



Midlands State University

OCCURANCE OF ORGANIC COMPOUNDS IN WATER AND SEDIMENTS
IN SEBAKWE RIVER

BY

CHARITY RUTANHIRA

R153765Z

Dissertation submitted in partial fulfillment of the requirements for the
Bachelors of Science Honors Degree in Applied Biosciences and Biotechnology

Department of Applied Biosciences and Biotechnology

Faculty of Science and Technology

MAY 2019

APPROVAL FORM

This is to certify that the dissertation entitled “ An investigation on the occurrence of organic compounds in water and sediment in Sebakwe River, Kwekwe”, submitted in partial fulfillment of the requirements for Bachelor of Science Honors Degree in Applied Biological Sciences and Biotechnology at Midlands State University, is a record of the original research carried out by Charity Rutanhira R153765Z under my supervision and no part of the dissertation has been submitted for any other degree or diploma.

The assistance and the help received during the course of this research have been duly acknowledged. Therefore, I recommend that it be accepted as fulfilling the dissertation requirements.

Name of supervisor(s)

Signature

Chairperson’s signature

ABSTRACT

Pollution of the aquatic environment is a major global concern as it is emerging that pollutants such as organic compounds are rising each day. The anthropogenic activities such as agricultural and wastewater effluent contribute to the pollution of aquatic resources. The aim of this study was to determine the spatial occurrence and concentration of organic compounds in water and sediment along Sebakwe River in Kwekwe. Water and sediment samples were collected once in January 2019 at six sites along Sebakwe River. The sampling points were selected to capture the different activities such as agriculture and sewage effluent discharge in the catchment with a potential to contribute organic pollutants in the aquatic environment. The water and sediment samples were analyzed for the presence of organic pollutants using a gas chromatography mass spectrometer at Central Veterinary Laboratory (CVL). The results showed that three different types of organic pollutants (pharmaceuticals, pesticide and food additives) were present in both the water and sediment samples. In addition, organic compounds naturally occurring in the environment were observed among all the sites. A total of 27 organic compounds were present in the sediment samples and 29 were present in the water samples. There was no significant difference in the concentration organic pollutants among the sites ($p > 0.05$). The occurrence of organic compounds such as pesticides were observed near areas with agricultural activities and pharmaceuticals were observed near the sewage effluent discharge point which suggests that the activities in the catchment have an influence on the type of organic compound found in the aquatic environment. The results from this study are important as they contribute to knowledge of the ecological health status of Sebakwe River. This information can be used by local environmental managers such as Environmental Management Agency (EMA) as baseline data for future monitoring studies and by Kwekwe City Council for the management activities in the catchment. Awareness programs are to be done so as to reduce organic compounds pollution of Sebakwe River and legislation on preserving natural resources is to be enforced in the catchment.

ACKNOWLEDGEMENTS

I would like to thank the Lord Almighty God for guiding me throughout my studies. A special thanks to my academic supervisor, Dr T. Dube for guiding me through the work. Many thanks to Mr. C. Mabugu , Billie Manhire and Maryleen Chibanda for their help in the sample collection and Mr T.Mhande for assisting me with the practical's at Central Veterinary Laboratory. I am grateful for my loving parents, for being my support system emotionally and financially throughout my studies.

DEDICATION

This is dedicated to my parents Mr and Mrs Rutanhira.

ACRONYMS AND ABBREVIATION

APIs – Active Pharmaceutical ingredients

CVL – Central Veterinary Laboratory

EC – European Commission

E.Coli - Escherichia coli

EMA – Environmental Management Agency

EMA act – Environmental Monitoring Act

EQS – Environmental Quality Standards

EU – European Union

GES – Good Ecological Status

HBCD - Hexabromocyclododecacane

MSFD – Marine Strategy Framework Directive

OC - Organochlorines

OP - Organophosphates

US – United State

WFD – Water Framework Directive

Table of Contents

Approval Form.....	iii
Abstract	iv
ACKNOWLEDGEMENTS.....	iii
DEDICATION.....	iv
ACRONYMS AND ABBREVIATION.....	v
CHAPTER ONE: INTRODUCTION.....	1
1.1 Background	1
1.2 Problem statement	3
1.3 Justification	3
1.4 General objectives	4
1.4.1 Specific objectives	4
CHAPTER 2: LITERATURE REVIEW	5
2.1 Organic compounds as pollutants of the aquatic system	5
2.2 Pesticides.....	5
2.2.1 Insecticides	5
2.2.2 Organochlorines (OC).....	6
2.2.3 Organophosphates (OP)	6
2.2.4 Pyrethroids.....	7
2.2.5 Other pesticides	8
2.3 Effects of pesticides on non-target pests.....	8
2.4 Pharmaceuticals	11
2.4.1 Effects of pharmaceuticals in the aquatic environment	12
2.5 Regulations on pollution	13
CHAPTER 3: MATERIALS AND METHODS	17

3.1. Area of study	17
3.2 Study design	17
3.2.1 Sediment and water sampling.....	18
3.3 Laboratory analysis.....	19
3.3.1 Preparation of reagents.....	19
3.3.2 Preparation of samples	19
3.3.2.1 Sediment.....	19
3.3.2.2 Water.....	20
3.4 Data analysis.....	20
3.4.1 Qualitative analysis.....	20
3.4.2 Quantitative analysis	20
CHAPTER FOUR: RESULTS	22
4.1 Qualitative analysis of the organic compounds in sediments and water	22
4.1.1 Organic compounds found in sediments from Sebakwe River	22
4.1.2 Organic compounds found in water from Sebakwe River	25
4.2 Quantitative analysis of organic compounds in river sediment and water	29
4.2.1 Quantitative analysis of organic compounds in sediments from Sebakwe River.....	29
4.2.2 Quantitative analysis of organic compounds in water from Sebakwe River.	30
CHAPTER 5: DISCUSSION	32
5.1 Qualitative and quantitative analysis of organic residues in water and river sediment.	32
5.2 Potential impact of organic pollutants to aquatic biota.....	34
5.3 Conclusion.....	35
5.5 Recommendations.....	35
References	37

List of appendices	page
Appendix 1: Chromatogram.....	46
Appendix 2: Spss output of naturally occurring compounds in sediment.....	46
Appendix 3: Spss output of pharmaceuticals in sediment.....	47
Appendix 4: Spss output of compounds of industrial type in sediment.....	47
Appendix 5: Spss output of pesticides in sediment.....	48
Appendix 6: Spss output of food additives in sediment.....	48
Appendix 7: Spss output of naturally occurring compounds in water.....	49
Appendix 8: Spss output of compounds of industrial type in water.....	49
Appendix 9: Spss output of pesticides in water.....	50
Appendix 10: Spss output of pharmaceuticals in water.....	50

List of Figures	page
Figure 3.1: Map showing sampling sites and catchment activities along Sebakwe River.....	18
Figure 4.1: The types of organic compounds in sediment from Sebakwe River.....	25
Figure 4.2: The types of organic compounds in water from Sebakwe River.....	28
Figure 4.3: Relative concentration of organic compounds found in sediment from Sebakwe River.....	29
Figure 4.4: Relative concentration of organic compounds in water from Sebakwe River.....	30

List of Tables	page
Table 4.1: Organic compounds present in sediment from Sebakwe River.....	22
Table 4.2: Organic compounds present in water from Sebakwe River.....	25

CHAPTER ONE: INTRODUCTION

1.1 Background

The pollution of the aquatic environment is now a major global concern (Elliott, 2003; Schriks *et al.*, 2010). This is due to the increasing human population, urbanization and rapid growth of economic activities (Dalton *et al.*, 2014). The growth of global economic activities has led to the release of more than 100,000 chemicals into the aquatic environment via atmospheric transport, runoff into waterways, or direct disposal (Dalton *et al.*, 2014).

The aquatic pollutants are broadly classified into organic and inorganic chemicals (Schriks *et al.*, 2010). The examples of these pollutants are: pesticides, herbicides, insecticides that are used in agriculture, chlorinated solvents used in many industrial processes and dry-cleaning activities, pharmaceuticals and chemical used in industrial processes such as preservatives (Bruchet *et al.*, 2005, Dalton *et al.*, 2014). The adverse effects of these organic pollutants on the aquatic environment are not fully understood and are worsened by their increased use (Malaj *et al.*, 2014 ; Torres *et al.*, 1996).

The aquatic chemical pollutants pose a serious long term risk when present in water bodies (Scherr and McNeely, 2007). For example, various pollutants such as metals, oil, pesticides, pharmaceuticals and preservatives when deposited into aquatic environment may accumulate in sediments over a long time (Pal *et al.*, 2010). Sediments may thus act as secondary sources of contaminants with potential for continuous release into the water (Scherr and McNeely, 2007).

Several pharmaceuticals and personal care products as well as artificial sweeteners are known as contaminants of emerging concern due to their frequent detection in environmental samples (Sharma *et al.*, 2019). Often, residues of these contaminants are collected in wastewater effluents after their consumption and due to their low removal in wastewater treatment plants (Schriks *et al.*, 2010). Irrigating using water containing pharmaceuticals could imply that crops may take up these compounds, being another route of human exposure (Köck-Schulmeyer *et al.*, 2013). Presence of the pharmaceuticals in the water could foster the dissemination of antibiotic resistance genes, which may interact with human intestinal flora and spread the resistance determinants, potentially impacting the human health (Sharma *et al.*, 2019).

The ecological effects of pesticides are varied and are often inter-related. For example, the effect of pesticides on aquatic species can be cumulative, synergistic or antagonistic (Grung *et al.*, 2015). Therefore accurate determination of risk posed to aquatic biota by the pesticides detected in water samples is difficult. Several studies have shown that pesticides are responsible for reducing aquatic insects such as mosquitoes, midges, blackflies and other invertebrates diversity (Bowmer, 2013). The occurrence of persistent pesticides residue, especially organochlorines (OC) in the environment is of great concern due to their tendency of long-range transport (Mahmood *et al.*, 2016). Organophosphorus pesticides are much more resistant to microbial degradation and have the tendency to concentrate in lipid rich tissues of aquatic organisms (Essumang and Chokky, 2009). Studies have shown that OC pesticides tend to accumulate more in aquatic organisms and they settle on the sediments (Akan *et al.*, 2014).

The ecological effects of pesticides extend beyond individual organisms and can extend to ecosystems (Grung *et al.*, 2015). The effects of pesticides at the ecosystem level are usually considered to be an early warning indicator of potential human health impacts (Grung *et al.*, 2015). For example, the rapidly increasing use of pesticides in agriculture, poses serious threat to the public health, fisheries and aquatic ecosystem through bioaccumulation and biomagnification (Mackay and Boethling, 2000). Bioaccumulation is the movement of a chemical from the surrounding medium into an organism, while biomagnification describes the increasing concentration of a chemical with increasing trophic level (Mackay and Boethling, 2000). The accumulation of these pollutants in higher trophic feeders therefore pose a health risk to human beings who consume contaminated fish (Grung *et al.*, 2015). Thus deaths and chronic diseases worldwide are sometimes reported to have resulted from pesticide poisoning (Rigotto *et al.*, 2013).

The impact of pesticides on the aquatic life is not fully documented and in some cases unreported (Sabra and Mehana, 2015). Thus, if continued will result in many aquatic species becoming extinct. There is therefore a need to monitor pesticide pollution in aquatic environment especially in the developing countries where there is scarcity of information.

1.2 Problem statement

An estimated 80 to 90% of land habited by people is under some form of productive livelihood activities (Scherr and McNeely, 2007). This includes almost a third of global land covered by agricultural activities ranging from cropping to pastures as the dominant land uses, therefore having an ecological effect on the overall landscape (Scherr and McNeely, 2007).

Agriculture is the backbone of Zimbabwe's economy. The agricultural activities are playing a role in the introduction of pesticides in the aquatic environment as they are widely used to increase yields and quality. Sebakwe River in Kwekwe is at risk of pesticide pollution because part of its catchment is dominated by commercial wheat production. These pesticides have a potential to pollute Sebakwe River through leaching, aerial sprays or soil erosion.

Stream bank cultivation is an old practice that is however facing a lot of resistance from modern environmental conservationists, environmental scientists and governing authorities. Despite the numerous environmental benefits of maintaining buffer zones, the practice is common among poor local communities. Along Sebakwe River, stream bank cultivation is common in the rural and resettled communities. This practice poses a risk to pesticide pollution to the river due the rampant use of chemicals in subsistence farming.

A potential source of organic compounds such as pesticides, preservatives and pharmaceuticals in the aquatic environment is sewage effluent. Surface runoff and wastewater effluents are among the most important entry pathways for organic compounds into aquatic environments (Köck-Schulmeyer *et al.*, 2013). Some industries release their waste effluent into the environment without proper treatment. For example, Kwekwe City Council was fined by Environmental Management Agency (EMA) for releasing raw sewage into Sebakwe River. Sewage effluent contains contaminates that include pesticides residues from domestic areas that have a negative effect on the aquatic ecosystem.

1.3 Justification

An increasing number of communities are drawing on water sources that are replenished directly or indirectly by wastewater effluents, leading to increasing concern that synthetic chemicals may contaminate ecosystems, and surface and drinking water supplies. Organic compounds enhance

economic potential in terms of increased production of food and amelioration of vector-borne diseases. However, their residues have resulted in serious health implications to humans and their environment (Forget, 1993). The organic pollutants pose potential risk to humans and unwanted side effects to the environment (Igbedioh, 1991).

Sebakwe River is a source of water for drinking, irrigation and many domestic activities. The quality of the water in the river has a direct impact on the health of the Kwekwe residence that relies on Sebakwe River as a water source. Individuals may be affected by drinking contaminated water or by eating contaminated fish from the river. The information on types of organic pollutants in Sebakwe River is of relevance to the health authorities of Kwekwe.

The ecological health status of Sebakwe River is important to local environmental authorities such as Environmental Management Agency and the Kwekwe City Council. The monitoring of organic pollutants in Sebakwe River provides a baseline data that can be used in future studies.

There are financial impacts associated with water pollution. When fresh water has been contaminated, they are deemed to be unsafe to drink and require treatment. Treating contaminated waters can be expensive. Considering the economic meltdown of Zimbabwe, spending money on treating contaminated water is economically unsustainable (Forget, 1993). Monitoring of organic pollutants will provide early warnings to the local authorities to act thereby reducing further pollution hence reducing costs associated with treatment of drinking water.

1.4 General objectives

The general objective of this study was to determine the organic compound residues in water and sediment in Sebakwe River.

1.4.1 Specific objectives

- To qualitatively assess organic compounds in water and sediment in Sebakwe River.
- To quantitatively assess organic compounds in water and sediment in Sebakwe River

CHAPTER 2: LITERATURE REVIEW

2.1 Organic compounds as pollutants of the aquatic system

Organic compounds are becoming a rising concern in the aquatic environment as they contaminate water sources. Persistent organic pollutants comprising organochlorines used for pest control and industrial purposes are becoming of concern worldwide (Goerke *et al.*, 2004). Examples of organic pollutants are pesticides, pharmaceuticals and preservatives. These could have been as a result of sewage effluent or industrial effluent that has been released into the water way.

2.2 Pesticides

Pesticides are natural or synthetic agents that are used to eliminate unwanted plant or animal pests (Goerke *et al.*, 2004). They can be classified either by target pest or by chemical identity or action of the pesticides. Classification by target pest is the most used method and examples of this classification are insecticides, herbicides, nematocides and rodenticides (Mahmood *et al.*, 2016). Pesticides can also be organized into classes according to their chemistry. Examples of this classification include organophosphates (OP), organochlorine (OC), Carbamates and Pyrethroids (Mahmood *et al.*, 2016). Pesticides such as organochlorines are of concern as they tend to persist in the aquatic environment which has a negative impact on aquatic biota and animals (Goerke *et al.*, 2004).

2.2.1 Insecticides

Insecticides are a group of chemicals that have been designed to eliminate insects. Their mode of action can be neurotoxic (Net *et al.*, 2015). The insecticides act on acetylcholinesterase which is

associated with the nervous system of insects. Insecticides that target multiple species have been developed. These include Dichlorvos, Cyhalothrin , Paraquat and Glyphosate. Alternatively, the insecticides are used in combination for effective control of the insects. The effect of pesticides at population level , depend on exposure and toxicity, as well as on different factors like life history, characteristics, timing of application, population structure and landscape structure (Mahmood *et al.*, 2016).

2.2.2 Organochlorines (OC)

Organochlorines are stable compounds which are persistent in the environment and tend to accumulate in fatty tissue (Miglioranza, *et al.*, 2002). The main use of OC's is to eradicate disease vectors such as mosquitoes. The OC's are also used in cultivation of grapes, lettuce, tomato, alfalfa, corn, rice, sorghum, cotton and wood, for preservation through elimination of termites, fungi and mites. The exposure of OC to insects is mainly by contact or ingestion (Goerke *et al.*, 2004).

Organochlorine pesticides are ubiquitous contaminants whose occurrence in the environment is of special concern because of their resistance to degradation and the toxicity of some of their constituents (Miglioranza *et al.*, 2002). In countries such as Argentina and Iran, an assessment on the presence of organochlorine pesticides was done (Miglioranza *et al.*, 2002; Kafilzadeh, 2015). The residues were found in water, sediment and aquatic biota. In the Antarctic, bioaccumulation of organochlorines was observed in the aquatic biota (Goerke *et al.*, 2004).

2.2.3 Organophosphates (OP)

Organophosphates are esters derived from phosphoric acid (Mahmood *et al.*, 2016). The action of OP in insects is through ingestion and contact (Mahmood *et al.*, 2016).The organophosphate

insecticides are most commonly used as they are less persistent in the environment in comparison to organochlorines and, hence they can be found both in drinking water and in food (Barky *et al.*, 2012). An example of an organophosphate pesticide is malathion. Malathion is a pesticide, commonly used by farmers in Zimbabwe. Malathion is an insecticide with a neurotoxin action that causes insect death by inhibiting the acetylcholinesterase enzyme (Barky *et al.*, 2012). Organophosphorus pesticides tend to bioaccumulate and biomagnify in aquatic biota (Mackay and Boethling, 2000).

2.2.4 Pyrethroids

Pyrethroids originate from natural insecticide derived from pyrethrum extract derived from chrysanthemum flowers, known as pyrethrins (Barky *et al.*, 2012). Subsequently, they are synthetically manufactured around 100 different commercial products. The insects are exposed to pyrethroids by contact or ingestion. They act on the central nervous system causing changes in the dynamics of the Na⁺ channels in the membrane of the nerve cell, causing it to increase its opening time prolonging sodium current across the membrane in both insects and vertebrates. These events can lead to neuronal hyper-excitation (Mahmood *et al.*, 2016). Among pesticides, Deltamethrin, which is type II pyrethroids, has a wide acceptability, and it is thoroughly used in agriculture and forestry because of its high activity against a broad spectrum of insect pests. The oral route constitutes the main sources of general population exposure to this pesticide which is ingested within food and water. Synthetic pyrethroids (also including sumithrin, fenvalerate, allethrin, permethrin, cypermethrin, and fenvalerate) have ability to disrupt biochemistry, hematology and reproduction. The effects of Deltamethrin on nervous, respiratory, and hematological systems in fish have been reported (Barky *et al.*, 2012). These pesticides tend to bioaccumulate and magnify in aquatic biota (Barky *et al.*, 2012).

2.2.5 Other pesticides

Herbicides are used on unwanted plants and examples are paraquat, glyphosate and propanil. Most herbicides tend to mimic growth hormone of plants. When the herbicides are present in the aquatic system, they result in the eradication of aquatic plants which are required by some aquatic organisms. Fungicides when applied to wood, they are called wood preservatives (Pal *et al.*, 2010). Fungi in the aquatic system help in the degradation of pollutants in water. Fungicides tend to eliminate some fungi resulting in accumulation of pollutants in the aquatic environment. Rodenticides kill mice, rats, moles and other rodents. They cause internal bleeding resulting in the death of the rodents. Fumigants are pesticides that exist as a gas or a vapor at room temperature and may be used as insecticides, fungicides or rodenticides, especially in closed storage places as they kill every living organism. They are extremely toxic, due to their physical properties, rapid environmental dissemination and human or animal absorption (Pal *et al.*, 2010). Examples include cyanide, aluminium phosphate and methyl bromide. Other pesticides include algaecides (to kill algae), miticides (to kill moths) and acaricides (to kill ticks) (Schriks *et al.*, 2010).

2.3 Effects of pesticides on non-target pests

While pesticides are commonly used in agriculture to protect crop production from harmful species, they can lead to the contamination of surface and ground waters. Urban effluents, agricultural runoff and leaching are the main sources of pesticides in surface and groundwater. Pesticides can cause neurological disorders, affect growth, malfunction of the immune and reproductive systems, cancer and endocrine disruption of the aquatic animals (Net *et al.*, 2015).

The application of pesticides in agriculture has become a major risk to the aquatic environment due to their toxicity and bioaccumulation (Net *et al.*, 2015). Moreover, pesticides are often

present in mixtures in natural environment instead of single compounds. It is known that pesticide mixtures can cause changes in their toxicity (Munze *et al*, 2017). Therefore, the actual field situations will be underrated based on experiments using only single pesticides, leading to underestimated ecological risk of compounds (Luo *et al.*, 2014; Shuman-goodier and Propper, 2016). It is therefore necessary to assess the effects of pesticide mixtures when evaluating their ecological risks on ecosystems (Wang, *et al*, 2018).

A broad range of non-target aquatic phytoplankton and higher trophic organisms like fish and fish predators are affected by pesticide pollution (Mondal, *et al*, 2018). Pesticides have mode of action that can pose risks to human health and the environment as the target systems or enzymes are similar to those in human beings (Turgut, 2007). As they are harmful to plant and animal life, they are also harmful to humans and especially developing children. Some pesticides are naturally derived from arsenic or plant extracts, while others are man-made chemicals. The widespread use of man-made pesticides began in the 1940s and 1950s when production rapidly grew and spread throughout the world (Barky *et al.*, 2012).

In humans organochlorines act primarily at the level of central nervous system altering the electrophysiological properties and enzymatic neuronal membranes, causing alterations in the kinetics of the flow of Na⁺ and K⁺ through the membrane of the nerve cell. This results in the spread of multiple action potentials for each stimulus , causing symptoms such as seizures and acute poisoning death from respiratory arrest (Mahmood *et al.*, 2016). High levels of exposure to organochlorines have been shown to cause cloracne, a type of acne cause by chlorine containing chemicals and skin rashes (Zhang, *et al*, 2004). There is some evidence that organophosphate insecticides affect the immune system and can cause psychiatric problems such as paranoid behavior, disorientation, anxiety and depression (Zhang *et al.*, 2004). Other pesticides may cause

muscle twitching, tremors, weakness, inability to breath, blurring of vision, vomiting, cramps, excessive perspiration, unconsciousness and even death in cases of high exposures. There are few studies on the long-term, low-level exposure of many types of pesticides (Zhang *et al.*, 2004).

Organophosphates in humans act on the central nervous system by inhibiting acetylcholinesterase, an enzyme that modulates the amount and levels of the neurotransmitter acetylcholine, disrupting the nerve impulse by serine phosphorylation of the hydroxyl group in the active site of the enzyme (Barky *et al.*, 2012). The symptoms of organophosphate poisoning causes loss of reflexes, headache, dizziness, nausea, convulsions, coma and even death. Also, described with alkylating properties ,which from the point of view of mutagenesis is paramount because they act directly on the deoxyribonucleic acid (DNA) adding alkyl groups methyl and ethyl mainly to the nitrogenous bases with nucleophilic groups capable of reacting with electrophiles (Mahmood *et al.*, 2016).

The threats associated with the use of these toxins cannot be overlooked. Accumulation of pesticides in the food chains is of greatest concern as it directly affects the predators and raptors (Zhang *et al.*, 2004). Indirectly pesticides can also reduce the quantity of weeds, shrubs and insects on which higher orders feed. Spraying of insecticides, herbicides and fungicide have also been linked to declines in the population of rare species of animals and birds. Additionally, their long term and frequent usage lead to bioaccumulation (Mahmood *et al.*, 2016).

Many pesticides are endocrine disrupting chemicals (EDCs) that alter fundamental physiological processes and lower fitness of exposed wildlife. At larger scales, pesticide contaminants affect

species interactions, decrease local and regional biodiversity, and even impair ecosystem function (Shuman-Goodie and Propper, 2016).

Organophosphates and carbamates are two structurally similar insecticide classes that also produced a large decrease in both swims peed and activity level (Barky *et al.*, 2012). They can disrupt thyroid hormone function, cause immune and nervous system toxicity, and impair metabolic function of non-target organisms. The use of several organophosphate insecticides has been discontinued in the United States, and a preliminary risk assessment by the Environmental Protection Agency has summarized significant human and environmental health concerns for seven additional organophosphates (Barky *et al.*, 2012). Carbamate insecticides exhibit similar toxicity to non-target organisms (Shuman-Goodie and Propper, 2016).

Aquatic toxicity assay has become a common method to assess the negative influence of toxic chemicals on the water environment. Fish are an essential component for the aquatic environment in conventional ecotoxicity test. Zebrafish (*Danio rerio*) has become an efficient and commonly used biological model for chemical toxicity screening due to its several advantages, such as easy handling, short life span, high fecundity, and high homology to mammalian species .It becomes urgently necessary to assess the negative influence of pesticides on *D. rerio*at different life stages since these animals are actually exposed to chemicals at different life stages or even during the whole life stage. Although many recent studies have been carried out on zebrafish, but only the effects of single pesticides have been investigated in most of these studies (Wang *et al.*, 2018).

2.4 Pharmaceuticals

Pharmaceutical products have been used for centuries but, from an ecotoxicological viewpoint, active pharmaceutical ingredients (APIs) are considered emerging environmental contaminants

since only recently there are suitable analytical and sampling techniques able to accurately quantify them in environmental matrices (Gonzalez-rey *et al.*, 2015).

As APIs are designed to be therapeutically active, the serious concern about the environmental fate related impacts in water quality status and potential effects on non-target organisms led to new EU and US legislative frameworks and directives. APIs and pesticides monitoring in natural waters is very complex due to their multiplicity in terms of e.g. physico-chemical properties, chemical structure and persistence in the environment (Gonzalez-rey *et al.*, 2015).

2.4.1 Effects of pharmaceuticals in the aquatic environment

Toxicity of pharmaceuticals (with special emphasis to veterinary drugs) has been demonstrated in various aquatic organisms. Aquatic organisms are particularly important targets, as they are exposed via wastewater residues over their whole life. Once inside the organism, the pollutant may promote a variety of effects, ranging from cellular impairment to lethality (Wagil *et al.*, 2015). The presence of pharmaceuticals in the aquatic system such as anti helminth drugs results in the killing of aquatic helminth and disrupting the ecosystem.

The prevalence of antimicrobial resistance, including multi-drug resistance continues to increase. The consequences of which are well known, yet action remains inadequate. Examples of antimicrobial resistance is the drug resistant tuberculosis (TB), enteric bacteria and many more (Coleman *et al.*, 2013; Pereira *et al.*, 2013; Harris *et al.*, 2014).

The presence of enteric bacteria in aquatic systems represents a public health risk. Enteric antibiotic resistant bacteria, selected in the intestinal tract of humans and animals under antibiotic therapy, may enter in water systems through discharges from livestock and poultry production, and municipal wastewater treatment plants (Coleman *et al.*, 2013). Rivers are the main receptacle

for pollution from these and other sources and constitutes efficient vectors for the spreading of antibiotic resistance (Pereira *et al.*, 2013).

Bacterial resistance is a rising problem all over the world, generated by processes of selection that result from the massive use of antibiotics. The sewage discharge of domestic effluents and from strongly selective sources such as hospitals, industries, aquaculture, and among others has led to an increase in the distribution and frequency of bacterial resistance genes in several environments, including fresh and marine waters (da Costa *et al.*, 2015). In Canada, antimicrobial resistant *E. Coli* has been found in drinking water (Harris *et al.*, 2014). The risk associated with antimicrobial resistance of aquatic animals and biota is that the gene may result in water borne diseases and the gene for resistance may be transferred from the aquatic animals to humans. This will result in one not being able to treat a number of diseases in that individual using the drug by which the individual is resistant to.

2.5 Regulations on pollution

The Water Framework Directive (WFD) of the European Commission (EC 2000/60/EC) describes the monitoring of priority substances and other pollutants in the surface waters of the European Union. The daughter directive 2008/105/EF of the European Parliament and the Council of the European Union has defined environmental quality standards (EQSs) for priority substances in water, with the aim to protect the aquatic environment from adverse effects of these substances. For some compounds, EQS values have been derived for biota to protect against indirect effects and secondary poisoning. Amongst the priority substances, specific compounds have been classified as priority hazardous substances, with the aim to cease or phase out their discharges, emissions and losses. The list of priority substances was recently revised (Directive 2013/39/EU). New priority substances were added by the European Commission,

amongst these are the biocides cybutryn (Irgarol) and terbutryn, the pesticides aclonifen, bifenox, cypermethrin and heptachlor/heptachlor epoxide and the brominated flame retardant hexabromocyclododecane (HBCD).

In Europe, the umbrella regulations for addressing the ecological quality of the water systems are the Water Framework Directive (WFD; 2000/60/EC), for lakes, rivers, transitional (estuaries and lagoons) and coastal waters, and the Marine Strategy Framework Directive (MSFD; 2008/56/EC) for marine waters. The ecological concept behind both directives is, in principle, very simple, and consists of comparing the current state of an area with that which would be expected under minimal or sustainable human use of that area and, in case of degradation, intervening to bring it back to the desired good status. A variety of indicators, target values and reference setting approaches for assessing good ecological status (GES) have been developed, inter-calibrated, discussed and published during the last decade, and the process continues (Van Hoey *et al.*, 2010).

Under the Common Implementation Strategy, guidance on chemical monitoring of sediment and biota has been published, which covers the requirements for compliance checking and temporal trend monitoring for biota and sediment. Several studies have been carried out in many European countries so as to implement the EU directive (Directive 2013/39/EU). In Denmark, a study was carried out in 2014 on biocides, pesticides and other chemicals in the aquatic environment (Van Hoey *et al.*, 2010; Vorkamp *et al.*, 2014). In Europe, a study on the use of benthic indicators as a way of detecting environmental hazards was done in 2010 and in Basque coast studies have also been done on how effective the directive is on monitoring and removal of harmful toxins in the environment (Van Hoey *et al.*, 2010; Borja *et al.*, 2011).

Many developing countries have no legislation to direct them on how to handle harmful substances in the environment. Some countries tend to use the legislation that is used in the developed countries. This legislation used is not effective in developing countries as the water systems are different and also different pollutants tend to affect these areas. Few developing countries (example, in Zimbabwe the Environmental Management Act of 2002) have managed to draft legislation on the way in which the environment can be protected from toxic compounds. However, the implementation of the legislation in developing countries is very difficult as economic challenges play a significant role.

In Zimbabwe there is use of the Environmental Monitoring Act (EMA act) (chapter 20:27) of 2002 is used in the monitoring of hazardous substances in the aquatic environment. Statutory instrument number 12 of 2007 addresses labeling, packaging, repackaging and sale of hazardous substances or articles containing hazardous substances in Zimbabwe. The regulations prescribe conditions which have to be observed by employers over the handling of hazardous substances at the workplace, conditions for transporting hazardous substances and procedures to be followed when there is an accidental spillage of hazardous substances in Zimbabwe. This is important as it is one of the routes by which chemical pollution of the aquatic environment occurs. The Environmental Management Agency is empowered to issue spot fines to any person who violates the law. In addition, any person whose substances affect the environment is liable to pay for the cost of restoring the environment i.e. the polluter pays principle. The offender is also liable to pay compensation for any damage caused by the offence to any person (EMA, 2002).

Environmental Management Act (2002) repealed The Natural Resources Act (Chapter 20:13), The Atmospheric Pollution Prevention Act (Chapter 20:03), The Hazardous Substances and Articles Act (Chapter 15:05) and The Noxious Weeds Act (Chapter 19:07). The Act creates a

framework for environmental management, make provision for the formulation of environmental quality standards, (e.g. air, water, noise, effluents, waste and hazardous substances), and develop the national environmental action plan. The Bill requires EIAs to be undertaken for prescribed activities, and specifies procedures for the administration of the EIA process.

Other Acts that are used in environmental monitoring in Zimbabwe are the Water Act, No. 31 of 1998 which regulates the planning and development of water resources, and provides a framework for allocating water permits. In association with this act, the Water (Waste and Effluent Disposal) Regulations of 2000 is specific on the quality is acceptable in terms of effluent released into rivers (EMA, 2002). Implementation of the EMA act is has been carried out by the Ministry of Water Resources and Development (EMA, 2002).

CHAPTER 3: MATERIALS AND METHODS

3.1. Area of study

Sebakwe River is in the Sanyati Catchment and located in the Midlands Province of Zimbabwe. It has a length 150 km from the source to mouth. Sebakwe River is a tributary of Munyati River which it joins in Zhombe East. The River descends from the south-western heel of Mtoro Hill with the elevation of 1580 m north-east of Chivhu. The climate is hot and wet during the summer rainy season from mid November to mid March, with a cool and dry weather from May to mid-August in the winter season and warm dry weather from August to mid November. Winters are mainly characterized with cold nights with a minimum temperature of 7 °C. The average temperature of the catchment is 19.4 °C and the average annual rainfall is 667 mm. The soil type in this area is loam. The catchment is characterised by agricultural activities, artisanal mining and human settlements. The water from the river is used for irrigating the commercial wheat farms that are found in the catchment (Figure 3.1). Below Sebakwe Dam are fishing activities and gold mining. The river is used as a water source for their domestic purposes and subsistence farming. Fish in the area are a source of income and as food to the residents in the area.

3.2 Study design

The sampling points were chosen to capture the different activities in the catchment. The first and second sites are located after the confluence of Sebakwe River and the point at which sewage effluent from the Kwekwe Sewage Treatment Plant (KSTP) is discharged (Figure 3.1). The third and fourth sites are upstream before the confluence. In this region, the catchment is mainly characterized by agricultural activity. The fifth site is located near the confluence of Mbembeswane River and Sebakwe River. The last sampling site is located in Mlala Park where agricultural activity is common.

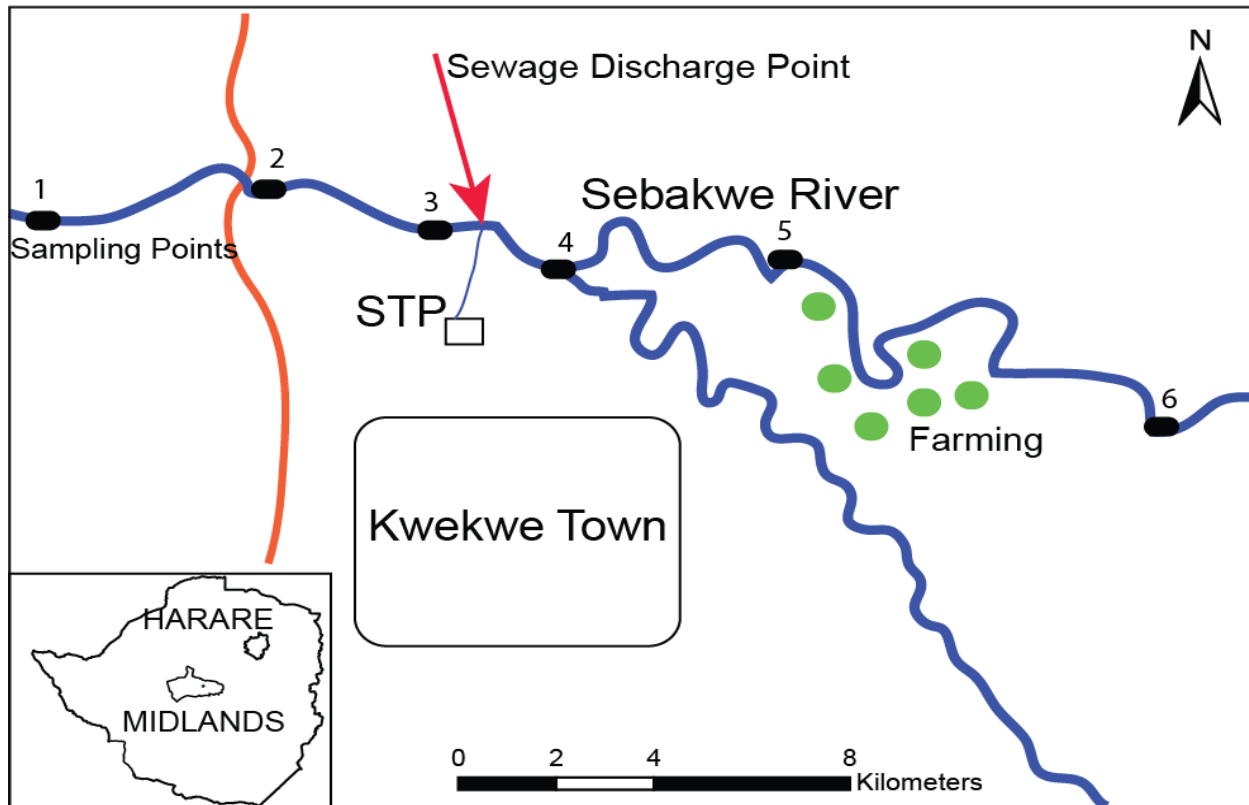


Figure 3.1: Map showing sampling sites and catchment activities along Sebakwe River.

3.2.1 Sediment and water sampling

The water and sediment samples were collected once in January 2019. The sediments were collected using a soil auger with a diameter of 10 cm. At each site, three samples were collected in a radius of 5 m. The samples from each site were mixed into one composite sample and placed into plastic bags. Water samples were collected from the same sites where sediments were collected. Each water sampling bottle was rinsed three times using the river. The sample bottle was immersed in the river and left under water until full. The sediment and water samples were stored in a cooler box which contained ice packs. They were then transferred into the refrigerator in the laboratory.

3.3 Laboratory analysis

3.3.1 Preparation of reagents

The extraction solvent was prepared by mixing methanol and chloroform in a ratio of 1:1. The solvent was used to dissolve the organic compounds in the samples. A mixture of methanol and chloroform was prepared because some organic compounds do not dissolve in methanol and in chloroform and vice versa (Kwak *et al.*, 2008; Dal Pra *et al.*, 2011). A volume of 500 ml of 99% methanol was mixed with 500 ml of < 99% of chloroform in a beaker. A salt was prepared so as to promote the separation of water and methanol. Using an analytical balance 4 g of anhydrous magnesium sulphate was weighed and placed in a tube and was mixed with 1 g of sodium chloride.

3.3.2 Preparation of samples

3.3.2.1 Sediment

Using an analytical balance, 20 g of each sediment sample was weighed and placed in a test tube. Using a measuring cylinder, 25 ml of the extraction solvent was added to each sample. The sample was mixed by shaking manually for 2 mins and then placed on a shaker for 10 mins. The samples were placed in a centrifuge for 10 mins at 4000 rpm. The supernatant from each sample was transferred into labeled test tubes. The test tubes were then placed into a drying block at 45 °C until dry. About 500 µl of chloroform was added to each test tube. Each test tube was then placed on a vortex until chloroform was mixed with the sample. The mixture was placed in labelled glass vials then placed in the gas chromatography mass spectrometer model GCMS-QP2020 for analysis.

3.3.2.2 Water

Using an analytical balance, 20 ml of each water sample was measured using a measuring cylinder and placed in a test tube. About 25 ml of the extraction solvent was added to each sample. This was mixed by shaking manually for 2 mins. The 5 g of anhydrous magnesium sulphate and sodium chloride salt prepared was added to the sample and mixed by shaking manually for 2 mins. The mixture was then placed on a shaker for 10 mins. After shaking, the sample was placed into the centrifuge for 10 mins at 4000 rpm. Chloroform is much denser than water resulting in layers forming with chloroform at the bottom leaving the water layer on top (Dal Pra *et al.*, 2011). The water layer was removed using a pipette. The remaining layer of chloroform was then placed in a labelled test tube for each sample. The test tubes were placed on the drying block until dry. About 500 µl of the sample was placed in each test tube and mixed using a vortex. The samples were then placed in vials then placed in the gas chromatography mass spectrometer model GCMS-QP2020 for analysis.

3.4 Data analysis

3.4.1 Qualitative analysis

A table containing the organic compounds highlighting the name of the compound, category of the compound and the potential source of the compound that was prepared. Bar graphs were plotted to show the number of compounds in each category in relation to the sampling sites.

3.4.2 Quantitative analysis

The Relative concentration of each analyte was estimated using the following equation:

Percentage concentration (% A) = [(Area of peak A)] / [total Area of peaks (A + B + C +...)]*

100, where A = area, A, B, C, ... = area of peaks (Appendix 1)

Bar graphs were used to show the relative concentrations of the organic compounds that were detected in the sediments and water samples from Sebakwe River. The data was tested for normality of residuals using Shapiro Wilk test. The water and sediment data did not conform to normality (Shapiro Wilk test; $p < 0.05$). A non-parametric test, Kruskal-Wallis test was used to test for the spatial variation of organic compounds amongst the six sites in Sebakwe River.

CHAPTER FOUR: RESULTS

4.1 Qualitative analysis of the organic compounds in sediments and water

The qualitative analysis of sediments and water showed that a number of organic compounds are present in Sebakwe River. The organic compounds present in Sebakwe River were grouped into five: pharmaceuticals, pesticides, food additives, compounds of industrial type and other compounds which naturally occur in the environment.

4.1.1 Organic compounds found in sediments from Sebakwe River

A total of 27 organic compounds were present in sediments. The most common type (14) of organic compounds present in the sediments were from plant and animal residue (Table 4.1 and Figure 4.1). Among the organic pollutants, pesticides were common with six residue types present among the sampling sites. There were three residues of pharmaceuticals, six pesticides, two food additives and one residue of industrial type among all the sites.

Table 4.1: organic compounds present in sediments from Sebakwe River

Compound	Description
Pharmaceuticals	
4-Imadazolidinone, 5-(phenylmethyl)-2-thioxo	Derived from ampicillin
Thiabendazole-13C6	Anthelmintic agent
p-Hydroxynobenzphetamine-2TFA	Synthetic drug

Table 4.1 continued

Compound	Description
Pesticides	
Ethofumesate	A herbicide
Dimethoate	An organophosphorous pesticide
Methoprene	An insecticide
Cenerin I	A member of pyrethins
Fonofos	An organophosphorous insecticide
Etrimfos	An insecticide
Food additive	
L-Ascorbic acid, 6-octadecanoate	Used as an anti oxidant
benzene,1,1',1''-[5-methyl-1-pentene-1,3,5-triyl]tris	Preservative
Industrial type	
Benzonitrile,m-phenyl-	Solventand versatile precursor to many derivatives
Other	
Benzene,(3-nitropropyl)-	
Thiocarbamic acid, N,N-dimethyl,S-1,3-diphenyl-2-butenyl ester	Found in mushroom
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide,trans-	Has a role as a human metabolite

Table 4.1 continued

Compound	Description
p-Hydroxynorbenzphetamine-2TMS	
Benzene,1,1'-[1-(2,2-dimethyl-3-butenyl)-1,3-propanediyl]bis-	
1,2-Propanediol,3-benzyloxy-1,2-diacetyl-	
1-Propene,3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	
EPN	Are entomopathogenic nematodes
1,2-Diphenyl-1-isocyanoethane	
1-Propene,3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	
Tetradecanoic acid,12-methyl-,methyl ester	
1-(+)-Ascorbic acid 2,6-dihexadecanoate	
Octadecanoic acid	An ester of glycerol in animal and plant fats
2-Methoxydecanoic acid	Carboxylic acids found in fruits
3-Octen-2-one,8-phenyl	Found in alcoholic beverages, raw fish and fried potatoes

The organic compounds naturally occurring in the environment such as octadecanoic acid were common among all the 6 sites (Figure 4.1). Sites one and two had four types of compounds each. Site three and five had three types of compounds and site four had two types of compounds

namely pesticides and naturally occurring compounds. Site six had no residues of pollutant type as naturally occurring residues were observed. In sites one and two, organic residues of industrial type and pharmaceuticals were common. Pesticide residues were absent at sites one and six while sites three, four and five had the same number of pesticides. Pharmaceuticals were detected at sites one, two and five. Preservatives were detected at sites one and three.

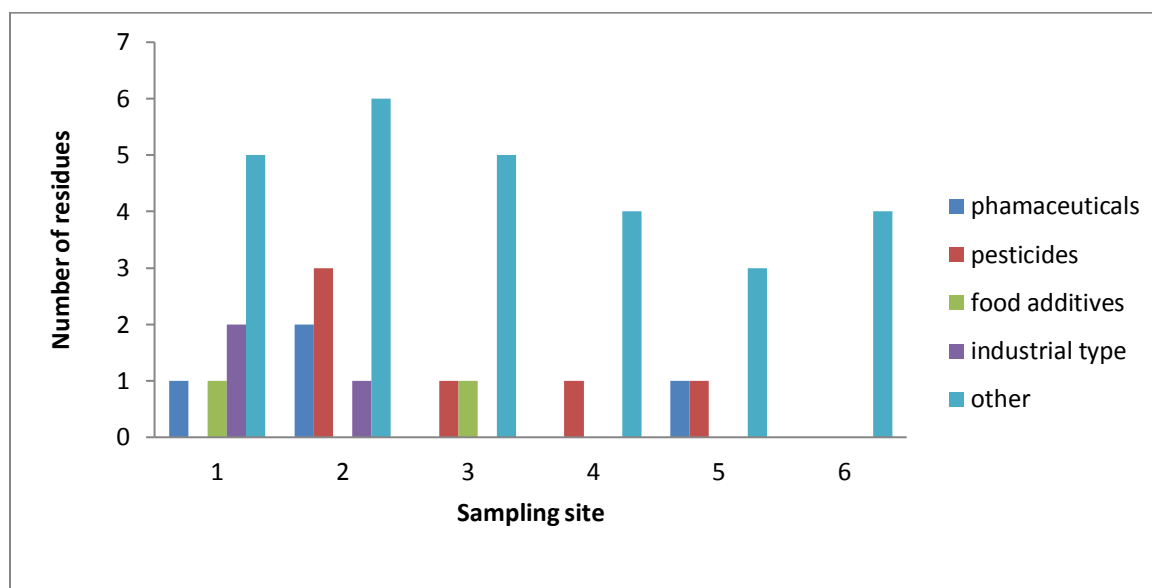


Figure 4.1: The types of organic compounds among six sampling sites found in sediment from Sebakwe River.

4.1.2 Organic compounds found in water from Sebakwe River

A total of 29 organic compound residues were detected in water samples from Sebakwe River. The largest numbers of residues present in water samples were naturally occurring non pollutant organic compounds (18). There were no food additives detected in the water samples. However six pesticides, four organic compounds of industrial type and one pharmaceutical residue were detected among the six sites (Table 4.2 Figure 4.2). Among the pesticides the organophosphates were common.

Table 4.2: Organic compounds present in water from Sebakwe River

Compound	Description
Pharmaceuticals	
Topiramate	Pain killer
Pesticides	
Prohydrojasmon-2	Plant growth regulator
Trichlofon	An organophosphate insecticide
Disulfoton	An organophosphate insecticide
Dichlorvos-d6	An organophosphate insecticide
Methoprene	An insecticide
Chlorethoxyfos	An organophosphate insecticide
N-(2-Methylbutyl)undeca-(2E,4E)-diene-8,10-dinamide	A bio active compound that can be used in pest control
Industrial type	
Heptacosane,1-chloro-	A common solvent for oils, fats and DDT
1-(+)-Ascorbic acid 2,6-dihexadecanoate	Antifoaming agent and fermentation nutrient
DEHP	Chemical that is added to plastics
Trihexadecyl borate	Welding fluxes intermediate
Phthalic acid, bis(7-methyloctyl) ester	A plasticizer
Other	

Table 4.2 continued

Compound	Description
Hexadecanoic, methyl ester	A metabolite
Octadecanoic acid	A human metabolite
Methyl stearate	An ester of glycerol in animal and plant fats
Tetracontane	
Methyl (13S)-(E)-13-trimethylsilyloxy-9,10-dimethoxy-11-octadecanoate	
Glutaric, tridec-2-yn-1-yl trans-4-tert-butylcyclohexyl ester	
Methoxyacetic acid, 3-pentadecyl ester	Bioactive compound
Heptadecanoic acid, 16-methyl-, methyl ester	A fatty acid found in mushroom
Pentadecanoic acid, 14-methyl-, methyl ester	A methylated fatty acid found in sea sponges
2-Methylhexacosane	
Heptadecane, 7-methyl-	
Methyl (13S)-(E)-13-trimethylsilyloxy-9,10-dimethoxy-11-octadecanoate	
Hexadecane	Essential oil found in black pepper
Sulfurous acid, butyl octadecyl ester	

Table 4.2 continued

Compound	Description
Nonadecanoic acid, ethyl ester	Fatty acid ethyl ester
Sulfurous acid, pentylundecyl ester	
Oxalic acid, isohexyludecyl ester	An essential oil
Nonadecane,9-methyl-	Essential oils from plants
Tetradecanoic acid	Found only in vegetable fats
Terephthalic acid,di(6-methylhept-2-yl) ester	

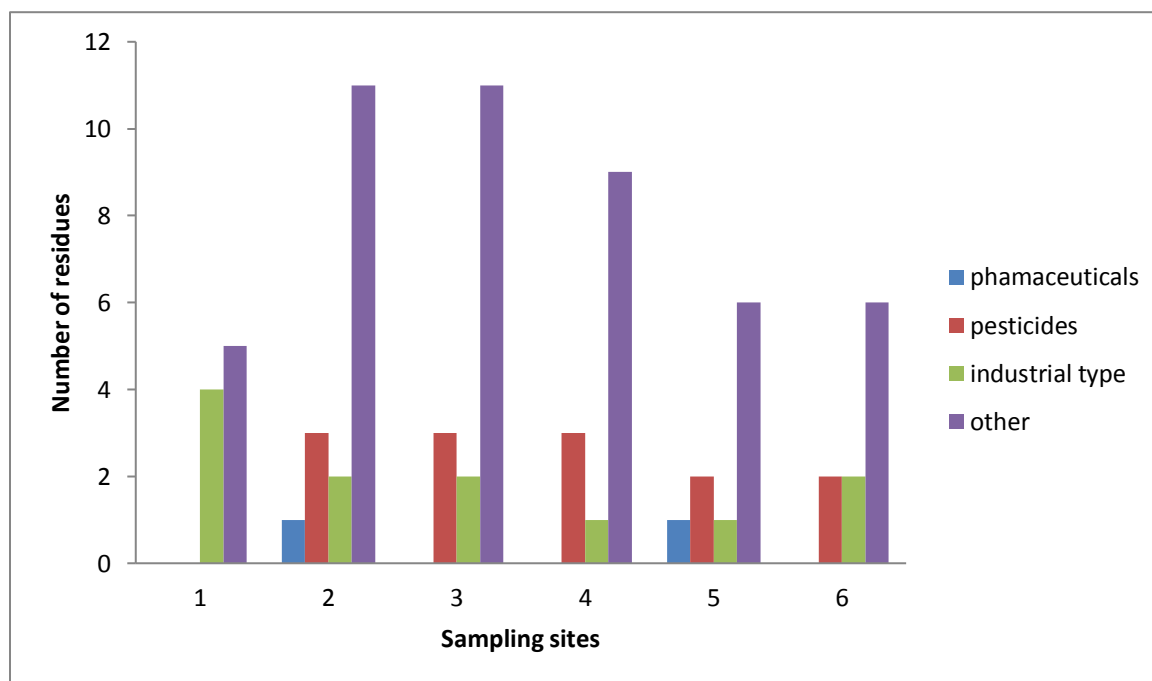


Figure 4.2: The types of organic compounds in water from Sebakwe River

Organic compounds naturally occurring in the environment had the highest number of residues throughout all the sites (Figure 4.2). Site one had one type of organic pollutant which is of industrial type. The most diverse organic residues were observed at sites two and five. The pesticide and industrial type residues were present among all the sites except at site one where pesticides were absent. Pharmaceuticals were observed at sites two and five.

4.2 Quantitative analysis of organic compounds in river sediment and water

4.2.1 Quantitative analysis of organic compounds in sediments from Sebakwe River.

Naturally occurring compounds had the highest concentration of organic residues compared to other compounds in sites three, four, five and six (Figure 4.3). The naturally occurring compounds ranged from 0.05 to 0.25 mol/ μ l. There was no significant difference in the concentration of naturally occurring organic residues ($p = 0.42$; 0.17 ± 0.08) amongst the sites (Appendix 3). The pharmaceutical concentration ranged from (0.01 to 0.02) mol/ μ l (Appendix 4). The concentration of pharmaceuticals were relatively high at sites one (0.29 ± 0) mol/ μ l and five (0.17 ± 0) mol/ μ l. There was no a significant difference in pharmaceuticals concentrations amongst the six sites ($p = 0.42$). The industrial type organic pollutants were present at sites one and two with mean values of (0.15 ± 0.01) mol/ μ l and (0.26 ± 0) mol/ μ l respectively. There was no significant difference in organic compounds of industrial type amongst the sites ($p = 0.42$; Appendix 5).

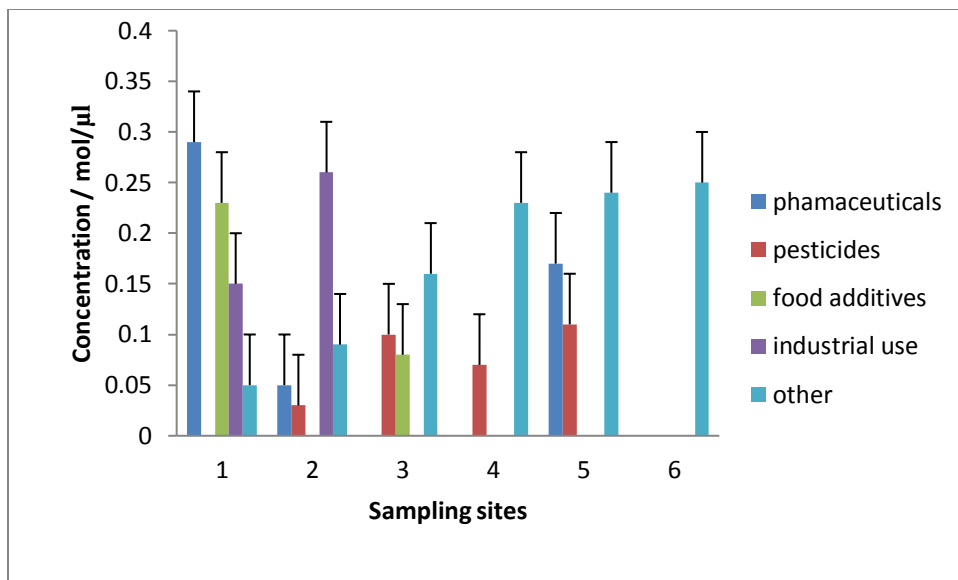


Figure 4.3: The relative concentration of organic compounds found in sediments from Sebakwe River.

The concentration of pesticides among the sites ranged from 0.03 to 0.11 mol/μl. There was no significant difference on the concentration of pesticides among the sites ($p = 0.42$; Appendix 6). The concentration of food additives was not significantly different amongst the sites ($p = 0.42$) ranging from 0.08 to 0.23 mol/μl (Appendix 7).

4.2.2 Quantitative analysis of organic compounds in water from Sebakwe River.

The highest concentrations of naturally occurring compounds were observed in all sites (Figure 4.4). The concentration of naturally occurring compounds ranged from 0.08 to 0.16 mol/μl. There was no significant difference in the concentration of naturally occurring compounds amongst sites ($p = 0.42$; Appendix 8).

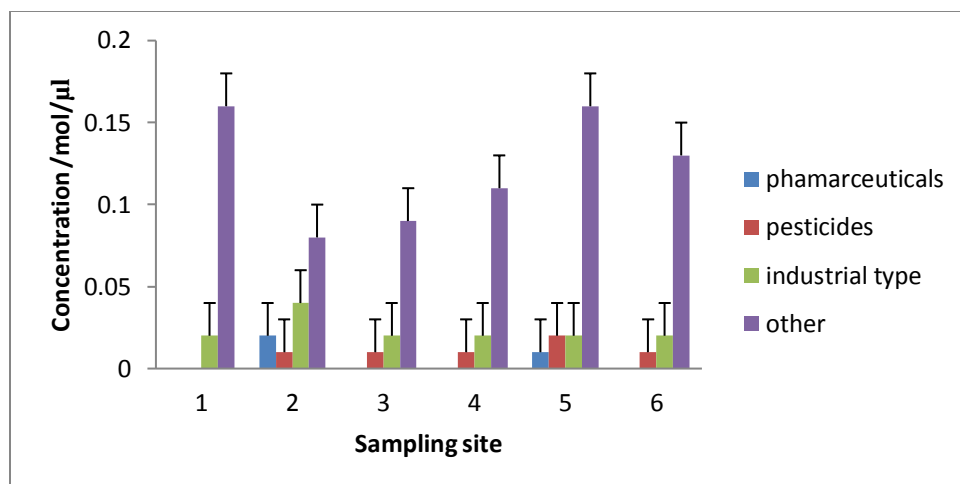


Figure 4.4: Relative concentration of organic compounds found in water from Sebakwe River.

The highest concentration of industrial type organic compound was observed at site two (0.04 ± 0.001) mol/μl compared to the other sites (Figure 4.4). The range of organic compounds of industrial type was 0.02 to 0.04 mol/μl. However there was no significant difference in the concentration of industrial type residues amongst the sites ($p = 0.42$; Appendix 9). The highest concentration of pesticides was observed at site five (0.02 ± 0.0003) mol/μl compared to other sites. There was no significant difference on the concentration of pesticides amongst the sites ($p = 0.42$; Appendix 10). Pharmaceuticals were not significantly different from each other ($p = 0.42$; Appendix 11).

CHAPTER 5: DISCUSSION

5.1 Qualitative and quantitative analysis of organic residues in water and river sediment.

The types of organic compounds present among the sites were related to the activities in the catchment such as farming and sewage disposal. The organic compounds present in sediments were those that had settled at the bottom such as: pharmaceutical (thiabendazole-13C6), a pesticide (dimethate), L-Ascorbic acid, 6-octadecanoate a food additive and phthalic acid which is a compound of industrial type. In water, pesticide compounds such as dichlorvos found were due to the agricultural activities done in the area. Among all sites, the naturally occurring compounds such as tetradecanoic acid, hexadecane, methyl stearate and heptadecanoic acid, 3-methyl ester from aquatic biota were present. These were not of significance to the study.

The organic pollutants observed in downstream sites one, two and three could have originated from the sewage effluent that is discharged into the water way from the sewage treatment plant. Similar studies in developed countries have shown sewage effluent contains organic pollutants such as pesticides and pharmaceuticals (Pal *et al.*, 2010; Bunzel *et al.*, 2013; Haarstad *et al.*, 2012; Münze *et al.*, 2017). The sewage treatment plant in Kwekwe is a Biological Nutrient Removal plant (BNR) designed to remove mainly solid wastes and nutrients. The BNR plant has no capacity to remove chemical pollutants such as pesticides, pharmaceuticals and food additives. In this study, pharmaceuticals such as antibiotics ampicillin (4-Imidazolidinone, 5-(phenylmethyl)-2-thioxo) and anti-inflammatory drugs anthelmintic agent (thiabendazole-13C6) were detected in the downstream sites. However, in this study, pharmaceuticals such as thiabendazole-13C6 were detected in the upstream sites near the confluence of Sebakwe River and Mbembeswane River. The catchment of Mbembeswane River includes a residential area which could have contributed the pharmaceutical pollutants in the upstream sites.

In this study, the pesticides were common in both upstream and downstream sites. Closer to site two downstream of the sewage effluent discharge point, stream bank cultivation of vegetables such as *Brassica oleracea* commonly known as chomolia was observed. The pesticides observed at site two were mainly insecticides such as chlorethoxyfos, etrimfos and trichlorfon. The upstream sites (four and five) were near the areas with intense commercial wheat farm agricultural activity where and the pesticides such as ethofumesate and disulfoton were detected in the aquatic environment. The results from this study confirm findings from similar studies that have shown that agricultural activities such as stream bank cultivation and farming contribute the pesticides in to the aquatic environment (Bowmer, 2013; Change, 2013; Le *et al.*, 2017). In this study, the concentration of pesticides in sites closer to commercial wheat farming were relatively higher compared to those near steam bank cultivation. This suggests that the scale of farming has an influence on the concentration of pesticides that are introduced in the aquatic environment. Large scale agriculture contributes pesticides in the aquatic environment (Larsen *et al.*, 2019).

The study showed that food additives such as benzene, 1, 1', 1''-[5-methyl-1-pentene-1, 3, 5-triyl]tris and L-ascobic acid,6-octadecanoate were observed in sites downstream of the sewage discharge point but absent in upstream sites. This suggests that the sewage effluent is a potential source of the food additives in Sebakwe River. Other studies have shown that the waste water effluent posses a number of food additives which end up in the aquatic environment (Kim *et al.*, 2011). Compounds of industrial type such as DEHP, phathalic acid were observed in all sites except in site one.

The concentrations of the organic compounds were not significantly different among the sites ($p > 0.05$). This suggests that the sources of the organic compounds are potentially the same. For site one pharmaceuticals were only found in the sediment and was absent in the water. This suggests that the pharmaceuticals found in the area were not water soluble. A study on the toxicity of antihelminthic drugs was carried out and among the physicochemical properties was that they have a low solubility level in water (Wagil *et al.*, 2015).

5.2 Potential impact of organic pollutants to aquatic biota

Organophosphate pesticides (e.g. dimethate) and pyrethroids (e.g. cenerin1) observed in this study have been found to affect photosynthesis diatoms such as *Amphora sp.* and *Navicula sp.* (Shoaib *et al.*, 2011). A study in Pakistan showed that organophosphates and pyrethroids have effects on the photosynthesis of two species of diatoms (Shoaib *et al.*, 2011). The organophosphates tend to destroy chloroplasts which are required for photosynthesis. The widespread use of pesticides in modern agriculture contributes to agricultural nonpoint source pollution in water bodies across the world threatening drinking water resources and broad range of non-target aquatic phytoplankton, zooplankton and higher trophic organisms like fish and fish predator (Mondal *et al.*, 2018).

A comprehensive study revealing the ecotoxicity of benzimidazoles such as thiabendazole-13C6 has been found to be toxic to duckweed (*L. minor*) and green algae (*S. vacuolatus*) (Wagil *et al.*, 2015). The benzimidazoles also affect *V. fischeri* and *D. magna* by affecting metabolism (Wagil *et al.*, 2015). The presence of antimicrobial drugs in the water results in antimicrobial resistance of microorganisms that are found in water such as *Escherichia coli* strains (da Costa Andrade *et al.*, 2015).

DEHP observed in this study belongs to the group of phthalates that undergo natural degradation in the environment with a half-life varying from few days to weeks in freshwater (Junaid *et al.*, 2018). DEHP metabolites are detected pre- dominantly in fish species due to their natural degradation in the aquatic environment, microbial biodegradation in water bodies and metabolic activity in fish. A result is bioaccumulation of DEHP metabolites in fish (Junaid *et al.*, 2018).The resulting elevated concentrations of DEHP in fish can cause serious ecological risks through the impairment of biochemical functions and reproduction in the aquatic species (Junaid *et al.*, 2018). DEHP, being an endocrine disruptor, can cause a wide range of toxic effects in animals and humans. DEHP can cause DNA damage mostly by initiating the accumulation of reactive oxygen species which may also lead to the perturbations related to mitochondrial membrane potential, and cell cycle (Junaid *et al.*, 2018).

5.3 Conclusion

This study has shown that there are organic pollutants in Sebakwe River originating from human activities such sewage effluent discharge and agriculture. This contributes to the deterioration of water quality of Sebakwe River. There is a need to closely monitor activities in the catchment to reduce the pollution of the river.

5.5 Recommendations

The sewage treatment plant in Kwekwe is to be able to remove chemical pollutants in the aquatic environment before they are discharged into Sebakwe River. This will reduce the occurrence of organic pollutants in the aquatic environment. When using pesticides farmers should favor the use of environmental friendly pesticides such as garlic spray for small scale farming in place of the organophosphate pesticides that tend to bioaccumulate. For commercial farming one can

carry out practices such as crop rotation in place of using pesticides as a way to remove pest in the field. Legislation which regulates the distance in which agricultural activities is to be done when a field is near a river is to be enforced so as to reduce contamination of the aquatic environment when chemicals are washed into the river. Also regulations on sewage effluent discharge are to be enforced so as to reduce pollution of the aquatic environment. Awareness programs are to be carried out to residents in Kwekwe on proper disposal of chemicals such as pharmaceuticals so as to reduce the number of organic pollutants that find their way to Sebakwe River.

References

- Akan, J.C., Sodipo, O.A., Mohammed, Z. and Abdulrahman, F., 2014. Determination of organochlorine, organophosphorus and pyrethroid pesticide residues in water and sediment samples by high performance liquid chromatography (HPLC) with UV/visible detector. *J Anal Bioanal Tech*, 5, pp.2.
- Barky, F.A., Abdelsalam, H.A., Mahmoud, M.B. and Hamdi, S.A., 2012. Influence of Atrazine and Roundup pesticides on biochemical and molecular aspects of *Biomphalaria alexandrina* snails. *Pesticide biochemistry and physiology*, 104, pp.9-18.
- Borja, Á., Galparsoro, I., Irigoien, X., Iriondo, A., Menchaca, I., Muxika, I., Pascual, M., Quincoces, I., Revilla, M., Rodríguez, J.G. and Santurtún, M., 2011. Implementation of the European Marine Strategy Framework Directive: a methodological approach for the assessment of environmental status, from the Basque Country (Bay of Biscay). *Marine Pollution Bulletin*, 62, pp.889-904.
- Bowmer, K., 2013. Ecosystem effects from nutrient and pesticide pollutants: catchment care as a solution. *Resources*, 2, pp.439-456.
- Bruchet, A., Hochereau, C., Picard, C., Decottignies, V., Rodrigues, J.M. and Janex-Habibi, M.L., 2005. Analysis of drugs and personal care products in French source and drinking waters: the analytical challenge and examples of application. *Water science and technology*, 52, pp.53-61.
- Bunzel, K., Kattwinkel, M. and Liess, M., 2013. Effects of organic pollutants from wastewater treatment plants on aquatic invertebrate communities. *Water research*, 47, pp.597-606.

Change, C., 2013. Human activities as a source of pollutants in water: Land Conversion, loss of forests and wetlands. *Water research*, 10, pp. 1-47.

Coleman, B.L., Louie, M., Salvadori, M.I., McEwen, S.A., Neumann, N., Sibley, K., Irwin, R.J., Jamieson, F.B., Daignault, D., Majury, A. and Braithwaite, S., 2013. Contamination of Canadian private drinking water sources with antimicrobial resistant *Escherichia coli*. *Water research*, 47, pp.3026-3036.

da Costa Andrade, V., Zampieri, B.D.B., Ballesteros, E.R., Pinto, A.B. and De Oliveira, A.J.F.C., 2015. Densities and antimicrobial resistance of *Escherichia coli* isolated from marine waters and beach sands. *Environmental monitoring and assessment*, 187, pp.342.

Dal Pra, V., Bisol, L.B., Detoni, S., Denti, M., Grando, J., Pollo, C., Pasquali, T.R., Hoffmann, A.E., Mazutti, M.A. and Macedo, S.M., 2011. Anti-inflammatory activity of fractionated extracts of *Salvia officinalis*. *Journal of Applied Pharmaceutical Science*, 1, p.67.

Dalton, R.L., Pick, F.R., Boutin, C. and Saleem, A., 2014. Atrazine contamination at the watershed scale and environmental factors affecting sampling rates of the polar organic chemical integrative sampler (POCIS). *Environmental pollution*, 189, pp.134-142.

Directive; 2013/39/EU

EC; 2000/60/EC

Elliott, M., 2003. Biological pollutants and biological pollution—an increasing cause for concern. *Marine Pollution Bulletin*, 46, pp.275-280.

Environmental Management Act (EMA act), 2002, Statutory Instrument No.13 of 2002 (Chapter 20:27), Zimbabwe.

Essumang, D.K., Togoh, G.K. and Chokky, L., 2009. Pesticide residues in the water and fish (lagoon tilapia) samples from lagoons in Ghana. *Bulletin of the Chemical Society of Ethiopia*, 23, pp.19-27.

Forget, G., Goodman, T. and De Villiers, A., 1993. *Impact of pesticide use on health in developing countries: proceedings of a symposium held in Ottawa, Canada, 17-20 Sept. 1990*. IDRC, Ottawa, ON, CA, pp.2.

Grung, M., Lin, Y., Zhang, H., Steen, A.O., Huang, J., Zhang, G. and Larssen, T., 2015. Pesticide levels and environmental risk in aquatic environments in China—A review. *Environment International*, 81, pp.87-97.

Goerke, H., Weber, K., Bornemann, H., Ramdohr, S. and Plötz, J., 2004. Increasing levels and biomagnification of persistent organic pollutants (POPs) in Antarctic biota. *Marine Pollution Bulletin*, 48, pp.295-302.

Gonzalez-Rey, M., Tapie, N., Le Menach, K., Dévier, M.H., Budzinski, H. and Bebianno, M.J., 2015. Occurrence of pharmaceutical compounds and pesticides in aquatic systems. *Marine pollution bulletin*, 96, pp.384-400.

Haarstad, K., Bavor, H.J. and Mæhlum, T., 2012. Organic and metallic pollutants in water treatment and natural wetlands: a review. *Water Science and Technology*, 65, pp.76-99.

Harris, S., Morris, C., Morris, D., Cormican, M. and Cummins, E., 2014. Antimicrobial resistant *Escherichia coli* in the municipal wastewater system: effect of hospital effluent and environmental fate. *Science of the Total Environment*, 468, pp.1078-1085.

Igbedioh, S.O., 1991. Effects of agricultural pesticides on humans, animals, and higher plants in developing countries. *Archives of Environmental Health: An International Journal*, 46, pp.218-224.

Junaid, M., Jia, P.P., Tang, Y.M., Xiong, W.X., Huang, H.Y., Strauss, P.R., Li, W.G. and Pei, D.S., 2018. Mechanistic toxicity of DEHP at environmentally relevant concentrations (ERCs) and ecological risk assessment in the Three Gorges Reservoir Area, China. *Environmental Pollution*, 242, pp.1939-1949.

Kafilzadeh, F., 2015. Assessment of organochlorine pesticide residues in water, sediments and fish from Lake Tashk, Iran. *Achievements in the Life Sciences*, 9, pp.107-111.

Kim, J.W., Ramaswamy, B.R., Chang, K.H., Isobe, T. and Tanabe, S., 2011. Multiresidue analytical method for the determination of antimicrobials, preservatives, benzotriazole UV stabilizers, flame retardants and plasticizers in fish using ultra high performance liquid chromatography coupled with tandem mass spectrometry. *Journal of Chromatography A*, 1218, pp.3511-3520.

Köck-Schulmeyer, M., Villagrasa, M., de Alda, M.L., Céspedes-Sánchez, R., Ventura, F. and Barceló, D., 2013. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. *Science of the Total Environment*, 458, pp.466-476.

Kwak, K., Rosenfeld, D.E., Chung, J.K. and Fayer, M.D., 2008. Solute– Solvent Complex Switching Dynamics of Chloroform between Acetone and Dimethylsulfoxide– Two-Dimensional IR Chemical Exchange Spectroscopy. *The Journal of Physical Chemistry B*, 112, pp.13906-13915.

- Larsen, A.E., Patton, M. and Martin, E.A., 2019. High highs and low lows: Elucidating striking seasonal variability in pesticide use and its environmental implications. *Science of The Total Environment*, 651, pp.828-837.
- Le, T.D.H., Scharmüller, A., Kattwinkel, M., Kühne, R., Schüürmann, G. and Schäfer, R.B., 2017. Contribution of waste water treatment plants to pesticide toxicity in agriculture catchments. *Ecotoxicology and environmental safety*, 145, pp.135-141.
- Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S. and Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the total environment*, 473, pp.619-641.
- Mackay, D. and Boethling, R.S., 2000. Bioconcentration and biomagnification in the aquatic environment. In *Handbook of property estimation methods for chemicals*, pp. 211-254.
- Mahmood, I., Imadi, S.R., Shazadi, K., Gul, A. and Hakeem, K.R., 2016. Effects of pesticides on environment. In *Plant, soil and microbes*, pp. 253-269.
- Malaj, E., Peter, C., Grote, M., Kühne, R., Mondy, C.P., Usseglio-Polatera, P., Brack, W. and Schäfer, R.B., 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. *Proceedings of the National Academy of Sciences*, 111, pp.9549-9554.
- Miglioranza, K.S., Sagrario, M.D.L.A.G., de Moreno, J.E.A., Moreno, V.J., Escalante, A.H. and Osterrieth, M.L., 2002. Agricultural soil as a potential source of input of organochlorine pesticides into a nearby pond. *Environmental Science and Pollution Research*, 9, pp.250-256.

Mondal, R., Mukherjee, A., Biswas, S. and Kole, R.K., 2018. GC-MS/MS determination and ecological risk assessment of pesticides in aquatic system: A case study in Hooghly River basin in West Bengal, India. *Chemosphere*, 206, pp.217-230.

MSFD; 2008/56/EC

Münze, R., Hannemann, C., Orlinskiy, P., Gunold, R., Paschke, A., Foit, K., Becker, J., Kaske, O., Paulsson, E., Peterson, M. and Jernstedt, H., 2017. Pesticides from wastewater treatment plant effluents affect invertebrate communities. *Science of the total environment*, 599, pp.387-399.

Net, S., Rabodonirina, S., Sghaier, R.B., Dumoulin, D., Chbib, C., Tlili, I. and Ouddane, B., 2015. Distribution of phthalates, pesticides and drug residues in the dissolved, particulate and sedimentary phases from transboundary rivers (France–Belgium). *Science of the total environment*, 521, pp.152-159.

Pal, A., Gin, K.Y.H., Lin, A.Y.C. and Reinhard, M., 2010. Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. *Science of the total environment*, 408, pp.6062-6069.

Pereira, A., Santos, A., Tacão, M., Alves, A., Henriques, I. and Correia, A., 2013. Genetic diversity and antimicrobial resistance of *Escherichia coli* from Tagus estuary (Portugal). *Science of the Total Environment*, 461, pp.65-71.

Rigotto, R.M., Silva, A.M.C.D., Ferreira, M.J.M., Rosa, I.F. and Aguiar, A.C.P., 2013. Trends of chronic health effects associated to pesticide use in fruit farming regions in the state of Ceará, Brazil. *Revista Brasileira de Epidemiologia*, 16, pp.763-773.

Sabra, F.S. and Mehana, E.S.E.D., 2015. Pesticides toxicity in fish with particular reference to insecticides. *Asian Journal of Agriculture and Food Sciences* , 3 , pp. 1571-2321.

Scherr, S.J. and McNeely, J.A., 2007. Biodiversity conservation and agricultural sustainability: towards a new paradigm of 'ecoagriculture' landscapes. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 363, pp.477-494.

Schriks, M., Heringa, M.B., van der Kooi, M.M., de Voogt, P. and van Wezel, A.P., 2010. Toxicological relevance of emerging contaminants for drinking water quality. *Water research*, 44, pp.461-476.

Sharma, B.M., Bečanová, J., Scheringer, M., Sharma, A., Bharat, G.K., Whitehead, P.G., Klánová, J. and Nizzetto, L., 2019. Health and ecological risk assessment of emerging contaminants (pharmaceuticals, personal care products, and artificial sweeteners) in surface and groundwater (drinking water) in the Ganges River Basin, India. *Science of the Total Environment*, 646, pp.1459-1467.

Shoaib, N.A.F.I.S.A., Siddiqui, P.J.A., Ali, A., Zaib-un-nisa, B. and Shafique, S., 2011. Toxicity of pesticides on photosynthesis of diatoms. *Pakistan Journal of Botany*, 43, pp.2067-2069.

Shuman-Goodier, M.E. and Propper, C.R., 2016. A meta-analysis synthesizing the effects of pesticides on swim speed and activity of aquatic vertebrates. *Science of the Total Environment*, 565, pp.758-766.

Torres, C.M., Picó, Y. and Manes, J., 1996. Determination of pesticide residues in fruit and vegetables. *Journal of Chromatography A*, 754, pp.301-331.

Turgut, C., 2007. The impact of pesticides toward parrotfeather when applied at the predicted environmental concentration. *Chemosphere*, 66, pp.469-473.

Vaj, C., Barmaz, S., Sørensen, P.B., Spurgeon, D. and Vighi, M., 2011. Assessing, mapping and validating site-specific ecotoxicological risk for pesticide mixtures: A case study for small scale hot spots in aquatic and terrestrial environments. *Ecotoxicology and environmental safety*, 74, pp.2156-2166.

Van Hoey, G., Borja, A., Birchenough, S., Buhl-Mortensen, L., Degraer, S., Fleischer, D., Kerckhof, F., Magni, P., Muxika, I., Reiss, H. and Schröder, A., 2010. The use of benthic indicators in Europe: from the Water Framework Directive to the Marine Strategy Framework Directive. *Marine Pollution Bulletin*, 60, pp.2187-2196.

Vorkamp, K., Bossi, R., Bester, K., Bollmann, U.E. and Boutrup, S., 2014. New priority substances of the European Water Framework Directive: biocides, pesticides and brominated flame retardants in the aquatic environment of Denmark. *Science of the Total Environment*, 470, pp.459-468.

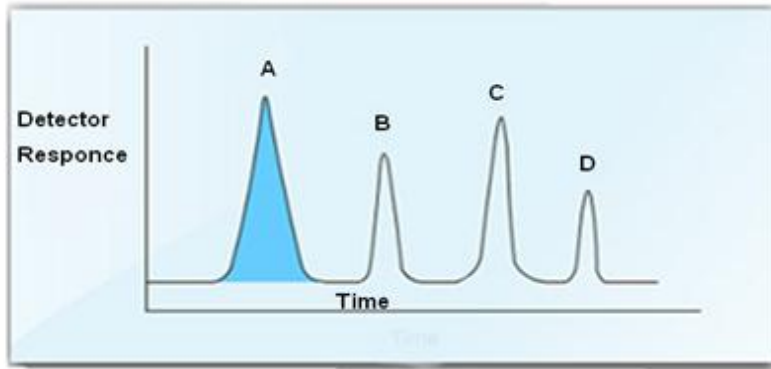
Wagil, M., Białk-Bielińska, A., Puckowski, A., Wychodnik, K., Maszkowska, J., Mulkiewicz, E., Kumirska, J., Stepnowski, P. and Stolte, S., 2015. Toxicity of anthelmintic drugs (fenbendazole and flubendazole) to aquatic organisms. *Environmental Science and Pollution Research*, 22, pp.2566-2573.

Wang, Y., Wu, S., Chen, J., Zhang, C., Xu, Z., Li, G., Cai, L., Shen, W. and Wang, Q., 2018. Single and joint toxicity assessment of four currently used pesticides to zebrafish (*Danio rerio*) using traditional and molecular endpoints. *Chemosphere*, 192, pp.14-23.

WFD; 200/60/EC

Zhang, Z., Huang, J., Yu, G. and Hong, H., 2004. Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. *Environmental Pollution*, 130, pp.249-261.

Appendix



Appendix 1: Chromatogram

$$\%A = \frac{\text{Area of Peak A} \times 100}{\text{Total Area of Peaks (A+B+C+D)}}$$

Appendix 2: Spss output of naturally occurring compounds in sediment.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
Other	6	.1700	.08462	.05	.25
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Other
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 3: Spss output of pharmaceuticals in sediment.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
other	6	.1700	.08462	.05	.25
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Other
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

Appendix 4: Spss output of compounds of industrial type in sediment.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
industrial type	6	.0683	.11143	.00	.26
Sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	industrial type
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 5: Spss output of pesticides in sediment.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
pesticides	6	.0517	.04875	.00	.11
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Pesticides
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 6: Spss output of food additives in sediment.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
additive	6	.0517	.09304	.00	.23
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Additive
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 7: Spss output of naturally occurring compounds in water.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
other	6	.1217	.03430	.08	.16
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Other
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 8: Spss output of compounds of industrial type in water.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
industrial ype	6	.0233	.00816	.02	.04
Sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	industrial ype
Chi-Square	5.000
Df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 9: Spss output of pesticides in water.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
pesticides	6	.0100	.00632	.00	.02
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Pesticides
Chi-Square	5.000
df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling

Appendix 10: Spss output of pharmaceuticals in water.

Descriptive Statistics

	N	Mean	Std. Deviation	Minimum	Maximum
phama	6	.0050	.00837	.00	.02
sampling	6	3.50	1.871	1	6

Kruskal-Wallis Test

Test Statistics^{a,b}

	Phama
Chi-Square	5.000
df	5
Asymp. Sig.	.416

a. Kruskal Wallis Test

b. Grouping Variable: sampling