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SPATIAL DISTRIBUTION AND ENVIRONMENTAL COMPARTMENTALIZATION OF DDT AND ITS METABOLITES IN DIFFERENT ENVIRONMENTAL MEDIA (SOIL,WATER AND PLANTS) IN TSHILAMUSI AREA, MUTALE DISTRICT IN LIMPOPO PROVINCE, SOUTH AFRICA

By

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A dissertation submitted in fulfilment of the requirements of the Masters in Environmental Science (MEnvSC) Degree

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DECLARATION

I TONDERAI MAKONI, hereby declares that the dissertation for the degree of Master of Environmental Sciences at the University of Venda for Science and Technology, hereby submitted by me, has not been previously submitted for a degree at this university or any other university, that it is my own work in design and execution and that all reference material contained therein has been duly acknowledged.

Signature...Makoni..... Date..29/06/2015....

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Finally, I would never have gone so far without the everlasting encouragements and considerable support from my family, they made this thesis possible.

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DEDICATION

I dedicate this thesis to my parents (Westa Netsi Kamwana and Claude Dota Makoni) and siblings Polite, Learnmore, Precious and Patience.

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ABSTRACT

DDT [1,1,1-trichloro-2,2-bis-(chlorophenyl)ethane] is a pesticide which has been banned in most developed countries but in South Africa it is still being used especially in the Limpopo Province for Indoor Residual Spray (IRS) to control malaria. The use of DDT has raised concern due to its persistence and long range transportable nature as well as toxic biological effects on the environment. The aims of the study were to determine the spatial distribution and concentration levels of DDT and its metabolites in the soil, water and plants found in and around the DDT spayed homesteads. Tshilamusi area was selected for the study and the area was divided into three zones with zone A being the zone of application and no spraying in zones B and C. Sampling was done a month after the IRS was completed. Thirty soil samples, eleven plant (leafy vegetables) samples and five tap water samples were collected and analysed for 4,4'-DDT, 4,4'-DDE and 4,4'-DDD residues. The three metabolites were present in all the soil and plant samples, with metabolite 4,4'-DDT being the most dorminant. In zone A the mean soil concentration of total DDT (∑DDT)was 65.69 µg/Kg which was the highest of all the zones followed by zone B and C which had 43.23 µg/Kg and 12.19 µg/Kg respectively. In plant samples 4,4'-DDT was detected in about 80% of the samples analysed and then 4,4'-DDE was the lowest at 40%. The highest concentrations (33.72 µg/Kg) levels in plants was detected in samples collected from zone A and the least concentration (3.84 µg/Kg) was detected in zone C. In soil samples, total DDT comprised of 50 % 4,4'-DDT whereas in plant samples it only accounted for approximately 35% of total DDT and moreover there were higher levels of ∑DDT in soils about three times more than the concentrations found in plants. DDT and its metabolites were found in soil zones B and C, which were never sprayed before and the same results were correlated by the results from plants. The most significant findings from this research is that DDT and it metabolites were detected in environmental media in areas far from the sprayed sites. The results show a strong correlation between distance and concentration levels of DDT and its metabolites.

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Keywords: *DDT, metabolite, Tshilamusi, spatial distribution, IRS, soil, water, plants*

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CHAPTER ONE: INTRODUCTION

1.1 Background

DDT [1,1,1-trichloro-2,2-bis-(chlorophenyl)ethane] is one of many synthetic chemicals that was produced and commercially used without proper toxicity tests (IPEP, 2006). It has been banned in most developed countries, but it is still being widely used in most developing countries mainly for the control of vector diseases like malaria (Dalvie, 2004). South Africa is one such developing country still using DDT, especially in the Limpopo Province for Indoor Residual Spray (IRS) to control malaria. The Vhembe district on the northern part of the province has a very high rate of malaria, hence this is where most of the DDT spraying takes place. IRS is done as stipulated under the Stockholm Convention (SC), which South Africa acceded to in 2002; the SC gives permission for the production and use of DDT to control disease vectors in line with WHO recommendations and guidelines (Bornman *et al.*, 2010).

In the Mutale district Municipality of Limpopo Province DDT has been sprayed annually since 1945 due to the high rate of malaria cases. Spraying is done on the indoor walls and the roof of traditional unpainted mud-walled thatched huts using DDT (WHO, 2002) to control malaria transmission by the *Anopheles funestus* and *Anopheles arabiensis* vectors (Barnhoorn *et al.*, 2009).

DDT together with its most persistent metabolite DDE is known to be an endocrine disrupting chemical (EDC) because they mimic and antagonize the actions of hormones. This basically means that the EDCs interact with the physiological system and cause alteration in the development, growth and even reproduction of organisms (Joblins and Tyler, 2003).

When an embryo is exposed to an endocrine disruptor chemical (EDC) like (DDT) in its stage of fetal development it can lead to male reproductive disorders such as undescended testes, intersex sub fertility and testicular cancer (Toppari et al., 1996; Bornman, 2010). Evidence has shown that healthy males in actively DDT sprayed areas had impaired semen quality and this was also supported by De Jager *et al* (2009) in his studies in Mexico. At times DDT can enter the body directly from unclothed, uncovered

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parts of the body i.e. hands, arms, chest, neck and face due to frequent contact for extended periods. Due to its high lipophilic nature (WHO, 1979) DDT is stored in the fatty tissues when inside the body and slowly released through urine and breast milk (Dalvie, 2004).

Studies by Tao et al (2009) have shown that DDT is mainly exposed to humans through food ingestion. The first step in the food chain accumulation would be the uptake of DDT by the roots of plants (Van Dyk, 2010). Taking into account that the majority of the people in the Vhembe District rely on their vegetables which they plant very close to their homesteads it therefore leaves them susceptible to DDT contamination. Their poultry meat is also likely to be affected in most cases as these animals tend to feed on the sprayed plants around the huts. Several researchers have found traces of DDT in chicken tissues including fat, muscle and even liver (Tao et al., 2009)

Previous studies have also shown that DDT from IRS can end up in the water thereby affecting fish. Aquatic organisms feed on other organisms at low trophic levels and then progressive biomagnifications of DDT happens in animals in higher trophic levels (Barnhoorn et al., 2009). According to Van Dyk et al (2010) large amounts of DDT were detected from indoor air and floor dust, outdoor soil and potable water at sprayed areas in Limpopo province. Indoor contamination can also be attributed to the precipitation of DDT particles on open food, water and utensils during spraying. Because DDT can also exist in the form of dust children tend to be the most affected especially as they play outside in the dust (Vieira et al., 2001)

DDT has been very successful in the elimination of malaria in a lot of countries mainly due to its persistence in the environment (Beard, 2006) but potential human health effects due to exposure to DDT must be given due consideration (Van Dyk et al., 2010). The application of DDT by IRS must be in such a way that it does not harm the environment especially humans. So the DDT concentrations in exposed biota, water and soil in malaria infected homes requires thorough understanding so as to identify exposure pathways and sinks, as well as possible risks to people and the ecosystem and to identify possible remedial interventions (Barnhoorn et al., 2009)

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According to Van Dyk et al (2010) there is very little available information on the DDT levels of exposure affecting those people staying in the sprayed homes hence the need for investigation of DDT contamination levels in the domestic environment. There is also need to evaluate the partitioning of DDT and its metabolites in different environmental compartments inorder to understand their mobility, degradation, biotransformation, and translocation pathways.

1.2 Problem statement

The use of DDT has been banned for international use, but in some countries like India, China and South Africa, DDT use has been restricted to Indoor Residual Spraying (IRS) for malaria control (Bornman et al., 2010). Several studies which have been carried out in DDT sprayed areas have shown that DDT may spread from inside sprayed homesteads into the whole ecosystem (Van Dyk et al., 2010). This is a major problem because DDT is toxic, persistent, resist normal processes that break down contaminants, can accumulate in the body fat of terrestrial animals and that of people thereby causing serious harm to the ecosystem (IPEP, 2006). The fact that DDT can travel great distances due to wind and water (runoff) currents has led to contamination in areas that have never been sprayed before. Also the concentrations of DDT and its metabolites DDD and DDE vary both spatially and from one environmental media to another with DDE being the most toxic (ATSDR, 2002).

1.3 Motivation

Several studies have been done in Limpopo and the world over on the impacts of DDT and its metabolites to human beings and the ecosystem as a whole. It has been concluded that exposure to DDT is associated with poorer semen quality in men leading to effects on testicular function and in women leads to pre-term births and underweight babies (IPEP 2006, Van Dyk et al., 2010). Most of these studies have been done mostly with data from the domestic environment of the sprayed homes. With time and due to the different agents of transport (water, wind) DDT can be transported over great distances and also due to its persistence in the environment.

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There has been little research on the spatial distribution of DDT and its metabolites from the sprayed area. Such a study would enable us to determine and understand how DDT is transported and how it ends up in those areas where it may cause harm to human beings and other terrestrial animals. DDT and its metabolites also have different toxic effects and their distribution in the ecosystem is also crucial in knowing how different organisms get to ingest the toxic metabolites.

1.4 Aim of the study

The overall aim of the study is to determine the spatial distribution and concentration levels of DDT and its various metabolites in the soil, water and plants found in and around the DDT spayed areas in Tshilamusi, Mutale district.

1.5 Specific objectives

- To determine the concentration levels of DDT and its metabolites in selected environmental media (soil, water and plants) around DDT sprayed areas in Tshilamusi, Mutale district.
- To evaluate the occurrence of DDT and its metabolites in soil, water and plants in areas adjacent to the DDT IRS homesteads in Tshilamusi, Mutale.
- Establish the spatial distribution patterns of DDT and its metabolites in the soils with distance from the IRS homesteads of Tshilamusi

1.6 Hypothesis

Concentration levels of DDT and its metabolites vary over space and from one environmental media to another.

1.7 Research questions

1) What are the concentration levels of DDT in the soil, water and plants of the sprayed homesteads in Tshilamusi?

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2) How do the concentration of DDT and its metabolites vary in the different environmental compartments with distance from IRS in Tshilamusi?

3) What is the spatial distribution of DDT and its metabolites in the soil around the sprayed homesteads in Tshilamusi?

1.8 Study area (Tshilamusi)

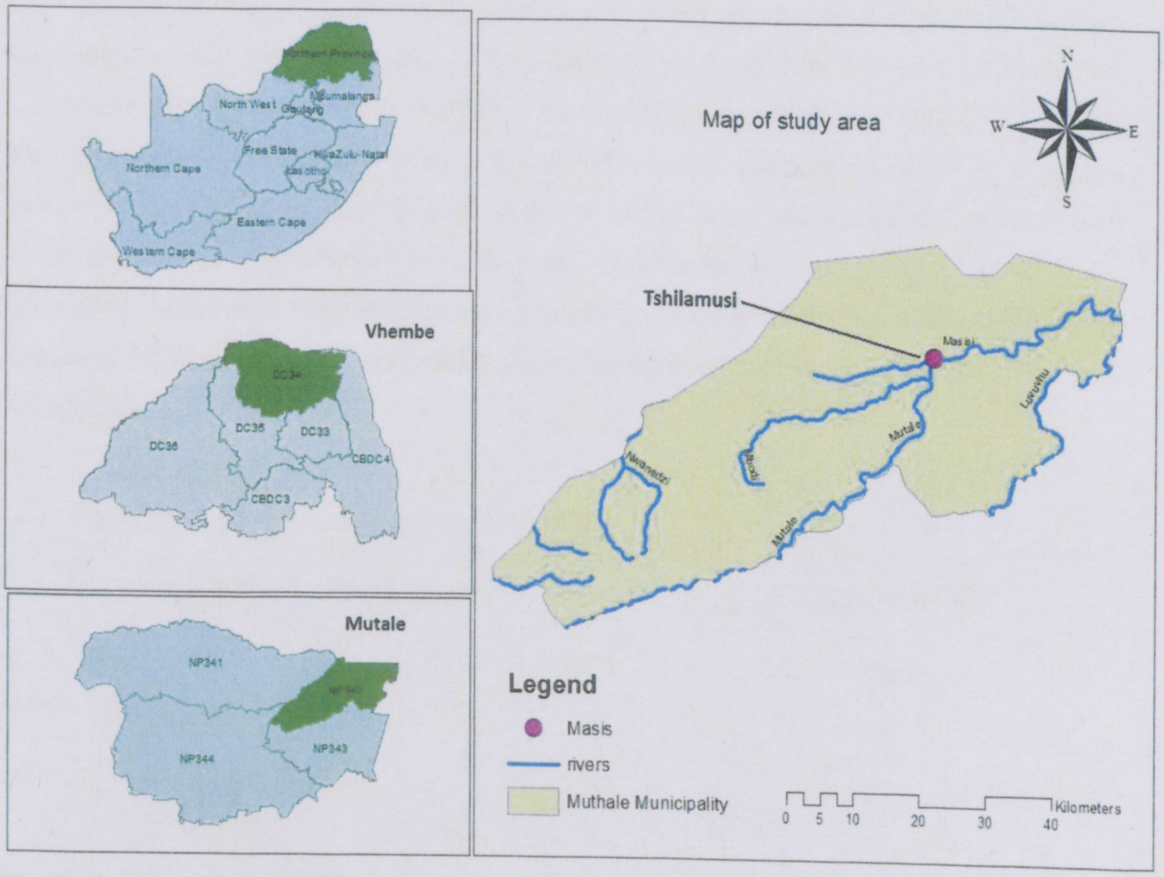


Figure 1.1: Map of Tshilamusi

In Tshilamusi, December is the warmest month of the year with an average temperature of 33.4 °C at noon. July is the coldest month with an average temperature of 20.7 °C at night. Tshilamusi has no distinct temperature seasons, the temperature is relatively constant during the year. Temperatures drop sharply at night. In winter there may be

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some days it freezes. Overall winters are mild in temperature, with the coldest month most often being July. The month of May is on average the month with most sunshine. Rainfall and other precipitation peaks is around February. The time around July is driest. Tshilamusi has a semi-arid (0.2 - 0.5 p/pet) climate. Most of the natural vegetation is still intact and the landscape is mostly covered with closed to open grassland. The climate is classified as a subtropical steppe (low-latitude dry) with a tropical dry forest biozone.

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CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

This chapter discusses the issues of DDT and malaria, mainly looking at the impacts of Indoor Residual Spraying (IRS) on the environment. The chapter will also look at the problem of malaria and how the international community is prescribing solutions for it. The impacts of IRS on humans, animals, water, and soil will also be thoroughly discussed.

DDT is one of many synthetic chemicals that were synthesized and used without adequate toxicity tests (ATSDR, 2002). Due to its long half life and harm to the ecosystem and humans it was classified as a persistent organic pollutant (POP) under the Stockholm Convention (IPEP, 2006). POP are defined as toxic substances composed of organic (carbon based) chemical compounds and mixtures. They are also a hazard to the environment due to their physiochemical properties; highly toxic, persistent, resist normal processes that breakdown pollutants, they bioaccumulate in the body fat of organisms, and can be transferred from mother to fetus. (WHO, 1979, WHO, 2007).

2.2 Physical – Chemical properties of DDT

The following are the chemical structures of 4,4'-DDT, 4,4'-DDE and 4,4'-DDD

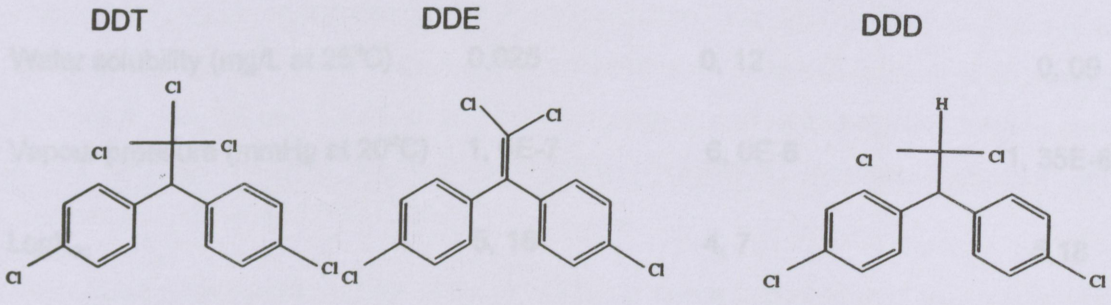


Figure 2.1: The chemical structure of **4,4'**-DDT, **4,4'**-DDE and **4,4'**-DDD

The DDT pesticide is available in different forms including aerosols, dustible powders, emulsifiable mixture of 3 forms p,p'-DDT (85%), o,p'-DDT (15%) and o,o'-DDT (trace

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amounts) (Metcalf, 1995). All of these metabolites are white, crystalline and almost odourless solids. Technical grade DDT may also contain DDE [1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene] and DDD [1,1-dichloro-2,2-bis(p-chloro-phenyl)ethane] as contaminants, both DDE and DDD are metabolites of DDT (ATSDR, 2002).

DDT is a very persistent compound in the environment with an approximate half-life of 15 years (EXTOXNET, 2001), and is also associated with a number of healthy problems such as breast cancer, diabetes, decreased semen quality, spontaneous abortion (Bornman, 2010). It is highly soluble in fats and most organic solvents but insoluble in water. Its breakdown products in the environment include DDE (1,1-dichloro-2,2-bis (p-dichlorodiphenyl)ethylene and DDD[1,1-dichloro-2,2bis(p-chlorophenyl)ethane.

DDT, DDE and DDD are present in soil, sediments, plants and moisture. The half-life of DDT is about 5 years in tropical areas and 20-30 years in temperate areas (ATSDR, 2000). While DDT and its derivatives may be present in soil, sediments and air, the ability of these chemicals to enter people directly through the skin and by inhalation is very limited in comparison to the amount absorbed from ingestion. A summary of the chemical properties of DDT,DDD and DDE are given in Table 2.1

Table 2.1: Chemical Properties of DDT and its metabolites

Property	p,p'-DDT	p,p'-DDE	p,p'-DDD
Molecular weight (g/mol)	354, 5	318.0	320.0
Water solubility (mg/L at 25°C)	0,025	0, 12	0, 09
Vapour pressure (mmHg at 20°C)	1, 6E-7	6, 0E-6	1, 35E-6
$LogK_{oc}$	5, 18	4, 7	5,18
Henry's Law Constant	8, 3E-6	2, 1E-5	4, 0E-6
Log K_{ow}	6.0	6.1	6.02

Source (ATSDR, 2000)

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2.3 Malaria and DDT

Malaria is a complex parasitic disease found mainly around the tropical areas and transmitted by mosquitoes of genus Anopheles (Van Dyk et al., 2010). In sub-Saharan Africa there are roughly 250 million cases of malaria annually which result in close to a million deaths, mostly children < 5years of age (WHO, 2008). It is important to note that the most crucial component of malaria control programme is vector control. This has led to the WHO reaffirming the importance of vector control through IRS as one of the most crucial strategies for reducing or interrupting malaria transmission in many countries.

Malaria imposes enormous human suffering and huge expenses on the poorest countries. In South Africa it is estimated that about 4,8 million people (10% of the population) are affected by the disease (Bornman et al., 2010). The mosquito *Anopheles arabiensis* is the most common malaria vector in South Africa, while the parasite *Plasmodium falciparum* accounts for the majority of malaria related morbidity and mortality (DoH, 2003; IPEP, 2006).

Manufacturing and utilization of DDT is strictly controlled by an international agreement known as the Stockholm Convention on POP. This Convention's mandate is to make sure humans and the environment are safe from persistent pollutants (Van Dyk et al., 2010). The DDT is very crucial when it comes to malaria vector control. Of the twelve insecticides mostly recommended for this intervention, it is DDT which has the longest residual efficacy after it has been sprayed on walls and ceilings (6-12months depending on dosage and nature of substrate). The other recommended insecticides tend to have a way shorter residual efficacy (pyrethroid: 3-6months; organophosphates and carbamates 2-6months) (IPEP, 2006)

The course of action promoted by the WHO has allowed and promoted the use of DDT for IRS globally, so as to be able to manage resistance of insecticide until such a time wherein suitable alternatives are available (WHO, 2007). The use of DDT for malaria control is only recommended where the intervention is appropriate and effective in the local epidemiologic situation (Van den Berg, 2009).

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At the World Malaria Day 2011 event it was noted at that point that new research showed that in some cases DDT spraying was not only effective, but had the potential to increase the transmission of malaria (Raghavendra et al.,2011). This is because some researchers have noted that some of mosquitoes become resistant to DDT's toxic effects are still being repelled by it. The problem is that the repellence is leading to the mosquitoes moving the the neighbouring homestead and bite there instead of residents of a house sprayed with DDT and this reduces the chances of the mosquito picking up the lethal dose of insecticide from sprayed huts (WHO, 2010). So this "behavioral avoidance" has been identified as the main reason for the reduction in effectiveness of most African anti-malaria programmes which are based on DDT.

The most notable problem associated with malaria vector control in most parts Southern Africa is the resistance *Plasmodium falciparum* develops to antimalarial drugs (Sharp and le Sueur, 1996). Malaria resistance has been reported in Africa and this includes report on resistance to chloroquine, sulfadoxine, mefloquine. Chloroquine resistance in Africa was first reported from both Kenya and Tanzania in 1979 and is now documented as occurring in all the Southern African countries. It was first detected in South Africa in 1985 and is now well established in the country (Sharp and Freese, 1995). According to Sharp and le Sueur (1996) biological systems are dynamic and malaria control must of necessity be based on sound scientific principles in order to be effective.

2.4 DDT as a global and South African problem

DDT was banned in most countries in the early 1970's, because of its toxic impacts on all living organisms. Prior to that it was used to control most disease carrying insects, like mosquitoes and tsetse fly and also to control insects on some agricultural crops (Fitzpatrick et al., 2000)

In China, DDT has been extensively used since the 1950's (Huang et al., 2000). As one of the biggest manufacturers of the DDT pesticide. China manufactured an estimated 203000- 381 000 MT annually of technical grade pesticides between 1985 and 1996, (Chen et al, 2007,Gao et al., 2008). Surface soil samples collected from China showed

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high mean concentration levels of DDT and all its metabolites (∑DDT) of 56,0±133 ng/g with a maximum value of 792ng/g. Since China is exempted from the Stockholm Convention on POP, it continues to produce 80 000 – 600 000 tons of the pesticide annually as raw and finished material for dicofol production (Huang et al 2007, Hu et al 2006)

Studies Gao et al (2008) showed that the high frequency of occurrence of DDT in most of Chinese rivers rarely exceeded the environmental quality standards for surface water for China. When compared to other parts of the world, surface water of China was moderately contaminated by p'p DDT with high concentrations in Yellow river and Huaihe river basins (Gao et al., 2008).

Illegal usage of DDT in farming is still happening in China mainly because this pesticide is very effective and cheap (Wang et al., 2008). Recent inputs of the DDT pesticide in many coastal areas have been recorded in some Asian countries including China, Vietnam, Indonesia, and Cambodia. Pollution of freshwater and aquatic life by DDT has also been detected in most countries and the low ratio of DDE to DDT in the aquatic suggests that new DDT is still a problem in Asia (Coots and Era-Miller, 2005;Kwong et al., 2008).

Recent studies in Lake Chelan, North Central Washington state showed elevated concentrations of DDT and its metabolites (DDE and DDD), occurring in aquatic species, sediments and tributaries of the lake that drain historically DDT application lands (Ellis et al., 2008). This goes on to show that DDT has a very high half life in the ecosystem. India is still engaged in large scale manufacture, use and export of some organochlorine pesticides (OCP) such as DDT (Li et al., 2003, Pozo et al., 2011). Previous studies in India have documented contamination of DDT in a range of environmental matrices including some limited measurements in air, soil, sediments and wildlife including mussels, birds, and marine and also in foodstuffs (Gupta, 2004; Ramesh, 1989; Pozo et al., 2011).

In the rural areas of Worka and Crojec in Poland the main sources of drinking water are wells located within the household area but considerable amounts of DDT has been

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detected in these wells. The occurrence of DDT in water samples goes on to prove that DDT is still persistent in the environment although its use was banned in Poland in 1975 (Badach, 2000).

Any soil with concetrations >0,5 mg of ∑DDT/kg is regarded as not suitable for agriculture in China. According to Gong et al (2006) the highest DDT and DDE contamination levels detected in China, Tianjin province, were 0,87 and 0,35mg/kg respectively while in the agricultural soils of New Zealand DDE contamination levels of 9,05 mg/kg were detected (Harris et al.,2000)

Africa has the highest incidences of malaria; 85% of cases and 90% of malaria-related deaths. The most efficient vector mosquitoes in the world is found on the African continent. This is mainly due to the climate of the sub-Saharan Africa is ideal for the transmission and the national treatment and control measures are constrained by the socio-economic factors in most African countries. Most of the people are also poor and rural based with less access to public health measures (IPEP, 2006).

In East Africa, Kenya, Uganda and Tanzania, adjoined by Lake Victoria have serious cases of DDT contamination reported. (Kihampa et al., 2010). In previous studies done in Uganda, Dieldrin was detected in water and sediments of Lake Kyoga. DDT and DDE were detected in human adipose tissues, in the Kampala area while DDT, Dieldrin and Lindane were detected in cow milk. In a more recent study aimed at providing baseline information on the current levels of organochlorine pesticides in the aquatic system of Lake Victoria, it was established that the ratios of DDT to DDE from the samples analysed suggests previous but no current use of the pesticide (Wasswa and Kiremire, 2001; ANCAP, 2004)

Despite the hot summer temperatures, which lead to the thriving of mosquitoes in Africa, DDT is still used to get rid of these malaria causing insects. Countries close to South Africa such as Zimbabwe, Mozambique also use DDT to prevent malaria and DDT contamination has also been detected in the sediments, water and even animals found in the sprayed areas in these countries (ANCAP, 2004).

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In South Africa DDT has been used since the 1940s for agriculture and mosquitoe eradication. Currently it's only used for IRS mainly in Limpopo province and KwaZulu Natal. The devastating effects of malaria on communities, tourism and agricultural development in the province of KwaZulu-Natal and Mpumalanga were the major motivations for control of the disease in the first half of the century (Sharp and le Sueur, 1996). Studies carried out in the sprayed areas have shown that DDT is present in the water, soil and even in some domestic animals and this poses a huge risk to human lives (Mabaso et al., 2004). The presence of DDT in these environmental media has led to contamination of the human tissue and evidence shows that there have been cases of cancer, damaged testes, and birth defects all which has been attributed to DDT (Bornman et al., 2005).

In 1994, bowing to international environmental pressure, South Africa was forced to replace DDT with synthetic pyrethroid insecticides. Malaria cases increased by 5 fold to 60 000 per year. In 1999 they reverted back to DDT house spraying which brought down the malaria incidences (Blumberg and Frean, 2007).

2.5 Malaria control programme in South Africa

South Africa is at the southern tip of malaria distribution in Africa. This means that small areas experience seasonal transmission leading to instability of malaria in these areas. South Africa is fortunate to have a well-run malaria control programme as well as advanced scientific, healthy and economic infrastructure (WHO, 2007).

DDT is distributed in boxes with 10 sachets each with 670g of DDT. A single sachet of DDT is mixed into 20L knapsack sprayer and then the solution is sprayed onto indoor walls at an application rate of 2 grams of DDT per m^2 leaving a white deposit (DoH, 2005).

Malaria mainly occurs in the Northern and Eastern parts of South Africa (low-latitudes areas) next to the borders with Mozambique and Zimbabwe. Most of the malaria transmission takes place in Limpopo, Mpumalanga and KwaZulu Natal provinces, with

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most fatalities being reported in the Limpopo province (DoH, 2006). According to Blumberg and Frean (2007) about 4,3 million South Africans are at risk of contracting malaria. South Africa's Malaria Control Programme uses the following strategies; vector control through IRS, case management, disease surveillance, epidemic preparedness and response, malaria education and communication. Of all these strategies Indoor Residual Spraying is the most common and effective (Van Dyk et al 2010).

In South Africa the DDT IRS malaria control program was started around the 1940s and 1950s and its use was credited for the removal of the *Anopheles Phenestus* mosquito which at the time was the major malaria vector in South Africa (Sharp and le Sueur, 1996). The use of DDT was stopped by the government in 1996 and moved to pyrethroid insecticides which worked well against the *Anopheles arabiensis*, which was at that time the only vector in the country. Later DDT was brought back in 2000 at the peak of a malaria epidemic associated with the emergence of a pyrethroid resistant strain of the *anopheles phenestus* in KwaZulu Natal (WHO, 2008).

An effective malaria control programme in South Africa has existed in those malaria prone areas for the past five decades, and indoor spraying with a residual insecticide to kill resting anopheles mosquitoes has been the cornerstone of control (Bornman et al., 2000). This resource-intensive intervention was hugely successful as evidenced by the reduction of more than 80% in the South African malaria endemic area. (WHO, 2000)

During the spraying some of the DDT is said to enter the atmosphere, suspended in particle form. The DDT residual coating prevents malaria transmission as a spatial repellent or contact irritant or by killing mosquitoes (indicating more than one mode of action) effectively preventing or interrupting transmission (Grieco et al 2007)

2.6 Breakdown and movement of DDT

2.6.1 Soil

Soil contamination by pesticides has been subject to several studies, mainly due to its important role in the distribution of contaminants to its environmental compartments

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(Dalla Villa et al., 2006). DDT and its metabolites last in the soil for a very long time even up to a hundreds of years (ATSDR 2002). To a larger degree DDT will be retained by soils and other soil fractions with higher proportions of soil organic matter. In cases were heavy application are or were made yearly DDT may accumulate in the top soil layers (ATSDR 2002)

The POPs which ultimately reach soils and aquatic sediments are subjected to several fate processes. The processes are normally divided into the following: physical transport losses including volatilisation and leaching of parent compound and metabolites; losses by chemical reaction including photolysis, hydrolysis, oxidation and reaction with mineral surfaces; biotic losses including bioaccumulation, transformation and mineralisation by soil and sediment microbial populations; and binding to environmental solids (Northcott and Jones, 2000)

The final result of these processes will lead to a decline in the amount of pesticide in the sediments and soils. However, a huge amount of organic compounds and/or their transformation products remains in soils and sediments in the form of labile and or bound residues. It is generally observed that the labile portion of compound remaining in soil and sediment decreases with time while bound residues increase. (Northcott and Jones, 2000)

Dalla Villa et al (2006) noted that the dissipation rate of organic compounds in soil was depended on several processes occurring simultaneously 1) chemical and biological degradation (2) run-off (3) volatization and leaching which depends on the climate of the region , soil properties and molecule physio-chemical properties. According to Gong et al (2004) the molecule properties which affect the dissipation of DDT in soil are water solubility (S) Henry's constant (H), soil-water partition coefficient (K_{ow}) which for p,p'DDT are S< 1mgL (EXTOXNET, 1986), H=3,4 x 10^{-4} at 25°C, Koc = 100000mLg and K_{ow} = 9,6x 10^{5} (ATSDR, 2002).

It is also important to note that the persistence of DDT and its metabolites in soil hugely affects its fate in the ecosystem. The DDT K_{ow} shows a high lipophilicity which promotes

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its sorption to the soil organic matter, thereby reducing leaching and increasing persistence (Sarkar et al., 2008).

Temperature, type of soil and whether the soil is wet are some of the factors that may affect the length of time that DDT will last in the soil. DDT disappears faster when the soil is flooded or wet than when it is dry (ATSDR, 2002). Organic carbon partition coefficient K_{oc} of $1,5x10^5$, $5x10^4$ and $1,5x10^5$ reported for 4,4'-DDT, 4,4'-DDE and 4,4'-DDD respectively suggest that these compounds adsorb strongly to soil rich in organic matter. So under aerobic conditions most of the DDT applied to soil will degrade to DDE. Under anaerobic conditions and in the presence of organic matter DDD is formed (Menchai et al., 2008).

Sometimes DDT is evaporated from soil surfaces and is also subjected to photo oxidation on soil surfaces but will not hydrolyze. There is a possibility of the DDT biodegrading in those soils which are flooded or under anaerobic conditions provided huge amounts of the required microorganisms are present (Rudd and Herman, 1972). In time DDT may be able to eventually leach into ground water mostly in those soils with little organic matter irrespective of the fact that DDT is immobile or slightly mobile. Compounds at the top soil are most likely to be broken down or otherwise dissipated than those below several inches (Bennet, 2001).

Organochlorine pesticides examined in a study in Poland showed persistence for many years in soil and were refractory to degradation by microorganisms, chemical reactions and sunlight (Badach, 2000). According to Gong et al (2006) after application, pesticides residues in soil remain in many areas with p,p-DDE being the most abundant metabolite. DDT and DDE usually show high hydrophobicity and adsorption mostly to soil particles leading to a reduction in leaching (Viera et al., 2001). The toxicities of DDT metabolites as probable carcinogens and endocrine disrupters, resistance to degradation leading to high persistence and 10^3 - 10^4 fold of bioaccumulation in a food chain qualify them as priority pollutants for remediation (ATSDR, 2002, Gong et al, 2006)

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In most countries risk- based levels and action plans for cleanup of ∑DDT have been initiated. In the United States of America, if DDE exceeds 2mg/kg in residential soils or 8,6mg/kg in industrial soils, remediation will be performed (Gong et al., 2006). Bioremediation is one method which can be used, its cost are comparatively low and its effective in treating polluted soils.

2.6.2 Water

Water is an essential part of our life, one of the most precious natural resources that we have. Currently, the pollution of our freshwater by organic compounds is of great ecological concern mainly in the areas with heavy farming where leaching of highly toxic substances into water supplies may result in long term consequences on human and animal health (Badach et al,. 2000).

Water monitoring of organochlorine pesticides (OCP) in South Africa, European Union, Asia and America (Iwata et al,.1994, Naude et al,. 1998), has shown residues of pesticides in environmental water systems though they have been banned for decades (Awofolu and Fatoki, 2003). The movement soils contaminated with pesticides into water remains a key risk exposure of benthic and other aquatic organisms to pesticide residues. Pollution of drainage channels by OCP including DDT pesticide has led to the subsequent near-shore contamination of marine ecosystems (Menchai et el., 2008)

Before the late 1970's, the contamination of underground from applied pesticides was not expected by many people. There was an assumption that pesticides in the environment would either breakdown or that the water will be cleansed by soil, sand, gravel and rock formations it reaches ground water (Buttler et al., 1998). According to Badach et al., (2000) persistence and adsorption are the two most important characteristics of a pesticide, affecting its potential to leach to the ground water. Basically adsorption is just how tightly a compound becomes attached to soil particulary pesticides that are strongly adsorbed (tightly held) will be less mobile in soil. If leached with water they will be less likely to reach ground water (Badach et al., 2000)

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Like any other organochlorine pesticide (OCP) DDT is photochemical, biological and chemical degradation resistant and persists in the environment for a long period of time. (ASTDR, 2002). It is highly lipophilic (high octanol-water partition coefficient K_{ow}) and hydrophobic (low solubility in water) with solubilities of 0.025, 012 and 0.090mg/L for p, p'-DDT, p, p'-DDE and p,p'-DDD respectively. So this means that DDT and its metabolites may be associated with either organic compounds of soils, sediments and biological tissues or dissolved organic carbon in aquatic systems (Vagi et al., 2007).

Photo degradation and biodegradation may be able to transform DDT, DDE and DDD in a water body. Photolysis mostly takes place in surface water and is dependent on the clarity of water especially since the shorter wave radiation does not penetrate far into the water. Direct photolysis of DDT and DDD are very slow in water and that of DDE will vary depending on photoperiod and brightness, resulting in different half-lives and depending on the season (Wang et al., 2008).

According to Sarkar and Gupta (1988) there are factors which are responsible for the degradation of DDT to DDE and these are: the alkaline nature of the marine system and their characteristics foe example salinity, clay mineral concentration, major elements and the presence and concentration of organic matter, the ability of marine benthic organisms to biodegrade DDT. These factors act in singly or in combination.

One of the most important reservoirs of DDT and its metabolite is marine sediments, in surface water DDT will bind to particles in the water, settle and be deposited in the sediments (Perez-Maldonado et al., 2010). Volatilization and sorption to biota and sediments are the main processes through which DDT undergo in the water bodies, with sorption being dependent on the amount of suspended particles available in the water. DDT alternative transformation in the aquatic environment is mostly by biotransformation. (Tao et al., 2007)

China is one country with massive production and usage of DDT and studies carried out by Gao et al (2008) showed the detection frequency of p, p'-DDT to be 63, 1% for all the consistent water samples collected. The concentrations ranged from 0, 14 to 368ng/L with a mean value of 14,6ng/l. Guo et al (2009), studied the concentration levels of DDT

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in various environmental compartments in the Pearl River Delta (PRD) in south China and noted that concentrations of DDTs (5, 33 - 9, 53ng/L) were significantly higher during low water flow season than during high flow season (0, 52 to 1,13ng/L). This suggests that the levels of DDTs in water are reflective of different water flow rates for example dilution effect might be a factor causing the lower levels of DDTs at higher water flows (Choi et al,.2011).

The most common method used for determining organochlorine pesticides in water is the Liquid/Liquid extraction (Awofolu and Fatoki, 2003, Sibali et al,.2009). A study by Sibali et al (2009) has shown that LLE is more effective than Solid Phase Extraction (SPE). The percentage recoveries which were obtained using SPE were lower when compared to LLE for all isomers of DDT, this was attributed to the dissolution of the standards into the plastic cartridges used for extraction

On the other hand there have been a lot of researchers who have also used SPE and have been able to come up with very good and convincing results (, Badach et al., 2000). With Solid Phase extraction most of the callenges associated with Liquid/Liquid extraction may be avoided, such as incomplete phase separations, less-than quantitative recoveries, use of expensive breakable glassware and large quantities of disposable organic solvents.

2.6.3Sediments

In the aquatic environment organic pollutants are strongly associated with sediments because of their hydrophobic properties and they tend to accumulate in sediments. Contaminated sediments, act as a pollutant sink, a carrier and future sources of pollutants(Choi et al., 2011). They might pose a danger for the associated living organisms and even for other aquatic organisms through the food web (Gao et al., 2008). So surface sediments samples are utilised in the monitoring and assessment programs to characterize contamination in fresh water and marine environments. Marine sediments are the most important reservoirs of organic pollutants like DDT (Yang et al., 2005), once disturbed the sediments can be resuspended and the

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contaminants can reenter the aquatic environment and circulate in the ecosystem resulting in second contamination (Wang et al., 2008)

Ecological risk was previously estimated by using total residue analysis. However according to Menchai et al (2008), the level of contaminants in soil or sediments may vary from the bioavailable part and might not directly relate to exposure and environmental risk to living organisms. Bioavailability is both matrix and contaminant dependent (Reid et al., 2000). This total residue analysis of soils and sediments alone is inadequate for predicting the likely exposure of biota to contaminants (Menchai et al, 2008)

Iwata et al (1994) analysed air, water, sediment and soil samples from Eastern and Southern Asia for the presence of OC pesticides to elucidate their geographical distribution. The distribution of OCP in sediments showed a smaller spatial variation on a global scale, indicating that OCPs released in the tropical environment are dissipated rapidly through air and water and released less in sediments. They noticed that environmental concentrations of DDT and its metabolites in tropical developing countries were higher than those observed in developed countries.

2.6.4 Plants

The uptake of DDT by plants is often the first step in food chain accumulation. Pollutants may enter the plant roots directly by partitioning from contaminated soil to the roots and then are translocated in the plant by the xylem. Studies on plant uptake of organic pollutants have been conducted for various plant species (Tao et al., 2005, Chen et al., 2007). In most cases whole roots were extracted and the data interpreted as the tissue concentration. As a matter of fact, hydrophobic pollutants often adsorb onto the root surface first before being incorporated into the tissue. Many factors including soil properties, plant species, root morphology and growth stages affect the adsorption and the absorption of organic pollutants by plant roots (Binet et al., 2000)

DDT and its metabolites have also been detected in beans, potatoes, turnip, wheat, however plants can only take up a portion of pesticides found in soil (Tao et al., 2004).

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Khan (1982) made a distinction between the bioavailable and non-bioavailable fraction of pesticides. He indicated that bioavailable fraction of a compound in soils can be taken up by plants and /or soil inhabiting animals while the non-available fraction cannot.

The uptake of hydrophobic organic pollutants by roots is often limited within the plant (Chen et al., 2007), so high concentrations of DDT in plant roots have been attributed to surface contamination. Binet et al (2000) concluded that metabolites of DDT (DDXs) adsorbed by non-mycorrhizal plant roots were more than twice of those absorbed by root tissue. High levels of root lipid content have been found favourable for the accumulation of lipophilic contaminants from the soil. Not only is the adsorption of DDXs a function of root surface area but absorption as well is directly influenced by root surface area (Chen et al., 2007).

Studies carried out in China by Chen et al (2007) postulated that absorption of DDXs by rice roots followed a series of steps: (1) transfer from bulk soil to the rhizosphere followed by (2) adsorption onto the root surface and then (3) absorption by root tissue. The same studies also concluded that indeed DDT did accumulate in the rhizosphere soil and this was dependent on site, compound and plant species specific (Trapp, 2000).

2.7 Impacts of DDT Indoor residual spraying on Human health

DDT is an endocrine disrupting chemical (EDC), it interferes with the body's hormone system (Dalvie, 2004). It is widely known to be very dangerous even at low doses posing danger to human health (Chen, 2003). EDC can affect fetus development and alter the ability of the body to fight disease and to reproduce especially during prenatal life.

DDT has been known to act as a stimulant and depressant of the central nervous system (WHO, 1979). Barnhoorn et al (2009) noted that single doses of 6 to 10mg/g may result in nausea, headaches, diarrhea and irritation of the mucous membrane, tumors and convulsions as well as affecting the central nervous system.

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In an analysis of international studies carried out by Carlsen et al (1992), there was evidence of a decline in human sperm concentration by about 40% and semen by 20% over the period 1938-1990. During the same period there was on increase in testicular cancer incidences as well as cryptorchidism and hypospadias in many countries worldwide (Dalvie et al., 2004). The deterioration of male reproductive health has been hypothesized as being caused by the presence of natural and synthetic chemicals such as DDT (Toppari et al 1996). Other authors have disputed semen quality deterioration (Cheek and McLachlan, 1998)

Most research studies done have linked DDT exposure to reproductive effects in humans which include environmental estrogen and anti-androgen effects on fetuses and breast feeding infants, decreased fertility and still births (WFPHA, 2000). Results from a study at Tshilidzini Hospital carried out by Bornman et al (2010) showed that of the 45 pregnant women admitted to the labour ward, the average p,p'-DDE concentrations in those women's blood was found to be 24,75mg/kg and went as high as 419,51mg/kg. In a Mexican study conducted by Beard (2006) 6% of breast fed babies had daily DDT intakes above recommended levels. Ironically it has also been suggested that increased levels of DDT are associated with a reduced period of lactation.

A number of case studies and small analytical studies which were undertaken in the early 1990s have also indicated that exposure to DDT maybe one of the significant environmental risk factors for breast cancer (Dong et al., 2010). Health effects of DDT and DDE most commonly suggested by studies in North America and Europe are early pregnancy losses, fertility loss, leukemia, pancreatic cancer and diabetes (Beard, 2006, Cox et al., 2007)

The concentration of DDT found in Limpopo are a case of concern because other studies have shown that DDE exposure of 10mg/kg causes pre-term births and under weight babies. Longernecker et al (2001) postulates that the higher the DDT levels in mothers the more likely are preterm births. He also goes on to link DDT contamination to the baby's size, with babies more likely to be small for their gestational age when born to mothers with higher levels of DDE.

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One recent study clearly documented neurological effects including developmental delays among babies and toddlers exposed to DDT in the womb(Gladen and Rogan, 1995). The same study also supported Longernecker et al (2001) linking exposure to reduced breast milk production among nursing women and other studies have found that the DDT breakdown product DDE can increase risks of premature delivery and reduced infant birth weight (PANNA, 2007).

When DDT is used for malaria control, it is usually sprayed on the walls inside homes, hence risk of exposure is very high (FAO, 2001). Researchers in Mexico and South Africa found elevated levels of DDT in the blood of those living where DDT was used to control malaria, breastfed children in those areas received more DDT than the amount considered "safe" by WHO standards (Waliszewski et al., 1996)

DDT is known to contaminate breast milk in lactating mothers. A study carried out in the province of KZN from clinics located in the areas which were exposed to agricultural and malaria control insecticides. The results showed higher levels of total DDT and its metabolites (4,48mg/kg milk fat) compared to the unsprayed areas (1,1mg/kg) (Curtis, 1994).

Perez-Maldonado et al (2010) notes that children are a highly vulnerable population due to the fact that the likely pathways of exposure to DDT are soil and dust ingestion, inhalation from household spraying and food ingestion. In support of this, ISAT (2002) found that high levels of DDT and its metabolites have been detected in children living in malaria prone areas when compared to children from non-malaria prone areas around the world.

After the reintroduction of DDT in South Africa, studies carried out by Okonkwo et al (2008) and Bouwman et al (2006) showed higher levels of DDT and its metabolites in human breast milk. Also noted were impaired semen quality in young men, urogenital birth defects in neonates and hormonal effects of long term occupational exposure to DDT in vector control workers (Bornman et al., 2005). Research in DDT levels in men and women in the endemic malaria areas of KZN showed 20 times the acceptable daily

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intake overall in the study and 31 times the acceptable daily intake in primiparous mothers (Sharp and le Sueur, 1996).

The evidence on the relation between pesticide contamination of drinking water and cancer was postulated by Badach (2000). The health effects of occupational and general population exposures to organochlorine compounds include neurological deficits, cancer-especially non-Hodgkin's' lymphoma and leukemia, developmental and reproductive impairment (Longnecker et al 1997).

The latest assessment of DDT by WHO states that inter alia "that there is an acute poisoning hazard for children with accidental ingestation of DDT" and also goes on to note that while exposures to residues of DDT-treated homes generally "are below potential levels of concern for populations" and that "in some areas, the exposures in treated residences have been higher than potential levels of concern...." Of particular concern would be women of child bearing age who live in DDT treated dwellings and transfer of DDT and DDE to the fetus in pregnancy and to the infant via lactation (Sharma, 1999; Herren and Mbogo, 2010)

The use of DDT for malaria eradication has caused a stir in the international community since the early 1970s (Sharma, 1987). Curtis and Lines (2000) argue that the illegal diversion of DDT intended for anti-malaria use to agriculture (which occurs as long as spray men are underpaid) might be the main source of detectable residues in agricultural products. They also go on to note that since DDT is sprayed on the inside surfaces of houses (especially mud walls), it is unlikely that much would enter the outside food chain as mud walls tend to be replastered every now and then (Raghavendra et al.,2011)

In many cases the results have not been consistent between studies, nevertheless these accumulating reports bear much concern particularly in relation to chronic effects. Breast cancer has been most rigorously studied: even though the majority of results show no causative association with DDT exposure (Biody et al., 2007). Recent studies by Cohn et al (2007) indicate an increased risk in women who were exposed at a young age.

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DDT is claimed to be an estrogen mimic (WWF, 1998) and possibly responsible for declining sperm count in European men. However according to WHO (1973), this decline has continued even though DDT usage is much less than it used to be. These conflicting reports just go on to show that there is need for long term research into the use of DDT for malaria prevention

2.8 Impacts of DDT on Wildlife and Aquatic health

Part of the success of DDT can be attributed to its persistence in the environment thus reducing the need for frequent application. However, chemical stability and an associated lipophilicity also results in DDT being bio persistant (WHO, 1991). This tendency is also shared by the key DDT metabolite (Dong et al, 2010). A large number of organisms particularly marine filter feeders, can also act as bioconcentrators (Gao et al , 2008), creating levels of DDT in their own flesh above ambient environmental concentrations. These traits result in accumulation of DDT through the food chain in particular predatory animals at the top of the food chain/ecological pyramid (Jensen et al, 1969)

Rachel Carson was a biologist with the United States fisheries and wildlife services. In 1962 she published a book, Silent Spring about the harm pesticides were doing to wildlife. One of the pesticides she was looking at was DDT which was having detrimental effects on the environment (Van Dyk et al, 2010). The major findings of her work were the thinning of eggshells as well as bioaccumulation and biotransformation of DDT. Her work led to the banning of DDT usage in agriculture in America and later on to the rest of the world (Carson, 1962)

The contamination by DDT and its metabolites in wildlife has been declining in most parts of the world since the early 1970s as evidenced by marked decrease in the levels of these compounds in fish, aquatic mammals, birds, invertebrates and many other species (Gao et al , 2008). In most studies p,p'-DDE had the highest frequency in fish,

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followed by p,p'-DDD and p,p'-DDT (Li et al 2006; Beard, 2006). The metabolite p,p'-DDE accumulates the most in fish mainly due to absorption of DDE from the diet rather than to recent exposures to DDT. Difference in exposures of benthic and pelagic feeders to DDT and its metabolites have been observed (Dong et al 2010).

In the marine environment there is evidence to suggest that benthic organisms feeding at the bottom of the oceans accumulate higher levels of p,p'-DDT and its metabolites p,p'-DDE and o,p'-DDE than do surface feeders (Awofolu and Fatoki, 2003). In a freshwater lake system, it was found that bioaccumulation of DDT was greater in the pelagic food web than in the benthic food web due to increase in mobility of pelagic organisms and their ultimate reliance on benthos. DDT from these aquatic food webs can further accumulate in organisms in higher trophic levels of the food chain (Badach et al 2000; Gao et al 2008).

Studies in animals suggest that exposure to DDT may impair immune competence (Van den Berg, 2009). Recent vivo studies have also demonstrated that p,p'-DDE which is the most environmentally relevant DDT metabolite, has anti androgen properties when administered to rodents at relatively high doses (PANNA, 2007), which corroborates the in vitro study especially the idea that p,p'-DDE functions as an antagonist after it has bound to the androgen receptor (ANACP, 2004). This androgen antagonism or antiadrogen activity can explain a number of reproductive and developmental effects in male rats of various ages exposed to p,p'-DDE. The effects include reduced anogenital distance and retention of thoracic nipples in pups exposed during gestation and lactation. Recents studies have also noted delayed puberty in rats exposed either during juvenile development or at very low doses during gestation and lactation (ATSDR, 2002)

Due to the fact that all vertebrates share a similar endocrine system the observed effects of DDT on wildlife will in most cases have similar effects on humans. As in the case with many organochlorine insecticides, a major target of acute DDT exposure is the nervous system (WHO 2007). Research by Blumberg and Fean (2007) has also supported the fact that DDT prevents androgen from binding to its receptor thereby blocking androgen from guiding normal sexual development in, male rats and resulting

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in abnormalities. Evidence has been found in alligators in which hatchlings from DDE painted eggs are sexually indeterminate possessing both male and female reproductive characteristics (Perez-Maldonado et al., 2010).

Contamination of fresh water and marine fish by DDT has been found in many countries and regions; and the low ratio of DDE to DDT in fish suggest that newly applied DDT is still a problem in South east Asia, where contaminated farmed seawater fish is of concern (Cheung et al., 2007). As a result DDT is expected to remain a continual threat to wildlife and aquaculture fish, thereby raising the issue of the safety of fish consumption given that aquaculture and fishery products are the popular diets of many Asians (Kwong et al., 2008)

A lot of research has been done on the bioaccumulation of DDT on fish as well as its biomagnification along the aquatic food chain (Kidd et al., 2001, Wang et al., 2005). Fish are known to metabolize DDT, but the biological fate of DDT in fish has not been properly understood. This is mainly due to many complex biological processes which occur in fish, such as the differential bioaccumulation and elimination of various DDT metabolites, biotranslocation of DDT among organs and biotransformation of DDT (Kwong et al., 2008).

Looking at DDT kinetics and biotransformation in fish Kwong et al (2008) concluded that DDT was absorbed by means of gills under waterborne exposure, and was quickly traslocated to other parts of the body through blood circulation. In the same study concentrations of DDT metabolites were found to be low which might be due to the slow DDT metabolism or conversion in fish. These findings were also supported by Lech and Bend (1980).

Mavura and Wangila (2001) noted that in water DDD was the most predominant of all the metabolites. However in fish it was the DDE that was more predominant (34,9 compared to 3,2 DDD). Another study by Mitemo and Gitau (2006) showed similar results/trend whereby 73% of fish samples were detected with p,p'-DDE compared with 9% p,p'-DDD and 11% p,p'-DDT. So both studies came to the conclusion that it is

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possible that fish are capable of accumulating this type of residue (DDE) better than the others, (ANACP, 2004).

2.9 Other vector control methods

Bed nets are another control method when it comes to malaria and in countries like Kenya they are the primary malaria prevention method (KMoH, 2001), however their use by the public is extremely low. Insecticide-Treated Nets or ITNs provide protection against adult mosquitoes. The netting material is treated with synthetic pyrethroid insecticide, which is relatively safe. The insecticide repels mosquitoes and inhibits them from enjoying their blood meal even when there are large holes in the nets. The most commonly used pyrethroids are permethrin, deltamethrin and lambda cyhalothrin (ATSDR, 2002). Several studies carried out in Ghana, Gambia, Kenya have concluded that ITNs tend to reduce child illness by 29% - 63% and childhood mortality by 17% – 60% depending on net coverage and malaria transmission pressure (IPEP, 2006)

Environmental management of vector control is another way of controlling malaria (van den Berg, 2009). Before the advent of pesticides, mosquito control depended mainly on identification and elimination of vector breeding spaces and water bodies in human habitats (Keiser et al., 2005). According to Walker and Lynch (2007), aquatic predators have also been used to control malaria vectors in some countries. Larvivorous fish have been reared and released in small tanks and well to control vector breeding but success has been limited to more or less permanent water bodies (van den Berg, 2009)

Some bacteria like *Bacillus thuringiensis israelensis* and *Bacillus sphaericus* have also been used as microbial larvicides. This is mainly due to the fact these bacteria produce toxins that are directly harmful to mosquitos and also they have a low risk to resistance development (Lacy, 2007). Field trails have shown that both bacteria have good potential to manage the breeding of mosquitos.

House spraying can also be used as a way to control malaria. Initially house spraying was dependent on DDT but gradually shifted away to organophosphates like malathion,

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fenitrothon and carbamates. Larviciding is the killing of mosquito larvae and is always a supplementary measure in the integrated Vector Control Programme. The organophosphate temophos is always used (WHO, 2008)

2.10 Conclusion

It is very important to note that malaria is a very dangerous disease affecting most of sub-Saharan Africa mainly due to the climatic conditions found in this area. The use of DDT for IRS has proven to be the most effective, easy and cheap way to combat this deadly disease. There is a huge cloud surrounding the use of DDT to fight malaria because of its long term effect on humans and wildlife. Evidence has shown that DDT has a tendency to bio accumulate in human tissue coupled with its persistence in the environment it become a very dangerous and toxic substance.

The main problem with the breakdown and translocation of DDT and its metabolites in the environment is that in the long run this toxic substance will accumulate in body fat and tissue to concentrations which can lead to cancer and birth defects. Furthermore DDT is now being detected in those areas which are outside of the spraying radius hence affecting species which were not meant to be affected. Tshilamusi is a rural area with mud huts hence DDT is still being sprayed in the area every year between October and April.

This study will contribute immensely to the community of Masisi because my findings can be used by the relevant departments in government in order to make sound decisions about the use of DDT to control malaria in the area. The spatial distribution of DDT will also help to determine if it is at an acceptable level or not. The results will be made available to the local community so that if the findings are detrimental to their health, the community can raise their concernes with an informed mind.

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CHAPTER THREE: RESEARCH METHODOLOGY

3.1 Sample collection

Soil, plant and water samples were collected from Tshilamusi area in Mutale district. A few homesteads were selected for the study and these sprayed houses where found within a radius of 30 meters. The study area was divided into three concentric circles with A being the area of heavy application, B is the area just outside the first zone and C is the outer core were no application of DDT takes place. In order to investigate the spatial distribution of DDT and its metabolites the sprayed homesteads in Tshilamusi were chosen because they are at an isolated area. This is important because all the detected concentrations will be from the sprayed homesteads only as the next houses are 4 kilometers away.

3.1.1 Soil

In the area of heavy application (zone A), 10 surface soil samples (0-5cm) were collected evenly around the concentric zone. In the next zones (B and C) 10 soil samples were also collected around each zone. At each sample location, 5 samples were collected at a 2 m x 2 m^2 plot (located on the crossing diagonals four in the corners and one in the crossing point and thoroughly mixed to form a composite sample (Gong *et al.*, 2004). All overlaying vegetation was removed prior to sampling and the soil samples were carefully screened to remove stones, leaves and other unwanted matter. The soil samples were collected using stainless steel scoops and they were stored in pre-cleaned amber glass containers. The soil samples were then sieved through a 2 mm mesh, wrapped in aluminum foil to prevent any reactions and contamination and stored at 4°C until further analysis.

Two sampling devices were carried to the field and brought back to the laboratory during the sampling period and treated as blanks. No detectable amounts of the target analytes were found in the field blanks. Prior to instrumental analysis a starndard solution of DDT was analysed to ensure no significant degradation of DDT occurred in the analytical system (EPA-recommended protocol suggest an acceptable breakdown magnitude of DDT less or equal to 20%: Foreman and Gates, 1997)

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3.1.2 Water

Drinking water in the Tshilamusi area was collected from tap water which comes from a drilled borehole. Water samples were collected from the 5 taps in the study area which were supplied by one borehole. Water samples were collected from all the taps using 1L Winchester bottles. Sampling was done three times at the beginning, middle and at the end of the spraying season. The bottles were rinsed with the water samples before collection. To preserve the samples they were kept in amber glass bottles and stored at 4°C until analysis (Sibali and Okonkwo, 2009).

3.1.3 Plants

Tshilamusi is an area where little agriculture is practiced due to the high temperatures and sandy soils. The locals only plant a few domestic vegetables like cow peas, tomatoes and spinach. In this study tomato and spinach leaves were collected as samples because these were the plants which were found often throughout the study area. Eleven plant samples of leaves were collected in a direction of North West to South East. This was done mainly because these were the only places were the plants were. These leaves were sampled from crops farmed by the local people for food mainly on their property and in fields. The samples were then collected in brown bags and stored at 4°C until chemical analysis. This was done to prevent any contamination and light penetration which might lead to the reaction of the samples (Van Dyk *et al.*, 2010).

3.2 Sample extraction and preparation

3.2.1Soil extraction

The sampled soils were sieved and all the unwanted material like leaves and stones removed to make it easy for extraction. Soil extraction was carried out using a Soxhlet extraction method (Fitzpatrick *et al.*, 2000). In this method firstly 10 grams of the soil sample was accurately weighed using a measuring balance, An equivalent amount of sodium suphate which had been previously dried at 60°C for 24hrs was placed in a

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cellulose extraction thimble together with the measured soil sample. A 100 ml of the extraction solvent (acetone:hexane 1:1 v/v) was put in the 250 ml round bottomed flask and fitted onto the Soxhlet extractor.

The extraction process was performed for 12 hours to make sure that there was complete extraction of the DDT into the solvent. Constant temperature and passage of water was monitored to make sure that all the solvent which evaporated would condense and drip inside the extraction thimble. A boiling chip was also put in the round bottomed flask to enhance and quicken the evaporation process. The nature of the Soxhlet extraction process allowed a "clean" solvent to pass through the sample at a rate of four times/hour. Thus for the extraction of DDT,DDD and DDE , the solvent passed through the contaminated soil sample 96 times at a temperature less than that of the solvent

The liquid extract was quantitatively transferred to a volumetric flask. The soil was extracted according to the above scheme with a 1:1, v,v mixture of acetone and hexane in accordance with solvent choice as recommended in US Environmental Protection Agency (EPA) method 3540C. The extracts were then concentrated to 1ml on a rotary evaporator at 30°C and dissolved in cyclohexane (2 mL) for cleanup (Kihampa *et al.*, 2010)

3.2.2 Water

The extraction and concentration of water samples were performed by Solid Phase Extraction (SPE) method with C18 (Backerbond spe-1000 column). Before extraction first the water samples were filtered and all the suspended material removed. All the organic solvents and water which were used during the extraction and elution procedures were HPLC grade. The column was conditioned by the gradual passing of 6ml of hexane. It was then desiccated under vacuum (25mm Hg) for 2 min. Once the column was dry, 12ml of methanol was passed through, followed by 6ml water passage. The samples were then allowed to pass through the pretreated column at a flow rate of 5ml/min. Subsequently the column was washed with 1ml HPLC grade water. The

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A glass column (4 mm i.d x 15 cm) was plugged with glass wool previously washed with cyclohexane. It was then packed with Florisil (2 g) followed by anhydrous sodium sulphate (10 g). After the samples have been put in, the column was rinsed with acetone/hexane (2mL: 1:9 v/v) and hexane (5 mL) to remove any impurities. The eluate was further concentrated to near dryness on a rotary evaporator at 40°C and reconstituted in Hexane (2mL) for GC analysis (Kihampa et al., 2010).

3.3 Analysis

Prior to analysis, DDT, DDE and DDD standards were run to check column performance, peak height and resolution. With each set of samples a solvent blank, a standard mixture and a procedural blank was run in sequence to check for contamination, peak identification and quantification. Compounds were mainly identified by their retention times. All results for soil and plant samples were reported on a dry weight basis. (Zhang et al., 2002).

3.3.1Gas Chromatography-Electron Capture Detector

Analysis was carried out with a Clarus 500 gas chromatography (Perkin Elmer) equipped with an electron capture detector (ECD-Ni^{63})coupled with a fused-silica capillary column. The oven temperature programme for optimal component resolution was as follows : initial temperature 185 °C for 4min then 230 °C for 4.5 min and 270 °C for 3 min. temperature programmed ramp rate was set at 70 °C/min. The injector port and detector temperatures were set at 270 °C and 300 °C, respectively. Purified nitrogen (99.99%) purchased and supplied by Afrox Limited, South Africa was used as the carrier gas with a flow rate of 63 ml/min. A Turbochrom 4.0 chromatography station was used for chromatographic data processing. The GC was operated in a split less mode and the injection volume was 1µl for each injection, reference standards were used to identify and quantify the residues (Badach *et al.*, 2000).

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A GC-MS was used to confirm the results. Data acquisition and processing was done using GC-MSD Chemostation Software. After confirmation quantification was done using the Turbochrom chromatograph station.

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CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Introduction

This chapter contains all the soil, water and plant analysis results from Tshilamusi area. The analysis was done on the spatial distribution of DDT and its metabolites in different environmental media. The chapter also tries to explain the causes of the differences in spatial distribution of DDT in the Tshilamusi soils and the impacts this has on the environment.

4.2 Occurrence and levels of DDT and its metabolites in the different soils zones of Tshilamusi area in Mutale district

The study area was divided into three zones A, B and C, and from these zones soil samples were collected for analysis at the University of Venda ,ERM laboratories.

4.2.1 Concentration levels of DDT and its metabolites in Zone A

Figure 4.1 shows the different metabolites and their concentration levels from the 10 samples collected in Zone A from Tshilamusi area. The metabolites measured in this case were 4,4'-DDT, 4,4'-DDE and 4,4'-DDD.

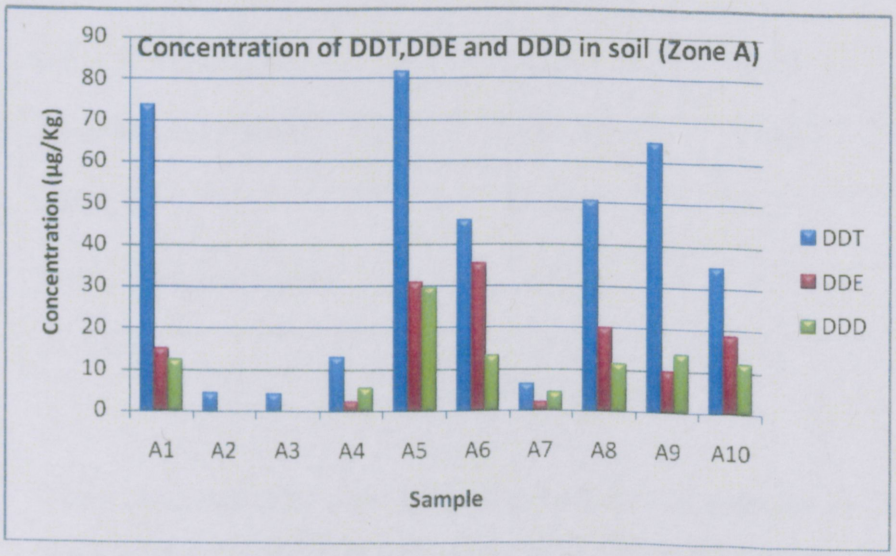


Figure 4.1: Concentrations of 4,4'-DDT, 4,4'-DDD and 4,4'-DDE in soil samples from Tshilamusi (Zone A).

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From the results (Figure 4.1), the metabolite 4,4'-DDT exhibited the highest concentration in all the samples and it was detected in all 10 samples. The other two metabolites occurred in the same 8 samples except in sample A2 and A3 with 4,4'-DDE having high concentrations than 4,4'-DDD in most of these samples except in samples A4, A7 and A9. Sample A5 provided the highest concentration for 4,4'-DDT and 4,4'-DDD whilst metabolite 4,4'-DDE had it highest concentration in sample A6.

From these results it can be noted that metabolite 4,4'-DDT was the most detected in all the samples from zone A and considering that the wettable powder used for IRS mainly consistutes 75% 4,4'-DDT it was no surprise to have a similar profile being detected (Bouwman et al, 2006). On the other hand Van Dyk et al (2010) notes that various factors also need to be taken into consideration regarding the different ∑DDT profiles in the different samples analysed. The factors to be considered are rate of metabolisation of DDT to 4,4'-DDD and 4,4'-DDE in the soil, exposure to 4,4'-DDD and 4,4'-DDE currently in the soil, ability of the various metabolites to accumulate and be stored in different media.

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The Table 4.1 below shows the statistical breakdown of all the samples collected from zone A in Thsilamusi area. Analysis was carried out for all the 3 metabolites from each sample collected so as to get a clear idea of the breakdown and concentration of the compounds.

In zone A, a total of 10 samples were also collected wherein 4,4'-DDT, 4,4'-DDE and 4,4'-DDD were detected in 100%, 80% and 80% of the samples respectively. Concentrations detected for 4,4'-DDT ranged from 4.08 to 81.45 µg/kg with a mean of 37.80 while 4,4'-DDE ranged from 1.80 to 35.1 µg/kg with a mean of 15.44 µg/kg. The highest detected concentration was 81.45 µg/Kg (4,4'-DDT) and the lowest was 1.80 µg/Kg (4,4'-DDE). The most predominant isomer in the samples collected was 4,4'-DDT (median=40.26 µg/kg) followed by both 4,4'-DDE (median=16.72 µg/kg and 4,4'-DDD (median=12.10 µg/kg).

Table 4.1: Statistical breakdown of concentrations of DDT and its metabolites in Zone A

	4,4'-DDT	**4,4'-DDE**	**4,4'-DDD**
Mean (µg/kg)	37.802	15.444	12.744
Standard deviation (SD)	29.855	11.045	7.612
Sample size (N)	10	8	8
Lower 95% conf. limit	16.447	6.209	6.379
Upper 95% conf. limit	59.158	24.68	19.109
Minimum	4.083	1.803	4.218
Median (50th percentile)	40.263	16.723	12.104
Maximum	81.456	35.1	29.37

These concentrations were far less than the ones detected by Zhang *et al* (2002) in China were 4,4'-DDE was the predominant metabolite reaches levels of 3538.50 µg/kg. Hence the lower values of total DDT found in zone A might be a result of proper spraying methods and no external sources of DDT other than from spraying. One-way

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Analysis of Variance (ANOVA) was used to measure the concentration variations among the three metabolites. The P value was 0.0255, which is significant. This means variation of concentration among metabolites means is significantly greater than expected by chance. The metabolite 4,4'-DDT had the highest standard deviation(SD) of 29.85 followed by 4,4'-DDE and 4,4'-DDD which had SD of 11.05 and 7.612 respectively.

4.2.2 Concentration levels of DDT and its metabolites in soils from Zone B

Figure 4 below shows the concentration values of the 10 soil samples collected from zone B in Tshilamusi. Three metabolites of DDT were analysed in every sample.

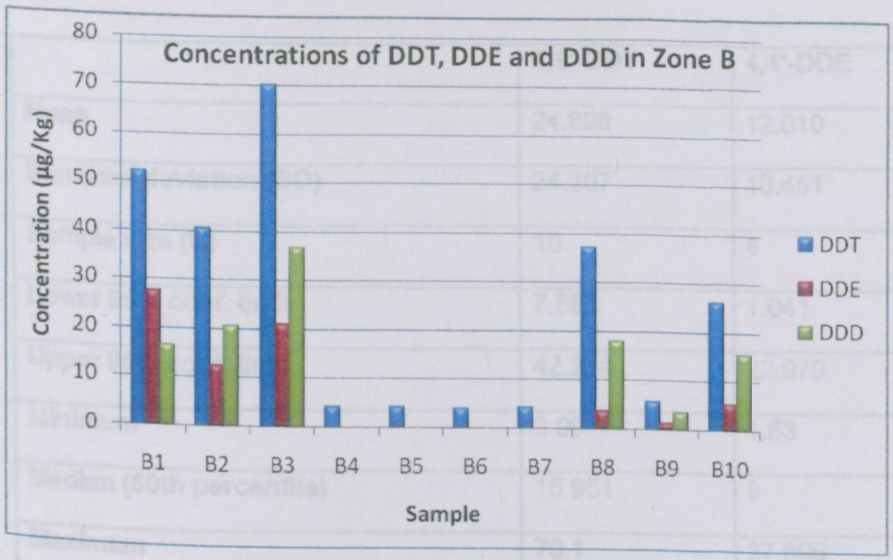


Figure 4.2: Concentration of 4,4'-DDT, 4,4'-DDE and 4,4'-DDD in soils from Tshilamusi (Zone B).

From Fig 4.2 above we can see that the distribution of metabolites was not the same throughout the samples collected. In samples B4, B5, B6 and B7 there was only one detected metabolite which is 4,4-DDT and it was present in all the samples although in varying amounts. The metabolites 4,4-DDD and 4,4-DDE were detected in the same 6 samples and the latter had the lowest concentrations among the 3 metabolite in all the samples except in sample B1 where it had a higher concentration than 4,4'-DDD. After DDT has been sprayed it is then converted to the other two metabolites DDE and DDD

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so the presence of these two metabolites in the same 6 samples mean that DDT in those samples had already started reacting and converting the pesticide to metabolites. So in the four samples wherein only 4,4'-DDT was detected it might be due to most recent spraying maybe on the same day hence no or little conversion had taken place.

The table 4.2 below shows the statistical breakdown of all the samples collected from zone B in Thsilamusi area. Analysis was carried out for all the 3 metabolites from each sample collected so as to get a clear idea of the breakdown and concentration of the compounds

Table 4.2: Statistical breakdown of the concentration of DDT and its metabolites in Zone B.

	4,4'-DDT	4,4'-DDE	4,4'-DDD
Mean	24.898	12.010	18.547
Standard deviation (SD)	24.207	10.451	10.733
Sample size (N)	10	6	6
Lower 95% conf. limit	7.583	1.041	7.282
Upper 95% conf. limit	42.214	22.979	29.813
Minimum	3.99	1.53	3.645
Median (50th percentile)	15.951	9	17.29
Maximum	70.1	27.696	36.86

In the 10 soil samples collected in zone B of Tshilamusi sampling site three metabolites of DDT were detected namely 4,4'-DDT, 4,4'-DDE and 4,4'-DDD with means of 24.89, 12.01 and 18.54 µg/kg respectively. The ranges of detection varied among the metabolites with 4,4'-DDT concentrations ranging from 3.99 to 70.1 µg/kg where as 4,4'-DDE ranged from 1.53 to 27.696 µg/kg and 4,4'-DDD concentrations ranged from 3.645 to 36.86 µg/kg. In this zone metabolites 4,4'-DDT, 4,4'-DDE and 4,4'-DDT were found at quantitative levels in 100%, 60% and 60% of the samples respectively. The presence of all the metabolites in the samples is similar to Van Dyk *et al* (2010) studies wherein all

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the metabolites were also detected and this might be a result of fresh DDT pesticide being applied hence it is continually being degraded and converted into other metabolites (Tavares et al.,1999).

The total DDT concentration from all the metabolites ranged between 1.53 and 70.10 µg/kg with 4,4'-DDE having the lowest and 4,4'-DDT having the highest concentrations. In this Zone the most predominant isomer was 4,4'-DDT (median=15.95) followed by both 4,4'-DDE (median=9 µg/kg) and 4,4'-DDD (median=17.29 µg/kg). This finding is consistent with the recent use of the pesticide as similar results were also found in Mozambique by Manaca *et al* (2012). In that study they found that the concentration of 4,4'-DDT was greater (nine times or more) than those of the other metabolites.

It is important to note that the conversion of 4,4'-DDT into 4,4'-DDE can start immediately after application but the half life of the former could be years (ATSDR, 2002: Bornman *et al.*,2010). This was also the same when it came to the Standard deviation with 4,4'-DDT having the highest followed by 4,4'-DDD then 4,4'-DDE. One-way Analysis of Variance (ANOVA) showed the P value is 0.4080, considered not significant hence variation among metabolites means is not significantly greater than expected by chance.

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4.2.3 Concentration levels of DDT and its metabolites in soils from Zone C

Figure 4.3 below shows the concentration values of the 10 soil samples collected from zone C in Tshilamusi. Three metabolites of DDT were analysed in every sample.

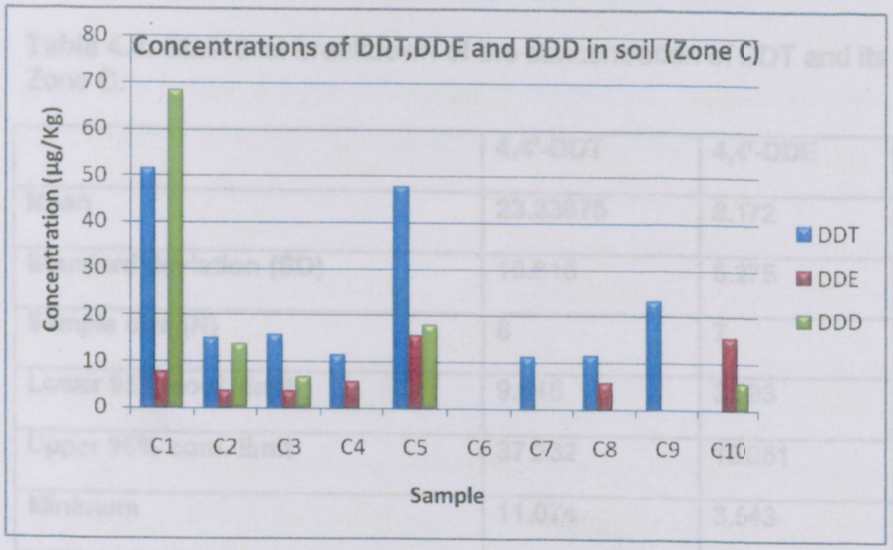


Figure 4.3: Concentration of DDT metabolites in soils of Tshilamusi (Zone C).

Fig 4.3 shows the concentrations of DDT metabolites detected from the soil samples. All the three metabolites were only detected together in 40% of the samples, whereas in the other 60% of the samples only two or one metabolites was detected as the other metabolites were below the detection limit. From these results (Fig 4.3) it can also be noted that the three metabolites were only detected together in only four samples (C1,C2,C3 and C5). The highest concentration of all the metabolites was 4,4'-DDD which was detected in sample C1 and 4,4'-DDT also exhibited its highest concentration in the same sample.

In sample C6 the concentration of all the metabolites were way below the detection limit of 0.5. The metabolite 4,4'-DDT occurred in all the samples except A6 and C10; and although 4,4'-DDD only occurred in 5 samples, it had high average concentration compared to 4,4'-DDE which occurred in 7 samples. The presence of more 4,4'-DDD and 4,4'-DDE compared to 4,4'-DDT means that there is less of fresh DDT and more metabolites indicating that a lot of degradation took place already. Since this area is far

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from the area of original application, less reaches zone B. This explains why there is presence of more metabolites from degradation.

The table below shows the statistical breakdown of three the metabolites from samples collected from zone C in Thsilamusi area.

Table 4.3: Statistical breakdown of the concentration of DDT and its metabolites in Zone C.

	4,4'-DDT	4,4'-DDE	4,4'-DDD
Mean	23.33875	8.172	22.422
Standard deviation (SD)	16.616	5.275	26.164
Sample size (N)	8	7	5
Lower 95% conf. limit	9.446	3.293	-10.06
Upper 95% conf. limit	37.232	13.051	54.904
Minimum	11.074	3.543	5.631
Median (50th percentile)	15.355	5.625	13.728
Maximum	51.263	15.69	68.337

Analysis of the distribution of DDT compounds and its metabolites from 10 soil samples in zone C of Tshilamusi sampling site has shown mean concentrations of 23.33, 8.17 and 22.42 µg/kg of 4,4'-DDT, 4,4'-DDE and 4,4'-DDD respectively. The standard deviation of the metabolites had 4,4'-DDD with the highest 26.16 µg/kg followed by 4,4'-DDT then 4,4'-DDE with the lowest 5,27 µg/kg. This might be as a result of less DDT pesticide reaching the area hence the higher proportion of DDT metabolites being found in the area. All the concentrations detected under 4,4'-DDT ranged from 11.074 to 51.26 µg/kg with a mean of 23.33 µg/kg which was higher compared to concentration values obtained by Choi et al (2011).

On the other hand 4,4'-DDE and 4,4'-DDD concentrations ranged from below detection limit (bdl) to 15.69 µg/kg and bdl to 68.337µg/kg respectively. In all the 10 soil samples collected 4,4'-DDT, 4,4'-DDE and 4,4'-DDD were detected at quantitative levels in 80%,

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70% and 50% of the samples respectively. The highest concentration levels were detected at 68.337 µg/kg (4,4'-DDD) whilst the lowest was 4,4'-DDE with 3.543 µg/kg. The total DDT concentration range of all the metabolites was between 3.543 µg/kg and 68.337 µg/kg in the soil samples collected. The metabolite 4,4'-DDD had the highest standard deviation of 26.164 µg/kg followed by 4,4-DDT then 4,4'-DDE with 5.275 µg/kg. This shows a huge difference in lowest and highest concentration values of 4,4'-DDD. The predominant isomer was 4,4-DDT (median=15.355 µg/kg) followed by 4,4'-DDE (median=5.625 µg/kg) and 4,4'-DDD (median=13.728 µg/kg).The P value is 0.2021, considered not significant. Variation of concentration among e metabolites means is not significantly greater than expected by chance.

4.3 Distribution and concentration of DDT and its metabolites in soils from Tshilamusi

The figure below shows the variation in mean DDT concentrations among the three zones A,B and C which were sampled as well as variations of mean concentrations of the metabolites in each zone.

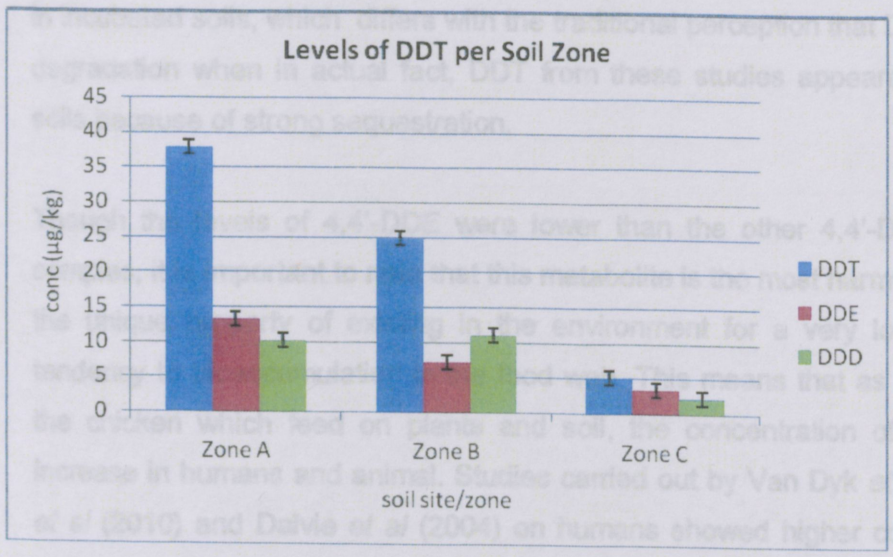


Figure 4.4: Figure 4.4. Concentrations of different metabolites of DDT per Soil Zone

From the results (Fig 4.4), it is clear that 4, 4'-DDT was the metabolite with the highest concentrations in each of the three zones. This might be an indication that the DDT in these soils was just recently deposited (Tao et al.,2007) or another unknown factor is

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slowing the breakdown of DDT to its metabolites. Two metabolites 4,4'-DDT and 4,4'-DDE show a decline in concentrations from zone A to C, the same cannot be said of 4,4'-DDD which had its highest mean concentration levels in zone B followed by zone A then very low concentrations in zone C. In zones A and B the mean concentration of 4,4'-DDT was approximately twice that of 4,4'-DDD and 4,4'-DDE but in zone C there was little difference in concentration between the three metabolite. In a study by Philips (2001) similar findings were also noted as all samples in that study consisted of 4,4'-DDT and the metabolite 4,4'-DDD had the lowest percentage (20%).

The proportions of total DDT occurring as 4,4'-DDE and 4,4'-DDD might indicate differences in the patterns of DDT breakdown from site to site. According to Bopp (1982) this pattern could be a result of anaerobic conditions which tend to favour conversion of DDT to 4,4'-DDD. In contrast the slightly higher ratios of 4,4'-DDE to 4,4'-DDT in other samples in zone C likely reflect aerobic conditions, because aerobic conditions favour the conversion of 4,4'-DDT to 4,4'-DDE. Various insitu studies (Aislabie et al., 1997; Corona-Cruz et al., 1999) showed remarkable degradation of DDT in incubated soils, which differs with the traditional perception that DDT is recalcitrant to degradation when in actual fact, DDT from these studies appeared to be retained in soils because of strong sequestration.

Though the levels of 4,4'-DDE were lower than the other 4,4'-DDD in some of the samples, it is important to note that this metabolite is the most harmful of them all. It has the unique property of existing in the environment for a very long time and has a tendency to bioaccumulation in the food web. This means that as as more people eat the chicken which feed on plants and soil, the concentration of 4,4'-DDE tends to increase in humans and animal. Studies carried out by Van Dyk *et al* (2010), Bornman *et al* (2010) and Dalvie *et al* (2004) on humans showed higher concentrations of this metabolites than the other metabolites of DDT higher up the food chain.

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The table below shows the statistical breakdown of all the 30 soil samples collected from Tshilamusi area. Comparison of total DDT was done among the 3 zones A, B and C.

The statistical breakdown and analysis of the ∑DDT of samples from all the samples in zones A, B and C. The DDT metabolites were detected in all of the samples in Zone A and zone B and there was 90% detection in zone C. When comparing the three zones zone A had the highest maximum concentrations of DDT detected which was 185.82 µg/kg followed by zone B with 127.97 µg/kg and zone C had the lowest detection of 27.28 µg/kg. The soil samples contained all the DDT isomers, but the 4,4'-DDE 185.82 µg/kg was high.

Table 4.4: Statistical breakdown of the occurrence and concentrations of 4,4'-DDT, 4,4'-DDD and 4,4'-DDE in soils of Tshilamusi homesteads.

	Zone A	Zone B	Zone C
N	10	10	9
Min	4.083	3.99	3.074
Max	185.82	127.97	27.277
Mean	65.6906	43.2331	12.18878
Std. error	18.17085	14.27981	2.476656
Stand. Dev	57.46128	45.15672	7.429968
Median	73.5075	29.0485	13.896

It is important to note that children play in the sand around the house and are probably exposed to these residues. In zone A the mean concentration was 65.69 µg/kg which was the highest of all of the zones followed by zone B and C which had 43.23 µg/kg and 12.18 µg/kg respectively This can be attributed to the fact that since A is the zone of application some of the DDT as dust or particles fall from the treated walls or roofs of the dwelling onto the ground (Van Dyk *et al.*,2010).

The standard deviation follow the same trend as that of the mean concentrations with zone A having the highest SD of 57.46 µg/kg followed by zone B with 45.16 µg/kg and

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zone C had the lowest SD of 7.43 µg/kg. The 4,4-DDT concentration detected from soils in Tshilamusi homesteads exhibited a larger standard deviation when compared to the other metabolites due to the higher values which were detected. The higher SD values could be as a result of dissimilar 4,4'-DDT breakdown and transformation after spraying (WHO, 2002). The noted variability of 4,4'-DDE may compound to the accumulated dispersion emanating from the dissimilar distribution of DDT due to IRS and from compound transformation.

A One-way Analysis of Variance (ANOVA) was used to check the variation of the different types of DDT at each soil Zone (A-C) at 0.05 level of significance. For Zone A the P value is 0.0066, considered very significant. Variation among different DDT metabolite means/averages is significantly greater than expected by chance. In Zone B the P value is 0.062, which is considered not significant. This means variation among different DDT variant means/averages is not significantly greater than expected by chance. For Zone C the P value is 0.16, considered not significant which means variation among different DDT metabolite means/averages not significantly greater than expected by chance.

The persistence of organochlorines in the environment have also been reported in other areas. For instance in China, 4,4'-DDE and 4,4'-DDD have been reported to be widely distributed in soil despite the discontinued use of the pesticide in 1983 (Wu *et al*, 2007). In this study of Tshilamusi homesteads, concentrations of the most dominant metabolite 4,4'-DDT ranged from 0 to 125 µg/kg . In Tanganyika 4,4'-DDT were detected with higher concentrations ranging from 1.1 to 636.7 µg/kg despite their discontinued use (Hellar and Kishimba, 2003). This just goes to show that the concentrations detected in Tshilamusi in which DDT is still being spread are lower than in other countries where DDT is no longer being used.

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4.4 Environmental compartmentalization of DDT and its metabolites in Tshilamusi

Once the DDT pesticide is sprayed on the walls of the huts in Tshilamusi, some of it will bind on to the walls and some will be released as dust and will end up on the soils, plants and water samples around the homesteads.

4.4.1 Type and levels of DDT in soils

The table below shows the type of metabolites and its concentration detected in all the soil samples collected from Tshilamusi rural village in Limpopo. It also shows the statistical breakdown of the 30 samples collected from the study area

Table 4.5: Type and level of DDT in all the soil samples collected from Tshilamusi homesteads.

	4,4-DDT	4,4-DDE	4,4-DDD
N	29	21	19
Min	3.99734	1.53	3.6443
Max	75.456	35.1	68.336
Mean	19.559	9.626	13.7282
Variance	653.5133	105.3056	85.64734
Stand. Dev	25.56391	10.26185	9.254585
Median	7.592	5.69	11.862
25 prcntil	4.2435	3.684	4.218
75 prcntil	43.195	19.245	16.47
Skewness	1.032521	1.072791	1.224721
Kurtosis	-0.3426479	0.06143375	1.566113
Coeff. Var	109.2808	89.84662	74.39786

Examination of the distribution of DDT compound and its metabolites in 30 soil samples from Tshilamusi has shown mean concentrations of 28.83, 12.46 and 17.12 µg/kg of 4,4'-DDT, 4,4'-DDE and 4,4'-DDD respectively. The concentration ranges varied among the three metabolites with 4,4'-DDT concentrations ranging between 3.99 and 75 µg/kg

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whereas 4,4'-DDE concentrations ranged from 1.53 to 35.1 µg/kg and lastly 4,4'-DDD with concentration ranges between 3.64 and 68.33 µg/kg. The differences in concentrations and residues in soil may be a result of soil-air exchange, degradation and other dissipative processes like leaching (Zhang *et al.*,2007)

In all the samples collected 4,4'-DDT, 4,4'-DDE and 4,4'-DDD were detected at quantitative levels in 93%, 70% and 63% of the samples respectively. The total DDT concentration range of all the metabolites ranged between 1.53 and 75 µg/kg with 4,4'-DDE having the lowest concentration and the highest belonging to 4,4'-DDT. The most predominant isomer was 4,4'-DDT (median=19.559 µg/kg) followed by 4,4'-DDE (median=9.626 µg/kg) and 4,4'-DDD (median=13.728). The dominance of 4,4'-DDT in 90 percent of the samples even the ones with low total DDT levels is mainly an indicator that the whole area has been sprayed recently (MISAU,2006). This is true in the sampled area of Tshilamusi where DDT is sprayed in the area from August up until March every year in order to get rid of the mosquitoes.

One-way Analysis of Variance (ANOVA) was used to measure the variations of metabolites in all the soil samples collected, P = 0.0078, considered very significant. So variation among metabolite means is significantly greater than expected by chance.

The 4,4'-DDT levels measured in Tshilamusi were significantly higher when compared those found in DDT treated soils Mexico (Waliszewski *et al.* 2004). On the other hand, they were lower than levels which were detected in Tanzania (Marco and Kishimba 2005). It has been noted that levels of DDT tend to increase in those commodities kept in DDT sprayed rural houses hence the presence of DDT and its metabolites in the soils outside these homesteads.

It is important to note that in most soils collected in this study 4,4'- DDD and 4,4'- DDE are the major primary degradation metabolites of DDT. More importantly, 4,4'-DDE is the major product in an aerobic environment while under anaerobic conditions 4,4'-DDD is produced (Wang *et al* 2007). In laboratory studies carried out by (Zhang *et al.*,2011) it was noted that 4,4'-DDE and 4,4'-DDD accumulated rapidly after the incubation began and reached peaks on day 15 because of significant early biodegradation of parent DDT

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in soils. After that the levels of 4,4'-DDE and 4,4'-DDD began to decrease, which might be attributed to the degradation rates of 4,4'-DDE and 4,4'-DDD exceeding that of DDT after day 15 (Reid *et al.*,2000). So, even though the total 4,4'-DDE accumulation in soils was supposed to have been produced by DDT degradation, some 4,4'-DDE was detected at the beginning of incubation. It can then be concluded that the accumulation dynamics of 4,4'-DDE and 4,4'-DDD as a result of the degradation rates of DDT, and that of 4,4'-DDE and 4,4'-DDD , which to some extent are governed by the sequestration rate (Khan,1982). These are the factors which might have resulted in the variations in residue levels and rate of metabolite occurrence in the soils of Tshilamusi.

There was significant in the DDT data and the CV varied from 74% to 109%. Skewness of total DDT concentration is 1.73 indicating that the distribution of total DDT it skewed mostly positively and suggested that higher total DDT concentration levels were present and the spatial distribution of total DDT is not homogeneous.

The ratio of DDT metabolites (4,4'- DDD and 4,4'- DDE) to the parent DDT , can be utilized as a way to determine if there are new sources by which DDT is entering the environment (Harner *et al.*, 1999). In this study the ratio was found to be less than 1.0 from all the samples. Generally it is accepted that, when the ratio is greater than 1, the sources of the DDT are old , otherwise, there is a suspicion of potential new sources (Wang *et al.*, 2007). The basis for this concept is that more and longer the time of spraying of DDT pollutants in soil, the more metabolites are generated by DDT degradation. Again, it is traditionally believed that DDE and DDD are more recalcitrant to degradation than DDT (Wang *et al.*,2007). Hence, as a result of the assumptions outlined above, some scholars suggested that the (4,4'- DDE+4,4'-DDD)/4,4'-DDT ratio can indeed show how long DDT has been in the environment and thus be used to differentiate new sources from old.

However Zhang *et al* (2011) argues that (4,4'-DDE+4,4'-DDD)/4,4'-DDT is not a reliable way to identify new DDT sources, he goes on to argue that this criterion is based on a controversial theoretical foundation. From their laboratory studies in China they noted that the most important elements that governed the ratio for aged DDT in soil were

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degradation and sequestration of both DDT and the metabolites DDE and DDD. The results noted the significant degradation of DDT, DDE, and DDD which led to the conclusion that the ratio is finally controlled by their differences in sequestration.

4.4.2 Distribution and concentration of DDT and its metabolites in plant samples from Tshilamusi

A total of 11 samples were collected around the study area of Tshilamusi and analysed for 4,4'-DDT, 4,4'-DDE and 4,4'-DDD. The table below illustrates the statistical breakdown of the plant samples.

Table 4.6: Statistical breakdown concentration values of DDT and its metabolites from plants samples.

	4,4'-DDT	4,4'-DDE	4,4'- DDD
Mean	5.9976	4.7175	3.891
Standard deviation (SD)	5.267	2.902	3.018
Sample size (N)	10	4	8
Std. error of mean(SEM)	1.665	1.451	1.067
Minimum	1.35	2.58	0.762
Median (50th percentile)	4.144	3.67	3.926
Maximum	19.383	8.95	8.16

Eleven samples were collected and anlysed and at least one of the metabolites was detected in all of the samples. 4,4'-DDT was the most common metabolite as it was detected in ten of the samples. The metabolite 4,4'-DDD was detected in about 80% of the samples analysed and then 4,4'-DDE had the lowest presence as it was detected in only about 40% of the samples. Looking at the mean concentration of these three metabolites 4,4'-DDT had the highest with 5.99 µg/kg compared to 4,4'-DDE (4.71 µg/kg) and then 4,4'-DDD (3.89 µg/kg). The lowest concentration detected was found to be that of 4,4'-DDD (0.762 µg/kg) whilst the highest maximum concentration was found in 4,4'-DDT which was 19.383 µg/kg. The highest standard deviation was found in 4,4'-DDT (5.26 µg/kg) followed by 4,4'-DDE with a standard deviation of 2.90 µg/kg.

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The high presence of 4,4'-DDT and 4,4'-DDE in plants could be attributed to their very high octanol:water partition coefficients, which means they are very soluble in lipids and ultimately tend to accumulate in lipid compartments in biological systems (Guo et al.,2009). The dorminance of 4,4'-DDT is a clear reflection that the DDT pesticide is still being sprayed in the area. Since only leaf samples were collected for the study it is expected that there will be more of the 4,4'-DDT because of the direct deposition of the pesticide as dust particles (Dalvie *et al.*,2010)

Table 4.7 shows the concentration of total DDT from all the samples analyses as well as the distance at which the samples were collected.

Table 4.7: Concentrations of DDT and its metabolites in plants samples with distance (m) from the sprayed area.

SAMPLE ID	DISTANCE IN METRES	TOTAL DDT µg/Kg
P 1	-150	3.84
P 2	-110	5.036
P 3	-90	13.63
P 4	-50	12.301
P 5	-20	24.235
P 6	0	33.723
P 7	10	19.63
P 8	20	4.146
P 9	75	4.827
P 10	100	9.606
P 11	118	9.939

Sample ID P6 represent the point source and the samples collected from north east are denoted by the negative numbers and the ones from the south east by the positive numbers.

From the results (Fig 4.7) it can be noted that the highest concentrations were detected at the source of application (Sample ID P6) where the total DDT detected was 33.72 µg/kg. The least concentration (3.84 µg/kg) was detected around 150m from the source in the north westerly direction but on the generally outlook samples from the southeasterly direction had lower ∑DDT concentrations compared to the ones from the

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northwesterly direction. The ∑DDT concentration in the south easterly direction was 48.148 µg/kg whilst the northwesterly detection amounted to 59.042 µg/kg.

According to Hellstrom (2004) the pathway by which organic pollutants enter the vegetation is a function of chemical and physical properties of each pollutant, such as, water solubility, hydrophobicity and vapour pressure, as well as environmental conditions, such as temperature, organic content of the soil, and plant species. Uptake of DDT into these plants around Tshilamusi might have occurred from air or soil, since leaves presents the biggest plant area by which uptake from air can happen. It is very important to note that DDT and its metabolites are hydrophobic and hence the accumulation of these chemicals is largely due to the large lipid covered surface of leaves. A high percentage of these compounds tend to be detected more in shoots, leaves and at times in shoots (Zhang *et al.*,2002)

In this study DDT was detected from plant (pumpkin and tomatoe) leaves which were analysed. However in some greenhouse and field studies (O'Connor *et al.*, 1990, Webber *et al.*, 1994) owhich looked at the uptake of DDT from soil have concluded that the only root uptake that can be seen are accumulation in the lipid-rich peels of e.g. carrot and beet. The studies did not show any convincing evidence of transport of DDT in plants to above ground parts (Hellstrom, 2004). So this goes on to suggest that most of the DDT residues detected from this study was from direct deposition of the compound onto the plant leaves.

The presence of DDT in the plant samples is also a major concern and needs to be thoroughly monitored. According to studies (Dalvie *et al.*, 2004) done in the rural Limpopo areas, it was found that vegetables are a big part of the VhaVenda diet and they eat them almost every day. Though the concentrations detected in plants were a bit lower than in the soils, there is a likelihood of bioaccumulation of these DDT metabolites in plants and eventually in chickens which ingest these plants. In Tshilamusi homesteads the vegetable samples were mainly contaminated with 4,4'-DDT and 4,4'-DDE. The contamination of these plants was likely to result from root uptake from the

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breakdown products of DDT which are present in the soil, as opposed to the aerial precipitation of DDT during IRS (Van Dyk *et al.*, 2010).

4.4.3 Concentration of DDT and its metabolites in water samples from Tshilamusi homesteads

Analysis of all the water samples collected from the five taps around the sprayed homesteads led to concentrations that were below the detection limit of 0.07µg/l. The levels of DDT detected in water samples were likely to pose no risk to the local people of Tshilamusi using water from these taps because the levels were all well below the drinking water guidelines of 20µg/l (WHO, 2002). On the other hand there is need to monitor these during and just after spraying as the levels may be higher during this period. Due to the fact that 4, 4'-DDT, 4,4'-DDE and 4,4'-DDD are highly soluble in lipids and coupled with a long half life results this might lead to high bioaccumulation as has been found elsewhere in South Africa (Barnhoorn *et al.*, 2009).

Due to the fact that the quantification limits for DDT pesticides were usually above the water quality criterion, it became important to look at the toxicity factor in this study even though the metabolites were not detected at the quantification limit of 0.07. If we consider that the relative criterion for water quality for 4,4'-DDE and 4,4'-DDT is 0.001 µg/L and the quantification limit was 0.07 µg/L. Hence we can conclude that the detection of DDT and DDE meant that these metabolites had already exceeded their quality criteria many times. So the occurrence of these metabolites in water sample is very significant and should be monitored.

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4.4.4 Occurrence and distributions of DDT and its metabolites in soil and plants

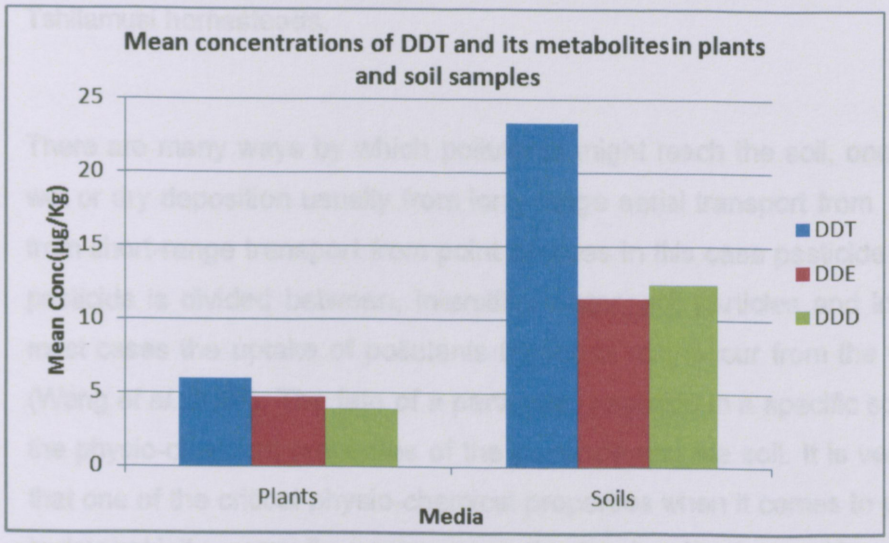


Figure 4.5: Comparison of mean concentration of ∑DDT in soil and plant samples

DDT was detected in both plants and soil samples though at different concentrations. Soil samples provided the highest ∑DDT concentration (125 µg/kg) of all the samples both soil and plants. Looking at the mean concentrations for both the plants and soils, it can be noted that in both media 4,4'-DDT was the dominant metabolite. On the other hand in plants 4,4'-DDE had higher concentration average than 4,4'-DDD but the opposite was true. Fig 4.5 above also shows that the means of metabolites in plants were almost similar as compared to metabolite means detected in soils where 4,4'-DDT was approximately twice the value of the other two metabolites.

The differences in concentrations and occurrence of DDT and its metabolites in different environmental media in Tshilamusi might be as a result of their physiochemical qualities like persistence, soil adsorption coefficient and water solubility (Tao *et al.*,2004). For example according to Wang *et al* (2007) 4,4'-DDE tend to have high soil adsorption coefficient (K_{OC}) coupled with low solubility in water, as well as a higher soil presence and its half life range from 50 days to 15 years. So due to the above properties DDT and its metabolites will therefore exhibit low degradation in soil hence their high detection in soil than water. The properties mentioned above mean that there can be

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contamination of nearby rivers as a result of erosion of the DDT sprayed soils from Tshilamusi homesteads.

There are many ways by which pollutants might reach the soil, one of them is through wet or dry deposition usually from long-range aerial transport from , and in other cases from short-range transport from point sources in this case pesticide spraying. The DDT pesticide is divided between, interstitial water, soil particles and interstitial air, and in most cases the uptake of pollutants by plants may occur from the water or air phases (Wang *et al.*,2007). The fate of a particular pesticide in a specific soil is dertermined by the physio-chemical properties of the pesticide and the soil. It is very important to note that one of the critical physio-chemical properties when it comes to pesticide pollution is hydrophobicity, normally expressed as the 1-octanol/water partition coefficient (Kow), or log Kow (Tao *et al.*,2007). This phenomenon explains why there was very little and at time no DDT residues detected in water samples whilst in plants samples DDT was detected even if the plants were a distance from the sprayed site.

In this study there were higher levels of ∑DDT in soils about three times more than the concentrations found in plants, whilst water samples had concentrations well below the detection limit. This variation is due to the transportation ability and accessibility of the pesticide to the media. In a study carried out in Limpopo, Van Dyk *et al* (2010) also noted that soil and vegetable samples had higher levels of DDT compared to water samples. The main reason for this would be that the source of water from Tshilamusi area is a community tap linked to a borehole hence there is less contamination. The slight contamination of the water might be attributed to contaminated containers used to fetch water which are usually stored inside the house. Just like in the study by Bornman *et al* (2010) 4,4'-DDT was the main metabolite found in the soil and plant samples, and is attributed to the continual spraying of DDT in this area hence the high presence of this compound.

An unpaired 't' test was used to check the variation of total DDT levels in different media (soil and plants) at 0.05 level of significance. Do the means of Plants and Soils differ

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significantly? The two-tailed P value was 0.0031, and was considered significant. So the difference in mean concentrations was quit huge and this is a concern which also warrants further study.

Further more the ratio of DDT/DDE in all matrices analysed was calculated and it was greater than 1. It is important to mention that the ratio of DDT/DDE can be used as a rough indication of the period of its application, a ratio of DDT/DDE near 1.0 or higher to 1.0 indicates use in the last 5 years (Perez Maldonado et al., 2010). Ratios of (DDD+DDE)/DDT greater than 1.0 shows aged residues in the soil. (Wang *et al* 2006). Often, the relative abundance of parent and metabolite is used to distinguish fresh (DDT/DDE>1) from aged (DDT/DDE<1) material (Pozo et al., 2011).

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4.5 Spatial distribution of DDT and its metabolites (∑DDT) in the soils from the DDT sprayed homesteads of Tshilamusi and surrounding areas

The Figure 4.6 shows the spatial distribution of ∑DDT from the samples area of Thilamusi. The figure was divided into three zones to clearly illustrate and show the differences in concentration from zone A to C

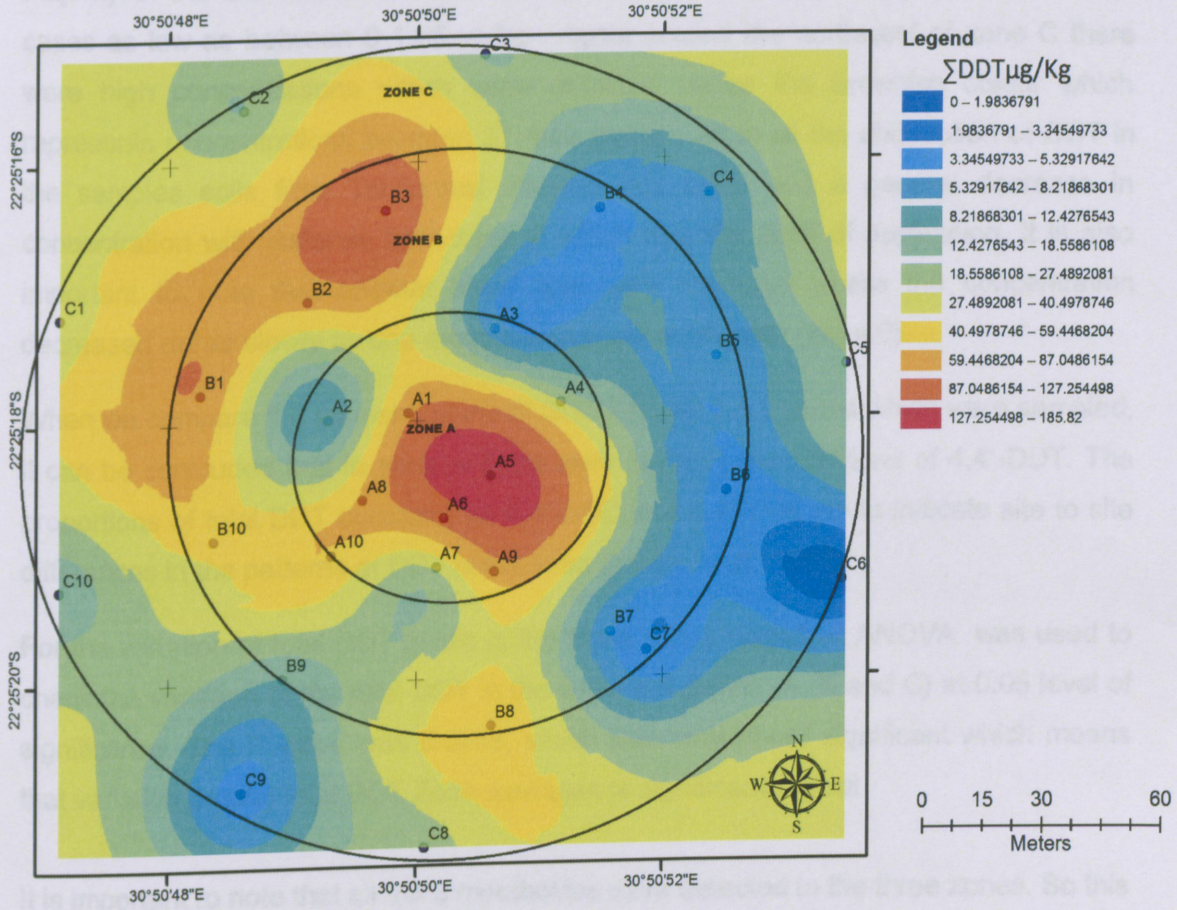


Figure 4.6: Map showing the zones and distribution of ∑DDT in the soils of Tshilamusi.

The map shows the spatial distribution of total DDT in the area of Tshilamusi. The sprayed homesteads are found in zone A which is at the centre. Figure 4.6 clearly illustrates that the distribution of DDT was mainly high at the centre around sample A5 and A6 as this was the area of heavy application which is dipicted by the red colour. Moving outwards in zone B there was a general decrease in concentrations except

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around B3 to the north west were concentrations between 87-127 µg/kg were also detected. To the east of zone B the concentration decreased rapidly as shown by the blue colour to concentrations below 18.55 µg/kg.

Moving on to the south east the DDT concentrations in zone B were slightly higher than the one on the eastern side but at the same time lower than in zone A. In Zone C the majority of the are had concentrations which were lower than 8 µg/Kg and in some cases as low as between 0-1.98 µg/kg . Again around the northwest of zone C there were high concentrations which were detected hence the brownish colour which represents concentrations between 27-40.9 µg/Kg . All in all the distribution of DDT in the samples soils from Tshilamusi showed that there was a general decrease in concentration with distance from zone A which was the zone of application. It is also important to note that another trend was also observed where the concentration decreased rather slowly as one move towards the north west (Fig 4.6).

When we compare the concentrations of DDT from all the 3 zones which were sampled, it can be concluded that in zone A there were higher concentrations of 4,4'-DDT. The proportions of total DDT occurring as 4,4'-DDD and 4,4'-DDE could indicate site to site differences in the patterns of DDT breakdown (Phillip *et al.*, 1997)

For the variation of total DDT levels in the three zones statistical ANOVA was used to check the variation of the total DDT in the three soil Zones (A, B and C) at 0.05 level of significance. The P value was 0.0258, which was considered significant which means that variation among total DDT Zone averages is significantly great

It is important to note that all the 3 metabolites were detected in the three zones. So this means that there is high probability of the DDT getting into the food web or affecting humans and animals (Cheung *et al.*,2010). These results from Tshilamusi raise concern regarding human exposure to the soils which are contaminated and most notably to children. Hwang *et al* (2008) states that children are most vulnerable due to their long exposure periods to the out door soil when they are playing and through other behavioral characteristics (Butte, 2004). For example ingestion of non-food items and regular hand to mouth contact. In a rural area like Tshilamusi with no pavements, small

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children spend most of their time outdoors playing and in many instances eat soil particles while playing hence there is high risk of exposure.

The levels of ∑DDT concentrations of plants in Tshilamusi do correlate with the results of soils concentrations. The thematic map (Fig 4.6) generated from the total DDT concentrations in soil show higher concentration in the inner zone as well as towards the North West. Similar results were generated from the analysis of plant samples which also showed higher concentration of ∑DDT in all the plants species collected from this area. This just goes to support the results of Gong *et al* (2006) who found that DDT pesticides tend to bioaccumulate in plants around the area where the soils are contaminated.

Once DDT has been sprayed on the walls of the huts it is now subject to different agents of weather and different physiochemical reactions which will determine the distance and rate of travel from the area of application (Zhang *et al.*,2002. In this study there was a huge difference in the total DDT detected in each of the 3 zones, with Zone A as expected having the highest concentrations followed by B then C. This can be attributed to the obvious fact that more DDT is found in the zone wherein its sprayed yearly and the fact that its bio persistence in soil is great and would require processes such as erosion, dispersion and heavy winds to move the DDT into other zones (Pozo *et al.*,2010).

These processes leads to the conclusion that pesticide movement in the environment is very complex because transfers in to different environmental compartments are always occurring continually all the time. Although long range transportation of pesticides is a possibility it does not necessarily mean that all pesticides sprayed will travel long distances or that they will end up in ground water (Kwong *et al.*,2010). This is true when we look at the Tshilamusi homesteads wherein the majority of the DDT was detected in the first two zones with the outer zone contributing about 8 % to the total DDT detected in all the zones.

Once a pesticide like DDT has been released into the environment two things are likely to happen, it might be degraded by the action of sunlight, water or other chemicals or

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microorganisms such as bacteria or the pesticide might may be broken down (ATSDR, 2002). The process of degradation often results in the formation of more toxic compounds like 4,4'-DDE and 4,4'-DDD, hence the presence of these compounds in this study.

In Tshilamusi homesteads notable concentrations of 4,4'-DDT, 4,4'-DDE and 4,4'-DDD were detected far away from the area of application in zone C. Similar findings were also noted by Martinez *et al* (2010) in a study of DDT levels in Mexico wherein concentrations of 4,4'-DDE ranged from 1 µg/kg to 7881 µg/kg in the outdoor soils far from the area of application. Gong *et al* (2004) goes on to mention that even if the pesticides are not volatile, the longer time that they persist might result, over time in measureable quantities of the pesticide moving through the atmosphere and accumulating in the unsprayed areas.

Looking at the spatial distribution of DDT and its metabolites in soil from Tshilamusi, there is a pattern which can be observed from the map (Fig 4.6). Although the concentrations decreased with distance from the area of application, it can also be observed that the decrease in concentration was at a lower rate when moving towards the North West and the opposite is true when moving towards the south east. The most logical reason for this variation from the general trend is the fact that in this area winds usually blow from south east to North West especially in the summer months and this is the time that application of DDT starts in the area.

Several studies have pointed to the fact that all pesticides, regardless of the medium that they are applied in have the potential to be transported by air (Dalla Villa *et al.*,2006: Yue *et al.*, 2011). Airborne pesticides like DDT can move long distances as they can attach to small particles such as soil or leaves that can be carried away by wind (Huang *et al.*, 2007). In Tshilamusi area the local folks usually sweep their huts and the surrounding area and this dust can be carried over distances by wind hence landing in places where DDT was not originally sprayed.

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The study results suggest that:

- Once DDT has been sprayed around the homesteads, with time it finds its way into different environmental media around the homesteads.
- The concentration levels of DDT and its metabolites from a recently sprayed areas vary significantly from one environmental media to another
- The metabolite 4,4'-DDT was the most dominant metabolite in soil and plant samples which were analysed.
- Distance plays an important role in determining concentration levels of DDT and its metabolites as the pesticide tend to reach areas which far away from the sprayed site.

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CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

From all the DDT metabolites analysed in this study 4,4'-DDT was the most dominant although the other metabolites 4,4'-DDE and 4,4'-DDD were also detected at significant levels. This is quite worrying because this is "fresh" DDT meaning it's as a result of continual spraying which is taking place in Tshilamusi. These concentrations in soils and plants might lead to further exposure to children and even adults who come into contact with the soil in their everyday lives.

In general the concentrations detected in and around Tshilamusi homesteads compares with values reported in other countries worldwide. Although the concentrations of pesticide residues reported under this investigation were low, it is crucial to note that soil pollution can play a vital role in the global fate and distribution of pesticides.

The detection of DDT and its metabolites in Zone C which is far away from the area of spraying is a cause for concern because these metabolites have a longer half- life which might lead to more accumulation of the compound. Detection in soil means that there is a possibility of DDT bioaccumulating in the food chain.

It is important to note that the quotient DDT/DDE in all matrices was always > 1. So there is reall need for more research and analysis in Tshilamusi area so that we can really determine to what extend people staying this area might be affected from IRS. In the mean time there is need for precautionary measures to be implemented, it is of utmost importance to initiate risk-reduction programmes which reduce exposure to the pesticide in Tshilamusi area.

The findings from this study should help in evaluation the safety regulations when it comes to Indoor Residual Spraying in order to reduce unnecessary pollution of the environment. The malaria control programme should include education regarding the correct and proper preparation of food (vegetables), washing of hands after exposure to soil and looking after the infants who usually play outside in the soil.

So as to develop and sustain high levels of protecting the environment, a good and solid monitoring program for the continual surveillance of DDT in Tshilamusi is required, and

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then the adoption of an efficient risk assessment criterion to identify the likely consequences of these pesticides in the various environmental media

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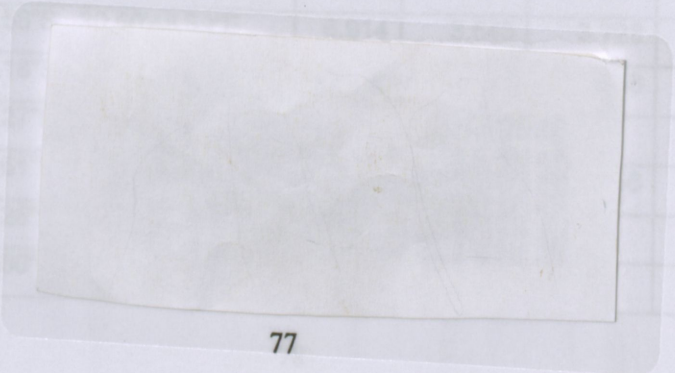
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APPENDICES

Appendix A: Distribution and concentration levels of DDT and it metabolites in all soil zones in Tshilamusi

	Sample ID	GPS	4,4-DDT	4,4-DDE	4,4-DDD	∑DDT
Zone A	A1	22 25'17.94"S 30 50'49.93"S	73.51	14.869	12.345	**100.724**
	A2	22 25'17.98"S 30 50'49.28"E	4.206	bdl	Bdl	**4.206**
	A3	22 25'17.30"S 30 50'50.63"E	4.083	bdl	Bdl	**4.083**
	A4	22 25'17.88"S 30 50'51.17"E	12.696	2.049	5.535	**20.28**
	A5	22 25'18.44"S 30 50'50.60"E	125.8	30.65	29.37	**185.82**
	A6	22 25'18.76"S 30 50'50.22"E	45.76	35.1	13.245	**94.105**
	A7	22 25'19.14"S 30 50'50.16"E	6.363	1.803	4.218	**12.384**
	A8	22 25'18.61"S 30 50'49.56"E	50.492	19.914	11.406	**81.812**
	A9	22 25'19.18"S 30 50'50.63"E	64.692	9.626	13.971	**88.289**
	A10	22 25'19.03"S 30 50'49.31"E	34.765	18.576	11.862	**65.203**
Zone B	B1	22 25'17.77"S 30 50'48.25"E	52.24	27.696	16.47	**96.406**
	B2	22 25'17.07"S 30 50'49.11"E	40.63	12.47	20.71	**73.81**
	B3	22 25'16.37"S 30 50'49.74"E	70.1	21.01	36.86	**127.97**
	B4	22 25'16.38"S 30 50'51.48"E	4.281	bdl	bdl	**4.281**
	B5	22 25'17.54"S 30 50'52.43"E	4.281	bdl	bdl	**4.281**
	B6	22 25'18.58"S 30 50'52.52"E	3.99	bdl	bdl	**3.99**
	B7	22 25'19.66"S 30 50'51.58"E	4.323	bdl	bdl	**4.323**
	B8	22 25'20.37"S 30 50'50.61"E	37.238	3.825	18.11	**59.173**
	B9	22 25'19.97"S 30 50'48.92"E	5.646	1.53	3.645	**10.821**
	B10	22 25'18.90"S 30 50'48.36"E	26.256	5.53	15.49	**47.276**
Zone C	C1	22 25'17.17"S 30 50'47.12"E	11.263	7.677	8.337	**27.277**
	C2	22 25'15.58"S 30 50'48.59"E	6.914	3.543	3.728	**14.185**
	C3	22 25'15.18"S 30 50'50.54"E	5.795	1.543	6.558	**13.896**
	C4	22 25'16.27"S 30 50'52.37"E	1.394	5.592	bdl	**6.986**
	C5	22 25'17.61"S 30 50'53.49"E	7.592	5.69	1.856	**15.138**
	C6	22 25'19.28"S 30 50'53.46"E	ND	ND	ND	**0**
	C7	22 25'29.80"S 30 50'51.87"E	3.074	bdl	bdl	**3.074**

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