Removal of DDT from Soil using Combinations of Surfactants

by

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Author’s Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

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ABSTRACT

Organochlorine pesticides (OCPs) were used in agriculture throughout the world for a long time because they are very effective for pest control, but OCPs such as DDT and its metabolites can threaten human health and ecological systems. Although DDT has been banned for use in Canada since 1972, it still persists in Canadian farmland at detectable levels due to its chemical stability. The soils contaminated with DDT require economical remediation strategies because of the low land value and rural location.

Although soil washing has been proposed as a possible economical technique to remove DDT, it has very low water solubility and so it is necessary to consider using surfactants to improve the soil-washing process. Building on previous research, we hypothesize that combinations of surfactants can be used to improve the performance of this remediation method.

The surfactants Tween 80, Brij 35, and sodium dodecylbenzene sulfonate (SDBS) were selected based on environmental and reported performance criteria. Combinations of surfactants were tested in both batch and leaching column experiments. Experiments indicated that removal efficiency and flowrate in leaching columns were optimized when a mixture of 2% Brij 35 and 0.1% SDBS was employed. The presence of Tween 80 was found to be less effective, possibly due to its higher biodegradability in the soil.

Since the measurement of surfactant concentration in the wash solution is important, several methods were tested before finally selecting a simple COD analysis as a surrogate parameter. Using the COD analysis, partitioning experiments were performed to measure the adsorption of surfactant on the soil. For economic reasons, it would be desirable to reuse the surfactant in a washing process. For this purpose, we employed activated carbon to selectively remove the more hydrophobic DDT from the surfactant solutions. Preliminary results have shown that carbon adsorption can remove some DDT, but additional work is required to understand and optimize the process.

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This thesis is dedicated to my wife Noemi and children

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for their moral support and understanding

throughout the period of my study.

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Chapter 1: Introduction

1.1 Preface

Since the organochlorine pesticides (OCPs) are very effective at pest control, they were used in agriculture throughout the world for a long time, but they introduced two significant problems: a) entry into the food chain where they can adversity affect man and animals, b) exposure, by workers to OCPs when they are spraying pesticides. OCPs such as DDT [Dichloro-Diphenyl-Trichloroethane or 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)-ethane] and their persistent metabolites can cause damage to ecological systems and threaten human health (Wang and Mulligan, 2004). The environmental fate of OCPs is summarized below:

For many years, DDT [$C_{14}H_9Cl_5$] was the most famous pesticide worldwide for the control of disease vectors and over a variety of agricultural crops. During the Second World War, DDT protected troops and civilians from typhus, malaria and other diseases. The DDT structure is shown in Figure 1.

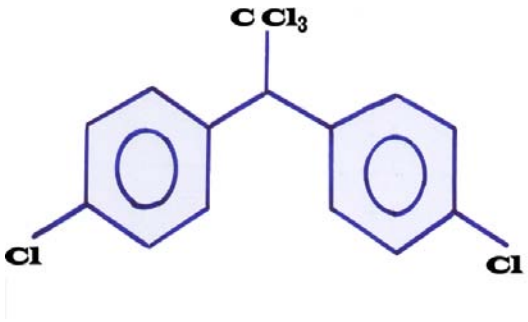


Figure 1. Structure of DDT. http://chemistry.about.com/od/factsstructures/ig/Chemical-Structures---D/DDT.-1Ks.htm

DDT has been banned for use in Canada since 1972, but it still persists in Canadian farmland at detectable levels because it is a highly stable compound in the environment (Turusov et. al, 2002). A global ban on DDT along with other twelve persistent organic pollutants was only imposed by the 2004 Stockholm Convention (UNEP, 2008). Despite the ban, DDT is still used in developing countries to control malaria under the supervision of United Nations (UN) (Thangavadivel et al., 2009). Due to its low water solubility, DDT tends to remain adsorbed to soil particles. Its resistance to biodegradation means leads to its persistence in the soil environment for long periods of

time. Most jurisdictions have identified maximum levels of DDT (and its intermediates) that are permitted in soil for various uses, which can pose problems for property owners who wish to sell or change the use of their contaminated land. For example, in Ontario the maximum permitted levels of DDT in soil for industrial use and non-potable groundwater is 1.4 mg/kg (similarly 4.6 and 0.52 mg/kg for DDD and DDE, respectively) (MOE, 2008) Therefore, it becomes necessary to identify and use techniques to clean the soil to a satisfactory level. Some toxic chemical are shown in Table 1.

Table 1. A summary of the history of some toxic chemicals (based on http://www.theglobaleducationproject.org/earth/toxics.php)

TOXIC CHEMICAL							
SUBSTANCE		DATE INTRODUCED	QUANTITY PRODUCED	TOXICITY LEVEL *	DATE BANNED		HUMAN CARCINOGEN (EPA)
					PRODUCTION	USE	
PERSISTENT ORGANIC POLLUTANTS (POPs)	PCBs	1929	1.5 MILLION TONS (TOTAL)	0.028 PPM, 0.005 PPM**	1979 (US)	IN USE (US)	PROBABLE
	DDT	1941	2 MILLION TONS (TOTAL)	5 PPM	1969 (SWEDEN) 1972 (US)		PROBABLE
	DIOXIN			0.00000003 PPM			POSSIBLE
	PBDEs	1970s	149 MILLION LBS (2001 ONLY)	3.52 PPM	PARTIAL 2005 – 2008		NO DATA
	HCB	1933		8 PPM	1981 (UK) 1970s		PROBABLE
	LEAD GASOLINE ADDITIVE	1923	7 MILLION TONS (US TOTAL)	0.0012 PPM 0.075 MG/M^3	1972 (US)	1996 (US)	PROBABLE***
MERCURY			2320 TONS (1998 ONLY)	0.009 MG/M^3			NOT CLASSIFIED
ASBESTOS		1857	> 30 MILLION TONS (TOTAL)	NO DATA	IN USE (US, CAN) 1999 (EU)		DEFINITE

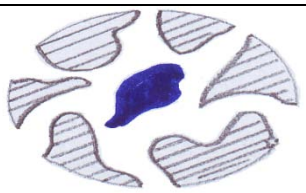
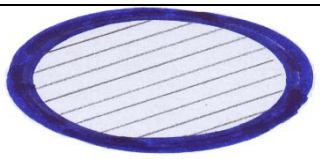
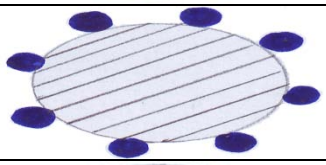
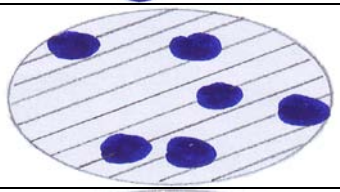
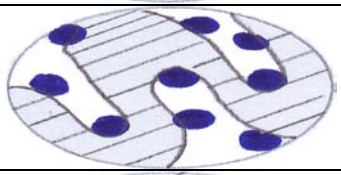
Note: All substances listed as "Probable" Human Carcinogens have been conclusively demonstrated to cause cancer in animals.

* Concentration in parts per million of body weight in food or milligrams per $meter^3$ in air at which a substance has been determined by the US EPA to have adverse non-cancer health effects. **Does not include carcinogenic effects.** ** PCB cogeners Aroclor 1016 and Aroclor 1254. *** Carcinogenesis data unavailable for tetraethyl lead. Data for "Lead and compounds" used.

1.2 Remediation Technologies

Before examining the various remediation technologies, it is very important to recognize the different physical forms possible for organic contaminants in soil. These are illustrated in Table 2. For example, DDT and petroleum pollution tend to present the form of type III and IV, ash and plastic (type I), petroleum's derivatives (type II), phenanthrene and pesticides (type V), and benzene and naphthalene tends to take the form of type VI (Harrison, 2001).

Table 2. Different physical forms of organic pollutants in soil: (I) solid particles; (II) liquid film; (III) adsorbed onto soil; (IV) absorbed into soil; (V) in soil macro pores; (VI) in soil micro pores [Paria, 2007].

TYPE	NAME	PHYSICAL FORM
I	Particulate Pollutant	
II	Liquid Film	
III	Adsorbed	
IV	Absorbed	
V	In water phase in pores	
VI	Solid or liquid in pores	

Many technologies have been tested or applied to remediate soil contaminated with inorganic and organic pollutants. According to Paria, (2007), in Table 3 are showed 863 technologies to remediate soil contaminated such as 499 *Ex situ* technologies (57%) and 364 *In situ* technologies (43%). For example, there are 20 physical separation in *Ex situ* technologies representing 2% (20/863) of total of technologies, and there are 213 soil vapor extraction *In situ* technologies representing 25% (213/863) of total.

Table 3: Technologies selected for source control at superfund remedial action sites (Fiscal year 1982–2002) [US EPA]. (Paria, 2007) A = Number selected, B = % of total

	REMEDIATION	A	B
EX SITU TECHNOLOGIES	**Physical Separation**	**20**	**2**
	Incineration (on-site)	**43**	**5**
	Bioremediation	**54**	**6**
	Thermal Desorption	**69**	**8**
	Chemical treatment	**10**	**1**
	Incineration (off-site)	**104**	**12**
	Solidification / Stabilization	**157**	**18**
	Other (ex situ)	**42**	**5**
	Soil vapor extraction	9	
	Neutralization	8	
	Soil washing	8	
	Mechanical soil aeration	5	
	Solvent extraction	5	
	Open burn / Open detonation	3	
	Phytoremediation	2	
	Vitrification	2	
	Total *Ex situ*	**499**	**57**

	REMEDIATION	A	B
IN SITU TECHNOLOGIES	**Soil vapor extraction**	**213**	**25**
	Bioremediation	48	6
	Solidification / Stabilization	48	6
	Flushing	**16**	**2**
	Chemical treatment	**12**	**1**
	Other (in situ)	**27**	**3**
	In situ thermal treatment	8	
	Multi-phase extraction	8	
	Neutralization	4	
	Phytoremediation	4	
	Vitrification	2	
	Electrical separation	1	
	Total *In situ*	**364**	**43**

Ex situ technologies 499 (57%) + *In situ* technologies 364 (43%) = **TOTAL 863 (100%)**

Excavation, removal and transportation of soil to treatment facilities represent major costs associated with the *ex situ* remediation of contaminated soil. Sometimes, building and other structures make impossible the *ex situ* remediation process. *In situ* remediation alleviates some of these problems, but additional costs and limitations exist due to the engineering and design of this process (Smith et. al, 2003).

The soils contaminated with DDT require economical remediation strategies because of cheap land value and rural location sites that are typically associated with such farmland contamination. For example, thermal destruction has showed a great efficiency in removing DDT, but these techniques are expensive and not economically possible in many applications. In contrast, bioremediation is generally considered an economical option, but it has serious limitations due to the low aqueous solubility and high hydrophobicity of DDT and slow treatment rates due to high degree of chlorination DDT. Therefore, bioremediation for DDT is often commercially unsuccessful (Juhasz et. al, 2002).

Soil washing has been proposed as a possibly economical technique, but in view of the low water solubility of DDT, it is necessary to consider using surfactants to improve this process. Surfactants are a class of natural and synthetic chemicals that promote the wetting, solubilization and emulsification of various types of organic and inorganic contaminants (Wang and Mulligan, 2004). As they are amphiphilic molecules with both hydrophilic and hydrophobic portions, many surfactants, can reduce the surface tension of water to approximately 25 $^{+}$- 5 mNm^{-1} depending on concentration and surfactant type, by acting as a bridge between the air and the liquid interface (Myers, 1999).

For soil-washing applications, surfactants have the ability to increase aqueous contaminant concentration through partitioning the solute into the hydrophobic interior of the micelles and forming spheroid or laminar structures with organic pseudo-phase interiors. Therefore, contaminants with low aqueous solubility can be dissolved in the hydrophobic interior of the micelles, thereby raising their apparent solubility. The minimum concentration at which this occurs is termed the critical micelle concentration (CMC) (Wang and Mulligan, 2004).

1.3 Scope of Research Project

This research project deals with the use of aqueous surfactant solutions such as Tween 80, Brij 35 and Sodium dodecylbenzene sulfonate (SDBS) to enhance the leaching process to remove DDT from contaminated soil. In order to accomplish this, it examines the behavior of a surfactant in the soil system, and later, combinations of two or three surfactants are considered. In the following chapter, some previous work on DDT remediation using surfactant washing is described, but the information is limited with varying levels of success. In this work, it is hypothesized that combinations of surfactants can be employed that will improve the performance of a remediation strategy.

1.4 Objectives of Current Research

The goal of this project is to study different surfactants for the removal of DDT from contaminated soil by a leaching process. More specifically, this entails the following aspects:

i) The use of small soil samples (10 g soil/ 25 ml aqueous solution) to determine the combination of surfactants that can remove the most DDT in the solution.

ii) Testing the best combination of surfactants in larger scale column leaching experiments (150 g soil / 100 ml solutions).

iii) Assessment of other important characteristics of the surfactant leaching process, such as surfactant losses through absorption and biodegradation.

Chapter 2: Theorical Background

2.1 Characterization of DDT

DDT was first synthesized in 1874 by Othmar Zeidler, but its excellent insecticidal properties were discovered by the Swiss chemist Paul Muller in 1939, who received the Nobel Prize in Physiology or Medicine in 1948 for this work. DDT was commercially introduced in 1942 by Geigy and produced on a large industrial scale in 1943 (Turusov et. al, 2002). The total cumulative global usage of DDT is estimated to have been 2.6 million tonnes from 1950 to 1993 (Voldner and Li, 1995).

DDT is still used to control mosquito vectors of malaria in the tropical regions of many countries such as Brazil, Colombia, Ecuador, Peru and Venezuela (Bate, 2001; Rodriguez-Morales et al., 2007). Table 4 shows the incidence of malaria, and the apparent inverse relationship between DDT use and malaria incidence. DDT has had a positive impact on controlling malaria, but as described below its other environmental impacts have been negative.

Table 4. House Spray Rates and Cumulative Malaria Cases in tropical countries. http://www.cis.org.au/policy/Spring01/PolicySpring01_1.html

YEAR								
1976	1980	1984	1988	1992	1996	2000	2004	2007
DDT House Spray Rate per 1,000 population (HSR)								
6000	5,000	1,800	1,600					
Cumulative Malaria Cases (x 1,000)								
	11	15	30	43	63	28	36	44

2.1.1 Environmental fate

Large quantities of DDT were released into the air during the period of agricultural or vector control applications. DDT is removed from the atmosphere by wet and dry deposition and diffusion into bodies of water (ATSDR, 2002). DDT and its metabolites have been detected in all places (air, water, soil and living organisms) around the world (Turusov, 2002).

Binelli and Provini (2003) established that DDT enters rivers and streams mainly through industrial point sources, runoff from agricultural fields and from atmospheric deposition due to volatilization as shown in Figure 2.

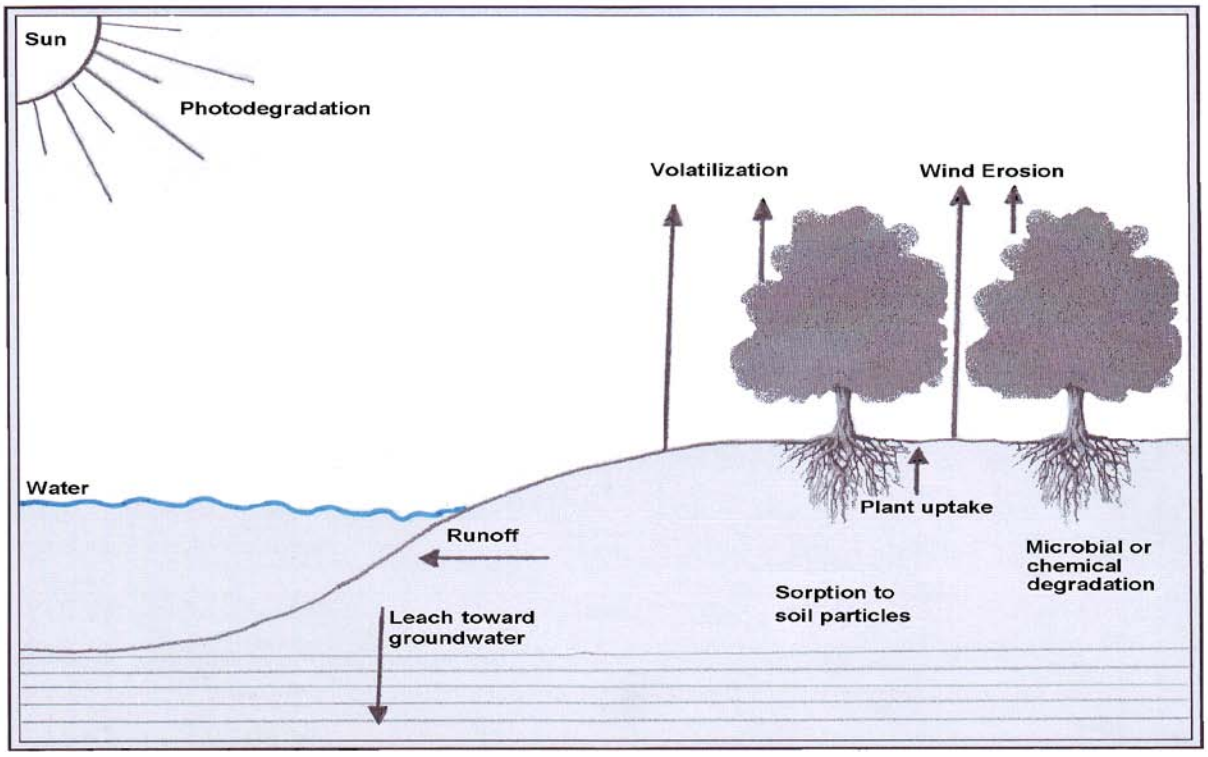


Figure 2. Pesticide fate processes. http://extoxnet.orst.edu/tibs/movement.htm

According to the World Health Organization (WHO) in 1989: “Volatilization loss will vary with the amount of DDT applied, proportion of soil organic matter, proximity to soil-air interface and the amount of sunlight”. The rate of volatilization can be low (<20% over 5 years) or as high as 50% in 5 months (Jorgensen, et al., 1991). As illustrated in Figure

2, DDT is able to leach into groundwater over long periods of time, especially from soils with little soil organic matter (Matsumura, 1985). In addition, it is very important to remember that DDT is retained to a greater degree by soils and soil fractions with higher proportions of soil organic matter due to its extremely low solubility in water (0.025 mg/L (25°C) - see Table 5), (WHO, 1989), but DDT in organic solvents is slightly soluble in ethanol, very soluble in ethyl ether and acetone (ATSDR, 2002). Table 5 summarizes the physico-chemical properties of DDT isomers and its known environmental breakdown products.

The half-life of DDT is a function of the sediment and soil conditions and ranges from 3 to 30 years (Dimond and Owen, 1996). Low water solubility, high stability and semi-volatility favor its long-range transport. However, the U.S. EPA (1989) reported that the half-life of DDT is 28 days in river water and 56 days in the lake water. The main pathways for this loss are: adsorption to water-borne particles and sedimentation, photodegradation, volatilization and aquatic organism that absorb and store it and its metabolites (ATSDR, 1994a).

2.1.2 Toxicology

DDT concentration tends to be fatal in adult animals only at very high concentrations by affecting the central nervous system (Cramer, 1972). Ingestion in humans can cause prickling of the tongue, nausea, dizziness, confusion, and headaches (Beard, 2006). Therefore, there are concerns that small quantities of DDT found in soils could be transferred to crops and then ingested by humans. IARC in 1991 classified DDT as carcinogenic to humans.

DDT is highly toxic to many aquatic invertebrate species (Johnson and Finley, 1980), and fish species (Hudson et al., 1984). Moreover, DDT can bioaccumulate in fish and other aquatic species, leading to long-term exposure (WHO, 1989). Table 6 shows the biological magnification of DDT up the food chain.

Table 5. Basic Properties of DDT, ATSDR (2002)

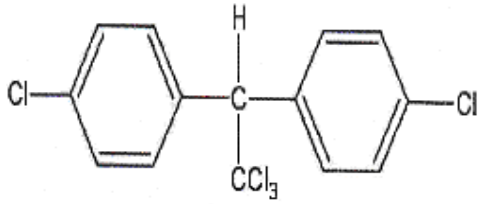
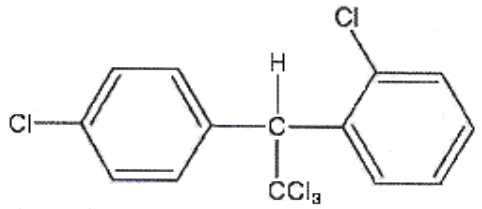
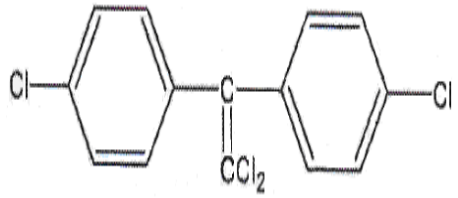
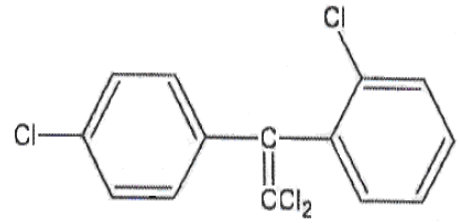
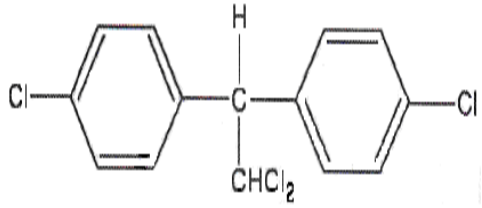
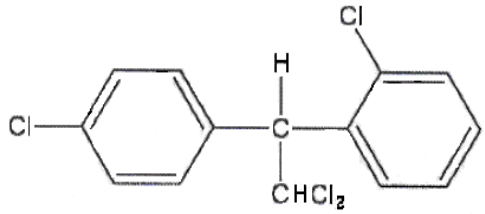
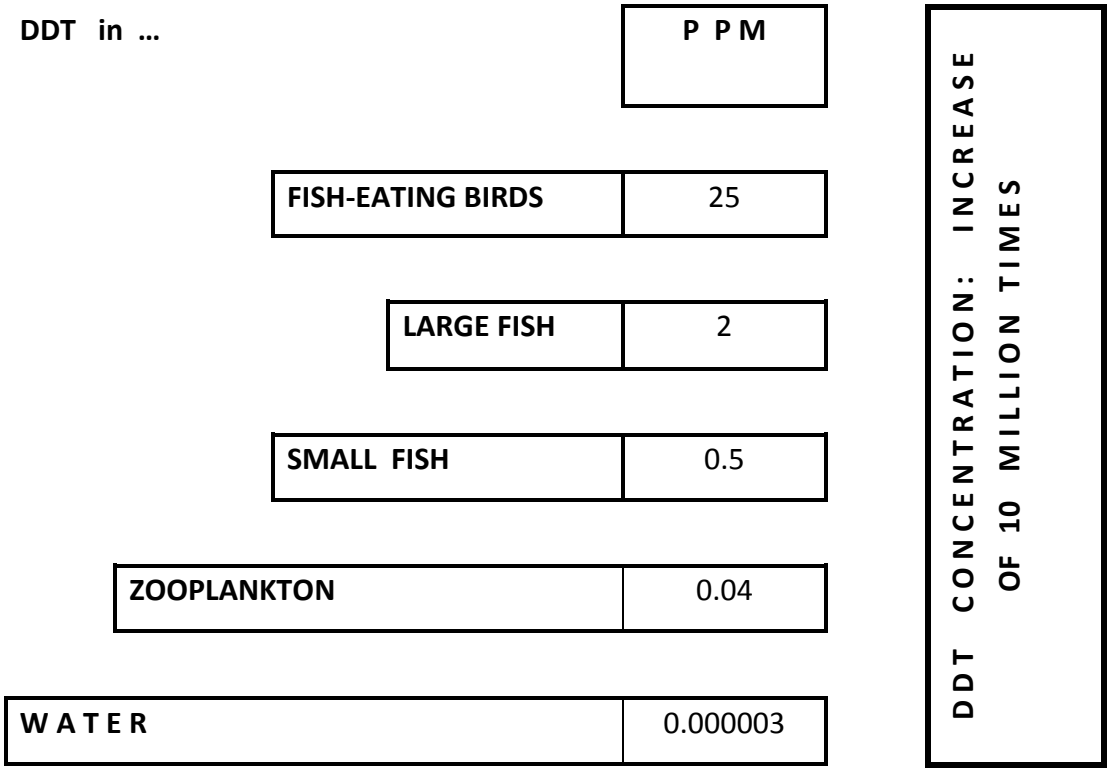
Structure	Name/Synonym	Properties
	1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane. **p,p'-DDT** 4,4'-DDT	Melting point: 109°C **Solubility (water): 0.025 mg/L (25°C)** Log Kow/Log Koc: 6.91 / 5.18 Henry's Law const.: 8.4 x 10^{-1} Pa m^3/mol
	1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethane. **o,p'-DDT** 2,4'-DDT	Melting point: 74.2°C Solubility (water): 0.085 mg/L (25°C) Log Kow/Log Koc: 6.79 / 5.35 Henry's Law const.: 6.0 x 10^{-2} Pa m^3/mol
	1,1,-dichloro-2,2-bis(p-chlorophenyl) ethylene. **p,p'-DDE** 4,4'-DDE	Melting point: 89°C Solubility (water): 0.12 mg/L (25°C) Log Kow/Log Koc: 6.51 / 4.70 Henry's Law const.: 2.12 Pa m^3/mol
	1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethylene. **o,p'-DDE** 2,4'-DDE	Melting point: no data. Solubility (water): 0.14 mg/L (25°C) Log Kow/Log Koc: 6.00 / 5.19 Henry's Law const.: 1.82 Pa m^3/mol
	1,1,-dichloro-2,2-bis(p-chlorophenyl) ethane. **p,p'-DDD** 4,4'-DDD **TDE**	Melting point: 109 - 110°C. Solubility (water): 0.090 mg/L (25°C) Log Kow/Log Koc: 6.02 / 5.18 Henry's Law const.: 4.1 x 10^{-1} Pa m^3/mol
	1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethane. **o,p'-DDD** 2,4'-DDD	Melting point: 76-78°C Solubility (water): 0.10 mg/L (25°C) Log Kow/Log Koc: 5.87 / 5.19 Henry's Law const.: 8.3 x 10^{-1} Pa m^3/mol

Table 6. Biological Magnification of DDT in a Food Chain. http://www.utc.edu/Faculty/Deborah-McAllister/educ575/wq04MichaelKavur/image004.jpg



2.2 Soil

Yong (1992) defines soil as “loose material composed of weathered rock, others minerals, and also partly decaying organic matter, that covers large parts of the land surface”. According to this definition it is very important to determine: i) the chemical and physical properties of soil to determine the operating parameters of remediation process, and ii) mechanism of the interaction between the soil and contaminant.

2.2.1 Chemical and physical properties of soil

The basic chemical and physical properties of the soil include: texture, structure, color, bulk density, drainage, calcium carbonate content, pH and acidity, and salinity. The soil particle classification according to MAFRI is shown in Table 7.

Table 7. Soil particle classification.
http://www.gov.mb.ca/agriculture/soilwater/soilmgmt/fsm01s01.html

	TYPE	m m
SOIL PARTICLE CLASIFICATION	G r a v e l	more than 2.00
	S a n d	between 0.05 – 2.00
	S i l t	between 0.002 - 0.05
	C l a y	less than 0.002

The texture of a soil which cannot be altered, is the relative proportion of clay particles [<0.002 mm diameter (clay is considered as a "heavy" soil because of the difficulty to physically move it)], silt [0.002 - 0.05 mm (medium material)], and sand [0.05 – 2.00 mm in diameter ("light" soils are easily tilled)]. Loams are medium textured soils made up of a mixture of clay, silt and sand. In agriculture, soil texture is less than 2.0 mm in diameter. Particles larger than 2.0 mm are classified as gravel and stones (MAFRI).

The structure lets soil particles cling together to form aggregates. There are peculiar soil structures such as prismatic, columnar, angular and subangular blocky, platy and granular. The most common structures of agricultural soils are either granular or blocky structure (MAFRI).

The colour is used as a soil classification criterion; for example, dark coloured topsoil indicates high organic matter content, whereas light-colored topsoil have low organic matter content (MAFRI).

Bulk density which is the apparent density of a soil, tends to be higher in sandy soils (approximately 1.3 g/cm^3) than in clayey soils (approximately 1.1 g/cm^3). In addition, the bulk density of compacted soil can be as high as 1.8 g/cm^3 (MAFRI).

Soil drainage is described in terms of the duration and frequency of time when the soil is not saturated. In fact, it is quantified by the speed and extent of water removal from the soil due to runoff (surface drainage) and downward flow through the soil profile (internal drainage). For example, sands in low-lying areas with high water tables are poorly drained (MAFRI).

Calcium carbonate content is expressed as the calcium carbonate equivalent and can range from 0% in extremely leached soil profiles to over 40% in the high lime tills. When calcium carbonate is contacted with HCl, it decomposes into carbon dioxide (CO_2). The depth at which this reaction occurs, gives an indication of internal soil and soil development (MAFRI).

Soil acidity is identified by its pH value. Soil pH affects the structure, chemical, and biological properties of soil. Since, soil pH affects crop fields, the crops also vary in their tolerance to various components of acidity. In practical terms, the soil is considered to be: very strongly acid when its pH is less than 5.1, strongly acid when its pH is between 5.1 and 5.5, moderately acid when its pH is between 5.6 and 6.0, neutral when its pH is between 6.5 and 7.5, alkaline when its pH is between 7.5 and 8.5, and finally alkali when its pH is more than 8.5. The extent and severity of soil acidity can be determined with careful sampling of fields. In some places in Canada such as Ontario, Saskatchewan, Alberta and northeast British Columbia, the pH of the soil is 6.0 or less under natural conditions (Canola-council)

Saline soils can be recognized by spotty growth of crops or by a white crust of salt that accumulates over the soil surface usually in low-lying areas. Salinity is the result of excess groundwater moving downward and laterally through the soil and dissolving and transporting soluble salts. The soil in Canada's prairie regions is relatively high in soluble salts. The dominant salts contain calcium, magnesium, sodium and sulphate (Canola-council).

2.2.2 Interactions between soil and contaminant

The mechanism of interaction is based on: i) precipitation, ii) complexation, and iii) sorption. Inorganic pollutants may undergo precipitation and complexation reactions, but sorption is the dominant mechanism with organic pollutants (Tan, 2000)

Sorption processes lead to the partitioning of the solutes (ions, molecules, and compound) between the soil particles and the liquid phase. These involve both chemical and physical processes. Chemical sorption occurs by chemical bonding, while physical

sorption involves the attraction of pollutants to the soil constituent's surfaces (from the aqueous solutions present inside the pore) due to electrostatic or hydrophobic interactions (Tan, 2000).

Sorption is a mechanism that retards contaminant migration in soil and groundwater. Sorption of organic contaminants in soil occurs via hydrophobic binding with soil organic matter (Karickhoff et al., 1979). For example, Shin et al. (1970) have shown that the adsorption of DDT is closely related to the organic matter content of the soils such as lipids, resins, polysaccharides, polyuronides, and humic matter which link with the DDT. Humic material represents a major adsorbent for DDT; the degree of sorption, however, is strongly connected with the degree of humification. A concentration-dependent sorption isotherm can be used to characterize sorption equilibrium. This concentration dependent sorption is often fitted with a Freundlich isotherm (Hamaker and Thompson, 1972).

In addition to contaminant-soil sorption, the interaction of surfactants with the soil must be considered. Nonionic surfactant molecules can sorb directly onto solid surfaces or can interact with sorbed surfactant molecules. The sorption mechanism depends on the surfactant dose and the nature of the sorbent (Edwards et al., 1994). Clunie et al. (1983) have made a special comparison between doses; for example, at low doses, the surfactant molecules may be sorb into a mineral surface or to a clean sediment with very few sorbed surfactant molecules. Sorption occurs mainly due to van der Waals interactions between the hydrophobic and the hydrophilic moieties of the surfactant and the surface. At higher surfactant doses, sorption usually entails the formation of more structured arrangements including the formation of monomer surfactant clusters on the surface or a second layer, that are governed mainly by interactions between hydrophobic moieties of the surfactant molecules.

2.3 Remediation of DDT from soils

The following summarizes some of the main techniques that have been applied or tested for DDT and related compounds:

2.3.1 Physical soil remediation

2.3.1.1 Excavation

This technique entails the removal of contaminated soil generally to disposal at a landfill. The process requires only short time, but it is very expensive because the excavation requires heavy machinery. After the excavation, it is necessary to replace it with new soil at extra cost (Heinegg et al., 2002), as well as to dispose the excavated contaminated soil in an acceptable manner, which is often a hazardous waste landfill. Landfilling and excavation involve obvious disposal and leaching problems (Evdokimov and Wandruszka, 1998).

2.3.1.2 Soil washing

This technique uses water, surfactant, or surfactant combined with solvents, and mechanical processes to scrub soils. The soil washing process separates fine soil (clay and silt) from coarse soil (sand and gravel). Soil washing can be cost-effective because it reduces the quantity of material that would require further treatment by another technology (Khan et al., 2004).

The two possible mechanisms to consider in remediation technologies using surfactants are micellar solubilization and mobilization by surface tension reduction. It is possible increase the efficiency of remediation of this technique when interfacial tension is 1 mN/m or lower. Under those conditions, a free hydrocarbon phase can flow spontaneously (Ganeshalingam et al., 1994). Using leaching, aqueous solutions containing the surfactants Triton X-100 removed 45% and polypropylene glycolethoxylate (PPG) removed 25% of DDT residues (Parfitt et al., 1995)

2.3.1.3 Soil vapor

Soil vapor also known as soil venting or vacuum extraction includes the installation of wells and pipes in the soil, through which soil contaminants are extracted. Vacuum is applied through the well near the source of contamination to evaporate the volatile constituents of the contaminated mass which are subsequently withdrawn through an

extraction well. The extracted vapors are treated with carbon adsorption before being released into the atmosphere (USEPA, 1995a). Due to its low volatility, DDT is not expected to be successfully remediated with this technique.

2.3.2 Biological soil remediation

2.3.2.1 Microbial

Microbial remediation refers to the use of microbes in degrading contaminants into less toxic form. Cost is generally low, but the timeframe can be very long (Heinegg et al., 2002). Bioremediation of DDT is generally unsuccessful and is not considered an economic remediation option due to serious limitations such as low aqueous solubility, high hydrophobicity and high degree of chlorination (resulting in low biodegradability). When degradation does occur, DDT degradation rates are extremely slow and the resultant transformation products (DDD and DDE) are more toxic and recalcitrant than the parent compound (Aislabie et al., 1997). As noted in section 1.1, the allowable concentration for the transformation product DDE is significantly lower than for DDT, meaning that biodegradation can actually increase the contamination problem.

2.3.2.2 Phytoremediation

This process uses plants to extract contaminants or to degrade them in the soil. Cost is generally low, but the timeframe is long and the effectiveness for DDT has not been conclusively demonstrated (Heinegg et al., 2002).

2.3.2.3 Fungal remediation

This technique is new and it involves the use of certain species of fungus to degrade contaminants (Heinegg et al., 2002). According Brown et. al. (1995), fungi utilize extracellular enzymes to cleave complex structures and make them more metabolically available. Thus, fungi are able to biodegrade complex polyaromatic hydrocarbons that are extremely recalcitrant to normal bacterial based processes. For example, White-rot fungi are organisms which can degrade lignin. Lignin is found in woody plants and is a very complex structure polymer. The complexity and irregularity of the lignin make it

resistant to absorption and degradation by intracellular enzymes. Because of low levels of key sources of carbon, nitrogen or sulfur nutrients, white-rot fungi produce enzyme (called lignin peroxidase) into extra-cellular environment to degrade lignin (Harjanto et. al., 2000).

2.3.3 Thermal and oxidative remediation

Vitrification is a method of stabilization/solidification that uses a powerful source of energy to melt soil or other earthen materials at extremely high temperatures of 1600 – 2000°C, immobilizing most inorganics and destroying organic pollutants by pyrolysis (Acard and Alshawabkeh, 1993).

In thermal desorption, the contaminated soil is excavated, screened, and heated to temperatures of 100 – 160 °C, to release it from the soil. Thermal desorption does not aim to destroy the organic but rather to change the form to a more treatable one; however, incineration (vitrification) aims to destroy the contaminants (Alpaslan and Yukselen, 2002).

Incineration is an accepted method for the clean-up of DDT, but it is expensive due to the energy costs involved. Although, it leads to the total destruction of the organic structure, it is a source of secondary pollution including NOx, SO_2 and particulate matter (Evdokimov and Wandruszka, 1998).

Other oxidative approaches have received some limited testing. For example, using supercritical fluid oxidation, the removal efficiency of DDT is > 99% (Modell, 1985). Using Fenton reaction chemistry (low pH, hydrogen peroxide, ferrous iron) in a slurry system, relatively low concentrations of H_2O_2 were sufficient to degrade about 50% of the DDT, while with higher concentration the degradation percentage was 75%. (Villa and Nogueira, 2006). Ultrasonic-driven advanced oxidation using 20 kHz high power ultrasound of 375 W/L has been used to degrade 75% of DDT (Thangavadivel et al., 2009). However, none of these approaches have found widespread acceptance, probably due to technical and economic barriers.

2.3.4 Removal efficiency

Analysis of the removal efficiency for some techniques used in the remediation of organochlorine insecticides showed that: i) thermal desorption could attain a removal efficiency > 98% (Troxler et al., 1993), ii) biological treatment by activated rotating biological contractor achieved a removal efficiency of chlordane between 75-96% (Sabatini et al., 1990), and iii) chemical destruction by superoxide radical in the presence of pyridine yielded a removal efficiency up to 99% (Matsunaga et al., 1991). Therefore, relatively high removal efficiencies are possible, although costs may be high.

2.4 Range cost of treatment

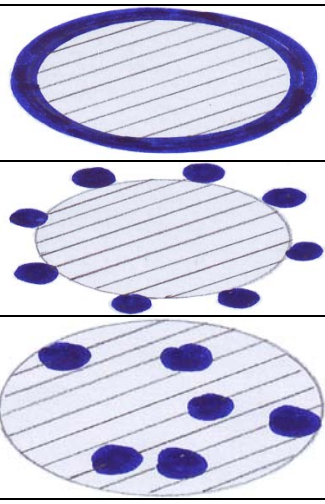
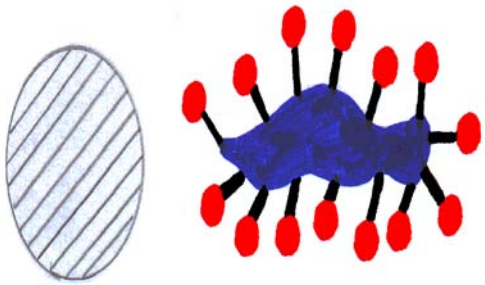
The costs shown below are general for polychlorinated biphenyls (PCBs) and not necessarily applicable specifically for DDT. As discussed in the previous sections, some techniques are not very effective for DDT, but the data shows below by Davila et. al. (1993) is useful for providing order of magnitude comparisons.

Type of treatment	Range of cost$ / ton
Incineration	$280 –1000
Thermal desorption	$ 90 – 380
Chemical dehalogenaton	$225 – 580
Solvent extraction	$110 – 540
Vitrification	$100 –1000
Solidification/Stabilization	$ 50 – 310
Soil washing	$ 60 – 230

Consequently, after examining the different techniques to remediate DDT from soil, it is very important to keep in mind that in the period 1940 – 1970, DDT and other chlorinated compounds were used to control pests, but caused serious pollution problems that persist in nowadays because they are highly hydrophobic and have low mobility in the soil where they accumulate.

Moreover, the soils contaminated with DDT require economical remediation strategies because of cheap land value and rural location sites. Although, soil washing may be the most economical process to clean up DDT, DDT has very low water solubility, and so it is necessary to consider using surfactants to improve the soil-washing process. For example, as illustrated in Table 8, a surfactant can capture the hydrophobic contaminant and remove it. For this reason, surfactants are particularly attractive for this soil washing process since they have low toxicity and fare more biodegradable than many organic solvent based systems (Xu et al., 2005).

Table 8. Surfactant's behavior (the surfactant is capturing the hydrophobic contaminant and removing it) http://www.pgbeautygroomingscience.com/2-in-1-shampoos.html

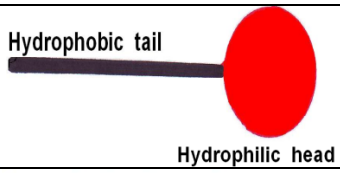
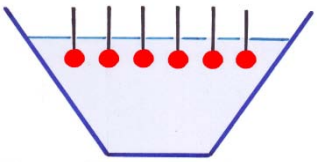
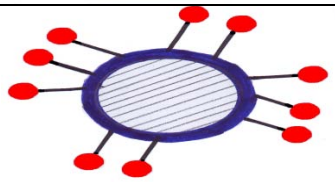
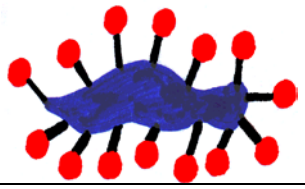
SURFACTANT BEHAVIOR	CONTAMINATED SOIL	SURFACTANT REMOVES CONTAMINANT
		

Finally, due to lack of specific information from the technical literature on the formulation of optimum surfactant mixtures, including data on interfacial tensions, the objective of this thesis is to investigate the effect on the recovery of the major fraction of the pollutant. These batch experiments must reproduce the same effects observed in leaching columns, which simulate the process at larger scales or field applications. Furthermore, lack of data about solubilization, emulsion stability, toxicity and biodegradability in many combinations requires more study.

2.5 Surfactant

The primary reason to use surfactant is to remove the pollutant in a short time period with less wash water required (Ganeshalingam et al., 1994). Surfactants (surface active compounds) are amphiphilic compounds (containing hydrophobic and hydrophilic portions; see Table 9) that reduce the free energy of the systems by replacing the bulk molecules of higher energy at an interface (Mulligan et. al., 2000). In other words, surfactants are a class of natural and synthetic chemicals that promote the wetting, solubilization, and emulsification of various types of organic and inorganic contaminants (Wang and Mulligan, 2004).

Table 9. Possible interactions of surfactants and hydrophobic contaminants such as DDT. http://www.funsci.com/fun3_en/exper2/exper2.htm

I		Surfactant's scheme of molecule.
II		Water's surface tension decreases because of surfactant in the solution. The hydrophilic head is in the water, but the hydrophobic tail is outside.
III		The hydrophobic tail of the surfactant is inserted into DDT to remove it. The surfactant can be showed as micelles, cylindrical or laminar forms.
IV		The hydrophobic head drives the DDT in the water.

There are four classes of surfactants: non-ionic, anionic, cationic, and amphoteric. Non-ionic and anionic surfactants are most favored for remediation techniques (Keller and Rickabaugh, 1992). Cationic surfactants are not normally used for soil washing because of their germicidal properties (Ganeshalingam et al., 1994). Cationic surfactants are

mainly used in household products as an active ingredient in fabric softeners and a few applications as shampoos (Rosen, 1989).

Non-ionic surfactants are supposed to be less toxic and more biodegradable than anionic and cationic ones. Differences may occur between classes of surfactants as well as within classes. For example, the non-ionic surfactant Tween 80 was found to be more biodegradable than Brij surfactants (Franzetti et al, 2008). Figure 3 illustrates the typical behavior of a surfactant in aqueous solution, as a function of the concentration.

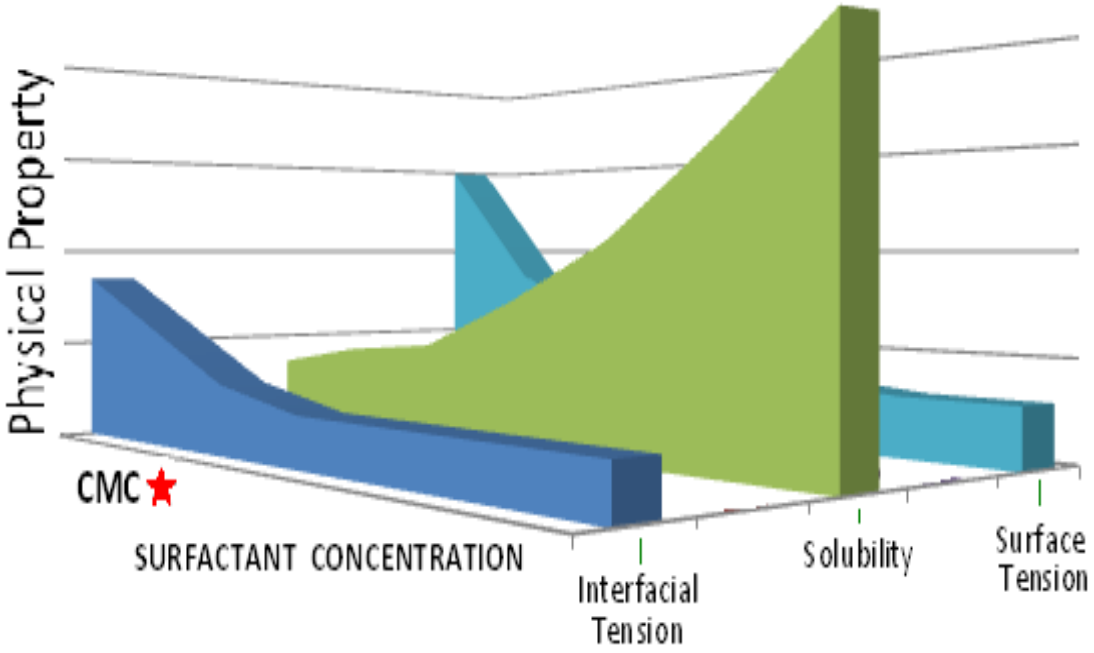


Figure 3. Schematic diagram of the variation of interfacial and surface tension, solubility with surfactant concentration ((Mulligan et. al, 2000)

Surfactants have the ability to increase aqueous contaminant concentrations by partitioning the solute into the hydrophobic interior of the micelles and forming spheroids or lamellar structures with organic pseudo-phase interiors (Wang and Mulligan, 2004). The micelles are generally spherical but may be cylindrical lamellar structures at higher concentrations as shown in Figure 4.

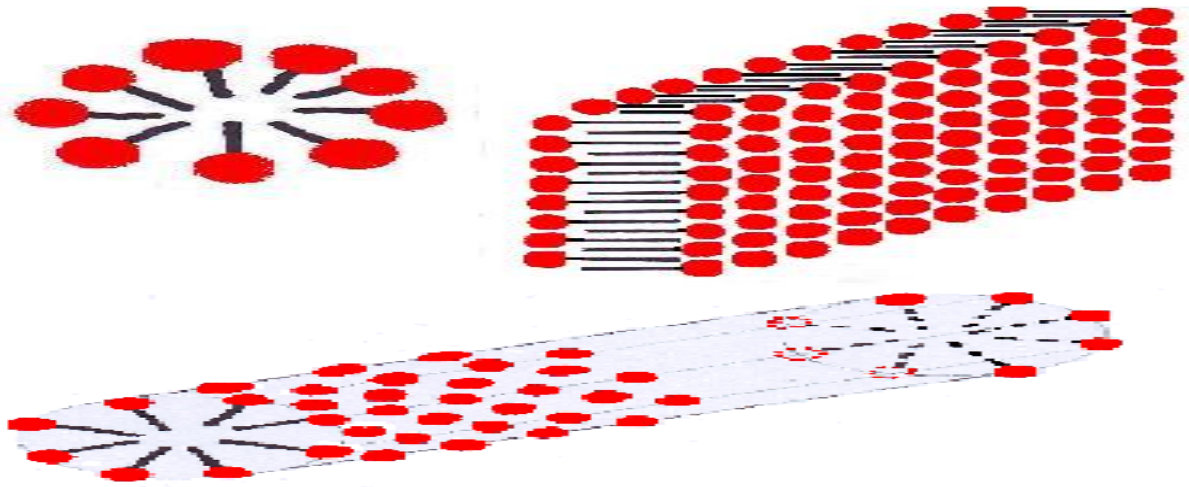


Figure 4. Schematic diagram of micelles. http://barrett-group.mcgill.ca/teaching/liquid_crystal/LC05.htm

The concentration of surfactant at which the thermodynamics of the surfactant-solvent system favor micelle formation (Figure 5) is called the critical micelle concentration (CMC) (Haigh, 1996). At concentrations above the CMC, surfactants have the ability to solubilize significantly more of a hydrophobic organic compound than would dissolve in water alone (Haigh, 1996). According to Figure 5, single molecules (i.e. monomers) are present at low concentrations in aqueous solution. However, beyond the CMC, the surfactant molecules aggregate, form micelles and reduce the thermodynamic energy in the system (Ahn et. al 2008).

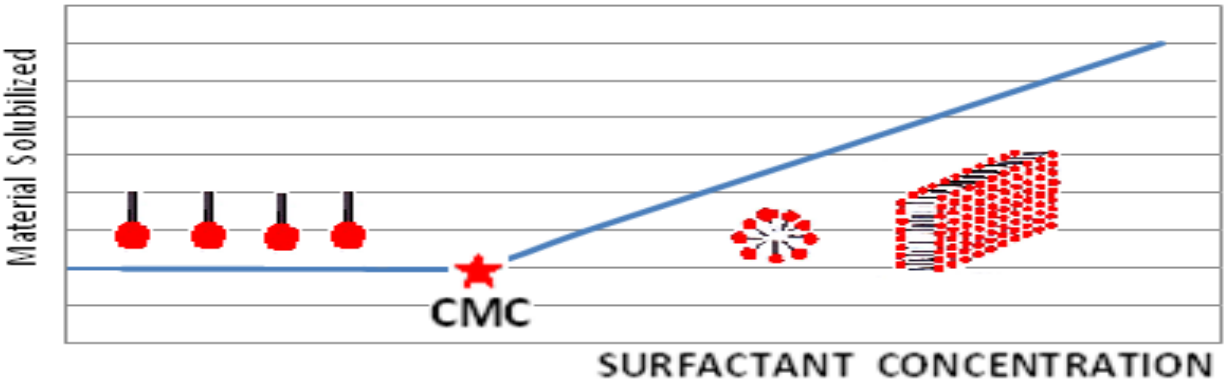


Figure 5. Graph of critical micelle concentration (CMC). (Haigh, 1996)

The CMC of surfactant in aqueous solution varies with surfactant structure, the temperature of the solution, the presence of electrolyte and various other organic compounds. However, generally anionic surfactants have much higher CMC's in aqueous solutions than a non-ionic surfactant with an equivalent hydrophobic group (Rosen, 1989).

The main factors that should be considered when selecting a surfactant are: i) effectiveness in removing the contaminant, ii) cost, iii) public and regulatory perception, iv) biodegradability and degradation products, v) toxicity to humans, animals and plants, and vi) ability to be recycled (Mulligan et al, 2000). In other words, the more important characteristics of a surfactant to consider are: biodegradability, low toxicity, solubility at groundwater (or environmental) temperatures, low adsorptivity onto soil, effectiveness at concentrations lower than 3%, low soil dispersion, low surface tension and low CMC (shown in Table 10) (Kimball, 1992).

2.6 DDT Recovery using surfactants

According Trochimczuk et al., (2003), many low molecular weight organic compounds are removed from aqueous solutions by adsorption using porous materials such as activated carbon and/or polymeric resins. The driving force of this process is interaction of the solute molecules with the sorbent surface and can be attributed to weak hydrophobic interactions, e.g., van der Waals forces or stronger interactions such as dipole–dipole and hydrogen bonding. For this reason, the interaction between sorbent and sorbate can be modified, changing the character of the sorbent surface. This will significantly influence sorbent capacity and selectivity (Trochimczuk et al., 2003). In addition, activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants. The high adsorption capacities of activated carbons are usually related to their high-surface-area, pore volume, and porosity. In addition, the adsorption capabilities of activated carbons strongly depend on the activation method and the nature of the source material (Ahmaruzzaman, 2008).

Table 10. Properties of common surfactants.
http://www.piercenet.com/browse.cfm?fldID=5558F7E4-5056-8A76-4E55-4F3977738B63

Surfactant	**Type**	**Agg. #**	**MW** mono (micelle)	**CMC** mM (%w/v)	**Cloud Point** °C	**Dialyzable**
Triton X-100	Nonionic	140	647 (90K)	0.24 (0.0155)	64	No
Triton X-114	Nonionic	–	537 (–)	0.21 (0.0113)	23	No
NP-40	Nonionic	149	617 (90K)	0.29 (0.0179)	80	No
Brij-35	Nonionic	40	1225 (49K)	0.09 (0.1103)	>100	No
Brij-58	Nonionic	70	1120 (82K)	0.08 (0.0086)	>100	No
Tween 20	Nonionic	–	1228 (–)	0.06 (0.0074)	95	No
Tween 80	Nonionic	60	1310 (76K)	0.01 (0.0016)	–	No
Octyl glucoside	Nonionic	27	292 (8K)	23-24 (~0.70)	>100	Yes
Octyl thioglucoside	Nonionic	–	308 (–)	9 (0.2772)	>100	Yes
SDS	Anionic	62	288 (18K)	6-8 (0.17-0.23)	>100	Yes
CHAPS	Zwitterionic	10	615 (6K)	8-10 (0.5-0.6)	>100	Yes
CHAPSO	Zwitterionic	11	631 (7K)	8-10 (~0.505)	90	Yes
Agg. # = Aggregation number, which is the number of molecules per micelle						

However, its high initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent (Memon et al., 2007). In order to overcome this problem, exploitation of newer, cheaper and indigenous waste materials for the removal of pesticides, organic and inorganic contaminants has become the focus of intense research. In other words, the search for an inexpensive and easily available adsorbent has led to more economic and efficient adsorbent from agricultural waste origin,

industrial by-products or natural materials such as chitosan, zeolites, clay, fly ash, red mud, sludges and oxides (Akhtar et al., 2007; Ahmaruzzaman, 2008).

Materials investigated for the removal of OPP pollutants include rice bran (Akhtar et al., 2005a), orange peel (Sivaraj et al., 2001), bagasse fly ash (Vinod et al., 2002), rice husk ash (Akhtar et al., 2006b), and other cellulosic materials such as sunflower stem and palm seed coat (Malik et al., 2005). Their lower cost, easy availability and easier regeneration have led to interest in their use as sorbents.

Soil washing process using surfactants will likely be expensive if the surfactant solution is only used once and then sent for disposal or treatment with the DDT solubilized in it. Therefore, it would be beneficial if the DDT could be removed from the surfactant solution, allowing for recycle or reuse of the solution (Boussahel et al., 2009) used several adsorbents including sawdust, cork waste and activated carbon to adsorb DDT from aqueous solutions (in the absence of surfactants). Therefore, it may be feasible to use an adsorbent such as activated carbon to remove DDT from the surfactant and allow reuse. It might also serve to concentrate recovered DDT in a small volume of adsorbent, which could reduce the ultimate disposal costs.

According to Baker et al. (1992), activated carbon has an extraordinarily large surface area and pore volume that gives it a unique adsorption capacity. Commercial food grade products range between 300 and 2,000 m^2/g. Some have surface areas as high as 5,000 m^2/g (Burdock, 1997)

Activated carbon has both chemical and physical effects on substances where it is used as a treatment agent. These effects can be classified as: (a) adsorption; (b) mechanical filtration; (c) ion exchange; and (d) surface oxidation.

2.6.1 Adsorption

Adsorption is the most studied of these properties in activated carbon. Physical adsorption involves the electrostatic attraction between the adsorbent and the adsorbate. In Figure 6, the carbon matrix represents the adsorbent and both large and small molecules are adsorbate. Chemical adsorption is the product of a reaction

between the adsorbent and the adsorbate (Cheremishinoff and Moressi, 1978). Adsorption capacity depends on: a) physical and chemical characteristic of the adsorbent and adsorbate, b) concentration of the adsorbate in the liquid solution, c) characteristics of the liquid phase (pH, temperature, etc) and d) contact time between the adsorbent and adsorbate (Cheremishinoff and Moressi, 1978).

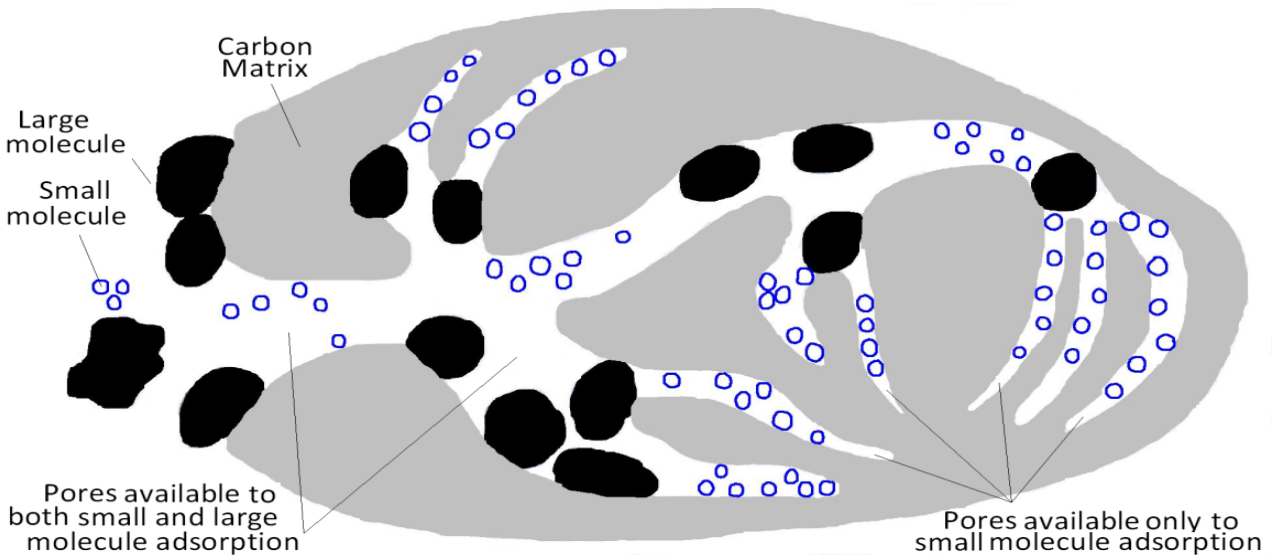


Figure 6. Molecular screening in the micropores of an activated carbon filter. http://www.waterprofessionals.com/wastewater/activated_carbon_filters.html

2.6.2 Mechanical filtration

According to Ahmedna et al., (2000), mechanical filtration involves the physical separation of suspended solids from a liquid passing through carbon arrayed as a porous media in a column or bed. In other words, the effectiveness of filtration depends on particle size, bulk density, and mechanical hardness. Moreover, while a smaller particle size results in a clearer liquid, it also slows the speed of processing. Bulk density determines how much carbon can be contained in a given container, while mechanical hardness is important because the particles must have sufficient strength to block the particulate matter being filtered (Ahmedna et al., 2000), and to avoid compaction.

2.6.3 Ion exchange

Ockerman (1991) defines ion exchange as a reversible chemical reaction between a solid and an aqueous solution that allows the interchange of ions. Ion exchange can be enhanced by chemical activation. For example, treatment of carbon with a base increases the capacity of carbon to exchange anions. Additionally, if only the sites are strong acid groups, the acidification of the surface makes carbon a powerful cation exchanger (Jankowka et al., 1991).

2.6.4 Surface Oxidation

The surface of activated carbon has an electrical double layer (Mattson and Marks, 1971). The type and net charge of functional groups bonded to the carbon surface is important in understanding the mechanism of adsorption between ionic adsorbates and the activated carbon (Ahmedna et al., 2000). Therefore, the diversity of functional groups on the carbon surface affects the surface behavior of carbon and thus enhances or reduces the affinity of carbon to the adsorbate via electrochemical mechanisms (Ahmedna et al., 2000).

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2.7 Solubilization Considerations for DDT

Investigations by Karagunduz et. al (2007) have demonstrated that higher weight solubilization ratio (WSR) values are needed for better solubilization of DDT. The solubility potential of a surfactant is characterized by the WSR which is defined as follows:

$$\mathbf{WRS} = [\, C_{DDT} - C_{DDT(CMC)} \,] / [\, C_S - CMC \,] \qquad (1)$$

where, C_{DDT} is the concentration of dissolved DDT (M/L^3), $C_{DDT(CMC)}$ is the concentration of DDT at CMC (M/L^3), C_S is the surfactant concentration (M/L^3) and **CMC** is the critical micelle concentration (M/L^3). However, other options to quantify the solubilization potential of surfactants are available. It is very important to remember that the

dissolution of hydrophobic organic contaminants (HOC) into a micellar phase is analogous to partitioning of HOC into organic matter.

Jafvert and van Hoof (1994) have shown that the distribution coefficient of hydrophobic organic contaminant (HOC) between water and surfactant micelles **(K_{mc})** can be determined using the following relationship:

$$K_{mc} = MSR / C_{aq} \quad (2)$$

where, C_{aq} is the molar aqueous (free- water) concentration and MSR is the molar solubility ratio defines as **$MSR = WSR \times (MW_S / MW_{DDT})$**, where **MW** is the molecular weight.

In the presence of surfactant, the solid-liquid distribution coefficient of DDT can be represented as follows:

$$K^* = \frac{Mass\ of\ sorbed\ DDT\ per\ mass\ solid-phase}{Mass\ of\ DDT\ in\ solution-phase\ per\ bulk\ liquid\ volume} = S^*_{DDT} / C^*_{DDT} \quad (3)$$

Kile and Chiou (1989) considered that C^*_{DDT} can be estimated using the following relationship:

$$C^*_{DDT} = C_{aqDDT} (1 + K_{mn}C_{mn} + K_{mc}C_{mc}) \quad (4)$$

where K_{mn} is the solute distribution coefficient between surfactant monomers and water (L^3/M), K_{mc} is the solute distribution coefficient between the surfactant micelle and water (L^3/M), C_{aqDDT} is the DDT concentration in the aqueous (water) phase (M/L^3), C_{mn} is the concentration of surfactant monomers (M/L^3), and C_{mc} is the concentration of surfactant micelles (M/L^3).

Karagunduz et. al (2007) reestablish that the sorption of DDT to solid phase can occur via a partitioning process and/or interaction with sorbed phase surfactant molecules. Chiou et. al (1979) noted that sorption of hydrophobic organic contaminants (HOC) can be described by a linear isotherm (Eq. 5).

$$S_{DDT} = K_D C_{DDT} \quad (5)$$

where $\mathbf{C_{DDT}}$ is the aqueous phase concentration of DDT (M/L^3), $\mathbf{S_{DDT}}$ is DDT mass sorbed on the soil (M/M) and $\mathbf{K_D}$ is the partition coefficient between soil and aqueous phase DDT concentration (L^3/M).

Rosen (1989) has mentioned that partitioning of organics to the sorbed surfactant phase is related to the amount of surfactant sorption, on solid particles which usually exhibits a Langmuir type of isotherms such as:

$$\mathbf{S_{SS} = bC_S S_m / (1 + bC_S)} \qquad \mathbf{(6)}$$

where **b** is Langmuir constant (L^3/M), $\mathbf{C_S}$ is aqueous phase surfactant concentration at equilibrium (M/L^3), $\mathbf{S_m}$ is maximum adsorbed surfactant mass (M/M) and $\mathbf{S_{SS}}$ is the adsorbed surfactant mass (M/M),

Studies by Karagunduz et al. (2007) showed that the sorption of DDT molecules from the aqueous phase (water) to sorbed phase of surfactant can be represented as follow:

$$\mathbf{S_{SS,DDT} = S_{SS}\, K_{ss}\, C_{aq,DDT}} \qquad \mathbf{(7)}$$

where $\mathbf{S_{SS}}$ is the mass of sorbed surfactant (M/M) and $\mathbf{K_{ss}}$ is the DDT distribution coefficient between sorbed surfactant and water (L^3/M).

Due to the sorption of aqueous phase ($K_{mm} > 0$) surfactant monomers associated with DDT molecules, an additional sorption term is required to quantify the sorption of DDT (Karagunduz et al., 2007). In other words, the **total sorbed DDT mass** will be a combination of Eqs. (5) and (7):

$$\mathbf{S^*_{DDT} = (K_D + S_{SS} K_{SS})\, C_{aq,DDT}}$$

$$\mathbf{S^*_{DDT} = K_D\,(1 + f_{SS/OC} K_{SS/OC})} \qquad \mathbf{(8)}$$

where $\mathbf{K_{SS/OC}}$ is equal to K_{SS}/K_{OC}, and $\mathbf{f_{SS/OC}}$ is equal to $\mathbf{S_{SS} f_{OC}}$.

The relationship developed by Sun et al. (1995) is obtained by combining Eqs. (3), (4) and (8).

$$K^* = (K_D + S_{SS}K_{SS}) / (1 + C_{mn}K_{mn} + C_{mc}K_{mc}) \quad (9)$$

when K^* is the apparent solute soil-water distribution coefficient (L^3/M) which tends to decrease at high surfactant concentrations (Karagunduz et al., 2007).

2.8 Surface Tension

Surface tension is used to quantify the critical micelle concentration (CMC) of surfactant (Muherei and Junin, 2009). As shown in Figure 7, surfactants exhibit a rapid fall in surface tension with concentration until the CMC is reached, where the surface tension becomes constant. In other words, above the CMC, the surface becomes fully loaded, with no further change in surface tension (Chu and Chan 2003).

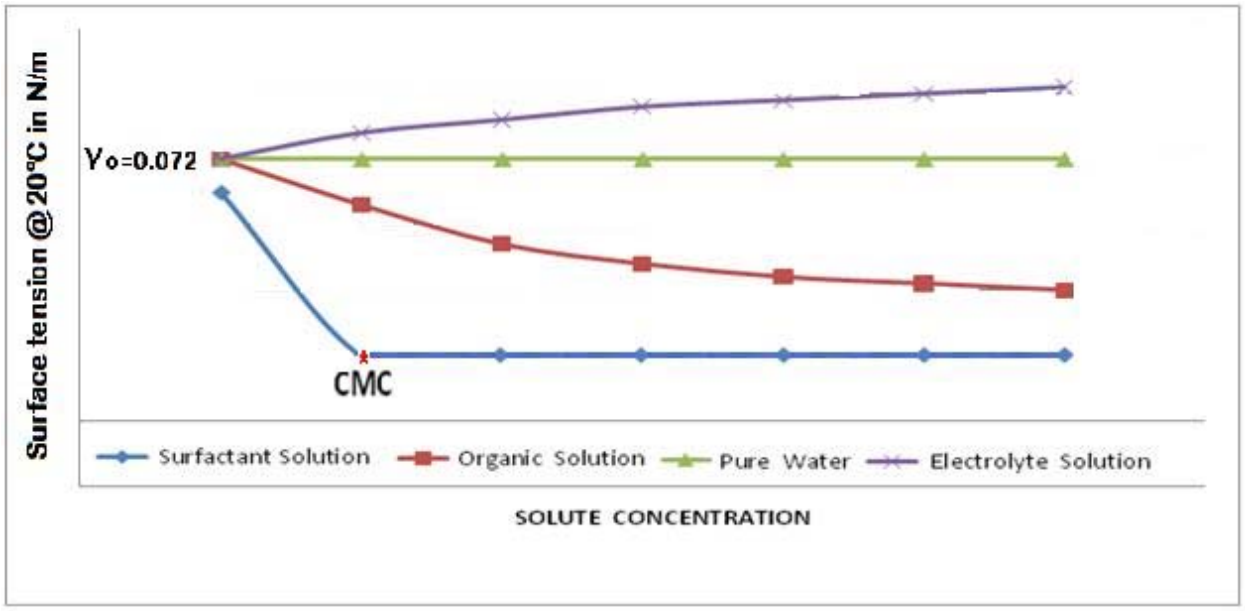

Figure 7. Surface tension vs solute concentration.
http://www.dur.ac.uk/sharon.cooper/lectures/colloids/interfacesweb2.html

Because they can reduce surface tension most effectively and have a low CMC (see Table 10), nonionic surfactants are often used in remediation process (Chu and Chan, 2003). The surface tension of the pure water @ 20°C in N/m is 0.072.

Chapter 3: Material and Methods

3.1 Sampling

Five soil samples were collected during the period from 28 August to 2 September 2008 from areas near agricultural land in southern Ontario. The specific location cannot be disclosed due to industrial confidentiality agreements. The sample material was obtained one meter below ground surface with the intention of reducing the presence of decaying organic matter. In the laboratory, the sample was dried and sieved with a # 12 screen (1.7 mm or 0.0661 inches; USA # 12 or Tyler = 10 Mesh) to remove large particles. Samples were stored at room temperature in clean 4L paint can containers, labelled #1 to #5.

3.2 Reagents

Hexane (purity>99.9%), ethanol (purity>99.9%), Tween 80 (purity>99%), Brij 35 (purity>99.9%) and SDBS (sodium dodecylbenzene sulfonate) (purity>99%) were purchased from Sigma Aldrich Chemical Company.

3.3 Surfactant Solution Preparation

Surfactant stock solutions were prepared by mixing a known percentage of surfactant into deionized water for different surfactant concentrations. The solutions were stirred for 10 min until all of the surfactant dissolved.

3.4 Soil Preparation

For each test, the samples were prepared with 25 ppm of DDT in soil. For the soil in these experiments, preliminary analyses showed that DDT concentrations were very low (less than 1μg/g). This soil was considered to be “clean”, relative to the concentrations that would be used in subsequent experiments. The following procedure was used in batch test samples preparation: First, 5 ml of a 50 ppm DDT solution in hexane was added to 10 g of soil. The solvent was then allowed to evaporate completely to yield soil with concentration of 25 ppm of DDT. In a similar way, leaching

column experiment samples were prepared, where 18.75 ml of a 200 ppm DDT solution in hexane was added to 150 g soil. Again the solvent was then evaporated completely.

3.5 Analytical Methods

3.5.1 COD Method

Chemical oxygen demand (COD) of surfactant solutions was measured as a surrogate analysis of the total concentration of surfactants in the aqueous washing fluids before and after leaching. According to Contreras et al., (2002), aggressive oxidizing agent (potassium dichromate) is used in the COD test. The reaction is performed in hot sulphuric acid solution and catalyzed by silver cation where the electrons from organic matter are transferred to dichromate. For this reason, the COD value does not include ammonia and only carbonaceous compounds are completely oxidized (Contreras et al., 2002). Hach Test 'n' tubes were used (0-1500 mg/L range) together with a Hach DR/2000 spectrophotometer and method number 435 (this method set at 620 nm for the high ranges where the amount of green Cr^{3+} are produced. Dilutions of about 1/20 of the surfactant solution were generally used to keep the concentration within the test kit range. The DDT concentration is negligible compared to surfactant concentrations, such that he majority of COD is attributed to surfactant. Blank experiments with water and surfactants contacted with soil did not indicate any significant interference by soil organics.

3.5.2 Water capacity test

Water capacity of soil samples was estimated by placing about 20 cm of soil into a 3.8 cm diameter column on bottom of about 3 cm of glass wool and 3 cm of glass wool over the soil. A measured amount of tap water was added slowly until the soil was completely saturated with a little water on top. The water that drained out of the bottom of the column was captured. Later, the column was drained for 2-3 days. After this, the water that was drained out was measured and compared with the total amount that was initially added.

3.5.3 Method to estimate the biodegradation rate of Brij 35 solution

Biodegradation rates of aqueous surfactant solutions were estimated by placing 100 mL of the solution into an Erlenmeyer flask and adding about 10 g of soil. A second (control) flask was prepared without the soil. The soil was swirled around for a few minutes then left to settle for 0.5 hours, at which point the liquid was decanted into a clean flask. Both flasks were agitated on a magnetic stirrer for several days and samples were withdrawn for COD analysis.

3.5.4 Tests with new soil

New soil was characterized after cleaning and removing rare particles such as plastic, metal and stones. The soil was dried and sieved (US # 12) to remove large particles. Then 10 g soil was placed in a small container to which 25 ml hexane was added. The soil was by a mechanical stirrer at 60 rpm for 24 hours and then left to settle for 1 hour. Finally, 1 μl of the liquid phase was introduced into a gas chromatograph for analysis.

3.5.5 Soil leaching batch test

A soil leaching batch was prepared by adding 5 ml of 50 ppm DDT solution in hexane to 10 g soil. The solvent was allowed to evaporate completely to leave behind approximately 25 ppm of DDT on the soil. The contaminated soil with DDT was put in a vial to which 25 ml of surfactant solution was added. The contents were mixed at 60 rpm for 24 hours and then left to settle for 1 hour. Then 10 ml of hexane was added to the 10 ml of leachate and stirred 30 more minutes in the roto-torque machine and then left to settle for another hour. Five ml of the resulting emulsion at the top was put into a closed vial to which 2 ml of ethanol was added to break up the emulsion. The contents were shaken gently for 10 seconds and allowed to settle for 1 minute. One μl from the top organic phase was removed for GC analysis.

3.5.6 Leaching column general test

Soil leaching column was prepared by making up a 200 ppm DDT solution in hexane and adding was added 18.5 ml of it to 150 g soil. The solvent was allowed to evaporate

completely to generate a soil sample containing approximately 25 ppm of DDT. Glass wool was put on the bottom of the column (2.5 cm x 30 cm). The contaminated soil with DDT was put into column and pressed down to make it compact, but not too hard. Again, glass wool was put on the top of the soil and then 250 ml of surfactant solution into column was added on top. Then 10 ml of hexane was added to the 10 ml of leachate from the first lot of 100 ml of recovered. The sample was stirred 30 minutes in the roto-torque machine and then left to settle for 1 hour. Five ml of the resulting emulsion at the top was put into a closed vial and 2 ml of ethanol was added to break up the emulsion. This was shaken gently for 10 seconds and allowed to settle for 1 minute. One μl from the top organic phase was analyzed by GC.

3.5.7 Leaching column global test

The global test considered 500 ml of surfactant solution and 100 ml of top water. Similar procedure in section 3.5.6 was made for the other four lots.

3.5.8 Gas Chromatographic Method

DDT, DDD, and DDE analyses were completed using gas chromatography. The samples (1 μL) were injected into a gas chromatograph (HP5890) equipped with a ^{63}Ni electron-capture detector (GC-ECD). The column used was an RTX-5 quartz capillary tube with an inner diameter of 0.53 mm, a film thickness of 0.50 μm and a length of 30 m. The column head pressure was set to 5 PSI. The carrier gas used was pure H_2 and the flow rate was 1 ml min^{-1}. The oven temperature started at 140°C and was increased to 280°C at 10°C min^{-1} with a final hold time of 2 min. Injector and detector interface temperatures were kept constant at 240 and 290°C, respectively. The peak height of speciation was used for quantification. Standard solutions of DDT, DDE and DDD were prepared in hexane at five different concentrations ranging from 0 ppm, 10 ppm, 50 ppm, 100 ppm and 200 ppm. Calibration was performed using linear regression analysis.

Figure 8 shows the flow sheet of the soil washing process used for testing mixtures of surfactants in this work.

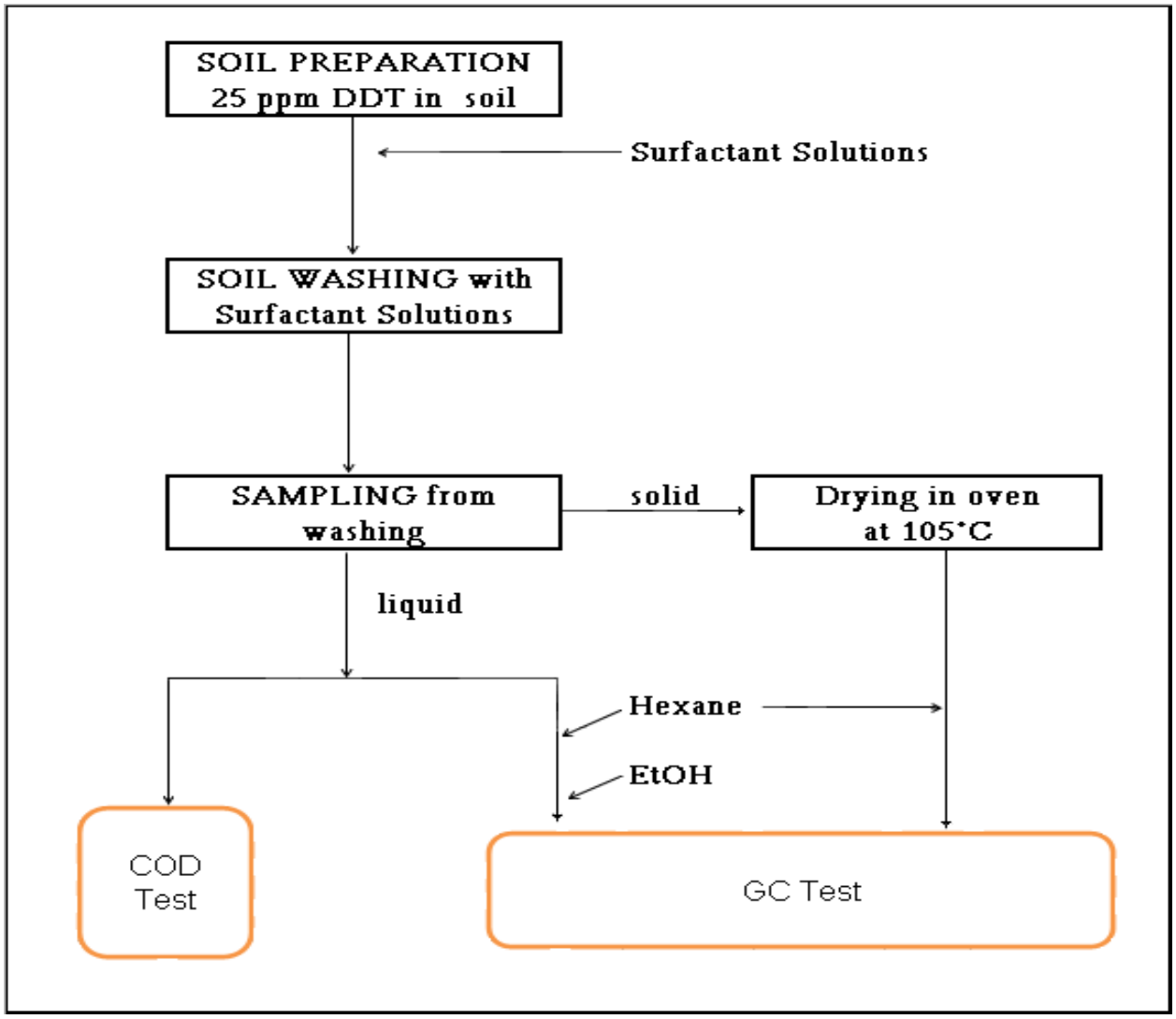

Figure 8. Flow sheet of the soil washing process used in this work. COD: Chemical oxygen demand, GC: Gas Chromatographic.

In other words, this flow sheet is the same to small and large scale. Initially, the soil was dried and sieved with a # 12 screen to remove larges particles such as plastic, metal and stones. First, the soil preparation is described in section 3.4 and soil washing with surfactant solutions is described in section 3.5.5 and 3.5.6. Second, sampling from washing considers both liquid and solid samples. The solid sample is dried a 105°C during 24 hours. Later, the exhausted soil was analyzed according section 3.5.4. Finally, the liquid samples were analyzed using section 3.5.1 (COD method) and 3.5.8 (Gas chromatographic method).

3.5.9 Carbon Adsorption Experiment

The removal of DDT, DDD, and DDE from surfactant solutions using activated carbon adsorption was tested by passing 500 mL (initial volume) of a 1% Brij + 0.1% SDBS surfactant solution (containing approximately 25 mg/L of each contaminant) through a column. The column contained 4 or 5 g of activated carbon (Sigma-Aldrich). The liquid passing through the column was collected and again passed through the column. This process was repeated several times. Samples were collected for DDT analysis after each pass. The COD of the surfactant solution was tested at the beginning and end. In one experiment, the carbon was reused for each pass, while in another case the carbon was replaced after each pass.

Chapter 4: Results and Discussion

4.1 Screening

In this research, the first screening and selection of surfactants was developed by a review of the available literature. According to Keller and Rickabaugh (1992), longer alkyl chain compounds display lower CMC's and so are potentially most effective. Based on this and considerations of environmental impact, expected performance, safety and cost, the nonionic surfactants Tween 80 and Brij 35 were selected for this study. Figure 9 shows the main structure of Tween and Brij surfactants.

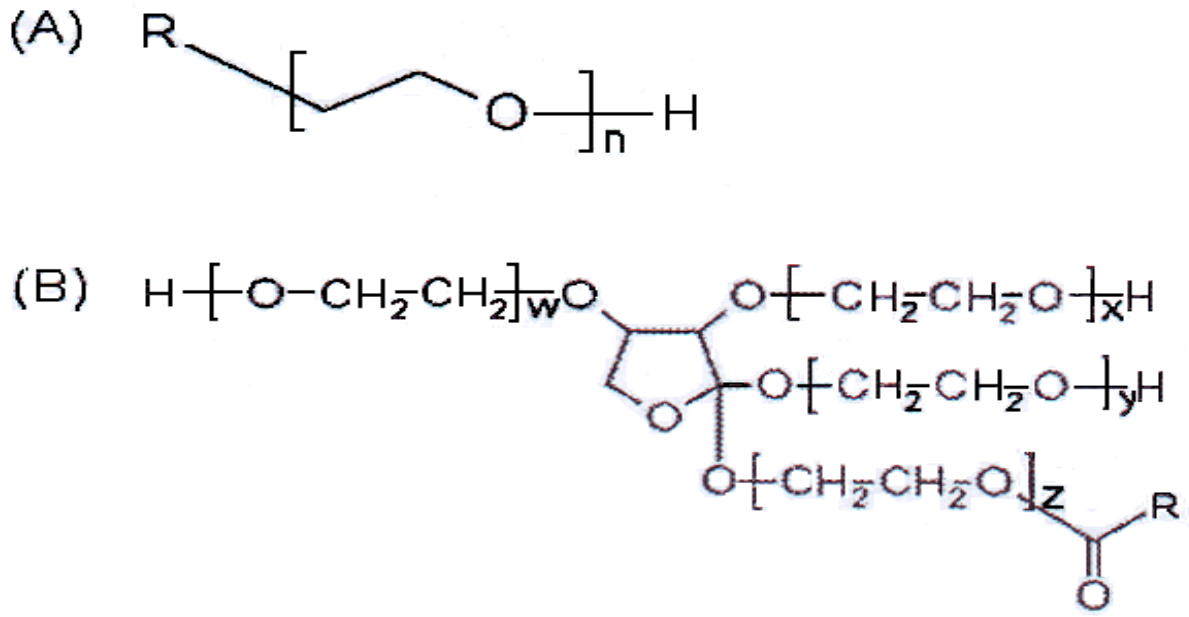

Figure 9. General formula: (A) Brij (polyethoxylates), (B) Tween (sorbitan derivates). R = alkyl chain, and n = number of ethoxylate groups present in the molecule. (Franzetti et. al, 2008)

A comparison of the surfactant considered for this study is summarized in Table 11.

Table 11. Surfactant's CMC. (Sigma, 2009)

Item		Surfactant					
		Tween **80**	**B**rij **35**	**T**riton X-**100**	**S**DS	**P**PG	**S**DBS
MW (g/mole)		1310	1225	625	288.4	1620	348.48
CMC	mg/L	35 - 45	92	110 -150	963 - 2420		
	%w/v	0.0016	0.1103	0.0155	0.17 - 0.23		
	mM	0.012	0.05 - 0.10	0.2 - 0.9	7 - 10	0.04	
Hazardous?		No	Yes			No	Yes
Environmental		A food-grade surfactant.		Octyl phenyl structure may be an endocrine disruptor.	Permitted in pharmaceuticals.	Some grades are only available as solids.	May have limited bio-degradability due to benzene ring structure.
Use for DDT?		Removed 72% of phenanthrene (0.2% Tween 80). Solubilized about 13% of DDT fro soil (0.75% Tween 80)	Increased DDT water solubility by $10^{5.8}$	Increased DDT water solubility by 10^{6}. Removed up to 45% of DDT (1% Triton X-100)	Increased DDT water solubility by $10^{5.4}$. Removed 25% of DDT after repeated washing (1% SDS concentration)	Removed up to 25% of DDT (2% PPG)	Solubilized 13% of DDT from soil (0.75% SDBS)
Adsorption to soil?		Moderate	Slight	Moderate	High		Very High

0-**Least**, 1-**Slight**, 2-**Moderate**, 3-**High**, 4-**Very High**; **SDS** = sodium dodecyl sulfate; **PPG** = polypropylene glycol ethoxylate; **SDBS** = sodium dodecylbenzene sulfonate; **Brij 35** = polyethylene glycol alkane ether; **Triton X-100** = polyoxyethylene octyl phenyl ether; **Tween 80** = polyoxyethylene sorbitan monoleate; SDS and SDBS are **anionics**; Brij 35, Tween 80, PPG and Triton X-100 are **non-ionics** surfactants.

4.2 Soil analysis

4.2.1 Soil pH

A sample of soil was taken from sample container # 1 and mixed with a small amount of deionized water to form a slurry sample. The pH was measured with a calibrated pH meter, and found to be 8.1 which puts it in the category of alkaline soil.

4.2.2 Moisture content

The original soil samples were sent to Maxxam Analytics (Waterloo, ON) for an independent analysis of DDT. It is very important to mention that the DDT data obtained by Maxxam are showed in Table 12 and Table 14.

Table 12. Soil analysis by Maxxam.

Maxxam Sample #	Description	Moisture Content (%)	**DDT** (μg/g)
101	Sample from site # 1	16	0.69
102	Sample from site # 2	14	1.50
103	Sample from site # 3	13	8.00
104	Sample from site # 4	15	1.40
105	Sample from site # 5	14	0.48

The samples were obtained from different locations at the same larger site. The results in Table 12 show that the soil samples are very heterogeneous with a wide range of DDT content and other metabolites. Using our own method to analyze DDT, the heterogeneous values were showed in Table 13 and even when samples are taken from the same container there is some difference. For example, two samples from container # 1 have different values, 0.1940 and 0.2468 due to this heterogeneity and analytical variance.

Table 13. Soil analysis in this work (10 g soil/ 25 ml hexane)

Container	Maxxam	This work (duplicates)					
#	(μg/g)	ng/μL		ave.	(μg/g)		ave.
1	**0.69**	0.1940	0.2468	0.2204	0.4849	**0.6171**	0.5510
2	**1.50**	0.4188	0.5330	0.4759	1.0470	**1.3325**	1.1897
3	**8.00**	2.1470	2.9648	2.5559	5.3674	**7.4121**	6.3897
4	**1.40**	0.3314	0.4218	0.3766	0.8285	**1.0545**	0.9415
5	**0.48**	0.1871	0.1909	0.1890	0.4678	**0.4772**	0.4725

This heterogeneity presents a challenge in performing experiments using the soil samples from the contaminated site. Taking everything into account, the variability of the DDT data is due primarily to the heterogeneity of the soil, and similar results were obtained by University of Guelph collaborators working with the same soil samples (data not shown). Comparison between Maxxam and our analytical method shows that the trends are similar, if the absolute values differ somewhat. Maxxam values tend to be higher, likely because of a more aggressive extraction process used in their analysis (i.e. Soxhlet extraction), versus the solvent micro-extraction technique used in this work.

The DDT analytical data showed in this thesis are reliable because each time that the sequence table to standard solution was worked out, the values in each standard solution (0 ppm, 10 ppm, 50 ppm, 100 ppm and 200 ppm) are similar. For example, if 1μL of a 50 ppm standard solution in hexane was introduced into GC, the value is identical.

Therefore, preliminary analyses in Table 13 show that DDT concentration is variable. For this reason, it was decided to work only with container # 5 because its DDT concentration was consistently very low (less than 1μg/g), and this soil was considered to be “clean”, relative to the concentrations that would be required for further experimental work (25 mg/kg, as discussed in Section 3.5.5). It was determined in preliminary experiments that these higher concentrations were necessary for adequate analytical sensitivity when testing surfactant leachates, and use of the original soil (without additional DDT) would not be practical.

4.3 Preliminary soil leaching test

Initially, 20 g of soil from site # 3 was used with 48 mL of surfactant solution. After two days of extraction, the aqueous phase was decanted and the soil contacted again with pure water, which was then decanted. The soil samples were sent to Maxxam for DDT analysis. The results are shown in Table 14.

Table 14. DDT remaining in the soil.

Maxxam Sample #	Description	**DDT** + DDD + DDE (μg/g)
1AS	1% Tween 80 solution.	10
2AS	0.5% Tween 80 solution.	10
3AS	1% Brij 35 solution	19
4AS	0.5% Tween 80 + 50 mg/L KCl	40
5AS	Water only	16

According to Table 14, initially Tween 80 solution achieved a better efficiency for DDT removal than Brij 35 solution at small scale (10 g soil). The addition of KCl did not enhance removal, in contrast to the results of Paria (2007), and possibly interfered with DDT removal, so this approach was not pursued further. Later, it will be seen that Tween 80 did not follow the same tendency in the subsequent tests because of its biodegradability into soil in large scale (150 g soil).

4.4 Surfactant Analysis Methods

In order to adequately assess the need for make-up amounts of Tween due to soil adsorption, a rapid method is needed to measure the concentration of the surfactant in leachates draining from the soil. This would be especially important for field applications of a washing process where quick feedback on the surfactant concentration in the wash stream would be desirable.

An initial attempt was made to measure the Tween 80 concentration with UV spectrophotometry. While pure standard solutions yielded UV absorbance peaks that could be used to quantify the surfactant, the presence of soil components extracted with the Tween 80 caused significant interference so that the approach was abandoned.

A “CTAS” method (cobalt thiocyanate active substances) was selected based on literature reports where it was applied to wastewater and industrial applications (Boyer et al., 1977; Holt et al., 1998). In this method, cobalt thiocyanate (a blue compound) is allowed to interact and bind with the non-ionic surfactant molecules (Tween 80) to form tetrathiocyanatocobaltate(II) complex that is transferred to a nonaqueous phase (dichloromethane) and measured using visible spectrophotometry. The cation associated with this complex is usually ammonium ion (Schmitt, 2001).

Two different applications of the method were attempted: 1) the aqueous surfactant was mixed with cobalt thiocyanate and then extracted into dichloromethane; and 2) the surfactant was extracted by dichloromethane by first (in an attempt to eliminate interfering compounds) and then complexed with cobalt thiocyanate in the organic phase in a slow process. Four standard solutions of Tween 80 were prepared for calibration purposes for analysis of the leachate samples from soil washing experiments, as well as water-only blanks.

After comparing the standard solutions with the leachates from soil washing experiments, it was concluded that the CTAS methods, while straightforward and rapid, were too non-specific for the non-ionic surfactant. Other soil components in the leachate were apparently complexing with the cobalt thiocyanate, leading to erroneously high readings. The water-only blanks did not have this problem with high readings. Therefore, it appears that the surfactant leaches hydrophobic compounds from the soil that interact with the CTAS reagent in addition to the surfactant itself. The conclusion is that the CTAS method does not appear to be a useful analytical method for monitoring surfactant concentrations in the wash solution.

According to Schmitt (2001), it is important to remember that the commercial nonionic surfactants do not absorb radiation in the visible spectrum, and the simplest form of spectrophotometric analysis of nonionics is the direct measurement of the UV absorbance of the sample, but because of the sensitivity of direct UV analysis to interference, it can only be used in well-defined situations.

In other words, the cobalt thiocyanate method is based upon formation of a tetrathiocyanatocobaltate(II) complex with materials containing polyether linkages which are extractable from water into organic solvents where ammonium ion is the cation associated with this complex. It was concluded that the CTAS methods did not work because of other soil components in the leachate were apparently complexed with the cobalt thiocyanate.

Subsequently, a COD (chemical oxygen demand) method was tested using a Hach Test-N-Tube reagent kit (0-1500 mg/L range). This method is fairly rapid (about 2 hours for a batch of samples) and can be performed in remote locations with portable equipment. COD is based in oxidative processes and the electrons from organic matter are transferred to dichromate, and interfering compounds would have to be readily oxidizable under the test conditions. Standards and samples were diluted 1/20 to keep the results within the acceptable range for the test method, which would further dilute any interfering compounds. Comparison of standards and samples from column washing did not indicate any significant interferences from soil compounds, and so it was concluded that the COD method is an adequate quick analysis for surfactant solutions. In other words, COD could be used as a surrogate indicator to analyze the changes in surfactant concentration during and after soil washing process. Typical COD values for the Tween 80 standards are shown in Table 15.

Table 15. COD measurement as an indicator for surfactant concentration.

Concentration	COD (mg/L) after 1/20 dilution
1.0 % Tween 80	1001
0.5 % Tween 80	301
0.1 % Tween 80	103
0.01 % Tween 80	12
0 (deionized water)	0

4.5 Surfactant Losses in Soil

Efficacy of a soil washing process depends in-part on minimizing the loss of surfactant via adsorption on the soil, since any lost surfactant must eventually be replenished to maintain the enhanced solubility of DDT in the aqueous solution. Therefore, several

tests were performed to quantify these losses (as characterized by COD change, as discussed in the previous section).

Previous studies suggest that losses might be in the range of 5 mg surfactant per g soil (Ahn et al., 2008), but it is likely that this loss is highly variable and dependent on the nature of the specific soil, such as the amount of organic material. Likewise, since the soil is a biologically active material, it is possible that some surfactant may be lost through biodegradation during the soil contact process. Experiments focusing on these are discussed in the following sections.

4.5.1 Soil Adsorption

Approximately 2 pore volumes of a 1% Tween 80 solution were passed through a column (approximately 2 cm diameter by 15 cm high) filled with soil from sample #3 (discussed above) six times in series (not recirculated), followed by 6 rinses with similar volumes of tap water. The concentration of surfactant in each wash was determined by the COD method, and the results are shown in Figure 10.

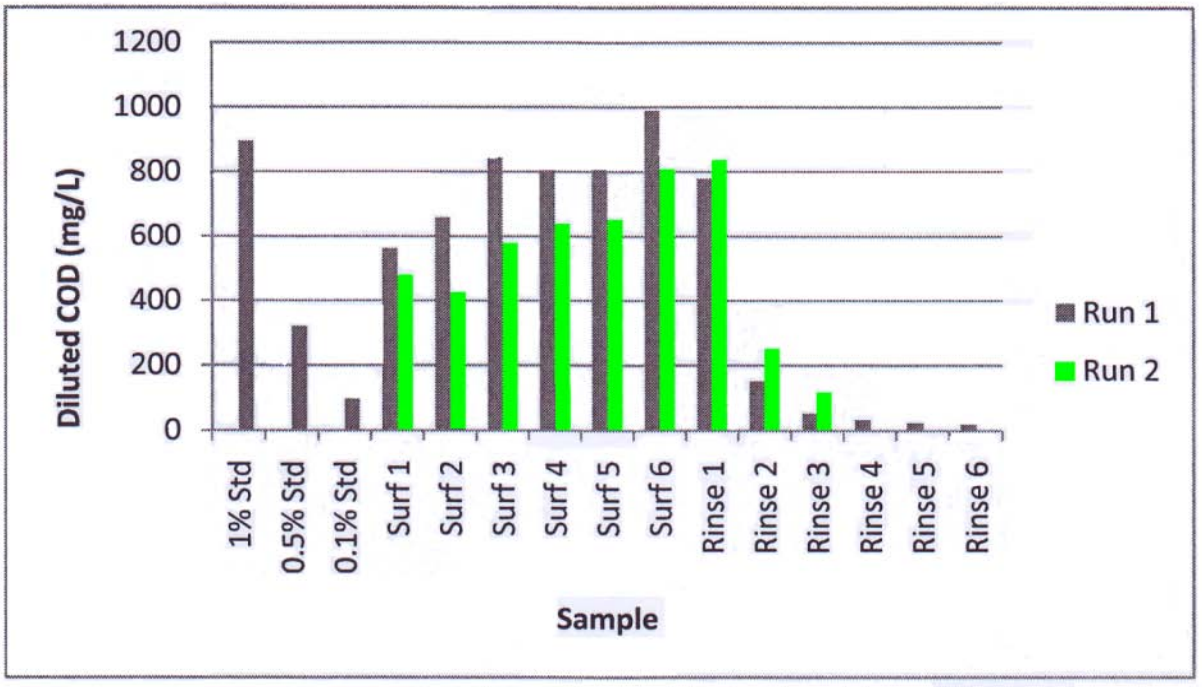

Figure 10. Column washing adsorption test results.

Figure 10 indicates that approximately 25% of the surfactant (as measured by COD) was adsorbed during the first 2 surfactant washes (Surf 1 and 2, compared to the 1% Std value), but subsequent washes approached the same value of COD as the initial surfactant solution. Furthermore, the first rinse with tap water (Rinse 1) appeared to desorb a significant amount of surfactant, while subsequent rinses had very little effect. This result was repeated a second time (Run 2) which showed similar trends with a fresh sample of the same soil. Even when adsorption occurs, the surfactant concentration in the solution leaving the column was above 0.5% (5000 mg/L), which is well above the CMC reported for Tween 80 (about 25 mg/L, Franzetti et al., 2006). Therefore, it would still be expected that significant amounts of DDT could be solubilized although a portion of the surfactant was lost through adsorption.

In a second adsorption test, a fixed volume of 1% Tween 80 was contacted with varying amounts of soil (from the same soil sample as the previous adsorption tests), and the COD was analyzed after a few hours of contact. The results are shown in Figure 11.

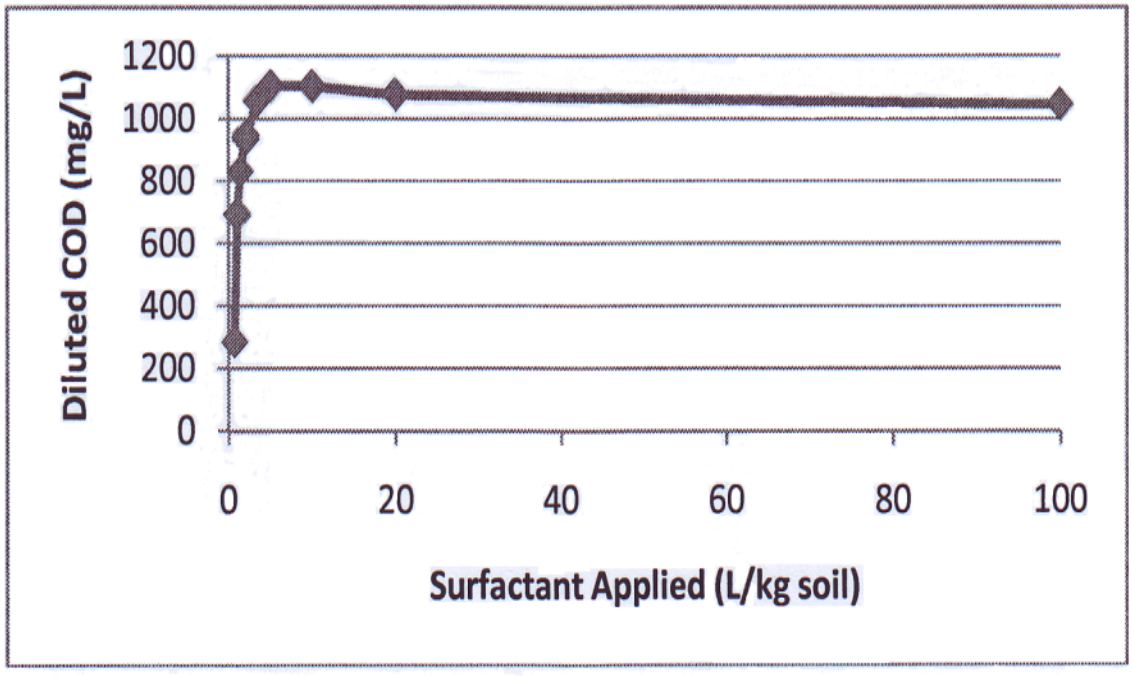

Figure 11. Second adsorption test: fixed amount of surfactant with varying amount of soil.

Figure 11 indicates that it requires about 5 L of surfactant solution (containing 1% Tween 80) to completely overcome the adsorption losses to 1 kg of soil, such that the remaining solution contains a significant amount of surfactant. Lower levels, such as 1 L/kg, are likely satisfactory since the adsorption does not deplete the surfactant concentration to a value below its CMC. At high values of surfactant applied (about 3 to 100 L/kg), the adsorption of surfactant is approximately 5 mg/g soil, which agrees well with Ahn et al. (2008). However, at low levels (less than 3 L/kg), the adsorption apparently increases to between 15 and 80 mg/g, with the adsorption increasing as the amount applied decreases. This result does not fit with standard adsorption theory, and suggests that there is another process occurring, especially when the surfactant/soil ratio is very low. It is believed that these results are confounded by simultaneous biodegradation of the surfactant, and this was explored further.

4.5.2 Surfactant Biodegradation

Another loss mechanism for surfactant is through biodegradation. Although this is desirable, since it minimizes the long-term impact on the soil, it is undesirable if it occurs too fast and the solubilization of DDT is affected during the soil washing process. A series of experiments were performed to assess the rate and extent of biodegradation in 1% Tween 80 solutions that had been passed through a soil sample (to inoculate them with soil microbes). These results are summarized in Figure 12, where Test 2-S is a sterilized control, and Test 3 is a mixture of 0.5% Tween 80 and 0.5% Brij 35.

The Test 1, Test 2 and Test 2-S were prepared with 1% Tween 80 solutions which original COD was 1600, but the Test 3 was prepared with a blend (0.5% Tween 80 + 0.5% Brij 35 solution) in which the initial COD was only 440, due to the lower Tween 80 concentration and lower inherent COD for Brij 35.

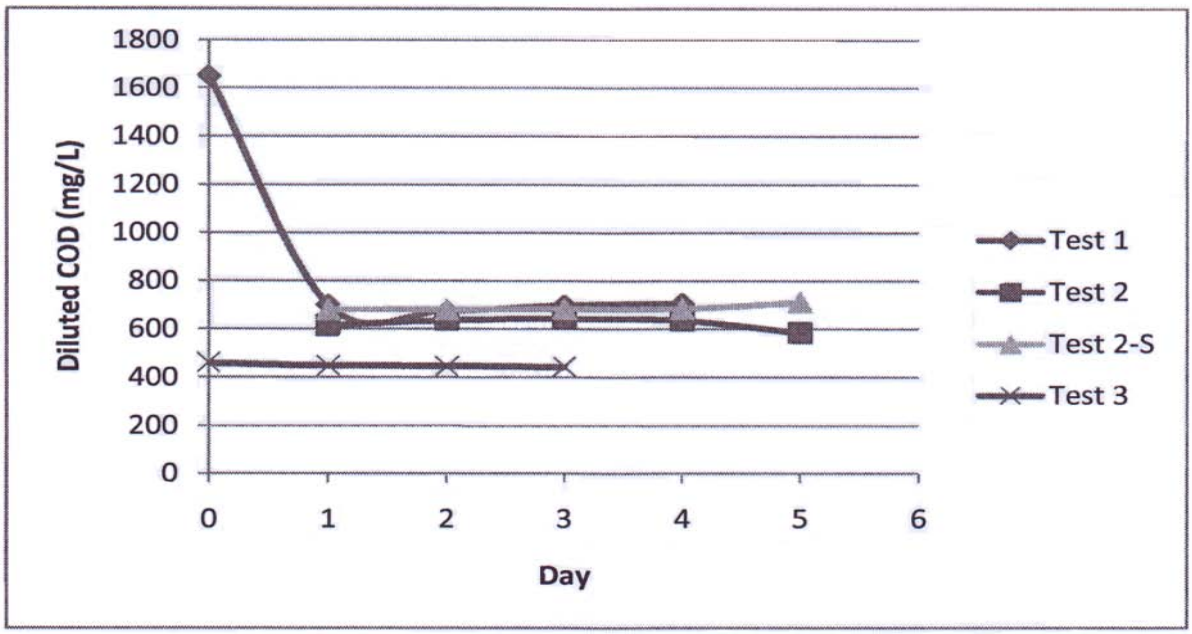

Figure 12. Surfactant biodegradation test. Test-1 and Test 2: 1% Tween 80 non-sterilized; Test 2-S: sterilized control; Test-3: mixture of 0.5% Tween 80 and 0.5% Brij 35 non-sterilized.

From Figure 12, a rapid decrease in COD is observed in the first 24 hours following contact with the soil (Test 1), after which the COD does not change significantly. In Test 2, the Day 0 sample was not available for analysis, but the trends in the following days are similar to Test 1. Test 2-S involved a portion of the surfactant solution that was steam sterilized to eliminate microbial activity, but showed no significant difference from that observed during Test 2. In Test 3, a surfactant blend was used (0.5% Tween 80 + 0.5% Brij 35), which suggested that the presence of Brij 35 (which is somewhat less biodegradable than Tween) appeared to stabilize the concentration. Further tests are required to confirm this result and to assess the adsorption and DDT solubilization of a surfactant blend.

4.6 Testing mixtures of surfactants

4.6.1 Small Scale Batch Experiment

According to the method described in section 3.5.5, the removal of DDT in a small scale was tested in the presence of several sets of surfactant combinations to yield the results shown in Table 16.

Table 16. Amount of DDT removed in batch system after 24 hrs.

Solution	ng/μL		ave.
2% Brij 35 + 0.5% SDBS	13.86	15.94	14.9
2% Brij 35 + 2% Tween 80	13.16	15.44	14.3
2% Brij 35	12.42	15.18	13.8
0.5% Brij 35 + 2% Tween 80	11.43	13.97	12.7
1% Brij 35 + 1% Tween 80	11.47	13.73	12.6
1% Brij 35 + 4% Tween 80	11.25	13.75	12.5
1.5% Brij 35	10.98	13.42	12.2
0.5% Brij 35 + 0.5% Tween 80	9.09	11.11	10.1
2% Brij35 + 0.5% SDBS + 0.5% EtOH	17.21	19.80	18.5
1% Brij 35 + 2% EtOH	8.92	10.68	9.8
2% Tween 80	5.22	6.38	5.8
1% Tween 80	3.07	3.53	3.3
1% Brij 35 + 1% EtOH	4.32	5.08	4.7

From Table 16, some observations can be made: 2% Brij 35 alone can achieve a good efficiency for DDT removal (13.8 ng/μL), while 2% Tween 80 only removes 5.8 ng/μL. The lower performance of Tween 80 is possibly due to the presence of a sorbitan carbon group and longer carbon branches, which reduce the ability of the surfactant micellar core to dissolve organics (Jafvert et al., 1994). In addition, this behavior is attributed to the strong interaction of Tween 80 with the soil (Karagunduz et al., 2007), although Tween 80 is also known to be more biodegradable than Brij 35, both in liquid and in solid phase (Franzetti et al., 2006). For example, in 2% Brij 35 + 0.5% SDBS solutions (nonionic-anionic mixed surfactant system), the presence of anionic surfactant greatly decreased the partitioning loss of nonionic surfactant (Paria, 2007). This may have led to the increase in DDT removal efficiency to 14.9 ng/μL due to higher cloud

points and lower kraft points than those of the single surfactant (Paria, 2007). In the 2% Brij35 + 0.5% SDBS + 0.5% EtOH system, there is a good potential to increase both the performance of contaminant extraction and the pollutant degradation.

Adding a solvent such as ethanol (EtOH) to the surfactant solution (both single or mixture of surfactants) can reduce the adsorption of surfactant to the soil particles and increase the efficiency of DDT removal from soil (Ganeshalingam et al., 1994). Ethanol concentrations of 2% enhanced extraction compared with concentration of 1%. The data from Table 16 are shown in Figure 13. The use of a co-solvent (ethanol) was tested for interest, although in practice it raises problems with potential air emissions due to evaporation and with worker safety due to flammability issues.

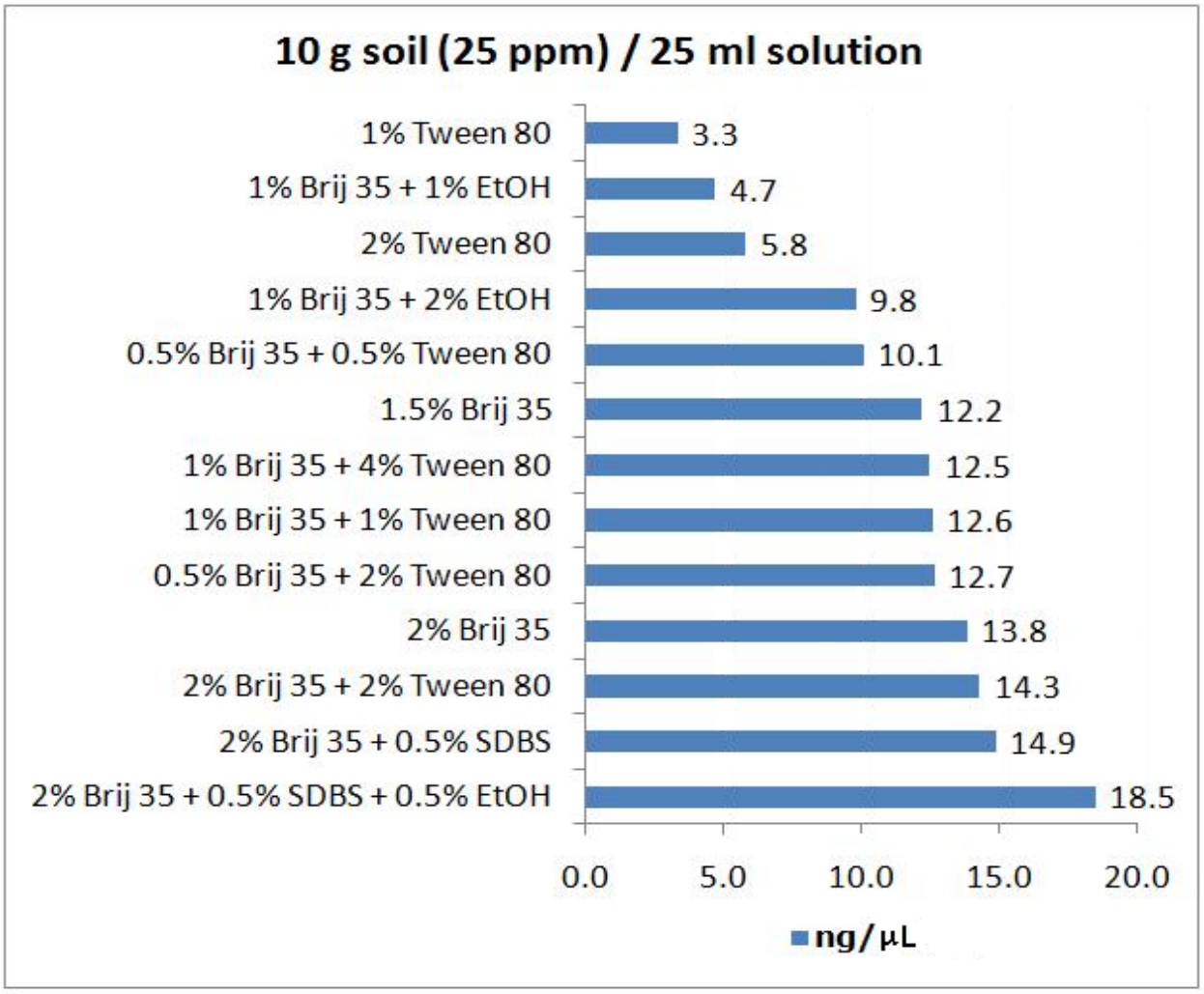

Figure 13. Extraction in small scale.

4.6.2 Larger Scale Leaching Column Experiments

Chandler et al., (1997) have shown that leachability depends on a number of physical parameters such as homogeneity, particle size, porosity, permeability of the solid phase influencing the flow rate and contact time between solution and solid, temperature, pH, redox condition, total organic carbon content, chemical reaction kinetics, chemical speciation of contaminants and complexation with other contaminants.

Since soil leaching is a passive form of washing, it was the recommended remediation technique because materials handling and soil/liquid separation would be avoided unlike other processes for soil excavation and mixing/washing (Evangelista et al., 1990).

Considering that the blend between Brij and SDBS gave the best results during the small scale experiments, this combination was tested in more detail in larger scale. The use of a co-solvent was abandoned because of the practical concerns. It has also been reported that the surfactant may create a bridge to link the solvent, pollutant, air and water molecules together, resulting in a stable and inseparable emulsion that can cause the failure of the soil-washing process (Chu and Kwan, 2003). Following the methods described in section 3.5.6, the removal of DDT in a leaching column was tested for several sets of surfactant combinations to yield the results shown in Table 17.

Table 17. Amount of DDT removed in leaching column experiments.

Solution	ng/μL		ave.
2% Brij 35 + 1% SDBS	44.43	47.17	45.8
2% Brij 35 + 0.1% SDBS	36.10	40.30	38.2
2% Brij 35	33.44	37.16	35.3
2% Tween 80	23.83	27.97	25.9
1% Brij 35	18.38	22.02	20.2
0.1% Brij 35 + 1% SDBS	16.20	19.80	18.0
1% Tween 80	15.36	18.04	16.7
0.5% Brij 35	12.33	15.07	13.7

4.6.3 Mass Balance

To assess DDT removal and the analytical methods, the following mass balances were performed:

Mass (μg) = (GC value) * (volume lot / volume sample) * (volume emulsion/ volume considered) * (volume hexane after EtOH). (10)

Where "GC value" comes from the calibrated gas chromatograph (38.2 ng/μL), "volume lot" represents the total volume in first lot (102 mL), "volume sample" considers only 10 mL from the first lot to be analyzed, "volume emulsion" is 10 mL of emulsion formed, "volume considered" is the 5 mL of emulsion to be mixed with 2 mL EtOH and then "volume hexane" after EtOH is the 4 mL of the final hexane phase where DDT content is recovered. The aqueous phase is 3 mL.

For example, the first 100 mL of leachate from the 2% Brij + 0.1% SDBS solution contained 38.2 ng/μL. In other words, 10 mL of leachate from the first lot was considered to be analyzed. This sample was combined with 10 mL of hexane and stirred in roto-torque machine during 30 minutes. As a result, there were 10 mL of emulsion. Then, 5 mL of the emulsion was combined with 2 mL ethanol to break the emulsion. It was produced two phases, the top-hexane phase (4 mL) and bottom-aqueous phase (3 mL). Finally, 1 μL of sample from top-hexane phase was injected into GC. Using equation **(10)** we have:

Mass (μg) = (38.2 ng/μL) * (102/10) * (10/5) * (4) = 3117.12 μg.

To prepare 25 ppm DDT in soil, 3750 μg of DDT was added to 150 g soil. Thus the % DDT recovered = 3117.12/3750 = 0.831 or **83.1 %**

Using the information from Table 17 and following the above example, the following DDT recoveries from the first 100 mL of leachate were obtained and shown in Table 18.

Table 18. DDT recovery (First 100 ml of surfactant solution.)

Solution	% Recovered
2% Brij 35 + 1% SDBS	99.7
2% Brij 35 + 0.1% SDBS	83.1
2% Brij 35	76.7
2% Tween 80	56.3
1% Brij 35	44.0
0.1% Brij 35 + 1% SDBS	39.2
1% Tween 80	36.3
0.5% Brij 35	29.7

The time required for passage of 100 mL of the surfactant solution is shown in Table 19.

Table 19. Time required for the passage of 100 mL of aqueous surfactant solution through the leaching column.

Solution	min
2% Brij 35 + 1% SDBS	1170
2% Brij 35 + 0.1% SDBS	100
2% Brij 35	86
2% Tween 80	118
1% Brij 35	70
0.1% Brij 35 + 1% SDBS	840
1% Tween 80	165
0.5% Brij 35	60

Considering Tables 18 and 19, it was noted that the combinations of 2% Brij 35 (non-ionic surfactant) and 1% SDBS (anionic surfactant) yielded the highest % recovery, but the time required (Table 19) for the passage of 100 mL of aqueous surfactant solution through the 150 g soil (25 ppm DDT) in leaching column was very high. Since the

kinetics of the process can have an impact on overall cost, the rates of removal of DDT were obtained using this data (Table 20).

Based on this, the solutions containing 1% SDBS are seen to have low DDT removal rates (Table 20). However, if the SDBS concentration is reduced to 0.1% SDBS or eliminated altogether, the time is also reduced so that the removed rate becomes more reasonable. In addition, 1% and 2% Tween 80 solutions yield moderate recoveries and rates because it adsorbs moderately onto soil. Finally, 0.5% – 2% Brij require only a short time to pass through column because Brij 35 only weakly adsorbs onto soil.

Table 20. Rate of removal of DDT in column leaching with different surfactant solutions.

Solution	ng/min
2% Brij 35 + 1% SDBS	0.039
2% Brij 35 + 0.1% SDBS	0.382
2% Brij	0.410
2% Tween 80	0.219
1% Brij 35	0.289
0.1% Brij 35 + 1% SDBS	0.021
1% Tween 80	0.101
0.5% Brij 35	0.228

The effect of SDBS on flowrate through the column is likely due to its anionic behaviour. Anionic surfactants have been known to disperse and suspend clay particulates in soil. This behavior was observed in sample vials prepared during this work. Suspension and dispersal of clay particles may cause blockage of flow channels in the leaching columns and therefore reduce flow rates. In any soil washing process that relies on gravity drainage, this will be a significant problem. Figure 14 shows graphically the values shown in Table 20.

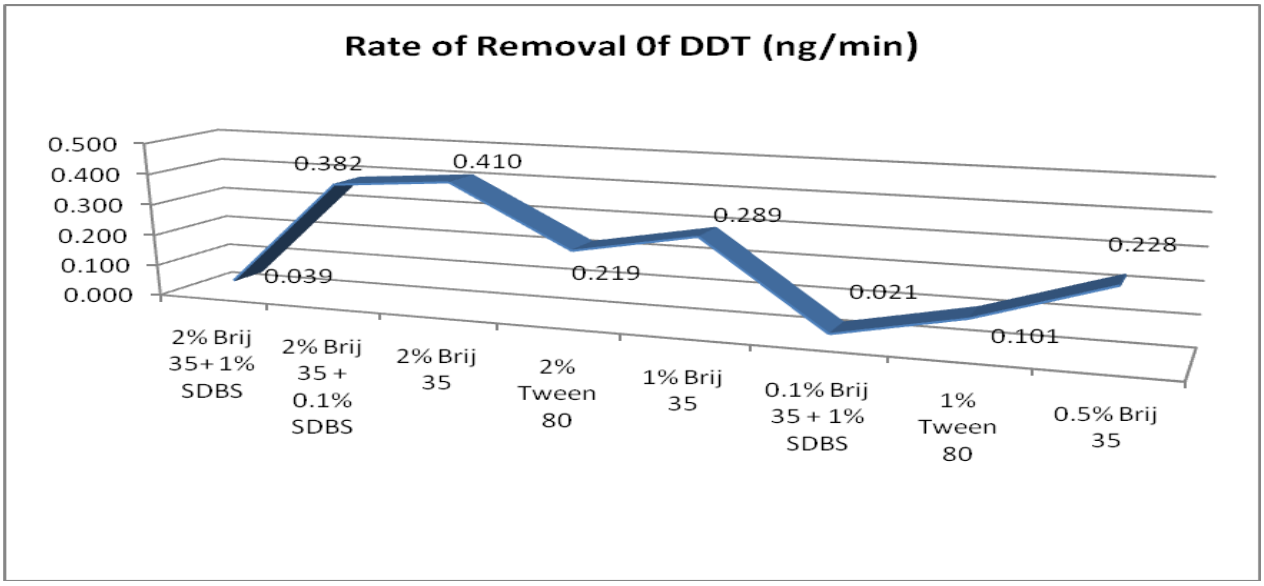

Figure 14. Rate of removal of DDT.

According to Figure 14, two combinations yield high removal rates of DDT, i.e. 2% Brij (0.410) and 2% Brij + 0.1% SDBS (0.382). For this reason, we have evaluated the reproducibility of these results following the same method as in the large scale leaching experiments.

To study the variability of the data obtained from the first 100 mL of leachate from both solutions, the method described in section 3.5.6 was used to yield the values shown in Table 21.

Table 21. Variations about the first 100 ml recovered leachate using two surfactant solutions

Run	ng/μL	
	2% Brij 35	2% Brij 35 + 0.1% SDBS
1	33.4	36.0
2	37.1	40.3
3	33.0	41.0
4	36.5	35.6
5	35.2	41.7
6	35.1	37.6
Average	35.0	38.7
Variation	+/- 1.6	+/- 2.6

According to Table 21, it can be seen that 2% Brij 35 solution can capture between 33.4 ng (2725 μg of DDT) and 36.6 ng (2987 μg of DDT) in the first 100 ml recovered. In a similar way, 2% Brij 35 + 0.1% SDBS solution can capture between 36.1 ng (2946 μg of DDT) and 41.3 ng (3370 μg of DDT) in the first 100 ml recovered.

Finally, a total mass balance for the 2% Brij 35 and 2% Brij 35 + 0.1% SDBS solutions yields the results in Tables 22 and 24, respectively.

Table 22. Mass Balance 2% Brij solution

Volume	2% Brij (ng)					%
ml	Run 1	Run 2	Run 3	Run 4	Average	Recovered
100	33.41	37.11	33.02	36.52	35.02	60.32
200	14.90	15.84	15.41	12.58	14.68	23.56
300	6.28	7.25	6.12	5.23	6.22	9.67
400	3.21	3.25	2.53	2.32	2.83	4.45
TW	1.70	1.84	0.90	0.65	1.27	2.01
						100.00

The results in Tables 22 and 23 indicate that 60.32% of the DDT is removed from the soil in the first 100 mL passed from the column and that the DDT concentration in the soil has been reduced from 25.0 to 9.92 ppm.

Table 23. Removal Time using 2% Brij Solution

Lot	Time lot (min)	Removal Time (min)	ppm in soil
	0	0	25.00
100	86	86	9.92
200	91	177	4.03
300	101	278	1.61
400	131	409	0.50
TW	160	569	0.00

The data from Table 23 are plotted in Figure 15.

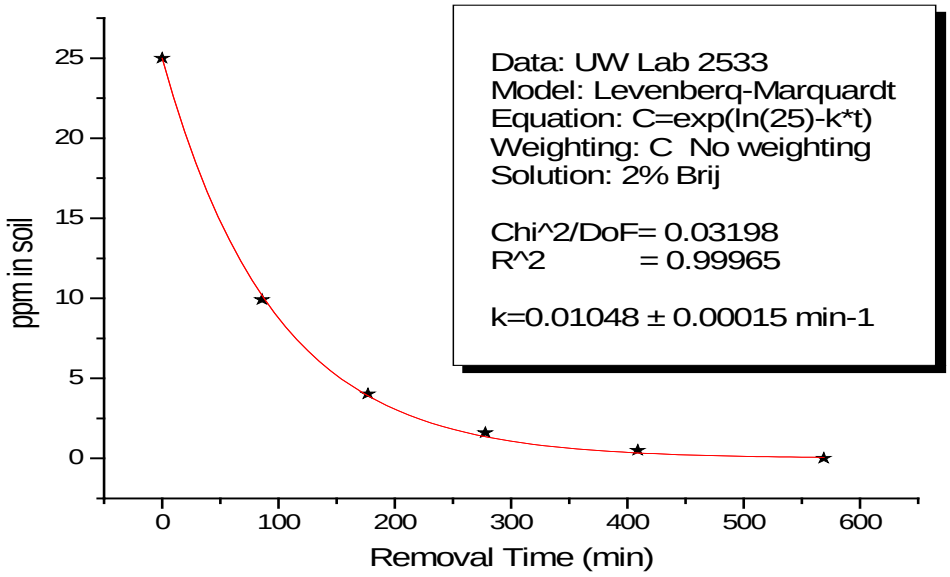

Figure 15. Removal Time using 2% Brij solution.

The decline in DDT concentration in the soil follows a first order kinetics (C_A=exp (lnC_{A0} – k*t)) where: K = 0.01048 min^{-1}, confidence interval = +- 0.00015 and Chi-sqr = 0.03198 (Method of fitting by Levenberq-Marquardt).

Table 24. Mass Balance 2% Brij + 0.1 % SDBS solution

Volume	2% Brij + 0.1% SDBS (ng)					%
ml	Run 1	Run 2	Run 3	Run 4	Average	Recovered
100	36.05	40.31	41.00	35.69	38.26	65.54
200	12.77	12.44	13.45	13.60	13.07	20.85
300	4.59	4.99	5.22	5.87	5.16	7.98
400	3.09	2.66	2.01	2.50	2.56	4.01
TW	0.92	0.84	1.20	1.18	1.03	1.62
						100.00

Following the same example above, 65.54% DDT is recovered in the first 100 mL from the column when 2% Brij 35 + 0.1% SDBS solutions is used. As shown in Table 25, only 8.61 ppm DDT remains in the soil.

Table 25. Removal time using 2% Brij 35 + 0.1% SDBS solution

Lot	Time lot (min)	Removal Time (min)	ppm in soil
	0	0	25.00
100	71	71	8.61
200	81	152	3.40
300	82	234	1.41
400	107	341	0.40
TW	139	480	0.00

The data from Table 25 is shown in Figure 16

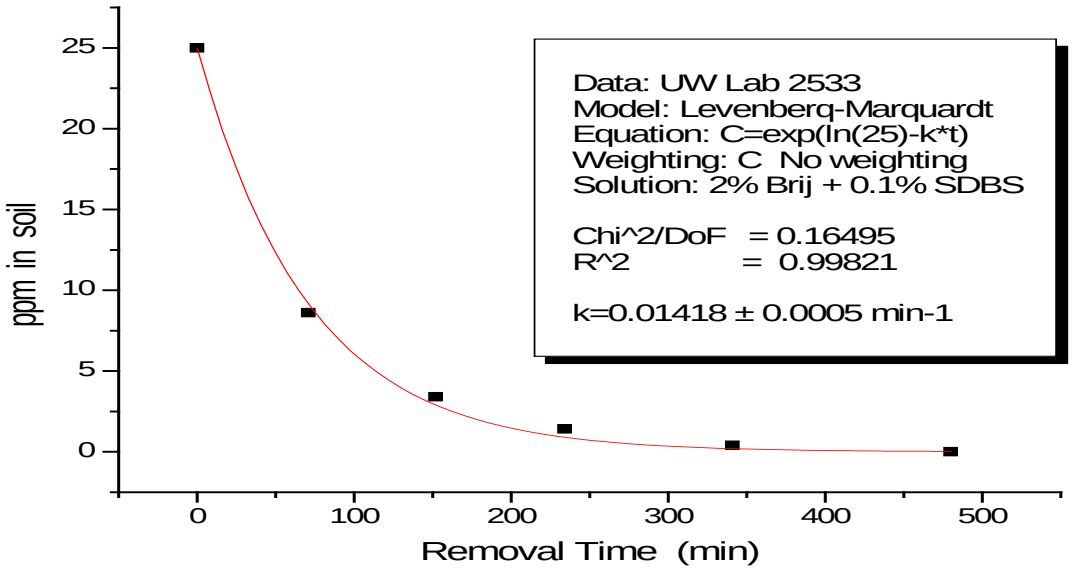

Figure 16. Removal Time using 2% Brij + 0.1% SDBS solution.

In similar way, the kinetics for DDT removed by a 2% Brij 35 + 0.1% SDBS solution shows first order behavior (C_A=exp(lnC_{Ao} – k*t)), where K = 0.01418 min^{-1}, confidence interval = +- 0.0005 and Chi-sqr = 0.16295 (Method of fitting by Levenberq-Marquardt).

The “cleaned” soil after each leaching process contains less than 1 ppm DDT. The average range is between 0.2 to 0.7 ppm.

According to Tables 22 and 24, we can conclude that the 150 g soil contaminated with DDT will be in better condition after contact with the first 300 or 400 mL of surfactant solutions in each process.

4.7 Recovery of Surfactant for Re-use

Up to this point, the importance of surfactants in the process of stripping of DDT from the soil is known. For economic reasons it would be desirable to continue to re-use the same surfactants once again or keep them clean for new work. One of the possible ways to do this is to use activated carbon to selectively remove the more hydrophobic DDT from the surfactant solutions. Ahn et al. (2008) used activated carbon to remove the hydrophobic polyaromatic phenanthrene from a Triton X-100 nonionic surfactant solution. Therefore, it was hypothesized that a similar approach might be successful in removing DDT from the surfactants used here.

To simulate the passage of surfactant solution through an activated carbon adsorption drum, such as might be used in the field, a volume of fresh contaminated surfactant solution was passed repeatedly through a column of activated carbon, as described in Section 3.5.9. DDT, DDD, and DDE concentrations were measured after each pass to yield the results are in Figure 17. In these experiments, 5 g of Sigma-Aldrich activated carbon were used in the column, while multiple volumes of 25 mL of contaminated surfactant solution were passed through the column. Figure 17 indicates that this activated carbon was capable of adsorbing the hydrophobic contaminants, although the amount removed was only about 50%. The shape of the curves in Figure 17 suggests that the adsorption capacity for the carbon was overwhelmed for this volume and concentration of fluid. In addition, the concentrations in the first pass are higher than expected and the curve does not follow a sigmoidal shape that might be expected for adsorption. This indicates either some type of adsorption interference by the surfactants or some analytical error.

Based on these preliminary results, it was estimated that the adsorption capacity of this carbon is in the range of 0.25 to 0.3 mg/g for each of the three contaminants, or approximately 0.85 mg/g for the total of DDT and its related compounds.

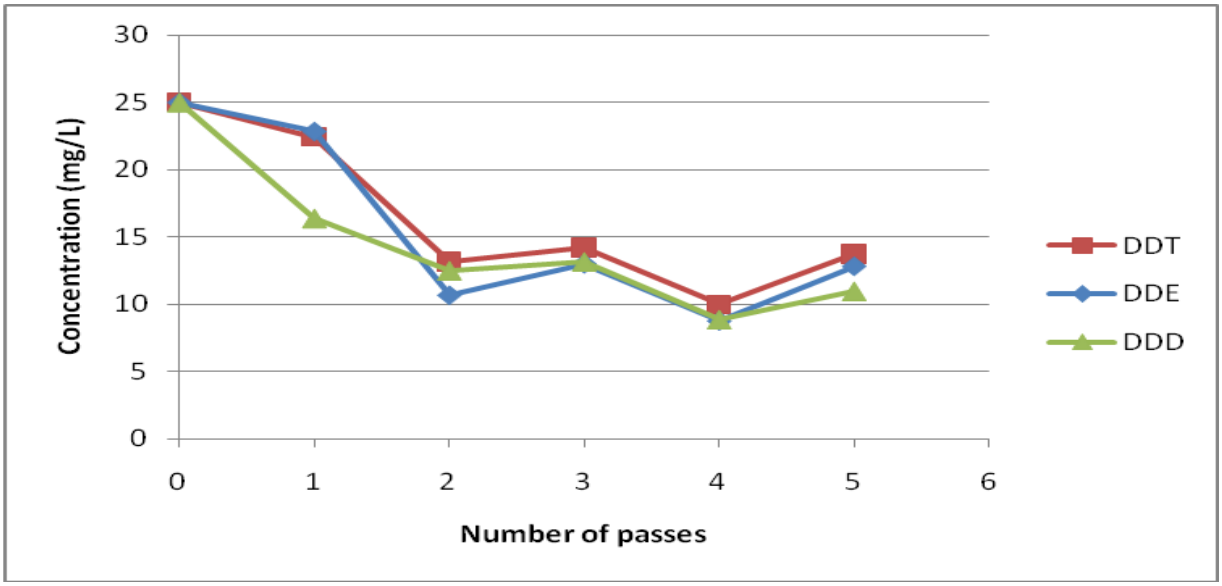

Figure 17: Change in contaminant concentration in the effluent from an activated carbon adsorption column (5 g), using 1% Brij 35 + 0.1% SDBS aqueous solution, 25 mL per pass.

To obtain a better understanding of the process, the adsorption experiment was repeated, but in this case a fresh amount of activated carbon (4 g) was used for each pass. An initial volume of 500 mL of surfactant solution was used so that it could be captured and re-used for each pass. This experiment was done to simulate the adsorption process in which a series of clean adsorption canisters were to be used in the field, and to determine more accurately when breakthrough might occur. These results are shown in Figure 18.

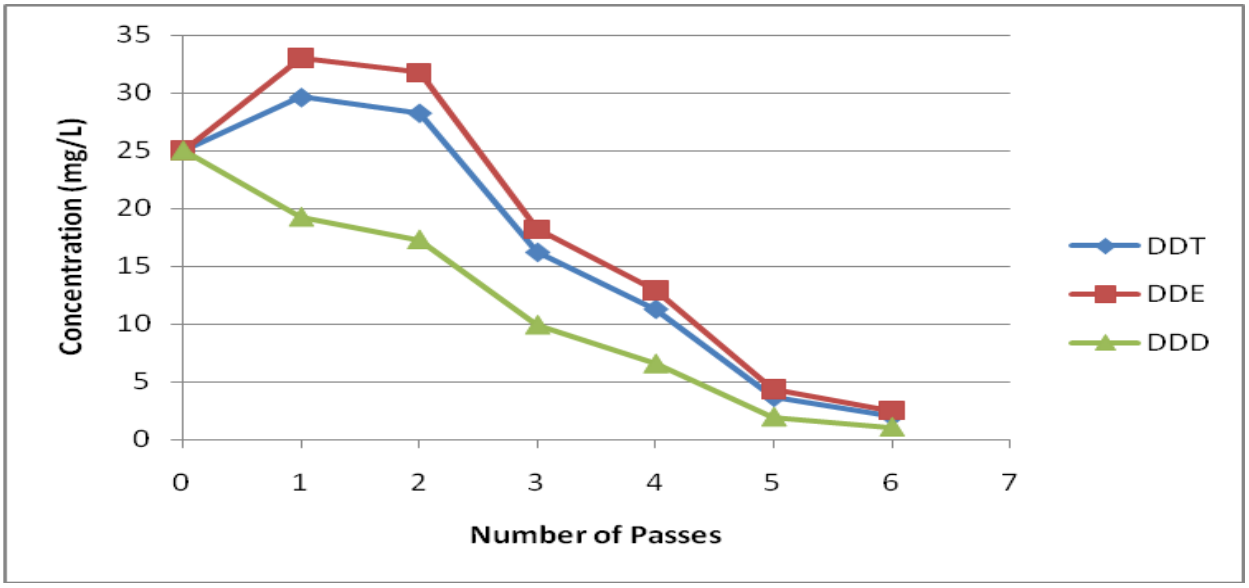

Figure 18: Change in DDT-related contaminant concentration in a 1% Brij 35 + 0.1% SDBS solution passed through 4 g beds of activated carbon, replaced after each pass.

Figure 18 indicates that relatively low values of contaminant concentration can be achieved when fresh activated carbon was used with each pass through the column. It is uncertain why the concentration appeared to increase for DDT and DDE in the first pass or two. This may have been due to a sampling and/or analytical artifact related to carbon fines in the samples being extracted for GC analysis. This apparent increase was noted in some other preliminary experiments, but since the focus of the work was on the low concentration endpoint shown in Figure 18, this problem was not pursued further during this work. Initially, 500 mL of contaminated surfactant solution was applied to the column in this work. After the 6th pass, approximately 305 mL of solution remained due to sampling losses for analysis.

In this experiment, the adsorption capacity was found to be approximately 3 mg/g for each of the contaminants (for a total of approximately 9 mg/g). This is much higher than the capacity estimated in the first experiment. One suggestion is that the adsorption is strongly kinetically controlled, due to the presence of the surfactants at concentrations that are much higher than the contaminants, on a relative basis. In repeating the flow through fresh carbon beds, there is additional time and fresh surface available to achieve

much higher loadings. This suggests that the kinetics of adsorption should be investigated in more detail for this system. However, these experiments do suggest that it may be feasible to selectively capture DDT from the surfactant solutions, as reported by Ahn et al. (2008) for capture of phenanthrene from Triton X-100 surfactant solution, and further work is necessary to optimize this process.

In the experiment shown in Figure 18, the surfactant solution COD was tested at the beginning and end, giving 363 and 736 mg/L, respectively. It might be expected that the COD would decrease during the experiment, due to some adsorption of surfactants onto the carbon (as noted by Ahn et al., 2008). The COD level increase could be due to interference from carbon-extracted components, but the lack of a significant decrease suggested that surfactant losses were apparently not severe. However, this will require further investigation to quantify the surfactant losses.

Chapter 5: Summary, Conclusions and Recommendations

5.1 Summary

Since 1972, DDT has been banned for use in Canada, but it still persists in Canadian farmland at detectable levels because it is a highly stable compound in the environment. Significant efforts have been made to remediate DDT contaminated soils. Several processes have been used such as bioremediation, incineration, thermal desorption, but these processes are impractically slow or too expensive.

Alternatively, a soil-washing process may extract and separate the contaminants from the soil, thereby reducing the quantity of contaminant for further treatment. Since DDT has very low water solubility, it is necessary to consider using surfactants to improve the soil-washing process. These surfactants are amphiphilic molecules with both hydrophilic and hydrophobic portions that have the ability to increase aqueous contaminant concentrations by partitioning the solute into the hydrophobic interior of the micelles and forming spheroid or lamellar structures with organic pseudo-phase interiors. The minimum concentration at which this occurs is called the critical micelle concentration (CMC).

To determine the effectiveness of the soil-washing process, column experiments were performed with contaminated soil and selected surfactant solutions. A single surfactant is selected based on various considerations such as effectiveness, cost, and environmental impact. Since the measurement of surfactant concentration in the wash solution is important, several methods were tested before finally selecting a simple COD analysis as a surrogate. Using the COD analysis, partitioning experiments were performed to quantify the adsorption of surfactant on the soil.

For economic reasons it would be desirable to reuse the surfactant in a washing process. For this purpose, it was hypothesized that activated carbon can selectively remove the more hydrophobic DDT from the surfactant solutions. Preliminary results have shown that carbon adsorption can remove some DDT, but additional work is required to understand and optimize the process.

5.2 Conclusions and Recommendations

- The non-ionic surfactants performed reasonably well for remediation of DDT in the soils used in this work. The Brij 35 surfactant was found to be effective and is recommended for continued work in this area. While Tween 80 exhibited similar soil washing properties, its apparent rapid biodegradability may be a problem for practical use in the field. Although biodegradability is a positive feature, this must be balanced with suitable lifetime for use in soil washing applications. Additional studies on biodegradation rates may be required in a pilot-plant test, although a lack of specific analytical methods for surfactants makes this difficult.

- The use of co-solvents in conjunction with the surfactant solutions can increase the capacity of extraction or cleanup of contaminated soil. However, if the risks of volatilization and flammability of the co-solvent would have to be addressed for field applications and may not be acceptable for environmental and safety reasons.

- The presence of SDBS in the surfactant solution at concentrations much higher than 0.1% causes significant flow problems in a soil column, possibly because of clay dispersion that slows the flow significantly or stops it altogether when the leachate reaches 150 ml in this work. While the presence of an anionic surfactant might prove beneficial for DDT removal, it may be limited due to this concern. However, if a mixing system was to be used instead (such as an agitated tank), the negative impact of SDBS on flow would not be important.

- Cloud and Kraft points should be studied with more details in future experiments to explain how these properties can affect the DDT removal process.

- Activated carbon appears to be a suitable approach for removal of DDT and its metabolites from surfactant solutions, to allow reuse or recirculation of the wash fluid. Additional confirmation work is required to determine the maximum capacity of the carbon, as well as the impact of other soil compounds that might be contained in the wash fluid. Likewise, surfactant losses due to adsorption on activated carbon should be quantified in more detail in a small pilot plant test using industrial materials.

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APPENDIX A

Cost of remediation technologies

Metal-contaminated soil (Evanko and Dzombak, 1997)

Type of treatment	Range of cost$ / ton
Electrokinetic	$100 –180
Pyrometal-lurgical	$230 – 590
Containment	$ 10 – 90
Soil flushing	$ 80 – 150
Vitrification	$420 – 880
Solidification/Stabilization	$ 80 – 300
Soil washing	$ 80 – 240

Polychlorinated biphenyls in soil (Davila et. al., 1993).

Type of treatment	Range of cost$ / ton
Incineration	$280 –1000
Thermal desorption	$ 90 – 380
Chemical dehalogenaton	$225 – 580
Solvent extraction	$110 – 540
Vitrification	$100 –1000
Solidification/Stabilization	$ 50 – 310
Soil washing	$ 60 – 230

APPENDIX B

Descriptive methods step by step

Analytical Methods

COD Method.

Chemical oxygen demand (COD) of surfactant solutions was measured as a surrogate analysis of the total concentration of surfactants in the aqueous washing fluids, before and after leaching. Hach Test 'n' tubes were used (0-1500 mg/L range) together with a Hach DR/2000 spectrophotometer and method number 435. Dilutions of about 1/20 of the surfactant solution were generally used to keep the concentration within the test kit range.

▲Put 0.1 mL sample + 1.9 mL water in vial.

▲Put the vials into reactor digest for 2 hours at 150°C.

▲Wait 10 minutes until the reactor reach 120°C. Later, wait 1 hour approximately until the vial reaches the temperature of the atmosphere.

▲Turn on the colorimetric machine.

▲Press: 435 READ/ENTER. The display will show: DIAL nm TO 435.

▲Rotate the wavelength dial until the small display shows: 620 nm.

▲Press: READ/ENTER.

▲Place the COD Vial Adapter into the cell holder with the marker to the right.

▲Clean the outside of the blank with a towel.

▲Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

▲Press: ZERO. The display will show: WAIT then: 0. mg/L COD

▲Clean the outside of the sample vial with a towel.

▲Place the sample vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

▲Press: READ/ENTER. The display will show: WAIT then the result in mg/L COD will be displayed.

Water capacity test.

The water capacity of soil samples was estimated by placing about 20 cm of soil into a (3.8 cm diameter) column, on top of about 3 to 5 cm of glass wool.

►Put about 3 – 5 cm of glass wool in the bottom of the column.

►Add about 20 cm of soil to the column. Press the soil down so that it is compact, but not too hard.

►Add a measured amount of tap water slowly until the soil is completely satured with a little water on top. Capture the water that drain out of the bottom of the column.

►Let it drains for 2 – 3 days. After this, measure the total amount of water that drained out, and compare with the total amount that was initially added.

Method to estimate the biodegradation rate of Brij 35 solution.

Biodegradation rates of aqueous surfactant solutions were estimated by placing 100 mL of the solution into an Erlenmeyer flask and adding about 10 g of soil. A second (control) flask was prepared without the soil. The soil was swirled around for a few minutes then left to settle for 0.5 hours, at which point the liquid was decanted into a clean flask. Both flasks were agitated on a magnetic stirrer for several days and samples were withdrawn for COD analysis.

▲Make up a 1% solution of Brij 35 (200 mL total).

▲Put 100 mL in each of two Erlenmeyer flasks.

▲To one flask, add about 10 g of soil from sample containers. Swirl it around for a few minutes; later, let it settle for half an hour, and the liquid decants into another flask (leaving behind as much of the soil as practical).

▲For the second flask, don't add anything.

▲Sample both flasks for COD.

▲Place both flasks on a magnetic stir plate and agitate gently overnight.

▲Continue agitation and sample for COD each day for the remainder of the week.

Finally, it compares the change in COD between the two flasks.

Test to new soil.

►Clean and remove rare particles in soil.

►Dry and homogenize the soil.

►Put 10 g in small container.

►Add 25 mL hexane into container.

►Mix it in roto-torque machine at 400 rpm for 24 hours.

►Let it rests for 1 hour.

►Take 1 μL from the liquid phase and place into a gas chromatographer to analyze.

Soil leaching batch test.

▲Make up a 50 ppm DDT solution in hexane.

▲To 10 g of soil, add 5 mL of 50 ppm solution.

▲Allow that the solvent evaporates completely. Now, the soil has 25 ppm of DDT.

▲Put the contaminated soil with DDT in a vial.

▲Add 25 mL of surfactant solution into vial.

▲Mix it in roto-torque machine at 400 rpm for 24 hours.

▲Let it rests for 1 hour.

▲Add an equal amount of hexane to the 10 mL of leachate.

▲Again mix for 30 minutes in roto-torque machine.

▲Let it rests for 1 hour.

▲Take 5 mL of the resulting emulsion at the top and place into a closed vial.

▲Add 2 mL of ethanol to break emulsion.

▲Shake gently for 10 seconds and let settle for 1 minute.

▲Take 1 μL from the top phase and place into a gas chromatographer to analyze.

Leaching column test.

►Make up a 200 ppm DDT solution in hexane.

►To 150 g of soil, add 18.5 mL of 200 ppm solution.

►Allow that the solvent evaporates completely. Now, the soil has 25 ppm of DDT.

►Put glass wool on the bottom of the column (2.5 cm x 30 cm); later, put the 150 g of contaminated soil with DDT into a column. Press the soil down so that it is compact, but not too hard. Finally, put glass wool on the top of soil.

►Prepare 500 ml of surfactant solution.

►Add 250 mL of surfactant solution into column, later 250 mL more of surfactant solution and finally add 140 mL of tap water.

►Take two samples of 10 mL each one from the first lot (100 mL) of recovered. Later, take two more samples of 10 mL each one from the second lot (100 mL) of recovered until reach 500 mL of recovered. In total 10 samples. To make a mass balance considers the average from each lot.

►Add 10 mL of hexane to each sample of 10 mL of leachate.

►Mix it in roto-torque machine at 400 rpm for 30 minutes.

►Let it rests for 1 hour.

►Take 5 mL of the resulting emulsion at the top and place into a closed vial.

►Add 2 mL of ethanol to break emulsion.

►Shake gently for 10 seconds and let settle for 1 minute.

►Take 1 μL from the top phase and place into a gas chromatographer to analyze.

Gas Chromatographic Method

DDT, DDD, and DDE analyses were completed using gas chromatography.

The samples (1μL) were injected into the gas chromatograph (HP5890) equipped a ^{63}Ni electron-capture detector (GC-ECD). The column used was an RTX-5 quartz capillary with an inner diameter of 0.53 mm, a film thickness of 0.50 μm, and a length of 30 m. The column head pressure was set to 5 PSI. The carrier gas used was pure H_2 and the flow rate was 1 mL min^{-1}. The oven temperature program started at 140°C; it was increased to 280°C at 10°C min^{-1} with a final hold time of 2 min. Injector and detector

interface temperatures were kept constant at 240 and 290°C respectively. The peak height of speciation was used for quantification. Standard solutions of DDT, DDE and DDD were made in hexane a five different concentration ranging from 0 ppm, 10 ppm, 50 ppm, 100 ppm and 200 ppm. Calibration was performed using linear regression analysis.

APPENDIX C

Data Base

Solution	**DDE**			**DDD**			**DDT**		
Batch System (10 g soil)	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**
2% Brij 35 + 0.5% SDBS + 0.5% EtOH	6.844	2.1e3		7.448	2.7e3		7.886	8.3e4	**18.5**
2% Brij 35 + 0.5% SDBS	6.851	1.7e3		7.455	2.2e3		7.893	6.8e4	**14.9**
2% Brij 35 + 2% Tween 80	6.815	3.8e3	0.34	7.374	3.2e3	0.44	7.857	7.8e4	**14.3**
2% Brij 35	6.848	1.6e3		7.410	4..8e3	0.47	7.891	6.4e4	**13.8**
0.5% Brij 35 + 2% Tween 80	6.805	3.0e3	0.23	7.365	2.0e3	0.23	7.847	7.8e4	**12.7**
1% Brij 35 + 1% Tween 80	6.805	3.1e3	0.27	7.364	2.7e3	0.38	7.848	6.6e4	**12.6**
1% Brij 35 + 4% Tween 80	6.806	3.1e3	0.25	7.366	2.0e3	0.24	7.848	7.9e4	**12.5**
1.5% Brij 35	6.838	3.1e3	0.04	7.397	1.4e4	2.62	7.880	1.1e5	**12.2**
0.5% Brij 35 + 0.5% Tween 80	6.802	2.4e3	0.21	7.362	2.3e3	0.32	7.845	5.3e4	**10.1**
1% Brij 35 + 2% EtOH	6.840	2.6e3		7.400	1.2e4	2.14	7.882	9.1e4	**9.8**
2% Tween 80	6.815	3.6e3	0.31	7.373	3.8e3	0.32	7.858	4.4e4	**5.8**
1% Brij 35 + 1% EtOH	6.842	1.6e3		7.401	9.0e3	1.46	7.884	4.5e4	**4.7**
1% Tween 80	6.806	2.1e3	0.13	7.364	2.6e3	0.26	7.851	2.3e4	**3.3**

Solution	**DDE**			**DDD**			**DDT**		
Leaching Column (150 g soil)	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**
2% Brij 35 + 1% SDBS	6.777	7.6e3	0.58	7.367	1.3e3	0.08	7.713	3.6e5	**45.8**
2% Brij 35 + 0.1% SDBS	6.703	9.6e3	0.35	7.257	4.8e4	2.70	7.739	4.3e5	**38.2**
2% Brij 35	6.677	5.1e3	0.26	7.236	2.6e3	0.15	7.714	2.9e5	**35.3**
2% Tween 80	6.801	9.2e3	0.62	7.358	1.4e4	1.30	7.843	2.0e5	**25.9**
1% Brij 35	6.801	1.2e3	0.08	7.358	9.1e3	1.09	7.842	1.3e5	**20.2**
0.1% Brij 35 + 1% SDBS	6.807	1.1e3	0.08	7.365	3.8e3	0.45	7.846	1.2e5	**18.0**
1% Tween 80	6.795	5.8e3	0.37	7.352	1.0e4	0.95	7.837	1.4e5	**16.7**
0.5% Brij 35	6.819	3.8e3	0.33	7.377	3.1e3	0.42	7.860	7.4e4	**13.7**

2% Brij:	**DDE**			**DDD**			**DDT**		
Run 1	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**
100	6.675	5.1e3	0.25	7.234	2.6e3	0.14	7.712	2.7e5	**33.41**
200	6.676	2.6e3	0.10	7.234	1.6e3	0.06	7.713	1.2e5	**14.90**
300	6.675	1.2e3	0.01	7.233	9.5e2		7.714	5.3e4	**6.28**
400	6.674	7.9e2		7.232	5.1e2		7.713	2.71e4	**3.21**
TW	6.671	4.7e2		7.229	5.9e2		7.711	1.5e4	**1.70**
Run 2									
100	6.679	5.4e3	0.27	7.237	2.7e3	0.16	7.716	3.0e5	**37.11**
200	6.679	2.8e3	0.11	7.236	2.0e3	0.10	7.716	1.3e5	**15.84**
300	6.671	1.4e3	0.03	7.230	9.2e2		7.710	6.1e4	**7.25**
400	6.674	8.2e2		7.232	6.6e2		7.713	2.7e4	**3.25**
TW	6.665	5.4e2		7.224	5.8e2		7.705	1.6e4	**1.84**

2% Brij: **Run 3**	**DDE**			**DDD**			**DDT**		
	R. T.	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**
100	6.724	4.7e3	0.24	7.217	4.2e2		7.761	3.0e5	**33.02**
200	6.700	2.7e3	0.14	7.257	2.0e3	0.13	7.738	1.4e5	**15.41**
300	6.689	1.5e3	0.07	7.246	1.2e3	0.05	7.727	6.2e4	**6.12**
400	6.687	8.7e2	0.04	7.245	8.2e2	0.02	7.725	3.0e4	**2.53**
TW	6.676	5.3e2	0.03	7.235	5.6e2	0.01	7.716	1.6e4	**0.90**
Run 4									
100	6.706	4.7e3	0.24	7.264	1.6e3	0.09	7.744	3.2e5	**36.52**
200	6.693	2.3e3	0.11	7.251	1.4e3	0.07	7.730	1.2e5	**12.58**
300	6.682	1.3e3	0.06	7.240	1.2e3	0.06	7.721	5.4e4	**5.23**
400	6.678	8.3e2	0.04	7.237	8.7e2	0.03	7.717	2.8e4	**2.32**
TW	6.675	5.0e2	0.02	7.234	9.4e2	0.04	7.715	1.4e4	**0.65**

2% Brij + 0.1% SDBS: Run 1	**DDE**			**DDD**			**DDT**		
	R. T.	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**	**R. T.**	**Area**	**ng/μL**
100	6.706	9.7e3	0.33	7.260	4.5e4	2.51	7.742	4.1e5	**36.05**
200	6.700	4.1e3	0.14	7.256	2.0e4	1.14	7.737	1.8e5	**12.77**
300	6.692	1.7e3	0.06	7.249	9.3e3	0.52	7.731	5.4e4	**4.59**
400	6.698	1.3e3	0.05	7.254	7.4e3	0.41	7.736	3.6e4	**3.09**
TW	6.702	5.5e2	0.02	7.258	3.0e3	0.17	7.741	1.1e4	**0.92**
Run 2									
100	6.700	1.1e4	0.36	7.254	5.3e4	2.96	7.736	4.5e5	**40.31**
200	6.697	3.8e3	0.13	7.252	1.9e4	1.06	7.734	1.4e5	**12.44**
300	6.691	2.0e3	0.06	7.247	9.2e3	0.52	7.729	5.8e4	**4.99**
400	6.699	1.4e3	0.05	7.255	7.0e3	0.39	7.737	3.1e4	**2.66**
TW	6.704	5.1e2	0.02	7.261	2.7e3	0.15	7.743	1.0e4	**0.84**

2% Brij + 0.1% SDBS: Run 3	DDE			DDD			DDT		
	R. T.	Area	ng/µL	R. T.	Area	ng/µL	R. T.	Area	ng/µL
100	6.699	7.9e3	0.63	7.260	6.0e3	0.77	7.744	2.6e5	**41.00**
200	6.673	2.6e3	0.14	7.231	2.7e3	0.18	7.710	1.3e5	**13.45**
300	6.669	1.3e3	0.07	7.227	1.5e3	0.08	7.706	5.4e4	**5.22**
400	6.682	8.6e2	0.04	7.239	8.0e2	0.02	7.721	2.6e4	**2.01**
TW	6.679	6.3e2	0.03	7.236	1.3e3	0.07	7.718	1.8e4	**1.20**
Run 4									
100	6.671	6.1e3	0.32	7.228	6.1e3	0.46	7.708	3.2e5	**35.69**
200	6.675	2.7e3	0.14	7.232	2.6e3	0.17	7.712	1.3e5	**13.60**
300	6.679	1.3e3	0.09	7.237	1.6e3	0.09	7.716	5.5e4	**5.87**
400	6.674	9.3e2	0.04	7.231	1.3e3	0.07	7.712	3.0e4	**2.50**
TW	6.670	6.7e2	0.03	7.228	1.3e3	0.07	7.709	1.8e4	**1.18**