DDT Characterization and Remediation Options at Point Pelee National Park

Caractérisation de DDT et des Options de Restauration au Parc national de la Pointe-Pelée

A Thesis Submitted to the Division of Graduate Studies
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by

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Dedicated in loving memory of my grandparents:

My very British Grandmother, Joan Penelope Clow (1923-2010), who told me I was obstreperous in a good way, my Grandfather Raymond Heber Clow (1918-1990) who I never had a chance to know, and my "near" grandparents: Art (1931-2009) and Barb (1932-2010) Lindop who unabashedly and enthusiastically cheered me on.

“No, no! The adventures first, explanations take such a dreadful time.”

― Lewis Carroll, Alice's Adventures in Wonderland & Through the Looking-Glass

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Abstract

Point Pelee National Park (PPNP), located in Leamington, ON, is heavily contaminated with the pesticide dichlorodiphenyltrichlorethane (DDT) which was liberally used for mosquito and pest control in the Park from the 1940s until the 1960s. Building on previous research, a comprehensive soil and sediment sampling and analytical program was carried out. Using the data obtained, contamination boundaries were defined and it was determined that DDT contamination was centred in three major hotspot areas. This information was mapped into an interactive Google Earth platform. DDT isomer analysis compared different groupings of samples, and determined that each of the soil hotspot areas have comparable degradation rates with half-lives ranging from 27 to 40 years. The sediments from the ponds and marsh areas had statistically different isomer compositions and degradation pathways than the soil with half-lives of 18 to 25 years. Finally, a remediation options analysis was conducted and courses of remedial action are suggested. This information and the Google Earth overlay is being provided to Point Pelee Park staff so they can more strategically approach long-term park management.

Keywords: Dichlorodiphenyltrichlorethane (DDT), Point Pelee National Park (PPNP), remediation, isomer, half-life, sampling program, hotspot, Google Earth

Résumé

Le parc national de Point Pelee (PNPP), situé à Leamingston Ontario, est largement contaminé avec le pesticide dichlorodiphenyltrichlorethane (DDT) qui fut largement utilisé pour le contrôle des moustiques et de la peste pendant les années 1940 jusqu'en 1960. Se basant sur des recherches antérieures, un programme d'échantillonnage et d'analyse de sédiments et de sols fut complété. En utilisant les données obtenues, les limites de la contamination ont été définies et il a été déterminé que la contamination au DDT était centrée autour de trois point chaud. Cette information a été cartographiée sur une plateforme interactive Google Earth. L'analyse d'isomère DDT a comparé les différents groupes d'échantillons, et a déterminé que les sols de chaque secteur avaient tous des taux de dégradations comparable avec des demi-vies de 27 à 40 ans. Les sédiments des secteurs de marais et d'étangs avaient des compositions d'isomère et des taux de dégradation statistiquement différents avec des demies-vie de 18 à 25 ans. Finalement, une analyse d'option de dépollution fut menée et les options d'analyse de dépollution sont suggérées. Cette information ainsi que l'information cartographiée de Google Earth sont également fourni aux employés du parc Pelee de manière a ce qu'ils puissent établir une meilleur stratégie de gestion du parc a long terme.

Mots clés: Dichlorodiphenyltrichlorethane (DDT), Parc national de la Pointe-Pelée, assainissement, isomère, la demi-vie, programme d'échantillonnage, point chaud, Google Earth

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List of Acronyms and Abbreviations

Acronym/Abbreviation	Definition
µg	Microgram
AC	Activated carbon
ANOVA	Analysis of variance
ASU	Analytical Services Unit
CCME	Canadian council of ministers of the environment
DCBP	Decachlorobiphenyl
DDE	Dichlorodiphenyldichloroethylene
DDD	Dichlorodiphenyldichloroethane
DDT	Dichlorodiphenyltrichlorethane
g	Gram
GC	Gas chromatography
GC/ECD	Gas chromatography with electron capture detection
GPS	Global positioning system
IDW	Inverse distance weighted
ISQG	Interim sediment quality guideline
K_{ow}	Partition coefficient
L	Litre
LC-Florisil	A trademark
m^2	square meters (area)
m^3	cubic meters (volume)
ml	Millilitre
$ng \bullet g^{-1}$	nanograms per gram (equivalent to PPB)
PEL	Probable effects level
ppb	Parts per billion
PPNP	Point Pelee National Park
QAQC	Quality assurance and quality control
RSD	Relative standard deviation
$ug \bullet L^{-1}$	Micrograms per litre
WHO	World Health Organization

CHAPTER 1 - Introduction

Due to its effectiveness and low cost, dichlorodiphenyltrichlorethane (DDT) was hailed as an instant solution for controlling insect borne diseases and agricultural pests beginning in the early 1940s. Between then and the 1960s, DDT was readily available to the Canadian public and widely used. DDT degradation in soil occurs at a very slow rate and its primary daughter products, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), are also toxic. DDT, DDE and DDD, which are collectively known as total DDT, all have low water solubility, persist in the environment, tend to accumulate in the upper soil layer, are mobile up the food chain, and bioaccumlate in mammals (Powter, 2002; Blus, 1996; Baird & Cain, 2008).

Point Pelee National Park (PPNP), in Leamington, Ontario, is the smallest of Canada's national parks and has been identified as a wetland of international significance (Dobbie *et al.*, 2007; Lynch-Stewart, 2008). During the time that DDT was available in Canada, PPNP was home to agricultural holdings and various recreational areas, on which DDT was liberally sprayed to control agricultural pests and mosquitoes. Although DDT has not been used in PPNP since 1967, there remain several areas in the park that are heavily contaminated with DDT. A number of studies were completed at PPNP to characterize DDT contamination which, in some areas, was found to be more than 14,000% above the Canadian DDT guidelines (Crowe & Smith, 2007). In addition, pilot-scale field trials of various DDT remediation techniques (Badley, 2003; Paul, in prep) were conducted. At the beginning of this project, a significant amount of information was available regarding past research and DDT concentrations at various locations around the park, however, a comprehensive picture of DDT concentration and spatial distribution did not exist.

The overall goals of this thesis were to quantity and map the DDT contamination in PPNP, and propose viable remediation options for the unique Park ecosystem. Following this brief introduction, a literature review (Chapter 2) outlines details of DDT's chemical characteristics, PPNP background information, DDT at PPNP including previous research, and possible DDT remediation methods. Additional sampling was required to comprehensively determine DDT's current spatial and concentration distribution. Using previous work to facilitate an initial understanding of DDT at PPNP, an iterative sampling plan was designed and implemented as described in Chapter 3, Methodology. An interactive mapping platform, found on the attached CD, was used to intuitively and flexibly compare result locations and concentration levels, and plan the iterative sampling based on maps created on a Google Earth platform. Chapter 3 also outlines sample collection and analysis procedures, as well as interpolation and statistical analyses.

Chapter 4, DDT Distribution in PPNP, presents the DDT analytical results of water, sediment and soil samples. Samples were collected throughout the Park to validate the results of previous studies, and reach a comprehensive understanding of contamination throughout the Park. Although water samples were all below the equipment detection limit, sediment and soil samples were well above the CCME guidelines (CCME, 1999). As the Park staff had specifically requested a study on soil contamination, sediment samples were not the main effort. Consequently, this chapter predominantly focuses on

the soil samples and their total DDT concentrations. Previous mapping used to represent contamination at the Park did not allow locations to be precisely identified, or additional sample locations to be added easily. In order to sample efficiently and to target specific areas, a Google Earth Map overlay was developed as described in the previous chapter 3. This powerful and intuitive platform enabled several major hotspots to be identified, and other areas to be disregarded. The major hotspot areas were interpolated with ArcGIS software which calculated the areas and volumes of soil associated with various levels of DDT contamination. These calculations became the basis of analysis in subsequent chapters.

DDT's half-life is affected by the degradation pathway that it has undergone since being applied to areas of the Park. Chapter 5 presents an analysis of DDT's degradation pathway which was completed in order to provide a PPNP specific estimate of time required for natural degradation to occur. Analysis of variance (ANOVA) was used to compare isomer percent composition between three major hotspots identified in Chapter 4, between soil and sediment samples, and between pre-existing (i.e. older) and current project (i.e. more recent) soil samples. Based on these findings, minimum and maximum half-lives were calculated.

In chapter 6, an initial remediation options analysis and several remediation recommendations for PPNP are presented. Environmental impact, cost, effectiveness, feasibility, and time were the criteria against which each remediation option was considered. This objective analysis led to three remediation option recommendations.

This project was conducted in support of PPNP's research goals to responsibly approach remediation of DDT contamination in the Park while avoiding ecosystem disturbances as much as possible. Park personnel will be provided with several tangible deliverables to assist their future remediation efforts. The mapping overlay, included in the attached disk, will assist future research or remediation implementation as more sample information can be easily added or compared. Additionally, the remediation options analysis and the associated assumptions will provide a starting point for the Park's anticipated remediation implementation. These tools will assist Parks Canada to make informed and proactive decisions related to DDT remediation.

CHAPTER 2 - Literature Review

2.1. DDT - A Historical Perspective

Dichlorodiphenyltrichlorethane (DDT) was first synthesized in 1874 by Othmar Zeidler. Sixty years later in 1939, Swiss research chemist Paul Hermann Muller stumbled upon DDT and recognized its potency against insects (Edwards, 2003). During World War II, DDT was adopted by the Allied Powers to control insect borne diseases (Fisher, *et al.*, 2011). It was used to control an October 1943 typhus epidemic in Naples, and during the evacuation of concentration camps. In 1948, Muller received the Noble Peace Prize for Physiology and Medicine because "DDT had passed its ordeal by fire with flying colours" (Bate, 2007). Following World War II, DDT was used around the world for agricultural activities and to control insect borne disease vectors. In 1955, the World Health Organization (WHO) launched a programme to eradicate malaria with the action plan heavily reliant upon DDT due to its insect repellency, irritancy, toxicity and persistence (Roberts, 2010). Although DDT was instrumental in eliminating malaria in many areas of the world, the disease was not eradicated globally and thus there remains an argument that DDT "should not be abandoned unless its known detrimental health effects are greater than the effects of uncontrolled malaria on human health" (Roberts, *et al.*, 1997).

Canada first recognized DDT as a pesticide when it was registered with the Pest Control Act in the 1940s (Environment Canada, 2012a), and it was made available to the Canadian public in 1945. Used extensively over the course of the next twenty years to control agricultural and forest pests, it was applied in Canada via aerial and land based spraying (CCME, 1999). In 1962, Rachel Carson's best seller *Silent Spring,* which focused on the impact of pesticides including DDT on human health and the environment, helped popularize the environmental movement. The American government formed the Environmental Protection Agency (EPA) and in 1971, held an eight month hearing focused on the future of DDT use. Around this same time, many first world countries began restricting and phasing out DDT. Over the course of twenty years, Canada gradually reduced DDT use, registered any remaining DDT stores, and finally disposed of all known remaining stockpiles by December 1990 (Environment Canada, 2012a).

DDT is still used and produced, predominantly in Africa, for indoor pest control in accordance with the World Health Organization's (WHO's) current anti-malaria policies. Additionally, there are concerns that uncontrolled and unenforced DDT use for indoor residual spraying (IRS) programmes has already led to DDT being traded on local markets for agriculture and termite control (van den Berg, 2008). As such, DDT continues to enter the world's food chains through airborne transmission, bioaccumulation and biomagnification. Although not recognized by the public consciousness, the United States also put policy in place to enable states to legally use DDT in the event of a medical necessity (Bate, 2007). The struggle between controlling disease vectors and the current and future environmental impact continues as many areas of the world still grapple with basic agricultural requirements and insect borne diseases.

2.2. DDT - A Scientific Description

Dichlorodiphenyltrichloroethane (DDT) is an anthropogenic product synthesized by a reaction between chloral (CCl_3CHO) and chlorobenzene (C_6H_5Cl) in the presence of sulfuric acid which acts as a catalyst (Figure 1).

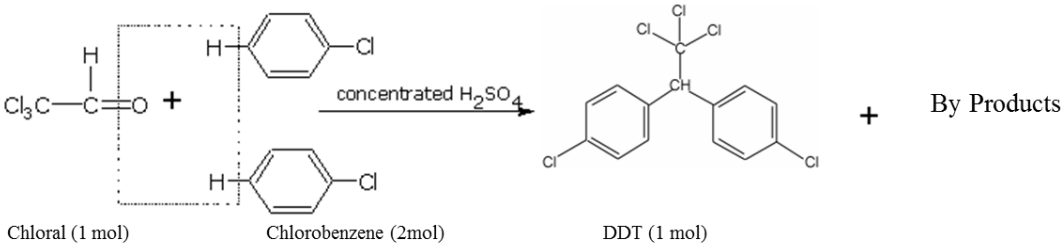


Figure 1. Synthesis of DDT. Information from US Department of Health and Human Services (2002). Image modified from Wikipedia (2012).

DDT follows two major degradation pathways breaking down into dichlorodiphenyldichloroethylene (DDE), and dichlorodiphenyldichloroethane (DDD) (Figure 2).

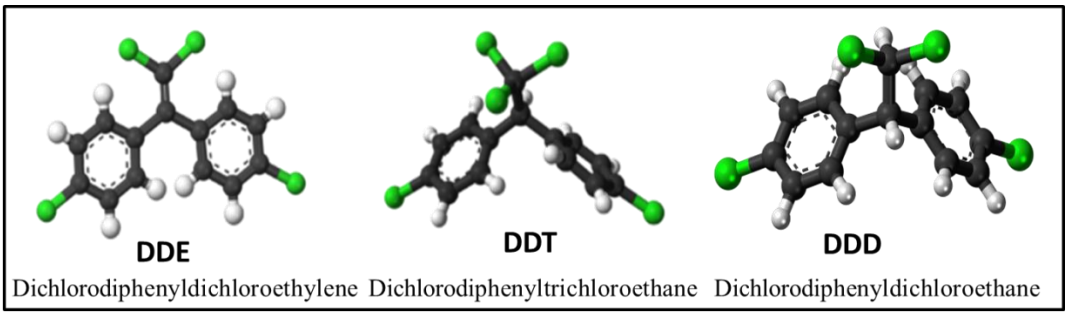


Figure 2 DDT, DDE and DDD ball and stick representation. Image modified from Wikipedia (2012).

DDE is formed through an elimination (dehydrohalogenation) reaction when DDT loses a hydrogen and chlorine atom (Baird & Cann, 2008). DDD is formed through hydrogenolysis of DDT (Larson & Weber, 1994), a chemical reaction that occurs when an organic molecule's bonds are broken and a hydrogen atom is simultaneously added (Figure 3).

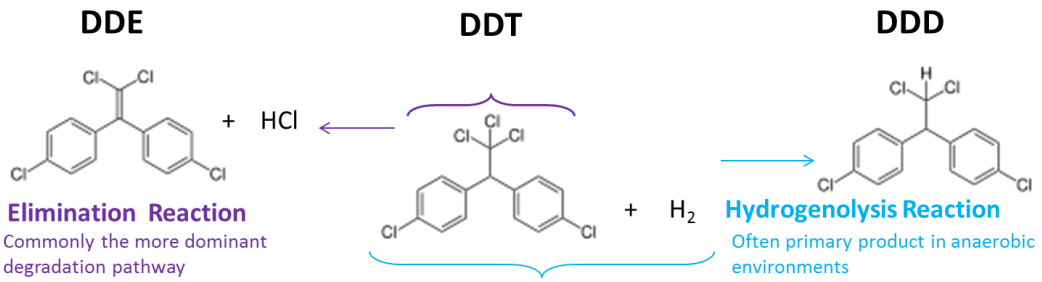


Figure 3. DDT Degradation Pathways. Schematic only, does not include by-products. Information from Larson & Weber (1994). Images modified from Wikipedia (2012)

Although DDE is generally the major degradation product of DDT, there are a number of environmental variables which influence which reaction pathway will dominate. DDE is the primary product in aerobic environments, and DDD dominates in anaerobic or aquatic environments (Gautam & Suresh, 2006). Other factors that affect degradation pathways include the pH of the water involved in the process (Larson & Weber, 1994), exposure to sunlight, DDT availability for degradation, temperature, and the presences of sulfate, organic content and metals (US Department of Health and Human Services, 2002).

In standardized conditions, DDT's reported half-life is very similar to that of DDD and DDE; in soil the half-life ranges from 2 to 15.6 years, in air 17.7 hours to 7.4 days, in surface water 7 days to 1 year, and in groundwater 16 days to 31.3 years (Howard, *et al.*, 1991). Factors that determine which degradation pathway is dominant also impact the length of the half-life (US Department of Health and Human Services, 2002).

Total DDT generally refers to the summation of all DDT related compounds contained within a sample including all isomers of DDT, DDE, and DDD (Figure 4). Technical grade DDT, a white crystalline or waxy solid at room temperature, consists of 77.1% *p,p'* DDT, 14.9% *o,p'*-DDT, 4.0% *p,p'*-DDE, 0.1% *o,p'*-DDE, 0.3% *p,p'*-DDD, 0.1% *o,p'*-DDD and 3.5% unidentifiable components (CCME, 1999).

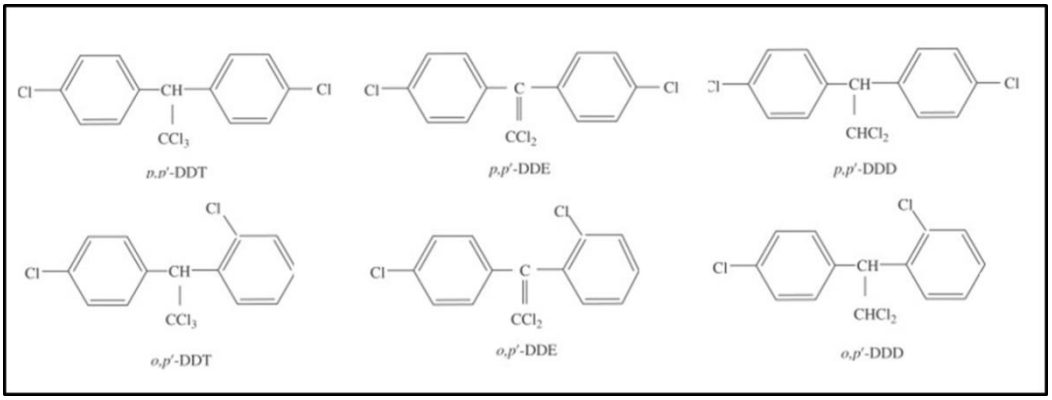


Figure 4. DDT, DDE and DDD Isomers (Wilson & Naidu, 2008).

DDT's success as an insecticide is due more to its bent molecular shape (Figure 2) than chemical interactions. Insects have a nerve channel through which muscle control impulses are transmitted. When DDT is absorbed by an insect, it becomes wedged into that nerve channel limiting the insect's ability to regulate nerve impulses which leads to twitches, convulsions and eventually death (Baird & Cann, 2008). Although DDT is more toxic due to its extra chlorine, DDD has a similar size, shape and effect upon insects, and was once marketed as a separate insecticide (Verschueren, 1996). DDE however, has a planar structure due to a double carbon bond (C=C) which makes the molecule largely ineffective as an insecticide (vanLoon & Duffy, 2000).

DDT, DDE and DDD meet Environment Canada's definition of being persistent contaminants based on their half-lives in various substances and their potential for global migration (Environment Canada, 2012b). DDT and its metabolites are non-polar, have low vapour pressure, low solubility in water, are thermally stable and preferentially accumulate in cells with high lipid content (Baird & Cann, 2008; CCME, 1999).

The partition coefficient $K_{ow,}$ measures the ratio of solubility between the octanol phase and the water phase at equilibrium (Larson & Weber, 1994). Log K_{ow} for DDT is 6.22 (Baird & Cann, 2008) and Environment Canada's criteria for substances that are bioaccumulated include those with a Log K_{ow} being greater than or equal to 5 (Environment Canada, 2012b).

Bioaccumulation (Figure 5) refers to the accumulation of substances within an organism that occurs when the organism is absorbing more of a substance through consumption of a contaminated food source and through direct contact with soil, air or water than it is releasing (Powter, 2002). DDT is more likely to be absorbed by live tissue rather than be adsorbed to sediments, and it biomagnifies, or increases in concentration, up the food chain as DDT is passed from prey to predator (CCME, 1999).

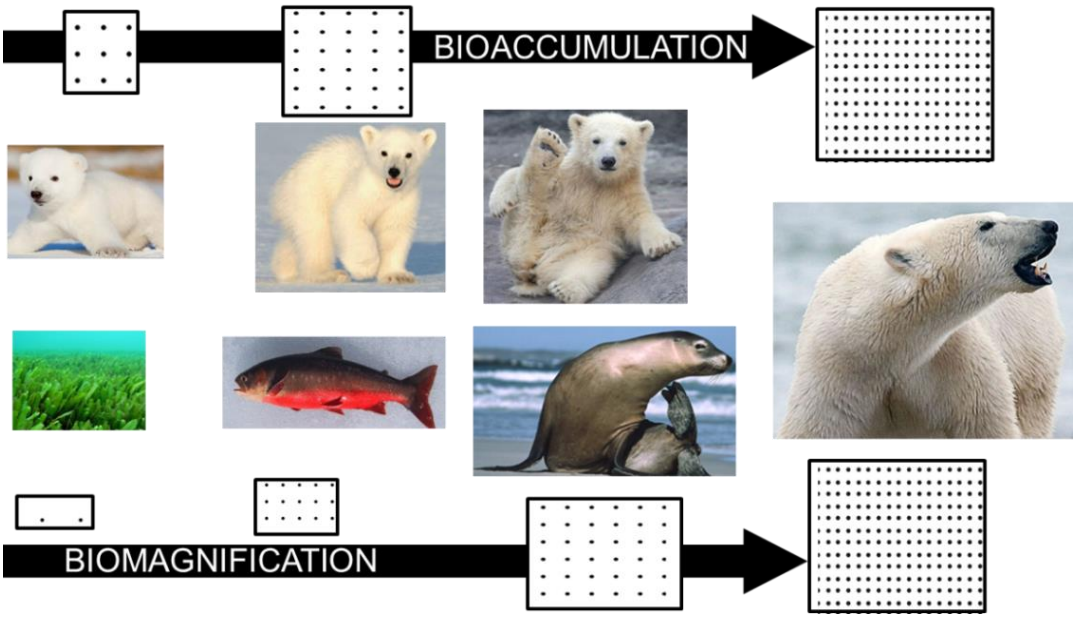


Figure 5. Bioaccumulation vs Biomagnification.

DDT can be lethal at very high concentrations, and large DDT burdens have been documented to thin eggshells; limiting bird and reptile reproduction (Blus, 1996). DDT has led to notable population declines in certain species including birds of prey which are at the top of the food chain (Baird & Cann, 2008). Humans are also affected by DDT. DDT and its metabolites can be passed from mother to infant through breastfeeding (Hoover, 1999), and has been linked to various forms of cancer (McGlynn, *et al.*, 2008) and other health concerns.

2.3. Point Pelee National Park; Historical Overview

Point Pelee National Park (PPNP), was established in 1918, and consists of only 16 square kilometres of land making it the smallest national park in Canada (Parks Canada, 2011). Located 50 km south-east of Windsor, Ontario, it consists of a long, narrow, triangular cuspate foreland extending almost 15 kilometers into Lake Erie and represents the southernmost tip of Canada (Figure 6). Seventy percent of PPNP is marshland (Trenhaile, *et al.*, 2000) covered by large cattail mats making it impassable. Most of the interior ponds can be accessed, but only by boat. Both the marsh and the interior ponds are cut off from Lake Erie by sandbars which run down the eastern and western edges of the park.

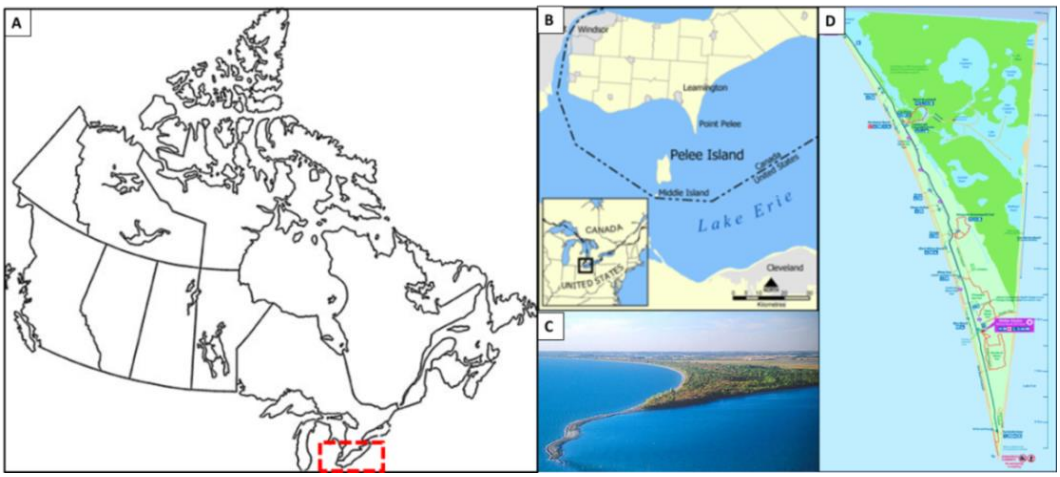


Figure 6. Four Views of Point Pelee National Park. A) Point Pelee and Lake Erie in Canada. B) PPNP's location in relation to Ontario and Lake Erie. C) An aerial view of the Park taken from the southeast. D) PPNP's current visitor's map. The light green colour represents largely forested land while the dark green colour represents marsh. The black line running along the length of the western edge of the park represents a dirt road currently used by tourists and park staff. The red lines indicate trails and boardwalks for tourists. Modified from images taken from Parks Canada (2011) and Wikipedia (2012).

During the latter part of the 19th century, PPNP supported a settlement of approximately 100 Chippewa Native Americans who grew corn and oats, and hunted and fished (Parks Canada, 2011). There continued to be a First Nations presence in PPNP until they were expelled from the park in the 20th century. As early as 1830, European settlers began arriving and, as the settlement flourished, land was cleared for agriculture, and livestock roamed freely. Larger native mammal species including deer and bears were decimated, and most of the marketable species of fish were overfished (Parks Canada, 2010). The introduction of many invasive non-native plants, large scale clearing of the original vegetation, and the local disappearance of several species have had lasting ecological impact on the area (Dobbie, *et al*., 2007).

Point Pelee became a popular tourist destination for cottages and camping beginning around 1910. One of the first preservationist parks, PPNP was founded in 1918 through the efforts of several ornithologists (Sandilands, 2000). To cater to the increasing tourist presence, the park established significant and environmentally damaging infrastructure including roads, parking lots, pavilions, and picnic grounds. In 1963, an unsustainable 781,000 people visited PPNP (Parks Canada, 2010). In 1972, the Point Pelee National Park Master Plan was implemented to emphasize ecological integrity and environmental principles. A property buyback programme was instituted, camping was phased out, and park traffic was curtailed (Crowe & Smith, 2007). The most current park management plan, published in 2010, documents a deliberate and environmentally conscious approach to running PPNP (Parks Canada, 2010).

Today, PPNP attracts over 300,000 day visitors annually and is considered biologically important due to bird migration and breeding, as well as the resident flora and fauna. Due to its location and climate, the park can be considered the only Carolinian forest in Canada's national parks (Trenhaile, *et al.*, 2000). With three separate protective designations (Dobbie, *et al.*, 2007), PPNP has been identified as a wetland of international significance (Lynch-Stewart, 2008). Containing multiple ecosystems and home to 66 designated species, PPNP is a priority site for the species at risk recovery program making it a leader in the field of protecting, reintroducing and creating recovery strategies for both flora and fauna (Parks Canada, 2010).

2.4. Point Pelee National Park; DDT Use, Persistence and Previous Studies

DDT was first used in 1948 at PPNP, shortly after it became available commercially. Until 1967 it was used extensively in the park's agricultural areas for pest control, and liberally on the roadways, campground and picnic areas to control mosquitoes (Russell & Haffner, 1997). The Great Lakes region, within which PPNP is located, was largely agricultural and DDT was commonly used throughout the area. By 1970, DDT use was no longer permitted at PPNP due to its detrimental impacts on the environment, humans and wild life (Crowe, *et al.*, 2004). In response to growing environmental concerns, including those associated with DDT, Canada and the United States signed the Great Lakes Water Quality Agreement in 1972. In 1978, the agreement was reviewed and renewed, and the 1987 protocol was added in that year. Both these additions specifically dealt with eliminating persistent substances (including DDT) and reinforcing government initiatives to support that goal (Bejankiwar, 2009). DDT remains a concern in the Great Lakes region, and the United States currently has an advisory against eating fish captured in Lake Erie for sport, and some wildlife in that area due to measured levels of a number of contaminants including DDT (The Lake Erie Lakewide Management Plan (LaMP) Work Group, 2008).

Historical land use of PPNP is now reflected in the names of various areas within the park (Figure 7). The majority of solid, non-marsh land on the west side of the park was used, first for agriculture, and then for camping. Most of the PPNP DDT soil studies conducted between 1995 and 2007 focused on areas of suspected DDT contamination (i.e. areas 2-7, Figure 7).

Figure 7. PPNP Landmarks and Areas with Elevated DDT levels. The red boxes show specific landmarks and areas of environmental concern: (1) Park boat house and access to Lake Pond. (2) Former Agricultural Area (Crowe & Smith, 2007). (3) Former Apple Orchard (Crowe, 1999). (4) Henry Community Youth Camp and Group Campground (no longer used for overnight camping). (5) Sleepy Hollow. (6) DeLaurier Homestead and maintenance compound, (abandoned). Formerly the operational centre for the apple orchards and DDT was possibly handled and stored here (Crowe, 1999). (7) Anders Field. (8) Visitor's Centre. Underlay from Arc GIS Explorer Desktop, a free internet mapping software which can be downloaded from: http://www.esri.com/software/arcgis/explorer.

In the 1990s, nearly 35 years after the last recorded application of DDT, PPNP wildlife studies found unexpectedly high levels of DDT in tissue samples. A 1993 field study collected seven Northern Spring Peppers (frogs) to evaluate their organochlorine pesticide burden and found DDT concentrations over 1,100 $ng \bullet g^{-1}$ (Russell, *et al*., 1995). While measuring the DDT burden on green frogs around the Canadian side of Lake Erie, PPNP was found to be the home of the frogs with the highest DDT burden at 3,000 $ng \bullet g^{-1}$, while the frogs from two other Lake Erie locations had a DDT burden < 1 $ng \bullet g^{-1}$. Four different types of frogs from PPNP were tested, and Northern Spring Peepers (frogs) were found to have the highest concentrations at 50,000 $ng \bullet g^{-1}$ (Russell, *et al*., 1999). Nestling tree swallows (birds) collected from contaminated areas were found to have contamination up to 300 $ng \bullet g^{-1}$ (Smits, *et al.*, 2005).

The results from the analyses of these soil samples revealed that DDT was still present in the park in high concentrations (Crowe & Smith, 2007) which prompted follow up soil studies. Hundreds of soil samples have since been collected at PPNP to determine the levels of total DDT contamination with many results testing well above established Canadian guidelines (Table 1). While soil and groundwater contamination is compared against total DDT and changes regarding land use, sediment contamination is compared against individual DDT, DDE and DDD levels and remains constant for all types of land use.

Table 1. Canadian Guidelines for DDT Levels in Soil, Groundwater and Sediments. Soil and groundwater guidelines represent total DDT and are differentiated by land use. Sediment guidelines are not differentiated by land use but do have both interim sediment quality guidelines (ISQG) and probable effect level (PEL). Guidelines are presented in $ng \bullet g^{-1}$. (CCME, 1999)

	Residential/Parkland	Agricultural	Commercial/ Industrial
Soil	700	700	12,000
Groundwater (fresh)	1.5	1.0	1.5
Sediment (fresh)	All Land Types		
	DDT	DDE	DDD
ISQG	1.19	1.42	3.54
PEL	4.77	6.75	8.51

A comprehensive report entitled '*Contamination of Soil, Sediments, and Biota with DDT and DDT Metabolites at Point Pelee National Park'*, was produced by the Great Lakes Institute for Environmental Research (Russell & Haffner, 1997). The report analyzed soil and sediment samples from 30 PPNP sites, green frogs from three sites, and snapping turtle eggs from three other sites (Figure 8-A). Two sites had high DDT soil concentrations (~1200 - 9000 $ng \bullet g^{-1}$), and another had very high DDT soil concentrations (~15,000 $ng \bullet g^{-1}$). Approximately 200-800 $ng \bullet g^{-1}$ of total DDT was found in frog tissue and snapping turtle egg samples.

For the 1999 Annual Meeting at the Parks and Research Forum of Ontario, Crowe (1999) published a paper involving 56 soil samples from three PPNP sites. At one site, close to the DeLaurier maintenance buildings (Figure 7, area 6), total DDT concentrations exceeded Canadian soil guidelines, but samples collected from the field and from depths greater than 60 cm were below guidelines which led to the assumption that the DDT source was generally from spills, and had not leached through the soil. All seven PPNP well sites were tested, and the groundwater was found to have no significant levels of DDT (Crowe, 1999).

In 22 of 37 soil samples collected DDT comprised 50-87% of the total DDT, with DDE being the second most prevalent (Crowe, 1999). Higher half-lives were found in areas such as a former orchard with sandy soil which would limit moisture content, thus

limiting microbiological activity and degradation. Conversely, lower half-lives were found in marsh sediments and areas with wetter, more organic rich soil where microbiological activity led to greater degradation of DDT. Crowe suggested that in the PPNP environment, DDT's half-life could range from ten to over forty years based on the microenvironment (Crowe, 1999).

Crowe also collaborated with Mills and Smith from the National Water Research Institute on a groundwater study (Crowe, *et al.*, 2003). Samples were collected from areas with the highest known DDT soil concentrations: i) the former orchard, ii) the Delaurier homestead, iii) Sleepy Hollow, iv) Anders Field, and v) an unnamed marshy area and uncultivated land for background levels (Figure 7). The study used a low detection limit (in the ppt range) and thus detected DDT in most of the samples with DDE dominating, followed by DDT and then DDD. Although the study did not find a correlation between DDT surface soil and groundwater concentrations, there was a correlation between soil surface and groundwater proportions of DDT, DDE and DDD (Crowe, *et al.*, 2003).

In 2003, a field trial was conducted to test the viability of mobilizing DDT with a starch surfactant (hydroxypropyl-β-cyclodextrin) at one of PPNP's most contaminated sites (Badley, 2003). A substantial decrease in the concentrations of DDT, DDE and DDD from the surface soil to levels below 700 $ng \bullet g^{-1}$ was shown. Side effects included vertical contaminant mobilization, and an increase of moisture and organic matter. DDT did not continue to degrade after weekly applications of hydroxypropyl-β-cyclodextrin ceased. A follow on project studied the vertical mobilization of DDT through some soil sampling and simulations (Mironov, 2004).

In 2004, Crowe *et al.* created a numerical model characterizing groundwater flow across the barrier bar between Lake Erie and the PPNP marsh. According to their model, where the bar is less than 325 m in width, the direction of groundwater flow fluctuates in response to lake and marsh variables causing the contaminants to alternate between spreading towards the lake and towards the marsh. However, the dominant direction of flow is from the marsh to the lake. When the barrier is wider than 350 m, the flow only moves from the lake to the marsh which means contaminants also move towards the marsh (Crowe, *et al*., 2004).

Lastly, Crowe worked with Smith to write *Distribution and Persistence of DDT in Soil at a Sand Dune-Marsh Environment: Point Pelee Ontario, Canada* (Crowe & Smith, 2007). They analyzed all available sample data (locations shown in Figure 8-B) and found the highest levels of total DDT in soil in the former agricultural areas (Figure 7, area 2). They expected that the anaerobic, flooded marsh would show greater levels of DDD and that the aerobic, sandy soils would show greater levels of DDE. They were surprised to find results that did not completely support that theory, and postulated that periodic flooding and draining of the soils adjacent to the marsh may have caused alternating aerobic and anaerobic conditions. Crowe and Smith (2007) expect that the total DDT in the former agricultural area will remain above CCME guidelines for decades to come.

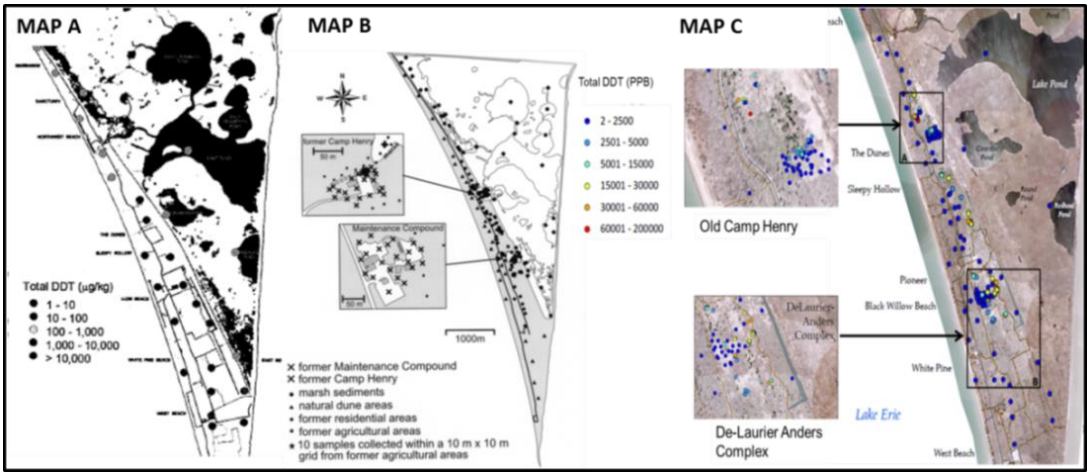


Figure 8. Three maps of DDT contamination in PPNP. Map A shows sites and concentrations of soil and sediment samples (Russell & Haffner, 1997). Map B shows all of the soil samples collected and analyzed at PPNP up until the spring of 2006 (Crowe & Smith, 2007). Map C was produced by PPNP in 2010 and includes all samples in Annex B.

Since 2007, PPNP personnel have produced a number of maps detailing DDT contamination (Figure 8-C). In accordance with the Park's mandate (Parks Canada, 2010), PPNP considered controlled burning of some areas to clear vegetation in order to eliminate invasive, non-native grasses and then reintroduce native plants (Dobbie, *et al*., 2007). In 2010, they contacted the Royal Military College (RMC) of Canada to investigate whether the presence of DDT affected their plans. If DDT is burned at less than 800 ^{0}C for less than 1.5 seconds, there is a marked increase in emissions from the combustions, and DDE forms in connection with the combustion of DDT which would cause significant environmental harm (Ahling, 1978). As a result, there have been several RMC led projects investigating various aspects of DDT in PPNP and possible remediation strategies. To date, RMC led research at PPNP has focused on phytoextraction and contaminant stabilization through activated carbon and biochar (Denyes, *et al.*, 2012).

2.5. Remediation Techniques Related to DDT in Soil

Generally initiated due to visible pollutants, historical information, or policy requirements, an environmental site assessment is "the process of developing an understanding of a site's current contamination levels and distribution through analyzing maps, local history, photographs, previous investigations, and physical site visits" (Fleming , *et al.*, 1991). At PPNP, further soil sampling was necessary to define areas of DDT contamination. As with any sampling program, there is a threshold of acceptable uncertainty after which more analyzed samples would no longer affect the decisions related to remediation (Norberg & Rosen, 2006). Once all the information has been gathered and analyzed, the requirement for remediation should be based on an assessment of risk or the probability that a substance or situation will produce harm, and the consequences of that harm (Figure 9). "Risk does not exist if exposure to a harmful substance or situation does not or will not occur" (Powter, 2002).

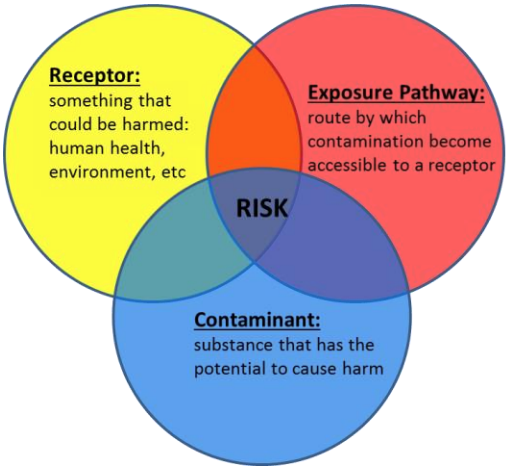


Figure 9. Venn diagram showing the relationship between receptor, exposure pathway, and contaminant that may create risk. Modified from Government of Canada (2012).

If remediation is required, the technique chosen for a site should depend on future land use, the type and levels of contamination, the budget, site accessibility, time, feasibility, and effectiveness. There is growing awareness that specific site and contaminant concerns, and a cradle to grave perspective (Diamond, *et al*., 1998) should be considered to ensure remediation does not cause a net environmental cost (Suer, *et al*., 2009). Options for dealing with a DDT contaminated site can be broken into four major categories: i) taking no direct remediation action, ii) excavation and removal of the contamination, iii) containing the contamination in place, and iv) *in situ* or *ex situ* soil treatment of the contamination.

2.5.i. No Direct Remediation Action

Although taking no action may, in some circumstances, be a viable option, it may also limit future site use (Diamond, *et al.*, 1998). Perpetual monitoring may be required to ensure that the contaminant remains immobile or continues to naturally attenuate in a manner that does not produce metabolites more toxic than the parent compound (Mulligan & Yong, 2004).

2.5.ii. Excavation and Offsite Disposal

Historically, excavation and off-site disposal has been a popular DDT approach for remediation of soil. The New York Department of Environmental Conservation recommends three main proven technological approaches for DDT contaminated soil, all of which require excavation as a first step: i) disposal at a hazardous waste facility, ii) incineration, and iii) thermal desorption (Division of Environmental Remediation, 2007). For DDT contaminated soil to be accepted at an Ontario hazardous waste facility, any liquid passing through the soil must extract less than 3000 $ng \cdot g^{-1}$ DDT solute (Environmental Protection Act, 2000), or it will require pre-treatment to bring it below that level. Incineration, the process of stimulating thermal decomposition via oxidation at

very high temperatures to destroy organic contamination within the soil, can be carried out on or off-site. Thermal desorption is similar to incineration, but vaporizes and captures organic contaminants instead of destroying them using oxidation. In ecologically sensitive areas, a remediation strategy heavily dependent on excavation may not be accepted, whereas a very deliberate and strategic excavation, or partial excavation, of small areas with extremely high levels of contamination may be more feasible.

2.5.iii. Containment

As landfill tipping fees and environmental concerns grow, there is increasing pressure to use non-excavation based remediation. Containment technologies are used at landfills and hazardous waste facilities, and *in situ* to decrease risk by making the contaminant inaccessible (Pearlman, 1999). These technologies include solidification, encapsulating with clean fill, and physical barriers including those formed with clay, impenetrable membranes, and chemically reactive barriers (Banerji, *et al*., 2007). The most common remediation containment strategy is partial isolation which is used to separate the hazard from the expected migration or exposure pathway, although long term monitoring may be required as physical barriers deteriorate over time (Barry, *et al.*, 1987). Remediation of DDT through containment has not been a popular technique because, as DDT is unlikely to dissolve in ground water, the contaminant naturally remains bioavailable but largely immobile. However, an emerging stabilization technology uses biochar or activated carbon (AC) to reduce bioavailability by adding it directly to the soil (Beesley, *et al*., 2011). The technique, which uses the additive's strong sorption properties, shows promise as being a cost effective solution for DDT. Preliminary results indicate biochar could be used to stabilize DDT (Denyes, *et al*., 2012).

2.5.iv. Soil Treatment

Soil treatment of DDT is complicated and involves removing DDT from the soil or groundwater either *in situ* or *ex situ*. It can be approached by exploiting DDT's various physiochemical properties, degrading it into innocuous or immobilized compounds through chemical technologies, or employing biological processes to degrade or remove it (Baird & Cann, 2008).

The Fenton reagent, high frequency ultrasound and electro-kinetic remediation are three techniques that have been researched for DDT remediation. The Fenton reagent uses hydroxyl radicals as an oxidizing agent and several studies have concluded that it shows potential value to pre-treat highly DDT contaminated soil (Villa & Nogueira, 2006). High frequency ultrasound process uses the mechanical vibration of sound waves to create vapour filled bubbles which facilitate the oxidization of organic compounds in aqueous solutions (Banerji, *et al*., 2007). Electro-kinetic remediation uses the flow of direct electrical current to increase solubility toward the anode and some work has been completed to find a compatible surfactant to help mobilize the DDT (Karagunduz, *et al*., *2007)*.

Phytoextraction, a subset of phytoremediation, uses plant roots to take up contaminants through natural transpiration processes and subsequently accumulates those contaminants (Ficko, *et al*., 2011). Substantial research has been conducted on the phytoextraction of DDT using both crop and native/naturalized plant species. Phytoextraction of DDT is a slow process, and depending of the concentration and soil characteristics, may take several years or even decades (Lunney, *et al*, 2004; Lunney, *et al*., 2010; MSc thesis in progress by Surmita Paul at RMC).

Surfactants are amphilphilic compounds (containing hydrophobic and hydrophilic portions) that are used to increase water solubility of contaminants for remediation during *in-situ* flushing. According to field studies, surfactants can accelerate remediation, including contaminants in the vadose and saturated zones, and hence large quantities of soil would not need to be excavated (Mulligan, *et al*., 2001; Badley, 2003). At PPNP starch surfactant (10% or 20% hydroxypropyl-β-cyclodextrin solutions) was tested to accelerate the effects of soil washing (Mironov, 2004; Badley, 2003). Before the appropriate remediation could be determined, additional information on the extent of DDT contamination was required.

CHAPTER 3 - Methodology

3.1. Experimental Design, Assumptions, and Iterative Process

There are numerous barriers to comprehensive quantification and characterization of DDT within Point Pelee National Park (PPNP) including the methodologies employed for previously conducted research. Multiple unrelated studies that involved collecting soil samples in the Park resulted in an amalgamated data set with a disproportionate number of samples collected from localized areas that were expected to have high DDT concentrations. Certain areas within regions of high concentration were well represented. However, the location of many boundaries between areas of high concentration and the distance over which that transition to uncontaminated soil took place remained uncertain. Additionally, most of those studies (outlined in Section 2.4) employed fairly small data sets. Even Crowe and Smith's 2007 paper, which was the most recent and comprehensive, did not provide clear boundaries for DDT contamination (Crowe & Smith, 2007). Maps provided by PPNP personnel, which consolidated previous information (Figure 8-C), had similar limitations. The current project was designed to fill in the data gaps and then use the complete data set to create a remediation plan for DDT contaminated soil at PPNP.

The initial assumptions and anticipated limitations detailed below comprised a methodical starting point for site assessment. They helped to shape an understanding of the remediation issues and focus the direction of the project. Specific concerns included the presence of possible unidentified 'hotspots' of DDT soil contamination and the challenge of comparing and manipulating existing data points due to different presentation formats. Also, while previous researchers had categorized, and in some cases sampled, hot spots employing a tight grid pattern, more information was required to define their outer edges.

A. Initially Known Facts/Assumptions:

   a. The flora and fauna found at PPNP is fragile and has international significance.

   b. PPNP is contaminated with DDT in at least four previously identified hotspot locations.

   c. These known hotspots have contamination two to three orders of magnitude above the acceptable Canadian soil guidelines.

   d. All known hotspots are between the main road and the western edge of the eastern marsh. This area was historically used for farming, growing orchards and camping.

   e. DDT has demonstrated a longer than normal half-life at PPNP which could be caused by the local aerobic and/or anaerobic environments.

f. Areas beyond the main paths, including known hotspots, are difficult to access due to thick underbrush, thriving poison ivy, marshy ground, and cattail marshes.

g. The eastern marsh, the southern tip of the peninsula, and the northern edge were not used for farming or camping and were likely not directly exposed to DDT.

h. DDT was exposed to the land mainly through spray based operations. Previous testing has shown the contamination remains in the top soil layer.

i. During the first research trip to PPNP for this project, staff provided an excel spreadsheet with 205 soil samples from previous studies including individual sample names, sample author, grid coordinates, elevation, DDT, DDE, DDD, and total DDT concentration, and a site description. This information was assumed accurate, used as the 'pre-existing' data set, and is recorded in Appendix B.

B. Known/Anticipated Limitations:

a. Pre-existing maps did not provide sufficient detail or allow for additional information to be accurately incorporated.

b. Pre-existing information may not have been accurately incorporated into existing maps.

c. Systematically sampling the entire park was not possible or economically feasible.

d. Remediation options considered had to complement PPNP's conservationist goals related to protecting and maintaining the Park's unique microclimates. Specifically, technologies which involve processes harmful or disruptive to the environment would not be acceptable options.

3.2. Sample Collection Process

Twenty-five surface soil samples, nine sediment samples, and four water samples were collected at PPNP in June 2012 with every tenth soil sample being comprised of a sample and a field duplicate. All sample locations were mapped using a handheld Magellan eXplorist 310 Global Positioning System (GPS) which is accurate within 3-5 m. A GPS waypoint was created for each sample within the Magellan eXplorist GPS programme, and hand written field notes including the coordinates were recorded.

Soil samples were collected in order to verify previous sample results, and to create boundaries between areas of known contamination and areas below the Canadian guidelines (Section 2.4, Table 1). Water and sediment samples were collected to confirm concentration levels in the marsh and ponds. Obvious geographic features such as the edge of the marsh land (A1 from Figure 10) and the ponds (B from Figure 10) were used to locate sampling locations away from areas that had been previously heavily sampled.

Soil samples of 50-150 g were collected using a clean trowel within 0-10 cm of the surface. Water and sediment sample locations were accessed by boat and were collected from along the edge of the transition between pond and cattail marsh where the water was approximately 2-4 feet deep. Underwater sediment samples were collected using a long handled spade shovel. Water samples were collected using 1 L sterile glass and plastic bottles. While the boat was stopped at the edge of the pond and cattail marsh, these bottles were carefully submerged into the pond water and allowed to fill.

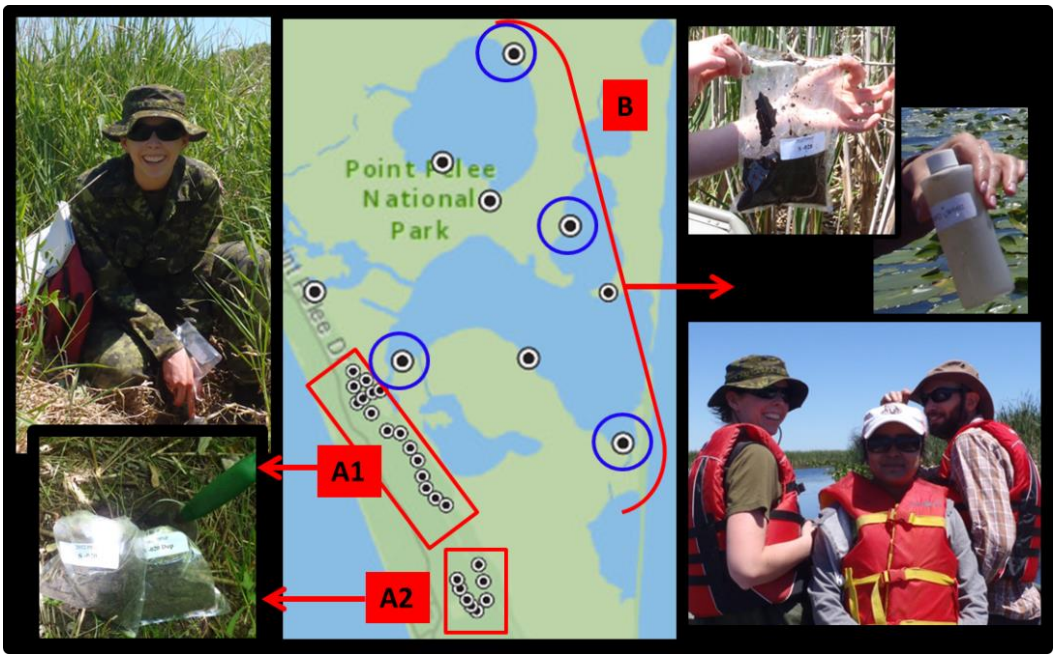


Figure 10. Overview of PPNP sample collection in June 2012. The map indicates where all samples were collected which were divided into several sections. Section A1 and A2) represents the locations of all soil samples. Pictures on the left show soil sample collection. Section B) all sediment and water sample locations; sediment samples were collected from every location indicated, water samples were collected from locations also circled in blue. These locations were only accessible by boat; pictures on right illustrate the process.

3.3. Laboratory Analysis Process

All samples were kept refrigerated 0.5 - 9.0 °C from the time the sample was collected until analysis. All samples were analyzed at Queen's University, by the Analytical Services Unit (ASU). For very wet samples, roughly 30 g of soil or sediment was air dried for at least 12 hours. Before analysis, a subsample of each sample was used to determine a wet/dry ratio. Next, 10 g of soil or sediment was accurately weighed into the soxhlet thimbles before adding 100 µL of decachlorobiphenyl (DCBP) and roughly 20 g of Ottawa sand and sodium sulphate. Each run also included one sample duplicate, one blank, and one control spike, and the solvent was methlyene chloride (DCM). Blanks were prepared with Ottawa sand. Control spikes are identical to blanks except that they also include 10 µL of Appendix 9 (Sigma-Aldrich). Following the soxhlet run (4-6 hours), the extracted sample was concentrated by rotoevaporation to 1 mL and applied to

a LC-Florisil solid phase extraction tube (Supelco^{TM}) and eluted with hexane. That extract was then diluted with hexane to 10 mL and a fraction of that was used to fill a 2 mL gas chromatography (GC) vial for analysis using a gas chromatograph with an electron capture detector (GC/ECD).

To prepare water samples for GC analysis, 500 ml of each sample was placed in a 1 L separator funnel and spiked with an internal standard, DCBP. 25 mL of methylene chloride was added to the separatory funnel and then shaken with frequent venting. The bottom layer was then decanted through a funnel containing anhydrous sodium sulfate and into a round bottom flask. This extraction step was repeated a total of three times with 75 mL collected in the round bottom flask. The solvent in the flask was then exchanged for hexane by rotary evaporating the original 75 mL down to 1 mL and adding 5 mL of hexane. The addition of 5 mL of hexane and subsequent evaporation with the rotoevaporator was repeated two more times stopping with a total volume of 1 mL on the final rotovaporization. The 1 mL remaining in the flask was pipetted onto a LC-Florisil solid phase extraction tube (Supelco^{TM}) and eluting with hexane.

All soil, sediment and water samples were analyzed using an Agilent 6890 or 7890 gas chromatograph equipped with a ^{63}Ni GC/ECD, a SPB^{TM}-1 fused silica capillary column (30 m, 0.25 mm ID x 0.25 μm film thickness). Each run included a spike, a blank and a control spike. Helium gas was used as the carrier gas with a flow rate of 2 mL/min and nitrogen was used as a makeup gas in the ECD. All values reported used ppm (μg/g) on a dry weight basis and all concentrations were corrected for surrogate recovery.

Quality assurance and quality control (QA/QC) was ensured by assessing blank, spike and duplicate data. DCBP extraction efficiency ranged from 77-112%, with an average of 97.9%. Except for one run, all analytical blanks were below the detection limit. The run with the blank above the detection limit was likely contaminated due to the high levels of contamination found within the other samples in that run. All control spikes ranged from 89.0-120% of the target with an average of 104%.

3.4. Amalgamating Information/Google Earth Platform

In order to target areas for additional sampling, collected data had to be presented geographically to enable comparison based on location and concentration. It became apparent that a new way of accessing and presenting the data was required to facilitate an iterative and targeted sampling strategy. A secondary objective was the creation of an accessible tool for the use of PPNP staff and future researchers working on other projects. These requirements are outlined in Table 2.

Table 2. Data Accessibility Requirements.

Comprehensive	Allows the user to accurately: - See each sample's concentration - See each sample's physical location within the park - See how each sample interacts or is related to other local samples - Target only areas of the park requiring further delineation - Gain an immediate 'big picture' understanding of the entire park's DDT contamination
Intuitive	- Allow the user to use, understand and manipulate the software with minimal experience or training - Information presented must be easily understood
Cost-Effective	- Inexpensive/Free
Flexible	- Allow additional sample points to be added - Allow future requirements to easily be imposed - Software must be accessible

After experimenting with several platforms, a Google Earth backbone was selected as it fulfilled all of the criteria, and clearly and intuitively presented information about both DDT locations and concentrations. All existing samples were programmed into an overlay to create an interactive data presentation format. The only major drawback to using a Google Earth platform was that each data point had to be added and manipulated individually while other platforms could upload data points via an excel spreadsheet.

Figure 11 is an example of the Google Earth display. Each coloured pin, (green, yellow, orange or red) represents one sample, and the concentration of each sample is listed in the adjacent similarly coloured text. The colours correspond to defined levels of contamination. Within the platform, the user can zoom in and out on specific areas and double click individual pins on the map, or the drop down menu on the left, for more information: the sample's name, by whom it was sampled, location (easting, northing, elevation), concentration (breakdown of DDT, DDE, DDD and total DDT in $ng \bullet g^{-1}$), and a site description.

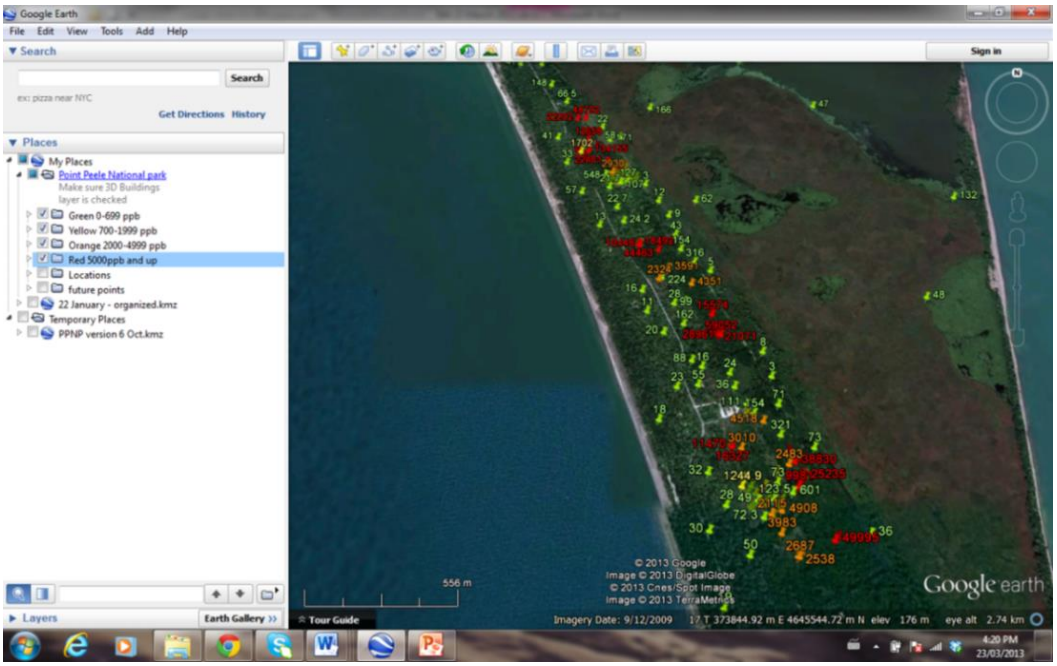


Figure 11. Example of Google Earth display with sampling overlay. Each colour represents a different level of DDT contamination: green = 0-700 ng•g^{-1}, yellow = 700-2,000 ng•g^{-1}, orange = 2000-5,000 ng•g^{-1}, and red = 5000 ng•g^{-1} and up.

Data captured in this tool can be manipulated and selectively displayed based on organizational layering (Figure 12). Patterns of contamination become more obvious as the user zooms in and out, and displays and compares various layers highlighting hotspots and areas requiring further study.

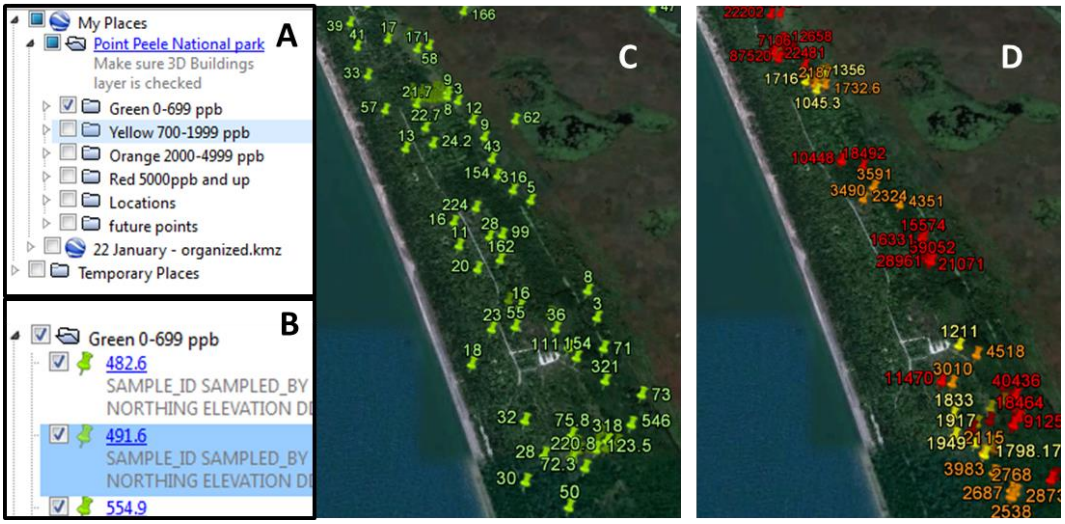


Figure 12. Example of layering flexibility. A) Individual samples are organized into appropriate layers based on contamination concentration. It is possible to select and display one, several, or all layers by checking the appropriate box. B) It is also possible to drill down into each layer and select individual or specific samples for display or further information. C) Only "green" samples, or those with a DDT concentration < 700 ng•g^{-1} were selected/displayed. D) Only samples with concentrations above 700 ng•g^{-1} are selected/displayed.

3.5. Second Iteration of Sampling

The second research trip was carried out 9 - 10 April 2013. The early spring was specifically chosen because the snow had melted but it was early enough to avoid PPNP's formidable undergrowth, poison ivy and insect population.

The objective of the second iteration of sampling was to further define the boundaries around areas of high concentration. For example, Figure 13, Map 1 shows all pre-existing samples within a small subsection of the Park. Figure 13, Section B shows 'red' and 'orange' samples which indicate pre-existing samples above Canadian guideline concentrations. Section B is part of a narrow band of land, extending both north and south, which was predominantly used for agriculture and directly contaminated with DDT. Sample collection was planned to radiate out from previous samples of high concentration towards areas of known low concentration to find the approximate contaminated/uncontaminated boundary.

Targeted sampling points were created seen in Figure 13, Map 2 as indicated by the pink and white pins. The pink pins denote the first planning cycle, and the white pins were added during the second planning cycle; but both were to be collected during the April research trip. These future points were chosen to surround the hotspots and determine how the contamination dissipates between the pre-existing red and green samples.

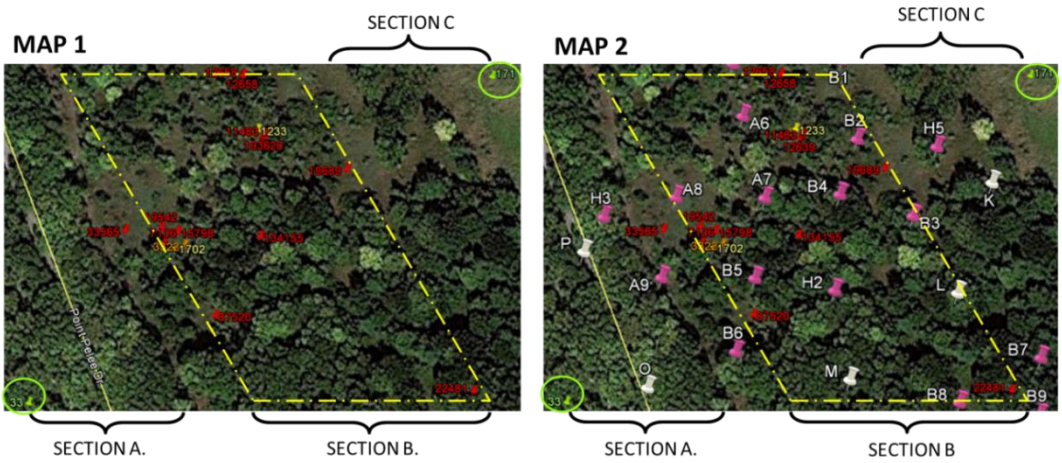


Figure 13. Creating a sampling plan. Map 1) a subsection of the Google Earth tool with all samples analyzed during the first iteration. Map 2) the same subsection with points indicating where future samples were planned. Sections A and C show areas of anticipated low contamination, while section B shows an area of anticipated high DDT concentration.

Once all the desired sample locations were mapped in Google Earth, GPS coordinates were mined (Figure 14). Those GPS coordinates in eastings and northings were then entered into a hand held Magellan eXplorist 310 GPS which was used while collecting the physical samples. The GPS was further loaded with a planned track route to most effectively reach all the desired sampling points.

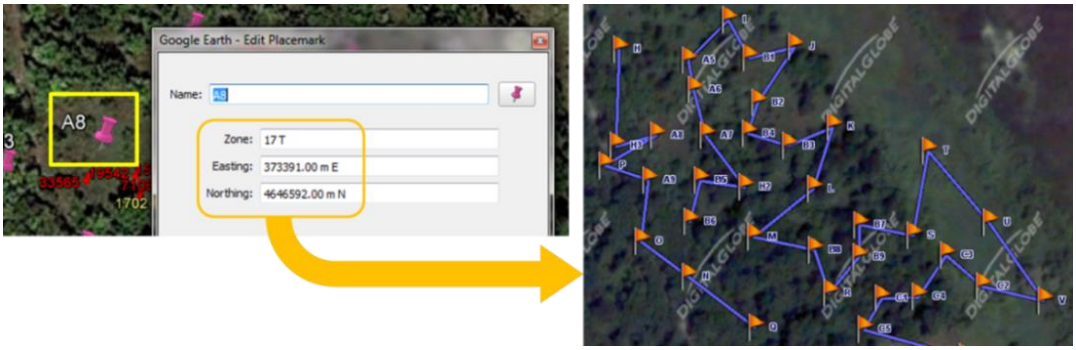


Figure 14. Mining sample coordinates. On the left, mining Google Earth for the GPS coordinates (easting and northing). On the right, the planned track route on the handheld Magellan GPS for some of the planned samples.

While in the field, the pre-programmed track route and planned sampling locations were followed as much as was practical, and extra samples were collected as appropriate. During this second PPNP sampling effort, a total of 170 soil samples were collected. Prior to DDT analyses, all soil sample locations were entered into the Google Earth map (white pins) as per Figure 15 such that samples could later be selected for analysis based on their location relative to previously existing samples. Once a sample was selected for analysis and analysed, the pin marking its location was changed from white to the appropriate colour based on its DDT concentration. Over five iterations, 115 samples were selected for analysis.

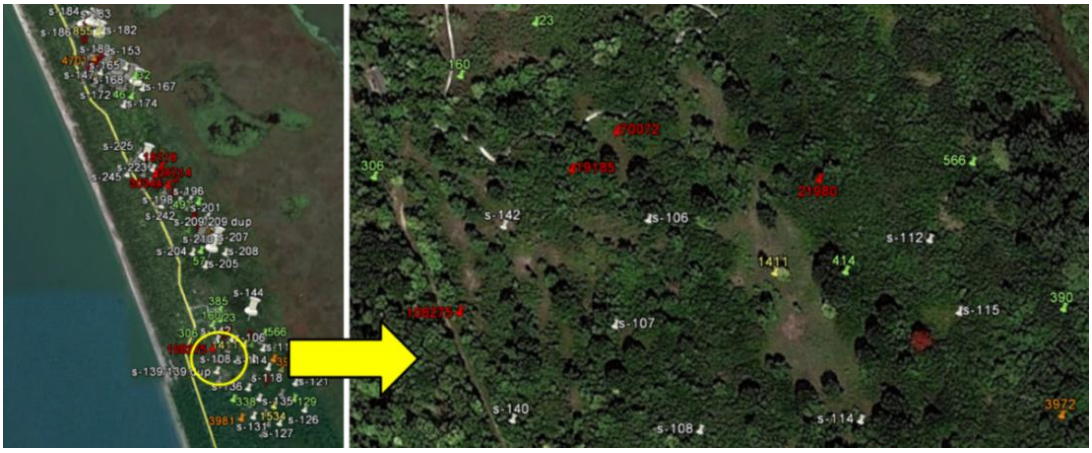


Figure 15. All samples collected during the second iteration. Samples in red, orange, yellow or green indicate the sample was analyzed. Samples in white (identified by the sample number rather than the concentration of total DDT) show samples that were not analyzed.

3.6. Data Analysis

3.6.i. Interpolative Mapping Software

Once the final iteration of analysis was completed, all samples were input into ArcGIS for interpolation using an inverse distance weighted (IDW) technique. ArcGIS, a

platform for designing and managing geographic knowledge, is a product of ESRI, a New York based firm specializing in geographic data (ESRI, 2011).

Inverse distance weighted (IDW) interpolation estimates the values of unknown points using the distances to, and values associated with, nearby known points. The closer the distance from the known point to the unknown point, the more effect it has on characterizing an unknown point. One of the other popular interpolation techniques, Kriging, uses a minimum variance method which is a less arbitrary and more precise weighting scheme (ESRI, 2011). However, IDW was selected because it requires fewer user inputs, and in densely sampled areas most interpolation methods provide similar results (Li & Heap, 2011).

The first step was to upload an excel spread sheet containing all sample data points to ArcGIS, plot the locations of each sample on a grid system, and store the information in a shapefile or geospatial vector data format. The uploaded data file was converted within ArcGIS to a raster or matrix of cells organized into rows and columns where each cell contains a value representing information. Although data stored in raster files may be affected by spatial inaccuracies, the simple structure is a powerful format for spatial analysis (Li & Heap, 2011). Next, the samples were interpolated using IDW. Part of the interpolation process requires setting grid-codes which in this case referred to levels of contamination. For this project, eight grid-codes were selected: 0-700 $ng \bullet g^{-1}$, 700-2,000 $ng \bullet g^{-1}$, 2,000-5,000 $ng \bullet g^{-1}$, 5,000-15,000 $ng \bullet g^{-1}$, 15,000-30,000 $ng \bullet g^{-1}$, 30,000-50,000 $ng \bullet g^{-1}$, 50,000-100,000 $ng \bullet g^{-1}$, and above 100,000 $ng \bullet g^{-1}$.

Inverse distance weighted (IDW) interpolation assigns values to non-sample locations using a weighted average of the values available from the known points, (i.e. sample locations). Some data points contribute more to calculating unknown points based on proximity; specifically the inverse distance to each known point. One of the assumptions related to IDW is that the contaminant decreases with distance from the sample location (ESRI, 2011).

Once the data set has been interpolated, ArcGIS can be used to solve for the area associated with each grid-code, which was set to correspond to concentration levels. First, the interpolated file (raster data set) was converted to polygon features. This converts the irregular interpolated shapes to polygons so the software can calculate area. All polygons for each grid code or concentration level are then linked even if they are not physically co-located. The area of the linked polygons can be found through the attribute table.

In order to ‘cut out’ or delete irrelevant parts of the interpolation, a new versions of the shape files had to be created and saved, and input as a layer on the base map. By combining the new shapefile with the interpolated polygon data and the ‘cut’ function, it was possible to re-calculate the area associated with the grid-codes or concentration levels for that new, smaller interpolated area.

3.6.ii. Statistical Isomer Assessment

To compare isomer composition regardless of sample concentration, it was necessary to transform each sample isomer from concentration to a percentage of total DDT by dividing each isomer's concentration by total DDT's concentration of that sample as per Appendix C.

To minimize Type I error and establish statistical difference between data sets, ANalysis Of VAriance (ANOVA) single factor test was used because it can simultaneously test two or more data sets of different sizes (Shaw & Mitchell-Olds, 1993). The ANOVA test null hypothesis assumes that there is no significant statistical difference between data sets. If this is proven untrue, the null hypothesis must be rejected. As described in Appendix C-2, all data can be shown to be approximately normally distributed. Appendix C-3 describes how ANOVA tests can be interpreted and all ANOVA test results can be found in Appendix C-4.

CHAPTER 4 - DDT Distribution in PPNP

Point Pelee National Park (PPNP) is highly contaminated with DDT. This research project was designed to build on Park staff's corporate knowledge of DDT, and previously conducted studies on the contaminant.

While some effort had been made to identify areas of high DDT concentration, most previous DDT research at PPNP concentrated on areas of known or probable contamination. Additional sampling was required to determine the contaminant's current spatial and concentration distribution. To achieve this objective, an iterative sampling and analysis plan was created and implemented. Previously existing and newly analyzed sample data were incorporated into Google Earth and ArcGIS to present a comprehensive picture of the DDT contamination at PPNP.

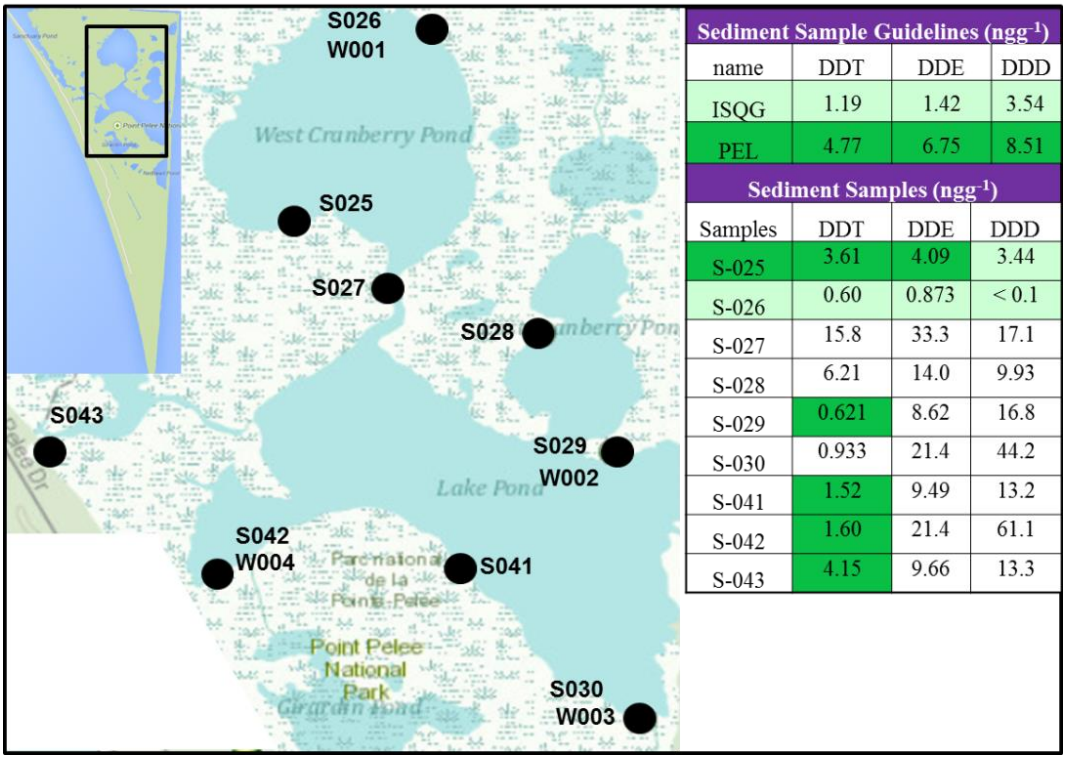
4.1. Water and Sediment Samples

Four water and nine sediment samples were collected from the ponds and marsh areas (Figure 16). All water samples were analyzed and determined to be below the method detection limit (<1.0 $ng \bullet g^{-1}$) (Appendix A) and thus the Canadian water guideline of 1.5 $ug \bullet L^{-1}$ DDT. Although water samples from the pond surfaces have not been previously sampled, an earlier study did sample groundwater at 16 sites within PPNP. The National Water Research Institute concluded that the concentration of DDT in the groundwater was less than 0.0005 $ng \bullet g^{-1}$ (Crowe, *et al*., 2003). While there was insufficient information to hypothesize about transport processes, it appeared unlikely that groundwater was a source of contamination to the marsh's open water.

Three literature sources (Russell & Haffner, 1997; Crowe, 1999; Crowe & Smith, 2007) refer to the application of commercial DDT directly onto open waters in the marsh at PPNP. The earliest source, a formal report produced for PPNP about DDT in the park, states that DDT was applied "by direct application to every body of water in the park by *tossit bomb*" and referenced unspecified park records (Russell & Haffner, 1997). Without providing any additional details regarding specific locations, quantity or frequency, the other two papers referring to *tossit bombs* only specify that DDT was, a) applied through "*toss bombs* at specific sites or pools of water" (Crowe, 1999), and b) applied to "some of the open water ponds of the marsh as *tossit bombs*" (Crowe & Smith, 2007). PPNP staff verbally indicated that DDT may have been applied to open water in the Park's marsh area, but were unable to definitively confirm this fact through corporate knowledge or available park records (Dobbie, pers comm).

DDT has low solubility (Agency for Toxic Substances and Disease Registry, 2012) and strongly sorbs to soil and sediment particles at PPNP (Russell & Haffner, 1997). The most likely method of DDT contaminant transport in the marsh and pond area is movement with sediments as they are eroded or moved in a suspended aqueous phase (Vinten, *et al*., 1983). In the 65 years since the earliest possible use of DDT at PPNP, any DDT applied to the open water likely sorbed to sediment particles, and may have been dispersed throughout the largely inaccessible pond and marsh system, or buried

under organic matter. For this project, sediment samples were collected from the top 0 - 0.1 m of the of the sediment layer which was below 0.6 – 1.2 m of water.



Sediment Sample Guidelines (ngg^{-1})			
name	DDT	DDE	DDD
ISQG	1.19	1.42	3.54
PEL	4.77	6.75	8.51

Sediment Samples (ngg^{-1})			
Samples	DDT	DDE	DDD
S-025	3.61	4.09	3.44
S-026	0.60	0.873	< 0.1
S-027	15.8	33.3	17.1
S-028	6.21	14.0	9.93
S-029	0.621	8.62	16.8
S-030	0.933	21.4	44.2
S-041	1.52	9.49	13.2
S-042	1.60	21.4	61.1
S-043	4.15	9.66	13.3

Figure 16. Sediment and water samples collected for this project. All water sample locations were co-located with sediment sample locations and are identified as W001, W002, W003, and W004. The location of each sediment sample in the embedded table is specified beside the appropriate indicator dot. In the sediment sample table, the light green indicates that sample's DDT concentration was less than the ISQG guideline, and dark green indicates that it was less than the PEL guideline.

Sediment samples had an average 37.1 ng•g^{-1} of total DDT, and ranged from 1.5 to 84.3 ng•g^{-1} (Appendix A). However, total DDT cannot be used to assess sediment concentrations as sediment guidelines differ for each component of total DDT (DDT, DDE and DDD), and each component has both an interim sediment quality guideline (ISQG) and a probable effects level (PEL) guideline. Only one sample was below the ISQG limits for all components, and only two were below the PEL guidelines for all components. Four other samples had DDT levels below the ISQG level, but all DDE and DDD levels were above the guidelines (Figure 16 and 17). These results are consistent with earlier studies. Previous sediment samples were collected from an unknown depth with a ponar dredge from two sites on PPNP's interior ponds and all samples had <150 ng•g^{-1} of DDT (Russell & Haffner, 1997). Other sediment samples collected from an unknown depth using a plexiglass tube had an average concentration of 28.3 ng•g^{-1} of total DDT (Crowe & Smith, 2007).

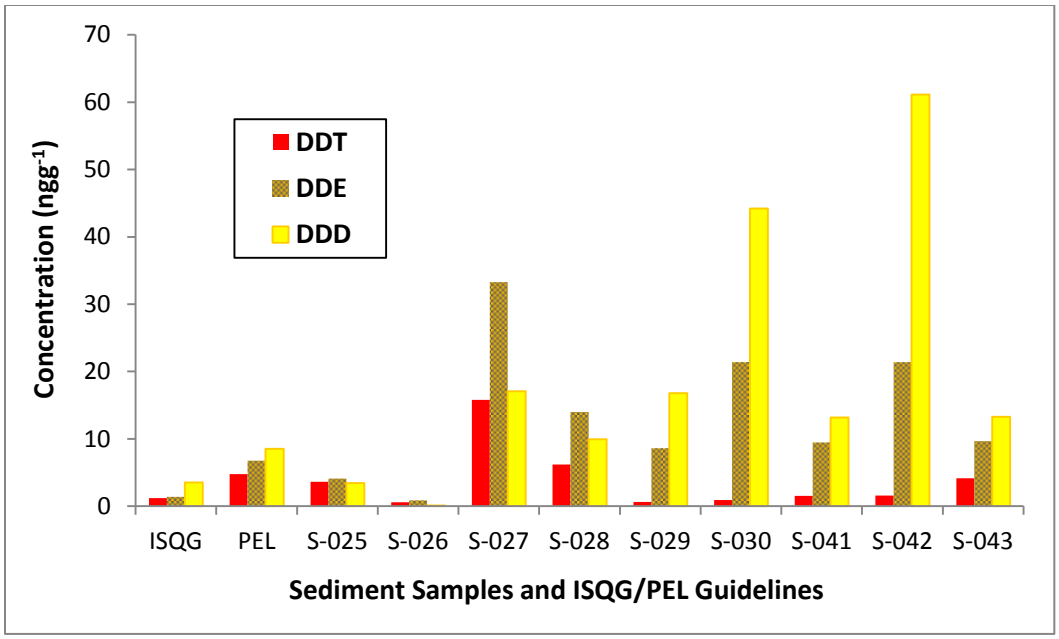


Figure 17. Sediment sample DDT, DDE and DDD concentrations. ISQG and PEL guidelines (CCME, 1999) are included for reference. Y axis is in ng•g^{-1}.

DDT is more likely to fully degrade in an anaerobic environment such as that found in a marsh than in an aerobic environment (Sudharshan, *et al*., 2012). Sediment samples revealed concentrations above the CCME guidelines, and DDT isomer analysis was conducted on these sediment samples (Chapter 5). However, as the ultimate goal of this project was to create a soil remediation options analysis plan (Chapter 6), no additional sediment samples were collected and sediment contamination was not further investigated.

4.2. Soil Samples

During two research trips to PPNP, 170 soil samples were collected of which 115 were analyzed. The locations of those 115 analyzed soil and sediment samples are shown in Figure 18-B and listed in Appendix A. Figure 18-A displays pre-existing samples, and Figure 18-C amalgamates all samples.

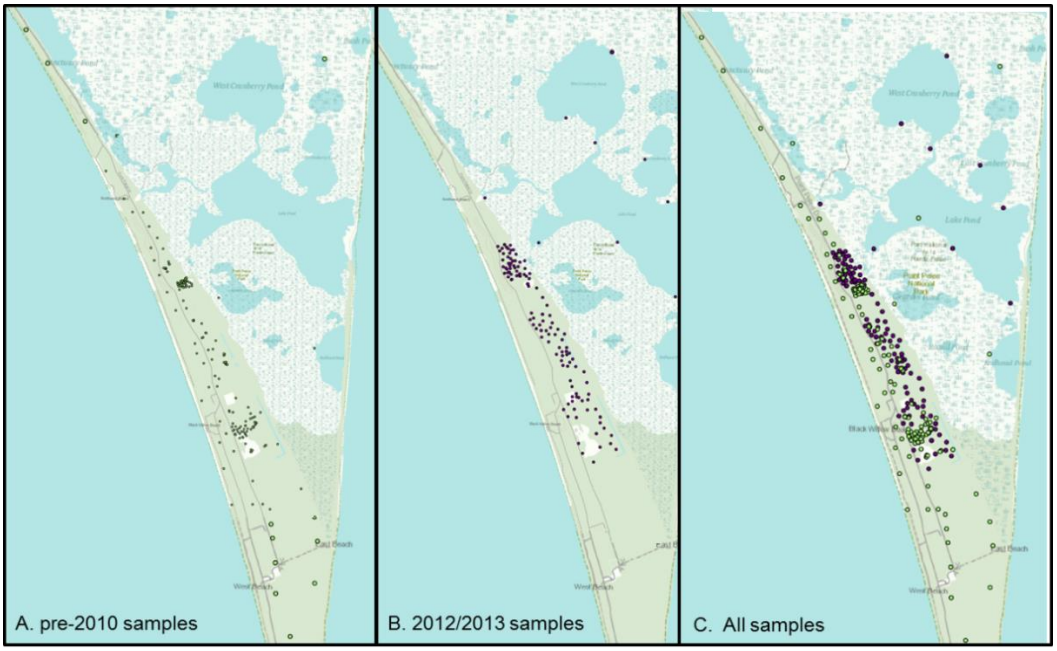


Figure 18. Analyzed soil sample locations. A) locations of pre-existing samples. B) locations of samples collected during this project. C) amalgamation of all sample locations where green dots indicate pre-existing samples and purple dots indicate new samples.

Of the soil samples collected during the April 2013 trip which subsequently analyzed, 50 are <700 ng•g^{-1} DDT with an average of 149 ng•g^{-1} DDT and the remaining 65 samples exceed the Canadian Guideline with an average of 23,000 ng•g^{-1}. Figure 19 shows the relationships between average concentration and the number of samples collected and analyzed within each designated concentration range.

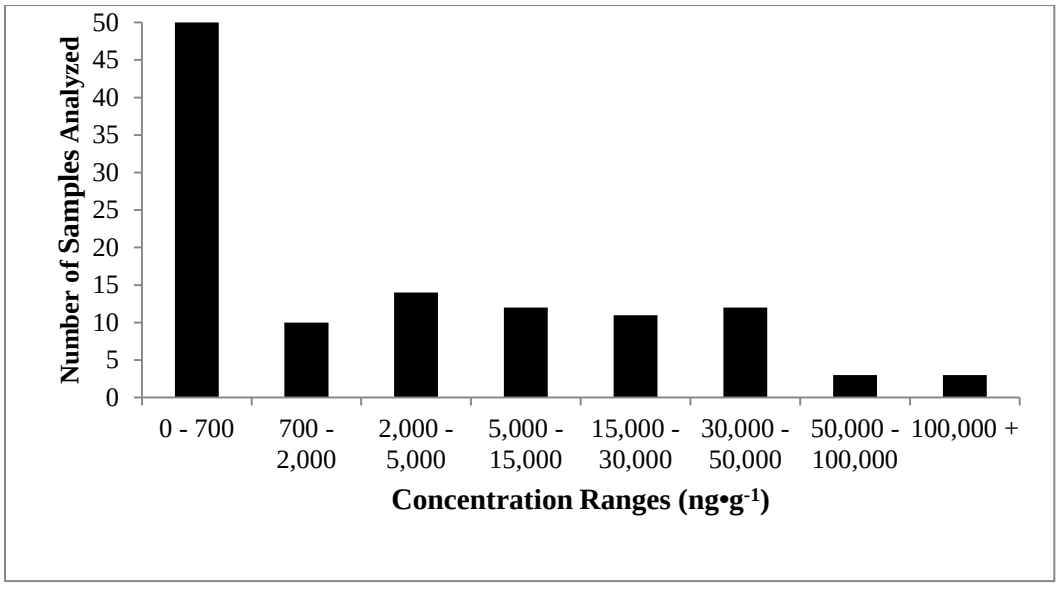


Figure 19. Number of soil samples analyzed at each concentration range. All concentrations in ng•g^{-1}

Information about both DDT location and concentration for all soil samples was programmed into Google Earth (Chapter 3) and can be viewed in greater detail via the attached disk. When the amalgamated set of data (Figure 18-C) was displayed on a Google Earth platform (Figure 20-A), each sample was marked with a colour related to its concentration level. This Google Earth overlay is compared to two maps produced by PPNP (Figure 20-B and C) which also use a Google Earth platform. They are based on historic aerial photographs and other documents from the Park's archives showing PPNP's best estimate of land use in 1931 and 1959 respectively (Point Pelee National Park, 2002). Within the original electronic file there are embedded labels which can be accessed when the map is displayed in Google Earth. These labels tag individual areas with PPNP's assumption of the original sites' use (e.g. cottages, orchards, fields, etc).

Figure 20-A indicates that the far northern and far southern areas do not have samples above the CCME criterion which is consistent with the land use shown in Figure 20-B and C. In the far northern area, there is no known land use as of 1931, and minimal land use as of 1959 consisting of a small cottage, an administrative building, and multiple marsh lookout points. In the far southern area, there is significant land use for fields and orchards as of 1931 (Figure 20-C). By 1959 (Figure 20-B), all land use in the far southern area is non-agricultural and consists of beaches, parking lots and access routes. The soil in the far southern area is sandy (Trenhaile, *et al*., 2000) and it is likely that the fields and orchard found in 1931 were abandoned prior to 1959 either due to a lack of agricultural success, or as part of the Park's shift to focus on conservation (Sandilands, 2000). As there are only low levels of DDT contamination in the far southern area, the fields and orchard were likely abandoned prior to 1948 when DDT was first used in the Park, or shortly thereafter. Previous sampling in the far northern and southern areas revealed an average DDT concentration of 19.5 $ng \bullet g^{-1}$ (Crowe & Smith, 2007). As this is below the CCME guidelines there is no evidence that these areas require remediation or further study.

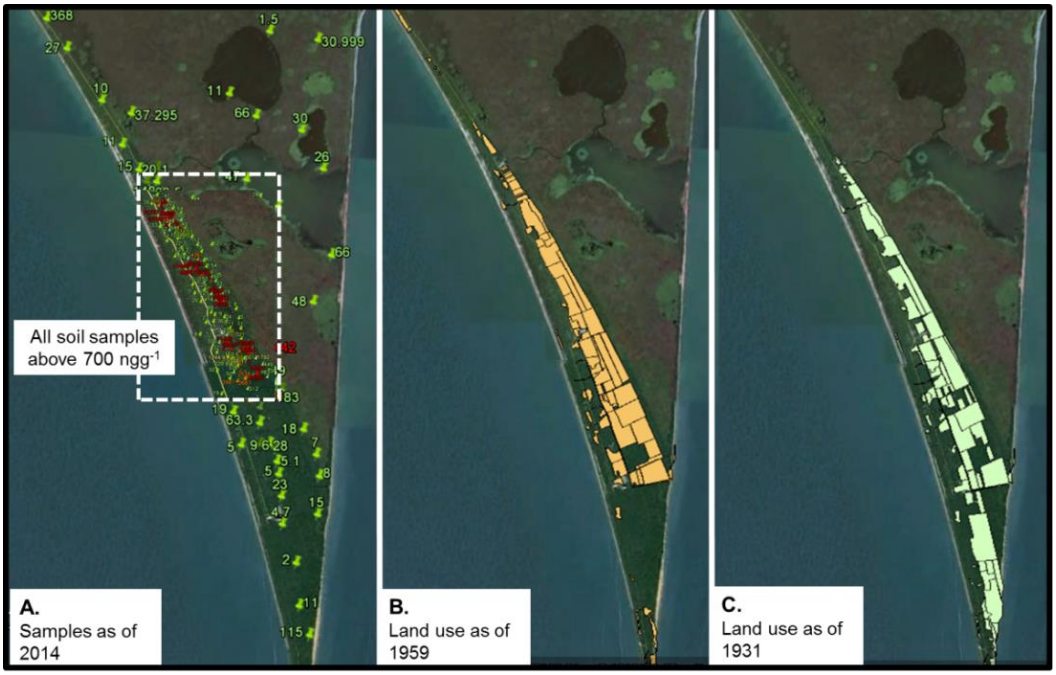


Figure 20. Google Earth depiction of sample locations and land use. A) All soil sample locations. All samples above 700 ng•g^{-1} are located mid-way down the peninsula highlighted with dashed white box. B) Land in use as of 1959; C) Land in use as of 1931 (Point Pelee National Park, 2002).

The dashed white box in Figure 20-A and 21- A indicates the area focused on for sampling as it contains all historic samples with concentrations exceeding 700 ng•g^{-1} DDT. Over 90% of samples above 700 ng•g^{-1} DDT are contained within areas previously used for agriculture and residences in 1931 (Figure 21-A). All samples above 700 ng•g^{-1} DDT except one, (which is within five meters) are contained in the areas identified for agriculture and cottage residences in 1959 (Figure 21-B). This illustrates that there has likely been little DDT mobility between the time of commercial DDT application, and sample collection; a period of 30 - 65 years. DDT generally does not migrate vertically or laterally. Two case studies on agricultural land in comparable climates found DDT's vertical movement was restricted to that caused by mechanical disturbance such as tilling and plowing, and lateral movement was insignificant and could be attributed to cultivation (Stewart & Chisholm, 1971; Martjn, *et al*., 1993). The assumption that DDT has not mobilized in PPNP is also supported by the low DDT concentration (<0.0005 ng•g^{-1}) in ground water in the Park (Crowe, *et al.*, 2003).

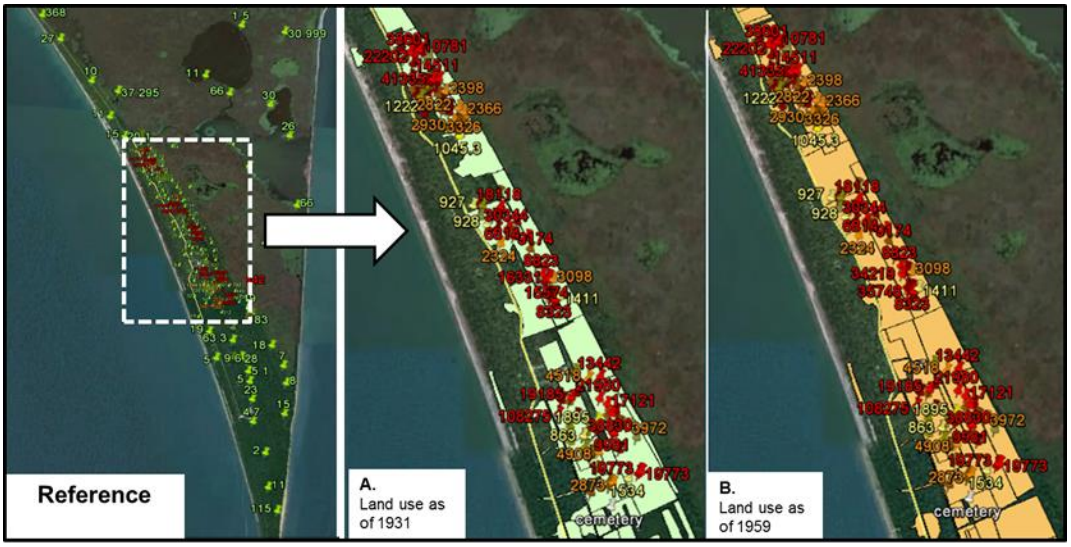


Figure 21. Historic PPNP land use. A) Land in use in 1931; B) Land in use in 1959. Both A) and B) are shown with sample locations and concentrations superimposed.

Distinct areas of higher DDT concentration can be identified by looking for tight groupings of red, orange and yellow pins representing samples with concentrations above 700 ng•g^{-1}. There are three major hotspot which are surrounded by green samples (i.e. those with low concentrations) (Figure 22-A). In Figure 22-C only samples with total DDT concentrations above 5,000 ng•g^{-1} are displayed, and distinct areas at this much higher DDT concentration are clearly visible. All samples above the guideline of 700 ng•g^{-1} are shown in Figure 22-B.

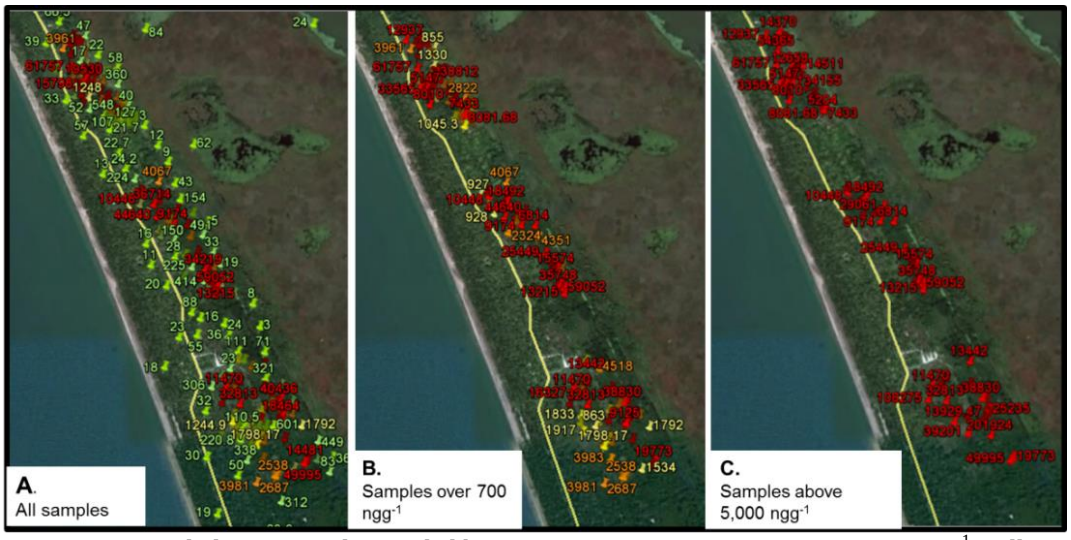


Figure 22. Sample locations colour coded by DDT concentration. Green = 0 - 700 ng•g^{-1}, yellow = 700 – 2,000 ng•g^{-1}, orange = 2,000-5,000 ng•g^{-1}, and red = 5,000 ng•g^{-1} and above. All maps in this figure include samples collected for this project 2012/2013 and previously existing samples. A) Samples at every concentration levels, B) All samples above 700 ng•g^{-1}, and C) All samples above 5000 ng•g^{-1}.

These distinct areas of higher DDT concentration are identified in Figure 23 and labeled as north, middle and south.

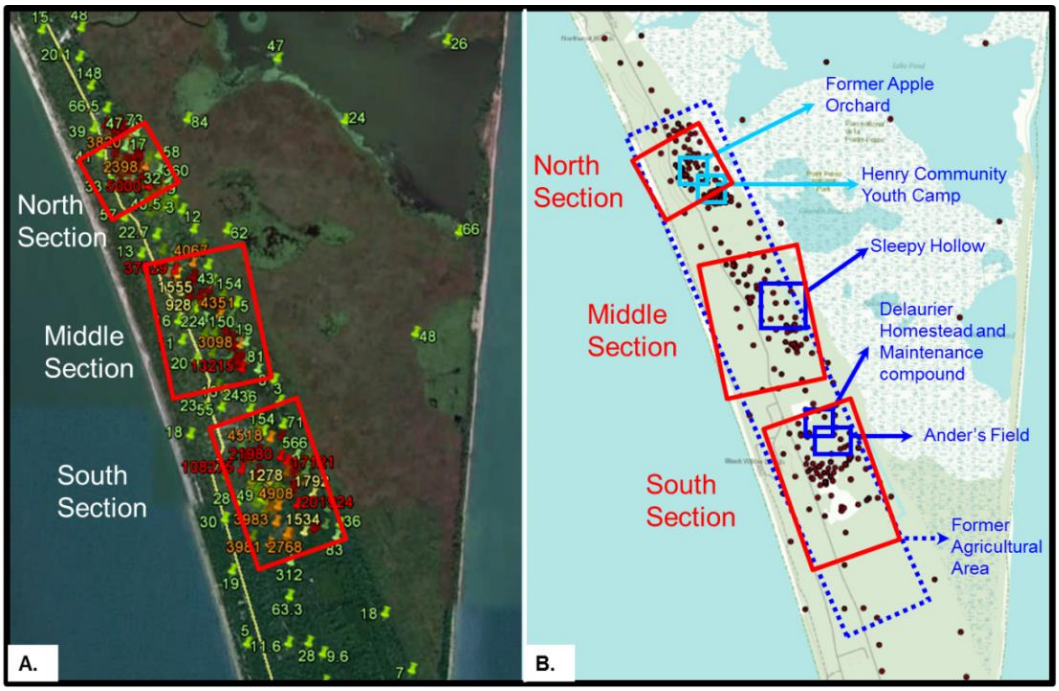


Figure 23. PPNP North, Middle and South area overview. A) All PPNP samples with concentrations exceeding Canadian DDT soil guidelines displayed in three sections: north, middle and south on a Google Earth backbone. B) Overlays of sample locations with north, middle, and south sections and historical names (identified in Chapter 2, Figure 7) on an ArcGIS platform.

All previous studies have used historic names (Figure 23-B) to describe the location of their samples. The former agricultural area runs through all three major hotspot sections (Figure 23-B). The north section includes the former apple orchard and the Henry Community Youth Camp. The middle section includes Sleepy Hollow, and the south section the Delaurier Homestead, maintenance compound and Ander's field. This thesis will predominantly use the nomenclature of north, middle and south sections as identifying locations.

Amalgamating the data from previous studies with this project's information resulted in 122 soil samples from the north, 43 from the middle, and 75 from the south sections over 700 $ng \bullet g^{-1}$ (Table 3). Details related to each soil sample can be accessed in Appendices A and B, and in the Google Earth map on the attached disk.

Table 3. Comparison of new and pre-existing data in the north, middle and south areas as shown in Figure 23. Concentrations are in $ng \bullet g^{-1}$.

	Number of samples above 700 $ng \bullet g^{-1}$		**Average concentration of samples above 700 $ng \bullet g^{-1}$**		**Maximum concentration within sample set**	
	This Study	*Pre-existing*	*This Study*	*Pre-existing*	*This Study*	*Pre-existing*
North	35	87	20,400	13,800	134,000	194,000
Middle	23	20	17,700	26,100	44,700	76,900
South	13	62	52,700	10,800	211,000	50,600

Crowe *et al.* (2007) found comparable DDT soil results to the current study for the maintenance compound in the south section, and Camp Henry in the north section. Their findings for the former residential and former agricultural areas, which cover portions of all three sections, are also consistent with current study results. A sub-area designated as former residential falls in the natural breakpoint between the north and middle section and is consistent with previous findings of lower levels of DDT in that sub-area (Crowe & Smith, 2007).

4.3. Interpolation

Google Earth and ArcGIS were both used for completion of this project although different legends are associated with each. As Google Earth shows individual samples, and the label indicates each sample's concentration, only a few concentration ranges were required. ArcGIS shows amalgamated and estimated levels of contamination. Hence, additional concentration ranges were selected to provide greater flexibility and more information for planning the remediation options (Figure 24).

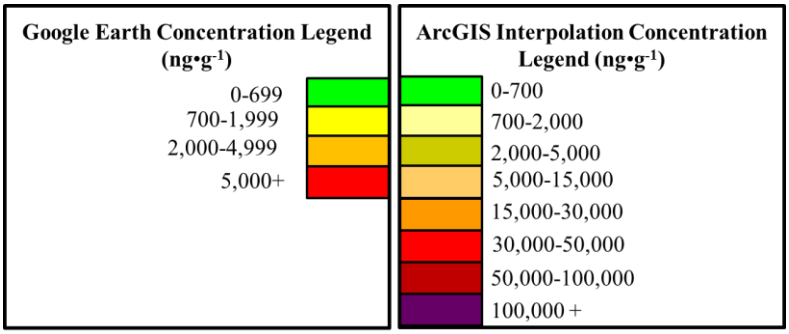


Figure 24. Google Earth vs ArcGIS DDT concentration legends.

ArcGIS software was used to interpolate data in order to refine the sections roughly identified in Figure 23, and find the area (m^2) associated with each level of contamination within those sections. The general process included mapping the entire data set, interpolating the entire area, and 'cutting out' or excluding sections of lower contamination to focus on the most contaminated areas.

The software's ability to calculate contamination levels decreases in areas with lower sample density such as the marsh and ponds, and the far north and south sections. As the marsh and ponds are beyond the scope of the remediation options analysis, and the far north and far south areas are below CCME guidelines, this does not pose a problem.

Figure 25 depicts approximately 850,000 m^2 and encompasses all samples above 700 $ng \bullet g^{-1}$. Figure 25-A shows the interpolative results based only on pre-existing samples, and Figure 25-B shows the results based on all samples. Through a visual inspection, areas associated with each concentration range in Figure 25-B are more clearly defined, and the calculated areas for most of the concentration ranges decreased when all samples are included. Specifically, there was a decrease of area in the concentration ranges of 700 – 5,000 $ng \bullet g^{-1}$ and 15,000 – 100,000 $ng \bullet g^{-1}$; additionally the area that is below the CCME guidelines of 700 DDT $ng \bullet g^{-1}$ increased. Consequently, the higher sample density in Figure 25-B resulted in the calculated areas at each concentration level being more

tightly characterized, illustrating the value of the additional samples collected and analyzed.

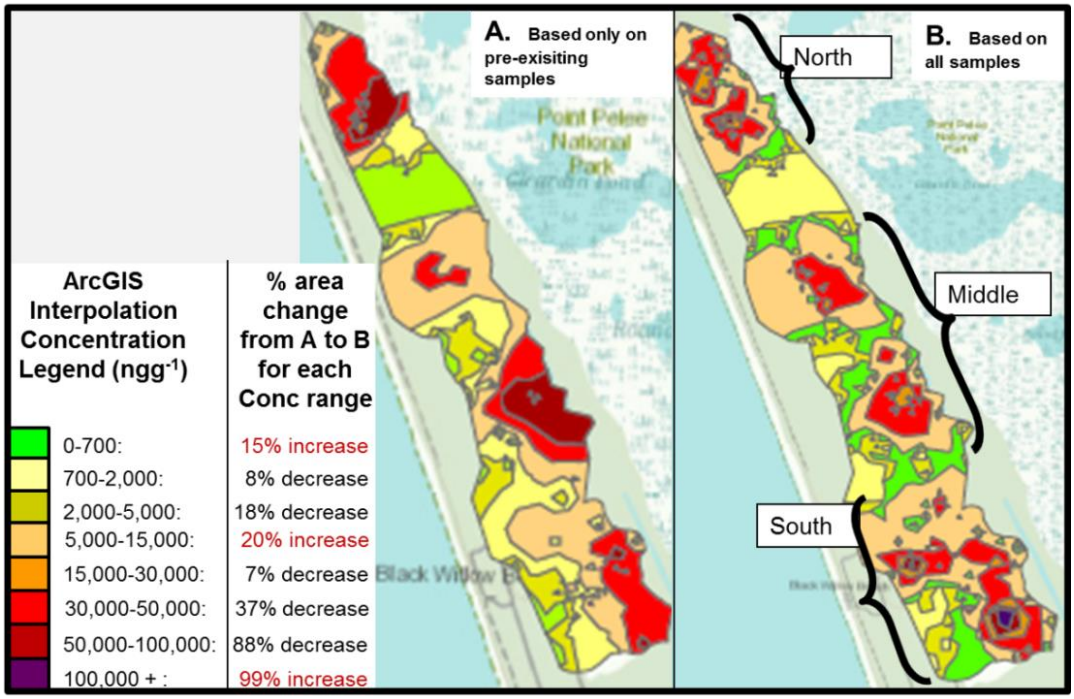
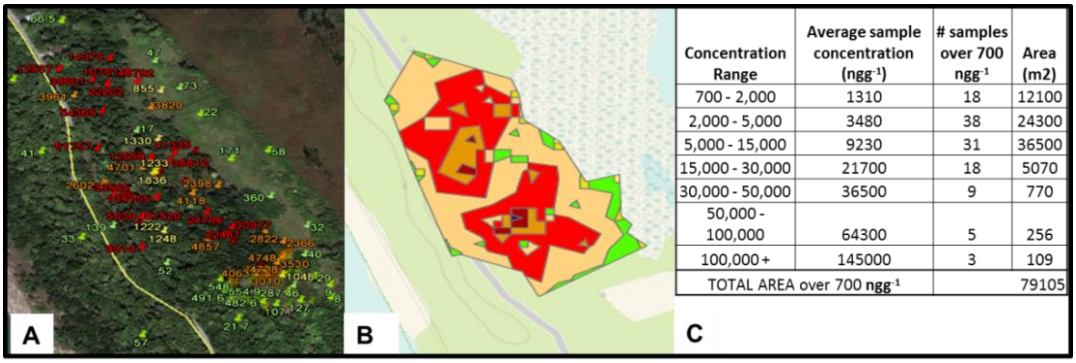


Figure 25. Overview of areas requiring further remediation. A) Interpolation results based on pre-existing samples only, B) Interpolation results based on all samples, and the general north, middle and south sections. An identical template was used to create the 'cut-out' so the overall area is the same.

4.3.i. North Section

The north section of DDT contamination at PPNP covers just over 79,000 m^2 and is heavily contaminated (Figure 26). The ArcGIS interpolation of this areas shows two hotspots (30,000 – 100,000 $ng \bullet g^{-1}$) approximately corresponding to the former apple orchard and Camp Henry, and connected by land contaminated above 700 $ng \bullet g^{-1}$. There is a well-established boundary line of samples between the hotspots' eastern edge and the marsh.

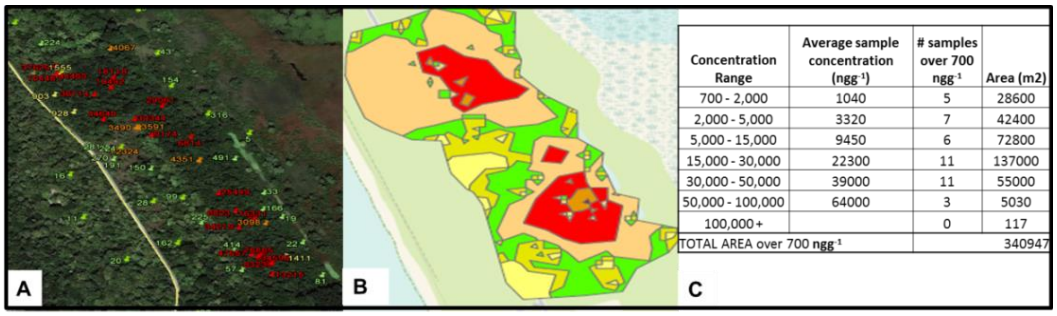


Concentration Range	Average sample concentration (ngg^{-1})	# samples over 700 ngg^{-1}	Area (m2)
700 - 2,000	1310	18	12100
2,000 - 5,000	3480	38	24300
5,000 - 15,000	9230	31	36500
15,000 - 30,000	21700	18	5070
30,000 - 50,000	36500	9	770
50,000 - 100,000	64300	5	256
100,000 +	145000	3	109
TOTAL AREA over 700 ngg^{-1}			79105

Figure 26. North section. A) All samples shown on Google Earth, and B) the corresponding interpolated ArcGIS. C) The mean, the number of samples, and area calculated for each concentration range.

4.3.ii. Middle Section

The middle section of DDT contamination in PPNP (Figure 27) contains two localized hotspots. This 340,000 m^2 area has well-defined boundaries along the eastern edge and lower western edge. The more southerly hotspot appears to correspond to Sleepy Hollow.

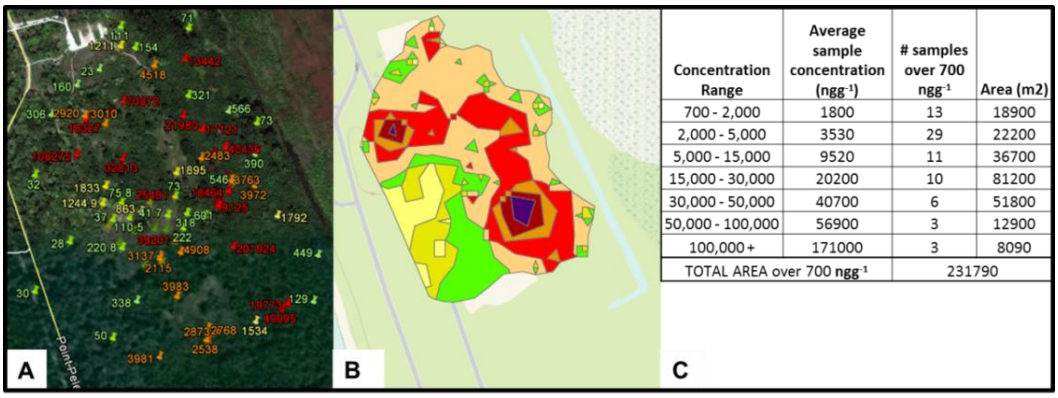


Concentration Range	Average sample concentration (ngg^{-1})	# samples over 700 ngg^{-1}	Area (m2)
700 - 2,000	1040	5	28600
2,000 - 5,000	3320	7	42400
5,000 - 15,000	9450	6	72800
15,000 - 30,000	22300	11	137000
30,000 - 50,000	39000	11	55000
50,000 - 100,000	64000	3	5030
100,000 +		0	117
TOTAL AREA over 700 ngg^{-1}			340947

Figure 27. Middle section. A) All samples shown on Google Earth, and B) the corresponding interpolated ArcGIS. C) The mean, the number of samples, and area calculated for each concentration range.

4.3.iii. South Section

The south section of DDT contamination in PPNP (Figure 28) with an area of 232,000 m^2, contains the highest concentrations of DDT contamination. Although not apparent in this diagram, there is a well-defined southern boundary around the larger hotspot in the bottom right which appears to centre on Anders Field. The hotspot in the top left is located on the maintenance compound at the Delaurier homestead. Crowe (1999) believed that high concentrations in the maintenance compound could be largely attributed to past spillage or disposal of DDT. While spillage may have been a contributing factor, the size of the area impacted suggests that DDT was actively applied to this area.



Concentration Range	Average sample concentration (ngg^{-1})	# samples over 700 ngg^{-1}	Area (m2)
700 - 2,000	1800	13	18900
2,000 - 5,000	3530	29	22200
5,000 - 15,000	9520	11	36700
15,000 - 30,000	20200	10	81200
30,000 - 50,000	40700	6	51800
50,000 - 100,000	56900	3	12900
100,000 +	171000	3	8090
TOTAL AREA over 700 ngg^{-1}		231790	

Figure 28. South section. A) All samples shown on a Google Earth, and B) the corresponding interpolated ArcGIS. C) The mean, the number of samples, and area calculated for each concentration range.

4.4. Volume Assumptions and Values

Total areas and volumes of DDT contaminated soil were calculated within each of the three sections at PPNP. As DDT contamination generally decreases with depth (Badley, 2003), and DDT at PPNP does not appear to extend beyond an 0.08 – 0.1 m depth (Crowe, 1999; Crowe *et al*., 2003; MSc thesis in progress by Surmita Paul at RMC), 0.1 m was used to calculate contaminated soil volumes for the north, middle and south section. Tables 4 – A and B show the area and volume respectively impacted above each concentration level. For example, ground contaminated by at least 15,000 $ng \bullet g^{-1}$ in the north section corresponds to 6,210 m^2 and 621 m^3 respectively.

Table 4. Table of soil areas and volumes impacted by DDT in each section.

TABLE A	Sum of Area (m^2) above each concentration level			Table B	Sum of Volume (m^3) above each concentration		
Conc range				Conc range			
(ngg^{-1})	North	Middle	South	(ngg^{-1})	North	Middle	South
above 0	105000	341000	235000	above 0	10500	34100	23500
above 700	79100	313000	216000	above 700	7910	31300	21600
above 2,000	66900	270000	194000	above 2,000	6690	27000	19400
above 5,000	42700	198000	157000	above 5,000	4270	19800	15700
above 15,000	6210	60200	75800	above 15,000	621	6020	7580
above 30,000	1140	5150	23900	above 30,000	114	515	2390
above 50,000	365	117	11000	above 50,000	36.5	11.7	1100
above 100,000	109		2900	above 100,000	10.9		290

Although areas and volumes from Table 4 were used to calculate costs in the remediation options analysis, remediation implementation planning should consider these to be minimum values. As interpolation does not create regular shapes, it will be difficult to accurately identify and remediate along exact concentration boundaries in the field. Remediation options are discussed in chapter 6.

CHAPTER 5 - Distribution of DDT, DDE and DDD, and DDT's Degradation Pathway Analysis

This section considers the relationships between individual DDT and its metabolites and their spatial distribution within Point Pelee National Park (PPNP), and how their relative prevalence was impacted by environment, and time. DDT's degradation pathways vary according to soil conditions and whether the environment supports aerobic or anaerobic degradation (Ricking & Schwarzbauer, 2012). The degradation pathway subsequently affects local DDT half-lives (Travares, *et al.*, 1999). DDT isomer analysis was also performed to provide an estimate of natural degradation and further information on isomer distribution.

5.1. ArcGIS and the Distribution of DDT, DDE and DDD

In addition to interpolating total DDT, ArcGIS was used to interpolate DDT, DDE and DDD individually (Figure 29). As the remediation options analysis focused on remediating total DDT, the areas calculated representing DDT, DDE and DDD individually were not used for this purpose. However, the interpolations did create a powerful visual representation of DDT's, DDE's and DDD's geographic prevalence in the Park. It is clear that DDE is the most prevalent, followed by DDT (not total DDT) and then DDD.

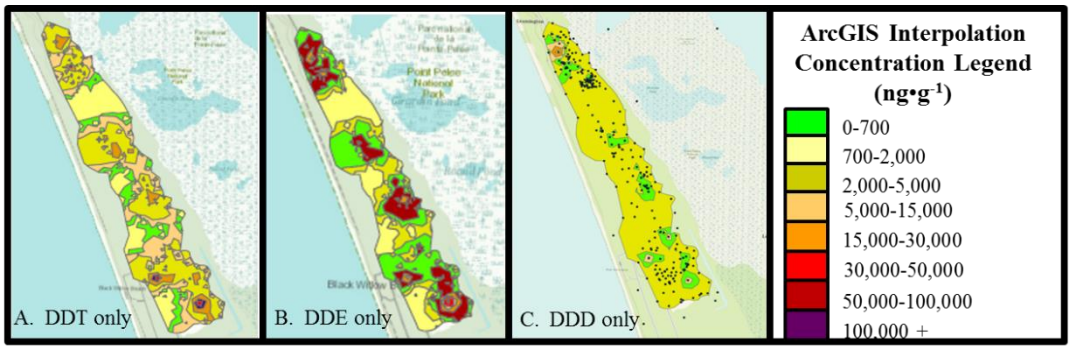


Figure 29. DDT, DDE and DDD interpolations. The identical area in all three panels is interpolated A) DDT, B) DDE, and C) DDD with the black dots indicating sample locations. The interpolation concentration legend is identical to that used in Chapter 4.

5.2. Project Soil Samples > 700 ng•g^{-1} vs Location

The three major hotspots sections (north, middle, and south) identified in Figure 23 contain all soil samples above the Canadian DDT guidelines (CCME, 1999). In order to assess any compositional differences between the three hotspot sections, a data set containing all project soil samples above 700 ng•g^{-1} was analyzed. Samples from previous studies were not included in case the composition had changed due to natural attenuation. By transforming each sample from concentration (ng•g^{-1}) to a percentage of total DDT (as per Appendix C), it was possible to compare total DDT's isomer composition across a broad data set (Wenrui, *et al.*, 2009). Histograms indicated that the

data sets were approximately normally distributed (Appendix C) and comparable to previous data sets representing samples from similar areas (Crowe & Smith, 2007).

In order to determine whether the percentage of DDT, DDE and DDD's isomers differed per section in a statistically significant manner, each isomer's data set was subjected to an ANOVA performed by excel software (Microsoft 2010). The set of tests indicated that there is a statistically similar composition in the north, middle and south sections of PPNP which implies that DDT in these sections are degrading in a similar manner (Ricking & Schwarzbauer, 2012) (Figure 30). Earlier hypotheses postulated that isomer composition of DDT and its subsequent degradation at PPNP is strongly affected by location (Crowe, 1999; Crowe *et al*., 2003; Crowe & Smith, 2007). This analysis indicates that this postulate does not apply within the north, middle and south sections.

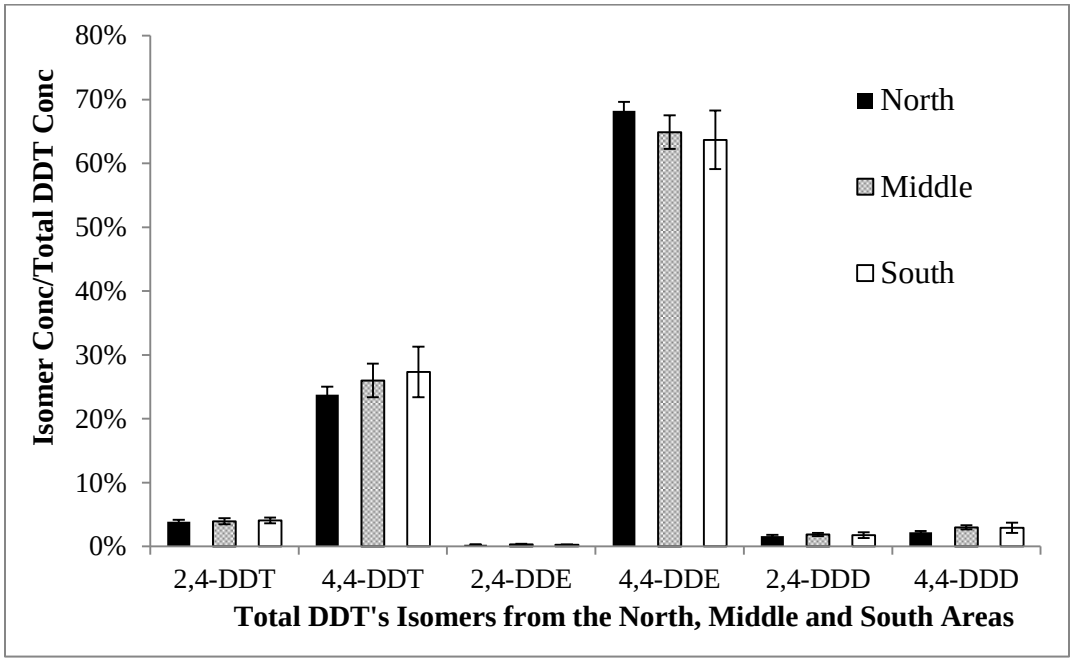


Figure 30. Comparison of the average percentage of each isomer in found in the north, middle and south sections from samples that have a total DDT concentration above 700 ng•g^{-1}. The error bars on the isomers in the north, middle and south sections indicate standard error which was calculated by dividing standard deviation by the square root of the sample size.

5.3. Soil Samples vs Sediment Samples

An ANOVA indicated that there are statistically significant differences between the percent of each DDT, DDE and DDD isomer in soil compared to sediment samples (Figure 31). This was expected as the DDD degradation pathway dominates in anaerobic environments (Ricking & Schwarzbauer, 2012), and is consistent with previous results (Crowe & Smith, 2007). When comparing current soil and sediment samples against original commercial DDT compositions, it is clear that degradation is taking place both in the soil and the sediment (Figure 31).

Soil samples were compared to the nine sediment samples to determine whether the composition differed between the land and marsh areas. Only current samples were considered so changes related to natural attenuation would not impact the analysis. Figure 31 compares the average percent concentration of commercial DDT, and DDT contaminated soil and sediment collected 2012-13.

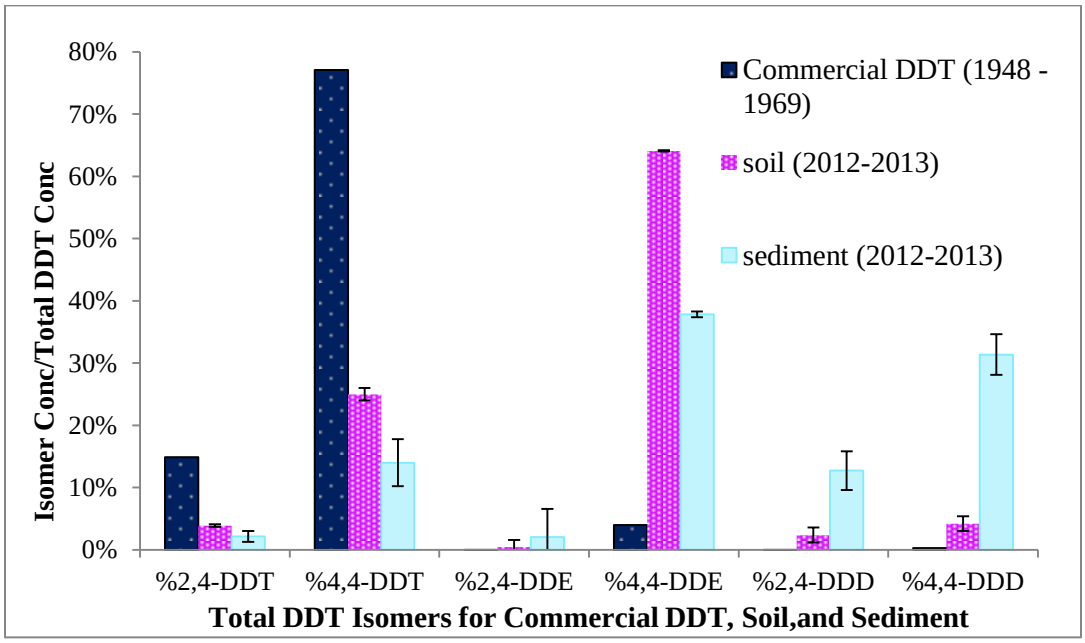


Figure 31. Graphical representation of the difference between the average isomer composition of soil and sediment samples. The soil and sediment data sets include samples collected for the current project.

5.4. Commercial DDT Versus Pre-existing and Current Soil Samples

A final application of ANOVA was conducted to compare the composition of commercial DDT, pre-existing soil samples, and project soil samples (Figure 32). Each comparison showed a statistically significant difference except for the percent of DDD between pre-existing and project soil samples.

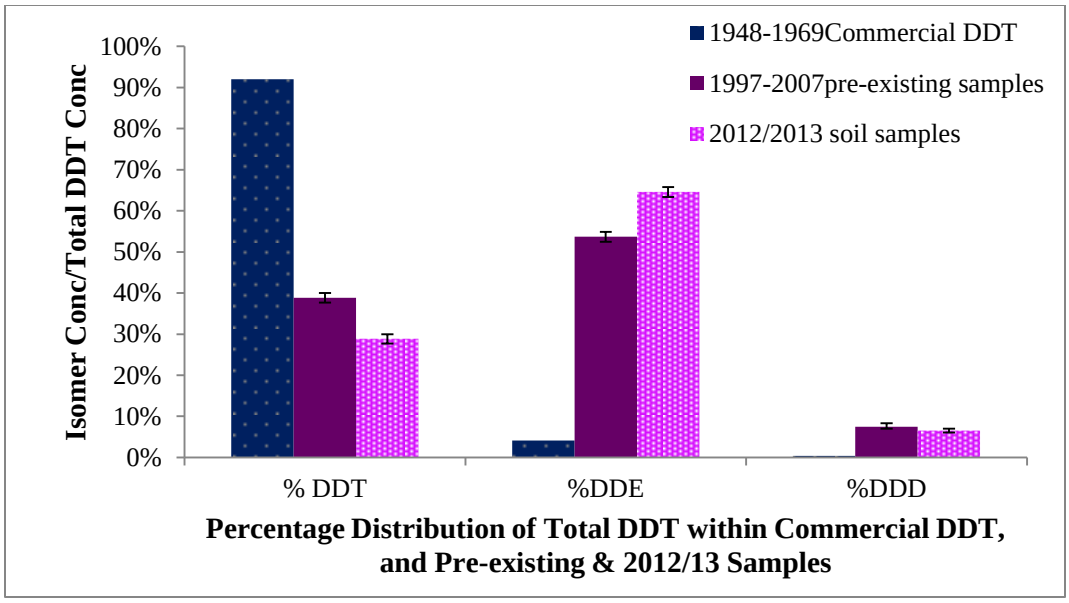


Figure 32. Total DDT composition average percentage comparison of commercial DDT, pre-existing samples and current soil samples.

Figure 32 also graphically illustrates the difference in DDT's composition between soil samples as it transitions from its original composition, to the composition captured in pre-existing samples (1997-2007), to the composition captured in project samples (2012-2013). As the average percentage of DDT decreases, the average percentage of DDE and DDD increases. Clearly, DDT degradation is taking place at PPNP.

5.5. DDT Degradation

Degradation of DDT and its derivatives can be expressed as a first order kinetic reaction, with the half-life equalling:

$$t_{\frac{1}{2}} = \frac{1}{t}\left[\ln\left(\frac{C_t}{C_0}\right)\right]\left[\ln\frac{1}{2}\right]$$

Where $t_{1/2}$ is the half-life of the initial concentration or C_0, and C_t is the concentration remaining after time t (Badley, 2003). To solve for the minimum and maximum half-lives, time (t) was based on the following assumptions:

A. All commercial DDT was assumed to be applied in 1948 or 1967; the earliest and latest dates of DDT application at PPNP.

B. All pre-existing samples were assumed to be collected in either 1999 or 2007, the earliest (Russell & Haffner, 1997) and most recent (Crowe & Smith, 2007) sample studies outside of this project.

C. All current samples were assumed to be collected in 2013 as 80% of the project samples were collected during the second field trip to PPNP in 2013.

Therefore, the minimum and maximum time (t) was 30 or 59 years for with pre-existing samples, and 46 or 65 years for current samples. The C_t/C_0 ratio is equivalent to the ratio between the percentage of an isomer in 2012-2013 or pre-existing samples and the percentage of the same isomer found within commercial DDT. The average composition by percent of DDT, DDE and DDD above 700 $ng \bullet g^{-1}$ was used as C_t because, as per section 5.2, 5.3, and 5.4, composition by percent is fairly consistent within a data set above the CCME guidelines. The composition of commercial DDT (C_0) was assumed to be equivalent to that described in section 2.2, and shown in Figure 31 and 31.

These calculations were verified by assuming the C_t/C_0 ratio was the ratio of the average percentage of current (2012-2013) samples compared to the average percentage of a pre-existing sample. Two cases existed based on the assumption that t was equal to the difference between 2013 and the most recent and earliest pre-existing studies; 6 and 14 years respectively.

Although it is possible to solve the C_t/C_0 ratio by imputing individual sample concentrations, this is not practical because it is not possible to select samples that were collected from the same location as the GPS used in 2013 has 3m uncertainty, and the coordinates of samples collected during earlier studies have an unknown associated uncertainty. Similarly, using average sample concentrations is impractical because the concentration range spans over 100,000 $ng \bullet g^{-1}$ and the spread of sample locations are not equivalent.

Table 5 presents the half-lives associated with four cases used to calculate the minimum and maximum amount of time that was available for degradation of DDT sorbed to soil and sediment.

Table 5. Half-Life Calculations. The minimum and maximum amount of degradation time for previous existing samples, current soil samples, and current sediment samples expressed in years.

Period of time used to calculate half-lives	Half-life calculated from previously existing soil samples			Half-life calculated from all 2012/2013 soil samples			Half-life calculated from 2012/2013 sediment samples		
	%DDT	%DDE	%DDD	%DDT	%DDE	%DDD	%DDT	%DDE	%DDD
1967-1999 (30 years)	24.1	-8.09	-7.09						
1948-2007 (59 years)	47.4	-15.9	-14						
1967-2013 (46 years)				27.5	-11.6	-11.4	18.3	-14	-6.78
1948-2013 (65 years)				38.9	-16.3	-16.1	25.9	-19.8	-9.58

Figure 33 shows the half-live of DDT graphed in an exponential decay for all cases presented in Table 5. The half-lives calculated for DDT based on previously existing samples (24 - 47 years) support the results of Crowe and Smith who postulated that the longest DDT half-lives at PPNP could be greater than 40 years (Crowe & Smith, 2007). The half-lives calculated using current samples gives a range of 27 - 39 years for soil, and 18 - 26 years for sediments. DDE and DDD both have negative half-lives for each category (Table 5) because DDT degrades into both DDE and DDD which creates a net increase during natural attenuation. As DDE and DDD are both independently harmful to the environment, DDT contamination must be addressed to slow their ongoing impact.

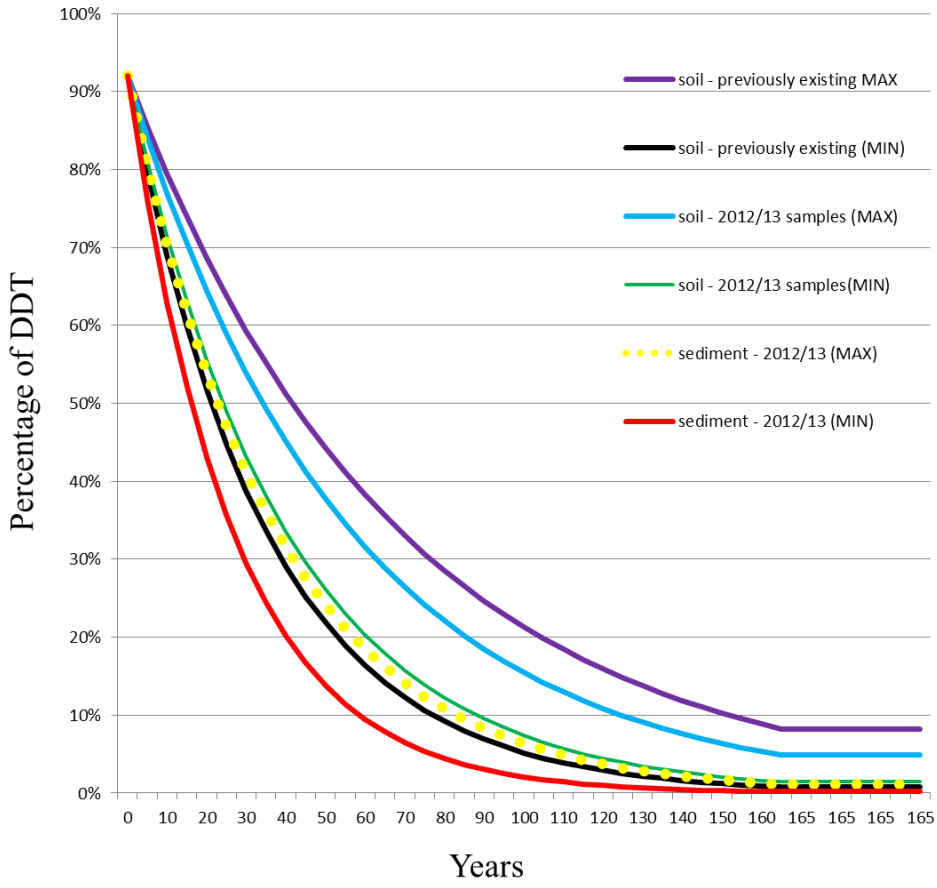


Figure 33. Exponential decay of possible half-lives of DDT.

CHAPTER 6 - Remediation Options Analysis

PPNP personnel are actively seeking appropriate technologies for remediating DDT soil contamination in the Park. In support of the PPNP's goals (Parks Canada, 2010), and specific a preliminary options analysis was conducted. This analysis used five evaluation criteria to quantify and compare five soil remediation options for PPNP. Natural attenuation and excavation/disposal were selected because they are typical options for DDT remediation, phytoextraction was selected because it is gaining traction as a valid technique, and stabilization with biochar and mobilization with a starch surfactant were selected because PPNP staff expressed specific interest as those technologies have been researched at the park.

Although the fenton process, high frequency ultrasound and electro-kinetic remediation are three techniques that are either used or being researched for DDT remediation, they are not viable options for PPNP and were rejected without further analysis. The fenton process was rejected because it requires H_2O and Fe^{2+} additives, there is contaminant mobility risk as contaminants are solubilized, the process has human health risks, and more research is required prior to practical application (Villa, *et al.*, 2008). High frequency ultrasound was not considered as it causes an insignificant amount of DDT degradation and further research is required (Thangavadivel, *et al.*, 2009). The electro-kinetic remediation was also not considered because it introduces external fluids and surfactants which may cause soil to become more acidic, DDT must be solubilized, and additional research is required (Karagunduz, *et al*., 2007).

6.1. Evaluation Criteria

Performance metrics allow the five remediation options to be assessed using a standardized set of criteria. For PPNP, five criteria were selected to reflect the park's specific concerns, goals and limitations. These five criteria are: i) environmental impact, ii) cost, iii) effectiveness, iv) feasibility, and v) time.

Criterion 1. Environmental impact of remediation is the most important factor for PPNP. As discussed in the Literature Review (Chapter 2), PPNP's three separate protective designations (Dobbie, *et al*., 2007) speak to the park's biological importance and international significance (Lynch-Stewart, 2008). One of the 2006 management plan objectives was to "provide the greatest possible protection to those features, processes, habitats or populations of species which are unique, sensitive, rare or endangered" (Dobbie, *et al.*, 2007). Given that PPNP staff believes DDT contamination contributed to the 50% decline in amphibian diversity over the past 50 years (Dobbie, *et al*., 2007), and they are working to reinvest in "restoration programs needed to reduce ecological stressors, such as…contaminants" (Parks Canada, 2010), Park staff want to minimize any negative impacts associated with remediation. Consequently, this criterion was assigned a 30% weighting.

Criterion 2. Aside from natural attenuation, most other remediation options can cost tens of thousands to millions of dollars, and PPNP's annual operating budget was less than three million dollars in 2006 (Dobbie, *et al*., 2007). As a governmental organization, PPNP must function within its allotted budget and adhere to federal contracting requirements. As it is unlikely the Park will be able to independently finance a significant remediation project, cost is just as much of a limiting factor as environmental impact. Consequently, the cost criterion was also given a weighting of 30%.

Criterion 3. Effectiveness refers to the amount of contamination that is likely to be removed from the site based on the reliability of the process or technology implemented. As a national park rather than a business oriented organization, PPNP staff works with, and sometimes approaches, research groups who experiment with cutting edge remediation techniques (Mironov, 2004; Badley, 2003; Paul, in progress). To meet conservation objectives in 2006, PPNP staff planned to "enable research…engage…the scientific community… and work with universities…to further collaborative research" (Dobbie, *et al.,* 2007). However, utilizing new techniques introduces additional challenges as they are less proven, and hence the risk of a successful outcome is increased. As remediation effectiveness is a very serious consideration, it was assigned a weighting of 20%.

Criterion 4. Feasibility is a measure of how easily an option can be implemented, and its impact on the site during implementation. Feasibility considerations include how implementation will impact visitors, site access, permits, federal regulations, effort required by the staff, technique availability, etc. As the Park staff is motivated and willing to actively work towards DDT soil remediation, most of these considerations can be managed, planned for, and mitigated. Consequently, feasibility was given a weighting of 15%.

Criterion 5. Of the five criteria being considered, time is the least important for PPNP personnel. Although a critical factor for many remediation projects, the Park's deadlines are largely self-imposed, and are related to other environmental projects such as implementing an alien plant management plan (Parks Canada, 2010). Park personnel are open to initiating a multi-year remediation project that could be undertaken in stages (Dobbie, pers comm). Long term implementation will have a manageable impact on the Park which is why time was assigned a weighting of only 5%.

6.2. Remediation Options Analysis Matrix

An options analysis matrix was created to allow direct comparison between each criterion for each remediation option presented (Table 6). Criteria were each assigned a percentage weighting (explained above) based on how important that criterion was to the Park's overall decision making process. Each remediation technique was then assessed against each criterion and assigned a score (0-4) which measures how well the remediation option was expected to perform based on each criterion. If a remediation technique was assigned a score of zero for a particular criterion, meaning there were significant risks and/or serious consequences, the remediation technique was not

considered for widespread implementation as it failed to meet the minimum critical requirements. Finally, the remediation options were quantitative ranked by adding the products of the weightings and scores for each remediation option:

$$overall\ remediation\ option\ score = \Sigma[(factor\ weighting)(assigned\ score)]$$

Table 6. Options Analysis Matrix. Criteria scoring: 0 = significant serious consequences or risks, 1 = negative consequences or risks, 2 = neutral, 3 = positive expected results, and 4 = very positive results and extremely low risk. Any remediation option assigned a score of zero for any criteria is not considered a valid option for large scale implementation at PPNP, and has been marked with an 'X' in the bottom row.

		Assigned Factor Scores					Calculated [(Weighting)(Score)]				
Factor	Factor Weighting	Natural Attenuation	Excavation & Disposal	Phyto-extraction	Biochar	Starch Surfactant	Natural Attenuation	Excavation & Disposal	Phyto-extraction	Biochar	Starch Surfactant
Environmental impact	30%	1	0	4	1	1	0.3	0	1.2	0.3	0.3
Cost	30%	4	0	3	2	0	1.2	0	0.9	0.6	0
Effectiveness	20%	0	4	3	3	2	0	0.8	0.6	0.6	0.4
Feasibility	15%	4	1	4	2	3	0.6	0.15	0.6	0.3	0.45
Time	5%	0	4	2	4	2	0	0.2	0.1	0.2	0.1
TOTAL=Σ[(score)(weighting)] for eliminated options							2.1	1.15			1.25
TOTAL=Σ[(score)(weighting)] for valid options							X	X	3.4	2	X

As metrics can skew how data is perceived, criteria weightings and assigned criteria scores should be reviewed by PPNP staff prior to moving forward with implementation. This analysis is also very situation specific; if PPNP's goals or limitations change, the park staff should re-evaluate all remediation options.

According to costs per volume identified in a study that considered 18 remediated sites in the United States of America and Canada, remediating all areas above 700 ng•g^{-1} at PPNP should range from \$21 - \$111 million, or \$31-\$163 m^{-3} (De Sousa, 2014). Generally these sites used a combination of techniques including capping, excavation and disposal, phyotextraction, and natural attenuation.

The natural attenuation, excavation and disposal and starch surfactant options were eliminated based on various criteria in the options analysis matrix (Table 6). However, strategic application of these options, particularly natural attenuation and excavation and disposal can become practical when applied in combination with other methods. The final recommendations as described below (section 6.4) were determined using both information presented in Table 6 and the practical application of combining these technologies.

6.3. Remediation Options Discussion

6.3.i. Natural Attenuation

Natural attenuation does not meet PPNP's minimum criteria. DDT at PPNP has been attenuating for 46-65 years and there are still many areas contaminated above 700 ng•g^{-1}.

The highest concentrations of DDT found could remain above 700 ng•g^{-1} for 220-342 years. In these areas, DDT is very stable, immobile, and persistent. Due to the significantly high concentration levels above CCME guidelines and concern regarding the ecological impact of DDT's bioavailability to resident fauna species (Smits, *et al*., 2005; Russell, *et al*., 1995), natural attenuation is not viable.

Although it should not be considered as a stand-alone solution, natural attenuation could be paired with other techniques: for example, by letting DDT contaminants continue to naturally attenuate in areas below a prescribed concentration that is still above CCME guidelines. This risk-based approach could be used to maximize available funding. For example, in the southern section (Figure 34), there is an area of light and dark yellow which indicates an area with concentrations up to 5,000 ng•g^{-1}. By not remediating that area, roughly 25% of the southern section can be disregarded, and resources can be focused on the areas of highest concentration. Remediating areas of very high concentration is the most efficient way to reduce overall concentration and risk associated with DDT bioavailability, as areas with lower concentration continue to slowly attenuate.

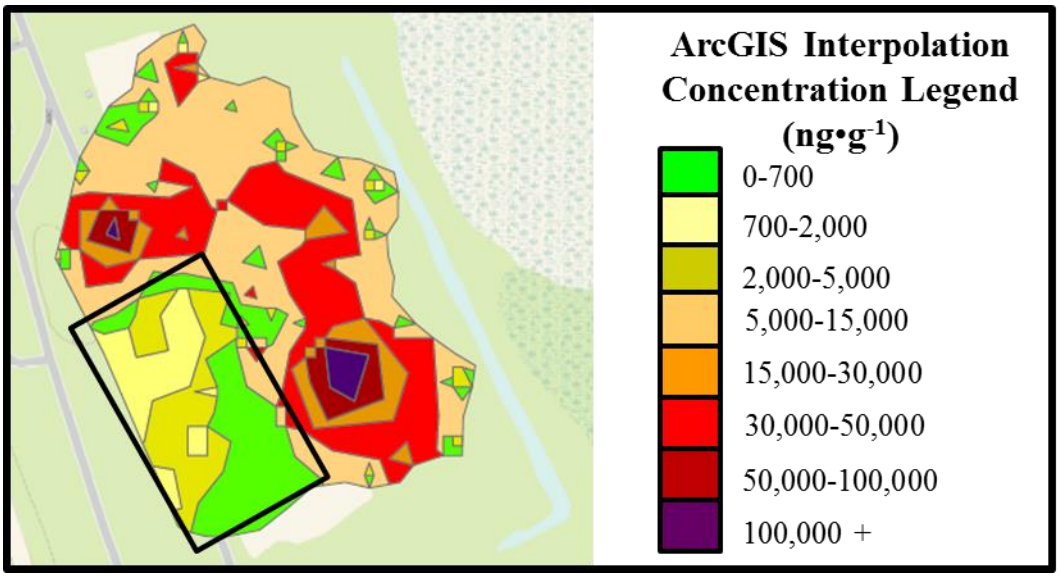


Figure 34. Example of where natural attenuation could realistically be implemented as shown by black outline.

While sediment remediation is not the focus of this remediation options analysis, it should be noted that the DDT degradation rate is significantly shorter in the marsh and pond areas. The half-life calculated for PPNP anaerobic environments was 18 - 26 years or approximately half of the half-life for the north, middle and southern sections. While the nine sediment samples collected had an average concentration of 37.1 ng•g^{-1}, which are significantly above the CCME guidelines for freshwater sediments, natural attenuation is a more acceptable option in this area due to the shorter half-life and lower DDT concentration.

6.3.ii. Excavation and Disposal

Excavation and disposal cannot be considered for blanket implementation at the Park due to environmental impact. This is traditionally the historically popular method for disposing of high levels of contaminated DDT soil because it is the most expedient method (Division of Environmental Remediation, 2007). However, excavation would consist of stripping 5-15 cm of topsoil from the affected areas which encompasses almost $1/16^{th}$ ($700{,}000 m^2$) of the Park's overall area. With this option, PPNP's staff was concerned about the large disruption to the Park's delicate environmental balance, impact on the birds that use PPNP as a migratory and breeding habitat, and various species at risk.

A North American company, Clean Harbor, runs a hazardous waste facility located in Sarnia, Ontario, approximately 150 km away from PPNP and they provided excavation estimates. Clean Harbor's estimate for hand excavation is approximately $500/cubic meter of soil removal (Fellner, per comm). Although using a hydrovac unit to remove the soil would reduce excavation costs to approximately $250/cubic meter, a hydrovac may have a greater impact on the environment. Unfortunately, Clean Harbor did not respond to follow up requests for information to give estimates for transportation or disposal.

Thomlinson Environmental Services has a hazardous waste facility near Hamilton, Ontario, approximately 300 km away from the Park. Thomlinson's Environmental Manager suggested hand excavation is unnecessary and a more efficient method, with a comparable level of environmental impact, would be to use a bobcat or small loader at approximately $150/hour including the operator. Assuming a bobcat could fill two to three 15 m^3 roll-off bins per day, using this method excavation would cost \$3-\$5/m^3 (Nagy, pers comm). Thomlinson's transportation cost estimate was \$88/m^3 or \$1,320/($15m^3$) bin. Finally, their disposal estimate ranged from \$150 - \$700/m^3 which would be based on soil density and the hazardous waste facility's determination of contaminant treatability (Nagy, pers comm). Based on all of this information, Table 7 lists the minimum and maximum costs associated with excavation, transportation and disposal. Note that this option does not include purchase, transportation or application of clean fill to replace the excavated soil.

Table 7. Excavation and Disposal Costs. \$241/ m^3 to \$1290/ m^3.

Excavation & Disposal	Sum of Volume (m^3) above each concentration level			Low Cost = [($3/m^3) excavation + ($88/m^3) transport + ($150/m^3) disposal]* Volume				High Cost = [($500/m^3) excavation + ($88/m^3) transport + ($700/m^3) disposal]* Volume			
Conc range							**Low cost**				**high cost**
(ngg^{-1})	North	Middle	South	North	Middle	South	**TOTAL**	North	Middle	South	**Total**
above 0	10500	34100	23500								
above 700	7910	31300	21600	$1,910,000	$7,540,000	$5,210,000	**$14,700,000**	$10,200,000	$40,300,000	$27,800,000	**$78,300,000**
above 2,000	6690	27000	19400	$1,610,000	$6,510,000	$4,680,000	**$12,800,000**	$8,620,000	$34,800,000	$25,000,000	**$68,400,000**
above 5,000	4270	19800	15700	$1,030,000	$4,770,000	$3,780,000	**$9,580,000**	$5,500,000	$25,500,000	$20,200,000	**$51,200,000**
above 15,000	621	6020	7580	$150,000	$1,450,000	$1,830,000	**$3,430,000**	$800,000	$7,750,000	$9,760,000	**$18,300,000**
above 30,000	114	515	2390	$27,500	$124,000	$576,000	**$728,000**	$147,000	$663,000	$3,080,000	**$3,890,000**
above 50,000	36.5	11.7	1100	$8,800	$2,820	$265,000	**$277,000**	$47,000	$15,100	$1,420,000	**$1,480,000**
above 100,000	10.9	0	290	$2,630	$0	$69,900	**$72,500**	$14,000	$0	$374,000	**$388,000**

Based on the assumptions in Table 7, it would cost $14.7-$78.3 million to excavate and dispose of all contaminated soil, or $728,000 - $3.89 million to remediate areas with concentrations above 30,000 ng•g^{-1}. Using this technique strategically, and targeting the areas with the highest concentrations (hotspots), would significantly decrease the Park's net contamination, and decrease ongoing risk. For example, there are two locations with a combined area of 3,010 m^2 or a volume of 301 m^3 that contain contamination >100,000 ng•g^{-1} (or 14,300% above CCME guidelines) and it would cost $72,000 - $388,000 to remediate those area through excavation and disposal.

6.3.iii. Phytoextraction

Phytoextraction is an emerging remediation technology. Costing this technology is site specific and a function of the estimated time required for remediation, site complexity, location, overhead charges, soil conditions, plant species, the number of seasons required, etc. According to Web-i, a University of Waterloo affiliated bioremediation company, an initial comprehensive site assessment can cost $5,000-$20,000 and it may include multiple site visits, extensive soil sampling, and greenhouse studies (Huang, pers comm). In their experience, the levels of contamination seen at PPNP could take up to 10 years to remediate. Using this information, the costing of phytoextraction is estimated to be $30 to $60/m^3 plus 10%-15% for overhead (Huang, pers comm).

Phytoextraction could pair with the research currently being conducted by RMC Master's Student, Surmita Paul who is investigating the abilities of native colonizers to extract DDT. She found that *S. scoparium* (little bluestem), *P. virgatum* (switchgrass) and *S. cryplandrus* (sand dropseed) could uptake 73,000 to 331,000 ng•m^{-2} per season from prepared, densely populated plots (Paul, in prep). If her research proves viable for large scale implementation, there would be limited environmental concerns as no alien species would be introduced into PPNP. The greatest barrier to this type of remediation is the multi-year fiscal commitment.

Table 8. Cost Estimate for Phytoextraction. $33-$69/m^3.

Phyto Conc range	Sum of Volume (m^3) above each concentration			Low Cost ($30/m^3) * Volume + 10% overhead			Low cost	High Cost ($60/m^3) * Volume + 15% overhead			high cost
(ngg^{-1})	North	Middle	South	North	Middle	South	**TOTAL**	North	Middle	South	**Total**
above 0	10500	34100	23500								
above 700	7910	31300	21600	$261,000	$1,030,000	$713,000	**$2,010,000**	$546,000	$2,160,000	$1,490,000	**$4,200,000**
above 2,000	6690	27000	19400	$221,000	$891,000	$640,000	**$1,750,000**	$462,000	$1,860,000	$1,340,000	**$3,660,000**
above 5,000	4270	19800	15700	$141,000	$653,000	$518,000	**$1,310,000**	$295,000	$1,370,000	$1,080,000	**$2,740,000**
above 15,000	621	6020	7580	$20,500	$199,000	$250,000	**$469,000**	$42,800	$415,000	$523,000	**$981,000**
above 30,000	114	515	2390	$3,760	$17,000	$78,900	**$99,600**	$7,870	$35,500	$165,000	**$208,000**
above 50,000	36.5	11.7	1100	$1,200	$386	$36,300	**$37,900**	$2,520	$807	$75,900	**$79,200**
above 100,000	10.9	0	290	$360	$0	$9,570	**$9,930**	$752	$0	$20,000	**$20,800**

Based on Web-i's estimates (Table 8), it could cost $2 - 4.2 million to remediate all contaminated areas, or $99,600 - $208,000 to remediate areas with concentrations above 30,000 ng•g^{-1}. Although there may be additional costs up to $20,000 for site assessment, this was not included as much of the onsite work has already been completed (Russell & Haffner, 1997; Crowe & Russell, 2007).

6.3.iv. Biochar Stabilization

Initial field and greenhouse studies, including those conducted at PPNP, indicate that biochar can be used to stabilize and decrease bioavailability of contaminants including DDT (Denyes, *et al*., 2012; Denyes, *et al.*, 2013). Denyes' research focused on soil that was well mixed with 2.8 - 11% weight of biochar, rolled end over end for greenhouse studies, and rototilled for field studies. Using these mixing protocols, bioavailibitily was almost immediately reduced, and soil did not need to be replaced or moved. To date, minimal work has been completed with respect to applying biochar to soil without mixing or disturbing the ground. However, based on previous research on the application of activated carbon to river sediments (Beckingham & Ghosh, 2011), Ms. Denyes postulates multiple applications over time may be required in order for the biochar to work into the soil via weathering processes (Denyes, pers comm).

Consequently, there are three scenarios for which there may be environmental impact. First, rototilling the entire area requiring remediation is only slightly less disruptive than excavation. Second, there are no long-term studies for biochar's fate as a result of being mixed into the soil. And third, application of biochar directly onto the soil surface could cause unanticipated issues such as creation of an immobile layer of biochar or various unknown ecological impacts.

Although biochar as a soil amendment to immobilize DDT is an extremely cost-effective remediation option at \$3-\$10/m^2 at PPNP, there could be significant labour related to application costs. As it is an unproven technology, there is no company that provides this service and the Park would have to make their own application arrangements. To rototill or mix the soil, Clean Harbor's labour rate of \$48/hour (Fellner, per comm) was used for the assumption that one cubic meter could be rototilled/hour which is equivalent to \$48/cubic meter. As the number of applications required still needs to be researched, the low and high costs were arbitrarily based on one and three applications respectively. Regardless of application style, costs related to the material range from \$3-\$10/m^2/application, or \$0.30 - \$1/m^3/application (Denyes, pers comm.).

Table 9. Cost Estimate for biochar, mixing with soil and surface application. \$48 - \$147m^{-3}.

Biochar + MIXING	Sum of Volume (m^3) above each			Mixing/low cost = [(\$0.3 biochar/m^3)+(\$48 for labour)]*				Mixing/ High Cost = [(\$1.00 biochar/m^3)+(\$48/m^3 for			
Conc range	concentration level			Volume			Low cost	labour)]*volume			high cost
(ngg^{-1})	North	Middle	South	North	Middle	South	TOTAL	North	Middle	South	Total
above 0	10500	34100	23500								
above 700	7910	31300	21600	\$382,000	\$1,510,000	\$1,040,000	**\$2,940,000**	\$388,000	\$1,530,000	\$1,060,000	**\$2,980,000**
above 2,000	6690	27000	19400	\$323,000	\$1,300,000	\$937,000	**\$2,560,000**	\$328,000	\$1,320,000	\$951,000	**\$2,600,000**
above 5,000	4270	19800	15700	\$206,000	\$956,000	\$758,000	**\$1,920,000**	\$209,000	\$970,000	\$769,000	**\$1,950,000**
above 15,000	621	6020	7580	\$30,000	\$291,000	\$366,000	**\$687,000**	\$30,400	\$295,000	\$371,000	**\$697,000**
above 30,000	114	515	2390	\$5,510	\$24,900	\$115,000	**\$146,000**	\$5,590	\$25,200	\$117,000	**\$148,000**
above 50,000	36.5	11.7	1100	\$1,760	\$565	\$53,100	**\$55,500**	\$1,790	\$573	\$53,900	**\$56,300**
above 100,000	10.9	0	290	\$526	\$0	\$14,000	**\$14,500**	\$534	\$0	\$14,200	**\$14,700**

Biochar + Surface Application	Sum of Volume (m^3) above each			1 surface application = [(\$0.30 biochar/m^3)+(\$48/application)]*(				3x surface application = [(\$1.00 biochar/m^3)+(\$48/application)]*			
Conc range	concentration level			1 applications)*volume			Low cost	(3 applications)*volume			high cost
(ngg^{-1})	North	Middle	South	North	Middle	South	TOTAL	North	Middle	South	Total
above 0	10500	34100	23500								
above 700	7910	31300	21600	\$382,000	\$1,510,000	\$1,040,000	**\$2,940,000**	\$1,160,000	\$4,600,000	\$3,180,000	**\$8,940,000**
above 2,000	6690	27000	19400	\$323,000	\$1,300,000	\$937,000	**\$2,560,000**	\$983,000	\$3,970,000	\$2,850,000	**\$7,800,000**
above 5,000	4270	19800	15700	\$206,000	\$956,000	\$758,000	**\$1,920,000**	\$628,000	\$2,910,000	\$2,310,000	**\$5,850,000**
above 15,000	621	6020	7580	\$30,000	\$291,000	\$366,000	**\$687,000**	\$91,300	\$885,000	\$1,110,000	**\$2,090,000**
above 30,000	114	515	2390	\$5,510	\$24,900	\$115,000	**\$146,000**	\$16,800	\$75,700	\$351,000	**\$444,000**
above 50,000	36.5	11.7	1100	\$1,760	\$565	\$53,100	**\$55,500**	\$5,370	\$1,720	\$162,000	**\$169,000**
above 100,000	10.9	0	290	\$526	\$0	\$14,000	**\$14,500**	\$1,600	\$0	\$42,600	**\$44,200**

Calculations based on the above assumptions (Table 9) indicate that, to remediate all areas above 700 ng•g^{-1}, it would cost approximately \$2.9 million for mixing, and \$2.9 - \$8.9 million for surface application. Only remediating areas above 30,000 ng•g^{-1} would cost approximately \$150,000 for mixing, and \$146,000 to \$444,000 for surface application.

6.3.v. Starch Surfactant

Another largely untested DDT remediation technique which shows promise is the application of starch surfactant (10% or 20% hydroxypropyl-β-cycloxdetrin solutions) to mobilize DDT used in conjunction with a soil flushing technique. During a field study, pore volumes (33.3 L) were applied weekly for 13-19 week to nine, 0.7 m^2 plot (Badley, 2003). Preliminary experiments from two McMaster MSc. students show 70-90% reduction of soil DDT, DDE and DDD, and a half-life of less than two months for displaced DDT (Mironov, 2004; Badley, 2003). Although hydroxypropyl-β-cyclodextrin is a naturally occurring substance, secondary effects from introducing large amounts of this surfactant are possible. This largely untested technology would require significant field testing to prove the benefits of the technique outweigh concerns, including those related to vertical DDT mobilization (Mironov, 2004).

This technique has unknown risks and therefore a potentially high environmental impact. No commercial company provides this particular soil washing function using starch surfactant. To implement this technique, PPNP personnel could obtain hydroxypropyl-β-cyclodextrin from Alfa Aesar (\$351/100g) or Sigma Aldrich (\$924/100g) and apply it weekly to the affected areas (Badley, 2003) which would cost \$9.51-\$144/m^3 of soil per application for just the active ingredient. Again using Clean Harbor's labor rates of

$48/man hour (Fellner, per comm), and assuming it takes one man-hour to apply water/starch mixture to nine 0.07 m^2 plots, it would cost \$76/m^3 per application.

Table 10. Cost estimate for application of starch surfactant. \$723 - \$10,994/m^3 per application, \$9,400 - \$208,000/m^3 for 13 – 19 applications.

Starch Surfactant Conc range	Sum of Volume (m^3) above each concentration level			Low cost = [(\$76/application)+(starch \$9.51/m^3)] *(13 applications)*area			Low cost	High cost = [(\$76/application)+(cost of starch \$114/m^3)]*(19 applications)*area			high cost
(ngg^{-1})	North	Middle	South	North	Middle	South	TOTAL	North	Middle	South	Total
above 0	10500	34100	23500								
above 700	7910	31300	21600	\$8,790,000	\$34,800,000	\$24,000,000	**\$67,600,000**	\$28,600,000	\$113,000,000	\$78,000,000	**\$220,000,000**
above 2,000	6690	27000	19400	\$7,440,000	\$30,000,000	\$21,600,000	**\$59,000,000**	\$24,200,000	\$97,600,000	\$70,100,000	**\$192,000,000**
above 5,000	4270	19800	15700	\$4,750,000	\$22,000,000	\$17,500,000	**\$44,200,000**	\$15,400,000	\$71,500,000	\$56,700,000	**\$144,000,000**
above 15,000	621	6020	7580	\$690,000	\$6,690,000	\$8,430,000	**\$15,800,000**	\$2,240,000	\$21,800,000	\$27,400,000	**\$51,400,000**
above 30,000	114	515	2390	\$127,000	\$573,000	\$2,660,000	**\$3,360,000**	\$412,000	\$1,860,000	\$8,640,000	**\$10,900,000**
above 50,000	36.5	11.7	1100	\$40,600	\$13,000	\$1,220,000	**\$1,280,000**	\$132,000	\$42,300	\$3,970,000	**\$4,150,000**
above 100,000	10.9	0	290	\$12,100	\$0	\$322,000	**\$335,000**	\$39,400	\$0	\$1,050,000	**\$1,090,000**

Based on the assumptions outlined in Table 10, it could cost \$67 to \$220 million to remediate all contaminated areas, or \$3.4 to \$10.9 million to remediate areas with concentrations above 30,000 $ng \bullet g^{-1}$. Unless a less expensive source of the starch surfactant (hydroxypropyl-β-cyclodextrin) can be found or a method that requires fewer applications, combining the cost and the risks associated with an untested technique, this option is not a valid option.

6.4. Remediation Recommendation

Although PPNP is dedicated to "actively managing ecological integrity issues to improve conservation" (Dobbie, et al., 2007), implementing a remediation option is a large fiscal commitment. When PPNP staff is ready to move forward with implementation, this preliminary remediation options analysis should act as a starting point for the decision making process. Constraints, particularly those related to available budget, target soil DDT concentration levels, and implementation timelines should be reviewed prior to selecting an option. Based on current criteria weightings and scores, three implementation options are presented as reasonable and viable.

6.4.i. Option 1

The first option is a three pronged approach: excavate and dispose of soil above 100,000 $ng \bullet g^{-1}$, phytoremediate areas with concentrations 5,000-100,000 $ng \bullet g^{-1}$, and let areas with concentrations below 5,000 $ng \bullet g^{-1}$ continue to naturally attenuate. This option would cost approximately $1.3 to $3.1 million. Although the areas being remediated using phytoextraction take a significant period of time to reduce in concentration, excavating the areas of extremely high concentration would immediately decrease DDT and offset the associated bioavailability risks.

6.4.ii. Option 2

a) This option comprises of phytoremediating all areas of PPPN that have concentrations above 700 $ng \bullet g^{-1}$. This would cost approximately $2 - $4.2 million and could be expected to take approximately 10 years (Huang, pers comm). This technique requires longer to implement, but it can be initiated without further field trials, and has a minimal environmental impact.

b) While remediating all areas with concentrations above 700 $ng \bullet g^{-1}$ is preferable, if it is too large a fiscal commitment, phytoextraction could be implemented on a smaller scale. For example, only implementing this technique on areas with concentrations above 5,000 $ng \bullet g^{-1}$ would cost $1.3 to $2.7 million, or above 30,000 $ng \bullet g^{-1}$ would cost approximately $99,600 - $208,000. It would be most effective to target areas of high concentration and leave the remaining areas to continue naturally attenuating.

6.4.iii. Option 3

The last option consists of further analysis by conducting multi-year testing on biochar stabilization and the efficacy of surface application. Although rough costs were provided in Table 9, additional testing is essential to refine application methods, expected results, and cost.

CHAPTER 7 - Conclusion

Dichlorodiphenyltrichlorethane (DDT) is an effective pesticide that was first used in World War II and quickly became an industry standard for pest control in agriculture and personal homes. It slowly degrades into dichlorodiphenyldichloroethylene (DDE) under aerobic conditions and into dichlorodiphenyldichloroethane (DDD) under anaerobic conditions. Total DDT, the combination of DDT, DDE and DDD, has been found to cause significant and prolonged harm to the environment. Point Pelee National Park (PPNP) holds multiple protective designations, is home to migratory birds, and is important to the effort of protecting significant endangered species. Due to the application of DDT on agricultural and recreational lands at PPNP from 1948 to 1967, some surface soil and sub-surface sediment is contaminated with DDT at levels three orders of magnitude above federal regulatory guidelines. This has environmental impacts on the fragile PPNP ecosystem because the contaminant remains bioavailable and is continuing to enter the food chain.

A number of DDT studies were conducted on wildlife (Russell, 1995; Russell, *et al*., 1997; Smits, 2005) and soil within the Park (Russell & Haffner, 1997; Crowe, 1999, Crowe, *et al*., 2003; Badley, 2003; Mironov, 2004; Crowe, *et al*., 2004; Crowe & Smith, 2007). The results from those studies presented concerning levels of DDT contamination which negatively affect this priority site for the species at risk recovery program. Although those previous studies illustrate DDT contamination is a continuing issue at the Park, the results were piecemeal and focused on specific areas of the Park and/or on specific organisms. This thesis focused on amalgamating relevant previous research, collecting more information as required, and producing tangible remediation recommendations.

In the initial phase of this project, a systematic and iterative sampling and sample analysis plan was conducted. During two site visits (June 2012 and April 2013), four water samples, nine sediment samples, and 115 soil samples were collected and analyzed from PPNP. A Google Earth platform was used to map, plan and track samples and their DDT concentrations geographically. The visual and intuitive representation allowed an efficient approach to sampling which included targeting specific geographic coordinates. Once the iterative sampling and analysis was complete, the Google Earth overlay included an amalgamated data set that could be represented geographically. The graphical presentation provides an intuitive and comprehensive method of viewing the information which allows the user to very clearly see gaps in sampling locations, areas with many high or low samples, and how samples change from high to low concentration.

Water samples analyzed for DDT showed the contaminant was below the equipment's detection limit. In sediment samples, DDT was found ranging from 1.5 to 167 $ng \bullet g^{-1}$ in the western ponds and marsh areas which is well above the CCME DDT sediment guidelines. The composition within the marsh was found to be statistically different from that in the soil areas, probably due to the anaerobic environment. The pond and marsh area compositional breakdown indicated that DDD is the dominant end product, and the half-life 18 - 26 years. Although sediment sample density was too low for interpolation, this project focused on soil contamination and thus sediment contamination was not

further investigated.

Visual inspection of all the mapped soil sample locations on a Google Earth overlay showed three major areas of concern. These hotspots contained samples with concentrations over 130,000 ng•g^{-1}, or 19,000% above the 700 ng•g^{-1} CCME DDT soil guidelines. Interpolating those major hotspots with ArcGIS enabled the calculation of soil areas and volumes requiring remediation totalling just less than 700,000 m^2. The interpolation created using input only consisting of pre-existing samples was compared to the interpolation created using all samples, the latter concentration range boundaries were much more clearly defined and the area associated with five of eight concentration ranges decreased. These more accurate boundaries increase the validity and usefulness of a remediation options analysis.

Isomer analysis showed there was no statistically significant difference between the compositions from samples collected in the three different hotspot areas. Composition of all current soil samples were also compared to previous soil samples and original commercial DDT composition. The only statistically significant similarity was the composition of pre-existing (Crowe & Smith, 2007) and current samples for DDD Isomer analysis further supported the new DDT half-life calculations of 27 - 38 years in soil and that it will take 220 to 342 years for PPNP's DDT in soil to naturally attenuate.

Using the additional soil results and defined DDT-contaminated areas, a remediation options analysis was conducted based on five performance metrics; environmental impact, cost, effectiveness, feasibility and time. Natural attenuation, excavation and disposal, phytoextraction, stabilization with biochar, and mobilization using a starch surfactant were considered, and three recommendations were proposed.

The first option is a combination approach involving i) excavating and disposal of the most contaminated soil, ii) phytoextraction to remediate the majority of contamination, and iii) allowing contamination close to the CCME guidelines to continue to naturally attenuate. This option is the most cost effective, immediately addresses the areas with extremely high levels of contamination, and follows up with a long term approach for the moderately contaminated areas. The second option exclusively applies phytoextraction to remediate all areas above the federal DDT guidelines. This approach requires a long commitment (potentially decades) but addresses all levels of contamination with minimal environmental impact. The third option consists of further testing to determine the suitability and viability of stabilization with biochar for park-wide application. Multi-year field tests should be conducted to develop surface application methods, confirm costing, and ensure there are no residual environmental concerns. The third option cannot be implemented immediately and requires additional research.

This thesis addressed a long standing issue of DDT contamination at PPNP. The consolidation of research, interactive map, and remediation recommendations will add practical value to PPNP and assist with the staff's goal of moving forward with remediation. The Google Earth overlay is a practical product that staff will be able to add to, and use to plan other conservation projects.

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Appendices

Appendix A. Raw Sample Data of samples collected for this thesis (2012-2013)

Table A-1. QAQC information for each run.

RUN	ΣDDT in spiked control in $ng \bullet g^{-1}$	% target for spiked control	ΣDDT in analytical blank in $ng \bullet g^{-1}$	% degradation	RSD	average extraction efficiency (%)
W	26.8	89.0%	< 1	10.3%	0%	77%
1	67.5	112%	< 1	4.1%	18.5%	110%
2	58.6	98.0%	< 1	4.1%	49.3%	89%
3	32.8	120.0%	< 1	4.6%	28.0%	96%
4	67.2	112%	< 1	4.7%	58.4%	96%
5	67.2	112%	< 1	3.6%	74.3%	90%
6	56.8	95.0%	< 1	11.1%	84.6%	94%
7 - McK	53.4	89.0%	< 1	7.4%	70.5%	92%
8	60.4	101%	< 1	not calculated	96.9%	99%
9	59.7	99.0%	< 1	not calculated	19.5%	105%
10	68.1	113%	< 1	not calculated	57.2%	112%
11	66.5	111%	< 1	10.4%	34.7%	97%
12	61.8	103%	< 1	5.3%	18.2%	103%
13	69.2	115%	< 1	14.8%	30.8%	108%
14	67.8	113%	4.5	5.0%	16.1%	96%
15	64.2	107%	< 1	not calculated	18.8%	98%
16	60.2	100%	< 1	not calculated	12.4%	97%
17	54.7	91.0%	< 1	6.2%	18.4%	103%

Table A-2. Water Samples. All results in ug•L^{-1}

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD
W	2012 ppnp w-001	374520	4648885	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
W	2013 ppnp w-002	375115	4647282.98	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
W	2014 ppnp w-003	375193	4646277	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
W	2015 ppnp w-004	373747	4646850	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

Table A-3. Sediment Samples. All results in ng•g^{-1}.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
4	2012 PPNP s-025	374036	4648171	< 1	3.31	< 1	3.9	< 1	2.7	11.1
4	2012 PPNP s-026	374520	4648885	< 1	< 1	< 1	0.8	< 1	< 1	1.5
5	2012 PPNP s-027	374344	4647907	2.2	13.7	< 1	33.0	4.2	12.8	66.2
5	2012 PPNP s-028	374872	4647732	< 1	5.3	1.4	13.0	2.9	7.0	30.1
5	2012 PPNP s-029	375115	4647283	< 1	< 1	< 1	8.3	5.3	11.5	26.0
5	2012 PPNP s-030	375193	4646278	< 1	< 1	2.5	18.9	12.7	31.5	66.6
5	2012 PPNP s-041	374581	4646855	< 1	1.2	< 1	8.9	4.2	9.0	24.3
5	2012 PPNP s-042	373747	4646850	< 1	1.6	< 1	20.8	16.9	44.2	84.1
5	2012 PPNP s-043	373178	4647323	< 1	4.1	< 1	9.5	4.1	9.2	27.1

Table A-4. Soil Samples. All results are in $ng \cdot g^{-1}$.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
1	2012 PPNP s-001	373445	4646577	6800	58800	454	64500	908	2680	134000
1	2012 PPNP s-002	373484	4646606	588	5280	47.2	13600	43.6	140	19700
1	2012 PPNP s-003	373549	4646645	< 1	8.4	< 1	146	1.7	13.6	171
1	2012 PPNP s-005	373508	4646727	< 1	4.9	< 1	15.3	< 1	1.1	21.9
1	2012 PPNP s-006	373422	4646788	2030	12900	156	33400	128	203	48800
1	2012 PPNP s-008	373538	4646508	1220	7480	90.0	13300	230	190	22500
1	2012 PPNP s-009	373640	4646388	10.7	42	< 1	68.8	< 1	3.6	127
2	2012 PPNP s-007	373420	4646699	< 1	4.7	< 1	10.9	< 1	< 1	17.4
2	2012 PPNP s-010	373726	4646370	< 1	1.0	< 1	1.5	< 1	< 1	2.91
2	2012 PPNP s-011	373789	4646271	< 1	4.9	< 1	6.2	< 1	< 1	12.4
2	2012 PPNP s-012	373836	4646187	< 1	3.1	< 1	5.0	< 1	< 1	9.4
2	2012 PPNP s-013	373867	4646081	1.9	12.1	< 1	27.7	< 1	< 1	43.3
2	2012 PPNP s-014	373890	4646002	< 1	66.6	< 1	78.2	1.2	7.4	154
2	2012 PPNP s-015	373951	4645933	18.8	105	1.4	172	3.5	15.8	316
2	2012 PPNP s-016	374020	4645885	< 1	1.3	< 1	3.2	< 1	< 1	5.5
3	2012 PPNP s-017	374228	4645485	< 1	3.2	< 1	4.0	< 1	< 1	8.26
3	2012 PPNP s-018	374257	4645372	< 1	< 1	< 1	2.2	< 1	< 1	3.0
3	2012 PPNP s-019	374276	4645249	5.25	22.9	< 1	32.7	3.3	6.9	71.3
3	2012 PPNP s-020	374209	4645179	110	821	5.4	3490	57.7	38.9	4520
3	2012 PPNP s-021	374173	4645213	15.1	45.4	< 1	82.2	4.53	6.9	155
3	2012 PPNP s-022	374146	4645253	12.6	48.1	< 1	37.4	3.9	9.3	112

Table A-4. Continued.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
3	2012 PPNP s-023	374101	4645328	3.5	17	< 1	10.8	1.3	3.7	36.3
3	2012 PPNP s-024	374083	4645390	1.7	9.2	< 1	12.5	< 1	< 1	24.8
4	2012 PPNP s-004	373599	4646660	< 1	2.8	< 1	50.9	1.6	3.1	58.8
6	2013 ppnp S-156	373495	4646584	58.2	573	3.3	3420	6.4	57.7	4120
6	2013 ppnp S-160	373514	4646501	119	1390	4.5	3050	51.9	241	4860
6	2013 ppnp S-163	373548	4646522	1540	8550	96.9	19800	327	664	31000
6	2013 ppnp S-168	373647	4646471	1.5	13.2	< 0	22.4	1.0	2.5	40.6
6	2013 ppnp S-169	373618	4646495	14.3	280	7.8	1930	43.2	95.7	2370
6	2013 ppnp S-184	373406	4646804	284	3300	9.8	6830	88.5	269	10800
6	2013 ppnp S-186	373360	4646791	1550	11100	50.2	25100	205	596	38600
6	2013 ppnp S-225	373693	4646052	1420	11900	40.6	23400	212	657	37600
7-McK	MD-1-6	373441	4646608	944	4330	70	13800	145	242	19500
7-McK	MD-2-6	373471	4646657	2040	8250	153	30300	274	317	41300
7-McK	MD-3-6	373427	4646631	210	737	39.2	3600	52.4	62.9	4700
7-McK	MD-4-6	373463	4646462	1690	9130	150	27100	290	451	38800
7-McK	MD-1-7	373420	4646533	1390	8500	79.6	19600	259	234	30100
7-McK	MD 2-7	373411	4646570	149	846	31	4030	44.9	46.9	5150
7-McK	MD-3-7	373434	4646538	46.6	200	4.3	952	5.9	14	1220
7-McK	MD-4-7	373398	4646583	568	3700	28.5	12800	73	122	17300
7-McK	MD_GH 2013-6	373452	4646631	1260	8050	57	13900	202	219	23700
8	2013 ppnp s-157	373530	4646597	51.4	675	2.5	1510	75.5	83.9	2400
8	2013 ppnp s-166	373651	4646523	< 1	2.4	< 1	24.3	3.5	2.5	32.7

Table A-4. Continued.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
8	2013 ppnp s-178	373373	4646734	2460	16300	205	31300	2730	1370	54400
8	2013 ppnp s-181	373454	4646770	2.7	27.1	1.8	750	42.9	30.5	855
8	2013 ppnp s-185	373385	4646829	729	3330	42.8	9610	256	403	14400
8	2013 ppnp s-193	373873	4645953	1000	7250	76.9	19400	349	986	29100
8	2013 ppnp s-219	373787	4646092	75.5	680	5.4	3420	76.7	78.3	4340
8	2013 ppnp s-222	373758	4645981	1290	6480	134	27400	671	740	36700
9	2013 PPNP s-111	374350	4645089	24.2	120	4.2	305	37.5	75.7	567
9	2013 ppnp s- 116	374400	4645006	11.6	79.8	1.2	230	19.1	48.7	390
9	2013 ppnp s-120	374441	4644888	132	616	9.9	727	91.1	217	1790
9	2013 ppnp s-123	374397	4644687	93.2	383	8.4	899	74.9	76.8	1530
9	2013 ppnp s-141	374058	4645010	4440	34700	295	63500	3890	1450	108000
9	2013 ppnp s-192	373854	4645882	996	1610	161	5620	356	431	9170
9	2013 ppnp s-206	374003	4645553	2.0	16.6	< 1	31.1	3.2	4.36	57.2
9	2013 ppnp s-215	373936	4645669	8.2	54.0	< 1	142	10.0	10.5	225
10	2013 ppnp s-217	374041	4645700	8.4	50.0	< 1	86	8.9	12.8	166
10	2013 ppnp s-189	373773	4645921	2040	14800	80.8	26500	478	758	44700
10	2013 ppnp s-195	373995	4645823	32.4	152	4.2	222	28.8	52.2	491
11	2013 ppnp s-100	374103	4645221	14.7	99.5	< 1	246	6.19	19.3	386
11	2013 ppnp s-102	374104	4645172	1.1	3.93	< 1	19	< 1	< 1	24
11	2013 ppnp s-103	374061	4645143	8.39	31.3	< 1	112	3.8	5.6	161
11	2013 ppnp s-104	374149	4645220	3910	21200	192	42100	1010	1660	70100
11	2013 ppnp s-105	374123	4645089	611	1970	45.5	16200	105	255	19200

Table A-4. Continued.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
11	2013 ppnp s-110	374263	4645081	907	5400	54.5	14900	172	547	22000
11	2013 ppnp s-209	374077	4645585	20.3	248	1.3	1070	18.9	54.7	1410
11	2013 ppnp s-213	373989	4645601	6.21	76.9	1.4	309	4.57	16.2	414
12	2013 PPNP s-143	374011	4645086	12.1	85.8	< 1	198	2.5	8.1	307
12	2013 PPNP s-119	374357	4644829	9380	108000	166	71900	617	2640	193000
12	2013 PPNP s-133	374170	4644727	12.6	56.9	< 1	262	2.73	4.15	338
12	2013 PPNP s-132	374212	4644622	38.9	430	2.5	3480	3.06	26.6	3980
12	2013 ppnp s-200	373966	4645740	1310	6280	86.2	16700	419	654	25400
13	2013 PPNP s-117	374398	4644945	93.1	722	9.8	2900	74.6	173	3970
13	2013 PPNP s-125	374508	4644724	5.2	36.2	1.2	59.1	6.24	21.1	129
13	2013 PPNP s-173	373631	4646414	2.82	17.9	5.2	22.6	1.5	3.6	53.4
13	2013 PPNP s- 191	373827	4645920	1630	7200	150	20000	487	878	30300
13	2013 PPNP s-203	374046	4645665	89.3	619	8.9	2180	59.9	141	3100
13	2013 PPNP s-214	373999	4645655	1320	12600	58.9	18300	431	1510	34200
13	2013 PPNP s-216	373995	4645695	403	3900	15.2	3710	105	690	8820
13	2013 PPNP s-220	373791	4646022	705	4300	46.3	12200	315	552	18100
13	2013 PPNP s-241	373778	4645851	5.5	36.9	1.3	226	4.53	6.65	281
14	2013 ppnp S-107	374146	4645001	1060	4700	139	25800	547	568	32800
14	2013 ppnp S-121	374518	4644812	31.3	176	1.2	164	16.4	61	450
14	2013 ppnp S-126	374567	4644664	2.9	21.3	< 1	43.4	3.86	11.7	83.3
14	2013 PPNP S-129	374328	4644529	5.9	41.3	< 1	235	13.5	16.5	313
14	2013 ppnp S-144	374268	4645189	523	3330	18.8	9010	169	392	13400

Table A-4. Continued.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
14	2013 ppnp S-151	373449	4646682	49.7	414	2.5	781	30.4	53.8	1330
14	2013 ppnp S-153	373499	4646660	685	2860	45.3	10400	168	353	14500
14	2013 ppnp S-158	373514	4646549	1020	4800	139	17700	417	711	24800
14	2013 ppnp s-159	373455	4646516	36.6	308	1.52	854	18.3	29.9	1250
15	2013 ppnp S-162	373549	4646495	190	1080	7.8	3500	89.5	133	5000
15	2013 ppnp S-164	373594	4646514	25.6	341	4.2	2240	110	102	2820
15	2013 ppnp S-165	373602	4646577	1.5	11.8	< 1	322	9.1	16.8	361
15	2013 ppnp S-180	373440	4646740	129	735	6.0	2760	86	104	3820
15	2013 ppnp S-182	373480	4646775	< 0	3.6	< 1	64.9	2.2	2.6	73.2
15	2013 ppnp S-183	373447	4646822	< 0	3.1	< 1	39.3	2.6	2.11	47
15	2013 ppnp S-187	373335	4646763	219	1220	12.3	2230	125	154	3960
15	2013 ppnp S-188	373315	4646811	999	2640	80.4	8480	367	372	12900
16	2013 ppnp S-194	373921	4645877	471	1040	53.4	4970	123	157	6810
16	2013 ppnp s-199	373852	4645801	2.6	21.5	< 1	110	6.3	9.7	150
16	2013 ppnp S-201	374043	4645740	< 1	4.14	< 1	23.2	2.3	337	33.1
16	2013 ppnp S-202	374073	4645681	< 1	2.4	< 1	12.0	1.7	3.76	19.8
16	2013 ppnp S-227	373366	4646667	4350	17400	237	38200	712	858	61800
16	2013 ppnp S-228	373371	4646596	28.3	724	1.4	1700	61.7	86.3	2600
16	2013 ppnp S-230	373424	4646487	508	1830	42.6	5070	227	333	8010
16	2013 ppnp S-232	373385	4646526	1.6	17.2	< 1	106	6.84	8.03	139
17	2013 ppnp S-207	374054	4645542	626	3440	34.4	8680	182	253	13200
17	2013 ppnp S-208	374139	4645539	3.9	21.3	1.2	36.9	3.8	14.5	81.6

Table A-4. Continued.

Run	Sample name	EASTING	NORTHING	2,4-DDT	4,4-DDT	2,4-DDE	2,4-DDE	2,4-DDD	4,4-DDD	Total DDT
17	2013 ppnp S-210	374107	4645619	< 1	5.7	< 1	15.5	< 1	1.6	22.8
17	2013 ppnp S-218	373670	4646106	7.1	46	< 1	153	6.6	11.4	225
17	2013 ppnp S-231	373458	4646458	1.1	11.8	< 1	37.2	1.3	1.4	52.8
17	2013 ppnp S-237	373656	4646036	5.2	589	< 1	303	12.8	18.2	928
17	2013 ppnp s-239	373691	4645982	29.1	266	1.7	528	44.6	34.9	904
17	2013 ppnp S-240	373723	4645940	21.7	97.3	1.6	758	32.1	18.1	929

Table A-5. Samples above 700 $ng \cdot g^{-1}$ from each section.

North		Middle	South
2012 PPNP s-001	2013 ppnp S-184	2013 ppnp s-189	2013 ppnp s-104
2012 PPNP s-002	2013 ppnp s-185	2013 PPNP s- 191	2013 S-105
2012 PPNP s-006	2013 ppnp S-186	2013 ppnp s-192	2013 ppnp S-107
2012 PPNP s-008	2013 ppnp S-187	2013 ppnp s-193	2013 S-110
2013 ppnp S-151	2013 ppnp S-188	2013 ppnp S-194	2013 PPNP s-117
2013 ppnp S-153	2013 ppnp S-227	2013 ppnp s-200	2013 PPNP s-119
2013 ppnp S-156	2013 ppnp S-228	2013 PPNP s-203	2013 ppnp s-120
2013 ppnp s-157	2013 ppnp S-230	2013 ppnp S-207	2013 ppnp s-123
2013 ppnp S-158	MD_GH 2013-6	2013 pppn S-209	2013 PPNP s-132
2013 ppnp s-159	MD 2-7	2013 PPNP s-214	2013 ppnp s-141
2013 ppnp S-160	MD-3-6	2013 PPNP s-216	2013 ppnp S-144
2013 ppnp S-162	MD-3-7	2013 ppnp s-219	
2013 ppnp S-163	MD-4-7	2013 PPNP s-220	
2013 ppnp S-164	MD-1-6	2013 ppnp s-222	
2013 ppnp S-169	MD-4-6	2013 ppnp S-225	
2013 ppnp s-178	MD-2-6	2013 ppnp S-237	
2013 ppnp S-180	MD-1-7	2013 ppnp s-239	
2013 ppnp s-181		2013 ppnp S-240	

Appendix B. Samples from other research

Table B-1. Paul's samples collected 2011-2012

Concurrent research conducted by Surmita Paul. Samples marked with an '*' are the samples used to capture GPS coordinates for each group. Not used for isomer analysis. All results in $ng \bullet g^{-1}$. Groups are identified following the table.

Sample Name	EASTING	NORTHING	DDT	DDE	DDD	TOTAL DDT	Group
T29804*	374180	4644900	109	314	6.65	429	1
T29806	374180	4644900	645	1310	28.2	1980	1
T29823	374180	4644900	76.7	190	8.8	276	1
T29832	374180	4644900	152	358	14.9	525	1
T29811	374180	4644900	460	714	28.1	1200	1
T29850*	374215	4644814	1500	5590	113	7200	2
T29852	374215	4644814	901	3760	54.6	4720	2
T29854	374215	4644814	1890	5370	103	7360	2
T29858	374215	4644814	629	2680	45.2	3360	2
T29861	374215	4644814	829	2650	75.7	3560	2
S29289	374215	4644814	1100	3390	160	4650	2
S29288	374215	4644814	896	4460	132	5480	2
S29287	374215	4644814	979	5340	268	6580	2
S29286	374215	4644814	807	2880	89.3	3770	2
S29282	374215	4644814	840	2930	149	3920	2
S29283	374215	4644814	1520	3930	206	5660	2
S29284	374215	4644814	529	1890	161	2580	2
S29285	374215	4644814	633	2840	140	3610	2
T29900*	373789	4645825	40	133	1.91	175	3
T29902	373789	4645825	59.8	170	5.46	235	3
T29904	373789	4645825	52.3	184	9.63	245	3
S29280	373789	4645825	68.5	313	15.7	397	3
S29278	373789	4645825	76.4	295	21.2	392	3
S29277	373789	4645825	54.6	227	11.8	294	3
S29279	373789	4645825	58	273	16.7	348	3
S29275	373789	4645825	35.4	173	13.3	221	3
S29276	373789	4645825	34.5	206	7.66	248	3
S29273	373789	4645825	29.9	190	7.63	227	3
S29274	373789	4645825	38.7	193	6.04	238	3
S29270	373789	4645825	52.3	168	6.3	226	3

Table B-1. Continued.

Sample Name	EASTING	NORTHING	DDT	DDE	DDD	TOTAL DDT	note
T29920*	373599	4646427	160	822	15.7	998	4
T29921	373599	4646427	648	2090	42.7	2780	4
T29924	373599	4646427	502	2330	37	2870	4
T29942	373599	4646427	87.7	314	10.4	412	4
T29945	373599	4646427	426	1120	31.2	1580	4
T29290*	373595	4646434	2210	6050	102	8360	4
T29291	373595	4646434	1030	3190	74.6	4300	4
T29292	373595	4646434	1280	3010	87.2	4380	4
T29293	373595	4646434	1100	2600	89	3780	4
T29982*	373425	4646543	5960	7780	223	14000	5
T29983	373425	4646543	9190	10600	373	20200	5
T29984	373425	4646543	26600	25600	869	53000	5
T29985	373425	4646543	6630	6350	208	13200	5
T29240	373425	4646543	9420	9830	379	19600	5
T29245	373425	4646543	18600	11400	693	30800	5
T29246	373425	4646543	13100	13500	729	27300	5
T29247	373425	4646543	7790	4310	381	12500	5
T29248	373425	4646543	45100	16800	2840	64800	5
T29249	373425	4646543	7080	25400	2760	35300	5
T29250	373425	4646543	12100	11000	737	23900	5
T29257	373425	4646543	77200	26300	4690	108000	5
S29263	373425	4646543	3410	3740	256	7410	5
S29264	373425	4646543	13100	6540	832	20500	5
S29261	373425	4646543	2190	1990	162	4340	5
S29262	373425	4646543	3930	3740	251	7920	5
S29268	373425	4646543	5250	6750	382	12400	5
S29269	373425	4646543	3150	3820	236	7210	5
S29266	373425	4646543	2250	3270	222	5740	5
S29267	373425	4646543	3950	5050	255	9250	5
T29950*	373448	4646621	3790	6170	144	10100	6
T29952	373448	4646621	5010	9990	215	15200	6
T29953	373448	4646621	10700	16200	414	27300	6
T29955	373448	4646621	8420	13600	327	22400	6
T29956	373448	4646621	14200	13800	565	28500	6
T29959	373448	4646621	2330	5850	173	8350	6

Table B-1. Continued.

Sample Name	EASTING	NORTHING	DDT	DDE	DDD	TOTAL DDT	note
T29970	373448	4646621	291	636	21.7	949	6
S29260*	374215	4644814	154	412	35.8	602	7
S29271	374215	4644814	692	2470	131	3300	7
S300109	374215	4644814	607	2680	87.1	3370	7
S300110	374215	4644814	772	2960	134	3870	7
S300112	374215	4644814	652	2630	101	3380	7
S300113	374215	4644814	490	2210	84.2	2780	7
S300114	374215	4644814	1440	3020	187	4650	7
S300106*	373789	4645825	36.3	157	8.73	202	8
S300107	373789	4645825	41	192	10.9	244	8
S300108	373789	4645825	15.9	106	5.8	128	8
S29242*	373425	4646543	2510	3880	140	6530	9
S300100	373425	4646543	1610	1810	126	3550	9
S300101	373425	4646543	2640	3090	159	5900	9
S300102	373425	4646543	2560	3340	194	6090	9
S300103	373425	4646543	2230	2240	162	4630	9
S300104	373425	4646543	1610	1500	132	3240	9
S300105	373425	4646543	2480	2630	178	5280	9

Groups:

1. Delaurier Maintenance Compound/RMC Site 1. Sampled in 2011.
2. Anders Field/RMC Site 2. Sampled in 2011.
3. Sleepy Hollow/RMC Site 3. Sampled in 2011.
4. Old Camp Henry/RMC Site 4. Sampled in 2011.
5. Former Agricultural Land 1/RMC Site 7. Sampled in 2011.
6. Former Agricultural Land 2/RMC Site 6. Sampled in 2011
7. Anders Field/RMC Site 2. Sampled in 2012
8. Sleepy Hollow/RMC Site 3. Sampled in 2012
9. Former Agricultural Land 1/RMC Site 7. Sampled in 2012.

Table B-2. Pre-existing samples. All results in $ng \bullet g^{-1}$.

Sample Name	Author	EASTING	NORTHING	DDT	DDE	DDD	Total DDT
CH-BH-1	EC-NWRI	373596	4646435	1790	1370	127	3290
CH-BH-2	EC-NWRI	373596	4646437	1520	1330	161	3010
CH-BH-3	EC-NWRI	373595	4646440	107	481	5.75	594
CH-BH-5	EC-NWRI	373597	4646433	155	402	11.1	567
CH-BH-6	EC-NWRI	373598	4646430	218	576	9.45	803
CH-BH-7	EC-NWRI	373599	4646427	7000	3180	310	10500
CH-BH-8	EC-NWRI	373598	4646436	4690	2040	700	7430
CH-BH-9	EC-NWRI	373601	4646437	1120	1010	72	2200
CH-BH-10	EC-NWRI	373605	4646438	1180	1110	67	2360
CH-BH-11	EC-NWRI	373594	4646434	2010	1210	184	3400
CH-BH-12	EC-NWRI	373592	4646433	1920	1100	204	3230
CH-BH-13	EC-NWRI	373587	4646431	1640	668	410	2720
C-1-5-0 cm	EC-NWRI	373589	4646387	218	255	10.2	483
C-1-9-0 cm	EC-NWRI	373627	4646403	1220	371	144	1730
C-3-1-0 cm	EC-NWRI	373544	4646390	249	224	18.2	492
C-5-1-0 cm	EC-NWRI	373537	4646408	186	354	14.8	555
C-5-5-0 cm	EC-NWRI	373574	4646424	111	235	12	358
C-5-7-0 cm	EC-NWRI	373593	4646431	1160	1290	89.4	2540
C-5-9-0 cm	EC-NWRI	373611	4646440	4160	133	493	4780
CH-22	EC-NWRI	373540	4646408	66	182	11.4	259
CH-23	EC-NWRI	373584	4646404	1270	810	107	2190
CH-24	EC-NWRI	373592	4646377	398	623	24.4	1050
CH-32	EC-NWRI	373624	4646439	259	122	39	420
CH-33	EC-NWRI	373616	4646434	410	378	260	1050
CH-34	EC-NWRI	373612	4646419	332	197	80	609
CH-36	EC-NWRI	373626	4646397	44.7	22.4	9.7	76.8
CH-SS-1-7	EC-NWRI	373581	4646395	80.9	165	6.1	252
CH-SS-2-3	EC-NWRI	373567	4646388	85	82	8	175
CH-SS-3-3	EC-NWRI	373563	4646397	111	217	10.1	338
CH-SS-4-2	EC-NWRI	373550	4646403	69.7	160	6.1	235

Table B-2. Continued

Sample Name	Author	EASTING	NORTHING	DDT	DDE	DDD	Total DDT
CH-SS-4-7	EC-NWRI	373597	4646423	151	374	17.5	543
RR-10	U. Windsor	373595	4646434	502	7090	486	8080
OC-BH-1	O'Connor	374268	4644895	129	176	13	318
OC-BH-3	O'Connor	374261	4644867	69	95	58	222
OC-BH-4	O'Connor	374244	4644841	1240	671	2	1910
OC-BH-5	O'Connor	374246	4644928	25	46	2	73
OC-BH-11	O'Connor	374136	4644839	79	60	2	141
WS-1-0 cm	EC-NWRI	374231	4644892	17.2	21	3.5	41.7
WS-7-0 cm	EC-NWRI	374215	4644809	646	1400	68	2120
WS-10-0 cm	EC-NWRI	374143	4644917	33.6	38	4.2	75.8
WS-11-0 cm	EC-NWRI	374107	4644916	303	921	20.9	1240
WS-12-0 cm	EC-NWRI	374227	4644864	43.5	67	13	124
WS-13-0 cm	EC-NWRI	374187	4644844	583	1300	65	1950
WS-14-0 cm	EC-NWRI	374185	4644797	38.3	29	5	72.3
WS-15-0 cm	EC-NWRI	374143	4644831	96	121	3.8	221
WS-16-0 cm	EC-NWRI	374166	4644862	23.7	19	6.3	49
WS-17-0 cm	EC-NWRI	374158	4644888	61	35	14.5	111
WS-18-0 cm	EC-NWRI	374126	4644885	18.8	15	3.2	37
WS-19-0 cm	EC-NWRI	374117	4644873	877	971	69	1920
WS-20-0 cm	EC-NWRI	374197	4644917	204	931	143	1280
WS-21-0 cm	EC-NWRI	374180	4644900	2000	11300	643	13900
WS-22-0 cm	EC-NWRI	374219	4644802	365	1370	60.2	1800
WS-23-0 cm	EC-NWRI	374206	4644866	116	540	30	686
RR-2	U. Windsor	375080	4648777	1.26	6.9	22.8	31
RR-5	U. Windsor	372890	4647963	0.5	17.6	19.2	37.3
RR-8	U. Windsor	374220	4647175	0.5	13	33.7	47.2
RR-12	U. Windsor	373965	4646270	4.51	36	21.8	62.3
RR-15	U. Windsor	374970	4645740	1.42	16.8	29.9	48.2
RR-23	U. Windsor	374830	4644265	4.19	13.5	1.27	18.9
RR-20	U. Windsor	374584	4644732	16.7	11.6	8.07	36.4
CH-28	EC-NWRI	373682	4646393	1.9	3.55	2.2	7.65
CH-29	EC-NWRI	373681	4646416	0.5	6.35	2.1	8.95
CH-30	EC-NWRI	373659	4646431	10.5	12.1	6.65	29.2
CH-31	EC-NWRI	373637	4646442	17	16.2	12.4	45.6
MS-14	EC-NWRI	373609	4646457	428	1850	1250	3530

Table B-2. Continued

Sample Name	Author	EASTING	NORTHING	DDT	DDE	DDD	Total DDT
MS-15	EC-NWRI	373617	4646468	885	1500	2360	4750
MS-16	EC-NWRI	373617	4646470	1290	1170	1760	4210
MS-17	EC-NWRI	373617	4646466	82	862	413	1360
MS-18	EC-NWRI	373619	4646472	160	884	576	1620
MS-19	EC-NWRI	373615	4646472	340	2040	940	3320
MS-20	EC-NWRI	373627	4646481	81.2	2850	400	3330
PP-DDT-S-01	EC-NWRI	373625	4646468	69	999	276	1340
RR-19	U. Windsor	374404	4645066	7.9	48.2	17	73.1
RR-25	U. Windsor	375007	4643719	1.52	5.92	0.691	8.13
PP-DDT-S-07	EC-NWRI	373861	4645331	10.3	11.9	1.25	23.5
PP-DDT-S-08	EC-NWRI	373808	4645582	8.59	11.6	0.67	20.9
PP-DDT-S-09	EC-NWRI	373715	4645789	6.47	9.77	0.67	16.9
PP-DDT-S-10	EC-NWRI	373514	4646137	6.17	6.47	0.67	13.3
PP-DDT-S-11	EC-NWRI	373342	4646506	13.3	19.2	1.12	33.7
PP-DDT-S-12	EC-NWRI	373975	4644750	25.4	4.58	0.67	30.7
PP-DDT-S-13	EC-NWRI	374018	4644478	9.41	8.56	1.16	19.1
PP-DDT-S-37	EC-NWRI	373423	4646328	14.6	41.7	1.4	57.7
PP-DDT-S-38	EC-NWRI	373289	4646662	9.67	30.3	1.97	42
PP-DDT-S-44	EC-NWRI	373978	4644972	8.32	22.9	1.12	32.3
PP-DDT-S-51	EC-NWRI	372970	4647309	6.91	8.61	0.44	16
PP-DDT-S-52	EC-NWRI	374043	4644844	6.81	20.1	1.84	28.7
RR-3	U. Windsor	372155	4648730	11.8	14.2	1.05	27
RR-4	U. Windsor	372550	4648120	5.01	5.33	0.123	10.5
RR-6	U. Windsor	372780	4647600	5.4	4.64	0.675	10.7
RR-7	U. Windsor	373060	4647170	17.8	21.9	0.868	40.6
RR-9	U. Windsor	373252	4646793	21.7	15.9	1.63	39.2
RR-13	U. Windsor	373736	4645685	4.37	6.39	0.27	11
RR-16	U. Windsor	373786	4645190	7.3	9.86	0.498	17.7
RR-18	U. Windsor	374123	4644659	13.9	35.5	1.2	50.7
RR-21	U. Windsor	374102	4644097	2.65	1.65	0.647	4.94
RR-26	U. Windsor	374564	4643172	3.27	1.43	0.05	4.75
RR-27	U. Windsor	374976	4643278	6.91	7.81	0.805	15.5
RR-28	U. Windsor	374718	4642720	1.15	0.661	0.05	1.86
RR-29	U. Windsor	374744	4642221	10.3	1.5	0.05	11.8
RR-30	U. Windsor	374858	4641879	56	57	2.68	116

Table B-2. Continued

Sample Name	Author	EASTING	NORTHING	DDT	DDE	DDD	Total DDT
OC-SS01	O'Connor	373381	4646783	7020	14900	249	22200
OC-SS02	O'Connor	373439	4646648	6210	6340	108	12700
OC-SS03	O'Connor	373787	4645999	4390	13900	200	18500
OC-SS04	O'Connor	373934	4645820	1460	2850	41	4350
OC-SS05	O'Connor	374042	4645594	22100	33300	428	55900
OC-SS06	O'Connor	374114	4645068	729	2260	23	3010
OC-SS07	O'Connor	374274	4645120	78	241	2	321
OC-SS08	O'Connor	374348	4644937	5290	13000	199	18500
OC-SS09	O'Connor	374446	4644710	16600	33200	260	50000
OC-SS10	O'Connor	374302	4644653	500	2010	25	2540
WS-2-0	EC-NWRI	374303	4644890	134	461	6.6	602
WS-3-0	EC-NWRI	374244	4644926	8100	17000	380	25500
WS-4-0	EC-NWRI	374249	4644973	638	1200	56	1900
WS-5-0	EC-NWRI	374246	4644844	28300	9900	1000	39200
WS-6-0	EC-NWRI	374255	4644821	2110	2700	97	4910
WS-8-0	EC-NWRI	374247	4644737	1520	2400	62	3980
WS-9-0	EC-NWRI	374113	4644949	294	1500	38	1830
CH-SS-6-2	EC-NWRI	373543	4646422	1060	568	84.8	1720
CH-SS-6-6	EC-NWRI	373580	4646437	2930	745	385	4060
CH-BH-4	EC-NWRI	373593	4646444	3360	1120	251	4730
CH-21	EC-NWRI	373551	4646422	1640	1120	191	2950
C-7-1-0 cm	EC-NWRI	373531	4646428	174	366	9.3	549
C-7-5-0 cm	EC-NWRI	373567	4646444	1590	620	719	2930
C-7-7-0 cm	EC-NWRI	373585	4646451	3580	916	797	5290
PP-DDT-S-02	EC-NWRI	374075	4645084	724	2140	54	2920
PP-DDT-S-05	EC-NWRI	373694	4646031	18600	24300	1570	44500
PP-DDT-S-06	EC-NWRI	373425	4646543	71700	14100	1720	87500
PP-DDT-S-17	EC-NWRI	373789	4645847	518	1770	40.3	2320
PP-DDT-S-18	EC-NWRI	374299	4645054	6010	10500	655	17100
PP-DDT-S-19	EC-NWRI	374321	4645010	18300	19000	1530	38800
PP-DDT-S-20	EC-NWRI	374343	4644964	18700	24600	1890	45300
PP-DDT-S-21	EC-NWRI	374343	4645020	11100	28100	1280	40400
PP-DDT-S-22	EC-NWRI	374297	4645000	446	1980	55	2480
PP-DDT-S-23	EC-NWRI	373703	4646034	494	1030	31.4	1560
PP-DDT-S-24	EC-NWRI	373702	4646026	1780	8430	244	10400

Table B-2. Continued

Sample Name	Author	EASTING	NORTHING	DDT	DDE	DDD	Total DDT
PP-DDT-S-25	EC-NWRI	374307	4644652	632	2010	47.5	2690
PP-DDT-S-26	EC-NWRI	374320	4644668	670	2160	43.5	2870
PP-DDT-S-27	EC-NWRI	374076	4645078	4810	11100	378	16300
PP-DDT-S-28	EC-NWRI	374077	4645076	3680	7580	216	11500
PP-DDT-S-29	EC-NWRI	373829	4645901	558	2870	66.4	3490
PP-DDT-S-30	EC-NWRI	373833	4645900	695	2810	87.7	3590
PP-DDT-S-31	EC-NWRI	374459	4644721	6930	12400	423	19800
PP-DDT-S-32	EC-NWRI	374458	4644722	4780	9410	296	14500
PP-DDT-S-33	EC-NWRI	374025	4645676	5600	10400	323	16300
PP-DDT-S-34	EC-NWRI	374020	4645682	10900	8890	347	20100
AO-plt1-Y02-1	EC-NWRI	374324	4644913	28100	18100	1450	47700
AO-plt1-Y02-2	EC-NWRI	374331	4644912	6680	11800	1520	20000
AO-plt1-Y02-3	EC-NWRI	374329	4644909	1660	7160	309	9130
AO-plt1-Y02-4	EC-NWRI	374329	4644914	4460	5100	416	9980
AO-plt1-Y02-5	EC-NWRI	374327	4644916	6330	11100	607	18000
AO-plt2-Y02-1	EC-NWRI	374352	4644953	19300	29800	1520	50600
AO-plt2-Y02-2	EC-NWRI	374358	4644959	1630	2670	107	4400
AO-plt2-Y02-3	EC-NWRI	374359	4644954	172	359	15.6	547
AO-plt2-Y02-4	EC-NWRI	374353	4644957	861	2810	89.8	3760
AO-plt2-Y02-5	EC-NWRI	374352	4644951	11500	12600	1180	25200
CH-plt1-Y02-1	EC-NWRI	373409	4646580	5470	9980	358	15800
CH-plt1-Y02-2	EC-NWRI	373402	4646582	10600	8500	437	19500
CH-plt1-Y02-3	EC-NWRI	373412	4646574	662	2610	50.7	3320
CH-plt1-Y02-4	EC-NWRI	373403	4646575	4010	2890	210	7110
CH-plt1-Y02-5	EC-NWRI	373408	4646573	537	1120	45.4	1700
CH-plt2-Y02-1	EC-NWRI	373445	4646624	314	889	30.8	1230
CH-plt2-Y02-2	EC-NWRI	373448	4646621	106000	76600	11400	194000
CH-plt2-Y02-3	EC-NWRI	373447	4646620	3000	9250	389	12600
CH-plt2-Y02-4	EC-NWRI	373448	4646622	5430	5500	552	11500
CH-plt2-Y02-5	EC-NWRI	373442	4646622	486	1300	45.9	1840
SH-plt1-Y02-1	EC-NWRI	374035	4645586	9390	14300	639	24300
SH-plt1-Y02-2	EC-NWRI	374031	4645583	15500	18700	1500	35700
SH-plt1-Y02-3	EC-NWRI	374034	4645587	35500	38600	2760	76900
SH-plt1-Y02-4	EC-NWRI	374036	4645584	15900	20100	1740	37700
SH-plt1-Y02-5	EC-NWRI	374031	4645586	15100	18800	719	34600

Table B-2. Continued

Sample Name	Author	EASTING	NORTHING	DDT	DDE	DDD	Total DDT
SH-plt2-Y02-1	EC-NWRI	374054	4645570	5620	1770	939	8320
SH-plt2-Y02-2	EC-NWRI	374050	4645568	17100	10500	1290	29000
SH-plt2-Y02-3	EC-NWRI	374053	4645567	30800	26600	1640	59100
SH-plt2-Y02-4	EC-NWRI	374044	4645569	8240	12100	773	21100
SH-plt2-Y02-5	EC-NWRI	374049	4645569	11900	15600	1010	28500
CHO-Pit1-000	NWRI-McM	373386	4646581	18300	13000	2220	33600
SHO-Pit1-000	NWRI-McM	374020	4645591	16400	30500	723	47700
AO-Pit1-000	NWRI-McM	374305	4644675	709	2030	33.1	2770
RR-14	U. Windsor	374019	4645665	5660	9700	212	15600
RR-17	U. Windsor	374145	4645216	607	576	27.6	1210
PP-DDT-S-03	EC-NWRI	373968	4645420	7.88	8.06	0.74	16.7
PP-DDT-S-04	EC-NWRI	373905	4645730	41.3	48.1	10.4	99.8
PP-DDT-S-14	EC-NWRI	373926	4645449	28.4	54.8	4.61	87.8
PP-DDT-S-15	EC-NWRI	373855	4645722	15.6	11.1	1.26	28
PP-DDT-S-16	EC-NWRI	373949	4645339	20.1	33.4	1.47	54.9
CH-25	EC-NWRI	373607	4646382	43.3	58.9	5.6	108
CH-26	EC-NWRI	373624	4646382	1.2	8.2	1.05	10.5
CH-27	EC-NWRI	373655	4646386	20.6	16.3	3.6	40.5
CH-35	EC-NWRI	373623	4646404	148	121	18.7	288
RR-1	U. Windsor	371925	4649080	78.6	285	4.49	368
RR-11	U. Windsor	373626	4646158	10.4	13.1	0.623	24.2
RR-22	U. Windsor	374504	4644050	3.27	4.76	1.57	9.6
RR-24	U. Windsor	374532	4643751	3.25	1.74	0.05	5.04
PP-DDT-S-35	EC-NWRI	373554	4646356	8.26	12.5	0.93	21.7
PP-DDT-S-36	EC-NWRI	373593	4646238	10.1	12.2	0.44	22.7
PP-DDT-S-39	EC-NWRI	373320	4646898	28.4	35	3.13	66.5
PP-DDT-S-40	EC-NWRI	373234	4647017	54.5	89.5	4.61	149
PP-DDT-S-41	EC-NWRI	373172	4647166	7.12	12	1.01	20.1
PP-DDT-S-42	EC-NWRI	373802	4645854	109	105	11.3	224
PP-DDT-S-43	EC-NWRI	373895	4645621	135	13.3	14.9	163
PP-DDT-S-45	EC-NWRI	374516	4643897	3.45	1.08	0.58	5.11
PP-DDT-S-46	EC-NWRI	374322	4644347	14.5	46.7	2.1	63.3
PP-DDT-S-47	EC-NWRI	374975	4643970	3.45	2.7	0.5	6.65
PP-DDT-S-48	EC-NWRI	374428	4644104	9.24	17.7	1.14	28.1
PP-DDT-S-49	EC-NWRI	374321	4644101	7.7	3.5	0.44	11.6
PP-DDT-S-50	EC-NWRI	374560	4643494	11.3	10.6	1.7	23.6

Appendix C. Statistical Analysis

C-1. Conversion from concentration to percentage.

To compare isomer composition, each isomer was converted to a percentage of total DDT using equations a-d.

$a)$ $$DDX = \sigma,\rho' DDX + \rho,\rho' DDX$$

$b)$ $$Total\ DDT = \Sigma DDX$$

$c)$ $$\sigma,\rho' DDX\%\ within\ Total\ DDT = \frac{y,\rho' DDX}{Total\ DDT}$$

$d)$ $$DDX\%\ within\ Total\ DDT = \frac{DDX}{Total\ DDT}$$

C-2. Normal Distribution.

Histograms showed approximate normal distribution.

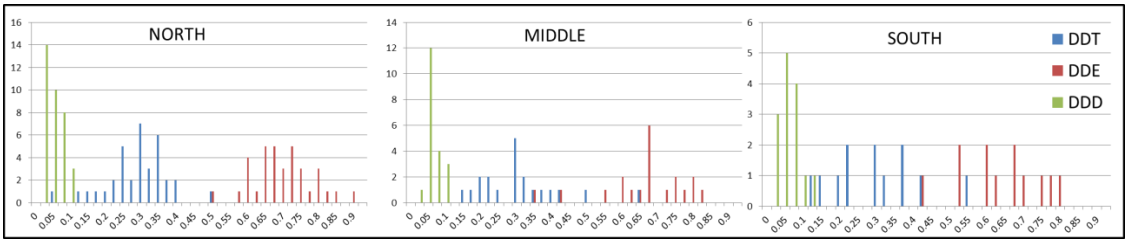

Figure C-2-1. Data sets from the north, middle and south sections from samples that were collected 2012-2013. Includes all data within those sections those sections above 700 $ng \bullet g^{-1}$.

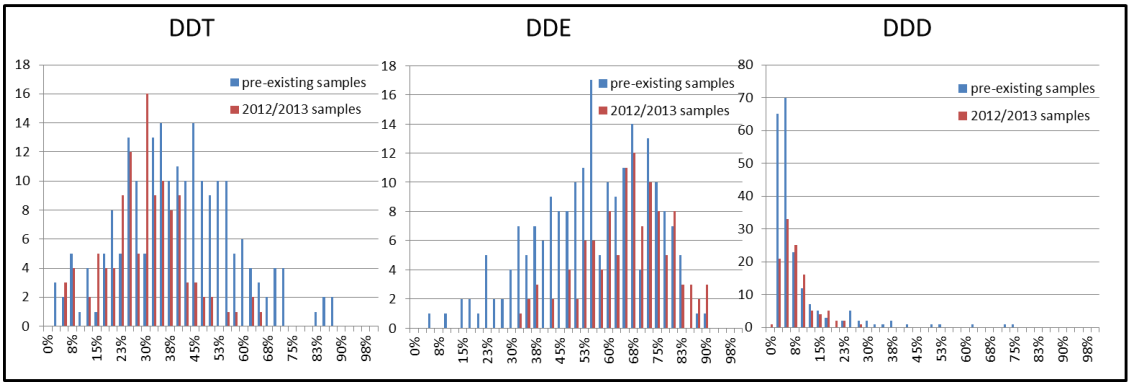

Figure C-2-2. Data sets of pre-existing and 2012/2013 data sets. Includes all soil samples from all concentration levels.

C-3. Interpreting ANOVA Tests

The variance is a measure of spread or how far each value in the data set is away from the mean. Because variance involves squaring, it does not have the same units of measurement as the original, but by taking the positive square root of variance, which equals standard deviation, the units are reinstated (Statistics Canada, 2013). Where s^2 is variance, and s is the standard deviation, $\bar{X}$ is the mean, and x is an individual sample:

$$Variance = s^2 = \frac{\Sigma\,(x-\bar{X})^2}{n-1} \qquad Standard\ Deviation = s = \sqrt{\frac{\Sigma\,(x-\bar{X})^2}{n-1}}$$

Information generated during an ANOVA test includes data on sum of squares (SS), degrees of freedom (df), mean squares (MS), F ratio (F), probability value

(p-value), and the critical F ratio (F crit). The sum of squares is related to variance and standard deviation, and measures the total variability of a set of samples around a particular number. SS_{total} measures the variability around the mean, $SS_{between\ groups}$ measures the sum of squares due to the difference between groups or data sets, and $SS_{within\ group}$ is the sum of squares error or the squared difference between the individual scores and their groups.

$$Sum\ of\ Squares = SS = \Sigma\ (x - \bar{X})^2 \qquad SS_{within} = SS_{total} - SS_{between\ groups}$$

The number of degrees of freedom is the number of independent pieces of data being used to make a calculation. Degrees of freedom can be used to determine whether a particular null hypothesis can be rejected based on the number of variables and samples in an experiment. Where *a* is the number of data sets, and N is the total number of samples:

$$df_{between} = a - 1 \qquad df_{within} = N - a \qquad df_{total} = N - 1$$

$$df_{total} = df_{groups} + df_{error}$$

Mean squares are estimates of variance and are computed by dividing the sum of squares by the degrees of freedom. If the means across a sample set is close, the number will be small. F ratio is the ratio of the variance between groups to the variance within groups and is used to test whether or not two variances are equal (University of Glasgow, n.d.). The probability value is the probability of obtaining an F ratio as large or larger than the one computed in the data assuming that the null hypothesis is true. The critical F ratio (F_{crit}) is the highest value of the F value that can be obtained without rejecting the null hypothesis.

If F is less than F_{crit}, the null hypothesis is accepted which means there is no significant statistical difference between the data sets. However, if F is larger than F_{crit}, the null hypothesis must be rejected if there is a significant statistical difference between data sets.

C-4. Table C-4-1 to C-4-6. ANOVA results comparing 2012-2013 soil samples from the north, middle and south sections.

The following tables show ANOVA test results using data sets from the north, middle, and south sections of samples with total DDT greater than 700 ng•g^{-1} that were collected 2012-2013. Each isomer is compared to the other isomers from the other sections. Because the F ratio is less than the F critical value for each test, the null hypothesis must be accepted and there is no statistically significant difference between the data sets.

Table C-4-1. 2,4-DDT

Groups	Count	Sum	Average	Variance		
north	35	1.36	0.0388	0.000302		
mid	20	0.79	0.0395	0.000497		
south	13	0.531	0.0409	0.000295		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0000433	2	0.0000216	0.0605	0.941	3.14
Within Groups	0.0232	65	0.000357			
Total	0.0233	67				

Table C-4-2. 4,4-DDT

Groups	Count	Sum	Average	Variance		
north	35	8.32	0.238	0.00592		
mid	20	5.2	0.26	0.0146		
south	13	3.55	0.273	0.0222		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0143	2	0.00717	0.626	0.538	3.14
Within Groups	0.744	65	0.0115			
Total	0.759	67				

Table C-4-3. 2,4-DDE

Groups	Count	Sum	Average	Variance		
north	35	0.105	0.00299	0.00000309		
mid	20	0.0637	0.00318	0.0000143		
south	13	0.033	0.00254	0.0000028		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00000334	2	0.00000167	0.265	0.768	3.14
Within Groups	0.00041	65	0.0000063			
Total	0.000413	67				

Table C-4-4. 4,4-DDE

Groups	Count	Sum	Average	Variance		
north	35	23.9	0.682	0.00707		
mid	20	13	0.649	0.0144		
south	13	8.28	0.637	0.0294		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0257	2	0.0128	0.963	0.387	3.14
Within Groups	0.867	65	0.0133			
Total	0.893	67				

Table C-4-5. 2,4-DDD

Groups	Count	Sum	Average	Variance		
north	35	0.562	0.0161	0.000161		
mid	20	0.376	0.0188	0.00011		
south	13	0.231	0.0178	0.000287		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.000101	2	0.0000504	0.297	0.744	3.14
Within Groups	0.011	65	0.000169			
Total	0.0111	67				

Table C-4-6. 4,4-DDD

Groups	Count	Sum	Average	Variance		
north	35	0.783	0.0224	0.000154		
mid	20	0.6	0.03	0.000238		
south	13	0.38	0.0293	0.000933		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00092	2	0.00046	1.43	0.247	3.14
Within Groups	0.0209	65	0.000322			
Total	0.0219	67				

C5. Table C-5-1 to C-5-6 ANOVA results comparing 2012-2013 soil and sediment samples.

The next tables shows ANOVA test results using 2012-2013 collected samples split into two data sets: a) an amalgamated data set from all samples from the north/middle/south section and b) sediment samples collected. Each isomer is compared to the other isomers from the other sections. Because the F ratio is greater than the F critical value for each test, the null hypothesis must be rejected, and there is a statistically significant difference between the data sets.

Table C-5-1. 2,4-DDT

Groups	Count	Sum	Average	Variance		
soil	115	4.48	0.039	0.000522		
Sediment	9	0.193	0.0215	0.000754		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00255	1	0.00255	4.76	0.0311	3.92
Within Groups	0.0655	122	0.000537			
Total	0.0681	123				

Table C-5-2. 4,4-DDT.

Groups	Count	Sum	Average	Variance		
soil	115	28.7	0.25	0.0116		
Sediment	9	1.26	0.14	0.0146		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.101	1	0.101	8.55	0.00413	3.92
Within Groups	1.44	122	0.0118			
Total	1.54	123				

Table C-5-3, 2,4-DDE.

Groups	Count	Sum	Average	Variance		
soil	115	0.518	0.0045	0.00013		
Sediment	9	0.182	0.0202	0.000214		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00207	1	0.00207	15.2	0.000157	3.92
Within Groups	0.0165	122	0.000136			
Total	0.0186	123				

Table C-5-4. 4,4-DDE.

Groups	Count	Sum	Average	Variance		
soil	115	73.7	0.641	0.0171		
Sediment	9	3.4	0.378	0.00977		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.578	1	0.578	34.7	3.45E-08	3.92
Within Groups	2.03	122	0.0166			
Total	2.61	123				

Table C-5-5. 2,4-DDD.

Groups	Count	Sum	Average	Variance		
soil	115	2.72	0.0236	0.000417		
Sediment	9	1.14	0.127	0.00539		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0895	1	0.0895	120	6.42E-20	3.92
Within Groups	0.0906	122	0.000743			
Total	0.18	123				

Table C-5-6. 4,4-DDD.

Groups	Count	Sum	Average	Variance		
soil	115	4.82	0.0419	0.0013		
Sediment	9	2.82	0.314	0.0269		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.617	1	0.617	207	4.65E-28	3.92
Within Groups	0.363	122	0.00298			
Total	0.98	123				

C6. Table C-6-1 to C-6-3. ANOVA results comparing pre-existing soil samples with 2012-2013 soil samples.

The following tables show ANOVA test results comparing pre-existing soil samples with 2012-2013 collected soil samples. Not every isomer concentration is available for pre-existing samples, so only DDT, DDE and DDD was compared. The null hypothesis is accepted for DDD but rejected for DDT and DDE. Consequently there is a statistically significant difference data sets for DDT and DDE, but not between DDD.

Table C-6-1. DDT.

Groups	Count	Sum	Average	Variance		
pre-existing samples	206	80	0.388	0.0307		
2012/2013 samples	115	33.2	0.289	0.0145		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.731	1	0.731	29.4	1.18E-07	3.87
Within Groups	7.94	319	0.0249			
Total	8.67	320				

Table C-6-2. DDE.

Groups	Count	Sum	Average	Variance		
pre-existing samples	206	111	0.537	0.0304		
2012/2013 samples	115	74.3	0.646	0.0165		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.877	1	0.877	34.5	1.07E-08	3.87
Within Groups	8.11	319	0.0254			
Total	8.99	320				

Table C-6-3. DDD.

Groups	Count	Sum	Average	Variance		
pre-existing samples	206	15.5	0.075	0.0129		
2012/2013 samples	115	7.54	0.0655	0.00261		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00664	1	0.00664	0.722	0.396	3.87
Within Groups	2.93	319	0.0092			
Total	2.94	320				

Appendix D. Contact Information

Environmental companies that provided information for remediation options can be contacted as follows:

Excavation and Disposal

Clean Harbors Canada Inc.

www.cleanharbors.com

520 Southgate Drive, Guelph, Ontario.

Terry Fellner, Director, National Remediation Group, Canada Region.

519-813-5526, fellner.terry@cleanharbors.com

Thomlinson Group

http://www.tomlinsongroup.com/environmental/environmental.html

970 Moodie Drive, Ottawa, Ontario.

Paul Nagy, Environmental Manager

613-822-2700

Phytoextraction

Web-I; *affiliated with the University of Waterloo*

www.web-i.com

Xiao-Dong Huang, Senior Scientist and Vice President.

519-888-4567 ext 35085,
xiaodong.huang@waterlooenvironmentalbiotechnology.com