EFFECT OF SUBSURFACE HYDROLOGY ON DDT DEGRADATION IN SOILS

THE EFFECT OF SUBSURFACE HYDROLOGY ON DDT DEGRADATION IN SOILS AT POINT PELEE NATIONAL PARK, ONTARIO, CANADA

By

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Abstract

Systematic soil sampling and analyses provided DDT, DDE and DDD, organic and mineral matter concentrations, as well as various soil physical and hydraulic properties from three study sites at Point Pelee National Park. A soil's physical properties, soil and water management practices, and DDT application history, can affect DDT degradation and change the relative amount of its metabolites. DDD is the principal product of the dechlorination of DDT in high moisture content, reducing anaerobic soil environments. The main degradation product in soils under aerobic conditions is DDE. %DDT, %DDE and %DDD abundances used in conjunction with soil environment characterization data, can be used to indicate not only whether DDT is degrading, but what environmental factors are controlling its degradation. At the Park, DDT is primarily lost from the soil by microbial degradation to DDE and DDD. %DDT, %DDE and %DDD ratios from each study site indicated that wetter more organic-rich soil environments degraded DDT to its metabolites at a faster rate than drier less organic-rich soils. Moreover, historical water level data was used to illustrate that this wetter study site was flooded for part of the year when adjacent marsh water levels were high. These conditions resulted in the accumulation of organic matter over time and the creation of alternating anaerobic/aerobic conditions in the soils resulting in an increased rate of degradation of DDT in these areas. Based on the relative %DDT in the soils at each study site, relative half-life estimates for the first order decay of DDT to its metabolites DDE and DDD were calculated. Half-life estimates for DDT at the wettest and most organic-rich study site range from 6 to 8 years; significantly lower than the two other study sites, which range from 15 to 30 years and are on the high end of the range reported in the literature.

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Notation

Notation	*Definition (dimension)*
ρ_b	bulk density (M/L^3)
θ_m	gravimetric water content (%)
ρ_s	average particle density (M/L^3)
θ_v	volumetric water content (%)
ρ_w	density of water (M/L^3)
∞	infinity (dimensionless)
a	cross-sectional area of glass tube (L^2)
A	cross-sectional area of soil sample (L^2)
a^*	radius of the test hole (L)
A-G	relative values of the decay constant (k)
C	shape factor; depends on H/a (dimensionless)
C_o	initial concentration (M/L^3)
C_t	concentration at time t (M/L^3)
d_{10}	diameter at which 10% of the grains are finer (L)
d_{50}	diameter at which 50% of the grains are finer (L)
DDD	Dichloro-Diphenyl-Dichloro-Ethane, daughter product of DDT
DDD-x	daughter product of DDD
DDE	Dichloro-Diphenyl-Dichloro-Ethylene, daughter product of DDT
DDE-x	daughter product of DDE
DDT	Dichloro-Diphenyl-Trichloro-Ethane
DDT_n	DDT at the n^{th} half-life step
DDT_{n-1}	DDT at the (n-1) half-life step
DDT_o	$DDT_{today} + DDE_{today} + DDD_{today}$ (or DDX)
DDT_oe^{-kt}	DDT remaining today
DDT_{today}	concentration of DDT today
DDX	DDT + DDE + DDD
DDX	o,p'-DDT + p,p'-DDT + o,p'-DDE + p,p'-DDE + o,p'-DDD + p,p'-DDD
$e^{-k_At} - e^{-k_Gt}$	degradation terms
GP	Guelph permeameter
GWC	gravimetric water content (%)
H_1	5 cm well head height (L)
H_2	10 cm well head height (L)
K	hydraulic conductivity (L/T)

k	rate or decay constant (L^{-1})
K_{fs}	field saturated hydraulic conductivity (L/T)
L^*	length of soil sample (L)
L_i	where i = 1, 2, 3, 4, 5; points on glass tube (L)
MM	mineral matter (%)
M_s	mass of oven-dried soil (M)
M_{Swet}	mass of moist soil (M)
M_w	mass of water (M)
n	0, 1, 2, 3…n
n	empirical constant affecting shape of retention curve in RETC
n	porosity (%)
OC	organic carbon (%)
OM	organic matter (%)
ON	organic nitrogen (%)
P	pressure (L of water)
PPNP	Point Pelee National Park
Q	reservoir constant times steady-state rate of fall (Q=XR) (L^3/T)
R_1	steady-state rate of fall of water in the reservoir at H_1 (L/T)
R_2	steady-state rate of fall of water in the reservoir at H_2 (L/T)
t	time (T)
$t_{½}$	half-life (T)
TDR	time domain reflectometry
V_s	contained volume of sample ring (falling head tests) (L^3)
V_T	total sample volume (L^3)
VWC	volumetric water content (%)
W_c	mass of crucible (M)
W_{csi}	mass of ignited soil and crucible (M)
W_{cso}	mass of oven dried soil and crucible (M)
W_s	mass of soil in sieve (M)
W_t	mass of entire sample (M)
α	empirical constant affecting shape of retention curve in RETC
α	ratio of K_{fs} to the matric flux potential; $0 < \alpha < \infty$ (L^{-1})
θ_r	residual water content (%)
θ_s	saturated water content (%)
φ_m	matric flux potential (L^2/T)

CHAPTER 1

1.0 Introduction

At Point Pelee National Park (PPNP), DDT was applied as a particulate spray for pest control in apple orchards and vegetable fields between 1948 and 1967. Supervised by Park personnel (Battin and Nelson, 1978), the picnic areas and campgrounds were also treated with DDT for mosquito control. It was manually shoveled out of dump trucks, carried by winds prevailing from the southwest, and deposited on plants and the ground surface. In addition, DDT wrapped in cheesecloth was applied as "toss bombs" at specific sites. It was used at PPNP due to its permanent-kill characteristics, relatively low cost and ease of use. Its application at PPNP ended in 1967.

By the mid-1990's, it was expected that DDT and its metabolites would no longer exist at PPNP. Studies on DDT in soil and groundwater were undertaken in 1994, 1996,

1998, 1999, and 2001 by various groups and continue to this day. Wildlife surveys undertaken by researchers from the University of Windsor (Russell et al., 1995; Russell and Haffner, 1997) detected DDT and its metabolites, DDE and DDD, in reptiles and amphibians. During 1998 they determined that the source of the contamination was the soil. Soil surveys later revealed high levels of DDT in several areas at the Park in concentrations that often exceeded the Ontario Ministry of Environment (OMOEE) limits for DDT for Recreational/Parkland land-use of 1.6 μg/g (OMOEE, 1997). This raised concerns about health risks to Park employees, visitors and wildlife. As a result, large sections of the park and some facilities were closed to the public pending remediation.

Also in 1998, Parks Canada requested the assistance of the National Water Research Institute (NWRI; Burlington, Ontario, Canada) of Environment Canada to further assess the extent of DDT, DDE and DDD contamination in the soil and groundwater in two specific areas of the Park. This study by Crowe (1999) confirmed, in part, that:

(a) DDT is present in the shallow soil and at concentrations that often exceed MOE limits for DDT in soil for Recreational/Parkland land-use of 1.6 μg/g;

(b) DDT concentrations are primarily confined to the upper 0 to 20 cm of the soil horizon, with concentrations decreasing with depth;

(c) DDT is essentially absent from the Park's drinking water;

(d) localized high soil concentrations are likely due to accidental spills or improper disposal; and

(e) DDT is not significantly mobile in the soil profile, thus retained essentially at the surface.

Crowe (1999) also suggested that soil conditions could influence DDT degradation rates. The half-life of DDT was estimated to range from a low of less than 10 years in the high organic matter marshy sediments to a high of greater than 40 years in the sandy soil, because these two areas exhibited different proportions of %DDT, %DDE and %DDD (Crowe, 1999).

This study hypothesizes that:

1. DDT, DDE and DDD concentrations used in conjunction with soil environment characterization data can be used to indicate not only where DDT is continuing to persist in soil at PPNP, but also what soil environmental factors are controlling its degradation.
2. The persistence of DDT, DDE and DDD in soil at PPNP varies significantly with location.
3. Soils at PPNP that are wetter and have historically been intermittently flooded will have significantly higher DDT degradation rates.
4. The depths to the water table and ground surface elevations are directly related to DDT degradation rates and pathways.

The specific objectives of this thesis are:

1. To physically and chemically characterize different soil environments at PPNP both spatially and with depth by examining:

a. DDT, DDE and DDD concentrations
b. soil types and structures
c. soil organic (%OC, %OM and %ON) and mineral matter contents
d. grain size distributions
e. bulk densities
f. porosities
g. soil moisture contents
h. hydraulic conductivities
i. soil water retention
j. historical and current Lake Erie, marsh and groundwater levels
k. topography and ground surface elevations

2. To determine if there exist statistically significant differences in these physical and chemical characteristics in the different soil environments both spatially and with depth at PPNP.
3. To assess whether these different soil environments affect DDT degradation rates and pathways.
4. To determine which soil environment degrades DDT at a faster rate and which promotes DDT persistence.
5. To determine relative DDT half-lives in these different soil environments.
6. To provide information to support future soil flushing remediation strategies.

1.1 Setting

Point Pelee, Ontario (41°54' North Latitude and 82°22' West Longitude; Figure 1) in the Essex County township of Mersea is the southernmost point of mainland Canada. Bounded by Lake Erie on the east, south and west and by farmland formed on a reclaimed portion of the marsh to the north, it extends southward 15.5 km from the northwestern shoreline of Lake Erie. Point Pelee is essentially a 50 km^2 cuspate foreland in which two barrier bars, or beach-dune complexes enclose a large marsh. Historically the marsh was much larger but the northern portion was drained for agricultural land. Only 11 km^2 of marsh remains and it is entirely within PPNP. PPNP occupies the southernmost 9 km of the cuspate. The marsh occupies about 66% of the total Park area (Battin and Nelson, 1978).

The current PPNP landscape is a product of various biophysical and cultural processes. Wave erosion and deposition have been and are of fundamental importance in its formation (Battin and Nelson, 1978). With erosion concentrated in high and deposition in low water periods, the shape of the southernmost 300 m of the peninsula is continually changing.

Unpublished reports by Terasmae (1970) and Vandall (1965) have suggested mechanisms for the formation of Point Pelee. Initially it was thought that Point Pelee was formed by the convergence of coastal drift from opposite directions, in the same manner as marine spits (Kindle, 1933). However, Coakley et al. (1998) and Battin and

Figure 1. Location of Point Pelee and Point Pelee National Park, Ontario, Canada. Point Pelee National Park (PPNP) occupies the southernmost 9 km of the point.

Nelson (1978) present a different evolutionary model. They state that the early history of the peninsula was associated with the advance and retreat of Late Wisconsin continental glaciers.

Point Pelee is a relict feature associated with the coastal processes and paleogeography of the western and central basins of Lake Erie more than 3500 years ago (Coakley et al., 1998). It owes its formation to the rise of lake levels in these basins, which caused the landward migration and eventual convergence of fringing beach sand dune complexes built up over the Pelee-Lorain moraine (Coakley et al., 1998). The Point Pelee foreland has undergone a progressive erosion in size up to two-thirds its original area and has been retrograding at decreasing rates since its formation (Coakley et al., 1998).

1.2 PPNP Soils

Relatively little research has been done on PPNP soils, so the soil profile data available is very limited. The last soil survey was performed at PPNP in 1938 (a copy of the soil survey report was last reprinted in 1989). In general, those on the western and eastern bars have been classified as Easport sands belonging to the Regosolic Soil Order (Canadian System of Soil Classification) and those in the center of the western bar have been classified as Marsh soil belonging to the Organic Soil Order (Canadian System of Soil Classification; Figure 2) (Richards et al., 1989).

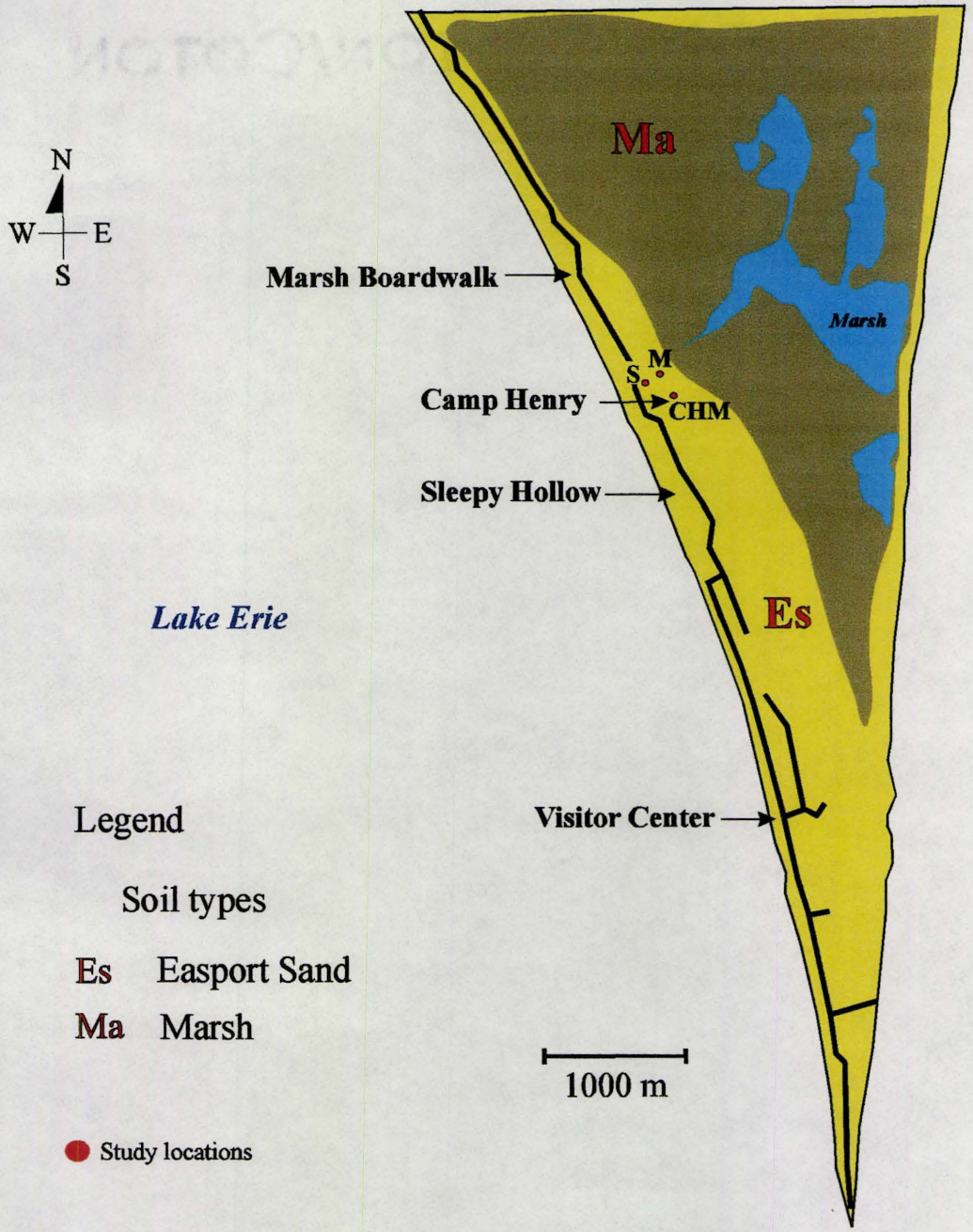


Figure 2. Soil types at PPNP according to the 1938 Soil Survey of Essex County map (report No. 11 of the Ontario soil survey, Richards et al., 1989).

Easport sands form on the flanks and hollows of dunes where leaves and other forest litter accumulate (Battin and Nelson, 1978). Because it is a droughty soil, the fertility levels are low enough that sufficient vegetative cover to prevent wind erosion is not produced (Richards et al., 1989). On the other hand the Marsh soil is an organic soil under water for all or part of the growing season. Both soils are very young in nature, 3500 years old or less. Thus, they exhibit little horizon differentiation.

According to Battin and Nelson (1978), the generalized Easport profile is: (a) an approximately one-half inch organic A layer; (b) a thin gray A horizon about 2 inches thick; (c) a yellow sandy B horizon, less then one inch thick; and (d) gray sand (the parent material C-horizon), however the exact location of this soil survey is unknown. Some evidence of thin buried soil profiles has been found. Both the Easport and the Marsh soils are stone free and the former is occasionally calcium-rich (Richards et al., 1989). This profile is different than what was seen in the field during this study, as will be explained in Section 4.2.

1.3 Climate and Vegetation

PPNP possesses a temperate climate, the warmest in Ontario and one of the warmest in Canada. The mean annual temperature is approximately 9°C, with January and July means being -3 and 23°C, respectively. The frost-free period is between 165 and 175 days, with a growing season commencing in early April, nearly a week earlier

than in any other area in the Province and averaging 218 days (Battin and Nelson, 1978; Canadian Climate Normals, 2002/03/13, Environment Canada).

The mean annual precipitation is approximately 890.8 mm with, January and July means being 47.2 mm and 78.9 mm, respectively (based on Environment Canada's Point Pelee Island station data from 1888 to 1987). This is within the range of the mean annual precipitation in southern Ontario, which ranges from 800 to 1000 mm (Canadian Climate Normals, 2002/03/13, Environment Canada). Another influential climatic element is wind, which prevails from the southwest at 11-16 km/hour across a 64 km stretch of open water (Lake Erie) and results in coastal erosion and the deposition of aeolian sands to form sand dunes.

PPNP, a blend of marsh, forest, field and beach, is a Ramsar site (wetland of international significance). The forest areas are typical of the Carolinean zone (National Library of Canada Electronic Collection, 2000/10/30, National Library of Canada). The grasslands are the habitat of mixed grasses and herbs. Mixed woods, such as maples and pines, are found at the north end and bounded by swampy terrain with cattails stretching across the marshland. Hardy plants survive on the beaches. Further up the beach, a variety of grasses help with soil stability.

1.4 History of PPNP Land-use

The Park was established May 29, 1918 as the first national park in Canada designated because of its unique fauna and flora. At that time several commercial, agricultural and recreational activities not conducive to a wildlife refuge (e.g., fishing, hunting, clearing, under-brushing, reforestation, beach protection and other activities) continued to exist within PPNP until the 1970's (Battin and Nelson, 1978).

A 12.1 hectares orchard began producing in the central part of the western bar in 1912. Small garden plots, some as large as 0.2 hectares, produced beans, peppers, tomatoes, watermelons, strawberries, while acreage not used for crop cultivation served as wood lots or grazing land (Battin and Nelson, 1978). By 1918, some interior sand dunes were flattened for the cultivation of asparagus, peaches and tobacco (Battin and Nelson, 1978). In 1923, apple orchards located on the western bar were abandoned to make way for summer homes and cottages. In 1954, some of the remaining apple trees were cut down and reforestation carried out in the following years (Government of Canada, 1938). By 1955, the demand for apples, peaches and asparagus had increased again to warrant the expansion of these orchards. Between 1955 and 1963 a total of 20.2 hectares were added to the existing 30.4 hectares of apple and peach orchards (Battin and Nelson, 1978).

During the 1960's and 1970's, property purchases by Parks Canada eliminated agricultural land-use from PPNP. Originally designated for campgrounds, the apple and

peach orchards were cut down and trees burned and bulldozed. At this point, no reforestation plantings were undertaken and there were no plans for any future developments (Battin and Nelson, 1978). However, after the late 1970's, some locations, mainly orchards, were reforested. Most of the trees used for replantation were black locust, an exotic species nonnative to the area and thus, all of the trees were cut down in the mid-1990's. Many other smaller areas, such as roads and cottage sites, were also replanted on a lesser scale (Smith, pers. comm., 2001).

Recreation was another important activity at PPNP. As early as the 1920's and 1930's, the Park was experiencing high visitor attendance and cottage development. In 1923, portions of private land were developed into "Lake Erie's finest summer home sites" (Point Pelee Park Company Limited, 1923; Anders, 1974). In the late 1930's, several existing camping areas were closed and fenced off to permit regeneration of trees, shrub and plant growth (Battin and Nelson, 1978). Houses and summer cottages remained in the Park until the mid-1970's and to this day a few private residences still exit. In 1972, family camping was eliminated, although two group campsites capable of holding 90 people still remained in operation. Only one restricted-use campground remained into the 1990's and still exists today.

1.5 History of DDT

There are several isomers of DDT, of which p,p'-DDT and o,p'-DDT are the most common. However, when referring to DDT, we are referring to the technical grade DDT produced and used for its insecticidal properties. Technical grade DDT was composed of approximately 14 chemicals, of which both DDD and DDE existed as by-products (Quensen et al., 1998; Sayles et al., 1997). The largest portion, approximately 65% to 80%, was the ingredient p,p'-DDT. The other components included 15-21% of o,p'-DDT, up to 4% p,p'-DDE, up to 0.1% o,p'-DDE, up to 0.3% p,p'-DDD, up to 0.1% o,p'-DDD, as well as other compounds (EHC 83, 1989; Table 1).

Table 1. Components of technical grade DDT (EHC 83, 1989).

Isomer	% Range	Isomer	% Range
p,p'-DDT	65-80	o,p'-DDT	15-21
p,p'-DDE	4	o,p'-DDE	0.1
p,p'-DDD	0.3	o,p'-DDD	0.1
m,p'-DDT	1	Other	1.5-3.5

A typical example of technical grade DDT has the following constituents: 77.1% p,p'-DDT, 14.9% o,p'-DDT, 0.3% p,p'-DDD, 0.1% o,p'-DDD, 0.1% p,p'-DDE, 4% o,p'-DDE, and 3.5% unidentified compounds (EHC 83, 1989). Collectively, the total of p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD is designated as DDX.

DDT is an anthropogenic, hydrophobic, toxic and persistent organochlorine (contains carbon, hydrogen and chlorine) that was one of the first synthetic pesticides to

gain wide acceptance (Quensen et al., 1998). It kills both target and non-target species in the immediate area of application by acting as a nerve poison (Bevenue, 1976). Its synthesis was reported in Germany as early as 1874. Prepared by a graduate student named Othmer Zeidler as part of his doctoral research at a German university (Friedman, 1992), Paul Hermann Müller, a Swiss citizen working for the Geigy Company (now Novartis) of Switzerland "rediscovered" it in 1938-1939 while screening hundreds of compounds for their insecticidal properties. He was searching for an insecticide against the clothes moth. This subsequently brought him the Nobel Prize for Physiology and Medicine in 1948 for his lifesaving discovery. Busvine (1989) has reviewed the factors contributing to the subsequent rise and decline in the use and popularity of DDT.

Before DDT there was no commercially available chemical compound that had its insecticidal properties and effectiveness. Furthermore, no pesticide had been given such thorough testing, and such widespread publicity (Corona-Cruz et al., 1999). DDT quickly proved to be cost-effective, a solution to the emerging problem of controlling insects and pests, and was ranked with penicillin as one of the great wonder drugs of modern chemistry.

During World War II, it was used by the military to control insect typhus spread by the body louse and mosquito borne malaria (Coulston, 1989). It was unavailable for civilian uses until Frank Mayo, an American entrepreneur, found the formula and recipe and began to manufacture it (Friedman, 1992). DDT was then used extensively after the war as an agricultural insecticide (Coulston, 1989). Its environmental persistence

provided effective, long-term control of insects and pests without reapplication, and allowed food to be grown safely and cheaply. Unfortunately, because of many of these properties, DDT was overused and abused before panic set in.

With the emergence of Rachel Carson's best selling novel Silent Spring in 1962, it became apparent that DDT was not only persisting, but bioaccumulating in the environment and biomagnifying in organisms including man threatening human and environmental health (Boul, 1994; You et al., 1996). "Bioaccumulation" refers to an increase in the concentration of DDT in the environment. "Biomagnification" refers to an increase in DDT as it is passed up the food chain. DDT and its metabolites are bioaccumulated by people through consumption of agricultural products grown on contaminated soils (Bates et al., 1994).

DDT is commonly found in soils that were once treated with it (EPA, 1986). Although these concentrations are generally low, uncertainty about the human and environmental health effects of DDT and its metabolites means that their reduction in the environment has become an important goal (Hileman 1993; Curtis, 1994). Pereira et al. (1996) observed that the adverse effects of DDT and its metabolites manifested themselves several decades after their introduction into the environment. Recently, DDT has been associated with several health problems, including the increased risk of breast cancer in women, alterations in reproductive functions in men (Cebrián, 1998) and endocrine disruption. Endocrine disrupters are chemicals that interfere with the endocrine system (consisting of glands and the hormones they produce that guide

development, growth, behaviour and reproduction) functions found in nearly all animals including man (Endocrine Disrupter Screening Program, March 27, 2001, US EPA).

Sales of DDT in Ontario reached a peak in 1969 (Figure 3) (Harris and Miles, 1975). In Ontario and Canada, DDT use was severely restricted in circa 1969 when Pollution Probe, a Canadian organization of students from the University of Toronto convinced the federal government to act. A ban (suspension of registration of all uses of DDT) ensued in Canada in 1985 with the understanding that existing stocks would be sold, used or disposed-of by the next registration date of December 31, 1990 (Environment Canada, 1997).

Today in Canada, DDT is regulated under the Pest Control Products Act and thus, the sale or use of DDT represents a violation of the Act (PMRA, 1996). Under the Canadian Environmental Protection Act (CEPA), DDT is included in the list of toxic substances requiring export notification (CEPA, Schedule II, Part II) and is under the grouping of "organohalogen compounds," a prohibited substance for ocean dumping (CEPA, Schedule III, Part I).

Today, under the Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem, DDT is included on the Tier I Substances List. DDT is also a target for elimination, as part of the proposed "Canada-United States Strategy for the virtual elimination of persistent toxic substances in the Great Lakes Basin" (Environment Canada, 1997).

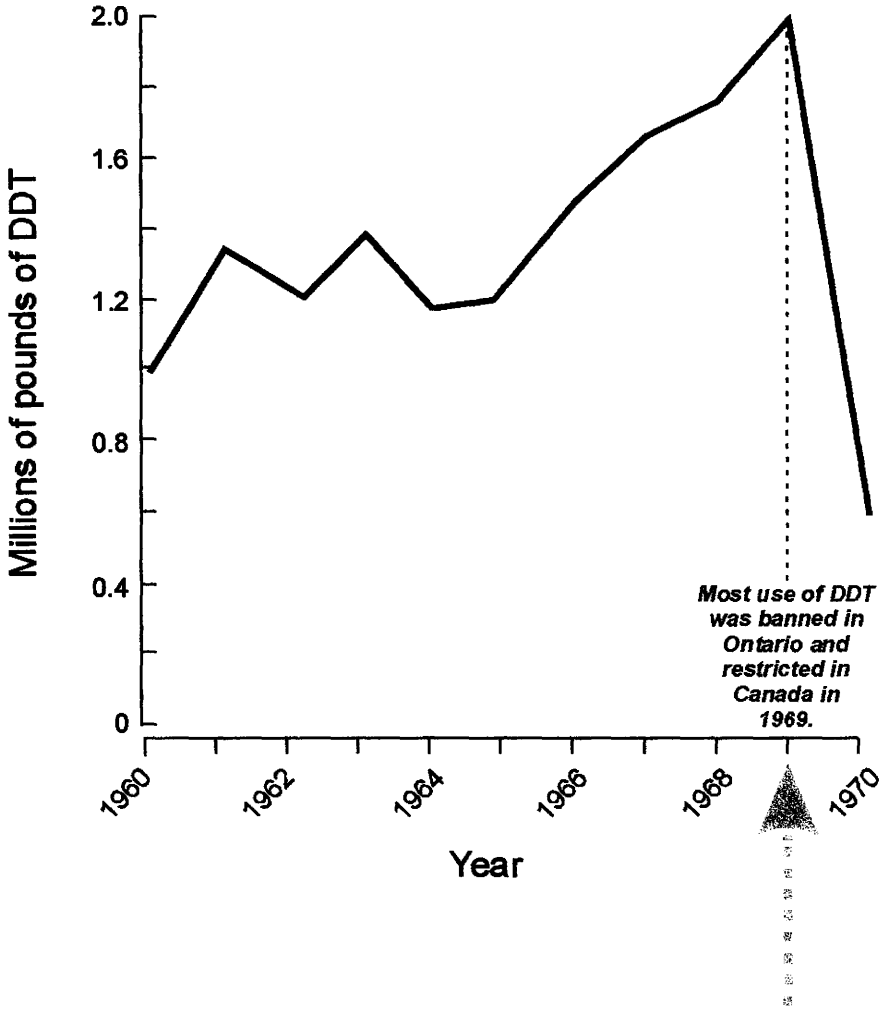


Figure 3. Agricultural sales of DDT (in millions of pounds) in Canada from 1960 to 1970. Most use of DDT was banned in Ontario and restricted in Canada in 1969 (modified from Harris and Miles, 1975).

DDT's persistence in the environment and the food chain is well known. However because of its low cost and effectiveness, it is still being globally distributed and used in developing countries for the control of malaria and dengue fever (Wayland et al., 1991; Cebrián, 1998; Hogue, 2000; Matthiessen, 1985; Woodwell et al., 1971; Ostromogil'skii et al., 1987). Global production for 1995 was estimated to be as high as 50 kilotonnes, with Italy, India, Indonesia listed by the UN Environment Program (UNEP) as basic producers (IPCS, 1995). In 1999, delegates from 110 countries met in Geneva and agreed that agricultural uses of DDT should be stopped and that the use of DDT for malaria control should be phased out in the near future. The World Wildlife Fund (WWF) suggested a phase-out date of DDT by 2007 as a motivational tool to accelerate the development and funding of alternatives (Hileman, 1999).

1.6 DDT in Soil

Soil is not an inert material and its interactions with DDT are complex. Its chemical, physical and biological properties (e.g., soil structure and texture, redox potential, pH, moisture content, organic matter content, mineral content, drainage, crop cover, microbial conditions, soil temperature) affect DDT's breakdown (Jury et al., 1984; Boul, 1994). In turn, the soil's chemical and physical properties are modified by the microorganisms in the soil. The top 10 cm of a soil contains a large number of organisms and microorganisms, the majority of which are beneficial in that they contribute to the

soil's structure, formation and fertility (Harris and Miles, 1975). Microbial degradation plays a major role in the fate of DDT accounting for most losses of DDT from soil (Edwards, 1966; Parr et al., 1970).

DDT can also be degraded in soil through chemical abiotic degradation, but according to Boul (1994) the conditions required for this degradation are such that they are not expected to occur frequently. For microbial degradation to occur however, the presence and number of microbes with the ability to degrade DDT and the environmental conditions that limit their growth, activity and access to the DDT are important conditions to consider (Aislabie et al., 1997). Microorganisms in both aerobic and anaerobic environments can transform DDT.

When soil environments and microbial conditions are such to promote DDT degradation, its predominant metabolites are DDE and DDD (Figure 4). Because all three compounds are man-made chlorinated chemical structures that do not closely resemble naturally occurring compounds, microbial systems cannot use them as substrates for degradation (Boul, 1994). Their microbial degradation is thus generally slow, resulting in their environmental persistence (Boul, 1994; Corona-Cruz et al., 1999; Johnsen, 1976; Garrison et al., 2000). Hence, DDX residues are found in various proportions in soils around the world. The chemical formulas of DDT, DDE and DDD are presented in Table 2.

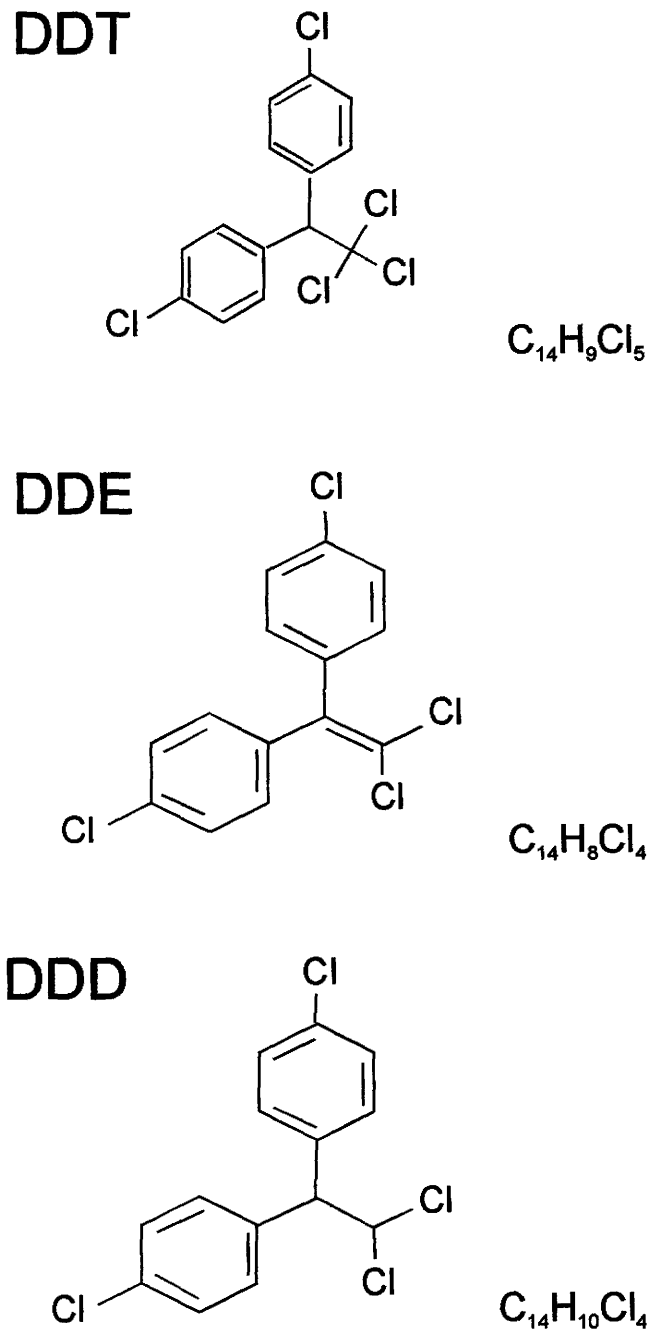


Figure 4. Molecular structure and chemical formula of DDT, DDE and DDD.

Table 2. Chemistry of DDT, DDE and DDD.

Abbreviation	Name	Formula
DDT	Dichloro-Diphenyl-Trichloro-Ethane	$C_{14}H_9Cl_5$ *Or* 1,1,1–trichloro-2,2-bis[p-chlorophenyl]-ethane
DDE	Dichloro-Diphenyl-Dichloro-Ethylene	$C_{14}H_8Cl_4$ *Or* 1,1'-[2,2-dichloroethenylidene]-bis[4-chlorobenzene]
DDD	Dichloro-Diphenyl-Dichloro-Ethane	$C_{14}H_{10}Cl_4$ *Or* 1,1'-[2,2-dichloroethylidene]-bis[4-chlorobenzene]

DDT and its metabolites may also be lost from soil by several other routes including: (a) volatilization; (b) leaching, run-off and erosion; and (c) uptake by plants and animals (Aislabie et al., 1997). These mechanisms are dependent on the physical properties of DDT and its metabolites, as well as the climate, geography and topography. Table 3 provides physical properties of DDT, DDE and DDD.

Table 3. Physical properties of DDT, DDE and DDD.

Property	DDT	DDE	DDD
Molecular mass (grams)	354.49[b]	318.03[b]	320.05[b]
Color	Colorless crystals, White powder[c]; White crystalline Powder[c]	White; no data	Colorless crystals, white powder; no data
Physical state	Solid[d]	Crystalline solid; no data	Solid
Melting point (°C)	109[b]; 74.2[e]	89[b]; no data	109-110[b]; 76-78
Boiling point (°C)	Decomposes; No data	336[b]; no data	350[b]; no data
Density (g/cm^3)	0.98-0.99	no data	1.385; no data
Odor	Odorless or weak Aromatic odor[e]	no data	Odorless; no data
Solubility:			
Water (mg/L)	0.025 at 25°C[b]; 0.085 at 25°C[b]	0.12 at 25°C[b]; 0.14 at 25°C[b]	0.090 at 25°C[b]; 0.1 at 25°C[b]
Organics	Slightly soluble in Ethanol, very soluble in ethyl ether and acetone[f]; no data[g]	Lipids and most Organic solvents; no data[g]	no data[g]; soluble in ethanol, isooctane, carbon tetrachloride[j]
Partition coefficients:			
Log K_{ow}	6.91[b]; 6.79[h]	6.51[b]; 6.00[b]	6.02[b]; 5.87[b]
Log K_{oc}	5.18[h]; 5.35[j]	4.7[i]; 5.19[i]	5.18[j]; 5.19[i]
Vapor pressure (torr)	1.60×10^{-7} at 20°C[b]; 1.1×10^{-7} at 20°C[b]	6.0×10^{-6} at 25°C[b]; 6.2×10^{-6} at 25°C[b]	1.35×10^{-6} at 25°C[b]; 1.94×10^{-6} at 30°C[b]
Henry's law constant ($atm\text{-}m^3/mol$)	8.3×10^{-6}[b]; 5.9×10^{-7}[b]	2.1×10^{-5}[b]; 1.8×10^{-5}[b]	4.0×10^{-6}[b]; 8.17×10^{-6}[b]

[a]All information obtained from HSDB 1999a, 1999b, 1999c, 1999d unless otherwise stated; [b]Howard and Meylan, 1997; [c]Verschueren, 1988; [d]NIOSH, 1985; [e]Sax, 1979; [f]Lide, 1998; [g]Chemical is expected to be soluble in most organic compounds; [h]Swann et al., 1981; [i]Sablejic, 1984; [j]Meylan et al., 1992 (values estimated).

Of particular interest: (a) DDT, DDE and DDD are practically insoluble in water; (b) their low vapour pressures (low volatility) indicate they are very stable when in contact with air; (c) their high organic carbon (K_{oc}) partitioning coefficients indicate that they are preferentially and strongly adsorbed onto soil organic matter; and (d) their high octanol-water partitioning coefficients (K_{ow}) indicate that the compounds are hydrophobic and thus have a strong preference to be dissolved in organic compounds instead of water. These properties mean that DDT, DDE and DDD are likely to be found in the top few centimeters of the soil profile and at much lower concentrations with depth.

1.7 Primary DDT Metabolites

The various degradation pathways and thus, the amounts of DDE and DDD produced from DDT degradation will depend on a number of factors, of which soil and associated microbial conditions are key. The degradation of DDT is more commonly observed under anaerobic conditions (Essac and Matsumura, 1980; Johnsen, 1976; Lal and Saxena, 1982; Rochkind and Blackburn, 1986).

According to Corona-Cruz et al. (1999), the pathway can be DDT → DDE → DDD, or from DDT to DDD directly. Quensen et al. (1998) and Heberer and Dünnbier (1999) suggested that the pathway could be DDT→ DDE and DDD (Figure 5). This is similar to the microbial pathway proposed by Wedemeyer (1968), Guenzi and Beard (1968), Menzie (1969), Langlois et al. (1973), Lal and Saxena (1982) and Rochkind and

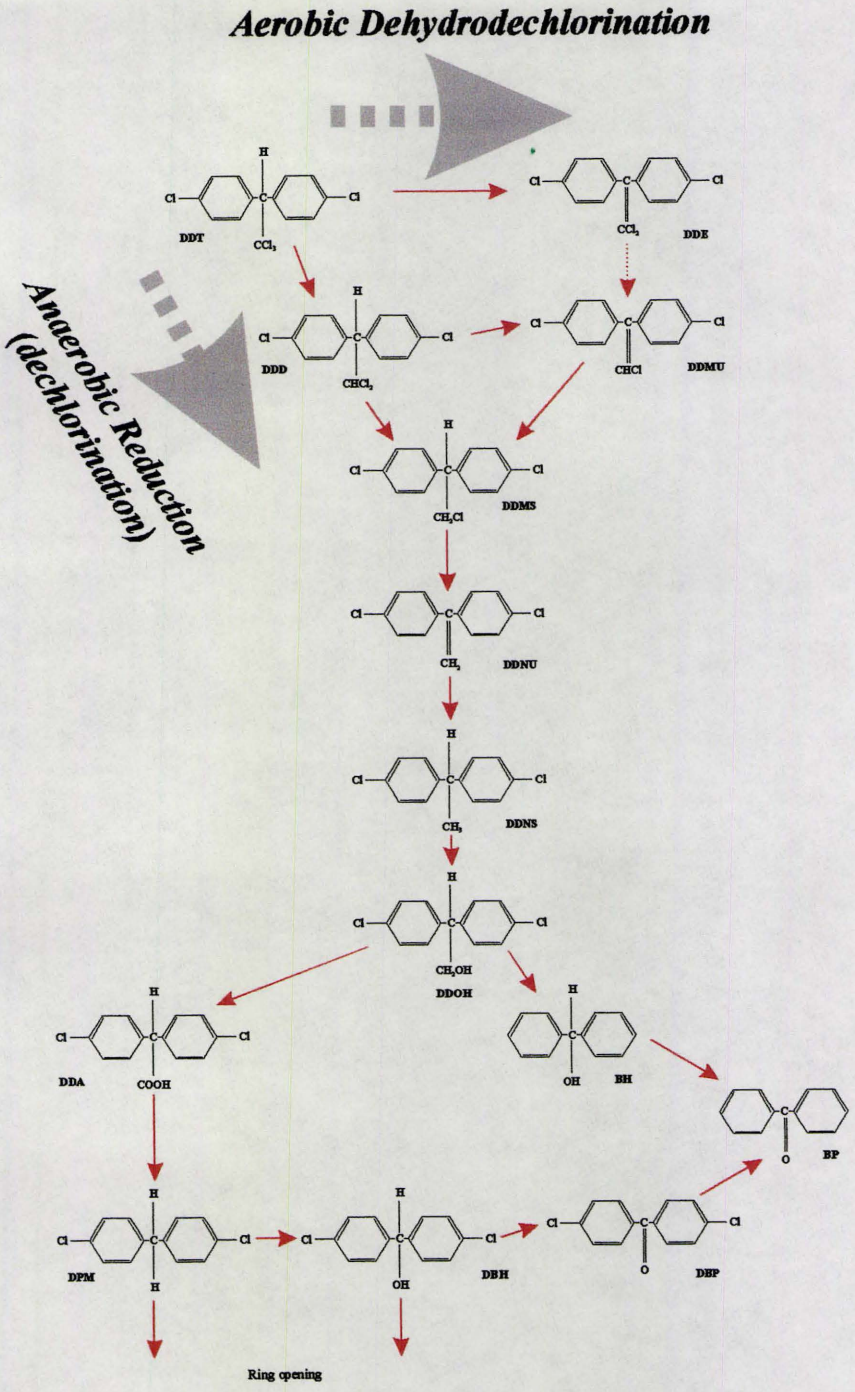


Figure 5. Aerobic and anaerobic degradation of DDT (modified from Quensen et al., 1998).

Blackburn (1986) which was: DDT → DDE → others, under aerobic (oxidative) conditions; and DDT → DDD → others, under anaerobic (reductive) conditions. According to Pfaender and Alexander (1972), the suggested pathway for the anaerobic degradation of DDT by bacteria is shown in Figure 6. Clearly, there is more than one DDT degradation pathway outlined in the literature. The degradation pathway focus of this study is DDT → primarily DDE under aerobic conditions and DDT → primarily DDD under anaerobic conditions, as shown in Figure 7.

As observed by Parr et al. (1970), Leahy and Brown (1994), Garrison et al. (2000), Wedemeyer (1968), Guenzi and Beard (1968), as well as Heberer and Dünnbier (1999), DDD is the main dechlorination product of DDT in anaerobic reducing conditions. Furthermore, according to Boul et al. (1994) and Farmer et al. (1974), anaerobic reducing conditions do not favour the formation of DDE. Stenersen (1965) described the anaerobic conditions required for the conversion of DDT to DDD. Its dechlorination, which can be microbially mediated (Wedemeyer, 1968) or the result of chemical reactions (Castro, 1964; Miskus et al., 1965; Glass, 1972; Zoro et al., 1974; Baxter, 1990), involves the loss of a chlorine atom. According to Renner (1998) and Parr et al. (1970), anaerobic dechlorination reduces toxicity, so the reaction of DDT to DDD is a detoxification step. Nonetheless, because DDD has properties similar to DDT, its accumulation in the soil is not desirable.

DDD is seldom reported to accumulate in aerobic soils, however DDE does. Boul et al. (1994), Farmer et al. (1974), Spencer et al. (1996), and Guenzi and Beard (1968)

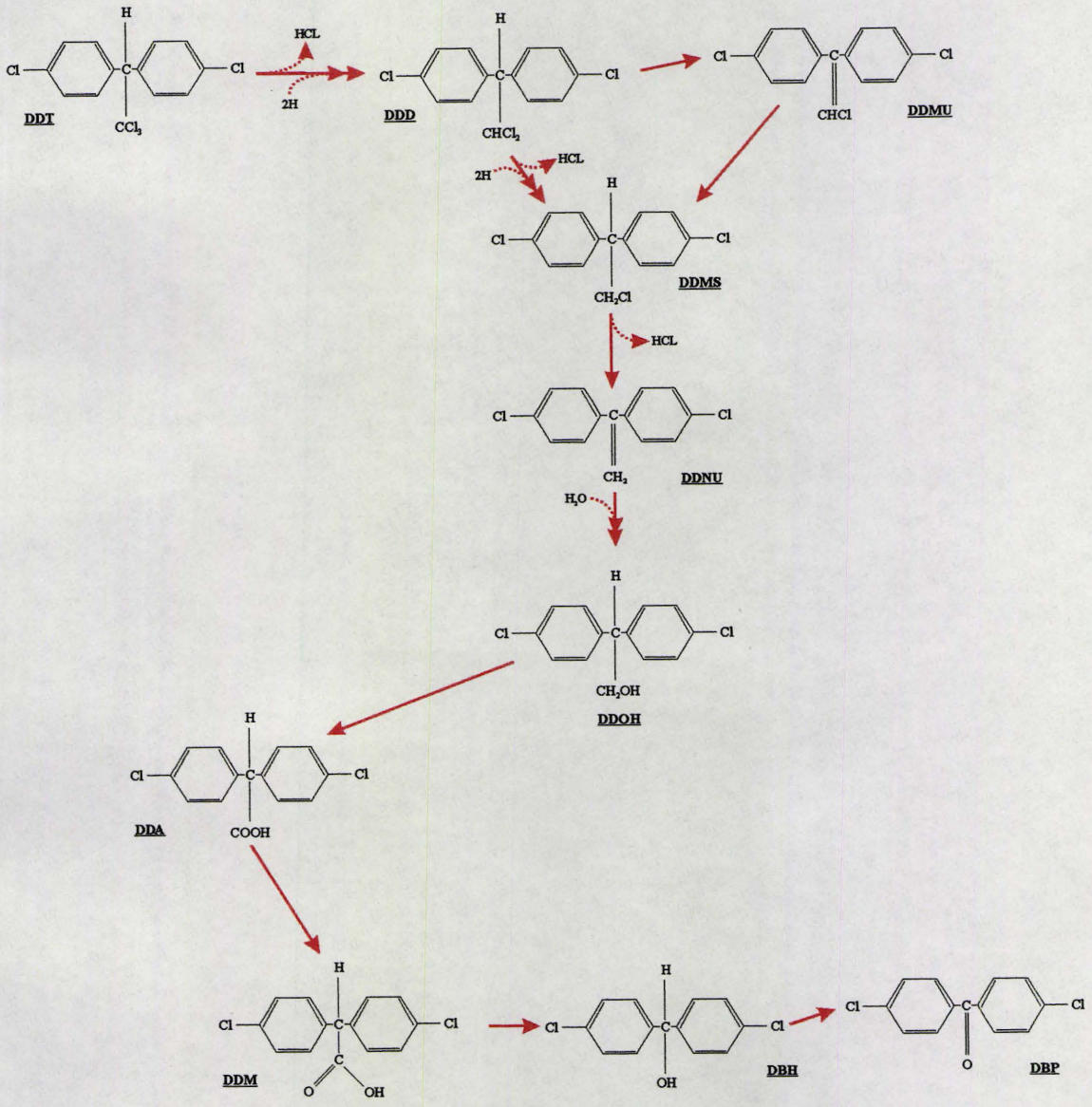


Figure 6. Anaerobic degradation of DDT by bacteria (modified from Pfaender and Alexander, 1972).

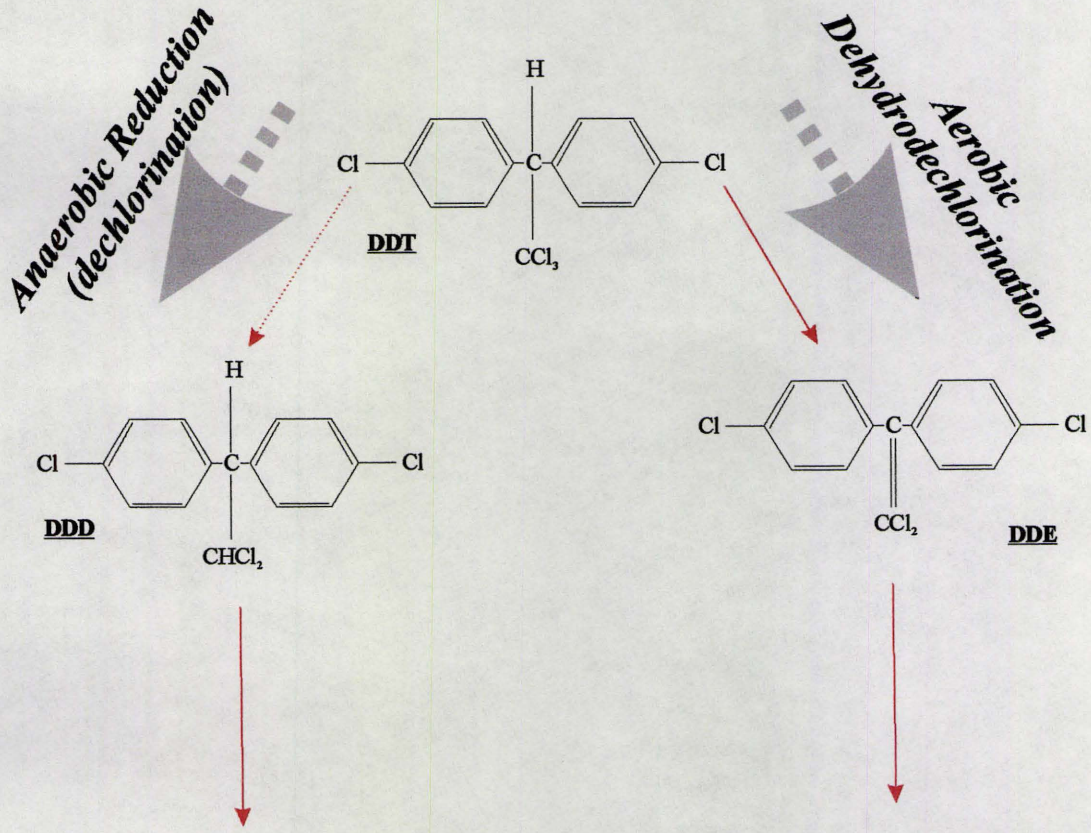


Figure 7. Degradation of DDT and focus of study.

observed that DDE was the main dehydrochlorination product of DDT in aerobic soils. DDT loses hydrogen chloride to form DDE through chemical reactions (Maugh, 1973) in basic or alkaline soil conditions (Lichtenstein et al., 1971; Parr et al., 1970; Nash et al., 1973) and through dehydrochlorination in bacteria and animals (Pfaender and Alexander, 1972; Guenzi and Beard, 1976). Like DDD, DDE is also less toxic than DDT (Sax, 1984). Nonetheless, like DDD, DDE has properties similar to DDT and hence DDE accumulation is not desirable.

DDE has been reported to bind more strongly to the organic matter in soils, in some cases apparently irreversibly (Hussain et al., 1994a; Zayed et al., 1994a and 1994b). Thus DDE is more persistent than both DDT and DDD and will not be readily lost by leaching, runoff and/or erosion. However, because the vapour pressure of DDE is several times greater than that of DDT, it is more readily lost by volatilization than DDT or DDD in aerobic soils (Spencer, 1975; Kawamoto and Urano, 1990).

1.8 DDT and Land-use at PPNP

Crowe et al. (2002) compiled DDT data from all the previous DDT studies at PPNP. This government report shows that because of the different soil and hydrological conditions, as well as former land-use areas within the Park, different concentrations of DDT, DDE, DDD and DDX, and thus different ratios of DDT to DDE, and DDT to DDD

are currently present in PPNP soils. According to Crowe et al. (2002), 7 distinct zones are defined:

1. *Former orchards* — including former agricultural areas such as vegetable fields, generally east of the road, generally higher ground surface elevation than the marshy areas and therefore typically not subject to flooding;
2. *Natural areas* — areas where there were never houses, agriculture, orchards; excluding marsh; generally the dune area west of the road;
3. *Marshy soil* — low-lying areas adjacent to the marsh which area intermittently saturated only flooded when the water level in the marsh is high; does not include former orchards;
4. *Former residential areas* — houses, cottages, trailer parks, picnic areas, etc.;
5. *Camp Henry* — area around the former buildings and the open fields;
6. *Maintenance Compound* — area within the perimeter of the Maintenance Compound (parking lots, storage areas, road, lawns, etc.);
7. *Marsh sediments* — within the marsh, always saturated

As stated in Crowe et al. (2002), Camp Henry and the Maintenance Compound are not land-use zones per-sae, but are designated as such because they have recently experienced intensive human activity and are of special concern to PPNP. The natural areas are also included because they may provide background concentrations of DDT, DDE, DDD and DDX to which other land-use zones may be compared.

Crowe et al. (2002) state that larger volumes of DDT were applied within the orchards than elsewhere in the Park. Their results show that soil samples from the former orchards have consistently higher DDX concentrations than the other land-use areas, ranging from 10^3 to 10^5 ng/g. In addition, soil samples from the natural areas and former residential areas show DDX concentrations that are consistently lower, ranging from 10^1 to 10^4 ng/g. Although DDT was not used extensively for pest control in the residential areas, some amount could have been transported there from the adjacent orchards by winds, and there is the possibility that some DDT may have been applied for mosquito suppression.

The study by Crowe et al. (2002) also shows that concentrations of DDX are consistently low in the marsh sediments. This may be because less DDT was applied in the marsh, and/or because anaerobic conditions increased the rate of degradation. Their study also shows that soil samples from the marshy soil, Camp Henry and the Maintenance Compound show considerable variability because of the inconsistent pattern of DDT application and the importance of fill to the Maintenance Compound. Furthermore, on the basis of the relative amounts of the compounds DDT, DDE and DDD in the soil, according to Crowe et al. (2002), the marsh sediments and marshy soil samples consistently exhibit the lowest proportion of DDT and the highest proportion of DDE and DDD.

CHAPTER 2

2.0 Study Sites

The three study sites within PPNP were selected in consultation with research scientists from NWRI and the Park Warden based on topography, hydrology and differing soil conditions. In addition, these sites were chosen because it was known that they contained high levels of DDX. Financial constraints impacted the study as well. Because the chemical analyses for DDT, DDE and DDD is so costly, the number of samples and therefore, the number of sites chosen for the study were limited to these three only. All three study sites are within a 93 m radius (Figure 8). A square-gridded area of 20 m x 20 m (400 m^2) was superimposed on each site to facilitate random sampling:

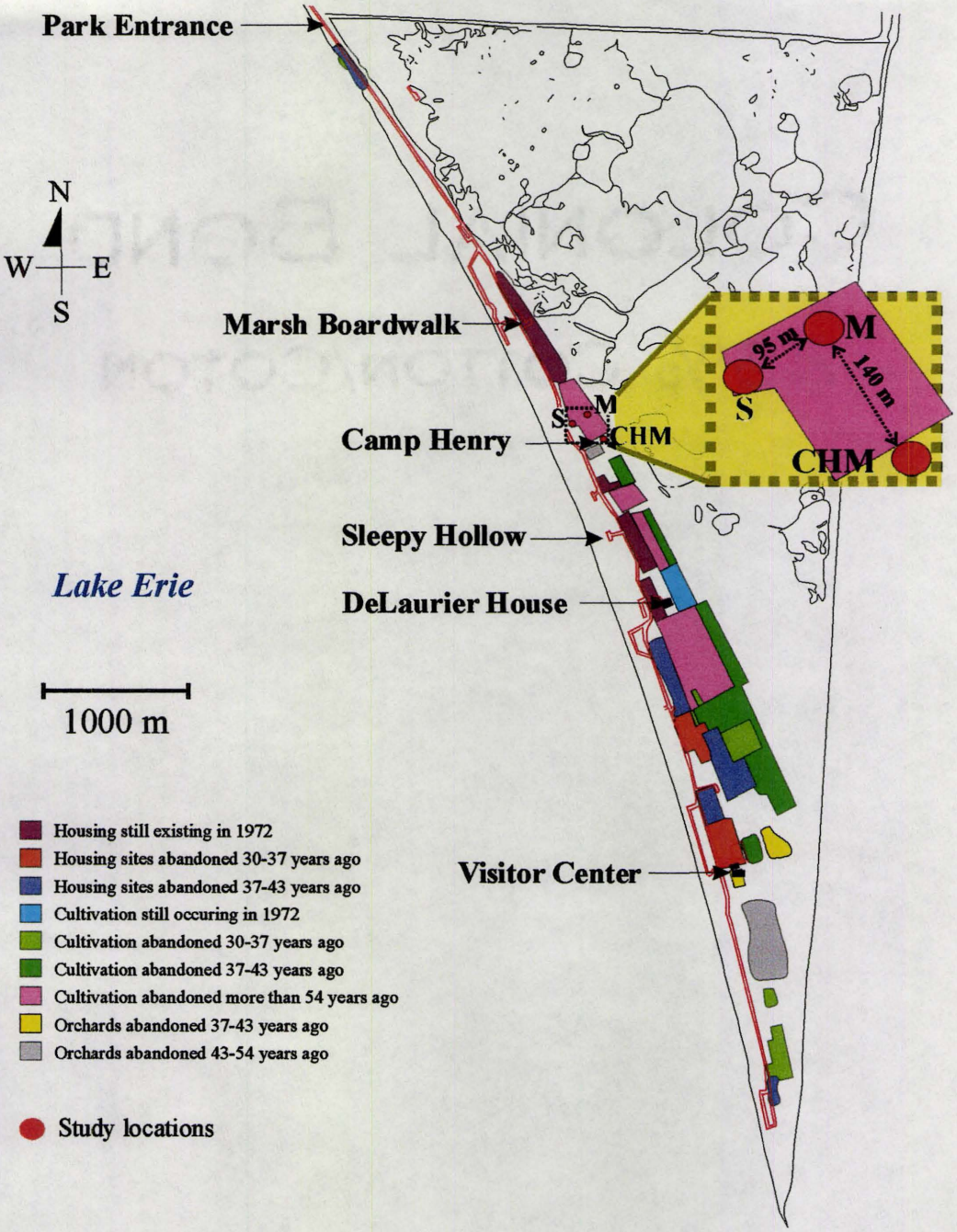


Figure 8. Land-use map of PPNP with location of study sites S, M and CHM (modified after Point Pelee map 4.9.2.3; Bayly and O'Neil, 1972; legend dates referenced from 2002).

1. *S* located in the relatively higher-lying (>175.1 m amsl) agricultural sandy soil of a former orchard area east of the main Park road and in a hollow; highest in ground surface elevation at ~176.6 masl. Cultivation here was abandoned more than 54 years ago (circa 1948). It is unclear what land-use activities existed here post-1948. Today, there are no specific land-use activities at S remaining.

2. *M* located in the relatively higher-lying (>175.1 m amsl) intermediate sandy more organic-rich soil of a former orchard area east of the main Park road adjacent to the marsh fringes and in a hollow; located approximately 95 m east of S; second highest in ground surface elevation at ~175.5 masl. Cultivation here was abandoned more than 54 years ago (circa 1948). It is unclear what land-use activities existed here post-1948. Today, there are no specific land-use activities at M remaining.

3. *CHM* located in the relatively lower-lying (<175.1 m amsl) organic-rich marshy soil east of the main Park road adjacent to the perimeter of the former orchard containing S and M, as well as adjacent to the perimeter of the marsh in a flood plain; immediately northeast of the former Camp Henry and approximately 140 m south of S and M; lowest in ground surface elevation at ~175.0 masl. There was no cultivation in this area.

The topography alternates between the relatively higher-lying areas of the sandy dunes and hollows (>175.1 m amsl) and the relatively lower-lying flood plains adjacent

to the marsh (<175.1 m amsl) (Figure 9). Leaf litter tends to accumulate in the hollows adjacent to the dunes, and these areas tend to have higher organic matter contents than the sandy dunes. S and M, adjacent to dunes, are in hollows. CHM is in a flood plain.

The thick organic layer at the lowest-lying site, CHM, is characteristic of its hydrologic history. CHM is a wetter study area that is flooded when the lake and marsh water levels are high (>174.0 m amsl). Snail shells found below ground surface at M and CHM are indicative of a wetter environment.

The vegetation at all three study sites is similar, but varied. S and the area around S consist of vegetation characteristic of the forest and grassland environment, such as short grasses, small to medium-sized trees and bushy shrubs. M and the area around M consist of vegetation intermediate between a forest and marshland. Tall grasses are common, however thorny vines, woody shrubs, and small to medium-sized trees can also be found. CHM and the area around CHM consist of vegetation more representative of a wet environment such as marshland. Tall sedge grasses prevail, however bushy shrubs and small to medium-sized trees can be found. The shallow root systems at all three study sites are extensive and an abundance of small, medium and large roots extend from the surface to approximately 20 cm depth depending on the location.

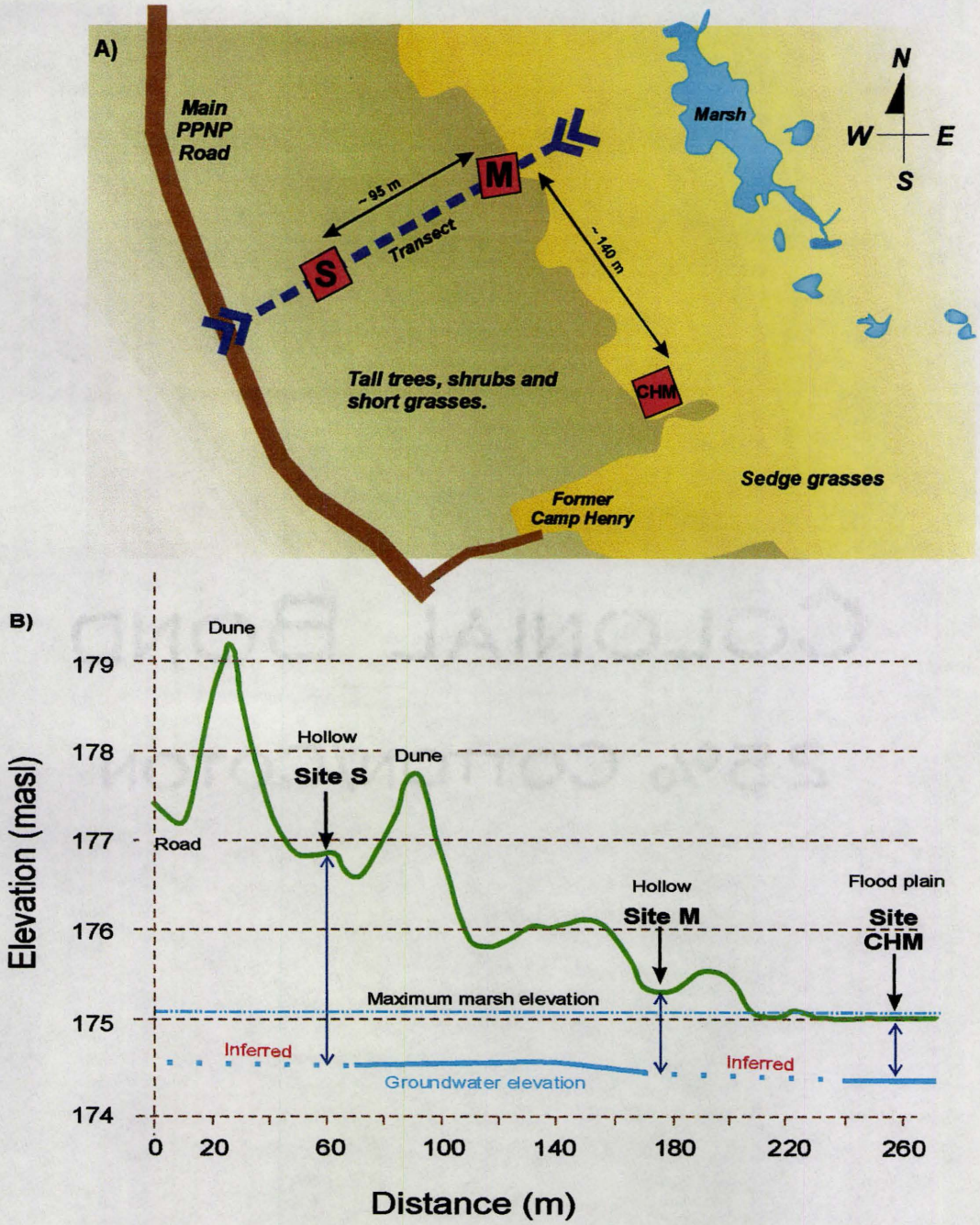


Figure 9. (a) Location of transect surveyed from the road through S and M; (b) topography along the transect surveyed (vertically exaggerated). The maximum marsh elevation is presented. Groundwater elevations were obtained April 26, 2001.

CHAPTER 3

3.0 Materials and Methods

A soil's physical properties, as well as the soil and water management practices imposed on soil, can affect the pathway of DDT breakdown. This, in turn, will change the relative amounts of DDT, DDE and DDD that will persist in the soil. In order to characterize the soil environments at PPNP, a combination of field and lab analyses were performed in conjunction with research scientists from the NWRI of Environment Canada.

Soil samples were first obtained from the three study sites to determine whether these different soil environments affect DDT degradation rates and pathways. Most importantly, the systematic sampling protocol provided %DDT, %DDE and %DDD abundances, total DDT (DDX), organic (%OC and %ON) and mineral (%MM) matter contents. It also provided grain size distributions, bulk densities, porosities, water

contents, hydraulic conductivities, as well as water retention data. In addition, depths to the water table were obtained at the three study sites, the study sites were surveyed for ground surface elevation and a transect was surveyed to determine the local topography (Figure 9). The UTM easting and northing coordinates of each sampling site were also obtained. Field and lab soil sampling methods to determine these parameters are described below. For further details on any of the following field and lab soil sampling methods, consult Methods of Soil Analysis, 2nd edition (Klute and Page, 1982). All the data sets were then compiled, verified and statistically analyzed subsequent to each field trip. In addition, the physical data sets were correlated, compared and contrasted to the corresponding chemical data sets to assess whether the different soil conditions at each location affected the rate and pathway of DDT degradation at that location.

3.1 Generating and Positioning Random Sampling Points within the Grids

In the field, the soil samples were acquired from 10 randomly selected sampling points to obtain unbiased samples. The 10 random sampling points within each study site were obtained using a random number generator tool in Microsoft® Excel 97. A 20m x 20m grid was first designed in CorelDRAW® 9.337 with 400 1m x 1m squares. Each small 1m x 1m square was then assigned a number from 1 to 400 sequentially starting from the top left corner to the bottom right corner. In Excel 97, the "RANDBETWEEN" function was used for numbers between 1 to 400 (=RANDBETWEEN(1,400)). These

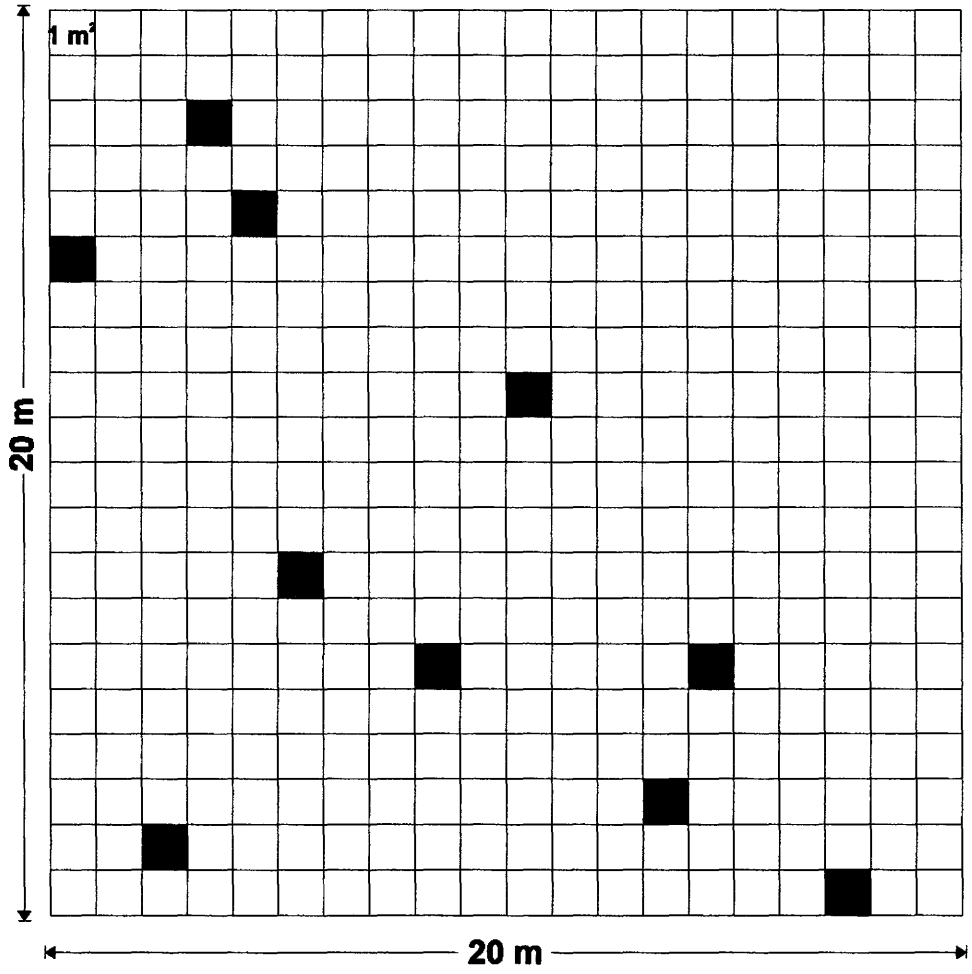
randomly generated numbers were used to select the corresponding numbered squares in the grid diagram (Figure 10).

In the field, a stake was first inserted into the ground at an arbitrary point within the first study site. A bearing of the PPNP main road was then recorded (340°N) with the Silva Model 530 Ranger Ultra Precision Compass (Johnson Worldwide Associates, Binghamton, NY, USA). Using this bearing, the second stake was positioned 20 m away from the first stake and parallel to the main road (340°N). At the first stake, the third stake was positioned perpendicular to the first using the initial bearing (340°N) plus 90° (70°N). The third stake was positioned 20 m away from the first stake. The fourth and last stake was then positioned 20 m away from the third by intersecting two 100 m measuring tapes. Based on the Pythagorean Theorem, the first measuring tape was extended diagonally 28.3 m from the first stake till it intersected with the 20 m mark on the second measuring tape extending from the third stake. This process was followed to get the grid layout for each study site.

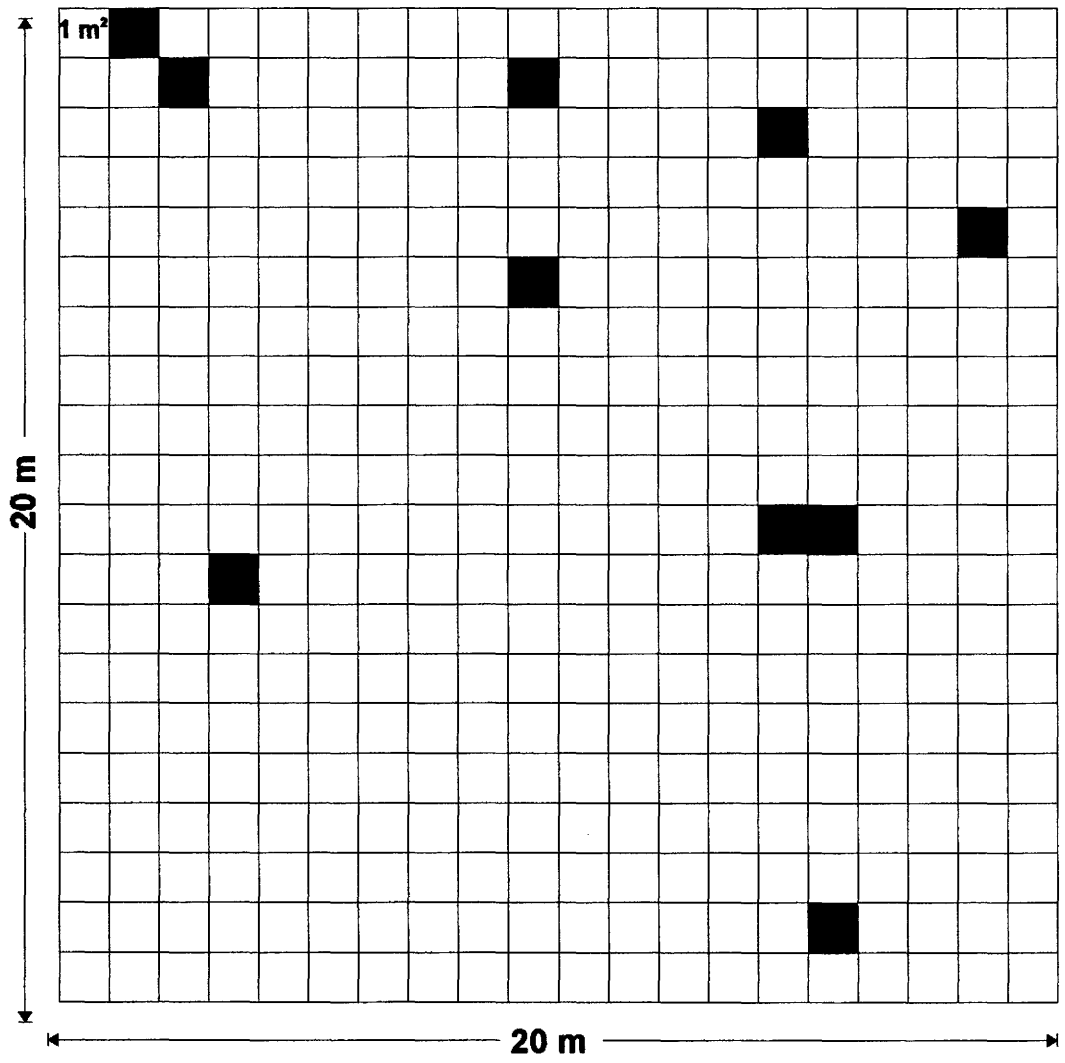
For the sampling point layout, a measuring tape was positioned joining the first and second stakes. A second measuring tape was then positioned joining the third and fourth stakes. A third measuring tape was then extended perpendicular to these measuring tapes. The sampling points were located by sliding the third measuring tape to the desired locations on the first and second measuring tapes. Metal stakes were then driven into the ground at these locations. The metal stakes were prelabeled S-1, S-2, S-3,..., S-10, M-1, M-2, M-3,..., M-10, as well as CHM-1, CHM-2, CHM-3,..., CHM-10.

Figure 10. Random sampling points within the 400 m^2 grids at S, M and CHM.

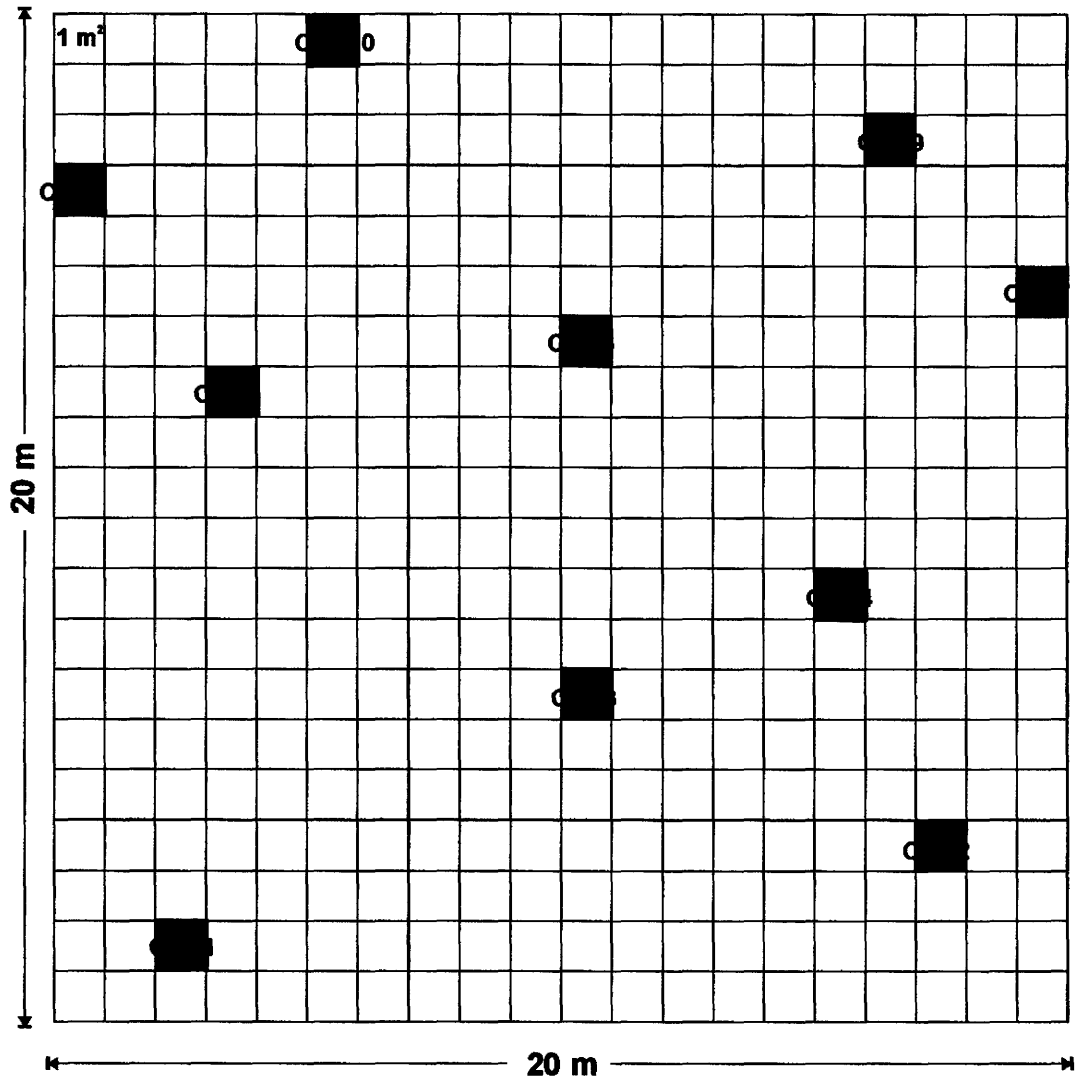
A) GRID 1: Sandy soil of former orchard (S)



B) GRID 2: Intermediate sandy to marshy soils of former orchard (M)



C) GRID 3: Marshy soils of Camp Henry (CHM)



All subsequent sampling was performed at these sampling points within each grid, unless otherwise noted.

3.2 Soil Sampling

Soil sampling for analyses of DDT, DDE, DDD, %OC and %ON was performed at the sampling points at S, M and CHM during two sampling trips in February 2001. Because of the uneven application of DDT at the Park and the known existence of DDT "hot spots", ten replicate samples were collected, subsequent to the removal of overlying snow and/or loose plant litter, from the 10 randomly selected sampling points within each 400 m^2 gridded area. Two shallow (from 0 – 5 cm depth) and two deep (from 10 – 15 cm depth) soil samples were collected at each of the ten randomly selected sampling points within each grid for a total of 40 samples per grid (total of 120 samples).

During these two sampling trips, disposable latex gloves were worn and the sampling stainless steel garden trowels and amber glass jars (120 and 250 mL) cleaned with a 50/50-acetone/hexane solution before and after each sample was collected. Amber glass jars were used to prevent photodegradation of the DDT, DDE and DDD and stainless steel trowels were used to minimize adsorption of DDT, DDE and DDD onto the trowel. All the soil samples were manually obtained from each sampling point with the handheld, stainless steel garden trowels and stored in the prelabeled amber glass jars. The jars were sealed with plastic lids with a piece of aluminum foil between the soil and

the plastic lid to minimize adsorption onto the plastic bottle cap surface. All the soil samples were transported in a cooler until stored in the lab refrigerator where they were kept until analyzed. All holes produced as a function of the sampling were permanently filled prior to leaving the Park.

3.3 Soil Analyses for DDT, DDE and DDD

Of the forty samples collected from each grid, twenty 250 mL samples (1 deep and 1 shallow) were obtained for organochlorine pesticide analyses, with a special focus on DDT, DDE and DDD. The other 20 samples were 120 mL samples (1 deep and 1 shallow) used for soil %OC and %ON analyses. Philip Analytical Services Corporation (PSC; Burlington, Ontario, Canada) used approximately 15 to 20 grams of the shallow and deep 250 mL samples for chemical analyses of a suite of organochlorine pesticides including the o,p'- and p,p'- isomers of DDT, DDE and DDD. The soil was analyzed using US EPA SW846 Method 8081B – modified. Method 8081 is a standard GC/MS procedure outlined in "Standard Methods for the Examination of Water and Wastewater", 19th Edition (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995).

Approximately 15 to 20 grams of wet soil were mixed with sodium sulfate. Surrogate standards were then added. The mixture was extracted with 3 x 80 mL of 50:50 v/v pesticide grade acetone:dichloromethane with a Polytron Ultrasonic probe.

Isooctane was added to the combined extract and then concentrated on a Snyder column to 1 mL. The injection volume used was 1 μL onto a dual column GC/ECD (Hewlett-Packard model 5890). The primary column was DB-5 and the secondary column was DB-1701. The responses were measured relative to the calibration curve. The surrogate and other QA/QC results had to fall within the specifications given in Method 8081B.

3.4 Soil Analyses for %OC and %ON

Twenty 120 mL samples (1 deep and 1 shallow) from each grid were analyzed for soil %OC and %ON analyses. At least 1 to 5 grams of dried soil from the shallow and deep 120 mL samples were chemically analyzed for soil %OC and %ON using method SOP 01-1090 (Standard Operating Procedure for the Analysis of Particulate Carbon and Nitrogen in Natural Waters and Sediment Using CHN Analyzer) by NWRI's National Laboratory for Environmental Testing (NLET; Environment Canada, Burlington, Ontario, Canada).

Samples analysed for organic carbon and organic nitrogen required an acid wash (2 mL of 6% sulphurous acid) procedure to remove inorganic forms. The PE 2400 Series II CHNS/O Analyser then used a combustion method to convert the sample elements to CO_2, H_2O and N_2. Halogens and sulphur were then removed by scrubbing reagents in the combustion zone. The resulting gases were homogenised and controlled to exact conditions of pressure, temperature and volume that were then allowed to depressurise

through a column where they were separated in a stepwise steady-state manner and detected as a function of their thermal conductivity.

The remaining portion of the samples used for organochlorine as well as %OC and %ON analyses were returned to McMaster University labs and used for ex-situ hydraulic conductivity (falling head) tests and grain size distribution analyses, respectively.

3.5 Relative DDT, DDE and DDD Degradation Half-lives

A measure of pesticide longevity, the half-life ($t_{½}$), is the time interval over which the mass level decreases to ½ or 50% from a given mass. This measure of degradation expresses loss as a first-order kinetic reaction, as shown in Eq. 1 and 2:

$$C_t/C_o = e^{-kt} \qquad \text{Eq. 1.}$$

$$t_{½} = (\ln 2)/k \qquad \text{Eq. 2.}$$

where $t_{½}$ is the half-life, C_t is the concentration at time t, C_o is the concentration at time zero, k is the decay constant, and t is the time since the chemical was last applied. To solve for the half-life of DDT at each site, two methods were used which assumed that the loss of DDT could be expressed as a first order decay process (Boul, 1994).

The first method involved the use of decay curves to simulate a half-life for the sample mean DDT/DDX currently remaining in soil at each site with the assumption that

further degradation of the daughter products DDE and DDD would not occur. That is, the initial DDT_o (C_o) was assumed to be expressed by $DDT_o = DDT_{today} + DDE_{today} + DDD_{today} = DDX_{today}$. This can be expressed with the following relationships:

$$\frac{DDT_{today}}{DDX_{today}} = \frac{DDT_{today}}{DDT_{today} + DDE_{today} + DDD_{today}}$$

Eq. 3.

where DDT_{today}, DDE_{today}, and DDD_{today} are the current observed concentrations.

Eq. 3 reduced to:

Eq. 4.

$$\frac{DDT_{today}}{DDX_{today}} = e^{-kt}$$

The term on the left side of the equation expresses the proportion of DDT remaining today relative to DDX. The DDT_t (C_t) for any time t between 0 and 50 years was then calculated with Eq. 1 and the mean k value expressing the mean half-lives at each site with Eq. 2. A plot of %DDT versus time passes through the mean %DDT remaining today for the appropriate k value and associated mean half-live ($t_{1/2}$) at S, M and CHM. Using this approach of assuming the original DDT concentration (C_o) is the DDX observed today generates a "conservative" estimate of the $t_{½}$ of DDT. That is, the half-live would not be expected to be shorter than the calculated value.

A second method was used to consider the effect of sequential degradation of the daughter products DDE and DDD. That is, to consider the case of the initial DDT concentration being greater than the sum of the DDT, DDE and DDD concentrations observed today. This method used an iterative procedure of sequential degradation of DDT, and production and degradation of the daughter products DDE and DDD to match the present day observed %DDT, %DDE and %DDD (DDT/DDX, DDE/DDX and DDD/DDX) at the study sites. The following relationships were used within a spreadsheet to estimate the half-lives at each site:

$$DDT_n = DDTn_{-1} * e^{-k_A t} \quad \text{Eq. 5.}$$

$$DDE_n = DDE_{n-1} * e^{-k_B t} + DDT_{n-1} * e^{-k_C t} \quad \text{Eq. 6.}$$

$$DDD_n = DDD_{n-1} * e^{-k_D t} + DDT_{n-1} * e^{-k_E t} \quad \text{Eq. 7.}$$

$$DDE\text{-}x_n = DDE\text{-}x_{n-1} + DDE_{n-1} * e^{-k_F t} \quad \text{Eq. 8.}$$

$$DDD\text{-}x_n = DDD\text{-}x_{n-1} + DDD_{n-1} * e^{-k_G t} \quad \text{Eq. 9.}$$

where DDE-x and DDD-x are the daughter products of DDE and DDD, respectively, DDT_n, DDE_n, DDD_n, $DDE\text{-}x_n$, and $DDD\text{-}x_n$ are the concentrations at the n^{th} DDT half-life step, while DDT_{n-1}, DDE_{n-1}, DDD_{n-1}, $DDE\text{-}x_{n-1}$, and $DDD\text{-}x_{n-1}$ are the concentrations at the *n-1* half-life step where n = 0, 1, 2, 3...n, t is the time in years, k_A to k_G are the decay constants and A, B, C, D, E, F, G are subscripts used to express the relative values of k. A, C and E express the relative values of k for DDT. B and F express the relative

values of k for DDE. E and G express the relative values of k for DDD. The $e^{-k_A t}$, $e^{-k_B t}$, $e^{-k_C t}$, $e^{-k_D t}$, $e^{-k_E t}$, $e^{-k_F t}$ and $e^{-k_G t}$ are the degradation terms.

DDT_o, DDE_o, DDD_o, DDE-x_o and DDD-x_o, i.e. at n = 0 (initial concentrations), were assumed to be the concentrations in technical grade DDT, i.e. 95%, 5%, 0%, 0% and 0% (EHC 83, 1989). Iterations were then calculated using a range of relative values of the degradation terms until the calculated %DDT, %DDE and %DDD matched the present day observed %DDT, %DDE and %DDD in soil at the study sites. The number of half-life steps required to reach the observed %DDT, %DDE and %DDD in soil today along with the time since DDT was last applied was used to estimate a half-life of DDT at S, M and CHM in shallow and deep soils at PPNP.

3.6 Percent Organic Matter by Loss on Ignition

Loss on ignition is a measure of the percent organic matter (%OM) in the soil. When the soil sample is heated to 550°C, the organic matter is burned off and %OM and percent organic carbon (%OC) can be determined (Klute and Page, 1982).

The samples were first oven dried to determine bulk densities, volumetric and gravimetric water contents, as well as porosities for another experiment. These oven-dried samples were then emptied into a clean, labeled, tared crucible and weighed. The muffle furnace was set to preheat at 550°C for 20 minutes before the samples were placed

in the oven. After a period of 12 hours in the furnace, the samples were removed and placed in desiccators to cool.

Once cool, the samples were reweighed and the loss on ignition calculated as follows:

$$\%OM = [(W_{cso} - W_c) - (W_{csi} - W_c)]/(W_{cso} - W_c) * 100 \qquad \text{Eq. 10.}$$

where W_{cso} is the mass of the oven dried soil and crucible, W_c is the mass of the crucible, and W_{csi} is the mass of the ignited soil and crucible. The %OC can then be calculated from the %OM by the following:

$$\%OC = \%OM/1.72 \qquad \text{Eq. 11.}$$

where 1.72 (Brady and Weil, 1999) is the accepted conversion factor for estimating %OC from %OM.

3.7 Particle Size Analysis

Particle size analysis is used in soil science to evaluate soil texture, which is based on different combinations of sands, silts and clays that make up the particle size distribution of a soil sample. The percent organic matter is not considered in this analysis. The USDA classification defines sands as <2000 to 50 μm, silts as <50 to 2 μm and clays as <2 μm (Klute and Page, 1982). Once the percentages of sand, silt and clay

are found through this analysis, the soil textural triangle can be used to determine the soil textural class name that applies to the sample.

The unused soil remaining from the samples used for organic carbon and organic nitrogen chemical analyses were transferred to clean, tared, lidless aluminum weighing dishes and oven dried at 105°C for 24 hours. Once dry, they were removed from the ovens and placed in desiccators containing active desiccant until cool, then weighed. The dried sand was then transferred to the nest of sieves: top lid, 2000, 1000, 500, 250, 106, 63 μm, and a bottom pan. The sieves were shaken on an electrically powered Cenco-Meinzer sieve shaker No. 18480 (Central Scientific Co., Chicago, IL, USA) for 10 minutes at level 3. The mass of each sand fraction in each individual sieve was then determined. The soil was carefully brushed out of the sieve and onto the paper towel with a brush. This was done for each sieve in the sieve stack, including the bottom pan (Klute and Page, 1982). The total mass that passed through the sieve stack was calculated. The percentage of soil caught by each sieve tray including the bottom pan was calculated using the following:

$$\% \text{ retained} = (W_s * 100)/W_t \qquad \text{Eq. 12.}$$

where W_s is the mass of the soil in sieve and W_t is the mass of the entire sample. The percent cumulative passing through each sieve was then calculated:

$$\%\text{cumulative passing in top sieve} = 100 - \%\text{caught in top sieve} \qquad \text{Eq. 13.}$$

and:

%cumulative passing = %cumulative passing from above sieve - %caught from current sieve

Eq. 14.

Subsequent to analyses, particle size distribution curves were plotted, in which the percentages of particles less than a given size were plotted against the logarithm of the particle diameter (sieve size) in mm. The d_{10} (diameter of grains at which 10% passes) and d_{50} (diameter of grains at which 50% passes) values, which are interpolation values between points, were determined from the curves.

3.8 Bulk Density

Bulk density is an indicator of the soil structure. The bulk density of a soil sample is equal to the ratio of the mass of dry solids to the total volume of the soil sample commonly expressed in units of g/cm^3. The mass of the sample is determined after drying the sample to a constant mass at 105°C (usually for 24 hours; Klute and Page, 1982). The equation for calculating the bulk density is:

$$\rho_b = M_s/V_T \qquad \text{Eq. 15.}$$

where ρ_b is the bulk density, M_s is the mass of oven-dried soil, and V_T is the total sample volume.

Soil sampling for bulk density was performed April 23 to 27, 2001. Two (1 shallow and 1 deep) 60 cm^3 disturbed soil samples were manually obtained from the original randomly selected sampling points using 60 cm^3 (approximately 3.3 cm height and 4.8 cm inner diameter) stainless steel coring rings. These samples were stored in prelabeled Ziploc® bags in a cooler and then in a lab refrigerator until analyzed. Twenty samples were obtained per grid for a total of 60 samples.

In addition, soil sampling for bulk density was performed in a soil pit dug with a shovel at each of the three study sites. Ten undisturbed 60 cm^3 soil cores were collected at 10 cm depth intervals from the surface to a depth of 100 cm. These ten undisturbed 60 cm^3 soil cores were stored in prelabeled Ziploc® bags in a cooler and then in a lab refrigerator until analyzed.

The 60 cm^3 field samples for bulk density obtained from study sites S, M and CHM were first transferred out of their coring rings or Ziploc® bags into clean, tared, prelabeled crucibles. They were then weighed and dried in 105°C ovens for 24 hours. Once dry, they were removed from the ovens and placed in desiccators containing active desiccant until cool and reweighed (Klute and Page, 1982). The bulk density was then calculated by dividing the oven-dry mass of the sample by the sample volume of 60 cm^3.

3.9 Porosity

The porosity is that portion of the soil occupied by air and/or water (void space). It is expressed as a percentage of the total volume. It can be calculated with the following formula:

$$\%n = [1 - (\rho_b/\rho_s)] * 100 \qquad \text{Eq. 16.}$$

where n is the porosity, ρ_b is the bulk density, and ρ_s is the weighted-mean particle density (Klute and Page, 1982).

Porosities were determined in conjunction with the bulk densities of the soil samples obtained from the study sites described in Section 3.8. The weighted mean particle densities were assumed to be 2.65 for the mineral matter and 1.6 for the organic matter (Brady and Weil, 1999).

3.10 Ex-situ Lab-based Gravimetric and Volumetric Water Contents

Water content is either a dimensionless ratio of two masses (gravimetric) or two volumes (volumetric). If water content is desired on a volume basis, the volume from which the sample was taken must be known. Gravimetric water contents may be determined from:

$$\theta_m = M_w/M_s \qquad \text{Eq. 17.}$$

When a bulk density is known, volumetric water contents may be obtained from the gravimetric water contents by:

$$\theta_v = (\rho_b/\rho_w) * \theta_m \qquad \text{Eq. 18.}$$

where θ_m is the gravimetric water content, θ_v is the volumetric water content, M_w is the mass of water, M_s is the mass of oven-dried soil, ρ_b is the bulk density, and ρ_w is the density of water (Klute and Page, 1982).

Soil water contents were determined in conjunction with the bulk densities of the soil samples obtained from the study sites described in Section 3.8. The bulk densities were determined with Eq. 15. Gravimetric water contents were determined using Eq. 17. The volumetric water contents were then determined with Eq. 18.

3.11 In-situ Field-based Volumetric Water Contents

In-situ (field-based) volumetric water contents were measured with the TDR (time domain reflectometry) method using a 20 cm single diode rugged (SDR - 20cm) probe (probe type number 12) with the Moisture•Point 917 (MP-917) system (Environmental Sensors Inc. [E.S.I.], Victoria, BC, Canada). Time domain reflectometry is a standard method that measures the propagation time of an electromagnetic wave as it travels through a probe buried in the soil. The longer the propagation times the higher the moisture content. When the TDR-probe is plugged into the MP-917 instrument and

MEASURE/DISPLAY is pressed, the instrument automatically engages the probe and processes the resultant waveforms. Propagation times, together with the probe length, as well as various soil and probe coefficients are directly converted into percent mean volumetric soil moisture contents by the instrument and output as numerical values on the display.

In-situ volumetric soil moisture contents between 0 and 20 cm were obtained with a 20 cm SDR TDR probe (SDR - 20cm) using the MP-917 system. The probe was inserted vertically at each of the ten sampling points previously sampled. In addition, the TDR probe was inserted horizontally at each of the depths in the soil pits previously sampled from 10 to 100 cm depth.

The TDR MP-917 system was first turned on by holding MODE down. At this point, the MP-917 displayed the current MODE. MODE was pressed to advance the MODE to 0 and MEASURE/DISPLAY was pressed to accept this MODE. At this point, the MP-917 displayed the current probe type. MODE was pressed again to advance to probe type 12 and MEASURE/DISPLAY was pressed to accept this probe type. The MP-917 was then turned off and turned on again while holding MODE down. To advance the current MODE to MODE 1, MODE was pressed and MEASURE/DISPLAY pressed to accept this MODE. The system was then turned off, the time delay/moisture switch was placed into the moisture position and the power was switched on. The 20 cm SDR probe was then inserted into the ground to take a reading. The MEASURE/DISPLAY was pressed twice to start the measuring process. Once the

numbers stopped flashing and a single number was displayed on the screen, the mean percent volumetric moisture content and time delay were recorded.

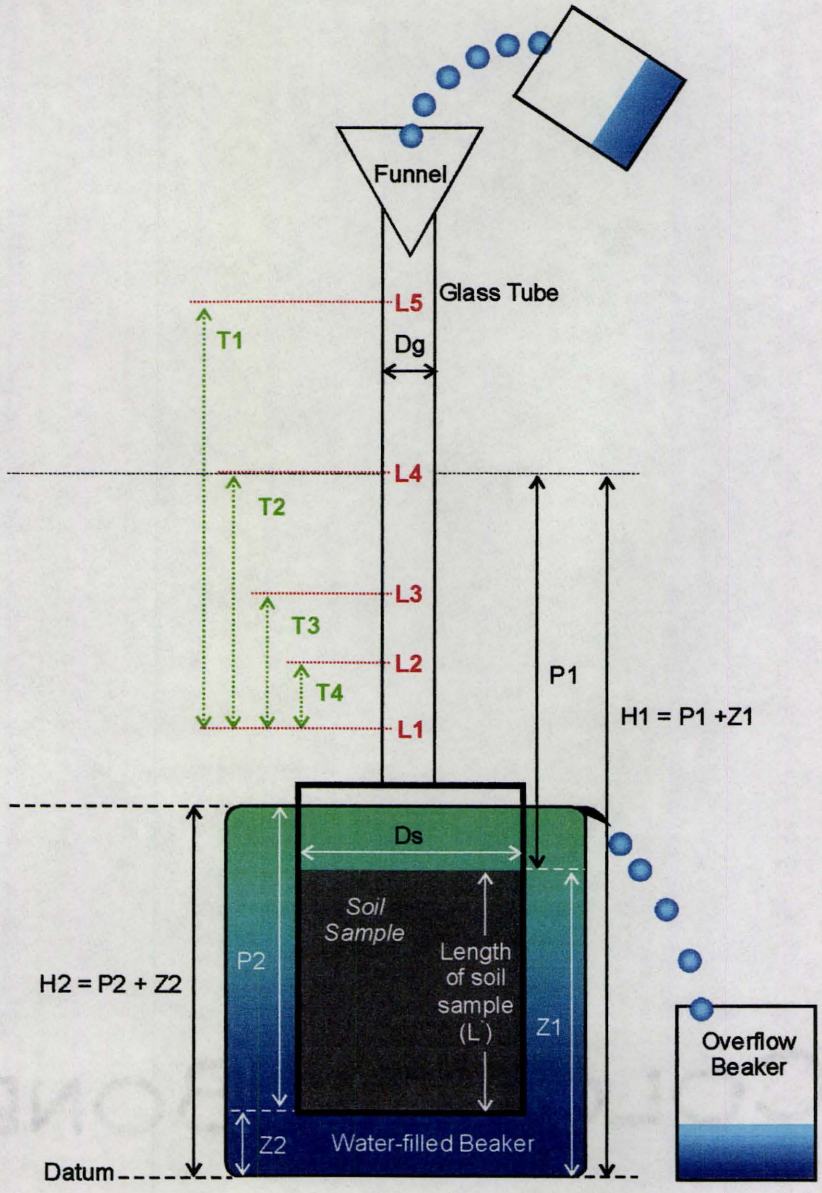
3.12 Ex-situ Lab Saturated Hydraulic Conductivities

The hydraulic conductivity (K) is an important hydraulic parameter governing the transmission of water in saturated and unsaturated soils. It is a measure of a soil's ability to transmit water. As the water content decreases from saturation, the large pores, which are most effective in conducting water, are the first to drain. Consequently, the hydraulic conductivity is a function of the soil water content (Klute and Page, 1982).

Ex-situ lab saturated hydraulic conductivities were measured with falling head permeameter tests (Figure 11). The falling head method for determining the hydraulic conductivity of saturated soils can be used with either repacked or undisturbed cores. Soil samples for determining the hydraulic conductivity by this method are usually held in metal or plastic cylinders to obtain one-dimensional flow.

If repacked soil samples are to be used, as in this study, a standard procedure for packing the soil cores to known bulk density is used. Sample cylinders with diameters on the order of 2 to 10 cm and lengths of 5 to 25 cm are practical for measurements in the laboratory (Klute and Page, 1982).

In this study, cores packed to the known bulk density were first prepared for the analyses. For each study site, the average bulk density of the soil samples was



Legend			
Dg	Diameter of glass tube	L1 to L5	Five points on glass tube
Ds	Diameter of soil sample	H	Hydraulic head
T1 to T5	Time	P	Pressure Head
		Z	Elevation from datum

Figure 11. Falling head permeameter apparatus used to determine hydraulic conductivities of repacked soil cores in the lab with the falling head method.

determined and used as a basis for repacking plastic cores approximately 4.5 cm in diameter and 7 cm in length (volume of the sample rings was approximately 110 cm^3). The packed cores were bound on the bottom with a J-cloth®. The cross-sectional area of the soil sample (A), the length of the soil sample (L^*) and the cross-sectional area of the glass tube (a) were determined. A 400 mL beaker was filled with approximately 300 mL of tap water and a 100 mL beaker was placed below the spout of the large beaker to catch the overflow.

Slowly, so as not to disturb the soil sample, the plastic cylinder containing the soil core was lowered into the large beaker of water to the point where the bottom half of the cylinder was submerged in the water. The plastic cylinder was held in this position until the soil sample reached natural saturation. A glass tube fitted into a rubber stopper was inserted into the top of the plastic cylinder and secured tightly. The cylinder was then further lowered and submerged below the water without touching the base of the beaker. The glass tube was clamped onto a support stand to hold in position and the experiments were run.

Five points on the glass tube were selected and measured using the counter top as the reference surface. Each point was labeled L_1, L_2, L_3, L_4 and L_5 (or L_i; where i = 1, 2, 3, 4, 5) and four differences in height were measured, such that L_5-L_1 resulted in the first difference in height, L_4-L_1 resulted in the second and so on. Using a funnel, water was poured into the glass tube until it was almost full. A stopwatch was then used to measure the time (t) for the water to pass from L5 to L1 and the time was recorded. The same

procedure was followed for the water to pass from L4 to L1, L3 to L1 and L2 to L1. The same procedure was repeated for all shallow and deep soil samples. The hydraulic conductivity was then calculated using Eq. 21 for each height difference for each sample (Klute and Page, 1982):

$$K = (aL^{*}/At) \log_e(L_i/L_{i+1}) \qquad \text{Eq. 19.}$$

An average hydraulic conductivity was then calculated for each sample.

3.13 In-situ Field Saturated Hydraulic Conductivities

The Model 2800K1 Guelph Permeameter (Soilmoisture Equipment Corp., Santa Barbara, CA, USA) was used to obtain in-situ field saturated hydraulic conductivities at five locations within the grid at each of the three study locations S, M and CHM. The Guelph Permeameter is a constant-head device that operates on the Mariotte siphon principle and provides a quick and simple method for determining field saturated hydraulic conductivity. The model comes as a complete field-ready kit, so that holes can be augured, measurements can be made and the results calculated very efficiently.

The method involves measuring the steady-state rate of water recharge into unsaturated soil from a hole in which a constant depth of water (head) is maintained. When this constant head of water is established in the cored hole, a "bulb" of saturated soil is formed whose exact shape depends on the type of soil, the radius of the hole and

the head of water in the hole. At this point, the outflow rate of water reaches a steady state measured as the rate of discharge from the instrument. This rate of constant outflow of water, together with the diameter of the hole and the depth of ponding in the hole can be used to accurately determine the field saturated hydraulic conductivity.

The constant head level in the hole is established by regulating the level of the bottom of the air tube located in the center of the permeameter. As the water level in the reservoir falls, a vacuum is created in the air space above the water. The vacuum can only be relieved when air that enters at the top of the air tube bubbles out of the air inlet tip and rises to the top of the reservoir. Whenever the water in the hole begins to drop below the air inlet tip, air bubbles emerge from the tip and rise into the reservoir air space. The vacuum is then partially relieved and water from the reservoir replenishes water in the hole and thereby maintains the constant level.

Holes 6 cm in diameter were augured using a hand-held soil auger provided in the Guelph Permeameter field-kit to depths of 15 cm and 30 cm. The soil auger provided was rotated in a clockwise direction while applying steady downward pressure on the handle until the bucket of the auger was filled with soil. The hole depth was then measured with a measuring tape and the entire process repeated if the required depth had yet to be reached. Once at the desired depth, the sizing auger provided in the kit was used as a finishing tool to produce a proper sized hole of uniform size, as well as to clean debris off the bottom of the hole.

The tripod was first assembled by connecting the tripod legs to the base and angled as needed. Next, the lower air tube was connected to the middle air tube at the base of the reservoir using the air tube coupling. The lower air tube was then pushed into the coupling until the ridge on the inside of the coupling snapped into the groove on the end of the lower air tube. The tripod bushing was slid onto the outside of the support tube with the wide end oriented up. With the support tripod bushing in place, the support tube was slid over the air tube and connected firmly into the recess at the bottom of the reservoir base. The support tube was then lowered into the tripod.

To support and stabilize the permeameter, the tripod provided was used. The upper air tube was connected to the top of the middle air tube with an air tube coupling. The air inlet tip was fully seated into the air tip seating washer by pushing down on the upper air tube. Once the air inlet tip was seated, the head height indicator was lowered and seated flush against the reservoir cap. The head scale was then lowered over the upper air inlet tube and fully seated against the bottom of the recess in the reservoir cap.

After the permeameter was assembled and mounted in the tripod, it was filled with water. The fill plug in the reservoir cap was first removed and the reservoir valve adjusted so that the notch was in the "up" or 12 o'clock position. The inner and outer reservoirs were now connected and ready for filling. Water was poured into the recess on the reservoir top cap. For convenience, the tube assembly was connected to the plastic water container to fill the permeameter. After filling, the fill plug was replaced and fully seated in the fill hole. The tripod was then centered over the hole and the permeameter

slowly lowered so that the support tube entered into the hole, being careful not to knock debris off the sides of the hole into the hole bottom.

The water level in the selected reservoir was recorded using scale stamped on the inner reservoir tube. Measurements at each depth were obtained with 5 cm of head in the hole, as well as 10 cm of head in the hole. A head height of 5 cm was first established. To establish a 5 cm head height (H_1), the air inlet tip was slowly raised by grasping the upper air tube until a head height of 5 cm was established, as indicated by reading the lower edge of the head height indicator against the head scale.

The rate of fall of the water level in the reservoir was observed. Readings were made at the regular time intervals. Determining whether to use the ½ minute or 2 minute sampling interval was left to the discretion of the operator. If the rate of flow was determined to be very fast, the 0.5 minute interval was used. If the rate of flow was slower, the 2 minute interval was used. If it was too slow to easily distinguish a drop in level between consecutive readings, usually 2 minute intervals, then the reservoir valve was turned so that the notch pointed down in the 6 o'clock position. Water was then supplied only from the small diameter inner reservoir, which resulted in a much greater drop in the water between readings.

The difference of readings at consecutive intervals, divided by the time interval, equals the rate of fall of water in the reservoir (R). The rate of fall of water in the reservoir was monitored until the "rate" of fall did not significantly change in three consecutive time intervals. This rate, R_1, is defined as "the steady-state rate of fall of

water in the reservoir at H_1." After completing the outflow measurements, the air inlet tip was raised to establish the second head height (H_2) of 10 cm. The rate of fall of water at this second head height (R_2) was then determined in the same way as for R_1.

The steady-state measurements were used to calculate the in-situ hydraulic conductivities in cm/sec using GP CAL (Zhang and Parkin, 1998) with $\alpha = 12\ m^{-1}$. A total of thirty readings of hydraulic conductivity were obtained using the one-ponded height method (Elrick et al., 1989). According to Elrick et al. (1989), the procedure suggested for the one-ponded height technique is:

(a) calculate the maximum K_{fs} by letting $\alpha \rightarrow \infty$ in Eq. 20, resulting in Eq. 21. This is equivalent to assuming zero capillarity because of extremely coarse soil texture, or very highly structured soil.

$$K_{fs} = CQ/(2\pi H^2+\pi a^{*2}C+2\pi H/\alpha) \qquad \text{Eq. 20.}$$

$$K_{fs} = CQ/(2\pi H^2+\pi a^{*2}C) \qquad \text{Eq. 21.}$$

K_{fs} is the field saturated hydraulic conductivity, Q is the reservoir constant (or the reservoir cross-sectional area) times the steady-state rate of fall (Q=XR), H is the ponded height, a^* is the radius of the test hole, and C is a dimensionless shape factor that depends only on the H/a^* ratio. The α parameter, which can be estimated from a site evaluation or from previous research, is the ratio of K_{fs} to the matric flux potential (φ_m).

According to Elrick et al. (1989), the choice of $\alpha = 12\ m^{-1}$ should be the first choice for most soils and can be used to provide the "best estimate" of K_{fs} using Eq. 20. It includes: (i) most structured soils from clays to clay loams; as well as (ii) unstructured

medium and fine sands and sandy loams. The choice of this α for most soils has some justification based on published results by White and Sully (1987). Fortunately, according to Elrick et al. (1989), the determination of K_{fs} is not strongly sensitive to the choice of α.

GP CAL (Zhang and Parkin, 1998), which uses Eq. 20 with the choice of $\alpha = 12$ m^{-1}, calculates the best K_{fs} estimate. As previously stated, this was the method used. To solve for the K_{fs} at S, M, and CHM with GP CAL (Zhang and Parkin, 1998), the necessary parameters were first input or changed from the default settings.

These included:

(a) changing the residual and saturated water contents (θ_r, θ_s);

(b) changing the reservoir constants (labeled on the water reservoirs being used for the experiment and recorded in the field during the in-situ hydraulic conductivity tests);

(c) changing the soil texture type to "medium sand" ($\alpha = 12$ m^{-1});

(d) inputting the hole radius as 3 cm;

(e) inputting the ponded height (H1) as 5 cm; and

(f) inputting the steady- state rate of fall (R1).

The units were altered to cm/sec and the "RUN" command was then selected from the menu to calculate the best estimate of K_{fs} in cm/sec and an α in /cm. The K_{fs} results are presented in Section 4.6.

3.14 Water Retention

The soil water characteristic curve, which is the relationship between the soil water content and the pressure head (or soil water suction), is a fundamental part of characterizing the hydraulic properties of a soil including solute migration and soil water drainage. Soil water varies nonlinearly with water content. Water retention in soil is thus primarily dependent on the particle-size distribution (texture) and structure of the soil (Salter and Williams, 1965; Richards and Weaver, 1944; Reeve et al., 1973; Sharma and Uehara, 1968; Croney and Coleman, 1954). The organic matter content and the composition of the soil water also play a role in determining the retention. Organic matter has a direct effect on the retention function because of its hydrophilic nature and an indirect effect because of the modification of the soil structure that is affected by the presence of organic matter.

In the literature, the relationship is defined by various names, including the moisture characteristic curve. The function relates a capacity factor, the water content, to an intensity factor, the energy-state of the soil water. In this study, the potential of the soil water is expressed in units of energy per unit weight of the soil water, which are head units with dimensions of length. In other words, the pressure head is expressed as the length of a column of water at the ambient temperature of the soil water system, or in this case, room temperature. In this study, the water content or wetness of the soil is

expressed on a volume basis, which is the most useful for analysis of water flow in soil profiles.

The traditional method of determining the water retention function involves establishing a series of equilibria between the water in the soil sample and a body of water at a known pressure or energy state. In this study, the soil-water system is in contact with the body of water via a water-wetted porous ceramic plate. These porous ceramic pressure plates are covered on one side by a thin neoprene diaphragm. An internal screen between the plate and diaphragm provides a passage for water flow. An outlet tube running through the plate connects this passage to an outflow tube that in turn connects to the atmosphere outside the extractor. At each equilibrium the volumetric water content (θ_v) of the soil is established in equilibrium with the pressure in the body of water and the gas phase pressure in the soil (P). The data pair (θ_{v1}, P_1) is one point on the retention curve. The drainage curve is mapped by establishing a series of equilibria by drainage from zero pressure to increasing pressures.

A soil pit was dug with a shovel at each study site for the collection of ten undisturbed 60 cm^3 soil cores at 10 cm intervals from the surface to 100 cm. A total of thirty soil cores were obtained. The cores were wrapped in cling wrap and aluminum foil and carefully placed in a prelabeled Ziploc® bag before being stored in a cooler for in-lab water retention studies.

In this study, the equipment for determining the retention function in the lab was the pressure plate apparatus, Cat. No. 1600 - 5 Bar Pressure Plate Extractor (Soilmoisture

Equipment Corp., Santa Barbara, CA, USA). It is a low-range pressure plate apparatus (especially suited to measurements in the pressure head range 0 to 5 bar or 0 to approximately 5000 cm of water), attached to a gaseous air pressure regulation system. It keeps the body of water under the porous plate at atmospheric pressure and raises the gas phase pressure applied to the soil sample so that no water in the system is actually subjected to pressures significantly less than atmospheric (Richards, 1941; Richards and Fireman, 1943).

Since the structure of the sample affects the water retention, especially in the low suction range, it is generally best to use samples of natural structure. A deaerated 0.005*M* $CaSO_4$ solution is suggested as a general test fluid (Klute and Page, 1982). Wetting with distilled or deionized water or tap water is not generally recommended. If the main drying curve is to be determined, as here, cores must be wetted in a manner that produces the "natural saturation". Soaking the cores in water that is at a level just below the top of the core is an easy method.

The 30 soil cores of natural structure obtained in the field were used. The ends of the cores were trimmed flat and bound on the bottom side by a tight weave cotton cloth. The pressure plates were wet in the recommended test fluid for 48 hours and the soil samples were wet until they reached natural saturation by immersing them in the test fluid to a level just below their tops. Although it is best to do this within the chamber in which the samples are to be drained to equilibrium, plastic dish bins were used instead.

Once the samples had reached natural saturation, they were transferred into the pressure chambers and the outflow tubes allowed to sit in outflow beakers. The chambers were then closed for pressurization. The desired gas pressure was applied to the system and the samples were allowed to come to equilibrium. For the 2 to 3 cm high core samples studied, an equilibration time of one to two weeks, depending on the applied pressure was found to be sufficient. While the samples were equilibrating, the regulated pressure applied to the apparatus was monitored. Core samples were pressurized from 0.2 psi (14.06 cm head) to 2.5 psi (175.77 cm head) (14.7 psi = 1052 cm water).

With pressures in the chamber above atmospheric, excess water in the soil pores was forced to drain into the ceramic plate and out through the outlet tubes positioned in beakers. Water drained from the soil into the ceramic plate until the effective curvature of the water films throughout the soil generated a capillary pressure that was in equilibrium with the applied pressure. At this point the flow of soil water ceased. When the air pressure in the extractor was increased, flow of soil moisture from the samples started again and continued until a new equilibrium was reached. At equilibrium, there is an exact relationship between the air pressure in the extractor, the soil water pressure head and the moisture in the soil samples.

The volumetric water content and bulk density of the samples were found when the retention studies were completed using the same samples (Sections 3.8 and 3.10). Data points of water content versus pressure head were then plotted and fitted with the

van Genuchten-Mualem retention curve model using the common assumption m=1-1/n. This was accomplished using the RETC V. 6.0, Code for Quantifying the Hydraulic Properties of Unsaturated Soil (van Genuchten et al., 1998). RETC is a computer program for describing the hydraulic properties of unsaturated soils. For instance, it may be used to fit several analytical models to observed water retention data.

Water contents at saturation, or θ_s (theta saturation), the residual water contents (θ_r) (both determined in McMaster University labs), were the only parameters input and "fitted" in RETC. The other parameters were provided by RETC (n, α) with "sand" used as an initial guess value for texture. Using "sand" provided reasonable estimates of the parameters to initiate the numerical fitting routine. The van Genuchten-Mualem analytical model assuming m=1-1/n was used to provide the "best-fit" to the observed data.

3.15 Depths to Groundwater

The positions of the water tables at S, M and CHM were determined once on April 26, 2001. A manually augured 6 cm borehole was located immediately adjacent to each grid so as not to disturb the grid. The holes were left open for 24 hours to establish natural water levels before measuring. A standard Solinst water level measuring tape was then used to measure depth to the water table. These water levels were compared to long-term monitoring data from nearby wells. The ground surface at the boreholes was

surveyed to obtain the elevation of the water table. These holes were filled subsequent to sampling.

3.16 UTM Coordinates and Ground Surface Elevations

UTM easting and northing coordinates (using the NAD-83 datum) were obtained with an Eagle Explorer Differential GPS (Eagle/Eagle, Mississauga, Ontario, Canada) operated by a CCIW technician. Additional UTM easting and northing coordinates were obtained with the Garmin GPS 12XL (Garmin Corp., Olathe, Kansas) using the NAD-83 datum. The Garmin GPS 12XL (Garmin Corp., Olathe, Kansas) was turned on by pressing the "lightbulb". To assure that the NAD-83 datum was used "page" was selected until the "main menu" appeared on the screen. The down arrow was then used to scroll down to the "setup menu" and "enter" was selected. At this point, "navigation" was selected, and "enter" was selected again. The down arrow was used to scroll down to "map datum" and "NAD-83" was selected.

To obtain UTM coordinates, the Garmin GPS 12XL (Garmin Corp., Olathe, Kansas) was turned on and when the screen displayed "North America City Data", "page" was selected until the screen displayed the "position," or the UTM coordinates. At this point, a minute or so was allowed for the UTM coordinates to become stable. This position was recorded. To turn off the GPS unit, the "lightbulb" was held until the screen turned black.

The boreholes, as well as the corners of each grid were surveyed for ground surface elevations with the Wild NA2000 Electronic Level with the assistance of a NWRI technician. In addition, a transect from the road to the marsh, through S and M at approximately 10 m intervals was surveyed for ground surface elevations and the UTM easting and northing coordinates of each survey point recorded.

3.17 Statistical Analyzes

The statistical analyses of all results were undertaken using SPSS 10.0 (Statistical Package for the Social Sciences, version 10.0). Analysis of variance (ANOVA) employing Tukey tests (SPSS, 2000) to determine significant differences between population means of the three study sites were performed. In addition, t-tests to determine significant differences between population means of the shallow and deep samples within each study site were performed.

All parameters were compared and contrasted using ANOVA in the following manner: (a) parameter X at CHM was compared to parameter X at M; (b) parameter X at CHM was compared to parameter X at S; and (c) parameter X at M was compared to parameter X at S. For instance the %DDT at CHM was compared to the %DDT at M and at S, and the %DDT at M was compared to the %DDT at S. Let us assume the first scenario "Is the %DDT at CHM significantly different than the %DDT at M?" If the P-value (or probability value) output by the software is less than the significance level set

by the user (default is typically 5% or 0.05; significant at the 95% confidence level; $P < 0.05$), it is correct to state that there is a significant difference in %DDT between CHM and M. However, if $P > 0.05$, there is no significant difference in %DDT between CHM and M.

Similarly, all shallow parameters from the three study sites were then compared and contrasted with their deep counterparts using Student t-tests. This was done in the following manner: (a) parameter X in shallow soils at CHM was compared to parameter X in deep soils at CHM; (b) parameter X in shallow soils at M was compared to parameter X in deep soils at M; and (c) parameter X in shallow soils at S was compared to parameter X in deep soils at S. For instance, the %DDT in the shallow soil at CHM was compared to the %DDT in the deep soil at CHM. If $P < 0.05$, there is a significant difference in %DDT between CHM-shallow and CHM-deep. If $P > 0.05$, there is no significant difference in %DDT between CHM-shallow and CHM-deep. Tables were then formulated to better illustrate which pairs showed significant differences (S) and which pairs showed insignificant differences (NS).

The following step in data analysis was to assess the degree of DDT degradation at each study site and determine which factors, if any, were influencing this degradation. To do so, several possible coupled relationships were examined for the studied sites: (a) whether ground surface elevation plays a role in the accumulation of soil organic matter; (b) whether ground surface elevation influences soil moisture; (c) whether soil moisture influences organic matter accumulation; (d) whether soil structure and texture influence

DDT degradation; (d) whether soil organic matter influences DDT degradation; (e) whether soil moisture influences DDT degradation; and (f) whether ground surface elevation influences DDT degradation. Graphs were produced to better illustrate some of the following relationships. The results are presented and discussed in Section 4.

CHAPTER 4

4.0 Results and Discussion

4.1 UTM Coordinates and Ground Surface Elevations of the Study Locations

The UTM easting and northing coordinates of the corners of each grid are presented in Table 4. In addition, the UTM easting and northing coordinates of the sites where samples were obtained with depth, for determination of the depth to ground water, as well as the sites for in-situ hydraulic conductivity sampling are presented.

Table 4. UTM easting and northing coordinates, as well as ground surface elevations at S, M and CHM at PPNP (Quadrant 17).

Site	Position ID	UTM E (m)	UTM N (m)	Ground Surface Elevation (masl)	Sampling Type
S	NW corner	0373418	4646551	176.58	Chemical and physical
S	NE corner	0373435	4646566	176.58	Chemical and physical
S	SW corner	0373428	4646532	176.81	Chemical and physical
S	SE corner	0373427	4646543	176.47	Chemical and physical
M	NW corner	0373522	4646610	175.62	Chemical and physical
M	NE corner	0373537	4646604	175.45	Chemical and physical
M	SW corner	0373524	4646594	175.68	Chemical and physical
M	SE corner	0373541	4646613	175.35	Chemical and physical
CHM	NW corner	0373613	4646483	174.99	Chemical and physical
CHM	NE corner	0373633	4646492	175.01	Chemical and physical
CHM	SW corner	0373625	4646450	174.96	Chemical and physical
CHM	SE corner	0373640	4646470	175.02	Chemical and physical
S	borehole	0373427	4646565	176.39	Depth to groundwater
M	borehole	0373527	4646623	175.40	Depth to groundwater
CHM	borehole	0373628	4646490	175.02	Depth to groundwater
CHM	CHM-6	0373623	4646482		K_{fs}
CHM	CHM-P1	0373622	4646475		K_{fs}
CHM	CHM-P2	0373621	4646468		K_{fs}
CHM	CHM-P3	0373618	4646484		K_{fs}
CHM	CHM-P4	0373634	4646481		K_{fs}
S	SP-1	0373414	4646551		K_{fs}
S	SP-2	0373421	4646545		K_{fs}
S	SP-3	0373423	4646541		K_{fs}
S	SP-4	0373417	4646538		K_{fs}
S	SP-5	0373417	4646564		K_{fs}
M	MP-1	0373529	4646618		K_{fs}
M	MP-2	0373521	4646621		K_{fs}
M	MP-3	0373531	4646625		K_{fs}
M	MP-4	0373522	4646606		K_{fs}
M	MP-5	0373510	4646621		K_{fs}
S	S-10 to S-100	0373427	4646565	176.39	TDR and physical
M	M-10 to M-100	0373527	4646623	175.40	TDR and physical
CHM	CHM-10 to CHM-100	0373628	4646490	175.02	TDR and physical

The UTM easting and northing coordinates of the transect from the road, through S and M are presented in Table 5.

Table 5. UTM easting and northing coordinates, as well as ground surface elevations of the transect from the road through S and M at PPNP (Quadrant 17).

Position ID	UTM E (m)	UTM N (m)	Ground Surface Elevations (masl)	Comment
1	0373429	4646543	176.85	bearing 70°E
2	0373439	4646545	176.62	~10 m E from Position 1
3	0373446	4646552	176.99	~10 m E from Position 2
4	0373457	4646554	177.74	~10 m E from Position 3
5	0373465	4646569	176.79	~10 m E from Position 4
6	0373480	4646566	175.87	~10 m E from Position 5
7	0373492	4646572	175.85	~10 m E from Position 6
8	0373493	4646582	176.04	~10 m E from Position 7
9	0373501	4646583	176.05	~10 m E from Position 8
10	0373511	4646583	176.11	~10 m E from Position 9
11	0373525	4646588	175.92	~10 m E from Position 10
12	0373528	4646599	175.36	~10 m E from Position 11
13	0373535	4646605	175.34	~10 m E from Position 12
14	0373545	4646605	175.53	~10 m E from Position 13
15	0373550	4646607	175.40	~10 m E from Position 14
16	0373552	4646600	175.03	~10 m E from Position 15
17	0373560	4646619	175.04	~10 m E from Position 16
18	0373570	4646613	174.85	~10 m E from Position 17
19	0373424	4646549	176.86	~10 m W from Position 1; bearing 250°W
20	0373406	4646526	177.31	~10 m W from Position 19
21	0373411	4646534	178.58	~10 m W from Position 20
22	0373393	4646540	179.23	~3.50 m W from Position 21
23	0373392	4646516	178.64	~10 m W from Position 21
24	0373375	4646532	177.25	~10 m W from Position 23
25	0373382	4646518	177.46	~10 m W from Position 24

Based on this data, S is highest in elevation and CHM is lowest in elevation.

4.2 Soil Texture and Structure

The type of soil is an important factor in determining DDT persistence. The structure of the soil is one of the main features influencing soil type. It depends partly on the parent material from which the soil is formed, on the percentages of the three main soil fractions (%sand, %silt and %clay), on its mineral content and on the recent history of the soil (agriculture, forest, recreation).

The structure and texture affect aeration and drainage. The 1938 Soil Survey of Essex County Report No. 11 (Richards et al., 1989) classifies the soils at the three study sites as Easport sands. However the standard "Easport sand" profile in Section 1.2 is different than what was actually seen in the field and what is described here. This may be due to several factors, some of which include: (a) the extent and sampling locations of the 1938 survey to characterize the different soil types at the Park; (b) the recent history of land-use at the Park; (c) the effects of erosion and deposition over time; and (d) the inherent variation in soil types between sampling points.

Based only on the soil horizons in the soil profile, the soils at S, M and CHM belong to the Regosolic Order. As such, they are too weakly developed to meet the requirements of any other order (Brady and Weil, 1999). At PPNP, this may be due primarily to a lack of time for development as Point Pelee is less than 4000 years old.

Humic Regosols have an Ah horizon at least 10 cm thick (Brady and Weil, 1999). As described in further detail below, the soils at S, M and CHM are thus Humic Regosols.

The sandy soil of S is characterized by a 5 cm dark brown soil layer consisting of slightly decomposed (Of - fibric) organic matter and an abundance of plant roots (Figure 12). The 5 cm layer beneath is composed of moderately decomposed organic matter (Om - hemic) and though abundant, less plant roots than the previous layer. The Ah layer beneath, approximately 30 cm thick, is composed of dark brown, well-sorted sand with the same root concentration as the previous horizon. The bottom layer C, of unknown vertical extent, consists of light brown, well-sorted, medium to coarse grained, aeolian sand.

The intermediate sandy/marshy soil of M is characterized by a 5 cm dark brown soil layer consisting of moderately decomposed (Om - hemic) organic matter and an abundance of plant roots. The 40 to 45 cm Ah layer beneath is composed of brown, well-sorted sand with an abundance of plant roots. The bottom layer C, of unknown vertical extent, consists of light brown, well-sorted, medium to coarse grained, aeolian sand. In contrast to the sandy soil, the presence of snail shells in this area an indication of a wetter environment.

Likewise, the marshy soil of CHM, adjacent to the former Camp Henry, contains an abundance of snail shells in the wet, upper few centimeters of the soil profile, and has the thickest organic horizon. The first 15 cm contains an accumulation of black soil rich in organic matter (Oh) with an abundance of plant roots. The underlying 2 to 5 cm are

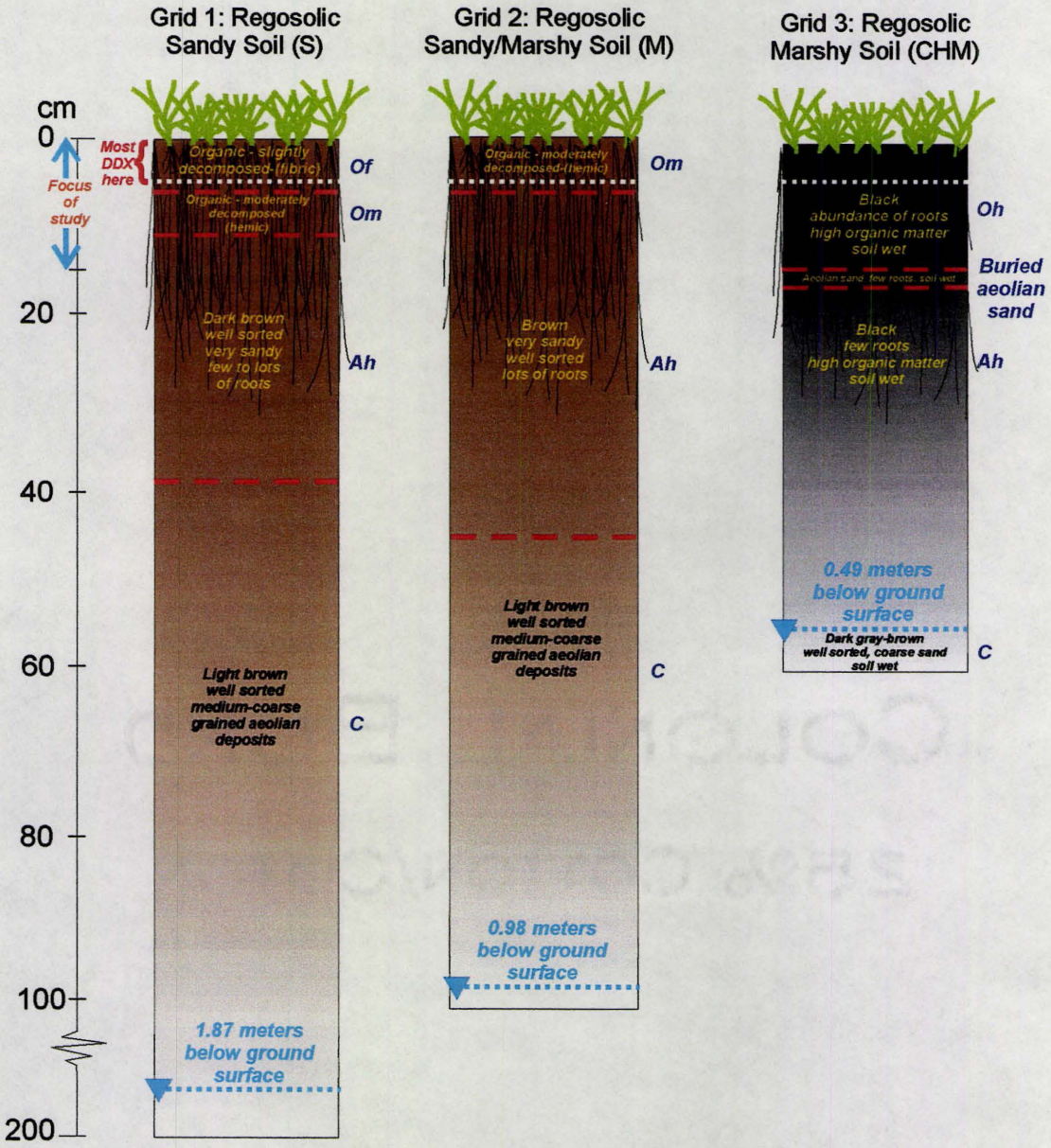
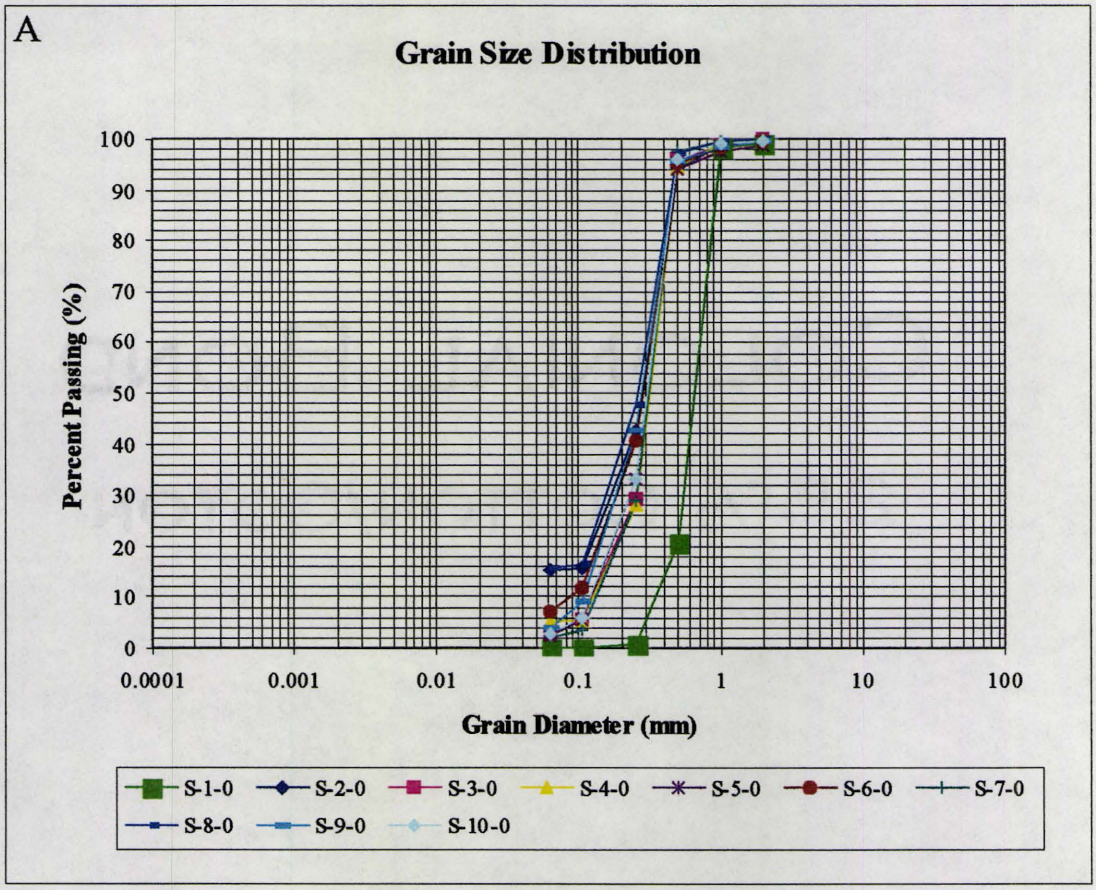


Figure 12. Soil profiles at PPNP study sites S, M and CHM, with depths to the water table.

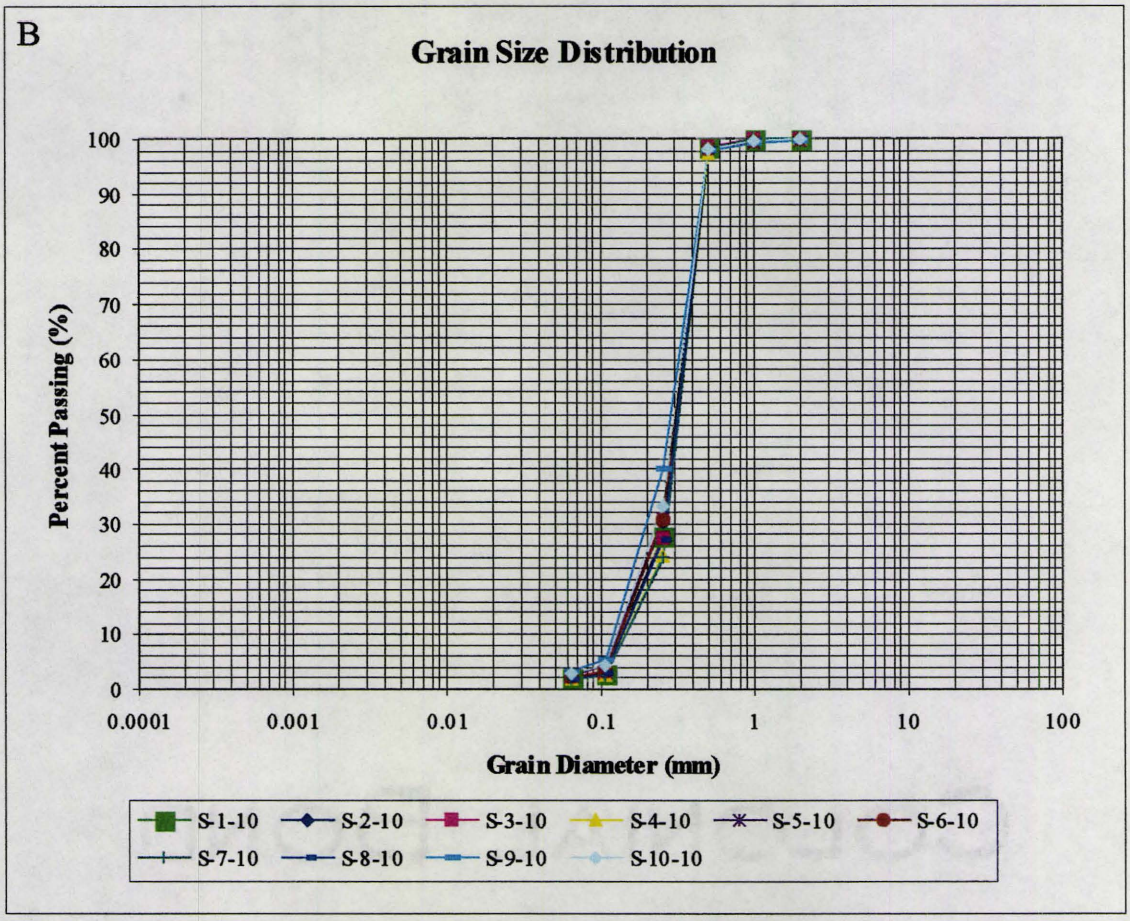
characterized by a buried horizon consisting of wet, aeolian sand with few roots. The wet Ah layer beneath (~40 cm) consists of black soil rich in organic matter, with few roots. The bottom layer C, of unknown vertical extent, consists of dark, gray-brown, well-sorted, coarse, wet sand.

The %silt and clay, %sand, and %gravel are presented in Table 6 and Figure 13. According to the soil textural triangle, the uppermost 0 to 15 cm of soil at CHM, M and S have a sandy texture and with the naked eye are hard to distinguish from one another (Figure 14). For further analyses, grain size distribution tests were performed on the shallow (0-5 cm) and deep (10-15 cm) soils obtained from the study sites according to Section 3.7. The d_{10} and d_{50} results of the grain size analyses are presented in Table 7.

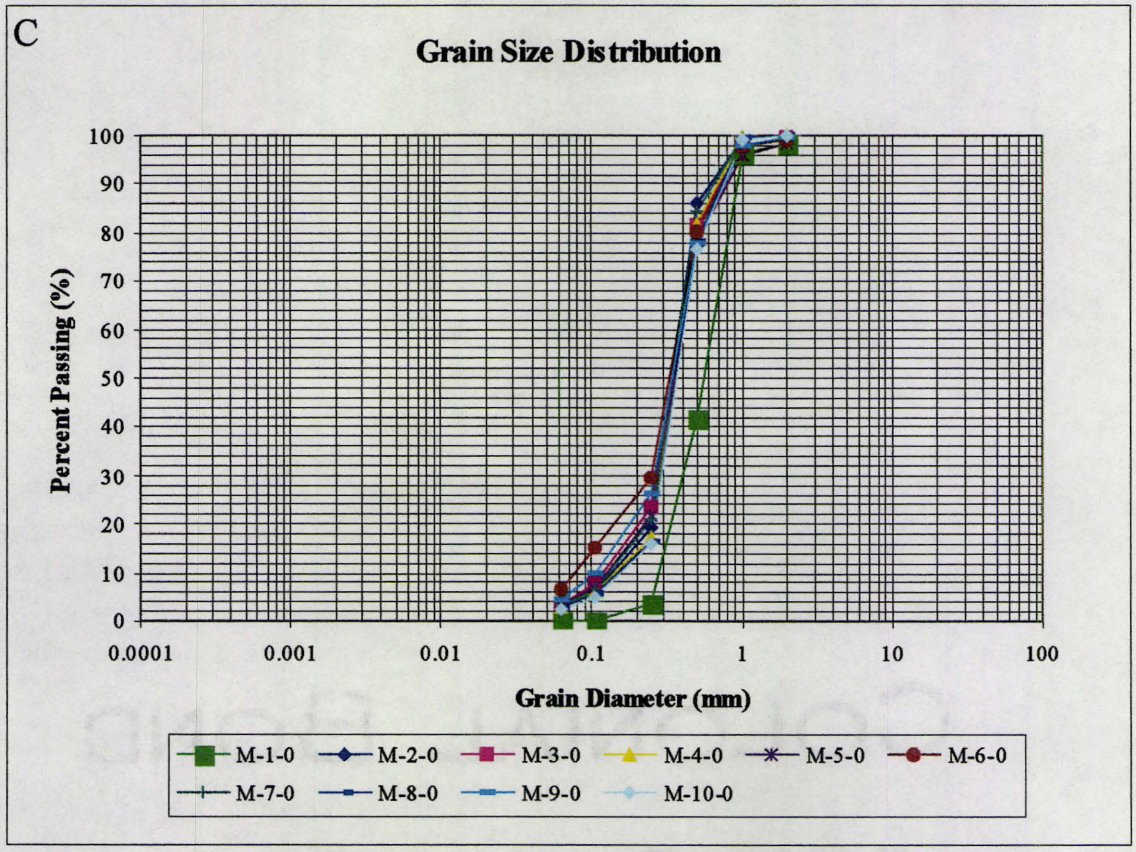
Figure 13. Grain size distribution curves at S, M and CHM in the shallow and deep soils.



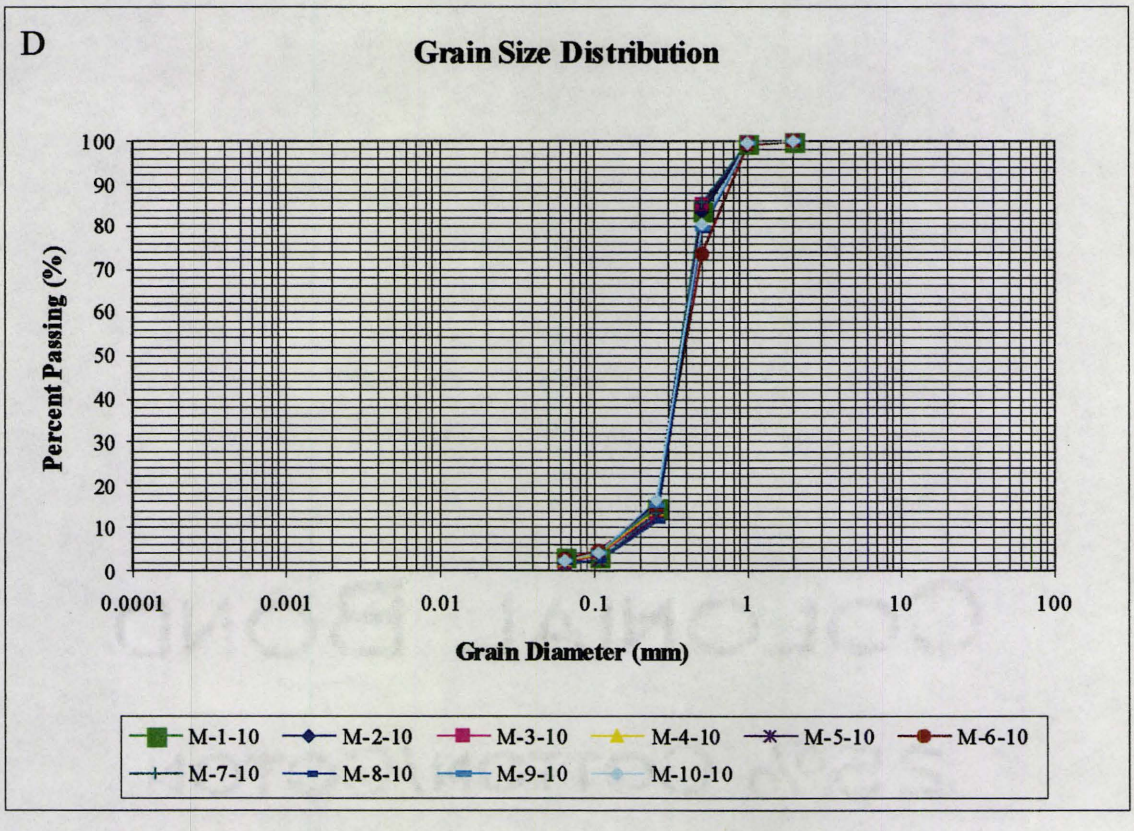
B


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
S-1-10
S-2-10
S-3-10
S-4-10
S-5-10
S-6-10
S-7-10
S-8-10
S-9-10
S-10-10

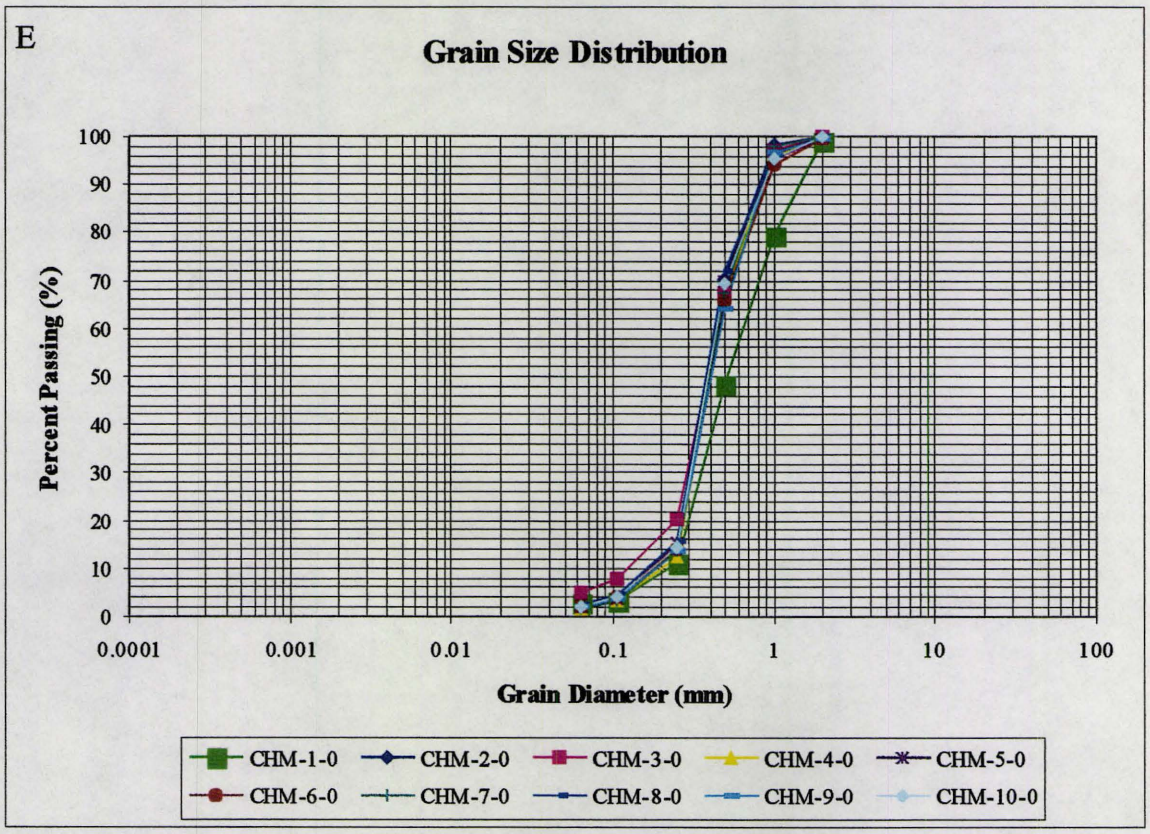
C


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
M-1-0
M-2-0
M-3-0
M-4-0
M-5-0
M-6-0
M-7-0
M-8-0
M-9-0
M-10-0

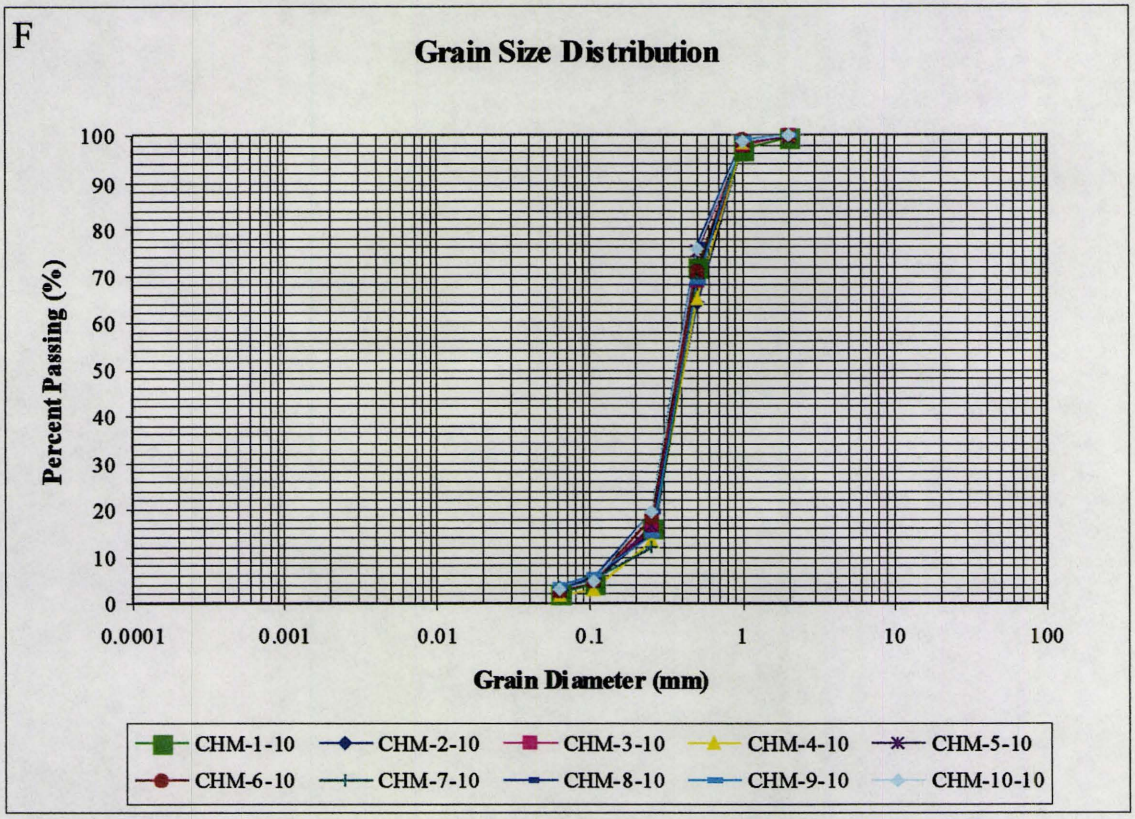
D


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
M-1-10
M-2-10
M-3-10
M-4-10
M-5-10
M-6-10
M-7-10
M-8-10
M-9-10
M-10-10

E


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
CHM-1-0
CHM-2-0
CHM-3-0
CHM-4-0
CHM-5-0
CHM-6-0
CHM-7-0
CHM-8-0
CHM-9-0
CHM-10-0

F


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
CHM-1-10
CHM-2-10
CHM-3-10
CHM-4-10
CHM-5-10
CHM-6-10
CHM-7-10
CHM-8-10
CHM-9-10
CHM-10-10

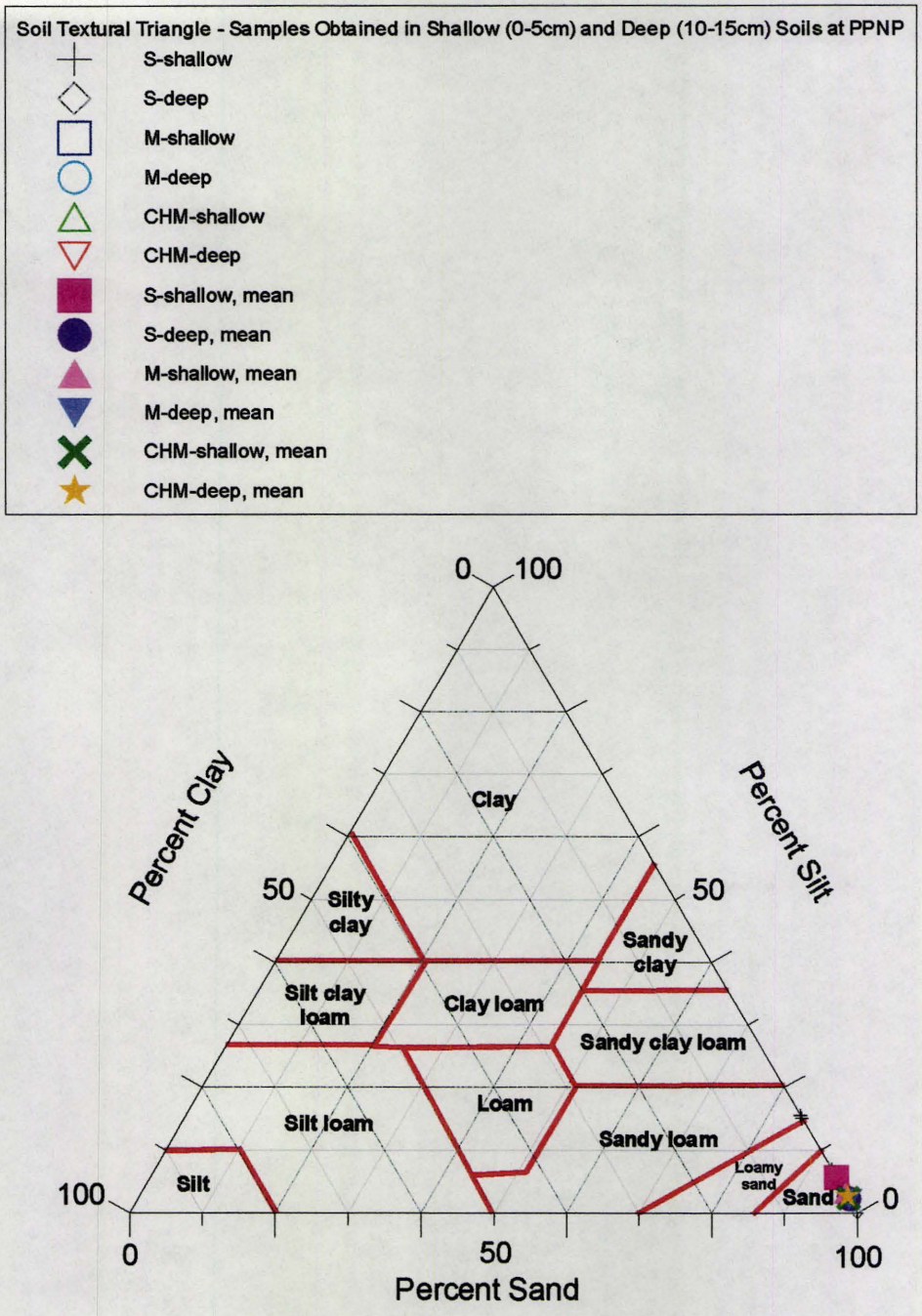


Figure 14. Soil textural triangle illustrating the texture of the shallow and deep soils at S, M and CHM.

Table 6. %Silt and clay, %sand and %gravel of shallow (0 – 5 cm) and deep (10 – 15 cm) soil samples from S, M and CHM at PPNP.

		SHALLOW					
	SILT and CLAY	SAND					GRAVEL
SITE ID	<0.063mm	Very Fine 0.05-0.1mm	Fine 0.1-0.2mm	Medium 0.2-0.5mm	Coarse 0.5-1mm	Very Coarse 1-2mm	>2mm
S-1-0	0.04	0.00	0.65	19.98	77.89	1.43	0.00
S-2-0	15.13	0.45	26.92	52.09	4.33	1.09	0.00
S-3-0	2.57	3.03	23.51	66.90	3.00	0.88	0.13
S-4-0	5.13	0.14	22.99	66.24	4.63	0.79	0.07
S-5-0	2.48	2.88	27.80	60.88	3.51	1.39	1.05
S-6-0	7.02	4.65	28.95	54.64	3.30	1.04	0.39
S-7-0	2.04	1.44	25.29	69.08	1.83	0.25	0.08
S-8-0	15.58	0.70	31.29	49.62	2.46	0.36	0.00
S-9-0	3.93	5.03	33.52	53.29	2.80	0.89	0.54
S-10-0	2.75	3.01	27.32	63.13	2.92	0.60	0.27
Mean	5.67	2.13	24.82	55.58	10.67	0.87	0.25
M-1-0	0.00	0.17	3.47	38.24	54.55	3.56	0.00
M-2-0	2.85	3.41	12.88	66.95	13.03	0.72	0.16
M-3-0	3.47	4.44	15.61	58.23	16.36	1.61	0.28
M-4-0	2.93	3.04	11.06	64.90	17.47	0.56	0.04
M-5-0	3.27	3.68	14.59	56.67	17.82	2.38	1.59
M-6-0	6.41	8.70	14.26	51.13	17.40	1.34	0.76
M-7-0	3.14	3.58	14.28	63.44	14.98	0.54	0.03
M-8-0	2.96	2.86	10.75	61.80	21.06	0.52	0.05
M-9-0	4.45	5.23	16.36	51.92	20.14	1.42	0.48
M-10-0	2.40	2.69	10.71	60.66	22.60	0.83	0.12
Mean	3.19	3.78	12.40	57.40	21.54	1.35	0.35
CHM-1-0	3.08	0.10	8.15	36.96	30.85	20.86	0.00
CHM-2-0	1.90	1.84	10.12	56.38	28.11	1.51	0.14
CHM-3-0	4.88	3.15	12.19	47.23	29.61	2.87	0.08
CHM-4-0	1.61	1.63	9.24	54.26	29.74	3.04	0.49
CHM-5-0	2.05	1.69	11.73	54.33	25.73	4.08	0.39
CHM-6-0	2.15	1.95	9.83	51.65	28.55	5.66	0.22
CHM-7-0	1.72	1.69	10.18	53.64	30.71	1.98	0.08
CHM-8-0	2.51	2.21	10.99	56.16	24.57	3.44	0.12
CHM-9-0	1.98	1.60	9.86	50.41	32.96	2.93	0.27
CHM-10-0	2.10	1.84	10.52	55.13	26.04	4.16	0.20
Mean	2.40	1.77	10.28	51.62	28.69	5.05	0.20

DEEP							
	SILT and CLAY	SAND					GRAVEL
SITE ID	<0.063mm	Very Fine 0.05-0.1mm	Fine 0.1-0.2mm	Medium 0.2-0.5mm	Coarse 0.5-1mm	Very Coarse 1-2mm	>2mm
S-1-10	2.06	0.92	24.78	70.76	1.43	0.05	0.00
S-2-10	2.77	1.46	26.09	67.60	1.66	0.25	0.16
S-3-10	1.84	0.92	24.61	71.24	1.30	0.07	0.03
S-4-10	1.72	0.69	21.91	73.30	2.21	0.15	0.02
S-5-10	2.47	1.72	26.97	66.94	1.32	0.18	0.40
S-6-10	2.25	1.17	27.29	67.51	1.57	0.15	0.06
S-7-10	1.73	0.71	21.56	74.31	1.53	0.12	0.04
S-8-10	1.86	0.87	24.51	70.86	1.69	0.13	0.09
S-9-10	3.37	2.18	34.64	57.71	1.55	0.28	0.27
S-10-10	2.82	1.43	29.10	64.78	1.66	0.12	0.08
Mean	2.29	1.24	26.30	68.25	1.61	0.16	0.12
M-1-10	3.06	0.05	11.79	69.11	15.50	0.49	0.00
M-2-10	2.15	2.06	11.98	67.32	15.76	0.60	0.12
M-3-10	2.03	1.50	9.71	71.72	14.46	0.52	0.05
M-4-10	2.11	1.41	10.81	66.22	18.83	0.59	0.04
M-5-10	1.61	0.83	10.22	71.99	14.78	0.49	0.08
M-6-10	2.68	2.15	10.52	58.42	25.45	0.71	0.06
M-7-10	1.23	0.95	11.37	72.18	13.97	0.29	0.01
M-8-10	1.62	0.86	9.10	67.45	20.65	0.30	0.01
M-9-10	2.32	1.98	10.83	64.41	19.89	0.47	0.09
M-10-10	2.46	1.66	12.34	64.31	18.74	0.44	0.05
Mean	2.13	1.35	10.87	67.31	17.80	0.49	0.05
CHM-1-10	2.04	2.16	12.13	55.57	25.10	3.00	0.00
CHM-2-10	2.83	1.72	10.82	48.86	34.21	1.46	0.10
CHM-3-10	2.68	2.44	10.52	53.36	28.94	1.92	0.13
CHM-4-10	1.61	1.38	10.17	51.91	33.20	1.54	0.19
CHM-5-10	2.35	2.23	11.96	58.76	23.23	1.20	0.27
CHM-6-10	2.66	2.18	13.29	52.81	28.24	0.76	0.05
CHM-7-10	3.29	1.71	7.02	57.15	30.12	0.58	0.12
CHM-8-10	2.89	2.60	13.96	56.95	22.70	0.81	0.09
CHM-9-10	3.70	2.07	8.62	54.14	30.66	0.77	0.04
CHM-10-10	2.85	1.95	14.65	56.24	23.06	1.11	0.14
Mean	2.69	2.04	11.31	54.57	27.95	1.32	0.11

Table 7. Grain size analyses results (d_{10} and d_{50}) of shallow (0 – 5 cm) and deep (10 – 15 cm) soil samples from S, M and CHM at PPNP.

	Shallow		Deep	
	d_{10} (mm)	d_{50} (mm)	d_{10} (mm)	d_{50} (mm)
S-1	0.35	0.61	0.14	0.31
S-2	-	0.28	0.12	0.30
S-3	0.12	0.31	0.15	0.31
S-4	0.13	0.31	0.15	0.31
S-5	0.13	0.30	0.13	0.30
S-6	0.09	0.28	0.13	0.30
S-7	0.14	0.31	0.15	0.32
S-8	-	0.27	0.14	0.31
S-9	0.11	0.28	0.12	0.28
S-10	0.12	0.30	0.12	0.30
Mean	0.15	0.33	0.14	0.30
M-1	0.28	0.54	0.17	0.35
M-2	0.14	0.33	0.17	0.35
M-3	0.12	0.35	0.19	0.36
M-4	0.16	0.35	0.17	0.37
M-5	0.13	0.35	0.20	0.37
M-6	0.08	0.33	0.17	0.38
M-7	0.14	0.34	0.19	0.36
M-8	0.15	0.36	0.22	0.37
M-9	0.11	0.35	0.17	0.38
M-10	0.17	0.38	0.17	0.36
Mean	0.15	0.37	0.18	0.37
CHM-1	0.22	0.51	0.16	0.38
CHM-2	0.18	0.40	0.17	0.40
CHM-3	0.12	0.39	0.16	0.39
CHM-4	0.20	0.40	0.19	0.40
CHM-5	0.17	0.39	0.16	0.37
CHM-6	0.18	0.40	0.16	0.38
CHM-7	0.19	0.40	0.19	0.40
CHM-8	0.16	0.38	0.15	0.37
CHM-9	0.18	0.41	0.17	0.40
CHM-10	0.18	0.40	0.15	0.36
Mean	0.18	0.41	0.17	0.39

In the table, the sample mean d_{10} grain size in the shallow soils is highest at CHM (0.18 mm) and the same at M (0.15 mm) and S (0.15 mm). The sample mean d_{50} in the shallow soils is highest at CHM (0.41 mm) and lowest at S (0.33 mm). ANOVA tests for the d_{10} of the shallow soils (Table 8) indicate that the three study sites have texturally similar soil types, all study sites being sandy in texture. ANOVA tests for the d_{50} of the shallow soils indicate that there are only significant differences between CHM and S.

Table 8. ANOVA results of d_{10} and d_{50} in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

d_{10} (0-5)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

d_{50} (0-5)	CHM	M	S
CHM	\	NS	S
M	NS	\	NS
S	S	NS	\

S: significant difference
NS: no significant difference

In the table, the sample mean d_{10} grain size in the deep soils is highest at M (0.18 mm) and lowest at S (0.14 mm). The sample mean d_{50} in the deep soils is highest at CHM (0.39 mm) and lowest at S (0.30 mm). ANOVA tests for the deep soils (Table 9) indicate that for d_{10}, only CHM and M have texturally similar soil types, but that for d_{50}, all study sites have texturally dissimilar soils.

Table 9. ANOVA results of d_{10} and d_{50} in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

d_{10} (10-15)	CHM	M	S
CHM	\	NS	S
M	NS	\	S
S	S	S	\

d_{50} (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	S
S	S	S	\

When comparing the shallow soils to the deep soils in the table, the sample mean d_{10} grain size is higher in the shallow soils at CHM and S, but lower in the shallow soils at M. The sample mean d_{50} grain size is higher in the shallow soils at CHM and S and the same in the shallow soils and deep soils of M. T-tests for CHM, M and S (Table 10) indicate that there are no significant differences in d_{10} and d_{50} between the shallow soils and deep soils.

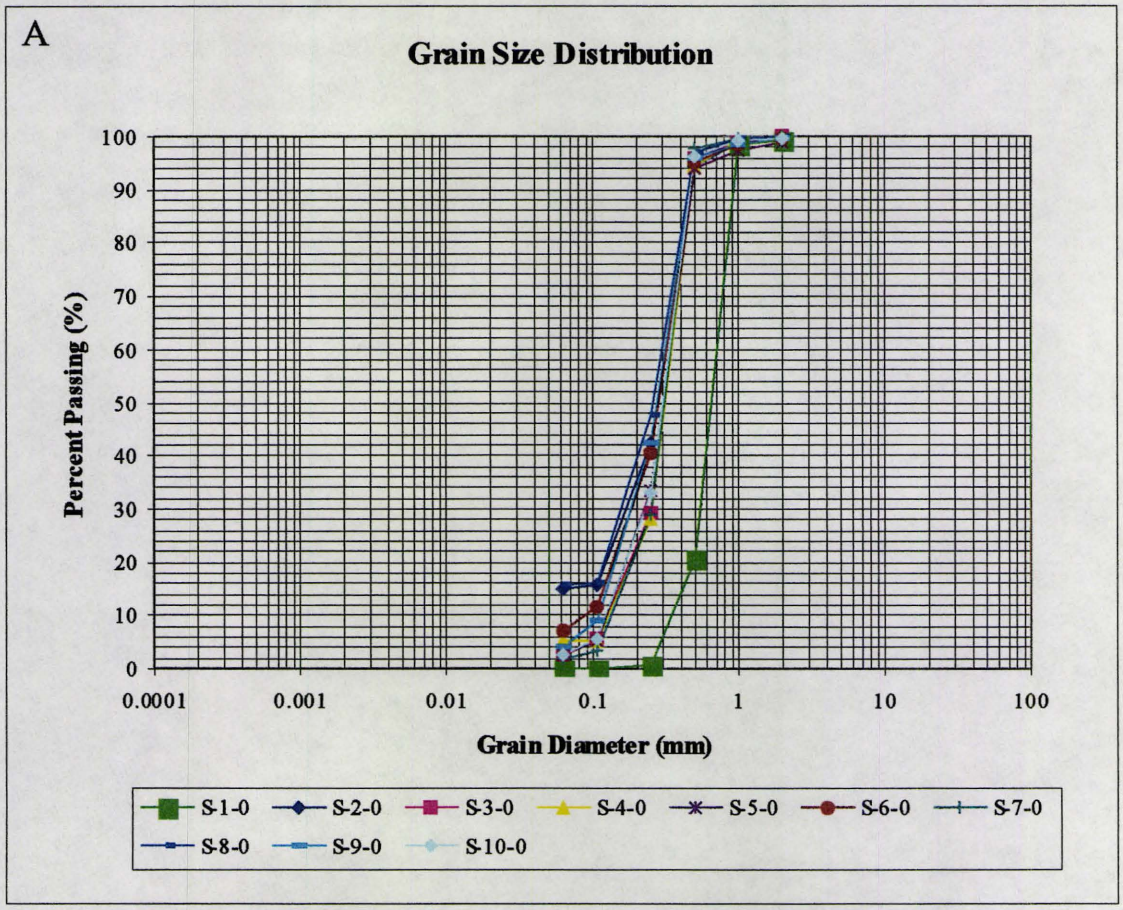
Table 10. T-test results of d_{10} and d_{50} between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

d_{10}	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	NS	\
S (10-15)	\	\	NS

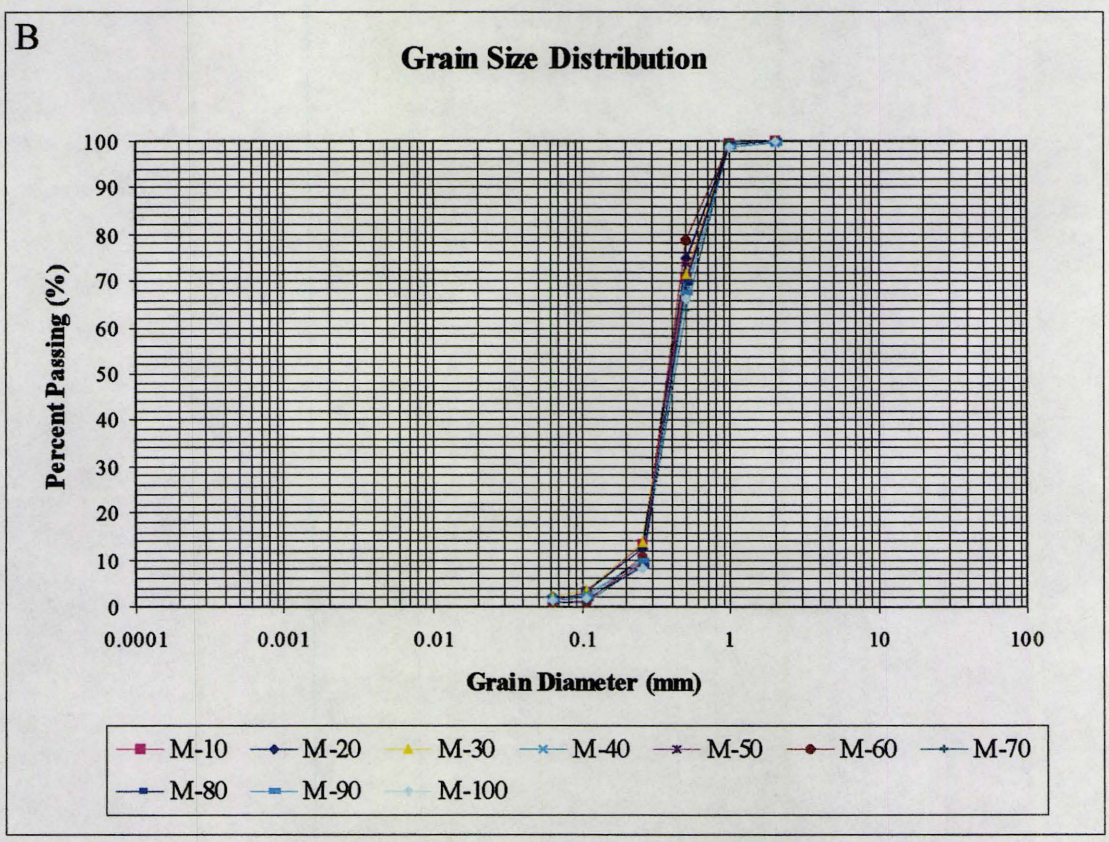
d_{50}	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	NS	\
S (10-15)	\	\	NS

The %silt and clay, %sand, and %gravel of soils from 10 to 100 cm depth are presented in Table 11 and Figure 15. According to the soil textural triangle, the soils at CHM, M and S with depth are also sandy in texture (Figure 16). To assess the grain size distribution of the soils in a vertical profile from 10 to 100 cm depth, the d_{10} and d_{50} were determined by analyses of soil cores obtained at 10 cm intervals at these locations at the study sites. These results are presented in Table 12.

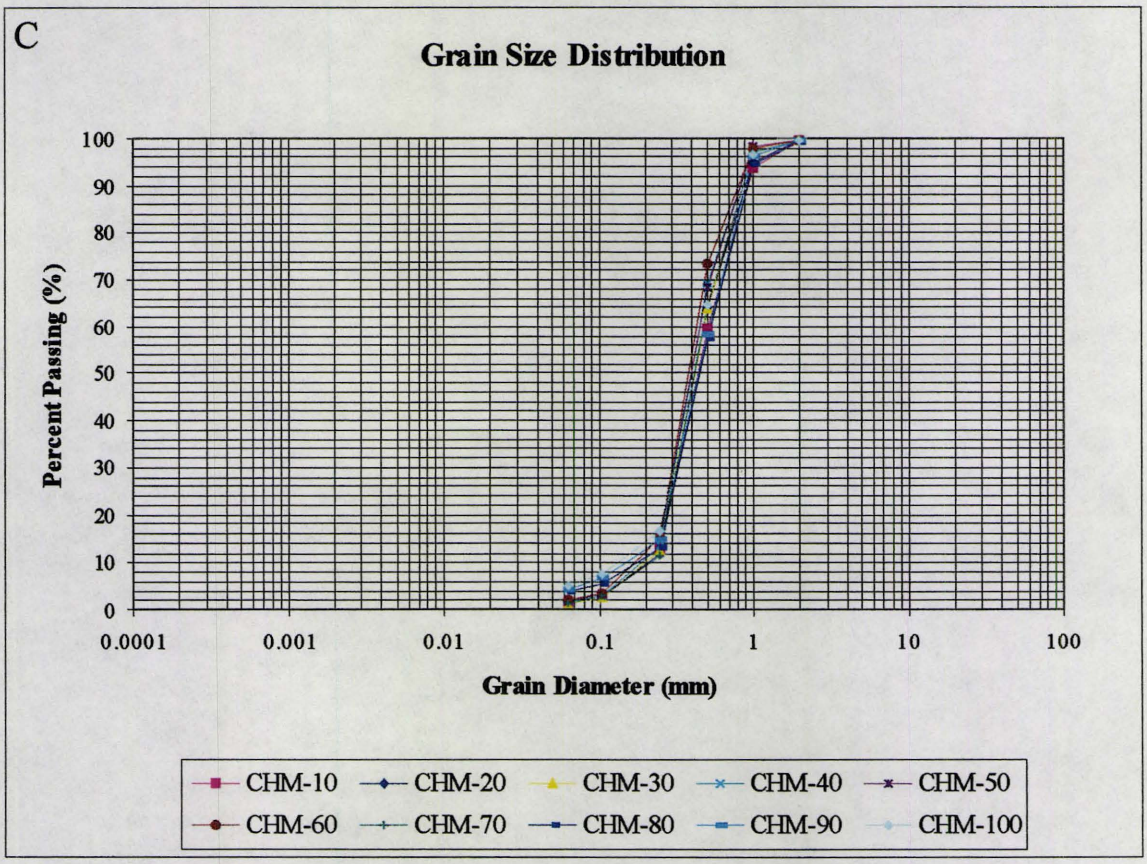
Figure 15. Grain size distribution analyses with depth.



B


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
M-10
M-20
M-30
M-40
M-50
M-60
M-70
M-80
M-90
M-100

C


Grain Size Distribution
Percent Passing (%)
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.001
0.01
0.1
1
10
100
Grain Diameter (mm)
CHM-10
CHM-20
CHM-30
CHM-40
CHM-50
CHM-60
CHM-70
CHM-80
CHM-90
CHM-100

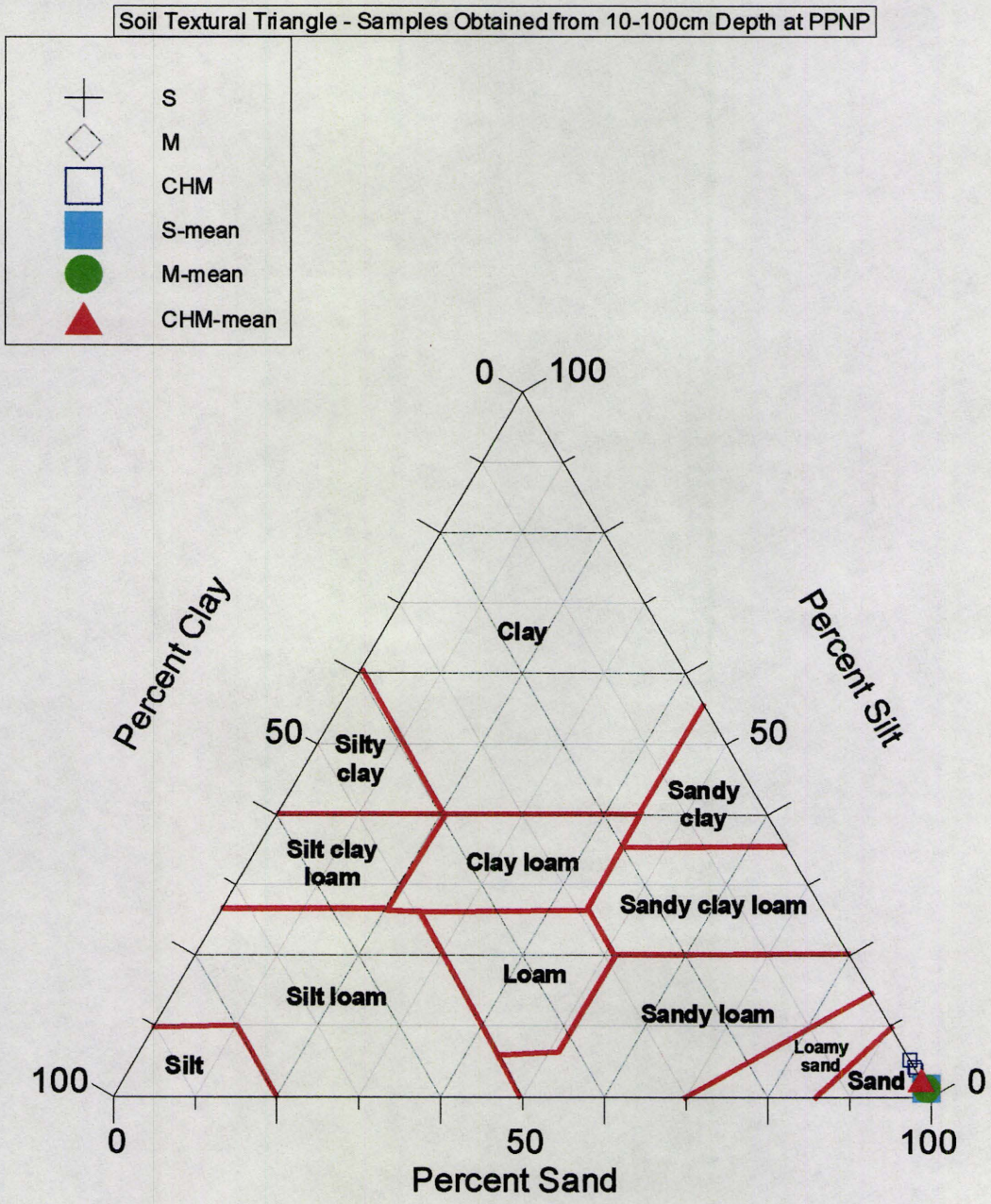


Figure 16. Soil textural triangle illustrating the texture of the soils with depth at S, M and CHM.

Table 11. %Silt and clay, %sand and %gravel of soil samples from 10 to 100 cm depth from S, M and CHM at PPNP.

	WITH DEPTH						
	SILT and CLAY	SAND					GRAVEL
SITE ID	<0.063mm	Very Fine 0.05-0.1mm	Fine 0.1-0.2mm	Medium 0.2-0.5mm	Coarse 0.5-1mm	Very Coarse 1-2mm	>2mm
S-10	1.64	3.5	29.2	50.3	9.6	3.7	2.10
S-20	2.22	2.0	29.5	61.3	3.7	1.0	0.22
S-30	1.33	1.3	36.3	58.6	2.1	0.2	0.14
S-40	2.06	1.1	33.3	61.6	1.8	0.2	0.10
S-50	1.58	1.3	38.0	57.0	1.8	0.2	0.04
S-60	0.79	0.4	32.2	64.1	2.0	0.3	0.13
S-70	0.55	0.4	31.9	64.9	2.1	0.1	0.01
S-80	0.81	0.4	23.9	72.4	2.2	0.2	0.02
S-90	0.48	0.3	28.3	68.2	2.6	0.2	0.00
S-100	0.65	0.1	20.8	75.9	2.2	0.2	0.03
Mean	1.2	1.1	30.3	63.4	3.0	0.6	0.3
M-10	1.4	1.7	10.1	57.2	28.9	0.4	0.20
M-20	2.04	1.2	9.3	62.4	24.4	0.5	0.10
M-30	1.95	1.6	10.0	57.7	28.2	0.5	0.03
M-40	1.64	0.8	7.5	59.3	30.0	0.5	0.24
M-50	0.71	0.4	8.3	64.5	25.7	0.2	0.05
M-60	0.64	0.3	9.8	67.9	21.1	0.2	0.00
M-70	0.66	0.4	7.8	55.0	35.7	0.5	0.01
M-80	1.29	0.5	6.9	61.0	29.5	0.6	0.14
M-90	0.14	0.8	7.9	57.6	31.2	0.9	0.48
M-100	1.25	0.6	6.2	58.0	32.8	0.9	0.16
Mean	1.2	0.8	8.4	60.1	28.8	0.5	0.1
CHM-10	1.23	1.4	9.8	47.0	34.2	6.0	0.41
CHM-20	1.61	1.1	9.1	52.2	30.9	4.6	0.48
CHM-30	1.34	1.4	9.7	51.3	33.1	2.6	0.43
CHM-40	1.74	1.3	10.3	56.0	28.4	1.9	0.36
CHM-50	1.63	1.7	11.8	53.1	30.0	1.5	0.35
CHM-60	1.96	1.6	11.6	58.1	24.8	1.4	0.48
CHM-70	1.36	1.5	8.5	53.3	32.5	2.5	0.35
CHM-80	3.78	1.8	7.3	44.3	37.4	4.7	0.72
CHM-90	4.16	2.5	8.0	43.7	38.0	3.4	0.35
CHM-100	5.19	2.5	8.8	48.1	31.8	3.0	0.52
Mean	2.4	1.7	9.5	50.7	32.1	3.2	0.4

Table 12. Grain size analyses results (d_{10} and d_{50}) of soil samples from 10 to 100 cm depth from S, M and CHM at PPNP.

	d_{10} (mm)	d_{50} (mm)
S-10	0.12	0.31
S-20	0.13	0.30
S-30	0.12	0.29
S-40	0.13	0.29
S-50	0.12	0.28
S-60	0.14	0.30
S-70	0.14	0.30
S-80	0.15	0.31
S-90	0.15	0.31
S-100	0.16	0.32
Mean	0.14	0.30
M-10	0.19	0.39
M-20	0.20	0.39
M-30	0.18	0.39
M-40	0.25	0.40
M-50	0.25	0.39
M-60	0.23	0.38
M-70	0.25	0.41
M-80	0.25	0.40
M-90	0.25	0.40
M-100	0.25	0.41
Mean	0.23	0.40
CHM-10	0.20	0.43
CHM-20	0.22	0.41
CHM-30	0.20	0.41
CHM-40	0.19	0.40
CHM-50	0.18	0.40
CHM-60	0.17	0.37
CHM-70	0.22	0.41
CHM-80	0.18	0.43
CHM-90	0.16	0.42
CHM-100	0.14	0.40
Mean	0.19	0.41

In the table, the sample mean d_{10} grain size is highest at M (0.23 mm) and lowest at S (0.14 mm). d_{10} ANOVA tests for the soils (Table 13) indicate that the three study sites have texturally dissimilar soil types with depth. There are significant differences in the d_{10} grain sizes of the soils at CHM, M and S.

Table 13. ANOVA results of d_{10} soil samples from 10 to 100 cm depth from S, M and CHM at PPNP.

d_{10} (10-100)	CHM	M	S
CHM	\	S	S
M	S	\	S
S	S	S	\

In the table, the sample mean d_{50} is highest at CHM (0.41 mm) and lowest at S (0.30 mm). d_{50} ANOVA tests for the soils (Table 14) indicate that two out of the three study sites have texturally dissimilar soil types with depth. There are only no significant differences in the d_{50} grain sizes of the soils at CHM and M.

Table 14. ANOVA results of d_{50} soil samples from 10 to 100 cm depth from S, M and CHM at PPNP.

d_{50} (10-100)	CHM	M	S
CHM	\	NS	S
M	NS	\	S
S	S	S	\

The percent mineral matter (%MM) contents of samples from the study sites, presented in Table 15, were determined in conjunction with the analyses for percent organic carbon (%OC) in McMaster University labs according to Section 3.6.

Table 15. %MM (McMaster lab) results of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

	Shallow	Deep
	%MM	%MM
S-P1	80.46	92.98
S-P2	52.70	97.47
S-P3	55.54	94.13
S-P4	62.08	97.57
S-P5	87.28	96.33
Mean	67.61	95.70
M-P1	84.91	94.87
M-P2	69.25	95.50
M-P3	52.80	94.90
M-P4	72.80	92.89
M-P5	90.62	98.18
Mean	74.07	95.27
CHM-6	79.19	88.63
CHM-P1	73.18	59.08
CHM-P2	79.21	79.90
CHM-P3	80.72	90.39
CHM-P4	68.61	79.92
Mean	76.18	79.58

In the table, the sample mean %MM in the shallow soils between sites is highest at CHM (76.18%) and lowest at S (67.61%). ANOVA tests for the shallow soils (Table 16) indicate that all three pairs show no significant differences. There are no significant differences in the mineral contents of CHM, M and S.

Table 16. ANOVA results of %MM (McMaster lab) in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

%MM (0-5)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

In the table, the sample mean %MM in the deep soils between sites is lowest at CHM (79.58%) and highest at S (95.70%). ANOVA tests for the deep soils (Table 17) indicate that two out of the three pairs show significant differences. For only S and M, there are no significant differences in mineral contents between the deep soils.

Table 17. ANOVA results of %MM (McMaster lab) in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%MM (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

When comparing the shallow soils to the deep soils, the soils at depth at CHM, M and S all have higher %MM than the shallow soils. T-tests for CHM (Table 18) indicate that there are no significant differences in the mineral contents between the shallow soils and deep soils. However, t-tests for M and S indicate that there are significant differences in the mineral contents between the shallow soils and deep soils.

Table 18. T-test results of %MM (McMaster lab) between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%MM	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

The bulk densities and porosities were determined according to Sections 3.8 and 3.9. The bulk density and porosity results for the shallow and deep soil samples are presented in Table 19.

Table 19. Bulk density and porosity results of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

	Shallow		Deep	
	Bulk Density (g/cm^3)	**Porosity (%)**	**Bulk Density (g/cm^3)**	**Porosity (%)**
S-1	0.38	82.0	1.03	51.6
S-2	0.31	85.5	0.32	84.9
S-3	0.21	90.0	1.13	46.9
S-4	0.47	77.7	0.88	58.5
S-5	0.29	86.5	1.44	32.1
S-6	0.39	81.5	0.96	54.6
S-7	1.26	40.6	1.30	39.0
S-8	0.53	75.0	1.05	50.4
S-9	0.79	62.9	1.19	43.8
S-10	0.64	69.9	1.25	41.3
Mean	0.53	75.1	1.06	50.3
M-1	0.65	69.6	1.20	43.4
M-2	0.79	63.1	1.34	36.8
M-3	0.44	79.3	1.15	45.8
M-4	1.14	46.3	1.16	45.4
M-5	0.84	60.5	1.44	32.0
M-6	0.30	85.9	0.99	53.4
M-7	0.30	85.9	1.27	40.2
M-8	0.84	60.6	1.09	48.7
M-9	0.66	69.1	1.08	49.1
M-10	0.61	71.1	0.91	57.1
Mean	0.66	69.1	1.16	45.2
CHM-1	0.46	78.2	0.46	78.1
CHM-2	0.54	74.7	0.81	62.0
CHM-3	0.34	84.2	0.48	77.6
CHM-4	0.59	72.1	0.74	65.1
CHM-5	0.57	73.3	0.82	61.6
CHM-6	0.53	75.2	0.71	66.6
CHM-7	0.81	62.1	1.02	51.9
CHM-8	0.53	75.1	0.64	69.7
CHM-9	0.69	67.6	1.07	49.7
CHM-10	0.44	79.1	0.56	73.9
Mean	0.55	74.2	0.73	65.6

All study sites show a high degree of variability in bulk density, as can be seen in Figure 17. In the table, the sample mean bulk density of the shallow soils is highest at M (0.66 g/cm^3) and lowest at S (0.53 g/cm^3). In the table, the sample mean porosity of the shallow soils is highest at S (75.1%) and lowest at M (69.1%). ANOVA tests for the shallow soils (Table 20) indicate that there are no significant differences between the three pairs; bulk densities and porosities of S, M and CHM are similar. In the table, the sample mean bulk density of the deep soils is highest at M (1.16 g/cm^3) and lowest at CHM (0.73 g/cm^3). In the table, the sample mean porosity of the deep soils is highest at CHM (65.6%) and lowest at M (45.2%). ANOVA tests for the deep soils (Table 21) indicate that there are significant differences between two out of the three pairs. For M and S only, there are no significant differences in bulk densities and porosities.

Table 20. ANOVA results of bulk density and porosity in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

Bulk density (0-5)	**CHM**	**M**	**S**
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Porosity (0-5)	**CHM**	**M**	**S**
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

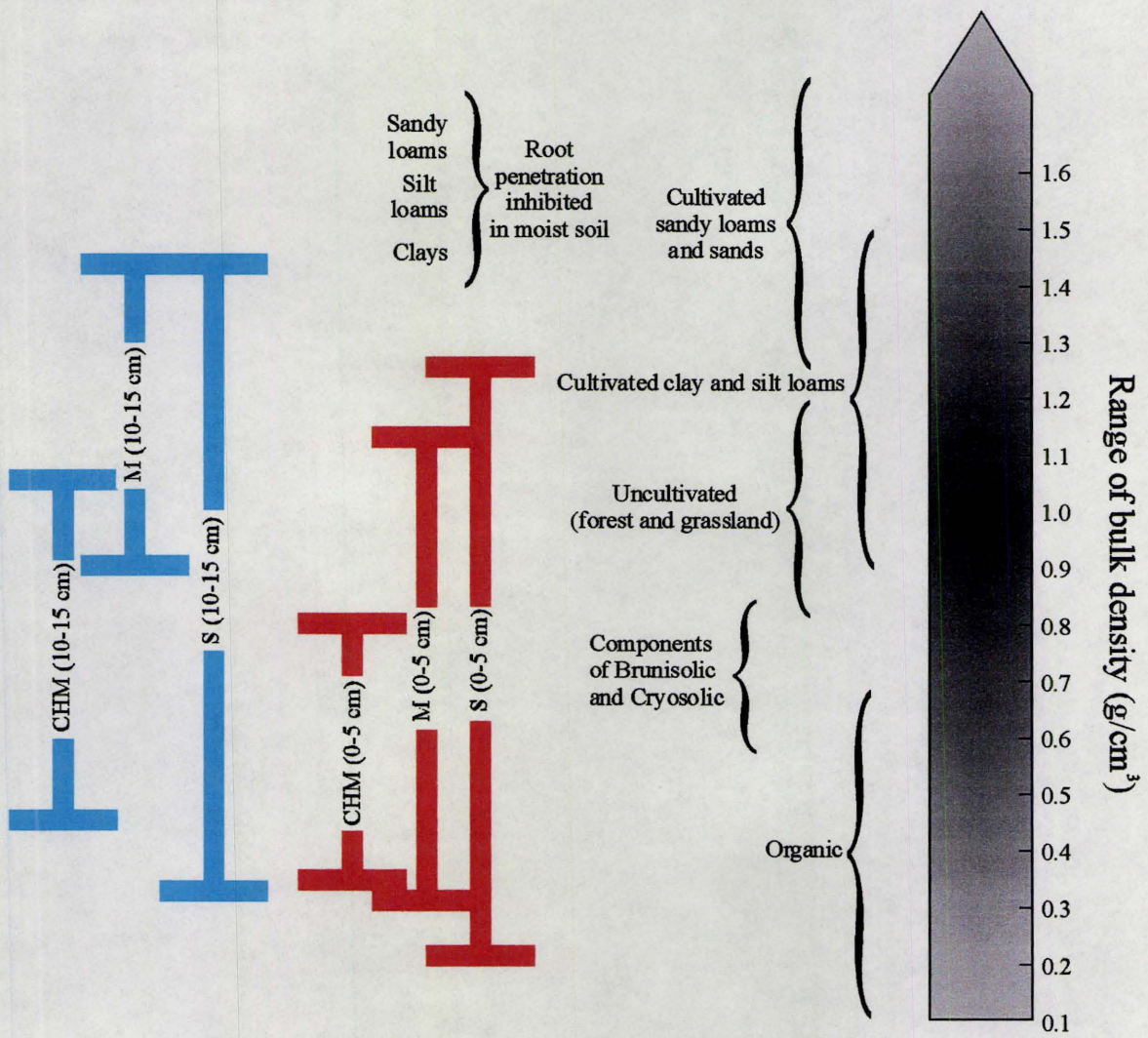


Figure 17. Variation in bulk density at S, M and CHM (modified from Fig. 4.15 in The Nature and Properties of Soils, 12th ed., by Brady and Weil, 1999).

Table 21. ANOVA results of bulk density and porosity in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Bulk density (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

Porosity (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

In the table, when comparing the shallow soils to the deep soils, the soils at depth at CHM, M and S all have higher sample mean bulk densities than the shallow soils. T-tests for study sites CHM, M and S (Table 22) indicate that there are significant differences in the bulk densities and porosities between the shallow soils and deep soils. This is consistent with higher organic matter contents in the shallow soils.

Table 22. T-test results of bulk density and porosity between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Bulk density	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	S	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

Porosity	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	S	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

The bulk density and porosity of soils from 10 to 100 cm depth are presented in Table 23.

Table 23. Bulk density and porosity results of soil samples from 10 to 100 cm depth from S, M and CHM at PPNP.

	Bulk Density (g/cm^3)	Porosity (%)
S-10	0.55	73.9
S-20	1.12	47.4
S-30	1.41	33.8
S-40	1.34	36.7
S-50	1.39	34.7
S-60	1.47	31.0
S-70	1.42	33.2
S-80	1.42	33.1
S-90	1.36	35.8
S-100	1.34	36.8
Mean	1.3	39.6
M-10	1.34	37.0
M-20	1.35	36.3
M-30	1.48	30.3
M-40	1.35	36.5
M-50	1.43	32.9
M-60	1.45	31.5
M-70	1.24	41.5
M-80	1.22	42.5
M-90	1.28	39.7
M-100	1.32	37.8
Mean	1.3	36.6
CHM-10	0.56	73.5
CHM-20	0.84	60.6
CHM-30	1.06	50.3
CHM-40	1.19	43.8
CHM-50	1.33	37.5
CHM-60	1.19	43.8
CHM-70	0.87	59.3
CHM-80	1.34	37.0
CHM-90	1.39	34.7
CHM-100	1.53	27.8
Mean	1.1	46.8

In the table, the sample mean bulk density is highest at S and M (1.3 g/cm^3) and lowest at CHM (1.1 g/cm^3). In the table, the mean porosity is highest at CHM (46.8%) and lowest at S and M (39.6% and 36.6%, respectively). Bulk density ANOVA tests for the soils (Table 24) indicate that the three study sites have similar bulk densities with depth. Porosity ANOVA tests for the soils (Table 24) indicate that there are no significant differences between S, M and CHM with depth.

Table 24. ANOVA results of bulk density and porosity from 10 to 100 cm depth from S, M and CHM at PPNP.

Bulk Density (10-100)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Porosity (10-100)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

In general, the first 0 to 15 cm of the soil profile at CHM are coarser soils than the soils at S and M. The first 0 to 15 cm of the soils at M are higher in mean %MM than the soils at S and CHM, which also have higher mean bulk densities than soils at S and CHM. The first 0 to 15 cm of the soils at CHM have higher mean porosities than the soils at S and M. However, with depth, the soils have similar bulk densities and porosities.

4.3 Soil Organic Matter

Soil organic matter (%OM) is generally used to represent the organic constituents in the soil, including undecayed plant and animal tissues, their partial decomposition products, and the soil biomass. Soil organic carbon (%OC) and soil organic nitrogen (%ON) are constituents of soil organic matter. Soil organic matter is an important factor to consider, because DDT, as a polar molecule, is readily adsorbed onto it. Because degradation reactions occur in soil water, DDT that is adsorbed will tend to persist, i.e. degrade more slowly. The OC:ON (C:N) ratio in soil is the ratio of carbon to nitrogen. The decomposition of matter is regulated in part by this ratio (Brady and Weil, 1999). The C:N ratio for optimal biological activity is about 25:1, with higher values being nitrogen limited and lower values being carbon limited. The average C:N ratio for soils is about 10:1 (Brady and Weil, 1999).

At PPNP, differences in the %OC, %OM,%ON and C/N that exist from site to site may be due to several factors. Some of the key factors include: (a) the land-use history at the Park (agricultural, recreational, housing); (b) the topography (dunes, hollows, flood plains); and (c) the hydrology (rise and fall of Lake and marsh levels, flooding). Some of the lesser factors include: (a) human activity (excavation of ditches, deposition of excavated material, burning of trees); and (b) erosion and deposition of aeolian sands atop surface soils.

The percent organic carbon (%OC) and percent organic nitrogen (%ON) determined by NLET (Environment Canada, Burlington, Ontario, Canada) are presented in Table 25. In the table, the sample mean %OC, %ON and %OM in the shallow soils are highest at CHM (12.79%, 1.22% and 22.01% respectively) and lowest at M (3.67%, 0.39% and 6.32% respectively). ANOVA tests for the shallow soils (Table 26) indicate that there are significant differences in the %OC, %ON and %OM between two out of the three pairs. There are only no significant differences in the %OC, %ON and %OM of M and S. However, for %OC/%ON, there are no significant differences between the soils at CHM, M and S.

*Table 25. %OC, %ON (NLET labs) and %OM (%OC*1.72) results of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.*

	Shallow				Deep			
	%OC	%ON	%OM	OC/ON	%OC	%ON	%OM	OC/ON
CHM-1	15.70	1.49	27.00	10.54	3.83	0.37	6.59	10.35
CHM-2	12.10	1.18	20.81	10.25	4.72	0.34	8.12	13.88
CHM-3	10.30	1.02	17.72	10.10	7.19	0.64	12.37	11.23
CHM-4	17.90	1.60	30.79	11.19	6.49	0.60	11.16	10.82
CHM-5	8.21	0.80	14.12	10.26	3.50	0.32	6.02	10.94
CHM-6	20.10	1.87	34.57	10.75	3.86	0.16	6.64	24.13
CHM-7	13.60	1.28	23.39	10.63	1.71	0.19	2.94	9.00
CHM-8	9.81	0.90	16.87	10.90	4.91	0.45	8.45	10.91
CHM-9	17.50	1.69	30.10	10.36	4.33	0.10	7.45	43.30
CHM-10	2.72	0.34	4.68	8.00	1.20	0.12	2.06	10.00
Mean	12.79	1.22	22.01	10.30	4.17	0.33	7.18	15.46
M-1	4.22	0.40	7.26	10.55	0.80	0.13	1.38	6.15
M-2	3.28	0.22	5.64	14.91	4.50	0.43	7.74	10.47
M-3	4.79	0.37	8.24	12.95	1.89	0.11	3.25	17.18
M-4	1.21	0.16	2.08	7.56	0.61	0.15	1.05	4.07
M-5	1.11	0.16	1.91	6.94	1.37	0.11	2.36	12.45
M-6	10.10	0.98	17.37	10.31	1.18	0.19	2.03	6.21
M-7	2.59	0.29	4.45	8.93	0.56	0.14	0.96	4.00
M-8	1.88	0.24	3.23	7.83	1.70	0.14	2.92	12.14
M-9	5.88	0.76	10.11	7.74	1.88	0.27	3.23	6.96
M-10	1.68	0.29	2.89	5.79	0.97	0.18	1.67	5.39
Mean	3.67	0.39	6.32	9.35	1.55	0.19	2.66	8.50
S-1	9.90	1.14	17.03	8.68	0.82	0.16	1.41	5.13
S-2	6.82	0.65	11.73	10.49	12.10	1.16	20.81	10.43
S-3	2.11	0.36	3.63	5.86	0.97	0.12	1.67	8.08
S-4	13.40	1.21	23.05	11.07	0.74	0.10	1.27	7.40
S-5	1.76	0.23	3.03	7.65	1.08	0.36	1.86	3.00
S-6	5.45	0.54	9.37	10.09	0.71	0.13	1.22	5.46
S-7	0.51	0.11	0.88	4.64	0.45	0.07	0.77	6.43
S-8	9.12	0.93	15.69	9.81	1.48	0.14	2.55	10.57
S-9	1.29	0.22	2.22	5.86	0.71	0.07	1.22	10.14
S-10	1.30	0.20	2.24	6.50	1.55	0.15	2.67	10.33
Mean	5.17	0.56	8.89	8.07	2.06	0.25	3.54	7.70

Table 26. ANOVA results of %OC, %ON, %OC/%ON (NLET labs) and %OM concentrations of soil sampling in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

%OC (0-5)		CHM	M	S
	CHM	\	S	S
	M	S	\	NS
	S	S	NS	\

%ON (0-5)		CHM	M	S
	CHM	\	S	S
	M	S	\	NS
	S	S	NS	\

%OM (0-5)		CHM	M	S
	CHM	\	S	S
	M	S	\	NS
	S	S	NS	\

%OC/%ON (0-5)		CHM	M	S
	CHM	\	NS	NS
	M	NS	\	NS
	S	NS	NS	\

In the table, the sample mean %OC and %ON in the deep soils are higher at CHM (4.17%, 0.33% and 7.18% respectively) and lowest at M (1.55%, 0.19% and 2.66% respectively). In the table, the sample mean %OC/%ON ratio in the shallow and deep soils is highest at CHM (10.30% and 15.46%, respectively) and lowest at S (8.07% and 7.70%, respectively). ANOVA tests for the deep soils (Table 27) indicate that there are no significant differences in the %OC, %ON and %OM for all three pairs. However, for %OC/%ON, there are only significant differences between the soils of CHM and S.

Table 27. ANOVA results of %OC, %ON, %OC/%ON (NLET labs) and %OM concentrations of soil sampling in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%OC (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

%ON (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

%OM (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

%OC/%ON (10-15)	CHM	M	S
CHM	\	NS	S
M	NS	\	NS
S	S	NS	\

In the table, when comparing the shallow soils to the deep soils, CHM, M and S have higher sample mean %OC, %ON and %OM in the shallow soils than in the deep soils. When comparing the shallow soils to the deep soils, %OC/%ON is higher in the deep soils at CHM, but higher in the shallow soils at M and S. T-tests for CHM, M and S (Table 28) indicate that there are significant differences in the %OC, %ON and %OM between the shallow soils and deep soils for CHM and M only. T-tests for CHM, M and S indicate that there are no significant differences in the %OC/%ON between the shallow soils and deep soils.

Table 28. T-test results of %OC, %ON, %OC/%ON (NLET labs) and %OM concentrations between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%OC	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	S	\	\
M (10-15)	\	S	\
S (10-15)	\	\	NS

%ON	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	S	\	\
M (10-15)	\	S	\
S (10-15)	\	\	NS

%OM	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	S	\	\
M (10-15)	\	S	\
S (10-15)	\	\	NS

%OC/%ON	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	NS	\
S (10-15)	\	\	NS

A plot of %ON versus %OC (Figure 18) for the shallow soils for each study site shows, an approximate ratio of 10:1 %OC to %ON at all three study sites. This is consistent with the average C/N ratio in most soils. At depth, the correlation is weaker, however the concentrations of %OC and %ON at most study sites are not as high. Because the NLET (Environment Canada, Burlington, Ontario, Canada) values for %OC didn't appear to agree with the bulk density values at the corresponding sampling points, 5 replicate samples were obtained at random from the study sites in the shallow (0-5 cm) and deep soils (10-15 cm), for a total of 30 samples. These samples were analyzed for

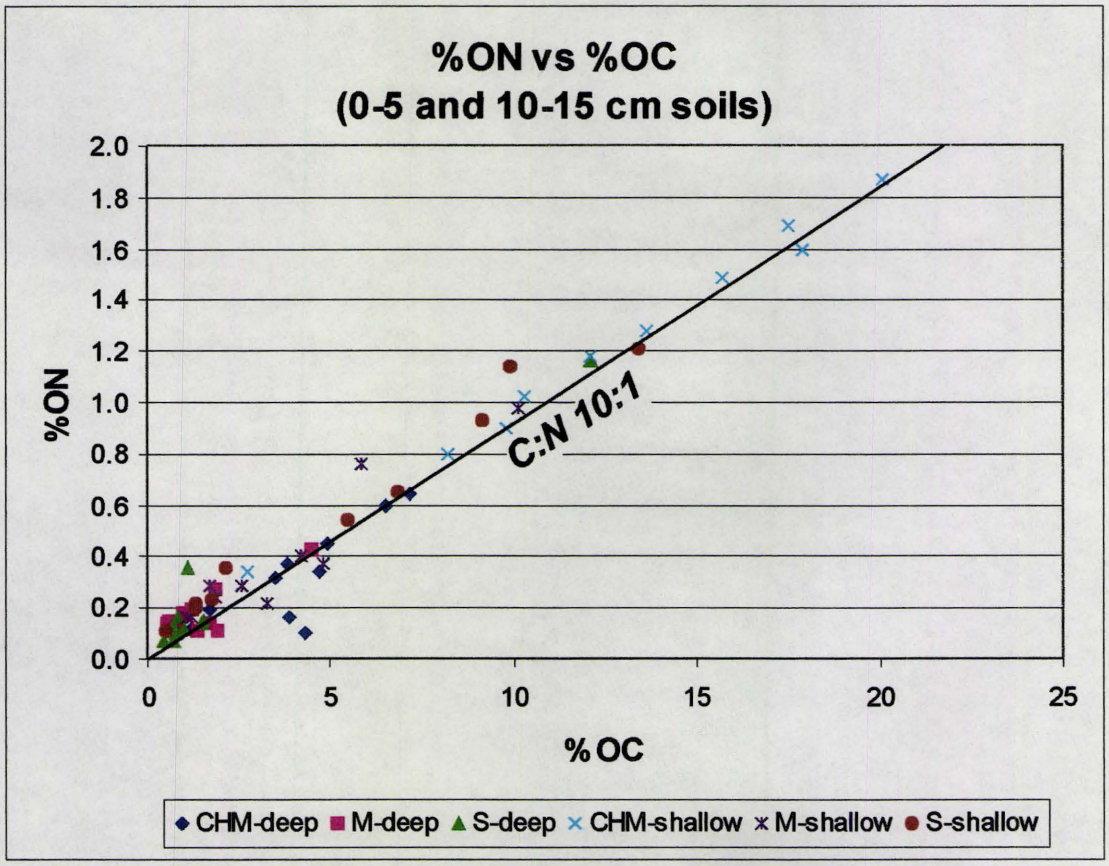


Figure 18. %ON vs %OC at S, M and CHM in the shallow and deep soils.

%OM and %OC according to Section 3.6 in McMaster University labs. The organic matter (%OM) contents, presented in Table 29, were determined in conjunction with the analyses for organic carbon (%OC).

Table 29. %OM and %OC (McMaster lab) results of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

	Shallow			Deep		
	%OM	**%OC**	**>17% OM = organic soil**	**%OM**	**%OC**	**>17% OM = organic soil**
S-P5	12.72	7.40	-	3.67	2.14	-
S-P4	37.92	22.05	Organic	2.43	1.41	-
S-P3	44.46	25.85	Organic	5.87	3.41	-
S-P2	47.30	27.50	Organic	2.53	1.47	-
S-P1	19.54	11.36	Organic	7.02	4.08	-
Mean	32.39	18.83	Organic	4.30	2.50	-
M-P5	9.38	5.46	-	1.82	1.06	-
M-P4	27.20	15.81	Organic	7.11	4.14	-
M-P3	47.20	27.44	Organic	5.10	2.97	-
M-P2	30.75	17.88	Organic	4.50	2.62	-
M-P1	15.09	8.77	-	5.13	2.98	-
Mean	25.93	15.07	Organic	4.73	2.75	-
CHM-P4	31.39	18.25	Organic	20.08	11.68	Organic
CHM-P3	19.28	11.21	Organic	9.61	5.59	-
CHM-P2	20.79	12.09	Organic	20.10	11.69	Organic
CHM-P1	26.82	15.59	Organic	40.92	23.79	Organic
CHM-6	20.81	12.10	Organic	11.37	6.61	-
Mean	23.82	13.85	Organic	20.42	11.87	Organic

In the table, the sample mean %OM and %OC in the shallow soils are highest at S (32.39% and 18.83%, respectively) and lowest at CHM (23.82% and 13.85%, respectively). ANOVA tests for the shallow soils (Table 30) indicate that there are no

significant differences in %OM and %OC between the three pairs. In the table, the sample mean %OM and %OC in the deep soils are highest at CHM (20.42% and 11.87%, respectively) and lowest at S (4.30% and 2.50%, respectively). ANOVA tests for the deep soils (Table 31) indicate that there are significant differences in %OM and %OC between two out of the three pairs. For S and M only, there are no significant differences in %OM and %OC.

Table 30. ANOVA results of %OM and %OC (McMaster lab) concentrations of soil sampling in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

%OM (0-5)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

%OC (0-5)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Table 31. ANOVA results of %OM and %OC (McMaster lab) concentrations of soil sampling in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%OM (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

%OC (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

In the table, when comparing the shallow soils to the deep soils, the sample mean %OM and %OC are higher in the shallow soils at CHM, M and S than in the deep soils. T-tests for CHM (Table 32) indicate that there are no significant differences in the %OM and %OC between the shallow soils and deep soils. T-tests for M and S indicate that there are significant differences in the %OM and %OC between the shallow soils and deep soils.

Table 32. T-test results of %OM and %OC (McMaster lab) concentrations between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%OM	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

%OC	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

When comparing the %OC and %OM NLET data to the %OC and %OM calculated in McMaster University labs (Table 33) of the shallow soils and deep soils, T-tests results indicate that there are no significant differences for CHM, but there are significant differences in the shallow soils for M and S only. This is due to discrepancies in the sampling depths. The samples analyzed for %OC and %OM my NLET contain lower %OM and %OC, because they were obtained in February when the ground surface was still frozen. The first 2 cm (approximately) of soil were thus discarded during the sampling. However, when the samples analyzed by McMaster University labs were

obtained, the first 2 cm were not discarded but rather, used as part of the study sample. This first 2 cm contained an abundance of roots at this time. We do not see this discrepancy at CHM, likely because the soil is very rich in organic matter to a greater depth, i.e. there is likely very little difference with %OM and %OC for the first 20 cm (approximately) of the soil profile at CHM.

Table 33. T-test results of %OM and %OC (NLET) %OM and %OC (McMaster lab) in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

		%OC-McMaster
CHM (0-5)	**%OC-NLET**	NS
CHM (10-15)	**%OC-NLET**	NS
M (0-5)	**%OC-NLET**	S
M (10-15)	**%OC-NLET**	NS
S (0-5)	**%OC-NLET**	S
S (10-15)	**%OC-NLET**	NS

		%OM-McMaster
CHM (0-5)	**%OM-NLET**	NS
CHM (10-15)	**%OM-NLET**	NS
M (0-5)	**%OM-NLET**	S
M (10-15)	**%OM-NLET**	NS
S (0-5)	**%OM-NLET**	S
S (10-15)	**%OM-NLET**	NS

Moreover, all five replicate shallow samples from CHM contained greater than 17% organic matter, which would make them organic horizons. In the deep soils, only three out of the five samples at CHM met the criteria of an organic horizon. In the shallow soils of M and S, three out of the five samples and four out of the five samples were organic horizons, respectively. The samples in the deep soils at M and S all had less than 17% organic matter. According to the PPNP Soil Survey of Essex County

Report No. 11 (Richards et al., 1989), in areas where there was a high concentration of crops, such as at M and S, the organic matter content of the soil has been lowered.

The mean %OM, %OC, %ON and C:N ratio of the first 0 to 15 cm of the soil profile are higher at CHM than M and S. The C:N ratio of approximately 10:1 is consistent with that of most soils. Most of the shallow soils at CHM, M and S classify as an organic horizon, however the deep soils at CHM also classify as an organic horizon.

4.4 Soil Moisture

Soil moisture is an important physical property for several reasons. Firstly, soil moisture controls the degree of anaerobiosis. Secondly, the presence of water increases microbial activity, which increases degradation reactions, such as the degradation of DDT to DDE and DDD. In particular, Guenzi and Beard (1976) observed that water had an influence on the rate of degradation of DDT in soil systems.

Soil moisture contents were determined according to Section 3.10, in conjunction with the bulk density analyses. The gravimetric water contents (GWC), volumetric water contents (VWC) and TDR-based water contents (volumetric) for the shallow and deep soil samples obtained from PPNP April 23 to 27, 2001 are presented in Table 34. In the table, the sample mean GWC and VWC in the shallow and deep soils are highest at CHM (88% and 44%; 70% and 45%, respectively) and lowest at M (37% and 19%; 10% and 12%, respectively).

Table 34. Results of %VWC (lab-based and TDR-based) and %GWC of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

	Shallow		Deep		0 – 20 cm
	%GWC – Lab	%VWC – Lab	%GWC– Lab	%VWC – Lab	%VWC – TDR
S-1	71	27	18	18	19.4
S-2	74	23	128	41	18.5
S-3	117	25	17	20	20.2
S-4	37	18	21	19	17
S-5	73	21	9	12	22
S-6	60	24	13	13	19.9
S-7	11	14	6	8	16.6
S-8	31	16	15	16	16.8
S-9	26	20	9	11	18.5
S-10	28	18	9	11	19.8
Mean	53	21	25	17	19
M-1	24	15	11	14	17.7
M-2	21	16	9	12	20.8
M-3	63	28	11	13	18.7
M-4	13	15	10	12	15.9
M-5	17	15	7	10	17.3
M-6	67	20	17	17	18.3
M-7	80	24	9	11	17.7
M-8	25	21	8	8	16
M-9	33	21	10	11	20.2
M-10	29	18	11	10	17.9
Mean	37	19	10	12	18
CHM-1	139	64	125	58	56.8
CHM-2	91	49	56	45	41.8
CHM-3	173	58	133	63	60.3
CHM-4	68	40	57	42	40.1
CHM-5	90	51	69	57	46.3
CHM-6	94	50	81	58	53.9
CHM-7	32	26	22	22	19.1
CHM-8	64	34	55	36	31.3
CHM-9	35	24	24	25	27.6
CHM-10	93	41	75	42	54
Mean	88	44	70	45	43

For the volume-based water contents (VWC and TDR), ANOVA tests for the shallow soils (Table 35) indicate that there are significant differences between two out of the three pairs; there are only no significant differences in volume-based water contents of M and S.

Table 35. ANOVA results of %VWC in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

%VWC (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

TDR (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

For the mass-based water contents (GWC), ANOVA tests for the shallow soils (Table 36) indicate that there are no significant differences between two out of the three pairs; there are only significant differences in the mass-based water contents of CHM and M.

Table 36. ANOVA results of %GWC in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

%GWC (0-5)	CHM	M	S
CHM	\	S	NS
M	S	\	NS
S	NS	NS	\

ANOVA tests for the deep soils (Table 37) indicate that there are significant differences between two out of the three pairs. There are only no significant differences in the water contents of M and S. Therefore, CHM is wetter than M and S.

Table 37. ANOVA results of %VWC and %GWC in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%VWC (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

%GWC (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

In the table, when comparing the shallow soils to the soils at depth, the shallow soils at CHM, M and S have a higher sample mean GWC than the soils at depth. The same trend is observed for the sample mean VWC in the shallow soils at M and S. The sample mean VWC at CHM is higher in the deeper soils. T-tests for CHM and S (Table 38) indicate that there are no significant differences in the volumetric and gravimetric water contents between the shallow soils and deep soils. However, t-tests for M indicate that there are significant differences in the volumetric and gravimetric water contents between the shallow soils and deep soils.

Table 38. T-test results of %VWC and %GWC between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

%VWC	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	NS

%GWC	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	NS

The mean soil moisture of the first 0 to 15 cm of the soil profile is higher in the soils at CHM than M and S. The mean soil moisture of the first 0 to 15 cm of the soil profile is lowest in the soils at M.

4.5 Lake, Marsh and Groundwater levels

The rise and fall of Lake Erie and marsh water levels are also of fundamental importance for this study, primarily because of their effects on other processes at PPNP. Effects such as: (a) the rise and fall of the water table; (b) the flooding of relatively lower-lying areas including CHM; (c) the moisture content of the soil; (d) the creation of anaerobic environments subsequent to flooding; and (e) the accumulation of organic matter in flooded soils, have a direct effect on DDT degradation.

The Lake and marsh share a common history. In 1971, a private agriculturist dredged a channel through the East Beach just north of the Park boundary to remove

"excess water" caused by high marsh water levels flooding the easterly relatively lower-lying portions of the Park (Anders, 1974; Department of Indian Affairs and Northern Development, no date). This subjected the Park marsh to direct Lake level fluctuations and storm action.

Over time, Lake levels and marsh levels have fluctuated by approximately 2 m and 1 m, respectively (Battin and Nelson, 1978). During the last seven years, the marsh elevation has been among the highest and lowest ever, as will be seen in Figure 20, ranging from 174.0 to 175.1 meters amsl (Crowe et al., 2002). Low water levels usually occur in November – December and high water levels in June – July. During low Lake and marsh levels, large marsh areas are exposed and dry. During high Lake and marsh levels (above 175.1 m amsl), the adjacent soils are flooded (Figure 19). For instance, a plot of the monthly mean Lake Erie water levels (Figure 20) indicates that the ground surface elevation of CHM was below that of the monthly mean Lake level elevation during1974, 1987 and 1997. Subsequently, CHM was flooded and S and M were not.

A flooded soil is different from a nonflooded soil in its physical, chemical and microbiological properties. A nonflooded soil is in an oxidized state (Sethunathan, 1973). Following flooding, oxygen interchange from the atmosphere to the soil is substantially restricted and the aerobic microorganisms consume the remaining "trapped" oxygen in the soil. A few days after flooding, a flooded soil consists of (Figure 21):

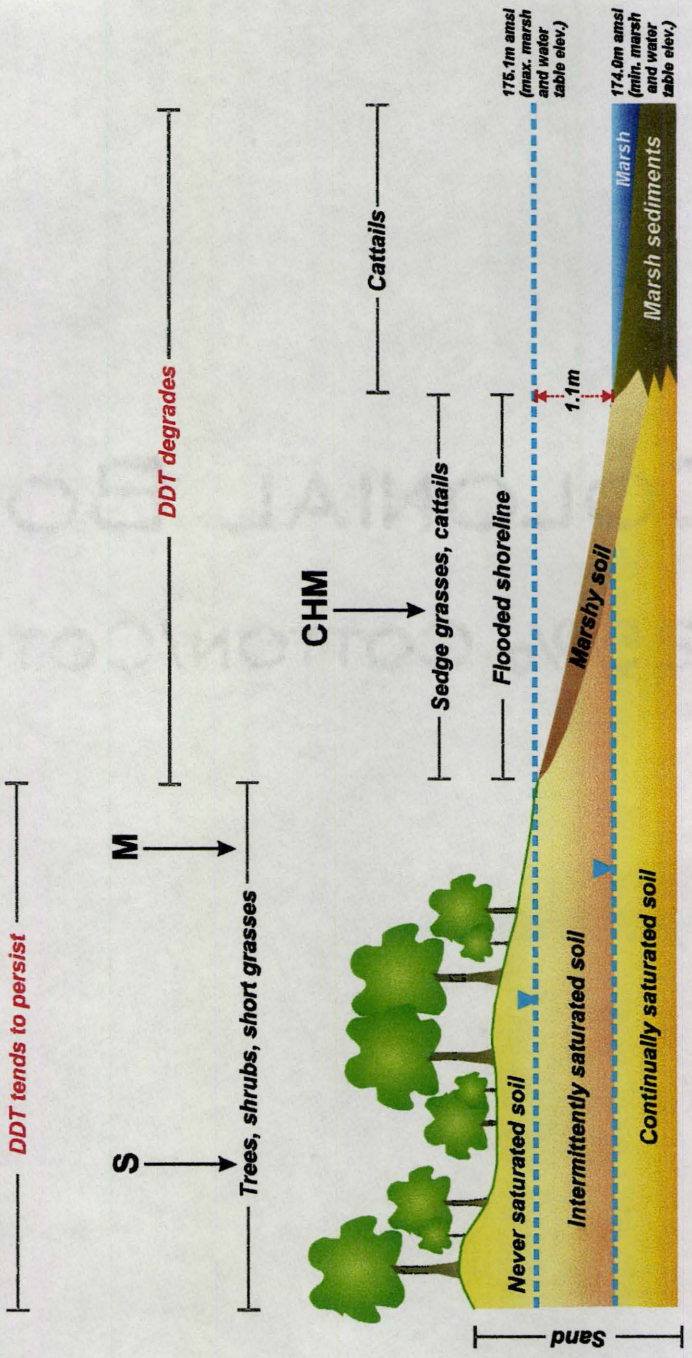


Figure 19. Cross-section from the marsh to the sand dunes illustrating the hydrological and soil conditions, as well as the local vegetation (modified from Crowe et al., 2002).

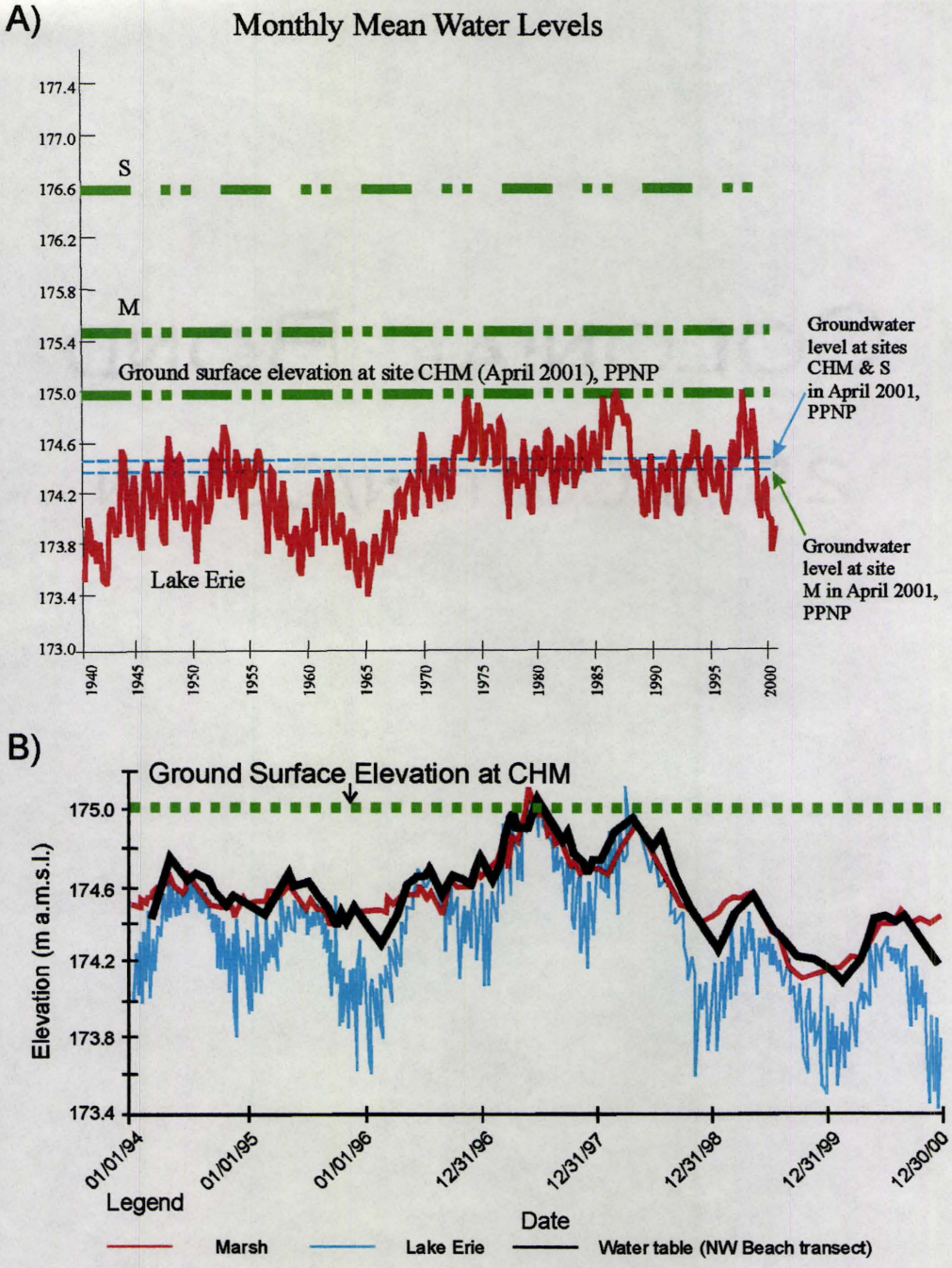


Figure 20. (a) Monthly mean Lake Erie Water levels, ground surface elevations, and water table elevations at study sites (U.S. Army Corps of Engineers); (b) water elevations at PPNP in Lake Erie, the marsh, and the water table from 1994 to 2000 (modified from Crowe et al., 2002).

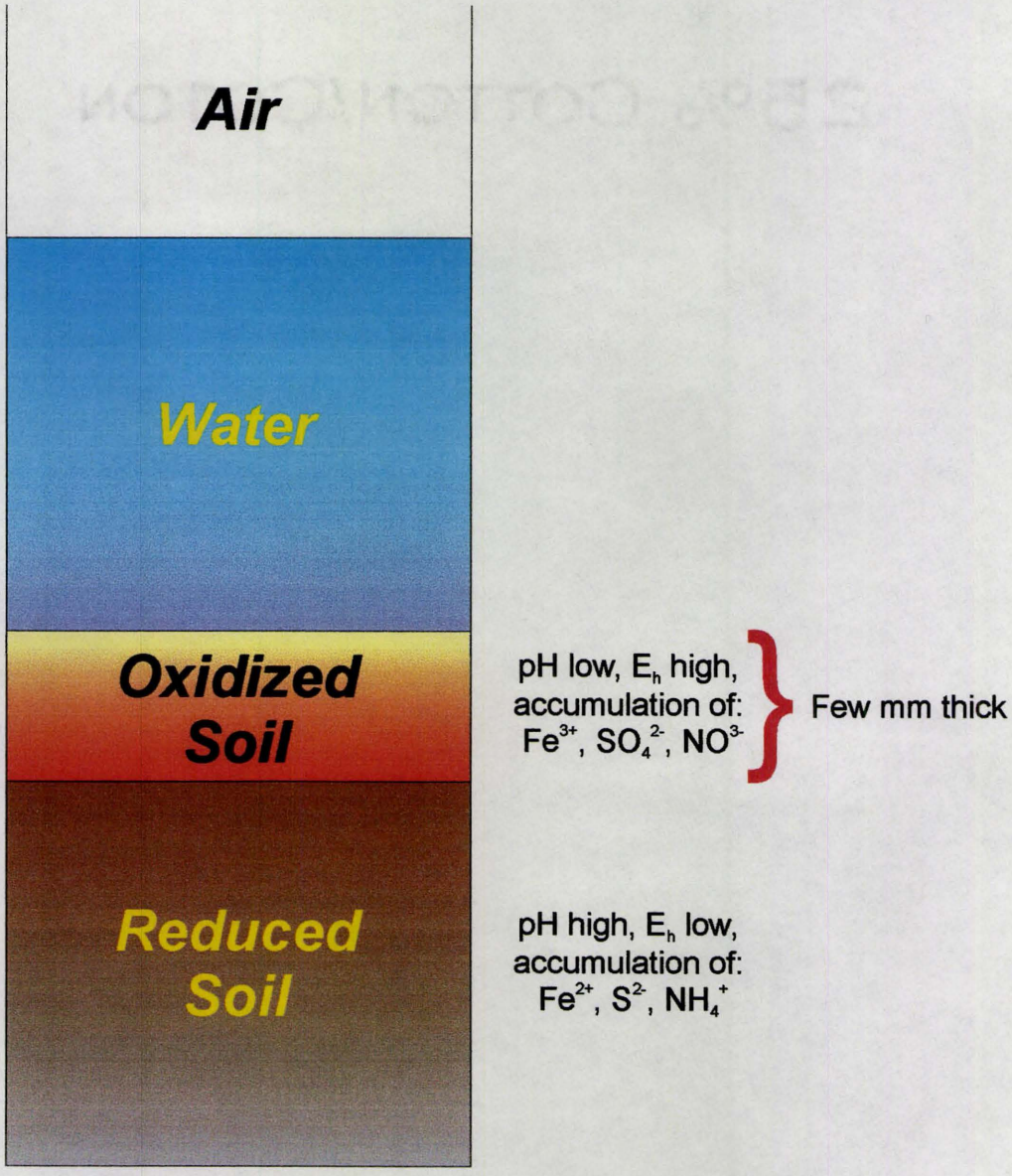


Figure 21. Schematic illustration of a flooded soil (modified from Sethunathan, 1973).

(a) standing water; (b) an upper, few mm thick oxidized soil layer; and (b) a reduced soil layer (Sethunathan, 1973).

In a flooded soil, the rate and pathway of DDT degradation differs from that in a nonflooded soil. For example, DDT is degraded to DDD in an anaerobic soil and to DDE in an aerobic soil. In studies by Samuel and Pillai (1989), 36.8% DDT, 48.5% DDE and 14.6% DDD were the main metabolites extracted from flooded soils after one month of incubation. However in unflooded soils, the main metabolites extracted after one month of incubation were predominantly DDT (92-96%) with some DDE.

Microbiological and physical mechanisms by which flooding could enhance the loss of DDT from soil are outlined by Boul et al. (1994). They include: (a) the creation of anaerobic environments in which microorganisms can degrade DDT to DDD; (b) the abiotic reductive dechlorination of DDT to DDD; (c) increased DDT loss through leaching, runoff and erosion; (d) increased export in plant and/or animal tissue due to increased productivity; (e) the promotion of volatilization; and (f) binding to soil particles and organic matter.

The rise and fall of the marsh also influence water table fluctuations. At PPNP, studies have shown that the water table fluctuates by up to 1 m from season to season and by up to 1.5 m from year to year (Crowe et al., 2002). Because of the relatively high K of the sands ($\sim 10^{-2}$ cm/s), the water table across a transect is essentially flat and does not vary by more than 20 centimeters relative to the lake level (Crowe et al., 2002). It may

rise to or above ground surface in some areas in very high lake level years (1984, 1987 and 1997 for instance) (Crowe et al., 2002).

As can be seen in Figure 22, the mean standard deviation of the water table at each well sampled by Crowe et al. (2002) over a period of 8 years indicates that the long-term depth to the water table is proportional to the elevation of the ground surface at the monitoring well. As the ground surface elevation increases, the depth to the water table increases. Thus, according to Crowe et al. (2002), the long-term mean depth to the water table can be estimated everywhere at PPNP based on ground surface elevation with the following:

Mean Water Depth (m) = [ground surface elevation (masl) – 174.56 (masl)]/0.976

Eq. 22.

During this study, groundwater levels were only obtained once during the year on April 26, 2001. These values are presented in Table 39. At this time, none of the studied areas were flooded by the marsh and water table elevations were well below that of ground surface. S, which is at the highest ground surface elevation, had the deepest water table at 1.87 meters below ground surface. M and CHM, at intermediate and lowest ground surface elevations respectively, had shallower water tables at 174.42 (0.98 meters below ground surface) and 174.53 (0.49 meters below ground surface) masl respectively. In February 2001, the water table at CHM was located at 55 cm below the surface and the soil was noticeably wet above it.

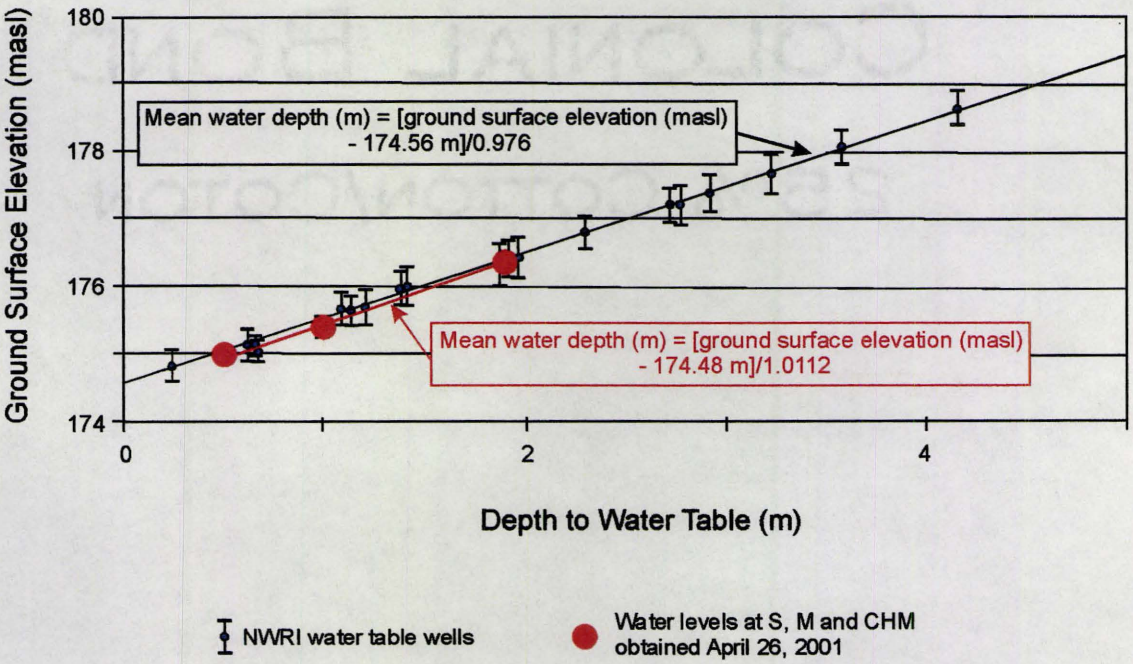


Figure 22. Relationship between depth to water table and ground surface elevation (modified from Crowe et al., 2002). The water levels at S, M and CHM plot approximately on the same curve as the NWRI water table wells.

Table 39. Groundwater levels obtained on April 26, 2001 from S, M and CHM at PPNP.

Site	Ground Surface Elevation (masl)	Groundwater Depth (m)	Groundwater Elevation (masl)
CHM	175.02	0.49	174.53
M	175.40	0.98	174.42
S	176.39	1.87	174.52

The water table across the transect running from the road through S and to the marsh is also essentially flat, which is consistent with observations by Crowe et al. (2002). In short, the ground surface elevation has no effect on the elevation of the water table at the study sites (Figure 22). As shown, the depth to water table at S, M and CHM is proportional to the to the elevation of the ground surface at the well hole. As the elevation increases, the depth to the water table also increases. Areas in the Park, such as CHM, that are relatively lower in ground surface elevation have surface soils that are thus closer to the water table. Areas such as S and M that are relatively higher in ground surface elevation than CHM have deeper depths to water table.

Because the S, M and CHM data points lie essentially on the same curve as those of Crowe et al. (2002), it is reasonable to assume that the long-term, mean depth to the water table at these sites can be estimated based on ground surface elevation with Eq. 22. The long-term, mean depth to the water table can this be based on the water table observations in local wells.

To assess the influence of ground surface elevation on soil VWC, a plot of ground surface elevation versus moisture content (%) was produced for samples obtained from

10 to 100 cm depth at 10 cm intervals, as well as for samples obtained at the 10 random sampling points within each site in the shallow (0-5 cm) and deep (10-15 cm) soils (Figure 23). As can be seen, according to the VWC contents obtained in the lab and in the field, CHM has the greatest VWC at surface and with depth, which means it is less well drained. This is consistent with its higher organic matter content. There is a higher degree of variability in the VWC with depth at CHM. CHM has a maximum moisture content at 20 cm depth and a minimum at about 80 cm depth. The lack of consistency between the TDR and lab data at CHM may be due to sample size. The change in VWC with depth at both S and M approximates zero.

The water table is deepest at S, the highest site topographically and shallowest at CHM, the lowest site topographically. During marsh levels above 174.0 m amsl, the soils at CHM only are flooded, because the maximum water levels do not exceed 175.1 m amsl and S and M have ground surface elevations that lie above 175.1 m amsl.

4.6 Hydraulic Conductivity

Up to this point, only the amount of water in the soil profile has been examined, but the hydraulic conductivity is also an important factor to consider in assessing DDT persistence. As seen in Sections 3.12 and 3.13, the hydraulic conductivity is an expression of how the soil transmits water. Ex-situ hydraulic conductivities were determined according to Section 3.12. In-situ hydraulic conductivities were determined

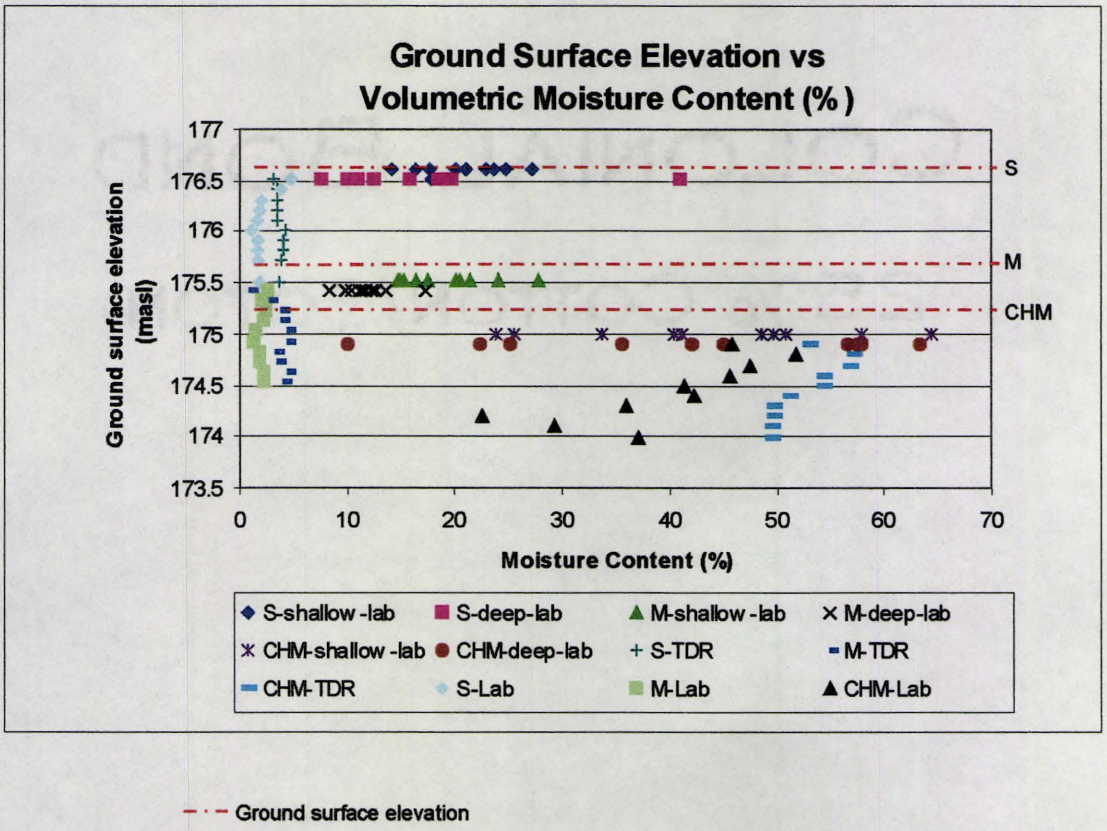


Figure 23. Moisture content as a function of ground surface elevation at S, M and CHM in the shallow and deep soils.

according to Section 3.13. In-situ and ex-situ hydraulic conductivities are presented in Table 40 and shown in Figure 24.

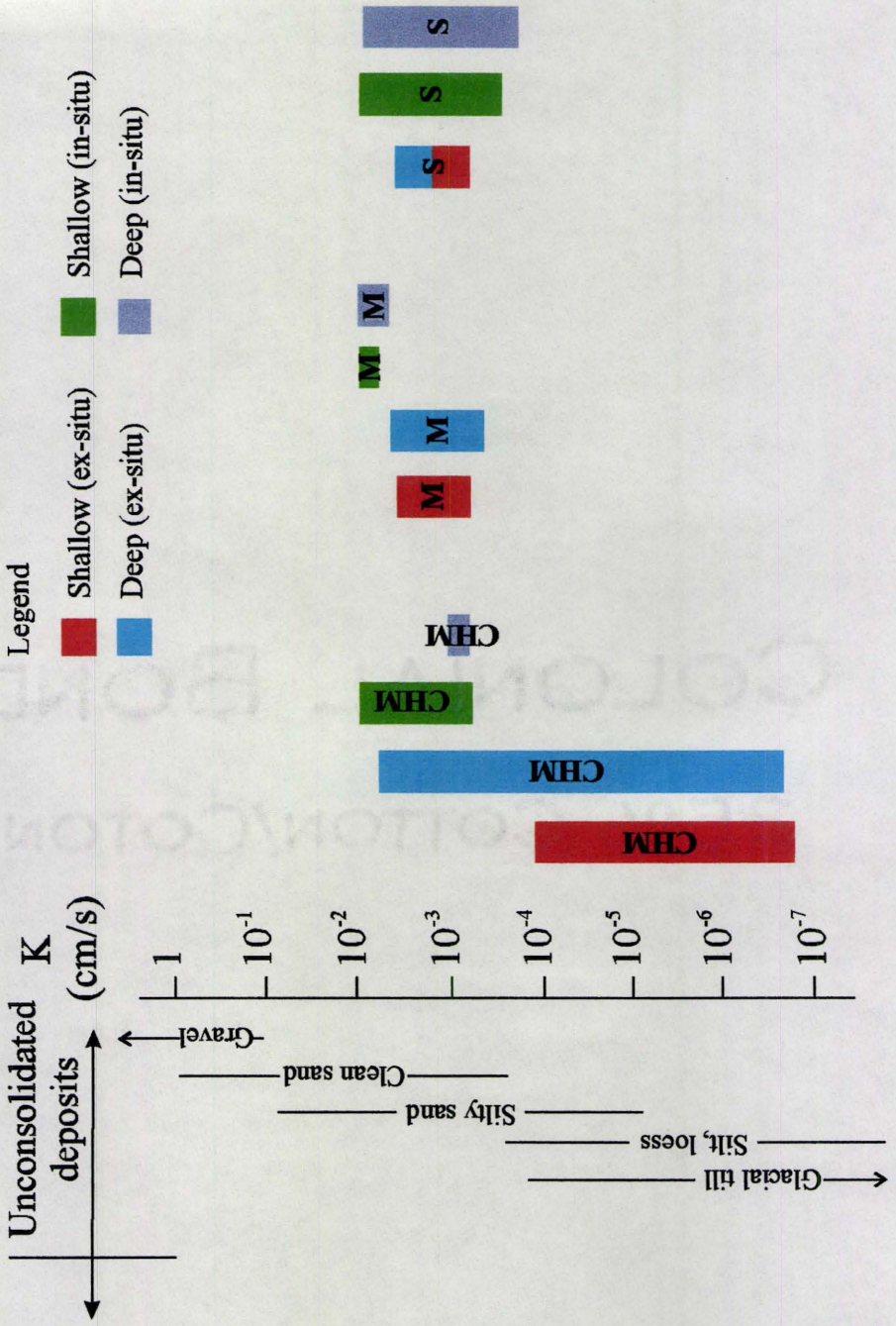


Figure 24. Variation in ex-situ and in-situ hydraulic conductivities at S, M and CHM (modified from Table 2.2, p. 29 in Groundwater by Freeze and Cherry, 1979).

Table 40. Ex-situ and in-situ hydraulic conductivity results (respectively) of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM.

	Shallow		Deep	
Site ID	**Mean Ex-situ K (cm/s)**	**Log Mean Ex-situ K (cm/s)**	**Mean Ex-situ K (cm/s)**	**Log Mean Ex-situ K (cm/s)**
S-1	1.46E-02	-1.84	7.82E-03	-2.11
S-2	2.19E-02	-1.66	1.35E-03	-2.87
S-3	1.58E-02	-1.80	4.00E-03	-2.40
S-4	2.24E-02	-1.65	3.16E-03	-2.50
S-5	2.47E-02	-1.61	3.66E-03	-2.44
S-6	1.55E-03	-2.81	5.61E-03	-2.25
S-7	4.00E-02	-1.40	6.91E-03	-2.16
S-8	2.24E-02	-1.65	4.95E-03	-2.31
S-9	1.93E-02	-1.71	3.07E-03	-2.51
S-10	3.79E-02	-1.42	3.65E-03	-2.44
Mean		-1.75		-2.40
M-1	2.35E-02	-1.63	3.87E-02	-1.41
M-2	1.15E-02	-1.94	4.52E-03	-2.35
M-3	2.70E-03	-2.57	1.76E-02	-1.75
M-4	1.60E-02	-1.80	1.56E-02	-1.81
M-5	4.87E-03	-2.31	3.38E-02	-1.47
M-6	2.32E-03	-2.63	3.31E-03	-2.48
M-7	2.76E-03	-2.56	3.69E-02	-1.43
M-8	4.65E-02	-1.33	3.54E-02	-1.45
M-9	2.05E-03	-2.69	6.27E-03	-2.20
M-10	1.14E-02	-1.94	5.59E-03	-2.25
Mean		-2.14		-1.86
CHM-1	7.60E-06	-5.12	6.76E-06	-5.17
CHM-2	9.80E-03	-2.01	2.18E-04	-3.66
CHM-3	2.87E-05	-4.54	4.15E-05	-4.38
CHM-4	6.55E-03	-2.18	1.43E-04	-3.85
CHM-5	6.80E-04	-3.17	4.04E-05	-4.39
CHM-6	3.29E-04	-3.48	1.67E-05	-4.78
CHM-7	5.78E-03	-2.24	2.49E-02	-1.60
CHM-8	1.47E-03	-2.83	2.13E-03	-2.67
CHM-9	3.90E-04	-3.41	2.34E-03	-2.63
CHM-10	4.57E-04	-3.34	3.06E-04	-3.51
Mean		-3.23		-3.67

Site ID	Shallow Depth (cm)	Shallow In-situ K_{fs} (cm/s)	Shallow Log in-situ K_{fs} (cm/s)	Deep Depth (cm)	Deep In-situ K_{fs} (cm/s)	Deep Log in-situ K_{fs} (cm/s)
CHM-6	15	2.13E-03	-2.67	30	1.06E-03	-2.97
CHM-P1	15	1.06E-02	-1.97	30	1.06E-03	-2.97
CHM-P2	15	4.25E-03	-2.37	30	2.13E-03	-2.67
CHM-P3	15	3.19E-03	-2.50	30	2.13E-03	-2.67
CHM-P4	15	2.13E-03	-2.67	30	2.13E-03	-2.67
Mean	15		-2.35	30		-2.77
M-P1	15	1.06E-02	-1.97	30	3.19E-02	-1.50
M-P2	15	1.06E-02	-1.97	30	1.06E-02	-1.97
M-P3	15	1.06E-02	-1.97	30	1.06E-02	-1.97
M-P4	15	1.49E-02	-1.83	30	2.13E-02	-1.67
M-P5	15	2.13E-02	-1.67	30	3.19E-02	-1.50
Mean	15		-1.87	30		-1.67
S-P1	15	8.50E-03	-2.07	30	8.50E-03	-2.07
S-P2	15	7.44E-03	-2.13	30	1.06E-02	-1.97
S-P3	15	1.06E-02	-1.97	30	1.06E-02	-1.97
S-P4	15	6.38E-03	-2.20	30	1.17E-02	-1.93
S-P5	15	8.50E-03	-2.07	30	1.06E-02	-1.97
Mean	15		-2.08	30		-1.98

Histograms were plotted that indicated that these hydraulic conductivities were not normally distributed, but that the log-hydraulic conductivities were normally distributed. Consequently, the analysis was undertaken using log-transformed data (i.e. using the log values of the hydraulic conductivities instead of the raw hydraulic conductivity values).

In the shallow soils, the mean in-situ log hydraulic conductivities are highest at M (-1.87 cm/s) and lowest at CHM (-2.35 cm/s). ANOVA tests for the shallow soils (Table

41) indicate that there are no significant differences between the log hydraulic conductivities at M and S only.

Table 41. ANOVA results of in-situ log hydraulic conductivities in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

Log K_{fs} (in-situ) (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

In the deep soils, the mean in-situ log hydraulic conductivities are highest at M (-1.67 cm/s) and lowest at CHM (-2.77 cm/s). ANOVA tests for the in-situ deep soils (Table 42) indicate that there are significant differences between two out of the three pairs; there are only no significant differences in the log hydraulic conductivities of M and S.

Table 42. ANOVA results of in-situ log hydraulic conductivities in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Log K_{fs} (in-situ) (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

When comparing the shallow soils to the deep soils, the mean in-situ hydraulic conductivities are higher in the deep soils for M and S, but higher in the shallow soils for CHM. T-tests for CHM, M and S (Table 43) indicate that there are no significant differences in the in-situ log hydraulic conductivities between the shallow soils and deep soils.

Table 43. T-test results of in-situ log hydraulic conductivities between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Log K_{fs} (in-situ)	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	NS	\
S (10-15)	\	\	NS

When tested in labs at McMaster University (ex-situ), the sample mean log hydraulic conductivities in the table for repacked shallow soil cores are highest at S (-1.75 cm/s) and lowest at CHM (-3.23 cm/s). ANOVA tests for the ex-situ shallow soils (Table 44) indicate that there are significant differences between two out of three pairs; there are only no significant differences in the log hydraulic conductivities of M and S.

Table 44. ANOVA results of ex-situ log hydraulic conductivities in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

Log K (ex-situ) (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

At depth, the sample mean ex-situ log hydraulic conductivities in the table are highest at M (-1.86 cm/s) and lowest at CHM (-3.67 cm/s). ANOVA tests for the ex-situ deep soils (Table 45) indicate that there are significant differences between two out of the three pairs; there are only no significant differences in the log hydraulic conductivities of M and S.

Table 45. ANOVA results of ex-situ log hydraulic conductivities in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Log K (ex-situ) (10-15)		CHM	M	S
	CHM	\	S	S
	M	S	\	NS
	S	S	NS	\

In the table, when comparing the shallow soils to the deep soils for the repacked soil cores, the sample mean ex-situ log hydraulic conductivities are higher in the deep soils for CHM and M, but higher in the shallow soils for S. T-tests for CHM and M (Table 46) indicate that there are no significant differences in the ex-situ log hydraulic conductivities between the shallow soils and deep soils. T-tests for S indicate that there are significant differences in the ex-situ log hydraulic conductivities between the shallow soils and deep soils.

Table 46. T-test results of ex-situ log hydraulic conductivities between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Log K (ex-situ)	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	NS	\
S (10-15)	\	\	S

The lower log hydraulic conductivities at CHM are consistent with the higher soil organic matter contents than both S and M present in the top 20 cm of the soil profile. Consequently, the shallow and deep soils at CHM should store more water than the soils at S and M, which are better at conducting water.

T-test results for comparing the in-situ log hydraulic conductivities to the ex-situ log hydraulic conductivities in the shallow and deep soils at S, M and CHM (Table 47) show that there are no significant differences at M, but that there are significant differences at S and CHM. These results suggest that for the most part, and certainly at S and CHM, the soil structure influences the hydraulic conductivity. It should be noted however, that the sample depths are different. For instance, the shallow ex-situ samples are from 0 to 5 cm depth, and the shallow in-situ samples are from 15 cm depth. Likewise, the deep ex-situ samples are from 10 to 15 cm depth, and the deep in-situ samples are from 30 cm depth.

Table 47. T-test results between in-situ log hydraulic conductivities and ex-situ log hydraulic conductivities in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

		Log K_{fs} (ex-situ)
S (0-5 cm)	**Log K_{fs} (in-situ)**	S
S (10-15 cm)	**Log K_{fs} (in-situ)**	S
M (0-5 cm)	**Log K_{fs} (in-situ)**	NS
M (10-15 cm)	**Log K_{fs} (in-situ)**	NS
CHM (0-5 cm)	**Log K_{fs} (in-situ)**	S
CHM (10-15 cm)	**Log K_{fs} (in-situ)**	S

In general, the mean in-situ and ex-situ hydraulic conductivities are highest at M and lowest at CHM.

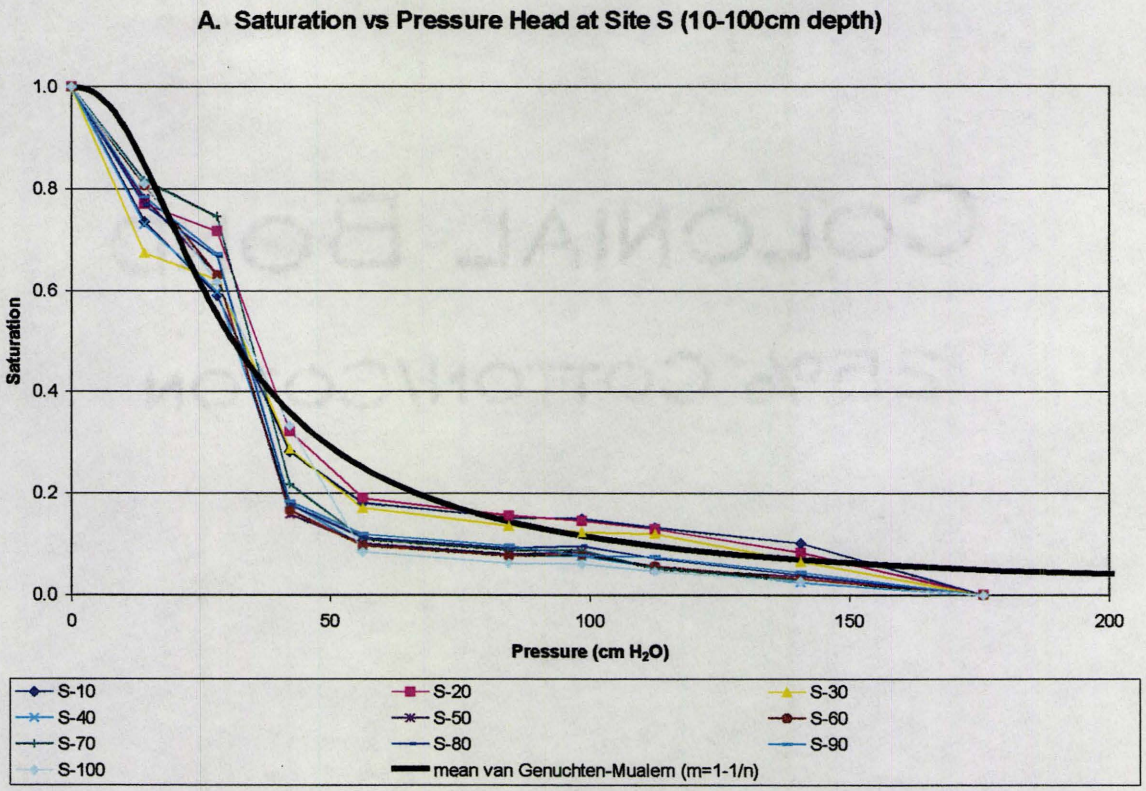
4.7 Water Retention

The water-retention characteristics of the soil are also important in assessing DDT persistence. As stated in Section 3.14, water retention is an expression of the soil's ability to store water. Table 48 presents the water contents at saturation and residual, as well as the n and α parameters provided by the numerical fitting routine initiated in RETC.

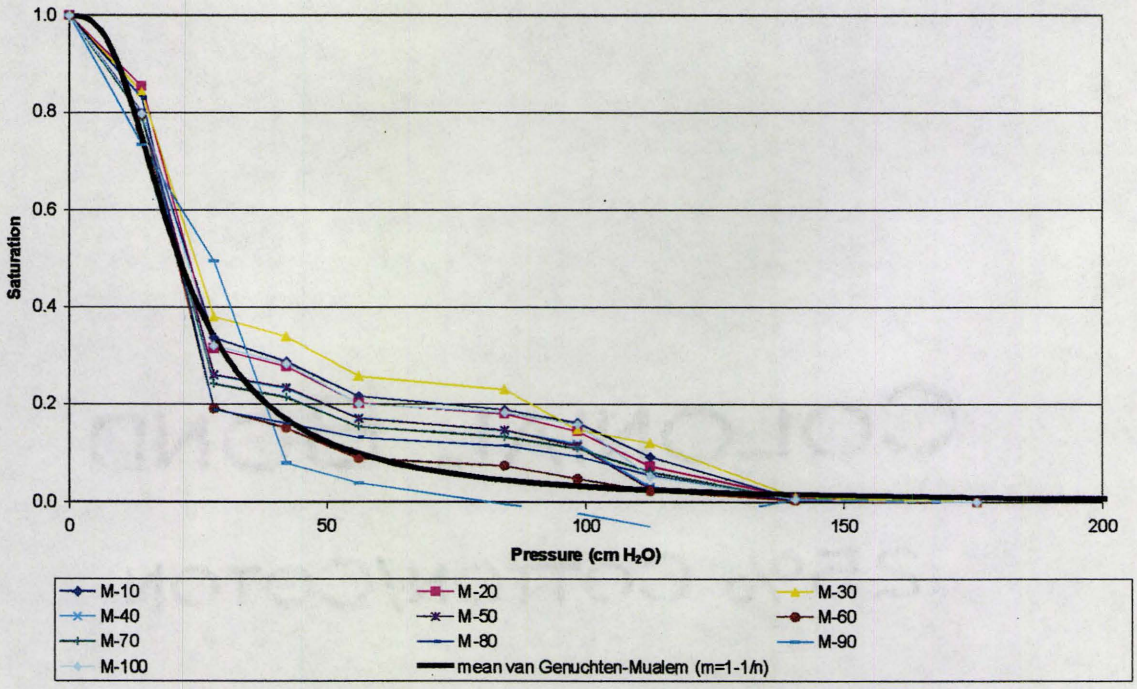
Moisture characteristic curves are presented in Figure 25. As can be seen in Figure 25, M has the lowest mean θ_s at 10 cm depth and CHM has the highest mean θ_s at 10 cm depth. S has the lowest θ_s at 100 cm depth and CHM has the highest mean θ_s at 100 cm depth. This means that CHM is the wetter site at the surface and with depth than both M and S. CHM has the highest θ_r at 10 cm depth and M has the lowest θ_r at 10 cm depth. CHM has the highest θ_r at 100 cm depth and M has the lowest θ_r at 100 cm depth.

This means that the soils at CHM initially drain their water faster than the soils at M and S, because the soils at CHM are generally coarser and have higher porosities than the soils at M and S. However, with increasing depth, they tend to retain their water to a greater extent than either M or S, because the mean %OM is higher and the mean hydraulic conductivity is lower with depth at CHM than M and S. The soils at M initially drain their water faster than the soils at S. This is likely because the soils at M are generally coarser and higher in mean %MM than the soils at S. In addition, the soils at M have the highest mean hydraulic conductivities. At the same pressures and same depths,

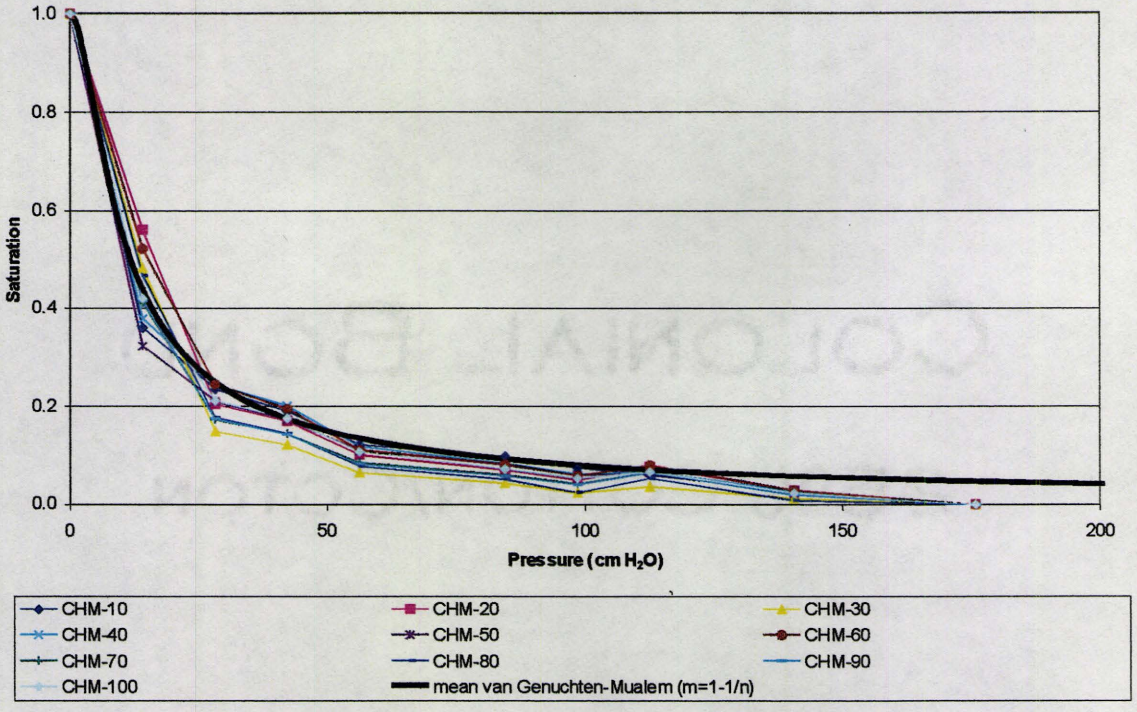
Figure 25. Moisture characteristic curves with depth at S, M and CHM.



B. Saturation vs Pressure Head at Site M (10-100cm depth)



C. Saturation vs Pressure Head at Site CHM (10-100cm depth)



M does not retain as much water as S and CHM. The soils at CHM with depth are unique. This data is consistent with the soil moisture observations at the sites. The mean soil moisture is higher in the soils at CHM than M and S. The mean soil moisture is lowest in the soils at M. Furthermore, the water table is deepest at S and shallowest at CHM.

The water content versus pressure head relationships plotted with this data also indicate that the air entry pressures are no more than a few cm thick (approx. 0 to 10 cm) in most soils at S and M, with a mean at approximately 5 cm. . The air entry pressures at CHM are less than 5 cm. In other words, the sandy texture of the soil is such that the capillary fringe (saturated soil under tension immediately above the water table) at all three sites is very narrow, however it is narrowest at CHM and does not exceed 5 cm. This means soil less than approximately 0 to 5 cm above the water table will be saturated and that the depth to saturated soil is 5 cm above the existing water table.

In short, the water content versus pressure head relationships indicate that the soils at CHM are quite different than those at S and M in that they retain more water, even with depth and increasing pressures. This is due to the higher organic matter content at CHM, which affects the texture and structure of the soil. In turn, the increased organic matter here affects the soil's water retention.

Table 48. Parameters input and provided (default parameters) for the calculation of moisture characteristic curves in RETC V. 6.0 (van Genuchten et al., 1998).

Site ID	θ_r (%)	θ_s (%)	n	α (/cm)
S-10	10	69	2.06	0.0555
S-20	5	56	1.8055	0.0667
S-30	4	61	1.8721	0.0719
S-40	2	55	1.9917	0.0809
S-50	2	53	1.9310	0.0796
S-60	2	49	1.9031	0.0745
S-70	1	49	1.7319	0.0743
S-80	2	49	1.8998	0.0792
S-90	1	47	1.8298	0.0783
S-100	1	46	1.7726	0.0744
Mean	3	53	1.8949	0.0764
M-10	0	58	2.2198	0.0636
M-20	0	50	2.4160	0.0580
M-30	0	55	2.1892	0.0581
M-40	0	51	2.3371	0.0610
M-40	0	51	2.5396	0.0625
M-60	0	47	3.4720	0.0586
M-70	0	51	2.5602	0.0621
M-80	0	48	3.1988	0.0581
M-90	0	52	4.0960	0.0421
M-100	0	51	2.6034	0.0639
Mean	0	51	2.9213	0.0578
CHM-10	30	75	1.3489	0.5618
CHM-20	13	49	2.4698	0.0866
CHM-30	9	45	2.7772	0.0956
CHM-40	27	72	1.3266	0.4980
CHM-50	25	71	1.2411	1.1182
CHM-60	16	46	2.1664	0.1045
CHM-70	14	49	2.0052	0.1574
CHM-80	11	50	2.2446	0.1162
CHM-90	13	50	2.1371	0.1420
CHM-100	16	54	1.7623	0.1871
Mean	17	56	1.2750	0.7425

4.8 Soil Moisture Content as a Function of Organic Matter and Ground Surface Elevation

Aside from changing a soil's structure and colour, organic matter also modifies a soil's water holding capacity. Water is readily adsorbed onto organic matter in soil. In this case, it will be free to degrade in the soil water. For instance, Harris (1964a) observed that organic matter strongly affected the amount of DDT adsorbed in moist soil but in dry soil, it had little effect.

The effects of organic matter accumulation in soil have frequently been examined with the effects of irrigation and flooding (Guenzi and Beard, 1967 and 1968; Parr et al., 1970; Castro and Yoshida, 1971 and 1974). Wahid and Sethunathan (1980) observed that in a flooded soil, less DDT was adsorbed onto the soil organic matter.

At CHM, the historic flooding conditions resulted in the accumulation of organic matter over time. Today, because these soils contain more organic matter, they have lower hydraulic conductivities, and tend to retain more water by capillary action. Plots (Figure 26) of %OC versus %VWC were produced to better assess the relationship between soil moisture and %OC in the shallow and deep soils at the three study sites. In general, CHM shows the highest degree of variability in accumulation of organic carbon with an increase in VWC. CHM also shows an increase in %OC as the VWC increases. M and S show lower degrees of variability in accumulation of organic carbon with an increase in VWC, as well as lower %OC and VWC.

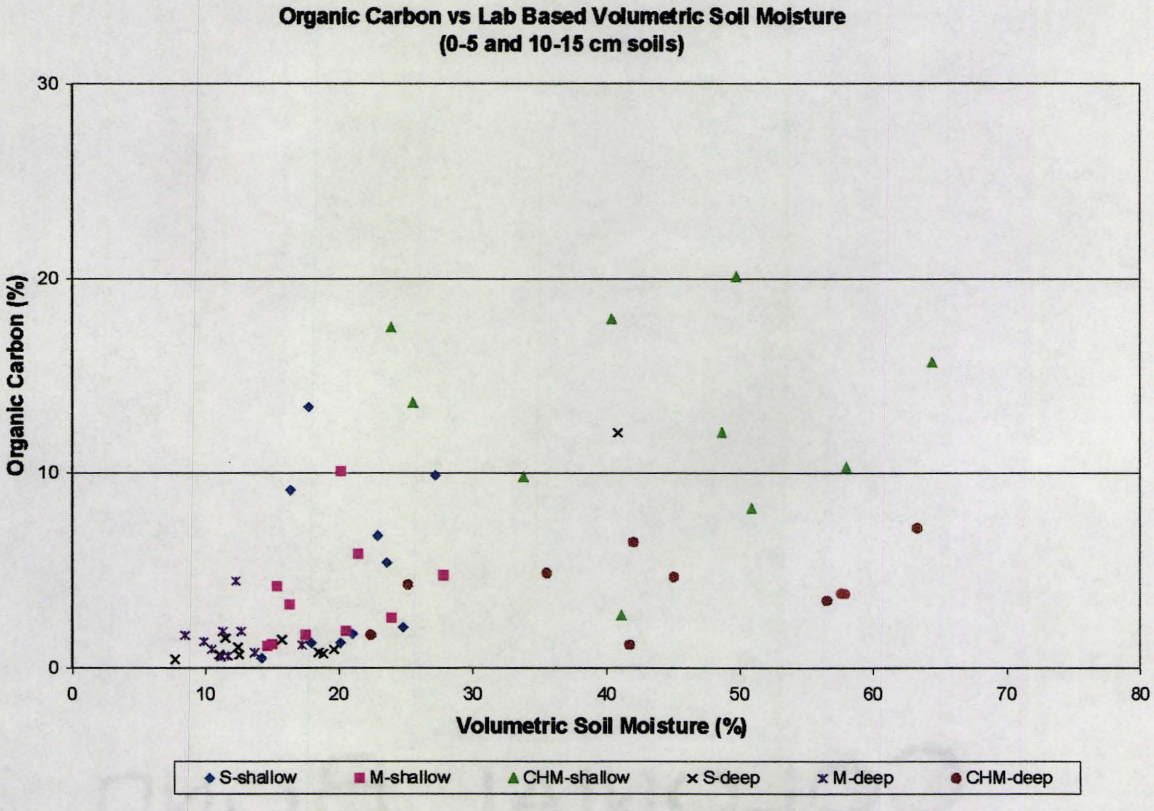


Figure 26. %OC vs volumetric moisture contents at S, M and CHM in the shallow and deep soils.

Plots (Figure 27) of ground surface elevation versus %OM were produced to betters assess the relationship between ground surface elevation and organic matter accumulation in the shallow and deep soils at the three study sites. According to the graph of ground surface elevation versus %OM, the shallow soils at M and S show a high degree of variability in organic matter. In the shallow soils between sites, S has the highest mean %OM and has the highest ground surface elevation. The higher %OM at S than CHM in these shallow soils may be due to the large amount of roots at S. CHM has the lowest mean %OM and the lowest ground surface elevation. In the deep soils, CHM shows the greatest degree of variability in organic matter. In the deep soils between sites, CHM has the highest mean %OM and has the lowest ground surface elevation. S has the lowest mean %OM and the highest ground surface elevation. The observations in the deep soils are consistent with the soil profiles at each study site.

4.9 DDT, DDE, DDD and DDX at S, M and CHM

At CHM, M and S, the p,p'- isomers of DDT, DDE and DDD were the most abundant. In the shallow soils at CHM, M and S, p,p'-DDX accounted for 92 to 98% of the total DDX (total DDX = p,p'-DDX + o,p'-DDX), while o,p'-DDX accounted for 2 to 8% of the total DDX. In the deep soils, p,p'-DDX accounted for 83 to 97% of the total DDX, while o,p'-DDX accounted for three to 17% of the total DDX. Because the o,p'-

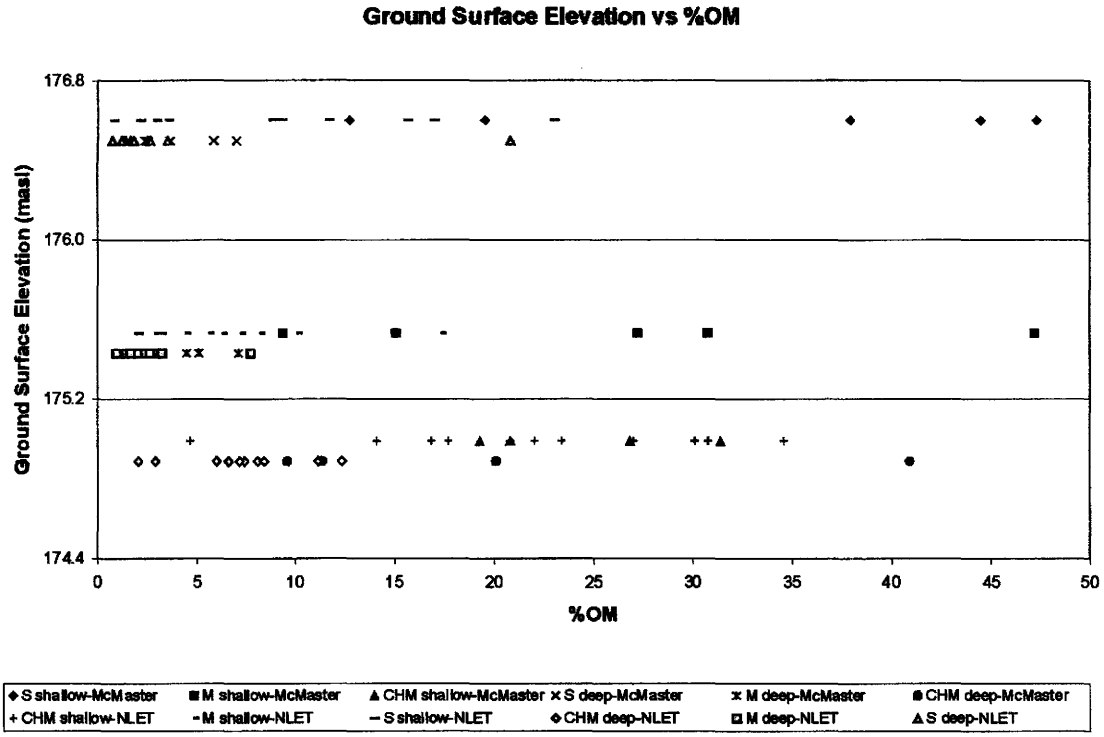


Figure 27. Ground surface elevation vs %OM at S, M and CHM in the shallow and deep soils.

isomers of DDT, DDE and DDD in soil at CHM, M and S were insignificant compared to the p,p'-isomers, the o,p' and p,p' isomers were added together such that:

$$DDT = p,p'\text{-}DDT + o,p'\text{-}DDT$$

$$DDE = p,p'\text{-}DDE + o,p'\text{-}DDE$$

$$DDD = p,p'\text{-}DDD + o,p'\text{-}DDD$$

$$DDX = p,p'\text{-}DDT + o,p'\text{-}DDT + p,p'\text{-}DDE + o,p'\text{-}DDE + p,p'\text{-}DDD + o,p'\text{-}DDD \quad \text{Eq. 23.}$$

The statistical analyses were performed on DDT, DDE, DDD and DDX. The raw concentration data of DDT, DDE, DDD and DDX are presented in Table 49 and Figures 28 and 29.

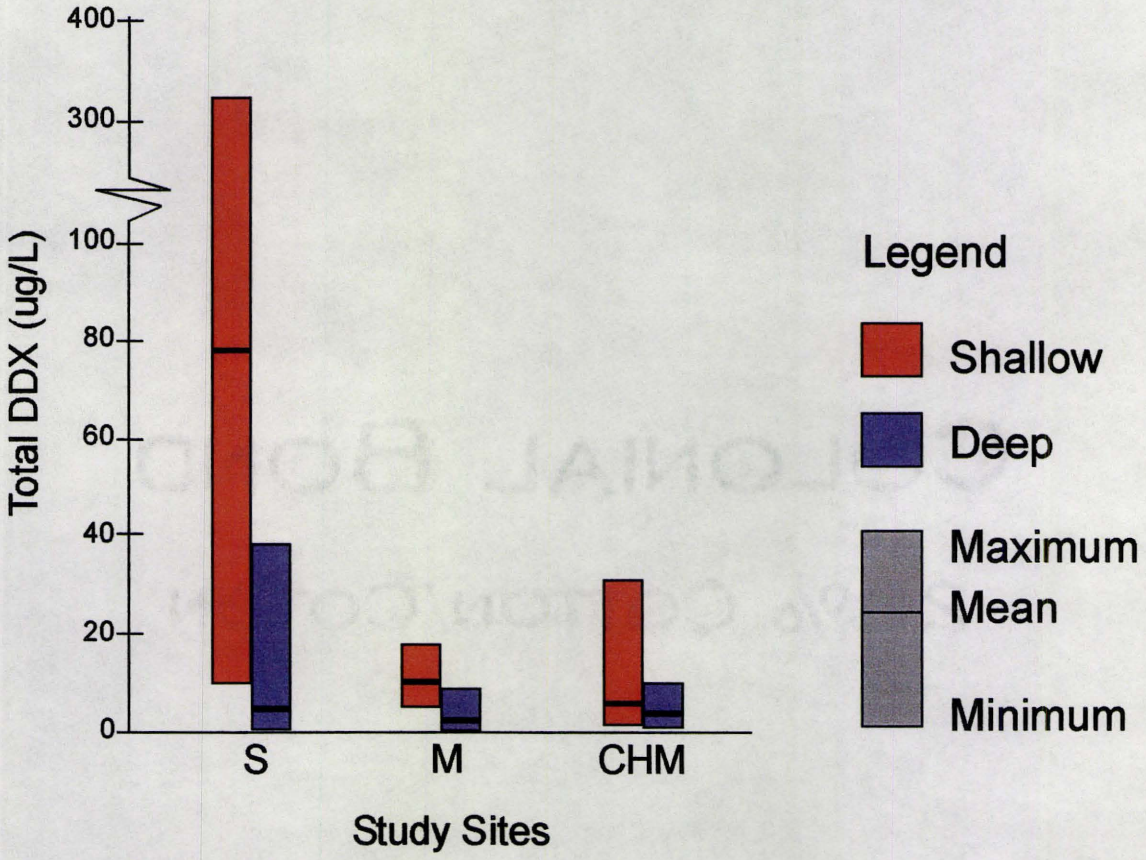
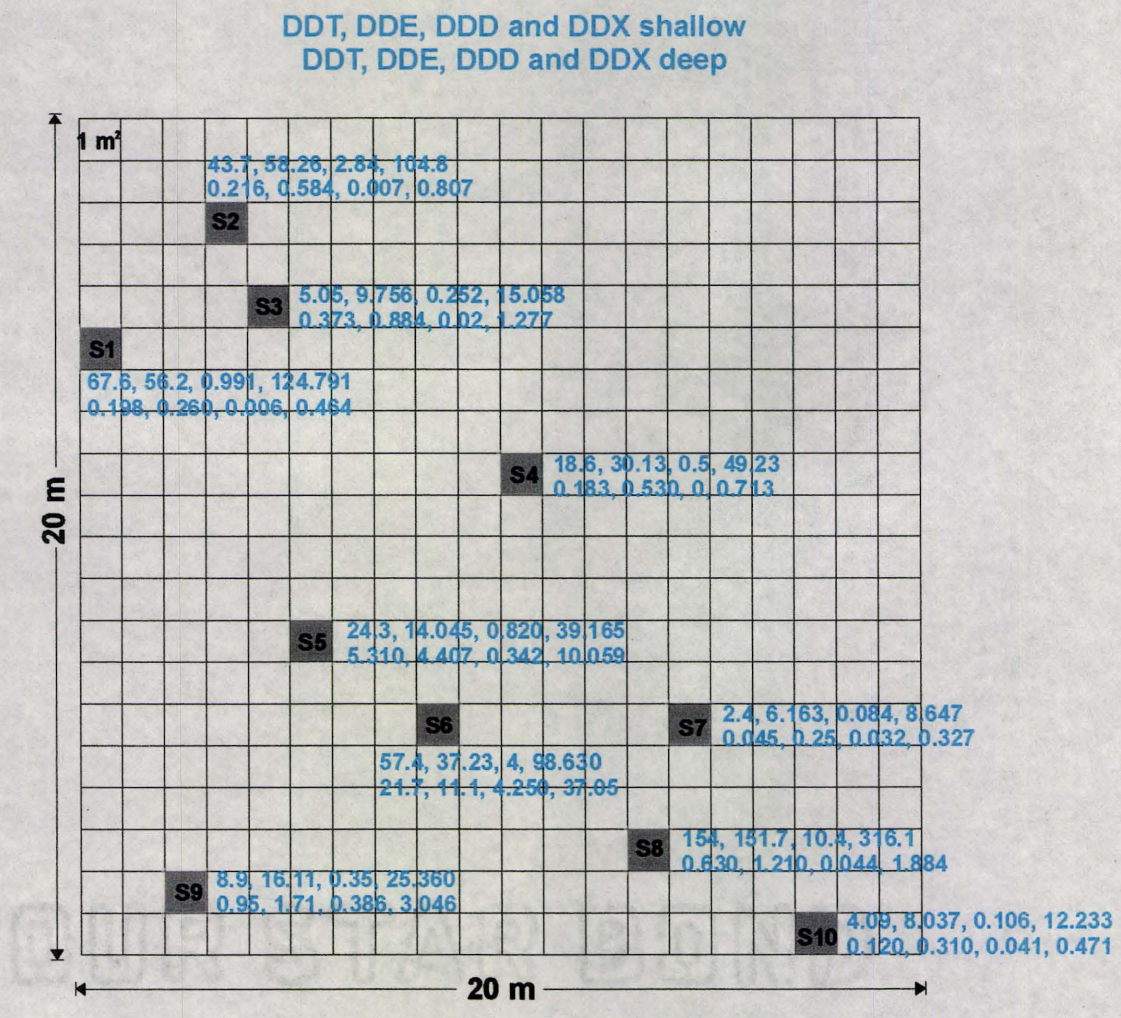


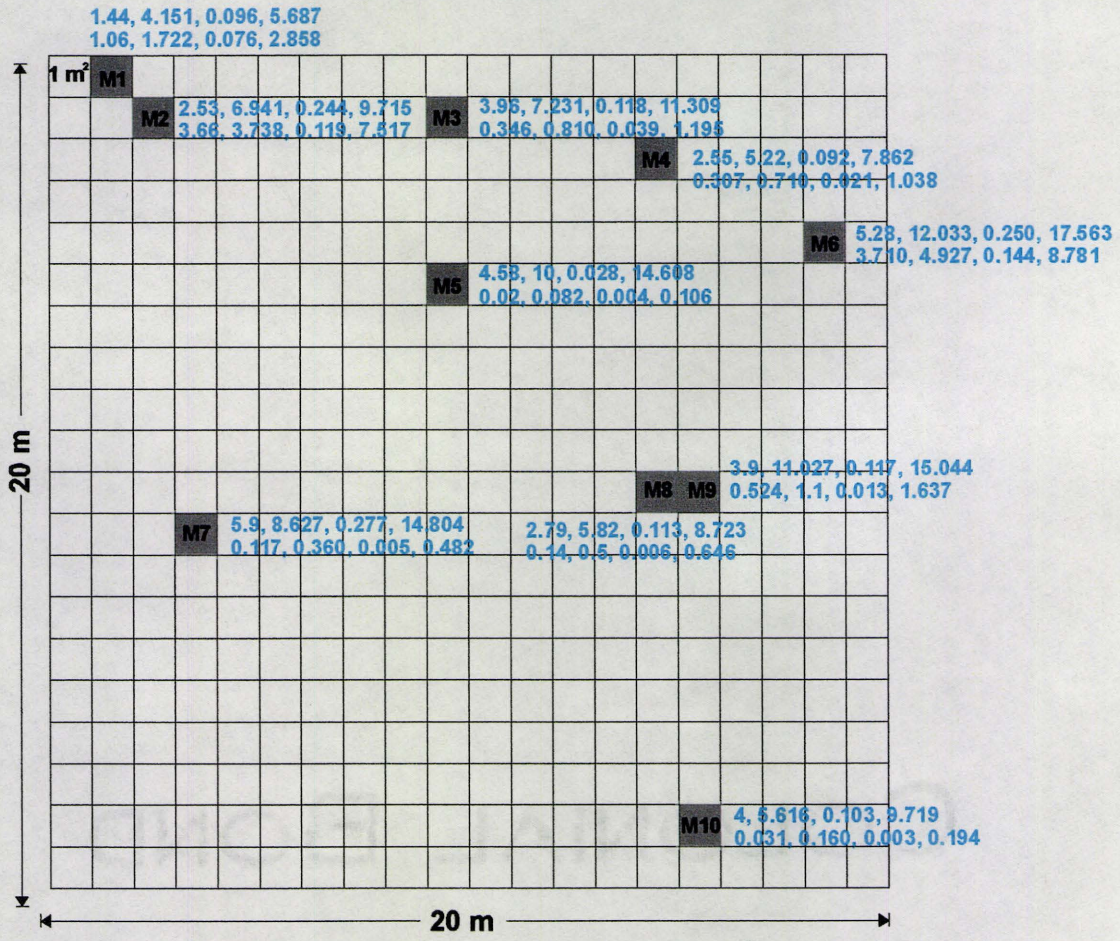
Figure 28. Bar graph illustrating the minimum, mean and maximum DDX (DDT + DDE + DDD) at S, M and CHM in the shallow and deep soils.

Figure 29. Variation in DDT, DDE, DDD and DDX in μg/g at the random sampling points at S, M and CHM.



B) GRID 2: Intermediate sandy to marshy soils of former orchard (M)

DDT, DDE, DDD and DDX shallow
DDT, DDE, DDD and DDX deep

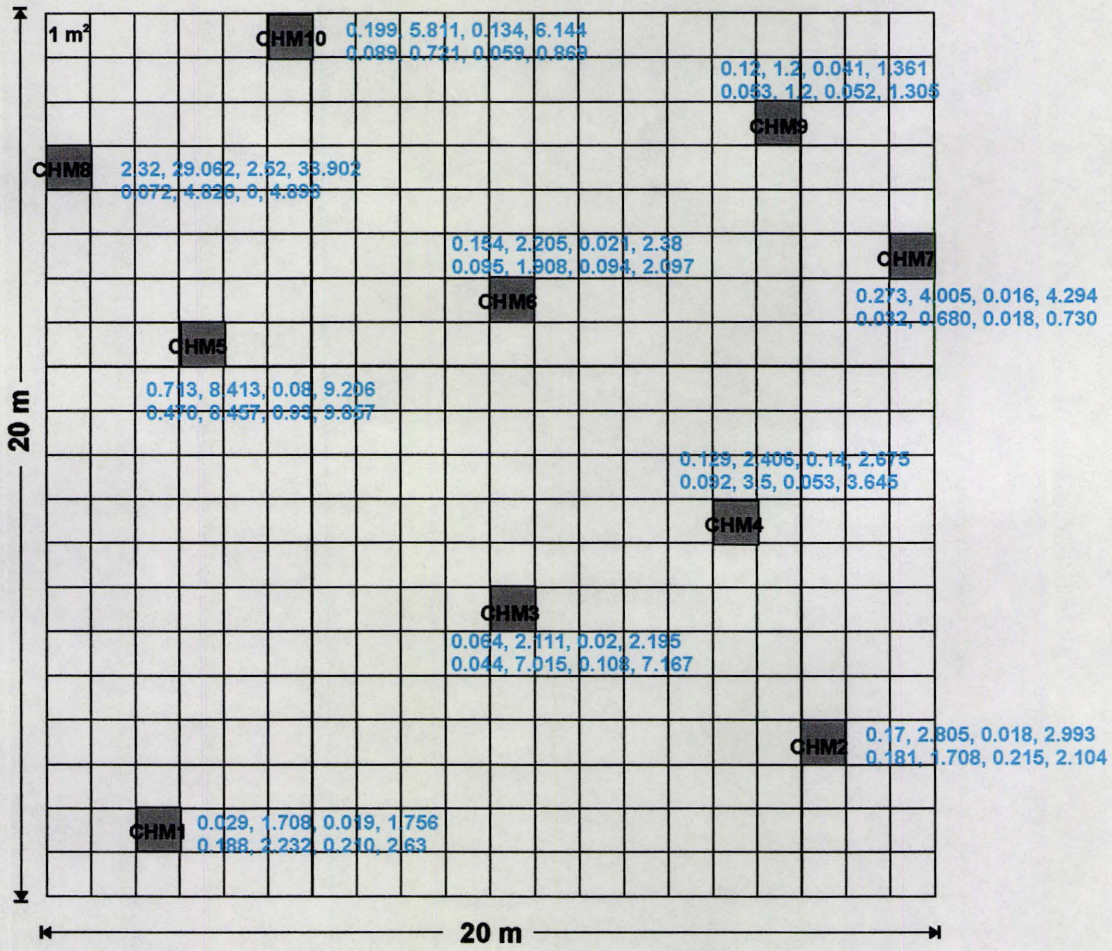


Average DDT, DDE, DDD and DDX shallow:
3.693, 7.667, 0.144, 11.503

Average DDT, DDE, DDD and DDX deep:
0.992, 1.411, 0.043, 2.445

C) GRID 3: Marshy soils of Camp Henry (CHM)

DDT, DDE, DDD and DDX shallow
DDT, DDE, DDD and DDX deep



Average DDT, DDE, DDD and DDX shallow:
0.417, 5.973, 0.301, 6.691

Average DDT, DDE, DDD and DDX deep:
0.132, 3.225, 0.174, 3.53

Table 49. DDT, DDE, DDD and DDX results of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP in µg/g.

	Shallow				Deep			
	DDT	**DDE**	**DDD**	**DDX**	**DDT**	**DDE**	**DDD**	**DDX**
CHM-1	0.029	1.708	0.019	1.756	0.188	2.232	0.210	2.630
CHM-2	0.170	2.805	0.018	2.993	0.181	1.708	0.215	2.104
CHM-3	0.064	2.111	0.020	2.195	0.044	7.015	0.108	7.167
CHM-4	0.129	2.406	0.140	2.675	0.092	3.500	0.053	3.645
CHM-5	0.713	8.413	0.080	9.206	0.470	8.457	0.930	9.857
CHM-6	0.154	2.205	0.021	2.380	0.095	1.908	0.094	2.097
CHM-7	0.273	4.005	0.016	4.294	0.032	0.680	0.018	0.730
CHM-8	2.320	29.062	2.520	33.902	0.072	4.826	0.000	4.898
CHM-9	0.120	1.200	0.041	1.361	0.053	1.200	0.052	1.305
CHM-10	0.199	5.811	0.134	6.144	0.089	0.721	0.059	0.869
Mean	0.417	5.973	0.301	6.691	0.132	3.225	0.174	3.530
M-1	1.440	4.151	0.096	5.687	1.060	1.722	0.076	2.858
M-2	2.530	6.941	0.244	9.715	3.660	3.738	0.119	7.517
M-3	3.960	7.231	0.118	11.309	0.346	0.810	0.039	1.195
M-4	2.550	5.220	0.092	7.862	0.307	0.710	0.021	1.038
M-5	4.580	10.000	0.028	14.608	0.020	0.082	0.004	0.106
M-6	5.280	12.033	0.250	17.563	3.710	4.927	0.144	8.781
M-7	5.900	8.627	0.277	14.804	0.117	0.360	0.005	0.482
M-8	2.790	5.820	0.113	8.723	0.140	0.500	0.006	0.646
M-9	3.900	11.027	0.117	15.044	0.524	1.100	0.013	1.637
M-10	4.000	5.616	0.103	9.719	0.031	0.160	0.003	0.194
Mean	3.693	7.667	0.144	11.503	0.992	1.411	0.043	2.445
S-1	67.600	56.200	0.991	124.791	0.198	0.260	0.006	0.464
S-2	43.700	58.260	2.840	104.800	0.216	0.584	0.007	0.807
S-3	5.050	9.756	0.252	15.058	0.373	0.884	0.020	1.277
S-4	18.600	30.130	0.500	49.230	0.183	0.530	0.000	0.713
S-5	24.300	14.045	0.820	39.165	5.310	4.407	0.342	10.059
S-6	57.400	37.230	4.000	98.630	21.700	11.100	4.250	37.050
S-7	2.400	6.163	0.084	8.647	0.045	0.250	0.032	0.327
S-8	154.000	151.700	10.400	316.100	0.630	1.210	0.044	1.884
S-9	8.900	16.110	0.350	25.360	0.950	1.710	0.386	3.046
S-10	4.090	8.037	0.106	12.233	0.120	0.310	0.041	0.471
Mean	38.604	38.763	2.034	79.401	2.973	2.125	0.513	5.610

Data in µg/g; limit for DDT for Recreational/Parkland land use is 1.6 µg/g (OMOEE, 1997); DDT MDL = 0.004 µg/g; DDE MDL = 0.004 µg/g; DDD MDL = 0.003 - 0.006 µg/g.

The sample mean DDX concentrations in the shallow and deep soils of all sites are above the Ontario Ministry of the Environment and Energy (OMOEE, 1997) and the Canadian Council of Ministers of the Environment (CCME, 2001) soil quality guidelines for Recreational/Parkland Land-use (Table 50). In the shallow soils, one sample mean DDT concentration at CHM is above the OMOEE (1997) guideline, as compared to nine at M and ten at S. In the deep soils, all sample mean DDT concentrations at CHM are below the guideline. Two sample mean DDT concentrations at M and S are above.

In the shallow soils, nine sample mean DDE concentrations at CHM are above the guideline, as compared to ten at M and S. In the deep soils, seven sample mean DDE concentrations at CHM are above the guideline, as compared to three at M and S. In the shallow soils, one sample mean DDD concentration at CHM is above the guideline, as compared to ten at M and three at S. In the deep soils, all sample mean DDD concentrations at CHM and M are below the guideline, as compared to nine at S.

In short, the mean sample DDT in the soils from 0 to 15 cm at CHM is below the Ontario Ministry of the Environment and Energy (OMOEE, 1997) soil quality guideline for Recreational/Parkland Land-use, while it is approximately 1.5 times above at M and approximately 10 times at S. The mean sample DDE in the soils at CHM, M and S are above the guideline on the order of 3x, 6x and 10x, respectively. This means that the mean concentration of DDE at CHM is three times the regulatory limit and so on. The mean sample DDD in the soils at CHM, M and S are below the guideline. As the data

suggests, the elevated levels of DDT, DDE and DDD at S make it the site of greatest concern.

Table 50. Soil quality guidelines for DDT.

	OMOEE (1997)[1]	CCME (2001)[2]
In Soil:	**(μg/g)**	**(μg/g)**
DDX	-	0.07
DDT	1.6	-
DDE	1.6	-
DDD	2.2	-

OMOEE: Ontario Ministry of Environment and Energy (OMOEE, 1997); CCME: Canadian Council of Ministers of the Environment (CCME, 2001); [1]soil quality guidelines for Recreational/Parkland Land-use in a potable groundwater situation; [2]soil quality guidelines for Recreational/Parkland Land-use.

It is probable that larger amounts of DDT were applied regularly in the orchards such as S and intermittently at other locations at PPNP. This is consistent with Crowe et al. (2002) and evident in Figures 28 and 29. These figures illustrate that the current DDX concentrations in the shallow and deep soils at S (79.401 μg/g; 5.610 μg/g, respectively) are still significantly higher than those at M (11.503 μg/g; 2.445 μg/g, respectively) or CHM (6.691 μg/g; 3.530 μg/g, respectively). Still today, DDX concentrations are highest in these former orchard areas and lower near the marsh.

These raw concentrations are not used to assess the degradation history at the study sites. And because data on historic DDT application to soils at the Park does not exist, only the relative amounts of DDT, DDE and DDD to DDX, as percent concentrations, can be used to assess the degradation history at the sites.

They were calculated in the following manner:

$$\%DDT = (DDT/DDX) * 100$$

$$\%DDE = (DDE/DDX) * 100$$

$$\%DDD = (DDD/DDX) * 100 \qquad \text{Eq. 24.}$$

The percentages of DDT, DDE and DDD of DDX at each study site are presented in Table 51 and Figures 30 and 31. Figure 30 shows the %DDT, %DDE and %DDD mean, maximum and minimum at each study site. The important trends in the shallow and deep soils are: (a) CHM generally has the lowest mean %DDT and the highest mean %DDE and mean %DDD; (b) S has the highest mean %DDT and the lowest mean %DDE and mean %DDD; and (c) M is a "middle" site in terms of mean %DDT, mean %DDE and mean %DDD. These trends will be seen again with elevation. It is also important to notice that there is generally a greater %DDT, %DDE and %DDD in the deep soils. Figure 31 illustrates the variation in %DDT, %DDE and %DDD within and between sites.

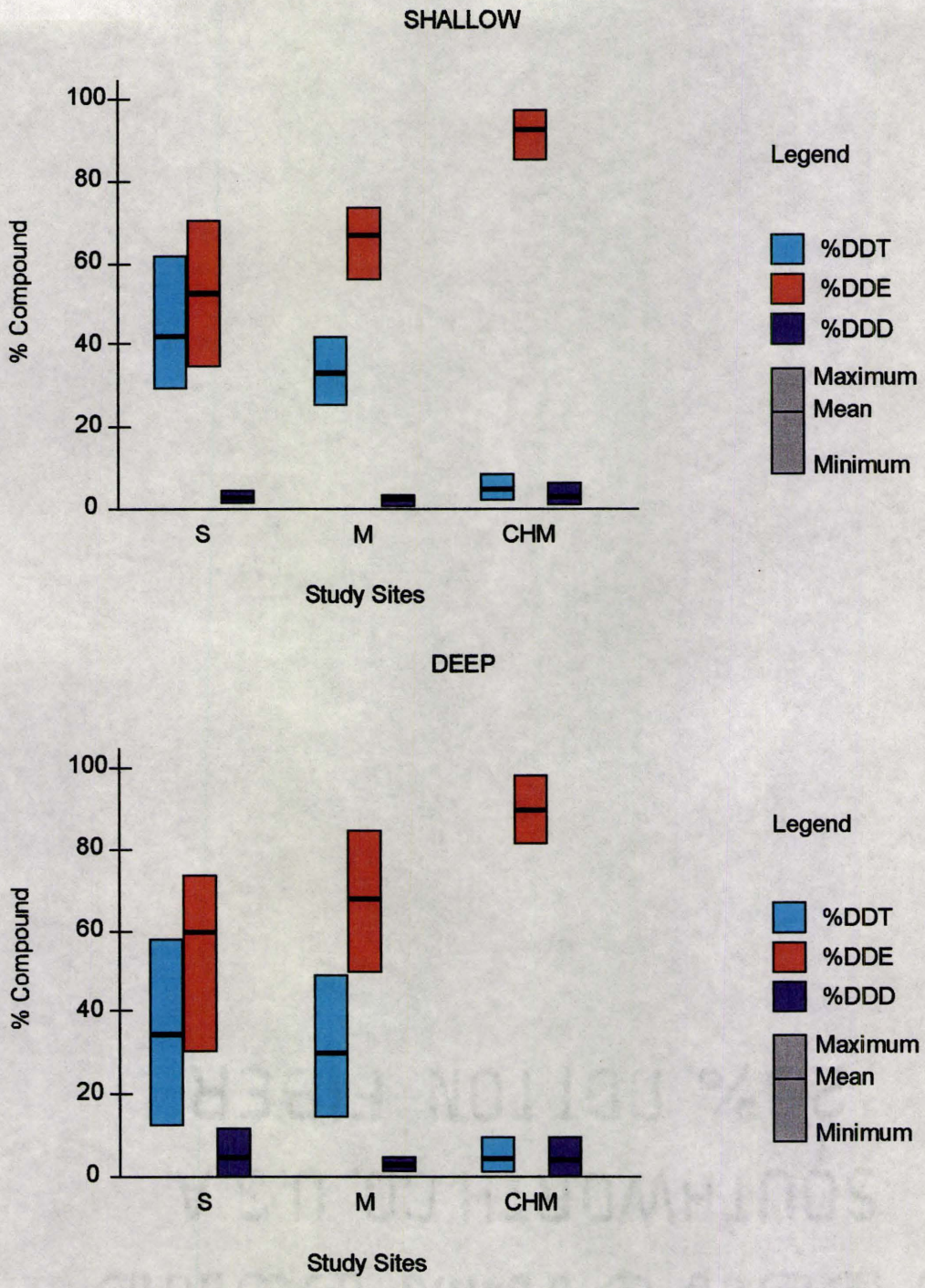
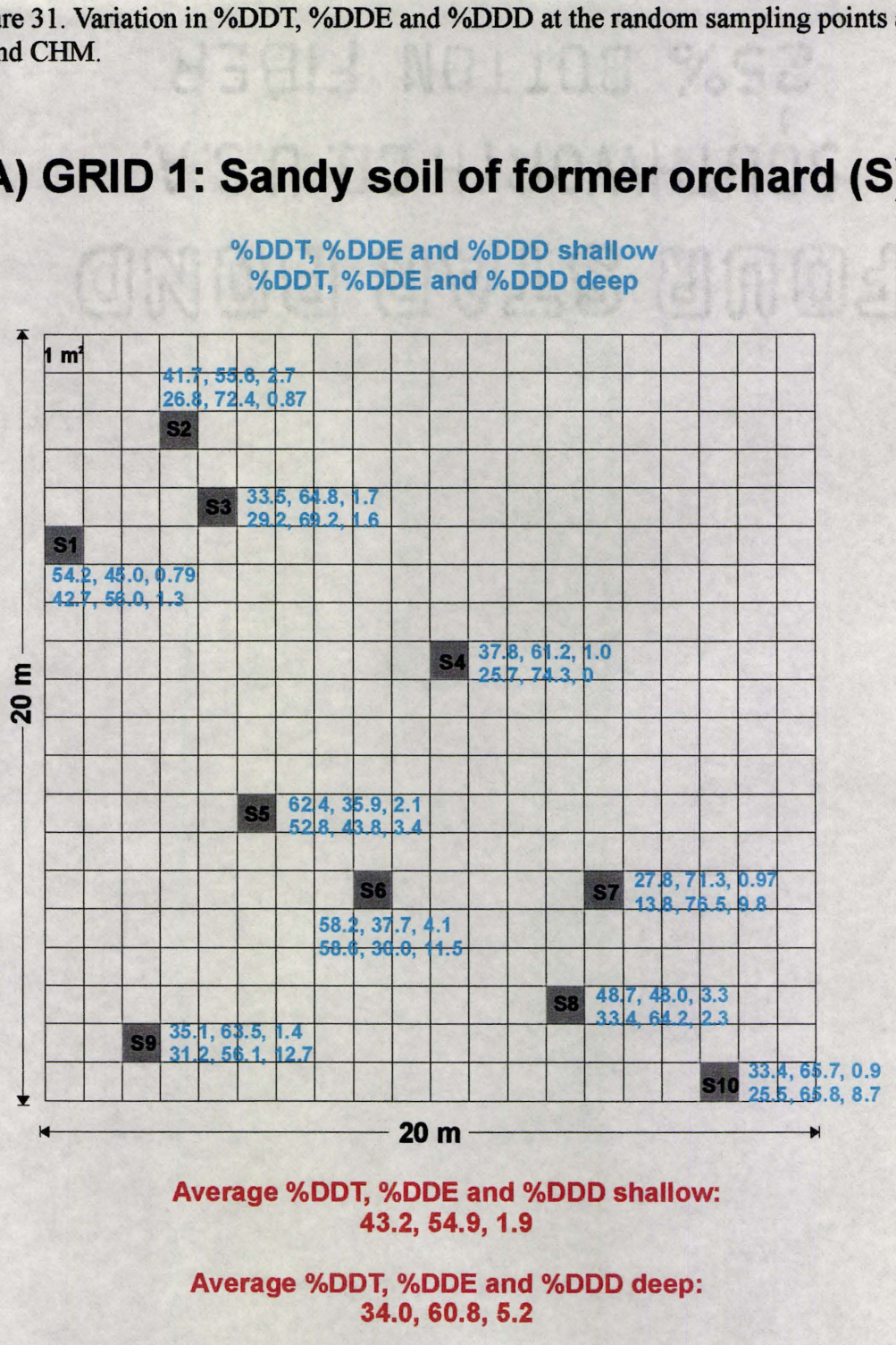


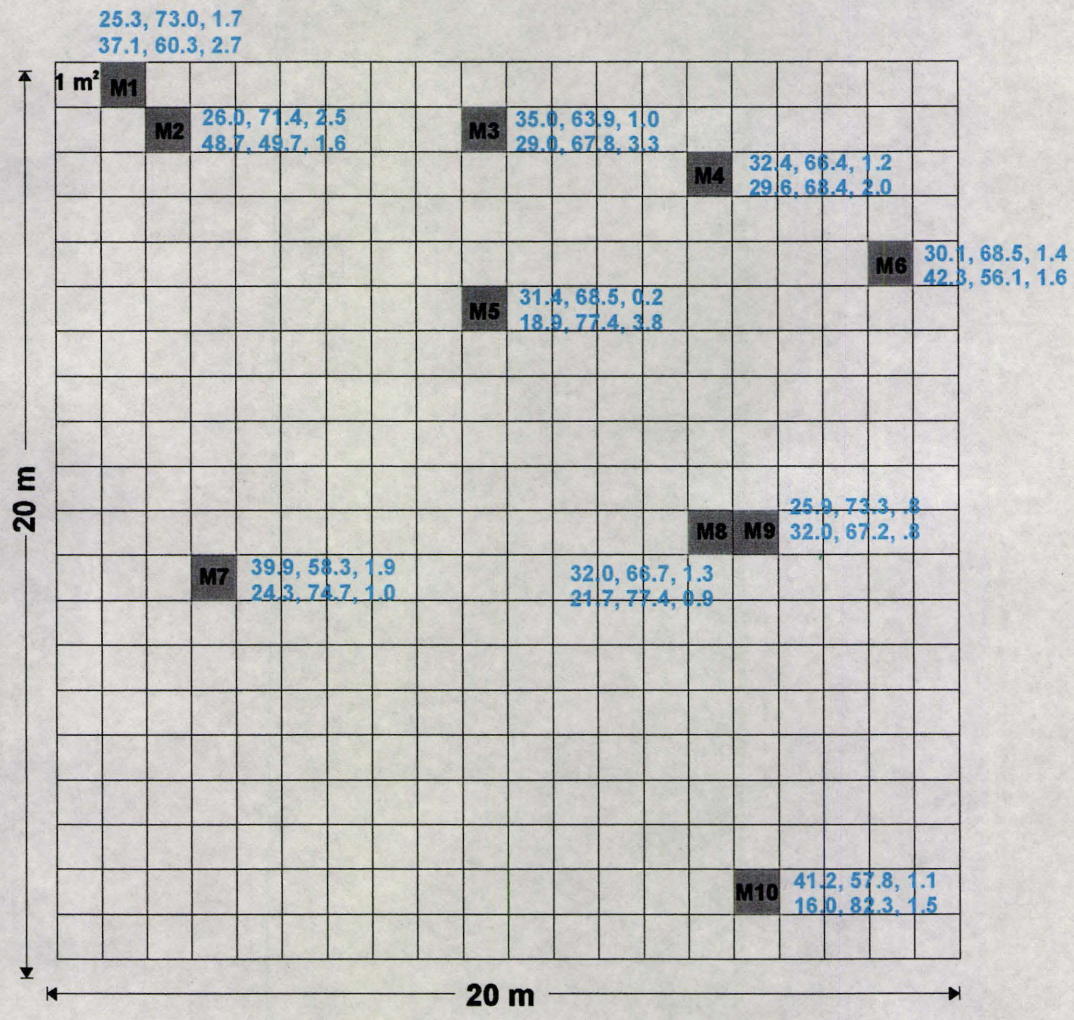
Figure 30. Bar graphs illustrating the minimum, mean and maximum %DDT, %DDE and %DDD at S, M and CHM in the shallow and deep soils at each site.

Figure 31. Variation in %DDT, %DDE and %DDD at the random sampling points at S, M and CHM.



B) GRID 2: Intermediate sandy to marshy soils of former orchard (M)

%DDT, %DDE and %DDD shallow
%DDT, %DDE and %DDD deep

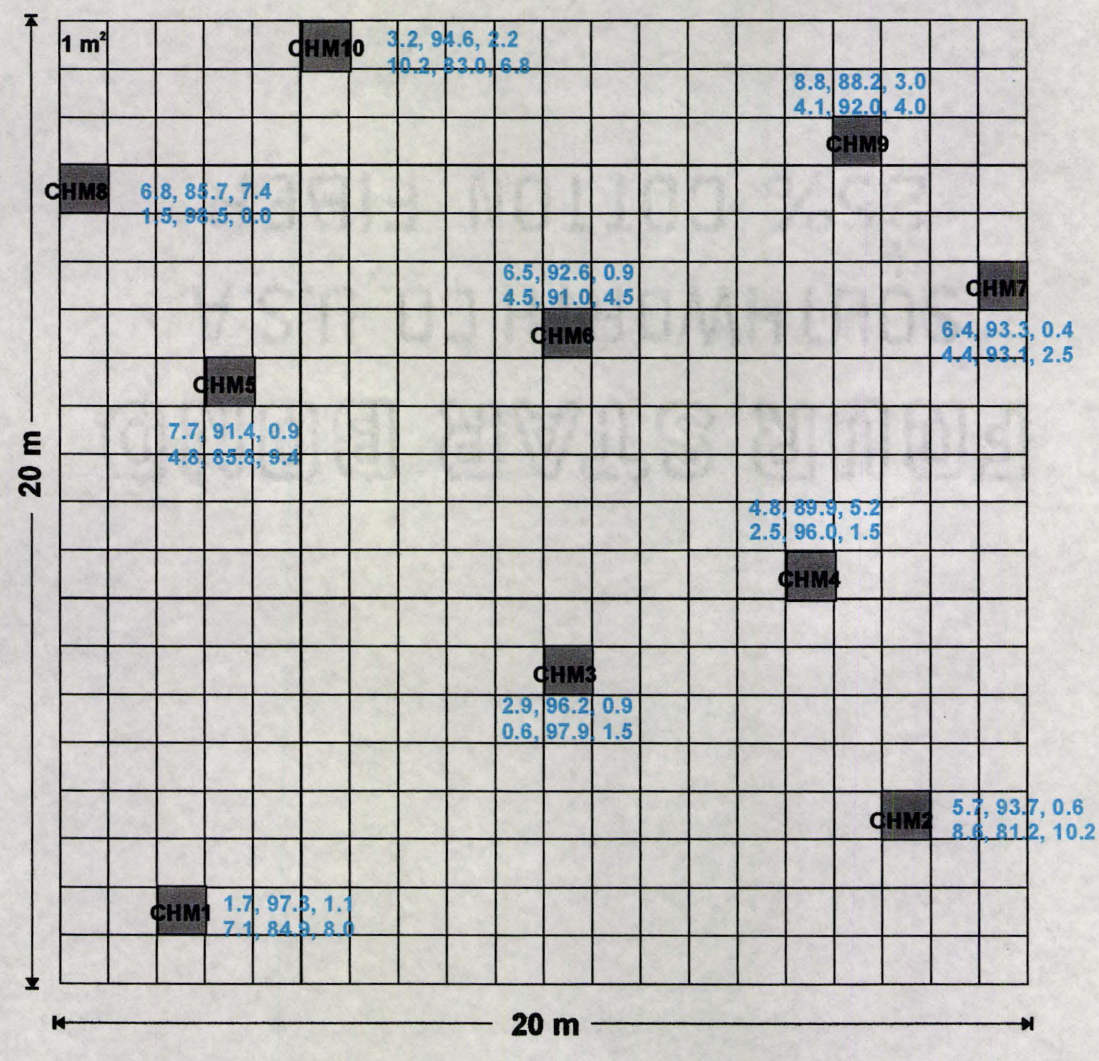


Average %DDT, %DDE and %DDD shallow:
31.9, 66.8, 1.3

Average %DDT, %DDE and %DDD deep:
29.9, 68.1, 1.9

C) GRID 3: Marshy soils of Camp Henry (CHM)

%DDT, %DDE and %DDD shallow
%DDT, %DDE and %DDD deep



Average %DDT, %DDE and %DDD shallow:
5.5, 92.3, 2.3

Average %DDT, %DDE and %DDD deep:
4.8, 90.3, 4.8

Table 51. %DDT, %DDE and %DDD (of the total DDX) results of soil sampling in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

	Shallow			Deep		
	%DDT	%DDE	%DDD	%DDT	%DDE	%DDD
CHM-1	1.7	97.3	1.1	7.1	84.9	8.0
CHM-2	5.7	93.7	0.6	8.6	81.2	10.2
CHM-3	2.9	96.2	0.9	0.6	97.9	1.5
CHM-4	4.8	89.9	5.2	2.5	96.0	1.5
CHM-5	7.7	91.4	0.9	4.8	85.8	9.4
CHM-6	6.5	92.6	0.9	4.5	91.0	4.5
CHM-7	6.4	93.3	0.4	4.4	93.2	2.5
CHM-8	6.8	85.7	7.4	1.5	98.5	0.0
CHM-9	8.8	88.2	3.0	4.1	92.0	4.0
CHM-10	3.2	94.6	2.2	10.2	83.0	6.8
Mean	5.5	92.3	2.3	4.8	90.3	4.8
M-1	25.3	73.0	1.7	37.1	60.3	2.7
M-2	26.0	71.4	2.5	48.7	49.7	1.6
M-3	35.0	63.9	1.0	29.0	67.8	3.3
M-4	32.4	66.4	1.2	29.6	68.4	2.0
M-5	31.4	68.5	0.2	18.9	77.4	3.8
M-6	30.1	68.5	1.4	42.3	56.1	1.6
M-7	39.9	58.3	1.9	24.3	74.7	1.0
M-8	32.0	66.7	1.3	21.7	77.4	0.9
M-9	25.9	73.3	0.8	32.0	67.2	0.8
M-10	41.2	57.8	1.1	16.0	82.5	1.5
Mean	31.9	66.8	1.3	29.9	68.1	1.9
S-1	54.2	45.0	0.8	42.7	56.0	1.3
S-2	41.7	55.6	2.7	26.8	72.4	0.9
S-3	33.5	64.8	1.7	29.2	69.2	1.6
S-4	37.8	61.2	1.0	25.7	74.3	0.0
S-5	62.0	35.9	2.1	52.8	43.8	3.4
S-6	58.2	37.7	4.1	58.6	30.0	11.5
S-7	27.8	71.3	1.0	13.8	76.5	9.8
S-8	48.7	48.0	3.3	33.4	64.2	2.3
S-9	35.1	63.5	1.4	31.2	56.1	12.7
S-10	33.4	65.7	0.9	25.5	65.8	8.7
Mean	43.2	54.9	1.9	34.0	60.8	5.2

Figure 32 is a ternary diagram illustrating the %DDT, %DDE and %DDD at each site, as well as the means. As can be seen, %DDT (DDT/DDX) at S, M and CHM was 95% of the total technical grade DDT when first applied. More than 30 years after the last known application, it has decreased to <1% at some sampling points, whereas the DDE and DDD (Figures 30, 32, 33 and 34) currently present have increased as percentages of the total and this, with different rates of degradation. In other words, with changes in the amount of DDT degradation, the ratio of DDT to DDE and DDD changed.

The mean data points for S in the shallow and deep soils plot at the right side of the triangle at approximately the center of the 1:1 line joining DDT and DDE. This means that there is an approximate 1:1 relationship between %DDT and %DDE. That is, for every one DDT being transformed, one DDE is being produced with very little DDD being produced. The mean data points for M in the shallow and deep soils plot just above the points for S. This means that at M, the same 1:1 relationship occurs, but to a greater extent. The mean data points for CHM in the shallow and deep soils plot above the two, at the apex of the triangle. This means that at CHM, the same 1:1 relationship of DDT to DDE transformation occurs yet again, but to an even greater extent still. In other words, the greatest transformation of DDT to DDE occurs at CHM>M>S.

This 1:1 relationship is shown in Figure 33. Again, this indicates that most of the DDT at these study sites is transformed to DDE. In both the shallow and deep soils, CHM shows the lowest %DDT and the highest %DDE. M and S display the same trend towards %DDE production, although they have higher %DDT and lower %DDE, an

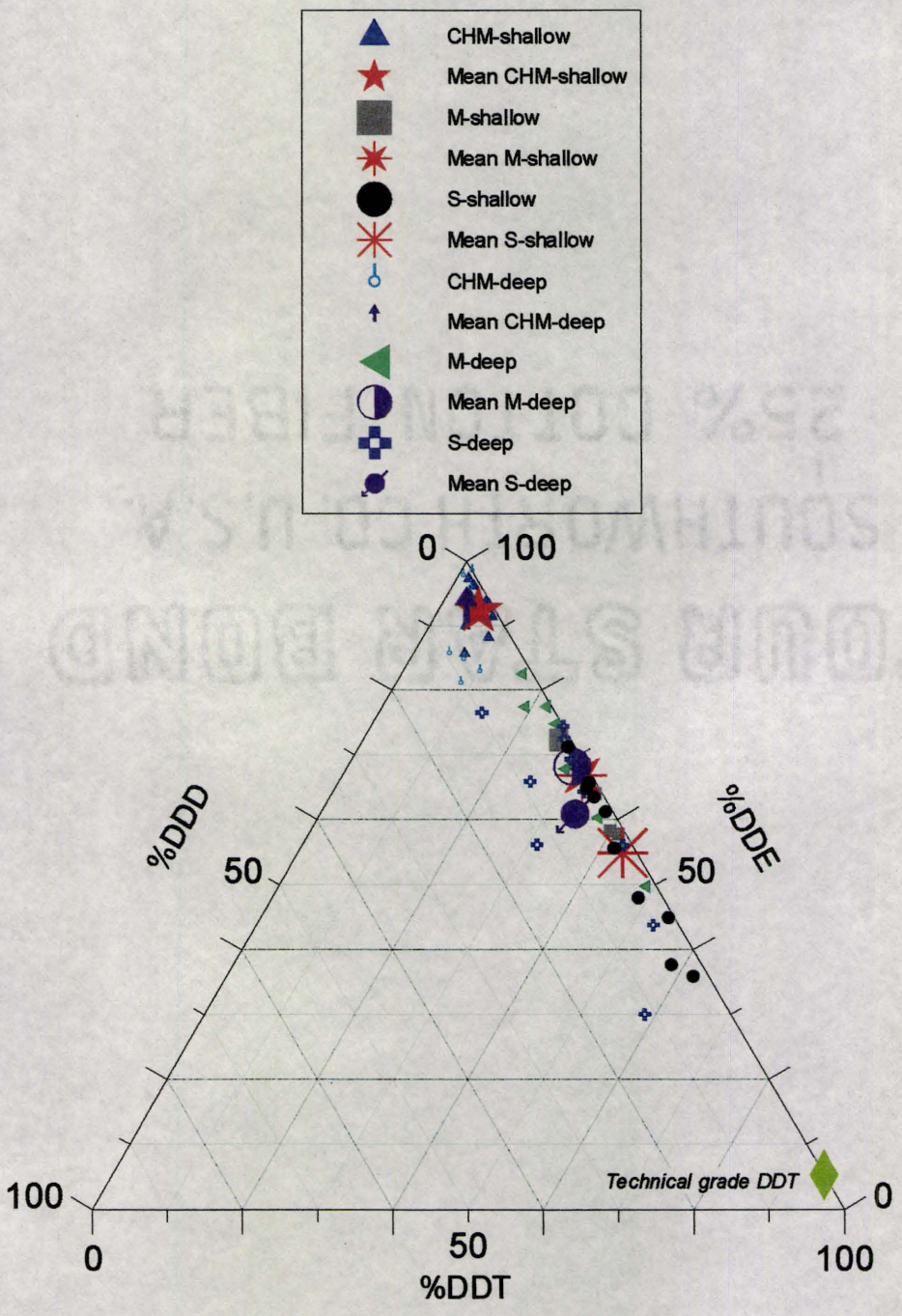


Figure 32. Ternary graph illustrating the %DDT, %DDE and %DDD in the shallow and deep soils at each site.

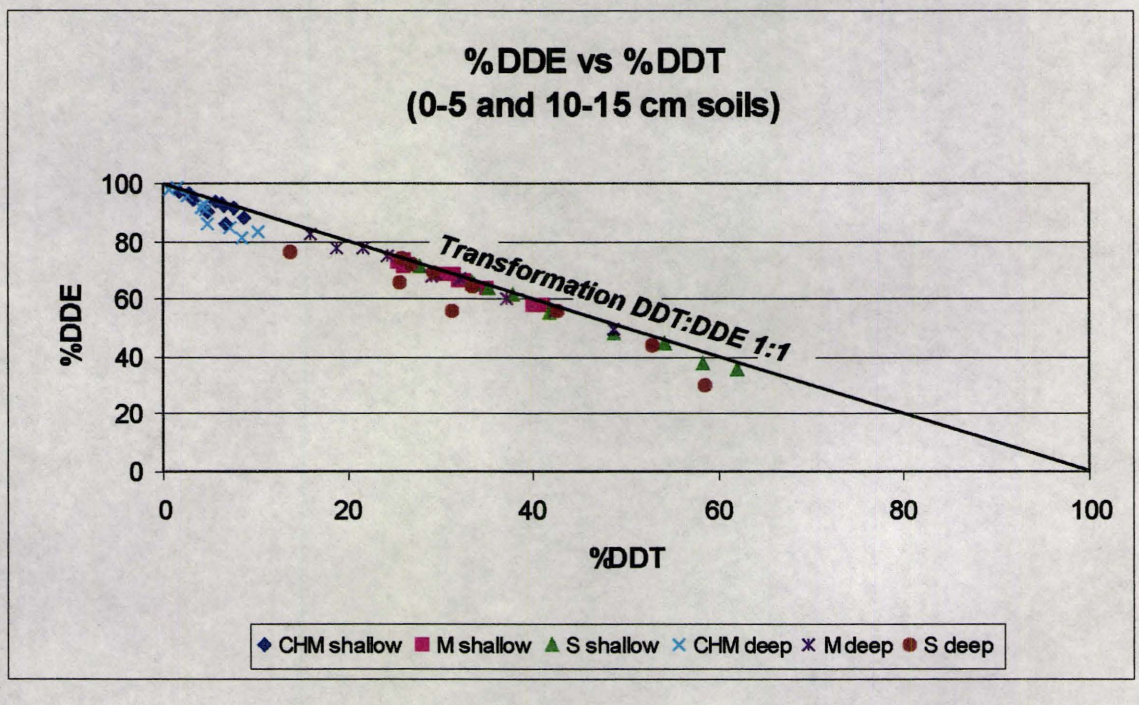


Figure 33. The transformation of %DDT to %DDE at S, M and CHM in the shallow and deep soils. Note the 1:1 relationship of %DDE production to %DDT degradation.

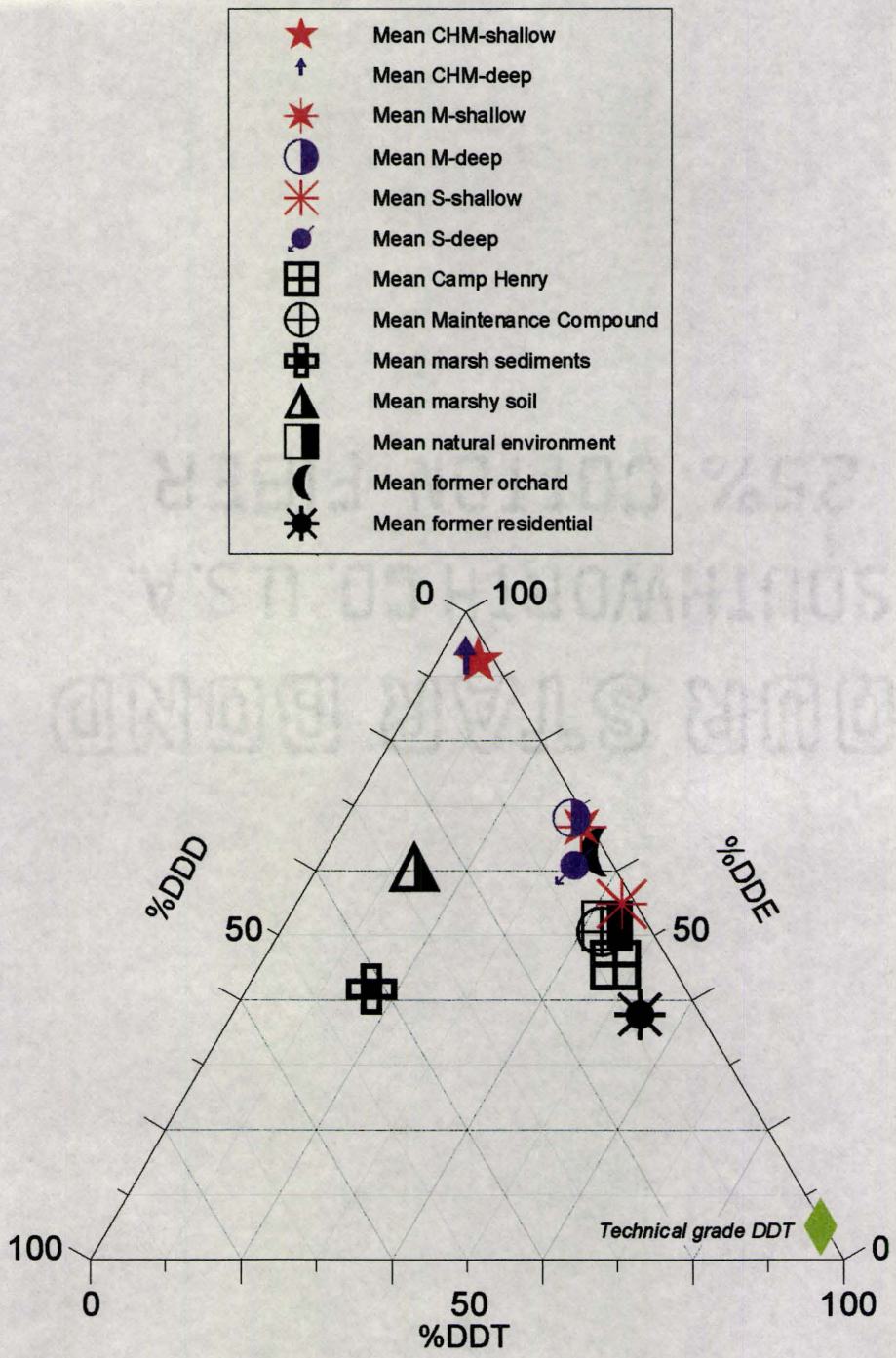


Figure 34. Ternary graph illustrating the mean %DDT, %DDE and %DDD in the shallow soils at the 7 land-use sites, as well as at S, M and CHM.

indication that the rates of degradation at these study sites are not as fast as those at CHM. S shows the highest degree of variability in %DDE versus %DDT in the shallow and deep soils. At CHM, M and S, there is a preference for the transformation of DDT to DDE, which is expected because of the aerobic conditions that predominate at these sites.

The data at CHM, M and S were also plotted with the historical land-use data (Figure 34) compiled by Crowe et al. (2002). For the most part, all samples plot along the 1:1 DDT:DDE line with the exception of the marshy soils and marsh sediments, which are primarily anaerobic environments favouring the transformation of DDT to DDD.

Clearly, the predominant metabolite at all three study sites is currently DDE. The trend at PPNP is similar to that in other parts of Canada and the world, where according to Harris and Miles (1975), DDE was the predominant metabolite in Ontario. Although its predominance was not satisfactorily explained at the time, it was thought that the conversion of DDT to DDE in soil was brought about by worms, reptiles and amphibians in the soil rather than soil microorganisms (Harris and Miles, 1975). Other studies also show that DDE made up the major proportion of DDX in American soil, orchard soil in England, and New Zealand soils with a known DDT application history (Ware et al., 1978; Cooke and Stringer, 1982; Boul et al., 1994).

DDT has primarily degraded to DDE and to a lesser extent, DDD, at a faster rate at the more organic-rich study site, CHM. For instance, in the shallow soils, CHM has the lowest sample mean %DDT and the highest sample mean %DDE and %DDD. The

faster degradation can be explained by its topography and related hydrology. Historically, CHM, located adjacent to the marsh, experienced flooding by marsh waters when water levels were high (>174.0 m amsl). This flooding created anaerobic environments, as indicated by the thick accumulation of organic matter. Fleming and Maines (1953) observed that DDT persisted longest in sand and least in organic-rich soil (muck).

The relationship between organic carbon (%OC), organic nitrogen (%ON) and DDT, DDE and DDD persistence in the shallow and deep soils at the three study sites were examined. In the shallow and deep soils, CHM, which has the highest %OC, also has the lowest %DDT and the highest %DDE. Boul et al. (1994) observed that the lower DDT concentrations in surface layers of soil (0-5 cm layer) were likely due to greater adsorption in areas with higher organic matter, perhaps in the top few mm. At PPNP, because DDT was applied aerially, it first made contact with the plant cover and surface soil. In the surface soil, DDT likely absorbed onto the OM, preventing it from migrating downwards.

Because all study sites show a high degree of variability in %DDT, %DDE, %DDD to %OC and %ON, it is likely that at PPNP, neither OC nor ON are limiting factors in the degradation of DDT to its metabolites. Furthermore, because the %DDT, %DDE and %DDD are sufficiently low relative to the %OM, it is likely that all potential adsorption sites are not filled. In other words, an increase or decrease in %OM generally shows no effect on the %DDT, %DDE and %DDD in the shallow or deep soils.

Because soils with higher organic matter contents tend to hold more water than other soil types, CHM remains wetter than the other studied locations, even with depth and even in dry years, as seen in Figure 25 and as was described in Section 4.7. In addition, the water table is less than half a meter below ground surface and the soils above it are noticeably wet.

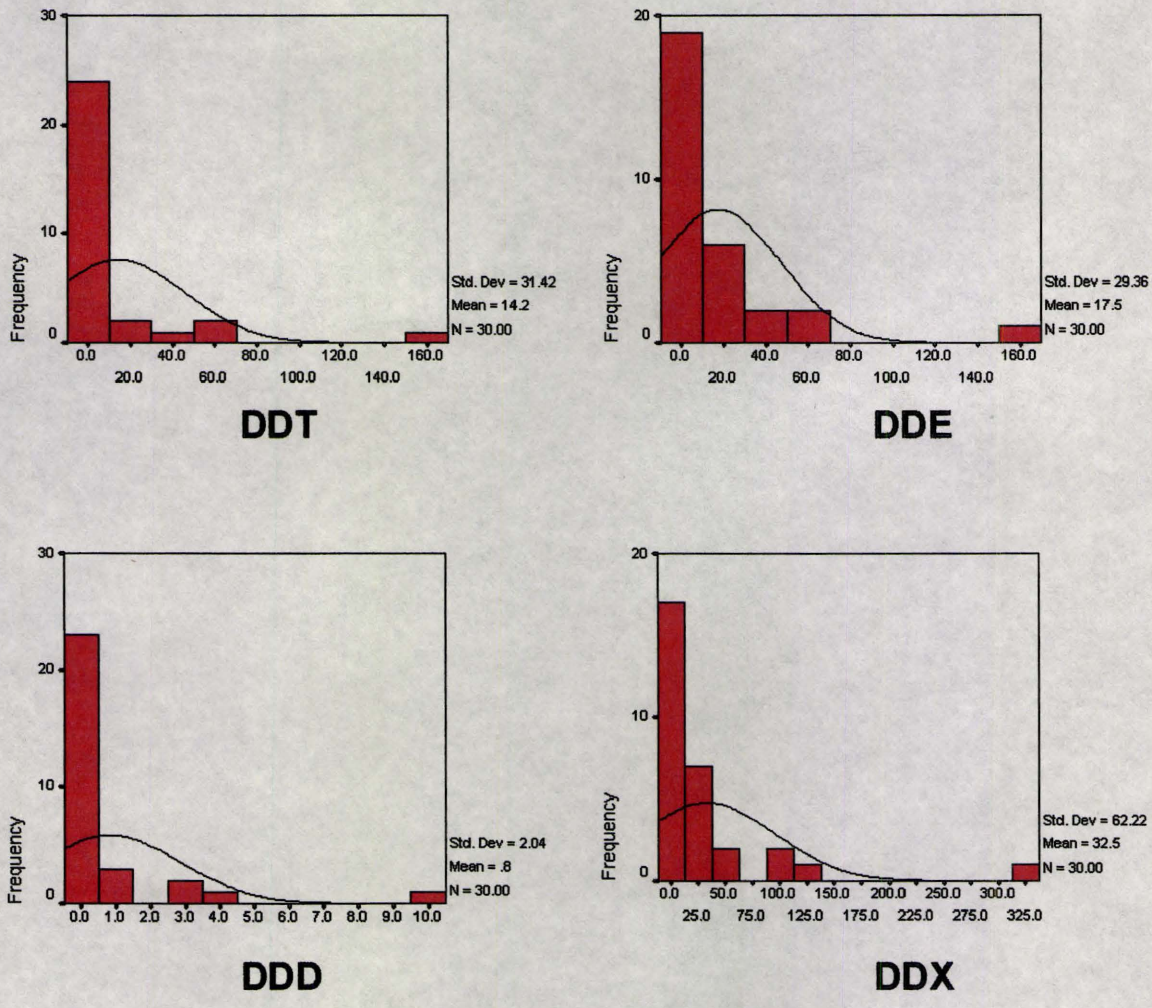
In addition, sites S and M have higher ground surface elevations, and have deeper depths to the water table, even in wet years. The surface soils here are never submerged by marsh waters and remain aerobic all year long. The lower organic matter contents mean that soils here don't retain as much water, even when conditions are wet. Because DDX levels are so low compared to the amount of organic matter, most of it is absorbed in the surface layers. There is thus little migration of any of the residues with infiltrating waters from the surface to the layers below.

To further assess the data, more rigorous statistical analyses were performed. DDT, DDE, DDD and DDX concentration histograms were first plotted (Figure 35) that indicated that these concentrations were not normally distributed, but that the log-concentrations were normally distributed. Consequently, the analysis was undertaken using log data (i.e. using the log values of the concentrations instead of the raw concentration values).

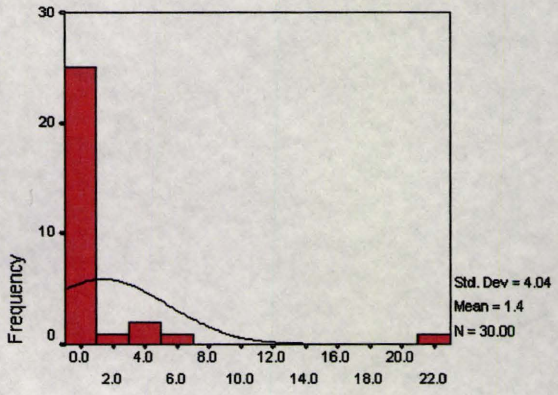
ANOVA tests for the shallow soils (Table 52) indicate that there are significant differences in log DDT and log DDX between the three pairs; log concentrations of DDT and DDX at S, M and CHM are dissimilar. However, ANOVA tests for the shallow soils

Figure 35. Concentration histograms and log concentration histograms of DDT, DDE, DDD and DDX in the shallow and deep soils.

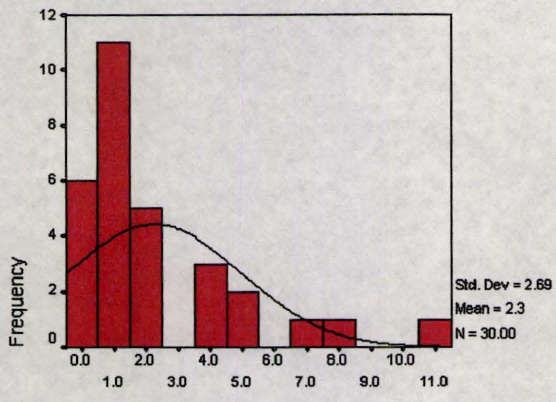
A. SHALLOW



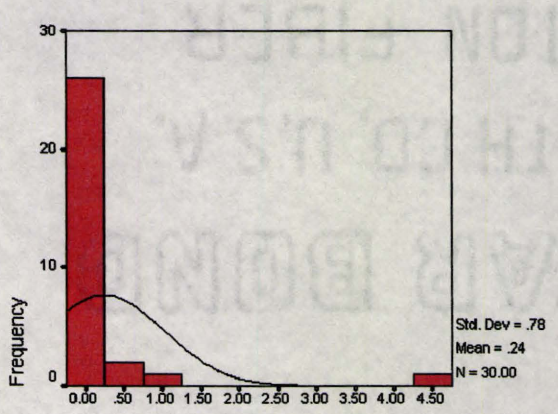
B. DEEP



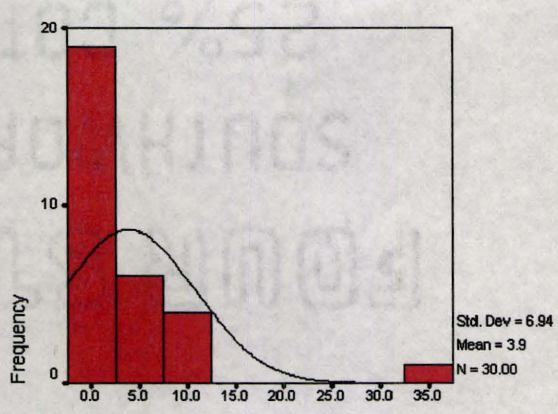
DDT



DDE

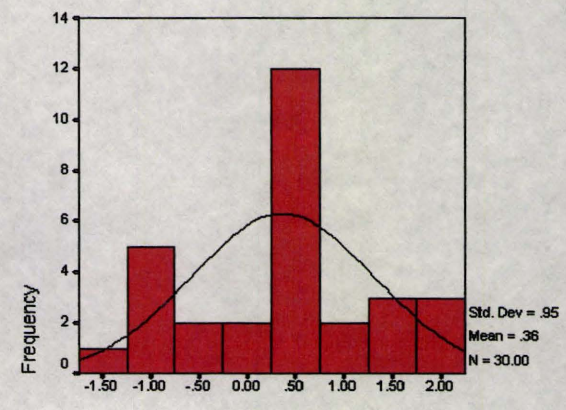


DDD

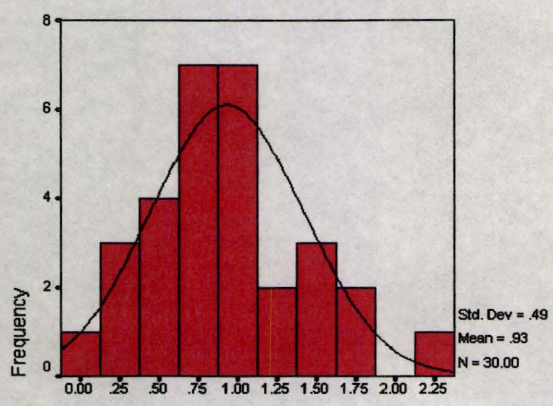


DDX

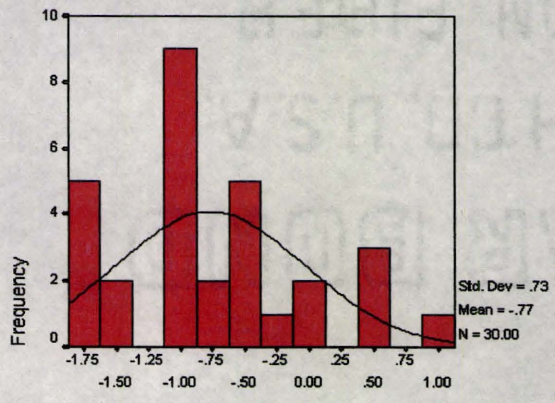
C. SHALLOW



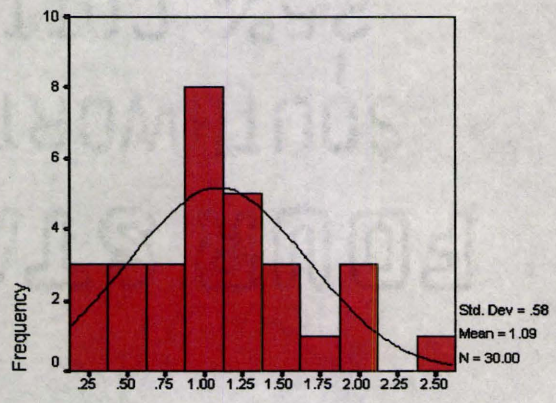
Log DDT



Log DDE

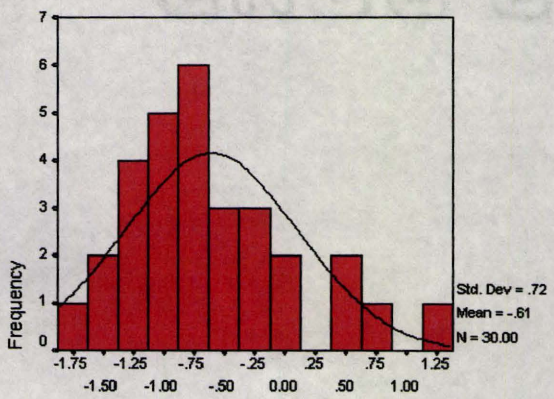


Log DDD

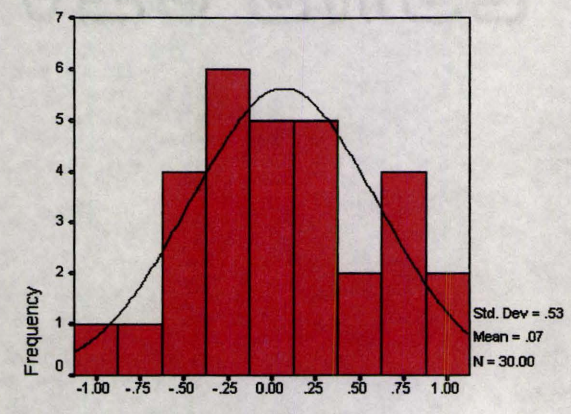


Log DDX

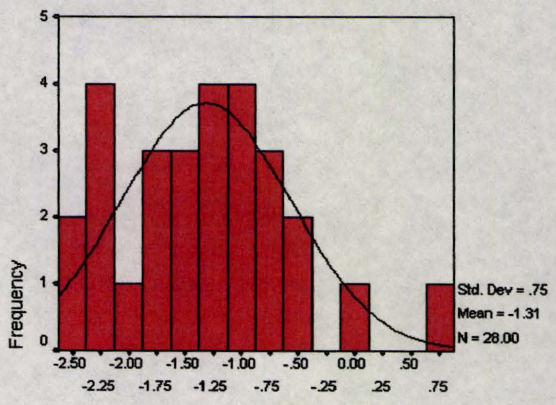
D. DEEP



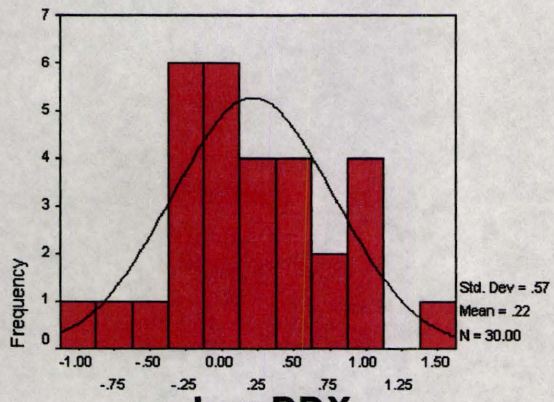
Log DDT



Log DDE



Log DDD



Log DDX

indicate that there are significant differences in log DDE and log DDD between two out of the three pairs; there are only no significant differences in the log concentrations of CHM and M.

Table 52. ANOVA results of the log concentrations of DDT, DDE, DDD and DDX of soil sampling in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

Log DDT (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	S
S	S	S	\

Log DDE (0-5)	CHM	M	S
CHM	\	NS	S
M	NS	\	S
S	S	S	\

Log DDD (0-5)	CHM	M	S
CHM	\	NS	S
M	NS	\	S
S	S	S	\

Log DDX (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	S
S	S	S	\

ANOVA tests for the deep soils (Table 53) indicate that there are no significant differences in log DDT, log DDE, log DDD and log DDX between the three pairs; log concentrations of DDT, DDE, DDD and DDX at S, M and CHM are similar.

Table 53. ANOVA results of the log concentrations of DDT, DDE, DDD and DDX of soil sampling in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Log DDT (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Log DDE (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Log DDD (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Log DDX (10-15)	CHM	M	S
CHM	\	NS	NS
M	NS	\	NS
S	NS	NS	\

Because of the low solubility of DDT, DDE and DDD, downward leaching in the soil horizons at the study sites was not a major route of loss. In fact, their solubility and their high organic carbon adsorption coefficients are the main reasons why sampling focused only on the O-horizons of the soil column. Most reports show negligible vertical movement of DDT in laboratory (Bowman et al., 1965; Guenzi and Beard, 1967) and field (Guenzi et al., 1971) studies. In studies by Guenzi and Beard (1967), during wetting and drying cycles, DDT remained in the first 0 to 3 cm of all soils tested.

Analyses of the PPNP data with depth confirm that raw concentrations of DDT and its metabolites are highest at the surface and decrease with depth. The shallow soils

at CHM, M and S have higher sample mean %DDT. The shallow soils at CHM also have a higher sample mean %DDE and %DDD. T-tests for CHM (Table 54) indicate that there are no significant differences in log DDT, log DDE, log DDD and log DDX between the shallow soils and deep soils. Contrary to what is expected, the shallow soils of M and S have lower %DDE and %DDD. T-tests for M and S indicate that there are significant differences in log DDT, log DDE, log DDD and log DDX between the shallow soils and deep soils.

Table 54. T-test results of the log concentrations of DDT, DDE, DDD and DDX between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Log DDT	**CHM (0-5)**	**M (0-5)**	**S (0-5)**
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

Log DDE	**CHM (0-5)**	**M (0-5)**	**S (0-5)**
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

Log DDD	**CHM (0-5)**	**M (0-5)**	**S (0-5)**
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

Log DDX	**CHM (0-5)**	**M (0-5)**	**S (0-5)**
CHM (10-15)	NS	\	\
M (10-15)	\	S	\
S (10-15)	\	\	S

The mean concentration of DDT in μg/g is highest at S and lowest at CHM. The mean concentration of DDE in μg/g is highest at S and lowest at M. The mean concentration of DDD in μg/g is highest at S and lowest at M. The mean concentration of DDX in μg/g is highest at S and lowest at CHM. The mean %DDT is highest at S and lowest at CHM. The mean %DDE is highest at CHM and lowest at S. The mean %DDD is lowest at S and similar at M and CHM.

4.10 DDT, DDE, DDD and DDX as a Function of Land-use

Very few studies (Truhlar and Reed, 1976; Johnson et al., 1988; Crowe et al., 2002) have examined compounds such as DDT in relation to land-use history. This relationship is important however because the analysis of DDT and its metabolites in soil is costly. Knowledge about it with relation to land-use will thus improve the design of the study and future land management practices.

To assess if former land-use practices influenced DDT persistence at the three study sites, the log concentrations of DDT, DDE, DDD and DDX from S, M and CHM were compared to the log concentrations of DDT, DDE, DDD and DDX from the 7 land-use zones identified by Crowe et al. (2002). This compiled data is from several different studies by several different groups and agencies over a period of several years. In addition, the samples were obtained from several different areas at the Park, from several different depths and were analyzed by different laboratories, likely with different

methodologies. The quality of this historical data is thus not great, but it can be used to show whether the data obtained from the study sites follows the same trends as these other land-use areas. These land-use areas were previously described in Section 1.8.

ANOVA tests for the shallow soils (Table 55) indicate that there are no significant differences in log DDT between: (a) CHM and the Maintenance Compound, Camp Henry, and the marshy soil; and (b) M and the former orchard. There are however, significant differences between the other pairs, as summarized in Table 55. The same tests indicate that there are no significant differences in log DDE between CHM and the former orchard and M and the former orchard. There are significant differences between the other pairs.

ANOVA tests for log DDD in the shallow soils indicate that there are significant differences between: (a) CHM and the former residential areas and natural environments; and (b) M and the former residential areas, natural environments, and the marsh sediments. The same tests indicate that there are no significant differences between S and the marshy soil. However, there are significant differences between the other pairs.

ANOVA tests for log DDX indicate that there are no significant differences between: (a) CHM and the former orchard and Camp Henry; and (b) M and the former orchard. There are significant differences between the other pairs.

Table 55. ANOVA results of the log concentrations of DDT, DDE, DDD and DDX between the shallow soils from S, M and CHM and the different land-use zones at PPNP.

Log DDT		**CHM**	**M**	**S**
	Former orchard	S	NS	S
	Former residential areas	S	S	S
	Maintenance Compound	NS	S	S
	Natural environment	S	S	S
	Camp Henry	NS	S	S
	Marsh sediments	S	S	S
	Marshy soil	NS	S	S
Log DDE		**CHM**	**M**	**S**
	Former orchard	NS	NS	S
	Former residential areas	S	S	S
	Maintenance Compound	S	S	S
	Natural environment	S	S	S
	Camp Henry	S	S	S
	Marsh sediments	S	S	S
	Marshy soil	S	S	S
		CHM	**M**	**S**
Log DDD				
	Former orchard	NS	NS	S
	Former residential areas	S	S	S
	Maintenance Compound	NS	NS	S
	Natural environment	S	S	S
	Camp Henry	NS	NS	S
	Marsh sediments	NS	S	S
	Marshy soil	NS	NS	NS
Log DDX		**CHM**	**M**	**S**
	Former orchard	NS	NS	S
	former residential areas	S	S	S
	Maintenance Compound	S	S	S
	natural environment	S	S	S
	Camp Henry	NS	S	S
	marsh sediments	S	S	S
	marshy soil	S	S	S

Table 55 identifies whether the degree of contamination is different at one land-use area relative to another. Table 56 presents results for the %DDT, %DDE and %DDD concentration data. This data addresses the pathway of degradation of DDT at PPNP.

Of interest are sites CHM and S because they are "opposites" with regards to DDT degradation at certain sites. For instance, ANOVA results of %DDT at CHM indicate that there are no significant differences between CHM and the marsh sediments and marshy soils, while all other pairs show significant differences. At S, there are significant differences between S and the marsh sediments and marshy soils, while all other pairs show no significant differences. Furthermore, ANOVA results for %DDE at CHM indicate that there are significant differences between CHM and the 7 land-use zones defined by Crowe et al. (2002), while at S, there are no significant differences between S and the 7 land-use zones. M is an "intermediary" between S and CHM showing significant differences and no significant differences in %DDT and %DDE when compared to the other 7 land-use zones. The ANOVA results for %DDD indicate that all three study sites show a similar pattern with respect to the other 7 land-use zones. In other words, there are only significant differences in CHM, M and S between the marshy soils and marsh sediments; all other pairs show no significant differences.

Table 56. ANOVA results of the percent concentrations of DDT, DDE, DDD and DDX between the shallow soils from S, M and CHM and the different land-use zones at PPNP.

% DDT		CHM	M	S
	Former orchard	S	NS	NS
	Former residential areas	S	S	NS
	Maintenance Compound	S	NS	NS
	Natural environment	S	NS	NS
	Camp Henry	S	NS	NS
	Marsh sediments	NS	NS	S
	Marshy soil	NS	NS	S

% DDE		CHM	M	S
	Former orchard	S	NS	NS
	Former residential areas	S	S	NS
	Maintenance Compound	S	NS	NS
	Natural environment	S	NS	NS
	Camp Henry	S	S	NS
	Marsh sediments	S	S	NS
	Marshy soil	S	NS	NS

% DDD		CHM	M	S
	Former orchard	NS	NS	NS
	Former residential areas	NS	NS	NS
	Maintenance Compound	NS	NS	NS
	Natural environment	NS	NS	NS
	Camp Henry	NS	NS	NS
	Marsh sediments	S	S	S
	Marshy soil	S	S	S

As previously stated, Figure 34 illustrates that other land-areas at PPNP display the same DDT degradation pathways as sites S, M and CHM. As can be seen, with the exception of the marshy soils and marsh sediments, most DDT at PPNP is transformed to

DDE. This is consistent with the fact that the transformation of DDT to DDE occurs under aerobic conditions that are found in areas well above the water table. The transformation of DDT to DDD favours anaerobic conditions, where the soil is flooded or wet for extended periods. In other words, the conversion of DDT to DDD is strongly dependent on the moisture conditions of the soil. However, the transformation of DDT to DDE occurs in both the anaerobic and aerobic environments, which is why it is always present as a daughter product of DDT.

Of interest, there is a significant difference in log DDT, log DDE, log DDD and log DDX between the soils of S and the former orchards as compiled by Crowe et al. (2002). However, there is no significant difference in %DDT, %DDE and %DDD between the soils of S and the former orchards as compiled by Crowe et al. (2002). There is a significant difference in log DDE, log DDX, %DDE and %DDD between the marshy soils of CHM and the marshy soils as compiled by Crowe et al. (2002). However, there is no significant difference in log DDT, log DDD, and %DDT between the marshy soils of CHM and the marshy soils as compiled by Crowe et al. (2002). These statistics suggest that the soils at S are similar to those of the former orchards and that the soils at CHM are similar to those of the marshy soils at PPNP with regards to %DDT concentrations.

4.11 DDT, DDE and DDD as a Function of Ground Surface Elevation

Since historic soil wetness has been a factor affecting DDT degradation and the water table at PPNP is essentially flat, ground surface elevation is directly related to historic soil wetness and intermittent flooding. Figure 36 is a plot of ground surface elevation versus the percent concentrations of DDT, DDE and DDD. Figure 36a shows that the %DDT is lowest at the site lowest in elevation, CHM and highest at the site that is highest in elevation, S. M is the middle site in terms of %DDT and elevation. Figure 36b shows that the %DDE, which is the predominant transformation product of DDT at S, M and CHM is highest at CHM and lowest at S, with M being the middle site again. Figure 36c shows that there is very little %DDD at CHM, M and S.

Because the soils at S and M are higher in ground surface elevation, even higher than the highest Lake and marsh water levels (>175.1 m amsl), they are never flooded. They have thus not accumulated as much organic matter as the soils of CHM, as seen in the soil profiles (Figure 12). This inherently means that, even in the wettest years (e.g. 1974, 1987 and 1997), they do not retain as much water, as illustrated in the moisture characteristic curves (Figure 25). The water table is also deep here, up to 2 m at S for instance. Because the capillary fringe is so narrow (approximately 5 cm thick; Figure 25), the soils above the water table are not noticeably wet and these soils remain aerobic all year. As can be seen from Figure 36, DDT is preferentially transformed to DDE in these aerobic soils, with smaller amounts of DDD.

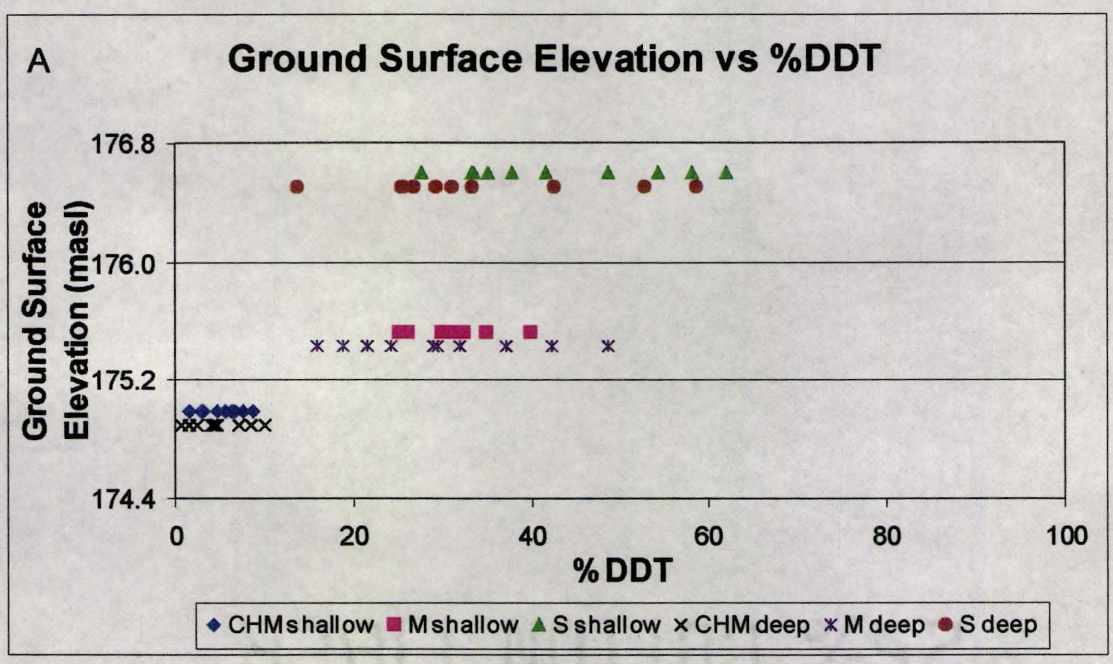
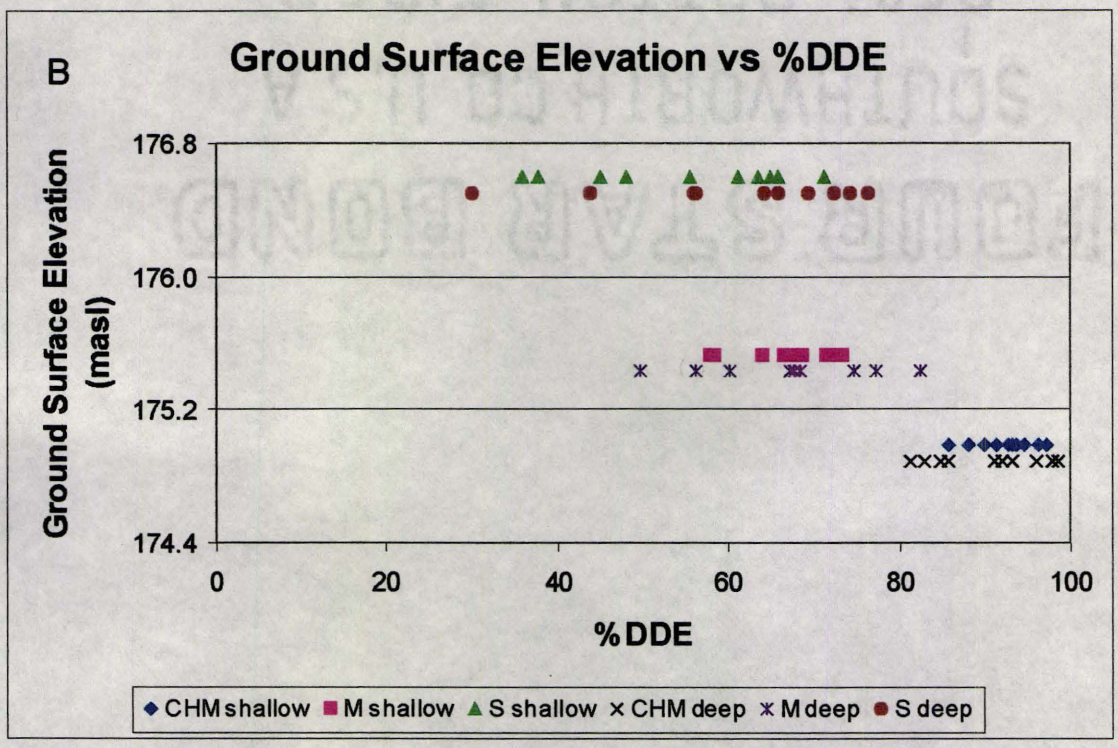
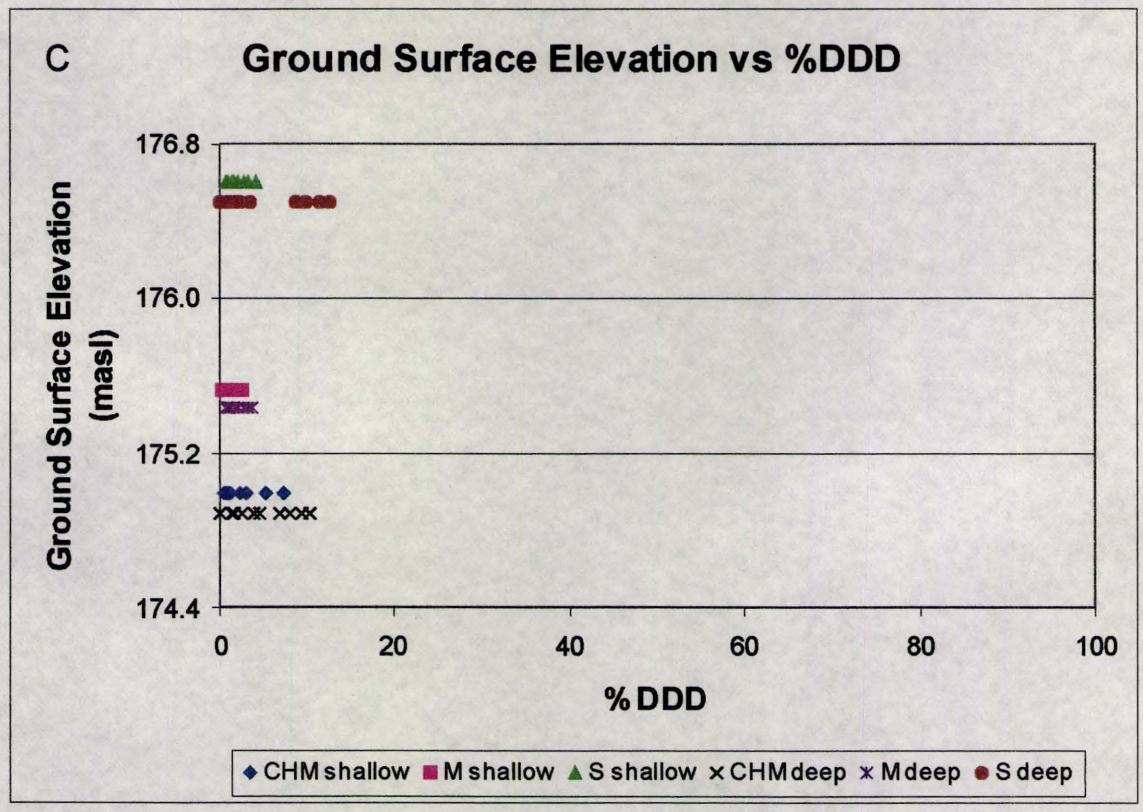


Figure 36. (a) Ground surface elevation vs %DDT at S, M and CHM in the shallow and deep soils; (b) ground surface elevation vs %DDE at S, M and CHM in the shallow and deep soils; (c) ground surface elevation vs %DDD at S, M and CHM in the shallow and deep soils.


B
Ground Surface Elevation vs %DDE
Ground Surface Elevation (masl)
176.8
176.0
175.2
174.4
0
20
40
60
80
100
%DDE
CHM shallow
M shallow
S shallow
CHM deep
M deep
S deep


C
Ground Surface Elevation vs %DDD
Ground Surface Elevation (masl)
176.8
176.0
175.2
174.4
0
20
40
60
80
100
% DDD
CHM shallow
M shallow
S shallow
CHM deep
M deep
S deep

On the other hand, DDT is preferentially transformed to DDE, with smaller amounts of DDD to an even greater extent at CHM, because it has a relatively lower-lying ground surface elevation and thus, very different hydrological conditions. The soils here were historically intermittently flooded (e.g. 1974, 1987 and 1997) by the marsh when Lake and marsh water levels were high (>174.0 m amsl). The resulting increase in mean soil moisture increased anaerobic environments within the soil. This in turn, led to an accumulation in organic matter, as can be seen in the soil profile (Figure 12). Today, even in very dry years, these soils are wetter than those of S and M, because they are able to hold more water (as seen in the moisture characteristic curves of Figure 25). The water table is also shallow here, less than half a meter in some areas. In addition, the capillary fringe in the shallow soils is often between 0 and 10 cm thick and thus, the soils above the water table are noticeably wet.

The data shows that CHM, which is lowest in elevation has the lowest mean %DDT and the highest mean %DDE. S, which is the highest in elevation, has the highest mean %DDT and the lowest mean %DDE. M is intermediate between the two. The mean %DDD is very low and approximately the same.

4.12 DDT Degradation at PPNP

Though the three study sites have texturally and compositionally similar soil types and are within a 93 m radius, they are characterized by different: (a) topographies; (b) hydrologic conditions; and (c) soil organic matter environments, which affect DDT degradation rates and pathways at each site.

It is well known that pesticides can be lost from soils in several ways (Edwards, 1966). At PPNP, it is suspected that a significant loss of DDT from soil over time did not occur at the study sites through (Figure 37): (1) volatilization; (2) leaching, runoff, erosion; and (3) plant uptake. Significant loss of DDT from soil over time occurred through microbial degradation. Volatilization would have been minimal at the study sites due to the temperate conditions. Runoff would be insignificant because of the high hydraulic conductivity, which would permit rapid infiltration and erosion would have been insignificant because of plant coverage. Consequently, microbial degradation would have been the major route of loss over time at the study sites.

Based on the data, we can now characterize the three study sites into two distinct environments, the first of which includes M and S and designated "sandy area", and the second of which includes CHM and designated "marshy area". The sandy area was formerly a cultivation area (orchards and vegetable fields abandoned in circa 1948) east of the main road that is now covered by grasses, even tall grasses in some areas, as well

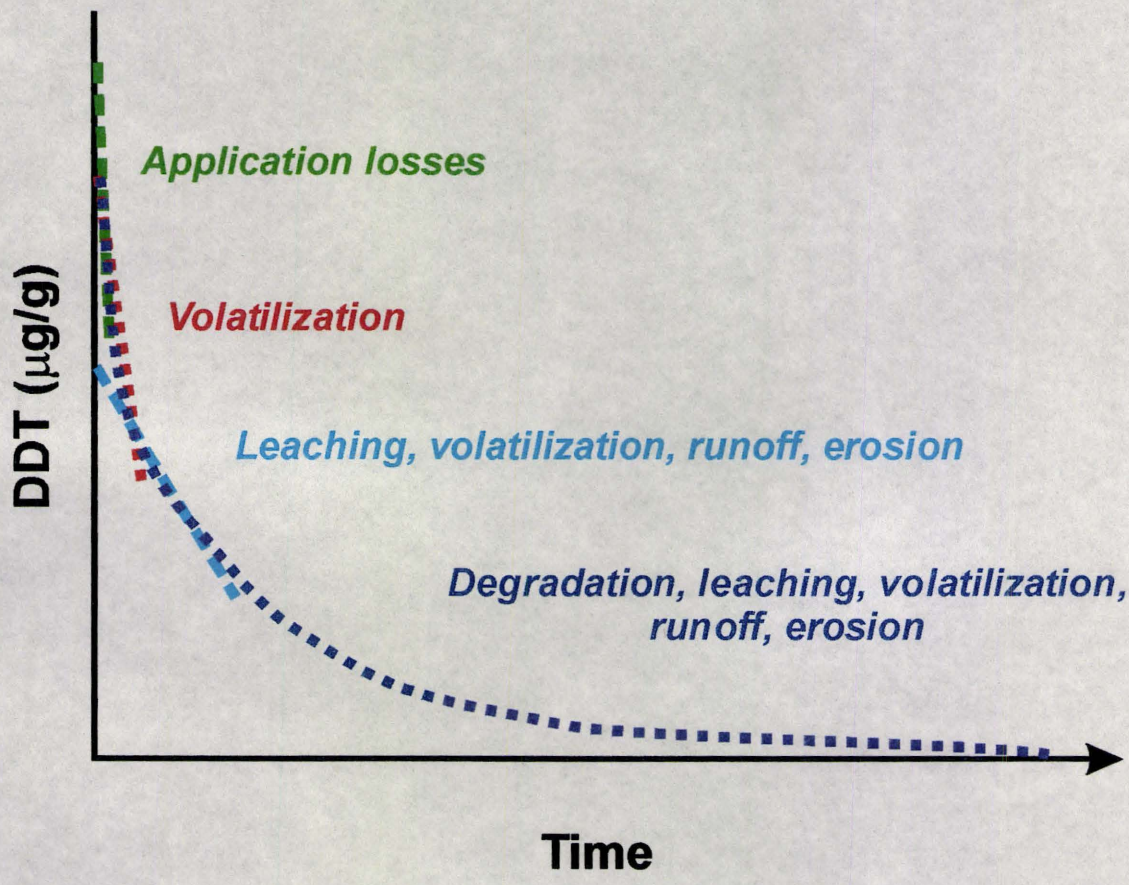


Figure 37. Theoretical breakdown curve for DDT in soil (modified from Edwards, 1966).

as trees and shrubbery common to a temperate environment. The local topography here is relatively higher-lying (>175.1 m amsl).

DDX concentrations and %DDT are highest here, with relatively lower levels of %DDE and %DDD. This indicates that this sandy area is more conducive to DDT persistence than DDT degradation and that degradation occurs at a slower rate here than at the marshy area, discussed below. The DDT degradation pathway is likely from DDT → DDE with DDT → DDD with a much lesser extent. The higher levels of %DDE than %DDD indicate that the soils here remain aerobic all year round.

The marshy area is quite different especially with regards to its land-use history and hydrology. It was formerly adjacent to a cultivation area (orchards and vegetable fields abandoned in circa 1948) east of the main road and just north of a former campsite. Because the area is located adjacent to the marsh fringes, the vegetation is characteristic of what one might find in a marsh. Sedge grasses common to a temperate climate, are common.

As a result of the relatively lower-lying ground surface elevation (<175.1 m amsl), the hydrological conditions here are very different. The soils tend to be seasonally wet soils here, that is, soils that are saturated with water and become anaerobic or "chemically reduced" for part of the year some years (e.g. 1984, 1987 and 1997). These soils characteristically have a thick organic soil layers.

DDX concentrations are lowest at the marshy area. The %DDT is also lowest here, with higher levels of %DDE and %DDD. Clearly, this environment is more

conducive to DDT degradation than DDT persistence with degradation occurring at a faster rate here than the previous environment. The degradation pathway is likely DDT → DDE under aerobic conditions, and DDT → DDD under anaerobic conditions. Because aerobic conditions prevail here, the %DDE in soils is still higher than the %DDD.

More specifically, the degradation of DDT here is likely due to the alternating aerobic-anaerobic conditions that result from the intermittent flooding by marsh waters. The alternating anaerobic and aerobic conditions occurring promote reductive dechlorination and ring cleavage reactions respectively (Aislabie et al., 1997). In studies by Corona-Cruz et al. (1999), Beunik and Rehm (1988), and Sethunathan (1973), coupled anaerobic-aerobic systems were the most effective at degrading DDT to DDD and DDE. These fluctuating anaerobic-aerobic conditions caused DDT metabolites stable under one environment to undergo rapid decomposition if the soil was reoxidized and vice-versa.

DDT degrades to its daughter products DDE and DDD to a greater extent in areas below 175.1 m amsl. These areas are flooded by the marsh for part of the year some years when water levels are above 174.0 m masl. DDT tends to persist at locations above 175.1 m masl. These areas are never flooded by the marsh when water levels are high.

4.13 Relative DDT Half-lives at PPNP

Because half-life estimates quoted here have been prepared on a concentration basis, the associated losses will not only include degradation processes but also losses to other environmental factors (Figure 37). Based on the present day sample mean %DDT at each study site in both the shallow and deep soils, half-life estimates for the first order decay of DDT to DDE and DDD, with no further degradation of DDE and DDD were calculated using Eq. 4 (Figure 38 and Table 57). The estimates of the mean relative half-lives of DDT in the shallow soils are 7 years at CHM, 18 years at M, and 25 years at S. Half-life estimates for DDT in the deep soils are 7 years at CHM, 17 years at M and 19 years at S.

ANOVA tests for the shallow soils (Table 58) indicate that there are significant differences in relative DDT half-lives between the three pairs; relative half-lives of DDT at S, M and CHM are dissimilar. ANOVA tests for the deep soils (Table 59) indicate that there are only significant differences in relative DDT half-lives between two out of the three pairs; there are no significant differences in relative DDT half-lives between M and S in the deep soils.

T-tests for CHM, M and S (Table 60) indicate that there are no significant differences in relative DDT half-lives between the shallow soils and deep soils.

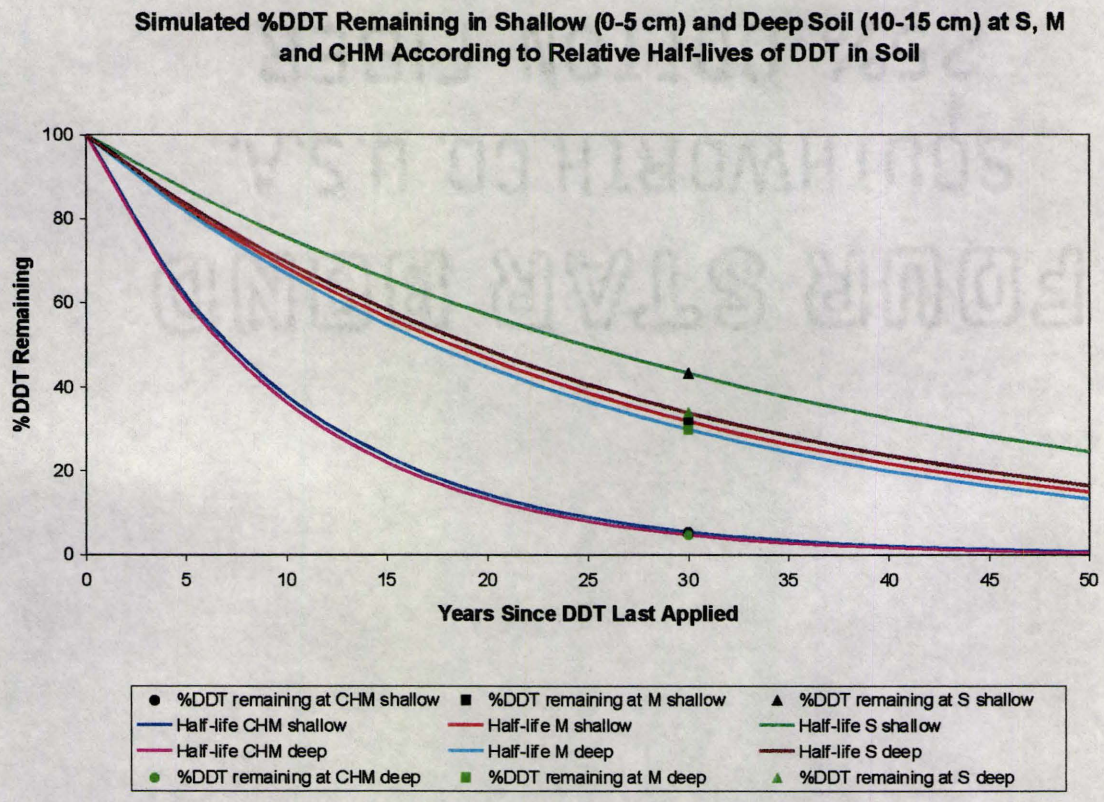


Figure 38. (a) Simulated %DDT remaining in the shallow and deep soils at PPNP according to various half-lives in soil.

Table 57. Relative half-life estimates of DDT with no further degradation of DDE and DDD in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

	Shallow $t_{½}$	Deep $t_{½}$
CHM-1	5	8
CHM-2	7	8
CHM-3	6	4
CHM-4	7	6
CHM-5	8	7
CHM-6	8	7
CHM-7	8	7
CHM-8	8	5
CHM-9	9	6
CHM-10	6	9
Mean	7	7
M-1	15	21
M-2	15	29
M-3	20	17
M-4	18	17
M-5	18	12
M-6	17	24
M-7	23	15
M-8	18	14
M-9	15	18
M-10	23	11
Mean	18	17
S-1	34	24
S-2	24	16
S-3	19	17
S-4	21	15
S-5	44	33
S-6	38	39
S-7	16	10
S-8	29	19
S-9	20	18
S-10	19	15
Mean	25	19

Table 58. ANOVA results of the relative DDT half-lives in the shallow (0 – 5 cm) soils from S, M and CHM at PPNP.

$t_{½}$ (0-5)	CHM	M	S
CHM	\	S	S
M	S	\	S
S	S	S	\

Table 59. ANOVA results of the relative DDT half-lives in the deep (10 – 15 cm) soils from S, M and CHM at PPNP.

$t_{½}$ (10-15)	CHM	M	S
CHM	\	S	S
M	S	\	NS
S	S	NS	\

Table 60. T-test results of the relative DDT half-lives between the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

$t_{½}$	CHM (0-5)	M (0-5)	S (0-5)
CHM (10-15)	NS	\	\
M (10-15)	\	NS	\
S (10-15)	\	\	NS

Because this method assumes no further degradation of the daughter products, it provided a conservative estimate of possible half-lives for DDT, i.e. these $t_{½}$ estimates provide an upper limit for degradation half-lives. However, it:

(i) did not provide a model of DDT decay that took into account the degradation of DDE and DDD at each site, i.e. DDE and DDD were assumed to persist

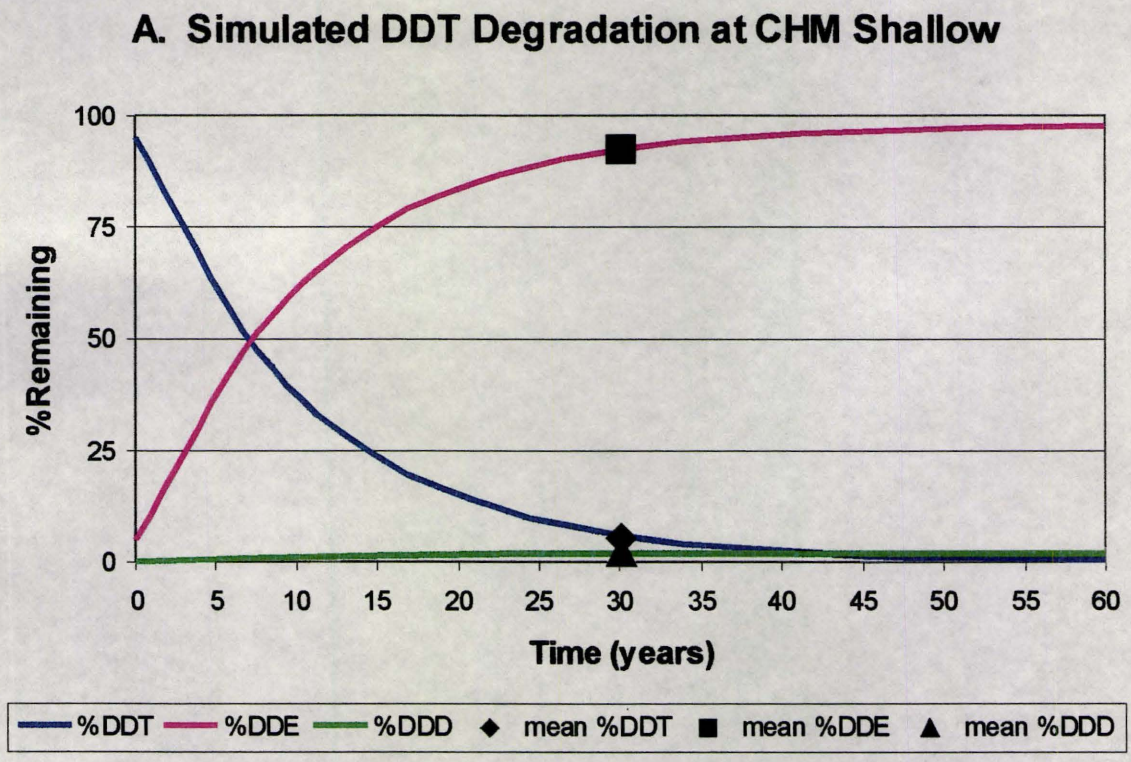
(ii) did not produce DDE/DDX and DDD/DDX ratios that matched the observed data at all 60 sampling locations.

The second method required the further degradation of DDE and DDD. Table 61 shows the $e^{-k_A t}$, $e^{-k_B t}$, $e^{-k_C t}$, $e^{-k_D t}$, $e^{-k_E t}$, $e^{-k_F t}$ and $e^{-k_G t}$ degradation terms that were required in the iterative procedure that includes further degradation of DDE and DDD to match the observed %DDT, %DDE and %DDD in the shallow and deep soils at S, M and CHM. Table 62 shows the half-life estimates for DDT using this method (Figure 39). In all cases, degrading DDE to its daughter products did not improve the match to the current observed %DDE at any of the sites. That means DDE persists in the shallow and deep soils. However, in all the deep soils and in the shallow soils at M, the degradation of DDD to its daughter products was required to match the current observed %DDD at those locations. In other words, although degrading DDE further did not improve the match to the current observed ratios of DDE/DDX, the further degradation of DDD did improve the match to the current observed ratios of DDD/DDX, especially in the deep soils.

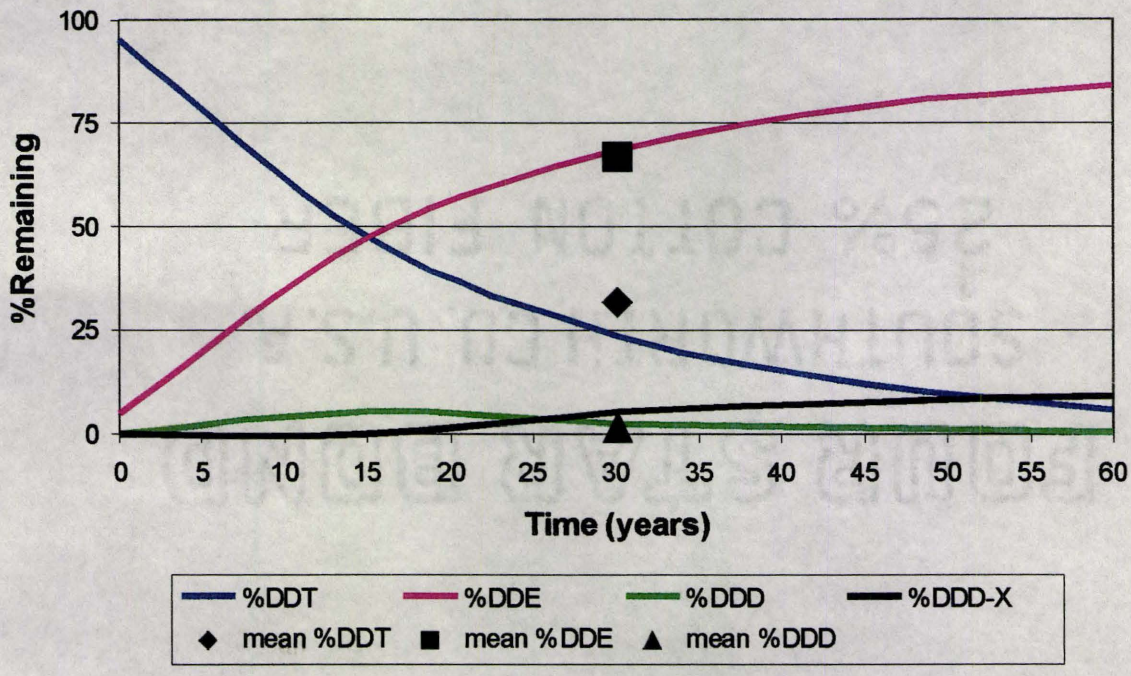
Table 61. Degradation terms used to run the iterations to estimate the relative half-lives of DDT in the shallow and deep soils at S, M and CHM.

		$e^{-k_A t}$	$e^{-k_B t}$	$e^{-k_C t}$	$e^{-k_D t}$	$e^{-k_E t}$	$e^{-k_F t}$	$e^{-k_G t}$
Shallow	**CHM**	0.50	0.00	0.49	0.00	0.01	0.00	0.00
	M	0.50	0.00	0.45	0.00	0.05	0.00	1.00
	S	0.50	0.00	0.49	0.00	0.01	0.00	0.00
Deep	**CHM**	0.50	0.00	0.47	0.91	0.03	0.00	0.09
	M	0.50	0.00	0.45	0.00	0.05	0.00	1.00
	S	0.50	0.00	0.41	0.05	0.09	0.00	0.95

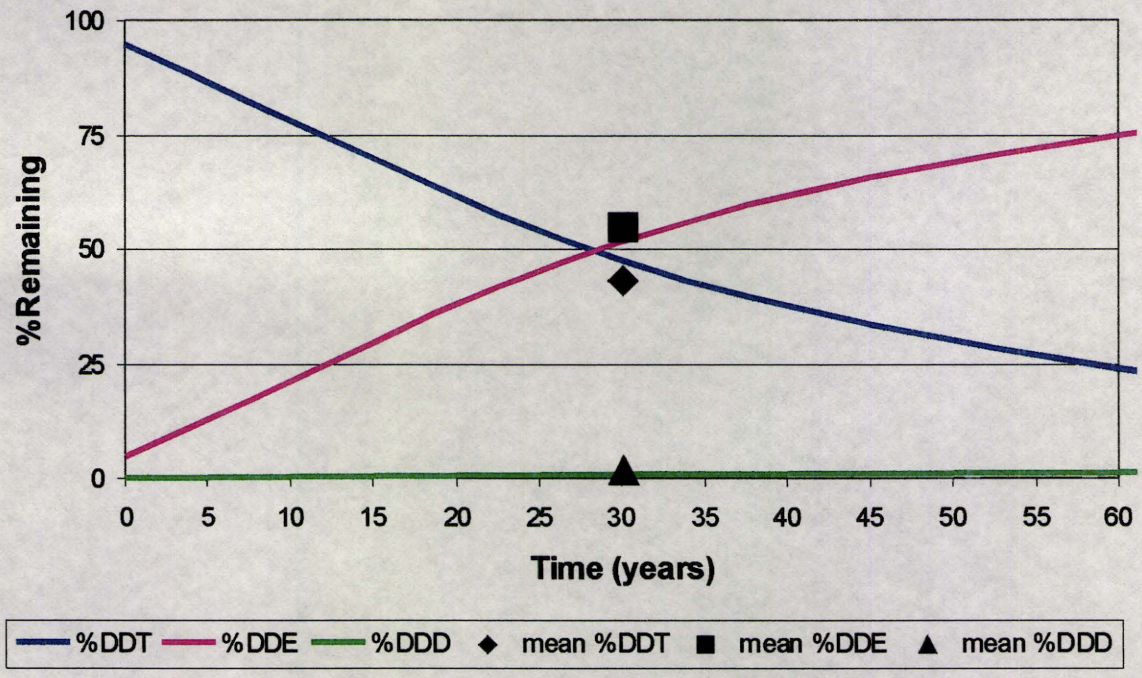
Figure 39. Degradation of DDT and production of DDE and DDD in the shallow and deep soils at S, M and CHM.



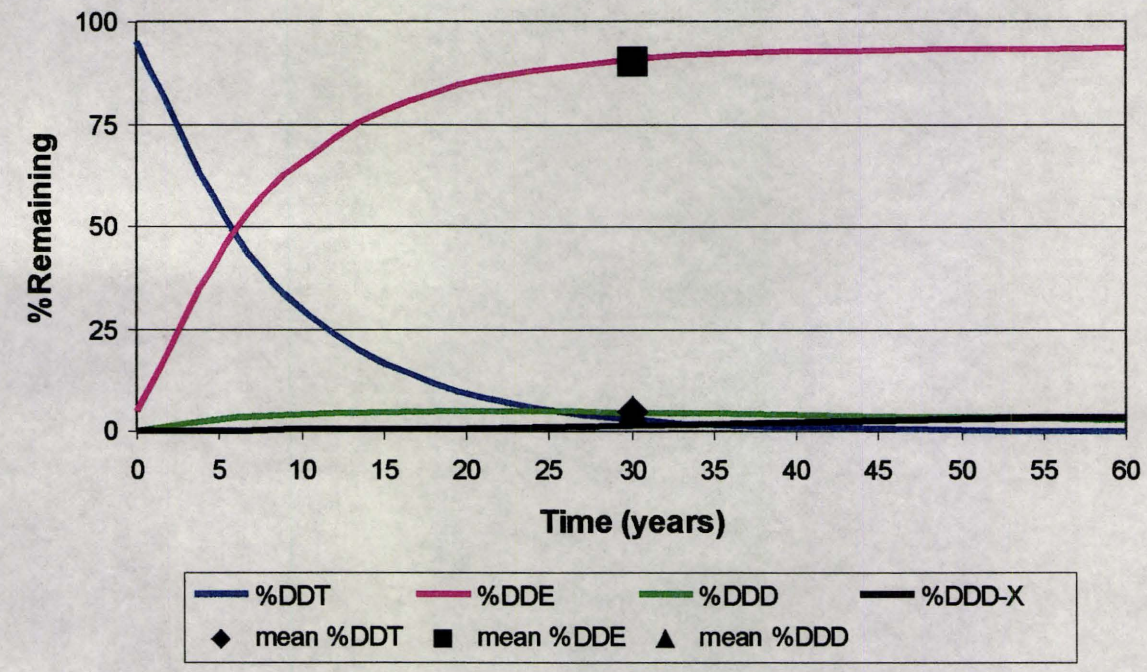
B. Simulated DDT Degradation at M Shallow



C. Simulated DDT Degradation at S Shallow



D. Simulated DDT Degradation at CHM Deep



E. Simulated DDT Degradation at M Deep

F. Simulated DDT Degradation at S Deep

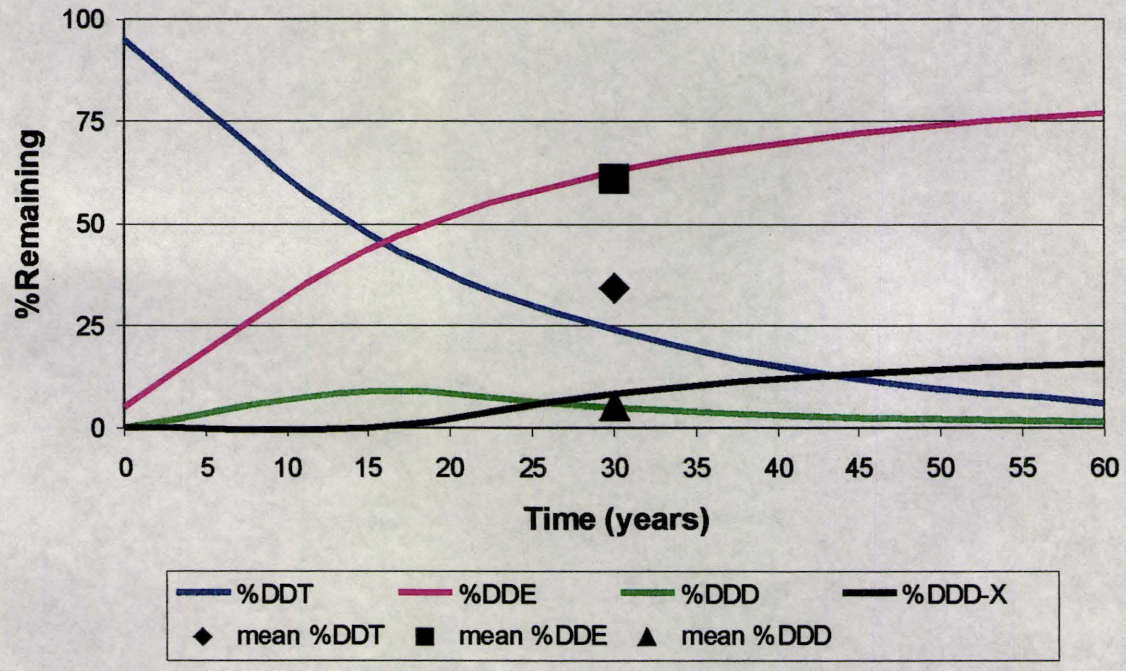


Table 62. Half-life estimates of DDT with further degradation of DDE and DDD in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Site	Shallow ($t_{1/2}$ years)	Deep ($t_{1/2}$ years)
CHM	8	6
M	15	15
S	30	15

The half-lives for DDT are 8 years at CHM, 15 years at M and 30 years at S in the shallow soils. Half-life estimates for DDT in the deep soils are 6 years at CHM, 15 years at M and 15 years at S.

Table 63. Half-life estimates of DDD in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils from S, M and CHM at PPNP.

Site	Shallow ($t_{1/2}$ years)	Deep ($t_{1/2}$ years)
CHM	-	9
M	11	11
S	-	15

The DDD in the shallow soils at CHM and S is assumed not to degrade. The half-life for DDD is 11years at M in the shallow soils. Half-life estimates for DDD in the deep soils are 9 years at CHM, 11 years at M and 15 years at S.

The difference in half-lives at the study sites reflects the varying soil and hydrological conditions. The longer half-lives of DDT at S and M reflect the drier soil conditions. The soil here is sandy, promoting rapid drainage and evaporation of soil

moisture. The shorter half-lives of DDT in CHM soils reflect the wetness and organic matter contents. Wetter, more organic-rich soil conditions promote microbial activity and consequently the degradation of DDT. Edwards (1966) observed that microorganisms were more active in wetter than in drier soil. Furthermore, it is reasonable to assume that the intermittent occurrence of flooding which would produce reducing conditions at CHM may account for a lower half-life of DDT at CHM.

The degradation of DDD at S, M and CHM in the deeper soils is possibly due to relatively lower oxygen levels. Lower oxygen or anaerobic conditions are known to increase the rates of degradation of DDT and DDD. In other words, because DDD is not observed to accumulate, its loss from soil must occur at a rate at least as great as that for its generation. The half-lives of DDT in the deep soils should be lower than those in the shallow soils to reflect these conditions. On the other hand, because DDE is observed to accumulate at S, M and CHM, its loss from soil must occur at a slower rate than its generation from DDT. The persistence of DDE in the shallow and deep soils is consistent with what is found in the literature for other sites with a DDT application history (Harris and Miles, 1975; Ware et al., 1978; Cooke and Stringer, 1982; Boul et al., 1994). The longer persistence of DDE in the deep soils at S cannot be sufficiently explained.

Estimating a DDT half-life with this iterative procedure, which includes the degradation of daughter products, was theoretically sound. Relative to the first method, which assumed no degradation of daughter products, this procedure provided:

(i) better estimates of DDT half-lives at each site using the relative abundances of DDT, DDE and DDD concentrations expressed as ratios of DDT/DDX (%DDT), DDE/DDX (%DDE) and DDD/DDX (%DDD) along with the known time since DDT was last applied

(ii) shorter half-lives of DDT because it included the degradation of DDE and DDD

(iii) a model of DDT decay and DDE and DDD production specific to each study site

(iv) DDE/DDX and DDD/DDX ratios that matched the observed data.

The half-life estimates calculated above are lower than those of Crowe (1999) who observed that the half-life of DDT in most of the sandy soil at PPNP probably exceeds 40 years, while the half-life in the marshy sediments is probably less than 10 years. Based on the relative calculated relative $t_{½}$ in Table 62 and the observed sample mean DDT concentrations in soils at S, M and CHM today, the time in years (from 2001) for DDT to reach acceptable values at or below regulatory limits are presented in Table 64.

Table 64. The time in years, based on the relative half-life estimates of the mean %DDT in the shallow (0 – 5 cm) and deep (10 – 15 cm) soils at S, M and CHM, for the mean DDT to reach acceptable values at or below regulatory limits.

Site	Shallow (years)	Deep (years)
CHM	140	100
M	320	290
S	740	310

Earlier studies have also indicated long persistence of DDT in soils under temperate climates (Dimond et al., 1970; Grau and Peterle, 1979). Lichenstein and Shulz (1959a), Stewart and Chisholm (1971), Keller (1970), Martijn et al. (1993), and Alexander (1994) estimated the half-life to range from 2 years to 15 to twenty years or more under field conditions for the aerobic degradation of DDT. Under anaerobic conditions, the biodegradation is faster, with half-lives estimated from 16 to 100 days (Castro and Yoshida, 1971).

Edwards (1966) calculated the 95% disappearance time for DDT in temperate soils to range from 4 to 30 years with a mean half-life of 10 years. Nash and Woolson (1967) gave a mean half-life of 10.5 years with a high of 35 years in several temperate agricultural soils. Metcalf and Pitts (1969) estimated a half-life of 2 to 4 years for DDT in temperate soils. Woodwell et al. (1971) estimated the mean half-life of DDT to be about 5.3 years in temperate soils. Menzie (1974) reported a half-life of 3 to 10 years in temperate soils. In a study by Dimond and Owen (1995), a half-life of 20-30 years was proposed for the DDT in forest soils in Maine. Using sediment cores from Lake Ontario, estimated half-lives of DDT ranged from 14 to 21 years (Oliver et al., 1989).

CHAPTER 5

5.0 Conclusions

Recent studies have shown that levels of DDT, DDE and DDD above OMOEE guidelines still exist in the shallow soils of certain areas at PPNP. Because of the potential risk to human, wildlife, and environmental health, it was important to understand why DDT is persisting in certain soil environments and what is controlling its degradation. The potential risk of DDT to human, wildlife and environmental health is a function of its persistence, its mobility, its volume or concentration in soil, as well as its toxicity to wildlife and humans. It was expected that different soil environments would have different concentrations and %DDT, %DDE and %DDD remaining as a result of different DDT application histories, degradation rates and pathways.

The study sites were chosen based on ground surface elevation and hydrology, and because we knew they all showed high levels of DDT Soil samples were obtained at

random from within the grids for chemical as well as physical analyses. Though the three study sites had texturally and compositionally similar soil types, bulk densities, porosities, and hydraulic conductivities, they were characterized by very different hydrological conditions. This resulted in significant differences in the relative amounts of %DDT, %DDE and %DDD still remaining in soil today.

The predominant daughter product of DDT degradation remaining at the studied sites was DDE, with smaller amounts of DDD. DDT has degraded to DDE and DDD at a faster rate at the more organic-rich study site, CHM. That can be explained by its topography and related hydrology. Historically, CHM, located adjacent to the marsh, experienced flooding by marsh waters when water levels were high (>174.0 m amsl). This flooding created anaerobic environments, as indicated by the thick accumulation of organic matter. Because soils with higher organic matter contents tend to hold more water than other soil types, CHM remains wetter than the other studied locations, even in dry years. In addition, the water table is less than half a meter below ground surface and the soils above it are noticeably wet. The height of the capillary fringe is no more than approximately 5 cm at each site.

During flooding, when the soils at CHM become anaerobic, DDT was preferentially degraded to DDD. However, the prevailing conditions here are low water levels. When the marsh water levels are low and the soils are not flooded, they may remain wet, but aerobic and DDT is preferentially degraded to DDE. This periodic flooding creates anaerobic-aerobic environments respectively, that causes DDT to

degrade to DDD and DDE faster at this study site. The residues then remain in the shallow soils, because they are adsorbed onto the organic matter there. There is thus little migration of any of the residues with infiltrating waters from the surface to the layers below.

In contrast, DDT degrades at a slower rate at higher ground surface elevations (>175.1 m amsl). Higher ground surface elevations have greater depths to the water table, even in wet years. The surface soils here are never submerged by marsh waters and remain aerobic all year long. The lower organic matter contents mean that soils here don't retain as much water, even when conditions are wet. Because DDX levels are so low compared to the amount of organic matter, most of it is sorbed in the surface layers. There is thus little migration of any of the residues with infiltrating waters from the surface to the layers below.

The study provided data characterizing different soil environments in terms of their propensity for degrading DDT. The assessment of soil environments also provided information required for the evaluation of the long-term patterns of contamination at PPNP - information that will be important for long-term land use planning within the park.

At PPNP, flat, relatively lower-lying sites (<175.1 m amsl) are expected to degrade DDT to its daughter products faster than the relatively higher-lying areas (>175.1 m amsl). It is these latter sites that should remain the target of desorption and flushing of DDT remediation studies. Furthermore, because of the high degree of variation in DDT,

DDE and DDD within and between sites, assessment programs should focus on obtaining replicated random samples within a targeted location. This kind of sampling program will provide more precise data in support of monitoring and management programs.

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8.0 Sample Identification

Table 65. Samples obtained at the sampling points below for various analyses.

	Samples obtained for bulk density, porosities, VWC, GWC, TDR, and grain size distribution analyses			
	Samples obtained for DDT, DDE, DDD, ON, OC, OM, MM, and ex-situ hydraulic conductivities analyses		Samples obtained for soil water retention studies	Samples obtained for K_{fs}
	Shallow Sites (0-5 cm)	Deep Sites (10-15 cm)	With Depth (10-100 cm)	
Site	**Sampling Point ID**			
S	S-1-0	S-1-10	S-10	S-P1
	S-2-0	S-2-10	S-20	S-P2
	S-3-0	S-3-10	S-30	S-P3
	S-4-0	S-4-10	S-40	S-P4
	S-5-0	S-5-10	S-50	S-P5
	S-6-0	S-6-10	S-60	
	S-7-0	S-7-10	S-70	
	S-8-0	S-8-10	S-80	
	S-9-0	S-9-10	S-90	
	S-10-0	S-10-10	S-100	
M	M-1-0	M-1-10	M-10	M-P1
	M-2-0	M-2-10	M-20	M-P2
	M-3-0	M-3-10	M-30	M-P3
	M-4-0	M-4-10	M-40	M-P4
	M-5-0	M-5-10	M-50	M-P5
	M-6-0	M-6-10	M-60	
	M-7-0	M-7-10	M-70	
	M-8-0	M-8-10	M-80	
	M-9-0	M-9-10	M-90	
	M-10-0	M-10-10	M-100	
CHM	CHM-1-0	CHM-1-10	CHM-10	CHM-6
	CHM-2-0	CHM-2-10	CHM-20	CHM-P1
	CHM-3-0	CHM-3-10	CHM-30	CHM-P2
	CHM-4-0	CHM-4-10	CHM-40	CHM-P3
	CHM-5-0	CHM-5-10	CHM-50	CHM-P4
	CHM-6-0	CHM-6-10	CHM-60	
	CHM-7-0	CHM-7-10	CHM-70	

	CHM-8-0	CHM-8-10	CHM-80	
	CHM-9-0	CHM-9-10	CHM-90	
	CHM-10-0	CHM-10-10	CHM-100	