ASSESSMENT OF PESTICIDE RESIDUES IN SURFACE AND GROUNDWATER IN TEA GROWING AREAS IN MULANJE, MALAWI

MSc (WATER RESOURCES MANAGEMENT) THESIS

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MZUZU UNIVERSITY

JULY 2024

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(BSc Environmental Science and Technology (Environmental Management)

A THESIS SUBMITTED TO THE FACULTY OF ENVIRONMENTAL SCIENCES OF MZUZU UNIVERSITY IN FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE DEGREE IN WATER RESOURCES MANAGEMENT

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DECLARATION

I hereby declare that this thesis titled, "*Assessment of Pesticide Residues in Surface and Groundwater in tea growing areas in Mulanje, Malawi*" has been written by me and is a record of my research work. All citations, references, and borrowed ideas have been duly acknowledged. It is being submitted in fulfillment of the requirements for the award of the degree of Master of Science Degree in Water Resources Management at Mzuzu University. None of the present work has been submitted previously for any degree or examination in any other University.

Name of Student: ENOCH ANDREW KAMWALA

Signature: ……………………….......………. **Date:** ……..................……………

CERTIFICATE OF COMPLETION

We, the undersigned, certify that this thesis is a result of the author's work and that to the best of our knowledge, it has not been submitted for any academic qualification within Mzuzu University or elsewhere. The thesis is acceptable in form and content, and that satisfactory knowledge of the field covered herein was demonstrated by the candidate through an oral examination held on………...

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Co-Supervisor: Associate Professor Elijah Wanda (Ph.D.)

Signature:

……………………...………………... Date………………………………………...

Head of Department: Dr. Brighton Chunga (Ph.D.)

DEDICATION

This accomplishment is dedicated to my wife Flossie and my daughters Pemphero, Rachel, my mother and my late dad for their support and encouragement.

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First, I thank the Almighty God for the gift of life, strength and wisdom that enabled me to accomplish my research project. With profound gratitude and great humility, I would like to acknowledge my supervisors Dr. Russel Chidya and Associate Professor Elijah Wanda who took their time to provide me with valuable information, guidance and mentorship towards the completion of this work. I am thankful to the Malawi Bureau of Standards (MBS), for offering me a scholarship that financed my studies and research work.

Special thanks to Edwin Mchirikizo from Mulanje District Water Development Office for granting me unlimited access to the Ruo River and surrounding boreholes in the tea estates. I am also indebted to the laboratory personnel; Happy Mhango, McDuff Luhanga, and Samson Nyirenda for their indispensable assistance during pesticide analysis at the Malawi Bureau of Standards Testing Laboratory. Special thanks should also go to Mayamiko Jumbe and Andrew Nyambalo who assisted me in getting water samples from the study sites.

Lastly, I thank my family members, fellow course mates and friends for their patience and moral support throughout my academics. I owe you a large debt of gratitude and I love you so much!

ABSTRACT

Malawi's tea industry, despite adopting an integrated pest management approach (IPM) emphasizing cultural and natural practices, struggles with the challenge of widespread illicit pesticide use by local farmers. This investigation aimed to assess the extent of pesticide residues in surface and groundwater within the tea-growing regions of Mulanje during both dry and rainy seasons. Levels of alpha-cypermethrin, cypermethrin, and deltamethrin were determined using Gas Chromatography-Mass Spectrometry (GC MS) and glyphosate, s-metolachlor, and terbuthylazine by Liquid chromatography-mass spectrometry-mass spectrometry (LC-MS/MS). Levels of pH, electrical conductivity (EC), total dissolved solids (TDS), temperature, and dissolved oxygen (DO) were measured in situ using the Multiparameter meter model HI98194. The human health risk assessment was evaluated using the hazard quotient. In the dry season, surface and groundwater exhibited varying levels: pH (6.66 – 7.71), EC (26 – 227 µS/cm), TDS (17 – 135 mg/L), TSS (0.47 – 26.9 mg/L), temperature (24.5 – 26.5°C), and DO (4.09 – 6.69 mg/L). In the rainy season, corresponding ranges were observed: pH (5.65 – 7.55), EC (8 – 243.67 µS/cm), TDS (5 – 148 mg/L), TSS (178 – 316 mg/L), temperature (23.0 – 25.0°C), and DO (3.43 – 4.86 mg/L). The levels of s-metolachlor ranged from below detection to 13.324 µg/L, while cypermethrin ranged from below detection to 1.137 µg/L for both seasons. Although these concentrations fell below the 300 µg/L guideline for Australia, they exceeded the European Union's 0.100 µg/L limits. Groundwater exhibited lower pesticide levels compared to surface water. The risk assessment of human health for chronic exposure for adults and children revealed some level of risk in surface and groundwater in the rainy season for cypermethrin and s – metolachlor. The study established the presence of s-metolachlor and cypermethrin residues in surface and groundwater, increasing the risk of adverse environmental and public health effects. Frequent monitoring of the contamination of the surface and groundwater in the tea estates to ensure that the limits are within the WHO regulations for drinking water is highly recommended.

LIST OF ABBREVIATIONS AND ACRONYMS

ANOVA	Analysis of Variance
CAS	Chemical Abstracts Service
DDT	Dichlorodiphenyltrichloroethane
EFSA	European Food Safety Agency
EU	European Union
FAO	Food and Agriculture Organization
FAOSTAT	Food and Agriculture Organization Statistics
GC MS	Gas Chromatograph Mass Spectrometer
GHS	Globally Harmonized System
HQ	Hazard Quotient
IARSC	International Agency of Research on Cancer
IPM	Integrated Pest Management
IUPAC	International Union of Pure and Applied Chemistry
LC-MS-MS	Liquid Chromatography Mass Spectrometer Mass Spectrometer
LD_{50}	Lethal Dose in 50% of the experimental population
LOD	Limit of detection
LOQ	Limit of quantification
MBS	Malawi Bureau of Standards
MZUNIREC	Mzuzu University Research Ethics Committee
PCA	Principal Component Analysis
PCB	Pesticides Control Board
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe
RQ	Risk Quotient
SPSS	Statistical Software for Social Sciences
TDS	Total Dissolved Solids

TRFCA	Tea Research Foundation of Central Africa
TRV	Toxicant Reference Value
TSS	Total Suspended Solids
US EPA	Environmental Protection Agency United States
USA	United States of America
WHO	World Health Organization
WRAs	Water Resources Areas
WRUs	Water Resources Units

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CHAPTER ONE: INTRODUCTION

1.1 Background

Most countries around the world use pesticides as a solution to deal with the challenges arising from the prevalence of pests (Maksymiv 2015). A pesticide, according to the United States Environmental Protection Agency (EPA US), is any chemical alone or in combination that is intended to prevent, eliminate, or keep a pest at bay, or reduce its population (Fan et al. 2014). Toxic compounds known as pesticides are dispersed into the environment to eradicate organisms including plants, bugs, mould, and rats (Kim et al. 2017). Pesticides are employed to kill undesired organisms in residential gardens, farms, and open spaces (Hassaan & El Nemr 2020). This category includes substances applied to crops before or after harvest to prevent crop degradation during storage or transit, as well as chemicals used as growth promoters, defoliants, drying agents, shrinking agents, or compounds to prevent early crop fall (Tano 2011). Pesticides function by luring pests in, enticing them, and then killing and controlling them (Kaur 2019).

At a global level, the total amount of pesticides used in agriculture in 2019 was 4, 190, 985 metric tons of active ingredients. China surpassed all other nations in 2019 to become the world's largest pesticide user, using nearly 1.7 million metric tons of pesticides for agricultural purposes. In 2019 Africa used 107, 864 metric tons of pesticides in agriculture, up from 65, 943 tons in 1990, a 70% increase over the same period. In the region of Southern Africa, pesticide use in 2019 was 27, 006 tons. In 2019, Malawi used 2, 358 metric tons of pesticides in agriculture (FAOSTAT 2021). Lakudzala (2013), claims that Malawi's expanding agriculture has increased the use of pesticides. Tobacco, tea, sugarcane, coffee, cotton, and maize are the crops in Malawi that utilize the most pesticides for both food production and commercial purposes (Ministry of Agriculture 2017).

By using pesticides, farmers have been able to produce more food and ensure that it is available to everyone. This has also reduced plant susceptibility to viruses and disease (Aktar et al. 2009). Farmers have been using pesticides to manage insects and weeds in agricultural operations, and reports of significant gains in agricultural output have been linked to pesticide use (Tudi et al. 2021). For example, a study done in Pakistan found that with the application of Rollup 7.2G and Pada 3G pesticides on Super Basmati rice, yields rose by 93.4% and 83.3%, respectively (Jamil Khan 2010). Kucharik & Ramankutty (2005) also reported that corn yields in the USA went from 30 bushels per acre to over a hundred bushels per acre over the period from 1920 to 1980. Pesticides are often utilized for safeguarding recreational turf, wood constructions, and hazards associated with trees and shrubs (Maksymiv 2015).

The use of pesticides has provided various benefits for farming, forestry, and the preservation and improvement of people and their communities' health (Aktar et al. 2009). However, the advantages that come with the use of pesticides have a hidden cost. In normal circumstances, a pesticide needs to be toxic to the pests it aims to manage, but not to harm other organisms, which is not what happens (Aktar et al. 2009). The pesticides can accumulate in plants as well as be transferred over great distances through the air, soil, and water, posing a major pollution source in ecosystems (Toumi et al. 2016). Even though pesticides enhance agricultural output, the toxins that accumulate along the food supply chain endanger animals (Jardim & Caldas 2012). These pesticides may be harmful to the surrounding areas and people's well-being. Pesticides are responsible for around 200,000 deaths per year due to acute poisoning (United Nations Human Rights 2017). WHO estimates that 3 million acute pesticide exposure cases emerge annually, with more than 300,000 fatalities: 99 percent of these episodes in countries with low and middle incomes (Gunnell & Eddleston 2003). In addition to genotoxicity, long-term pesticide exposure can result in immune system problems, cancers, reproductive system defects, hormonal imbalances that cause conception and bosom discomfort, a disorder of the nervous system, and mental issues, among other things (Koli et al. 2019).

The use of groundwater in or near agricultural land, especially in rural regions where it may be used for household supply, is a source of international concern for pesticide contamination of groundwater and surface water. Pesticide droplets moving in the air, water flowing freely over the surface, and diffusion from sprayed agricultural areas are all possible sources of pollution (Bortoluzzi et al. 2007). Studies on the incidence of chemical contaminants in the Deomoni River, which runs through India's tea fields, have shown that the river contains chlorpyriphos and ethion (Singh et al. 2015). Similarly, research on the prevalence and destiny of metolachlor in some catchment areas in the United States of America (USA) revealed that it was present in both surface and groundwater (Rose et al. 2018). Also, pesticide residues such as lindane and cypermethrin were detected in Weruweru, Tanzania which ranged from below the detection limit to 45.7ug/l in surface water (Mohamed 2014). At the national level, several types of research on water-related contamination were conducted. For example, Lakudzala (2013) did a study on surface and groundwater for atrazine and metolachlor contamination in Zomba, Thondwe area which is mainly a tobacco growing area, and found that both surface and groundwater were contaminated.

Since Malawi is a farming nation that mainly depends on its agriculture industry, the effects of pesticide use are particularly pertinent. Malawi's reliance on smallholder farming further highlights the hazards connected with pesticide usage if not properly handled. An increasing reliance on pesticides is highlighted by concerning statistics from Malawi's Ministry of Agriculture and Food Security, which shows a consistent rise in pesticide imports (Government of Malawi,2021) As most people in this nation are employed in agriculture, serious concerns exist over the effects this usage spike will have on the environment and public health.

This research investigated the residual concentrations of selected pesticides in surface and groundwater in water bodies surrounding selected tea-producing sites in Mulanje, Malawi. It also investigated the way pesticide concentrations in rivers, boreholes, and dams relate to physicochemical water quality indices. The list of selected pesticides investigated were alpha-cypermethrin, cypermethrin, deltamethrin, s-metolachlor, terbuthylazine, and glyphosate. The pesticides were selected because they constitute a list, which have been recommended by the Tea Research Foundation of Central Africa (TRFCA) for utilization in tea estates in Malawi.

1.2 Problem statement

The widespread use of pesticides in tea plantations, driven by the necessity to combat pests in monoculture crops, poses a critical environmental and public health concern (Gurusubramanian 2008). The escalation of pesticide concentrations in surface and groundwater, documented in various regions, raises alarming issues about their potential impact on human and ecological systems. highlight the profound health risks associated with the accumulation of pesticides in the food chain, emphasizing the urgent need for comprehensive investigation and mitigation(Sharma et al. 2019). Pesticides migrate up the food chain, causing biomagnification. Low quantities of pesticides enter the food chain at lower trophic levels, but they build up at higher trophic levels, endangering the health of both humans and animals (Lushchak et al. 2018). Pesticides represent a risk to biological systems' health because of their quick solubilization in fat and ability to accumulate poisons in species which are not their primary concern (Agrawal et al. 2010).

Several studies have indicated incidences of surface and groundwater contamination arising from the utilization of pesticides and the discharge of wastes containing pesticides. For instance, in Thondwe, Zomba, a region known mostly for its tobacco cultivation, atrazine, and metolachlor were found. (Lakudzala 2013). Pesticides such as cypermethrin and glyphosate are among the pesticides that are authorized for use in Malawi's tea plantations, although it is unknown how much of these chemicals remain in the waterways. Prior research along the Ruo River in Mulanje on the effect of different land uses by Kambwiri et al. (2014) only concentrated by analyzing physicochemical parameters, leaving a substantial void in our understanding of actual pesticide pollution levels.

Despite the purported implementation of Integrated Pest Management (IPM) as the recommended approach in Malawi's tea industry by TRFCA, reports by Soko (2018), reveal the illicit use of pesticides acquired from neighboring countries, undermining the effectiveness of IPM. This discrepancy highlights the crucial research gap and the shortcomings of current pest control methods, as does the lack of reliable studies explicitly evaluating pesticide residue levels in tea plantations in Mulanje. The potential risks associated with pesticides, whether as metabolites or parent residuals in food and water sources, as emphasized by (Riaz et al. 2018) necessitate urgent attention to safeguard the well-being of communities relying on tea plantation waterways for domestic use . Failure to address these issues promptly jeopardizes the long-term quality of surface and groundwater, threatening the safety and health of the surrounding communities.

1.3 Study objectives

1.3.1 Main objective of the study

The main objective of the study was to assess pesticide residues in the surface and groundwater around tea growing regions of Mulanje, Malawi.

1.3.2 Specific objectives

The study had the following specific objectives:

a. To determine the levels of temperature, pH, total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), electrical conductivity (EC) and their relationship with the occurrence concentrations of pesticides in the surface and groundwater.

b. To assess levels of pesticide residues (alpha-cypermethrin, cypermethrin, glyphosate, deltamethrin, s-metolachlor, and terbuthylazine) in surface and groundwater in Mulanje.
c. To assess the risks posed by pesticides to humans on the use of the ground and surface water for human consumption in Mulanje.

1.3.3 Hypothesis of the study

(a) There is no significant difference in the levels and relationship of physicochemical water parameters and pesticide residues of the surface and groundwater in the dry and rainy seasons.
(b) There is no significant difference in the levels of pesticide residues on the surface and groundwater in the dry and rainy seasons.
(c) There is no significant risk of pesticides to humans on the use of the surface and groundwater for human consumption.

1.4 Significance of the study

Surface and groundwater are adversely impacted by the destruction of the surrounding area, agriculture, and pesticide use, manufacturing and mine operations, and insufficient sanitation facilities (Government of Malawi 2021a). This can affect the use of the surface and groundwater for drinking, agriculture, recreation, and other domestic purposes. Therefore, there is a need to estimate the quality of the surface and groundwater for various purposes. Since tea is the second-largest pesticide consumer after tobacco, it is important to investigate the pesticides' effects on both surface and groundwater. As a result, a better understanding of the impacts of these pesticides on water bodies will be obtained, paving the way for better pesticide management.

The community around these tea estates will be made aware of the quality of the surface and groundwater for drinking and other domestic purposes. This will therefore help the local communities to make informed decisions. The estate owners will also be aware of the concentrations of pesticides in the water bodies and take appropriate action wherever necessary. It is also intended that the data and information gathered would contribute to policy discussions and help the authorities formulate policies on pesticide residues and public health.

The study's findings and recommendations may be valuable to policymakers and academicians in developing and implementing appropriate developmental programs and policies to use and handle them properly over the long run. The findings can also be utilized as supplemental data to aid in the development of mitigation measures to prevent pesticide-related water pollution and strategies to assure safe water quality for the community around the tea estate plantations. In addition, this research will further serve as a starting point for more studies on the subject in the field of study.

1.5 Ethical consideration

The study sought ethical clearance approval from the Mzuzu University Ethical Clearance Committee (MZUNIREC). The MZUNIREC approved fieldwork with Protocol Reference number MZUNIREC/DOR/23/03 (Appendix A). A letter of consent was obtained from the Mulanje District Water Development Office for access to the tea estates for water sampling (Appendix B).

1.6 Study limitations

This study only focused on tea estates in Mulanje, the Southern part of Malawi. Therefore, future research must take into consideration other tea-growing areas in the district of Thyolo, the Southern part of Malawi, and Nkhata Bay in the Northern part of Malawi. The study had also a limitation on the reference standards of Sulphur and copper oxychloride, which failed to do a quantitative analysis of the two pesticides, used in the tea plantations in Malawi.

CHAPTER TWO: LITERATURE REVIEW

2.1 Pesticides and their historical perspective

The use of pesticides traces back to 1000 BC when the Greeks utilized sulfur to control insects and weeds (Oberemok et al. 2015). Arsenic sulfides were recorded in China by 900 A.D to suppress garden insects., and in the 1600s, arsenic became the Western world's first documented insecticide (Özkara et al.2016). Various substances, such as tobacco, hydrated lime, copper sulfate, hydrocyanic acid, and carbon disulfide, were employed for pest control in different periods. Until the mid-1930s, pesticides were mainly natural or inorganic.

In the early 1930s, the introduction of synthetic organic insecticides, including dinitro compounds and thiocyanates, marked a significant shift. This era saw the discovery and widespread use of synthetic pesticides like DDT, organophosphates, and pyrethroids, particularly between 1935 and 1950 (Abubakar et al. 2019). DDT, a notable chlorinated hydrocarbon pesticide, gained prominence but faced criticism due to environmental concerns, notably highlighted by Rachel Carson in her 1962 book "Silent Spring."

Despite the decline in DDT production in the U.S. after the 1960s, it is still utilized globally for disease vector control. The 1970s and 1980s witnessed ongoing research leading to the development of safer pesticides, including glyphosate, sulfonylurea, imidazolinone herbicides, dinitroanilines, and the aryloxyphenoxypropionate and cyclohexanediones families (George & Shukla 2011)..

2.2 Pesticide uses in Malawi

In Malawi, the Pesticides Act of 2018 (Chapter 35.03) empowers the Pesticide Control Board for the control and management of the importation, exportation, manufacture, distribution, storage, disposal, sales, repackaging and use of all pesticides (Government of Malawi 2018). The farmers in Malawi use insecticides, fungicides, herbicides, fumigants, nematicides, acaricide, and rodenticides (Soko 2018). Herbicides are mostly used in sugar plantations, whereas fumigants are mostly dominant in the tobacco industries. Insecticides are mostly used in field crops, particularly maize. According to TRFCA, the tea farmers spraying calendar normally falls between May to July and October to November. These are the period when certain pests such as bugs and thrits are known to be most active. The frequency of application mostly depends on the observed outbreaks of pests. Malawi does not manufacture pesticides hence all pesticides used in the country are imported. Some chemical companies import pesticides into the country and in turn, supply them to various stakeholders for both crop and livestock production(Government of Malawi 2021b). The pesticides used in weed and anthropoid pest control in sugarcane farming include Metryn Acetochlor and Profenofos (Kasambala Donga & Eklo 2018). According to Kamanula et al. (2011), actellic super dust (pirimiphos-methyl, permethrin) and Shumba super (Fenitrothion, Deltamethrin) are used to control pests in stored maize and beans. Lakudzala (2013), also reported the use of atrazine and metolachlor in tobacco, coffee, cotton, and sugarcane farming.

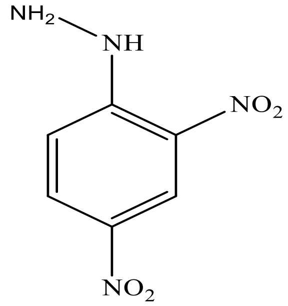
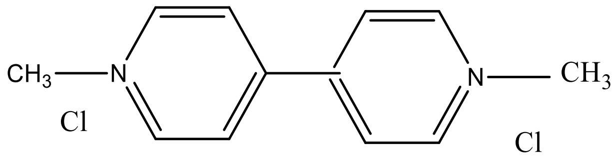
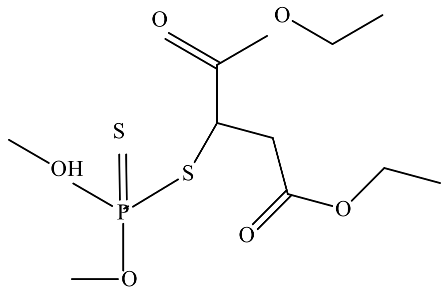
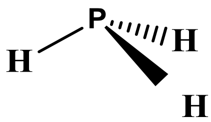
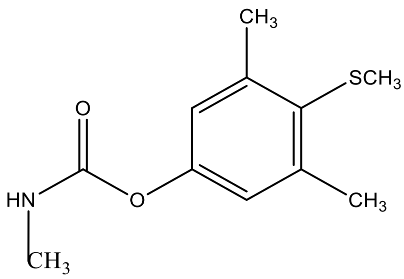
2.3 Pesticides classification

Pesticides fall into several categories depending on their uses and physical and chemical characteristics since they vary from one class to the next (Hassaan & El Nemr 2020). Pesticides have been categorized into the following groups depending on the kinds of organisms they are meant to manage fungicides, insecticides, bactericides, algicides, germicides, nematicides, larvicides, herbicides, and rodenticides (Abubakar et al. 2019). Pesticides could also be classified based on their nature and the nature of the active ingredients, which gives a hint about the efficacy, and physical and chemical properties of the pesticides. Based on this chemical composition, there are four main groups, and these are organophosphates, organochlorines, carbamates, and pyrethroids (Akashe et al. 2018; Kaur et al. 2019; Tudi et al. 2021). Presently, the WHO recommends the classification of pesticides as hazards, and in 2009, after revision, the classes were harmonized with acute toxicity hazard categories of the globally harmonized system (GHS) (Akashe et al. 2018).

2.3.1 Classification based on mode of entry

In this method, the pesticides are classified by the way they enter the organism, Table 1 (Yadav & Devi 2017).

Table 1. Classification based on the mode of entry (Yadav & Devi 2017b).

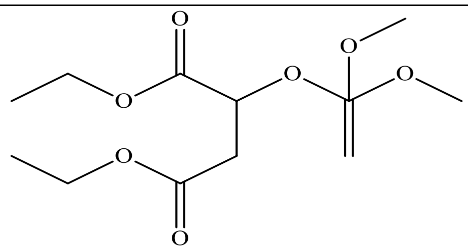
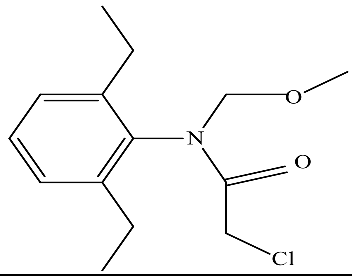
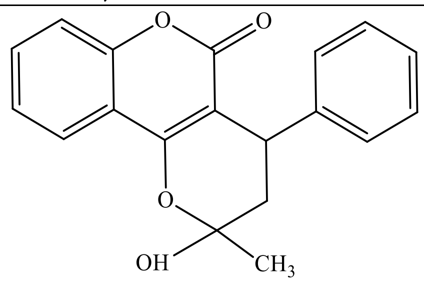
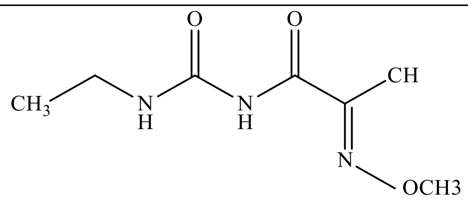
Type of Pesticide	Description	Examples	Structure
Systemic Pesticides	These are pesticides that are ingested and transferred to unprocessed tissue	2,4 –D	
Contact pesticides	It kills pests that encounter the plant	Paraquat	
Stomach poisons	It enters through the mouth and digestive system	Malathion	
Fumigants	Pesticides work by producing vapor and entering the pest's body via the tracheal system.	Phosphine	
Repellents	Repellents do not kill but are unpleasant enough to keep pests away from treated areas.	Methiocarb	

2.3.2 Classification based on function and pest organisms they kill

With this approach, pesticides are categorized according to the organism of the target pest, and they are given special names to represent their function. These pesticides' group names are formed by adding the Latin word “cide” to the end of the names of the pests they are designed to kill. However, not all pesticides have the term "cide" at the end (Yadav & Devi 2017). Additionally, some pesticides are categorized by their purposes such as growth regulators, defoliants desiccants, repellents, attractants, and chemosterilants (Chandra Yadav &

Linthoingambi Devi 2017a). By this classification, Table 2 lists the pesticides that are used most frequently.

Table 2. Classification of pesticides based on pest organisms they kill and pesticide function (Yadav & Devi 2017b).

Type of pesticide	Target pests/Functions	Examples	Structures
Insecticides	Kills insects	Azadirachtin, DDT, chlorpyrifos, malathion	 Malathion
Herbicides	Undesired vegetation	Alachlor, paraquat, 2,4-D	Alachlor 
Rodenticides	Substances used to kill rats and related animals	Strychnine, Warfarin, zinc phosphide	
Fungicides	Chemicals that are used to prevent or kill the growth of fungi.	Cymoxanil, thiabendazole, Bordeaux mixture.	 Cymoxanil

2.3.3 Classification based on chemical composition of pesticides

The chemical composition and nature of active ingredients are the most common and useful methods of classifying pesticides (Yadav & Devi 2017). Information on the various pesticides' effectiveness in addition to their physical and chemical properties is provided by this categorization. Understanding the chemical and physical features of pesticides is extremely helpful in deciding on the mode of application, safety measures to be taken during the application, and application rates. Pesticides are grouped into four different primary classes depending on their chemical composition: organochlorines, organophosphorus, carbamates and permethrin, and pyrethroids (Kaur et al. 2019).

2.3.3.1 Organochlorines

Organochlorines (OC) are a class of frequently used insecticides that are chlorinated chemicals. These substances fall under the category of persistent organic pollutants (POPs) with a high level of environmental persistence (Jayaraj et al. 2016). Although the OC insecticides were formerly used to successfully combat typhus and malaria, they are now prohibited in most industrialized nations (Aktar et al. 2009). Due to the high bio-accumulative potential and toxicity in living organisms, OCPs may be a serious threat to ecological integrities and humans (Mahmood et al. 2014). A live thing's skin, lungs, and gut wall are all entry points for organochlorines into the circulatory system (Singh et al. 2015). Common examples of OCPs include DDT, lindane, endosulfan, aldrin, and dieldrin (Abubakar et al. 2019b).

2.3.3.2 Organophosphorus

Most organophosphates (OPs) are alkyl-, alkoxy-, alkylthio-, or amido-group-containing alkyl-, amide-, or thiol-derivatives of phosphoric, phosphonic, or phosphonic acids. According to Marrazza (2014), X is the acyl residue, which might contain labile aliphatic, aromatic, or heterocyclic groups that are fluorine-, cyano-, substituted, or branched. The structure of organophosphates is seen in Figure 1. The OPs have also been misused as chemical warfare agents and are known to be the most toxic pesticides to vertebrate animals. The bioaccumulation of OPs in the environment leads to the contamination of air, water, soil, and agricultural resources. The OPs penetrate the body mainly through inhalation, ingestion, injection, or cutaneous (Hassani et al. 2017). The most used OP pesticides are chlorpyrifos, paraoxon, 98 malathion, parathion, coumaphos, diazinon, methyl parathion, fenitrothion, and cyanophos (Pundir et al. 2019). People are susceptible to several neurotoxic diseases brought on by organophosphorus esters, icing cholinergic syndrome, intermediate syndrome, organophosphate-induced delayed polyneuropathy (OPIDP), and chronic organophosphate-induced neuropsychiatric illness (COPIND) (Jokanović & Kosanović 2010).

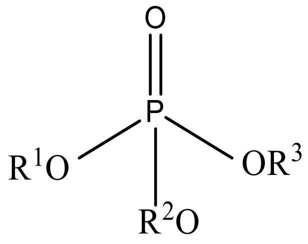


Figure 1 Structure of the organophosphate

2.3.3.3 Carbamates

The most extensively used insecticides on a worldwide scale are carbamate pesticides (CMs). These compounds, which are produced from carbamic acid, are perhaps the insecticides with the widest range of biocidal effects. Figure 2 shows the structure of the physiologically active carbamates. Acetylcholinesterase activity (AChE) is inhibited by CMs pesticides, which makes them also capable of reversibly inhibiting neuropathic target esterase (Bini Dhouib et al. 2016).

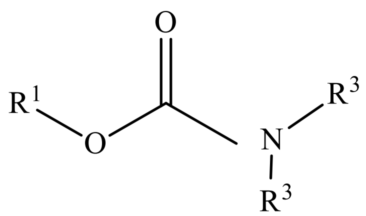


Figure 2 Structure of carbamate pesticides

2.3.3.4 Pyrethroids

Pyrethroids are a class of synthetic insecticides. Their chemical structure of them is based on pyrethrins, which are organic compounds found in *Chrysanthemum cineraraefolum flowers*. The combination of an acid and an alcohol moiety with an ester constitutes the fundamental pyrethroid structure (Saillenfait et al. 2015). They have been used on a global scale since the 1980s because of their ability to produce the desired outcome and low doses to cause poisoning toxicity in comparison to other insecticides like organophosphorus and carbamic ester compounds (Yoo et al. 2016). The main commercially available pyrethroids include allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, deltamethrin, permethrin, d-phenothrin, permethrin, and tetramethrin (Saillenfait et al. 2015).

2.3.4 Classification based on the toxicity of pesticides.

Depending on the health risks associated with pesticides and the toxic behavior of pesticides, the WHO classified them into four categories (Kim et 2017). The WHO experimented on rats and other laboratory animals by administering a dose of pesticide orally and dermally. They then estimated the median lethal dose (LD_{50}) that produces death in 50 percent of exposed animals to reach this conclusion. Numbers I through IV represent, in order of decreasing toxicity, very poisonous, highly toxic, moderately toxic, and somewhat toxic, respectively. At present, the widely used 'WHO-recommended classification of pesticides by hazard suggests allocating pesticides to the specific WHO Hazard classes. After revision in 2009, these classes were harmonized with the GHS Acute Toxicity Hazard Categories (World Health Organization & International Programme on Chemical Safety 2010) The classification of pesticides according to toxicity level is summarized in Table. 3 and the revised GHS classification of pesticides is shown in Table 4.

Table 3. The World Health Organization recommended classification of pesticides.

	Class	**Lethal Dose $_{50}$ for rats (Mg/kg body wt.)**		**Examples**
		Oral	Dermal	
I a	Extremely hazardous	<5	<50	Parathion, Dieldrin, Phorate
I b	Highly hazardous	≤ 20	≤ 50	Aldrin, Dichlorvos
II	Moderately hazardous	≤ 2000	≤ 2000	DDT, Chlordane
III	Slightly hazardous	> 2000	> 2000	Malathion
U	Not likely to present acute hazard	≥5000	≥5000	Carbetamide, Cycloprothrin

Table 4. The Globally Harmonized System Classification of Pesticides.

GHS Category	Classification Criteria			
	Oral		Dermal	
	Lethal Dose $_{50}$ (mg/kg bw)	Hazard Statement	Lethal Dose $_{50}$ (mg/kg bw)	Hazard Statement
1	< 5	Fatal when eaten	< 50	Lethal in touch with skin
2	≤50	Fatal when eaten	≤200	Lethal in touch with skin
3	≤300	Toxic when eaten	≤1000	Lethal in touch with skin
4	≤2000	Harmful when eaten	≤2000	Harmful in touch with skin
5	2000 – 5000	May be harmful	2000 – 5000	May be harmful

2.4 Commonly used pesticides in the study

In the current section, refer to the introduction chapter, and the last paragraph in the background section where the rationale for selecting these pesticides in the study has been justified.

2.4.1 Cypermethrin

Synthetic pyrethroid insecticide cypermethrin is widely used in residential, agricultural, and zoological applications to treat cracks, crevices, and specific areas to control insects (Yadav 2018). When ingested or absorbed directly via the skin, cyclomethrin is a moderately hazardous substance. The primary signs and symptoms of dermal exposure include irritability, itching of the skin and eyes, numbness, tingling, and burning sensations, loss of bladder control, convulsions, and occasionally even death. According to the WHO, cypermethrin is a synthetic pyrethroid insecticide of class II. Chemically, cypermethrin is known as an alpha-cyano-3-phenoxybenzyl ester of the dichloro analog of chrysanthemic acid, 2, 2-dimethyl-3-(2, 2-dichlorovinyl) cyclopropane carboxylic acid (Table 5). The molecule possesses three chiral centers: one on the alpha cyano carbon and two on the cyclopropane ring. Four cis- and four trans-isomers are frequently used to categorize these isomers, with the cis group representing the more potent Cypermethrin insecticides. A study in Gella, Nigeria indicated the existence of cypermethrin residues in all the water samples analyzed ranging between 25 and 61.5×10^{-3} µg/l (Sudi 2017). Similarly, a study on water samples indicated cypermethrin levels ranging from 8.115–15.460 mg/L in surface water and 4.48–12.18 mg/L in groundwater concentrations during the rainy season was above the recommended limits (Kanyika-Mbewe et al. 2020).

2.4.2 Glyphosate

Glyphosate [(N-phosphonomethyl) glycine] (GLY) is a non-selective and broad-spectrum herbicide that is extensively used around the world Glyphosate-based herbicides are employed to eradicate undesired vegetation from agricultural areas, and they also eliminate any plants that lack genetic resistance (Table 5) (Gill et al. 2018). Its global use has increased due to the widespread use of certain agricultural practices such as no-till cropping and the widespread use of glyphosate-resistant genetically modified crops (Heler et al. 2012). Products containing glyphosate are very harmful to all animals, including people. Symptoms include eye and skin irritation, headache, nausea, numbness, elevated blood pressure, and heart palpitations (Valle et al. 2019). In Spain, water samples revealed a mean glyphosate concentration of 200 ng/L and a maximum glyphosate concentration of 2.5 g/L (Sanchís et al. 2012). Additionally, in South Africa, 0.42 g/L of glyphosate was found at a farm's in-flow dam following a spraying event (Horn et al. 2019).

2.4.3 Deltamethrin

Using the esterification of [1R,3R, or cis], deltamethrin is a pyrethroid made up of a single isomer of 8 streamers. -2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylic acid with (alpha S) -or (+) -alpha-cyano-3-phenoxybenzylalcohol or by selective recrystallization of the racemic esters produced by esterifying the (1R, 3R or cis) -acid with the racemic or (alpha R), (alphas), or (alpha RS + -alcohol (Table 5) (Ismail et al. 2015). Monitoring of deltamethrin residues in surface winter ranged from Not Detected (ND) to 0.108 µg/l in winter and ND to 0.087 µg/L in summer in Chenab River, Pakistan (Riaz et al. 2018). Also, the levels of deltamethrin ranged from 12.5-37.5 x 10^{-3} mg/L. The highest level of deltamethrin was in the water source, Kurbaca Pond,37.5 x 10^{-3} mg/L, and the lowest in Bogga Earth Dam, South Africa,12.5 x 10-3 mg/L (Horn et al. 2019).

2.4.4 S-Metolachlor.

S-metolachlor is a selective chloroacetanilide herbicide that is heavily used on annual grassland weeds, maize, soybeans, peanuts, and other crops. It is 2-chloro-N-(2-ethyl-6-methyl phenyl)-N-[(1S)-2-methoxy-1-methylethyl] acetamide (Table 5) (Gutowski et al. 2015). The physical and chemical properties of S – metolachlor are represented in Table 5. Herbicide penetration and exit into the soil matrix, in addition to how they reach ground and surface water, and even the atmosphere, are all regarded to be aspects of herbicide transport. The three main methods by which S-metolachlor can enter different environments are runoff, volatilization, and leaching (Zemolin et al. 2014).

2.4.5 Alpha- Cypermethrin

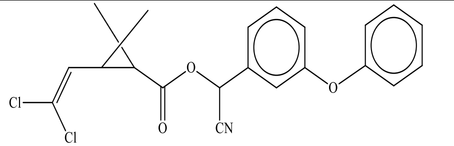
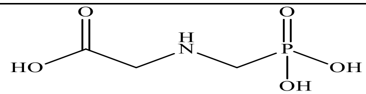
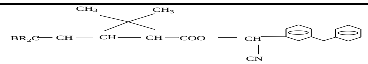
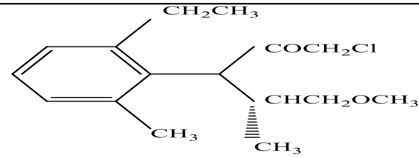
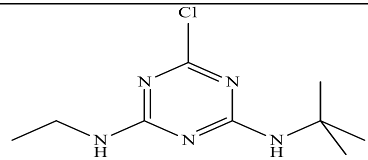
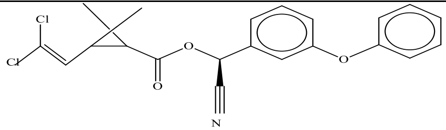
Due to the presence of a cyano group at the alcohol molecule's -carbon, alpha-cypermethrin, which belongs to the class II pyrethroids, is frequently employed to combat insect pests in gardens, fruits and vegetables, and woodland trees (Ghazouani et al. 2020). Alpha-Cypermethrin is also used as an insecticide in indoor environments (Saillenfait et al. 2015). The protected area of Zobnatica Lake tested positive for alpha-cypermethrin during a screening analysis (Mihajlović et al. 2021)

2.4.6 Terbuthylazine

Terbuthylazine is a herbicide with selective action that is often utilized in agricultural and forestry operations as a chloro-s-triazine herbicide to control vegetation (Watt et al. 2010).

Preemergence selective herbicide terbuthylazine (N2 -tert-butyl-6-chloro-N4 -ethyl-1,3,5-triazine-2,4-diamine) is administered directly to the soil and is largely taken by roots (Table 5) (Cañero et al. 2011). In Zagreb, Croatia, terbuthylazine has been detected in drinking water samples up to 25ng/L and in groundwater up to 16ng/L (Fingler et al. 2017).

Table 5.Chemical and physical properties of selected pesticides in this study

Compound	**IUPAC Chemical name**	**Relative Molecular mass g/mol**	**Solubility in water at 20ºC mg/l**	**Density g/ml**	**Vapor pressure 20 °C (mPa)**	**Chemical structure**
Cypermethrin	[cyano-(3-phenoxyphenyl) methyl]3-(2,2-dichloethynyl)-2,2-dimethylpropane-1-carboxylate	416.3	0.009	1.30	6.78×10^{-3}	
Glyphosate	N-(phosphonomethyl)glycine	169.09	10,000 – 15,700	1.71	0.0131	
Deltamethrin	[(*S*)-cyano-(3-phenoxyphenyl) methyl] (1*R*,3*R*)-3-(2,2-dibromo ethenyl)-2,2-dimethyl cyclopropane-1-carboxylate	505.2	0.002-0.0002	0.55	1.24×10^{-5}	
S-metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(2S)-1 methoxy-2-propanyl] acetamide.	283.79	480	1.12	3.7	
Terbuthylazine	N-tert-butyl-6-chloro-N-ethyl-1,3,5-triazine-2-4-diamine	229.71	8.5	1.19	0.152	
Alpha cypermethrin	[(S)-cyano-(3-phenoxyphenyl) methyl] (1R,3R)-3-(2,2-xylene ethenyl dichloroethane)-2,2-dimethyl cyclopropane)-dimethyl cyclopropane carboxylate	416.3	0.01.	1.28	3.8×10^{-4}	

2.5 Sources of entry of pesticides into the environment

Both point sources and nonpoint sources allow pesticides to enter water bodies. Chemical runoff from incorrect storage, loading, and disposal as well as improper pesticide application to water bodies are examples of point sources that come from a fixed site (Syafrudin et al. 2021a). Farming operations are the formation of non-point sources of pesticides because runoff and erosion from such fields cause pesticides to slowly seep into the ground and surface water (Aydinalp & Porca 2004). A typical form of point source contamination is the direct transport of pesticides into groundwater. In this case, the chemicals penetrate water wells and cause spills and inappropriate pesticide disposal. Insecticide use in urban areas is regarded as a point source of pesticides in surface waters. The non-point source is the dispersion of pesticides across a wide region, via the watersheds, and eventually into the water bodies over an extended period (Syafrudin et al. 2021a).

2.6 The risk associated with pesticides.

The length of time of contact and how toxic the components are both affect the risk of health risks brought on by exposure to pesticide residue (Kim et al. 2017). Human health hazards have been recorded, ranging from immediate symptoms like headaches to long-term ones such as cancer, reproductive harm, and endocrine disruption (Berrada et al. 2010). When consumed or absorbed directly via the skin, cyclomethrin is a moderately potentially dangerous substance. The most common effects of dermal exposure include irritability, itchiness in the skin and eyes, numbness, tingling, and burning sensations, loss of bladder control, coordination problems, seizures, and occasionally fatalities (Sharma et al. 2019). Glyphosate is the world's most used herbicide (Benbrook 2016). There has been an ongoing debate regarding the toxicity of glyphosate (Bai & Ogbourne 2016); (Mesnage & Antoniou 2017). For example, the incidence of liver and kidney cancers in studies on chronic feeding led the International Agency of Research on Cancer (IARSC) to categorize glyphosate as a category 2a carcinogen (Benbrook 2016). Later, in 2016, this was denied (Brusick et al. 2016). Glyphosate exposure has been linked to reproductive toxicity and birth defects (Garry et al. 2002). According to the European Food Safety Agency (EFSA), terbuthylazine is very harmful to aquatic organisms and presents a significant danger to plants that are not aimed at off-field areas (Kaur 2019).

2.7 Water Quality and pesticides use.

Pesticides present a challenge for safeguarding water quality because of their widespread application (Agrawal et al. 2010). Pesticides can enter water bodies by direct application, spray drift, aerial spraying, air fallout, soil erosion and runoff from agricultural regions, discharge of home and industrial sewage, leaching, reckless dumping of empty containers, and equipment cleaning. These pesticides in water bodies can degrade the water's quality and eventually pose a hazard to non-target creatures that are part of the food chain (Kaushik et al. 2010). Most pesticides fall into one of many toxic categories, and they can pollute the environment and marine resources (Musa et al. 2019). National governments have put in place guidelines for pesticide levels in drinking water to safeguard the public's health. Several guideline values are present and a select handful of them have been developed by the WHO, the US, Australia, the EU, and Japan (Syafrudin et al. 2021b). A maximum contamination level of 100 ng L-1 for a single pesticide and 500 ng L-1 for all pesticides is specified by the EU Drinking Water Regulations established by the EU directives (European Union 2014). Malawi's national standards for drinking water do not have limits for the pesticides under study. The WHO and the Australian government's recommended values for pesticide concentration in drinking water are presented in Table 6.

Table 6. Drinking water recommended values.

Pesticide	Australian Drinking Water Guidelines (mg/L) max	WHO (mg/L) max	EU (mg/L) max
Cypermethrin	0.20	na	0.0001
Alpha-Cypermethrin	0.20	na	0.0001
Deltamethrin	0.04	na	0.0001
Glyphosate	1.00	na	0.0001
S Metolachlor	0.30	0.010	0.0001
Terbuthylazine	0.01	0.007	0.0001

na = not applicable

2.8 Occurrence of pesticides in surface and groundwater

The existence of pesticides in the water is triggered by chemical waste from factories and runoff from agricultural fields (Syafrudin et al. 2021a). Surface and groundwater pollution due to pesticides is a worldwide concern (Aktar et al. 2009). The deliberate release of pesticides into the environment has resulted in pesticides being transported off-field into water bodies, where they may impair the quality of the surface water by posing a risk to aquatic life and, on rare occasions, human health through consumption of contaminated water or fish (Ippolito & Fait 2019). Several factors, including the land-use context, the hydrologic system's characteristics, and the pesticides' historical and current use, impact how widely various pesticides are spread in streams and groundwater (Syafrudin et al. 2021a).

Pesticides were found in a variety of surface waters, including the Deomoni River in the Terai region of West Bengal, India (Singh et al. 2015), northeastern Greece (Vryzas et al. 2009), Nile River, Cairo, Egypt (Shalaby et al. 2018), and from four sub-basins, Argentina (De Gerónimo et al. 2014). In comparison to groundwater, (Lari et al. 2014) discovered that surface water included higher quantities of OCIPs and OPPs. Similarly, Meffe & de Bustamante (2014), reported the highest concentrations of terbuthylazine, metolachlor, glyphosate, diuron, and terbutryne herbicides in surface water in comparison to groundwater.

The widespread contamination of water by pesticides has also been reported. The mentioned studies highlight the concerning presence of pesticides in surface water, emphasizing specific cases in Portugal and the United States. In the case of the Alquera reservoir in the Guadiana basin in south Portugal, a risk assessment of pesticides in surface water revealed alarming findings. Out of the twenty-five pesticides assessed, twenty-three were detected in some or all of the water samples analyzed. Notably, the pesticides bentazone, terbuthylazine, and metolachlor were found to be the most abundant. Terbuthylazine, in particular, was consistently present in all water samples, reaching a maximum concentration of 532 ng/l as reported by Palma et al. (2014a). Similarly, a study conducted in the United States focused on the occurrence of fungicides and other pesticides. The findings indicated a higher prevalence of pesticides in surface water compared to other environmental matrices, such as groundwater. Among the 63 surface water samples analyzed, at least one pesticide was detected in 62 of them, according to Orlando et al. (2009)

These studies underscore the widespread contamination of surface water with various pesticides, posing potential risks to both environmental ecosystems and human health. The detection of a significant number of pesticides, including those with high abundance, emphasizes the urgent need for effective water quality management and the adoption of sustainable agricultural practices to minimize the adverse impacts of pesticide runoff into surface water bodies. The results also highlight the importance of ongoing monitoring and regulatory measures to address and mitigate the risks associated with pesticide contamination in water resources.

2.9 Risk assessment

Risk assessment, as defined by the US EPA, is the process of assessing the likelihood that a pesticide will have adverse effects on human health and the environment. An evaluation of the type and likelihood of harmful health consequences for individuals, who may be in contact with chemicals in contaminated environmental media, either now or in the future, is known as a human health risk assessment. To determine the probability that the ecosystem may be influenced by exposure to one or more environmental stressors, such as pollutants, land use change, disease, and invasive species, an ecological risk assessment is used. In general, the ecological risk assessment of pesticides is represented as the ratio of anticipated environmental concentration (PEC) to the projected no-effect concentration (PNEC), which is determined by the combination of environmental exposure and ecotoxicological effects (PNEC) (Palma et al. 2014b). People are constantly exposed to different chemicals through their diet and the environment and this cannot be ignored (Reffstrup et al. 2010).

Risk assessment is a technique used by regulatory agencies like the US EPA to characterize the risk category of a chemical compound using the risk quotient (RQ) index and risk evaluation for compounds that are cancerous and non-carcinogenic to human health using the hazard quotient (HQ). To gauge the risk of chemical exposure to certain species in the immediate natural environment, the risk quotient (RQ) model was developed. RQ is defined as a ratio of an ambient concentration (exposure) that has been measured or calculated to a toxicant reference value (TRV). Equation 1 is used to get the RQ for a single pesticide, i.(Faggiano et al. 2010). According to risk quotients of concern reported by (Sánchez-bayo et al. 2002), low risk, medium risk, and high risk are indicated by RQ < 0.1, 0.1 ≤ RQ < 1, and RQ ≥ 1, respectively.

$$Risk\ Quotient(RQ) = RQi = \frac{Exposure}{Toxoxity} = \frac{MECi}{TRVi} = \frac{MECi}{LC50orEC50} \qquad \text{Equation 1}$$

Where MECi denotes the pesticide's measured environmental concentration and TRVi denotes the pesticide's toxic reference value (LC50, the half-lethal concentration for 50% of the tested species' population, or EC50, the effective concentration for 50% of the tested species' population). Carcinogenic risk (R) is computed using Equation. 2 for the potentially carcinogenic substances (Kim et al. 2013).

$$R = CDI \times SF \times ADAF \qquad \text{Equation 2}$$

where SF stands for the cancer slope factor (mg/kg/day), which calculates the probability that a substance will cause cancer if ingested by mouth, and ADAF is the age-dependent adjustment factor (10 for children under 2 years old, 3 for children between 2 and 16 years old, and 1 for people over 16 years old). The cancer slope factor's default modifications, known as ADAF values, consider the increased risk of developing cancer from early life exposures. Several studies have been conducted on risk assessment using the HQ for health risk assessment. For example, Chidya et al. (2022) discovered the HQ values below the limit of danger (HQ=1) and concluded that the Kurose River water posed minimal dangers to the safety of people, making it safe for ingestion. Similarly, a study on the Jiulong River in South China by Zheng et al. (2016) found the HQ value not more than 0.01, suggesting that the harm to human health from pesticides in river water was minimal and hence safe for consumption.

2.10 Physico-chemical water quality parameters in relationship to pesticide residues

Pesticide levels in rivers can vary depending on the physicochemical quality of the environment such as pH, TSS, TDS, DO, EC and temperature. The pace of breakdown of the pesticides is influenced by the physicochemical properties of the water and the amount of time the pesticide is in contact with it (Ccanccapa et al. 2016). The temperature has an impact on other parameters including the chemical property of dissolved oxygen (Arora 2018). The temperature of the water in a river also affects how quickly chemical reactions occur. Many chemical processes in a river will occur more quickly in warm water, which affects the water's quality (Adeniran 2018). The pH of water causes some pesticides to undergo degradation through the hydrolysis process. In the pH range of 8 to 9, the hydrolysis rate can be quick. The rate of hydrolysis will roughly be tenfold for each pH point increase (Deer & Specialist 2001). DO is one of the most important markers for lake, river, and stream water quality. It is a crucial sign of water pollution. Better water quality is associated with higher dissolved oxygen concentrations (Omer no date). The soil sorption coefficient (Kd) and soil organic sorption coefficient (Koc) provide information on the pesticide's capacity to cling to soil particles and particles suspended in water.). Pesticides with high Kd or Koc values have strong soil and water organic matter binding properties. Therefore, fewer pesticides are left to attach to the suspended particles as there is more sediment and organic matter in the water (Whitford et al. no date).

CHAPTER THREE: MATERIALS AND METHODS

3.1 Description of the study area

3.1.1 Location

The study was conducted in Mulanje, the Southern part of Malawi, which borders Mozambique, to the east. Mulanje had a total population of 684,107 people by the year 2018 (National Statistical Office 2019). It is around 65 kilometers from Blantyre, a major business center. The total area of the district is 2,005 square kilometers, which is 2.2 percent of the total surface area of Malawi and is the 6th largest in the southern part of Malawi. The study area lies between longitude 35 38'51" east, latitude 16 2'14" south, and longitude 35 42'26" east, latitude 16 5'39" south (Figure 3). The study area is drained by the Ruo River, which passes through the three tea estates of Ruo, Suaz, and Bluefield. The research area's map, shown in Figure 3, includes twelve sample locations and Table 7 shows the descriptions of the sampling points. The primary source of water for irrigation for these tea farms is the Ruo River. The area of study also includes Muluzi dam located in Bluefield estate, which is used for irrigation as well as for domestic and two boreholes in Bluefield and one borehole in Suaz Estate. It will also include the Muluzi River and Nsuwadzi River, which are tributaries of the Ruo River.

3.1.2 Weather and Climate

The study area has a tropical environment, which has rainy and dry seasons. The dry season starts from May to October, whereas the wet season starts from November to April. The study area receives 74.7 mm of rainfall each month on average. The average yearly temperature measured is 24.25 °C. With a mean temperature of 35 °C, the warmest months are from September to April, while the coldest months are from May to August (Government of Malawi 2017).

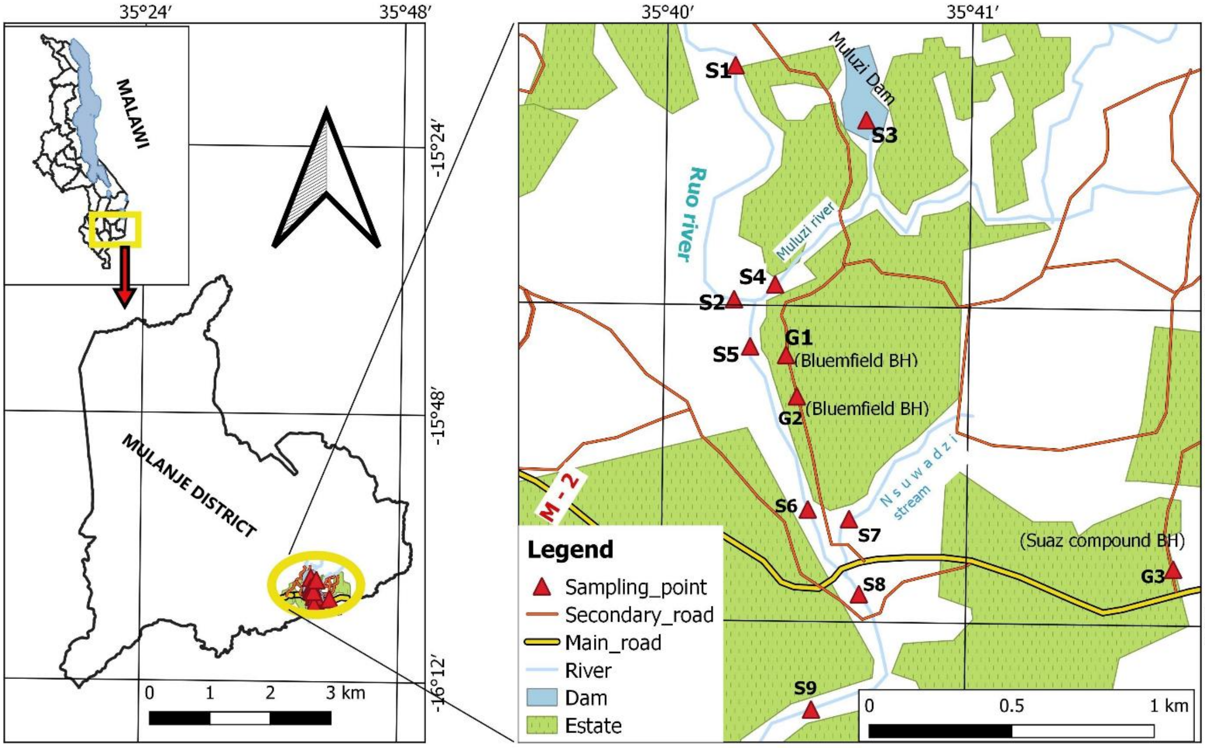


Figure 3 Map of Mulanje District showing the study areas.

3.1.3 Land use and social-economic activities

Mulanje's total land area is 205 600 hectares, of which 12 147 hectares are under the ownership of tea estate. Communities depend on the area beside rivers for farming, which makes it conducive to agriculture. Subsistence farming is a common practice among farmers who cultivate crops like vegetables and maize to make ends meet. The majority of the locals who live close to the tea estates make their living there. In addition, they cultivate cassava, bananas, maize, and pineapples to supplement their income. The Ruo River, which flows through the Ruo tea estate, is utilized to generate electricity through hydroelectric power.

Table 7. Sampling stations showing codes, names, and description of the sites.

Site code	Site name	Coordinates	Description
S1	Upstream Ruo Estate	16º 2 '45" S and 35º 39' 52" E	Used for irrigation by the estates and domestic purposes by the surrounding communities
S2	Downstream Ruo Estate	16º 3' 34.6" S and 35º 52 '65" E	Used for irrigation by the estates and domestic purposes by the surrounding communities
S3	Muluzi dam	16º 2'57.7" S and 35º 40'24.9" E	Used for both irrigation and domestic purposes
S4	Muluzi river	16º 3' 32.4" S and 35º 40' 1.4" E	Used for both irrigation and domestic purposes
S5	Upstream Bluefield Estate	16º 3' 46.7" S and 35º 39' 56.8" E	Used for irrigation by Bluefield tea estate as well as for domestic purposes
S6	Downstream Bluefield Estate	16º 4' 23.5" S and 35º 40' 10.8" E	Used for irrigation by Bluefield tea estate as well as for domestic purposes
S7	Nsuwadzi stream	16º 4'25.5" S and 35º 40' 19.9" E	Used for irrigation by Bluefield tea estate as well as for domestic purposes
S8	Upstream Suaz Estate	16º 4'41.8" S and 35º 40'23.17" E	Used for irrigation by the Suaz tea estate as well as for domestic purposes
S9	Downstream Suaz Estate	16º 5'8.5" S and 35º 40'11.4" E	Used for irrigation by the Suaz tea estate as well as for domestic purposes
G 1	Bluefield borehole 1	16º 3'48.3" S and 35º 40'5.95" E	Within the compound of the Bluefield tea estate, the water is used for drinking
G 2	Bluefield borehole 2	16º 3'58.4" S and 35º 40'8.7" E	Within the compound of the Bluefield tea estate, the water is used for drinking
G 3	Suaz compound borehole	16º 4'36.3" S and 35º 41'37.4" E	Within the compound of the Suaz estate, the water is used for drinking

3.1.4 Hydrology

There are multiple rivers and streams that run down the mountain amid the study's undulating topography. Ruo, Likhubula, Lichenya, and Thuchila are the principal rivers. The Ruo River has three significant tributaries: Likhubula, Lichenya, and Thuchila. Specifically, the Ruo merges with the Shire River in the Chikwawa District. The district's plain zone, which is a section of the Thuchila-Phalombe plain and is generally flat-lying at 600 meters above sea level, contains sections of the southwest, west, and north-western areas (Government of Malawi 2017).

The Ruo River is the main tributary of the Shire River in southern Malawi and Mozambique. It is a part of the Mulanje Massif in Malawi and makes up 80 km of the boundary between Malawi and Mozambique. At Chiromo, it merges with the Shire River. It is a river that is a part of the system of surface water resources border (Government of Malawi 2017). The country's drainage system is made up of 17 Water Resources Areas (WRAs), two of which, Lake Chilwa and Lake Chiuta, drain into lakes other than the Lake Malawi/Shire System. From the 78 Water Resources Units, additional divisions are established from the Water Resources Areas (WRUs) (Government of Malawi, 2021)**.** Malawi's southern Mulanje Massif and Shire Highlands are part of the Ruo River's catchment. The Thuchila River, which drains the Thuchila plain between Mulanje's southwest and Shire Highlands' southeast slopes, is its primary tributary. Near Sandama, the Ruo and Thuchila come together. Another area drained by the Ruo, and its left bank tributaries is the Milange District in neighboring Mozambique. The eastern Shire Highlands' southern region is drained by the Ruo, which has a catchment area of around 4,900 square kilometers. The river frequently floods severely due to strong discharge on occasion (Government of Malawi 2017).

3.1.5 Geology

Mulanje has three unique rock types: granite on the mountain, aegirine, and nepheline in the vicinity of the Mulanje district (Government of Malawi 2017). The earliest rocks in the Mulanje are part of a gneissic basement. Several partially overlapping, subcircular, primarily syenitic plutons from the Upper Jurassic to Lower Cretaceous Chilwa Alkaline Province intrude on this region (Le Couteur & Eng 2011). The existence of the various rocks offers a chance to promote mining. There are four main types of soil in Mulanje. These include clay loam soils, sandy clay loam soils, sandy loam soils, and clay soils (Government of Malawi 2017). The interaction between groundwater and the minerals in the rock or sediment that the water is passing through determines the chemical properties of the water (Panno & Hackley 2010).

3.2 Research Design and Methods

The study was a quantitative experimental study design where samples collected were analyzed for physico-parameters and selected pesticides in a laboratory. This involved measuring the quantities of the parameters in the sample to give an understanding of the concentrations of the pollutants present in the water environment. To achieve an in-depth understanding of the stated objectives, the study collected samples from 12 purposively selected sites (Figure 7) in the dry and rainy seasons to compare seasonal variations of the occurrence in the surface water and groundwater. The summary of the methodology section is presented in the methodology matrix in Table 8.

Table 8: Methodology matrix

Objective	Data to be Used (Variables)	Method of data collection	Data analysis method	Data Analysis tools
To determine the levels of temperature, pH, total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), electrical conductivity (EC) and their relation with occurrence concentrations of pesticides in the surface and groundwater.	pH, Temperature, TSS, DO alpha-cypermethrin, cypermethrin, glyphosate, deltamethrin, s-metolachlor, and terbuthylazine	Insitu analysis using pH/DO meter and gravimetric. -GC-MS/LC-MS-MS for pesticides	Descriptive analysis: One-Way Analysis of Variance (ANOVA), graphs and tables. Principal Component Analysis (PCA), Pearson's correlation	SPSS, Excel
To assess levels of pesticide residues (alpha-cypermethrin, cypermethrin, glyphosate, deltamethrin, s-metolachlor, and terbuthylazine) in surface and groundwater in Mulanje	alpha-cypermethrin, cypermethrin, glyphosate, deltamethrin, s-metolachlor, and terbuthylazine	GC-MS/LC-MS-MS for pesticides	Descriptive analysis: One-Way Analysis of Variance (ANOVA) and graphs and tables	SPSS, Excel,
To assess the risks posed by pesticides to humans on the use of the ground and surface water for human consumption in Mulanje	alpha-cypermethrin, cypermethrin, glyphosate, deltamethrin, s-metolachlor, and terbuthylazine	GC-MS/LC-MS-MS for pesticides	Calculation of Hazard quotient, risk quotient and interpretation according to risk.	SPSS, Excel

3.3 Sample collection

One-liter amber glass bottles were used for the collection of the samples. The samples were collected twice, in the dry and rainy seasons. Triplicates of samples from the upstream and downstream of the Ruo River cutting through the three tea estates of Suaz, Ruo, and Bluefield estates and from Muluzi dam, Muluzi river, and Nsuwadzi stream were collected representing a total of fifty-four (54) samples for the dry and rainy season. Another triplicate of borehole samples was collected from the three boreholes in dry and rainy seasons. located in the Bluefield and Suaz tea estates for the two seasons. In total 72 samples were collected. The sampling locations were chosen based on their ease of access and closeness to the tea gardens. To prevent spreading air bubbles through the samples or trapping them in sealed bottles, sample bottles were cautiously filled to the point of overflow after being washed three times with the water sample. The collected water samples were preserved in ice-cooled boxes and transported to the Malawi Bureau of Standards (MBS) laboratories for analysis. Samples were kept at 4°C after being transported to the laboratory and extraction was completed in 48 hours.

3.4 Analytical quality control and reliability

Recovery efficiencies were evaluated by spiking blank samples (n=5) with 10µg/L pesticide standard solutions. Spiked sample blanks underwent the same extraction, cleanup, and analysis steps as real samples. For analysis, the samples were collected in triplicate. Recoveries were calculated as described in Equation 3. The recovery performance of the extraction method was found to range from 74.9 ± 2.2 to 89.8 ± 1.5 percent. The results fell within the typical permissible limits of 70% to 120% (SANTE 2021). The lack of targeted analytes in the blank reference samples supported the validity of the analytical techniques employed to identify pesticide residues. The chromatographic response's effectiveness on LC MS - MS was also evaluated. (Appendix C).

$$\text{Recovery}(\%) = \text{Amount}\left(\frac{\text{Recovered}}{\text{Spiked}}\right) \times 100 \qquad \text{Equation 3}$$

Blank samples were used in the analysis to give confidence in assuring that the reported results found in the samples are real and not the result of contamination. A blank sample refers to a sample without the analyte going through all the steps of the procedure with the reagents only. The limit of detection (LOD) and limit of quantification (LOQ) of pesticide residue was calculated based on the residual standard deviation of the regression line (σ) and the slope (s) of the calibration curve using LOD=3.3 × σ /S and LOQ=10 × σ/S (Chidya et al. 2022). The LOD and LOQ ranges for all the pesticides were 0.01 – 0.03 µg/L and 0.04 – 0.08 µg/L, respectively.

3.5 Reagents and Standards

Pesticides reference standard solution containing S metolachlor, Terbuthylazine, Cypermethrin, Alpha-cypermethrin, Deltamethrin, and Glyphosate was obtained from Restek USA through Leco Africa Pty Ltd. Chemicals of QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) extraction pouch which contains chemicals such as primary secondary amines (PSA), carbon-18 (C18), graphitized carbon black (GCB), magnesium sulfate ($MgSO_4$), and sodium acetate (NaOAc) were individually purchased from Agilent Technologies, USA. All other chemicals such as analytical grade anhydrous magnesium sulfate ($MgSO_4$) acetonitrile (MeCN), and acetic acid (HOAc) 1% HOAc in MeCN. —prepared on a v/v basis (e.g., 10 mL glacial HOAc in a 1 L MeCN solution), anhydrous sodium acetate (NaOAc), primary secondary amine (PSA) sorbent, helium gas) high purity w of HPLC grade from Sigma-Aldrich, and Rankem Chemicals (Gurugram, Haryana, India).

3.6 Cleaning of sample glassware and sample preparation

All glassware was washed with acetone, thoroughly rinsed with distilled water, and then dried in an oven for about five hours. The collected samples (1000 mL) were filtered through a Whatman filter paper No 1 to remove debris, suspended materials, and extracted by the QuEChERS method. The water samples were placed in a centrifuge tube containing 1 mL of 1% acetic acid (HOAc) in MeCN and 0.5 g anhydrous MgSO4 /NaOAc (4/1, w/w) per g sample. The resulting mixture was shaken and centrifuged. This final extract was transferred to autosampler vials for analysis by gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem-mass spectrometry (LC/MS/MS) to identify and determine levels of pesticide residues.

3.7 Pesticide residues analysis

The extracted pyrethroid, viz. cypermethrin, deltamethrin, and alpha-cypermethrin were analyzed from water samples by using Gas Chromatography-Mass Spectrophotometry (GC MS) (Agilent 7890A GC system in tandem with 5975C mass spectrometer detector) fitted with reverse phase sorbets C18 Column (250 mm × 4.6 mm ID; pore size 5 µm) The initial oven temperature was maintained at 75 ^{o}C for 0.5 min, then increased to 150 ^{o}C at a rate of 8 ^{o}C min-1 and again to 280 ^{o}C at a rate of 10 ^{o}C min-1 for 10 min. Helium (He) head pressure on the column was set at 10 psi and constant flow was 1.0 mL/min with systems capable of electronic pressure/flow control. A 10-µL analyte was introduced to the GC MS system. The flow rate was adjusted to 1 mL/ minute at 30 °C.

The extracted herbicides viz terbuthylazine, glyphosate, and S -Metolachlor were detected from the water samples by using Liquid Mass Spectrophotometry- Mass Spectrophotometry (LC-MS/MS) (Agilent HPLC 1290 series in tandem with triple quad 6460 LC/ MS). The LC-MS/MS was used for the herbicide's analysis because of the polar components and that they are thermally labile hence the difficulty in accurately analyzing the GC-MS. The LC conditions were a 15 cm long, 3.0 mm id, 3 mm particle size C18 column, a flow rate of 0.3 mL/min, and gradient elution with an initial condition of 25% MeOH in 5 mM formic acid solution taken linearly in 15 min to 90% MeOH in 5 mM formic acid solution and held for 15 min. The mobile phase used was a composition of acetonitrile 100 percent with 0.1 percent formic acid as an additive.

3.8 Physico-chemical quality parameter analysis

Levels of pH, temperature, dissolved oxygen (DO), and total dissolved solids (TDS) were determined in the field right at the point of sampling, using the Multiparameter meter model HI98194. All parameters were determined and recorded three times on-site to ensure that the readings taken were accurate.

The total suspended solids were determined by gravimetry by filtering 100 mL of water through a Whatman GF/A glass fiber filter on a buncher funnel attached to a vacuum pump. The filter papers were then placed on glass Petri dishes and dried in an oven at temperatures of 103 °C – 105 °C- before and after filtration with cooling to room temperature in desiccators weighing until a constant mass was achieved. TSS was calculated from the difference between the mass of the filter paper after and before filtering divided by the sample volume.

3.9 Human health risk assessment

In the present study, the potential non-carcinogenic health risks associated with the consumption of contaminated surface and groundwater with cypermethrin and S-metolachlor pesticide residues were assessed based on the hazard quotient (HQ). Pesticides are potentially dangerous to people and can have both short- and long-term adverse effects on health, depending on the amount and routes to which a person is exposed (US EPA 2015). Therefore, the noncarcinogenic risks posed by those Cypermethrin and S metolachlor pesticides through the consumption of drinking water from various regions of Ruo were calculated. Hazard Quotients (HQ) were calculated to assess non-carcinogenic risk for chronic and acute exposure.

3.9.1 Chronic exposure

The chronic daily intake (CDI) of cypermethrin and s-metolachlor pesticides through the ingestion of water was calculated according to Equation 4 (Hu et al. 2011).

$$CDI = \frac{C \times IRi \times EFi}{BWi \times AT} \quad \text{Equation 4}$$

where C denotes the median and highest recorded amounts of each pesticide in water as measured in milligrams per liter (mg/L), EFi denotes the exposure frequency (365 days/year for both ages), EDi denotes the exposure duration (6 years for children and 70 years for adults), BWi denotes the total body mass of the exposed person (20 kg for children and 70 kg for adults), AT denotes the mean life expectancy (2 190 and 25 550 days for children and adults, respectively) and the IRi represent the water ingestion rate (0.87 L/ day for 6 years age of children and 1.41 L/day for 70 years of age of adults) (Fijałkowska et al. 2022).

The HQ is the ratio between the calculated chronic daily intakes (CDI) of pesticide to the oral reference dose (RfD) for the same pesticide. The RfD values for Cypermethrin and S-metolachlor are 0.01 and 0.19, respectively. The RfD value is represented by mg/kg bw/ day. The HQ is an accurate assessment of the potential for contact or a measured risk of developing non-cancerous medical effects following a typical exposure period. Equation 5 depicts how this is computed (Shi et al. 2011).

$$Hazard\ Quotient\ (HQ) = \frac{CDI}{RfD} \quad \text{Equation 5}$$

3.9.2 Acute exposure

The average daily intake (ADI) of Cypermethrin and S-metolachlor was calculated using Equation. (6) (Jaipieam et al. 2009).

$$Dpot = C \times IngR \qquad \text{Equation 6}$$

Where:

Dpot = Potential Dose

C (μg/L) = Pesticide concentration,

IngR (L/day) = Intake/Ingestion Rate of water

The potential dose was converted to an Average Daily Intake by dividing it by the body weight.

$$ADI = \frac{Dpot}{BW} \qquad \text{Equation 7}$$

Where:

BW = Body Weight

The hazard quotient for the acute exposure was calculated using Equation 8.

$$HQ = \frac{ADI}{RfD} \qquad \text{Equation 8}$$

The danger is regarded to be minor to low and the exposed population of receptors will not encounter adverse effects if the value of HQ is less than or equal to 1.0. However, if the HQ value is greater than 1.0, there may be an undesirable effect, and the likelihood of harm will be moderate to high (Sparling 2016).

3.10 Relationship of physico-chemical water parameters and the concentrations of pesticides.

The statistical analysis was conducted by the IBM Statistical Package for Social Sciences (SPSS) version 22.0. Pearson correlation was performed to determine the relationship between the concentration of pesticides and the physicochemical water parameters.

The principal component analysis (PCA) was also used to assess the relation between the physico-chemical water quality parameters and the occurrence of pesticide residues in the surface and groundwater. The PCA in varimax rotation mode was performed on the mean S metolachlor and cypermethrin residues data. The analysis was done in two parts, dry and rainy seasons for S metolachlor and cypermethrin. From the analysis of the dry season, the variables were reduced to three principal components from the data set with Eigenvalues > 1. Measurements below the detection limit were taken as zero during the PCA.

3.11 Comparison of pesticide residues levels with WHO Water Standards and Other Worlds Standards.

The comparison was carried out between the WHO, EU and Australian water standards and the mean concentrations of both Cypermethrin and S-metolachlor in groundwater or surface water regardless of the season. The values for the dry and rainy seasons on each pesticide were combined and the means were computed which was compared with the three water standards. The t-test was used for the comparison of the pesticide's residues against the water standards.

3.12 Statistical Analysis and data management

The statistical examination was performed by using the IBM Statistical Package for Social Sciences (SPSS) version 22.0. Microsoft Excel (2019) software was used for descriptive analysis such as means, ranges and standard deviation as well as a graphical presentation of the data obtained. The PCA was used to extract principal components using varimax rotation. A one-way analysis of variance (ANOVA) was used to look at significant differences in the physicochemical parameters evaluated and the amounts of pesticide residues recorded from the various sites in the dry and rainy seasons. Pearson's correlation and t-test were done to determine whether there was a connection between pesticide residue levels and the physical-chemical characteristics of water and to compare the mean levels of pesticide residues in surface and groundwater and the WHO water standards. The 95% confidence level ($p < 0.05$) was used for the statistical significance testing.

CHAPTER FOUR: RESULTS

4.1 Physico-chemical parameters in surface and groundwater

The results of the physico-chemical parameters of water samples namely pH, temperature, total dissolved solids, dissolved oxygen, conductivity, and total suspended solids from the sites in the tea growing areas for surface and groundwater in the dry and rainy seasons have been summarized in Appendix. D and E.

4.1.1 pH of the water

The measured pH for surface water varied between 7.30 and 7.70 with an average value of 7.42±0.14 during the dry season. The pH during the rainy season varied between 6.34 and 7.55 with a mean value of 6.68±0. 37. The measured pH for the groundwater ranged from 6.70 to 6.90 with a mean value of 6.78 ±0.11 during the dry season. During the rainy season, the pH for groundwater ranged from 5.65 to 5.93 with an average value of 5.77 ± 0.15. Analysis of Variance (ANOVA) shows that there are significant differences ($p<0.05$) in pH mean between surface and groundwater in the dry and rainy seasons. (Appendix E). The trends and patterns of pH values in the dry and rainy seasons are presented in Figure 4.

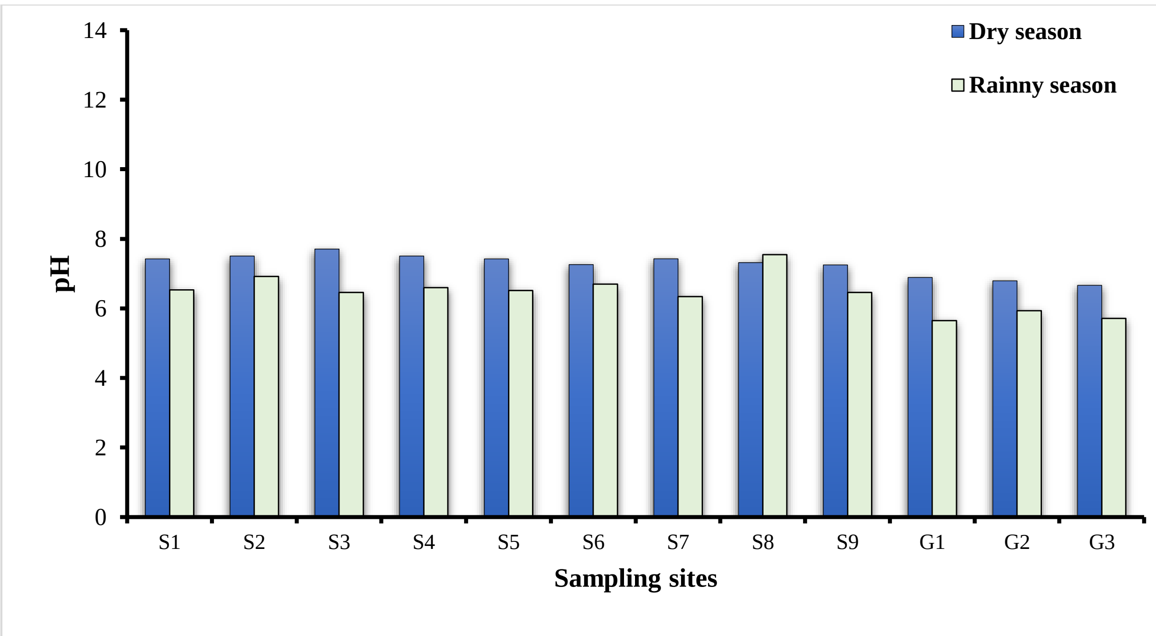


Figure 4 pH of surface and groundwater

4.1.2 Total suspended solids

The total suspended solids (TSS) for surface water during the dry season ranged from 0.47 mg/L to 26.90 mg/L with a mean value of 9.12±8.16 mg/L. During the rainy season, TSS ranged from 178.00 mg/L to 260.00 mg/L with a mean value of 216.00 ± 32.60 mg/L. The TSS for groundwater ranged from 4.60mg/l to 17.20 mg/l with a mean value of 12.73 ± 7.06mg/L During the rainy season the TSS for groundwater ranged from 206.00 mg/L to 316.00 mg/L with a mean value of 246.17±60.66mg/L. Analysis of Variance (ANOVA) shows that there are no significant differences ($p>0.05$) in the total suspended solids mean between surface and groundwater in the dry and rainy seasons. (Appendix E). The trends and patterns of TSS content for surface and groundwater in the dry and rainy seasons are presented in Figure 5.

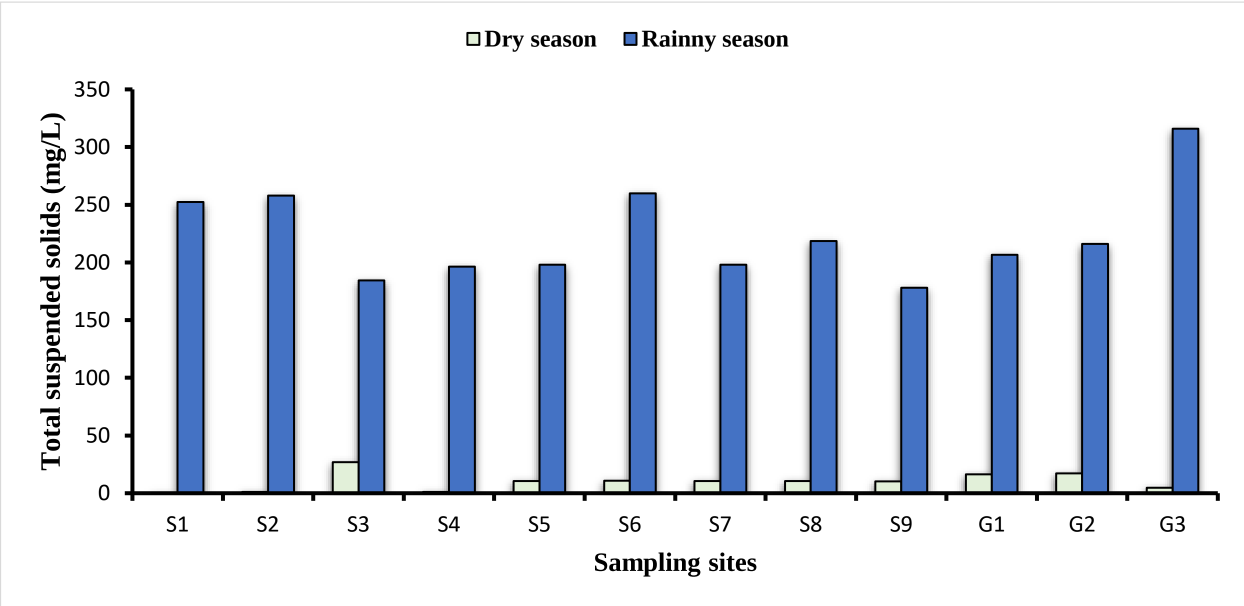


Figure 5 Total suspended solids for surface and groundwater

4.1.3 Total dissolved solids of water

The total dissolved solids (TDS) for surface water ranged from 17.0 mg/l to 27.0 mg/l with a mean value of 21 ± 2.78mg/L. During the rainy season, the TDS ranged from 5.00 mg/L to 25.00 mg/L with a mean value of 11.33±7.28 mg/L. The TDS for groundwater during the dry season ranged from 63.33 mg/L to 135.00 mg/L with a mean value of 88.22 ±40.54mg/L. During the rainy season the TDS for groundwater ranged from 57.00 mg/L to 148.33 mg/L with a mean value of 89.33 ±50.90mg/L. Analysis of Variance (ANOVA) shows that there are significant differences ($p<0.05$) in TDS mean between surface and groundwater in the dry and rainy seasons. (Appendix E). The trends and patterns for surface and groundwater in the dry and rainy seasons are Figure 6.

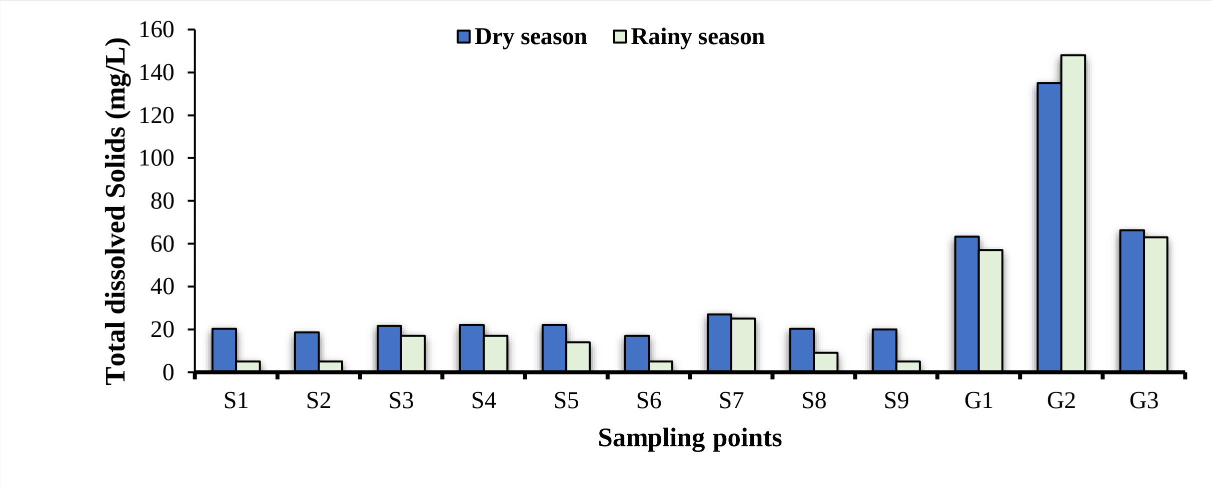


Figure 6 Total dissolved solids for surface and groundwater

4.1.4 Dissolved Oxygen of water

The dissolved oxygen (DO) content for surface water ranged from 4.64 mg/L to 6.69 mg/L with a mean value of 5.91 ± 0.81 mg/L during the dry season. During the rainy season, the DO ranged from 4.07 mg/L to 4.86 mg/L with a mean value of 4.59 ± 0.23 mg/L. The DO for groundwater in the dry season ranged f from 4.10 mg/L to 5.50 mg/L with a mean value of 4.85 ± 0.71mg/L During the rainy season the DO for ground water ranged from 3.43 mg/L to 3.99 mg/L with a mean value of 3.72 ± 0.28 mg/L. Analysis of Variance (ANOVA) shows that there are significant differences ($p<0.05$) in DO mean between surface and groundwater in the dry and rainy seasons. (Appendix F). The trends and patterns of for surface and groundwater in dry and rainy seasons are presented in Figure 7.

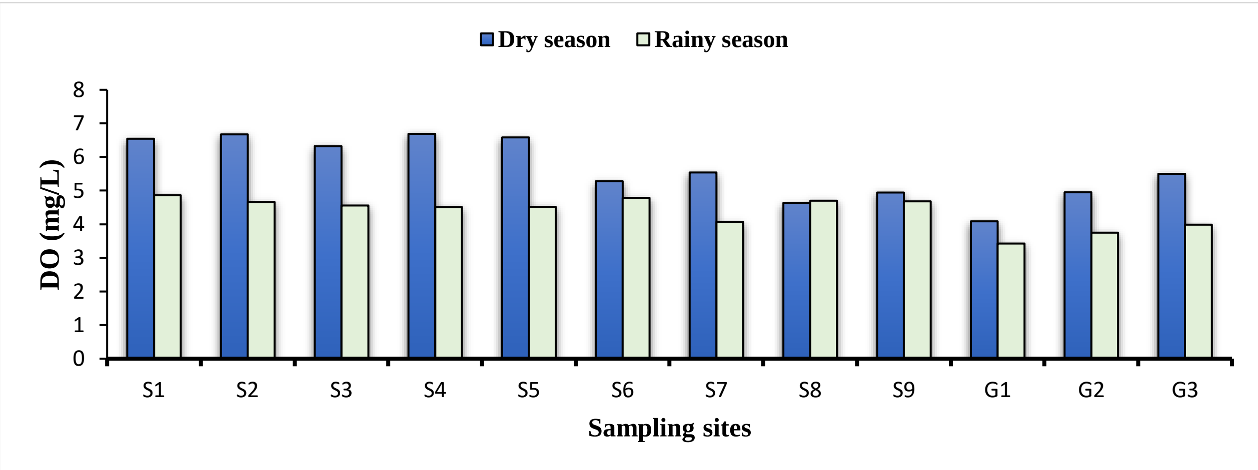


Figure 7 Dissolved Oxygen for surface and groundwater.

4.1.5 Temperature of water

The temperature for surface water varied between 24.48 °C and 26.45 °C with a mean value of 25.48±0.62 °C. During the rainy season, the temperature varied between 24.26 °C and 25.05 °C with an average value of 24.74±0.31 °C. The temperature for the groundwater varied between 25.40 °C and 25.90 °C with an average value of 25.58±0.24 °C during the dry season. During the rainy season, the temperature for groundwater varied between 24.8.0 °C and 24.9 °C with a mean value of 25.85±0.24 °C. Analysis of Variance (ANOVA) shows that there are no significant differences ($p>0.05$) in temperature mean between surface and groundwater in the dry and rainy seasons. (Appendix E). Temperature trends and patterns of the surface and groundwater during the dry and rainy seasons are presented in Figure 8.

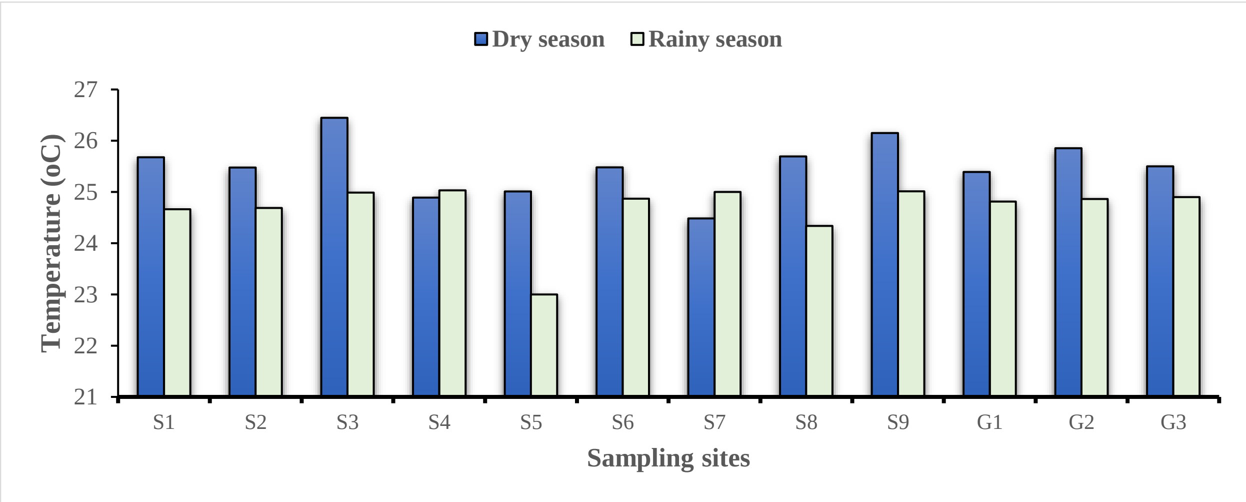


Figure 8 Temperature of surface and groundwater

4.1.6 Electrical conductivity of water

The electrical conductivity (EC) for surface water varied between 26.33μS/cm and 45.33 μS/cm with an average value of 33.67±5.12μS/cm during the dry season. During the rainy season, the EC varied between 8.00 μS/cm and 43.33μS/cm with an average value of 22.67±14.32μS/cm. The EC for the groundwater varied between 139.00μS/cm and 195.00μS/cm with a mean value of 163.33±28.71μS/cm during the dry season. During the rainy season the EC for groundwater varied between 60.20μS/cm and 93.33μS/cm with a mean value of 80.84±18μS/cm. Analysis of Variance (ANOVA) shows that there are significant differences ($p<0.05$) in EC mean between surface and groundwater in the dry and rainy seasons. (Appendix E). The trends and patterns of EC of the surface and groundwater during the dry and rainy seasons are presented in Figure 9.

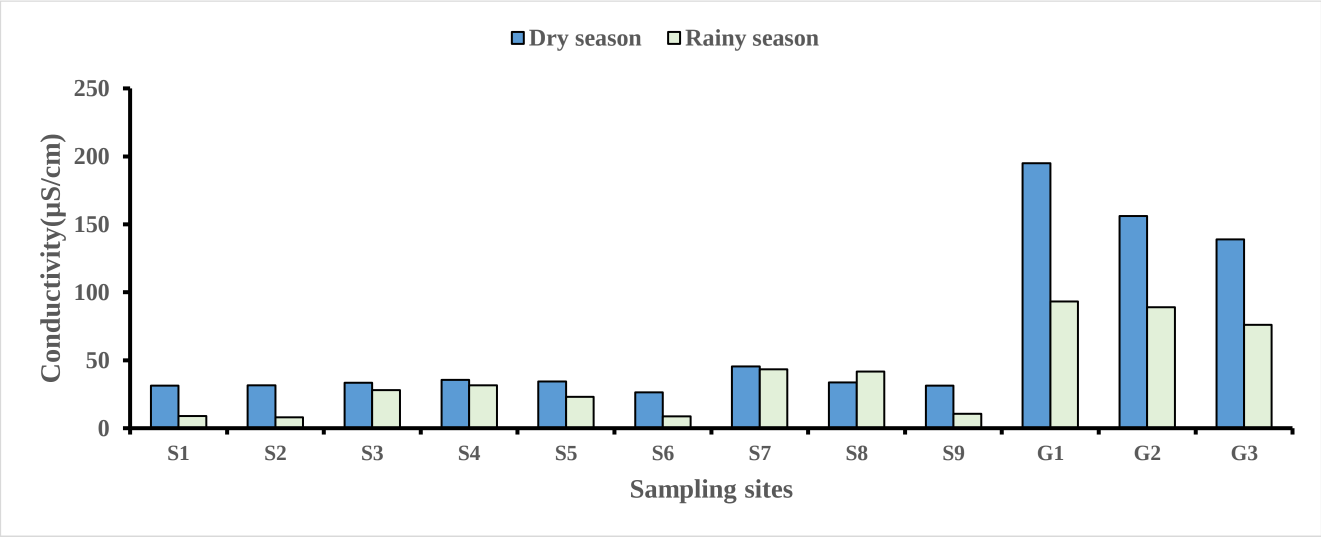


Figure 9 Electrical Conductivity of surface and groundwater

4.2 Occurrence of pesticide residues in surface and groundwater

Two pesticide residues were detected in surface and groundwater, these were S- metolachlor, and cypermethrin whilst alpha-cypermethrin, deltamethrin, glyphosate, and terbuthylazine were below detection limits in both surface and groundwater. The pesticide concentrations in surface and groundwater (mean and frequency of detection) are summarized in Table 10 and Table 11. The frequency of detection was in the order of cypermethrin (100% of the samples) both in the dry and rainy seasons and in S metolachlor (66.7%) in the dry season and 77.8 % in the rainy season.

Table 9: The mean concentrations of pesticides in surface water

Site	Cypermethrin		Terbuthylazine		Alpha cypermethrin		Deltamethrin		S metolachlor		Glyphosate	
	Mean pesticide concentrations in surface water(µg/L)											
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
S1	0.536	1.118	bdl	bdl	bdl	bdl	bdl	bdl	0.614	5.427	bdl	bdl
S2	0.713	1.009	bdl	bdl	bdl	bdl	bdl	bdl	0.918	2.545	bdl	bdl
S3	0.252	0.688	bdl	Bdl	bdl	bdl	bdl	bdl	0.493	5.036	bdl	bdl
S4	0.461	0.769	bdl	bdl	bdl	bdl	bdl	bdl	1.99	10.964	bdl	bdl
S5	0.870	1.137	bdl	bdl	bdl	bdl	bdl	Bdl	bdl	bdl	bdl	bdl
S6	0.952	1.068	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S7	0.365	0.528	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.115	bdl	bdl
S8	0.092	0.834	bdl	bdl	bdl	bdl	bdl	bdl	0.399	10.814	bdl	bdl
S9	0.098	0.679	bdl	bdl	bdl	bdl	bdl	bdl	0.325	13.324	bdl	bdl
FD %	100	100	-		-		-		66.7	77.8		

bdl: below the detection limit, FD: frequency of detection, S: Surface water, G: Groundwater

Table 10: The mean concentration of pesticides in groundwater

Site	Cypermethrin		Terbuthylazine		Alpha cypermethrin		Deltamethrin		S metolachlor		Glyphosate	
	Mean pesticide concentrations in groundwater(µg/L)											
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
G1	bdl	1.047	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
G2	bdl	1.024	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
G3	bdl	0.763	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
FD%	-	100	-	-	-	-	-	-	-	-	-	-

bdl: below the detection limit, FD: frequency of detection, S: Surface water, G: Groundwater

During the dry and rainy seasons, the following results were obtained for cypermethrin and s - metolachlor pesticides.

4.2.1 Occurrence of cypermethrin

Samples taken during the dry season at points G1, G2 and G3 showed below detection levels whereas point S6 showed a relatively high level of cypermethrin (0.952 µg/L) and lowest at S8 (0.092 µg/L). During the rainy season, the lowest level was at point S7 (0.528 µg/L). Point S5 had a high level of 1.137 µg/L. There were detectable levels of the pesticide higher in the up streams (points S1, S5, and S8; 1.118, 1.137 and 0.834 µg/L, respectively than in the downstream at points S2 (1.009µg/L) S6 (1.068 µg/L) and S9 (0.679 µg/L) (Figure 10). Analysis of Variance (ANOVA) shows that there are significant differences ($p<0.05$) in cypermethrin mean between surface and groundwater in the dry and rainy seasons. (Appendix F).

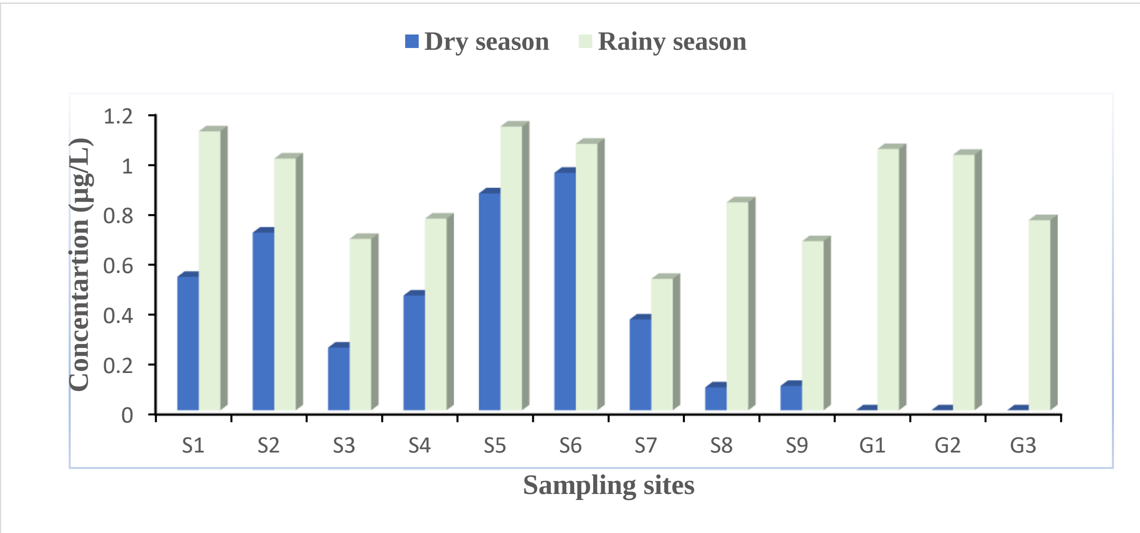


Figure 10 Levels of Cypermethrin

4.2.2 Occurrence of S metolachlor

Samples taken during the dry season at points S5, S6 and S7 showed below detection levels whereas point 4 had a relatively high level of metolachlor (1.990 ug/L), and point S9 had the lowest detectable level of the pesticide (0.325 ug/L). During the rainy season, the level at points S5 and S6 remained below detection level, and the level at point S7 increased to 1.115 ug/L whereas point 9 had a relatively high level of metolachlor at 13.324. There were below detection levels of S metolachlor at points G1, G2 and G3 during both the dry and rainy seasons (Figure 11). Analysis of Variance (ANOVA) shows that there are no significant differences ($p<0.05$) in s - metolachlor mean between surface and groundwater in the dry and rainy seasons. (Appendix F).

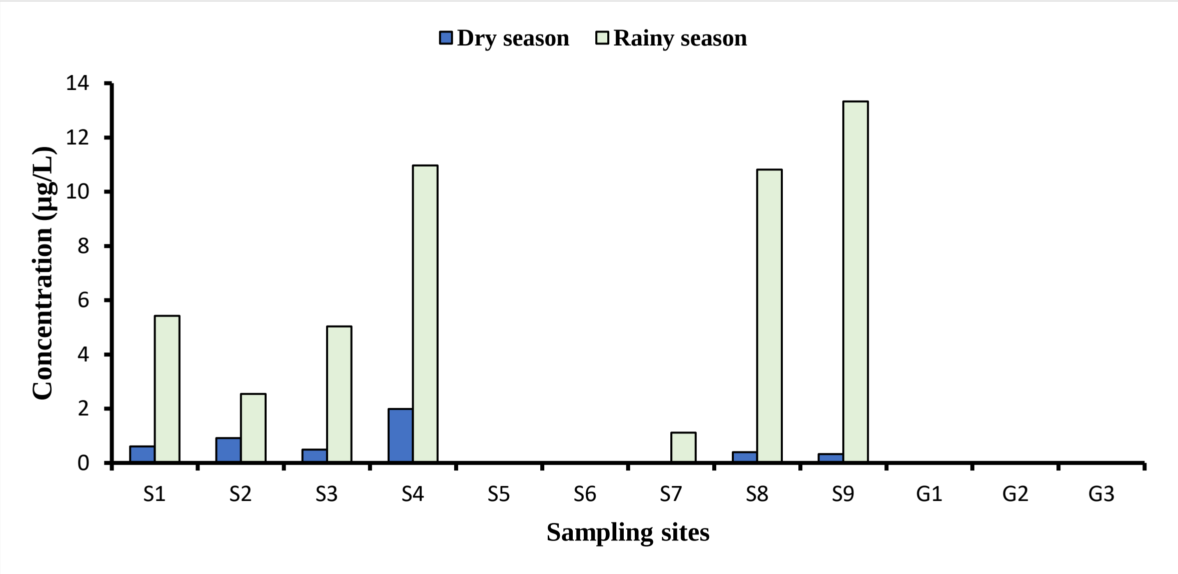


Figure 11 Levels of S – metolachlor

4.3 Comparison of the physico-chemical parameters and pesticide residues with the World Health Organization and other globally recommended drinking water standards.

The levels of physico-chemical parameters and pesticide residues obtained for the surface and groundwater were compared with the WHO, EU, and Australian drinking water standards. The range of S metolachlor for Surface water: (bdl-1.990 µg/L) and bdl for groundwater during the dry season and bdl-13.324 µg/L for surface water and bdl for groundwater during the rainy season respectively (Table 10 and Table 11) obtained in this study were within the Australian Drinking Water Quality Recommended Guideline Value of 300µg/L S metolachlor residue maximum allowed concentration. The levels of S metolachlor residue obtained during the rainy season at sites S4 (10.964 µg/L), S7 (10.814 µg/L), and S9 (13.324 µg/L) were above the WHO

Recommended S metolachlor Residue Limit (10 µg/L). During the dry season, all the sites were within the WHO Recommended S metolachlor Residue Limit whereas sites S5, S6, S7, G1, G2 and G3 were within the EU drinking water limit of individual pesticide of 0.1 µg/L During the rainy season S5, S6, G1, G2 and G3 were within the EU drinking water limit of individual pesticide of 0.1 µg/L. In general, the levels of S metolachlor residue obtained for groundwater were below the WHO, EU, and Australian recommended drinking water standards for the dry and rainy seasons. The levels of Cypermethrin for the rainy season for both the surface and groundwater were above the EU drinking water limit of individual pesticides of 0.1 µg/L whereas all the sites expect groundwater G1, G2 and G3 and surface water from sites S8 and S9 were within the EU drinking water limit during the dry season.

The mean pH values for surface water during dry (7.42) and rainy (6.68) seasons were within the WHO acceptable limits of 6.5-8.5 recommended for drinking water levels. The mean pH values for groundwater during the dry season (7.42) were within the WHO acceptable limits whilst during the rainy season it was below the WHO acceptable limits of 6.5-8.5 recommended for drinking water levels. The mean TDS for both surface and groundwater during the dry and rainy seasons were within the WHO acceptable limits of 1000mg/L recommended for drinking water levels (World Health Organization 2008)

4.4 Relation between physical chemical water parameters and pesticide residues using Pearson Correlation Analysis.

4.4.1 pH

The relationship between pH and levels of S metolachlor and cypermethrin residues in the water samples was assessed using Pearson correlation as shown in Table 12. The correlation showed that there was a statistically significant correlation ($p<0.05$) between pH and S metolachlor concentration in the surface and groundwater in the dry season and rainy seasons. The R-value (0.535) showed that the pH increases with increasing S metolachlor concentration and vice versa during the rainy season. The R-value (0.503) also showed that the pH increases with the increase in S metolachlor concentration and vice versa during the dry season. However, the correlation between pH and Cypermethrin was significant in the dry season ($r=0.561$, $p=0.03$) and a negative insignificant correlation in the rainy season ($r = -0.011$, $p = 0.49$).

4.4.2 Temperature

The relation of temperature on s - metolachlor and cypermethrin residues concentration was evaluated using Pearson correlation as shown in Table 12. The correlation showed that there was no statistically significant relationship ($p>0.05$) in temperature changes on s - metolachlor concentrations in the surface and groundwater for the dry and rainy seasons. The R-value (0.206) showed that temperature increases with increasing s - metolachlor concentration and vice versa during the rainy season. The R-value (-0.113) showed that temperature decreases with increasing s - metolachlor concentration and vice versa during the dry season and it was insignificant. There was a negative significant relationship between temperature and cypermethrin ($r = -0.508$, $p = 0.05$) in the dry season and a negative insignificant relationship ($r = -0.351$, $p = 0.133$) in the rainy season.

4.4.3 Dissolved Oxygen

The relation of dissolved oxygen on s - metolachlor and cypermethrin residue concentration was assessed using Pearson correlation. The correlation showed that there was a statistically significant relationship ($p<0.05$) between DO and s - metolachlor concentration in the surface and groundwater in the dry season and rainy seasons. The R-value (0.515) showed that the DO increases with increasing s - metolachlor concentration and vice versa during the rainy season. The R-value (0.563) also showed that the DO increases with the increase in s - metolachlor concentration and vice versa during the dry season. The correlation between DO and cypermethrin was significant in the rainy season ($r=0.623$, $p=0.015$), and a low correlation and insignificant correlation in the dry season ($r = 0.043$, $p = 0.445$).

4.4.4 Total dissolved solids

The relation of total dissolved solids on s - metolachlor and cypermethrin residue concentration was assessed using Pearson correlation. The correlation showed that there was a negative statistically significant relationship ($p<0.05$) between total dissolved solids and cypermethrin concentrations in the surface and groundwater in the rainy season. The R-value (-0.564) showed that total dissolved solids decrease with increasing cypermethrin concentration and vice versa during the dry season. Similarly, the R-value (-0.440) showed that total dissolved solids decrease with increasing s - metolachlor concentration and vice versa during the rainy season and in the dry season ($r=-0.354$, $p=0.129$). However, there was a positive correlation between TDS and Cypermethrin concentration ($r=0.121$, $p=0.34$) though insignificant.

4.4.5 Total suspended solids.

The relation of total suspended solids on s - metolachlor and cypermethrin residue concentration was assessed using Pearson correlation. There was a negative insignificant correlation between TSS and s - metolachlor in the rainy season ($r = -0.422$, $p = 0.086$) and dry season ($r=-0.467$, $p=0.06$). The R-value (0.286) showed that total suspended solids increase with increasing cypermethrin concentration and vice versa during the dry season but insignificant ($p>0.05$). The R-value (-0.340) showed that total suspended solids decrease with increasing cypermethrin concentration and vice versa during the rainy season.

4.4.6 Electrical conductivity

The relation of electrical conductivity on s - metolachlor and cypermethrin residues concentration was assessed using Pearson correlation There was a negative insignificant correlation between EC and S metolachlor in the rainy season ($r = -0.387$, $p = 0.107$) and dry season ($r=-0.343$, $p=0.138$). The R-value (0.105) showed that EC increases with increasing cypermethrin concentration and vice versa during the dry season but is insignificant ($p>0.05$). The R-value (-0.560) showed that total suspended solids decrease with increasing cypermethrin concentration and vice versa during the dry season.

Table 11: Relation between physicochemical water parameters and pesticides during the dry and rainy seasons

	Cypermethrin	S Metolachlor	TSS	TDS	Temp	DO	pH	EC
Dry season								
Cypermethrin	1							
S – Metolachlor	0.17	1						
TSS	-0.34	-0.467	1					
TDS	-0.564*	-0.354	0.292	1				
Temp	-0.351	-0.113	0.466	0.133	1			
DO	0.623*	0.563*	-0.397	-0.434	-0.176	1		
pH	0.561*	0.503*	-0.027	-0.779**	-0.039	0.646*	1	
EC	-0.560*	-0.343	0.28	0.999**	0.129	-0.423	-0.771**	1
Rainy season								
Cypermethrin	1							
S – Metolachlor	-0.409	1						
TSS	0.286	-0.422	1					
TDS	0.121	-0.44	0.099	1				
Temp	-0.508*	0.206	0.093	0.166	1			
DO	0.043	0.515*	0.009	-0.767**	-0.175	1		
pH	-0.011	0.535*	-0.137	-0.638*	-0.24	0.791**	1	
EC	0.105	-0.387	0.083	0.994**	0.153	-0.750**	-0.568*	1

*. Correlation is significant at the 0.05 level (1-tailed).

**. Correlation is significant at the 0.01 level (1-tailed).

4.5 Relation between physico-chemical water parameters and pesticide residues using Principal Component Analysis.

The PCA with the varimax rotation results are summarized in Table 13. The Kaiser-Meyer-Olkin (KMO) measure of adequacy was 0.512 at 0.000 significance. The three PCs were extracted, which explained 81.56% of the observed variations during the dry season. Similarly, three principal components were extracted during the rainy season from the data set with Eigenvalues >1, which explained 78.06% of the observed variations. The KMO measure of sampling adequacy was 0.579 at 0.00 significance. The PC1 was associated with TDS, pH, EC, and cypermethrin. The PC2 was associated with TSS, DO and S-metolachlor whilst PC3 was associated with TSS and temperature during the dry season. In the rainy season, PC1 was associated with TDS, DO, pH, EC and s - metolachlor and PC2 was associated with temperature whilst PC3 was associated with TSS.

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Table 12: Principal Component loading for the dry and rainy seasons

Parameter	Dry season			Rainy season		
	PC 1	**PC 2**	**PC 3**	**PC 1**	**PC 2**	**PC 3**
Cypermethrin	**0.70**	0.09	-0.46	-0.03	-0.77	0.38
S – Metolachlor	0.17	**0.92**	-0.05	**0.50**	0.44	-0.04
TSS	-0.04	**-0.51**	**0.72**	-0.05	-0.05	**0.96**
TDS	**-0.93**	-0.17	0.09	**-0.93**	-0.02	0.07
Temperature	-0.08	0.03	**0.89**	-0.18	**0.90**	0.20
DO	0.46	**0.67**	-0.20	**0.92**	-0.06	0.08
pH	**0.85**	0.38	0.14	**0.82**	-0.11	-0.12
EC	**-0.93**	-0.15	0.09	**-0.91**	-0.03	0.05
Eigenvalue	3.18	1.76	1.59	3.49	1.61	1.15
% of variance	39.73	21.94	19.94	43.63	20.11	14.32
Cumulative %	39.73	61.67	81.56	43.63	63.74	78.06

Suspended solids, TDS: Total Dissolved Solids, DO: Dissolved Solids, EC: Electrical Conductivity TSS: Total Suspended Solids

*Bold-faced indicates high loadings

4.6 Human health risk assessment of s - metolachlor and cypermethrin in surface and groundwater

4.6.1 Risk assessment for chronic exposure

Risk assessment of s - metolachlor and cypermethrin residues intake from chronic exposure was estimated as Chronic Daily Intake (CDI). For chronic exposure to s - metolachlor, the HQ for surface water in the dry season ranged from 0 to 0.344 (Adults) and 0 to 0.733 (Children); and 0 to 1.413 (Adults) and 0 to 3.050 (Children) in the rainy season while the hazard quotient for groundwater was nil for both seasons for adults and children (Table 13). For chronic exposure to cypermethrin, the HQ for the surface water in the dry season ranged from 0.042 to 0.446 (Adults) and 0.084 to 0.896 (Children); and 1.145 to 2.466 (Adults) and 2.297 to 4.945 (Children) in the rainy season while the HQ for groundwater ranged from 0.343 to 0.396 (Adults) and from 0.679 to 0.784 (Children) in the dry season and from 1.655 to 2.271 (Adults) and 3.319 to 4.554 (Children) in the rainy season (Table 13).

4.6.2 Risk assessment for acute exposure

S - metolachlor and cypermethrin residue levels in surface and groundwater water were used to assess human exposure through oral intake/ingestion. The population groups considered in this study were adults and children. The HQ for acute exposure of s - metolachlor to surface water ranged from 0 to 0.086 for adults; 0 to 0.173 for children in the dry season and 0 to 0.537 for adults and 0 to 1.159 for children in the rainy season. For groundwater, the hazard quotient (HQ) was nil for adults and children in both seasons. (Table 14). The HQ for acute exposure of cypermethrin to surface water ranged from 0.005 to 0.056 for adults; 0.01 to 0.111 for children in the dry season and 0.294 to 0.485 for adults and 0.459 to 0.972 for children in the rainy season. For groundwater, the hazard quotient (HQ) was 0.042 to 0.049 for adults and (0.084 to 0.097) for children in the dry season and 0.331 to 0.454 for adults, and 0.664 to 0.911 for children in the rainy season. (Table 14). Statistically, all variables expect chronic exposure to s metolachlor and chronic exposure to cypermethrin to children have p values less than 0.05 as such there was no significant risk to human health.

Table 13: Human health risk assessment of s – metolachlor and cypermethrin residues in water samples due to chronic exposure

Site	S - metolachlor								Cypermethrin							
	Surface water				Groundwater				Surface water				Groundwater			
	Dry season		Rainy Season		Dry season		Rainy Season		Dry		Rainy		Dry		Rainy	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
S1	0.106	0.226	0.575	**1.242**	na	na	na	na	0.446	0.882	**2.424**	**4.862**	na	na	na	na
S2	0.159	0.338	0.270	0.583	na	na	na	na	0.400	0.791	**2.189**	**4.389**	na	na	na	na
S3	0.085	0.182	0.534	1.153	na	na	na	na	0.269	0.532	**1.492**	**2.993**	na	na	na	na
S4	0.344	0.733	**1.162**	**2.510**	na	na	na	na	0.308	0.609	**1.668**	**3.345**	na	na	na	na
S5	0.000	0.000	0.000	0.000	na	na	na	na	0.453	0.896	**2.466**	**4.945**	na	na	na	na
S6	0.000	0.000	0.000	0.000	na	na	na	na	0.042	0.084	**2.317**	**4.646**	na	na	na	na
S7	0.000	0.000	0.118	0.255	na	na	na	na	0.209	0.413	**1.145**	**2.297**	na	na	na	na
S8	0.069	0.147	**1.146**	**2.476**	na	na	na	na	0.326	0.644	**1.809**	**3.628**	na	na	na	na
S9	0.056	0.120	**1.413**	**3.050**	na	na	na	na	0.237	0.469	**1.471**	**2.949**	na	na	na	na
G1	na	Na	Na	na	0.000	0.000	0.000	0.000	na	na	na	na	0.347	0.686	**2.271**	**4.554**
G2	na	Na	Na	na	0.000	0.000	0.000	0.000	na	na	na	na	0.396	0.784	**2.221**	**4.454**
G3	na	Na	Na	na	0.000	0.000	0.000	0.000	na	na	na	na	0.343	0.679	**1.655**	**3.319**

S: Surface water, G: Groundwater, na: not applicable

Table 14: Human health risk assessment of s – metolachlor and cypermethrin in water samples due to acute exposure

Site	S - metolachlor								Cypermethrin								
	Surface water				Groundwater				Surface water					Groundwater			
	Dry season		Rainy Season		Dry season		Rainy Season		Dry season			Rainy season		Dry season		Rainy season	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult		Children	Adult	Children	Adult	Children	Adult	Children
S1	0.027	0.053	0.219	0.472	na	na	na	na	0.055		0.110	0.485	0.972	na	na	na	na
S2	0.040	0.080	0.103	0.221	na	na	na	na	0.049		0.098	0.438	0.878	na	na	na	na
S3	0.021	0.043	0.203	0.438	na	na	na	na	0.033		0.066	0.298	0.599	na	na	na	na
S4	0.086	0.173	0.442	0.954	na	na	na	na	0.038		0.076	0.334	0.669	na	na	na	na
S5	0.000	0.000	0.000	0.000	na	na	na	na	0.056		0.111	0.493	0.989	na	na	na	na
S6	0.000	0.000	0.000	0.000	na	na	na	na	0.005		0.010	0.463	0.929	na	na	na	na
S7	0.000	0.000	0.045	0.097	na	na	na	na	0.026		0.051	0.229	0.459	na	na	na	na
S8	0.017	0.035	0.436	0.941	na	na	na	na	0.040		0.080	0.362	0.726	na	na	na	na
S9	0.018	0.028	0.537	**1.159**	na	na	na	na	0.029		0.058	0.294	0.590	na	na	na	na
G1	na	na	Na	na	0.000	0.000	0.000	0.000	na	na	na	na	na	0.043	0.085	0.454	0.911
G2	na	na	Na	na	0.000	0.000	0.000	0.000	na	na	na	na	na	0.049	0.097	0.444	0.891
G3	na	na	Na	na	0.000	0.000	0.000	0.000	na	na	na	na	na	0.042	0.084	0.331	0.664

S: Surface water, G: Groundwater, na: not applicable

CHAPTER FIVE: DISCUSSION

5.1 Physico-chemical parameters

The mean pH of the surface water was observed to be near neutral in the dry season (7.42) and slightly acidic during the rainy season (6.68). The pH values were higher in the dry season than in the rainy season. This is in agreement to the results by Nienie et al. (2017) who observed higher pH values in the dry season than in the rainy season. Similar results were also observed in rivers running through an intensive agricultural area in Kilimanjaro, Tanzania by Hellar-Kihampa (2011). The decrease in pH during the rainy season may be attributed to the rise in the water table during rainfalls, which in turn may increase the H^+ concentration. The mean pH of the groundwater was also near neutral in the dry season (6.78) and acidic in the rainy season (5.77). Similarly, there was a decrease in pH during the rainy season and pH values were higher in the dry season than in the rainy season. In general, the mean pH was higher in surface water than in groundwater in both seasons. Statistically, there was a significant difference in the pH mean between surface and groundwater in both dry and rainy seasons ($p < 0.05$). (Appendix E).

The mean concentration of TDS in the surface water (21 mg/L) during the dry season decreased during the rainy season (11.3 mg/L). The increase in the concentration of TDS during the dry season could be a result of increased concentrations of salts, and organic and inorganic materials due to evaporation and decreased levels of water in the river. This is consistent with studies conducted in the Majidun area of Ikorodu, Lagos State, Nigeria by Awoyemi et al. (2014) where it was observed that TDS was higher in surface water during the dry season than rainy season. However, this is in contrast to a study conducted in the Etche River, Niger Delta area of Nigeria by Akintoye et al. (2014) where it was observed that TDS was higher in the rainy season than the dry season. The mean concentration of TDS was higher in groundwater (89.33 mg/L) than in surface water (21 mg/L) in both seasons. This is in agreement with a study conducted in Noyyal River and groundwater quality of Perur, India by Usharani et al. (2010) where it was observed that TDS was higher in groundwater (616 mg/L) than in surface water (302mg/L). This could be attributed to groundwater moving through the rocks and sediments that make up an aquifer, some of the minerals in those rocks, and sediment. Statistically, there was a significant difference in the TDS means between surface and groundwater in both dry and rainy seasons ($p < 0.05$). (Appendix E).

The mean TSS measured in the surface water (9.12 mg/L) in the dry season increased during the rainy season (216 mg/L). Similarly, the mean TSS was higher in the groundwater was higher in the rainy season (246.78 mg/L) than in the dry season (12.73 mg/L). In general, TSS was higher in both surface water and groundwater in the rainy season than in the dry season. This is similar to what Lydia et al. (2018) in the Ainabkoi sub-county, Uasin Gishu County, Kenya, Makwe & Chup (2013) in groundwater around Karu abattoir, Nigeria, and Agbaire & Oyibo (2009) reported in their studies higher The higher TSS in the rainy season could be due to the increase in water flow rate which comes with it sediments and soil particles. Statistically, there was no significant difference in the total suspended solids mean between surface and groundwater in both dry and rainy seasons ($p > 0.05$). (Appendix E).

In this study, DO was higher during the dry season (4.09 – 6.69 mg/l) than in the rainy season (3.43 – 4.46mg/l). The results on DO are in contrast with results observed in Mullai Periyar River, Tamil Nadu, India by Roshinebegam et al.(2014) where DO was higher in the rainy season than in the dry season. The warm temperatures during the dry season enhance the solubility of oxygen in water hence the higher DO in the dry season than in the rainy season. The concentrations of DO in the study area were above 3.0 mg/l and therefore, the river water is suitable for domestic and recreational purposes according to WHO. Statistically, there was a significant difference in the DO mean between surface and groundwater in the rainy season ($p < 0.05$) and an insignificant difference in the dry season ($p > 0.05$). (Appendix F).

The temperature ranged from 24.34 to 25.03 °C during the rainy season and 24.48 to 26.45 °C during the dry season. However, this is in contrast to what was observed by Ugbaja & Ephraim (2019) in part of Oban massif, Nigeria where the temperature was higher during the rainy season than during the dry season. The lowest temperature of water samples was recorded in the upper stream (S5) of the river in Bluefield estate for the rainy season. Statistically, there was no significant difference in the temperature mean between surface and groundwater in both dry and rainy seasons ($p > 0.05$). (Appendix E).

The levels of conductivity were generally higher in the dry season (26 – 227 µs/cm) than during the rainy season (8 – 243.7 µs/cm). The high conductivity during the dry season could be related to the high concentration of total dissolved solids (TDS) that results in an increase in the concentration of salts, and organic and inorganic materials (Lawson 2011) and could also be attributed to the concentration effect as a result of reduced water volume. A similar trend was observed for the Kontagora reservoir, Niger State, Nigeria by Ibrahim et al. (2010). The results are also in line with a similar work in Ikorogo, Lagos State, Nigeria by Okoya et al. (2014). Statistically, there was a significant difference in the conductivity mean between surface and groundwater in both dry and rainy seasons ($p < 0.05$). (Appendix E)

5.2 Occurrence of s -metolachlor

It was observed that there were higher levels of s - metolachlor in the rainy season (bdl – 13.324 µg/L) than during the dry season (bdl – 1.199 µg/L) in the surface water. The findings also revealed that s - metolachlor had a higher frequency of detection during the rainy season (77.8%) than during the dry season (66.7%). The highest recorded, site S9 (13.324ug/L) was probably due to the closeness of the gardens to the water sources. This finding was, however, higher than what was observed in a study conducted covering the main rivers and lakes of Northern Greece (Macedonia, Thrace and Thessaly) by Papadakis et al. (2015) who reported 0.41 ug/L as the highest concentration. In general, the mean concentration of S metolachlor was higher in the rainy season than in the dry season. This could probably be due to the runoff during the rainy season and that the pesticides applied in the dry season might have stayed in situ because there is no water to carry it to water bodies and the application of herbicides is mostly done during the rainy season. However, the measured mean concentrations of s - metolachlor observed at all the sampled sites were above the EU MRL of 0.1 µg/L for individual pesticide residue concentrations. The use of S metolachlor in the control of weeds by the tea estates in the study area might have accounted for its detection levels in the water samples analysed. Statistically, there was no significant difference in the s - metolachlor mean between surface and groundwater in both dry and rainy seasons ($p > 0.05$). (Appendix F).

5.3 Occurrence of cypermethrin

In the present study, it was observed that the mean concentration of cypermethrin was higher in the rainy season (0.528 – 1.118µg/L) than in the dry season (bdl – 0.952µg/L). This could probably be due to the runoff during the rainy season and the application of herbicides is mostly done during the rainy season These findings were however higher than the findings of Fosu-Mensah et al. (2016) who reported cypermethrin in the range of bdl – 0.04µg/L at Cocoa farms in Ghana and Feo et al. (2010) who reported a concentration of 0.057 µg/L max in the Ebro River Delta in NE Spain. In contrast, Ismail et al. (2012) reported a higher concentration of cypermethrin of 3970µg/L in surface water during the wet season in the irrigation canals in the

Munda Irrigation Scheme Kedah, in Malaysia than in the present study. Statistically, there was a significant difference in the cypermethrin mean between surface and groundwater in the dry season ($p < 0.05$) and there was no significant difference in the rainy season ($p > 0.05$). (Appendix F).

It was also observed that the levels of cypermethrin in the rainy season were below the WHO health-based limit (10 µg/L) and Australian health limits (200 µg/L) but they exceeded the EU guideline limit of 0.1 µg/L. Likewise, the measured mean concentrations of cypermethrin observed at all the sampled sites in the dry season were above the EU MRL of 0.1 µg/L for individual pesticide residue concentrations except points S8, S9, G1, G2 and G3.

5.4 Human health risk assessment of s - metolachlor and cypermethrin in surface and groundwater

The HQs for human health risks of the pesticides for the surface and groundwater are presented in Table 14 and Table 15. The HQ ranged from 0.01 to 2.56 for adults and children for the cypermethrin during the dry season and from 0.005 to 1.908 for adults and children in the rainy season. There is generally no health risk associated with drinking groundwater by adults and children through acute exposure. However, children from site S9 are potentially at risk; due to acute exposure to s - metolachlor in surface water. S - metolachlor and cypermethrin showed low HQ values below the threshold value for acute exposure in the rainy and dry seasons for both adults and children. This implied that the surface and groundwater were relatively safe for human consumption as they posed a low potential risk to humans through drinking water. The results were similar to those by Chidya et al. (2018) who observed that the water from the Kurose River, Japan posed a low risk to humans. On the other hand, cypermethrin showed HQ value above the threshold value for chronic exposure during the rainy season for adults and children.

5.5 Relation of physico-chemical water parameters and pesticides using principal component analysis.

From the findings, it was observed that pH correlated highly and positively to cypermethrin and s - metolachlor both in the dry and rainy seasons for groundwater and surface water, thus from the study, cypermethrin and S-metolachlor levels in groundwater and surface water are pH-dependent. (Table 13). The DO correlated highly and positively with S metolachlor in the dry season, implying that S-metolachlor levels in the surface water were also influenced by DO. (Table 13). These results were consistent with the significant coefficients (Pearson correlation coefficient) between pH and Cypermethrin ($r=0.558$, $p<0.05$) and between DO and s - metolachlor ($r=0.563$, $p<0.05$) (Table 12). The observed correlation between pH and the pesticide levels (cypermethrin and -metolachlor) suggests that the acidity or alkalinity of the water (pH) is influencing the concentrations of these pesticides.

The conductivity and total dissolved solids (TDS) clustered strongly together and decreased with increasing cypermethrin levels. (Table 13). This implies that conductivity and TDS correlated inversely with levels of cypermethrin. There was a negative but strong correlation between S metolachlor levels and TDS and EC. (Table 13). This suggests that the presence of cypermethrin in the water is associated with a decrease in conductivity and TDS. In general, the physico-chemical parameters with strong loadings (TDS, pH, DO and EC) had a strong positive or negative correlation with cypermethrin and s - metolachlor.

5.6 Relation of physico-chemical water parameters and pesticides using Pearson Correlation Analysis

The study revealed various relationships between the measured indexes in the dry and rainy seasons. The strong positive correlation between pH and (cypermethrin and s - metolachlor) and DO and (cypermethrin and s - metolachlor) indicates that the pH and DO of water could have enhanced the adsorption of these pesticide compounds. These findings agree with those of (Javaid et al. 2023) where pH was positively correlated with cypermethrin residues Thus, an increase in pH and DO results in a corresponding increase in concentrations of cypermethrin and S metolachlor, respectively. In addition, the positive correlation between TDS and (cypermethrin) and TSS and (cypermethrin) suggests that these pesticide residue levels in water possibly increased with the TDS and TSS content of the water during the rainy season. On the other hand, the negative correlation between temperature and (cypermethrin) indicates that these pesticide residue levels in the water decrease with an increase in water temperature and vice versa.

Based on Table 11 during the dry season, the study discovered a significant positive connection between DO ($R=0.623$, $p < 0.05$) and cypermethrin concentration. Table 11 also shows a strong positive correlation between pH and cypermethrin, pH and s - metolachlor, and DO and s - metolachlor. However, the researcher discovered a negative correlation between cypermethrin and TDS (-56.4%), conductivity (-56%), TSS (-34.0%), and Temperature (-35.1%). and between s - metolachlor and TDS (-46.7%), conductivity (-34.3%), TSS (-34.0%), and temperature (-11.3%).

Based on Table 12 during the rainy season, the study discovered a weak positive correlation between Cypermethrin concentration and TSS, TDS, DO, and EC while the rest showed a negative correlation. This agrees with the findings of (Kanyika-Mbewe et al. 2020) where pH had a negative correlation with cypermethrin. On the other hand, there is a weak positive correlation between S metolachlor and pH, DO, and temperature. However, the researcher discovered a negative correlation between s - metolachlor and TDS (-33.6%), conductivity (-32.9%), and TSS (-15.5%).

CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The purpose of this research was to assess levels of pesticide residues in the surface and groundwater around tea-growing regions of Mulanje, Malawi. The study established that out of the six pesticides investigated only two, namely s - metolachlor and cypermethrin were detected in surface and groundwater samples. The levels of s - metolachlor and cypermethrin were found to be higher in surface water than in groundwater. Cypermethrin was found in all the surface water both in the dry and rainy seasons while S – metolachlor was not found in any of the groundwater in both seasons. The groundwater and surface water analyses indicated that parameters EC, temperature, TDS, DO and pH were lower in the rainy season than in the dry season and TSS was lower in the dry season than in the rainy season.

In this study, it was further established that the levels of cypermethrin and s – metolachlor in groundwater were below the WHO recommended limits, which is an indication of less contamination and therefore fit for human consumption based on these parameters.

The risk assessment results indicated that cypermethrin and s - metolachlor did not pose a health risk to adults and children for both surface and groundwater in the dry season. However, surface and groundwater did pose a health chronic risk to adults and children during the rainy season.

The study using principal component analysis identified pH as one of the physico-chemical parameters influencing cypermethrin residue in surface water. The concentrations of cypermethrin were significantly correlated to DO in the dry season. In the rainy season, s-metolachlor exhibited a positive association with DO and pH and a negative correlation with TSS, TDS, temperature, and EC. These variables were correlated negatively with cypermethrin.

6.2 RECOMMENDATIONS

Based on the results obtained from this study, the following are recommendations:

i. There is a need for frequent monitoring of the contamination of the surface and groundwater in the tea estates especially during the rainy season when the occurrence of pesticide residues is higher than during the dry season, to ensure that the limits are within the WHO regulations for drinking water.

ii. To educate the local populace about the possible dangers of drinking water during the rainy season and the importance of using alternative water sources or water treatment.

iii. To reduce their negative effects on water quality, it is necessary to incorporate these pesticides in national standards and to implement laws governing their use, paying special attention to those that have been identified—s - metolachlor and cypermethrin.

iv. There is a need to conduct periodic health assessments, especially during the rainy season, to ensure that the identified health risks are continually monitored and addressed promptly if needed.

v. To effectively address and manage pesticide pollution in water sources, it is imperative to promote collaboration among pertinent parties, such as agricultural authorities, environmental organizations, and local populations.

vi. To lessen the dependency on chemical pesticides and embrace a more environmentally friendly and sustainable method of pest management, it is necessary to encourage and support the use of Integrated Pest Management techniques.

6.3 FURTHER RESEARCH

There is a need to conduct further studies in other districts of Thyolo and Nkhatabay where tea plantation is done to ascertain the state of water concerning pesticide contamination.

REFERENCES

Abubakar, Y., Tijjani, H., Egbuna, C., Adetunji, C.O., Kala, S., Kryeziu, T.L. & Patrick-Iwuanyanwu, K.C., 2019b, 'Pesticides, history, and classification', *Natural Remedies for Pest, Disease and Weed Control*, pp. 29–42, Elsevier.

Adeniran, A., 2018, 'Hydrology : Current Research', 9(1), 1–20.

Agbaire, P.O. & Oyibo, I.P., 2009, 'Seasonal variation of some physico-chemical properties of borehole water in Abraka, Nigeria'.

Agrawal, A., Pandey, R.S. & Sharma, B., 2010, 'Water Pollution with Special Reference to Pesticide Contamination in India', *Journal of Water Resource and Protection*, 02(05), 432–448.

Akashe, M.M., Pawade, U.V. & Nikam, A.V., 2018, 'Classification of pesticides: a review', *International Journal of Research in Ayurveda and Pharmacy*, 9(4), 144–150.

Akintoye, O.A., Obi, C.N., Etim, O.A., Olorundami, T., Ukata, S.U. & Harrison, E.U., 2014, 'Seasonal Variation in the Physico-chemical Characteristics of Surface Water in EtcheRiver, Niger Delta Area of Nigeria', *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 8(7), 01–07.

Aktar, W., Sengupta, D. & Chowdhury, A., 2009, 'Impact of pesticides use in agriculture: Their benefits and hazards', *Interdisciplinary Toxicology*, 2(1), 1–12.

Arora, P., 2018, 'Physical , Chemical and Biological Characteristics of Water (e Content Module) Paper Name : 5 Water Resources and Management Module : 26 Physical , Chemical and Biological Characteristics of Water Development Team', (September).

Aydinalp, C. & Porca, M.M., 2004, The effects of pesticides in water resources efectele pesticidelor asupra resurselor de apă, vol. 5.

B S Ismail, Siti Humaira Haron, & Mohd Talib Latif, 2012, *Pesticide Residue Levels in The Surface Water of The Irragation canals in Malaysia.pdf*.

Bai, S.H. & Ogbourne, S.M., 2016, ‘Glyphosate: environmental contamination, toxicity and potential risks to human health via food contamination’, *Environmental Science and Pollution Research*, 23(19), 18988–19001.

Benbrook, C.M., 2016, ‘Trends in glyphosate herbicide use in the United States and globally’, *Environmental Sciences Europe*, 28(1), 1–15.

Berrada, H., Fernández, M., Ruiz, M.J., Moltó, J.C., Mañes, J. & Font, G., 2010, ‘Surveillance of pesticide residues in fruits from Valencia during twenty months (2004/05)’, *Food Control*, 21(1), 36–44.

Bini Dhouib, I., Annabi, A., Jallouli, M., Marzouki, S., Gharbi, N., Elfazaa, S. & Lasram, M.M., 2016, ‘Carbamates pesticides induced immunotoxicity and carcinogenicity in human: A review’, *Journal of Applied Biomedicine*, 14(2), 85–90.

Bortoluzzi, E.C., Rheinheimer, D.S., Gonçalves, C.S., Pellegrini, J.B.R., Maroneze, A.M., Kurz, M.H.S., Bacar, N.M. & Zanella, R., 2007, Investigation of the occurrence of pesticide residues in rural wells and surface water following application to tobacco, vol. 30.

Brusick, D., Aardema, M., Kier, L., Kirkland, D. & Williams, G., 2016, ‘Critical Reviews in Toxicology Genotoxicity Expert Panel review: weight of evidence evaluation of the genotoxicity of glyphosate, glyphosate-based formulations, and aminomethylphosphonic acid’.

Cañero, A.I., Cox, L., Redondo-Gómez, S., Mateos-Naranjo, E., Hermosín, M.C. & Cornejo, J., 2011, ‘Effect of the herbicides terbuthylazine and glyphosate on photosystem II photochemistry of young olive (Olea europaea) plants’, *Journal of Agricultural and Food Chemistry*, 59(10), 5528–5534.

Ccanccapa, A., Masiá, A., Andreu, V. & Picó, Y., 2016, ‘Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers (Spain)’, *Science of the Total Environment*, 540, 200–210.

Chandra Yadav, I. & Linthoingambi Devi, N., 2017, *Pesticides Classification and Its Impact on Human and Environment Development of pesticide runoff model for controlling risk of pesticides loss in upland field View project Monitoring and Sources Assessment of Persistent Organic Pollutants in Nepal:Implication on human health View project 7 Pesticides Classification and Its Impact on Human and Environment*, vol. 6.

Chidya, R., Derbalah, A., Abdel-Dayem, S., Kaonga, C. & Sakugawa, H., 2022, 'Ecotoxicological and human health risk assessment of selected pesticides in Kurose River, Higashi-Hiroshima City (Japan)', *Water Environment Research*, 94(1).

Chidya, R.C.G., Abdel-dayem, S.M., Takeda, K. & Sakugawa, H., 2018, 'Spatio-temporal variations of selected pesticide residues in the Kurose River in Higashi-Hiroshima city, Japan', *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 53(9), 602–614.

De Gerónimo, E., Aparicio, V.C., Bárbaro, S., Portocarrero, R., Jaime, S. & Costa, J.L., 2014, 'Presence of pesticides in surface water from four sub-basins in Argentina', *Chemosphere*, 107, 423–431.

Deer, H.M. & Specialist, E.P., 2001, 'Effect of water pH on the c chemical s stability of pesticides'.

European Union, 2014, 'European Union (DRINKING WATER) REGULATIONS 201', S.I 122.

Faggiano, L., Zwart, D.D., García-berthou, E., Lek, S. & Gevrey, M., 2010, 'Science of the Total Environment Patterning ecological risk of pesticide contamination at the river basin scale', *Science of the Total Environment, The*, 408(11), 2319–2326.

Fan, A.M., Ting, D., Environmental, C. & Agency, P., 2014, 'Environmental Fate and Behavior What Are Pheromones?', 3, 898–901.

FAOSTAT, 2021, *FAOSTAT :Pesticides Use in FAO, United Nations*.

Feo, M.L., Ginebreda, A., Eljarrat, E. & Barceló, D., 2010, 'Presence of pyrethroid pesticides in water and sediments of Ebro River Delta', *Journal of Hydrology*, 393(3–4), 156–162.

Fijałkowska, R.K., Dragon, K., Drożdżyński, D. & Górski, J., 2022, 'Seasonal variation of pesticides in surface water and drinking water wells in the annual cycle in western Poland , and potential health risk assessment', *Scientific Reports*, (0123456789), 1–12.

Fingler, S., Mendaš, G., Dvoršćak, M., Stipičević, S., Vasilić & Drevenkar, V., 2017, 'Herbicide micropollutants in surface, ground and drinking waters within and near the area of Zagreb, Croatia', *Environmental Science and Pollution Research*, 24(12), 11017–11030.

Fosu-Mensah, B.Y., Okoffo, E.D. & Mensah, M., 2016, ‘Synthetic Pyrethroids Pesticide Residues in Soils and Drinking Water Sources from Cocoa Farms in Ghana’, *Environment and Pollution*, 5(1), 60.

Garry, V.F., Harkins, M.E., Erickson, L.L., Long-Simpson, L.K., Holland, S.E. & Burroughs, B.L., 2002, ‘Birth defects, the season of conception, and sex of children born to pesticide applicators living in the Red River Valley of Minnesota, USA’, *Environmental Health Perspectives*, 110(SUPPL. 3), 441–449.

George, J. & Shukla, Y., 2011, ‘Pesticides and cancer: Insights into toxicoproteomic-based findings’, *Journal of Proteomics*, 74(12), 2713–2722.

Ghazouani, L., Feriani, A., Mufti, A., Tir, M., Baaziz, I., Mansour, H.B. & Mnafgui, K., 2020, ‘Toxic effect of alpha cypermethrin, an environmental pollutant, on myocardial tissue in male wistar rats’, *Environmental Science and Pollution Research*, 27(6), 5709–5717.

Gill, J.P.K., Sethi, N., Mohan, A., Datta, S. & Girdhar, M., 2018, ‘Glyphosate toxicity for animals’, *Environmental Chemistry Letters*, 16(2), 401–426.

Government of Malawi, 2000, ‘Pesticides Act 2000’, (12).

Government of Malawi, 2017, ‘Republic of Malawi Mulanje District Council’.

Government of Malawi, 2021a, National Water Policy.

Government of Malawi, 2021b, Republic of Malawi Ministry of Agriculture Agricultural Sector Wide Approach Support Project II (ASWAp-SP II AF).

Government of Malawi,2021, 2021, no date, Republic of Malawi Ministry of Agriculture Agricultural Sector Wide Approach Support Project II (ASWAp-SP II AF).

Gunnell, D.J. & Eddleston, M., 2003, ‘Suicide by intentional ingestion of pesticides: A continuing tragedy in developing countries’, *International Journal of Epidemiology*, 32(6), 902–909.

Gurusubramanian, G., 2008, *Pesticide usage pattern in tea ecosystem, their retrospects and alternative measures The diversity of Amphibians and Reptiles of Mizoram using classical taxonomy and DNA barcoding View project*.

Gutowski, L., Baginska, E., Olsson, O., Leder, C. & Kümmerer, K., 2015, ‘Assessing the environmental fate of S-metolachlor, its commercial product Mercantor Gold® and their photoproducts using a water-sediment test and in silico methods’, *Chemosphere*, 138, 847–855.

Hassaan, M.A. & El Nemr, A., 2020, ‘Pesticides pollution: Classifications, human health impact, extraction and treatment techniques’, *Egyptian Journal of Aquatic Research*, 46(3), 207–220.

Hassani, S., Momtaz, S., Vakhshiteh, F., Maghsoudi, A.S., Ganjali, M.R., Norouzi, P. & Abdollahi, M., 2017, ‘Biosensors and their applications in detection of organophosphorus pesticides in the environment’, *Archives of Toxicology*, 91(1), 109–130.

Helander, M., Saloniemi, I. & Saikkonen, K., 2012, ‘Glyphosate in northern ecosystems’, *Trends in Plant Science*, 17(10), 569–574.

Hellar-Kihampa, H., 2011, ‘Pesticide residues in four rivers running through an intensive agricultural area, Kilimanjaro, Tanzania’, *Journal of Applied Sciences and Environmental Management*, 15(2).

Horn, S., Pieters, R. & Bøhn, T., 2019, ‘A first assessment of glyphosate, 2,4-D and Cry proteins in surface water of South Africa’, *South African Journal of Science*, 115(9–10).

Hu, Y., Qi, S., Zhang, Junpeng, Tan, L., Zhang, Jiaquan, Wang, Y. & Yuan, D., 2011, ‘Assessment of organochlorine pesticides contamination in underground rivers in Chongqing, Southwest China’, *Journal of Geochemical Exploration*, 111(1–2), 47–55.

Ibrahim, B., Auta, J. & Balogun, J., 2010, ‘An assessment of the physico-chemical parameters of Kontagora reservoir, Niger state, Nigeria’, *Bayero Journal of Pure and Applied Sciences*, 2(1), 64–69.

Ippolito, A. & Fait, G., 2019, ‘Pesticides in surface waters: from edge-of-field to global modelling’, *Current Opinion in Environmental Sustainability*, 36, 78–84.

Ismail, B.S., Mazlinda, M. & Tayeb, M.A., 2015, *The Persistence of Deltamethrin in Malaysian Agricultural Soils (Kekekalan Deltametrin dalam Tanah Pertanian Malaysia)*, vol. 44.

Jaipieam, S., Visuthismajarn, P., Sutheravut, P., Siriwong, W., Thoumsang, S., Borjan, M. & Robson, M., 2009, ‘Organophosphate Pesticide Residues in Drinking Water from Artesian

Wells and Health Risk Assessment of Agricultural Communities, Thailand', *Human and Ecological Risk Assessment: An International Journal*, 15(6), 1304–1316.

Jamil Khan, M., 2010, *Use of Pesticides and Their Role in Environmental Pollution Phosphate Sorption in Calcareous Soil Series View project Sustainable Management of High Altitude Mountainous Sites in the Changing World Climate View project*.

Jardim, A.N.O. & Caldas, E.D., 2012, 'Brazilian monitoring programs for pesticide residues in food - Results from 2001 to 2010', *Food Control*, 25(2), 607–616.

Javaid, Z., Ghazala, Ibrahim, M., Mahmood, A. & Bajwa, A.A., 2023, 'Pesticide Contamination of Potable Water and Its Correlation with Water Quality in Different Regions of Punjab, Pakistan', *Water*, 15(3), 543.

Jayaraj, R., Megha, P. & Sreedev, P., 2016, 'Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment', *Interdisciplinary Toxicology*, 9(3–4), 90–100.

Jokanović, M. & Kosanović, M., 2010, 'Neurotoxic effects in patients poisoned with organophosphorus pesticides', *Environmental Toxicology and Pharmacology*, 29(3), 195–201.

Kamanula, J., Sileshi, G.W., Belmain, S.R., Sola, P., Mvumi, B.M., Nyirenda, G.K.C., Nyirenda, S.P. & Stevenson, P.C., 2011, 'Farmers' insect pest management practices and pesticidal plant use in the protection of stored maize and beans in Southern Africa', *International Journal of Pest Management*, 57(1), 41–49.

Kambwiri, A.M., Changadeya, W., Chimphamba, J. & Tandwe, T., 2014, *Land use Impacts on Water Quality of Rivers Draining from Mulanje Mountain:A case of Ruo River in Southern Malawi*.

Kanyika-Mbewe, C., Thole, B., Makwinja, R. & Kaonga, C.C., 2020, 'Monitoring of carbaryl and cypermethrin concentrations in water and soil in Southern Malawi', *Environmental Monitoring and Assessment*, 192(9).

Kasambala Donga, T. & Eklo, O.M., 2018, 'Environmental load of pesticides used in conventional sugarcane production in Malawi', *Crop Protection*, 108, 71–77.

Kaur, G., 2019, ‘Herbicides and its role in Induction of Oxidative Stress- A Review’, *International Journal of Environment, Agriculture and Biotechnology*, 4(4), 995–1004.

Kaur, R., Mavi, G.K., Raghav, S. & Khan, I., 2019, ‘Pesticides Classification and its Impact on Environment’, *International Journal of Current Microbiology and Applied Sciences*, 8(03), 1889–1897.

Kaushik, A., Sharma, H.R., Jain, S., Dawra, J. & Kaushik, C.P., 2010, ‘Pesticide pollution of River Ghaggar in Haryana, India’, *Environmental Monitoring and Assessment*, 160(1–4), 61–69.

Kim, H.H., Lim, Y.W., Yang, J.Y., Shin, D.C., Ham, H.S., Choi, B.S. & Lee, J.Y., 2013, ‘Health risk assessment of exposure to chlorpyrifos and dichlorvos in children at childcare facilities’, *Science of the Total Environment*, 444, 441–450.

Kim, K.H., Kabir, E. & Jahan, S.A., 2017, ‘Exposure to pesticides and the associated human health effects’, *Science of the Total Environment*, 575, 525–535.

Koli, P., Bhardwaj, N.R. & Mahawer, S.K., 2019, ‘Agrochemicals: Harmful and beneficial effects of climate changing scenarios’, *Climate Change and Agricultural Ecosystems: Current Challenges and Adaptation*, pp. 65–94, Elsevier.

Kucharik, C.J. & Ramankutty, N., 2005, ‘Trends and Variability in U.S. Corn Yields Over the Twentieth Century’, *Earth Interactions*, 9(1), 1–29.

Lakudzala, D.D., 2013, ‘International Letters of Chemistry’, *Physics and Astronomy*, 1, 33–45.

Lari, S.Z., Khan, N.A., Gandhi, K.N., Meshram, T.S. & Thacker, N.P., 2014, ‘Comparison of pesticide residues in surface water and ground water of agriculture intensive areas’, *Journal of Environmental Health Science and Engineering*, 12(1).

Lawson, E.O., 2011, ‘Physico-chemical Parameters and Heavy Metal Contents of Water from’.

Le Couteur, P.C. & Eng, P., 2011, ‘Geological Report on the Chambe Basin Area of Exclusive Prospecting License EPL0325/11 Mulanje Massif,Southern Malawi, East Africa’, 101.

Lushchak, V.I., Matviishyn, T.M., Husak, V.V., Storey, J.M. & Storey, K.B., 2018, ‘Pesticide toxicity: A mechanistic approach’, *EXCLI Journal*, 17, 1101–1136.

Lydia, M.K., Wilkister, N.M., Samuel, M.M. & Isaiah, T., 2018, 'Assessment of physico-chemical characteristics of groundwater among different farm sizes in Ainabkoi sub-county, Uasin Gishu County, Kenya', *African Journal of Environmental Science and Technology*, 12(11), 408–416.

M. Awoyemi, O., C. Achudume, A. & A. Okoya, A., 2014, 'The Physicochemical Quality of Groundwater in Relation to Surface Water Pollution in Majidun Area of Ikorodu, Lagos State, Nigeria', *American Journal of Water Resources*, 2(5), 126–133.

Mahmood, A., Malik, R.N., Li, J. & Zhang, G., 2014, 'Levels, distribution pattern and ecological risk assessment of organochlorines pesticides (OCPs) in water and sediments from two tributaries of the Chenab River, Pakistan', *Ecotoxicology*, 23(9), 1713–1721.

Maksymiv, I., 2015, 'Pesticides: Benefits and Hazards', *Journal of Vasyl Stefanyk Precarpathian National University*, 2(1), 70–76.

Makwe, E. & Chup, C., 2013, 'Seasonal variation in physico-chemical properties of groundwater around Karu abattoir', *Ethiopian Journal of Environmental Studies and Management*, 6(5), 489–497.

Marrazza, G., 2014, 'Piezoelectric biosensors for organophosphate and carbamate pesticides: A review', *Biosensors*, 4(3), 301–317.

Meffe, R. & Bustamante, I. de, 2014, 'Emerging organic contaminants in surface water and groundwater: A first overview of the situation in Italy', *Science of the Total Environment*, 481(1), 280–295.

Mesnage, R. & Antoniou, M.N., 2017, 'Facts and Fallacies in the Debate on Glyphosate Toxicity', *Frontiers in Public Health*, 5.

Mihajlović, I., Živančev, N., Sremački, M., Milovanović, D., Špánik, I., Novaković, M. & Petrović, M., 2021, 'Screening analysis of pesticides in the protected area of Zobnatica Lake', *IOP Conference Series: Materials Science and Engineering*, 1163(1), 012030.

Ministry of Agriculture, I. and W.D., 2017, *Pesticides Risk Reduction in Malawi(FSP)*, Lilongwe.

Mohamed, J., 2014, ‘Degradation of Water Resources by Agricultural Pesticides and Nutrients, Weruweru, Tanzania’, *Iranica Journal of energy and environment*, 5(2).

Musa, M., Buwono, N.R., Iman, M.N., Ayuning, S.W. & Lusiana, E.D., 2019, *Pesticides in Kalisat River: water and sediment assessment 1,2*, vol. 12.

National Statistical Office, 2019, Malawi population and housing census report-2018 *2018 Malawi Population and Housing Main Report*.

Nienie, A.B., Sivalingam, P., Laffite, A., Ngelinkoto, P., Otamonga, J.-P., Matand, A., Mulaji, C.K., Mubedi, J.I., Mpiana, P.T. & Poté, J., 2017, ‘Seasonal variability of water quality by physicochemical indexes and traceable metals in suburban area in Kikwit, Democratic Republic of the Congo’, *International Soil and Water Conservation Research*, 5(2), 158–165.

Oberemok, V.V., Laikova, K.V., Gninenko, Y.I., Zaitsev, A.S., Nyadar, P.M. & Adeyemi, T.A., 2015, ‘A short history of insecticides’, *Journal of Plant Protection Research*, 55(3), 221–226.

Omer, N.H., no date, ‘Water Quality Parameters’, 1–18.

Orlando, J.L., Smalling, K. l, Reilly, T.J., Fishman, N.S., Boehlke, A., Meyer, M.T. & Kuivila, K.M., 2009, ‘Occurence of Fungicides and Other Pesticides in Surface Water,Groundwater and Sediment fron Three Targeted -Use Areas in The United States,2009’.

Özkara, A., Akyil, D. & Konuk, M., 2016, ‘Pesticides, Environmental Pollution, and Health’, *Environmental Health Risk - Hazardous Factors to Living Species*, InTech.

Palma, P., Köck-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I.R., López de Alda, M. & Barceló, D., 2014a, ‘Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal)’, *Science of the Total Environment*, 488–489(1), 208–219.

Palma, P., Köck-Schulmeyer, M., Alvarenga, P., Ledo, L., Barbosa, I.R., López de Alda, M. & Barceló, D., 2014b, ‘Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal)’, *Science of the Total Environment*, 488–489(1), 208–219.

Panno, S. & Hackley, K., 2010, ‘Geologic influences on water quality’, *Geol. Illinois*, (January 2010), 337–350.

Papadakis, E.N., Vryzas, Z., Kotopoulou, A., Kintzikoglou, K., Makris, K.C. & Papadopoulou-mourkidou, E., 2015, ‘Ecotoxicology and Environmental Safety A pesticide monitoring survey in rivers and lakes of northern Greece and its human and ecotoxicological risk assessment’, *Ecotoxicology and Environmental Safety*, 116, 1–9.

Pundir, C.S., Malik, A., & Preety, 2019, ‘Bio-sensing of organophosphorus pesticides: A review’, *Biosensors and Bioelectronics*, 140.

Reffstrup, T.K., Larsen, J.C. & Meyer, O., 2010, ‘Risk assessment of mixtures of pesticides. Current approaches and future strategies’, *Regulatory Toxicology and Pharmacology*, 56(2), 174–192.

Riaz, G., Tabinda, A.B., Kashif, M., Yasar, A., Mahmood, A., Rasheed, R., Khan, M.I., Iqbal, J., Siddique, S. & Mahfooz, Y., 2018, ‘Monitoring and spatiotemporal variations of pyrethroid insecticides in surface water, sediment, and fish of the river Chenab Pakistan’, *Environmental Science and Pollution Research*, 25(23), 22584–22597.

Rose, C.E., Coupe, R.H., Capel, P.D. & Webb, R.M.T., 2018, ‘Holistic assessment of occurrence and fate of metolachlor within environmental compartments of agricultural watersheds’, *Science of the Total Environment*, 612, 708–719.

Roshinebegam, K., Selvakumar, Sundaraj & Selvakumar, S, 2014, ‘Seasonal Changes in Physico-Chemical Parameters of Mullai Periyar River, Tamil Nadu, India’.

Saillenfait, A.M., Ndiaye, D. & Sabaté, J.P., 2015, ‘Pyrethroids: Exposure and health effects - An update’, *International Journal of Hygiene and Environmental Health*, 218(3), 281–292.

Sánchez-bayo, F., Baskaran, S. & Robert, I., 2002, ‘Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture’, 91(2002), 37–57.

Sanchís, J., Kantiani, L., Llorca, M., Rubio, F., Ginebreda, A., Fraile, J., Garrido, T. & Farré, M., 2012, *Determination of glyphosate in groundwater samples using an ultrasensitive immunoassay and confirmation by on-line solid-phase extraction followed by liquid chromatography coupled to tandem mass spectrometry, Analytical and Bioanalytical Chemistry*, vol. 402, 2335–2345, Springer Verlag.

SANTE, 2021, ‘Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes’, *Sante/2020/12830*, (February), 1–50.

Shalaby, S.E.M., El-Saadany, S.S., Abo-Eyta, A.M., Abdel-Satar, A.M., Al-Afify, A.D.G. & Abd El-Gleel, W.M.M., 2018, ‘Levels of pesticide residues in water, sediment, and fish samples collected from Nile River in Cairo, Egypt’, *Environmental Forensics*, 19(4), 228–238.

Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G.P.S., Handa, N., Kohli, S.K., Yadav, P., Bali, A.S., Parihar, R.D., Dar, O.I., Singh, K., Jasrotia, S., Bakshi, P., Ramakrishnan, M., Kumar, S., Bhardwaj, R. & Thukral, A.K., 2019, ‘Worldwide pesticide usage and its impacts on ecosystem’, *SN Applied Sciences*, 1(11).

Shi, W., Zhang, F., Zhang, X., Su, G., Wei, S., Liu, H., Cheng, S. & Yu, H., 2011, ‘Identification of trace organic pollutants in freshwater sources in Eastern China and estimation of their associated human health risks’, *Ecotoxicology*, 20(5), 1099–1106.

Singh, S., Sarkar, S., Bhattacharjee, S., Rai, B.K., Pal, J., Bahadur, M., Bhutia, D. & Rai, K., 2015, ‘Analyses of pesticide residues in water, sediment and fish tissue from river Deomoni flowing through the tea gardens of Terai Region of West Bengal, India.’, *International Journal of Fisheries and Aquatic Studies*, 3(2), 17–23.

Soko, J., 2018, ‘Agricultural Pesticides Use in Malawi’, *Journal of Health & Pollution Volume*, 8(20).

Sparling, D.W., 2016, ‘Chemical Stressors and Ecological Risk’, *Ecotoxicology Essentials*, 391–415.

Sudi, I., 2017, ‘Assessment of Herbicides and Pesticides Residues in Gella Surface Water’, *Asian Journal of Advances in Agricultural Research*, 3(1), 1–9.

Syafrudin, M., Kristanti, R.A., Yuniarto, A., Hadibarata, T., Rhee, J., Al-Onazi, W.A., Algarni, T.S., Almarri, A.H. & Al-Mohaimeed, A.M., 2021a, ‘Pesticides in drinking water-a review’, *International Journal of Environmental Research and Public Health*, 18(2), 1–15.

Syafrudin, M., Kristanti, R.A., Yuniarto, A., Hadibarata, T., Rhee, J., Al-Onazi, W.A., Algarni, T.S., Almarri, A.H. & Al-Mohaimeed, A.M., 2021b, ‘Pesticides in drinking water-a review’, *International Journal of Environmental Research and Public Health*, 18(2), 1–15.

Tano, J., 2011, *Identity, Physical and Chemical Properties of Pesticides*.

Toumi, H., Burga-Perez, K.F. & Ferard, J.F., 2016, 'Acute and chronic ecotoxicity of carbaryl with a battery of aquatic bioassays', *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 51(1), 57–62.

Tudi, M., Ruan, H.D., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C. & Phung, D.T., 2021, 'Agriculture development, pesticide application and its impact on the environment', *International Journal of Environmental Research and Public Health*, 18(3), 1–24.

Ugbaja, A.N. & Ephraim, B.E., 2019, 'Physicochemical and bacteriological parameters of surface water quality in part of Oban Massif, Nigeria', *Global Journal of Geological Sciences*, 17(1), 13.

United Nations Human Rights, 2017, *Report of the Special Rapporteur on the right to food 34th session of the Human Rights Council*, Geneva.

US EPA, O., 2015, *Human Health Issues Related to Pesticides*.

Usharani, K., Umarani, K., Ayyasamy, P.M., Shanthi, K. & Lakshmanaperumalsamy, P., 2010, 'Physico-Chemical and Bacteriological Characteristics of Noyyal River and Ground Water Quality of Perur, India', *Journal of Applied Sciences and Environmental Management*, 14(2).

Valle, A.L., Mello, F.C.C., Alves-Balvedi, R.P., Rodrigues, L.P. & Goulart, L.R., 2019, 'Glyphosate detection: methods, needs and challenges', *Environmental Chemistry Letters*, 17(1), 291–317.

Vryzas, Z., Vassiliou, G., Alexoudis, C. & Papadopoulou-Mourkidou, E., 2009, 'Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece', *Water Research*, 43(1), 1–10.

Watt, M.S., Wang, H., Rolando, C.A., Zaayman, M. & Martin, K., 2010, 'Adsorption of the herbicide terbuthylazine across a range of New Zealand forestry soils', *Canadian Journal of Forest Research*, 40(7), 1448–1457.

Whitford, F., Johnson, B., Bledsoe, L., Wise, K. & Obermeyer, J., no date, 'Water quality'.

World Health Organization, 2008, *Guidelines for drinking-water quality [electronic resource]: incorporating 1st and 2nd addenda,Vol.1, recommendations*, 3rd ed, World Health Organization, Geneva.

World Health Organization & International Programme on Chemical Safety, 2010, 'The WHO recommended classification of pesticides by hazard and guidelines to classification 2009', *The WHO recommended classification of pesticides by hazard and guidelines to classification : 2009*, 78.

Yadav, B., 2018, 'Cypermethrin Toxicity: A Review', *Journal of Forensic Sciences & Criminal Investigation*, 9(4).

Yoo, M., Lim, Y.H., Kim, T., Lee, D. & Hong, Y.C., 2016, 'Association between urinary 3-phenoxybenzoic acid and body mass index in Korean adults: 1st Korean National Environmental Health Survey', *Annals of Occupational and Environmental Medicine*, 28(1).

Zemolin, C.R., Avila, L.A., Cassol, G.V., Massey, J.H. & Camargo, E.R., 2014, 'Environmental fate of S-metolachlor - A review', *Planta Daninha*, 32(3), 655–664.

Zheng, S., Chen, B., Qiu, X., Chen, M., Ma, Z. & Yu, X., 2016, 'Distribution and risk assessment of 82 pesticides in Jiulong River and estuary in South China', *Chemosphere*, 144, 1177–1192.

APPENDICES

Appendix A: Ethical approval letter

MZUZU UNIVERSITY

DIRECTORATE OF RESEARCH

Mzuzu University
Private Bag 201
Luwinga
Mzuzu 2
MALAWI
TEL: 01 320 722
FAX: 01 320 648

MZUZU UNIVERSITY RESEARCH ETHICS COMMITTEE (MZUNIREC)

Ref No: MZUNIREC/DOR/23/03 **10/01/2023.**

Enock Kamwala,
Mzuzu University,
P/Bag 201,
Luwinga,
Mzuzu 2.

ekamwala@gmail.com

Dear Enock,

RESEARCH ETHICS AND REGULATORY APPROVAL AND PERMIT FOR PROTOCOL REF NO: MZUNIREC/DOR/23/03: A COMPARATIVE ASSESSMENT OF PESTICIDE RESIDUES IN SURFACE AND GROUNDWATER IN TEA GROWING AREAS IN MULANJE, SOUTHERN MALAWI

Having satisfied all the relevant ethical and regulatory requirements, I am pleased to inform you that the above referred research protocol has officially been approved. You are now permitted to proceed with its implementation. Should there be any amendments to the approved protocol in the course of implementing it, you shall be required to seek approval of such amendments before implementation of the same.

This approval is valid for one year from the date of issuance of this approval. If the study goes beyond one year, an annual approval for continuation shall be required to be sought from the Mzuzu University Research Ethics Committee (MZUNIREC) in a format that is available at the Secretariat. Once the study is finalised, you are required to furnish the Committee with a final report of the study. The Committee reserves the right to carry out compliance inspection of this approved protocol at any time as may be deemed by it. As such, you are expected to properly maintain all study documents including consent forms.

Wishing you a successful implementation of your study.

Committee Address:

Secretariat, Mzuzu University Research Ethics Committee, P/Bag 201, Luwinga, Mzuzu 2; E-mail address: mzunirec@mzuni.ac.mw

Yours Sincerely,

Gift Mbwele

SENIOR RESEARCH ETHICS ADMINISTRATOR

For: CHAIRMAN OF MZUNIREC

MZUZU UNIVERSITY
RESEARCH ETHICS COMMITTEE
10 JAN 2023
PRIVATE BAG 201, LUWINGA
MZUZU 2

Appendix B: Letter of consent

Phone: (265) 01 466 086
Fax No: (265) 01 466 086
Email: mjdistrictcouncil@yahoo.com
Communications should be addressed to:

District Water Development Officer
P.O. Box 223
Mulanje

DISTRICT WATER DEVELOPMENT OFFICE

s

Ref.N0.: DWDO-MJ/02/11/2022 → Wednesday, 02 November 2022.

To: Whom it may concern

Dear Sir/Madam,

- <u>RE: PERMISSION TO ACCESS RUO RIVER AND SURROUNDING BOREHOLES FOR POSTGRADUATE STUDIES</u>

Refer to above captioned subject matter.

The bearer of this letter, Enoch Andrew Kamwala with Reg. No. MScWRM0920 postgraduate student from Mzuzu University has been given permission by our office to access Ruo river and surrounding boreholes to collect samples for research purpose.

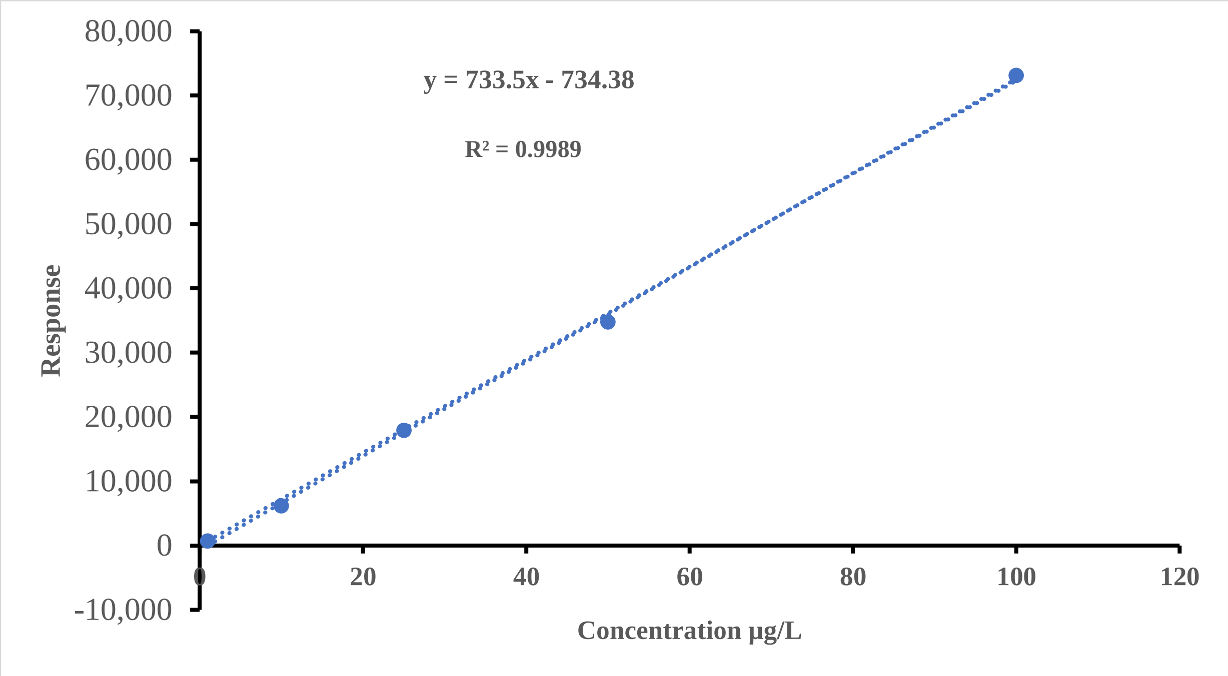
May you please assist him by allowing him entry through your estates to access Ruo river and surrounding boreholes.

Should you require further information, please do not hesitate to contact the undersigned.

Yours faithfully,

Edwin Mchirikizo
<u>District Water Development Officer</u>

Appendix C: Performance of chromatographic response on LC MS MS



Appendix D: The mean and range of physico-chemical properties of surface water in the dry and rainy seasons

Site	Season	pH		TSS(mg/L)		TDS(mg/L)		EC		Temperature(oC)		DO(mg/L)	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
S1	Dry	7.42	7.32 - 7.42	0.5	0.4 - 0.6	20	18 - 20	31	30 – 32	25.7	25.3 - 25.9	6.54	6.33 - 6.85
	Rainy	6.53	6.53 - 6.60	252.7	215 - 254	7	5 - 8	9	9 – 10	24.7	24.7 - 24.8	4.85	4.83 - 4.86
S2	Dry	7.51	7.47 - 7.56	1.0	0.8 - 1.2	19	18 - 19	32	31 - 32	25.5	25.4 - 25.6	6.67	6.44 - 6.88
	Rainy	6.92	6.90 - 7.11	257.0	255 - 259	8	7 - 8	8	8 - 9	24.6	24.6 - 24.7	4.66	4.63 - 4.70
S3	Dry	7.71	7.68 - 7.73	26.9	26.0 - 27.5	22	20 - 23	33	32 - 35	26.5	26.3 - 26.6	6.32	6.16 - 6.66
	Rainy	6.46	6.45 - 6.47	185.3	184 - 187	20	17 - 23	26	28 - 29	25.0	25.0 - 25.1	4.48	4.36 - 4.56
S4	Dry	7.51	7.50 - 7.52	1.0	9.3 - 11.5	22	21 - 24	36	35 - 47	24.6	24.6 - 25.3	6.69	6.63 - 6.76
	Rainy	6.60	6.53 - 6.61	195.3	193 - 198	17	17 - 18)	31	28 - 38	25.0	25.0 - 25.1	4.4	4.26 - 4.51
S5	Dry	7.43	7.20 - 7.55	10.6	9.3 - 11.5	22	21 - 23	34	33 - 36	24.9	24.9 - 25.3	6.58	6.23 - 6.78
	Rainy	6.52	6.44 - 6.61	197.7	196 - 200	14	14 - 15	23	23 - 24	24.3	23.0 - 24.9	4.44	4.33 - 4.52
S6	Dry	7.26	7.22 - .31	10.0	176 - 182	17	16 - 18	26	26 - 27	25.5	25.5 - 25.6	5.28	5.00 - 5.50
	Rainy	6.70	6.58 - 6.83	251.0	230 - 290	6	5 - 7	8	8 - 9	24.9	24.8 - 24.9	4.82	4.82 - 4.86
S7	Dry	7.43	7.33 - 7.51	1.2	0.9 - 1.5	27	25 - 28	45	44 - 46	24.5	24.4 - 24.5	5.54	5.40 - 5.60
	Rainy	6.34	6.32 - 6.36	197.7	201 - 208	26	25 - 28	43	42 - 46	25.0	25.0 - 25.1	4.3	4.07 - 4.56
S8	Dry	7.32	7.28 - 7.38	10.4	10.0 - 10.8	20	19 - 21	34	32 - 35	24.7	25.6 - 25.8	4.64	4.56 - 4.70
	Rainy	7.55	7.31 - 7.84	212.0	197 - 240	17	16 - 19	41	40 - 43	24.4	24.3 - 24.4	4.68	4.67 - 4.68
S9	Dry	7.25	7.24 - 7.26	10.0	9.2 - 10.7	20	19 - 22	31	31 - 32	26.2	25.8 - 26.8	4.94	4.82 - 5.02
	Rainy	6.46	6.38 - 6.55	179.3	176 - 82	6	5 - 8	10	9 - 11	25.0	25.0 - 25.1	4.67	4.65 - 4.68

Appendix E: The mean and range of physico-chemical properties of groundwater water in the dry and rainy seasons

Site	Season	pH		TSS		TDS		EC		Temperature		DO	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
G1	Dry	6.89	6.88 - 6.90	15	14.0 - 15.6	63	60 – 67	195	186 – 205	25.4	25.3 - 25.5	4.09	3.95 - 4.20
	Rainy	5.65	5.51 - 5.78	6.3	204 – 209	56	54 – 57	93	91 – 95	24.5	24.8 - 25.0	3.51	3.41 - 3.70
G2	Dry	6.79	6.78 - 6.82	22.4	22.1 - 22.9	135	133 – 136	156	152 – 161	25.9	25.6 - 26.1	4.95	4.45 - 5.52
	Rainy	5.93	5.85 - 6.00	4.7	212 – 218	46	143 – 148	89	88 – 89	24.9	24.9 - 25.1	3.75	3.67 - 3.82
G3	Dry	6.66	6.63 - 6.72	4.4	3.6 - 5.0	66	65 – 68	139	136 – 145	25.5	25.4 - 25.6	5.50	5.32 - 5.55
	Rainy	5.72	5.70 - 5.73	314.7	312 - 317	61	58 - 63	76	73 - 79	25.0	24.9 - 25.1	4.21	3.99 - 4.42

Appendix F: ANOVA physico-chemical water parameters between surface and groundwater

Table 1. ANOVA pH between surface and groundwater

		Sum of Squares	df	Mean Square	F	Sig.
pH Dry Season	Between Groups	0.938	1	0.938	49.036	0.000
	Within Groups	0.191	10	0.019		
	Total	1.129	11			
pH Rainy Season	Between Groups	1.859	1	1.859	16.535	0.002
	Within Groups	1.124	10	0.112		
	Total	2.983	11			

Table 2. ANOVA Total Suspended Solids between surface and groundwater

		Sum of Squares	df	Mean Square	F	Sig.
Suspended Solids Dry Season	Between Groups	29.340	1	29.340	0.464	0.511
	Within Groups	632.032	10	63.203		
	Total	661.372	11			
Suspended Solids Rainy Season	Between Groups	2,047.563	1	2,047.563	1.291	0.282
	Within Groups	15,863.167	10	1,586.317		
	Total	17,910.729	11			

Table 3. ANOVA Temperature between surface and groundwater

		Sum of Squares	df	Mean Square	F	Sig.
Temperature Dry Season	Between Groups	0.023	1	0.023	0.073	0.793
	Within Groups	3.158	10	0.316		
	Total	3.181	11			
Temperature Rainy Season	Between Groups	0.125	1	0.125	0.370	0.557
	Within Groups	3.377	10	0.338		
	Total	0.502	11			

Table 4. ANOVA Electrical Conductivity between surface and groundwater

		Sum of Squares	df	Mean Square	F	Sig.
Conductivity Dry Season	Between Groups	28,056.250	1	28,056.250	27.378	0.000
	Within Groups	10,247.667	10	1,024.767		
	Total	38,303.917	11			
Conductivity Rainy Season	Between Groups	34,348.444	1	34,348.444	21.578	0.001
	Within Groups	15,917.988	10	1,591.799		
	Total	50,266.433	11			

Table 5. ANOVA Dissolved Oxygen between surface and groundwater

		Sum of Squares	df	Mean Square	F	Sig.
Conductivity Dry Season	Between Groups	28,056.250	1	28,056.250	27.378	0.000
	Within Groups	10,247.667	10	1,024.767		
	Total	38,303.917	11			
Conductivity Rainy Season	Between Groups	34,348.444	1	34,348.444	21.578	0.001
	Within Groups	15,917.988	10	1,591.799		
	Total	50,266.433	11			

Appendix G: ANOVA Pesticide residues between surface and groundwater

Table 1: ANOVA Cypermethrin between surface and groundwater

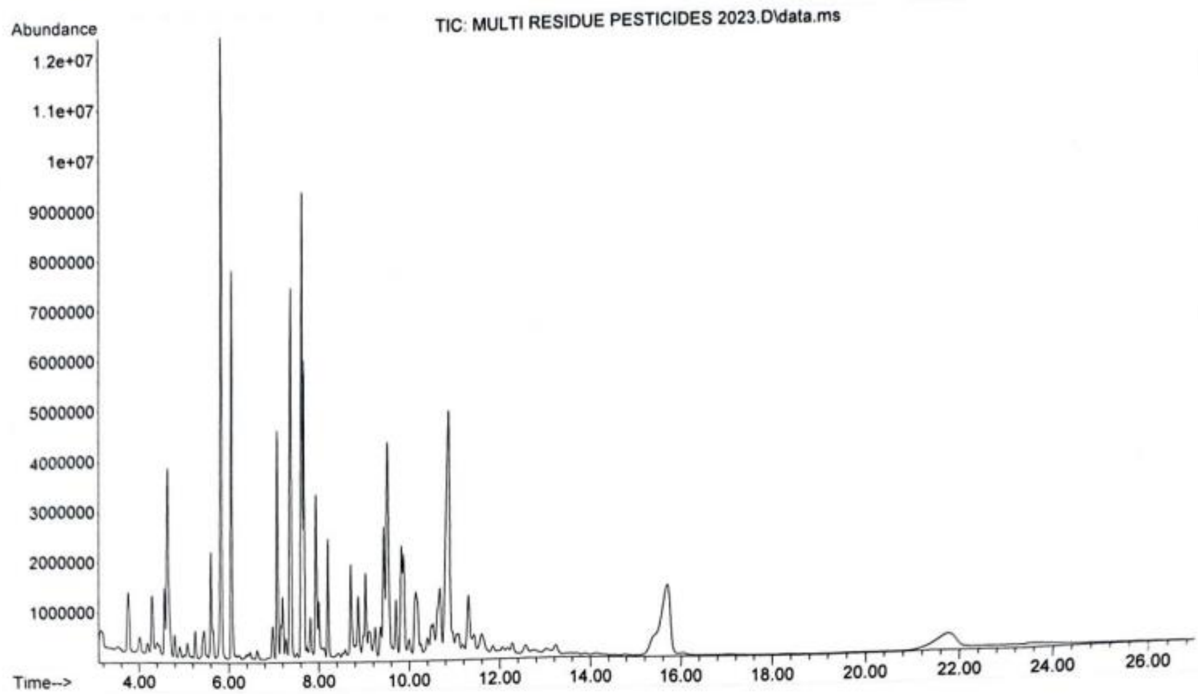
		Sum of Squares	df	Mean Square	F	Sig.
Cypermethrin Dry Season	Between Groups	0.523	1	0.523	6.584	0.028
	Within Groups	0.794	10	0.079		
	Total	1.317	11			
Cypermethrin Rainy Season	Between Groups	0.013	1	0.013	0.286	0.605
	Within Groups	0.439	10	0.044		
	Total	0.452	11			

Table 1: ANOVA S – metolachlor between surface and groundwater

		Sum of Squares	df	Mean Square	F	Sig.
S Metolachlor Dry Season	Between Groups	0.624	1	0.624	1.954	0.192
	Within Groups	3.192	10	0.319		
	Total	3.816	11			
S Metolachlor Rainy Season	Between Groups	67.308	1	67.308	3.236	0.102
	Within Groups	207.981	10	20.798		
	Total	275.290	11			

Appendix H: Some chromatograms and sample printout results from GC MS analysis

nstrument :   GCMS MBS
ample Name: BLUE FIELD BH 1
isc Info   :
ial Number: 1



MALAWI BUREAU OF STANDARDS   Quantitation Report   (Not Reviewed)

Data Path : C:\msdchem\1\data\
Data File : Water Sample
Acq On   : 17 February 2023 15:49
Operator : LUHANGA
Sample   : Bloomfield BH1 (Dry season)
Misc   :
ALS Vial : 1   Sample Multiplier: 1

Quant Time: 17 16:12:09 2023
Quant Method : C:\msdchem\1\methods\CHEMETRIXLFK_laboratorya.M
Quant Title :
QLast Update : February 17:16:03 2023
Response via : Initial Calibration

Compound	R.T.	QIon	Response	Conc	Units	Dev(Min)
Target Compounds						Qvalue
1) Cypermethrin	3.764	43	304427	0.000	ppb	93
2) Deltamethrin	14.624	41	161152	0.000	ppb	98
3) Alpha-cypermethrin	26.180	90	250045	0.000	ppb	96

manual integration (+) = signals summed

MALAWI BUREAU OF STANDARDS Quantitation Report (Not Reviewed)

Data Path : C:\msdchem\1\data\
Data File : Water Sample
Acq On : 15 April 2023 15:49
Operator : LUHANGA
Sample : Bloomfield BH1 (Rainy season)
Misc :
ALS Vial : 1 Sample Multiplier: 1

Quant Time: April 15 16:12:09 2023
Quant Method : C:\msdchem\1\methods\CHEMETRIXLFK_laboratorya.M
Quant Title :
QLast Update : 15 April 16:11:03 2023
Response via : Initial Calibration

Compound	R.T.	QIon	Response	Conc	Units	Dev(Min)
Target Compounds						Qvalue
1) Cypermethrin	4.201	44	203642	1.047	ppb	93
2) Deltamethrin	14.938	37	151941	0.000	ppb	98
3) Alpha-cypermethrin	25.911	83	230072	0.000	ppb	96

manual integration (+) = signals summed

nstrument : GCMS MBS
ample Name: BLUE FIELD BH 2
isc Info :
al Number: 1