SEASONAL VARIATION OF CARBARYL AND CYPERMETHRIN IN SOILS, GROUND WATER AND SURFACE WATER IN A COTTON GROWING AREA OF LISUNGWI IN NENO DISTRICT, MALAWI

M.Sc. (WATER RESOURCES AND SUPPLY MANAGEMENT) THESIS

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THE POLYTECHNIC

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M.Sc. (Water Resources and Supply Management) Thesis

By

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Submitted to the Department of Physics and Biochemical Sciences, Faculty of Applied Sciences in partial fulfillment of the requirements for the degree of Master of Science in Water Resources and Supply Management

University of Malawi

The Polytechnic

October, 2017

DECLARATION

I, Charity Beauty Kanyika – Mbewe, declare that this is my own work and has not been presented or submitted elsewhere for any award. All additional sources of information have been acknowledged.

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Charity Beauty Kanyika Mbewe

Date: _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

CERTIFICATE OF APPROVAL

We, the undersigned, certify that we have read and hereby recommend for acceptance by the University of Malawi a thesis entitled *'Seasonal variation of Carbaryl and Cypermethrin in soils, ground water and surface water in a cotton growing area of Lisungwi in Neno district, Malawi.'*

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Date : _____

DEDICATION

This thesis is dedicated to my family: my dear husband Willard Kamowa – Mbewe, my son Cleophas Mbewe, my dad Wiyule Kanyika and mum Mercy Mwamondwe–Kanyika, my brothers and sisters.

ACKNOWLEDGENTS

I express my sincere gratitude to my supervisors, Dr. Chikumbusko Chiziwa Kaonga and Dr. Bernard Thole of University of Malawi, The Polytechnic for their valuable and generous contribution towards the completion of this work. They provided me with guidance, motivation, excellent supervision, inspiration and encouragement. I could not have imagined having better supervisors for my study. Besides my supervisors, I would like to thank the Soroptimist International Great Britain and Ireland (SIGBI) for the research grant.

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ABSTRACT

Pesticides play a vital role in crop production in Malawi through the reduction of insects, weeds, plant diseases and other pests. However pesticides contaminate the environment including catchment areas which in turn may affect both human health and aquatic life. This study was conducted to assess the presence of pesticides, Carbaryl and Cypermethrin in water and soil from Lisungwi area, Neno district, southern Malawi. The area from which samples were collected is dominated by high pesticide usage especially in cotton fields. Carbaryl (a carbamate) and Cypermethrin (a pyrethroid) are the mostly used pesticides in cotton production hence being the main focus of the study. In this study, soils, surface water and ground water samples were collected in both the rainy season and dry season to assess the presence of Carbaryl and Cypermethrin. This was in addition to the assessment of selected physico-chemical parameters which included nitrates, phosphates, pH, temperature, total dissolved solids and electrical conductivity using standard methods especially from American Public Health Association (APHA), and Association of Official Analytical Chemists (AOAC). Carbaryl and Cypermethrin were extracted using organic solvents, and quantified using HPLC-DAD and UV spectrophotometer, respectively. There were no guideline values for Carbaryl from World Health Organization (WHO) and Malawi Bureau of Standards (MBS). Furthermore, no guideline value for Cypermethrin was highlighted by MBS. The results showed that all physico-chemical parameters were within accepted limits set by World Health Organization (WHO) and Malawi Bureau of Standards (MBS) except for phosphates and electrical conductivity. The results further confirmed the presence of both Carbaryl and Cypermethrin residues in water (both surface and groundwater) and soil samples. The average concentration of Carbaryl for surface water in rainy season was 0.14 ± 0.08 ppm, and 0.26 ± 0.12 ppm in groundwater. The average concentration of Carbaryl residue in the surface water was 0.05 ± 0.07 ppm and 0.01 ± 0.01 ppm in ground water

during the dry season. There were no significant differences in Carbaryl residues in the surface water and ground water in rainy season and dry season ($p > 0.05$). Furthermore, average Carbaryl residue for soil in the rainy season was 1.23 ± 0.48 ppm and 1.19 ± 0.04 ppm in the dry season. Carbaryl residues in soil was statistically significant in the rainy season than dry season ($p < 0.05$). There was no significant difference ($p > 0.05$) in the concentration for the Cypermethrin residue in the rainy season in the surface water (Mean = 11.16 ± 3.3) as compared to ground water (Mean = 7.27 ± 2.89). Cypermethrin concentration in surface water for the dry season was not statistically significant ($p > 0.05$) (Mean = 3.95 ± 5.53) compared to ground water (Mean = 7.23 ± 4.95). The average concentration of Cypermethrin residue in soil samples for the rainy season was 0.29 ± 1.02 ppm and in the dry season it was 0.04 ± 0.00 ppm. Cypermethrin in soil was not statistically significant ($p > 0.05$) in the rainy season as compared to the dry season.

Carbaryl residues in water and soil were above Australian guideline (0.003 mg/L) and Canadian guideline (0.09 mg/L) for drinking water in both seasons. Cypermethrin residues in water were above United States Maximum Residual Limit (US MRL), (0.05 µg/L), WHO limit (0.05 µg/L) in both seasons. The soil samples exceeded the US MRL guideline value (0.05 mg/Kg) in the rainy season only. The water and soil in the study area get contaminated easily with the pesticides applied in the cotton fields. Among others, it is recommended that there is a need for the routine monitoring of pesticide residues in the study area so as to reduce and control environmental pollution.

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ACRONYMS AND ABBREVIATIONS

AOAC	Association of Official Analytical Chemists
APHA	American Public Health Association
AR	Analytical Reagent
EC	Emulsifiable concentrate
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
FS	Flowable concentrate for seed treatment
GoM	Government of Malawi
GIS	Geographical Information System
HLC	Henry's Law constant
HPLC	High Performance Liquid Chromatography
LC	Lethal concentration
mL	Mill liter
NO_3^-	Nitrates
NRSC	Natural Resources Conservation Services

OC	Organochlorines
OP	Organophosphate
ppb	parts per billion
TB	Tablet
UNEP	United Nations Environment Programme
USEPA	United states –Environmental Protection Agency
WHO	World Health Organization
WP	Wettable powder
WS	Water soluble
μg	Microgram

APPENDICES

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND

Agriculture is the mainstay of Malawi`s economy which employs 85% of the population, contributes 35% of Gross Domestic Product (GDP) and 90% of foreign exchange (Kachule, 2011). Furthermore, about 65 % of raw materials to manufacturing sector in Malawi are also attributed to the agricultural sector (Government of Malawi [GoM], 2006). Cotton is one of the important sources of foreign exchange which is slowly becoming vibrant at smallholder sub-sector level (GoM, 2006). About 90,000 families are supported by cotton farming in Malawi (Mwatuwa, 2009). Despite the role played by cotton to the economy of the country, cotton growing is done by smallholder farmers of late. Large commercial farms had been abandoned due to progressively declining profitability at the international market for five consecutive years beginning from the 1998-1999 growing season (GoM, 2004). This has also been reflected in Figure 1.

The available and suitable land for cotton production is continually declining due to environmental degradation and this includes soil erosion and soil exhaustion, leading to poor plant nutrition (Food and Agriculture Organization [FAO], 2000). According to GoM (2010), sustainable agricultural production systems in Malawi have been greatly affected by environmental degradation. Despite high input rates of herbicides, pesticides and spraying machines, cotton production has been low since 1990 as compared to the previous years (Mwatuwa, 2009).

Substantial pesticides' usage in cotton cultivation helps in weed and pests control especially during growing season (Scott, 2008). Subsequently this leads to water pollution as a result of run-off from the fields due to inappropriate water management and irrigation technology. Fertilizers, salts and residues of pesticides washed from the fields and drainage, accumulate in the water bodies and this in turn affects aquatic life (Sallenave, 2016). Thus, one of the major sources of ground water pollution and drinking water pollution, with either nutrients or pesticides is agricultural activities (Kishimba & Mihale, 2004).

1.1.1 Cotton production

Cotton, *Gossypium hirsutum* (L.), is one of the native crops to sub-tropical regions of the world, and its use has been known since 2000 years ago (Kamminga, 2008). It is one of the perennial crops grown in tropical climates but cultivated as an annual crop through destructive harvesting at the end of the season. As a member of the *Malvaceae* family, cotton is the world's most widely grown fiber crop accounting for over 35% of the total world fiber use (United States Department of Agriculture [USDA], 2011).

According to United States Department of Agriculture Foreign Agriculture Service [USDA FAS], (2016), the present world production of cotton lint is about 22.5 million tons annually as portrayed in Table 1. Although the area under cotton production has been fluctuating over the decades in Figure 1 because of unstable world markets as reported by USDA FSA, (2016), the crop is still one of the most important economic crops worldwide, produced on approximately 2.5% of the world's arable land. In Malawi, cotton production has been increasing over the years

until 2015, when production became constant and remained as such, as presented in Figure 1.

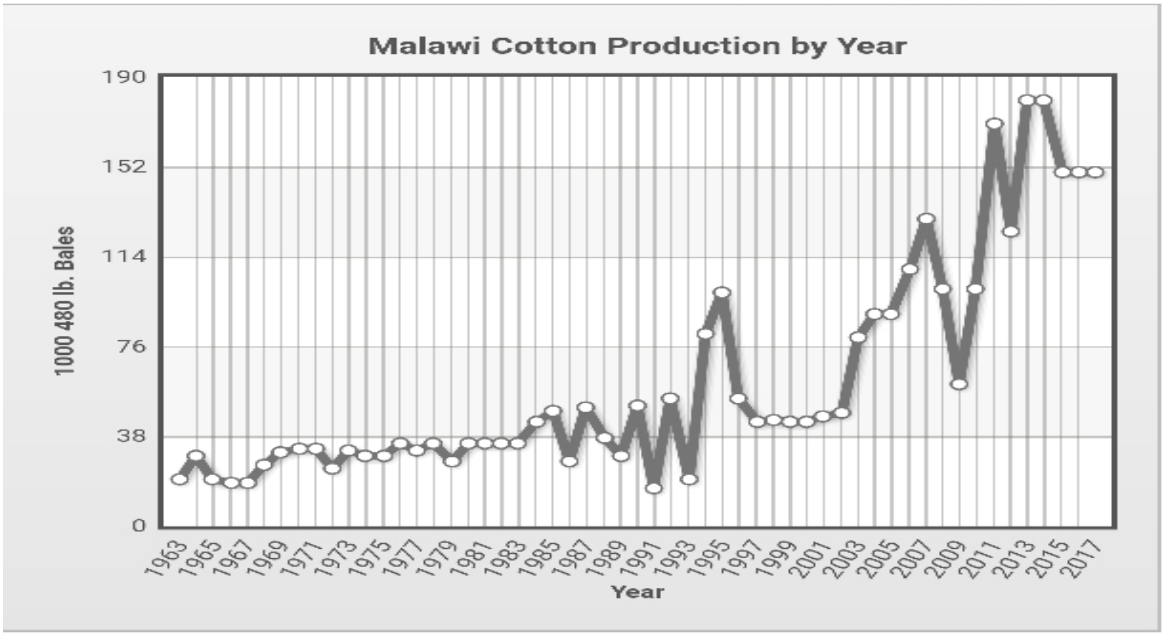


Figure 1: Malawi cotton production by year (Source: Index Mundi, 2017)

Table 1: The world's top cotton producers for the past 6 years (Source; USDA FAS, 2016)

Cotton production (in 1,000 MT)	**2012/13**	**2013/14**	**2014/15**	**2015/16**	**2016/17**
India	6,205	6,750	6,423	5,748	5,879
China	7,620	7,131	6,532	4,790	4,572
United States of America	3,770	2,811	3,553	2,806	3,519
Pakistan	2,025	2,068	2,308	1,524	1,796
Brazil	1,306	1,742	1,524	1,285	1,415
Australia	1,002	893	501	566	871
Uzbekistan	1,002	893	849	827	806
Others	4,047	3,920	4,261	3,466	3,629
Total world production	26,976	26,207	25,951	21,012	22,486

Cotton in Malawi is grown in three main areas; the lower Shire which accounts for up to 50% of the total production, the Southern Region upland areas, accounting for 30% of production and Lakeshore areas, accounting for 20% of production (Kenamu & Phiri, 2014). It is grown mainly in areas where climate and soils are not suitable for tobacco. The crop ranks fourth as a foreign exchange earner for the country after tobacco, tea and sugarcane (GoM, 2006). One of the districts where cotton is grown in Malawi is Neno which is part of the Southern Region upland areas as shown in Figure 3.

Neno district engages over 90% of the population on customary land which is allocated to individual households and overseen by the chiefs. Cotton is grown within lower Neno which is low lying, hotter and often receives little rainfall. Since cotton tolerates drier conditions, it is grown and regarded as the chief cash crop for the area (Nyirenda, 2011). Despite its production, Malawi is ranked third in southern Africa (Index Mundi, 2017). This is also shown in Table 2.

Table 2: Cotton production in Southern Africa (Source; IndexMundi , 2017).

Cotton production (in 1000 480 lb. Bales)	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
Zambia	192	184	240	207	170	185
Zimbabwe	276	262	195	55	155	160
Malawi	125	180	180	150	150	150
Mozambique	170	140	125	90	115	105
South Africa	28	44	86	46	69	70
Angola	5	5	5	5	5	5
Lesotho	0	0	0	0	0	0
Total production	796	815	831	553	664	675

1.1.2 Pesticides used in cotton and their significance

Cotton production relies heavily on pesticide usage (Ministry of Agriculture [MoA], 2005). However, the use of pesticides in cotton is relatively lower as compared to tobacco, coffee and sugarcane due to low hectarage (Kapeya, Daudi, & Maulana 2003). Various types of pesticides are used in the cotton fields. These include organophosphates, carbamates, pyrethroids, chloronicotinyl, and thianicotinyl as shown in Table 3.

The types and amount of pesticides used has been increasing over the years, thereby increasing pest resistance. Organochlorine pesticide residues are regarded as one of the important classes of contaminants, owing to their toxicity, persistence and bioaccumulation (Zhou, Zhu, Yang, & Chen 2006). Residues and degradation products of these organochlorine pesticides are still being detected in water, soil, air, sediments and biota in previous application sites as well as non-application areas despite the banning or restriction in the use and application of these chemicals in many countries (Zhou et al. 2006).

Cotton production is improved with the use of pesticides, but their excessive use results into the presence of their residues in both water and soil. These would contaminate both ground and surface water (Lakudzala, 2009). In Neno district, Malawi, one of the cotton growing areas is Lisungwi. The area has Lisungwi river; a perennial river passing through it. Lisungwi area also has boreholes and wells located within the vicinity of farmers' cotton fields as indicated in Figure 4.

Table 3: Recommended pesticides for cotton pest control in Malawi (MoA, 2005).

Common name	Chemical group	Trade names	Common Formulations	Target Pests
Imidacloprid	Chloronicotinyl	Gaucho	WS	Aphids, elegant grasshopper, termites, and other early pests
Thiamethoxam	Thianicotinyl	Cruiser	FS	Aphids, elegant grasshopper, termites, and other early pests
Carbaryl	Carbamate	Sevin	WP	All cotton pests except African bollworm, aphid, red spidermite, lygus and helopeltis
Profenofos	Organophosphate	Curacron	EC	All cotton pests except African bollworm, aphid, red spidermite, lygus and helopeltis
Triazophos	Organophosphate	Hostathion	EC	All cotton pests except African bollworm, aphid, red spidermite, lygus and helopeltis
Dimethoate	Organophosphate	Rogor	EC	Aphid, red spider smite
Cyfluthrin	Pyrethroid	Baytroid	EC	Aphids, cotton leafworm, boll weevil.
Cypermethrin	Pyrethroid	Cymbush	EC	Boll weevil, aphids, cotton leafworm, cotton budworm, pink bollworm.

EC: Emulsifiable concentrates, **FS**: Flowable concentrate for seed treatment, **WP**: Wettable powder and **WS**: Wettable soluble.

1.1.3 Pesticide usage regulation in Malawi

Malawi as a country that depends heavily on agriculture, uses a considerable number and amount of pesticides to combat pest problems. The Pesticides Act No 12 of 2000 enables the Malawi

government to have control on the importation, exportation, manufacture, distribution, storage, disposal, sales, repackaging and use of all pesticides in Malawi (GoM, 2000). All of the available pesticides used in Malawi are imported by chemical companies which in turn supply to various stakeholders for both crop and livestock production (Ministry of Agriculture and Food Security, 2017). Despite the law, a lot of Malawians trade in, and access unregulated and illegal chemical pesticides through districts that are close to bordering countries, as smuggling of such pesticides is common along the borders. This then affects the environment, plants and human life (Ministry of Agriculture and Food Security, 2017). It is clearly stipulated in Section 17 of the Act that no person shall import, manufacture or sell pesticide, which has not be registered under this Act (GoM, 2000). Therefore, importation of pesticides by farmers is completely prohibited, for fear that they may import unrecommended and substandard pesticides which upon using, may introduce toxic chemicals into the environment, resulting into the development of pest resistance and even economic loss to the farmers and eventually to the country.

1.2 PROBLEM STATEMENT AND JUSTIFICATION OF THE STUDY

Water quality degradation due to excess nutrients from fertilizers, and pesticides, washed to the rivers, lakes and groundwater are major concerns in Malawi (Nyasulu, 2010). As mentioned earlier, cotton production has been associated with heavy use of pesticides so as to increase yield (Scott, 2008). Carbaryl and Cypermethrin are some of the pesticides used in cotton fields. These are potential hazards to human beings through contamination of different components of the environment such as surface water, aquifers, soil and air (Gill & Garg, 2014). Despite having few recorded studies available on the existence of pesticides in Malawi, the findings of these few studies highly indicate pesticides contamination. One of these recorded studies detected pesticide

residues in Lilongwe River (Malawi Economic Report on Environmental Policy [MEREP], 1995).

Although some studies have been done on the sorption and degradation of pesticides in soil, there is a knowledge gap on Carbaryl and Cypermethrin residue accumulation in soils, as well as in surface and ground water within cotton growing areas. This is what prompted this study in which Carbaryl and Cypermethrin were assessed in water and soil samples from a cotton growing area of Lisungwi in Neno district, Malawi.

1.3 OBJECTIVE OF THE STUDY

1.3.1 Main objective

The main objective of the study was to assess the levels of Carbaryl and Cypermethrin in surface water, ground water and soils in a cotton growing area of Lisungwi in Neno district, Malawi.

1.3.2 Specific objectives

The specific objectives of the study were:

i. To determine physico-chemical parameters like pH, electrical conductivity, total dissolved solids (TDS), nitrates and phosphates in surface water, ground water and soil in Lisungwi area.

ii. To determine the concentration of Carbaryl and Cypermethrin during rainy and dry season in surface, ground water and soil in Lisungwi area.

iii. To compare the levels of physico-chemical parameters and pesticides in surface water, ground water and soils in Lisungwi area for rainy and dry season.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 PESTICIDES

Pesticides are substances or mixtures of substances intended for preventing, destroying, repelling, attracting or mitigating any pest (Arias – Estevez, Lopez – Penago, Martinez – Carballo, Simal – Gondara, Mejuto, & Gacia – Rio, 2008). The term normally covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators and others. Pesticides tend to improve quality and quantity of agricultural productivity through reduction and elimination of negative impacts of pests (Garcia, 2012). Ideally a pesticide must be lethal to the targeted pests, but not to non-target species, including man. Unfortunately, this is not the case, so the controversy of use and abuse of pesticides is a common occurrence. The rampant use of these chemicals, under the adage, "if little is good, a lot more will be better" has played havoc with human and other life forms (Aktar, Sengupta, & Chowdhury 2009).

2.2 CLASSIFICATION OF PESTICIDES

Pesticides are classified according to their use (herbicides, insecticides, fungicides, acaricides, rodenticides, and bacteriocides) and chemical structure (organic and inorganic). Inorganic pesticides are naturally occurring non-carbon elements which are environmentally stable, non-volatile and soluble in water (Kinyuzu, 2015). Most of the inorganic pesticides contain metals such as arsenic, cyanide, mercury and thallium which result into the pesticides being persistent and having bio-accumulative properties (Hassall, 1990). On the other hand organic pesticides are

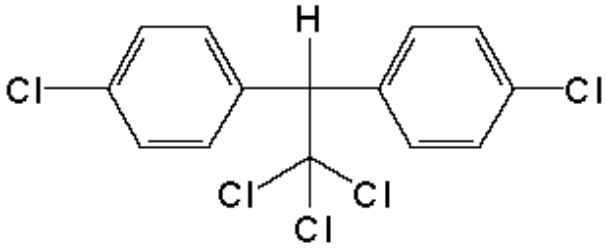
synthetic compounds with aliphatic or aromatic hydrocarbon chains classified in terms of their active ingredients, such as carbamates, pyrethroids, organophosphates and chlorinated hydrocarbons (Wasswa, 2008).

2.2.1 Organophosphates

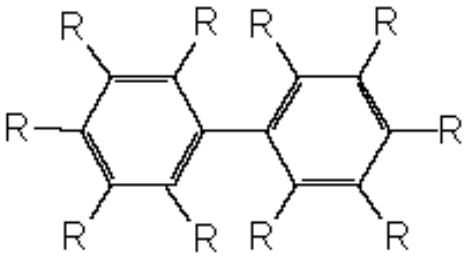
Organophosphates are phosphoric acid esters or thiophosphoric acid esters developed between 1930s and 1940s. They are highly toxic to mammals and affect the nervous system by disrupting acetyl cholinesterase activity. This has resulted into loss of reflexes, headache, dizziness and death (Garcia, Cortés Ascencio, Gaytan Oyarzun, Hernandez, & Alavarado, 2012)

2.2.2 Organochlorines

Organochlorine pesticides are highly persistent in the environment as such tend to accumulate in fatty tissues of animals due to their stability (Waliszewski et al. 2004). They are used in the eradication of vectors that carry parasites which cause diseases such as malaria and typhus. They are also used in agriculture (Garcia, 2012). They include chlorinated derivatives of biphenyl ethane (dichlorodiphenyltrichloroethane – DDT), hexachlorobenzene (HCB), the group of hexachlorocyclohexane (α-HCH, β-HCH, γ-HCH, δ-HCH, or lindane), the group of cyclodiene (aldrin, diedrin, endrin, chlordane, nonachlor, heptachlor and heptachlor-epoxide), and chlorinated hydrocarbons (dodecachlorine, toxaphene, and chlordecone) (Porto, Melgar, Kasemodel, & Nitschke, 2011).



DDT



Polychlorinated Biphenyls

2.2.3 Pyrethroids

Pyrethroid pesticides originate from natural insecticides which are derived from pyrethrum extract which comes from chrysanthemum flowers, known as pyrethrins. They were introduced in the 1980's and are currently manufactured around 100 different commercial products (Sorgob & Vilanova, 2002). They act on the central nervous system leading to neuron hyperexcitation (Garciaet al. 2012).

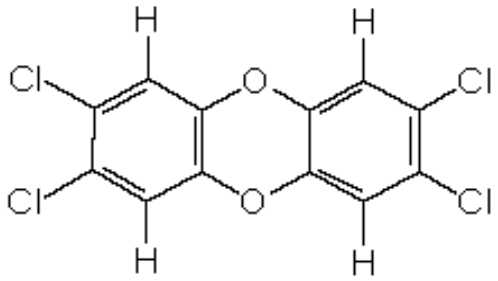
2.2.4 Persistent organic pollutants (POPs)

Persistent Organic Pollutants are chemicals that persist in the environment and bio-accumulate through the food chain (Ashraf, 2017). These are mainly: Pesticides, industrial chemicals, industrial by-products, and unintended by-products of burning processes called (UPOPs). The dirty twelve POPs are highlighted in table 4

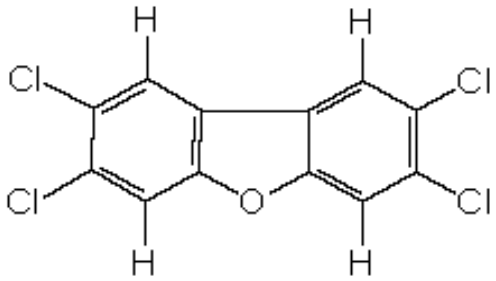
Table 4: The Dirty Twelve POPs, (POPs and Stockholm Convention: Resource guide, 2001).

Compound	Regulation
Aldrin	Applied to soils to kill termites, corn-worms and grasshoppers (Banned 1992)
Chlordane	Control termites and insects (Restricted to Citrus).
DDT	Restricted to Malaria.
Dieldrin and (HCB)	Control termites and textile pests and also insects in soils for Agriculture (Banned in 1983).
Dioxins	From Incomplete combustion during manufacture of pesticides and chemicals, bleaching of paper, metal recycling, car exhaust, tobacco smokes, wood and waste burning and coal, etc. They are highly carcinogenic.
Endrin	Insecticide on leaves of crops – cotton and grain. (Banned 1980).
Furans	Products same as Dioxins, including being found in commercial mixtures of PCBs.
Heptachlor	Kills soil insects and termites, i.e. in cotton. (Banned 1976).
Hexachlorobenzene (HCB) & Dieldrin	Kill fungi (Banned 1983).
Mirex	Used in plastics, rubber, electrical goods and as Fire Retardant (Not used in South Africa).
Poly Chlorinated Biphenyls (PCBs)	Used in transformers.
Toxaphene	Banned 1970

Dioxins and Furans Pose Concerns for Health and Environment World-wide. Polychlorinated dibenzo-para-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two of the twelve initial POPs included in the Stockholm Convention. In its decision 19/13 C of February 7, 1997 (UNEP Governing Council, 1997).



2,3,7,8-TCDD



2,3,7,8-TCDF

2.2.5 Carbamates

Carbamate pesticides are derived from dimethyl n-methyl carbamic acid (NH_2COOH) and are used to kill or control insects (Garcia, 2012). Functional groups are ethyl carbamates and carbamic acid that are inter-related structurally. They include Aldicarb, Carbaryl, Propoxur, Oxamyl and Terbucarb. Carbaryl was the first carbamate introduced in 1956 and is widely used throughout the world (Fishel, 2014). They are less persistent than organochlorines and organophosphates (Sorgob & Vilanova, 2002).

2.3 CARBARYL AND CYPERMETHRIN

2.3.1 Carbaryl

Carbaryl (1-naphthyl-N-methyl carbamate) is a carbamate insecticide which is registered to control a broad spectrum of insects in more than 120 different crops and non-crop use sites including home and garden uses (Garber, Jones, & Steeger, 2007). It was introduced in 1956 by Union Carbide Corporation to substitute organochlorine pesticides (Ribera et al. 2001) which are said to be persistent in the environment. Sevin® is the common trade name used among others. Garber et al., (2007) highlights the active ingredient (a.i) use rate that it ranges from 0.53-6.4 pounds/acre. Carbaryl is available in different formulations such as a wettable powder, pellets, granules, suspensions, and solutions.

2.3.2 Cypermethrin

Cypermethrin [(±)-B-Cyano-(3phenoxyphenyl) methyl (±)-cis/trans-3-(2,2-dichlorovinyl)-2,2 dimethylcyclopropane carboxylate] is a synthetic, pyrethroid insecticide with high insecticidal activity, low avian and mammalian toxicity, and adequately stable in air and is used in controlling pests in many crops (Dhundhel & Rai, 2011). Lepidopterous pests of cotton, fruit, and vegetable crops are controlled by Cypermethrin and is available as an emulsifiable concentrate or wettable powder (Chen, Luo, Hu, Lai, Geng, & Huang, 2012). Recently, accelerated use of Cypermethrin in agricultural fields has been observed for crop protection. This has resulted into the accumulations of Cypermethrin in the soil, water and sediments (Karthigayani, Denis, Annadurai Rexlin Andrew Remy, & Shettu, 2014).

2.4 PHYSICAL AND CHEMICAL PROPERTIES OF PESTICIDES

2.4.1 Physical properties of pesticides

Pesticides mode of action, dosage, mode of application and environmental chemo dynamics is determined by their physical properties such as molecular weight, vapour pressure, solubility, octanol/water partition coefficient (K_{ow}), soil adsorption coefficient and Henry's constant (Zacharia, 2011).

The vapour pressure refers to the ability of a substance to change to gaseous state. Substances with high vapour pressure are said to cause vapour drift and environmental pollution while those with low vapour pressure remain in the water if they are soluble and accumulate in the soil or biota if insoluble in water (Zacharia, 2011). Solubility of a substance is the possibility of a particular substance to dissolve in a solvent. Temperature, pH, polarity of the substance, hydrogen bonding, molecular size and method used are said to have an effect on the measurements of solubility (Gunasekara, 2007). It is clearly stated that pesticides with high

solubility in water tend not to accumulate in soil or biota due to their polar nature, hence degradation through hydrolysis (Zacharia, 2011).

Octanol/water partition coefficient-K_{ow} is a measured ratio of the dissolved mass of the substance between equal layers of n-octanol and water at equilibrium.

$$K_{ow} = \frac{\text{concentration in } n-\text{Octanol phase}}{\text{Concentration in water phase}}$$

K_{ow} values are expressed as Log K_{ow} which implies that log to the base 10 of K_{ow} with the values ranging from -3 to 7. It is a good indicator for bioaccumulation and systematic mode of action of pesticides in organisms and food chains. For example bioaccumulation effects to organisms and food chains are observed when pesticides have a positive correlation between Log K_{ow} and systematic translocation of pesticides. Their metabolites in the plants transvascular system occur when K_{ow} are generally low thus ≤ 2 (Ssebugere, 2015). Furthermore, polarity of the pesticides and the general physical factors influences K_{ow}. Polar pesticides are more soluble in water leading to low K_{ow} values, and K_{ow} increase when molecular surface area, molar volume, molecular weight, and density increase (Zacharia, 2011).

Soil adsorption coefficient, (K_{oc}/K_d), is one of the major factors that determines the destination of pesticides in the environment and decides their degradation process (Zachariah, 2011). Most of the pesticides are not very soluble in water (non-polar and hydrophobic), that in turn are pushed onto soils and sediments which contain non-polar organic matter. Therefore it is defined as the ratio (at equilibrium) of the mass of a substance, adsorbed onto a unit mass of soil, relative to the mass of the substance remaining in water solution. Its value is dependent on the organic matter content of the soil, polarity of the chemical and soil pH.

$$K_{oc} = \frac{K_d \times 100}{\%\ \text{organic carbon}}$$

Sorption Coefficient, K_d, measures the amount of pesticides adsorbed onto soil per amount of water without considering the organic matter content of the soil (Lakudzala, 2009). K_{oc} is the preferred parameter used to determine the soil's ability to adsorb pesticides due to its consideration of organic matter content in the soil (Zacharia, 2011).

$$K_d = \frac{\text{Concentration of a chemical in soil}}{\text{Concentration in water}}$$

Henry`s law constant, (H` or HLC), is the measure of the concentration of a chemical in air over its concentration in water. This expresses the tendency of a substance to volatilize from aqueous solution to air (gaseous state). It is usually calculated as the ratio of vapor pressure (in Pascal) x molecular weight / solubility (mg/L).

$$H' = \frac{16.04 \times P \times M}{T \times S}$$

Where P = Vapor pressure

M = Molecular mass

T = Temperature

S = Solubility

Henry's law constant plays a great role in the environment, the higher the HLC value of a pesticide the greater the chances of volatilization from the water into the air. The HLC value is also an integral part in calculating the volatility of a chemical (Zacharia, 2011). Conversely, pesticides with low HLC value persist in water and get adsorbed onto the soil and sediment.

2.4.2 Chemical properties of pesticides

Pesticides undergo a complex series of interdependent processes known as chemodynamics once released to the environment. These processes are determined by its inherent physico-chemical properties and partly by environmental parameters such as pH, temperature, moisture, precipitation, salinity, light intensity and topography (Zacharia, 2011). The pesticides' persistence, distribution and their ultimate fate in the environment such as transportation, retention, degradation and biota uptake are determined by these chemical processes. Besides these chemodynamic processes, degradation is of much significance since it entails the chemical transformation of the pesticides in the environment hence chemical properties. Therefore, degradation of pesticides is the breakdown or chemical transformation of pesticide molecules into other forms that are not necessarily simpler nor less toxic compared to the parent molecule. Degradation products of some pesticides (Dichlorodiphenyltrichloroethane, DDT to Dichlorodiphenyldichloroethane, DDD and Dichlorodiphenyldichloroethylene, DDE) are also toxic and act as a pesticide (Kumar, Sharma, & Ahluwalia, 2017).

Generally, the rate at which pesticides degrade is described as half–life ($t_{1/2}$). Half–life is defined as the time required for the depletion of half (or 50%) of the amount of pesticide present initially (Zacharia, 2011). Degradation processes can be chemical (occurs in water or atmosphere) or biological (occurs in soil or living organisms). Chemical degradation results into reactions such as oxidation, reduction, hydrolysis and photolysis while biological degradation results into reactions such as oxidation, reduction, hydrolysis and conjugation (Çelebi, Oturan, Zazou, Hamdani, & Oturan, 2015).

2.4.2.1 Oxidation and reduction of pesticides

Oxidation of pesticides is the reaction between dissolved oxygen in the environment and the pesticides. The primary agents are singlet oxygen, ozone, hydrogen peroxide, or other hydroxy radicals, which are regarded as the primary agents of oxidation in water or atmosphere (Çelebi, et al. 2015).

Pesticides undergo a reduction process where reducing agents in the environment are usually H^+ (Zacharia, 2011). Malathion performs reduction reaction in acidic/aquatic environment. Replacement of any ethyl group with H^+ results into the construction of two functional isomeric molecules of Malathion monoacid (Kumar et al. 2017).

2.4.2.2 Hydrolysis reaction of pesticides

Hydrolysis plays a vital role in the chemical degradation of pesticides. Hydrolysis is a pH and temperature dependent reaction where pesticides react with water molecules involving specific catalysis by hydrogen ion (proton) or hydroxide ion and sometimes inorganic compounds such as phosphate ions present in the aquatic environment (Katagi, 2002). Most organophosphates and carbamates have particularly shown to be highly responsive to hydrolysis reaction under alkaline condition (Jaiswa, Verma, & Yadav, 2016). A pesticide that is very soluble in water will tend not to accumulate in soil or biota because of its stronger polar nature. This suggests that it will degrade via hydrolysis which is the reaction that is favored in water (Zacharia, 2011).

2.4.2.3 Photodegradation and biodegradation of pesticides

Photolysis or photodegradation is described as the breakdown or transformation of pesticides by sunlight that causes a rapture of chemical bonds (Zacharia, 2011). Organic molecules get excited after absorbing photons, releasing electrons hence changing the molecule (Linde, 1994).

Biodegradation is the breakdown or transformation of pesticides by microbial agents and this process normally occurs in water and soil to remove pesticides especially carbamates, organochlorines, and organophosphates used in agriculture (Jaiswa et al. 2016). Microbial degradation is highly affected by the amount and nature of pesticides present in the soil, the microbial population in the soil and other soil conditions that favour microbial activities such as warm temperature, favorable pH, adequate soil moisture, aeration and high organic matter content (Zacharia, 2011). The microorganisms participating in biodegradation include fungi, bacteria, actinomycetes and viruses that use pesticides as their substrate (Kaloyanova & Simeonova, 1994).

2.4.3 physico-chemical indicators for water quality

pH is a measure of the activity of solvated hydrogen ion which measures hydrogen ion concentration (Estefan, Sommer, & Ryan, 2013). It is as well described as negative logarithm of Hydrogen ion concentration.

$$pH = - \log [H^+]$$

Therefore, pH measures acidity and alkalinity of a substance. pH beyond permissible limits corrode water supply system, give metallic taste to water and affect mucous membrane of cells (Estefan, et al. 2013).

Electrical Conductivity (EC) is the measure of the ability of a solution to carry an electric current or the concentration of soluble salts in the sample at any particular temperature (Estefan, et al. 2013). The EC measurement is a function of dissolved CO_2, turbidity, temperature and the nature of various ions, their relative concentration and the ionic of water (Bani, 2015). Therefore, EC is a valuable indicator of the minerals dissolved in water.

Total dissolved solids (TDS) are any minerals, salts, metals, cations or anions dissolved in water. Total Dissolved Solids comprise combined content of inorganic substances (calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates) and some small amounts of organic matter that are dissolved in water. High concentration of TDS imparts salty taste to water and also effects plumbing appliances (Dezuane, 1997).

Temperature plays a vital role in the aquatic environment. Generally, both biological and chemical processes are temperature dependent. There is a great variation in its measurements especially in natural water bodies probably due to seasons, depth of water, gain or loss of heat in shallow waters close to the land and latitude among others (Saad, Massoud, Amer, & Ghorab, 2017).

Nitrates (NO_3^-) and phosphates (PO_4^{3-}) are some of the common water pollutants associated with fertilizers. Increased acidity and higher concentrations of nutrients, salts, metals and other chemicals are clearly manifested by pollution and contamination from these sources (Akoto Gyamfi, Darko, & Barnes, 2014). PO_4^{3-} is essential for crop production such as stimulation of early root formation and growth, giving a rapid and vigorous start to plants, promoting flower and seed production as well as needed in the genetic coding material which controls cell division among other functions (Estefan, et al. 2013). High nitrate and ammonia concentrations in drinking water impart negative effects on human health; Pregnant women, babies, individuals suffering from methemoglobin reductase (Mussa, Elferjani, Haroun, & Abdelnabi, 2009). Methemoglobinemia, i.e., 'blue baby syndrome' is linked with high nitrate concentrations in water.

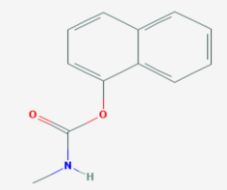
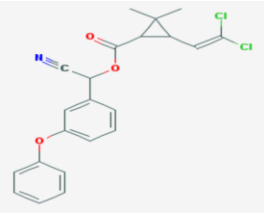
Phosphorus has the potential to cause algal blooms and explosive growth of bacteria, and consequently poor water quality, eutrophication, poor aesthetic appeal and unpleasant odors

(Carpenter, 2005). The available forms of nitrogen and phosphates are water soluble and move rapidly through the soil profile with rainfall and irrigation.

2.5 PHYSICAL AND CHEMICAL PROPERTIES OF CARBARYL AND CYPERMETHRIN

Table 5 below shows the physical and chemical properties of Carbaryl and Cypermethrin. The physical and chemical properties of these pesticides are further discussed below.

Table 5: Physical and chemical properties of Carbaryl and Cypermethrin

Chemical property	Carbaryl	Cypermethrin
Chemical formula	$C_{12}H_{11}NO_2$ or $CH_3NHCOOC_{10}H_7$ [a]	$C_{22}H_{19}Cl_2NO_3$
Structure		
Molecular Weight	201.2 g/mol [a]	416.29716 g/mol
IUPAC chemical name	1- naphthyl N-methylcarbamate	(R,S)-alpha-Cyno-3-phenoxybenzyl-2,2-dimethyl (1R, 1S)-cis,trans-3-(2,2-dichlorovinyl) cyclopropane-carboxylate
Density	1.228 g/cm^3 [b]	1.12 g/ml at 22°C [i], 1.249 g/cm^3 at 20°C[h]
Melting point	145°C [b]	60-80 °C for pure isomers [i]
Boiling point	210°C [n]	170-195°C [h]
Vapour pressure	0.041 mPa at 23.5°C [a]	4×10^{-8} mmHg at 70°C [i]
Solubility in water	120 mg/L at 20°C [a],104 mg/L at 25°C [a] 40 mg/L at 40°C[d]	Insoluble in water [i] ; 4×10^{-3} mg/L [k]
Heny's law constant	2.74×10^{-9} atm m^3 g/mol at 25°C [a]	2.5×10^{-7} atm m^3 g/mol at 20°C [l]
Octanol-water coefficient (K_{ow})	2.36 [e]	6.60 [k]
Soil adsorption coefficient (K_{oc})	290 [f]	4.5[k]

[a] Tomlin, (2003); [b] Lide, (2007); [d] Meister, (2001); [e] Hansch *et al.*, (1995); [f] Phillips and Bode (2004); [h] USEPA, (1989); [i] Meister (1992); [k] Mcbean, (2008); [l]Jones (1995). [m] EXTOXNET, (1993). [n] EFSA Scientific Report (2006).

2.6 VOLATILIZATION OF CARBARYL AND CYPERMETHRIN

Physical-chemical properties such as vapour pressure, water solubility, Henry's law constant, octanol-water partition coefficient (K_{ow}), and the organic carbon-water partition coefficient (K_{oc}) play a vital role in the transportation of pesticides (Ssebugere, 2015). Literature states that vapor pressure, solubility and Henry's law constant affect the volatilization of the pesticides (Larson & Weber, 1994). Low vapor pressure and low Henry's law constant of Carbaryl as shown in Table 4 suggests that it will not volatilize from aqueous solutions. Carbaryl however has been detected in the atmosphere as spray drift immediately after application (Gunasekara, 2007; Kaloyanova & Simeonova, 1994). Despite the presence, studies noted that all the detections decayed to relatively low concentrations within 2 hours after application.

Like Carbaryl, Cypermethrin has low vapor pressure and Henry's law constant, as shown in Table 3 and a water solubility of 4×10^{-3} mg/L (Mcbean, 2008) that depicts that there is no tendency of volatilization from an aqueous solution. Cypermethrin as one of the pyrethroids enters the aquatic environment through surface run-off due to high K_{ow} and low Henry's Law constant as shown in Table 4. Feo, Ginebreda, Elijarrat, E., and Barcelo´, (2010) indicates that substances with lower values of Henry Law constant than 3×10^{-7} atm m^3 g/mol are considered as non-volatile hence pesticide persistence in water and adsorption onto the soil and sediment (Zacharia, 2011). As a result no volatilization is expected on dry soil surfaces based on vapor pressure. Therefore low mobility in the environment is a function of high K_{ow} and K_{oc}, and low half-life.

2.7 SOLUBILITY OF CARBARYL AND CYPERMETHRIN

Carbaryl is moderately soluble in water and its solubility is affected by changes in temperature and organic solvents as indicated in the Table 4. Gunasekara (2007) states that solubility is

accelerated with the increase in temperature and amount of organic solvents used. Carbaryl can be introduced to the groundwater through leaching due to its partial solubility in water. A study done in the United States of America (USA) revealed that Carbaryl is detected in both surface and ground water (Gunasekara, 2007). Mcbean, (2008) reports that Cypermethrin has a negligible solubility (4×10^{-3} mg/L) in water, as such it is regarded as insoluble resulting into high tendency to adsorb to soil particles (USDA, Soil conservation Service, 1990). Therefore, there is low potential to contaminate groundwater. This behavior of Cypermethrin is echoed by Dubey & Fulekar, (2013).

2.8 SORPTION OF CARBARYL AND CYPERMETHRIN

Studies reveal that Carbaryl undergoes sorption despite its ability to dissolve in water. For example; rapid Carbaryl sorption is observed at 0.5 hours (Ahmad, Kookana, Alston, & Bromilow, 2001a) and 3 hours (Jana & Das, 1997). However, Carbaryl is persistent from two to sixteen weeks (Ren, Zhang, Zhao, & Hongwen, 2016). Furthermore, Carbaryl adsorbs more readily in acidic soil since its degradation occur in alkaline medium. Its K_{oc} value is 290 which corresponds to a medium of strong adsorption. The adsorption and desorption properties of Carbaryl makes it to remain in the top layers of the soil when applied under agricultural conditions (Kaloyanova & Simeonova, 1994).

In addition, both clay minerals and organic matter contributes to the sorption of Carbaryl. Recent studies indicate mineral interactions between exchangeable cations and carbonyl group from Carbaryl (Fernandes de Oliveira et al. 2005). According to Shen (2001) Carbaryl sorption is dependent on the presence of specific exchangeable cations (Mg^{+2} and Na^{+1}) interacting strongly with partial negative charges of the double-bonded oxygen atom on the insecticide.

Sorption process of Cypermethrin is dominated by organic carbon or organic matter on the particle surfaces which removes it from the aqueous phase of water and causing it to bind to sediments (Oudou & Hansen, 2002).

2.9 DEGRADATION OF CARBARYL AND CYPERMETHRIN

Generally degradation is classified in two ways; abiotic (hydrolysis, and photolysis,) and biotic (microbial) for Carbaryl (Gunasekara, 2007) and Cypermethrin in water and soil (Jones, 1995).

2.9.1 Hydrolysis

There is an effective hydrolysis of Carbaryl in water as a function of pH. Carbaryl is stable in acidic conditions with pH ranging from 3 to 4, it is reported that its half -life is 10 to 17 days at pH 7, 3 hours at pH 9 with temperature being at 25 ºC (Tomlin, 2003), and 1.3 to 1.9 days at pH 8 (Gunasekara, 2007). Greater amounts of Carbaryl are detected in water at pH 4, rather than at higher pH such as pH 6 and 8 (Xu, 2002). Ren, et al. (2016) indicates that Carbaryl undergoes 50% loss at 20 ºC and pH 8 in 4 days.

Additionally, temperature variation has an impact in the hydrolysis of Carbaryl; thus increase in temperature elevates the hydrolysis (Ghauch, Gallet, Charef, Rima, & Martin-Bouyer, 2001). A series of studies were conducted at different temperatures to study temperature dependence of the rate of hydrolysis. Results showed an increase in the reaction velocity due to increase in temperature, consequently decreasing Carbaryl residues (Starner, Kuivila, Jennings, & Moon, 1999).

Carbaryl like other carbamates undergoes hydrolysis by esterase's and is oxidized by cytochrome P450-mediated momnooxygenases (CYP) to form both hydrolysis and hydroxylation products respectively (Tang, Cao, Rose & Hodgson, 2002). Main hydrolaxylation products includes 5-

hydroxycarbaryl (5-hydroxy 1-naphthyl N -methylcarbamate), 4-hydroxycarbaryl (4-hydrox 1-naph-thyl N-methylcarbamate) and Carbaryl methylol (1-naphthyl N-methy – (hydroxymethyl) carbamates.

Hydrolysis is regarded as one of the key players in the degradation of Cypermethrin. It is well highlighted that hydrolysis of Cypermethrin is pH dependent, thus at alkaline conditions (1.9 hours at 50 ^{o}C), neutral condition (4.73 days at 50 ^{o}C) and relatively stable in acidic conditions (> 1 year at 50 ^{o}C) (Agriphar, 2013). According to Tallur, Megadi, & Ninnekar, (2008), the principal degradation route of Cypermethrin is through hydrolysis of ester linkages that leads to the formation of 3-phenoxybenzoic acid (PBA) and cyclopropanecarboxylic acid derivatives principally, 3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropanecarboxylic acid, DCVA. Furthermore, Cypermethrin hydrolyses slowly in neutral or acidic aqueous solution and more rapid alkaline solution at pH 9 more especially in surface water (Dubey & Fulekar, 2013).

2.9.2 Photolysis

Photolysis of pesticides in water and soil for both Carbaryl and Cypermethrin has been reported (Brahimia & Richard, 2003; Jones, 1995). Evidence to suggest that photodegradation plays a great role in loss of Carbaryl in clear surface waters exposed to sunlight for long periods has been stated (Kaloyanova & Simeonova, 1994). Ultra violet (UV) radiation affects the cleavage of the ester bond as well as the occurrence of other modifications in the Carbaryl molecule. It is clearly stated that natural sunlight causes decomposition of Carbaryl. The formation of a greater number of degradation products is due to the extreme UV irradiation (Kaloyanova & Simeonova, 1994).

Field studies show that Carbaryl get photolyzed into 1, 2-naphthoquione, 1, 4-naphthaoquinone, 2-hydroxy-1,4naphthoquinone, and 7-hydroxy-1,4-naphthoquinone (Brahimia & Richard, 2003). As naphthoxyl radicals are produced from Carbaryl in water, hemolytic cleavage of the carbon

oxygen bonds is demonstrated. Furthermore, transformation of solvated electrons into super-oxide anions recombines with radical cations or with 1-naphthoxyl radicals (Brahimia & Richard, 2003).

Light is considered important in photo degradation of Cypermethrin on soil surface and water. Rapid photodegradation is experienced in Cypermethrin with a half-life of 8 to 16 days with main products as 3-phenoxybenzaldehyde, DCVA and 3-phenobenzoic acid, DCVC (Jones, 1995).

2.9.3 Microbial degradation

Several studies have reported microbial degradation of Carbaryl. Doddamani & Ninnekar (2001) highlighted microbial degradation of Carbaryl by *micrococus sp.* to salicylic and gentrisic acid which are then oxidized to maleylpyruvate. Furthermore, constant degradation rate of Carbaryl can be observed within 120 days leaving behind 15-20% of the parent compound in the soil as monitored by the release of ^{14}C carbon dioxide (Doddamani & Ninnekar, 2001). In aerobic soils, Carbaryl has a half-life of 7 days and 28 days in anaerobic soils (Extension Toxicology Network [EXTOXNET], 1993).

Cypermethrin undergoes degradation and its half-life ranges from 2 to 8 weeks in aerobic conditions and is more persistent in anaerobic soil conditions (EXTOXNET, 1993). However, it can be significantly more persistent, as it is indicated in the findings of the study that was carried out in Ontario, Canada where Cypermethrin is reported to have persisted between 4 and 12 months in agricultural soils (Cox, 1996). Microbes also play a significant role in the degradation of Cypermethrin. Although studies stipulate that degradation of Cypermethrin is more slowly in anaerobic and water logged conditions (Walker & Keith, 1992), degradation is even slower in sterilized versus natural soils, which illustrates the importance of microorganisms (Rahman, Rahman, & Hossain, 2015). In sterile aerobic soils, the half-life is reported to be 20 to 25 weeks

and in aerobic soils it ranges from 6-20 days (Walker & Keith, 1992). Additionally, Rahman et al. (2015) indicates that increased Cypermethrin persistence is observed in soil with high organic matter, high clay content, reduced microbial activity and anaerobic conditions. As a result it has a strong affinity to bind to organic matter, since it is fairly immobile in the soil (Jones, 1995). It is also noted that degradation of Cypermethrin is rapid in sandy clay and sandy loam soils than on clay soils, and more rapid in soils that are low in organic material especially under laboratory conditions.

It is well stated that increased bacterial growth in minimal medium increases biodegradation of Cypermethrin (Pankaj, Sharma, Gangola, Kjhati, Kumar, & Srivastava, 2016). Similar findings were obtained by Singh, Walker, Morgan, & Wright, (2004).

2.10 PESTICIDES IN SOILS

2.10.1 Transport of pesticides in soils

Soil is regarded as a primary reservoir of the pesticides through direct application of the chemicals to the soil surface, incorporation in a few inches of the soil surface or off-target drift during application to crops. Kishimba & Mihale (2004) claim that the possible carryover of the pesticides in the soil and their biologically active degradation products has been a major concern to crops grown in the later seasons. They also add that biological effects on organisms in terrestrial and aquatic ecosystems include bioaccumulation and transfer through food chains, surface and ground water contamination, and effects to the soil fertility.

Pesticides undergo a series of transformation and distribution processes while in the soil. These transformation processes may cause the degradation of pesticides through several mechanisms such as oxidation, reduction, or hydrolysis (Berkowitz, Dror, & Yaron, 2008). The pesticides that

enter the unsaturated soil profile through various ways are transported by the water flux downwards and are adsorbed, desorbed and or degraded as they pass through the soil.

A big role of the mobility processes of the pesticides is played by soil texture (percentage of sand, silt, and clay) and structure. Himel, Chaster, Loats, and Bailey, (1990) explained the role of the soil in the transportation of the pesticides. Sandy soils allow water to move easily through them but do not attach easily to pesticides and have less population of soil organisms. On the other hand clay soils and organic matter slows down water motion, attach easily to pesticides and have higher diversity and population of soil organisms that metabolize the pesticides (Evangelou, 1998). The duration of the presence of the pesticides in the soil depends on how strongly it is bound by soil components and how fast degradation is done (Lyman, Warren, Patrick, Reidy & Levy, 1992).

2.10.2 Application of pesticides

Both surface and groundwater get contaminated due to the mode of pesticide application; pesticides applied using an aeroplane can lead to spray drift where pesticides hit non target species. This leads to direct poisoning of the freshwater species. Ground water on the other hand, is impacted by deep percolation, which can also be contaminated by pesticides and fertilizers (Katagi, 2013). The rate at which the pesticides pass through the soil depend on the properties of the pesticides, soil, and the prevailing environmental conditions.

2.11 PESTICIDES IN WATER

2.11.1 Pesticides transport in water

Water carries pesticides through wet and dry deposition, run-off from surfaces, infiltration of the water through the drains, rivers, streams, as well as open ditches (Leonard, 1990). Water moving

at high velocity carries heavier pesticides; thus the faster the water moves the farther the pesticides are transported. Leonard (1990) highlights that pesticides may be deposited onto the sediments at the bottom of the water, on surface float or may diffuse into the water column more especially in the open water systems.

2.12 MOBILITY OF PESTICIDES

Pesticides distribution originates from various pathways, which includes volatilization, leaching, runoff, and absorption by plants as indicated in figure 2. The physico–chemical properties of pesticides and the adsorption– desorption equilibrium in soil are the main factors involved in these processes (Sánchez-Brunete, Albero, & Tadeo, 2008; and Schreck, Geret, & Treilhou, 2008).

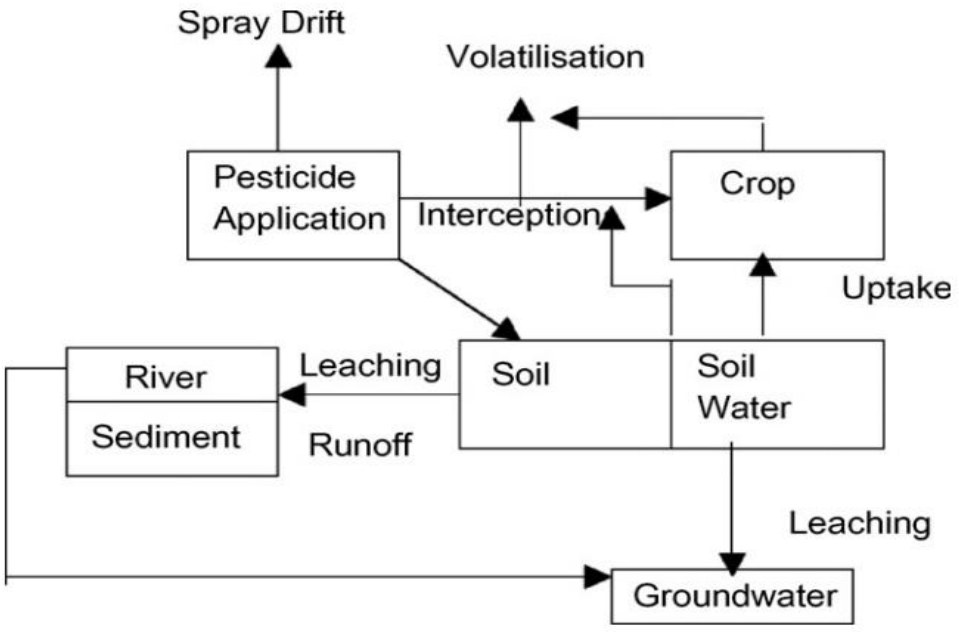


Figure 2: Pathways of a pesticide applied to a crop**.** Ideally, at least one includes its contact with the targeted pest (Source: Arias-Estévez et al. 2008).

2.13 PESTICIDES AND THE ENVIRONMENT

2.13.1 Effects of Carbaryl and Cypermethrin in the environment

Nitrogenous fertilizers such as ammonium sulphate and urea increase the persistence of Carbaryl in the flooded laterine soil (Kaloyanova & Simeonova, 1994). Additionally, effects of Carbaryl on non-targeted organisms has been documented. Fish and other aquatic organisms are exposed to Carbaryl which results into death (Toumi, Burga – Perez, & Ferad 2015).

Cypermethrin reduces the population of insects and other anthropods that prey on unwanted insects in the fields biologically. They also play a vital role in pollination (Cox, 1996). Its toxicity has been documented as affecting bees, spiders, predatory mites, red spider mite, predatory beetles, and aquatic insects such as caddisflies, mayflies, damselflies, brown trout and diving beetles (Siegfried, 1993; and Baatrup & Bayley, 1993).

Cypermethrin causes both median lethal or sub-lethal effects on fish. The median lethal concentration (the concentration that kills 50 percent of a population of test animals; LC50) for most fish is less than 5 Parts per billion. Their nervous systems are sensitive to pyrethroids hence their (fish) inability to breakdown pyrethroids as mammals and birds do (World Health Organization [WHO], 1989). Additionally, it is clearly stated that Cypermethrin bioconcentrates in fish. For example rainbow trout bioconcentration factors ranging from 180 to 438 depending on water type, and valuing up to 1200 have been reported (Cox, 1996).

2.13.2 Pesticides and aquatic life

Clean water is not only essential to human health, but also it is vital to functioning of aquatic ecosystems. These aquatic ecosystems have both economic and intrinsic values (Sallenave, 2016). However, there has been an increasing concern over effects of human activities on water

quality and aquatic life. Pesticides are one group of toxic compounds that can have a profound effect on water quality and aquatic ecosystems. Studies have reported disruption of endocrine system in fish, decline of amphibians, death of fish and as well as general effect on aquatic organisms (Sallenave, 2016).

Carbaryl as one of the carbamates does not persist in the environment but has short term cumulative effects on the reproduction of aquatic organisms (Gunasekara, 2007). Similar findings were highlighted by Tripathi and Singh (2004), that glycogen, pyruvate, total protein and nucleic levels in aquatic organisms were reduced after 96 hours of exposure to Carbaryl. Furthermore, no Carbaryl accumulation has been observed since it is rapidly metabolized to non-toxic substances which are eliminated in urine and faeces (Gunasekara, 2007). Although the persistence of Carbaryl in water may be limited under standard conditions, aquatic organisms may experience long-term exposure to the pesticide. Exposure of fish to Carbaryl depletes glycogen levels in liver and muscles (Canadian Council of Ministers of the Environment [CCME], 2009). Various studies have reported effects of Carbaryl on fish (Toumi et al. 2015). However, low Carbaryl concentrations had no effect on the aquatic plants (Brogan & Relyea, 2017).

Toxicity of Cypermethrin has been reviewed by Parithabhanu and Deepak, (2014) who report that it adversely affects fish and other aquatic organisms. Cypermethrin residue in water results into the death of fish due to decrease in oxygen content. Long-term fish exposure to Cypermethrin reduces survival rate of fish (Karthigayani, et al. 2014). Previous studies indicated the bioaccumulation of Cypermethrin in fish due to acidic conditions through gills uptake. It has already been reported that pesticide, xenobiotic and other chemicals are accumulated over a period of time in natural waters which may ultimately result in toxicity risk to aquatic organisms (Parithabhanu & Deepak, 2014).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 STUDY AREA

The study was conducted in Lisungwi, Neno district, which is located in southern Malawi (Figure 3). The monitoring program was done for a period of seven months between February 2016 to August 2016 (dry and rainy season) which covers the period when pesticides are applied.

3.1.1 Geographic location and climatic condition of the study area

Neno district is one of the 28 administrative districts of Malawi with a total land area of about 1469 km^2. The district shares boundaries with Ntcheu, Balaka, Zomba, Blantyre, Chikwawa, and Mwanza districts. It is located in the southern region of the country at latitude 15º33'35" South and longitude 34º30'16" East. The climate of Neno is subtropical characterized by two main seasons which are rainy and dry seasons. The rainy season is from November to March and the dry season runs from April to October. The area experiences rainfall averaging 500 to 1200 mm per annum. The mean annual temperatures for the area range from 8ºC t in the high altitude areas to 35 ºC in low lying areas within the shire valley (Nyirenda, 2011).

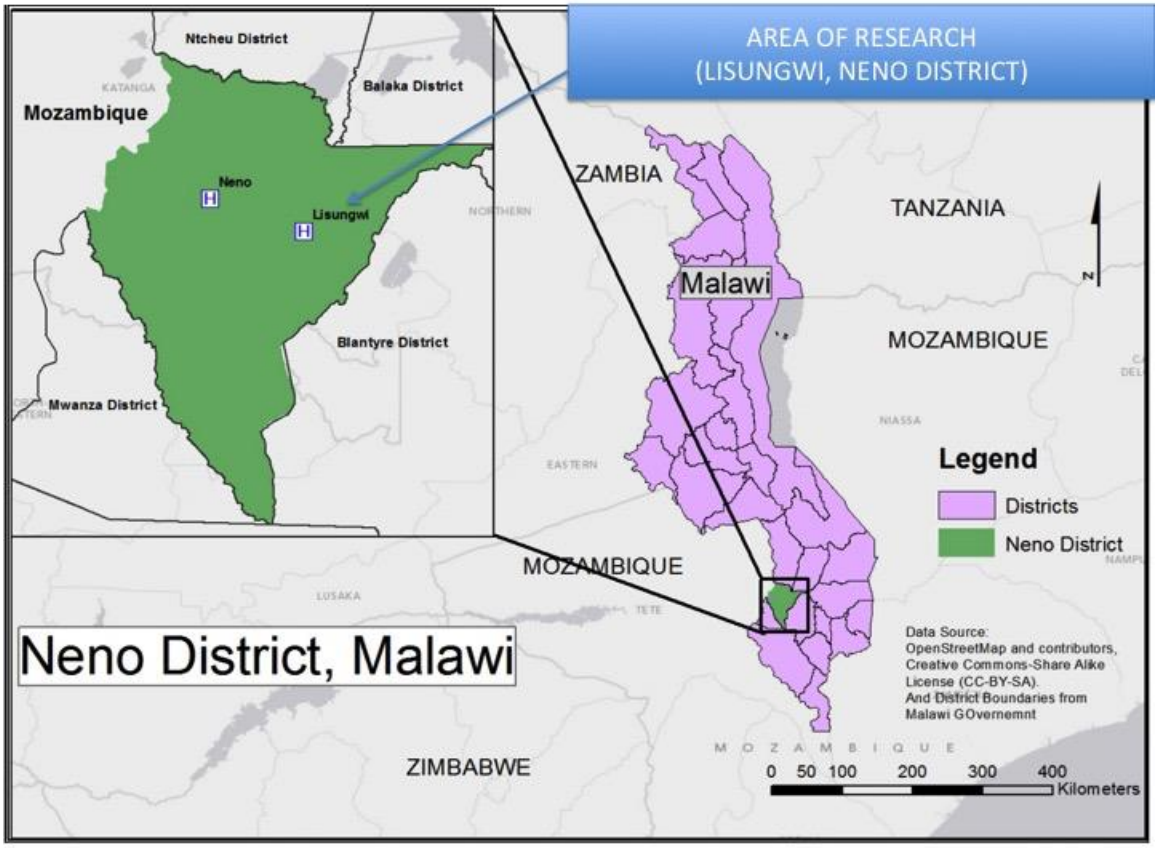


Figure 3: Map of Malawi showing the study area (Partners in Hope, 2013).

3.2 WATER AND SOIL SAMPLING

Samples were collected using systematic random sampling where all fields had chances to be selected.

3.2.1 Sample collection

Figure 4 below shows the water and soil collection points. Arch GIS tool was used to come up with sampling sites in the map.

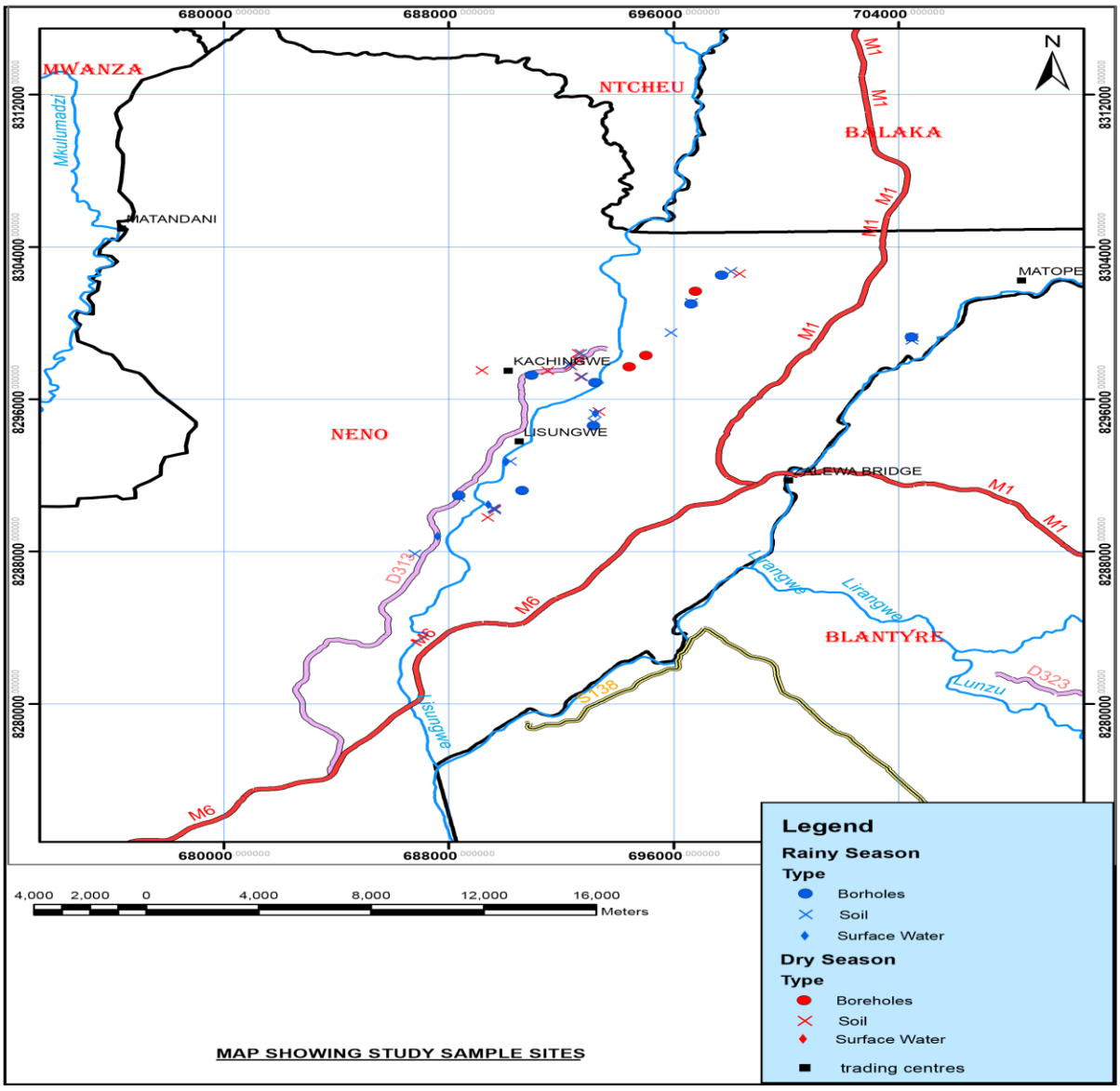


Figure 4: Map showing sampling points in Lisungwi, Neno, Malawi.

Soil samples were collected from 11 and 16 locations in triplicates during dry and rainy season, respectively. The total number of soil samples is shown in Table 6. The samples were collected in dry and rainy season so as to capture seasonal variations. A total of 66 water samples were collected and the summary is shown in Table 6. Thirty six (36) of these water samples were

collected in the rainy season in which twenty four (24) samples were collected from the boreholes, three (3) water samples were collected from the shallow wells and nine (9) water samples were collected from surface water sources (rivers and swamps). Thirty samples (30) were collected in the dry season where eight samples (8) were collected from boreholes and two samples (8) were collected from the surface water (Lisungwi River) in triplicates both upstream and downstream. Collected water samples were put in a cooler box with ice blocks at 4^{o}C according to methods by Laxen & Harrison, (1981) and transported to the laboratory where they were refrigerated upon arrival.

One litre teflon bottles were used in the water sample collection, and they were pre- cleaned with 1:1 v/v HCl before sample collection. The bottles were rinsed three times with the sample to be collected. Surface water samples were collected in the flowing river at 0.1m depth in the direction of current while ground water was collected after running the borehole for 20 minutes in order to flash out the stagnant water.

Five sub-soil samples were collected from each cotton field following systematic random sampling procedure described in Katalin (2011). Samples were collected at four corners of each rectangular cotton field and one at the central location using an auger at the depth of up to 30cm (USEPA, 2014) where diagonals of the field ("X" shaped sampling pattern) was employed as shown in the Figure 5.

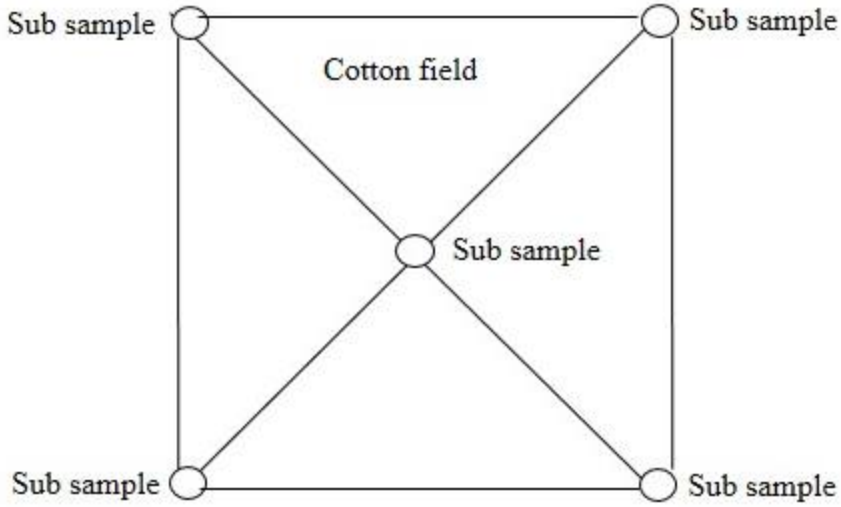


Figure 5: Field sampling procedure for soil sample testing (Katalin, 2011).

A composite sample was made by combining the five collected soil samples (sub-samples) using a hand shovel in a bucket; subsequently transferred into an aluminum foil and then put in polythylene bags.

Table 6: Water and soil samples collected during the surveys.

Sampling point	Dry season	Rainy season	Totals
Shallow well	0	3	3
Surface water	6	9	15
Bore holes	24	24	48
Soil	33	48	81
Totals	63	84	147

3.3 INSTRUMENTS USED

All analytes were determined using standard methods as described by the US Environmental Protection Agency [EPA], (2007), the Association of Official Analytical Chemists [AOAC], (2002) and the American Public Health Association [APHA], (1995). Temperature, pH, electrical

conductivity, total dissolved solids were measured as recommended by APHA (1995). Phosphates and Cypermethrin were analysed according to AOAC (2002) standard methods while nitrates according to standard methods from APHA (1995). Carbaryl was analysed according to US EPA (2007).

Nitrates and Phosphates concentrations were analyzed in the laboratory using UV/Visible spectrophotometer (Milton Roy and electronic 20 model) in chemistry laboratory at University of Malawi – The Polytechnic. Carbaryl and Cypermethrin were analyzed using HPLC (Agilent Technologies and 1260 Infinity) and UV/VIS Spectrophotometer (T90+UV/Vis Spectrometer PG Instrument T90 Ltd and wagtech model), respectively in a chemistry laboratory at University of Malawi – Chancellor College.

Equipment used for field measurements included a pH/Temperature meter (Wagtech International, WE 30200). This was used to measure pH and Temperature. Electrical conductivity meter (Batch Company MP-4 model) was used to measure conductivity whereas TDS meter (Hach Company) was used to measure total dissolved solids as recommended by APHA (1995).

Soil pH and electrical conductivity were determined using 1:1 (w/v) soil/water mixture as described in Mussa, et al. (2009). Soil sample portions of 20 g were weighed using a beam balance (ADAM equipment Company and AFA210LC model) then 20 ml of distilled water was added. The mixture was shaken and allowed to stay for 30 minutes and measured with a pH meter and electrical conductivity meter.

3.4 LABORATORY CHEMICALS AND REAGENTS

3.4.1 Determination of nitrates in water

Nitrates react with sodium salicylate under strongly acidic conditions. Addition of excess sodium hydroxide solution produces the sodium salt of the organic nitro complex. The nitro compound is

soluble in water and produces a strongly yellow solution. The color intensity is proportional to the amount of Nitrate in the sample and is measured on a spectrophotometer (Milton Roy and electronic model 20) at 410 nm.

3.4.1.1 Reagents

3.4.1.1.1 Sodium Salicylate (0.5% w/v)

Sodium salicylate of concentration 0.5% w/v was prepared by dissolving 0.5 ± 0.01 g of laboratory grade sodium salicylate in 100 mL distilled water in a volumetric flask. This was stored in a refrigerator.

3.4.1.1.2 Sodium Hydroxide (25% w/v)

Sodium hydroxide of concentration 25% w/v was prepared by dissolving 25 ± 0.1 g of sodium hydroxide (NaOH) in 70 mL of distilled water and left to cool; quantitatively transferred to 100 mL volumetric flask and diluted to the mark.

3.4.1.1.3 Stock Solution for Nitrate Determination: 1 mL = 500μg NO_3^-

Potassium nitrate was dried at 110 °C in the oven. A mass of 0.815 ± 0.001g (0.008 mol) of analar potassium nitrate was dissolved in 100 mL of distilled water, quantitatively transferred to 1 L volumetric flask and diluted to the mark with distilled water.

3.4.1.2 Standard Nitrate (working solution A), 1mL = 50μg NO_3^-

To a 100 mL volumetric flask, 10 mL of standard nitrate (stock) solution were pipetted and diluted to the mark with distilled water.

3.4.1.3 Standard Nitrate (working solution A) Series

Nitrate containing standards were prepared as follows: 0 (blank), 2, 4, 6, and 8 mL of standard Nitrate working solution A were separately dispensed into a 100 mL pyrex beaker using a micro burette. Using a pipette 2.0 mL of sodium salicylate (0.5% w/v) was added in each of the beakers and mixed well, in turn evaporated to dryness in a water bath. Beakers were allowed to cool and 1.0 mL of concentrated sulphuric acid was pipetted into each beaker and allowed to stand for 10 minutes. Each beaker was diluted to approximately 50mL with distilled water. 10.0 ml of sodium hydroxide (25% w/v) was added into each beaker using a burette, mixed thoroughly then allowed to cool. Thereafter, the mixtures were quantitatively transferred to a 100 mL volumetric flask and diluted to the mark with distilled water.

The resulting concentration ranges were: 0, 1, 2, 3 and 4 mg/L. Using a UV/Vis spectrophotometer, absorbance was measured against a blank (100% transmission) in a 10.0 cm cell at a wavelength of 410 nm. The signals of those standard solution series was used to establish a calibration curve (Appendix 5a, and 5b for water and soil samples).

For water samples, 5 mL of each sample was used for analysis. Mean concentration of each were calculated and recorded. Using a calibration curve, concentration in μg NO_3^- were calculated using y = 0.2295x – 0.0152; R^2 = 0.9998 and y = 0.0455x + 0.002; R^2 = 0.9987. Where y = absorbance, x = concentration in μg NO_3^-.

Nitrate content (mg L^{-1}) was calculated by $$y = \frac{\mu gNO_3^- \times df}{V}$$

Where y = nitrate content in mg/L

df = dilution

V = Volume used

3.4.2 Determination of Nitrates in soil samples

3.4.2.1 Soil sample extraction

To 250 mL stopper conical flask, 50 g of each of the weighed soil samples were transferred and shaken using a mechanical shaker for 10 minutes with exactly 50 mL of distilled water 1:1 w/v. The equilibration was allowed to take place by leaving the samples for 30 minutes after shaking. The samples were filtered into Buchner funnels by using filter papers whatman no. 42. Then the procedure as stated in section 3.4.1.3 was followed.

3.4.3 Determination of available Phosphates in water by phosphovanadomolybdate method

The phosphovanadomolybdate complex was formed between Phosphate, Ammonium vanadate and Ammonium molybdate indicated by a bright yellow colour and its absorbance was measured at 465 nm. UV/Visible range spectrophotometer (Milton Roy and electronic model 20) was used.

3.4.3.1 Reagents

3.4.3.1.1 Ammonium vanadate solution

Ammonium vanadate solution was made by dissolving 2.5 g Ammonium vanadate (NH_4VO_3) in 500 mL of boiling distilled water in 1 L volumetric flask. The solution was cooled to 60 ^oC and then 20 mL of concentrated Nitric acid were added. The solution was cooled to room temperature then diluted with distilled water to the mark and stoppered.

3.4.3.1.2 Ammonium molybdate solution

Ammonium molybdate solution was prepared by dissolving 50 g Ammonium molybdate [$(NH_4)_6MO_7O_{24}.4H_2O$] in warm distilled water using 1 L volumetric flask and in turn diluted to the mark with distilled water.

3.4.3.1.3 Combined reagent (Vanadate-molybdate solution)

Vanadate-molybdate solution was made by transferring 500 mL of Ammonium vanadate to 1 L volumetric flask followed by 500 mL of Ammonium molybdate and then mixed. Light green color was observed.

3.4.3.1.4 Standard Phosphate solution (1ml = 0.05mg P)

To 1 L volumetric flask, 0.2197 g of analytical grade potassium dihydrogen phosphate (KH_2PO_4) was dissolved and diluted to the mark with distilled water.

3.4.3.2 Standard Phosphate working solution

A series of Phosphate standards 0 (blank), 1, 2, 4, and 8 mL were prepared and pipetted in separate and clearly labeled 50 mL volumetric flasks representing 0, 0.05, 0.1, 0.2, and 0.4 mg Phosphate, respectively. 10 mL of combined reagent (Vanadate-molybdate reagent) were added to the series of the standards. The standards were in turn diluted to the mark with distilled water and allowed to stay for 10 minutes while the reaction was taking place. Yellow colour was observed and the color intensity showed the amount of phosphate in the standards. A blank solution was used to calibrate the spectrophotometer and absorbance of the standards was measured on the spectrophotometer at a wavelength of 465 nm.

A beer lambert's plot was plotted with the concentration on the x- axis and absorbance on the y-axis (appendix 5c and 5d for rainy and dry season, respectively) where concentration was calculated using $y = 0.85x - 0.003$ and $R^2 = 0.9997$ and $y = 0.0237x + 0.002$, $R^2 = 0.9991$.

3.4.3.3 Water sample preparation for phosphate determination

Water samples were prepared by pipetting 10 mL of each water sample to 50 mL conical flask and 10 mL of Vanadate-molybdate reagent was added. Each sample was diluted to 50 mL using a

cornical flask. Samples were allowed to stay for 10 minutes for the reaction to take place. Absorbance was measured using a spectrophotometer at a wavelength of 465 nm. Finally the concentration was calculated using the Beer-Lambert's plot and then multiplied by 5 (dilution factor) to get the original concentration.

3.4.4 Determination of available Phosphates in soil -Ascorbic acid method

Phosphorus was extracted from the soil using Bray No. 1 solution as extractant (Bray, 1995). The extracted Phosphorus was measured colourimetrically based on the reaction with Ammonium molybdate and development of the 'Molybdenum blue' colour. The absorbance of the compound was measured at 882 nm in a spectrophotometer and is directly proportional to the amount of Phosphorus extracted from the soil.

3.4.4.1 Bray No. 1 extracting solution

Bray No. 1 extracting solution was made by dissolving 2.22 g Ammonium flouride A.R. (NH_4F) in distilled water and transferring the solution to a 2 L volumetric flask. Thereafter, 5 mL of concentrated hydrochloric acid was added and topped up with distilled water to the mark.

3.4.4.2 Reagent A

Reagent A was prepared by dissolving 17.4 g of ammonium molybdate A.R. [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 200 mL of warm distilled water. Then 0.392 g potassium antimonyl tartrate A.R. ($KSbO.C_4H_4O_6$) was dissolved separately in 150 mL volumetric flask with distilled water. 500 mL of deionized water was placed in a 2 L volumetric flask and 200 mL concentrated sulphuric acid was slowly added with mixing and consequently allowed to cool. Cooled ammonium molybdate and potassium antimonyl tartrate solutions were added, then mixed and topped up with distilled water.

3.4.4.3 Reagent C

Reagent C was prepared by dissolving 0.53 g L-Ascorbic Acid A.R. ($C_6H_8O_6$) in distilled water and transferred to a 500 mL volumetric flask. Then 70 mL of Reagent A was added and topped up with distilled water.

3.4.4.4 Standard Phosphorus Solution (P = 50 mg/L)

To 100 mL of deionized water, 0.2195 g potassium dihydrogen orthophosphate A.R. (KH_2PO_4) was dissolved and transferred to a 1 L volumetric flask. 5 mL concentrated sulphuric acid (A.R.) was added and topped up with distilled water.

3.4.4.5 Phosphorus working standard Solution (P = 2.50 mg/L)

To 100 mL volumetric flask, 5 mL standard phosphorus solution was pipetted and topped up with distilled water.

3.4.4.6 Standard reference preparation

A set of reference standards (0.125, 0.250, 0.500, 0.750, 1.000 and 1.250 mg/L) were prepared by pipetting 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50 mL of 2.5 mg/L Phosphorus working standard solution into a colourimeter tube. Reagent C (2.45, 2.40, 2.30, 2.20, 2.10, and 2.00 mL) was mixed in separate Phosphorus working standard solution and allowed to stand for 30 minutes. Absorbance of the standards was measured and recorded at a wavelength of 882 nm. Finally a graph from the standards data was plotted and was used to determine the concentration of Phosphorus in sample solutions (appendix 5e and 5f for rainy and dry season, respectively).

3.4.5 Soil sample preparation

Soil samples were prepared by dispensing 7 mL Bray extracting solution into 1 g oven-dried soil contained in the centrifuge tube. The tubes were stoppered and shaken vigorously for 1 minute. The tubes were in turn transferred to the centrifuge and spun at 6000 rpm for 5 minutes. 0.50 mL of the supernatant was dispensed into a colourimeter tube then 2.0 mL of reagent C was added to each tube. These were mixed and allowed to stand for 30 minutes before absorbance was measured using a spectrometer at 882 nm. Using a calibration curve (appendix 5e and 5f for rainy and dry season soil samples, respectively), concentration in mg/L were calculated using $y = 0.85x - 0.003$; $R^2 = 0.9997$ and $y = 0.815x - 0.0065$; $R^2 = 0.9993$.

Available phosphorus content of soil samples were calculated using the equation below:

$$Available\ phosphorus\ (^{mg}/_{Kg}) = \frac{C \times 14}{ODW}$$

Where: C = Phosphorus concentration (mg/L)

ODW = Oven-dry sample weight (g)

14 = Dilution factor

3.5 PESTICIDES ANALYSIS

All reagents used were of analytical reagent grade and double distilled water was used throughout.

3.5.1 Determination of Carbaryl in water and soil

3.5.1.1 Equipment

Carbaryl residues in water and soil were analyzed using High Performance Liquid Chromatography, HPLC (Agilent Technologies 1260 Infinity) equipped with an auto injector (G1329b 1260 ALS) with sample loop size 10 µL and Diode Array Detector (G1315D 1260 DAD, Agilent). The oven temperature was maintained at 40°C, and the system had an Acclaim 120-C18, 150 mm × 3mm ID column (particle size 3 µm), part number 063691. A guard column (Acclaim 120-C18, 5 µm, 10 mm × 2.1 mm ID), part number 069689 was fitted before the analytical column. The flow rate was 0.8 mL/min; absorbance 280 nm. The mobile phase consisted of (A. Acetonitrile, B. 5 mM Ammonium acetate, pH 5.0, with acetic acid) (EPA method 8318a). A mixture of acetonitrile and distilled water (60:40) was used as the mobile phase with isocratic elution.

3.5.1.2 Reagents

All reagents were of HPLC grade and included Acetonitrile (CH_3CN), Methanol (CH_3OH) and Methylene chloride.

3.5.1.2.1 Carbaryl Standard Stock solution (1000 mg/L)

Carbaryl stock solution was made by dissolving 0.050 g of Carbaryl in Methanol and was diluted to the mark in 50 mL volumetric flask. The solution was refrigerated in glass vials with PTFE-lined screw caps.

3.5.1.2.2 Intermediate Standard solution (50 mg/L)

Carbaryl intermediate standard solution was prepared by pipetting 2.5 mL of Carbaryl stock solution into 50 mL volumetric flask and diluted to the mark with Methanol. The solution was refrigerated in glass vials with PTFE-lined screw caps.

3.5.1.3 Working Standard solutions

Series of standards (0.5, 1.0, 2.0, 3.0 and 5.0 mg/L) were prepared by adding 0.25, 0.5, 1.0, 1.5 and 2.5 mL of intermediate standard solution to a 25 mL volumetric flask and diluted to the mark with Methanol. Standards were filtered using a disposable 0.45-µm filter.

20 µL of Methanol (solvent of blank) was analyzed prior to calibration of Carbaryl standards starting with the lowest standard and ending with the highest standards. Standards were loaded into the autosampler vials and then loaded into the HPLC autosampler. Peak areas (peak heights) were recorded and the calibration curve was prepared by plotting a peak area against concentration. The best line of fit through the data points was determined where a linear equation was derived from it as $y = 574x - 17.993$ and $R^2 = 0.9993$. The calibration curve was used to calculate the concentration of both soil and water samples as shown in appendix 5g.

3.5.1.4 Water sample preparation

100 mL of each water sample was put into 250 mL separatory funnel where 30 mL of Methylene chloride was added and then shaken vigorously for about 2 minutes. Phases were allowed to separate and consequently the organic layer was transferred into a clean 100 mL volumetric flask. The extraction was repeated two more times using fresh portions of solvents. All the three extracts were combined in a 100 mL volumetric flask and diluted to the mark with Methylene chloride. The extract was then filtered using a disposable 0.45 µm filter into a labelled auto-sampler vial and then loaded into the HPLC autosampler.

3.5.1.5 Soil sample preparation using EPA method 8318a

Sample portion extraction was done as described by USEPA, (2007). Soil portions of 2.5 ± 0.1 g were weighed and put into separate 250 mL volumetric flask with PTFE-screw cap. 50 mL of acetonitrile was then added to the portion of each sample and shaken for two hours on a platform shaker. The mixture was allowed to settle for about 5-10 minutes and then the extract was decanted into 250 mL centrifuge tube in order to separate the solid particles from the liquid. The extraction was repeated two more times using 20 mL of Acetonitrile and shaking for 1 hour each time. All the three extracts were combined in the centrifuge tube and later centrifuged at 200 rpm for 10 minutes. The supernatant was carefully decanted into a 100 mL volumetric flask and diluted to the mark with Acetonitrile. The extract was then filtered using a disposable 0.45 µm filter into a labelled auto-sampler vials and loaded into the HPLC autosampler.

3.5.1.6 Liquid chromatography (HPLC-DAD) results and calibration curve.

The retention time for chromatograms for Carbaryl standards was 2.267 minutes and an example of chromatograms is indicated in appendix 4. The calibration curve for Carbaryl is shown in appendix 5g where $y = 574.8x - 17.93$ and $R^2 = 0.9993$.

3.5.2 Determination of Cypermethrin in water and soil using Uv/Vis Spectrophotometer

According to Dhundhel & Rai (2011) Cypermethrin is hydrolyzed to Cyanide ion in an acidic medium which in turn reacts with bromine water to form cyanogen bromide. Excess of bromine is removed in the solution by addition of Potassium iodide solution which reacts with p-aminoacetophenone reagent. Absorption of violet color is measured at 400 nm using a UV/Vis spectrophotometer (Wagtech PG instrument T90 model).

3.5.2.1 Reagents

3.5.2.1.1 Sodium Hydroxide (20%)

Sodium hydroxide (20%) was prepared by dissolving 20 g of the analyte in 70 mL of distilled water and allowed to cool; then made up to 100 mL volume in a flask with distilled water.

3.5.2.1.2 Potassium iodide (0.1%)

Potassium iodide (0.1%) was prepared by dissolving 0.1 g of the analyte in 100 mL volumetric flask with distilled water and diluted to the mark with distilled water.

3.5.2.1.3 Hydrochloric acid (3%)

Hydrochloric acid (3%) was made by pipetting 3 mL of Hydrochloric acid in 100 mL volumetric flask (v/v), then diluting with distilled water and then it was made up to the mark.

3.5.2.1.4 P-aminoacetophenone (1%)

P-aminoacetophenone (1%) was made by dissolving 1 g of the reagent with absolute ethanol in 100 mL volumetric flask and then it was diluted to the mark with alcohol.

3.5.2.2 Cypermethrin stock solution (1000 ppm)

Cypermethrin stock solution (1000 ppm) was prepared by dissolving 0.1 g of pure reagent powder in dichloromethane (DCM) solvent to 100 mL in a volumetric flask and it was diluted to the mark using DCM. The solution had a concentration of 1000 ppm.

3.5.2.3 Cypermethrin intermediate solution (100 ppm)

Cypermethrin intermediate solution was made by pipetting 10 mL of Cypermethrin Stock solution into 100 mL volumetric flask, and then diluting it to the mark using DCM. The solution had a concentration of 100 ppm.

3.5.2.4 Cypermethrin working standards

A series of Cypermethrin containing standards were prepared by diluting 1.0, 2.0, 3.0, 4.0 and 5.0 mL of Cypermethrin intermediate solution into 100 mL with dichloromethane in separate volumetric flasks and the concentration for the solutions made were 1.0, 2.0, 3.0, 4.0, and 5.0 ppm, respectively.

3.5.2.5 Working standards preparation for analysis

To 0.5, 1, 1.5, 2, and 2.5 mL of Cypermethrin working standards, 4 mL of 20% sodium hydroxide was added in 50 mL volumetric flasks. The solution was kept for 10 minutes at room temperature for complete hydrolysis and neutralized with 0.1N HCl. Then 2 mL of 0.1% potassium iodide was added followed by one drop of concentrated HCl, to liberate iodine and then followed by the addition of 2 mL of 1% p-aminoacetophenone reagent. The solutions were thoroughly shaken and kept for 15 minutes for colour development. A violet color was observed and solutions were diluted to the mark with distilled water. Absorbance for both standards and samples were measured at 400 nm. Calibration curve was then constructed as indicated in appendix 5h and Cypermethrin content in samples was established from the calibration graph: $y= 0.0052x – 0.0002$ and $R^2 = 0.9991$. For water samples 25 mL of each sample was used.

3.5.2.6 Soil sample preparation

Soil samples were prepared by mixing 2.5 g of each soil sample portions with dichloromethane, DCM and then filtered using Whatman No. 40 cm filter paper. The filtrate of each sample portion were quantitatively transferred into separate 50 mL graduated flask and made up to the mark with DCM. 25 mL of each aliquots were taken in a 50 mL graduated tube, and then analyzed as recommended by procedures in 3.5.2.5.

3.6 DATA ANALYSIS

The experiment for each sample was performed in triplicate and results were expressed as means of the three triplicates. Data was organized using 2013 Microsoft office excel and statistical analyses were performed using IBM SPSS statistics version 20. Statistical significance was tested using independent samples t – test and correlation was used to measure the linear association between variables.

CHAPTER 4

4.0 RESULTS AND DISCUSSION

4.1 Results for pH, temperature and electrical conductivity

Findings for pH, temperature and electrical conductivity measured from surface water, ground water and soil samples are presented in Table 7.

Table 7: Physical parameters of water and soil samples

Sample type	**Seasonal ranges**			**Seasonal mean ± standard deviation**		
	pH	Temperature (°C)	EC (µS/cm)	pH	Temperature (°C)	EC (µS/cm)
RSW	6.8-7.3	30-35.1	164.7-808.4	7.02±0.19	31.90±2.35	436.58±314.0
RGW	6.0- 6.8	29.8-42.7	175.3-2196.0	6.42±0.28	32.67±4.99	1173.42±894.2
RS	5.5-7.2	-	17.9-103.5	6.73±0.36	-	46.80±21.6
DSW	7.6-7.7	23.7-24.5	198.8-219.3	7.66±0.07	24.10±0.61	209.0±14.5
DGW	6.7-7.1	25.3-42.1	1030.7-2293.0	6.79±0.12	29.18±5.33	1508.2±431.4
DS	5.8-6.5	-	215.2-372.6	5.99±0.23	-	288.75±45.4

EC – Electrical conductivity, **RSW**- surface water in rainy season, **RGW** – Ground water in rainy season, **RS**- Soil in rainy season, **DSW** – Surface water dry season, **DGW** – Ground water in dry season, **DS** – Soil in dry season.

4.1.1 pH

A small difference was observed between the range of pH in surface water (6.8 – 7.3) and ground water (6.0 – 6.8) in the rainy season as shown in Table 7. This shows that during the rainy season, the pH was slightly acidic to neutral as indicated in Figure 6. The surface water was associated with a slightly higher pH (Mean = 7.02, Standard deviation = 0.19) as compared to

ground water pH (Mean = 6.42, Standard deviation = 0.28). Statistical analysis showed that in the rainy season, the mean pH in the surface water was significantly higher ($p < 0.05$) than that of ground water samples. In the dry season, the pH ranges were 7.6 – 7.7 in surface water and 6.7 – 7.1 in ground water. This indicates that surface water pH was also significantly higher ($p < 0.05$) than ground water pH. The WHO (2008) recommends a pH range of 6.5 to 9.5 while Malawi Bureau standards' recommended range is 6.5 and 9.0 (MS, 2013) for drinking water, as shown in Table 14. The results of this study indicate that the pH falls within the acceptable limits of Malawi standards and WHO. Additionally, the water pH findings in this study compared well with those found for water supplies in Malawi (Grimason, Morse, Beattie, Masangwi. Jabu, Taulo, & Lungu, 2012).

The range of soil pH was 5.8 – 6.5 and 5.5 – 7.2 in the dry season and rainy season, respectively. The soil pH was significantly higher ($p < 0.05$) in the rainy season as compared to the dry season. The lower pH values found in this study especially in the rainy season could be attributed to the decomposition process of organic matter, which consumes dissolved oxygen, yielding carbon dioxide gas and hydrogen ions (Ajibade, Ayodele, & Agbede, 2008).

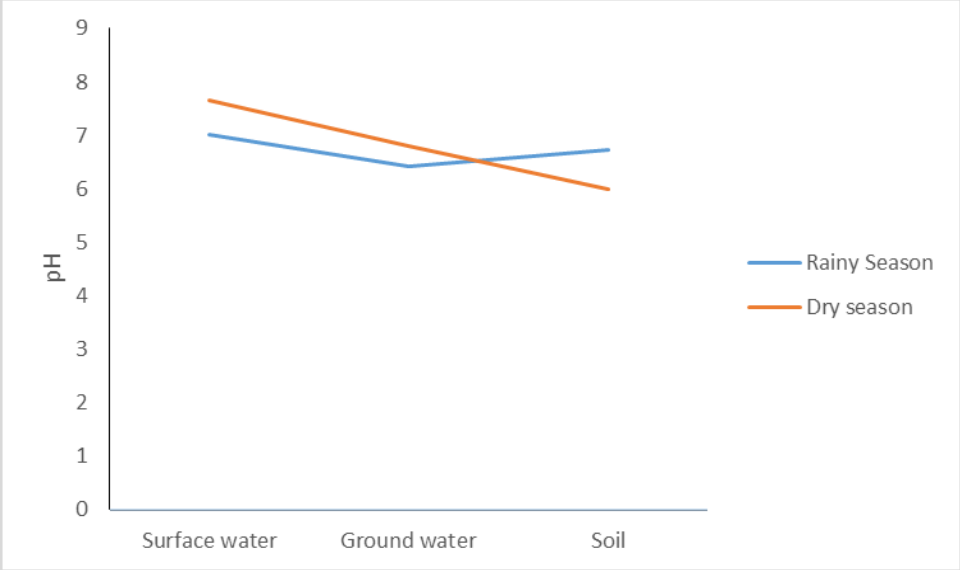


Figure 6: Comparison of pH during the rainy and dry season.

4.1.2 Temperature

The temperature ranges for water samples were as follows 30 – 35.1 °C in surface water and 29.8 – 42.7 °C in ground water in the rainy season. In the dry season, temperature range in surface water was 23.7 – 24.5 °C while in ground water, it was 25.3 – 42.1 °C. The temperature in surface water was slightly lower (Mean = 31.90, Standard deviation = 2.35) as compared to that of ground water (Mean = 32.67, Standard deviation = 4.99).

The recommended temperature for aquatic life in the tropical environment ranges from 21 °C to 32 °C and below 40 °C for drinking water (Ajibade et al. 2008). This shows that the results for this study fall within the stated range mostly for surface water and ground water. However, no recommended temperature for drinking water is stipulated by either Malawi standards or WHO. A number of studies (WHO, 2008; and Oyem, Oyem, & Ezeweali, 2014) have indicated the negative effects of high water temperature on water quality. These effects include decreases in solubility of various gases such as carbon dioxide, oxygen, methane and nitrogen.

4.1.3 Electrical conductivity and total dissolved solids

The study showed marked differences in the electrical conductivity and total dissolved solids values. Electrical conductivity ranges for surface water was 164.7 – 808.4 µS/cm, ground water was 175.3 – 2196.0 µS/cm and soil was 17.9 – 103.5 µS/cm in the rainy season. In the dry season, the electrical conductivity for surface water was 198.8 – 219.3 µS/cm, ground water was 1030.7 – 2293.0 µS/cm and soil was 215.2 – 372.6 µS/cm. The conductivity of surface water was the lowest (Mean = 436.58, Standard deviation = 313.96). By comparison, ground water was associated with a numerically higher electrical conductivity (Mean = 1173.42, Standard deviation = 894.24) as compared to surface water. This is normal because the surface water passes through soils and stones dissolving minerals before being ground water. The conductivity of surface water was significantly lower than that of ground water ($p > 0.05$) in the dry season which was also the case in dry season.

The total dissolved solids (TDS) in water samples in the rainy season ranged from 82.4 – 404.2 mg/L with the mean of 218.3 mg/L in surface water and 87.7 – 1098 mg/L in ground water with a mean concentration of 584.5 mg/L. The TDS in surface water was significantly lower ($p > 0.05$) than that of ground water samples in the rainy season. In the dry season, TDS values for water samples ranged from 99.38 – 109.63 mg/L with mean value of 104.5 mg/L in surface water and 515.33 – 1146.83 mg/L in ground water with mean value of 754.1 mg/L. The TDS in the surface water was significantly lower ($p > 0.05$) than that of ground water samples in the dry season. High values of electrical conductivity shows the presence of inorganic ions such as H^+, Na^+, K^+, Mg^{2+} , Ca^{2+} , Cl^-, SO_4^{2-}, HCO_3^- among others, in reasonable concentrations in both surface water and soil as reported by Uwidia & Ukulu, (2013).

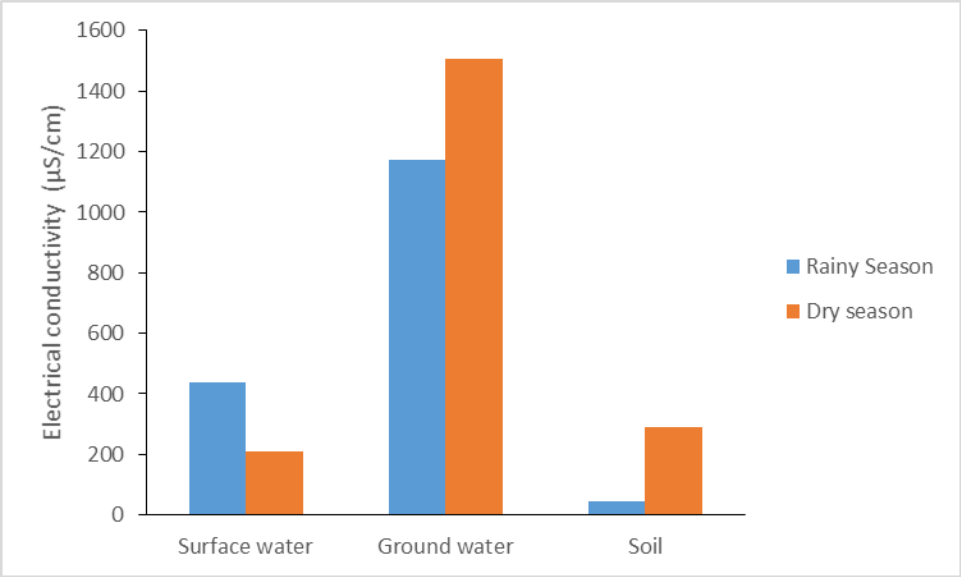


Figure 7: Comparison Electrical conductivity during rainy and dry season.

Furthermore, the electrical conductivity for ground water was lower in the rainy season than in the dry season as shown in Table 7 and Figure 7. The lower values in the rainy seasons were due to the leaching of the mineral salt from the bedrock and re-suspension of solids. However, all the samples were above the limits as recommended by WHO and Malawi Bureau Standards (Table 14). Lower conductivities in the ground water of the rainy season were attributed to dilution effect.

The findings of the current study indicate that concentration of TDS was lower in the rainy season than in the dry season. The degree of relation between EC and TDS concentration of samples showed that TDS concentration was increasing proportionally with EC value. Generally, an increase in concentration of total dissolved solids (TDS) in water results into an increase in conductance (Tutmez, Hatipoglu & Kaymak, 2006). All samples were within the WHO standards except for ground water samples (> 1000 mg/L). This could be due to the presence of inorganic minerals in the aquifers (Uwidia & Ukulu, 2013).

4.2 Results for Nitrates and Phosphates

The results for nitrates and phosphates are shown in Table 8.

Table 8: Results for Nitrate and Phosphate

Sample type	Seasonal ranges		Seasonal mean ± standard deviation	
	Nitrate (ppm)	Phosphate(ppm)	Nitrate (ppm)	Phosphate(ppm)
RSW	n.d – 35.73	2.61 – 3.25	12.82 ± 13.88	2.98 ± 0.23
RGW	n.d – 36.87	1.75 – 2.82	15.95 ± 11.37	2.28 ± 0.31
RS	9.3 – 107	1.86 – 12.43	35.52 ± 24.53	6.51 ± 3.03
DSW	n.d – 10.55	2.67 – 5.98	5.27 ± 5.27	4.32 ± 1.65
DGW	n.d – 154.81	1.69 – 12.17	50.19 ± 56.15	6.09 ± 3.45
DS	11.34 – 136	2.25 – 14.76	44.51 ± 34.95	7.12 ± 3.11

RSW – surface water in rainy season, R**GW** – Ground water in rainy season, R**S** – Soil in rainy season, **DSW** – Surface water in dry season, **DGW** – Ground water in dry season and **DS** – Soil in dry season, **n.d** – not detected

4.2.1 Nitrates

As shown in Table 8, Nitrate concentration ranged from 0.00 – 35.75 ppm, and 0.00 – 36.87 ppm in surface water and ground water, respectively during rainy season; from 0.00 – 10.55 ppm and 0.00 – 154.81 ppm in surface water and ground water, respectively in dry season. Nitrate concentration range was, 9.3 – 107 ppm and 11.34 – 136 ppm in soil during rainy and dry season, respectively. The Nitrate concentration in surface water was significantly lower ($p > 0.05$) than that of ground water samples in the rainy season. However, Nitrates in surface water was significantly higher ($p > 0.05$) than that of ground water in the dry season. Nitrate concentration in soil during the rainy season was significantly lower than dry season ($p > 0.05$).

Previous studies indicate that higher nitrate levels are usually built up during the dry season and that high levels of nitrates are only observed during early rainy seasons, because initial rains flush out deposited nitrates from near–surface soils (Adeyemo, Adedokun, Yusuf, & Adeleye 2008). This is the case with the surface water (Figure 8). The content of nitrates in all samples were lower than the WHO standards of nitrates contents in potable water (< 50 mg/L) as indicated in Table 14.

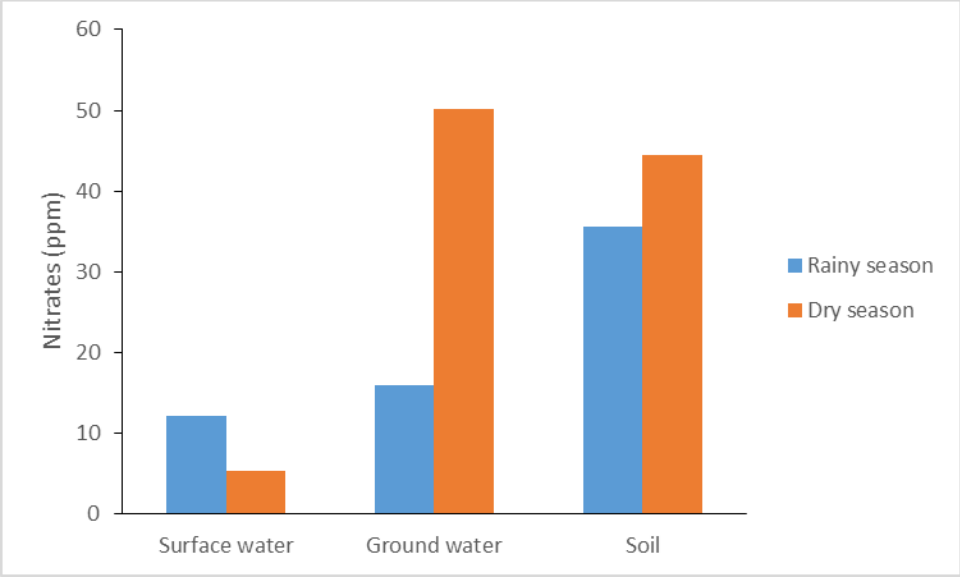


Figure 8: Comparison of Nitrates during rainy and dry season.

4.2.2 Phosphates

The range of Phosphate in surface water was 2.61 – 3.25 ppm and in ground water was 1.75 – 2.82 ppm in the rainy season. On the contrary, the surface water Phosphate range in the dry season was 2.67 – 5.98 ppm and ground water 1.69 – 12.17 ppm. In the soil, the range was 1.86 – 12.43 ppm in the rainy season and 2.25 – 14.76 ppm in the dry season. The mean concentration in surface water (Mean = 2.98 ppm, Standard deviation = 0.27 ppm) was slightly higher than that of ground water (Mean = 2.27 ppm, Standard deviation = 0.35 ppm) (Table 8). Phosphate

concentration was significantly higher in surface water than ground water ($p < 0.05$) in the rainy season (Figure 9), but in the dry season there were no significant differences ($p > 0.05$). Furthermore, Phosphate concentration was not statistically significant in rainy season ($p > 0.05$) than dry season in the soil samples.

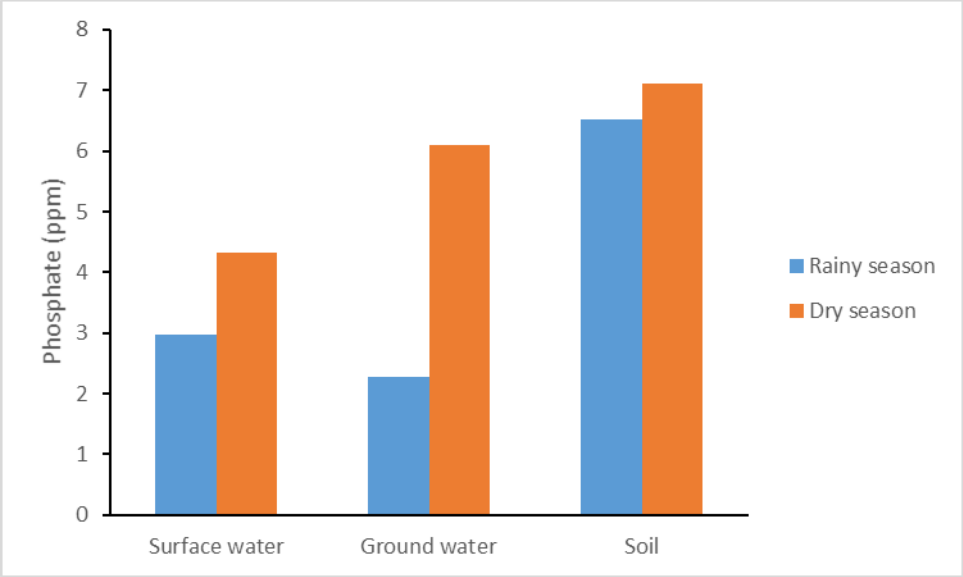


Figure 9: Comparison of Phosphates during rainy and dry season

Phosphate concentration as found in the current study was higher in both surface water and ground water as compared to WHO standards (Table 14). Phosphates in natural waters originate principally from sewage, effluents, farmyard manures, and detergents from washing powders, fertilizers among others (Sajidu, Masamba, Henry, & Kuyeli 2007). The concentration of phosphates found in this study is consistent with Sajidu et al. (2007) who did a study in Blantyre streams where phosphate concentrations ranged from 0.63 to 5.50 mg/L.

4.3 Results for Carbaryl and Cypermethrin

Results (range and mean) for Carbaryl and Cypermethrin in dry season and rainy season are shown in Table 9. The results are for surface water, ground water and soil.

Table 9: Carbaryl and Cypermethrin residues (ppm) in water and soil.

Sample type	**Range (ppm)**		**Mean ± SD (ppm)**	
	Carbaryl	Cypermethrin	Carbaryl	Cypermethrin
RSW	0.08 – 0.25	0.04 – 15.46	0.14 ± 0.08	11.16 ± 3.3
RGW	0.15 – 0.49	0.04 – 12.18	0.26 ± 0.12	7.27 ± 2.89
RS	1.13 – 1.30	0.08 – 0.49	1.23±0.48	0.29 ± 1.02
DSW	0.04 – 0.16	0.04 – 7.73	0.05 ± 0.07	3.95 ±5.53
DGW	0.07 – 0.10	0.04 – 18.82	0.10 ±0.01	7.23 ± 4.95
DS	1.13 – 1.25	0.00 – 0.075	1.19 ± 0.04	0.04±0.00

RSW – Surface water in rainy season, R**GW** – Ground water in rainy season, R**S** – Soil in rainy season, **DSW** – Surface water dry season, **DGW** – Ground water in dry season, **DS** – Soil in dry season.

4.3.1 Carbaryl

The concentration of Carbaryl decreased in surface water, ground water and soil samples over the seasons i.e. the concentration was high in rainy season as compared to dry season as shown by mean values in Table 9. The average concentration of Carbaryl for surface water was 0.14 ± 0.08 ppm, and ground water was 0.26 ± 0.12 ppm in the rainy season. After rainy season 36% of Carbaryl remained in surface water, and 38% in ground water. The results showed that there was a rapid dissipation of Carbaryl in surface and ground water which indicates that degradation process had occurred. Based on these results for Carbaryl (that it was higher in rainy season than

dry season), there is an indication that photodegradation seems to be the main dissipation process for this pesticide. Statistical analysis (independent sample t-test) showed that there were no significant differences ($p > 0.05$) in Carbaryl concentration for surface water and ground water in both the dry season and rainy season. This could point to the fact that the concentration of Carbaryl in ground water is dependent on its levels in surface water.

The average concentration of Carbaryl for soil in rainy season was 1.23 ± 0.48 ppm (Table 9). After rainy season 97% of Carbaryl remained in the soil. Statistical analysis (independent sample t-test) showed that the concentration of Carbaryl in soils was significantly higher ($p < 0.05$) in rainy season as compared to dry season. This is an indication that the concentration of Carbaryl in soils is based on the quantities that are applied in a particular season but that it gets degraded over time. A lot of this pesticide is applied in cotton fields during the rainy season, hence its availability in soils (Figure 10).

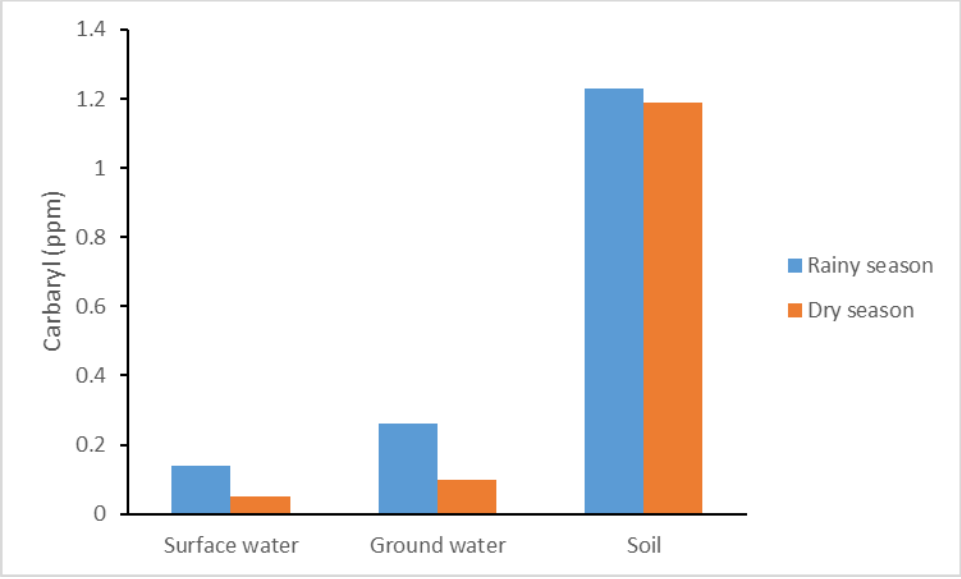


Figure 10: Comparison of Carbaryl levels during rainy and dry season.

This study detected Carbaryl in both surface and ground water in dry season although the concentration was less for this season as compared to the rainy season. Similar results have been reported for Carbaryl residues presence in surface and ground water within 2 to 8 months after application on well drained loamy soil on a river bed (Gunasekara. 2007). Various studies have reported effects of Carbaryl on fish (Toumi et al. 2015). Other studies revealed that low Carbaryl concentrations had no effect on the aquatic plants (Brogan & Relyea, 2017), which implies that high concentrations are potentially dangerous to aquatic plants. The Carbaryl concentrations as found in this study have a potential of causing problems to both plants and aquatic life.

The study also noted a drastic reduction of Carbaryl in soil during the dry season as compared to the rainy season. Variations of this pesticide residue in soil depends on several factors. Studies have shown that environmental factors such as soil type, soil aeration and soil temperature influence the rate of degradation (Canadian Council of Ministers of the environment, 2009). Hydrolysis, photolysis, oxidation as well as microorganisms are other factors (Gunasekara, 2007 & Xu, 2002).

4.3.2 Cypermethrin

The concentration of Cypermethrin was noted to have decreased in both surface water and ground water as well as in soil samples over the seasons. For instance, it was higher in rainy season as compared to dry season as shown by mean values in Table 9. The initial average concentration of Cypermethrin found in surface water was 11.16 ± 3.3 ppm, in ground water was 7.27 ± 2.89 ppm and in soil it was 0.04 ± 0.00 ppm in the rainy season. In the dry season 35% of Cypermethrin remained in the surface water, and about 99% in ground water. An independent sample t-test showed that there were no significant differences ($p > 0.05$) in Cypermethrin when concentrations of surface water were compared to those of ground water in rainy season and dry

season. This also points to the fact that the concentration of Cypermethrin in ground water was dependent on its levels in surface water which was also the case with Carbaryl (Figure 11).

The average concentration of Cypermethrin in soil samples was 0.29 ± 1.02 ppm (Table 9), and after rainy season 14% of Cypermethrin remained in the soil in the dry season. There were no significant differences ($p > 0.05$) in Cypermethrin concentration for soil samples in the dry season when compared to the rainy season. This is pointing to the fact that the degradation of Cypermethrin in soils is slow i.e. the pesticide is persistent in soils.

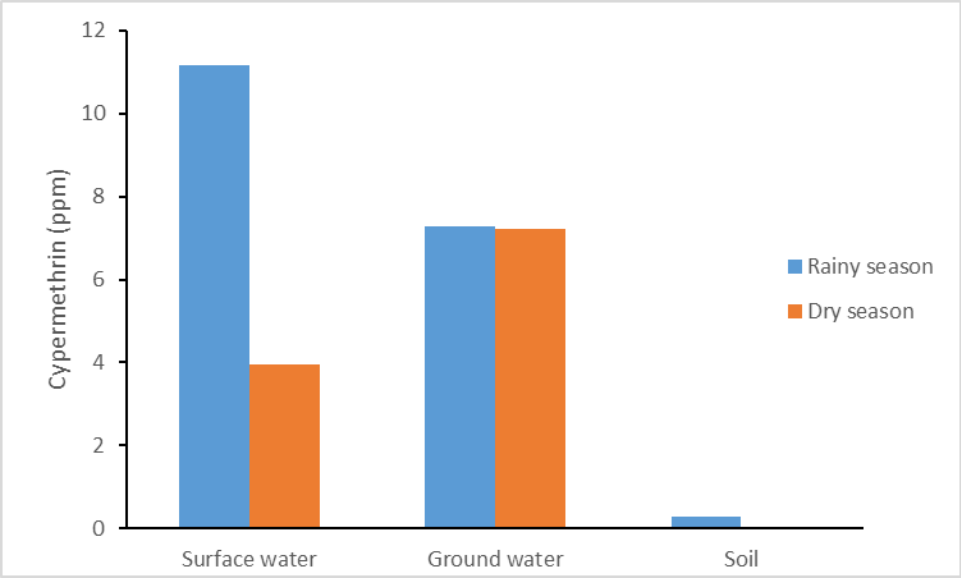


Figure 11: Cypermethrin levels during rainy and dry season

Cypermethrin residues in surface water and ground water decreased sharply from the rainy season to the dry season. This decrease in water samples can be associated with degradation of Cypermethrin. The presence of Cypermethrin in water as shown in this study is a cause for concern because it negatively affects aquatic organisms. For example, long term exposure to Cypermethrin by fish reduces their survival rates (Karthigayani, et al. 2014).

A decrease in Cypermethrin residues in soil was observed during the dry season i.e. the concentration of Cypermethrin in soil was low as compared to the rainy season. This is attributed to degradation. According to Vig, Singh, Agarwal, Dhawan, and Dureja, (2008) the degradation of Cypermethrin is facilitated by microorganisms. Slow degradation has been observed in anaerobic and waterlogged conditions and increased persistence is observed in soils with high organic matter, high clay content, reduced microbial activity and anaerobic conditions (Goswami Pati, Chowdhury, & Mukhopadhyay, 2013). Despite the role played by microbes in the degradation of Cypermethrin, studies have also reported the decrease in population of other types of microbes which probably do not adapt to the insecticide (Goswami et al. 2013).

Additionally the degradation of Cypermethrin in soil has been attributed to hydrolysis. Dubey & Fulekar, (2013) highlights the hydrolysis of Cypermethrin as a principal degradation route and leads to the formation of 3-phenoxybenzoic acid (PBA) and cyclopropanecarboxylic acid derivatives.

4.4 CORRELATION BETWEEN PHYSICO-CHEMICAL PARAMETERS AND PESTICIDES (CARBARYL AND CYPERMETHRIN) IN WATER SAMPLES

4.4.1 Rainy season

Pearson's product-moment correlation coefficient (r) indicated a weak positive correlation between Cypermethrin and pH ($r = 0.426$, $p > 0.05$), with water pH explaining 18% of the Cypermethrin variation. A weak positive correlation was also noted between Nitrate and Cypermethrin ($r = 0.018$, $p > 0.05$), with nitrate concentration in water explaining 3% of the Cypermethrin variation. This was also the case between Phosphate and Cypermethrin ($r = 0.280$, $p > 0.05$), with phosphate concentration in water explaining 8% of Cypermethrin variation.

However, there was a weak negative correlation between electrical conductivity and Cypermethrin (r = -0.143, p > 0.05), with water electrical conductivity explaining 2% of the Cypermethrin variation. Temperature and Cypermethrin correlation was also weak (r = -0.13, p > 0.05) with water temperature explaining 2% of the Cypermethrin variation. Similarly electrical conductivity and Cypermethrin correlation was also weak (r = -0.143, p > 0.05), with water electrical conductivity explaining 2% of the Cypermethrin variation. On the other hand, there was a strong positive correlation between Temperature and Carbaryl (r = 0.536, p > 0.05), with water Temperature explaining 29% of the Carbaryl variation. A medium positive correlation between electrical conductivity and Carbaryl was also noted (r = 0.477, p > 0.05), with water conductivity explaining 23% of the Carbaryl variation. Furthermore, a strong positive correlation was noted between Nitrate and Carbaryl (r = 0.764 p < 0.05), with Nitrate concentration in water explaining 58% of the Carbaryl variation. However, a weak positive correlation between Phosphate and Carbaryl (r = 0.049 p > 0.05), with Phosphate concentration in water explaining 0% of the Carbaryl variation was noted. There was also a weak negative correlation between pH and Carbaryl (r = -0.064, p > 0.05), with water pH explaining 4% of the Carbaryl variation (Table 10). It is normally expected that temperature should negatively correlate with pesticide concentration. This is because high temperatures encourage pesticide degradation. However, this doesn't seem to be the case as observed in this study, more especially in the rainy season (Appendix 6). The positive correlation between pesticides and temperature in the rainy season was therefore attributed to temperature variations during this pesticide application period.

Table 10: Correlation coefficients for the relationship between physico-chemical parameters, Carbaryl and Cypermethrin for water in the rainy season.

Parameter 1	Parameter 2	Coefficient (r)	*p*-Values	Significance
Cypermethrin	pH	0.426	0.167	Ns
Cypermethrin	EC	-0.143	0.659	Ns
Cypermethrin	Temperature	0.13	0.969	Ns
Cypermethrin	Nitrate	0.018	0.955	Ns
Cypermethrin	Phosphate	0.280	0.378	Ns
Carbaryl	pH	-0.064	0.843	Ns
Carbaryl	EC	0.477	0.116	Ns
Carbaryl	Temperature	0.536	0.073	Ns
Carbaryl	Nitrate	0.764**	0.004	**
Carbaryl	Phosphate	0.049	0.879	Ns

Ns not significant, ** significant at $p = 0.01$ (2 tailed)

4.4.2 Dry season

The Pearson's product-moment correlation coefficient (r) indicated a strong positive correlation between electrical conductivity and Cypermethrin ($r = 0.590$, $p > 0.05$), with electrical conductivity explaining 35% of the Cypermethrin variation. A medium positive correlation between Nitrate and Cypermethrin was also observed ($r = 0.489$, $p > 0.05$), with nitrate concentration in soil explaining 24% of the Cypermethrin variation. However, there was a medium negative correlation between pH and Cypermethrin ($r = -0.468$, $p > 0.05$), with water pH explaining 22% of the Cypermethrin variation. This was also the case between temperature and

Cypermethrin (r = -0.205, p > 0.05), with water temperature explaining 4% of the Cypermethrin variation. There was a weak negative correlation between Phosphate and Cypermethrin (r = -0.238, p > 0.05) with Phosphate concentration in water explaining 6% of the Cypermethrin variation. Furthermore, there was a strong positive correlation between electrical conductivity and Carbaryl (r = 0.584, p > 0.05), with water electrical conductivity explaining 34% of the Carbaryl variation. A moderate positive correlation between Nitrate and Carbaryl was observed (r = 0.332, p > 0.05), with Nitrate concentration in water explaining 11% of the Carbaryl variation. There was a weak positive correlation between Phosphate and Carbaryl (r = 0.186, p > 0.05), with Phosphate concentration in water explaining 3% of the Carbaryl variation. Finally, there was a strong negative correlation between pH and Carbaryl (r = -0.710, p < 0.05), with water pH explaining 50% of the Carbaryl variation, and there was no correlation between temperature and Carbaryl (r = -0.031, p > 0.05), with water temperature explaining 0% of the Carbaryl variation (Table 11).

The negative correlation between pesticide concentration and temperature in water during dry season is an indication that the pesticide was decomposing or degrading at high temperatures (Appendix 7). The decrease of Cypermethrin as a function of temperature has been reported by Parithabhanu & Deepak (2014). Furthermore, inverse relationship between temperature and Carbaryl is clearly highlighted by Starner et al. (1999), suggesting that the half-life of Carbaryl is affected by temperature variations.

Table 11: Correlation coefficients for the relationship between physico-chemical parameters, Carbaryl and Cypermethrin for water samples in the dry season

Parameter 1	Parameter 2	Coefficient (r)	*p*-Values	Significance
Cypermethrin	pH	-0.468	0.173	Ns
Cypermethrin	EC	0.590	0.073	Ns
Cypermethrin	Temperature	-0.205	0.571	Ns
Cypermethrin	Nitrate	0.489	0.152	Ns
Cypermethrin	Phosphate	-0.238	0.508	Ns
Carbaryl	pH	-0.710*	0.021	*
Carbaryl	EC	0.584	0.076	Ns
Carbaryl	Temperature	-0.031	0.932	Ns
Carbaryl	Nitrate	0.332	0.349	Ns
Carbaryl	Phosphate	0.186	0.606	Ns

Ns not significant, * significant at $p = 0.05$ (2 tailed)

4.5 CORRELATION COEFFICIENTS BETWEEN PHYSICO-CHEMICAL PARAMETERS AND PESTICIDES (CARBARYL AND CYPERMETHRIN) IN SOIL SAMPLES

4.5.1 Rainy season

The Pearson's rank correlation coefficient (r) test showed a strong negative correlation between Cypermethrin and pH (r = -0.922, p = 0.05), with soil pH explaining 85% of the Cypermethrin variation. There was a moderate negative correlation between Cypermethrin and electrical conductivity (r = -0.372, p > 0.05), with soil electrical conductivity explaining 14% of the Cypermethrin variation. Furthermore, a weak negative correlation between Cypermethrin and

Phosphate was observed (r = -0.214, p > 0.05), with Phosphate of the soil explaining 5% of the Cypermethrin variation. Also a weak negative correlation between Cypermethrin and Nitrate was observed (r = -0.168, p > 0.05), with Nitrate in the soil explaining 3% of the Cypermethrin variation. However, there was a strong positive correlation between Carbaryl and pH (r = 0.931, p = 0.00), with soil pH explaining 87% of the variation in Carbaryl concentration. There was also a moderate positive correlation between Carbaryl and electrical conductivity (r = 0.379, p > 0.05) with electrical conductivity of soil explaining 14% of the variation in Carbaryl concentration. However, there was a weak negative correlation between Carbaryl and Nitrates (r = -0.217, p > 0.05) with Nitrates in soil explaining 5% of the variation in Carbaryl concentration. Finally a weak negative correlation between Carbaryl and phosphate was observed (r = -0.216, p > 0.05), with phosphate in soil explaining 5% of the variation in Carbaryl concentration (Table 12). The strong positive and negative correlations between the pesticides and the pH is an indication that their availability depends on whether the soil pH is high or low. The correlation results for Cypermethrin are pointing to the fact that this pesticide is inversely related to pH (Appendix 8). On the other hand, the Carbaryl results are pointing to the fact that this pesticide's availability in soil is directly proportional to pH. Almost similar results were also noted in water samples.

This is clear evidence that stability of some pesticides in the environment is affected by pH. High water pH lowers the half-life of hydrolysis for Carbaryl and Cypermethrin as indicated by Schilder (2008). Carbaryl is more susceptible to hydrolysis under alkaline conditions than other fungicides, herbicides, or growth regulators. Furthermore, the effect of pH on degradation of Carbaryl and Cypermethrin is also given by Jaiswal et al. (2016). For example, alkaline conditions are favorable for hydrolysis of Carbaryl and Cypermethrin (Jaiswal et al, 2016 and Deer & Beard, 2001).

Table 12: Correlation coefficients for the relationship between physico-chemical parameters, Carbaryl and Cypermethrin.

Parameter 1	Parameter 2	Coefficient (r)	*p*-Values	Significance
Cypermethrin	pH	-0.922**	0.000	**
Cypermethrin	EC	-0.372	0.156	Ns
Cypermethrin	Nitrate	-0.168	0.533	Ns
Cypermethrin	Phosphate	-0.214	0.425	Ns
Carbaryl	pH	0.931**	0.000	**
Carbaryl	EC	0.379	0.148	Ns
Carbaryl	Nitrate	-0.217	0.419	Ns
Carbaryl	Phosphate	-0.216	0.421	Ns

Ns not significant ** significant at $p = 0.01$ level (2 tailed)

4.5.2 Dry season

The Pearson's rank coefficients showed that there was a weak positive correlation between Cypermethrin and pH ($r = 0.222$, $p > 0.05$), with soil pH explaining 5% of the Cypermethrin variation. However, there was a moderate negative correlation between Cypermethrin and electrical conductivity ($r = -0.444$, $p > 0.05$), with soil electrical conductivity explaining 20% of the Cypermethrin variation. A weak negative correlation was noted between Cypermethrin and Nitrate ($r = -0.267$, $p > 0.05$), with Nitrate in soil explaining 7% of the Cypermethrin variation, and also between Cypermethrin and Phosphate ($r = -0.107$, $p > 0.05$), with Nitrate in soil explaining 1% of the Cypermethrin variation. Furthermore, there was a strong positive correlation between Carbaryl and Phosphate ($r = 0.551$, $p > 0.05$), with phosphate concentration in soil explaining 30% of the Carbaryl variation. There was weak positive correlation between Carbaryl and pH ($r = 0.125$, $p > 0.05$), with soil pH explaining 2% of the Carbaryl variation;

between Carbaryl and Nitrate (r = 0.244, p > 0.05), with nitrate concentration in soil explaining 6% in Carbaryl variation. On the other hand, there was no correlation between Carbaryl and electrical conductivity (r = 0.044, p > 0.05), with soil electrical conductivity explaining 0% of the Carbaryl variation (Table 13). In the dry season, the correlations of the pesticides were not similar to what was found in the rainy season. Appendix 8 and 9 gives the difference in correlation during rainy and dry season. As explained above, the correlations of the pesticides and physicochemical parameters in water were almost similar to what was found in the soils (as indicated on pH correlations above). The differences in correlations in dry and rainy season are attributed mainly to movement of the pesticides. In rainy season, the soil water content is high, as such the pesticides can easily move about unlike during the dry season.

Table 13: Correlation coefficients for the relationship between physico-chemical parameters, Carbaryl and Cypermethrin.

Parameter 1	**Parameter 2**	**Coefficient (r)**	***p*-Values**	**Significance**
Cypermethrin	pH	0.222	0.512	Ns
Cypermethrin	EC	-0.404	0.217	Ns
Cypermethrin	Nitrate	-0.267	0.428	Ns
Cypermethrin	Phosphate	-0.107	0.754	Ns
Carbaryl	pH	0.125	0.715	Ns
Carbaryl	EC	0.044	0.898	Ns
Carbaryl	Nitrate	0.244	0.470	Ns
Carbaryl	Phosphate	0.551	0.079	Ns

Ns – not significant

Table 14. Acceptable limits for drinking water

Quality parameter	MBS	WHO
pH	6.5 – 9.0	6.5 – 9.5
Temperature (°C)	-	-
Electrical conductivity (µS/cm)	70 – 150	250
Total dissolved solids (mg/L)	-	1000
Phosphate (mg/L)	0.15	0.05
Nitrate (mg/L)	50	50
Cypermethrin (µg/L)	-	0.05
Carbaryl (µg/L)	-	-

MBS Malawi Bureau of standards **WHO** World Health organization – No recommendation

There were no WHO and MBS standards for Carbaryl in drinking water. However, Australian standards for Carbaryl in drinking water is 0.003 mg/L and Canadian standard is 0.09 mg/L (Hamilton et al. 2003). The results for Carbaryl concentration in water as found in this study were above both the Australian and Canadian standards for drinking water.

The mean concentration of Cypermethrin found in this study in the rainy season, was above the US maximum residual limit (MRL) for agricultural soils of 0.05 mg/Kg (Fosu–Mensah, Okoffo, & Mensah 2016) but below US MRL in the dry season. Furthermore, findings of the current study showed that water samples were above US MRL of 0.05 µg/L during both rainy season and dry season. The pesticide values that were above the standards are a cause for concern which calls for continuous monitoring of water and soils in the study area.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The study has shown that boreholes, wells and soils in Lisungwi are polluted as far as the levels of electrical conductivity, Phosphates, Carbaryl and Cypermethrin is concerned. The levels for most parameters in the groundwater and soils are above acceptable limits for drinking water.

The pH in all sample types were within acceptable limits of drinking water in both seasons. Although literature on temperature standards for surface water and ground water is missing, higher mean water temperatures as observed in this study have the potential to cause negative impacts. On the other hand higher conductivities (above WHO standards) were observed in the ground water than surface water and in soil during all seasons. Furthermore, total dissolved solids were within the acceptable limits by WHO in all samples except the ones for ground water.

Nitrates and Phosphates were detected in all samples for both seasons. Nitrate concentrations were within WHO and MBS standards for drinking water in all samples except for ground water of the dry season. Furthermore high Phosphate concentrations were observed in all sample types in both seasons, which happened to be above MBS and WHO standards. Therefore the water quality in the study area was compromised with anthropogenic sources which include application of fertilizers.

This study also detected Carbaryl and Cypermethrin in both water and soil samples. Generally there was a high frequency of occurrence for these two pesticides detected in water and soil samples. The concentration of Carbaryl in soils were above Australian guideline value and

Cypermethrin residues were generally above their respective US MRLs for agricultural soils except for the dry season samples. The presence of these pesticide residues in the soils cause contamination of water bodies through surface run off and leaching. Furthermore, Carbaryl and Cypermethrin were detected in all water samples collected in the rainy season and dry season. Carbaryl detected was above Australian guideline value and Cypermethrin was above US MRL standards. The water and soil in the study area get contaminated easily with the pesticides applied in the cotton fields. Pesticide residues in water samples in the cotton growing area of Lisungwi could be traced through drift when spraying, and could be carried from treated area through runoff. Some of it could also have leached to ground water.

5.2 RECOMMENDATIONS

From the study, it is recommended that;

i. Farmers should be sensitized on pesticides use (safety measures and mode of application) so as to protect the environment.

ii. Remediation measures such as oxidation should be employed to remove or minimize the concentrations of pesticides in the environment in order to reduce the environmental and public health risks.

iii. Farmers should be advised to use chemical pesticides at a minimum rate to keep the environment safe.

iv. Farmers should be trained on biological pest control through integrated pest management in order to reduce chemical pesticide use.

v. Domestic water wells or boreholes should be sited at longer distances from cotton fields to reduce the potential of pesticide contamination.

5.3 AREAS FOR FURTHER RESEARCH

More work needs to be done in the following areas:

i. Assessing the mobility of Carbaryl and Cypermethrin in both water and soil in relation to residue content in both surface and ground water.

ii. Studying the sorption of Carbaryl and Cypermethrin in soils.

iii. Monitoring the factors that affect degradation of Carbaryl and Cypermethrin in water and soils.

iv. Comparing Carbaryl and Cypermethrin levels in sediments and surface water.

v. Assessing the effect of organic matter and moisture on degradation of Carbaryl and Cypermethrin.

vi. Assessing the potential effects Carbaryl and Cypermethrin aquatic life

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APPENDICES

Appendix 1: Sample collection form for both water and soil samples.

VH	Sample type	pH	EC μS/cm	Temperature (◦C)	S	E	Elevation (m)	Relevant information

VH: Village Headman **EC**: Electrical conductivity **E**: E – Coordinates

S: S – Coordinates

Appendix 2: Geographical data and field information of the sampled areas in dry season

VH	TA	Sample Type	S	E	Elevation (m)
Chaponda	Sayimon	GW (BH)	15°55'31.76"	035°04'24.30"	292
Moffat	Sayimon	Soil	15°27'52.60"	034°45'54.70"	350
Moffat	Sayimon	Soil	15°27'37.71"	034°46'03.44"	353
Moffat	Sayimon	Soil	15°33'27.33"	034°45'50.68"	-
Moffat	Sayimon	SW –River	15°27'31.78"	034°45'54.89"	-
Moffat	Sayimon	GW – BH	15°27'06.76"	034°46'35.13"	366
Chaponda	Sayimon	Soil	15°25'07.42"	034°48'00.22"	386
Chaponda	Sayimon	Soil	15°24'50.93"	034°48'06.32"	391
Kanseru	Sayimon	SW – River	15°23'46.11"	035°48'09.61"	373
Mapundi II	Sayimon	GW – BH	15°23'49.18"	034°46'45.00"	391
Mapundi II	Sayimon	Soil	15°23'41.75"	034°47'04.43"	396
Mapundi II	Sayimon	Soil	15°23'33.77"	034°47'31.87"	406
Limani	Sayimon	Soil	15°23'23.99"	034°47'41.06"	407
Limani	Sayimon	Soil	15°23'11.74"	034°47'40.12"	409
Mkundika	Sayimon	Soil	15°23'51.44"	034°47'43.67"	403
Mkundika	Sayimon	GW – BH	15°24'01.23"	034°48'00.66"	390
Funsani	Sayimon	GW – BH	15°23'34.14"	034°48'41.26"	413
Limani	Sayimon	GW – BH	15°23'14.87"	034°49'01.11"	418
George	Sayimon	GW – BH	15°21'24.65"	034°49'59.19"	448
Chikwekwe	Sayimon	Soil	15°20'50.74"	034°50'41.15"	463
Chikwekwe	Sayimon	GW – BH	15°20'53.98"	034°50'51.54"	466

VH: Village Headman **TA**: Traditional Authority **E**: E Coordinates **S**: S Coordinates

G – BH: Ground water – Borehole **SW:** Surface water

Appendix 3: Geographical data and field information of the sampled areas in rainy season.

VH	GVH	Sample type	S	E	Elevation
Mwingitsa	Sayimon	Soil	15º26.282’	034º46.359’	351
Mwingitsa	Sayimon	SW-River	15º26.305’	034º46.256’	-
Moffat	Sayimon	Soil	15º27.667’	034º46.056’	-
Moffat	Sayimon	Soil	15º27.677’	034º46.058’	-
Moffat	Sayimon	Soil	15º27.625’	034º46.022’	342
Moffat	Sayimon	SW-River	15º27.525’	034º45.921’	-
Mofffat	Sayimon	GW-BH	15º27.113’	034º46.587’	359
Chaponda	Sayimon	Soil	15º25.143’	034º48.006’	379
Chaponda	Sayimon	GW-Shallow well	15º25.251’	034º47.989’	368
Chaponda	Sayimon	Soil	15º24.905’	034º48.030’	384
Mkundika	Sayimon	SW-River	15º24.905’	034º48.031’	366
Mkundika	Sayimon	GW-BH	15º24.021’	034º48.012’	382
Mussa	Sayimon	Soil	15º23.859’	034º47.757’	391
Mussa	Sayimon	Soil	15º23.521’	034º47.502’	398
Mussa	Sayimon	GW-BH	15º23.821’	034º46.750’	-
Ngwenyama 1	Ngwenyama	Soil	15º28.934’	034º44.478’	338
Lembani	Ngwenyama	SW-Swamp	15º28.431’	034º44.923’	329
Nelesani	Sayimon	Soil	15º27.312’	034º45.330’	369
Nelesani	Sayimon	GW-BH	15º27.261’	034º45.329’	357
Ngwenyama 2	Kasamba	Soil	15º23.195’	034º47.728’	-
Limani	Kasamba	Soil	15º22.585’	034º49.515’	434
George	Kasamba	Soil	15º21.725’	034º49.916’	434
George	Kasamba	GW-BH	15º21.770’	034º49.902’	428
George	Kasamba	GW-BH	15º20.944’	034º50.503’	451
Chikwekwe	Kasamba	Soil	15º20.833’	034º50.686’	446
Gobede	Somisomi	Soil	15º22.770’	034º54.307’	453
Gobede	Somisomi	GW-BH	15º22.679’	034º54.291’	460
Gobede	Somisomi	Soil	15º22.687’	034º54.308’	459

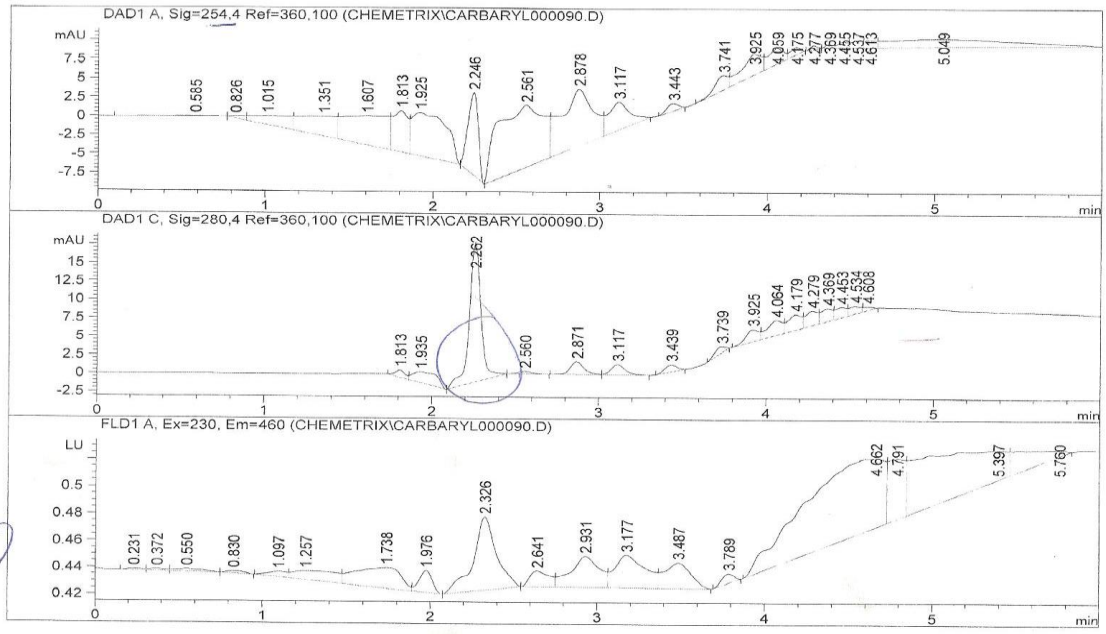
VH: Village Headman **GVH:** Group Headman **E**: E Coordinates **S**: S Coordinates

SW: Surface water **GW – BH**: Ground water – Borehole

Appendix 4: An example of a chromatogram of Carbaryl standards.

Data File C:\CHEM32\1\DATA\CHEMETRIX\CARBARYL000090.D
Sample Name: std3

Acq. Operator : SYSTEM
Acq. Instrument : Agilent Location : Vial 3
Injection Date : 7/22/2016 12:47:25 Inj Volume : 10.000 µl
Method : C:\CHEM32\1\METHODS\CARBARYL.M
Last changed : 7/22/2016 11:28:17 by SYSTEM
(modified after loading)
Method Info : analysis of carbaryl



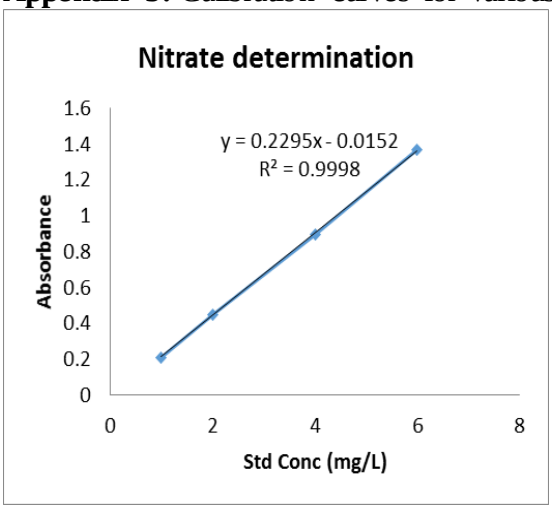
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

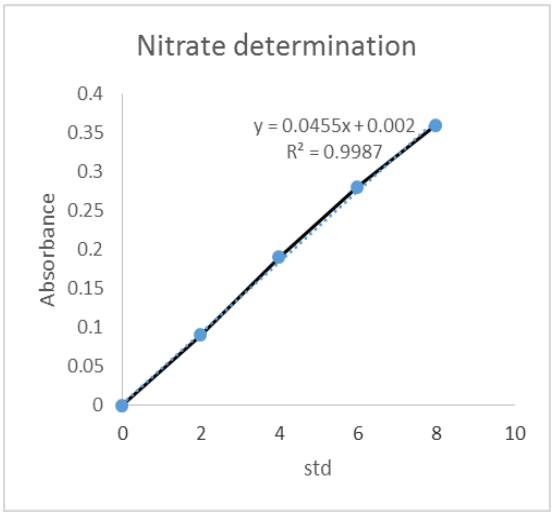
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.585	BB	0.2764	1.12490	4.92583e-2	0.1583
2	0.826	BV	0.0989	1.94776	2.61368e-1	0.2741
3	1.015	VV	0.2256	19.61176	1.12391	2.7603
4	1.351	VV	0.1847	37.77598	2.64358	5.3169
5	1.607	VV	0.2281	69.96075	3.84908	9.8469

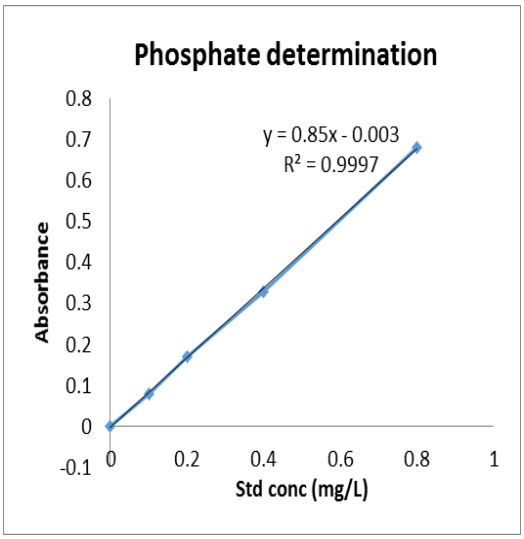
Appendix 5: Calibration curves for various analyses.



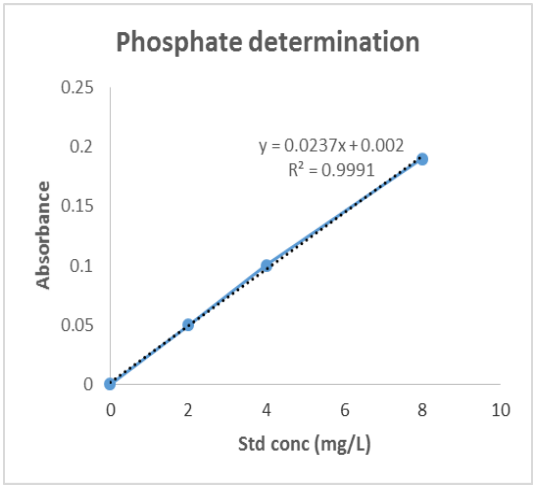
Appendix 5 a.: Standard nitrate curve for water samples in rainy season.



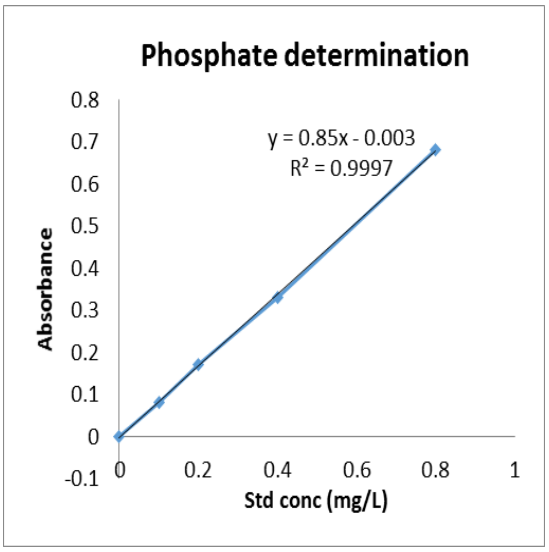
Appendix 5 b : Standard nitrate curve for water samples analysis in the dry season.



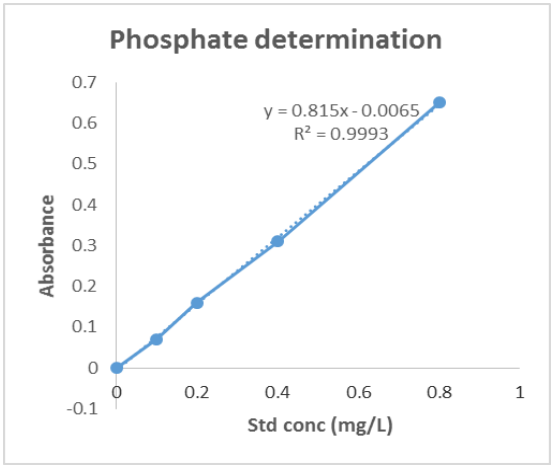
Appendix 5 c: Standard curve for phosphate determination in water samples of the rainy season



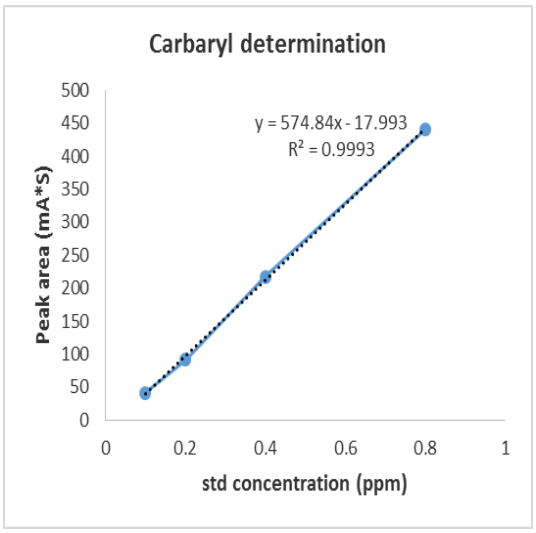
Appendix 5 d: Beer-Lambert plot for water samples in the dry season



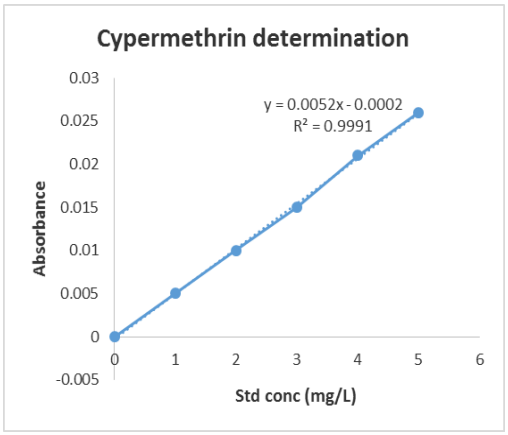
Appendix 5 e: Standard curve for phosphate determination of soil samples in the rainy season



Appendix 5 f: Standard curve for phosphate determination for soil samples in the dry season

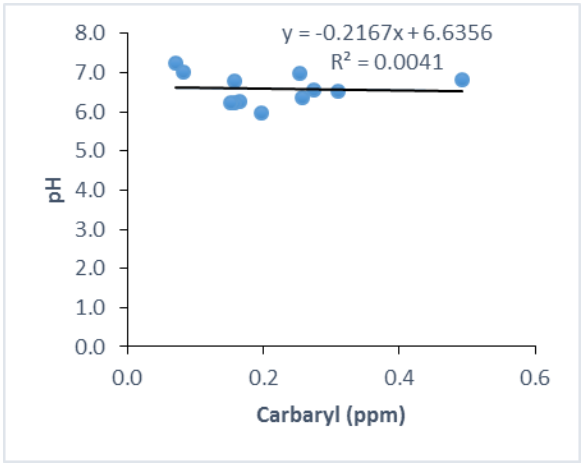


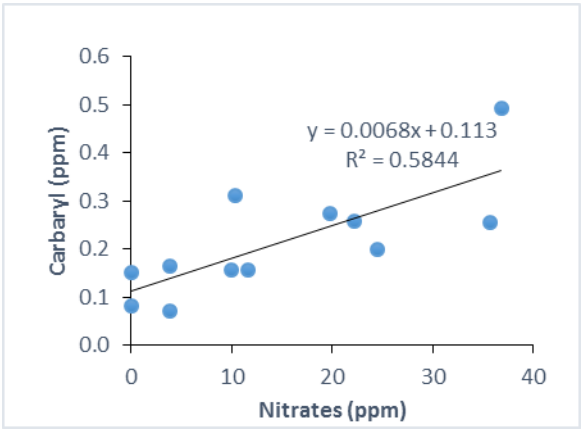
Appendix 5 g: Calibration curve for Carbaryl standards

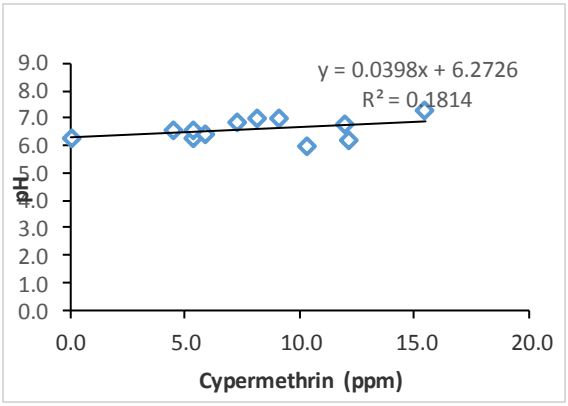


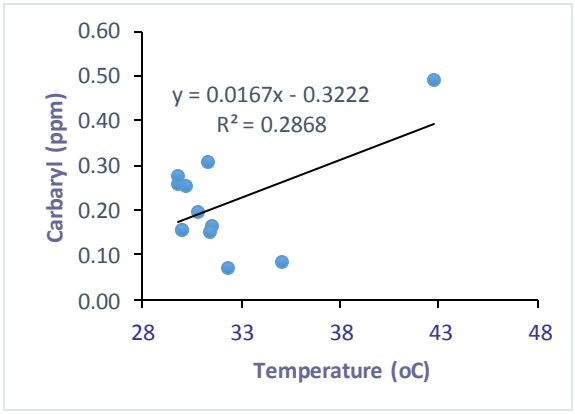
Appendix 5 h: Calibration curve for Cypermethrin for both water and soil samples.

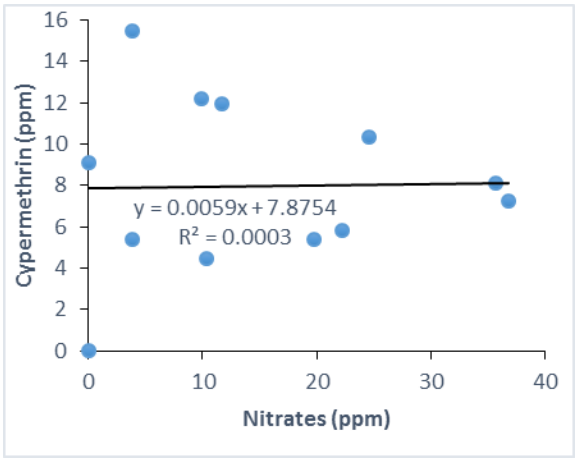
Appendix 6: Correlation between parameters of water samples during rainy season

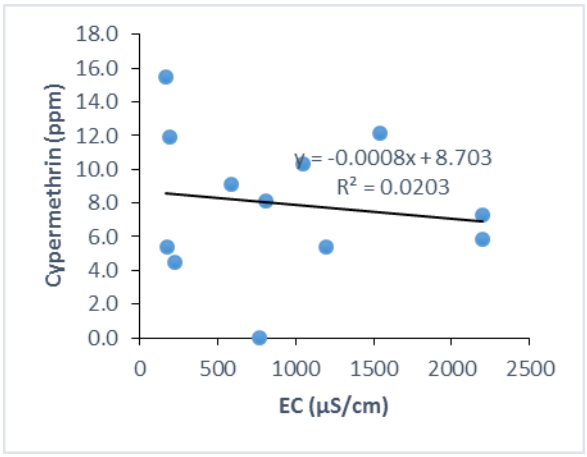


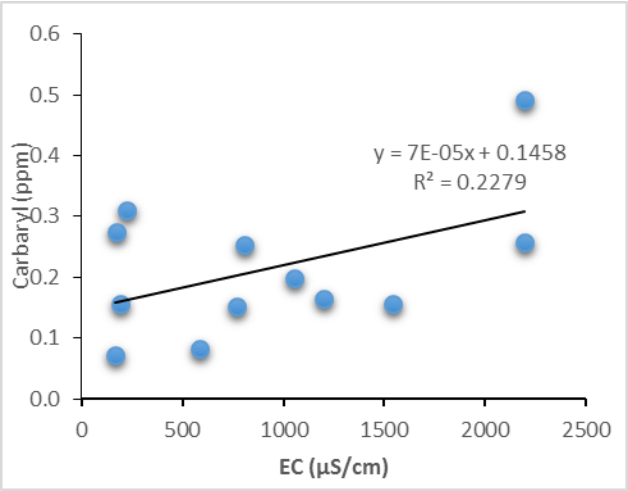


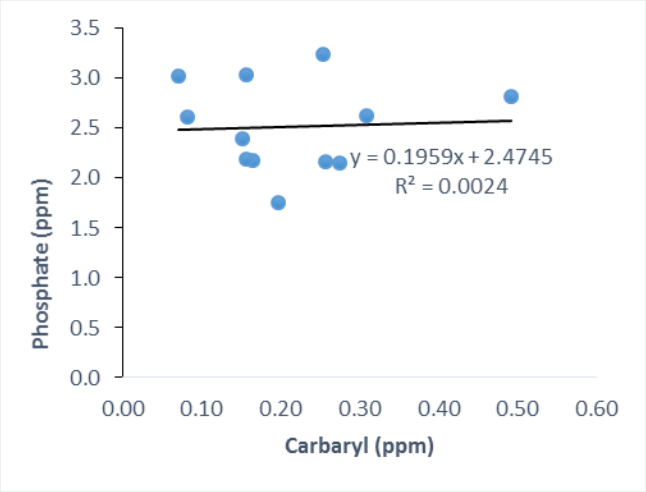


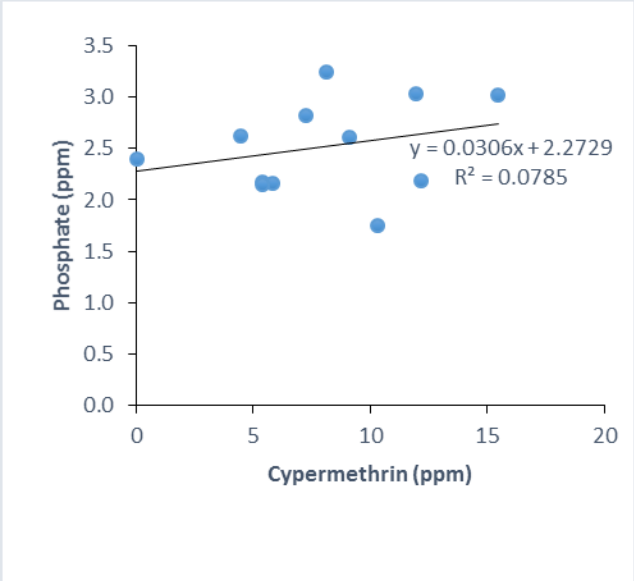




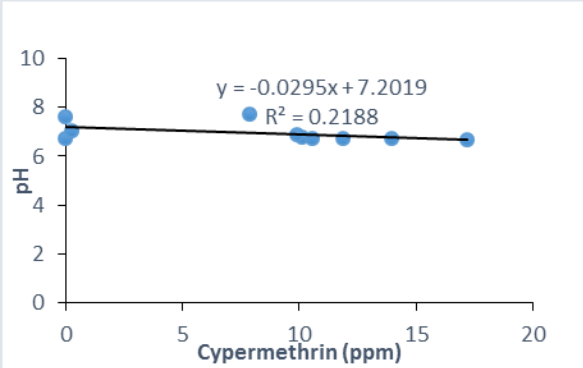


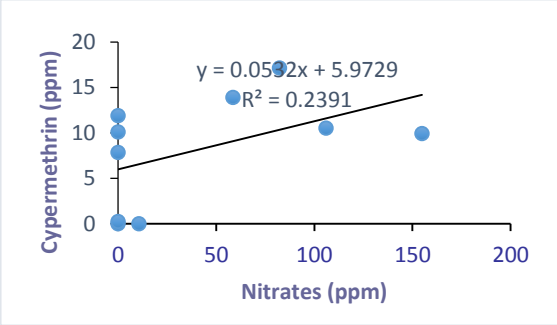

0.6
0.5
0.4
0.3
0.2
0.1
0.0
Carbaryl (ppm)
y = 7E-05x + 0.1458
R² = 0.2279
0
500
1000
1500
2000
2500
EC (µS/cm)

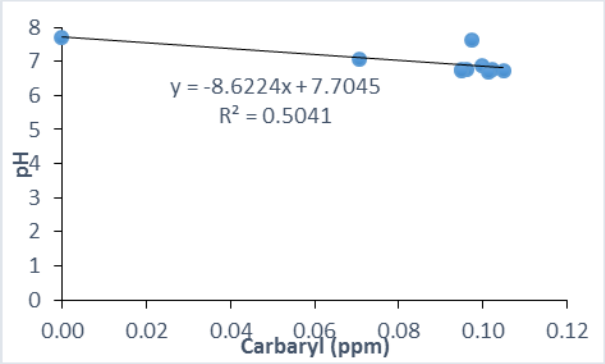

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Phosphate (ppm)
y = 0.1959x + 2.4745
R² = 0.0024
0.00
0.10
0.20
0.30
0.40
0.50
0.60
Carbaryl (ppm)

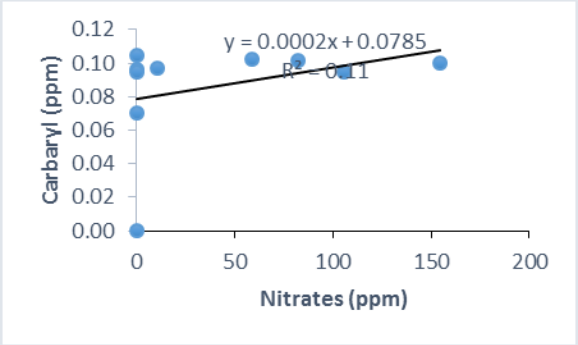

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Phosphate (ppm)
y = 0.0306x + 2.2729
R² = 0.0785
0
5
10
15
20
Cypermethrin (ppm)

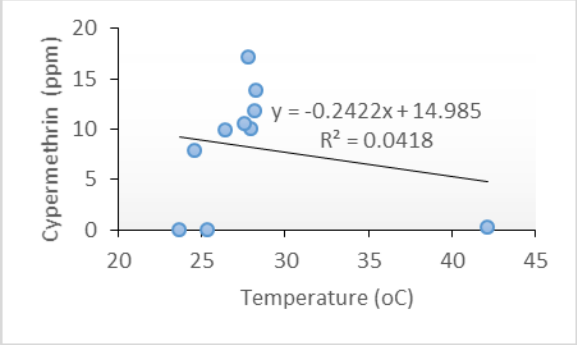
Appendix 7: Correlation between parameters of water samples during dry season

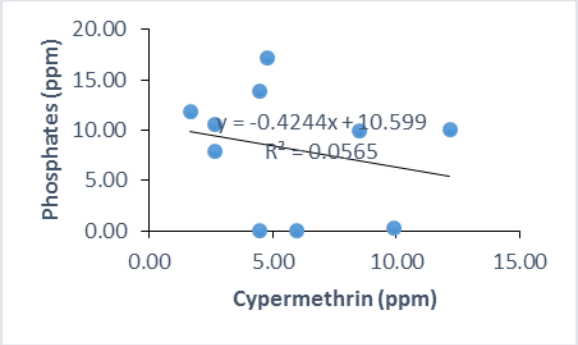


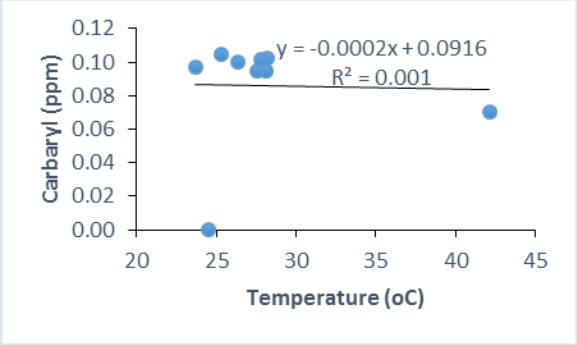


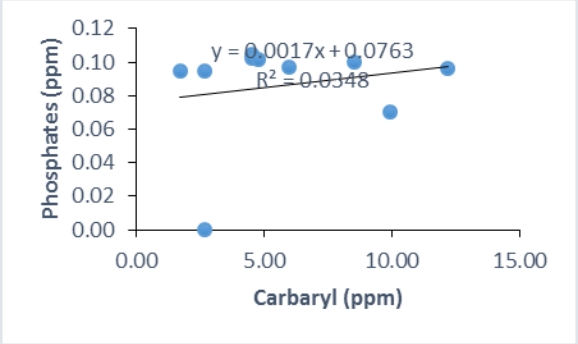


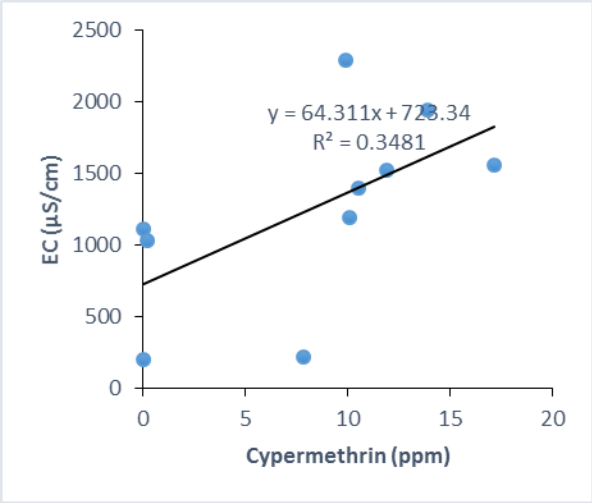


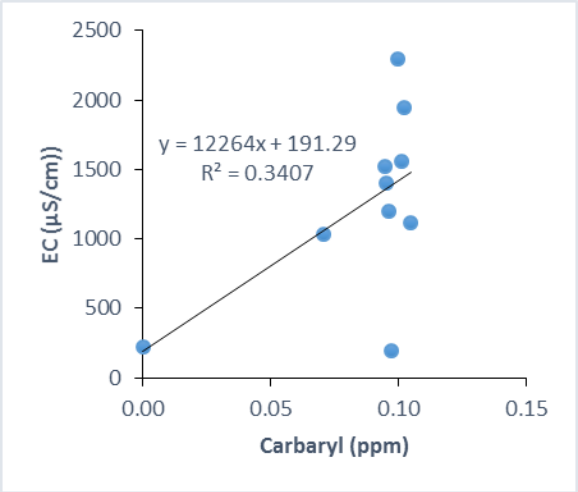




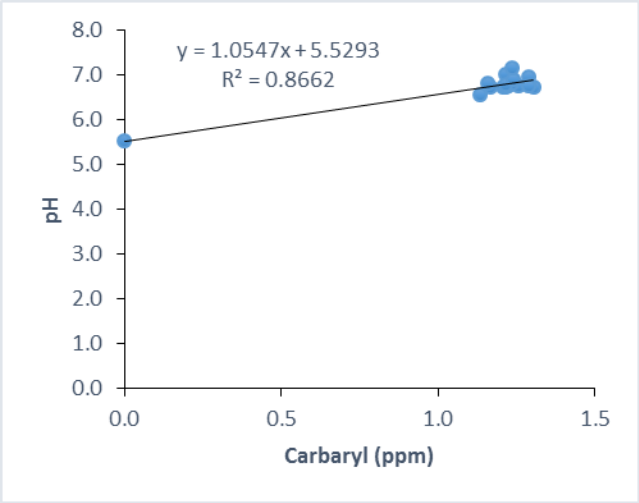


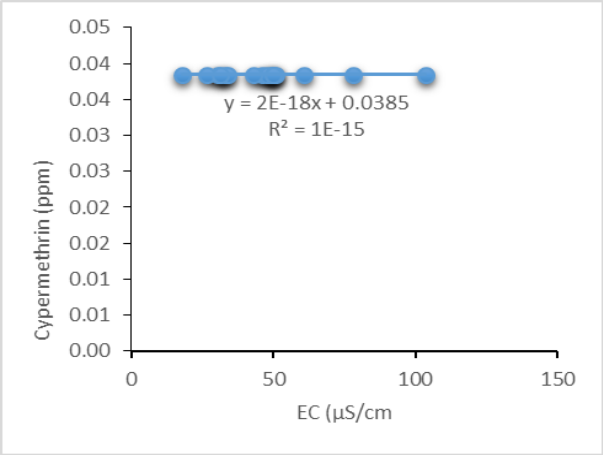


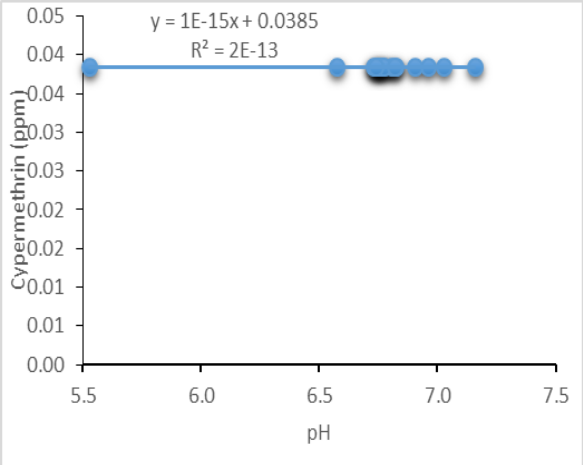

2500
2000
1500
1000
500
0
EC (µS/cm)
y = 64.311x + 728.34
R² = 0.3481
0
5
10
15
20
Cypermethrin (ppm)

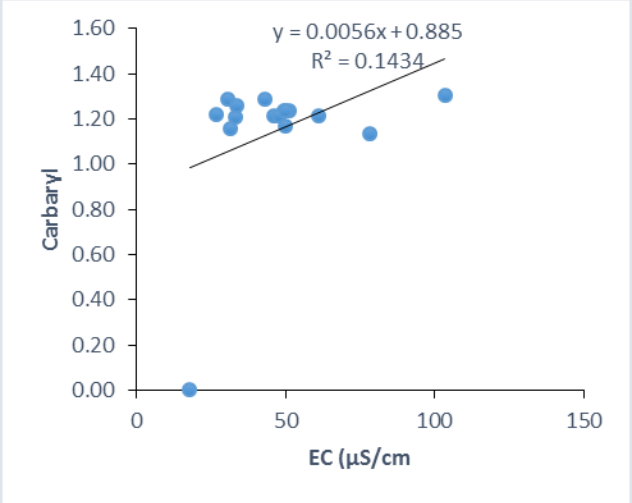

2500
2000
1500
1000
500
0
EC (µS/cm))
y = 12264x + 191.29
R² = 0.3407
0.00
0.05
0.10
0.15
Carbaryl (ppm)

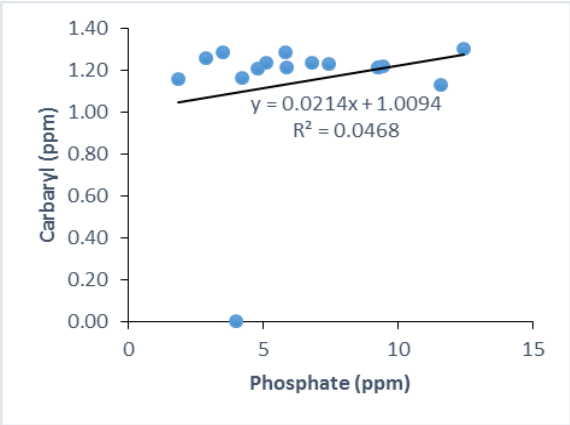
Appendix 8: Correlation between parameters of soil samples during rainy season

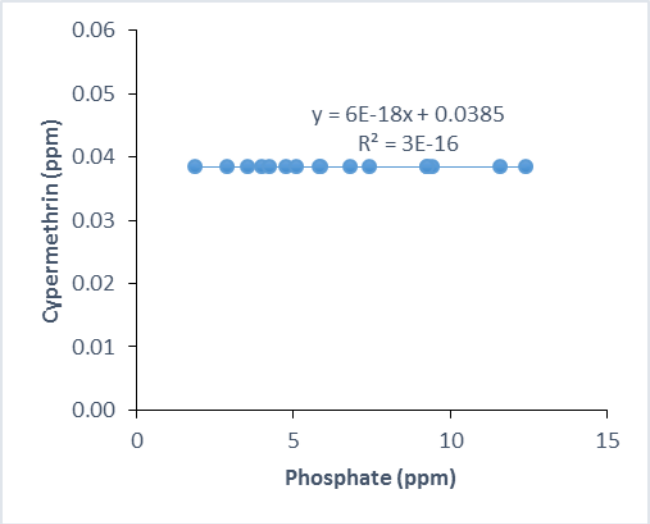


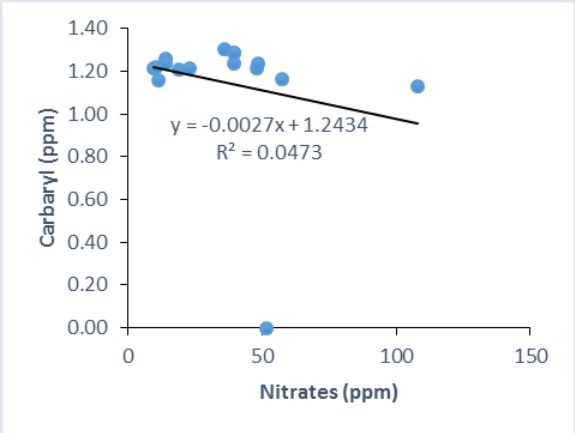


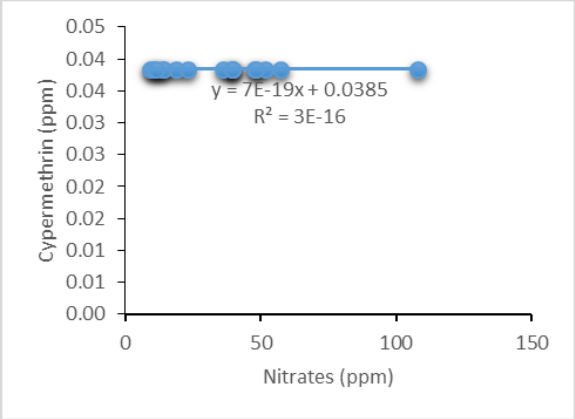





y = 0.0214x + 1.0094
R² = 0.0468
Carbaryl (ppm)
Phosphate (ppm)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
5
10
15


y = 6E-18x + 0.0385
R² = 3E-16
Cypermethrin (ppm)
Phosphate (ppm)
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
5
10
15


y = -0.0027x + 1.2434
R² = 0.0473
Carbaryl (ppm)
Nitrates (ppm)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
50
100
150


y = 7E-19x + 0.0385
R² = 3E-16
Cypermethrin (ppm)
Nitrates (ppm)
0.05
0.04
0.04
0.03
0.03
0.02
0.02
0.01
0.01
0.00
0
50
100
150

Appendix 9: Correlation between parameters of soil samples during dry season