table 3.4. Continued*

| Time, days | Net Infiltration Caused by precipitation, cm/day | Prescribed Flux, cm/day |
|---|---|---|
| 354 | 0.035 | -0.14 |
| 384 | 0.03 | -0.12 |
| 415 | 0.0375 | -0.15 |
| 446 | 0.0375 | -0.15 |
| 485 | 0.05 | -0.20 |
| 507 | 0.05 | -0.20 |
| 537 | 0.05 | -0.20 |
| 568 | 0.05 | -0.20 |
| 599 | 0.05 | -0.20 |
| 638 | 0.0625 | -0.25 |

| # Day | Date | Comments |
|---|---|---|
| 0 | June 11, 2002 | No applications, setting up the grid |
| 6 | June 17, 2002 | 3 pore volumes of 10% solution to 3 plots and 3 pore volumes of 20% solution to 3 plots |
| 14 | June 25, 2002 | ——— // ——— |
| 27 | July 8, 2002 | ——— // ——— |
| 29 | July 10, 2002 | ——— // ——— |
| 34 | July 15, 2002 | ——— // ——— |
| 41 | July 22, 2002 | ——— // ——— |
| 49 | July 30, 2002 | ——— // ——— |
| 56 | August 6, 2002 | ——— // ——— |
| 62 | August 12, 2002 | ——— // ——— |
| 69 | August 19, 2002 | ——— // ——— |
| 76 | August 26, 2002 | ——— // ——— |
| 84 | September 3, 2002 | ——— // ——— |
| 90 | September 9, 2002 | ——— // ——— |
| 97 | September 16, 2002 | 3 pore volumes of 10% solution to 3 plots |
| 104 | September 23, 2002 | ——— // ——— |
| 118 | October 7, 2002 | 6 pore volumes of 10% solution to 3 plots |
| 132 | October 21, 2002 | ——— // ——— |
| 146 | November 4, 2002 | No applications, final sampling of soil |
| 485 | October 6, 2003* | Groundwater sampling |
| 638 | March 8, 2004* | ——— // ——— |

**this study*

**Table 3.5: Schedule of Activities (Badley, 2003)**

| Time, days | Concentration Value, % |
|---|---|
| 6 | 0 |
| 6.125 | 15 |
| 14 | 0 |
| 14.125 | 15 |
| 27 | 0 |
| 27.125 | 15 |
| 29 | 0 |
| 29.125 | 15 |
| 34 | 0 |
| 34.125 | 15 |
| 41 | 0 |
| 41.125 | 15 |
| 49 | 0 |
| 49.125 | 15 |
| 56 | 0 |
| 56.125 | 15 |
| 62 | 0 |
| 62.125 | 15 |
| 69 | 0 |
| 69.125 | 15 |
| 76 | 0 |
| 76.125 | 15 |
| 84 | 0 |
| 84.125 | 15 |
| 90 | 0 |
| 90.125 | 15 |

| Time, days | Concentration Value, % |
|---|---|
| 97 | 0 |
| 97.125 | 10 |
| 104 | 0 |
| 104.125 | 10 |
| 118 | 0 |
| 118.25 | 10 |
| 132 | 0 |
| 132.25 | 10 |
| 146 | 0 |
| 172 | 0 |
| 203 | 0 |
| 234 | 0 |
| 262 | 0 |
| 293 | 0 |
| 323 | 0 |
| 354 | 0 |
| 384 | 0 |
| 415 | 0 |
| 446 | 0 |
| 485 | 0 |
| 507 | 0 |
| 537 | 0 |
| 568 | 0 |
| 599 | 0 |
| 638 | 0 |

**Table 3.6: The Cyclodextrin Concentration Values for Variable Boundary Conditions for the Cyclodextrin Applications Simulation**

### *3.2.2.6 Variable Flux Boundary for DDT Mobilization Simulation*

During the field experiment (Badley, 2003), the DDT concentration in soil remained at about the same value after ten pore volumes had been applied. Therefore the mass mobilization of DDT occurred only during the first ten applications. As described in Chapter 2, Table 2.15 and Table 2.18 the total mass of DDT leached from the system to groundwater equals 12.0g (arithmetical average data) or 3.37g (ln-transformed data). The arithmetical average was used for simulations. The average mobilization of DDT occurred according to an approximaty exponential decline, therefore, the total mass removed was distributed between the applications using an exponential decline. The total mass of DDT removed from the soil is 12g. To calculate the DDT concentration in leached solution the mass of DDT removed with each application was divided by the volume of each application (200L). The solute concentrations used in the simulation, are given in Table 3.7 and Table 3.8.

| # pore volumes | Leached mass remained in the soil, g | Mass removed with each application, g | DDT Concentration in the solution, g/L | DDT Concentration in the solution, mg/L |
|---|---|---|---|---|
| 0 | 12.00 | 0.00 | 0 | 0 |
| 1 | 7.00 | 5.00 | 0.02500 | 25.00 |
| 2 | 4.50 | 2.50 | 0.01250 | 12.50 |
| 3 | 3.00 | 1.50 | 0.00750 | 7.50 |
| 4 | 2.20 | 0.80 | 0.00400 | 4.00 |
| 5 | 1.50 | 0.70 | 0.00350 | 3.50 |
| 6 | 1.00 | 0.50 | 0.00250 | 2.50 |
| 7 | 0.60 | 0.40 | 0.00200 | 2.00 |
| 8 | 0.30 | 0.30 | 0.00150 | 1.50 |
| 9 | 0.05 | 0.25 | 0.00125 | 1.25 |
| 10 | 0.00 | 0.05 | 0.00025 | 0.25 |

**Table 3.7: Mass Removal and Solution Concentration with Each Pore Volume Used in HYDRUS Simulations**

| Time, days | Concentration Value, mg/L |
|---|---|
| 6 | 0 |
| 6.125 | 25.00 |
| 14 | 0 |
| 14.125 | 12.50 |
| 27 | 0 |
| 27.125 | 7.50 |
| 29 | 0 |
| 29.125 | 4.00 |
| 34 | 0 |
| 34.125 | 3.50 |
| 41 | 0 |
| 41.125 | 2.50 |
| 49 | 0 |
| 49.125 | 2.00 |
| 56 | 0 |
| 56.125 | 1.50 |
| 62 | 0 |
| 62.125 | 1.25 |
| 69 | 0 |
| 69.125 | 0.25 |
| 76 | 0 |
| 76.125 | 0 |
| 84 | 0 |
| 84.125 | 0 |
| 90 | 0 |
| 90.125 | 0 |

| Time, days | Concentration Value, mg/L |
|---|---|
| 97 | 0 |
| 97.125 | 0 |
| 104 | 0 |
| 104.125 | 0 |
| 118 | 0 |
| 118.25 | 0 |
| 132 | 0 |
| 132.25 | 0 |
| 146 | 0 |
| 172 | 0 |
| 203 | 0 |
| 234 | 0 |
| 262 | 0 |
| 293 | 0 |
| 323 | 0 |
| 354 | 0 |
| 384 | 0 |
| 415 | 0 |
| 446 | 0 |
| 485 | 0 |
| 507 | 0 |
| 537 | 0 |
| 568 | 0 |
| 599 | 0 |
| 638 | 0 |

**Table 3.8: The Concentration Values for Variable Boundary Conditions for the DDT Mobilization by Cyclodextrin Simulation**

## *3.3 Results and Discussions*

### 3.3.1 The Single Application to One Plot Simulation

The simulation "single application to one plot" demonstrates, both visually and quantitatively, the infiltration event during the application of one treatment of cyclodextrin solution and the 7 days following the application. Figure 3.6 shows the advance of the cyclodextrin concentration front during the 3-hour period of application of cyclodextrin solution. The front reached the material boundary between the A and B horizons at approximately 2 hours after the beginning of application. Figure 3.6 shows that between 2 and 2.5 hours the wetting front vertical migration is slowed down by the capillary barrier effects at the interface. Additional horizontal migration is associated with that effect. At about 2.5 hours the wetting front penetrates the A-B boundary and vertical migration continues. At the end of the 3-hour application period most of cyclodextrin solution is still within the A horizon which is the zone with the highest DDT concentrations and the primary targeted zone of the pilot scale field remediation experiment. Figure 3.7 is a plot of moisture content during the same simulation presented in Figure 3.6. Figure 3.7 shows that the application of cyclodextrin solution caused near saturation conditions within the entire thickness of the A horizon within the treatment plot. That high moisture content condition could generate low air and oxygen contents which favor the microbially mediated generation of lower oxidation reduction potentials and possibly anaerobic conditions, which are known to promote DDT degradation to DDD (Guenzi and Beard, 1968; Aislabie et al., 1997). Microbial degradation of the

cyclodextrin in solution could hasten the onset of anaerobic conditions because microorganisms may consume the oxygen.

Figure 3.7 shows that during the 7-day period following the application of the cyclodextrin solution (i.e. the period prior to the next application of the cyclodextrin solution), the shallow soil drains and the applied solution percolates deeper into the profile towards the water table. The condition at 7 days represents the initial conditions at the beginning of the next treatment application. At that time the moisture content as decreased to values is close to the original value (Figure 3.7), but still remaining cyclodextrin solution. The residual cyclodextrin solution remaining in the soil potential provides good conditions for cometabolic degradation of DDT (Figure 3.8).

Figure 3.8 shows the concentration of the cyclodextrin plume distribution 7 days after the initial application. The solution infiltrated about 1.5m downward and 20cm to the sides. The highest concentration of cyclodextrin solution is under the treatment plot within the A horizon, but the mass of cyclodextrin within A horizon is much less than during and immediately after the application, because the water content is significantly lower than the earlier near saturation values (Figure 3.8).

These results from the simulation of a single application to one plot provide visual and quantitative demonstration of the nature of the infiltration event of the cyclodextrin treatments. They are consistent with field observations (Badley, 2003) early in the study in that high moisture contents were observed during application of the solution and at the time of the next application field measurements of moisture content showed lower values. The A horizon was the primary target of cyclodextrin application. The simulation shows

that volume and rate of application of the cyclodextrin solution was such that high moisture contents were achieved within the A horizon aided by the capillary barrier effects at the A-B material boundary. Simulations presented later in this chapter will show the subsurface horizontal interaction of the infiltration of the cyclodextrin solution on adjacent plots and the net cumulative effects of all the infiltration to the treatment grid.

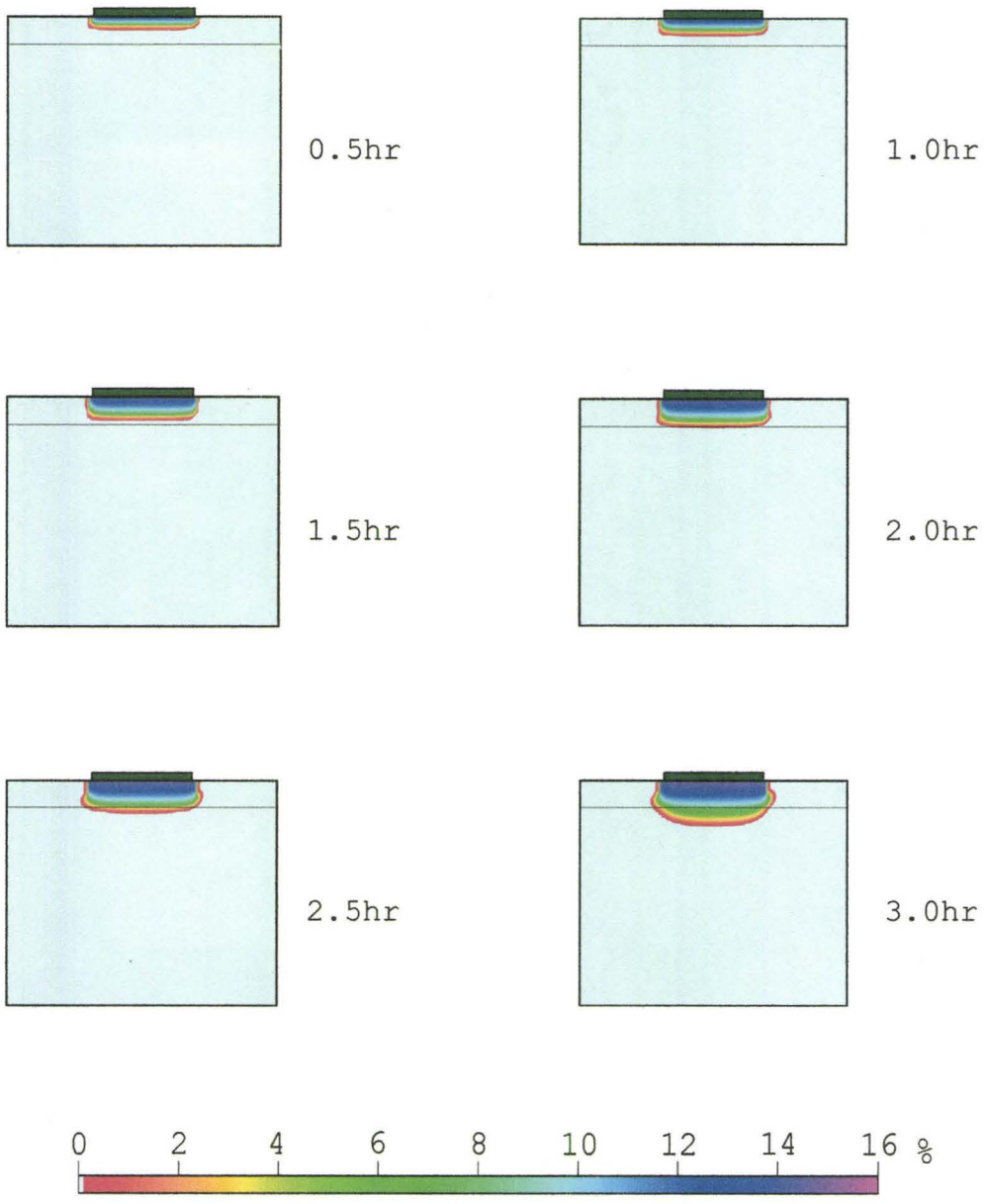


**Figure 3.6: The Results of Cyclodextrin Concentration Distribution of the Single Application to One Plot Simulation for First 3 Hours with 30minutes Intervals (the Domain is 160cm Deep and 190cm Wide)**

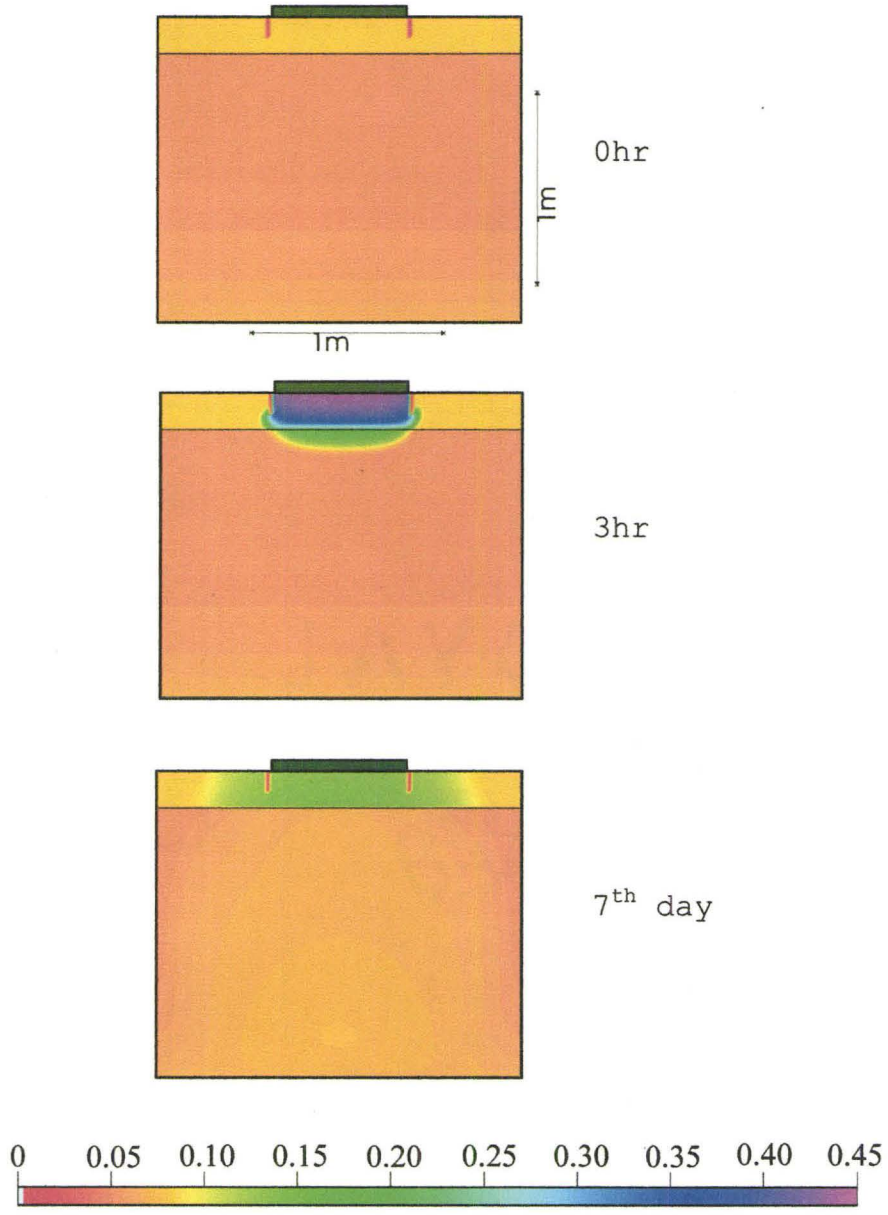


**Figure 3.7: The Results of Volumetric Moisture Content Distribution of the Single Application to One Plot Simulation at the Initial Time, at the End of Cyclodextrin Application and on 7th Day after Application of Cyclodextrin Solution**

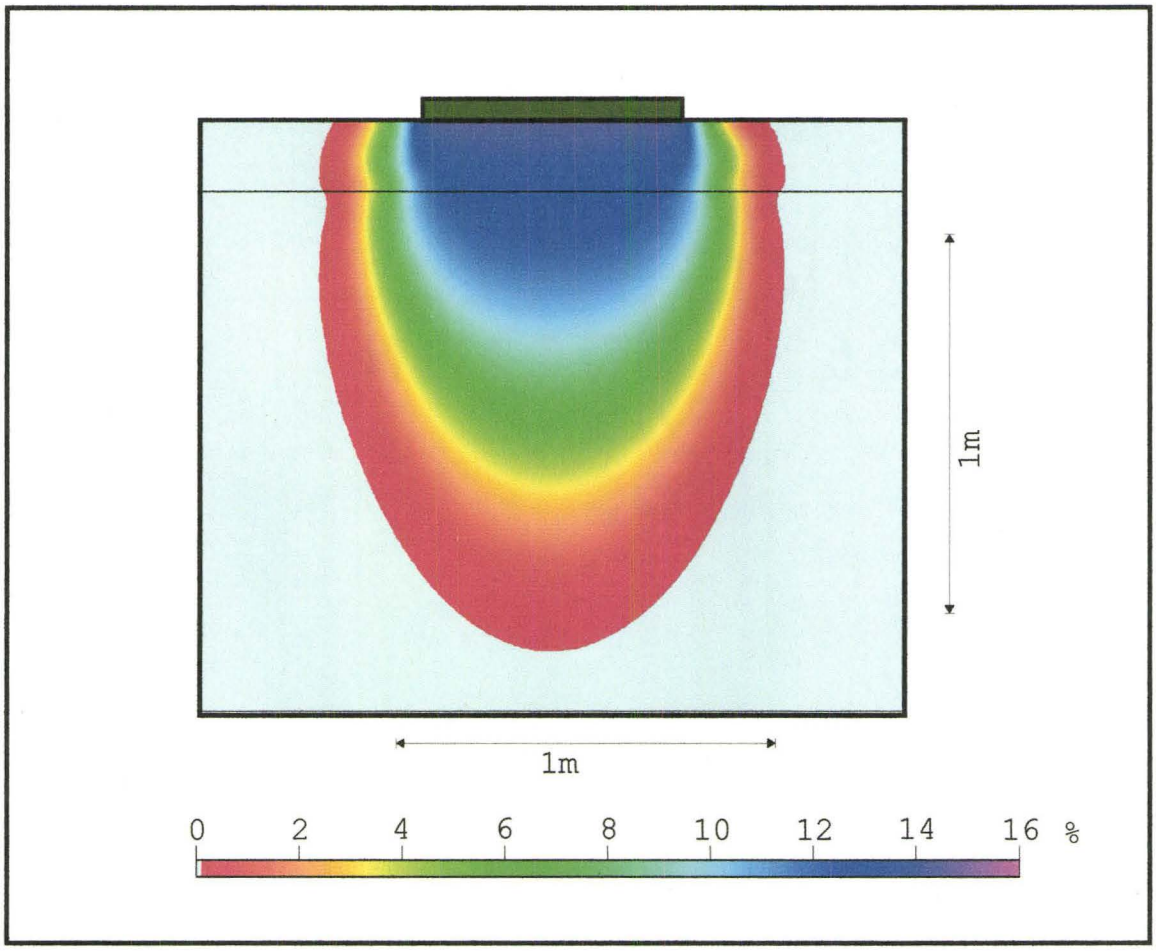


**Figure 3.8: The Results of Cyclodextrin Concentration Distribution of the Single Application to One Plot Simulation on 7th Day after Application of Cyclodextrin Solution**

### 3.3.2 The Cyclodextrin Applications Simulation

The Cyclodextrin Applications Simulation demonstrated the infiltration of cyclodextrin solution to all the plots within the remediation grid during the pilot-scale field experiment and the 16 months after the treatments were completed.

For the following discussion of the figures of the cyclodextrin applications simulation, the size of the cyclodextrin plume is defined by the minimum contour output by HYDRUS-2D model. The minimum value of the contour corresponds to 1/128 times the maximum value contoured. Specifically, HYDRUS 2D generates plots using 128 colours each representing a contour interval between zero and the maximum value contoured. For Figure 3.9, that is 0.125%, which is 1/128 of 16%. This means that if one is interested in the extent of the plume using a concentration value less than 0.125%, the plume is larger than that seen on the figures. The 0.125% contour serves the purpose here.

Figures 3.9, 3.10 and 3.11 show the cyclodextrin concentration distribution after three hours, 24 hours, and 7 days since the beginning of the first application respectively. The simulated first application lasts for three hours. At the end of the first application, the solution infiltrates about 35-40 cm below the surface (Figure 3.9) and the maximum mass of cyclodextrin remains within the A horizon. At 24 hours after the beginning of application of the solution, it has percolated to at depth of about 1.0-1.2m (Figure 3.10) and spread about 30cm from the edges of remediation grid. This horizontal spread of the plume is due to the combined effect of advection due to horizontal capillary driven infiltration and the relatively high values of the longitudinal and transverse dispersivities,

i.e., 45cm and 4.5cm respectively. Those dispersivities correspond to the late-time travel distance (size) of the plume. HYDRUS 2D does not include scale dependent dispersivities. Consequently, at early times and associated shorter travel distances the specified dispersivities are relatively large.

Before the second application, seven days since the first application, the plume infiltrates to at depth of about 2.1 to 2.3m (Figure 3.11). Figure 3.12 shows the corresponding water contents at seven days. At this time the solution has substantially drained from the A horizon, but the water contents in the A horizon within remediation grid still has about 5% higher moisture content than were initially present. Some local mounding of the water table is expressed by the 20 cm of fully saturated soil above the depth of water table (Figure 3.12), whereas the input hydraulic functions express a capillary fringe in the sand of approximately 5 to 10cm.

The cyclodextrin plume reaches the simulated water table depth after application of two pore volumes, just before the scheduled third application (Figure 3.13). Figure 3.13 shows horizontal migration of the plume to the right at depth 2.2m, which is 20 cm above the water table. This is due to the local mounding effect created by the additional influx of percolating water and groundwater flow toward the right within the capillary fringe.

Figure 3.14 shows the cyclodextrin concentration distribution two weeks after the last cyclodextrin solution application, which corresponds to the time of final soil sampling by Badley (2003). The plume is 5 to 6m wide in the vadoze zone, 8 to 9m wide within the unconfined aquifer, and extends to depth of 5m below the surface. The flux of

water from the vadoze zone generates a local water table mound that causes a local divergent hydraulic gradient that generates some flow (to the left) against the local background groundwater flow (to the right). That same effect increased the hydraulic gradient generating flow down the local groundwater background gradient (to the right). The net effect was that the solute plume was transported 2m to the left and 4m to the right of the horizontal the edges of remediation grid.

A minimum estimate to flush out a conservative compound like cyclodextrin solution from the vadoze zone is that at least one residual pore volume of clean water should pass through the unsaturated zone. The average width of the plume in the vadoze zone at the end of the experiment is 600cm; the water table is 240cm below the surface. For 2D system the volume of soil that needs to be flushed is approximately 144,000cm$^3$, the average residual water content is approximately 0.10, therefore the residual pore volume is about 14,400cm$^3$. The average precipitation rate is 890mm a year (Environmental Canada, 2004) which is 53,400cm$^3$ over the area of plume in 2D system. The average net infiltration at PPNP is about 40% (Crowe et al., 2004) which is about 21,360cm$^3$. Therefore, using the estimated residual water content above and assuming simple piston displacement, it should take not less than eight (8) months for the cyclodextrin solution to be flushed out from the vadoze zone into the aquifer.

Figure 3.15 shows the cyclodextrin concentration distribution about one year after the end of the pilot-scale field experiment (485 days since the remediation began) and corresponds to when the October groundwater sampling was conducted. The plume migrated 9m to the right of the edge of remediation grid. The center of mass is located 1

to 2m to the right of the remediation grid and about 1m below the water table. The 0.125% concentration contour of the plume has reached a depth of about 6m below the surface.

As depicted in Figure 3.16, sixteen months after the end of the field experiment which corresponds to the March 2004 groundwater sampling, the plume of cyclodextrin had spread 10m to the right of the application grid. At that time the concentration of cyclodextrin in the vadoze zone is less than 4% of its initial value and the maximum concentration in the center of plume is only 6 to 7%. As described above the simulated net infiltration rate was set to relatively low values, 10-25% of the average precipitation rate depending on the time of year, to better match the vertical position of the center of the plume. What consequence is that the amount of water that has passed through the vadoze zone is insufficient to flush all the cyclodextrin solution from the vadoze zone.

The possibility that cyclodextrin solution may remain in the soil for a prolonged period of time provides the conditions for further co-metabolic degradation of DDT. This persistence of cyclodextrin is consistent with observations by Asmaa (2004) that reducing conditions persisted 10 months after application stopped.

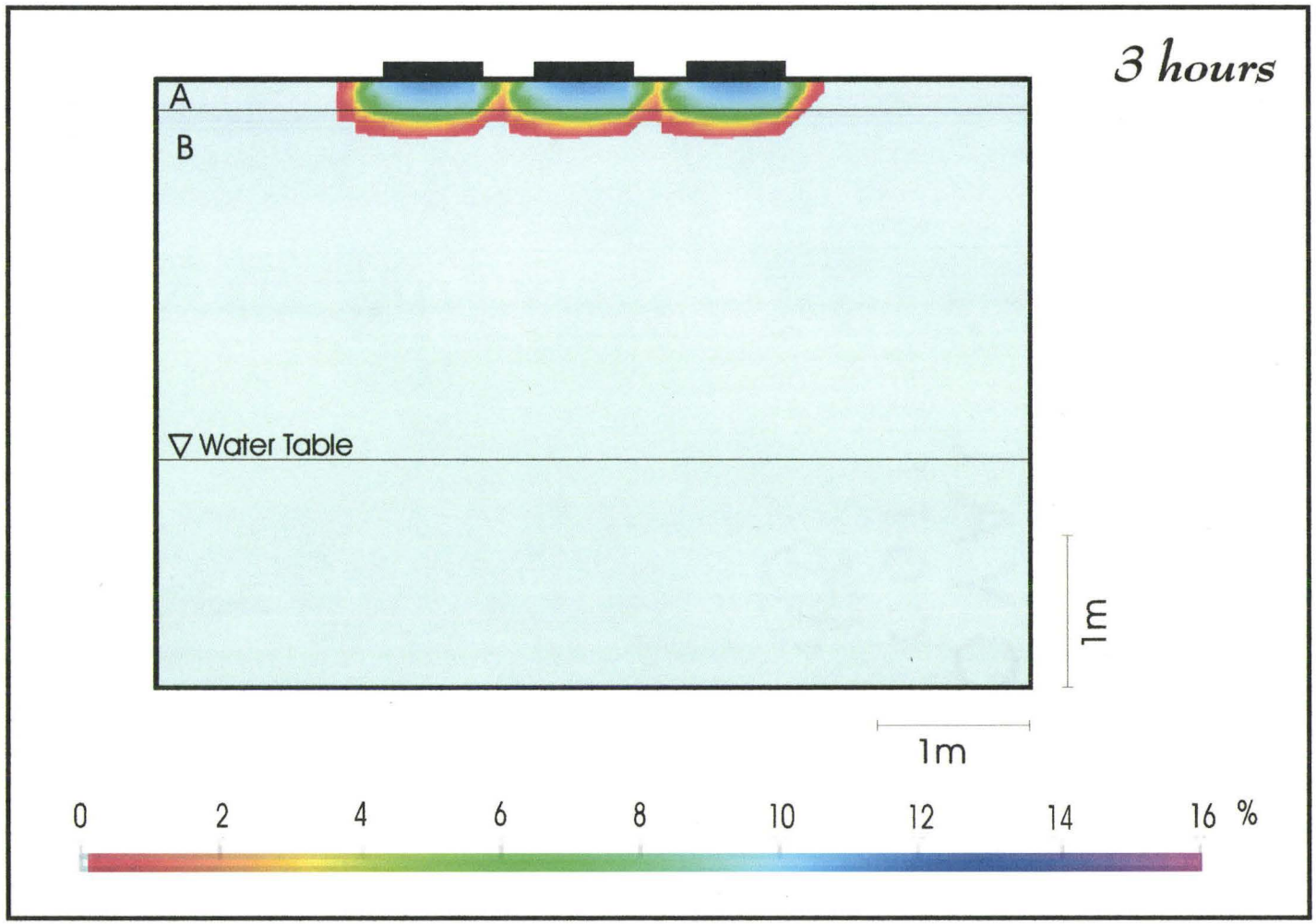


**Figure 3.9: The Cyclodextrin Concentration Distribution after Three Hours since the Beginning of the First Application of Cyclodextrin Solution**

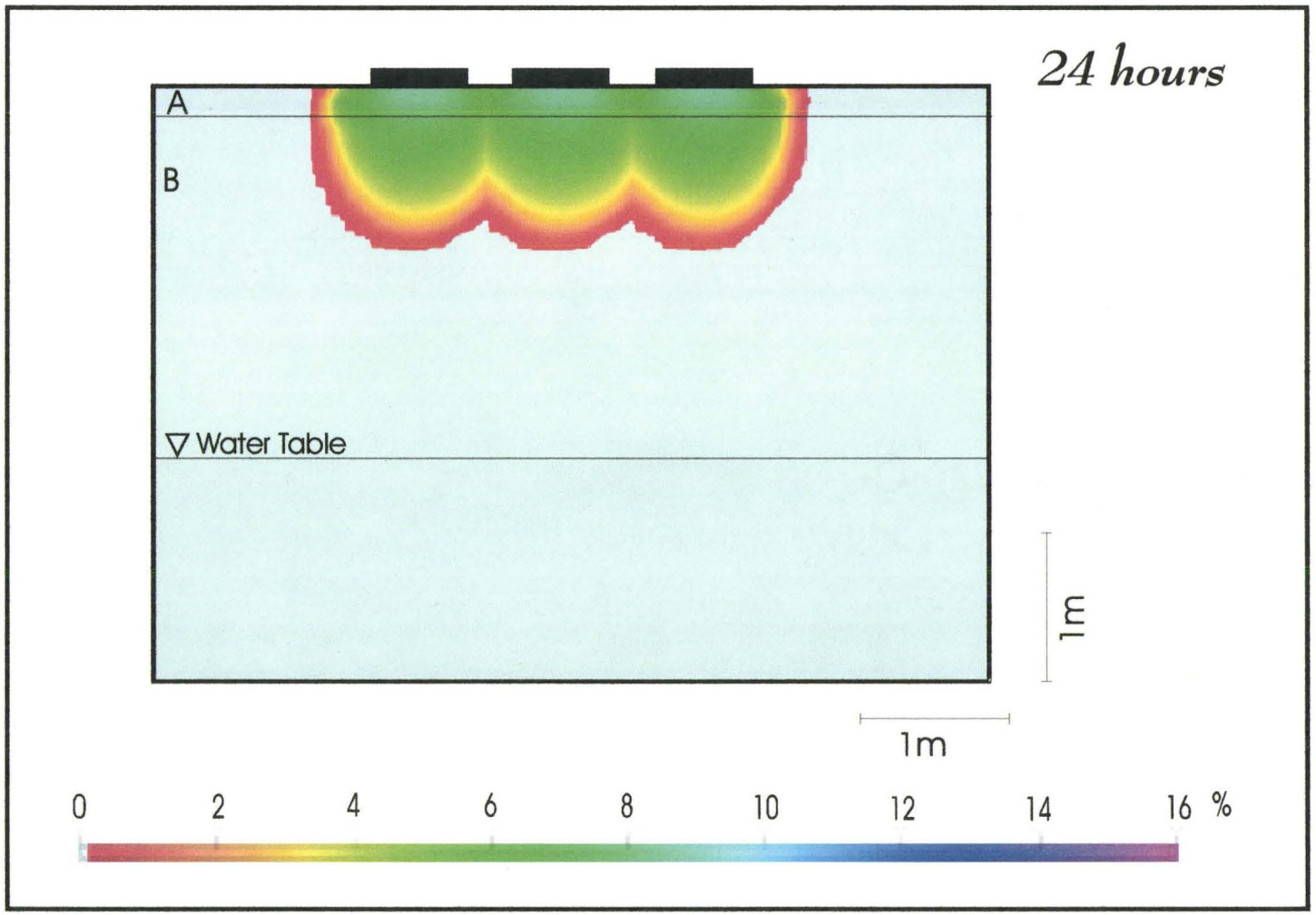


**Figure 3.10: The Cyclodextrin Concentration Distribution after 24 Hours since the Beginning of the First Application of Cyclodextrin Solution**

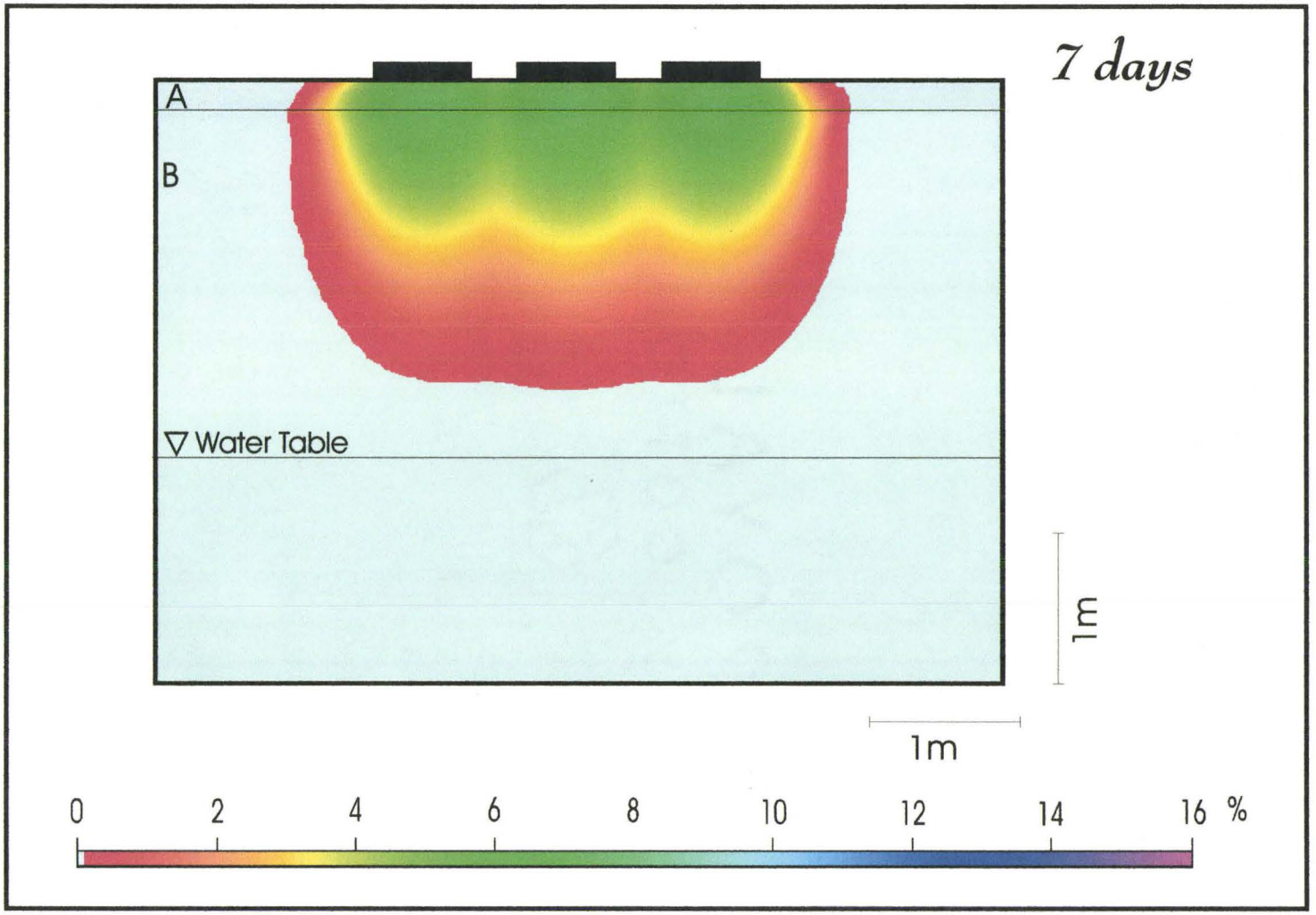


**Figure 3.11: The Cyclodextrin Concentration Distribution after 7 Days since the Beginning of the First Application of Cyclodextrin Solution**

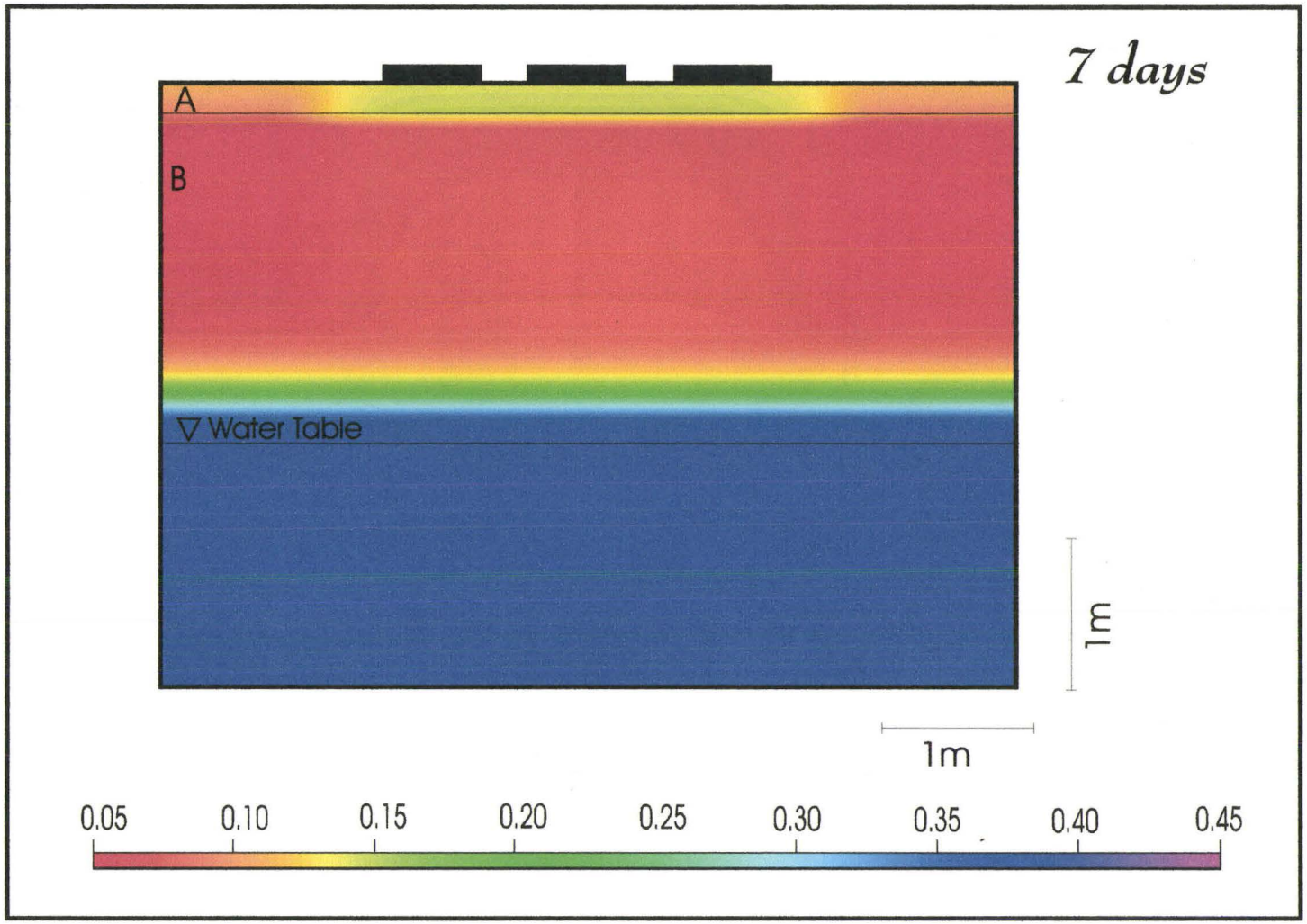


**Figure 3.12: The Volumetric Water Content Distribution after 7 Days since the Beginning of the First Application of Cyclodextrin Solution**

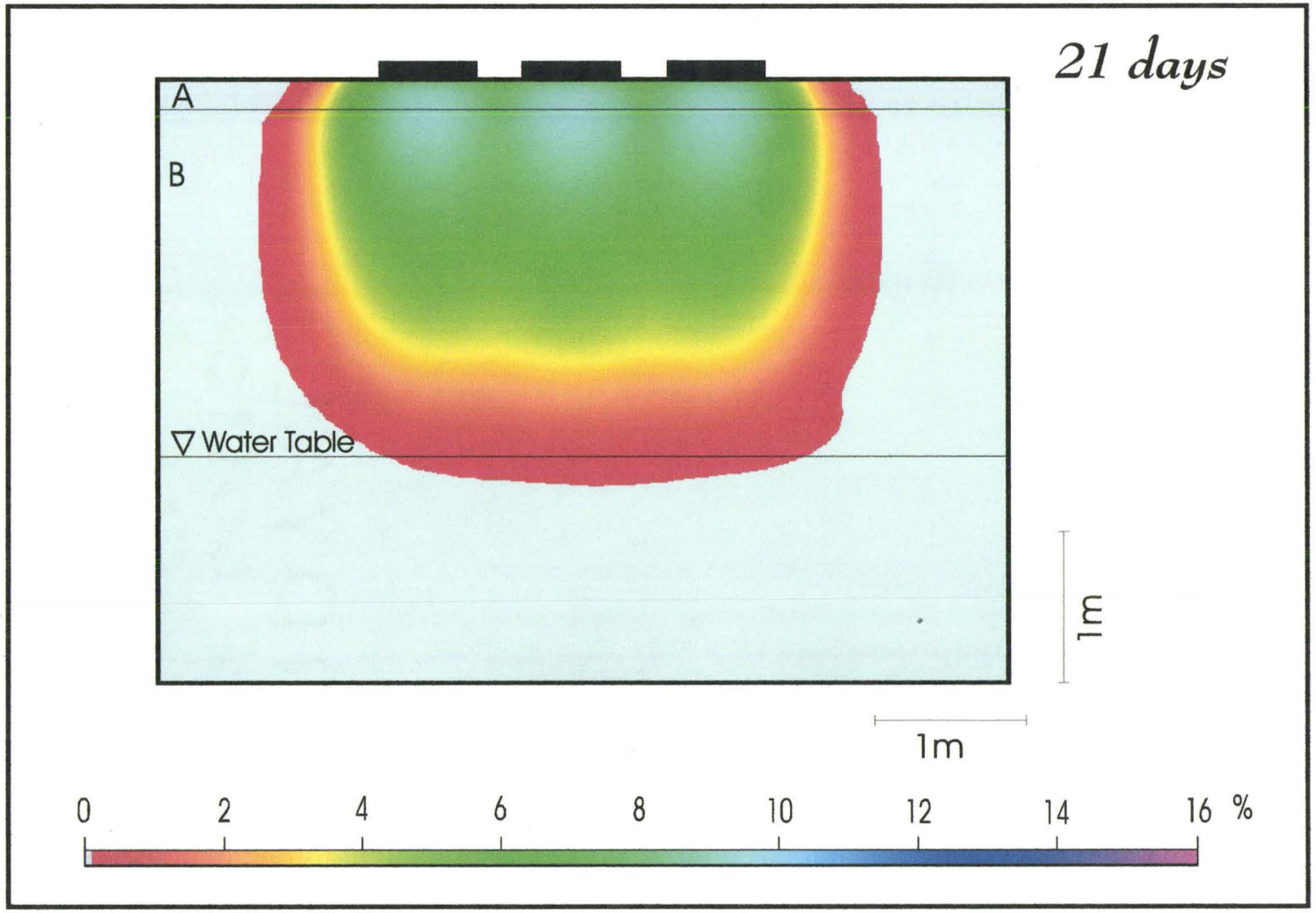


**Figure 3.13: The Cyclodextrin Concentration Distribution after Three Weeks since the Beginning the First Application of Cyclodextrin Solution, when the Cyclodextrin Plume Reached the Water Table**

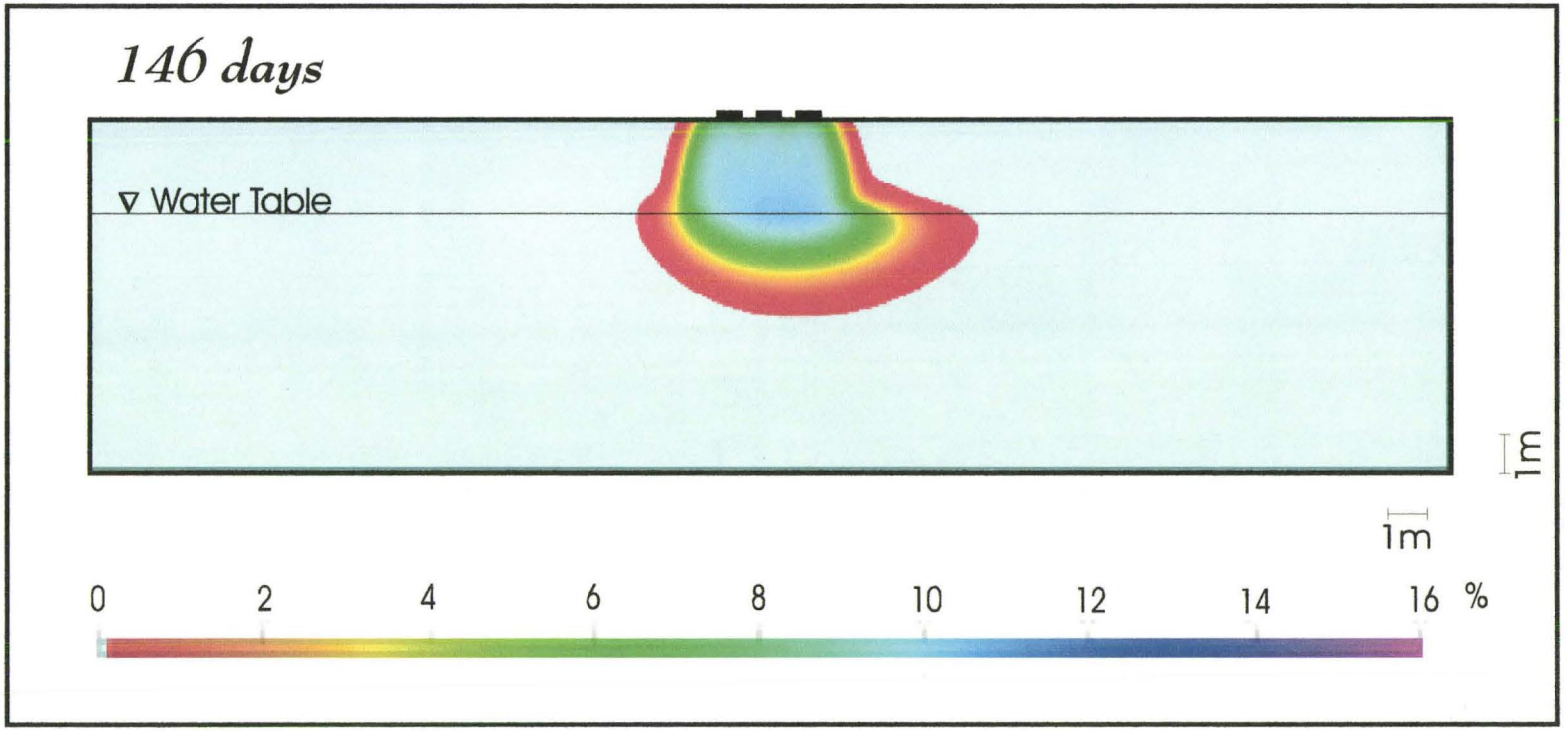


**Figure 3.14: The Cyclodextrin Concentration Distribution after Two Weeks after the Last Application of Cyclodextrin Solution**

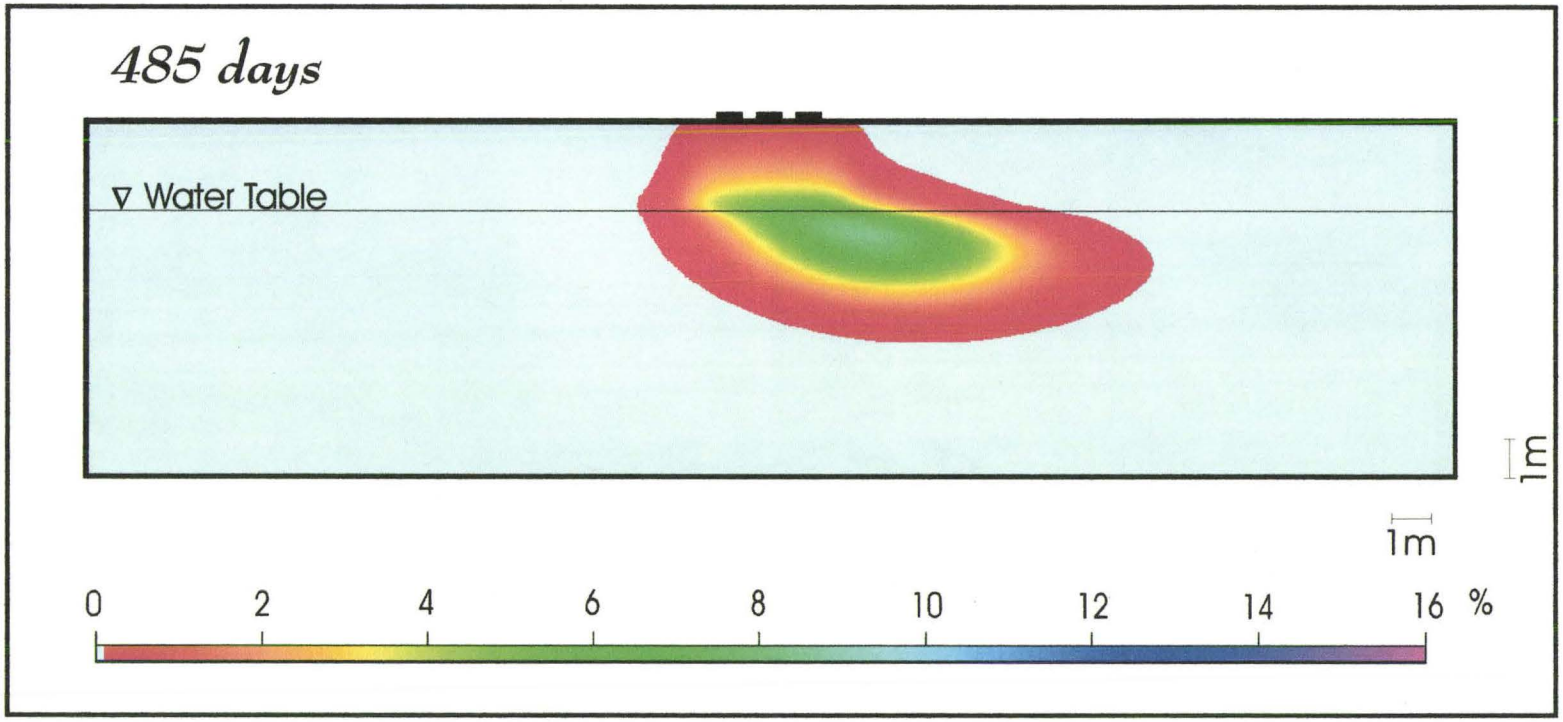


**Figure 3.15: The Cyclodextrin Concentration Distribution after about One Year after the End of the Pilot-Scale Field Experiment (485 Days since the Remediation Began) and Corresponds to when the October Groundwater Sampling was Conducted**

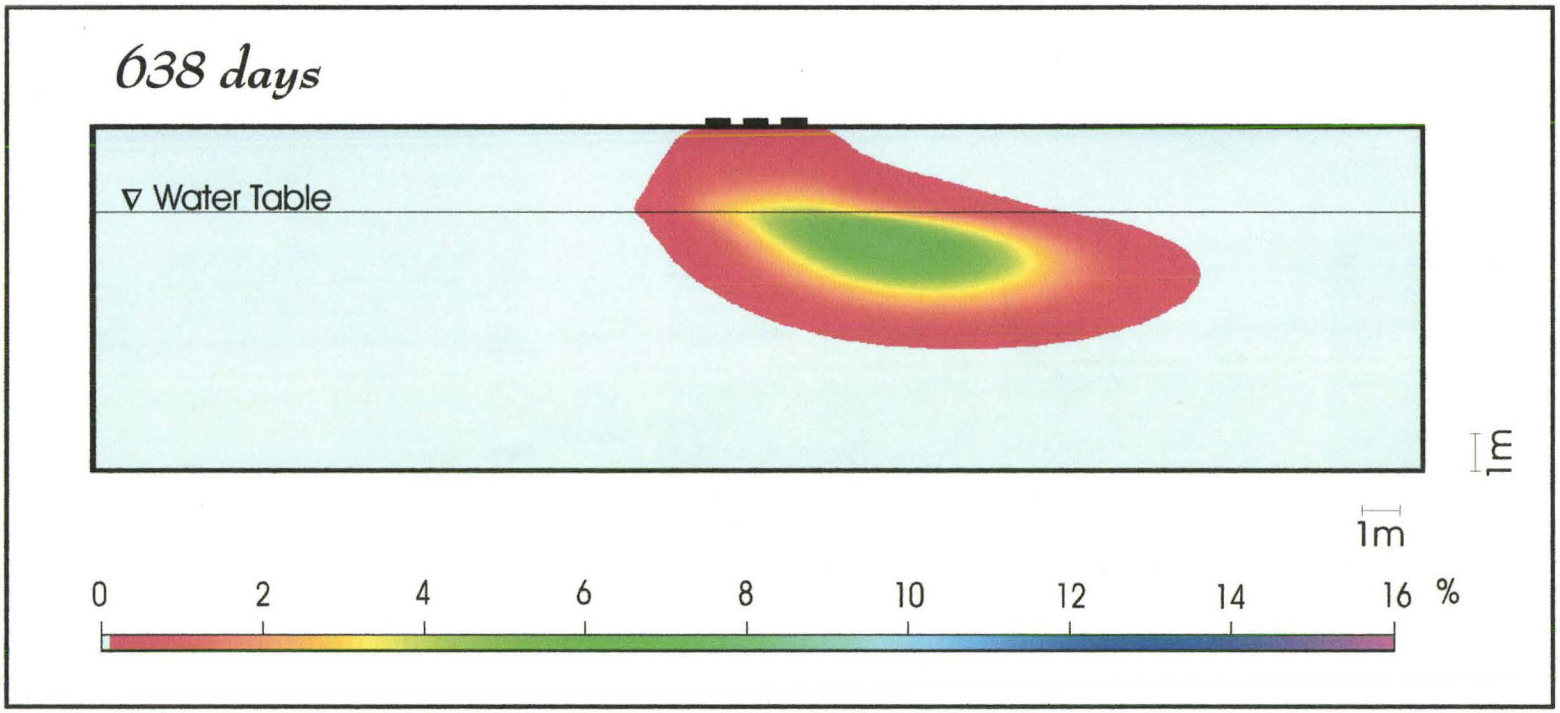


**Figure 3.16: The Cyclodextrin Concentration Distribution after about Sixteen Months after the End of the Pilot-Scale Field Experiment (638 Days since the Remediation Began) and Corresponds to when the March Groundwater Sampling was Conducted**

### 3.3.3 The DDT Mobilization Simulation

The DDT flux from the application plots at the surface in this simulation are set to match the observed exponential mass loss of DDT from the shallow soil during the field remediation trials conducted by Bradley (2004). The DDT mobilization simulation further matches the field observations by using exponential removal of DDT from soil during the first 10 applications of cyclodextrin and then no mass removal (i.e., zero mass flux) during the last 9 applications of cyclodextrin solution (Badley, 2003).

For the following discussion of the DDT mobilization simulation, the size of the DDT plume is defined by the minimum contour set by HYDRUS-2D model; the value was 0.16mg/L for Figures 3.17; 3.18 and 3.19, and 0.01mg/L for Figure 3.20. Note that the lower concentration contour in Figure 3.12 delimits a larger DDT plume than in the other figures.

During application of first ten pore volumes the DDT plume is similar to the cyclodextrin solution simulations discussed earlier in this chapter. Most, i.e. 75%, of the DDT mass infiltrated during the first three applications, and then the concentration of DDT in the simulated solution declines exponentially (Table 3.7).

Figure 3.17 shows the distribution of DDT concentration after application of 10 pore volumes which corresponds to the final application that mobilized (input) DDT. The DDT plume is about 5m wide in the vadoze zone and about 6.5m wide at the level of water table. The minimum contour of the DDT plume reaches a depth of 4m below the

surface. The center of mass is at depth of the water table with DDT concentrations about 3-4mg/L, which is less than 12-16% of the maximum applied concentration.

The cyclodextrin solution behaves as a conservation solute and the DDT is associated with the cyclodextrin. Therefore, approximately the same volume of zero-concentration water as the volume of applied cyclodextrin solution that mobilized DDT would be the minimum volume required to pass through the unsaturated zone to flush out the DDT containing cyclodextrin solution. After infiltration of the first 10 pore volumes which contained DDT, an additional cumulative amount of 600L of solution with no DDT was applied to the three plots over 7 applications (Table 3.5). This is not enough to flush out the DDT in solution in the vadoze zone.

Figure 3.18 shows the DDT concentration distribution at the end of the field experiment. The depression in the shallow portion of the DDT plume within the vadoze zone was caused by the later applications of 600L of solution containing no DDT, because Badley (2003) showed that no DDT was removed after application of 10 pore volumes of cyclodextrin solution. The regions of higher DDT concentrations near the surface and 1m to the left and to the right of the edges of the application grid are a result of the combined effect of horizontal infiltration by capillarity, transverse dispersion, and low net precipitation infiltration. This persistent "halo" around the remediation grid will contribute to a "tailing effect" in the displacement (flushing) of DDT from the vadoze zone. At this time, the center of mass is about 1m below the water table and the DDT concentration there is about 1-2mg/L.

The DDT concentration distribution one year after the end of the cyclodextrin applications is shown on Figure 3.19. This corresponds to the date in October 2003 when groundwater samples were collected. The minimum concentration contour for DDT concentration is 0.16mg/L [$1.6\times10^5$ng/L]. The simulated DDT concentrations are 5 orders of magnitude higher than was measured in groundwater samples collected at the site. This large difference in concentrations suggests that degradation of DDT is likely playing a primary role at the site. That is, the simulated mass transport processes of advection and dispersion were not sufficient to explain the observed concentrations.

Figure 3.20 is a plot simulated DDT concentrations 16 months (t=638days) after the last application, which was the time of the March 2004 groundwater sampling. The minimum concentration contour for DDT on this plot is 0.01mg/L [$10^4$ng/L], which is lower than on the previous figures. The center of mass is located at 3 to 4m to the right from the right edge of the grid and about 3.5m below the surface (Figure 3.20). The sample location and concentration of DDT in groundwater is superimposed on the simulation. The maximum concentration in the plume is about 1.4mg/L. The range of DDT concentrations measured in the groundwater samples collected in March 2004 was 0.46 to 89.00ng/L (0.00000046 to 0.000089 mg/L) (Figure 3.20). That is approximately 5 orders of magnitude below the simulation results, which is similar to the difference observed relative to the October 2003 sampling and simulations discussed above.

Comparison of the DDT mobilization simulation with both the October 2003 and March 2004 groundwater concentration values reveals a large amount of "missing" DDT mass. That is, more than 99.9% of DDT removed from the shallow soil by the

cyclodextrin solution is not accounted for in the groundwater samples. The simulations of the conservative transport of DDT with cyclodextrin suggest that if the DDT where only mobilized within the infiltrated solutions the sample locations should have detected it. Given the large amount of missing mass, the possibility that local groundwater velocities were higher than reported by Crowe et al. (2004) and used in the simulations and therefore the infiltrated plume had migrated beyond the sampled area was addressed with an additional simulation.

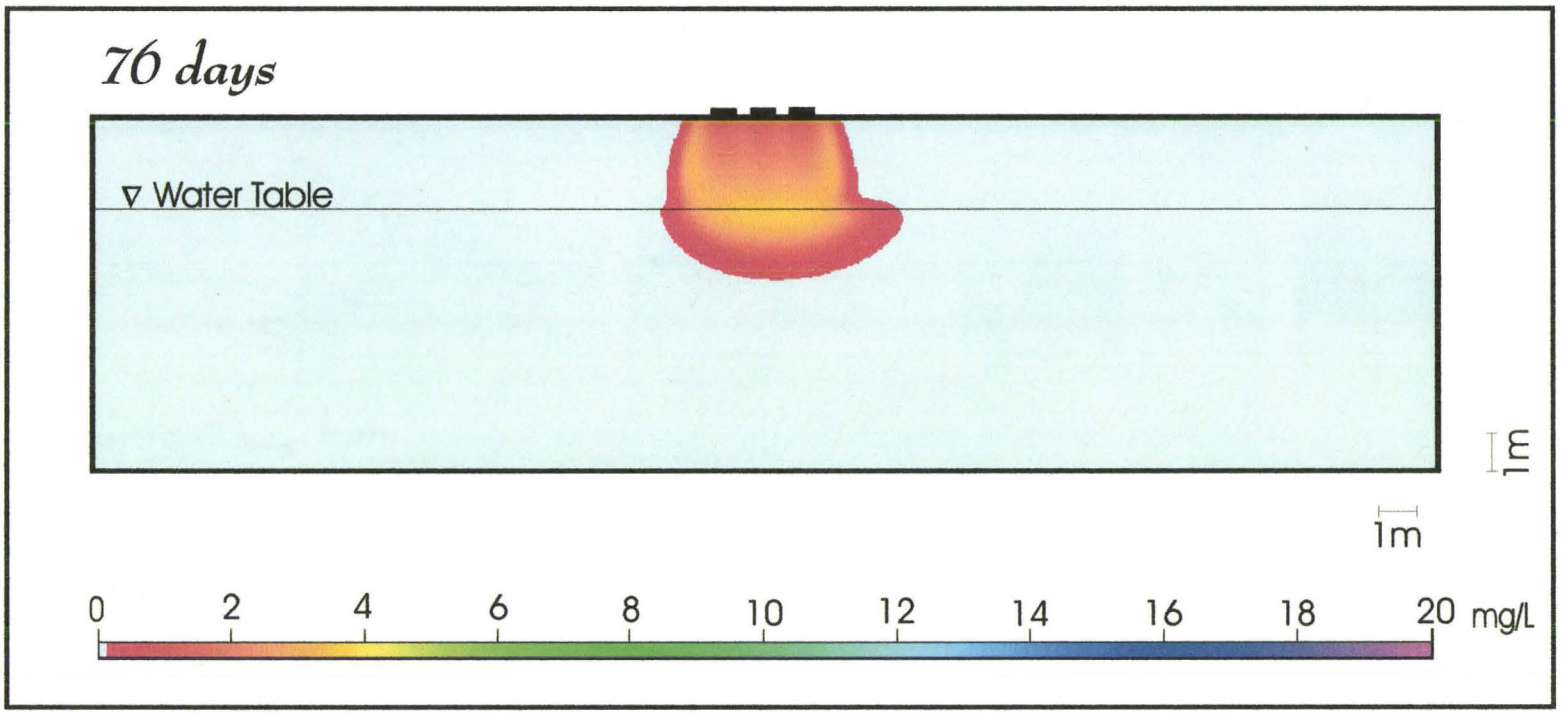


**Figure 3.17: The DDT Concentration Distribution after Application of 10 Pore Volumes of Cyclodextrin Solution, 76 Days since the Beginning of the Pilot-Scale Field Experiment**

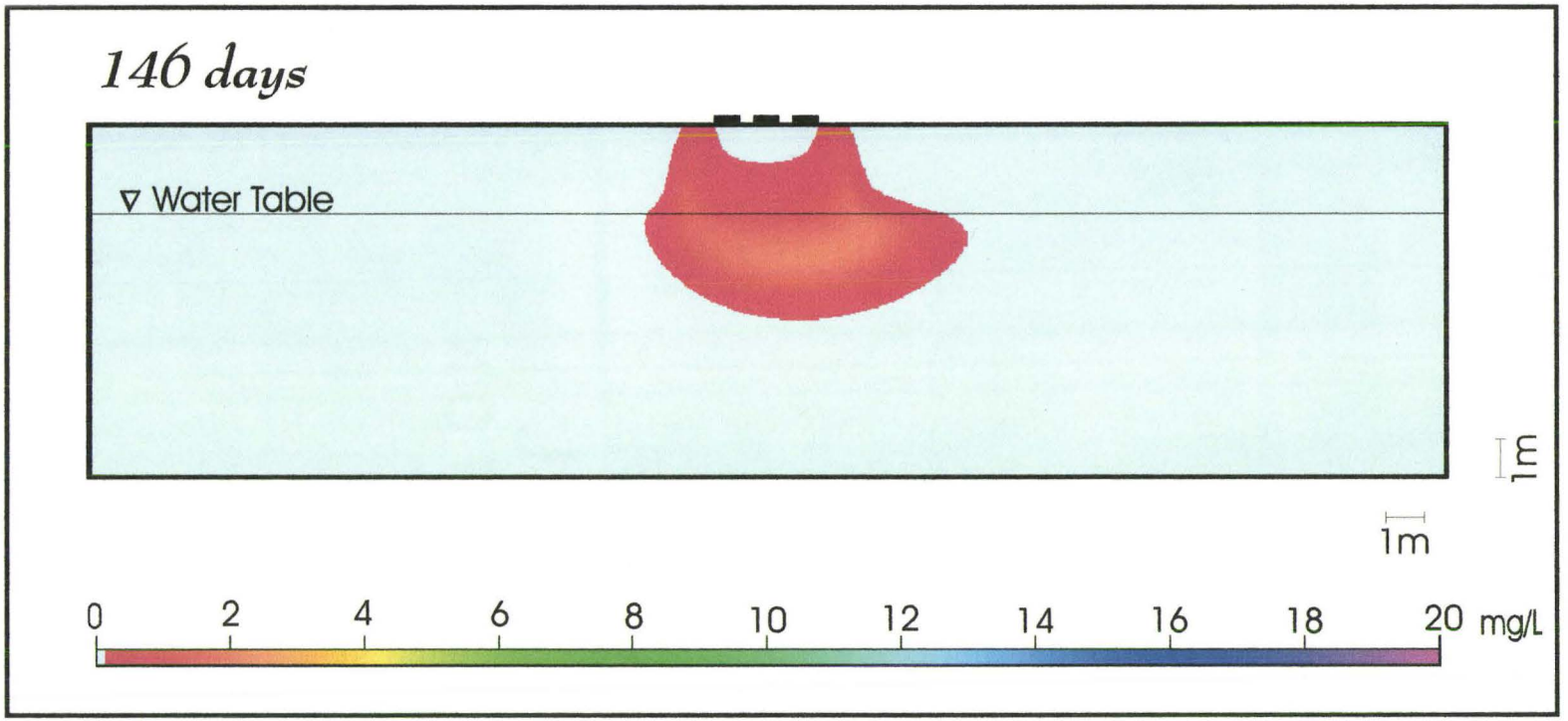


**Figure 3.18: The DDT Concentration Distribution after Two Weeks after the Last Application of Cyclodextrin Solution**

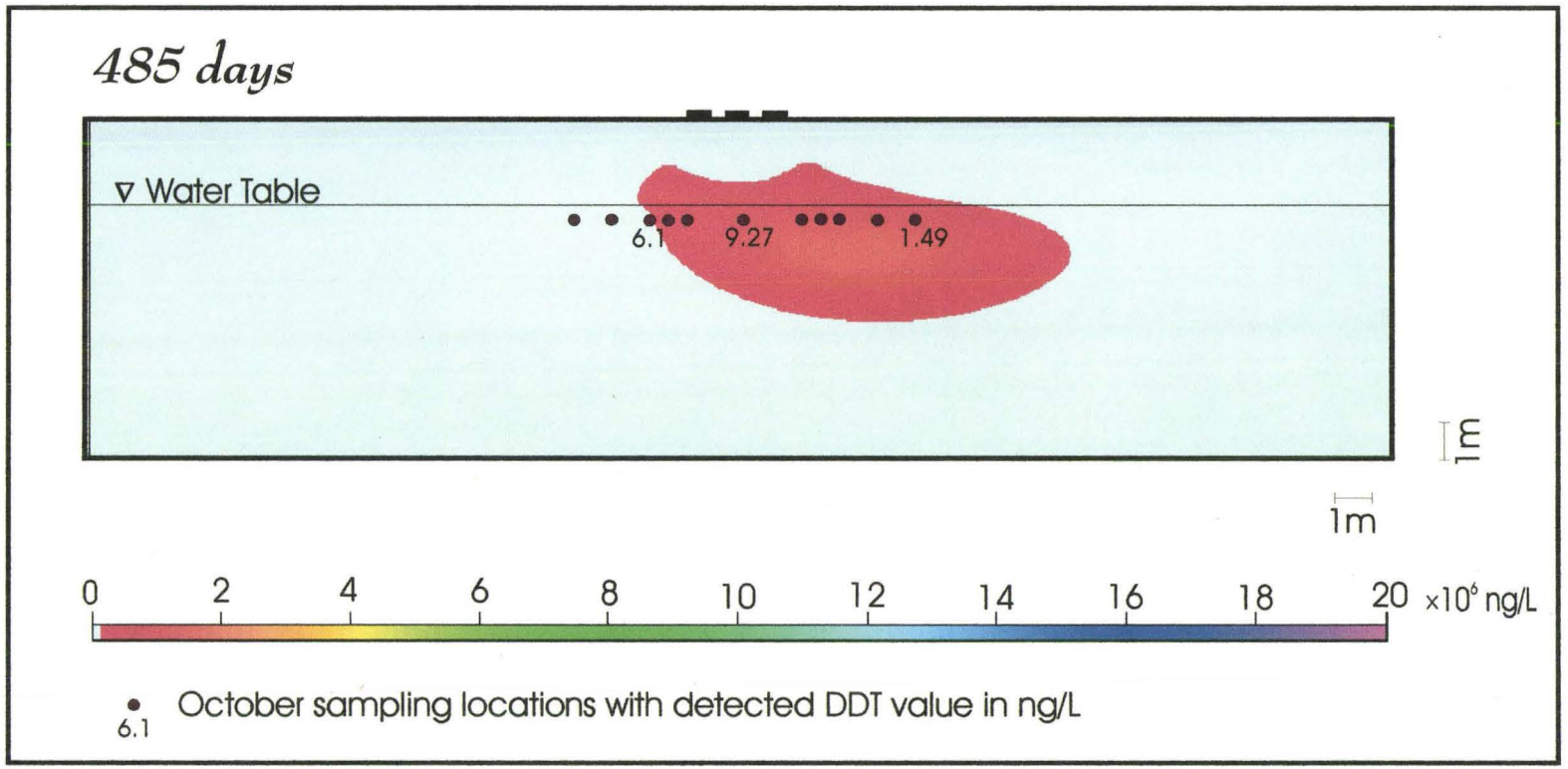


**Figure 3.19: The DDT Concentration Distribution after about One Year after the End of the Pilot-Scale Field Experiment (485 Days since the Remediation Began) and Corresponds to when the October Groundwater Sampling was Conducted**

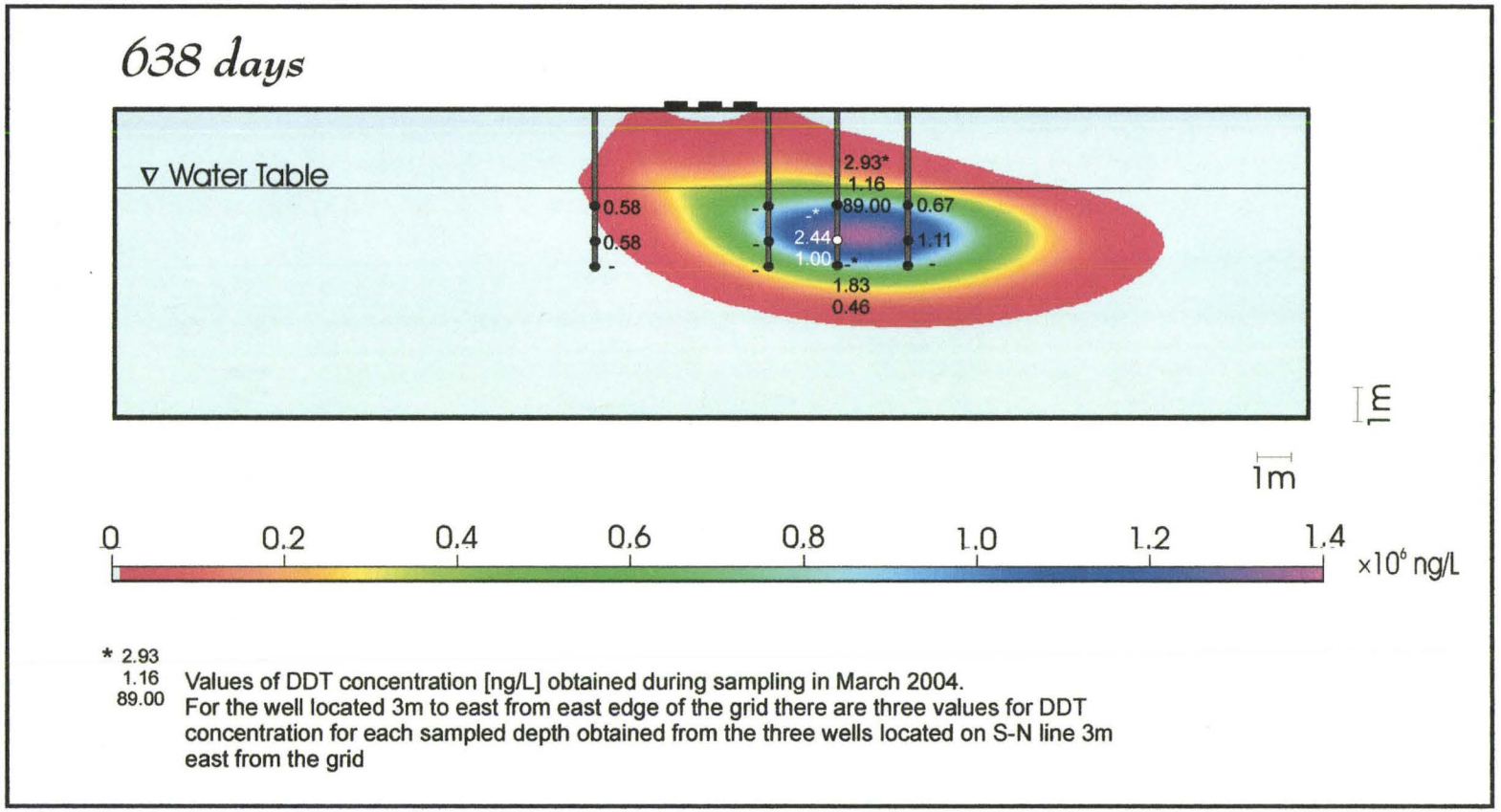


**Figure 3.20: The DDT Concentration Distribution after about Sixteen Months after the End of the Pilot-Scale Field Experiment (638 Days since the Remediation Began) and Corresponds to when the March Groundwater Sampling was Conducted**

### 3.3.4 The High Groundwater Velocity Simulation

Given the large amount of missing mass, the possibility that the infiltrated plume had migrated beyond the sampled area was addressed with an additional simulation. The local groundwater velocities by Crowe et al. (2004) were based on decades water level records, slug tests, and numeric simulations. Crowe et al. (2004) reported an average groundwater flow velocity in the study area of 0.5 to 1.0 m/yr with lower velocities in drier years. The years of interest to this study 2002, 2003, and 2004 were relatively dry years at PPNP. In personal communications with Dr. Crowe, Dr. Smith, and a fellow M.Sc. student working on groundwater studies at PPNP, Ryan Mills, and based on the historic data at PPNP it was decided that 2 m/yr was probably higher than would have been the case during the study period. It was decided to double that number to 4 m/yr as a "safety factor" in that estimation. The groundwater background gradient in HYDRUS 2D was set to a value that generated 4 m/yr groundwater velocity toward the marsh to the east, i.e. a horizontal hydraulic gradient of 0.0008. In addition, a higher net infiltration rate equal to the average precipitation rate for winter months and half of the average precipitation rate during summer months to account for loss by evatransportation was used to increase groundwater velocities further. The values for net infiltration from January though December is 0.2; 0.2; 0.25; 0.26; 0.13; 0.14; 0.12; 0.15; 0.15; 0.2; 0.2; 0.2 cm/day respectively. The dispersivity values were set to one-tenth of the travel distance, i.e. 60cm for longitudinal and one tenth of that, i.e. 6cm for transverse. This constitutes an extreme estimate on the high end of possible flow conditions. The purpose

was to determine if reasonable groundwater conditions could generate sufficient advection and dispersion to transport the DDT outside the sampled area. The results of this simulation represent the maximum reasonably possible travel distance of the DDT plume.

Figure 3.21 shows the DDT concentration distribution generated with the high groundwater velocity simulation. The center of mass moved about 16m to the right (east) from the grid. The minimum contour represents a DDT concentration of $2.7\times10^{3}$ng/L (0.0027 mg/L) with the maximum concentration being $3.5\times10^{5}$ng/L (0.350 mg/L). The locations of groundwater samples are also shown on Figure 3.21 with DDT concentration values detected in March 2004 samples. All sampling point on the right side from the grid fall into the contour, therefore the predicted concentration for these points is above 2700ng/L. The highest detected value of DDT concentration in March 2004 is 89ng/L, which is still more than one order of magnitude lower the concentrations simulated with the high groundwater velocity. The DDT concentration values for the rest of the groundwater samples are three to four orders of magnitude below the predicted values. This supports the idea that the groundwater sampling scheme collected samples from locations that, if DDT was conserved, should have exhibited DDT concentrations much higher than observed. That is further evidence that substantial DDT degradation, probably microbially mediated, was likely a primary mechanism in the fate of DDT during the remediation activities.

Given the significance of this observation a closer look at the simulated versus observed groundwater concentrations of DDT is warranted.

Figures 3.22; 3.23; and 3.24 are graphs of the DDT concentration along cross-sectional lines within the simulation domain. The lines are labeled A-A, B-B and C-C respectively and correspond to those shown on Figure 3.21. Each of these lines corresponds to one of the sampling depths from the groundwater sampling conducted in March 2004. All the DDT concentrations observed in groundwater samples are 3 to 5 orders of magnitude smaller then the simulated values. This fact indicates that even using extreme possible values of groundwater velocity and net infiltration, which were unlikely to be present in the actual system, the DDT concentration at the sample well locations is below the expected values. Therefore the only reasonable remaining explanation of the large DDT loss is co-metabolic microbial degradation enhanced by cyclodextrin, because cyclodextrin solution does not sorb in porous media (Brusseau, 1994).

A further point about the simulations is that the DDT entrained with cyclodextrin was treated as a conservative solute exhibiting ideal behavior. It is common to observe "tailing effects" in most groundwater transport problems in the field. Consequently, the simulated groundwater concentrations on the trailing edge of the groundwater plume are lower than would be commonly expected. A type of "flow geometry" induced tailing effect was discussed above relative to the infiltration of the cyclodextrin solution at the sides of the remediation grid.

Figure 3.25 is a graph of the DDT concentrations with depth along the cross-sectional line D-D shown on Figure 3.21. This line is located 3m to the left from the outlined DDT plume. For the case of simulated high groundwater velocity and high net infiltration rate it might be expected that there would be no mass of DDT to the left (west)

of the grid. Figure 3.25 shows that there is mass of DDT 1m to the left (west) from the remediation grid. The concentration values are below 500ng/L. This is the tailing effect in the system created by horizontal infiltration of the solution containing DDT along the sides of the grid in the vadoze zone. The later applications of solutions within the grid do not displace these waters vertically. Displacement of this water is a slow process due to low net infiltration rates and it can be a relatively long source of leaching to groundwater. The presence of this readily explainable in hind-sight tailing effect in the simulated system attests to the value of using a fully unsaturated-saturated flow and transport model such as HYDRUS-2D rather than a standard saturated zone groundwater model with inputs from the vadoze zone expressed as boundary fluxes at the water table.

The longitudinal dispersivity value is estimated as one tenth of a travel distance. Another simulation with high groundwater velocity and high net infiltration values was completed using lower dispersivities values (10 for longitudinal and 1 for transverse), in order to exclude the possibility that simulated concentrations of DDT are present in the sampled area during March 2004 only due to dispersivity. These values are not likely to represent the actual system. Figure 3.26 is graph of the DDT concentration along the cross-sectional line within the simulated domain at depth 3m below the ground surface. Simulated concentration of DDT at the sampling point located 5m east from the edge of remediation grid is about 150ng/L that is 2-3 order of magnitude above the values detected during groundwater sampling at this location in March 2004. This is further evidence that substantial DDT degradation was likely the primary mechanism in the fate of DDT during the remediation activities.

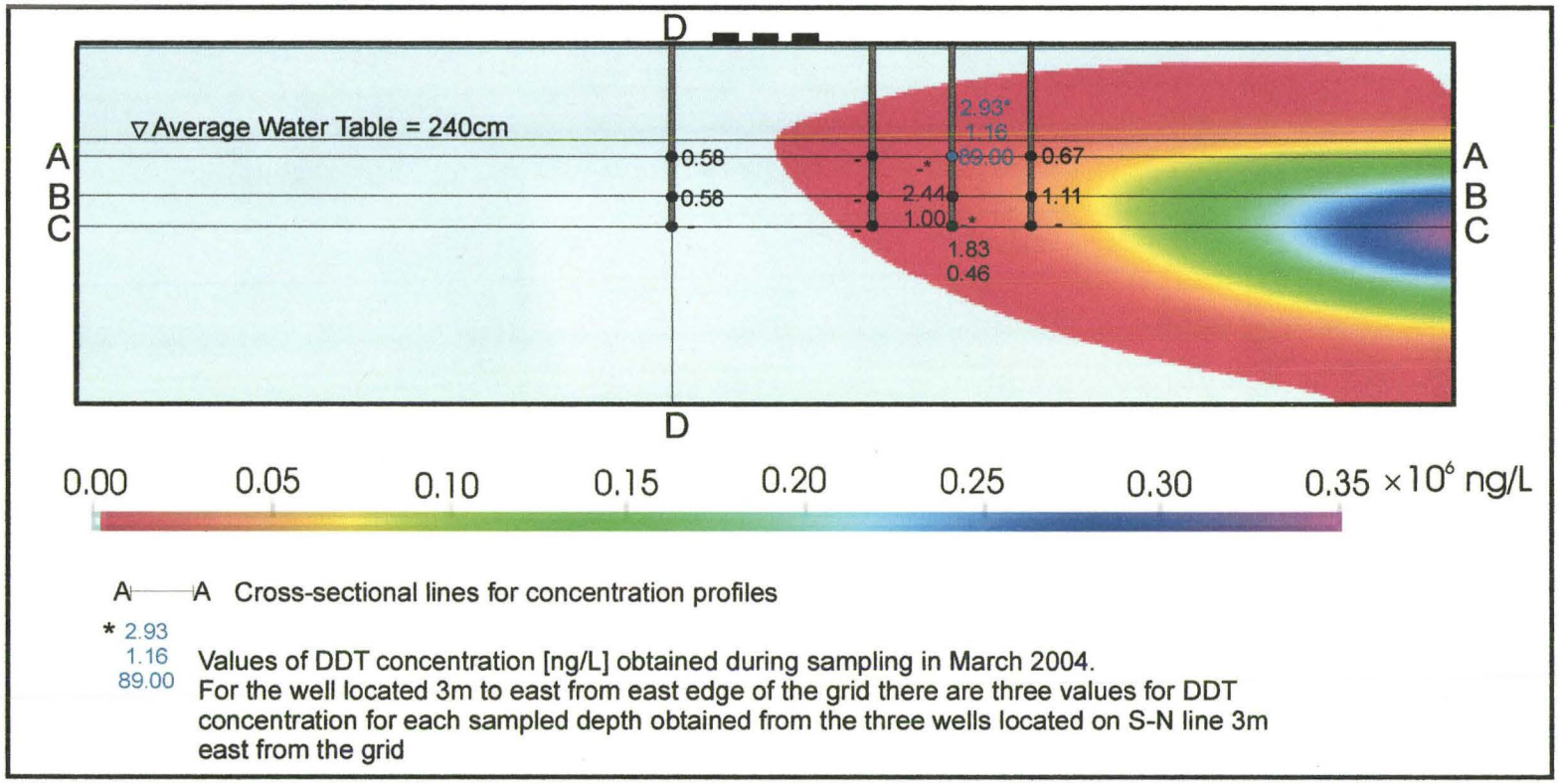


**Figure 3.21: The DDT Concentration Distribution Generated with the High Groundwater Velocity Simulation after about Sixteen Months after the End of the Pilot-Scale Field Experiment (638 Days since the Remediation Began) and Corresponds to when the March Groundwater Sampling was Conducted**

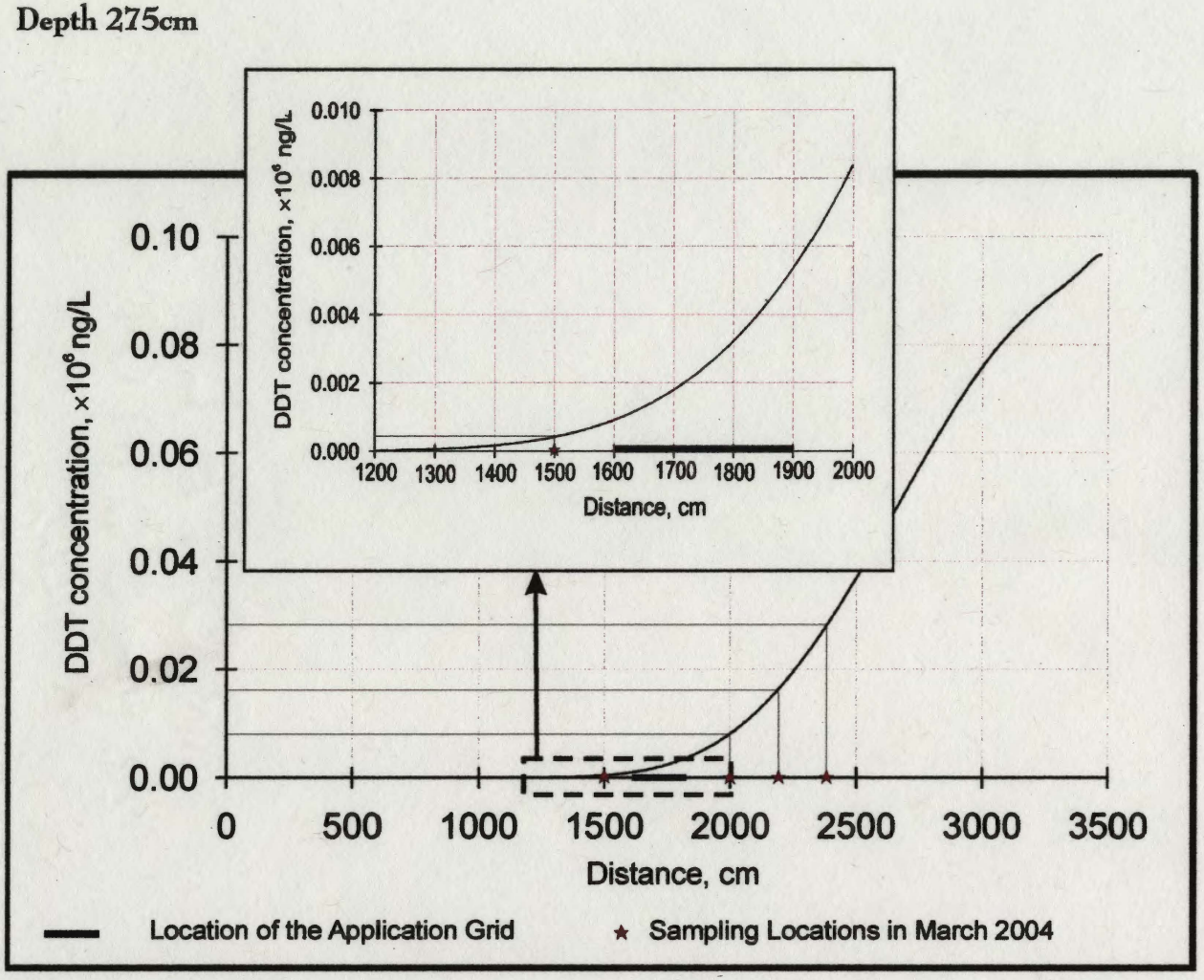


**Figure 3.22: The Cross-Sectional Profile A-A (Figure 3.21) of DDT Concentration Distribution at Depth 275cm Generated with the High Groundwater Velocity Simulation, 638 Days since the Remediation Began and Corresponds to when the March Groundwater Sampling was Conducted**

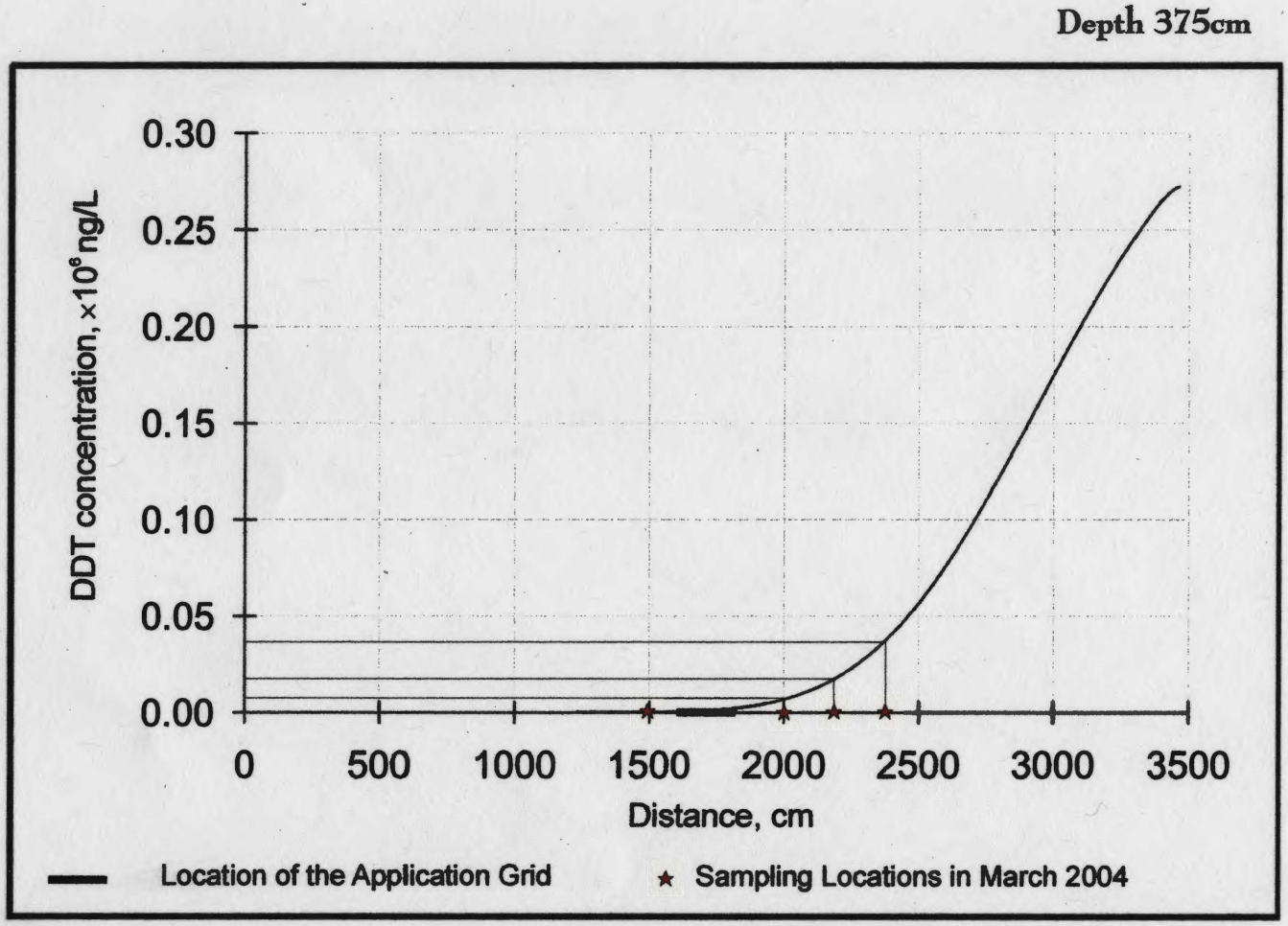


**Figure 3.23: The Cross-Sectional Profile B-B (Figure 3.21) of DDT Concentration Distribution at Depth 375cm Generated with the High Groundwater Velocity Simulation, 638 Days since the Remediation Began and Corresponds to when the March Groundwater Sampling was Conducted**

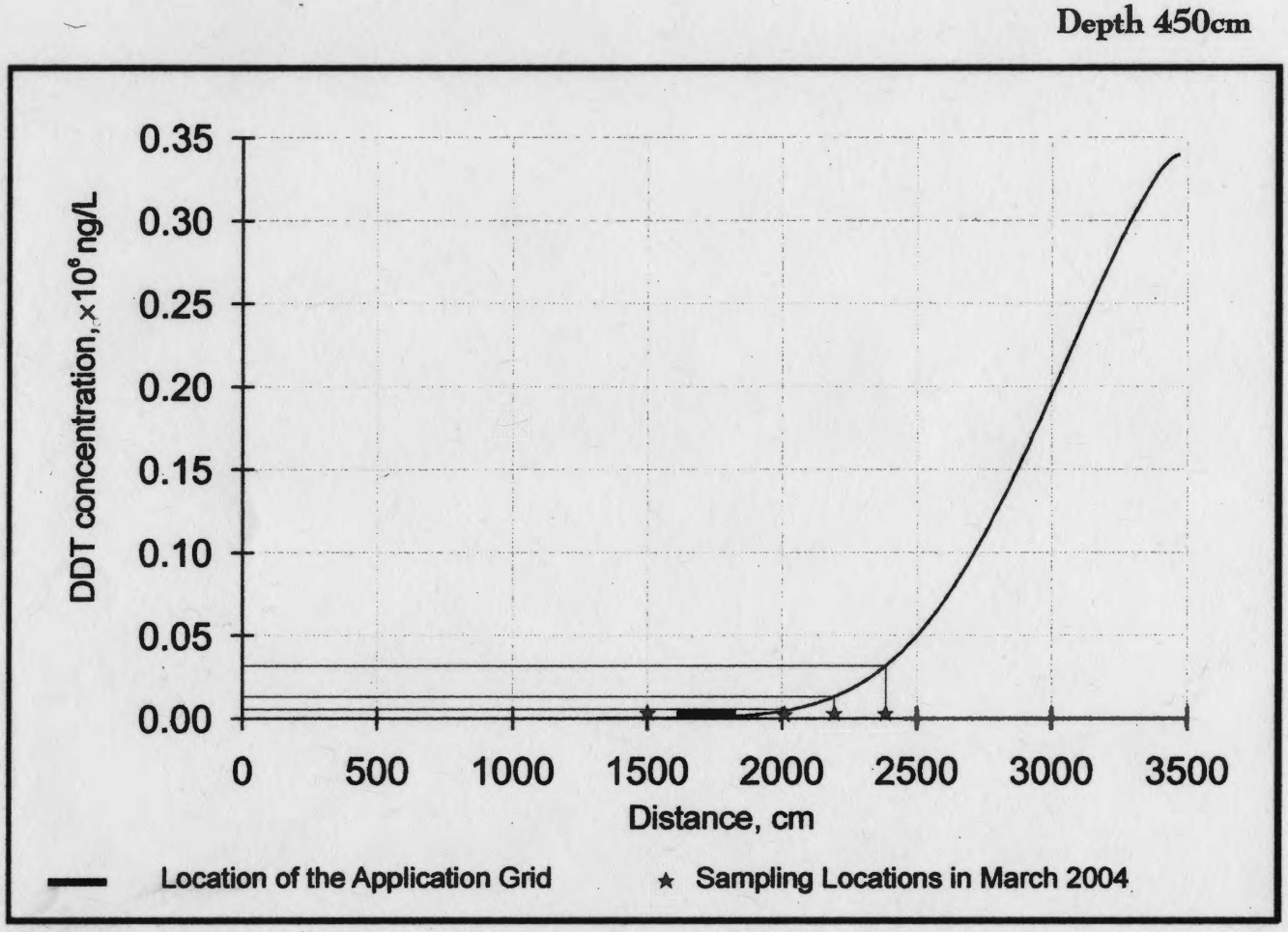


**Figure 3.24: The Cross-Sectional Profile C-C (Figure 3.21) of DDT Concentration Distribution at Depth 450cm Generated with the High Groundwater Velocity Simulation, 638 Days since the Remediation Began and Corresponds to when the March Groundwater Sampling was Conducted**

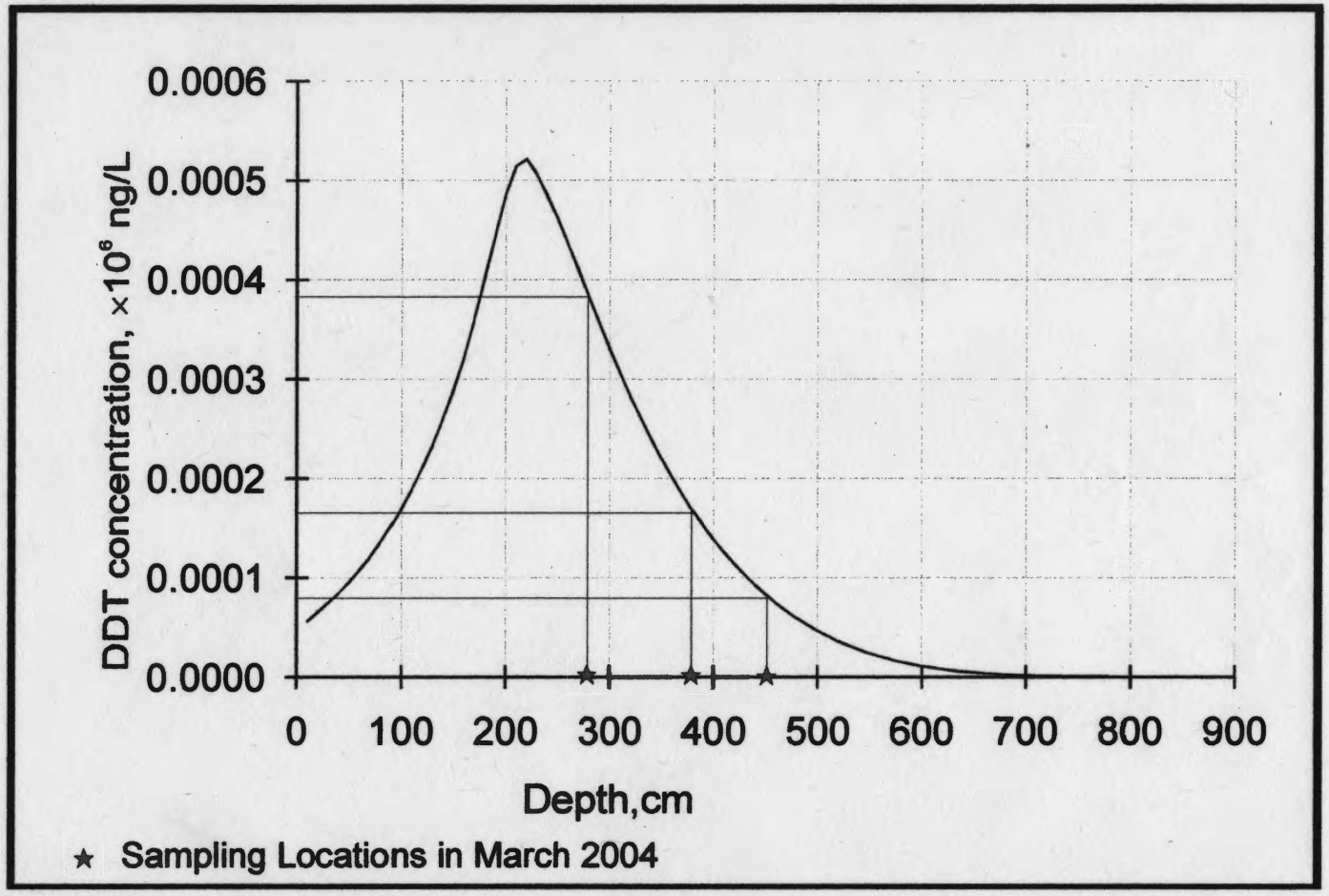


**Figure 3.25: The Cross-Sectional Profile D-D (Figure 3.21) of DDT Concentration Distribution with Depth 100cm West from the Remediation Grid Generated with the High Groundwater Velocity Simulation, 638 Days since the Remediation Began and Corresponds to when the March Groundwater Sampling was Conducted**

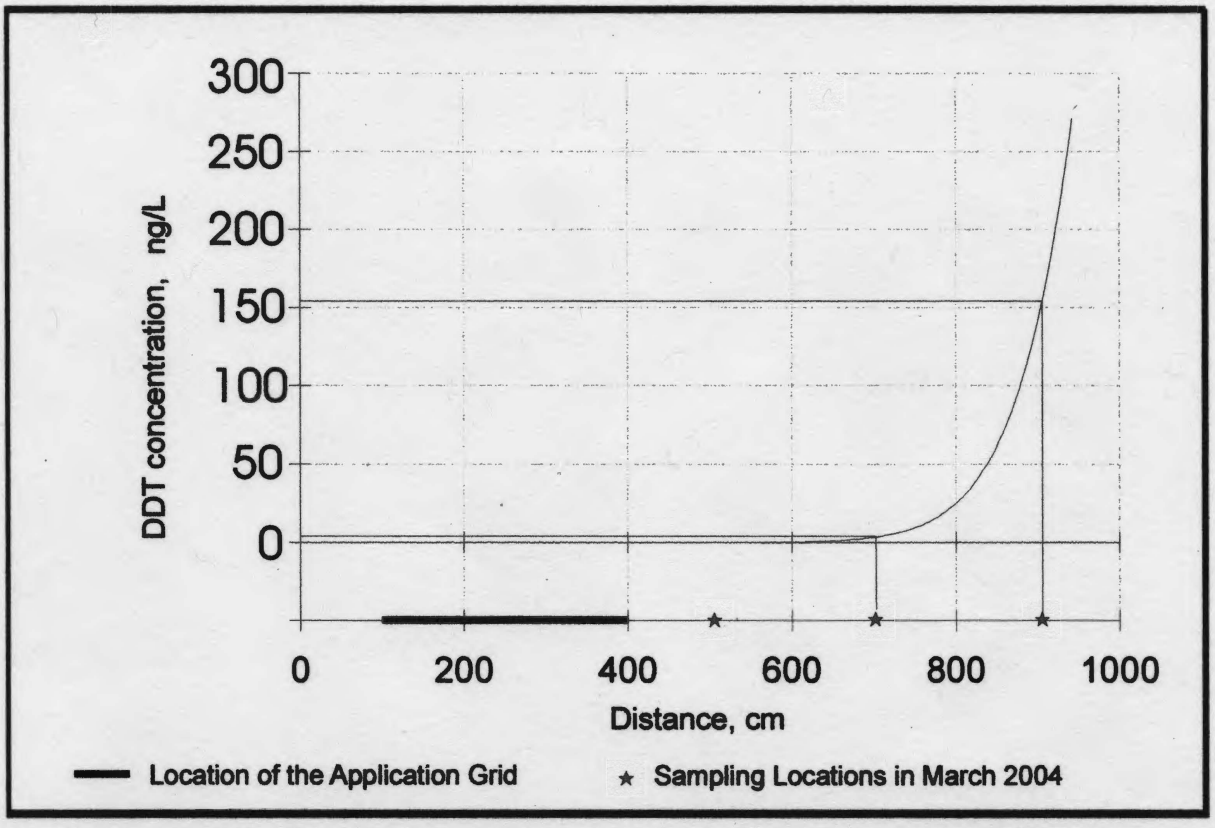


**Figure 3.26: The Cross-Sectional Profile of DDT Concentration Distribution at Depth 300cm Generated with the High Groundwater Velocity Simulation with Low Dispersivities Values, 638 Days since the Remediation Began and Corresponds to when the March Groundwater Sampling was Conducted**

# 4. Pump-and-Treat Method

## *4.1 Introduction*

During the pilot-scale experiment conducted by Badley (2003), DDT was flushed into the groundwater. During the year after the experiment the contaminated plume spread about 4 to 6 meters west and east from the edges of the application grid. It can be

expected that the contaminated plume may chemically and/or biologically degrade before it reaches the wetland or it is expected to be adsorbed by the organic sediments. If groundwater concentration of DDT is at unacceptable levels, action to clean up the system can be undertaken. Given that cyclodextrin has been shown to be a non-sorbing (conservative) solute, the pump and treat method should be effective in removing the cyclodextrin plume and its associated compounds.

## 4.2 Methods

The solution for remediation of this system is the "pump-and-treat" method. The studied site is a good candidate for this kind of remediation. There is no further release of contamination into the plume; the soil profile consists of relatively homogeneous material with high conductivity (Table 3.2). The cyclodextrin is a conservative compound, i.e. doesn't exhibit retardation.

For a pump-and-treat system the minimum total pumping rate should be the amount of water passing through the plume's maximum cross-sectional area (McKillip, 2002). Based on groundwater sampling conducted in October 2003 and November 2004 the width of the plume is approximately 500cm. The aquifer saturated thickness is estimated to be 660cm. Therefore the maximum cross-sectional area is approximately $3.3\times10^5$ cm$^2$. The minimum pumping rate can be calculated based on Darcy's Law:

$$Q = \frac{q}{n} A \qquad (4.1)$$

where $Q$ [$L^3/T$] is bulk well discharge, $q$ [L/T] is the Darcy velocity, or the specific discharge, $n$ is porosity, $\frac{q}{n}$ equals to 1m/year for the studied system, $A$ [$L^2$] is cross-sectional area.

The calculated minimum pumping rate is 90,410$cm^3$/day, which equals to about 4L/hr.

The equation of the line, which contours the capture zone with a pumping rate (Q) (McKillip, 2002 after Javandel and Tsang, 1986), is

$$x = \frac{-y}{\tan\left(\frac{2 \cdot \pi \cdot q \cdot B \cdot y}{Q}\right)} \tag{4.2}$$

where $x$, $y$ [L] are Cartesian coordinates where the origin is at the well; $q$ [L/T] is the Darcy velocity; $B$ [L] is aquifer thickness, $Q$ [$L^3/T$] is minimum pumping rate.

The distance to the downgradient stagnation point is given by (McKillip, 2002):

$$x_0 = \frac{-Q}{2 \cdot \pi \cdot q \cdot B} \tag{4.3}$$

As $x$ approaches infinity the maximum width of the capture zone is given by (Javandel and Tsang, 1986):

$$2y_{max} = \frac{-Q}{q \cdot B} \tag{4.4}$$

For the studied system the distance to the downgradient stagnation point is equal to 80cm and the maximum width of the capture zone is 500cm. The capture zone line is presented in Figure 4.1. To bring this graph closer to our system the sign of $x$ coordinate was changed, because the groundwater flow is from the left to the right.

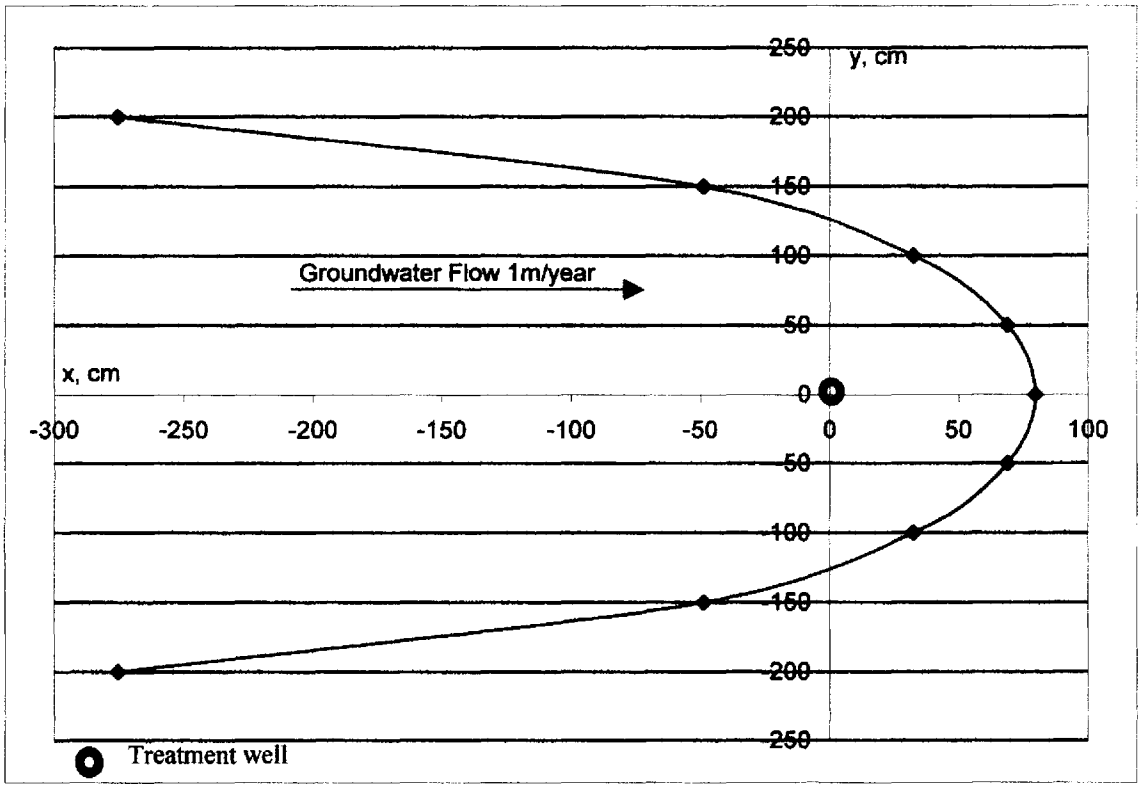


**Figure 4.1: The Capture Zone Plot, with the Pumping Rate of 90,410cm$^3$/day and the Pumping Well located at the origin. The Hydraulic Gradient Slope from Left to Right**

The minimum time required for pump-and-treat of a conservative compound, i.e. without retardation, can be found by the following equation (Domenico and Schwartz, 1998):

$$t_c = \frac{V_T}{Q} \tag{4.5}$$

where $V_T$ is the total volume of contaminated water and $Q$ is the pumping rate from a single recovery well. This equation assumes that no uncontaminated water flows to the well. This is unrealistic assumption, therefore the time of pump-and-treat method in a real system will be much higher.

The total volume of contaminated water can be found by multiplication of the length, width and height of the plume multiplied by porosity. For the studied system the length of the plume was estimated though numerical modeling and is equal to approximately 18m. The height of the plume is the thickness of aquifer, which is equal to 6.6m. The width of the plume is based on groundwater sampling conducted in October 2003 and in March 2004 and is 5m. The average porosity for the system is 0.42. Therefore the total volume of contaminated water at the moment of groundwater sampling in March 2004 is approximately $240 \times 10^6 cm^3$.

With the minimum pumping rate ($90410 cm^3$/day) the time required for the system clean-up is estimated to be greater than 7.5 years. To reduce operation time of the treatment well 5 times, the pumping rate should be increased 5 times. With the pumping

rate equal to 452,000cm$^3$/day the time required for the system clean-up is about 1.5 years. This pumping rate is approximately 20L/hour.

The model HYDRUS-2D was used to simulate the "pump-and-treat" system. The DDT mobilization simulation required a larger domain and the Pump-and-Treat simulations were based on the results of DDT mobilization simulation. The input data for these simulations are present in Table 4.1. The size of the domain for these simulations is 5470cm in horizontal dimension and 900cm in vertical dimension. The distance between nodes in vertical dimension is 20cm. In horizontal dimension the domain is divided in three zones: 1) 270cm under the application plots, the distance between nodes is 10cm, 2) 500cm to the right and to the left from the edges of application grid, the distance between nodes is 20cm, 3) 2100cm from the edges of the domain, the distance between nodes is 30 cm. The distance between nodes was increased for reducing time of running the simulations. The application plots are located 2600cm from the edges of the domain for minimizing boundary effect on the solute transport during the Drain simulation. The rest of the parameters are the same with DDT mobilization simulation described in Chapter 3 (Tables 3.1; 3.4 and 3.8; Figure 3.5).

Two cases for pump-and-treat method were simulated: the first one is one pumping well for extracting DDT contaminated water and the second one is one pumping well for extracting DDT contaminated water combined with one injection well for injection of treated water. The second case represents a system with water treatment facilities, for example reverse osmosis, directly on the site. Therefore the contaminated

water is withdrawn down groundwater flow within the plume and is being injected up groundwater flow past the edge of the plume.

For the first case the pumping well was placed 530cm to the right from the right edge of the application grid. The treatment well is screened from the water table depth 250cm to the depth of the aquitard 880cm. The total number of nodes is 32. The initial distribution of the DDT concentration is present in Figure 4.2. The pumping rate was calculated for a 3D system. To convert it to 2D system the pumping rate was divided by the width of the plume, 500cm. Therefore the pumping rate for the simulation is $900cm^3/day$, which is equal to approximately $30cm^3/day$ per well node. With this rate the system should be cleaned up in not less than about 1.5 years.

For the second case the pumping well was placed 10m to the right from the right edge of the remediation grid and injection well was placed 5m to the left from the edge of the remediation grid (Figure 4.3). Both wells are screened from the water table depth 250cm to the depth of the aquitard 880cm. The total number of nodes for each well is 32. The initial distribution of the DDT concentration is present in Figure 4.4. The preliminary simulations showed that if pumping rate is equal to injection rate the DDT plume moves to the right beyond the capture zone of pumping well due to increased gradient between pumping and injection wells. The pumping rate for this simulation was $40cm^3/day$ for each node, which is equal to $640,000cm^3/day$ for a 3D system. The injection rate was $30cm^3/day$ for each node, which is equal to about $480,000cm^3/day$ for a 3D system. This difference between pumping and injection rates corresponds very well with real systems,

the treatment facilities produce some volume of highly concentrated solution, which has to be discarded somewhere else due to its toxicity.

**Table 4.1: Summary for Input Data in HYDRUS-2D simulations**

| **Model*** | **1** | **2** |
|---|---|---|
| **Main Processes** | | |
| ▪ Water Flow | ✔ | ✔ |
| ▪ Solute Transport | ✔ | ✔ |
| **Geometry Information** | | |
| ▪ Length Units | cm | cm |
| *Geometry Type* | | |
| ▪ Rectangular | ✔ | ✔ |
| ▪ Type of Flow | vertical | vertical |
| *Soil Profile* | | |
| ▪ Number of materials (Heterogeneity) | 2 | 2 |
| ▪ Number of Layers (Mass Balance) | 2 | 2 |
| **Time Information** | | |
| ▪ Time Units | days | days |
| *Time Discretization* | | |
| ▪ Initial Time | 0 | 638 |
| ▪ Final Time | 638 | 1500 |
| ▪ Initial Time Step | 0.001 | 0.001 |
| ▪ Minimum Time Step | 0.0001 | 0.0001 |
| ▪ Maximum Time Step | 1 | 1 |
| *Boundary Conditions* | | |
| ▪ Number of Time-Variable Boundary Records | 51 | 1 |
| **Print Options** | | |
| ▪ Number of Print Times | 1 | 20 |
| **Iteration Criteria** | | |
| *Iteration Criteria* | | |
| ▪ Maximum Number of Iterations | 50 | 50 |
| ▪ Water Content Tolerance | 0.001 | 0.001 |
| ▪ Pressure Head Tolerance | 0.1 | 0.1 |
| *Time Step Control* | | |
| ▪ Lower Optional Iteration Range | 3 | 3 |
| ▪ Upper Optional Iteration Range | 7 | 7 |
| ▪ Lower Time Step Multiplication Factor | 1.5 | 1.5 |
| ▪ Upper Time Step Multiplication Factor | 0.7 | 0.7 |
| *Internal Interpolation Tables* | | |
| ▪ Lower Limit of the Tension Interval | 0.001 | 0.001 |
| ▪ Upper Limit of the Tension Interval | 250 | 250 |
| *Initial Conditions* | | |
| ▪ In the Pressure Head | ✔ | ✔ |
| ▪ In theWater Content | | |

*Table 4.1. Continued*

| **Model*** | **1** | **2** |
|---|---|---|
| **Soil Hydraulic Model** | | |
| ▪ van Genuchtem-Mualem | ✔ | ✔ |
| ▪ Hysteresis | No | No |
| **Water Flow Parameters** | | |
| *A Horizon* | | |
| ▪ $Q_r$ | 0.0465 | 0.0465 |
| ▪ $Q_s$ | 0.5656 | 0.5656 |
| ▪ Alpha | 0.0649 | 0.0649 |
| ▪ n | 1.9929 | 1.9929 |
| ▪ $K_s$ | 493.02 | 493.02 |
| ▪ I | 0.5 | 0.5 |
| *B Horizon* | | |
| ▪ $Q_r$ | 0.0531 | 0.0531 |
| ▪ $Q_s$ | 0.3933 | 0.3933 |
| ▪ Alpha | 0.0316 | 0.0316 |
| ▪ n | 4.3647 | 4.3647 |
| ▪ $K_s$ | 1369.46 | 1369.46 |
| ▪ I | 0.5 | 0.5 |
| **Solute Transport – General Information** | | |
| *Time Weighting Scheme* | | |
| ▪ Crank-Nicholson Scheme | ✔ | ✔ |
| *Space Weighting Scheme* | | |
| ▪ Galerkin Finite Elements | ✔ | ✔ |
| ▪ Mass Units | % | % |
| ▪ Stability Criteria | 2 | 2 |
| ▪ Use Tortuosity Factor | ✔ | ✔ |
| ▪ Number of Solutes | 1 | 1 |
| ▪ Pulse Duration | 146 | 146 |
| **Solute Transport Parameters** | | |
| *A Horizon* | | |
| ▪ Bulk Density | 0.97 | 0.97 |
| ▪ Longitudinal Dispersivity | 30 | 30 |
| ▪ Transverse Dispersivity | 9 | 9 |
| *B Horizon* | | |
| ▪ Bulk Density | 1.43 | 1.43 |
| ▪ Longitudinal Dispersivity | 30 | 30 |
| ▪ Transverse Dispersivity | 9 | 9 |

* 1. DDT mobilization by Cyclodextrin
2. Pump-and-Treat

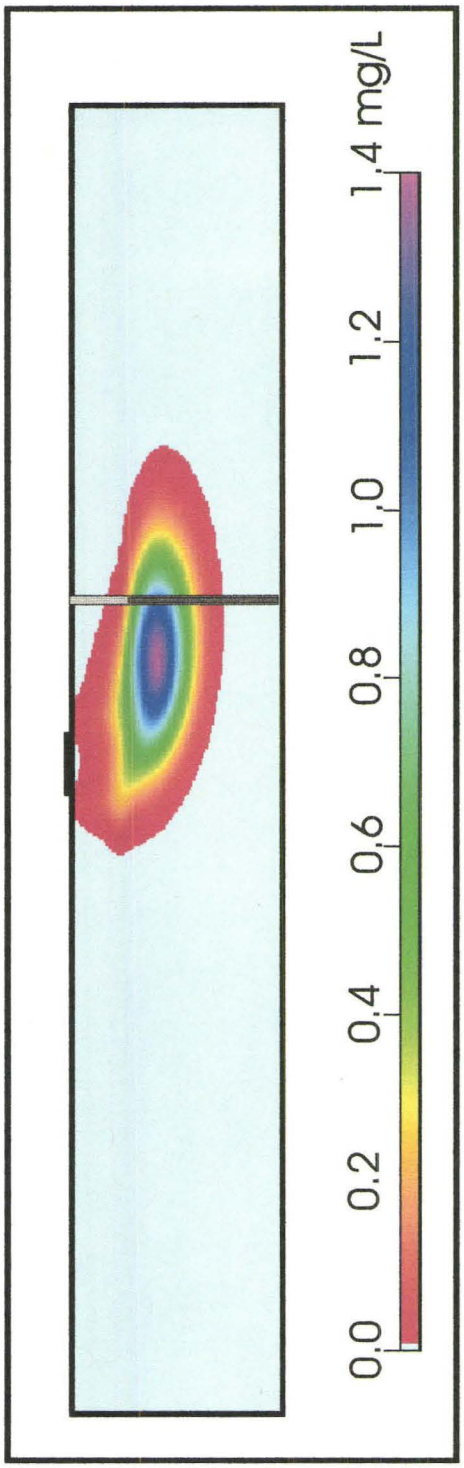


**Figure 4.2: The Initial Concentration Distribution for the Drain Simulation with One Pumping Well (the Size of the Domain is 5470cm×900cm)**

**Figure 4.3: The Initial Concentration Distribution for the Drain Simulation with One Pumping Well and One Injection Well (the Size of the Domain is 5470cm×900cm)**

## 4.3 Results and Discussions

The purpose of two drain simulations was to demonstrate the pump-and-treat method in the studied area and to understand which processes affect the time of remediation by pump-and-treat method.

The drain simulation with one pumping well achieved the decrease in DDT concentration by 100 times after 2 years of pumping. Figure 4.4 demonstrates the distribution of DDT concentration after a half-year of pumping. As shown in this figure the direction of the flow is toward the well capturing the plume. This simulation reveals the tailing effect of the pump-and-treat method, even if there is no retardation simulated. As indicated in the Figure 4.5, after 1 year of pumping well operation, the plume distribution in the vadoze zone is wider than in the aquifer. The solute percolates downward very slowly due to low net infiltration rate caused by precipitation. After 2 years of the simulated treatment well operation the maximum plume concentration reduced from 1.4mg/L to 0.011mg/L (Figure 4.6). This reduction in 100 times could be enough for a real system installed at the pilot-scale field experiment, because the concentration values which were revealed during the sampling in October 2003 and March 2004 are thousands times below the simulated concentration values.

It was expected that combination of pumping and injection wells would reduce the DDT concentration in groundwater faster than only one pumping well. But reduction in 100 times was reached also in 2 years of the pump-and-treat system operation. This can

be due to increase in distance of pumping well location from the remediation grid, so the well pumps out more clean groundwater from the right side of the well due to boundary effect - the higher hydraulic gradient is created and also the center of mass of the plume has to travel some distance towards the pumping well. Figure 4.7 shows the DDT concentration distribution after half-year of the system operation. Apparently the size of the plume is larger that for simulation with one pumping well at that time (Figure 4.4). The same tailing effect was observed during the drain simulation with two wells. The size of the plume is much wider in the unsaturated zone than in the saturated (Figure 4.8), which is caused by the low net infiltration rate. Flushing the contaminant from the vadoze zone is a slow process. After two years of system operation the maximum DDT concentration was reduced by 100 times (Figure 4.9).

The tailing effect induced by slow infiltration of solution from unsaturated zone causes the increase in time of remediation. The decision for this problem could be the application of one pore volume of clean water, which is equal to the void space occupied by contaminated solution on the surface above the plume in the unsaturated zone, to flush out the contamination from the vadoze zone and then the pump-and-treat method could be applied to the system. Also for further evaluation of the pump-and-treat method the simulations could be run in a larger domain to eliminate the boundary effect, which was observed in the described two drain simulations.

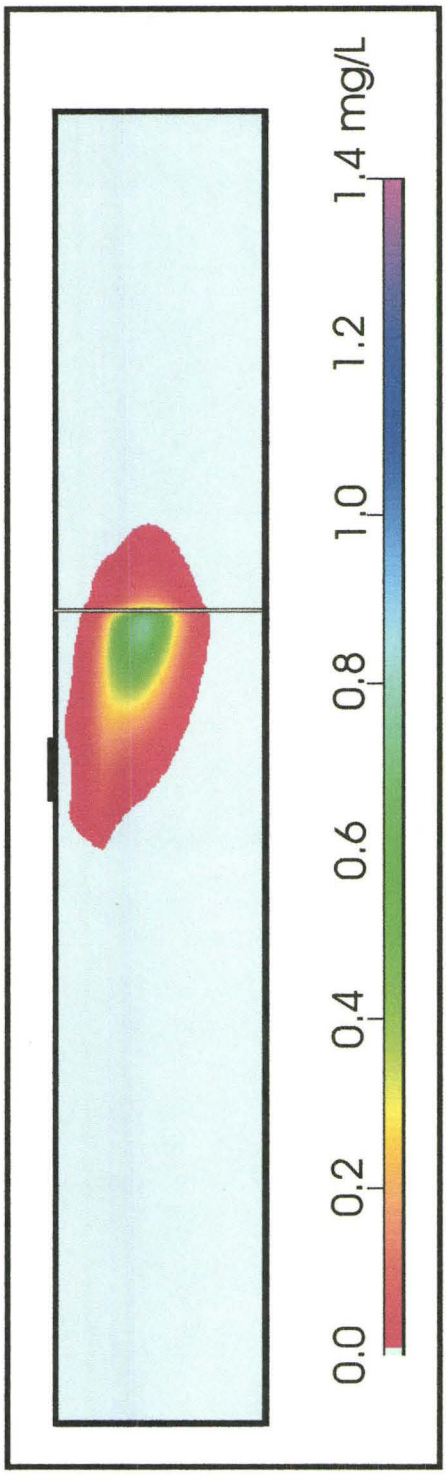


**Figure 4.4: The Concentration Distribution for the Drain Simulation with One Pumping Well after ½ Years ($t_{HYDRUS}$=810days) of Well Operation (the Size of the Domain is 5470cm×900cm)**

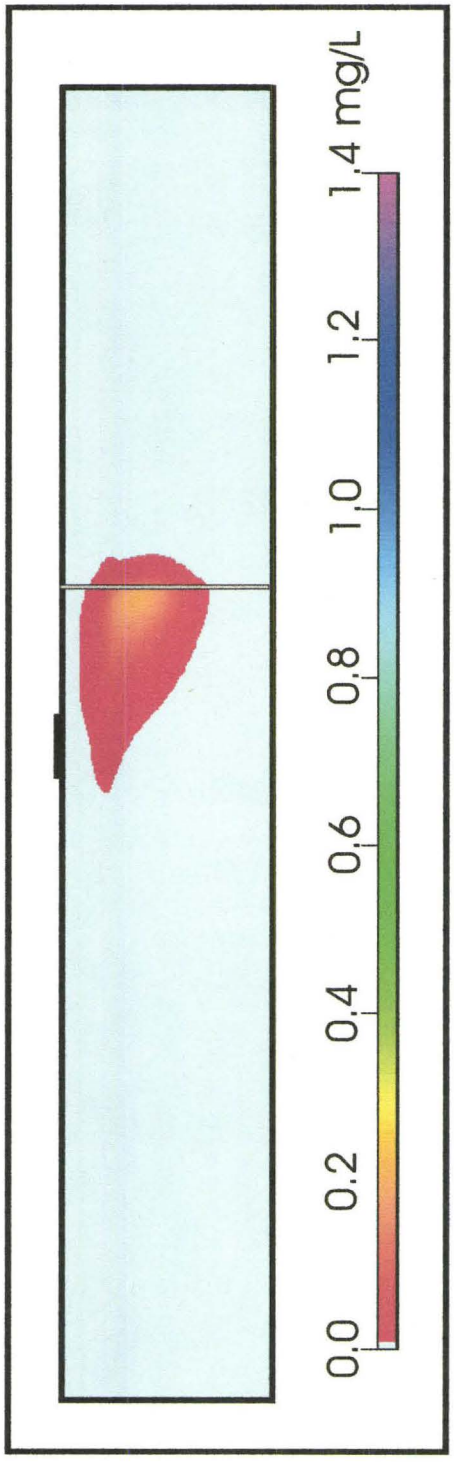


**Figure 4.5: The Concentration Distribution for the Drain Simulation with One Pumping Well after 1 Years ($t_{HYDRUS}$=1000days) of Well Operation (the Size of the Domain is 5470cm×900cm)**

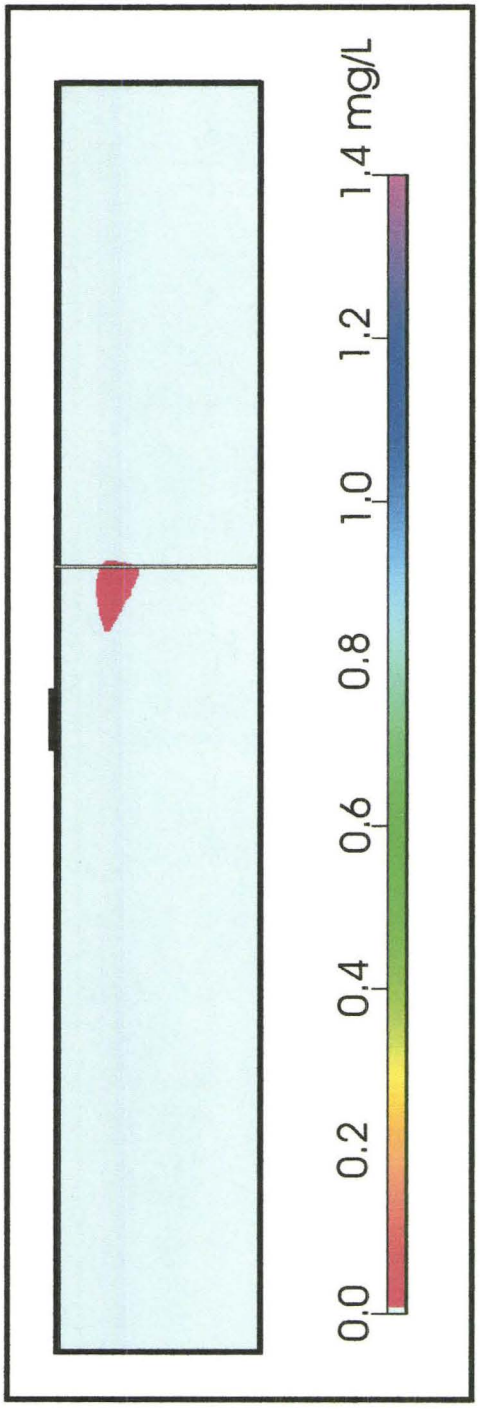


**Figure 4.6: The Concentration Distribution for the Drain Simulation with One Pumping Well after 2 Years ($t_{HYDRUS}$=1365days) of Well Operation (the Size of the Domain is 5470cm×900cm)**

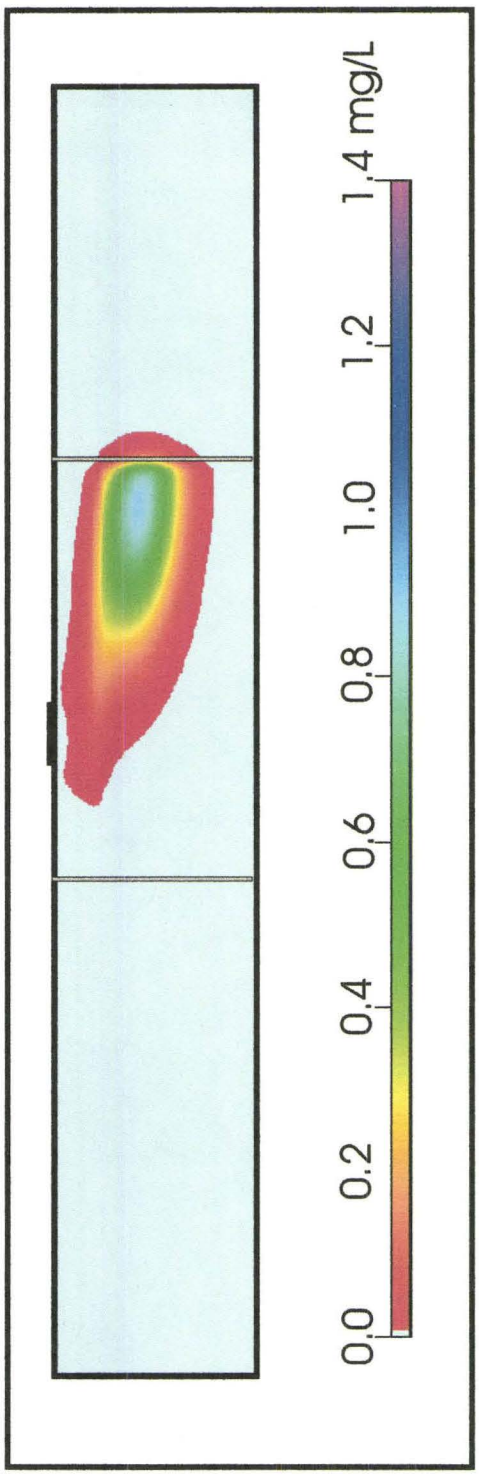


**Figure 4.7: The Concentration Distribution for the Drain Simulation with One Pumping Well and One Injection Well after ½ Year ($t_{HYDRUS}$=820days) of Well Operation (the Size of the Domain is 5470cm×900cm)**

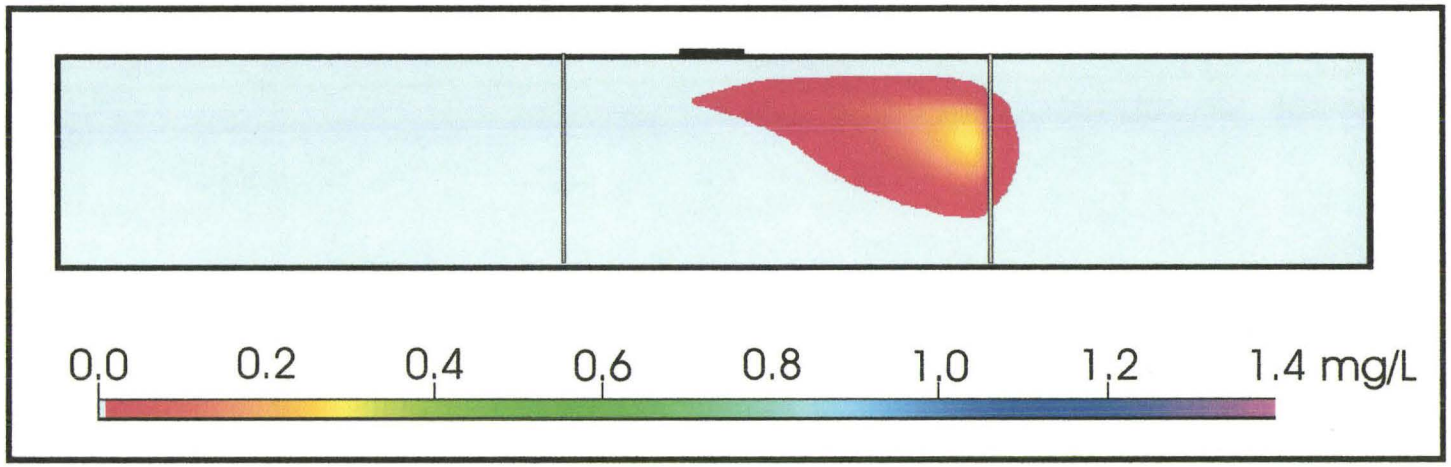


**Figure 4.8: The Concentration Distribution for the Drain Simulation with One Pumping Well and One Injection Well after 1 Year ($t_{HYDRUS}$=1000days) of Well Operation (the Size of the Domain is 5470cm×900cm)**

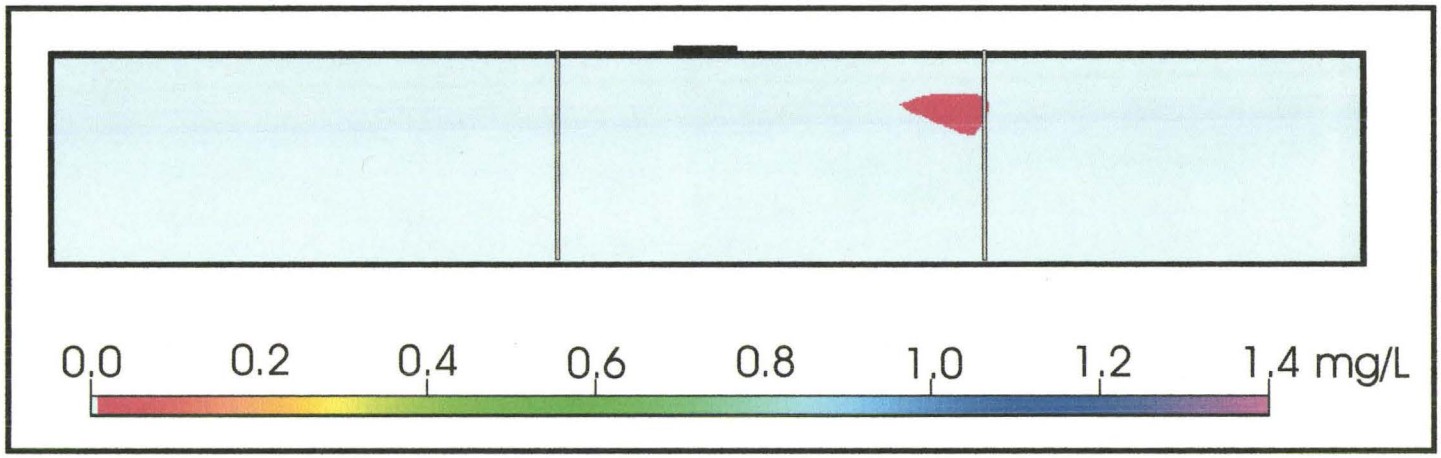


**Figure 4.9: The Concentration Distribution for the Drain Simulation with One Pumping Well and One Injection Well after 2 Years ($t_{HYDRUS}$=1365days) of Well Operation (the Size of the Domain is 5470cm×900cm)**

# 5. Conclusions and Recommendations

## *5.1 Conclusions*

Due to agricultural land-use in the period from 1948 to 1967, the shallow soils in the former agricultural areas in Point Pelee National Park have DDT, DDE and DDD concentrations above the regulatory limits. This is a potential health risk for people and wildlife in the park.

Recent studies reported high persistence of DDT and its metabolites in the shallow soils in Point Pelee National Park. The estimated half-life for DDT is in the range of 15-30 years for the former orchard area. A pilot-scale field remediation experiment involving the application of hydroxypropyl-β-cyclodextrin to soils resulted in a substantial decrease of the DDT, DDE and DDD concentrations.

Soil sampling within the remediation grid 10 months after the treatments had stopped revealed no additional degradation of the DDT, DDE or DDD. Semple and Doick (2003) reported that the portion of organic contaminants extracted by solutions of cyclodextrin correlates very well with the portion of contaminants which is bioavailable. Probably, within this study, the first few applied pore volumes the cyclodextrin solution extracted all DDT, DDE and DDD which could be mineralisable and leached it to groundwater. This supposition is verified by the research of Fava et al. (1998). They have shown that the second addition of cyclodextrin was much less effective than the first for polychlorobiphenyl aerobic biodegradation and dechlorination in the soil. They suggested that this effect could be due to the fact that the primary and more bioavailable fraction

was already metabolized with the first addition of cyclodextrin or due to a quick metabilization of the new added cyclodextrin by the microorganisms already adapted to the metabolisation of these substrates.

The percentage of removed contaminants from soil calculated using arithmetical mean data from 2002 and 2003 is 86%, 72% and 79% for DDT, DDE and DDD respectively in the 10% plots and 80%, 58% and 57% for DDT, DDE and DDD respectively in the 20% plots. Due to the fact that concentrations of DDT and its metabolites may have ln-normal distribution, mass loss was calculated with ln-transformed data. The percentage of removed contaminants from soil calculated using ln-transformed data from 2002 and 2003 is 74%, 65% and 61% for DDT, DDE and DDD respectively in the 10% plots and 62%, 45% and 18% for DDT, DDE and DDD respectively in the 20% plots. This mass loss can be attributed to mobilization of DDT and its metabolites by cyclodextrin solution and/or co-metabolic degradation.

The concentrations found in groundwater samples taken in October 2003 and March 2004 were 10-100 times above the background values. This is a direct indication of mobilization of DDT and its metabolites by cyclodextrin solution to groundwater. Assuming that the groundwater sampling scheme represents the extent of the groundwater plume, the estimated mass in groundwater is 0.0035% and 0.012% of mass lost from soil, based on the arithmetical and ln-transformed soil data, respectively. This reduction in mass would be attributed to the biological and/or cometabolic degradation as enhanced by the presence of cyclodextrin in solution. The resultant estimated half-life of DDT in the

pilot-scale field experiment is less than two month which is substantially less than the 15 to 30 years observed for untreated soils within Point Pelee National Park.

The numerical model HYDRUS 2D was useful for further evaluations of the mass and distribution of DDT in the subsurface, both above and below the water table. Brusseau et al. (1994) demonstrated that cyclodextrin solutions are conservative (non-reactive) and travels through soil with no retardation. Based upon the flow velocities reported by Crowe et al. (2004), the simulated solute transport without retardation or degradation generated a March 2004 DDT plume with a center of mass located 3-4m to the east from the east edge of the remediation grid and approximately 3.5m below the surface. The maximum concentration in the simulated plume was approximately 1.4mg/L. The DDT concentrations detected during March 2004 groundwater sampling are 2 to 8 orders of magnitude below these simulated with numerical model using a non-reactive solute. Even when extreme possible values of groundwater velocity and net infiltration were input to the model the simulated values of DDT concentration are 3 to 5 orders of magnitude above the observed values in groundwater samples. Therefore it was concluded that enhanced degradation of DDT must have been induced within the system by the presence of the cyclodextrin solution.

There are several effects and processes that the cyclodextrin solution application could induce in the studied DDT contaminated soil. First, the cyclodextrin solution can mobilize the DDT and transport it to groundwater by forming inclusion complexes. This fact was confirmed by elevated groundwater concentrations compared to background values. This mobilization process has been demonstrated by Brusseau et al. (1994) and

Schepanow (2002). Second, the cyclodextrin solution can increase the bioavailability of DDT and its metabolites by increasing the solubility of DDT in the aqueous medium as was shown by Schwartz and Bar (1995), Fava et al. (1998) and Semple and Doick (2003). Third, cyclodextrin solution can reduce the toxicity of the soil and promote the growth of microbial cultures which are capable of degrading DDT and its derivatives. Gaw et al. (2003) reported a strong negative correlation between degradation of DDT to DDE and concentration of copper in soil, i.e., the presence of toxic compound can reduce the ability of microbial community to degrade DDT to DDE. The reduction in soil toxicity by application of cyclodextrin was demonstrated by Schwartz and Bar (1995) and Fava et al. (1998). Forth, Foght et al. (2001) stated that the biodegradation of DDT and its metabolites is co-metabolic and requires an alternate carbon source as a growth substance. Gray et al. (1999) reported a reduction in DDT concentration by 98% in 14 weeks during *ex-situ* bioremediation of DDT contaminated soil using a compost window amended with organic material and alteration of aerobic and anaerobic conditions. In this study it appears that cyclodextrin probably was used by degrading bacteria as an alternate carbon source and promote more intensive degradation of DDT and its metabolites.

The results of this study lead to the conclusion that more than 99.9% of the mass of DDT, DDE and DDD that was initially present in the soil was broken down by enhanced microbial degradation caused by the application of cyclodextrin solutions. Based on the observations that treatment plots had increased organic content after remediation (Badley, 2003), no increase in DDT concentration was observed during final sampling at depth 80cm in November 2002 (Badley, 2003) and less then 0.1% of the

DDT mass lost from soil was found in groundwater in the vicinity of remediation grid it can be concluded that co-metabolic degradation of DDT and its metabolites likely occurred within the A-horizon during the application of cyclodextrin solution.

However, while this large proportional mass loss is a highly desirable outcome the concentration of some soil samples collected within the remediated soil are still above the regulatory limits set by the Ontario Ministry of Environment and Energy for Parkland/Recreational Land-Use. Further study of cyclodextrin applications for remediation of contaminated soils and groundwaters is warranted. That is particularly true for situations which involve sensitive lands that require relatively low impact remediation methods that do not remove the local flora and leave the existing soil intact.

## 5.2 Recommendations

Badley's (2003) work has concluded that the application of cyclodextrin is an excellent remediation method for DDT contaminated soils. However, before this remediation technology is recommended for commercial use, further investigations of the local groundwater should be completed. That should include more extensive sampling in the area of remediation grid to confirm that the groundwater velocities and direction considered in this study were correct. In addition, the groundwater in the vicinity of remediation grid should be sampled and analyzed for cyclodextrin concentration in order to delineate the cyclodextrin plume and estimated the mass of cyclodextrin in the groundwater. The distribution of cyclodextrin concentrations could be correlated with the DDT plume to confirm DDT fate estimates. Also, a study of the long term fate of cyclodextrin in groundwater including estimates of the degradation rate of cyclodextrin would be valuable for future applications of this remediation method.

The soil treated with cyclodextrin solution should be further investigated to determine the microorganisms responsible for the enhanced degradation of DDT, DDE and DDD in the presence of cyclodextrin. Therefore if the soil chosen for this treatment has insufficient microorganisms capable of co-metabolicly degrading DDT and its metabolites, it may be possible to spike that soil with microorganisms from Badley's (2003) experiment.

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# Appendix A: Results of Soil Sampling in September 2003 Provided by National Laboratory for Environmental Testing (NLET)

| | | ng/g (wet weight) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | control | control | control | control | control | control | control | control | control |
| NLET SAMPLE # | | 9035 | 9036 | 9037 | 9044 | 9045 | 9046 | 9047 | 9048 | 9049 |
| Client Sample # | | Plot5-a | Plot5-b | Plot5-c | Plot8-a | Plot8-b | Plot8-c | Plot9-a | Plot9-b | Plot9-c |
| SAMPLE WET WEIGHT (g) | | 17.97 | 20.23 | 20.63 | 20.3 | 20.34 | 20.33 | 20.26 | 20.05 | 20.21 |
| | | | | | | | | | | |
| Surrogates | | % | % | % | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 91 | 73 | 93 | 90 | 104 | 89 | 83 | 94 | 79 |
| 1,2,4,5-Tetrabromobenzene | | 111 | 88 | 113 | 101 | 105 | 103 | 98 | 100 | 87 |
| d-HCH | | 101 | 87 | 126 | **50** | 97 | 95 | **34** | 95 | 78 |
| Analytes | Detection Limit (ng/g) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) |
| o,p-DDE | *0.29** | 367 | 158 | 149 | 38.3 | 7.61 | 98.0 | 182 | 210 | 76.2 |
| p,p-DDE | 2.25 | 38700 | 16600 | 11400 | 2530 | 929 | 12500 | 15400 | 13000 | 6870 |
| op-DDD | *0.58** | 240 | 103 | 240 | 7.99 | 5.82 | 169 | 178 | 223 | 99.1 |
| p,p-DDD | 0.76 | 211 | 222 | 347 | 19.5 | 13.6 | 335 | 212 | 344 | 185 |
| o,p-DDT | 4.85 | 4610 | 2420 | 1760 | 61.5 | 21.3 | 492 | 1630 | 1780 | 632 |
| p,p-DDT | 2.07 | 5540 | 12400 | 7960 | 177 | 209 | 4520 | 5110 | 17500 | 2310 |

Note: Values reported below detection limit are nominal.
* - Instrument Detection Limits

Concentrations of DDT, DDE and DDD within the soil of control plots

| | | ng/g (wet weight) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 10% | 10% | 10% | 10% | 10% | 10% | 10% | 10% | 10% |
| NLET SAMPLE # | | 9026 | 9027 | 9028 | 9038 | 9039 | 9040 | 9041 | 9042 | 9043 |
| Client Sample # | | Plot2-a | Plot2-b | Plot2-c | Plot6-a | Plot6-b | Plot6-c | Plot7-a | Plot7-b | Plot7-c |
| SAMPLE WET WEIGHT (g) | | 14.56 | 20.09 | 20.14 | 20.5 | 20.65 | 20.38 | 20.06 | 20.91 | 20.26 |
| | | | | | | | | | | |
| Surrogates | | % | % | % | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 85 | 100 | 89 | 91 | 94 | 88 | 91 | 84 | 100 |
| 1,2,4,5-Tetrabromobenzene | | 107 | 105 | 109 | 119 | 97 | 101 | 101 | 90 | 108 |
| d-HCH | | 97 | 99 | 65 | int | 93 | 93 | 94 | 93 | 95 |
| Analytes | Detection Limit (ng/g) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) |
| o,p-DDE | *0.29** | 130 | 63.6 | 107 | 64.1 | 92.1 | 111 | 18.5 | 46.2 | 248.0 |
| p,p-DDE | 2.25 | 13500 | 3490 | 10700 | 8510 | 9140 | 11200 | 1130 | 4460 | 186 |
| op-DDD | *0.58** | 330 | 42.3 | 412 | 98.9 | 140 | 127 | 11.3 | 110 | 95.6 |
| p,p-DDD | 0.76 | 531 | 71.2 | 485 | 232 | 168 | 218 | 21.1 | 111 | 102 |
| o,p-DDT | 4.85 | 1110 | 153.0 | 1320 | 647 | 378 | 705 | 35.4 | 179 | 1000 |
| p,p-DDT | 2.07 | 7560 | 768 | 9990 | 3670 | 3600 | 3600 | 135 | 1160 | 3870 |

Note: Values reported below detection limit are nominal.
* - Instrument Detection Limits

Concentrations of DDT, DDE and DDD within the soil of 10% plots

| | | ng/g (wet weight) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 20% | 20% | 20% | 20% | 20% | 20% | 20% | 20% | 20% |
| NLET SAMPLE # | | 9023 | 9024 | 9025 | 9029 | 9030 | 9031 | 9032 | 9033 | 9034 |
| Client Sample # | | Plot1-a | Plot1-b | Plot1-c | Plot3-a | Plot3-b | Plot3-c | Plot4-a | Plot4-b | Plot4-c |
| SAMPLE WET WEIGHT (g) | | 20.22 | 20.31 | 20.5 | 20.76 | 20.71 | 20.28 | 20.73 | 16.58 | 20.88 |
| | | | | | | | | | | |
| Surrogates | | % | % | % | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 87 | 88 | 96 | 90 | 97 | 86 | 79 | 85 | 96 |
| 1,2,4,5-Tetrabromobenzene | | 88 | 92 | 113 | 108 | 119 | 106 | 109 | 114 | 115 |
| d-HCH | | 102 | 101 | 105 | 96 | 99 | 93 | 99 | 101 | 97 |
| Analytes | Detection Limit (ng/g) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) | ng/g (w/w) |
| o,p-DDE | *0.29** | 122 | 95.4 | 203 | 55.4 | 121 | 188 | 186 | 548 | 103 |
| p,p-DDE | 2.25 | 9220 | 8040 | 19100 | 10200 | 11100 | 12700 | 18600 | 39500 | 10800 |
| op-DDD | *0.58** | 153 | 176 | 603 | 225 | 280 | 308 | 586 | 3050 | 355 |
| p,p-DDD | 0.76 | 158 | 174 | 895 | 357 | 373 | 357 | 609 | 2750 | 534 |
| o,p-DDT | 4.85 | 404 | 266 | 1090 | 988 | 985 | 1050 | 1100 | 2750 | 870 |
| p,p-DDT | 2.07 | 2160 | 1910 | 8170 | 5810 | 5940 | 4920 | 9920 | 24400 | 5720 |

Note: Values reported below detection limit are nominal.
* - Instrument Detection Limits

Concentrations of DDT, DDE and DDD within the soil of 20% plots

# Appendix B: Locations for groundwater sampling on October 6-10th and March 8-10th

| | Sample Name | Sample location |
|---|---|---|
| 1 | REM-GW-W000-270 | 0 cm west of grid, 270 cm below surface |
| 2 | REM-GW-W050-270 | 50 cm west of grid, 270 cm below surface |
| 3 | REM-GW-W100-270 | 100 cm west of grid, 270 cm below surface |
| 4 | REM-GW-W200-270 | 200 cm west of grid, 270 cm below surface |
| 5 | REM-GW-W300-270 | 300 cm west of grid, 270 cm below surface |
| 6 | REM-GW-E000-270 | 0 cm east of grid, 270 cm below surface |
| 7 | REM-GW-E050-270 | 50 cm east of grid, 270 cm below surface |
| 8 | REM-GW-E100-270 | 100 cm east of grid, 270 cm below surface |
| 9 | REM-GW-E200-270 | 200 cm east of grid, 270 cm below surface |
| 10 | REM-GW-E300-270 | 300 cm east of grid, 270 cm below surface |
| 11 | REM-GW-N000-270 | 0 cm north of grid, 270 cm below surface |
| 12 | REM-GW-N100-270 | 100 cm north of grid, 270 cm below surface |
| 13 | REM-GW-S000-270 | 0 cm south of grid, 270 cm below surface |
| 14 | REM-GW-S100-270 | 100 cm south of grid, 270 cm below surface |

**List of Groundwater Samples Extracted on October 6-10$^{th}$**

| # | Sample Name | Sample location |
|---|---|---|
| 1a | REM-GW-W100-275 | 100 cm west of grid, 275 cm below surface |
| 1b | REM-GW-W100-375 | 100 cm west of grid, 375 cm below surface |
| 1c | REM-GW-W100-450 | 100 cm west of grid, 450 cm below surface |
| 2a | REM-GW-E100-275 | 100 cm east of grid, 275 cm below surface |
| 2b | REM-GW-E100-375 | 100 cm east of grid, 375 cm below surface |
| 2c | REM-GW-E100-450 | 100 cm east of grid, 450 cm below surface |
| 3a | REM-GW-E300-275 | 300 cm east of grid, 275 cm below surface |
| 3b | REM-GW-E300-375 | 300 cm east of grid, 375 cm below surface |
| 3c | REM-GW-E300-450 | 300 cm east of grid, 450 cm below surface |
| 4a | REM-GW-E500-275 | 500 cm east of grid, 275 cm below surface |
| 4b | REM-GW-E500-375 | 500 cm east of grid, 375 cm below surface |
| 4c | REM-GW-E500-450 | 500 cm east of grid, 450 cm below surface |
| 5a | REM-GW-E300N-275 | 300 cm east of grid, 250 cm north of E300, 275 cm below surface |
| 5b | REM-GW-E300N-375 | 300 cm east of grid, 250 cm north of E300, 375 cm below surface |
| 5c | REM-GW-E300N-450 | 300 cm east of grid, 250 cm north of E300, 450 cm below surface |
| 6a | REM-GW-E300S-275 | 300 cm east of grid, 250 cm south of E300, 275 cm below surface |
| 6b | REM-GW-E300S-375 | 300 cm east of grid, 250 cm south of E300, 375 cm below surface |
| 6c | REM-GW-E300S-450 | 300 cm east of grid, 250 cm south of E300, 450 cm below surface |
| 7a | REM-GW-N100-275 | 100 cm north of grid, 275 cm below surface |
| 7b | REM-GW-N100-375 | 100 cm north of grid, 375 cm below surface |
| 7c | REM-GW-N100-450 | 100 cm north of grid, 450 cm below surface |
| 8a | REM-GW-S100-275 | 100 cm south of grid, 275 cm below surface |
| 8b | REM-GW-S100-375 | 100 cm south of grid, 375 cm below surface |
| 8c | REM-GW-S100-450 | 100 cm south of grid, 450 cm below surface |

**List of Groundwater Samples Extracted on March 8-10th**

# Appendix C: Calculations of Statistical Analysis of Independent Samples

t-Test: Two-Sample Assuming Unequal Variances

| | *initial DDT* | *10% DDT* |
|---|---|---|
| Mean | 26.09273548 | 3.767 |
| Variance | 1659.681084 | 7.78552072 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 30 | |
| t Stat | 3.043041656 | *S* |
| P(T<=t) one-tail | 0.00241771 | |
| t Critical one-tail | 1.697260359 | |
| P(T<=t) two-tail | 0.00483542 | |
| t Critical two-tail | 2.042270353 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *initial DDT* | *20% DDT* |
|---|---|---|
| Mean | 26.09273548 | 5.207166667 |
| Variance | 1659.681084 | 28.4146176 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 31 | |
| t Stat | 2.826752602 | *S* |
| P(T<=t) one-tail | 0.004080631 | |
| t Critical one-tail | 1.695518677 | |
| P(T<=t) two-tail | 0.008161262 | |
| t Critical two-tail | 2.039514584 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *10% DDT* | *20% DDT* |
|---|---|---|
| Mean | 3.767 | 5.207166667 |
| Variance | 7.78552072 | 28.4146176 |
| Observations | 27 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 39 | |
| t Stat | -1.243768409 | *NS* |
| P(T<=t) one-tail | 0.110504558 | |
| t Critical one-tail | 1.684875315 | |
| P(T<=t) two-tail | 0.221009116 | |
| t Critical two-tail | 2.022688932 | |

**Statistical Comparison of DDT Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval), data from year 2002 and 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *initial DDE* | *10% DDE* |
|---|---|---|
| Mean | 24.45435839 | 6.852434444 |
| Variance | 891.3354704 | 15.61343504 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 31 | |
| t Stat | 3.250098062 | *S* |
| P(T<=t) one-tail | 0.001388728 | |
| t Critical one-tail | 1.695518677 | |
| P(T<=t) two-tail | 0.002777455 | |
| t Critical two-tail | 2.039514584 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *initial DDE* | *20% DDE* |
|---|---|---|
| Mean | 24.45435839 | 10.29987778 |
| Variance | 891.3354704 | 62.47568776 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 35 | |
| t Stat | 2.5394904 | *S* |
| P(T<=t) one-tail | 0.007849384 | |
| t Critical one-tail | 1.689572855 | |
| P(T<=t) two-tail | 0.015698769 | |
| t Critical two-tail | 2.030110409 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *10% DDE* | *20% DDE* |
|---|---|---|
| Mean | 6.852434444 | 10.29987778 |
| Variance | 15.61343504 | 62.47568776 |
| Observations | 27 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 38 | |
| t Stat | -2.027140013 | *S* |
| P(T<=t) one-tail | 0.02485268 | |
| t Critical one-tail | 1.685953066 | |
| P(T<=t) two-tail | 0.04970536 | |
| t Critical two-tail | 2.024394234 | |

**Statistical Comparison of DDE Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval), data from year 2002 and 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *initial DDD* | *10% DDD* |
|---|---|---|
| Mean | 2.328613226 | 0.493502593 |
| Variance | 10.28485885 | 0.230375297 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 32 | |
| t Stat | 3.145791709 | *S* |
| P(T<=t) one-tail | 0.001783647 | |
| t Critical one-tail | 1.693888407 | |
| P(T<=t) two-tail | 0.003567294 | |
| t Critical two-tail | 2.036931619 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *initial DDD* | *20% DDD* |
|---|---|---|
| Mean | 2.328613226 | 1.004503704 |
| Variance | 10.28485885 | 1.435867946 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 39 | |
| t Stat | 2.134134486 | *S* |
| P(T<=t) one-tail | 0.019587401 | |
| t Critical one-tail | 1.684875315 | |
| P(T<=t) two-tail | 0.039174802 | |
| t Critical two-tail | 2.022688932 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *10% DDD* | *20% DDD* |
|---|---|---|
| Mean | 0.493502593 | 1.004503704 |
| Variance | 0.230375297 | 1.435867946 |
| Observations | 27 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 34 | |
| t Stat | -2.057001109 | *S* |
| P(T<=t) one-tail | 0.023711467 | |
| t Critical one-tail | 1.690923455 | |
| P(T<=t) two-tail | 0.047422933 | |
| t Critical two-tail | 2.032243174 | |

**Statistical Comparison of DDD Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval), data from year 2002 and 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *initial lnDDT* | *10% lnDDT* |
|---|---|---|
| Mean | 2.185688721 | 0.838029318 |
| Variance | 3.047546183 | 1.53954356 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 54 | |
| t Stat | 3.419441423 | *S* |
| P(T<=t) one-tail | 0.00060071 | |
| t Critical one-tail | 1.673565748 | |
| P(T<=t) two-tail | 0.001201419 | |
| t Critical two-tail | 2.004881026 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *initial lnDDT* | *20% lnDDT* |
|---|---|---|
| Mean | 2.185688721 | 1.212565847 |
| Variance | 3.047546183 | 1.069091295 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 50 | |
| t Stat | 2.62047115 | *S* |
| P(T<=t) one-tail | 0.005799472 | |
| t Critical one-tail | 1.675905423 | |
| P(T<=t) two-tail | 0.011598944 | |
| t Critical two-tail | 2.008559932 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *10% lnDDT* | *20% lnDDT* |
|---|---|---|
| Mean | 0.838029318 | 1.212565847 |
| Variance | 1.53954356 | 1.069091295 |
| Observations | 27 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 50 | |
| t Stat | -1.204951087 | *NS* |
| P(T<=t) one-tail | 0.116947233 | |
| t Critical one-tail | 1.675905423 | |
| P(T<=t) two-tail | 0.233894467 | |
| t Critical two-tail | 2.008559932 | |

**Statistical Comparison of Ln-transformed DDT Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval), data from year 2002 and 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *initial lnDDE* | *10% lnDDE* |
|---|---|---|
| Mean | 2.670356056 | 1.627933702 |
| Variance | 1.181311469 | 0.889858885 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 56 | |
| t Stat | 3.910363999 | *S* |
| P(T<=t) one-tail | 0.000125702 | |
| t Critical one-tail | 1.672522103 | |
| P(T<=t) two-tail | 0.000251403 | |
| t Critical two-tail | 2.003239388 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *initial lnDDE* | *20% lnDDE* |
|---|---|---|
| Mean | 2.670356056 | 2.074013127 |
| Variance | 1.181311469 | 0.602535056 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 54 | |
| t Stat | 2.426024408 | *S* |
| P(T<=t) one-tail | 0.009317933 | |
| t Critical one-tail | 1.673565748 | |
| P(T<=t) two-tail | 0.018635867 | |
| t Critical two-tail | 2.004881026 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *10% lnDDE* | *20% lnDDE* |
|---|---|---|
| Mean | 1.627933702 | 2.074013127 |
| Variance | 0.889858885 | 0.602535056 |
| Observations | 27 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 50 | |
| t Stat | -1.897371338 | *NS* |
| P(T<=t) one-tail | 0.03178063 | |
| t Critical one-tail | 1.675905423 | |
| P(T<=t) two-tail | 0.06356126 | |
| t Critical two-tail | 2.008559932 | |

**Statistical Comparison of Ln-transformed DDE Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval), data from year 2002 and 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *initial lnDDD* | *10% lnDDD* |
|---|---|---|
| Mean | -0.323418037 | -1.265335961 |
| Variance | 3.246360964 | 1.54859083 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 53 | |
| t Stat | 2.339661274 | *S* |
| P(T<=t) one-tail | 0.011550525 | |
| t Critical one-tail | 1.674115993 | |
| P(T<=t) two-tail | 0.023101051 | |
| t Critical two-tail | 2.005745046 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *initial lnDDD* | *20% lnDDD* |
|---|---|---|
| Mean | -0.323418037 | -0.529656903 |
| Variance | 3.246360964 | 1.23317983 |
| Observations | 31 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 51 | |
| t Stat | 0.531807334 | *NS* |
| P(T<=t) one-tail | 0.298584255 | |
| t Critical one-tail | 1.675284693 | |
| P(T<=t) two-tail | 0.597168511 | |
| t Critical two-tail | 2.007582225 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *10% lnDDD* | *20% lnDDD* |
|---|---|---|
| Mean | -1.265335961 | -0.529656903 |
| Variance | 1.54859083 | 1.23317983 |
| Observations | 27 | 27 |
| Hypothesized Mean Difference | 0 | |
| df | 51 | |
| t Stat | -2.291973618 | *S* |
| P(T<=t) one-tail | 0.013034207 | |
| t Critical one-tail | 1.675284693 | |
| P(T<=t) two-tail | 0.026068413 | |
| t Critical two-tail | 2.007582225 | |

**Statistical Comparison of Ln-transformed DDD Concentration Samples for Each Group of Plots (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval), data from year 2002 and 2003**

**DDT 2002 vs 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *DDT 10% 2002* | *DDT 10% 2003* |
|---|---|---|
| Mean | 3.434922222 | 4.431155556 |
| Variance | 5.336400791 | 13.21873002 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 11 | |
| t Stat | -0.749829162 | *NS* |
| P(T<=t) one-tail | 0.234545775 | |
| t Critical one-tail | 1.795883691 | |
| P(T<=t) two-tail | 0.46909155 | |
| t Critical two-tail | 2.200986273 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *DDT 20% 2002* | *DDT 20% 2003* |
|---|---|---|
| Mean | 3.45225 | 8.717 |
| Variance | 7.499547184 | 55.622775 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 9 | |
| t Stat | -2.049774859 | *NS* |
| P(T<=t) one-tail | 0.03531974 | |
| t Critical one-tail | 1.833113856 | |
| P(T<=t) two-tail | 0.070639479 | |
| t Critical two-tail | 2.262158887 | |

**Statistical Comparison of DDT Concentration Samples within 10% and 20% plots for years 2002 and 2003 (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval)**

**DDE 2002 vs 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *DDE 10% 2002* | *DDE 10% 2003* |
|---|---|---|
| Mean | 6.767735 | 7.021833333 |
| Variance | 13.27189145 | 22.49247008 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 13 | |
| t Stat | -0.141242254 | NS |
| P(T<=t) one-tail | 0.444921901 | |
| t Critical one-tail | 1.770931704 | |
| P(T<=t) two-tail | 0.889843801 | |
| t Critical two-tail | 2.16036824 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *DDE 20% 2002* | *DDE 20% 2003* |
|---|---|---|
| Mean | 7.62305 | 15.65353333 |
| Variance | 26.10907232 | 99.19770962 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 10 | |
| t Stat | -2.273868893 | S |
| P(T<=t) one-tail | 0.023132696 | |
| t Critical one-tail | 1.812461505 | |
| P(T<=t) two-tail | 0.046265391 | |
| t Critical two-tail | 2.228139238 | |

**Statistical Comparison of DDE Concentration Samples within 10% and 20% plots for years 2002 and 2003 (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval)**

**DDD 2002 vs 2003**

t-Test: Two-Sample Assuming Unequal Variances

| | *DDD 10% 2002* | *DDD 10% 2003* |
|---|---|---|
| Mean | 0.556565 | 0.367377778 |
| Variance | 0.29521013 | 0.094554337 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 24 | |
| t Stat | 1.153353367 | NS |
| P(T<=t) one-tail | 0.130061431 | |
| t Critical one-tail | 1.710882316 | |
| P(T<=t) two-tail | 0.260122861 | |
| t Critical two-tail | 2.063898137 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *DDD 20% 2002* | *DDD 20% 2003* |
|---|---|---|
| Mean | 0.843255556 | 1.327 |
| Variance | 0.720467439 | 2.960071 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 10 | |
| t Stat | -0.796431216 | NS |
| P(T<=t) one-tail | 0.222138881 | |
| t Critical one-tail | 1.812461505 | |
| P(T<=t) two-tail | 0.444277763 | |
| t Critical two-tail | 2.228139238 | |

**Statistical Comparison of DDD Concentration Samples within 10% and 20% plots for years 2002 and 2003 (t-Test: Two-Sample Assuming Unequal Variances at the 95% confidence interval)**

t-Test: Two-Sample Assuming Unequal Variances

| | *lnDDT 10% 2002* | *lnDDT 10% 2003* |
|---|---|---|
| Mean | 0.761944631 | 0.99019869 |
| Variance | 1.534394825 | 1.70385263 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 15 | |
| t Stat | -0.435611156 | *NS* |
| P(T<=t) one-tail | 0.33466112 | |
| t Critical one-tail | 1.753051038 | |
| P(T<=t) two-tail | 0.66932224 | |
| t Critical two-tail | 2.131450856 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *lnDDT 20% 2002* | *lnDDT 20% 2003* |
|---|---|---|
| Mean | 0.864964518 | 1.907768505 |
| Variance | 0.985850222 | 0.56403487 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 21 | |
| t Stat | -3.042948943 | *S* |
| P(T<=t) one-tail | 0.003091481 | |
| t Critical one-tail | 1.720743512 | |
| P(T<=t) two-tail | 0.006182961 | |
| t Critical two-tail | 2.079614205 | |

**Statistical Comparison of Ln-transformed DDT Concentration Samples within 10% and 20% Plots for Years 2002 and 2003 (t-Test: Two-Sample Assuming Unequal Variances at the 95% Confidence Interval)**

t-Test: Two-Sample Assuming Unequal Variances

| | *lnDDE 10% 2002* | *lnDDE 10% 2003* |
|---|---|---|
| Mean | 1.67152072 | 1.540759666 |
| Variance | 0.698708535 | 1.3944619 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 12 | |
| t Stat | 0.297063518 | *NS* |
| P(T<=t) one-tail | 0.385748721 | |
| t Critical one-tail | 1.782286745 | |
| P(T<=t) two-tail | 0.771497441 | |
| t Critical two-tail | 2.178812792 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *lnDDE 20% 2002* | *lnDDE 20% 2003* |
|---|---|---|
| Mean | 1.799623997 | 2.622791388 |
| Variance | 0.566756744 | 0.245677437 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 23 | |
| t Stat | -3.395147673 | *S* |
| P(T<=t) one-tail | 0.001243799 | |
| t Critical one-tail | 1.713870006 | |
| P(T<=t) two-tail | 0.002487598 | |
| t Critical two-tail | 2.068654794 | |

**Statistical Comparison of Ln-transformed DDE Concentration Samples within 10% and 20% Plots for Years 2002 and 2003 (t-Test: Two-Sample Assuming Unequal Variances at the 95% Confidence Interval)**

t-Test: Two-Sample Assuming Unequal Variances

| | *lnDDD 10% 2002* | *lnDDD 10% 2003* |
|---|---|---|
| Mean | -1.212291831 | -1.37142422 |
| Variance | 1.873932964 | 1.03182031 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 21 | |
| t Stat | 0.34023618 | *NS* |
| P(T<=t) one-tail | 0.36852925 | |
| t Critical one-tail | 1.720743512 | |
| P(T<=t) two-tail | 0.7370585 | |
| t Critical two-tail | 2.079614205 | |

t-Test: Two-Sample Assuming Unequal Variances

| | *lnDDD 20% 2002* | *lnDDD 20% 2003* |
|---|---|---|
| Mean | -0.718333201 | -0.152304307 |
| Variance | 1.408401723 | 0.774689255 |
| Observations | 18 | 9 |
| Hypothesized Mean Difference | 0 | |
| df | 21 | |
| t Stat | -1.396342326 | *NS* |
| P(T<=t) one-tail | 0.088598773 | |
| t Critical one-tail | 1.720743512 | |
| P(T<=t) two-tail | 0.177197546 | |
| t Critical two-tail | 2.079614205 | |

**Statistical Comparison of Log-transformed DDD Concentration Samples within 10% and 20% Plots for Years 2002 and 2003 (t-Test: Two-Sample Assuming Unequal Variances at the 95% Confidence Interval)**

# Appendix D: Results of Groundwater Sampling in October 2003 Provided by National Laboratory for Environmental Testing (NLET)

| Sample Number | | | | 200308309 | 200308310 | 200308311 | 200308312 | 200308313 |
|---|---|---|---|---|---|---|---|---|
| ENV Project/Cruise # | | | | n/a | n/a | n/a | n/a | n/a |
| ENV Station - Mon \| Con Station | | | | n/a | n/a | n/a | n/a | n/a |
| Client # - Begin/End Depth (m) | | | | REM-E000-270 | REM-E050-270 | REM-E100-270 | REM-E200-270 | REM-E300-270 |
| Sampling Date | | | | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 |
| Date Last Analyzed | | | | Dec-10-2003 | Dec-10-2003 | Dec-10-2003 | Dec-10-2003 | Dec-10-2003 |
| Date Received | | | | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 |
| Date Expected | | | | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 |
| Date Accepted | | | | Dec-10-2003 | Dec-10-2003 | Dec-10-2003 | Dec-10-2003 | Dec-10-2003 |
| | OC1-W | S61 | | | | | | |
| | | | | | | | | |
| A2572 | NG/L | | A-HCH | < 0.20 C | < 0.20 C | < 0.20 C | < 0.20 C | < 0.20 C |
| A2573 | NG/L | | HCB | < 0.62 C | < 0.62 C | < 0.62 C | < 0.62 C | < 0.62 C |
| A2574 | % | | 1245TTBB | 126 C | 123 C | 126 C | 122 C | 104 C |
| A2575 | NG/L | | G-HCH | < 0.15 C | < 0.15 C | < 0.15 C | < 0.15 C | < 0.15 C |
| A2576 | % | | D-HCH | 112 C | 106 C | 108 C | 123 C | 87 C |
| A2577 | NG/L | | HEPTCHLR | < 0.82 C | < 0.82 C | < 0.82 C | < 0.82 C | < 0.82 C |
| A2578 | NG/L | | ALDRIN | < 0.61 C | < 0.61 C | < 0.61 C | < 0.61 C | < 0.61 C |
| A2579 | NG/L | | HPTCLEPX | < 0.17 C | < 0.17 C | < 0.17 C | < 0.17 C | < 0.17 C |
| A2580 | NG/L | | G-CHLRDN | < 0.33 C | < 0.33 C | < 0.33 C | < 0.33 C | < 0.33 C |
| A2581 | NG/L | | A-ENDSLF | < 0.22 C | < 0.22 C | < 0.22 C | < 0.22 C | < 0.22 C |
| A2582 | NG/L | | A-CHLRDN | < 0.31 C | < 0.31 C | < 0.31 C | < 0.31 C | < 0.31 C |
| A2583 | NG/L | | DIELDRIN | < 0.35 C | < 0.35 C | 0.55 C | 0.63 C | 3.37 C |
| A2584 | NG/L | | P,P-DDE | < 1.28 C | < 1.28 C | 1.93 C | 2.73 C | 10.1 C |
| A2585 | NG/L | | ENDRIN | < 0.55 C | < 0.55 C | < 0.55 C | < 0.55 C | < 0.55 C |
| A2586 | NG/L | | B-ENDSLF | < 0.88 C | < 0.88 C | < 0.88 C | < 0.88 C | < 0.88 C |
| A2587 | NG/L | | P,P-DDD | < 2.24 C | < 2.24 C | < 2.24 C | < 2.24 C | < 2.24 C |
| A2588 | NG/L | | O,P-DDT | < 0.75 C | < 0.75 C | < 0.75 C | < 0.75 C | 1.49 C |
| A2589 | NG/L | | P,P-DDT | < 1.30 C | < 1.30 C | < 1.30 C | < 1.30 C | < 1.30 C |
| A2590 | % | | END-KETO | 124 C | 121 C | 120 C | 129 C | 89 C |
| A2591 | NG/L | | MTHXYCHL | < 7.90 C | < 7.90 C | < 7.90 C | < 7.90 C | < 7.90 C |
| A2592 | NG/L | | MIREX | < 1.41 C | < 1.41 C | < 1.41 C | < 1.41 C | < 1.41 C |

| Sample Number | | | | 200308314 | 200308315 | 200308316 | 200308317 | 200308318 |
|---|---|---|---|---|---|---|---|---|
| ENV Project/Cruise # | | | | n/a | n/a | n/a | n/a | n/a |
| ENV Station - Mon \| Con Station | | | | n/a | n/a | n/a | n/a | n/a |
| Client # - Begin/End Depth (m) | | | | REM-W000-270 | REM-W050-270 | REM-W100-270 | REM-W200-270 | REM-W300-270 |
| Sampling Date | | | | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 |
| Date Last Analyzed | | | | Dec-10-2003 | Dec-10-2003 | Jan-23-2004 | Jan-23-2004 | Jan-23-2004 |
| Date Received | | | | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 |
| Date Expected | | | | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 |
| Date Accepted | | | | Dec-10-2003 | Dec-10-2003 | Jan-23-2004 | Jan-23-2004 | Jan-23-2004 |
| | OC1-W | S61 | | | | | | |
| | | | | | | | | |
| A2572 | NG/L | | A-HCH | < 0.20 C | < 0.20 C | < 0.20 C | < 0.20 C | < 0.20 C |
| A2573 | NG/L | | HCB | < 0.62 C | < 0.62 C | < 0.62 C | < 0.62 C | < 0.62 C |
| A2574 | % | | 1245TTBB | 142 C | 113 C | 114 C | 104 C | 99 C |
| A2575 | NG/L | | G-HCH | < 0.15 C | < 0.15 C | < 0.15 C | < 0.15 C | < 0.15 C |
| A2576 | % | | D-HCH | 108 C | 123 C | 101 C | 100 C | 107 C |
| A2577 | NG/L | | HEPTCHLR | < 0.82 C | < 0.82 C | < 0.82 C | < 0.82 C | < 0.82 C |
| A2578 | NG/L | | ALDRIN | < 0.61 C | < 0.61 C | < 0.61 C | < 0.61 C | < 0.61 C |
| A2579 | NG/L | | HPTCLEPX | < 0.17 C | < 0.17 C | < 0.17 C | < 0.17 C | < 0.17 C |
| A2580 | NG/L | | G-CHLRDN | < 0.33 C | < 0.33 C | < 0.33 C | < 0.33 C | < 0.33 C |
| A2581 | NG/L | | A-ENDSLF | < 0.22 C | < 0.22 C | 0.33 C | < 0.22 C | < 0.22 C |
| A2582 | NG/L | | A-CHLRDN | < 0.31 C | < 0.31 C | < 0.31 C | < 0.31 C | < 0.31 C |
| A2583 | NG/L | | DIELDRIN | 21.8 C | 28.7 C | 298. C | 22.2 C | 2.68 C |
| A2584 | NG/L | | P,P-DDE | 1.87 C | 2.45 C | 17.0 C | < 1.28 C | 1.64 C |
| A2585 | NG/L | | ENDRIN | < 0.55 C | < 0.55 C | 1.01 C | < 0.55 C | < 0.55 C |
| A2586 | NG/L | | B-ENDSLF | < 0.88 C | < 0.88 C | < 0.88 C | < 0.88 C | < 0.88 C |
| A2587 | NG/L | | P,P-DDD | < 2.24 C | < 2.24 C | < 2.24 C | < 2.24 C | < 2.24 C |
| A2588 | NG/L | | O,P-DDT | < 0.75 C | < 0.75 C | 2.14 C | < 0.75 C | < 0.75 C |
| A2589 | NG/L | | P,P-DDT | < 1.30 C | < 1.30 C | 3.96 C | < 1.30 C | < 1.30 C |
| A2590 | % | | END-KETO | 117 C | 132 C | 143 C | 97 C | 1 C |
| A2591 | NG/L | | MTHXYCHL | < 7.90 C | < 7.90 C | < 7.90 C | < 7.90 C | < 7.90 C |
| A2592 | NG/L | | MIREX | < 1.41 C | < 1.41 C | < 1.41 C | < 1.41 C | < 1.41 C |

| Sample Number | | | | 200308319 | 200308320 | 200308321 | 200308322 |
|---|---|---|---|---|---|---|---|
| ENV Project/Cruise # | | | | n/a | n/a | n/a | n/a |
| ENV Station - Mon \| Con Station | | | | n/a | n/a | n/a | n/a |
| Client # - Begin/End Depth (m) | | | | REM-N000-270 | REM-N100-270 | REM-S000-270 | REM-S100-270 |
| Sampling Date | | | | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 | Oct-08-2003 |
| Date Last Analyzed | | | | Jan-23-2004 | Jan-23-2004 | Jan-23-2004 | Jan-23-2004 |
| Date Received | | | | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 | Oct-20-2003 |
| Date Expected | | | | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 | Feb-09-2004 |
| Date Accepted | | | | Jan-23-2004 | Jan-23-2004 | Jan-23-2004 | Jan-23-2004 |
| | OC1-W | S61 | | | | | |
| | | | | | | | |
| A2572 | NG/L | | A-HCH | < 0.20 C | < 0.20 C | < 0.20 C | < 0.20 C |
| A2573 | NG/L | | HCB | < 0.62 C | < 0.62 C | < 0.62 C | < 0.62 C |
| A2574 | % | | 1245TTBB | 113 C | 103 C | 98 C | 100 C |
| A2575 | NG/L | | G-HCH | < 0.15 C | < 0.15 C | < 0.15 C | < 0.15 C |
| A2576 | % | | D-HCH | 122 C | 93 C | 97 C | 114 C |
| A2577 | NG/L | | HEPTCHLR | < 0.82 C | < 0.82 C | < 0.82 C | < 0.82 C |
| A2578 | NG/L | | ALDRIN | < 0.61 C | < 0.61 C | < 0.61 C | < 0.61 C |
| A2579 | NG/L | | HPTCLEPX | < 0.17 C | < 0.17 C | < 0.17 C | < 0.17 C |
| A2580 | NG/L | | G-CHLRDN | < 0.33 C | < 0.33 C | < 0.33 C | < 0.33 C |
| A2581 | NG/L | | A-ENDSLF | < 0.22 C | < 0.22 C | < 0.22 C | < 0.22 C |
| A2582 | NG/L | | A-CHLRDN | < 0.31 C | < 0.31 C | < 0.31 C | < 0.31 C |
| A2583 | NG/L | | DIELDRIN | < 0.35 C | < 0.35 C | 1.70 C | < 0.35 C |
| A2584 | NG/L | | P,P-DDE | < 1.28 C | < 1.28 C | 9.14 C | < 1.28 C |
| A2585 | NG/L | | ENDRIN | < 0.55 C | < 0.55 C | < 0.55 C | < 0.55 C |
| A2586 | NG/L | | B-ENDSLF | < 0.88 C | < 0.88 C | < 0.88 C | < 0.88 C |
| A2587 | NG/L | | P,P-DDD | < 2.24 C | < 2.24 C | < 2.24 C | < 2.24 C |
| A2588 | NG/L | | O,P-DDT | < 0.75 C | < 0.75 C | 1.33 C | < 0.75 C |
| A2589 | NG/L | | P,P-DDT | < 1.30 C | < 1.30 C | 7.94 C | < 1.30 C |
| A2590 | % | | END-KETO | 118 C | 86 C | 91 C | 108 C |
| A2591 | NG/L | | MTHXYCHL | < 7.90 C | < 7.90 C | < 7.90 C | < 7.90 C |
| A2592 | NG/L | | MIREX | < 1.41 C | < 1.41 C | < 1.41 C | < 1.41 C |

# Appendix E: Results of Groundwater Sampling in March 2004 Provided by National Laboratory for Environmental Testing (NLET)

03-517 **Concentration :ng/L**

| NLET SAMPLE # / Client Sample # | | 12859 REM-W100-275 | 12860 REM-W100-375 | 12861 REM-W100-450 | 12862 REM-S100-275 | 12863 REM-S100-375 | 12864 REM-S100-450 |
|---|---|---|---|---|---|---|---|
| **Surrogates** | | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 50 | 69 | 64 | 62 | 70 | 61 |
| 1,2,4,5-Tetrabromobenzene | | 56 | 76 | 74 | 72 | 84 | 71 |
| d-HCH | | 70 | 77 | 69 | 71 | 79 | 68 |
| **Analytes** | **Detection Limit (ng/L)** | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L |
| o,p-DDE | ***0.29**** | | | | | | |
| Dieldrin | 0.38 | 10.7 | 1.38 | 0.47 | | | |
| p,p-DDE | 0.56 | 2.77 | 0.80 | | | 3.11 | |
| op-DDD | ***0.58**** | | | | | | |
| p,p-DDD | 0.19 | | | | | | |
| o,p-DDT | 1.21 | | | | | | |
| p,p-DDT | 0.51 | 0.58 | 0.58 | | | 2.60 | |

*** - Instrument Detection Limits**

**-- - less than detection limit**

**03-517** **Concentration :ng/L**

| NLET SAMPLE # / Client Sample # | | 12865 REM-N100-275 | 12866 REM-N100-375 | 12867 REM-N100-450 | 12868 REM-E100-275 | 12869 REM-E100-375 | 12870 REM-E100-450 |
|---|---|---|---|---|---|---|---|
| **Surrogates** | | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 71 | 77 | 53 | 74 | 60 | 67 |
| 1,2,4,5-Tetrabromobenzene | | 78 | 86 | 75 | 73 | 70 | 89 |
| d-HCH | | 79 | 92 | 75 | 76 | 82 | 78 |
| **Analytes** | **Detection Limit (ng/L)** | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L |
| o,p-DDE | ***0.29**** | | | | | | |
| Dieldrin | 0.38 | | 0.46 | | | | |
| p,p-DDE | 0.56 | 0.81 | 4.03 | | 0.97 | | 0.65 |
| op-DDD | ***0.58**** | | | | | | |
| p,p-DDD | 0.19 | | | | | | |
| o,p-DDT | 1.21 | | | | | | |
| p,p-DDT | 0.51 | | 2.81 | | | | |

*** - Instrument Detection Limits**

**– - less than detection limit**

**03-517** **Concentration :ng/L**

| NLET SAMPLE # / Client Sample # | | 12871 REM-E300S-275 | 12872 REM-E300S-375 | 12873 REM-E300S-450 | 12874 REM-E300N-275 | 12875 REM-E300N-375 | 12876 REM-E300N-450 |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| **Surrogates** | | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 57 | 59 | 58 | 60 | 57 | 65 |
| 1,2,4,5-Tetrabromobenzene | | 63 | 67 | 74 | 72 | 65 | 73 |
| d-HCH | | 71 | 73 | 75 | 70 | 71 | 75 |
| **Analytes** | **Detection Limit (ng/L)** | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L |
| o,p-DDE | ***0.29**** | | | | 0.21 | | |
| Dieldrin | 0.38 | 0.36 | | | 3.41 | | |
| p,p-DDE | 0.56 | 3.97 | | | 34.8 | | |
| op-DDD | ***0.58**** | | | | 1.30 | | |
| p,p-DDD | 0.19 | | | | 3.39 | | |
| o,p-DDT | 1.21 | | | | 7.72 | | |
| p,p-DDT | 0.51 | 2.93 | | | 81.3 | 1.00 | 0.46 |

*** - Instrument Detection Limits**

**-- - below detection limit (levels near but below detection limit still reported)**

03-517

Concentration :ng/L

| NLET SAMPLE # / Client Sample # | | 12877 REM-E500-275 | 12878 REM-E500-375 | 12879 REM-E500-450 | 12880 REM-E300-275 | 12881 REM-E300-375 | 12882 REM-E300-450 |
|---|---|---|---|---|---|---|---|
| **Surrogates** | | % | % | % | % | % | % |
| 1,3,5-Tribromobenzene | | 69 | 61 | 62 | 81 | 75 | 62 |
| 1,2,4,5-Tetrabromobenzene | | 77 | 69 | 74 | 77 | 84 | 76 |
| d-HCH | | 69 | 79 | 83 | 72 | 84 | 75 |
| **Analytes** | **Detection Limit (ng/L)** | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L |
| o,p-DDE | ***0.29**** | | | | | | |
| Dieldrin | 0.38 | | | | 0.36 | 0.38 | 0.35 |
| p,p-DDE | 0.56 | 0.81 | 1.26 | | 1.51 | 3.53 | 2.22 |
| op-DDD | ***0.58**** | | | | | | |
| p,p-DDD | 0.19 | | | | | | |
| o,p-DDT | 1.21 | | | | | | |
| p,p-DDT | 0.51 | 0.67 | 1.11 | | 1.16 | 2.44 | 1.83 |

*** - Instrument Detection Limits**

**-- - below detection limit (levels near but below detection limit still reported)**