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ASSESSMENT OF SELECTED AGROCHEMICALS IN WASTEWATER FROM HORTICULTURAL FARMS IN ARUSHA AND THEIR REMOVAL BY CONSTRUCTED WETLANDS

By

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ABSTRACT

Commercial horticulture has been growing rapidly and has a significant contribution to food security and economic growth in Tanzania. The growth of horticulture industry has been associated with an increase in consumption of agrochemicals on farms. However, wastewaters containing agrochemicals are usually discharged from horticulture farms into the environment without proper treatment. Apparently, the effects of these agrochemicals on the environment are very complex, and therefore, their undesirable transformations can contaminate water, soil, sediments and biota and consequently cause adverse effects on human health and the environment. This study was aimed at investigating the levels of agrochemicals in wastewater discharged from selected horticultural farms in Arusha and their removal by constructed wetlands. The study reviewed literature on the use of agrochemicals in Tanzania and analysed wastewater discharged from horticulture farms for nutrients and pesticide levels. The literature review on agrochemical use showed that inorganic fertilizers, insecticides, fungicides and herbicides are mostly used in horticultural fields. The analysis of wastewater from five horticulture farms detected NO_3^-, PO_4^{3-}, BOD_5 and permethrin in the wastewater discharged into the environment at concentration levels above the Tanzanian allowable limits for discharge. The mean concentration levels ranged from (4.5 - 64) ppm for NO_3^-, (3 - 48) ppm for PO_4^{3-}, (57-119) ppm for BOD_5 and (0.4 - 0.8) ppm for permethrin insecticide. This study investigated the influence of macrophyte type towards removal of Cu, Fe, Mn, Zn, Endosulfan, L-Cyhalothrin and Permethrin by using bucket experiments and influence of flow rate towards removal of Cu, Zn and Mn in horizontal subsurface flow constructed wetlands (HSSFCWs). The results from the bucket experiments showed a significant positive effect of macrophytes on the removal of Cu, Fe, Mn and Zn. In the HSSFCWs experiments, the removal of heavy metals was as high as 95 % on the average and was found to be independent of flow rate and the difference was statistically insignificant (P>0.05). It was observed that regardless of the mechanisms involved in the removal of heavy metals in the HSSFCWs, the overall removal is not limited to transport processes within the wetlands. The conclusion drawn from this research is that agrochemicals are a problem in the environment and constructed wetlands can be used as treatment options for wastewater before it is discharged into the environment.

DECLARATION

I, EMMY SOLOMON LEMA, do hereby declare to the Senate of Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

Emmy Solomon Lema

23rd Dec 2014

Name and signature of candidate

Date

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Name and signature of supervisor 1

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23rd DEC 2014

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Date

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for examination of a dissertation entitled; Assessment of Agrochemicals in Wastewater from Horticulture Farms in Arusha and their Removal by Constructed Wetlands, in fulfilment of the requirements for the Degree of Doctor of Philosophy in Environmental Science and Engineering (EnSE) at Nelson Mandela African Institution of Science and technology (NM-AIST).

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DEDICATION

To God Almighty - Ancient of days, who makes all things possible

In Loving Memory of My Father – the source of inspiration

To my Mother - who supports me in what I do

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LIST OF ABBREVIATIONS

APHA	American Public Health Association
ANOVA	Analysis of Variance
BTEX	Benzene Toluene, Ethylbenzene and Xylene
CAN	Calcium Ammonium Nitrate
COSTECH	Tanzania Commission for Science and Technology
CWs	Constructed Wetlands
DAP	Di-Ammonium Phosphate
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DNT	Dinitrotoluene
EMA	Environmental Management Act
EPA	Environmental Protection Agency
ESRF	Economic and Social Research Foundation
FWS	Free Water Surface
GC/MS	Gas Chromatography/Mass Spectrometry
GCLA	Government Chemist Laboratory Agency
GDP	Gross Domestic Product
GPS	Geographical Positioning System
HCH	Hexachlorocyclohexane
HODECT	Horticultural Development Council of Tanzania
HSSFCWs	Horizontal Subsurface Flow Constructed Wetlands
IUCN	International Union for Conservation of Nature
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
IPM	Integrated Pest Management
LLE	Liquid-liquid Extraction
MAFSC	Ministry of Agriculture, Food Security and Cooperatives
MDG	Millennium Development Goals
MoW	Ministry of Water
MRP	Minjingu Rock Phosphate

NAIVS	National Agricultural Input Voucher Scheme
NEP	National Environmental Policy
NPK	Nitrogen, Phosphorus and Potassium
OECD	Organisation for Economic Co-operation and Development
PAHs	Polycyclic Aromatic Hydrocarbons
PCE	Perchloroethylene
PCPs	Personal care products
POPs	Persistent Organic Pollutants
SEAMIC	Southern and Eastern African Mineral Centre
SPSS	Statistical Package for the Social Sciences
SSA	Sub Saharan Africa
SSF	Subsurface Flow
TCE	Trichloroethylene
TDS	Total dissolved solids
TKN	Total Kjeldahl Nitrogen
TNT	Trinitrotoluene
TPRI	Tropical Pesticide Research Institute
TSP	Triple Super Phosphate
TZS	Tanzania Water Quality Standards
UNEP	United Nations Environment Programme
UNS	United Nations Summit
URT	United Republic of Tanzania
USEPA	United States Environmental Protection Agency
VSSFCWs	Vertical Subsurface Flow Constructed Wetlands
VPO	Vice President's Office
WHO	World health organization of UN

LIST OF SYMBOLS

µg/l	microgram per litre
µs/cm	micro Siemens per centimetre
Bdl	below detection limit
BOD-5	5-day biological oxygen demand
DO	Dissolved oxygen
EC	Electrical conductivity
HCl	Hydrochloric acid
Kg/ha	Kilogram/hacter
L	Litre
L/min	Litre/minute
LoD	Limit of Detection
M	Meters
Mg/l	Miligram/litre
Min	Minute
Ml	Milliliter
N	Number of samples
^{o}C	Degree celsius
pH	Hydrogen ion concentration
ppm	Parts per million
SD	Standard deviation

CHAPTER ONE

General Introduction and Background

1.1. Summary

This chapter mainly focuses on the background information of the study, particularly the issue of horticultural water pollution, its origin, impacts, and the challenges in wastewater treatment. The chapter also gives an overview of the potential role of constructed wetlands for the remediation of such polluted wastewater. The chapter also details the specific objectives of the research and the research questions.

1.2. Background information

It is well known that clean water is essential for life and a basic natural resource for socio-economic development and management of natural ecosystems. On the other hand, water and wastewater management for human health and economic development has always been an issue of environmental concern all over the world. The overexploitation of waters and natural resources to produce goods and services also generate wastes which may compromise the quality of surface waters to meet the standards for various end uses. The problem of wastewater management is a growing concern in developing countries due to high costs of wastewater management and treatment and Tanzania is reported to experience the same challenges (Masoud, 2009; Kivaisi, 2001).

Proper disposal of wastewater and protection of the environment is among the prerequisite for the achievement of the Millennium Development Goal (MDG 7), which calls for environmental sustainability by integrating the principles of sustainable development into country policies and programmes, and reverse of environmental pollution processes as well as loss of environmental resources (UNS, 2010). In Tanzania, the National Environmental Policy 1997 (NEP) and Environmental Management Act, 2004 (EMA) have identified environmental pollution as one of the key problems that call for urgent attention (VPO, 2008). However, like many developing countries, Tanzania is still facing environmental problems of diverse nature and some of which are growing day by day (Mato, 2002). The modernization and expansion of horticulture call for careful consideration of the adverse effects on the environment that may be caused by the intensified irrigation practices, and the use of agrochemicals (pesticides, fertilizers) (URT, 2004c). Nevertheless, with increasing modernization of horticulture, agrochemicals have been widely used in Tanzania horticulture industry (Agenda, 2006; MAFC, 2011).

Contamination due to horticultural wastewater containing agrochemicals constitutes one of the biggest threats for aquatic ecosystems, and human health. Discharging wastewater that are rich in N and P into surface waters cause eutrophication, a condition in an aquatic ecosystem where high nutrient concentrations stimulate blooms of algae and aquatic plants (Kalf, 2002). The most notable impacts of eutrophication are excessive algal blooms and cyanobacteria which contain toxins that have detrimental effects on human and environmental health. When the algae and plants decompose, they induce anoxic conditions in water which in turn cause death of fish and increased particulate turbidity (Kalff, 2002). Humans can be impacted by eutrophication due to impairment of water as a source of drinking, recreational and also increased costs of water treatment. Eutrophication was also recognized as a pollution problem in some agricultural areas in Tanzania (Nonga *et al.*, 2011; Kulekana, 2004). Several chemical contaminants from horticultural fields. containing agrochemicals have been reported in effluents and are likely to jeopardise the quality of water bodies that support fishery industry. Literature has also shown that the pollution with pesticides in Lake Victoria caused banning export of Nile Perch fillets to European Union Countries which consequently led to loss of jobs and foreign currency between 1996-2000 (Aksoy and Beghin, 2004).

Tanzania's economy depends significantly on the growth of its agricultural sector. The horticulture subsector has grown significantly in the last decade and has contributed to the country's food security, nutrition improvement and economic growth (HODECT, 2010). One of the most important horticultural productions in Arusha is both small scale and large scale cultivation of vegetables, hybrid seeds, fruits and flower cuttings. In order to increase crop productivity and control weeds, pests and diseases affecting crops, agrochemicals such as fungicides, pesticides, herbicides, and chemical fertilizers have been widely used (Nonga *et al.*, 2011). However, there is a growing concern that intensive horticultural practices and the use of agrochemicals may have adverse effects to the environment and human health (URT, 2004c). Studies have shown that improper disposal or applications of pesticides and fertilizers in agricultural fields have caused contamination of water, soil, sediments and biota (Heller *et al.*, 2013; Mohammed and Khamis, 2012; Nonga *et al.*, 2011; Heller, 2011; Kihampa, 2010a, 2010b; Kulekana, 2004; Mihale *et al.*, 2004). However, wastewaters are frequently released to the environment without proper treatment in many developing nations

(Breisha and Winter, 2010). Apparently little is known about the levels of agrochemical residues from effluent wastewater from horticulture farms in Arusha. Some studies performed in different countries have found that there is a significant correlation between environmental pollution and health effects (Sarkar *et al.*, 2008; Soltaninejad *et al.*, 2007; Liney *et al.*, 2006; Weis, 2006). There is a need to protect the general public from the risk of exposure to agrochemicals through consumption of contaminated water or food chain. For the protection of human health, wastewater regulations are established by different organisations such as USEPA, WHO, EPA and European Union Commission to minimise human and environmental exposure to hazardous chemical substances. This includes setting limits on types and concentration levels that may be discharged from wastewater effluents. Tanzania water quality standards to protect human exposure from pollutants have been issued and they contain permissible limits for municipal and industrial effluents discharged directly into water bodies. Therefore there is a need of pre-treatment of wastewater from horticulture farms before discharge into receiving waters to reduce the concentration of contaminants in wastewater effluents to the levels that are permissible for use.

Conventional wastewater treatment techniques for the removal of agrochemicals include physical and/or chemical treatments, but these techniques are often expensive for developing countries like Tanzania and produce hazardous by-products that require appropriate disposal. The use of CWs for pollutants removal is gaining acceptance as one of the management practice (Rose *et al.*, 2006). Despite increasing application of CWs in wastewater treatment in Tanzania (Njau and Renalda, 2010), this technology has not been well understood in mitigating agrochemical pollution. This has limited the effective application of this technology in the horticultural industry in Tanzania and these systems have been less utilized (Kivaisi, 2001).

A "constructed wetland" is defined as a wetland specifically constructed for the purpose of pollution control through wastewater management, at a location other than existing natural wetlands (Upadhyay, 2004). Therefore, constructed wetlands (CWs) are designed and constructed to mimic natural wetlands by introducing vegetation, soils and the associated microbial assemblages to drive wastewater treatment process (Vymazal, 2009). The CWs are apparently the most suitable technologies in developing countries because they are generally less costly to construct, operate and maintain (Kadlec and Wallace, 2009; Vymazal, 2002; 2009; Kaseva, 2004). In addition they are of low energy consumption, have high pollutant removal efficiencies and have ability to treat different types of wastewater from various sources (Vymazal, 2009; Njau *et al.*, 2010; Greenway, 2005; Zhang *et al.*, 2012). Even though the potential for the application of wetland technology for treatment of wastewaters in Tanzania is enormous because of warm climate and richness in aquatic macrophyte species diversity, the rate of adoption of the technology has been very slow (Kivaisi, 2001). Indeed some wetland macrophyte species have natural ability to absorb and degrade trace elements. Nevertheless little information is available on phytoremediation capability of these macrophytes in Tanzania. This has limited their use in treatment of wastewater in horticulture farms. Therefore, there is still room for investigation of the feasibility of using CWs for the treatment of agrochemicals in wastewater from horticulture farms.

1.3. Research problem and justification

The use of certain agrochemicals like pesticides and fertilizers in horticulture farms is associated with contamination of the environment (Nonga *et al.*, 2011; Kihampa *et al.*, 2010a, 2010b; Tirado, 2007; Kulekana, 2004, Hellar and Kishimba, 2005). Arusha region in Tanzania has also been reported to use large amounts of pesticides than other regions in Tanzania (Agenda, 2006) and the survey of agrochemicals sold in Arusha listed 21 insecticides and fungicides, majority of which have been classified as moderately hazardous by WHO (AGENDA, 2006; WHO, 2005). Despite the hazardous nature of these pesticides, the horticulture industry has been constrained by excessive and unsafe use of these agrochemicals in production practices (AGENDA, 2006; Ngowi, 2007, Nonga *et al.*, 2011).

The horticulture farms consume commercial fertilizers in order to improve soil fertility and enhance crop productivity. Most of the inorganic fertilizers which are commonly used in the farms have been reported to contain traces of heavy metals (Benson *et al.*, 2014; Rauf., 2007; Nziguheba and Smolders, 2008). Furthermore, the survey of the horticulture farms and literature have shown that majority of the farms don't have wastewater treatment facilities (Lema *et al.*, 2014b). Consequently discharges of untreated and poorly treated wastewaters from horticulture farms may affect the quality of receiving water bodies if control measures are not effective. There is enough evidence that pesticides and heavy metals cause contamination of receiving water bodies and exposure risks to human health, aquatic organisms and wildlife (Ngowi, 2002; McCauley *et al.*, 2006; Soltaninejad *et al.*, 2007; Weiss *et al.*, 2006; Liney *et al.*, 2006; Lasat, 2002; Oversch *et al.*, 2007; Ullah *et al.*, 2009). Nonetheless, little information is available on the levels of agrochemical residues from wastewater in horticulture farms. Due to the potential of agrochemical contamination of water resources, there is a need of designing wastewater treatments that are cost effective and efficient in removing pesticides and heavy metals from the wastewater. Constructed wetlands are sustainable options because they have proven record of removing various pollutants from wastewaters (Njau *et al.*, 2003; Kadlec and Knight, 1996; Kadlec and Wallace, 2008; Bwire *et al.*, 2011; Nyomora *et al.*, 2012; Zurita *et al.*, 2009; Njau and Renalda, 2010). The performance of CWs have been reported to be influenced by the various physical, biological and chemical factors however little is known on the influence macrophyte types and water flow rate in removing agrochemicals from wastewaters in the climate prevalent in Arusha region.

1.4. Objectives

1.4.1. General objective

The general objective of this research was to investigate the levels of selected agrochemicals in wastewaters from horticultural farms in Arusha and evaluate their removal by using constructed wetlands.

1.4.2. Specific objectives

i. To establish baseline information on the use of agrochemicals in horticulture farms in Arusha.
ii. To assess residual levels of selected agrochemicals in wastewater from horticulture farms in Arusha.
iii. To evaluate the influence of macrophyte plant types towards phytoremediation of wastewater contaminated by agrochemicals.
iv. To understand the influence of flow rate on the removal of selected agrochemicals in wastewater in horizontal subsurface flow constructed wetlands (HSSFCW).

1.5. Research questions

The proposed research work was designed to answer the following questions:

i. Which agrochemicals are commonly used in horticultural farms in Arusha?
ii. What are the residual levels of selected agrochemicals in wastewater from horticulture farms?

iii. How do macrophyte plant types influence phytoremediation of agrochemicals?

iv. Is the removal of selected agrochemicals influenced by flow rate of wastewater in CWs?

1.6. Significance of the study

Agrochemical removal from wastewater effluents is of great importance because of their well-known toxicity to the environment and human health. This study focused on the removal of agrochemicals which will protect the aquatic environment and public health from exposure risks related to toxic effects of these agrochemicals. The knowledge of the quality of wastewater discharged from horticulture farms can help to develop solutions to manage horticulture wastewater. Greater understanding of influence of macrophyte type and flow rate would be useful in designing constructed wetland treatment systems. The results of this study will benefit horticultural farmers by providing them with environmentally friendly and cost effective technology to remove agrochemicals from wastewater. The discharge of wastewater that meets the discharge standards will protect the quality of water for different end uses and also sustain aquatic ecosystems.

CHAPTER TWO

Agrochemicals use in Horticulture Industry in Tanzania and their Potential Impact to Water Resources[1]

ABSTRACT

The objective of this review was to analyze the existing information on the use of agrochemicals (Fertilizers and Pesticides) in the Tanzanian horticulture industry especially the Northern regions and their potential to impacting water resources. Agrochemicals play an important role in horticulture, and have been widely used in Tanzania for crop protection and increasing productivity. Apart from these benefits, agrochemicals have the potential to impair the quality of water resources for different end uses. Majority of communities in Tanzania depend on surface water from rivers and lakes for potable uses such as washing, drinking and domestic animals also drink from these sources. Reports from studies done in Northern Tanzania have indicated the presence of significant levels of pesticides, phosphates and nitrates in surface water. It is apparent that most of the horticultural farms in Northern Tanzania are located on gently sloping land adjacent to water bodies. Thus discharges of wastewaters from horticulture farms may affect the quality of water resources through run-off and groundwater through infiltration if proper management of the agrochemicals is not well adhered to. The agrochemicals that have been widely used and identified as potential environmental pollutants from their use as horticultural chemicals are reviewed. The potentially adverse impacts of these agrochemicals to water resources are discussed. The review concludes with a discussion of the directions for further investigation.

2.1. Introduction

Agrochemicals are commercially produced, usually synthetic chemical compounds such as fertilizers, pesticides including insecticides, herbicides, fungicides that are used to improve the production of crops in agricultural industries. The current system of agriculture industry in Tanzania promotes the reliance on agrochemicals, both synthetic fertilizers and pesticides. Agriculture, which by definition includes horticulture, continues to play a predominant role in Tanzanian economy. It contributes about 45.6% of the Gross Domestic Product (GDP), generates about 60% of the total export earnings and employs about 80% of the labour force in 2005 (MAFS, 2007).

The existing diversity of agro-climatic zones in Tanzania implies that wide ranges of horticultural crops can be grown. Despite high production potential in many parts of the

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country at the moment, horticulture is well developed in the Northern regions (like Arusha, Kilimanjaro and Tanga) and the Southern highlands (Mbeya and Iringa). However, more than 85% of commercial horticultural investment is concentrated in the Northern part of Tanzania, especially in Arusha and Kilimanjaro regions. The lack of proper infrastructure, access to markets and investment programmes form major bottlenecks to other regions with potential to develop commercial and export-oriented horticulture industries (Nyambo and Verschoor 2005). The development of the horticulture industry in Tanzania has had a positive impact on people in Northern regions through employment generation over a period when employment in another important export sector such as coffee went down significantly.

The commercial horticulture crops grown in these regions include fruits, vegetables, spices, herbs and ornamental (flowers). In recent years there has been an increase in demand and production of horticulture products (ESRF, 2010). However, the horticultural productivity in a tropical country like Tanzania is severely limited by incidences of pests and diseases affecting crops. To cope with pest and disease problems, Farmers rely heavily on the use of pesticides. Different classes of pesticides have been commonly used such as organochlorines, carbamates, organophosphorous, pyrethroids and atrazines (Henry and Kishimba, 2002; Ngowi, 2007; Nonga *et al.*, 2011). Some of the organochlorine pesticides like dichlorodiphenyltrichloroethane (DDT), γ-hexachlorocyclohexane (HCH) and aldrin are reported being persistent in the environment and have been banned in developed countries in Europe and America in accordance with the Stockholm Convention on persistent organic pollutants (POPs) (Vijgen *et al.*, 2011). Tanzania banned the use of DDT in agriculture in the early 1990s (Henry and Kishimba, 2003) and the pesticides were replaced by pyrethroids such as cypermethrin, deltamethrin, permethrin and cyhalothrin. Other pesticides include organochlorines like endosulfan and chlorothalonil; organophosphorous insecticides (chlorpyrifos, dimethoate, profenofos, diazinon and fenitrothion) and carbamates (mancozeb, carbaryl and metalaxy). However, some of other pesticides like HCH are still used on horticulture crops in Tanzania (Kihampa *et al.*, 2010a, 2010b) despite the fact that this pesticide is not registered by the Tanzania licensing authority (Anon, 2002). They are being used because of their low cost and usefulness in agriculture (Agenda, 2006). Some of the pesticides are imported and sold under different names (Henry and Kishimba, 2003).

Despite the problems of pests and diseases affecting crop productivity, Tanzania like many other Sub-Saharan African (SSA) countries is reported to experience soil fertility decline

(Ehui and Pender, 2005). Most soils have low nutrient content particularly in nitrogen and phosphorus (Ndakidemi and Semoka, 2006; Hartemink, 2006). The decline in soil fertility is among the reasons for decline in crop productivity and yields in several SSA countries. The use of fertilizers has been an important input in agriculture to improve soil fertility (Todd *et al.*, 2012) and consequently increase productivity (Zhu and Chen, 2002). Globally, the use of fertilizers has increased tremendously and is generally responsible for the green "revolution" i.e. the massive increase in production obtained from the same surface area of land with the help of inorganic fertilizers and intense irrigation. Studies done in China reported a significant positive linear correlation between annual food production and chemical fertilizer nitrogen consumption for a consecutive period of 50 years (Zhu and Chen, 2002). The most commonly used fertilizers include different nitrogen and phosphate fertilizers. However, in SSA countries, the low productivity of crops has been linked to poor resource endowments, minimal use of inputs (fertilizer, improved seeds, and irrigation), and adverse policies (Kwadwo *et al.*, 2012).

Whilst agrochemicals have been the most common strategy for fertilizing soils, control pests and crop diseases, but also constitute a major factor affecting the environment and human health. Cases of organochlorine pesticide contamination and human health impacts have been reported around the world including in developing countries like Tanzania (Henry and Kishimba, 2002; Weiss *et al.*, 2006; Liney *et al.*, 2006; Kihampa *et al.*, 2010a). The consequences of excessive and inappropriate use of nitrogen and phosphorus fertilizers in agriculture can significantly contribute to surface and underground water pollution. Drinking water polluted with nitrates poses health risks, especially to children being vulnerable to Methaemoglobinemia. Nutrients from agricultural activities have resulted in eutrophication of water bodies (Kalff, 2002; Kulekana, 2004; Nonga *et al.*, 2011). Once the quality of water is changed by the presence of these agrochemicals, it becomes potentially harmful to life forms, instead of sustaining them. Thus, despite their role in the horticulture industry, evaluating their potential to impacting the water resources especially in the Northern Tanzania is of great importance. This will make available the information about the potential threat they may pose to both surface and groundwater sources. This review therefore analyses their types and quantities in use and pattern of use so as to evaluate any potential for polluting such water sources. It finally recommends on the best practices and measures that need to be taken to prevent potential environmental damage.

2.2. Agrochemicals in use in Tanzania

2.2.1. Fertilizers imports and use

In Tanzania, most of the fertilizers are mainly an imported commodity with exception of Minjingu Rock Phosphate (MRP) which is obtained locally from major deposits of phosphate produced in the Northern part of Tanzania. Over the years, fertilizer imports have increased and can be attributed to the Government supported input subsidy program, the National Agricultural Input Voucher Scheme (NAIVS). The program was first started in 2007 and was then scaled up in 2009. In 2007, Tanzania imported 169,027 metric tons of fertilizer, an amount that increased to 318,060 tons in 2011(World Bank, 2012) as shown in Fig. 2.1.

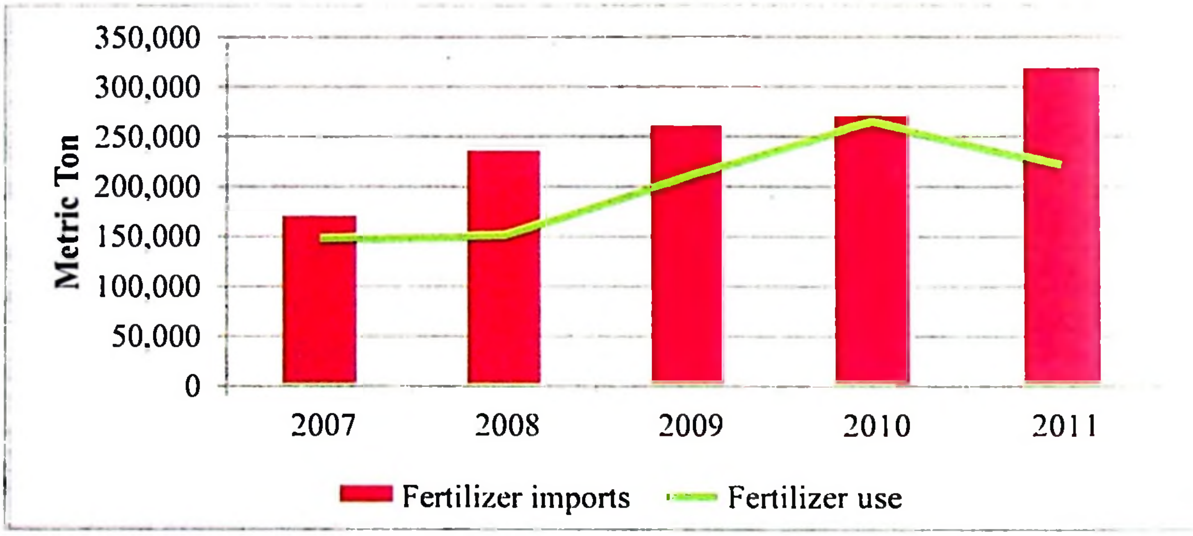

Figure 2.1: Fertilizer imports and use in Tanzania (Source: World Bank, 2012)

Alongside imports, fertilizer use has also increased since the re-introduction of subsidy on fertilizer use (MAFC, 2011). From 2008 to 2010, there was a sharp increase in total fertilizer use (Fig. 2.1). Despite this increase, the average fertilizer application rate of 19.3 kg/ha in Tanzania is lowest compared to other countries in Africa (World Bank, 2012). For example, Kenya and South Africa's fertilizer application rates are 100 kg/ha and 20 kg/ha respectively. The reason for the low usage in Tanzania could be attributed by the fact that the country's agriculture is dominated by small-scale subsistence farming and that most farmers do not have the capacity to purchase fertilizers and also they have not been sensitized on the benefits of using artificial fertilizers. On the other hand, in 2011 the use of fertilizers dropped due to prices being high as shown in Fig. 2.1.

2.2.2. Types and quantities of fertilizers used in Tanzania.

Inorganic fertilizers commonly used in Tanzania include Urea, Di-Ammonium Phosphate (DAP), Calcium Ammonium Nitrate (CAN), various Nitrogen, Phosphorus and Potassium (NPK) grades, Muriate of Potash (MOP); comprising 71% of imported fertilizers in 2009/10 and Minjingu Rock Phosphate (MRP). Urea and DAP accounted for about half the total volume of fertilizer used in 2009/10. This is because the NAIVS vouchers subsidize for their purchase and hence farmers are having difficulty to pay the portion of the fertilizer cost not covered by the subsidy. NPK fertilizers consistently account for 21 %, MRP (13 %), CAN about 9 %, Sulphate of Ammonia (S/A) 5.1 %, other fertilizers 0.9 % and Triple Super phosphate (TSP) 0.3 % (MAFC, 2011). Low quantities of foliar fertilizers (liquid) are used mainly in horticulture industries. These types and quantity are as summarized in Fig. 2.2.

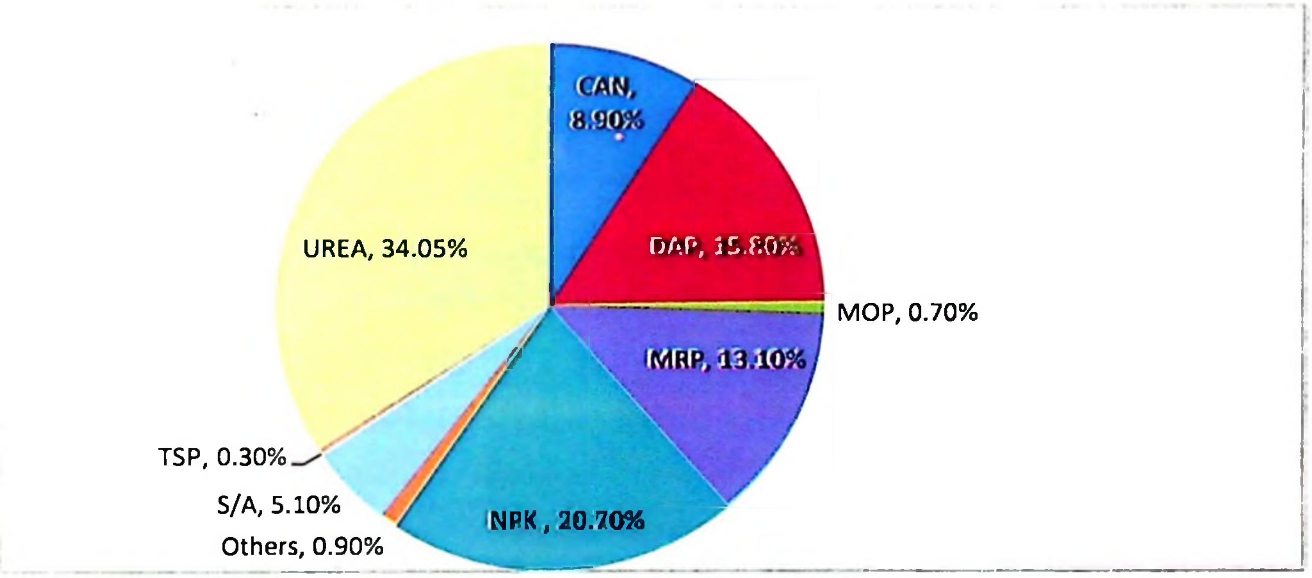

Figure 2.2: Quantity of fertilizer use and type share to the total 2009/10. {Source: (MAFC, 2011)}.

2.2.3. Pesticide use in Tanzania

Pesticides are defined by the Tropical Pesticide Research Institute (TPRI) Act No.18 of 1979 as "any matter of any description (including acaricides, arboricides, herbicides, insecticides, fungicides, molluscides, nematicides, hormonal sprays and defoliants) used or intended to be used, either alone or together with other material substances) for the control of weeds, pest and disease in plants, or for the control of the external vectors of veterinary or medical disease and external parasites of man or domestic animals or for the protection of any food intended for human or human consumptions" (Agenda, 2006).

A large number of pesticides have been extensively used to maintain high agricultural yields and eradicate vector-borne diseases in Tanzania in the last decades (Agenda, 2006). Although it is not possible to obtain figures for quantity of pesticides used or sold to the agricultural sector, however, the available information indicates that Tanzania imports over tons of pesticides from European and North-American countries (Kaoneka and Ak'habuhaya, 2000) and the importation rose following the liberalization of agrochemicals trade in the country (Ngowi, 2002). From 2000 to 2003 the imports of pesticides increased from 500 to 2500 tons per year. By the year 2006, a total number of brands of registered pesticides were 682 (Agenda, 2006). It is estimated that 81% of pesticides are used in livestock and agricultural sectors and only 19% is used for non-agricultural purposes (Agenda, 2006).

2.2.4. Types of pesticides used in Tanzanian horticultural farms

The horticulture industry in Tanzania mostly uses different classes of pesticides and herbicides such as organochlorines, carbamates, organophosphorous, pyrethroids and atrazines (Ngowi, 2002; Agenda, 2006; Nonga *et al.*, 2011). Table 2.1 shows different types of pesticides used in Northern Tanzania (Ngowi, 2002; Agenda, 2006; Nonga *et al.*, 2011). It is estimated that more than 40 different pesticides are used in horticulture of which the most widely used are insecticides (59%), fungicides (29%), with the remaining (12%) being herbicides (Ngowi, 2007). Insecticides are mostly used because insect pests are the most serious problem in horticulture production. Fungicide usage indicates that fungal attacks rank second to insect pests. Herbicides are least in use because weeding can be easily done manually by deploying community members (Ngowi, 2007). The most widely used pesticide types are organophosphates, carbamates and pyrethroids. Although Tanzania has a regulatory system on registration and trading of pesticides, however, the pesticides which are imported and used in Tanzania includes both the registered and unregistered (Table 2.1). The use of unregistered or banned pesticides can cause unreasonable risk to the environment and human health. Smallholder horticulture farmers in Tanzania have been reported to lack adequate knowledge in proper use and management of pesticides (Ngowi, 2007; Nonga *et al.*, 2011). Improper use of pesticide has been found to cause various forms of cancer, birth defects, sterility, damage of liver, kidney, neural organs and deaths (Ngowi, 2002; McCauley *et al.*, 2006; Soltaninejad *et al.*, 2007; Weiss, *et al.*, 2007; Aktar *et al.*, 2009).

Notwithstanding these effects, Table 2.1 shows that some of the pesticides used in horticulture include those which are categorized by WHO as Class 1a (extremely hazardous), Class Ib (highly hazardous). Respective examples include aldicarb and carbofuran which belong to the carbamate class of pesticides and are marked as "restricted use pesticides" by the US Environmental Protection Agency (USEPA). In addition, majority of the pesticides used are in Class II (moderately hazardous) and a few in Class III (slightly hazardous) or U (Unlikely to present acute hazard). The pesticides used have implications on health because some of them are classified to be carcinogenic, cholinesterase inhibitors and others suspected to be endocrine disruptors. A few examples include aldicarb, carbofuran, cypermethrin and dimethoate classified by the USEPA as possible human carcinogens and cholinesterase inhibitors. Endosulfan, lambda-cyhalothrin and chlorpyrifos are listed by WHO as moderately hazardous pesticides however they are suspected to be endocrine disrupting chemicals. Due to the associated risks of toxicity, these pesticides have been banned in the European Union, but are still being used in developing country like Tanzania. There are strong indications that there are substantial human health problems associated with the use of pesticides in horticultural farming in Tanzania but these are inadequately documented (Ngowi, 2007).

Table 2.1 Types of pesticides used in horticulture in Northern Tanzania

Trade name	Active ingredient	Chemical group [a]	WHO Class [b]	Health effects [c]	Amount used /yr	Registration status
			Insecticides			
Thionex / Thiodan	Endosulfan	OC	II	Suspected EDC	940 L	Registered
Selectron	Profenofos	OP	II	CI	619 L	Registered
Karate	Lambda-cyhalothrin	P	II	Suspected EDC	565 L	Registered
Dimethoate	Dimethoate	OP	II	CI	154 L	Registered
Bamethrin	Deltamethrin	P	II	CI	150 L	Registered
Helarat	Lambda-cyhalothrin	P	II	Suspected EDC	175 L	Registered
Rogor	Dimethoate	OP	II	CI, C	128 L	Registered
Dursban	Chlorpyrifos	OP	II	EDC, CI	108 L	Registered
Zetabestox	Zeta-cypermethrin	P	II		102 L	Registered
Antokil	Chlorpyrifos	P	II	EDC, CI	165 L	Registered
Diazinon	Diazinon	OP	II	CI	120 L	Unregistered
Profecron	Profenofos	OP	II	CI	143 L	Registered
Polytrin	Cypermethrin	OP	U	C	NK	Unregistered
Selecron	Profenofos	OP	II	CI	NK	Registered
Furadan	Carbofuran	C	IB	CI, EDC	254 Kg	Registered
Malathion	Malathion	OP	III	CI	192 Kg	Registered
Shumba super	Fenitrothion + Deltamethrin	OP/P	II	CI	145 Kg	Registered
Actellic super	Pirimiphos-methyl	OP	III	CI	21 Kg	Registered
Permethrin	Permethrin	P	II	Neurotoxin	NK	Unregistered
Propamocarb hydrochloride	Pyrethrins	P	None		NK	Unregistered
Termik	Aldicarb	C	IA	EDC, CI	NK	Unregistered
Diazol	Diazinon	OP	II	CI	NK	Unregistered
Carbaryl	Carbaryl	CA	II	CI	NK	Unregistered
			Herbicides			
Kalachi	Glyphosate	OP	III		452 L	Registered
Balton	2-4-D Amine	AA	U		331	Registered
Roundup	Glyphosate	OP	III		338 L	Registered
Mamba	Glyphosate	OP	III		200 L	Registered
			Fungicides			
Victory	Metalaxyl	A	NK		1400 Kg	Registered
Farmerzeb	Mancozeb	C	II	CI	501 Kg	Registered
Red copper	Copper oxide	Cu	III		560 Kg	Registered
Cuprocaffaro	Copper oxychloride	Cu	II		210 Kg	Registered
Blue copper	Copper sulphate	Cu	II		370 Kg	Registered
Dithane	Mancozeb	C	III	CI	1596 Kg	Registered
Antracol	Dithiocarbamate	D	III		165 L	Registered
Ridomil	Metalaxyl / Mancozeb	C	IIB	C / CI	127 Kg	Registered
Bayleton	Tridimefon	T	III	PC	65 L	Registered
Indofil	Mancozeb	C	III	CI	52 Kg	Registered
Ivory	Mancozeb	C	IB	CI	145 Kg	Registered
Linkonil	Chlorothalonil	OC	IIB	C	63 Kg	Registered

Thiovit	Sulphur	S	U	Irritant	124 Kg	Registered
Banko plus	Chlorothalonil Carbendazil	OC	IIB	C	NK	Registered
Bravo	Chlorothalonil	OC	IIB	C	115 Kg	Registered
Rova	Chlorothalonil	OC	IIB	C	12 Kg	Registered
Meltatox	Triforine		U	Irritant	NK	Unregistered
Milthane	Mancozeb	C	U	CI	NK	Unregistered

Foot note:

[a] C = carbamate, D = dithiocarbamate, P = pyrethroid, OP = organophosphate, A = acylalanine, AA = aryloxyalkanoic acid, Cu = inorganic copper, T = tridimefon, S = suphur.

[b] Ia = extremely hazardous; Ib = highly hazardous; II = moderately hazardous; III = slightly hazardous; U= unlikely to present acute hazard in normal use, NK = not known.

[c] CI = Cholinesterase inhibitor, C = Carcinogenic, PC = Possible carcinogenic, EDC = endocrine disrupting chemical.

Source: (Agenda, 2006; Ngowi *et al.*, 2007 and Nonga *et al.*, 2011).

2.3. Potential impacts of agrochemicals to water resources

Agriculture has been identified as the major user of water in most countries (OECD, 2010) and also contributes to water pollution from excess nutrients, pesticides and other pollutants. Majority of the farms are therefore located in areas where water supply is assured. Sources of water include springs, rivers and boreholes. Consequently, discharges of untreated and poorly treated wastewaters from horticulture farms may affect the quality of water resources for different end uses. Rural communities depend on surface water from rivers and lakes for potable uses such as washing, drinking and domestic animals also drink from these sources. Horticulture activities can contribute to water quality impairment through the release of agrochemicals particularly nutrients from inorganic fertilizers and pesticides. Majority of horticulture farmers in Tanzania lack appropriate knowledge of proper management of agrochemicals (Ngowi, 2007) and have been using them without proper advice from agriculture officers (Nonga *et al.*, 2011). Unlike the misuse including overdosing, farmers apply agrochemicals by use of Knapsack sprayers and the sprayers washing is often done in rivers. Also, the remnants of these agrochemicals are discarded by pouring them on the ground or burying (Nonga *et al.*, 2011). Empty containers are disposed within farms or in designated waste pits. This improper management of agrochemicals may cause pollution of water resources. Many of these pollutants may reach surface and ground water resources through runoff, discharges and percolation, where they can cause significant water pollution (Aktar *et al.*, 2009). Several authors have discussed research on the potential for agrochemicals pollution by fertilizers and pesticides used in horticulture. A summary of the key findings reviewed is provided hereafter.

2.3.1. Eutrophication

Eutrophication is generally defined as an increase in nutrients such as nitrogen and phosphorus in aquatic ecosystems that lead to increase in primary productivity. The consequences from this eutrophication are algal blooms increased water turbidity, oxygen depletion and fish deaths (Kalf, 2002). Monitoring of rivers and lakes in many parts of the world including Tanzania has shown significant concentration of nutrients. For example in Lake Manyara in Tanzania, big blooms of blue green algae (cyanobacteria) have been observed in the lake, and this was associated with high nutrient loads and eutrophication. High levels of phosphates were detected in the lake and were associated with high uses of fertilizers (Nonga *et al.*, 2011). Fertilization and eutrophication are among the factors reported to foster increases of phytoplankton in particular in water bodies and other water weeds in lakes (Nonga *et al.*, 2011). The eutrophication effect of Lake Victoria in Tanzania is also anticipated to be arising from the increased inflow of nutrients, particularly nitrates and phosphates (Kulekana, 2004).

2.3.2. Nitrate pollution

Excess application of inorganic nitrogenous fertilizers in horticulture can contribute directly to water nitrate pollution through fertilizer use. When too much nitrogen fertilizer is applied to crop soils, the excess that is not used by the plants eventually runs-off polluting groundwater, rivers, and lakes. Groundwater wells in vegetable farming areas in the Philippines were polluted with nitrates levels above WHO limits (Tirado, 2007). This pollution was related to intensive use of nitrogen fertilizers are applied in excess. Drinking water polluted with nitrates poses health risks, especially to children. A known human health risk is nitrate contamination in infant methemoglobinemia (blue-baby syndrome), a condition where nitrates are converted into nitrites in the digestive system, impairing the ability of infants' blood to carry oxygen. Concentration of nitrates in drinking water may be below levels at which acute health effects have been observed. However, continued exposure may result in chronic effects (i.e., reproductive impairments, cancer, etc.) to humans or other organisms.

2.3.3. Pesticide pollution

The contamination of the environment with pesticide residues in environmental matrices could result in water pollution and thus endangering human health and non-target species.

Cases of water pollution as well as soil and food contamination in Tanzania and elsewhere have been documented (Henry and Kishimba, 2002; Hellar and Kishimba, 2005; Mihale *et al.*, 2004; Aktar *et al.*, 2009; Kihampa *et al.*, 2010a, 2010b; Chowdhury *et al.*, 2012) and some health effects have been correlated with pesticide pollution (Ngowi, 2002; Agenda, 2006). As part of this review, surface water and ground water is the compartment of concern.

2.3.3.1. Surface water contamination

Pesticides can reach surface water through runoff from wastewater effluents and from soil deposits. Around the globe, pesticides and metabolites have been detected in major rivers and lakes from different countries. Water samples collected from paddy and vegetable fields in Bangladesh were reported to be highly polluted with pesticide residues (Chowdhury *et al.*, 2012). The presence of these pesticide residues were attributed by their intense use by the farmers living in the sampled areas.

In studies conducted in Tanzania, significant levels of pesticide residues in water, soil and sediments have been reported (Henry and Kishimba, 2002; Hellar and Kishimba, 2005; Kihampa *et al.*, 2010a, 2010b). Their analysis indicated among other pesticides, residues of DDT and its metabolites DDE and DDD; HCH isomers and endosulfan in water, sediments and soil samples from agriculture farms despite the ban of these pesticides in Tanzania (TPRI, 2002). Similar results of organochlorine pesticide such as DDT and HCH were also determined in water sampled in Simiyu river catchment (Tributary Lake Victoria) (Rwetabula, 2007). The Simiyu catchment was considered to be one of the main contributors to the deterioration of Lake Victoria quality due to agricultural activities using agrochemicals (Ningu, 2000). In Northern part of Tanzania, pesticide residues such as lindane, chlorpyrifos, endosulfan, DDE and DDD was determined in soil samples collected from tomato fields in Arusha (Kihampa *et al.*, 2010a). In addition, residues of organochlorine pesticides aldrin, dieldrin, heptachlor epoxides, HCH, endosulfan and DDT were detected in river water near Tanganyika sugar cane plantations (TPC) in Kilimanjaro, with mean concentrations ranging from 1.1 to 636.7 ng/l (Hellar and Kishimba, 2005). These findings are similar to those observed in a study conducted by Kihampa *et al.* (2010b) where significant concentrations of lindane, chlorpyrifos, and endosulfan was detected in irrigation effluent from horticulture farms in Arusha. The high levels of pesticides detected were associated to the intensity of agricultural activities due to pesticide use as well as pesticide application history among the areas.

Contamination of the water bodies by pesticides, either directly or indirectly, can lead to ecotoxiological effects to aquatic organisms, wildlife as well as human health if used for public consumption (Soltaninejad *et al.*, 2007). Toxic pesticide residues which can also pollute water bodies used for drinking are toxic to fish and can accumulate in many aquatic organisms and affect the top predators. Historically, most of the fish in Europe's Rhine River were killed by the discharge of pesticides, and at one time, fish populations in the Great Lakes became very low due to pesticide contamination (Adedeji and Okocha, 2012). In the United States of America, there were incidences of DDT pollution that caused thinning of eggshells and the migration of the bald eagle population (Liroff, 2000).

2.3.3.2. Ground water contamination

Groundwater pollution due to pesticides is a worldwide problem. Over the past two decades, pesticides and their metabolites have been detected in ground water. During one survey in India, 58% of drinking water samples drawn from various hand pumps and wells around were contaminated with organochlorine pesticides above the EPA standards (Kole and Bagchi, 1995). Similar contamination has also been reported in Tanzania. Some wells in Tanzania which are also used for domestic purposes by villagers are contaminated by DDT with mean total levels of 9 μg/l (Mihale and Kishimba, 2004). This concentration is higher than those allowed by the WHO for drinking water, therefore is a risk to consumers.

In addition, analyses of ground water in Tanzania indicated some trace concentrations of endosulfan sulphate (Henry and Kishimba, 2002) and Lindane (Mihale and Kishimba, 2004). Endosulfan is an organochlorine pesticide which is persistent to environmental degradation as compared to other classes of pesticide and thus has the potential to bio-accumulate in fish, wildlife and human tissues and cause toxicity effects. Notwithstanding these effects, endosulfan is among the insecticides reported to be used intensively in horticulture crops in Northern Tanzania. Endosulfan sulphate was the most abundant residue detected in horticulture fields in the area and high levels have been reported in environmental matrices (Kihampa *et al.*, 2010a, 2010b). The high uses of these pesticides call for the need to monitor their residues in the environment because once the ground water source is polluted with pesticides, it may take many years for the contamination to dissipate or be cleaned up (US EPA, 2001). Clean-up may also be very costly and complex, if not impossible especially for a developing country like Tanzania.

2.4. Conclusion and Recommendations

Agrochemicals are widely used in Tanzania horticulture and their use has significantly increased in the recent years. Many important benefits are achieved by the use of agrochemicals such as increased yields of plant crops. However, agrochemical use comes at a significant cost. Indiscriminate use of certain agrochemicals like pesticides and fertilizers has been associated with contamination of the environment and potential impacts to water resources. There are significant contribution of fertilizer application and eutrophication of some rivers and lakes in Tanzania from high use of nitrogen and phosphate fertilizers in areas with intense horticulture. Pesticide residues have been detected in soil, surface water and ground water across countries. Results from different literature show that organochlorine pesticides are by far the most frequently detected in environmental samples. These chemicals are persistent in the environment and thus there is a need to ensure regulations governing their ban for use are strictly enforced.

Farmer's limited knowledge on proper use and management of agrochemicals is among the factors that cause indiscriminate use and pollution of the environment. However, opportunities for preventing pollution by these agrochemicals include the following measures:

i. Education and sensitization of farmers against illegal and indiscriminate use of agrochemicals (pesticides and fertilizers);
ii. Promotion of integrated pest management (IPM) to ensure responsible use of pesticides so as to minimize potential adverse impacts on human health and environment;
iii. Continual monitoring of levels of agrochemicals in different environmental compartments for regulatory control;
iv. Further research work is recommended to ascertain the levels of agrochemicals in wastewater.

CHAPTER THREE

Assessment of Agrochemical Residues in Wastewater from Selected Horticultural Farms in Arusha, Tanzania[2]

ABSTRACT

Arusha region in Tanzania has been involved for quite some time on commercial horticulture. The use of agrochemicals results to increased crop productivity and consequently offers farmers major economic returns. However, the use of agrochemicals and the adjacency of horticultural farms to streams and rivers have the potential to contribute to water pollution if control measures are not effective. We analysed the physical and chemical parameters of wastewater discharged from five horticultural farms in Arusha and detected BOD, nitrates (NO_3^-), phosphates (PO_4^{3-}), sulphates (SO_4^{2-}) and permethrins insecticide in the effluents discharged into the environment. The mean concentration levels ranged from (56.60-279) ppm for BOD_5, (4.5 - 64) ppm for NO_3^-, (3 - 48) ppm for PO_4^{3-}, (91 - 139) ppm for SO_4^{2-} and (0.4 - 0.8) ppm for permethrin. Of all the five farms monitored, five farms had high levels of BOD, four farms had high levels of PO_4^{3-}, three farms had high levels of NO_3^- and one farm had high levels of permethrin above the allowable limits for discharge into receiving water bodies. It may be concluded that the continued agrochemical use may lead to contamination of adjacent water resources which may in the long run cause adverse health effects to the downstream water users. Continual monitoring of agrochemical residues is recommended to inform and ensure compliance with the stipulated standards and regulations for wastewater discharge.

3.1. Introduction

Horticulture, as one of the major economic activities in Tanzania, has much to contribute to water pollution through the use of agrochemicals. The need to increase crop productivity has led to extensive use of pesticides, fertilizers and promotion of irrigation in horticultural practices (MoW, 2012). Arusha is among the regions in Tanzania with increased agrochemical use and intensive horticulture practices (Nonga *et al.*, 2011; Agenda, 2006). On the other hand, both expansion of horticultural activities and the intensive use of these agrochemicals when not well managed may lead to adverse impacts on the environment (Lema *et al.*, 2014). Horticulture in Tanzania has been reported to be constrained by excessive and unsafe use of agrochemicals in production practices (HODECT, 2010; Ngowi 2007; Nonga *et al.*, 2011). Indiscriminate uses of agrochemicals present one of the main environmental and human health problems in many developing countries. For example in

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[2] International Journal of Environmental Sciences, 2014, 5(2)

Tanzania, the excessive and inappropriate uses of nitrogen and phosphorous fertilizers in horticulture have resulted to nutrient enrichment (eutrophication) of surface waters (Kulekana, 2004; Nonga *et al.*, 2011). The consequences from this eutrophication are increase in big blooms of blue green algae which cause oxygen depletion and fish deaths (Kalff, 2002).

Over the years, various types of pesticides such as organophosphates, organochlorines, and carbamates have been extensively used by farmers in Tanzania (Ngowi, 2002, 2007; Henry and Kishimba, 2003; Hellar and Kishimba, 2005 and Agenda, 2006). Although organochlorine pesticides were banned for use in many countries in European Union and America due to their high toxicity (Moore *et al.*, 2009), Tanzania is still using endosulfan which is a chlorinated insecticide. Endosulfan is persistent to the environment even after long-term applications and its residues are being detected in horticultural areas (Kihampa *et al.*, 2010a, 2010b; Haarstad *et al.*, 2012). However, organophosphorous insecticides like (chlorpyrifos, dimethoate, profenofos, diazinon and fenitrothion) and carbamates (carbofuran, mancozeb, carbaryl and metalaxy) have been widely used in many countries including Tanzania due to their broad spectrum activity, low persistence and mammalian toxicity as compared to the organochlorines. Currently the organophosphorous pesticides are being replaced by the more efficient and safe pyrethroid class of insecticides like permethrin, cypermethrin, deltamethrin and lambda-cyhalothrin (Ngowi, 2007). Although these pesticides are regarded as safe for use due to their relatively fast degradation rates, however a review of the literature shows that they are toxic even at trace level concentrations of 0.1 μg/L (Chowdhury *et al.*, 2012). For example, in trace amounts, chlorpyrifos which is an organophosphorous insecticide has been reported to cause neurological disorders due to its cholinesterase inhibition and endocrine disrupting effects. Furthermore, carbofuran, which is a carbamate, has been reported to cause cholinesterase inhibition and endocrine disrupting effects (Chowdhury *et al.*, 2012).

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Due to the widespread, long term uses and the chemical properties of agrochemicals, their residues are being detected in environmental matrices. Toxic chemical residues usually reach the aquatic environment through nonpoint and point pollution sources by direct run-off or leaching of these chemical compounds or by careless disposal of empty containers or the washing of equipment after their application (López-Blanco *et al.*, 2005; Sattler *et al.*, 2007). The environmental contamination into water resources is now a topic of considerable environmental interest due to the increasing number of toxic chemical compounds detected and has required the establishment of strict international and local regulations aimed at minimizing these inputs (Gomez *et al.*, 2012). A primary concern about wastewater from horticulture is their effect on water quality and the subsequent impacts on human health and the environment. Disposal of wastewater into natural systems will in most cases have a detrimental effect on the future use and sustainability of these resources (Lema *et al.*, 2014). Problems related to the release of nutrient enriched wastewater and pesticide leaching has been observed worldwide (Kalf, 2002; Camargo and Alonso, 2006; Carvalho, 2006; Aktar *et al.*, 2009; Kimani *et al.*, 2012). However the use of agrochemicals in Tanzania horticulture industry is increasing (Ngowi, 2007; Kihampa *et al.*, 2010a, 2010b and Nonga *et al.*, 2011).

It is apparent that horticulture industries in Tanzania are located adjacent to water resources and hence putting stress on the quality of the receiving waters such as streams, rivers and lakes (Lema *et al.*, 2014). These water resources from intensive horticultural areas are more vulnerable to agrochemical contamination, which is a major concern if the water is intended for human and animal consumption. In many cities of developing countries including Tanzania, these water resources are used as sources of water for domestic use and livestock (Nonga *et al.*, 2011). Therefore, agrochemical residues from wastewater have the potential of impairing the quality of water resources for different end uses. Currently, information on agrochemical residues from wastewater discharged from horticulture farms in Tanzania is inadequate. It is in this regard that this study was undertaken to obtain information on the characteristics and levels of agrochemical residues from wastewater in selected horticulture farms. Knowledge of the quality of the wastewater produced from these farms can help to develop solutions to manage horticulture wastewater. The study will also be helpful for developing sustainable techniques for the treatment of horticulture wastewater before discharge.

3.2. Material and methods

3.2.1. Study area

The study was done in selected horticulture farms in Arumeru district in Arusha located in the North of Tanzania (All sites are shown in Fig. 3.1). Arusha was chosen as the study area because of its known history of growing commercial horticulture crops where such activities are practiced in Arumeru and Arusha Districts. In Arumeru district, commercial horticulture farms are located in two major locations: at Usa river area and Nduruma areas. These farms comprise of large scale farms growing horticulture crops which supply to the European markets such as in the Netherlands, Germany, Sweden, and Norway among others. These farms have been established in Tanzania because of the advantage of the good climate which allows such crops to be grown all year round and also on the basis of cheaper labour costs compared to Europe. The crops grown in the area includes hybrid seed production (produce and supply seeds required by vegetable growers), nursery industry (production of fruit trees for fruit growers) and cut flower farming (roses and chrysanthemum). These crops are grown in greenhouses where agrochemicals are applied through the use of drip irrigation systems.

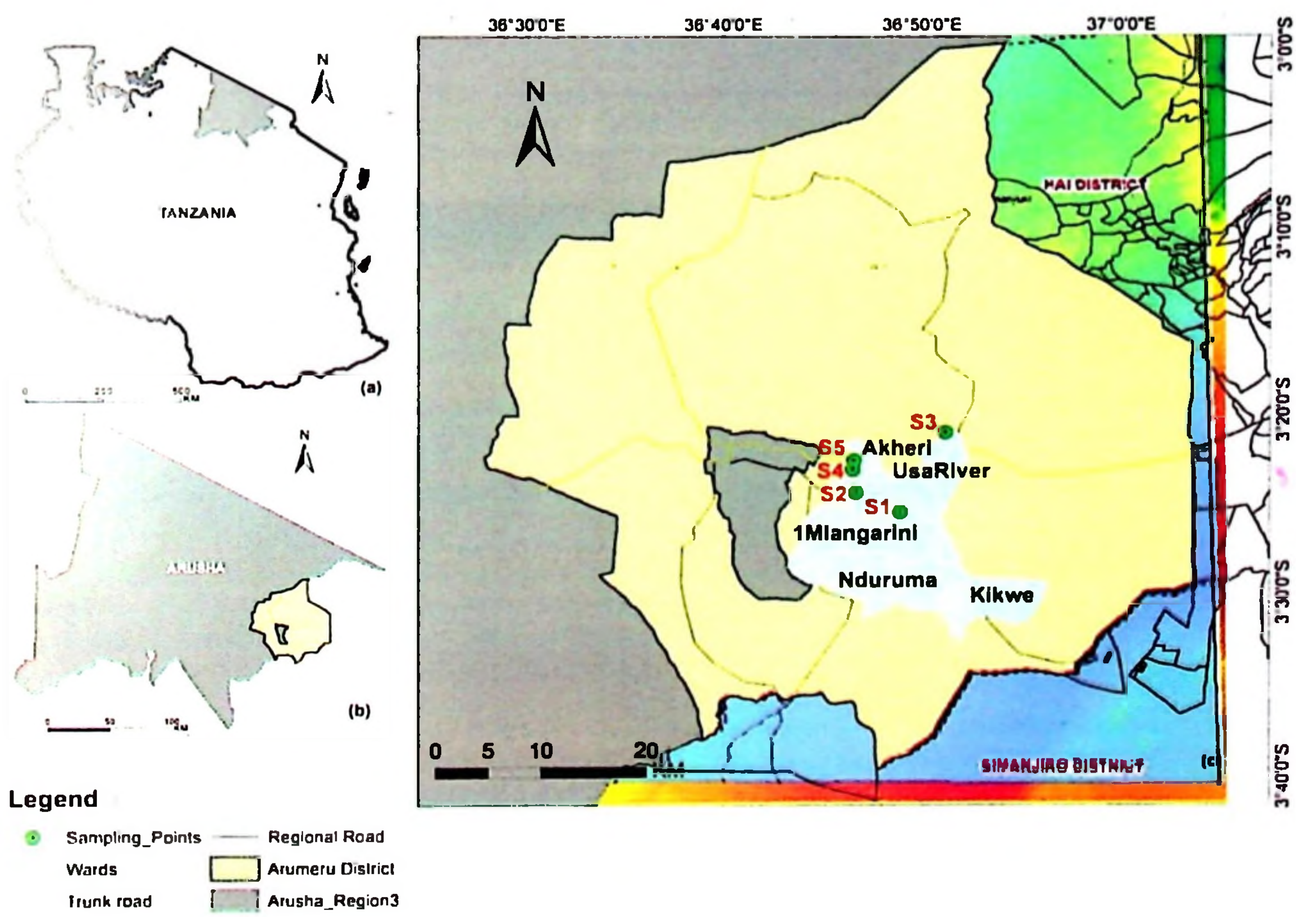

Figure 3.1: Map of the study area with indication of the sampling sites.

The wastewater draining from greenhouse fertigation units and processing areas is either retained in wastewater ponds or filtered through a series of wetland systems for treatment before disposal. It was not possible to monitor wastewater quality from all the farms in the region due to limited time and budget. A purposive sampling was made and five horticulture farms from the two major locations were selected to investigate the potential of agrochemical pollution of environment. Sampling points were selected and located by Geographical

Positioning System (GPS) instrument. Site observations were used to obtain information about agrochemical use and horticultural practices.

3.2.2. Sample collection and characterization

3.2.2.1. Nutrients and other physical parameters

Wastewater effluents were collected on weekly basis for two months consecutively during the season in September 2013 and October 2013. Sampling for was done by using 500 ml new polyethylene bottles which had previously been washed thoroughly with detergent, rinsed with tap water and soaked overnight with dilute HCl (10 %), followed by rinsing with deionized distilled water prior to usage. During sampling, they were again rinsed three times with sample water and filled to the brim with wastewater (APHA, 1998). The samples were then labelled and transported to the laboratory using ice-cooled boxes. In the laboratory, the samples were analysed for 10 parameters, namely temperature, pH, conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), 5-day biological oxygen demand (BOD_5), nitrate (NO_3^-), phosphate (PO_4^{3-}), chloride (Cl^-), and sulphate (SO_4^{2-}) as per the methods described in standard methods (APHA, 1998). The nutrient levels (nitrates, phosphates, ammonium and sulphates) were determined using water quality laboratory series HACH - DR (2700) Spectrophotometer, and BOD_5 was determined using BOD_5 OxiTop kit. Field determinations of temperature, pH, conductivity, total dissolved solids and oxygen were measured in-situ using portable EC/ pH/TDS/temperature meter and dissolved oxygen measured using a handheld oxygen meter. Descriptive statistics (mean and standard deviation) of the results obtained was determined using Origin 8.0 software (Origin Lab Corporation, Northampton, MA, USA).

3.2.2.2. Sampling and extraction

Sample collection was done using standard methods as described by Akerblom (1995). Upon reaching the laboratory, the samples were immediately extracted by liquid-liquid extraction (LLE) method (Siegel and Lee, 2004). The 1-L unfiltered water sample was quantitatively transferred in a 2-L separating funnel and the sampling bottle rinsed with 60 ml hexane: acetone 1:1. The rinsate was then mixed with the sample in the separating funnel. The combined contents were extracted successively with hexane: acetone 1:1 (3x60 ml). The organic phase was filtered through a plug of glass wool containing anhydrous sodium sulphate (ca 20 g) for drying and drawn into an Erlenmeyer flask. The aqueous layer was repeatedly extracted with a mixture of hexane: acetone (1:1 v/v, 60 ml) as above. After the extraction procedure, the volume of the extract was concentrated to 2 mls using a rotary evaporator at 40 °C and the final volume adjusted by evaporating under gentle stream of nitrogen gas to 1 ml. The water extracts appeared clean and were not subjected to further clean up, and hence was stored at -5 °C freezer ready for GC/MS analysis.

3.2.2.3. Analytical quality assurance

Analytical grade reagents and chromatographic solvents hexane, acetone and dichloromethane supplied by Sigma - Aldrich Chemical Co Ltd (Germany) were used. Samples were quantified using pesticide standard mixture which had over 99 % certified purity. Laboratory glassware were thoroughly cleaned with detergents, rinsed with distilled water and acetone, and then dried in an oven overnight before use. Blanks and recovery experiments were run to check the contamination from the solvents used. The results showed no significant peaks in the chromatograms of the blanks. The recoveries of the method were determined by spiking matrix blank with pesticides at concentrations ranging from 0.01 - 1.1 μg/ml for each analyte. The percentage mean recoveries ± SD (n=4): chlorpyrifos 80.1 ± 2.9 %, endosulfan 87.3± 0.7 %, cypermethrin was 70 ± 2.4 % and carbofuran 84.5 ± 0.7%. The results indicate that the recovery was within the normal acceptable range of 70-120 % (Akerblom, 1995). The lower limit of detection in the GC/MS was 0.01 ppm.

3.2.2.4. Analysis and quantification

Analysis of pesticide residues was done using gas chromatography (Agilent Technologies, 7890A GC System with auto sampler 7683B series injector) coupled with mass spectrometer (Agilent Technologies, 5975C inert XL EI/CIMSD with Triple-Axis Detector). The GC/MS analysis parameters and operating conditions were as follows: Helium was used as a carrier gas at a flow rate of 1.2 mls/min; the oven temperature programme was 50 °C held for 1 min at a rate of 10 °C /min to 160 °C then held for 5 minutes and finally by 3 °C /min to 300 °C and held for 18.5 min. The temperature of the injection port was 250 °C. The MS detector temperature was 250 °C (transfer line temperature) and 230 °C (ion source). Pesticide residues were identified and quantified by comparing their retention times and peak heights with respect to external reference standards.

3.3. Results and Discussion

A summary of the physical and chemical parameters of the measured wastewater for all the sampling sites, their units, methods of analysis and maximum acceptable standards are summarized in Table 3.1. The results for each variable were compared against Tanzania allowable water quality standards and WHO standards where possible.

Table 3.1: Mean (±) standard deviation values of physical and chemical parameters determined in wastewater in selected horticulture farms in Arusha (n = 5)

Sites / Variables	S1	S2	S3	S4	S5	Method of analysis	TZS allowable limits
pH	8.5 ± 0.7	7.9 ± 0.6	8.7 ± 0.7	6.9 ± 2	7.1 ± 0.2	pH metry	6.5 – 9.0
TEMP (° C)	19.9 ± 1.1	19.8 ± 1.5	20.1 ± 1.9	21 ±0.6	21.8 ± 0.7	Thermometry	20 – 35
EC (μs/cm)	784.7 ± 67.1	1442 ± 46	1045.1 ±137.8	1102.6 ±79.6	663.3 ±81.9	EC meter	-
TDS (ppm)	496.6 ± 11.4	876.4 ±48.7	636.8 ±99.1	695.2 ±33	423 ±54	TDS meter	2000
DO (ppm)	6.1 ±1	1.6 ±0.3	3.9 ±0.3	2.5 ±0.2	5.9 ±1.3	Do meter	3
BOD_5 (ppm)	109.9 ± 27	79.2 ±8.7	118.6 ±22	279.1 ±141	56.6 ±7.4	Manometric	30
NO_3^- (ppm)	8.1 ± 2.5	22.2 ± 6.5	64.1 ± 9.7	4.5 ± 0.6	27 ± 14	Colorimetry	20
PO_4^{3-} (ppm)	3.2 ± 2.4	17.4 ±16.9	47.6 ±16.1	15.7 ± 1.9	9.1 ± 4.8	Colorimetry	6
SO_4^{2-} (ppm)	91.4 ± 3.5	132.4 ± 8.6	139 ± 33.4	118.6 ± 11.9	106.1 ± 13.7	Colorimetry	500
Cl^- (ppm)	84.9 ± 50.6	90.5 ± 40	121.4 ± 47.9	419.4 ± 24	122.5 ± 45.9	Titrimetry	200
Permethrin (ppm)	bdl	bdl	0.6 ± 0.3	bdl	bd	GC/MS	0.01
Chlorpyrifos (ppm)	bdl	bdl	bdl	bdl	bdl	GC/MS	0.01
Endosulfan (ppm)	bdl	bdl	bdl	bdl	bdl	GC/MS	0.01
Carbofuran (ppm)	bdl	bdl	bdl	bdl	bdl	GC/MS	0.01

bdl = below detection limit. TZS = Tanzania water quality standards.

3.3.1. pH

This is the concentration of hydrogen ions in solution and indicates the level of acidity or alkalinity of an aqueous solution. If the pH of the wastewater is outside the range of 6-9, there may be considerable interference with chemical and biological processes in the aquatic environment. Low pH causes the immobilization of toxic elements and compounds thereby increasing their availability to aquatic plants and animals. For example increasing the solubility of micronutrients particularly phosphates and elements like manganese, zinc, iron and copper (UNEP, 2001). From the results of the study, the mean levels of pH varied between 6.89 and 8.66. These values are typical values normally experienced in surface waters and are within the TZS allowable limits of 6.5-9.0 for wastewater discharge (MoW, 2012).

3.3.2. Temperature

Temperature is an important parameter for its effect on other properties of wastewater since it controls the rates of biological and chemical processes in water. Temperature affects the oxygen content of water, rate of photosynthesis by aquatic plants and metabolic rate of organisms. The mean temperatures observed range between 19.86 (± 1.13) °C and 21.84 (± 0.66) °C are typical for these climate conditions and are within the TZS allowable limits of 20-35 °C for discharge (MoW, 2012). The variation of temperature observed is attributed to change in weather conditions and time between the times of monitoring.

3.3.3. Conductivity (EC)

Conductivity is a measure of waters potential to conduct an electric current and is a useful indicator of salinity or total salt content. The mean EC values detected in the wastewater vary considerably between 663.34 (± 81.89) to 1442.01 (± 46.1) µs/cm. The natural range of EC in water falls within the range of 10 - 1000 µs/cm (MoW, 2012). The higher EC values (i.e. over 1000 µS/cm) detected in site S2, S3 and S4 suggests that the wastewater is polluted and contains excess dissolved salts than normal. In general water can be affected by the presence of inorganic dissolved solids (i.e. chloride, nitrate, sulphate, and phosphate anions; or sodium, magnesium, calcium, iron, and aluminium cations. The use of agrochemicals (i.e. fertilizers and pesticides) could be the main reason for the high conductivity values detected in the sampled sites. Although conductivity appears to have no health significance but high levels of salts in wastewater can increase salinity of the receiving water resources and consequently cause adverse ecological effects on aquatic biota (Morrison *et al.*, 2001).

3.3.4. Total Dissolved Solids (TDS)

The mean concentration of TDS in wastewater ranged from 423 (± 54) ppm to 876.44 (± 48.68). High values were 876.44 (± 48.68) ppm, 636.8 (± 99.1) ppm and 695.2 (± 33.02) ppm for sampling site S2, S3 and S4 respectively. The principal constituents that contribute to high TDS values are usually dissolved salts such as calcium, magnesium, sodium, potassium, chloride, sulphate and nitrate. The high levels detected in the sampling sites could mostly emanate from agrochemical based fertilizers. High concentrations of TDS limit the suitability of water as drinking sources and irrigation supply (Razowska-Jaworek and Sadurski, 2005). The WHO limit for drinking water is a TDS of 1,000 ppm. However the levels detected in all sampling sites were within the TZS allowable limits for discharge which is 2000 ppm.

3.3.5. Dissolved oxygen (DO)

Dissolved oxygen (DO) is one of the most important parameter in assessing the quality of water and understanding the physical and biological process prevailing in the water (Sinha *et al.*, 2000 and Efe, 2005). Dissolved oxygen concentrations in unpolluted water usually range between 8 to 10 ppm and concentrations below 5 ppm adversely affect aquatic life (Rao, 2005). The mean DO levels detected in the study ranged between 1.56 (± 0.33) ppm to 6.05 (± 1.02) ppm. Very low levels were detected in sampling sites S2 and S4 with mean values of 1.56 (± 0.33) ppm and 2.47 (± 0.23) ppm respectively. The DO levels in these sites fell short of the Tanzania recommended standard for discharge into receiving waters (Tanzania Water Utilization, 1981). The low DO concentrations could be due to excess inputs of nutrient rich effluents and other organic matter which can cause an oxygen deficient situation to occur.

3.3.6. Biological oxygen demand (BOD)

Biological oxygen demand is the amount of oxygen used by microorganisms (e.g. aerobic bacteria) whilst consuming organic material in a wastewater sample. It is also taken as a measure of the concentration of organic materials present in any water. The greater the BOD values means the wastewater is more concentrated with organic materials (APHA, 1998). The mean values of BOD obtained from the sampling sites ranged from 56.6 (± 7.4) ppm to 279.1 (± 141.01) ppm. The levels obtained in all the sampling sites were higher than the TZS maximum permissible value of 30 ppm for discharge into receiving waters. These high results are an indication of contamination due to excessive concentration of nutrients and other organic materials discharged from the sampling sites.

3.3.7. Nitrates (NO_3^-)

The values of nitrates varied between 4.5 (± 0.57) ppm to 64.08 (± 9.68) ppm. The highest NO_3^- levels recorded are 22.16 (± 6.5) ppm, 64.08 (± 9.68) ppm and 27.44 (± 14.4) ppm in site S2, S3 and S5 respectively. The high levels detected exceeded the TZS allowable value of 20 ppm for discharge into receiving waters. These values indicate possible contamination from direct and indirect discharges of nitrogen containing fertilizers and sewage. Nitrate is very mobile and can enter surface and ground water. Releasing effluents rich in nitrates may lead to the growth of blue green algae, which could release toxic substances (cyanotoxins). The water cyanotoxins are known to have caused death of farm livestock (Morris *et al.*, 2001). Drinking water contaminated with nitrate may give rise to a health condition known as methaemoglobinemia or blue baby syndrome especially to infants (Akinbile, 2006).

3.3.8. Phosphates (PO_4^{3-})

Phosphate is a constituent is used extensively in fertilizers to replace and/or supplement natural quantities on agricultural lands. Runoff from agricultural areas is a major contributor of phosphates in surface waters. Phosphate levels in the wastewater from the monitored sites ranged between 3.22 (± 2.37) ppm to 47.64 (±16.12) ppm. High concentrations exceeding the TZS permissible value of 6 ppm was detected in sites S2, S3, S4 and S5 with mean concentrations of 17.39 (±16.92) ppm, 47.64 (±16.12) ppm, 15.69 (±1.86) and 9.11 (±4.84) ppm respectively. The high levels detected are an indication of possible pollution of wastewater containing phosphate based fertilizers. High concentrations of phosphates may lead to eutrophication - a process which causes surface waters to become enriched with nutrients so that algae and cyanobacteria can grow rapidly and deplete the oxygen needed by aquatic organisms and other recreational uses of water. Eutrophication was observed in the sampling sites during reconnaissance survey (via visual inspection) with the presence of algal blooms.

3.3.9. Sulphates (SO_4^{2-})

Sulphate is one of the least toxic anion however consumption of water containing concentrations in excess of 600 ppm could result in cathartic effects (WHO, 1996). The mean concentration of sulphate ranged between 91.42 (± 3.50) ppm to 139 (± 33.42) ppm. These values are below the TZS allowable limit of 500 ppm for the discharge of wastewater into receiving waters. Sulphate in water may be contributed by natural and anthropogenic sources, however the use of sulphate containing fertilizers have been reported to contaminate surface waters (IUCN, 2010). The results obtained from this study can be related to the use of sulphate fertilizers.

3.3.10. Chlorides (Cl^-)

Chloride in the form of chloride ion is one of the major inorganic anions commonly found in most waters due to salt deposits and discharge of effluents. Chloride concentration detected in the sampled sites ranged between 84.89 (± 50.57) ppm to 419.44 (± 24) ppm. Except for the highest concentration of 419.44 (± 24) ppm detected in site S4, the levels observed in the remaining sites were within the TZS allowable limits of 200 ppm for discharge.

3.3.11. Pesticides

The results of the study (Table 3.1) showed that out of the four pesticides screened in wastewater from the sampled sites, the study detected one pesticide permethrin during the time of monitoring. Permethrin is a synthetic pyrethroid and is widely used in agriculture. High concentration was detected at site S3 with a mean concentration of 0.63 (± 0.26) ppm. These findings are consistent with other studies that obtained information on the types of pesticide use in horticulture (Ngowi, 2007). The levels are indicative of usage of permethrin pesticide in the sampled site. However, the pesticides were trivial to be detected in other sampling site. The reason could be explained by the fact that permethrin and many other pyrethroids are highly hydrophobic and binds strongly to suspended solids, dissolved organic matter and sediments (Liu *et al.*, 2004; Lee *et al.*, 2004). Within a few hours of discharge they will rapidly dissipate from the water column (Allan *et al.*, 2005). They are easily degraded in the environment via photolysis and microbial biodegradation.

Furthermore, as can be observed in Table 2.1, chlorpyrifos, endosulfan and carbofuran insecticide residues were not detected in the wastewater in any of the sampled sites during the time of investigation. The non-detection could be explained by the fact that the selected horticulture farms are large scale commercial farms cultivating crops such as seeds and cut-flowers (roses and chrysanthemum) for export to European countries (Cooksey, 2011) and may be restricted from using some of these toxic pesticides like the banned endosulfan and carbofuran (Thompson, 2009). However, this was in contrary to a study done in small scale horticulture farms in Northern Tanzania, where detectable levels of endosulfan and chlorpyrifos insecticides were observed in effluent samples (Kihampa, 2010b). Indiscriminate uses of pesticides in smallholder vegetable farmers in Northern Tanzania have been reported (Ngowi *et al.*, 2007). Nevertheless, in the present study, the non-detection of chlorpyrifos insecticide which has been reported to be commonly used in horticulture may indicate that it was either not used during the months in which the sampling took place or it may have dissipated from the water column owing to its relatively fast degradation rate. Although results for most targeted pesticides were trivial to be detected in wastewater samples, but soil can act as a sink for most pesticides (Kihampa *et al.*, 2010a; Kishimba and Mihale, 2004), from which they can be released into the environmental matrices and bio-accumulate through food chain to an extent high enough to cause adverse health effects to consumers.

3.4. Conclusion and Recommendations

Based on the results of this study, wastewater samples collected from selected horticulture farms in Arusha detected high levels of nitrates (NO_3^-), phosphates (PO_4^{3-}) and permethrins insecticide in the effluents discharged into the environment. The mean concentration levels ranged from (4.5 ppm - 64.08 ppm) for NO_3^-, (3.22 ppm - 47.64 ppm) for PO_4^{3-} and (0.39 ppm - 0.80 ppm) permethrin. Of all the farms monitored, eighty (80) % had high levels of PO_4^{3-}, sixty (60) % had high levels of NO_3^- and twenty (20) % had high levels of permethrin above the allowable limits for discharge into receiving water resources. The findings indicate that these concentration levels were above the allowable limits for wastewater discharge in receiving waters. Accordingly, if such levels are not controlled, continued agrochemical use may lead to pollution of adjacent water resources which may in the long run cause adverse health effects to the downstream users. It is recommended that continual monitoring of effluents is essential to inform and ensure compliance with the stipulated standards and regulations for wastewater discharge. Importantly, farmers need to ensure that mitigation measures such as wastewater management strategies and treatments on site are efficient to prevent contamination of the environment. Further research is recommended to determine the levels of agrochemical residues in sediments, soils and biota around horticultural fields on a wider perspective in the course of assessing the extent of agrochemical contamination.

CHAPTER FOUR

Influence of Macrophyte types towards Phytoremediation of Wastewater contaminated by Agrochemicals in a Tropical Environment[3]

ABSTRACT

The presence of agrochemicals in wastewater from agricultural fields poses major environmental and human health problems which may be solved by phytoremediation technologies. Phytoremediation is the use of plants to remediate contaminants in the environment. Bucket experiments were conducted to evaluate the influence of four aquatic macrophytes (*Cyperus papyrus*, *Typha latifolia*, *Cyperus alternifolius* and *Phragmites mauritianus*) towards phytoremediation of agrochemicals from simulated wastewater in Arusha, Tanzania. The selected agrochemicals belonged to different categories namely heavy metal based (Cu, Fe, Mn and Zn) and pesticides (L-Cyhalothrin, Endosulfan and Permethrin). The change in mean concentration of the agrochemicals was described by first-order reaction kinetics. The results indicated that the removal rate constants were greater for the bucket experiments planted with the macrophytes than for the control group. Furthermore, the rate of removal varied between the treatments for the different categories of agrochemicals. As far as heavy metals are concerned, *Cyperus papyrus* had a greater removal Cu and Fe with the *k* values of 0.338 d^{-1} and 0.168 d^{-1} respectively and *Typha latifolia* had a greater removal of Mn and Zinc with *k* values 0.420 d^{-1} and 0.442 d^{-1} respectively. On the other hand, the pesticides endosulfan and permethrin were greatly removed by *Cyperus papyrus* with *k* values 0.086 d^{-1} and 0.114 d^{-1} respectively. Lastly, L-Cyhalothrin was removed greatly by *Typha latifolia* with *k* value of 0.116 d^{-1}. Generally, the results demonstrated that aquatic macrophytes can influence the reduction of agrochemicals in wastewater.

4.1. Introduction

The use of agrochemicals such as chemical fertilizers and pesticides are integral part in the current agriculture production system around the globe. Accordingly, their uses have been a common practice particularly in many nations in the tropical world (Carvalho, 2006). In humid tropics of Africa, these agrochemicals have been extensively used to control pests and diseases affecting crop productivity and improve soil fertility. In Tanzania, the need to increase crop productivity has led to extensive use of pesticides, fertilizers and promotion of

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irrigation in horticultural practices (MoW, 2012). However the excessive and indiscriminate uses of these agrochemicals create environmental problems such as contamination of soil and water resources (Lema *et al.*, 2014a).

Pollution by agrochemicals is one of the most significant threats to the integrity of the world's surface waters. In Tanzania, agriculture has been categorized as one of the most polluting industries releasing effluents containing agrochemicals (Mwegoha, 2008). The agrochemicals of main ecological concern are heavy metal based fertilizers, fungicides and pesticides because they are toxic and persistent in the environment and hence they can eventually bio-accumulate to higher levels that could affect human being (Dipu *et al.*, 2011) and other living organisms. Although heavy metals occur naturally in soils in small quantities but the major sources emanate from micro nutrients applied on agricultural fields as such as zinc, manganese, molybdenum, iron, nickel, phosphates, aluminium, selenium and copper. These trace elements are essential for the growth and health of plants but they are highly toxic when the concentration exceeds certain limits.

Earlier information on the types of pesticides used in Tanzania revealed that different classes of pesticides are being used in agriculture like organochlorines (endosulfan); organophosphates (chlorpyrifos, dimethoate, profenofos, diazinon and fenitrothion); carbamates (carbofuran, mancozeb, carbaryl and metalaxy) and pyrethroids (permethrin, cypermethrin, deltamethrin and lambda-cyhalothrin (Lema *et al.*, 2014a; 2014b 'in press'). Due to the widespread, long term use and the chemical properties of these pesticides, their residues end up in the environment and are being detected in various environmental matrices including the biota.

Studies done in Tanzania and elsewhere have indicated significant agrochemical contamination of soil and water resources (Fianko *et al.*, 2011; Kihampa *et al.*, 2010; Moore *et al.*, 2009; Hellar and Kishimba, 2005). Application of copper based fungicides has been reported to cause soil contamination by copper (Mirlean *et al.*, 2006). The application of phosphate fertilizers to the agricultural soil has led to increase in heavy metals like cadmium, copper, zinc and arsenic (Zarcinas *et al.*, 2004). Although some farms in Tanzania treat their wastewater effluents in a suitable way, others lack convenient treatment systems thus discharging untreated or poorly treated wastewater into the natural environment (Lema *et al.*, 2014b 'in press'). The continual discharges of effluents containing these agrochemicals can increase the accumulation of toxic chemicals and thereby threatening the aquatic ecosystem and human health (Sasmaz *et al.*, 2008).

Due to their toxic properties and adverse negative effects on the environment, several strategies have been developed to remove contaminants from the environment. Conventional wastewater treatment techniques for removal of agrochemicals from agriculture runoff include physical and/ or chemical treatments such as isolation, containment, coagulation-flocculation, reverse osmosis, ion exchange, electrochemical treatment, etc. However, these technologies are impractical and expensive for developing countries like Tanzania and often require a large excess of chemicals and generate large volumes of sludge and hazardous by-products that require appropriate and costly disposal methods. Due to the above-mentioned constraints of conventional technologies, phytoremediation methods using aquatic macrophytes are the need for developing countries because they are environmentally friendly, effective and cheaper to establish and operate.

4.1.1. Phytoremediation using aquatic macrophytes

Macrophytes are aquatic plants and are regarded as important component of aquatic ecosystem due to their roles in oxygen production, nutrient recycling, controlling water quality, sediment stabilization and providing shelter for aquatic life (Ravena, 2001). Phytoremediation takes advantage of the natural processes of macrophytes and their roles in pollutant removal. These processes include water and chemical uptake, metabolism within the macrophytes, and the physical and biochemical impacts of root system. Aquatic macrophytes are more suitable for wastewater treatment than terrestrial plants because of their relatively fast growth rate and larger biomass production, higher capability of pollutant uptake and better purification effects due to direct contact with contaminants in water.

The word phytoremediation comes from the Greek word phyto which means plant and Latin word remediation which means to remove, which refers to a diverse collection of plant based technologies that use plants to clean contaminants (Cunningham, 1997). Phytoremediation technology is relatively a new approach and has gained importance during the last two decades (Dhir, 2010). This technique can be applied to both organic and inorganic pollutants (Garbisu and Alkorta, 2001) present in solid substrates (e.g. soil), liquid substrates (e.g. water) and air (Lone *et al.*, 2008). Chemical substances that can be subjected to phytoremediation include metals (Pb, Zn, Cd, Cu, Ni, Hg etc.), metalloids (As, Sb), inorganic compounds (NO_3^-, NH_4^+, PO_4^{3-}), radionuclides (U, Cs, Sr), petroleum hydrocarbons (BTEX), pesticides (atrazine, bentazone, chlorinated and nitroaromatic compounds), explosives (TNT, DNT), chlorinated solvents (TCE, PCE) and industrial organic wastes (PCPs, PAHs) and landfill leachates (Khan *et al.*, 2004).

4.1.2. Phytoremediation mechanisms

There are several mechanisms by which phytoremediation can occur (Fig. 4.1). Each of these mechanisms will have an effect on the volume, mobility, or toxicity of contaminants, as the application of phytoremediation is intended to do (EPA, 2000).

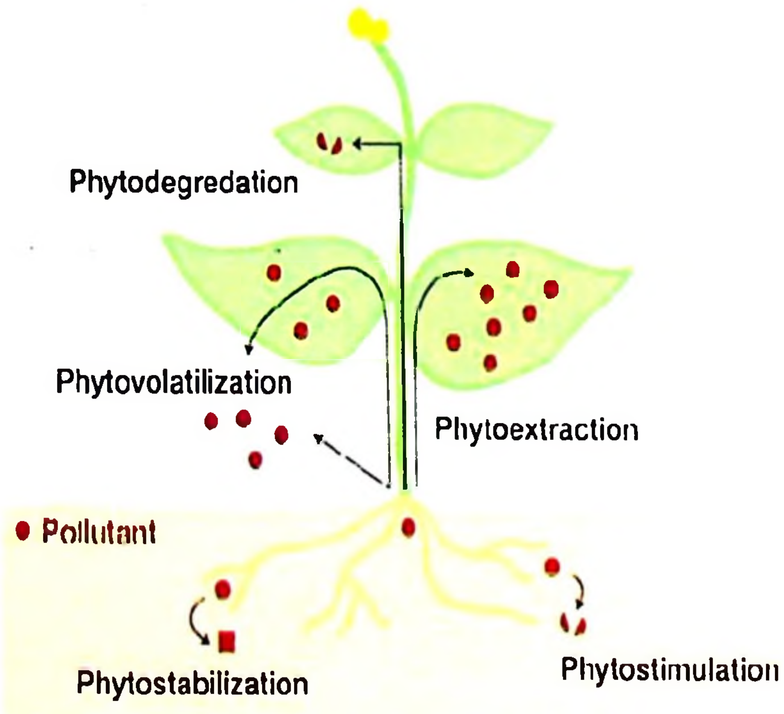


Figure 4.1: Phytoremediation through the use of plants

4.1.2.1. Phytodegradation or phytotransformation

This is the breakdown (degradation) of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants surrounding the plant through the effect of enzymes produced by the plants (Sursala *et al.*, 2002). Phytodegradation has been observed to remediate some organic contaminants, such as chlorinated solvents, herbicides, and it can address contaminants in soil, sediment, or water (EPA, 2000).

4.1.2.2. Rhizodegradation or phytostimulation

This refers to the breakdown of contaminants within the plant root zone, or rhizosphere through microbial activity. Microorganisms (yeast, fungi, and bacteria) are enhanced in the rhizosphere because the plant roots release natural substances like sugars, alcohols, acids, enzymes, and other compounds that contain organic carbon that is used as source of energy and food for microorganisms (Chang *et al.*, 2005). The roots also provide additional surface area for microbial growth and aeration. The rhizodegradation process has been investigated and found to be successful in treating a wide variety of mostly organic chemicals, including petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), pesticides etc. (EPA, 2000).

4.1.2.3. Phytoextraction or phytoaccumulation

This is the uptake of contaminants by plant roots and the translocation/accumulation (phytoextraction) of contaminants from the soil into the plants biomass (shoots and leaves). This process occurs when the sequestered contaminants are not degraded in or emitted from the plant rapidly and completely, resulting in an accumulation within the plant tissue (Sursala *et al.*, 2002). The process involves the removal of contaminants (metals, radionuclides, and certain organic compounds) from the environment by direct uptake into the plant tissue.

4.1.2.4. Phytovolatilization

Phytovolatilization is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant through contaminant uptake, plant metabolism, and plant transpiration. Phytovolatilization has mainly been applied to groundwater, but it can be applied to soil, sediments, and sludge. Phytovolatilization may be applied to both organic and inorganic contaminants (USEPA, 2000).

4.1.2.5. Phytofiltration of Rhizofiltration

Is used to remediate surface water, wastewater or groundwater and is defined as the use of plants to absorb, adsorb, concentrate and precipitate contaminants from polluted waters by their roots. The most appropriate plant for a rhizofiltration system is one capable of rapid growth, high root biomass, and has the ability to remove contaminants from the water in relatively high concentrations (Tome *et al.*, 2008).

The most important factor in successful implementation of phytoremediation is the selection of appropriate plant which should have high uptake of both organic and inorganic pollutants, grow well in polluted environments and easily controlled (Roongtanakiat *et al.*, 2007; Stefani *et al.*, 2011). Careful selection of plant and plant variety is critical, first, to ensure that the plant is appropriate for the climatic and soil conditions at the site, and second, for effectiveness of the phytoremediation of the pollutant at hand (Mwegoha, 2008). Research experiences have demonstrated the feasibility of different macrophytes species for the removal of chemical pollutants from different types of wastewater. Amongst them include cattail (*Typha sp*) and common reed (*Phragmites sp*); vetiver grass (*Vetiveria zizanioides*) (Bwire *et al.*, 2011; Nyomora *et al.*, 2012); water hyacinth (*Eichhornia crassipes*), rye grass (*Lolium multiflorium*), Duckweed (*water Lemna*) etc. However, majority of the documented work available on literature has been carried out in developed countries under temperate climatic conditions and their performance may differ in tropical conditions in Africa due to climatic factors. The potential for phytoremediation technology in the tropic environment is high due to the prevailing climatic conditions which favours plant growth and stimulates microbial activity (Zhang *et al.*, 2010).

Information on the capability of phytoremediation of agrochemicals removal is limited (Kovacic *et al.*, 2006). Tanzania lacks information on potential local plant species that may be used for phytoremediation (Mwegoha, 2008). Further studies in tropical countries like Tanzania, will add more information about the phytoremediation effectiveness of the locally available species. The objective of the study was to investigate the influence of different types of macrophytes towards agrochemical removal. The knowledge about the potential macrophyte plants towards agrochemical removal will provide insight into choosing appropriate macrophytes which may be suitable in wetland phytoremediation processes in agricultural environment.

4.2. Materials and Methods

4.2.1. Site of the study

The research study was conducted between October 2013 and March 2014 in a ventilated greenhouse located at the premises of Nelson Mandela African Institution of Science and

Technology (NM-AIST) in Arusha, Tanzania. The site is at an altitude of 1204 m above sea level and at a geographical location of coordinates S 03° 23. 945′and E 036° 47.671′. The dominant climate is tropical –savannah type of climate with clearly rainy and dry seasons.

4.2.2. Preparation of wastewater

Analytical grade heavy metal salts of copper sulphate ($CuSO_4.5H_2O$), zinc sulphate ($ZnSO_4.7H_2O$), manganese sulphate ($MnSO_4.4H_2O$), iron sulphate ($FeSO_4.7H_2O$) and formulated pesticides endosulfan, lambda cyhalothrin (L.cyhalothrin) and permethrin were used to prepare the artificial wastewater by diluting with tap water to a final concentration of 5 ppm. These initial concentrations were to simulate typical concentrations reported in runoff from horticultural farms and were also at concentration levels capable of being detected by analytical instruments.

4.2.3. Experimental setup and operation

The experimental system was bucket experiments and consisted of 15 plastic buckets and a 500 L bulk tank for wastewater storage. The plastic bucket reactors had a capacity of 100 litres and were filled with gravel of porosity of 0.3, giving a total working volume of 30 L. Healthy young seedlings of *Cyperus papyrus*, *Typha latifolia*, *Phragmites mauritianus* and *Cyperus alternifolius* that had similar biomass were collected from natural wetlands in Arusha and were planted into 12 buckets while 3 unplanted buckets were set as controls (Plate 1). The experiment was conducted in triplicates. These macrophytes were selected on the basis of local availability and they also grow well in tropic regions. The macrophytes were watered on daily basis with tap water and occasionally enriched with Hoagland solution as source of nutrients. The acclimatization period observed was 3 months during which the plants appeared green, healthy and with new grown shoots (Plate 2). Prior to the start of the experiment, sewage with water addition (1:1) and glucose 22.5 ppm was applied to the system for seven days to establish bacterial inoculation and generation of biofilms on the surface of the gravel. Thereafter, artificial wastewater from the 500 L storage tank was fed into the system at the start of the batch experiment. During the whole experimental period, the water volume was kept constant by adding tap water to compensate for water lost through evapotranspiration (Soltan and Rashed, 2003).

Plate 1: Buckets planted with macrophytes in October 2013

Plate 2: Buckets with the established macrophyte in January 2014

4.2.4. Sampling and measurement

4.2.4.1. Heavy metal based agrochemicals

Sampling was done as per standard methods specified in (APHA, 1998). The waste water was collected by using a 250 mls. polyethylene sampling bottles at 09hrs on every sampling day.

The sampling was done at initial start-up (day 0), day 1, day 4, day 8, day 12 and finally day 16. All samples were filtered using 0.45 μm filters (Whatman filter papers) and preserved by acidifying with analytical grade HNO_3 to pH < 2 and kept at 4 °C. The concentrations of heavy metal based agrochemicals in the waste water samples were analysed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (manufactured by Horiba Jobin Yvon, France) with detection limits of 0.01 ppm for Cu, Zn, Mn and Fe respectively.

4.2.4.2. Pesticide agrochemicals

Effluent water samples were collected using standard methods as described by Akerblom (1995). Effluent water was sampled before the start of the experiment (day 0), day 1 and every four days at about 09hrs on every sampling day. Upon reaching the laboratory, the samples were immediately extracted by liquid-liquid extraction (LLE) method (Siegel and Lee, 2004). The 1-L unfiltered water sample was quantitatively transferred in a 2-L separating funnel and the sampling bottle rinsed with 60 ml hexane: acetone 1:1. The rinsate was then mixed with the sample in the separating funnel. The combined contents were extracted successively with hexane: acetone 1:1 (3x60 ml). The organic phase was filtered through a plug of glass wool containing anhydrous sodium sulphate (ca. 20 g) for drying and drawn into an Erlenmeyer flask. The aqueous layer was repeatedly extracted with a mixture of hexane: acetone (1:1 v/v, 60 ml) as above. After the extraction procedure, the volume of the extract was concentrated to 2 mls using a rotary evaporator at 40 °C and the final volume adjusted by evaporating under gentle stream of nitrogen gas to 1 ml. The water extracts appeared clean and were not subjected to further clean up, and hence was stored at -5 °C freezer ready for GC/MS analysis. Analysis of pesticides was done using gas chromatography (Agilent Technologies, 7890A GC System with auto sampler 7683B series injector) coupled with mass spectrometer (Agilent Technologies, 5975C inert XL EI/CIMSD with Triple-Axis Detector). The GC/MS analysis parameters and operating conditions were as follows: Helium was used as a carrier gas at a flow rate of 1.2 mls/min; the oven temperature programme was 50 °C held for 1 min at a rate of 10 °C /min to 160 °C then held for 5 minutes and finally by 3 °C /min to 300 °C and held for 18.5 min. The temperature of the injection port was 250 °C. The MS detector temperature was 250 °C (transfer line temperature) and 230 °C (ion source). Pesticide residues were identified and quantified by comparing their retention times and peak area with respect to external reference standards.

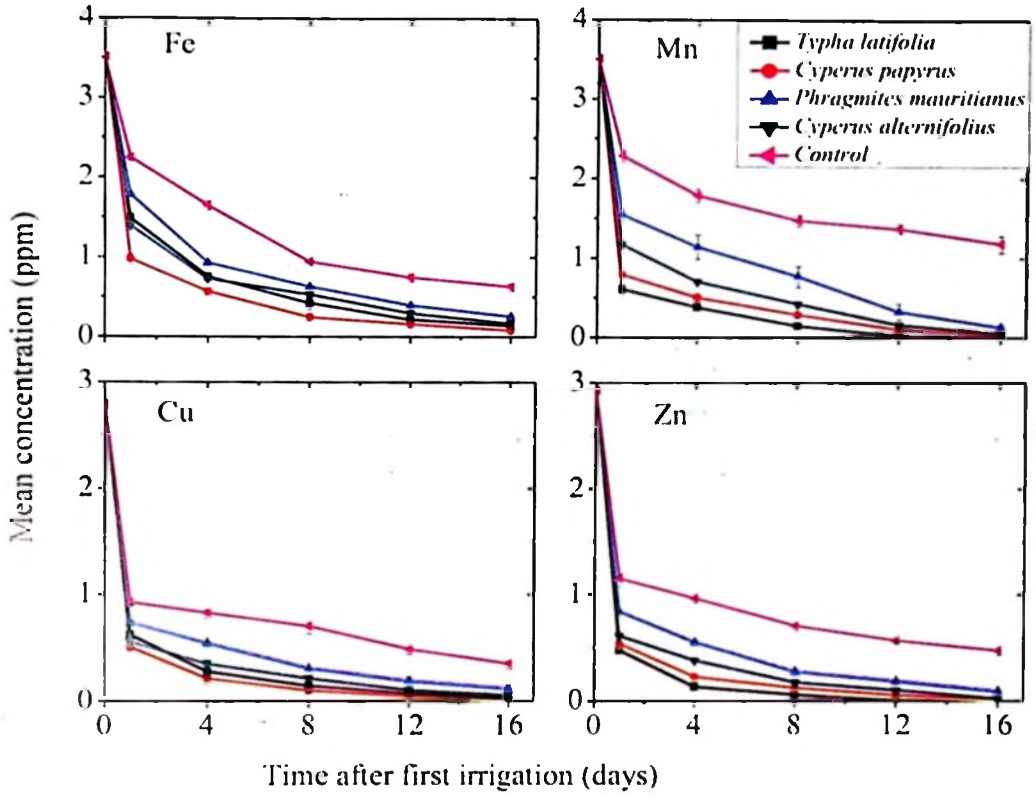
4.2.5. Statistical Analysis

Descriptive statistics (mean and standard deviation) of the results was determined using Origin 8.0 software (Origin Lab Corporation, Northampton, MA, USA). The data obtained were analysed using SPSS 16.0 for windows package (SPSS, Inc., Chicago, IL, USA). The data was subjected to a one-way analysis of variance (ANOVA) to test the overall variations and differences in mean concentrations of agrochemicals in wastewater in the batch reactor systems. Furthermore, post hoc Tukey test was used to assess the significant differences between the planted batch treatment groups relative to control. Differences at $P<0.05$ were considered statistically significant.

4.3. Results and Discussion

4.3.1. Influence of macrophyte types in heavy metal removal

The performance of the different types of macrophytes towards removal of metals from wastewater is shown in Fig. 4.2. The data analysis revealed significant differences ($P < 0.05$) in the removal of heavy metals between the planted batches as compared to the control. Fig. 4.2 shows that the concentration of heavy metals decreased with time, however a rapid drop in concentration levels was observed during day 1. This could be a result of dilution in the batch reactor system because it is not completely dry at start of the experiment. Similarly, this might be associated to the different multiple mechanisms taking place in the batch reactors such as adsorption, precipitation, co-precipitation, complexation and ion exchange (Matagi, 1998) before attaining equilibrium.



Footnote: Fe = Iron, Mn = Manganese, Cu = Copper, Zn = Zinc

Figure 4.2: Variation of heavy metal removal in wastewater in planted treatments and control.

4.3.1.1. Influence of macrophyte types in Iron (Fe) removal

According to Fig. 4.2, the results showed that macrophytes are capable in removing Fe from the wastewater. After 16 days retention in the wastewater, there was a significant difference ($P<0.05$) in mean concentration of Fe in the planted systems relative to control. Among the various types of macrophytes, the highest removal capability was observed in buckets planted with *Cyperus papyrus* and *Typha latifolia*, and then followed with *Cyperus alternifolius* and *Phragmites mauritianus* where the initial concentration of iron (3.515 ppm) dropped to 0.077(±0.021) ppm, 0.142(±0.015) ppm, 0.170(±0.042) ppm and 0.252 (±0.026) ppm respectively. This observation revealed that macrophytes have different capabilities influencing the magnitude of Fe removal from wastewater. According to Jayaweera, 2008; Maine, 2009 and Khan *et al.*, 2009, have highlighted that the mechanisms involved in Fe removal from wastewater are rhizofiltration and chemical processes such as precipitation. Similarly, macrophytes can play an important role in metal removal through adsorption and uptake by plants (Kadlec and Wallace, 2008). However, in the control systems, the decrease in the mean levels of iron to 0.624(±0.048) ppm can be related to other non phyto mechanisms for heavy metal removal such as adsorption to substrates (e.g. gravel, particulates and soluble organics), by cation exchange and chelation, and precipitation as insoluble salts as explained by Kadlec and Knight (1996).

4.3.1.2. Influence of macrophyte types in Manganese (Mn) removal

As shown in Fig. 4.2, the mean concentration levels of manganese decreased during the 16 days retention time. There was a significant ($P<0.05$) decrease in the mean concentration of manganese in the wastewater for the buckets planted with macrophytes relative to control. The levels of manganese concentration decreased from 3.508 ppm to 0.001(±0.001) ppm, 0.017(±0.006) ppm, 0.045(±0.012) ppm, and 0.127(±0.033) ppm, for the planted systems with *Typha latifolia*, *Cyperus papyrus*, *Cyperus alternifolius* and *Phragmites mauritianus* respectively. The highest removal capability was influenced by *Typha latifolia* and *Cyperus papyrus* causing a reduction of manganese in wastewater to almost completion. The control group also showed a decrease in levels of manganese concentration to 1.177(±0.104) ppm over the 16 day retention time. This decrease in the control group could be attributed to mechanisms such as adsorption to substrate, chemical precipitation and microbial interactions as explained by (Kadlec and Wallace, 2008). Generally, the overall results indicated that aquatic macrophytes were effective in phytoremediation of manganese. According to Italiya *et al.* (2013), plants possess mechanisms which are able to stimulate metal bioavailability in the rhizosphere and enhance adsorption and uptake into their roots.

4.3.1.3. Influence of macrophyte types in Zinc (Zn) removal

As shown in Fig. 4.2, the mean concentration levels of zinc decreased during the 16 days retention time. There was significant difference ($P<0.05$) in the mean concentration levels of zinc between planted and control system. In the buckets planted with macrophytes, the concentration levels of zinc reduced from initial concentration of 2.921 ppm to 0.001(±0.001) ppm, 0.001(±0.001) ppm, 0.091(±0.007) ppm and 0.025(±0.022) ppm in the buckets with *Typha latifolia*, *Cyperus papyrus*, *Phragmites mauritianus* and *Cyperus alternifolius* respectively. The greater removal occurred in the buckets planted with *Typha latifolia* and *Cyperus papyrus*, where the levels of zinc almost reached to completion on day 16 retention time. The control system also showed a reduction in the mean concentration of zinc to 0.459

(±0.019) ppm. This reduction in control system can be due to mechanisms such as adsorption onto particulates and settlement. Similar studies indicated that more than 50 % of the heavy metals can be easily adsorbed onto particulate matter in the wetland and thus be removed from the water column by sedimentation (Sheoran and Sheoran, 2006).

4.3.1.4. Influence of macrophyte types in copper (Cu) removal.

The results shown on Fig. 4.2 indicate that the mean concentrations of copper in wastewater decreased with time. A sharp decrease in concentration was observed during day 1 exposure perhaps owing to the multi mechanisms for heavy metal removal in the bucket experiments. As far as heavy metals are concerned, generally for the batch reactor systems, most removal takes place during the initial stages, and the rate slows after wards. This phenomenon has been observed by other authors (Lim *et al.*, 2008; Aisien *et al.*, 2010). As shown in the figure, the buckets planted with macrophytes significantly affected the reduction in copper concentration ($P<0.05$) as compared to control. On the other hand, *Cyperus papyrus* and *Typha latifolia* achieved the greatest reduction in mean levels of copper from initial concentration of 2.778 ppm to 0.001(±0.001) ppm and 0.023(±0.013) ppm respectively, followed by *Cyperus alternifolius* 0.055(±0.022) ppm and *Phragmites mauritianus* 0.0116(±0.035) ppm. The mean levels of copper observed in the control were 0.338± (0.033) ppm. The significant reduction in levels of copper in the planted systems with the macrophytes relative to control may be influenced by plant uptake and filtration effect of the roots system. Statements that of (Kadlec and Wallace, 2009; Carvalho *et al.*, 2012) may confirm that macrophytes can contribute directly through uptake, sedimentation, adsorption and other mechanisms in the rhizosphere.

4.3.2. Influence of macrophyte types in pesticide removal

According to Fig. 4.3, the data obtained during the study revealed that all the buckets planted with macrophytes caused a reduction in the mean concentration of the pesticide levels from the wastewater during the 12 days experimental period. However, it appeared that there was no statistical significant difference between the planted treatments relative to control group at $\alpha = 0.05$ level. The variation of pesticide removal in wastewater in the planted systems and control is shown in Fig. 4.3.

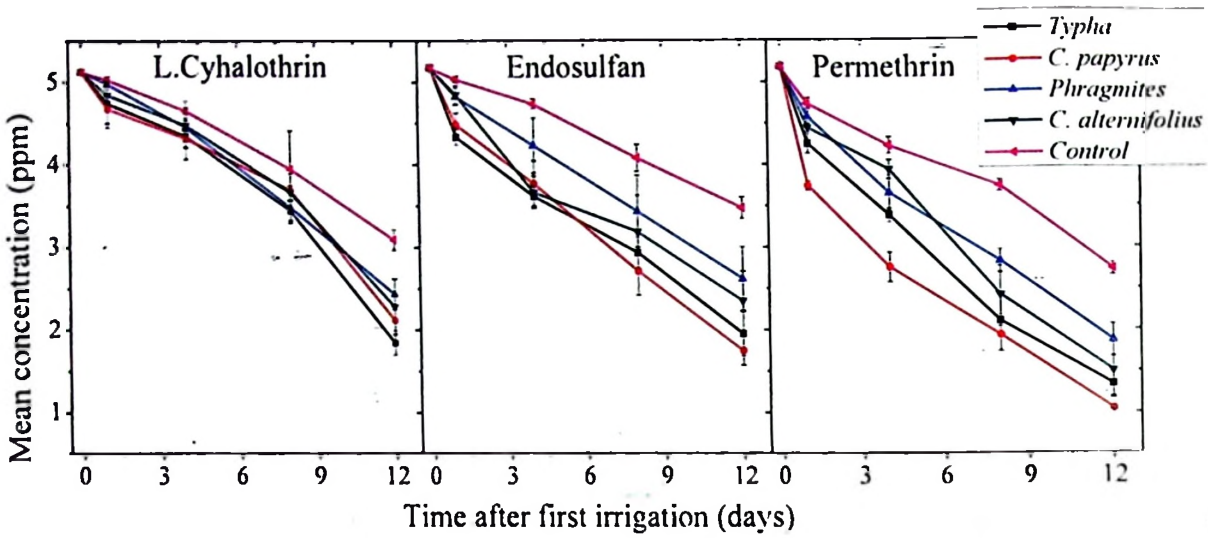


Figure 4.3: Variation of pesticide removal in wastewater in planted treatments and control

4.3.2.1. L. Cyhalothrin removal

The variation of pesticide removal in wastewater in the buckets planted with macrophytes (treatments) and control is shown in Fig. 4.3. Statistical analysis showed that there were no observed significant differences (P>0.05) in L. Cyhalothrin removal between planted and control. However, the study has observed that over the 12 days experimental period, *Typha latifolia* showed the greatest reduction of L. Cyhalothrin in wastewater from initial concentration of 5.132 to 1.184(±0.147) ppm, followed by *Cyperus papyrus*, *Cyperus alternifolius* and *Phragrmites mauritianus* with mean concentrations of 2.116(± 0.290) ppm, 2.285(± 0.186) ppm and 2.437(±0.186) ppm respectively. Meanwhile, the mean concentration of wastewater in the control group was 3.093(±0.126) ppm. These results demonstrate that the planted systems had a better removal of L. Cyhalothrin in wastewater as compared to the control. Macrophytes can increase pollutant removal including pesticides either directly through uptake or indirectly through enhanced rhizosphere degradation (Moore *et al.*, 2006). Though, the reduction in the control group could be explained by the lipophilic nature of the pesticide. The pesticide L. Cyhalothrin is a pyrethroid insecticide and their molecules rapidly dissipate from the water column and are strongly adsorbed to particulates and other aquatic organisms. Li-Ming *et al.* (2008) observed that L. Cyhalothrin residues in water decrease rapidly if suspended and/or aquatic organisms (algae, macrophytes or aquatic animals) are present. The better performance in planted systems is influenced by the macrophytes which serve as sites for adsorption, absorption and degradation of the pesticide.

4.3.2.2. Endosulfan removal

The difference observed in the removal trends (Fig. 4.3) was found to be not statistically significant at α = 0.05 level between the planted systems. Likewise, there was no statistical significant difference between the planted and the control. However, the analysis of wastewater measured daily for 12 days in the bucket experiments showed that the initial concentration of endosulfan (5.180 ppm) decreased with time (Fig. 4.3). Among the planted systems, *Cyperus papyrus* and *Typha latifolia* showed highest reduction of endosulfan in wastewater to mean levels of 1.742(±0.171) ppm and 1.954(±0.265) ppm respectively, followed by *Cyperus alternifolius* and *Phragmites mauritianus* where the mean concentration levels dropped to 2.349(±0.383) ppm and 2.349(±0.358) ppm respectively. Meanwhile, the mean concentration of endosulfan in wastewater reduced to 3.475(±0.131) ppm in the control group. The results demonstrated that slightly better endosulfan removal was affected by the planted systems as compared to control. The results were indicative that macrophytes may influence the removal of endosulfan through several phytoremediation mechanisms such as plant uptake, phytodegradation, and sorption through the root system (rhizosphere). Pesticides that are sorbed are more likely to remain in the root zone where they may be available for plant uptake and microbial or chemical degradation (Kerle *et al.*, 2007). However, the decrease in the control group may be influenced through sorption and bioremediation mechanisms due to the presence of biofilm, gravel and organic matter in the reactor system (Braeckevelt *et al.*, 2007).

4.3.2.3. Permethrin removal

There was no observed statistical significant differences in permethrin removal between the planted systems at α = 0.05 level during the 12 day operation of the system (Fig. 4.3). Likewise, no statistical significant difference was noted between the planted and the unplanted. However, the analytical results of the levels of permethrin in the wastewater decreased with time. Among the planted systems, *Cyperus papyrus*, *Typha latifolia* and *Cyperus alternifolius* had a higher removal ability of permethrin from initial concentration of 5.187 ppm to 1.037(±0.005) ppm, 1.338(±0.151) ppm and 1.500(±0.330) ppm respectively, followed by *Phragmites mauritianus* where the mean concentration levels dropped to 1.865 (±0.196) ppm. The least removal ability was observed in the control group with a reduction of permethrin to mean concentration of 2.728(±0.076) ppm. The decrease in pesticide concentration in the control group can be explained by adsorption to substrates such as gravel and other particulates in the reactor. However, it appeared that the macrophytes in the planted systems have shown a higher removal capability towards permethrin in the wastewater. This phenomenon may be influenced by several mechanisms such as phytodegradation, rhizofiltration, or uptake by plants as explained by Brix, (1994); Kadlec *et al.*, (2000); and USEPA, (2000).

4.3.3. Kinetics of agrochemical removal

The change in mean concentrations of the selected agrochemicals in the bucket experiments was described by first-order reaction kinetics and mathematically expressed as:-

$$r = -kC$$

$$\frac{dC}{dt} = -k\,C$$

$$\frac{dC}{C} = -k\,dt$$

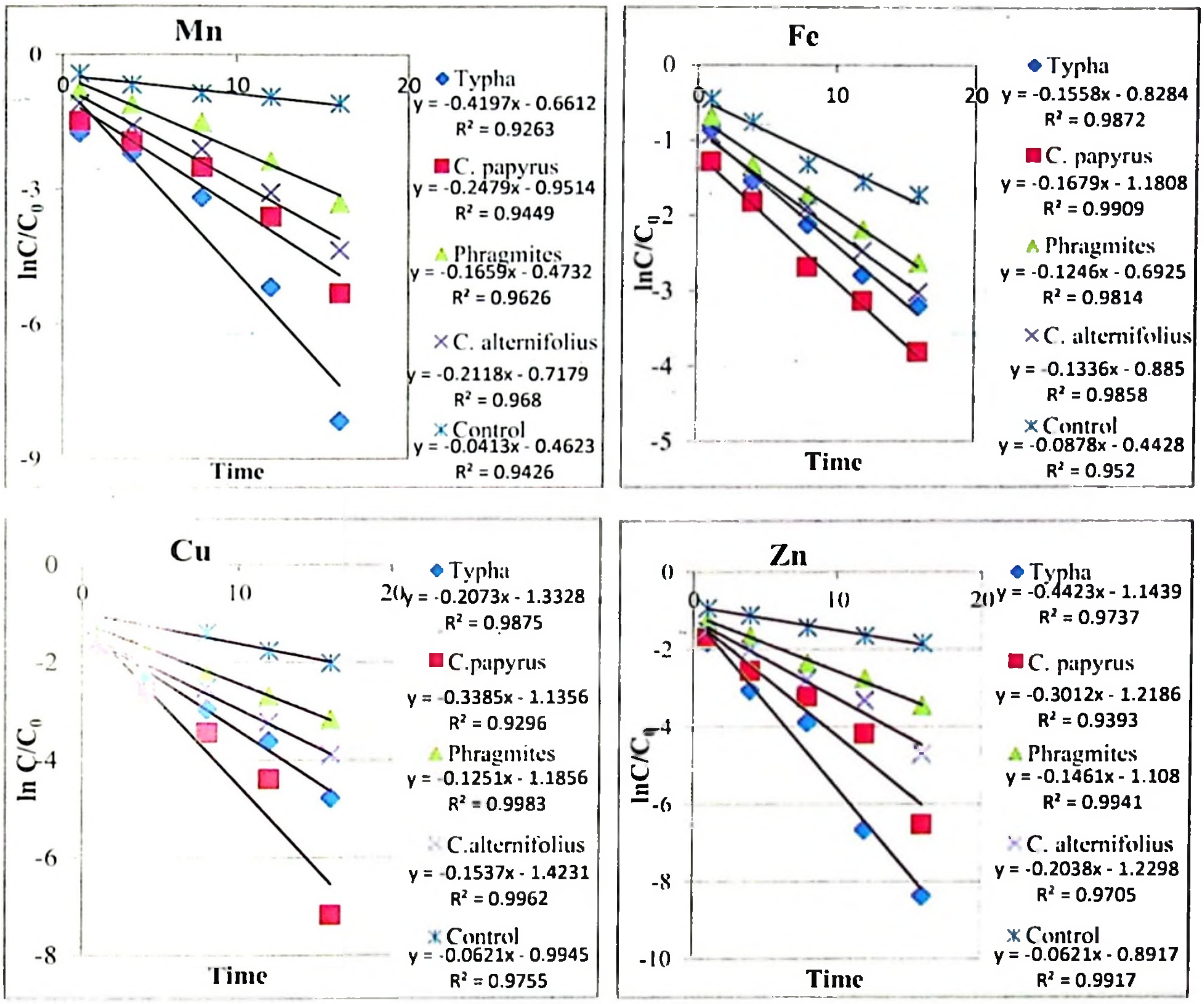
$$\int_{C_0}^{C} \frac{dC}{C} = -k \int_{t0}^{t} dt$$

$$\ln\frac{C}{C_0} = -kt \quad \text{---} \quad \text{(Eq. 1)}$$

Where C was the concentration of the respective agrochemicals (mg/l) at time t (d), C_0 being the initial concentration (mg/l) and *k*, the first–order rate constant (t^{-1}). A graph of ln C/C_0 versus time was produced and the slope *k* determined. The value of *k* was used to determine the removal of the agrochemicals with respect to the bucket experiments. A higher removal rate constant implied a reduction of the concentration levels of the respective agrochemicals.

4.3.3.1. Kinetics of heavy metal removal

When ln C/C_0 was plotted against t, linear relationships were obtained and the rate constants *k* was obtained as the -slope of the line. All samples observed a linear fit with $R^2 \geq 0.9$ (Fig. 4.4). The results obtained have shown that the magnitude of *k* values was greater for the planted systems than for the control. Furthermore, the rate of removal varied between the planted systems for the different types of heavy metals. Among the planted systems, *Cyperus papyrus* had a greater removal Cu and Fe with the *k* values of 0.3385 d^{-1} and 0.1679 d^{-1} respectively and *Typha latifolia* had a greater removal of Mn and Zinc with *k* values 0.4197 d^{-1} and 0.4423 d^{-1} respectively. The findings have also revealed that macrophytes differ in their affinity towards different types of heavy metals. Similarly, the rate of removal of heavy metals were much higher that the pesticides.



Footnote: Fe = Iron, Mn = Manganese, Cu = Copper, Zn = Zinc

Figure 4.4: Determination of first-order kinetic constant (*k*) for heavy metal removal

4.3.3.2. Kinetics of pesticide removal

The results for the kinetic parameters for the pesticides (Fig. 4.5) indicated that all samples observed a linear fit with $R^2 \geq 0.9$. The amount of *k* values was greater for the planted batch treatments than for the control. Furthermore, the rate of removal varied between the planted systems for the different types of pesticides. Among the planted systems, *Cyperus papyrus* showed the highest *k* value for both endosulfan and permethrin removal with *k* values of 0.086 d^{-1} and 0.114 d^{-1} respectively. Likewise *Typha latifolia* had the highest *k* value of 0.116 d^{-1} for the removal of L-Cyhalothrin.

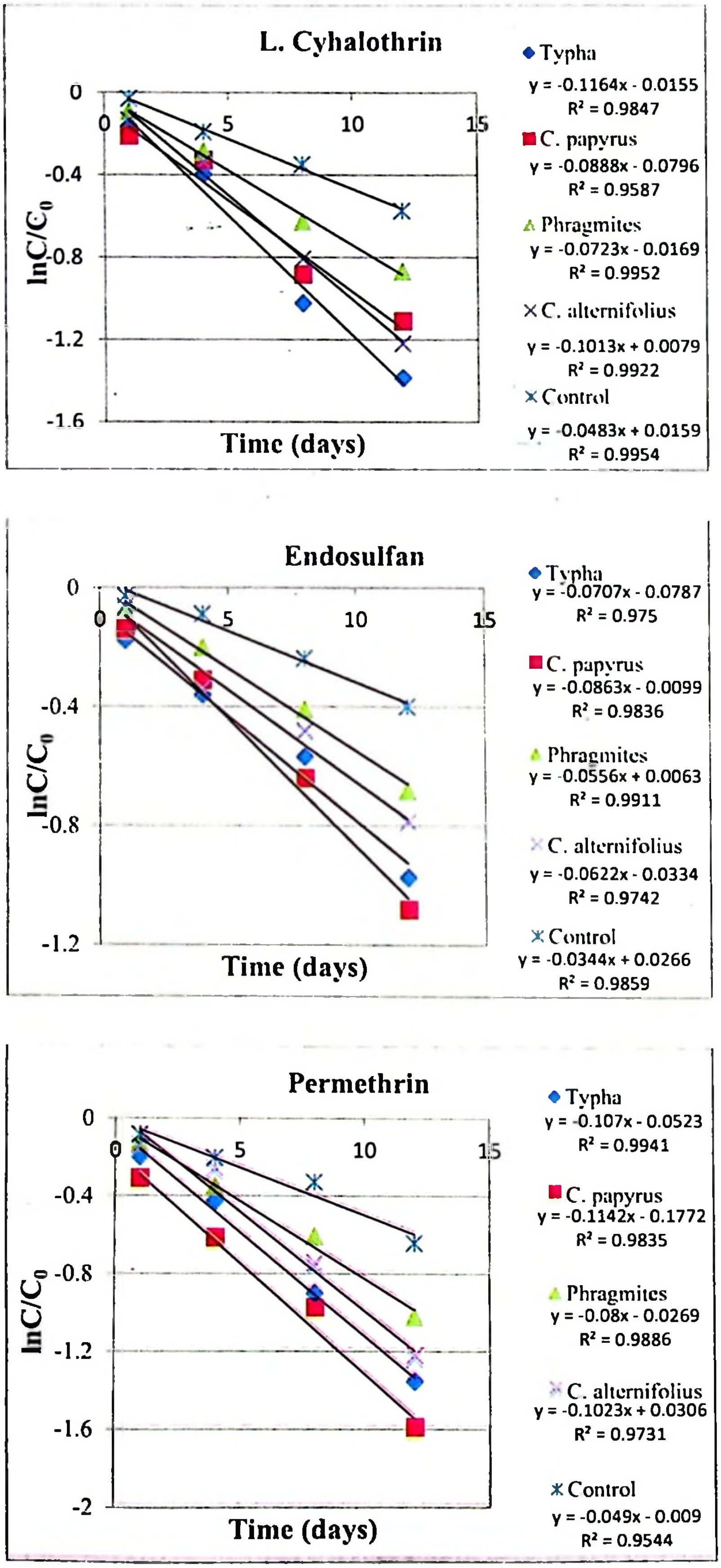


Figure 4.5: Determination of first-order kinetic constant (k) for pesticide removal

4.4. Conclusion and Recommendations

Water pollution by agrochemicals from agricultural runoff is a serious environmental problem in many parts of the world including Tanzania. Agrochemicals cannot be degraded easily and thus require a preventative approach for a successful outcome. In this study, the influence of four aquatic macrophytes *Cyperus papyrus*, *Typha latifolia*, *Cyperus alternifolius* and *Phragmites mauritianus* towards agrochemical phytoremediation in wastewater were investigated. The results revealed that planted systems work better than unplanted systems in the removal of agrochemical residues from wastewater. These results prove their suitability for use in phytoremediation of agrochemicals. Furthermore, the study has demonstrated that plant type has influence on the removal of agrochemicals where in this study, *Cyperus papyrus* and *Typha latifolia* showed higher removal capability for most agrochemicals, followed by *Cyperus alternifolius* and *Phragmites mauritianus*. The findings have also shown that the rate of removal of heavy metals were much higher than the pesticides. Therefore, in designing wastewater treatment systems for agricultural and industrial lands, removal of pesticide should be used to size the systems. It is recommended that the experiments conducted in this research could be up-scaled to include treatment of actual wastewater from agricultural industries to establish their long term characteristics under various environmental conditions like organic loading and velocity.

CHAPTER FIVE

Influence of Flow Rate in Horizontal Subsurface Flow Constructed Wetlands on the Removal of Heavy Metal-based Agrochemicals from Wastewater

ABSTRACT

Four horizontal subsurface flow constructed wetlands (HSSFCWs), were established to evaluate the influence of flow rate on the removal of simulated wastewater contaminated with Cu, Zn and Mn. These heavy metals are among the constituents in commercial fertilizers, herbicides and pesticides used in horticulture. In this work, two HSSFCWs cells were planted with *Typha latifolia* and two wetland cells were left unplanted as control. The capacity of the HSSFCW cells to treat wastewater was 210 L each. The HSSFCWs were operated at four flow rate settings of 1.5 L/min, 3.0 L/min, 4.5 L/min and 6.0 L/min. Each flow rate was allowed to run for five days before switching to another flow rate. It was observed that the planted and control wetlands removed 96.1% and 93 % of Cu; 98.7% and 96.3% of Zn; and 97.3% and 94.8% of Mn respectively. When the planted wetlands were compared to the control it was observed that the planted systems performed better than the control and the difference was statistically significant at 95% confidence level ($P<0.05$). However, we also found out that the removal of heavy metals does not depend on flow rate (differences were statistically insignificant i.e. $P>0.05$). The conclusions drawn from these observations are that the removal of heavy metals in HSSFCWs is independent of flow rate and the planted wetlands perform better in terms of Cu, Zn and Mn removal compared to unplanted.

5.1. Introduction

A heavy metal is a generic term that refers to any element with a density greater than 5 g/cm^3 and usually indicates metals and metalloids associated with pollution and toxicity (Ramola and Singh, 2013). However, they also include elements those which are required at low concentrations such as Cu, Zn, Fe, Co, Mn, Se, Mo, B and Ni (Adriano, 2001) for plant growth and for animal and human health. Heavy metals are stable in the environment and therefore tend to accumulate in environmental matrices such as water, soil and sediments to levels that can cause toxicity to the environment and human health (Dipu *et al.*, 2011). Recent studies done in Tanzania have detected high levels of heavy metal contaminants in agricultural sediments and water (Kihampa, 2013), soil (Lema *et al.*, 2014; Mwegoha and Kihampa, 2010) and in vegetables (Mohammed and Khamis, 2012). Since heavy metal contamination in the environment threatens the quality of agricultural food crops, water and human health (Lasat, 2002; Oversch *et al.*, 2007) we need to identify their sources and design sustainable remediation or control measures. The most important anthropogenic sources of heavy metals are solid and liquid wastes from municipal, agricultural, mining and industrial process activities (Adriano, 2001). While most of wastewaters can easily be channelled through sewerage systems to wastewater treatment facilities, the wastewaters from agricultural activities such as horticulture may usually not be well treated before their discharge into receiving water bodies.

5.1.1. Heavy metal-based agrochemicals in horticulture

The most important heavy metal agrochemicals in horticulture include Arsenic (As), Cadium (Cd), Copper (Cu), Zinc (Zn), Nickel (Ni), Molybdenum (Mo), Manganese (Mn), Mercury (Hg), Selenium (Se), Lead (Pb), Iron (Fe), Vanadium (V), etc. Inorganic fertilizers and pesticides are the most significant sources of these heavy metals (Adriano, 2001). Traces of some heavy metals are present in fertilizers in order to supply micronutrients to plants or they are the active ingredients in pesticides and fungicides used in horticulture. For instance Bordeaux mixture is a fungicide comprised of Copper sulphate ($CuSO_4$) and calcium hydroxide ($Ca(OH)_2$); Copper trihydroxyl chloride ($Cu_2(OH)_3Cl$) is an agricultural fungicide and bactericide; Lead arsenate ($PbHAsO_4$) is an insecticide and herbicide; Manganese sulphate ($MnSO_4$), Zinc sulphate (ZnSO4), Iron sulphate (FeSO4) , and Molybdenum are used as fertilizers to supply nutrients in plants (El Hadri *et al.*, 2012; Sherene, 2010; Mirlean *et al.*, 2006; Zarcinas *et al.*, 2004; Lu *et al.*, 1992). In addition, traces of heavy metals have been detected in industrial fertilizers (Rauf *et al.*, 2007), and also in phosphate fertilizers marketed in Nigeria (Benson *et al.*, 2014) and in 12 European countries (Nziguheba and Smolders, 2008).

5.1.2. Contamination by heavy metal-based agrochemicals

In terrestrial ecosystems, soils are the major recipients of heavy metal-based agrochemicals while in aquatic ecosystems, water and sediments are the major sinks for heavy metals. Recent research study done in Tanzania on the levels of heavy metal concentrations in soil from four sampled areas detected high levels of Cu, Zn, Cr, Ni, Hg, Pb and V, which were beyond acceptable limits in soil (Lema *et al.*, 2014). These high levels were correlated to extensive uses of fertilizers and pesticides in agricultural fields. Some of these heavy metals may eventually be leached directly into ground and or into the surface waters. Cases of surface and ground water pollution by heavy metals have also been linked to fertilizer use.

Begum *et al.* (2008) detected high levels of Zn and Pb in Cauvery River in India and extensive use of fertilizer was a key source. In Pakistan, the use of fertilizers, herbicides and pesticides are reported among the primary causes of ground water contamination by heavy metals Zn, Pb, Fe and Pb above permissible levels set by WHO (Ullah *et al.*, 2009).

Although these heavy metal-based agrochemicals are useful for the growth and productivity of horticulture crops, they may be toxic to different forms of life including humans when occurring in environment at concentrations above acceptable limits. Humans can be exposed by ingestion of contaminated drinking water or through the food chain. For example Mn is known to cause neurological effects following extended exposure to very high levels above 0.4 mg/l (WHO, 2008). In addition, drinking Cu-contaminated drinking water above 2 mg/l can cause gastrointestinal effects and Zn levels above 3 mg/l in drinking water are not acceptable to consumers (WHO, 2008).

Wastewaters from horticulture can intensify the heavy metal contamination of drinking water sources and hence pose a significant threat to health and survival of aquatic ecosystems and the public. However, in most developing countries there are very few conventional wastewater treatment plants designed to remove trace contaminants due to high capital investment, operational and maintenance costs (Newman and Reynolds, 2004). Nonetheless, natural and constructed wetlands are best and affordable options for treatment of municipal, industrial and agricultural wastewater in developing countries. Evidences have shown that constructed wetlands can significantly reduce contaminants in agricultural runoff (Dierberg *et al.*, 2002; Moore *et al.*, 2000). It is therefore imperative to design intervention measures for remediating and limiting the contaminants from untreated wastewaters from horticulture farms.

5.2. Wastewater treatment using constructed wetlands

Constructed wetlands (CWs) are designed and established to treat wastewater by mimicking the chemical, biological and physical processes that occur in natural wetlands (Kadlec and Knight, 1996). There are various types of CWs that exist and the two major categories are: Free Water Surface (FWS) wetlands and Subsurface Flow (SSF) wetlands (Kayombo *et al.*, 2001). The advantages and disadvantages of these types are well documented in the literature (Kayombo *et al.*, 2001). The SSF wetlands are categorized into the following subtypes according to the water current direction; Horizontal Subsurface Flow Constructed Wetlands

(HSSFCWs) or Vertical Subsurface Flow Constructed Wetlands (VSSFCWs). These systems have been reported to be effective at removing pollutants at high application rates (Shutes, 2001). For the purpose of this research, only HSSFCWs are considered (Fig. 5.1) which usually consist of gravel or rock beds and are planted with wetland vegetation. The wastewater is fed at the inlet and flows through a porous medium under the surface of the bed in a more or less horizontal path until it reaches the outlet zone where it is collected and discharged (Fig. 5.1) (Vymazal, 2010).

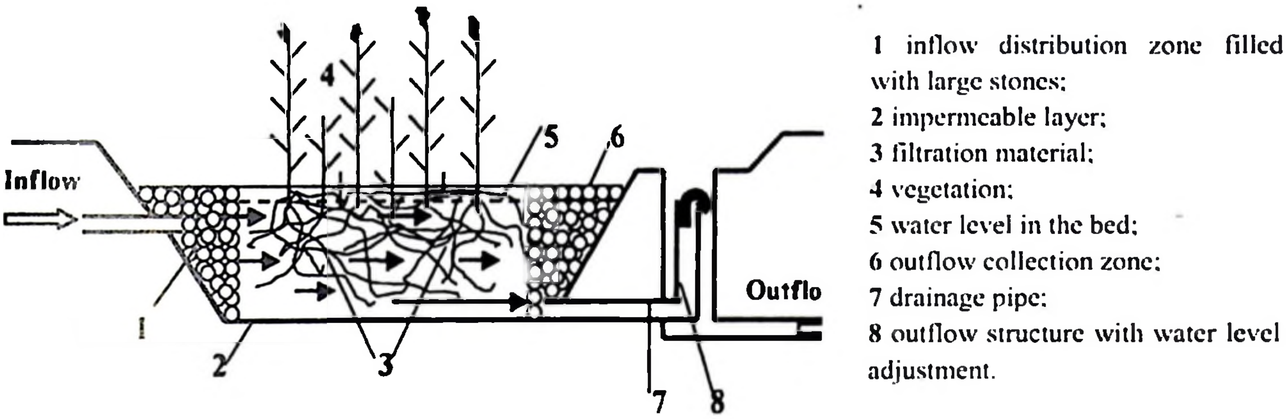


Figure 5.1: Schematic layout of a HSSFCW (Vymazal, 2010).

Horizontal subsurface flow constructed wetlands have been used successfully to treat domestic and municipal wastewaters but of recently, this technology has been used for the treatment of various types of wastewater such as agricultural runoff, land fill leachate, tannins and industrial wastewaters, and various runoff waters (Njau *et al.*, 2003; Kadlec and Knight, 1996; Kadlec and Wallace, 2008; Bwire *et al.*, 2011; Nyomora *et al.*, 2012; Zurita *et al.*, 2009; Njau and Renalda, 2010). In addition, HSSFCWs have been used to remove heavy metals from wastewater (Bwire *et al.*, 2011; Maine *et al.*, 2009; Khan *et al.*, 2009).

5.2.1. Processes of heavy metal removal in constructed wetlands (CWs)

In CWs, heavy metal removal processes are very complex and these processes involve a combination of physical processes (sedimentation), chemical processes (adsorption, precipitation, complexation, etc.) and biological processes (plant uptake and microbial activity) (Lesage, 2006; Matagi, 1998; Brix, 1994; Kadlec and Knight, 1996). These processes affect the mobilization and immobilization of heavy metals. These processes may occur in various compartments of the wetland (water, biota, substratum, suspended solids) and the rate depends on environmental conditions such as temperature, oxygen and pH (Matagi, 1998).

5.2.1.1. Plant uptake

Wetland plants can uptake essential metals such as Fe, Mn, Cu, Zn, Mo and Ni from water and soil in order to sustain their metabolism (Adriano, 2001). The ability of wetland plants to assist in heavy metal removal has been recently investigated and studies have shown that plants differ in their ability to sequester toxic elements (Lema *et al.*, 2014; Brankovic *et al.*, 2011). The cattails (*Typha latifolia*) and *Cyperus papyrus* are particularly effective in heavy metal removal from wastewater (Lema *et al.*, 2014; Sasmaz *et al.*, 2008). Nonetheless, heavy metal removal through uptake by plants in constructed wetlands plays a minor role compared to other processes (Lizama, 2012; Lesage *et al.*, 2007; Stottmeister, 2006).

5.2.1.2. Sedimentation

Sedimentation is the tendency of particles in suspension to settle out of the fluid in which they are entrained. This physical process plays an important role in the removal of heavy metals associated with particulate matter. The particles may settle out of the water column by gravity to the bottom of the wetland. In this way heavy metals are removed from wastewater and trapped in the wetland medium, thus protecting the ultimate receiving aquatic environment (Matagi, 1998).

5.2.1.3. Adsorption

Adsorption involves the binding of dissolved substances in solution to solid particles by cation exchange (Dhir, 2010). This occurs by electrostatic attraction when heavy metal cations are bound to the solid surfaces that contain a residual negative charge on its surface. In constructed wetlands, heavy metals are adsorbed in various wetland media containing clay colloids, organic matter, sulphides, carbonates, etc. About 50 % of heavy metals may easily be adsorbed onto particulates within the wetland and thus be removed from the water component by sedimentation (Matagi, 1998). On the other hand, researchers who investigated adsorption capacities of wetland media suggested that adsorption onto mature biofilm was responsible for high removal efficiencies of heavy metals (Garcia, 2010).

5.2.1.4. Precipitation

This is one of the major mechanisms by which heavy metals are removed from water in wetlands and deposited in sediments. In HSSFCWs, heavy metals may easily precipitate as sulphides and carbonates at neutral and basic pH (Gambrell, 1994). It has been reported that precipitation with sulphides is an important removal mechanism in HSSFCWs (Garcia, 2010). This is because HSSFCWs provide anoxic zones where sulphate reducing bacterial (SRB) convert sulphates to sulphides. Optimal conditions for SRB are a pH above 5.5 and an organic carbon source such as organic matter, glucose, alcohols (Garcia *et al.*, 2001). The organic carbon represented by CH_2O may combine with sulphate in the present of SRB to produce the sulphide ions and bicarbonate ions (Eq. 1). The alkalinity generated in the form of bicarbonate (HCO_3^-) will help to neutralize acidity and raise pH. The soluble sulphides produced during the reaction (Eq. 1) combines with divalent metals ions (Me^{2+}) to form insoluble metal sulphide precipitates (Eq. 2). On the other hand, the bicarbonate ions (HCO_3^-) produced either from (Eq. 1) of through dissolution of carbonates form wetland medium may combine with metal ions and precipitate them as metal carbonates ($MeCO_3$) in the HSSFCWs (Eq. 3). Although metal carbonates are less stable than metal sulphides but may influence the initial precipitation of metals (Sheoran and Sheoran, 2006).

$$2\ CH_2O\ (aq) + SO_4^{2-}\ (aq) \rightarrow H_2S\ (aq) + 2\ HCO_3^-\ (aq) \quad \text{------------------------------} \quad (1)$$

$$H_2S\ (aq) + Me^{2+}\ (aq) \rightarrow MeS\ (s) \downarrow + 2H^+\ (aq) \quad \text{--} \quad (2)$$

$$Me^{2+}\ (aq) + HCO_3^-\ (aq) \rightarrow MeCO_3\ (s) \downarrow + H^+\ (aq) \quad \text{--} \quad (3)$$

5.2.2. Transport processes within the wetland

In subsurface flow wetlands, many reactions are also microbial mediated which means they are the result of the microbial activity of bacteria, fungi, yeasts and algae (Matagi, 1998; Das and Karthika, 2008). These microorganisms form thick coatings of microbial communities (biofilms) onto the immersed solid surfaces in the wetlands. The microbial activity within the biofilms formed on surfaces of wetland media are responsible for processing of chemical pollutants (Kadlec and Wallace, 2009). Heavy metals can be removed directly from wetlands through metabolic uptake and to a great extent through bio-sorption process (Matagi, 1998). The bio-sorption process involves binding of the positively charge metal ions to the cell surfaces which contain negatively charged functional groups (Das and Karthika, 2008; Macek and Mackova, 2011) and diffusion through microbial cell walls and membrane (Matagi, 1998). The overall microbial removal mechanism is influenced by the transfer of the heavy metals from the water phase to the solid surfaces containing the biofilms responsible for microbial processing as well as the binding sites for sorption processes (Kadlec and Wallace, 2009). The dissolved materials in the wetlands are transported from the bulk of the water to the surrounding solid surface and then diffuse through stagnant water layer to the surface and penetrate the biofilm while undergoing chemical transformation (Fig. 5.2). According to Njau *et al.* (2011) the transfer of the chemical constituents from the bulk water to the surface of the biofilm is influenced by flow velocity of wastewater, where by higher velocities produce turbulences and better transfer.

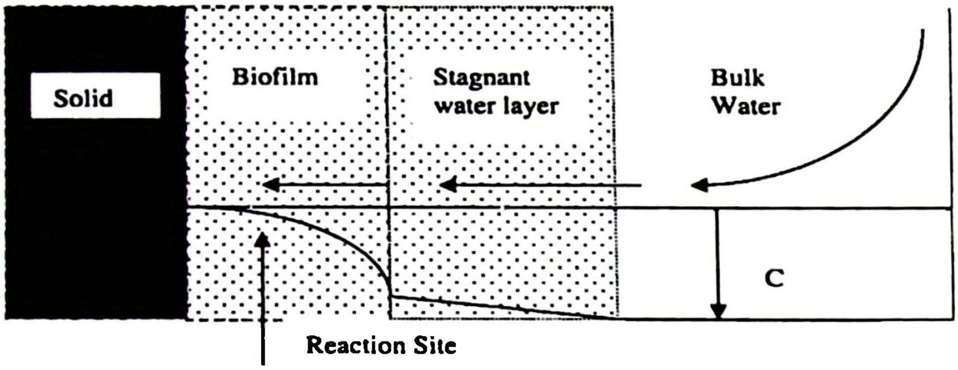


Figure 5.2: Pathway for the movement of a pollutant from the water across a diffusion layer into a reactive biofilm (Kadlec and Knight, 1996).

The control of flow velocity has been observed to improve removal of pollutants such as BOD, NO_3^-, NH_3, TKN and Faecal coliforms in HSSFCWs (Njau *et al.*, 2011; Lohay *et al.*, 2012). Apparently, studies have not been done to look at the influence of flow rate on heavy metal removal from wastewater in constructed wetlands. It is speculated that the higher flow rate would lead to better treatment due to enhanced transport processes within the boundary layer where dissolved substances have to pass to reach the reacting site within the biofilm. Therefore, the objective of this study was to ascertain whether or not flow rate has influence on the removal of heavy metals in wastewater.

5.3. Materials and Methods

5.3.1. Site of the study

The research study was conducted between January 2014 and July 2014 in a ventilated greenhouse located at the premises of Nelson Mandela African Institution of Science and

Technology (NM-AIST) in Arusha City, Tanzania. The site is at an altitude of 1204 m above sea level and is located at S 03° 23. 945′ and E 036° 47.671′. The dominant climate is tropical -savannah type of climate with two rainy seasons which starts from September to December for short rains and in Feb-June for long rains. The average annual temperatures are between 21 °C in the highlands and 24 °C at lower altitudes.

5.3.2. Preparation of wastewater

The wastewater was prepared in the laboratory with analytical grade heavy metal salts of copper sulphate ($CuSO_4.5H_2O$), zinc sulphate ($ZnSO_4.7H_2O$), and manganese sulphate ($MnSO_4.4H_2O$) which was followed by dilution with tap water to a final concentration of 10 ppm of the respective heavy metal-based agrochemicals. These initial concentrations were used to simulate typical concentrations of Zn, Cu and Mn reported in wastewater runoff from horticultural farms and the concentrations were above the limit of detection (LoD) of the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Horiba Jovin Yvon, France).

5.3.3. Experimental setup and macrophyte establishment

The experimental set up comprised of 4 identical HSSFCW cells enclosed in greenhouse. The wetlands cells were constructed of concrete and had dimensions of 150 cm length, 50 cm width and 100 cm height, and were filled with 12-20 mm gravel of 0.35 in porosity to a depth of 80 cm. Each of the wetland cells was connected to a feeding tank of 500 L. The wetland comprised of two planted cells and two unplanted cells (Plate 3). The planted cell had cattails (*Typha latifolia*) which were collected from natural wetlands in Arusha, while the unplanted cell was set as control. *Typha latifolia* was a macrophyte of choice in the study because of its local availability, rapid growth rate and high potential for phytoremediation of heavy metals (Lema *et al.*, 2014c). After the transplantation, the wetland cells were irrigated with water and Hoagland's solution as source of nutrients to establish the macrophytes. The acclimatization process was 3 months and at this time the macrophytes had healthy and new green shoots (Plate 4). Prior to the start of the experiment, 400 L of sewage-water mixture and 22.5 mg/l glucose was added to each wetland cell. The wetland cells were left to stand for seven days to allow ample time for the bacterial inoculants to establish and formation of biofilms on the surface of the gravel.

Plate 3: Macrophytes in HSSFCWs at the planting time in March 2014

Plate 4: Macrophytes fully established in HSSFCWs in June 2014

5.3.4. Operation procedure

The wetland cells were operated as semi-batch recycle system where the prepared wastewater with known concentrations of target agrochemicals was continuously recycled by using a pump between a 500 L reservoir tank and the respective wetland reactors for the whole treatment period. The schematic representation of the wetland cell is shown in Fig. 5.3. The wetland cells were operated at 4 different flow rates: 1.5 L/min, 3.0 L/min, 4.5 L/min and 6.0 L/min. The flow rates were set by using a rotameter mounted on the wetland cells and by regulating the respective valves. During each flow rate setting, sampling and monitoring of wastewater characteristic was done at the outlet of the feeding tank on daily basis for 5 consecutive days. At completion of each experimental run, the system was flushed with tap water several times and 400 L of fresh sewage-water mixture (1:1) and glucose 22.5 ppm were applied to the system for seven days to establish bacterial inoculants and generation of biofilms on the surface of the gravel. New wastewater was prepared and fed to the system between each flow rate change over.

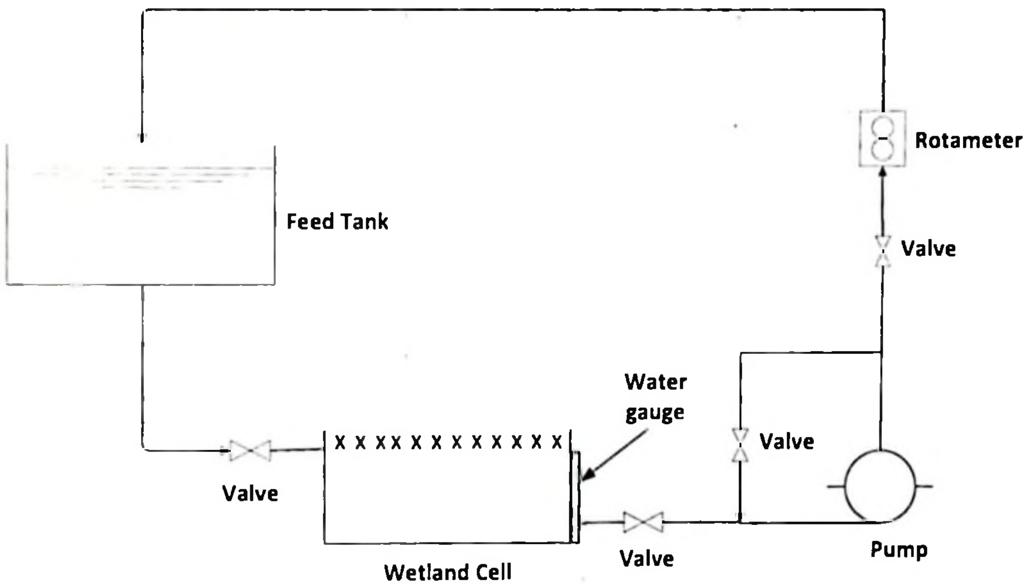


Figure 5.3: Semi-Batch Recycle System

5.3.5. Sampling and measurement

5.3.5.1. Physical chemical parameters

Field determinations of temperature, pH and dissolved oxygen (DO) were measured in-situ following standard methods (APHA, 1998). The measurements were done by using Eijkelkamp 18.52 SA Model PH/Mv/EC/T/Sa/TDS/DO multi-parameter from Eijkelkamp Agrisearch Equipment, The Netherlands.

5.3.5.2. Heavy metal-based agrochemicals

Samples of the simulated wastewater effluents were collected on daily basis at 10hrs from 11th June - 27th July, 2014 at the outlet of the respective CW cell's storage tank. Sampling was done on day 0 (start), day 1, day 2, day 3, day 4 and day 5. The samples were collected using unused polyethylene sampling bottles (250 ml). The bottles were previously washed thoroughly with detergent, followed by rinsing with tap water. Then they were soaked overnight in (10 %) HCl followed by rinsing with deionized distilled water prior to usage. During sampling, they were again rinsed three times with sample water. Soon after sampling, all the samples were filtered using 0.45 μm Whatman filter papers, carefully labelled and preserved by acidifying with analytical grade HNO_3 to pH < 2 and kept at 4 °C until analysis. The concentrations of Cu, Mn and Zn in the wastewater samples were analysed at the Southern and Eastern African Mineral Centre (SEAMIC), an ISO 9001-2000 certified lab. The analysis was done by using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Horiba Jobin Yvon, France) with detection limits of 0.01 mg/l, 0.01 mg/l and 0.01 mg/l for Cu, Mn and Zn respectively.

5.3.6. Data analysis

Descriptive statistics (mean and standard deviation) of all variables measured were calculated and graphs were plotted using Origin 8.0 software (Origin Lab Corporation, Northampton, MA, USA). The data obtained were analysed using SPSS 16.0 software for windows package (SPSS, Inc., Chicago, IL, USA). The significant differences in the mean concentrations were analyzed using one-way ANOVA followed by post hoc Tukey's tests (at $\alpha=0.05$ level). Mean differences between planted and control systems were assessed by Paired-Samples T-Test at a significance level at 95% confidence level. Where applicable, values are presented as the mean ± standard error.

The percentage removal of heavy metals was calculated according to Equation 4.

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100\ \% \qquad (4)$$

Where c_i and c_f are the initial and final concentrations of the respective heavy metals in (mg/l).

5.4. Results and Discussion

There were four variables measured in the simulated wastewater; temperature, dissolved oxygen (DO), hydrogen ion concentration (pH), and heavy metal-based agrochemicals (Cu, Mn and Zn). The results of temperature, DO, and pH in both the planted cells and control at different flow rate settings are summarized in Table 5.1. These results are further discussed in sections 5.3.1 to 5.3.3. The mean concentrations of Mn, Cu and Zn analysed in both planted and control wetland cells at various flow rates introduced in the HSSFCWs are presented in Fig. 5.8 and further discussed from sections 5.3.4 to 5.3.6.

Table 5.1: Descriptive statistics of physical chemical parameters in HSSFCWs over 5 day's experimental period at different flow rates

Flow rate	Location	Variable	Units	N	Mean	SE
1.5 L/min	Planted cell	Temp	°C	6	21.99	0.19
		DO	mg/l	6	3.60	0.20
		pH	-	6	8.05	0.06
	Control cell	Temp	°C	6	22.28	0.11
		DO	mg/l	6	2.98	0.18
		pH	-	6	7.84	0.02
6.0 L/min	Planted cell	Temp	°C	6	21.73	0.01
		DO	mg/l	6	5.02	0.27
		pH	-	6	8.27	0.03
	Control cell	Temp	°C	6	22.18	0.13
		DO	mg/l	6	4.81	0.21
		pH	-	6	8.11	0.11
3.0 L/min	Planted cell	Temp	°C	6	21.78	0.06
		DO	mg/l	6	3.90	0.27
		pH		6	7.78	0.06
	Control cell	Temp	°C	6	21.97	0.11
		DO	mg/l	6	3.51	0.43
		pH	-	6	7.62	0.06
4.5 L/min	Planted cell	Temp	°C	6	21.78	0.11
		DO	mg/l	6	4.83	0.12
		pH		6	8.00	0.01
	Control cell	Temp	°C	6	22.16	0.14
		DO	mg/l	6	4.40	0.18
		pH	-	6	7.88	0.01

5.4.1. Temperature

Temperature is an important abiotic factor in the functioning of a wetland because it has a strong influence on the bio-chemical processes in wetlands. Temperature varies diurnally and seasonally (Kayombo, 2001). The mean temperatures recorded ranged between 21.73 ± 0.01 °C and 21.99 ± 0.19 °C in the planted cells and 21.97 ± 0.11 °C and 22.28 ± 0.11 °C in the unplanted cells (Table 5.1). There was no significant difference observed in the mean temperatures between the planted and unplanted cells ($P>0.05$). However, the mean temperatures were lower in the planted cells than in the unplanted cells. This may be attributed to the fact that plants provided some shade to the wetland media which cooled the temperatures slightly in the planted cells. The average temperatures in this study were relatively lower than those reported in similar HSSFCW studies done in Dar es Salaam City in Tanzania (Njau *et al.*, 2003; Bwire *et al.*, 2011). The difference is attributed to lower annual temperatures in Arusha as compared to Dar es Salaam. However, the temperatures recorded in the study was conducive enough to promote microbial activities and health growth of macrophytes since wetlands function at optimal temperatures range of (20 to 35) ^{0}C (Kadlec and Reddy, 2001).

5.4.2. Influence of flow rate on dissolved oxygen (DO)

Dissolved oxygen is an important factor for many biological and chemical processes in wetland systems. It enters wetlands via inflows or by diffusion on the water surface when the surface is turbulent. Oxygen is also produced by photosynthesis of plants and algae. Dissolved oxygen of many wastewaters is usually low, however, oxidation can be promoted in constructed wetland systems through processes that provide oxygen such as water inflows, or by diffusion on the water surface when the surface is turbulent (Kayombo *et al.*, 2001). The data obtained in Fig. 5.4 showed that the mean levels of DO ranged from 3.60 ± 0.19 mg/l to 5.02 ± 0.27 mg/l in the planted cells and 2.98 ± 0.18 mg/l to 4.81 ± 0.21 mg/l in the control cells. There was a significant difference in mean levels of DO between planted and control ($P<0.05$). The high content of DO levels in the planted cells is attributed to macrophytes' photosynthetic activity in the water phase and some work has shown that aquatic plants contribute to oxygen transfer in wetlands (Colmer, 2003). When the flow rates were increased gradually in the HSSFCWs, the concentration of DO values also increased. Results presented in Fig. 5.4 showed a linear relationship between flow rates and DO values of the wastewater. This showed that when water is flowing at high velocities, aeration is increased and DO levels are also increased. Studies have shown that high turbulence conditions in constructed wetlands increase oxygen transfer rates (Rousseau and Santa, 2007).

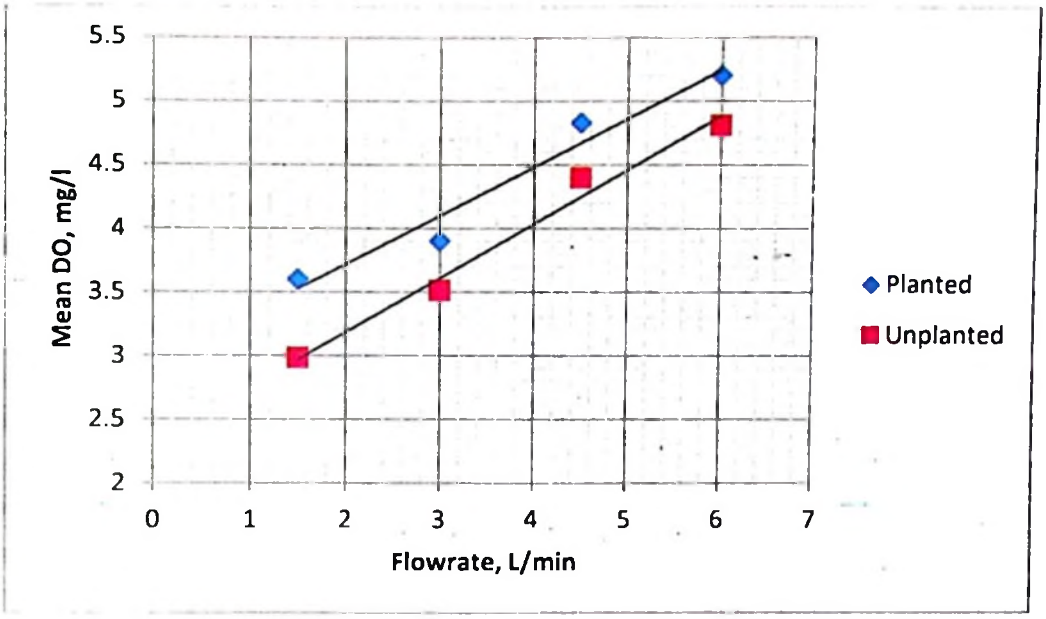


Figure 5.4: Mean variation of DO in HSSFCWs at different flow rates

5.4.3. Hydrogen ion concentration (pH)

The hydrogen ion concentration (pH) has significant influence on a number of reactions within wetlands and treatment processes (Kadlec and Knight, 1996) and a pH of 6-8 is optimal for promoting aquatic organism's health (Kayombo, 2001). In this study we monitored pH and obtained mean pH levels in both planted and control wetland cells ranging from 7.78 ± 0.06 to 8.27 ± 0.03 in the planted cells and 7.62 ± 0.10 to 8.11 ± 0.11 in the control cells (Fig. 5.5) and this pH was within the normal pH range in natural wetlands. At near neutral or alkaline pH, heavy metals are effectively immobilized (Gambrell, 1994) and the pH of the wastewater recorded in our study might have influenced precipitation of the heavy metals to some extent. The general trend in pH was observed to increase with flow rate with exception of the difference observed at flow rate of 3.0 L/min which cannot be adequately explained. However, there was a significant difference ($P<0.05$) in mean pH between the planted and control wetland cells. The possible explanation of the difference in pH between planted and control wetlands may be related to photosynthetic activities of the wetland plants (Equation 5). During photosynthesis, CO_2 is consumed from the water column faster than it can be replaced by bacterial respiration (Kayombo *et al.*, 2001). A decrease in the dissolved CO_2 concentration in the water results in a lower concentration of carbonic acid (H_2CO_3) in solution as shown in Equation 6. As the H_2CO_3 concentration in the water decreases, the concentration of H^+ decreases (Equation 7), as a result the pH within the wetland increases.

$$6H_2O + 6CO_2 + \text{Light energy} \rightarrow C_6H_{12}O_6 + 6O_2 \quad \text{------------------------------------ (5)}$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad \text{------------------------------------ (6)}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad \text{------------------------------------ (7)}$$

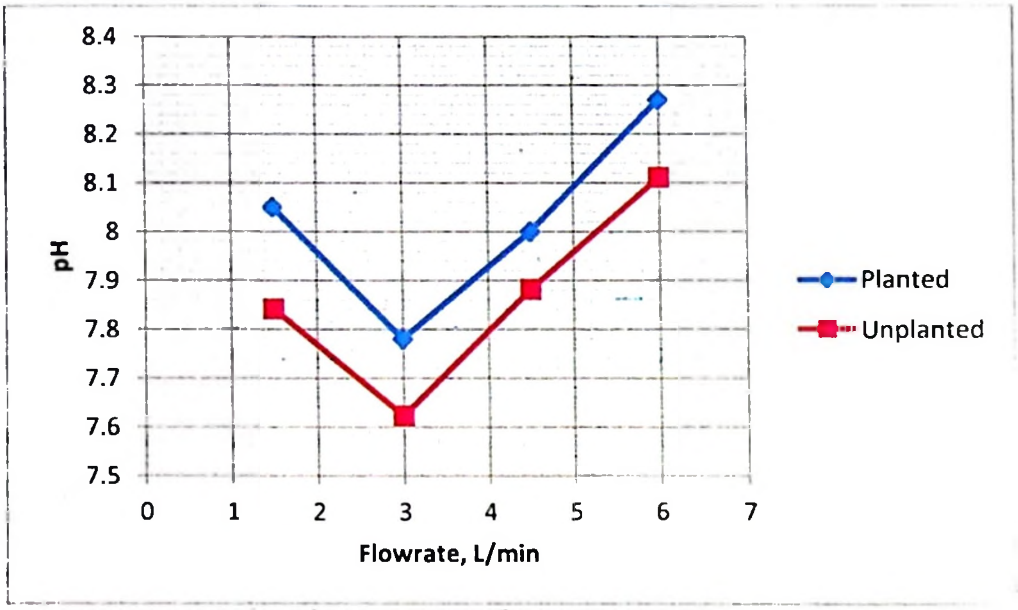


Figure 5.5: Mean variation of pH in HSSFCWs at different flow rates

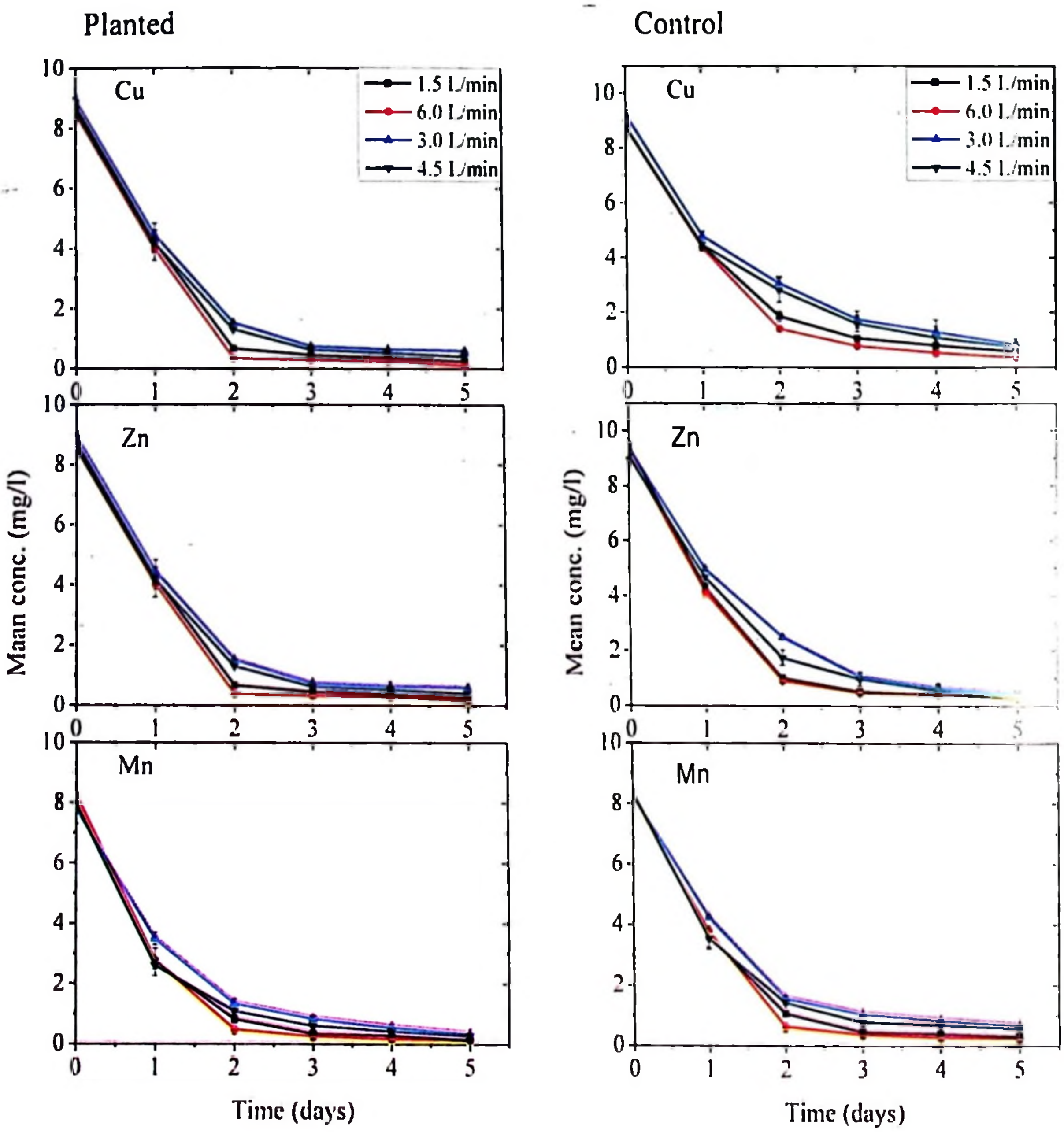
5.4.4. Influence of flow rates on the removal of copper in HSSFCWs

The results showed no consistent trend in the concentration levels of Cu as the flow rates were increased gradually in the HSSFCWs cells (Fig. 5.6). For the planted cells, it was observed that at flow rates 6.0 L/min and 1.5 L/min, there were 98.9 % and 97.1 % removal efficiency respectively, which was followed by 95.2 % removal at flow rates of 4.5 L/min and 93.3 % at flow rates of 3.0 L/min. This indicated that the 6.0 L/min flow rate treatment was equally efficient as the 1.5 L/min flow rate treatment. In the control wetlands, the same trend was also observed whereby Cu removal efficiency was 96.1 %, 93.5 %, 91.5 % and 91.0 % at flow rates 6.0 L/min, 1.5 L/min, 4.5 L/min and 3.0 L/min respectively. Statistical data analysis showed no significant difference ($P>0.05$) in mean concentration of copper in wastewater at different flow rates. This was indicative that flow rates variation did not have a significant influence on copper removal in HSSFCWs although other researchers have reported that control of flow velocity improves the removal of nutrients and faecal coliforms in wastewater (Njau *et al.*, 2011; Lohay *et al.*, 2012). In this study, the removal of Cu in the wastewater could be attributed to the combination of bio-chemical processes which occur simultaneously in the wetlands compartments. Literature has shown that microbial sulphate reduction followed by sulphide precipitation is the most important process for metal removal inside HSSFCWs. The average pH of 6-8 recorded in this study (Table 5.1) and the presence of organic matter in the prepared wastewater is conducive for conditions where SRB influence precipitation of Cu ions from the wastewater as described in the precipitation reactions (Equations 1 and 2).

On the other hand, this study observed a significant difference ($P<0.05$) in mean concentration levels of copper between planted and control cells. The results were in agreement with other findings that reported influence of plants towards heavy metal removal (Njau *et al.*, 2003; Garcia *et al.*, 2010; Nyomora *et al.*, 2012; Maine *et al.*, 2009; Lema *et al.*, 2014c). The planted cells performed better than control because the presence of plants play an important role in wetlands by providing organic matter as carbon sources for microbial activity and additional sites for pollutant adsorption (Weis & Weis, 2004). However, without any plants, as organic matter is used up in microbial mediated reactions and over time the substrate will become devoid of binding sites, thus decreasing the capacity of the substrate to maintain metal immobilizing capacity (Jacob and Otte, 2004).

5.4.5. Influence of flow rates on the removal of zinc (Zn) in HSSFCWs

The concentration levels of Zn in the wastewater decreased with time but there was no consistency in the removal as the flow rates were increased gradually (Fig. 5.6). High removal of Zn was observed at the following flow rates 6.0 L/min and 1.5 L/min with removal efficiencies of 99.6 % and 98.9 % respectively, which was followed by 4.5 L/min and lastly 3.0 L/min with removal efficiencies of 98.6 % and 97.7 % respectively. In the control wetlands, similar trend was observed whereby the removal Zn efficiency was 97.5 %, 96.5 %, 96.0 % and 95.1 % at flow rate 6.0 L/min, 1.5 L/min, 4.5 L/min and 3.0 L/min respectively. The analysis of variance showed no significant difference ($P>0.05$) in the mean concentrations of heavy metals between the flow rate treatments. The findings suggest that removal of zinc in the wetland cells was independent of flow rate and that other biochemical mechanisms are more significant. However, in this study we observed that planted wetland cells performed better than unplanted wetland cells. The t-test showed that the differences in mean concentration levels of Zn between planted and control were statistically different ($P<0.05$). This trend has also been reported in our previous study due to the influence of macrophytes in phytoremediation of heavy metals (Lema *et al.*, 2014c).



Footnote: Fe = Iron, Mn = Manganese, Cu = Copper, Zn = Zinc

Figure 5.6: Variation of mean concentrations of Cu, Zn and Mn in planted and unplanted control with time at different flow rates.

The results for Zn removal in HSSFCWs obtained in this study were also found to be higher than those reported in other studies done under temperate conditions. Maine *et al.* (2006) in their study on the treatment of wastewater in a constructed in Argentina got a mean removal efficiency of 59 %. In Belgium, a study evaluated Zn removal in wastewater and obtained 85 % (Lesage *et al.*, 2006). Yeh *et al.* (2009) evaluated three surface flow constructed wetlands in Taiwan and obtained a 92 % removal of Zn in wastewater. This shows that HSSFCWs are more efficient in tropical environments because of optimal temperature conditions for chemical and biological processes. The HSSFCWs acts like anaerobic reactors and the most likely reduction mechanism of zinc removal is precipitation of insoluble sulphide minerals. Sulphide minerals of zinc have exceedingly low solubility products (Stumm and Morgan, 1996) and precipitate from solution as described in the precipitation reactions (Equations 1 and 2). Other research results have indicated that in wetland systems, more than 50 % of zinc can readily be adsorbed onto particulate matter (Sheoran and Sheoran, 2006). Although this study did not measure turbidity of the wastewater, however, the wastewater had organic matter content from the seeding of sewage, and some algae which grew in the wetland cells therefore, the particulate matter, the wetland media and substrate could be important sites for adsorption of Zn and finally be removed from the water column. Likewise, zinc could also be assimilated as essential nutrient through plant uptake and microbial metabolism.

5.4.6. Influence of flow rates on the removal of manganese (Mn) in HSSFCWs

Manganese removal like the other heavy metals monitored in this study did not show consistent trend with increase in the flow rates (Fig. 5.6). The results obtained in the planted cells showed that at flow rates of 6.0 L/min and 1.5 L/min, there were 99.1 % and 98.1 % of Mn removal respectively, which was followed by 96.5 % removal at flow rate of 4.5 L/min and 95.5 % removal at flow rate of 3.0 L/min. In the control cells, the same trend was observed whereby the removal efficiency was 99.1 %, 98.1 %, 93.1 % and 91.8 % for the flow rates of 6.0 L/min, 1.5 L/min, 4.5 L/min and 3.0 L/min respectively. The data analysis showed no statistical significant difference ($P>0.05$) in the mean concentration levels of Mn between the flow rate treatments. However, when the planted wetlands were compared to unplanted, the differences in mean concentration levels in Mn were statistically different ($P<0.05$). Almost complete removal was observed in the planted wetlands and this was attributed to the influence of macrophytes to contribute to heavy metal removal from the wastewater. Similar results showing performance of macrophytes in wastewater treatment have also been reported by other researchers (Bwire *et al.*, 2011).

The overall removal of Mn in the HSSFCW cells was suggested to be influenced by precipitation mechanism. However, the chemistry of Mn in solution is different from Cu and Zn because it is an extremely mobile metal ion. Literature shows that Mn does not readily form an insoluble sulphide phase and thus it is not removed to a great extent in wetlands by sulphate reduction but may precipitate as $MnCO_3$ under reducing conditions (Hallberg and Johnson, 2005) and high pH of the water (pH > 7.2) as explained in precipitation reactions (Equation 3). According to Maine *et al.* (2006), wastewater containing high pH and calcium carbonate concentrations favoured heavy metal retention in sediments. Based on the results of pH values of the wastewater recorded in this study (Fig. 5.5) were high enough to influence precipitation with carbonates as shown in precipitation reactions (Equation 3). Another possible mechanism that could explain the removal of Mn in this experiment is sorption of dissolved Mn onto the wetland substrate, plant uptake and microbial metabolism (Lesage *et al.*, 2007). This mechanism has been observed by other researchers to be an important method of metal removal (Garcia *et al.*, 2001; Sheoran and Sheoran, 2006).

5.5. Conclusion and recommendations

Experiments performed in this study showed that HSSFCW's are capable of removing heavy metal-based agrochemicals from wastewater with removal efficiencies above 95 % on the average. When the planted systems were compared to those without plants it was also observed that planted systems outperformed the unplanted systems in removing heavy metals and the difference was statistically significant at 95 % confidence level. However, it was observed that there was no statistical significant difference (P>0.05) in the mean concentrations of heavy metals between the flow rate treatments. The control of flow velocity has been observed to improve removal of BOD, NO^-_3, NH_3, TKN and Faecal coliforms in wastewaters (Njau *et al.*, 2011; Lohay *et al.*, 2012). In this study it was speculated that higher flow rates might influence the removal of Cu, Zn and Mn in the HSSFCWs. In contrast, the levels of heavy metals in wastewater in the HSSFCWs did not decrease with gradual increase in flow rate. From the present observation, it can be concluded that regardless of the mechanisms involved in the removal of heavy metals, the overall removal is not limited by mass transfer step. Diffusion therefore is not the rate limiting step.

CHAPTER SIX

General Discussion, Conclusion and Recommendations

6.1. Summary

The general objective of this research was to investigate the levels of selected agrochemicals in wastewater from horticulture farms in Arusha and to evaluate their removal in constructed wetland systems. This chapter discusses the implications of the main findings of this research and re-examines the specific objectives presented in Chapter one. Based on the findings of this research it also makes general conclusion and recommendations for reducing pollution from agrochemical use in horticulture.

6.2. General Discussion

Following the review of literature on agrochemical use in Tanzania (Chapter two), the findings revealed that agrochemicals have been widely used in Arusha region because of the need to increase productivity of horticultural crops which are also on high demand in the region. The most important categories of agrochemicals used in horticultural fields in this region include insecticides, fungicides and inorganic fertilizers containing N and P. Some of these fertilizers include Urea, NPK, CAN, DAP, TSP, $ZnSO_4$, $MnSO_4$, $FeSO_4$, etc. The insecticides include Endosulfan, L. Cyhalothrin, Chlorpyrifos, Carbofuran, Permethrins and fungicides include $CuSO_4$, $Cu_2(OH)_3Cl$, etc. However, some of these agrochemicals contain chemical elements and compounds which are toxic to human health and the environment (WHO, 2005; Akinbile, 2006; Tirado, 2007). Notwithstanding these effects, horticultural farmers discharge their treated and poorly treated wastewater to the environment. A few studies have been done in Arusha horticulture fields and findings reported pesticides residues (Kihampa *et al.*, 2010a; 2010b) and nutrients (Nonga *et al.*, 2011) in environmental matrices and the contamination was related to the use of agrochemicals. However, these studies were done in small scale farms, and there is limited information about contamination of wastewater emanating from large-scale farms.

Chapter three therefore discusses the findings of the assessment of agrochemical residues in wastewaters from selected horticultural farms in Arusha. In this work, the research was focused on large-scale horticulture farms and the parameters of interest included nitrates (NO_3^-), nitrates (PO_4^{3-}), sulphates (SO_4^{2-}), chlorides (Cl^-), Permethrins, Chlorpyrifos, Endosulfan and Carbofuran. In this study NO_3^-, PO_4^{3-} and Permethrins concentrations in the wastewater discharged into the environment were detected at the levels exceeding allowable limits for discharge as per the Tanzania water quality standards (MoW, 2012). Our results confirm the high usage of nitrogen and phosphate containing fertilizers and permethrin insecticides in horticulture fields. Other studies conducted in small scale horticulture farms reported detectable levels of chlorpyrifos, and endosulfan, but these pesticides were not detected in the large scale horticulture farms (Chapter three). Their non-detection suggested that they might have dissipated out of the water column or they were not used during the time of the investigation. However, soils and sediments often act as a sink for most pesticides from which they can be released into the water sources and bio-accumulate in biota through food chain to the levels high enough to cause adverse health effects to organisms or humans. Therefore continual discharges of wastewater containing agrochemicals may lead to the environmental contamination. With this investigation, work on treatment using phytoremediation technology was proposed. Macrophytes are major components in phytoremediation technologies, yet little is known about their capability in Tanzania. Greater understanding of influence of macrophyte type would be useful in designing wastewater treatment systems.

This work also investigated the influence of different species of aquatic macrophytes (*Cyperus papyrus*, *Typha latifolia*, *Cyperus alternifolius* and *Phragmites mauritianus*) towards phytoremediation of Cu, Fe, Mn, Zn, Endosulfan, L. Cyhalothrin and Permethrin (Chapter four). The removal of these agrochemicals in the batch experiments was described by first-order reaction kinetics, and the results indicated that the removal rate constants were significantly greater ($P<0.05$) in planted batch reactors compared to unplanted reactors. These performances were encouraging and support their potential suitability for use in the treatment of horticultural wastewaters. An important finding observed was that different macrophytes demonstrated different removal rates towards agrochemicals. The macrophyte *Cyperus papyrus* had the highest removal of Cu, Fe, Ensosulfan and Permethrin. On the other hand, *Typha latifolia* showed the highest removal of Mn, Zn and L-Cyhalothrin. Therefore, the removal of agrochemicals by different macrophytes depends on among other factors, the type of macrophytes species because they have been reported to exhibit differences in uptake of agrochemicals. According to Brankovic *et al.* (2011), great differences in heavy metal bioaccumulation can be observed within different species of the same genus under the same environmental conditions because the uptake of heavy metals is regulated by plant organism via physiological mechanism. Generally, it appeared that macrophytes *Cyperus papyrus* and *Typha latifolia* have considerable impact on the mitigation of agrochemicals as compared to *Cyperus alternifolius* and *Phragmites mauritianus*. The differences found between the different types of macrophytes suggest that *Cyperus papyrus* and *Typha latifolia* could be used to mitigate agrochemicals in wastewater. From a management perspective, our results provide necessary information for their use in wetland systems when treating wastewater contaminated with agrochemicals.

In chapter five we established HSSFCW cells to understand the influence of flow rate on the removal of heavy metal-based agrochemicals (Cu, Zn and Mn) from simulated wastewater. These heavy metals are among the contaminants in commercial fertilizers, herbicides and pesticides (Adriano, 2001) and they may eventually be present in trace amounts in wastewaters from horticultural farms. The study revealed that HSSFCWs removed about 95 % of the three heavy metals on the average, at flow rates ranging from 1.5 L/min to 6.0 L/min. The variation in flow rate did not significantly improve removal of heavy metals in wastewater. Analyses of the above experiments revealed that both high flow rates and low flow rates were very similar in terms of heavy metal removal and the same trends were observed in planted and control experiments. However, the results in the present study are not consistent with results of removal of other wastewater pollutants reported by Njau *et al.* (2011) and Lohay *et al.* (2012) where flow velocity significantly affected the removal of BOD, NO^-_3, NH^-_3, TKN and Faecal coliforms in wastewaters. It can be inferred that flow rate is not an important environmental variable in the removal of heavy metal-based agrochemicals in HSSFCWs.

6.3. Conclusion

This dissertation has evaluated and compiled results of a research study to assess agrochemicals in wastewater from horticulture farms in Arusha and their removal by constructed wetlands. The review of agrochemical use in Arusha clearly indicated that fertilizers and pesticides are widely used in horticulture farms. The residues of PO_4^{3-}, NO_3^- and permethrins were detected at concentration levels above the allowable limits for discharge into receiving water resources. Keeping in view of this scenario, phytoremediation using bucket reactors and lab scale HSSFCWs were studied for the removal of agrochemicals in wastewater. This research revealed the capability of using aquatic macrophytes (*Cyperus papyrus* and *Typha latifolia*) for the treatment of wastewater contaminated with agrochemical residues. Experimental HSSFCWs showed that flow rate does not play a significant role in the removal heavy metal-based agrochemicals although it is an important environmental variable in the transfer of other pollutants within wetlands. The results obtained demonstrated that HSSFCWs effectively removed heavy metal-based agrochemicals from the simulated wastewater. The successful removal of these agrochemicals makes CWs as sustainable technologies for the treatment of wastewater from horticultural farms.

6.4. Recommendations

i. While this research work has demonstrated the potential for the use of macrophyte plants and constructed wetlands for the removal of agrochemicals in wastewater from horticulture farms, there is an obvious need for Farmers to utilize these phyto technologies since they offer a sustainable solution to water pollution control.

ii. This research work was limited to the study of few types of agrochemicals due to analytical constraints. More studies are needed to establish for example the fate of pesticides in the wetlands.

iii. Further work to investigate agrochemical residues in soil, sediment and biota around horticulture fields because soil and sediments often act as a sink for agrochemicals from which they can be released into the water sources and bio-accumulate in biota through food chain to the levels high enough to cause adverse health effects to organisms or humans.

iv. Literature review findings indicate that pesticides and inorganic fertilizers are commonly used in horticulture farms in Arusha. It is recommended that Farmers be educated and sensitized about integrated pest management to ensure responsible and safe use of agrochemicals so as to minimize the potential for environmental pollution.

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APPENDICES

Appendix 1. Laboratory analytical results for physical-chemical parameters in wastewater from horticulture farms

Sites	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Date			pH					Temperature (0C)					EC (µs/cm)		
15/9/13	9.10	7.40	7.90	7.10	7.40	21.70	18.10	18.20	21.10	21.10	996.60	1414.00	848.00	1022.00	773.16
20/9/13	7.81	7.54	9.20	6.88	6.96	19.80	21.20	23.20	21.10	21.80	714.90	1498.90	1050.00	1128.00	653.86
25/9/13	9.10	8.07	8.70	6.80	6.97	18.80	18.40	19.70	20.10	22.90	601.50	1397.00	1111.00	1228.00	662.82
3/10/13	8.70	7.64	8.03	6.98	7.10	19.10	19.90	20.20	20.80	21.80	688.00	1416.00	1219.60	1064.00	543.82
10/10/13	7.80	8.90	9.48	6.69	7.14	19.90	21.30	19.30	21.80	21.60	922.60	1484.17	997.00	1071.00	683.02
Date			NO^-_3					Cl^- (ppm)					SO^{2-}_4 (ppm)		
15/9/13	7.40	11.90	54.80	4.40	11.60	67.48	58.50	52.00	44.00	94.00	90.00	123.00	175.00	104.00	98.00
20/9/13	5.10	20.20	53.20	4.60	43.90	169.90	159.50	99.97	559.80	202.40	91.00	142.00	105.00	112.00	115.00
25/9/13	12.10	25.50	75.30	bd	14.10	52.98	82.47	157.45	332.39	99.96	90.00	134.00	120.00	125.00	122.00
3/10/13	8.40	24.29	70.10	5.20	35.90	44.20	72.86	172.44	560.00	96.00	88.60	139.00	175.00	117.00	87.30
10/10/13	7.69	28.90	67.00	3.80	31.70	89.92	79.16	124.96	601.00	120.00	97.50	124.00	120.00	135.00	108.00
Date			DO (ppm)					BOD-5 (ppm)					TDS (ppm)		
15/9/13	4.39	1.86	3.80	2.41	7.16	145.00	93.00	91.00	172.50	44.00	637.00	848.40	509.00	654.00	497.00
20/9/13	6.60	1.50	3.80	2.56	5.86	72.10	71.00	113.00	430.00	60.00	457.00	956.00	630.00	721.00	418.00
25/9/13	5.90	1.44	4.40	2.70	6.82	121.00	76.00	107.00	435.00	63.00	385.00	838.20	667.00	736.00	423.00
3/10/13	6.30	1.90	3.70	2.10	3.82	96.00	82.00	142.00	156.00	58.00	413.00	849.60	780.00	680.00	345.00
10/10/13	7.05	1.09	4.19	2.59	6.02	115.50	74.00	140.00	202.00	58.00	591.00	890.00	598.00	685.00	432.00

Date	Permethrin (ppm)					Chlorpyrifos (ppm)					Endosulfan (ppm)					Carbofuran (ppm)				
15/9/13	bdl	bdl	0.70	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
20/9/13	bdl	bdl	0.39	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
25/9/13	bdl	bdl	0.80	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
3/10/13	bdl	bdl	0.82	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
10/10/13	bdl	bdl	0.44	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl

Appendix 2. Laboratory analytical results for heavy metal agrochemicals in bucket experiments

Plant type	Time (d)	Fe (ppm)			Mn (ppm)			Cu (ppm)			Zn (ppm)		
		Pot 1	Pot2	Pot3	Pot 1	Pot2	Pot3	Pot 1	Pot2	Pot3	Pot 1	Pot2	Pot3
Typha latifolia	0	3.515	3.515	3.515	3.508	3.508	3.508	2.778	2.778	2.778	2.921	2.921	2.921
	1	1.492	1.587	1.369	0.677	0.503	0.641	0.587	0.631	0.650	0.490	0.465	0.476
	4	0.767	0.819	0.678	0.425	0.307	0.412	0.241	0.208	0.385	0.109	0.145	0.151
	8	0.535	0.460	0.266	0.161	0.114	0.156	0.139	0.135	0.156	0.091	0.012	0.074
	12	0.249	0.150	0.247	0.016	0.008	0.035	0.076	0.040	0.107	0.000	0.000	0.011
	16	0.138	0.117	0.170	0.000	0.000	0.003	0.012	0.008	0.050	0.000	0.000	0.002
C. papyrus	0	3.515	3.515	3.515	3.508	3.508	3.508	2.778	2.778	2.778	2.921	2.921	2.921
	1	1.101	0.896	0.913	0.756	0.824	0.782	0.507	0.489	0.476	0.504	0.533	0.549
	4	0.647	0.501	0.544	0.419	0.597	0.480	0.264	0.183	0.141	0.174	0.268	0.201
	8	0.286	0.207	0.219	0.224	0.327	0.296	0.085	0.071	0.098	0.113	0.134	0.081
	12	0.201	0.116	0.136	0.096	0.106	0.078	0.039	0.014	0.045	0.067	0.038	0.021
	16	0.118	0.049	0.063	0.015	0.029	0.007	0.004	0.000	0.002	0.012	0.000	0.000
Phragmites	0	3.515	3.515	3.515	3.508	3.508	3.508	2.778	2.778	2.778	2.921	2.921	2.921
	1	1.748	1.831	1.755	1.421	1.551	1.668	0.708	0.729	0.764	0.831	0.852	0.832
	4	0.966	0.947	0.865	0.856	1.165	1.394	0.513	0.532	0.574	0.508	0.560	0.584
	8	0.660	0.623	0.593	0.498	0.878	0.922	0.296	0.311	0.307	0.232	0.276	0.312
	12	0.395	0.358	0.426	0.132	0.362	0.481	0.124	0.264	0.169	0.155	0.186	0.208
	16	0.237	0.216	0.302	0.086	0.102	0.192	0.074	0.186	0.089	0.089	0.103	0.080
C. alternifolius	0	3.515	3.515	3.515	3.508	3.508	3.508	2.778	2.778	2.778	2.921	2.921	2.921
	1	1.447	1.456	1.265	1.065	1.294	1.154	0.542	0.566	0.565	0.582	0.625	0.640
	4	0.755	0.739	0.682	0.683	0.716	0.702	0.321	0.425	0.307	0.368	0.372	0.413
	8	0.605	0.526	0.457	0.378	0.486	0.404	0.191	0.267	0.188	0.172	0.132	0.223
	12	0.362	0.306	0.221	0.137	0.196	0.149	0.086	0.136	0.099	0.091	0.062	0.151
	16	0.249	0.153	0.107	0.029	0.069	0.036	0.025	0.097	0.042	0.007	0.000	0.069
Control	0	3.515	3.515	3.515	3.508	3.508	3.508	2.778	2.778	2.778	2.921	2.921	2.921
	1	2.179	2.240	2.310	2.424	2.274	2.157	0.922	0.905	0.911	1.146	1.028	1.251
	4	1.527	1.721	1.689	1.930	1.779	1.638	0.871	0.751	0.822	0.976	0.909	0.978
	8	0.913	0.973	0.929	1.325	1.533	1.559	0.798	0.608	0.657	0.718	0.636	0.728
	12	0.640	0.788	0.796	1.250	1.444	1.415	0.416	0.481	0.526	0.561	0.572	0.534
	16	0.529	0.686	0.656	0.969	1.294	1.269	0.358	0.273	0.382	0.490	0.424	0.463

Appendix 3. Laboratory analytical results for pesticide agrochemicals in bucket experiments

Plant type	Time (d)	L. Cyhalothrin (ppm)			Endosulfan (ppm)			Permethrin (ppm)		
		Pot1	Pot2	Pot3	Pot1	Pot2	Pot3	Pot1	Pot2	Pot3
Typha latifolia	0	5.13248	5.13248	5.13248	5.17995	5.17995	5.17995	5.18679	5.18679	5.18679
	1	4.46654	4.24626	4.34466	4.20221	4.52156	4.28365	4.41258	4.31748	4.01725
	4	3.31248	3.68649	3.34144	3.83175	3.41147	3.60157	3.46920	3.45560	3.21512
	8	2.13209	1.64749	1.75476	3.18720	2.55929	3.05232	2.23524	2.03604	2.03491
	12	1.10279	1.29059	1.45268	2.26130	1.42650	2.17350	1.63674	1.23238	1.14600
C. papyrus	0	5.13248	5.13248	5.13248	5.17995	5.17995	5.17995	5.18679	5.18679	5.18679
	1	4.32205	4.13455	4.01533	4.22565	4.71043	4.52570	3.74751	3.63528	3.83325
	4	4.01175	3.75554	3.31765	3.38535	4.30344	3.63266	2.93796	2.39379	2.92328
	8	2.27817	2.51639	1.55271	2.61070	3.26262	2.26231	2.13957	1.55232	2.08119
	12	2.00165	1.82565	1.23266	1.76630	2.02563	1.43316	1.02855	1.03469	1.04645
Phragmites	0	5.13248	5.13248	5.13248	5.17995	5.17995	5.17995	5.18679	5.18679	5.18679
	1	4.88805	4.63531	4.52240	5.01356	4.65336	4.82253	4.61043	4.45399	4.66400
	4	3.94377	3.83536	3.78409	4.78086	4.29059	3.63319	3.23524	3.78480	3.93524
	8	2.88473	2.71520	2.61173	3.82796	3.91698	2.56581	2.56930	2.85057	3.04676
	12	2.01356	1.92156	2.51938	2.65265	3.26365	1.93810	1.55462	1.81255	2.22645
C. alternifolius	0	5.13248	5.13248	5.13248	5.17995	5.17995	5.17995	5.18679	5.18679	5.18679
	1	4.21540	4.52819	4.71040	4.67552	4.81565	5.05545	4.53297	4.35962	4.43297
	4	3.50335	3.78896	3.70060	4.05681	3.43758	3.50784	4.13751	3.92450	3.74113
	8	1.70636	2.86477	2.28410	3.48490	3.75874	2.31829	3.10946	2.08570	2.05679
	12	1.67552	1.81565	1.05545	2.65852	2.75236	1.63565	2.12890	1.35823	1.01240
Control	0	5.13248	5.13248	5.13248	5.17995	5.17995	5.17995	5.18679	5.18679	5.18679
	1	5.06855	4.90792	4.96621	5.06855	5.07915	4.96621	4.60390	4.78483	4.91752
	4	4.45216	3.67755	4.58661	4.63605	4.83297	4.74843	4.27167	4.03448	4.36944
	8	4.09060	3.09085	3.67356	3.97026	4.40606	3.87099	3.77511	3.59605	3.82145
	12	3.27812	2.25323	3.14651	3.36220	3.73614	3.32659	2.84310	2.58429	2.75530

Appendix 4. Laboratory analytical results for pH, temperature and dissolved oxygen in HSSFCWs

Flow rate (L/min)	Time (d)	pH				Temperature				Dissolved oxygen (DO)			
		Control		Planted		Control		Planted		Control		Planted	
		Cell1	Cell3	Cell2	Cell4	Cell1	Cell3	Cell2	Cell4	Cell1	Cell3	Cell2	Cell4
1.5	0	7.95	7.89	8.36	8.00	22.30	22.20	21.90	22.00	2.00	2.00	4.90	4.30
	1	8.02	8.01	8.40	8.30	22.00	22.30	21.30	22.00	3.00	2.50	3.50	4.10
	2	7.91	7.93	8.02	8.05	22.50	23.00	21.70	22.00	2.80	3.00	3.10	3.20
	3	7.80	7.86	7.97	8.00	23.00	22.30	22.80	22.30	3.10	3.00	3.30	3.50
	4	7.83	7.81	8.04	8.01	23.00	22.80	23.00	22.50	2.90	3.30	3.30	3.60
	5	7.46	7.58	7.64	7.78	21.00	21.00	21.30	21.10	2.70	2.70	3.30	3.50
6.0	0	8.35	8.35	8.58	8.44	22.30	22.10	22.10	21.90	5.00	5.10	5.30	4.80
	1	8.26	8.25	8.51	8.48	22.40	22.10	23.00	23.00	5.00	4.70	5.45	5.20
	2	8.28	8.28	8.46	8.48	22.50	23.00	23.00	23.00	5.00	4.30	5.60	5.60
	3	8.24	8.24	8.42	8.33	21.90	22.30	22.10	22.00	5.10	4.50	4.50	4.70
	4	7.93	7.92	8.03	8.04	22.90	22.80	22.80	22.90	4.60	4.90	4.40	4.80
	5	7.62	7.60	7.63	7.75	20.90	21.00	21.00	21.00	5.00	4.50	4.50	5.40
3.0	0	7.98	8.09	8.35	8.30	22.00	22.00	21.40	21.40	4.30	3.50	3.70	4.10
	1	7.90	8.10	8.21	8.21	22.00	22.30	22.30	22.00	3.55	3.50	3.70	3.35
	2	7.64	7.75	7.76	7.87	22.00	22.30	22.30	22.00	2.80	3.50	3.70	2.60
	3	7.29	7.40	7.57	7.61	21.70	22.20	22.10	22.20	3.90	2.30	3.90	3.90
	4	7.30	7.41	7.31	7.52	21.80	21.80	21.30	21.50	4.20	3.20	4.20	4.40
	5	7.00	7.50	7.20	7.50	21.70	21.80	21.40	21.60	4.20	3.20	4.20	4.40
4.5	0	8.10	8.13	8.21	8.18	22.80	22.50	22.50	22.10	4.20	4.30	4.50	4.60
	1	8.01	8.06	8.10	8.10	21.80	21.90	21.70	21.80	4.40	4.55	4.55	4.30
	2	8.00	8.06	8.10	8.10	21.80	21.90	21.70	21.90	4.60	4.10	4.80	4.60
	3	8.03	7.86	8.13	8.20	22.20	22.70	22.40	22.60	4.80	4.30	5.10	5.20
	4	7.76	7.64	7.87	7.88	21.70	22.30	22.30	21.70	4.90	4.20	4.80	4.90
	5	7.49	7.42	7.60	7.55	22.10	22.20	22.40	22.20	4.73	4.90	4.58	4.80

Appendix 5. Laboratory analytical results for heavy metal agrochemicals in the HSSFCWs

Flow rate (L/min)	Time (d)	Zn Concentration				Cu concentration				Mn Concentration			
		Control		Planted		Control		Planted		Control		Planted	
		Cell1	Cell3	Cell2	Cell4	Cell1	Cell3	Cell2	Cell4	Cell1	Cell3	Cell2	Cell4
1.5	0	9.41	9.35	9.47	9.46	9.00	8.62	8.64	8.86	8.24	8.28	8.17	7.95
	1	3.93	3.69	4.27	4.34	4.64	4.25	4.84	3.60	3.27	3.97	3.18	2.27
	2	0.47	0.41	1.01	1.02	2.06	1.68	0.76	0.58	1.16	0.98	0.96	0.69
	3	0.31	0.20	0.58	0.46	1.16	0.96	0.48	0.43	0.52	0.41	0.32	0.37
	4	0.21	0.15	0.43	0.35	0.90	0.72	0.36	0.35	0.44	0.37	0.32	0.26
	5	0.09	0.10	0.37	0.29	0.62	0.52	0.26	0.23	0.36	0.28	0.17	0.13
6.0	0	9.35	9.01	9.10	9.31	8.70	8.86	8.58	8.42	8.21	8.28	8.19	8.25
	1	4.18	3.07	4.25	3.94	4.32	4.39	4.09	3.87	3.87	3.55	2.59	2.78
	2	0.22	0.27	0.85	0.86	1.44	1.34	0.32	0.34	0.63	0.48	0.34	0.45
	3	0.12	0.15	0.42	0.41	0.80	0.72	0.26	0.28	0.32	0.27	0.14	0.20
	4	0.14	0.11	0.36	0.35	0.62	0.42	0.20	0.26	0.23	0.19	0.06	0.12
	5	0.05	0.04	0.22	0.23	0.38	0.30	0.09	0.11	0.18	0.15	0.04	0.09
3.0	0	9.12	9.42	9.28	9.53	9.12	9.38	8.86	9.12	8.22	8.33	7.31	8.29
	1	4.09	3.93	5.03	4.92	4.65	4.96	4.34	4.60	4.30	4.19	3.29	3.71
	2	1.60	1.51	2.59	2.42	3.32	2.82	1.54	1.52	1.65	1.53	1.19	1.50
	3	0.78	0.54	1.23	0.93	2.06	1.44	0.72	0.78	1.08	1.04	0.76	0.94
	4	0.24	0.25	0.81	0.53	1.74	0.86	0.64	0.66	0.89	0.82	0.45	0.67
	5	0.19	0.23	0.56	0.35	1.04	0.63	0.58	0.62	0.73	0.63	0.32	0.38
4.5	0	9.08	8.98	9.09	9.10	8.84	8.78	8.64	8.62	8.19	8.60	8.02	7.92
	1	3.86	3.80	4.89	4.45	4.42	4.53	4.23	4.13	3.20	3.89	2.48	2.75
	2	1.08	1.08	2.03	1.48	3.26	2.38	1.28	1.34	1.50	1.37	1.05	1.14
	3	0.52	0.39	1.23	0.73	1.90	1.30	0.62	0.64	0.94	0.66	0.57	0.65
	4	0.19	0.22	0.74	0.39	1.50	0.68	0.54	0.52	0.71	0.69	0.43	0.45
	5	0.13	0.12	0.50	0.21	0.92	0.58	0.48	0.34	0.61	0.55	0.22	0.35

Appendix 6. Hoagland solution recipe used in the study

Macronutrients

Chemical name	Formula	grams/litre	Final concentration (mM)
Potassium dihydrogen phosphate.	KH_2PO_4	340	1
Potassium nitrate	KNO_3	1265	5
Calcium nitrate	$Ca(NO_3)_2{\cdot}4H_2O$	2952.5	5
Magnesium sulphate	$MgSO_4{\cdot}7H_2O$	1232.5	2

The chemicals were dissolved in 250 L of tap water in the order listed in the table.

Micronutrients stock solution (makes 1 litre)

Chemical name	Formula	grams/litre	Final concentration (µM)
Manganese sulphate	$MnSO_4{\cdot}H_2O$	2.00	11.8
zinc sulphate heptahydrate	$ZnSO_4{\cdot}7H_2O$	0.22	0.7
Copper sulphate pentahydrate	$CuSO_4{\cdot}5H_2O$	0.08	0.32
Ammonium heptamolybdate	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	0.2	0.16
Boric acid	H_3BO_3	2.86	46.3
Iron chelate	Fe-EDTA	50	5

0.25 L of each micronutrient stock solution was added to 250 L of tap water used for irrigation.