

**INVESTIGATION OF SOME HEAVY METALS IN WATER, SOIL AND SPINACH
SAMPLES FROM FARMLANDS SURROUNDING KWARI POND, KWANGILA**

ZARIA

BY

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JUNE, 2016

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BY

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(M.Sc/SCIE/1436/2010 – 2011)

P15SCCH8020

**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL,
AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF
SCIENCE (MSc) IN ANALYTICAL CHEMISTRY**

**DEPARTMENT OF CHEMISTRY,
AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA**

JUNE, 2016

DECLARATION

I, **ABDULLAHI, Zulaihat Bello** hereby declare that this thesis has been written by me and that the information contained herein is a record of my own research work. It has not been presented in any form for the award of any degree at the Ahmadu Bello University or any other University.

All sources of information obtained from other literary publications have been duly acknowledged by means of references.

ABDULLAHI, Zulaihat Bello
M.Sc/SCIE/1436/2010-2011
P15SCCH8020

Date

CERTIFICATION

This thesis entitled “A STUDY OF SOME HEAVY METALS IN WATER, SOIL AND SPINACH SAMPLES FROM FARMLANDS SURROUNDING KWARI POND, KWANGILA” by ABDULLAHI, ZULAIHAT BELLO meets the regulations governing the award of the degree of M.Sc in Analytical Chemistry of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Date

DEDICATION

This research work is solely dedicated to my Parents, Malam Abdullahi Abdurrahman and Habiba Musa Haman for their support throughout the course of my studies

ACKNOWLEDGMENTS

All praise is to Almighty Allah whose mercy encompasses all things and peace and salutation be upon our master Mustapha Muhammad, the best in the universe as child and the most chaste as a grown up, also upon his immaculate family, the thoroughly purified and his chosen companions.

I wish to express my sincere gratitude to all those who contributed towards making this work possible. I am particularly indebted to my Supervisors, Prof C.E. Gimba and Dr. (Mrs). H.Omenesa.

Through the many constructive discussions along the course of this research, they provided an invaluable guidance. It was their technical and moral support that brought this work to completion.

My deepest appreciation goes to my wonderful parents, Malam Abdullahi Abdurrahman and Malama Habiba Musa for all their love, encouragement, support and understanding throughout my studies. You are among the best parents in the world and I love you both. Also, I am deeply indebted to my esteemed Husband and mentor, Malam Bello Garba; for his support and encouragement. But for you, this would not have turned to reality. Thank you.

I would like to express my sincere appreciation to Malam Muhammad Lawal for his helpful suggestions and thoughtful and critical evaluation of this work. Special thanks go to Malam Bashir Multi-user laboratory for his invaluable advices and encouragement. Thank you all.

Special thanks are also given to my fellow classmates; Queendalin, Safiyya, Elija, Muhammad, and Amina Kudu for their cheerful help and the pleasant environment for work they have created.

My brothers and sisters, Amina Abdullahi, Zainab Abdullahi, Habiba Abubakar Anas Abdullahi, Ahmad Abdullahi, Abbas Abdullahi, Idris Abdullahi, Yusuf Abdullahi, Yunusa Abubakar, Umar Musa, Yaaji Galadima and Hauwa Galadima for your prayers and encouragement.

Finally, my deepest appreciation and love go to my Husband, Bello Garba and my lovely children Fatima Bello, Hayatu Bello, Baqir Bello ,Khadija Bello and Zainab Bello: what can I say but to thank the Almighty Allah for bringing us together? You have been there for me through thick and thin. I love you all my life.

ABSTRACT

The levels of Cd, Zn, Mn, Cr and Pb were investigated in spinach plant irrigated with pond water using Atomic Absorption Spectroscopy. The physico-chemical parameters and the levels of the metals in the pond water samples were analyzed also. The temperature, salinity, conductivity and dissolved oxygen of the pond water were within permissible limits; however, the pH was slightly above the permissible limit. The levels of Cd, Mn and Cr 0.53, 0.94 and 5.22mg/L respectively (all through the months) in the pond water were higher than the US permissible limits for irrigation water (0.01, 0.2 and 0.1mg/L respectively), while the level of Zn was higher in the month of May only and Pb was higher in the months of May and April. The concentration of the metals in the soil samples from the three farmlands was generally of the order Mn>Cr>Pb>Zn>Cd and the mean concentrations of Cr (26.8mg/kg), Pb (20.3mg/kg) and Zn (12.7mg/kg) were below the WHO/FAO recommended maximum limits of (100, 85 and 200mg/kg) respectively except for Mn(91.9mg/kg) and Cd(1.7mg/kg) with allowable limits of 80 and 0.8mg/kg. The general trend of the metals in the spinach samples was observed to be Mn>Zn>Cr>Pb>Cd, the mean concentrations of Cd(1.52mg/kg), Cr (17.37mg/kg) and Pb (13.73mg/kg) were higher than the WHO/FAO allowable limits of 0.30mg/kg, 1.50mg/kg and 10.0mg/kg for Cd, Cr and Pb respectively. On the other hand, the mean concentrations of Zn (21.8mg/kg) and Mn (40.0mg/kg) were below the WHO permissible limits (50.0, 200.0mg/kg).The transfer factor of the metals from the soil to the spinach plant in farm 1 followed the order Zn>Cd>Cr>Mn>Pb while orders of Zn>Cd>Pb>Cr>Mn and Cd>Zn>Pb>Cr>Mn were observed for farms 2 and 3 respectively. Since the concentrations of the metals in the spinach (vegetable) were higher than permissible limits, consumption over time

might present problems as the tendency for the soil to accumulate and transfer metals to the spinach cultivated increases which will subsequently get to man through the food chain.

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LIST OF ACROYNMS

AAS	Atomic Absorption Spectroscopy
FAAS	Flame Atomic Absorption Spectroscopy
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
XRF	X-ray Fluorescence Spectroscopy
PIXE	Particle Induced X-ray Emission Spectroscopy
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
NAA	Neutron Activation Analysis
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry for Hg
LDPE	Low density polyethylene
HDPE	High-density polyethylene
PTFE	Polytetrafluoroethylene
ANOVA	Analysis of variance
C_v	Coeffient of variation

LIST OF SYMBOLS

Cd	Cadmium
Pb	Lead
Hg	Mercury
Ni	Nickel
Co	Cobalt
Cr	Chromium
Cu	Copper
Se	Selenium
Zn	Zinc
Mn	Manganese
Fe	Iron
Ag	Silver
Al	Aluminium
HClO ₃	Perchloric acid
HNO ₃	Nitric acid
HCl	Hydrochloric acid
Cl ⁻	Chloride

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Heavy metals are general terms, which apply to the group of metals and metalloids with atomic density greater than 4 g/cm^3 , (Huton and Symon, 1988; Nriagu, 1999; Garbarino *et al.*, 1995; Hawkes, 1997). This classification includes transition metals and higher atomic weight metals of group III to V of the periodic table. Heavy metals include lead, cadmium, zinc, copper, Iron to mention a few (Duruibe *et al.*, 2007). They are among the major contaminants of food supply and are considered as problem to the environment (Zaidi *et al.*, 2005). Heavy metals contamination may occur due to irrigation with contaminated water, the addition of fertilizers, metal-based pesticides, industrial emissions, transportation, harvesting process and storage. Advancement in technology has lead to high levels of industrialization leading to the discharge of effluent bearing heavy metals into our environment. The various activities by man in recent years have increased the quantity and distribution of these heavy metals in the atmosphere, land and water bodies (Gustar, 1974).

Odoh and Kolawale (2011) observed that long term irrigation with heavy metals contaminated water may lead to the accumulation of heavy metals in agricultural soils and plants. Accumulation of heavy metals in the edible and non-edible parts of vegetables creates serious environmental concern (Vousta *et al.*, 1996). Toxicity of heavy metals such as Cd, Pb, and Hg to man, other animals and organisms are well known as they are not required by man even in small amounts (Cui *et al.*, 2004).Vegetables constitute an important part of the human diet since they contain carbohydrates, proteins, as well as vitamins and minerals. Heavy metals are one of a

range of important types of contaminants that can be found on the surface and in the tissue of fresh vegetables (Bigdeli and Seilsepour, 2008). A number of elements, such as lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), chromium (Cr), Copper (Cu) and Selenium (IV) (Se) can be harmful to plants and humans even at quite low concentrations (Bowen, 1979). Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of industrial and urban wastes (Buchaver, 1973). Soil is also polluted through application of chemical fertilizers (like phosphate and Zn fertilizers), and herbicides (Demirezen and Aksoy, 2004). Heavy metal accumulation of soils is of concern in agricultural production due to its adverse effects on food quality, crop growth (Ma *et al.*, 1994; Msaky and Calvert, 1990; Fergusson, 1990) and environmental health.

1.2 STATEMENT OF THE PROBLEM

Kwari pond is the only source of water used to produce substantial amount of irrigated vegetables from the surrounding farmlands. This practice has been going on for decades. Concern over possible heavy metal contamination of the pond arises following the construction of Kaduna- Kano express highway, establishment of Maraba Clinic, block making industries, the springing-up of residential houses together with their dumpsites and domestic wastewater disposal points in the vicinity of the pond. The possible sources of heavy metal pollution to the pond include storm runoff of oil spillage from hollow block producing industries and a major highway (Kaduna – Kano highway) which discharge directly into the pond and untreated hospital waste generated from Maraba Clinic which may find its way into the pond from the clinic waste disposal points. Also, the location of dumpsites and household liquid waste disposal

points within the pond catchments further increases the likelihood of heavy metals getting into the pond through leachate and storm runoff.

1.3 JUSTIFICATION

The presence of heavy metals in irrigation water constitutes a considerable health risk to the consumers of the farm products. For example, irrigation water that is chronically contaminated with dissolved cadmium (Cd) results in kidney damage and hypertension in the consumers. Exposure to lead (Pb) impacts negatively upon intelligence and behaviour of young children (Roy, 1999). Various regulatory bodies have specified the minimum quality of water required for irrigation, the constituents of soil for farming activities and allowable metal (s) concentration in food substances in order to ensure safe practice and also to safeguard human health. Hence, the need to investigate the quality of water from Kwari pond since it is being used for irrigation of surrounding farmlands in order to ensure compliance with world standard and regulations.

1.4 Aim

The aim of this research is to investigate the levels of Cr, Cd, Pb, Zn and Mn in water, soil and spinach samples from farmlands surrounding Kwari pond and to determine the physico-chemical parameters of water samples from Kwari Pond for its stability for irrigation since reports relating to the analyses of water, soil and vegetation around Kwari pond are not available in literature.

1.5 OBJECTIVES

The objectives of this research are to:

- (i) Assess the levels of Cr, Cd, Pb, Zn and Mn in the water, soil and spinach samples from and around Kwari pond;
- (ii) Compare the levels of Cr, Cd, Pb, Zn and Mn in the samples with the regulatory standards
- (iii) Determine the concentration of the relevant physico-chemical parameters for water quality requirement for irrigation; and
- (iv) Make recommendations on the suitability or otherwise of Kwari pond water for irrigation farming.

1.6 SCOPE AND LIMITATIONS OF THE RESEARCH

1.6.1 SCOPE

The levels of heavy metals (Cr, Cd, Pb, Zn and Mn) would be determined in samples of water, soil and spinach using Atomic Absorption Spectrometry (AAS), the physico-chemical parameters of the pond. The results obtained would be compared with regulatory standard for each metal in irrigation water, soil and spinach samples

1.6.2 .LIMITATIONS

Only the listed metals would be assessed in the water, soil, and spinach samples. A total of 72 samples of water, soil and spinach are to be collected for the purpose of this investigation.

CHAPTER TWO

LITERATURE REVIEW

2.1 HEAVY METALS AND THEIR OCCURRENCE

Metals with density or specific gravity greater than 5g/cm^3 are known as heavy metals. They are commonly referred to as trace metals because they are present at much lower concentrations in water compared to major ions SO_4^{2-} , Cl^- , NO_3^- , Mg^{2+} and Ca^{2+} (Radojevic and Bashkin, 1999). Heavy metals are poisonous to living organisms and are sometimes referred to as toxic metals. Metals most often involved in human poisoning are Pb, Hg, As and Cd. Some heavy metals, such as Zn, Cu, Cr, Fe and Mn, are required by the body in small amounts, but can be toxic in larger quantities (Duffus, 2002).

Heavy metals occur naturally in the ecosystem with large variations in concentrations. In modern times, anthropogenic sources of heavy metals, i.e. pollutions from the activities of humans, have introduced some of these heavy metals into the ecosystem. The presence of heavy metals in the environment is of great ecological significance due to their toxicity at certain concentrations, translocation through food chains and non biodegradability which is responsible for their accumulation in the biosphere (Aekola *et al.*, 2008).

Heavy metals like iron, tin, copper, manganese and vanadium occur naturally in the environment and could serve as plant nutrients depending on their concentrations. Mercury, lead, cadmium, silver, chromium and many others that are indirectly distributed as a result of human activities could be very toxic even at low concentrations. These metals are non-biodegradable and can undergo global ecological circles (Oluyemi *et al.*, 2008).

The problem of environmental pollution due to toxic metals has attracted the attention of researchers worldwide. The toxic heavy metals entering the ecosystem may lead to geoaccumulation, bioaccumulation and biomagnification. Heavy metals like Fe, Cu, Zn, Ni and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Ward, 1995).

2.2 SOURCES OF HEAVY METAL CONTAMINATION

Heavy metals are introduced to environment either by natural means or anthropogenic activities.

(a) Natural sources: In nature, excessive levels of trace metals may occur by geographical phenomena like volcanic eruptions, weathering of rocks; leaching into rivers, lakes and oceans due to action of winds.

(b) Anthropogenic sources: In ancient times, heavy metals were released in small amounts while mining and smelting of metal ores in open fires. With the industrial revolution, metals are extracted from natural resources and processed in industries from where heavy metals leak into atmosphere. Similarly, traces of heavy metals get deposited in the environment through discharge; domestic waste, agricultural runoff and automobile exhausts.

According to Hariprasad and Dayananda(2013) the various sources through which heavy metals reach the environment are:

- (i) Smelting or processing of ores of metals,
- (ii) Mining
- (iii) Dumpsites
- (iv) Burning of fossil fuels such as coal, petrol and kerosene oil,

- (v) Storm runoff containing compounds of heavy metals from agricultural farmlands
- (vi) Discharge of industrial, domestic and hospital waste
- (vii) Storm runoff of oil spillage from highways and automobile exhaust. .

Wastewater from urban area is being used profitably to irrigate crops in the vicinity of cities from time unknown. It is still considered rich in plant nutrients and organic matter. However, the situation has changed now because, in many cities and towns the wastewater is sold for secondary use and it is a good source of income to municipalities (Saleem *et al.*, 2005). Heavy metal is present in diminutive quantities in the water and is further added due to soil erosion and leaching of minerals. However, in the recent past, freshwater pollution due to heavy metals has become a hazard due to discharge of industrial effluents. Heavy metals like Mn, Fe, Ni, Cu, Zn and Cr are essential for the growth of organisms, while Pb, Cd, Hg and Ag are not biologically essential, but definitely toxic. Even the essential heavy metals if beyond optimum threshold levels could be hazardous and toxic. After entering the water, metals may precipitate, get adsorbed on solid surface, remain suspended in water or taken up by fauna. A very important biological property of metal is its tendency to accumulate (Eralagere and Bhadravathi, 2008).

The main sources of heavy metals to vegetable crops are their growth media (soil, air and water) from which these are taken up by the roots or foliage. Most of our water resources are gradually becoming polluted due to the addition of foreign materials from the surroundings. The foreign materials, according to Karnataka State Pollution Control Board (KSPCB) (2002), include organic matter of plant and animal origin, land surface washing, and industrial and sewage effluents. Rapid urbanization and industrialization with improper environmental planning often

lead to discharge of industrial and sewage effluents into lakes. The lakes have a complex and fragile ecosystem, as they do not have self cleaning ability and therefore readily accumulate pollutants (Akinola *et al.* 2006).

Municipal waste contains such heavy metals as As, Cd, Cu, Fe, Hg, Mn, Pb, Ni and Zn which end up in the sink when they are leached out from the dumpsites. Soil is a vital resource for sustaining two human needs of quality food supply and quality environment. Plants grown on a land polluted with municipal, domestic or industrial wastes can absorb heavy metals in form of mobile ions present in the soil through their roots or through foliar absorption. These absorbed metals get bioaccumulated in the roots, stems, fruits, grains and leaves of plants (Fatoki, 2000).

2.3 METHODS FOR INVESTIGATING HEAVY METALS IN ENVIRONMENTAL SAMPLES

According to EPA reference document (EPA-600/R-94/111), the presence of heavy metals in various samples can be investigated using any of the following methods:

- (i) Flame Atomic Absorption Spectroscopy (FAAS)
- (ii) Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
- (iii) X-ray Fluorescence Spectroscopy (XRF)
- (iv) Particle Induced X-ray Emission Spectroscopy (PIXE)
- (v) Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)
- (vi) Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

- (vii) Neutron Activation Analysis (NAA)
- (viii) Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) for Hg
- (ix) Ion chromatography for soluble metals
- (x) Electron Microscopy for qualitative analysis

However, the FAAS method has the following advantages over others:

- (i) Greater sensitivity and detection limits than other methods
- (ii) Direct analysis of some types of liquid samples
- (iii) Low spectral interferences
- (iv) Very small sample size
- (iv) It can be use to detect the presence of metals individually (García and Báez, 2012)

2.3.1 Atomic Absorption Spectroscopy (AAS)

The use of Atomic Absorption Spectroscopy (AAS) for the determination of heavy metals in both aqueous and solid samples has been sanctioned by Environmental Protection Agency (EPA-600/R-94/111, method 200.9, section 1.0). Atomic absorption spectroscopy (AAS) provides procedures for the determination of dissolved and total recoverable elements in ground water, surface water, drinking water, storm runoff, industrial and domestic wastewater. The method is also applicable to the determination of total recoverable elements in sediment, sludges, and soil.

The AAS is a standard laboratory analytical technique in which trace metals in solution are detected in elemental form in a flame. There are two main AAS techniques, flame atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS). Both techniques are based on similar principles used for measuring metals in solution. However, they differ in the method used for sample introduction into the instrument. In FAAS, the sample is atomised with a nebuliser and introduced into a flame, normally an air/acetylene flame. A graphite furnace electrothermal atomiser is used in GFAAS.

Upon introduction of the metal solution into the instrument, the solution is vaporised by the flame or a furnace, and the trace metal to be detected is dissociated from its chemical bonds into its elemental form. A hollow cathode or electrodeless discharge lamp provides characteristic radiation energy for the metal. The wavelength of this emitted radiation must match the absorption wavelength of the metal to be determined. The amount of energy absorbed by the metal atoms is related to their concentration. Since each metal absorbs light at a characteristic wavelength, analysis for each metal requires a different light source, and only one element can be determined at a time.

Atomic absorption spectroscopy measurements are subject to interferences for example: background, spectral, ionisation, chemical and physical interferences. Appropriate choice of filter media and matrix matching of the samples to standards tend to minimise interference (US EPA, 1999b). Overall, AAS has less interference than other techniques used for measuring metals in air samples. High-volume samplers are normally used for sampling when FAAS or GFAAS analysis is planned. Both techniques are destructive and require that the sample be

extracted or digested before introduction into system as a solution. The detection limit of the GFAAS is normally about two orders of magnitude better than the FAAS.

2.4 SAMPLE COLLECTION TECHNIQUE

2.4.1 Water Sample Collection Technique

The sample collection method developed by the Environmental Protection Agency (EPA-600/R-94/111, method 200.9, section 8.0) stated that Water samples should be collected at a depth of 10 cm below the water surface and away from the edge to avoid surface debris and sediment disturbance in plastic bottles. The pH of all aqueous samples must be measured prior to aliquoting to ensure proper preservation of the sample. The method further highlighted that properly preserved samples can be held for up to six months before analysis (EPA, 1994). Sample containers, sampling devices, glass and plastic material should be carefully cleaned before use, by soaking in 10% nitric acid (USEPA, 2001). At the time of collection, the aqueous sample must be filtered preferably using glass or plastic filtering apparatus, to avoid contamination of the sample. A portion of the filtered sample should be used to rinse the filter flask. The required volume of filtrate is then collected and acidified with (1+1) nitric acid immediately following filtration to $\text{pH} < 2$ (EPA, 1994).

Table 2.1: Sampling procedures for heavy metals determination in surface water

Dissolved (soluble)	Al, Ag, As (total, III, V), B, Ba, Be, Ca, Cd, Co, Cr (total, III), Cu, Fe (total), Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se (total, IV, VI), Sn (not including tributyl tin as Sn), Ti, U, V & Zn
Sample requirements	Filtered sample
Volume	250 mL, unless speciation of As (total, trivalent, pentavalent) and/or Cr (total, trivalent) is required, in which case 500 mL is required.
Container	Plastic Bottle cap must have a teflon liner, Use new pre-cleaned acid rinsed bottles
Collection technique	Decant from collection vessel and filter immediately. Filtered sample is placed directly in sample bottle.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter C.
Treatment to assist preservation	After filtration, add 10% nitric acid (concentrated HNO ₃) to pH <2 D (if bottle from laboratory does NOT already have 2 mL present in pre-prepared bottles). Do not pre-rinse these sample bottles. Refrigerate at 1–4°C or freeze
Filling technique	If the sample bottles contain acid do not pre rinse them, otherwise, pre rinse bottle with filtered sample three times, then add filtered sample and add acid preservative. Fill to the shoulder of bottle.
Maximum sample holding time and storage conditions	1 month if at 1–4°C, and pH < 2, 6 months if frozen
Units of measurement	mg/L or µg/L (mg metal/L or µg metal/L)
Analysis method	Measured by a range of methods: ion chromatography, colorimetry, ICPMS, ICP-AES, flame ASS, graphite furnace ASS, or cold vapour generation AAS methods.
Comments	Samples for total metal concentrations are not filtered. Generally, all metals/metalloids can be analyzed from the same sample bottle, except for when the special Hg analysis or speciation analysis is required. Safety note: Use the appropriate personal protective equipment (e.g. safety glasses and gloves) when filling the sample bottles for dissolved metal analysis. Avoid contact or accidental splashing with the concentrated nitric acid preservative present in the bottles. Concentrated nitric acid is corrosive and care should be taken to avoid any eye or skin contact, or inhalation of fumes. If eyes or skin are exposed to the acid, wash thoroughly and with copious amounts of water and seek medical attention.

Source: Government of Australia (Department of Water, 2009)

The recommendations further added that samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Re-use of filter paper is strictly discouraged (Government of Australia, 2009). Plastic sample bottles should not be made from low density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or fluoropolymer (e.g. nalgene, teflon (polytetrafluoroethylene, PTFE)).

2.4.2 Soil Sample Collection Technique

According to EPA document (EPA/600/R-92/128) sampling constants can be used to determine the size of soil sample that should be used for collecting samples in the field. The sampling constants are determined upon data collected from two sets of samples from the site. The site should be divided into nine or more approximately equal rectangular or square cells. A series of small random samples of weight W_1 should be taken from each cell. This should then be followed by taking a second series of random samples of weight W_2 from the same cells. The weight of the large sample should be ten or more times the weight of the small sample. The mean (M) and the variance (S^2) for each set of samples should be calculated (subscripts identify each individual sample), A and B are then calculated according to the following equations:

$$A = (W_1 W_2 (S_1^2 - S_2^2)) / (W_2 - W_1) \quad (2.1)$$

$$B = S_1^2 - (A/W_1) = S_2^2 - (A/W_2) \quad (2.2)$$

The optimum sample weight (W_{opt}) has been reported in several references (Ingamells and Switzer, 1973; Ingamells, 1974; Ingamells and Pitard, 1986; Pitard, 1989b;) to be:

$$W_{opt} = A/B \quad (2.3)$$

A method employed by Evaristo (2013) outlined the use of composite soil samples from each sampling plot. Each composite soil sample should comprise of soil sub samples to be obtained from different points randomly located in each sampling plot. The soil sub samples should be obtained from the depth of 0-20 cm using the soil auger. The depth of 20 cm was chosen because that is part of the sub soil used for crop growing and roots penetrate to such depth to extract nutrients and other elements necessary for plant growth (Gupta and Varshney, 1989).

2.6 PREVIOUS RESEARCHES ON HEAVY METALS CONTAMINATION OF ENVIRONMENTAL SAMPLES

Rajesh *et al.*, (2004) reported that sewage effluents of municipal origin contain appreciable amount of major essential plant nutrients and therefore the fertility levels of the soil are improved considerably under sewage irrigation of crop fields. However, studies showed that treated sewage water contains variable amounts of heavy metals such as Pb, Ni, Cd, Cu, Hg, Zn and Cr, which have the potential to contaminate crops growing under such irrigation scheme (Lokeshwari and Chandrappa, 2006). Plants grown in the neighbourhood of major motorways have been reported to contain metals such as Pb and Cd from motor vehicle emissions (Sharma and Prasade, 2010; El-Gamal, 2000; Luilo and Othman, 2006). Other sources of heavy metals to roadside environments are vehicle component wear, engine oil consumption and corrosion of batteries and other vehicle metallic parts (Sharma and Prasade, 2010).

In a study on the impact of heavy metal contamination of water, soil and cultivated vegetation around Bellandur Lake, Lokeshwari and Chandrappa (2006) discovered that Fe, Cr and Pb

showed 50% higher concentration during rainy season, while Cd showed higher concentration during dry season. A marginal difference in concentration is found for Cu and Ni between wet and dry seasons. Zn showed less seasonal variation. Higher concentration of Fe, Cr and Pb during the rainy season is probably due to rainfall and run-off which cause erosion, thereby introducing into the lake soil, silt and even discarded iron waste besides wastewater from drains nearby, the high level of Cd during dry season might be due to concentration effects. Tsafe *et al.*, (2012) evaluated the heavy metals (Al, Fe, Mn, Mg, Zn, Pb, Ni, Cr, Co, Cu, Cd) uptake of vegetables grown in Yargalma in northern Nigeria using flame Atomic Absorption Spectrophotometer. The results showed high concentration of metals in the soil with Al being the highest (3111.29 mg/Kg) and the lowest was Cd (0.965 mg/Kg). However, the vegetables, had the highest concentration of Fe (54.05 mg/Kg) and the lowest was in Cd (0.5 mg/Kg).

Using Particle Induced X-ray Emission (PIXE) spectrometry, Wilberforce and Nwabue (2012) analyzed soil and plant samples for heavy metals (As, Cd, Cr, Pb and Zn) contents in Enyigba and Abakaliki. The results showed that the levels of $Pb > Ni > Cd$ in Enyigba top soil was above the US-EPA Regulatory Limits in that order. Also elevated concentrations of heavy metal values in the vegetable from Enyigba were observed, while in Abakaliki the levels of arsenic and lead in bitter leaf and garden egg leaf exceeded WHO (1988) Maximum Limit (WHO-ML = 0.1ppm for As and 0.3ppm for Pb).

Also, using the Atomic Absorption Spectrometer (AAS) technique, Evaristo (2013) analyzed samples of wastewater used for irrigation, soil and vegetable crops for heavy metals comprising chromium, cobalt, copper, lead and nickel. The results indicated that the concentration of heavy

metals in the water, soil and crop samples at the two study sites in Peri-urban areas in Zambia exceeded WHO (1988) acceptable limits.

The heavy metals widely used in the manufacture of household appliances, paints, photographic paper, photo chemicals e.t.c., lead to pollution of ground and surface water systems through anthropogenic activities (WHO, 1988 and Hutchinson *et al.* 1993). According to the Food and Agricultural Organization (FAO, 1992) the major constituents of typical domestic wastewater are:

- (i) Calcium Carbonate (CaCO_3)
- (ii) Phosphorus (P)
- (iii) Nitrogen (N)
- (iv) Chloride (Cl)
- (v) Oil and Grease
- (vi) Total Solids (TS)
- (vii) Total Dissolved Solids (TDS)
- (viii) Suspended Solids (SS)
- (ix) BOD_5

Eralagere and Bhadravathi (2008), tested water samples from Jannapura Lake which receives untreated domestic wastewater from residential areas, using Atomic absorption spectrophotometer. Their result showed that the concentration of all the heavy metals of concern (Cu, Zn, Pb, Cd and Ni) in the water exceeded the permissible limits for WHO (1988) Standards. Additionally, solid waste dumpsites contribute to heavy metals contamination of the environment (soil, water, food crops etc) (Abdus-Salam; Olarinoye *et al* and Odukoya *et al.*, 2009). Dauda *et*

al (2013) discovered significant concentration of heavy metals (Cr, Cd, Pb and Cu) in several dumpsites across Bauchi Metropolis.

The major tools of building block producing industry are the molding machine and a diesel engine that powers it. The moulding machine requires lubrication to ensure minimum wear and long machine life. Lubricating oil from petroleum fractions are mainly composed of paraffinic, naphthenic, and small amounts of aromatic hydrocarbons while metalo-organic compounds are usually added as additives (Aucellio, 2007).

In a comparative study to investigate the common metals that appear in used lubrication oil, Aucellio (2007) discovered significant quantities of Aluminum, Copper, Lead and Silver in the used oil than in the virgin oil. The author attributed this to the wearing of bearings and Iron shaft of the molding machine. Also, cases of contamination of the receiving environment (soil, water, food crops) due to the discharge from hospital dumpsites and incinerators have been reported. Sunday and Agbaji (2012) discovered significant concentrations of Pb, Fe, Mn, Cr, and Cd from dumpsites of Ahmadu Bello University Teaching Hospital in Zaria.

It was also observed that organic materials, such as farm manures, bio-solids or composts contain higher concentration of trace elements and are responsible for increases in total amount of Cu, Zn, Pb, Cd, Fe and Mn in the receiving environment (Yang *et al.*, 2005).

According to the US Environmental Protection Agency (1996), road runoff carries millions of gallons of improperly discharged used motor oil which pollute streams, lakes, and coastal areas. This should be cause for concern since one gallon of used oil can contaminate one million gallons of water. Manitoba Association for Resource Recovery Corporation (MARRC) (2001)

described used oil as the “single largest environmentally hazardous recyclable material.” Heavy metals in storm-water runoff are of particular concern because of their toxicity, pervasiveness, and persistence. In an early study, Ellis *et al.* (1987) found that heavy metals can make highway runoff chronically toxic to receiving waters. Many pollutant loadings exhibit seasonal variations: winter brings high concentrations of chlorides and sulfates from de-icing salt (Legret and Pagotto, 1999) while irregular rainfall complicates runoff management. Gaffield *et al.* (2003) examine impacts from heavy metals in storm-water, which can often be traced to motor vehicle sources. According to Van Metre *et al.*, (2000), vehicles (through tire wear, oil leaks, or car exhaust) are a significant source of heavy metals in water bodies. Over a long, dry season pollutants accumulate on road surfaces and enter receiving waters during the first storm event (Han *et al.*, 2006).

2.7 ALLOWABLE LIMITS OF HEAVY METALS IN VARIOUS SAMPLES

Water sample

Table 2.2: National and International standards

Metals	Water sample (mg/L)		
	FEPA	Dutch standard	USEPA
Pb	1.0	5.0	0.015
Zn	50	---	2.0
Cr	0.02---2.0	0.1	0.10
Fe	1.0	---	0.30
Mn	0.02—0.10	---	0.05
Cd	0.2---1.80	0.01	0.005
Cu	2.0--- 4.0	0.2	1.00
Ni	0.02--- 0.10	0.2	0.05

Source: Aremu *et al.* (2010) - FEPA /USEPA and Muhammad *et al.*, (2011) - Dutch standard

Soil sample

Table 2.3: International standards

Metals(mg/kg)	Soil sample			
	USEPA	Dutch Standard	Great Britain	Wu Yao-guo
Pb	300	85	400	216.93
Zn	200	—	300	118.06
Cr	400	100	50	44.72
Fe	No Limit	—	—	—
Mn	80	—	—	—
Cd	3.0	0.8	3	0.55
Cu	50	36	100	54.13
Ni	50	35	50	—

Source: Tsafe *et al.*, (2012) - USEPA /Great Britain /Wu Yao-guo and Muhammad *et al.* (2011) -

Dutch standard

Vegetable crop (spinach) sample

Table 2.4: International standards

Metals(mg/kg)	Vegetable Crop sample	
	WHO/FAO	Indian
Pb	10	2.5
Zn	50.0	50.0
Cr	1.50	20.0
Fe	5.0	—
Mn	200	—
Cd	0.3	1.5
Cu	40.0	30.0
Ni	—	1.5

Source: Tsafe *et al.*, (2012) – WHO (2005) /FAO /Indian

CHAPTER THREE

MATERIALS AND METHODS

The reagents and equipment used in order to achieve the objectives of this research work are listed in Appendix I. All reagents used were of analar grade.

3.1 Description of the Study Area

Kwari pond is located near Kwangila, Zaria, along Kaduna-Kano highway on latitude $11^{\circ} 08.127'N$ and longitude $007^{\circ}42.404'E$. The pond is surrounded by Kaduna-Kano Highway to the North, Kwangila residential houses and their dumpsites to the West, Maraba Clinic and Farmlands to the South and hollow block producing factories to the East. The surrounding farmlands rely entirely on the pond for irrigation farming during dry season. Substantial quantities of vegetable crops such as tomatoes, spinach (*Amaranth caudatus*), lettuce (*lactucasativa*), pepper and Onion (*Allium cepa*) are produced annually from the irrigation practice.

By virtue of its location, the pond is subjected to various forms of pollution from anthropogenic sources. The following were identified as possible sources of heavy metal pollution of the pond:

- (i) Domestic Liquid Waste from Kwangila residential houses
- (ii) Leachate from dumpsites near the pond
- (iii) Storm runoff from hollow block producing industries
- (iv) Maraba Hospital Waste
- (v) Storm runoff containing compounds of heavy metals from agricultural farmlands
- (vi) Contaminated Storm Washed off of Kaduna-Kano Road Highway

The map of Kwangila Zaria showing the sampling points(F1, F2 and F3) is shown in Figure 3.1, photographs of the pond and farm lands are also presented in Figures 3.2-- 3.4.

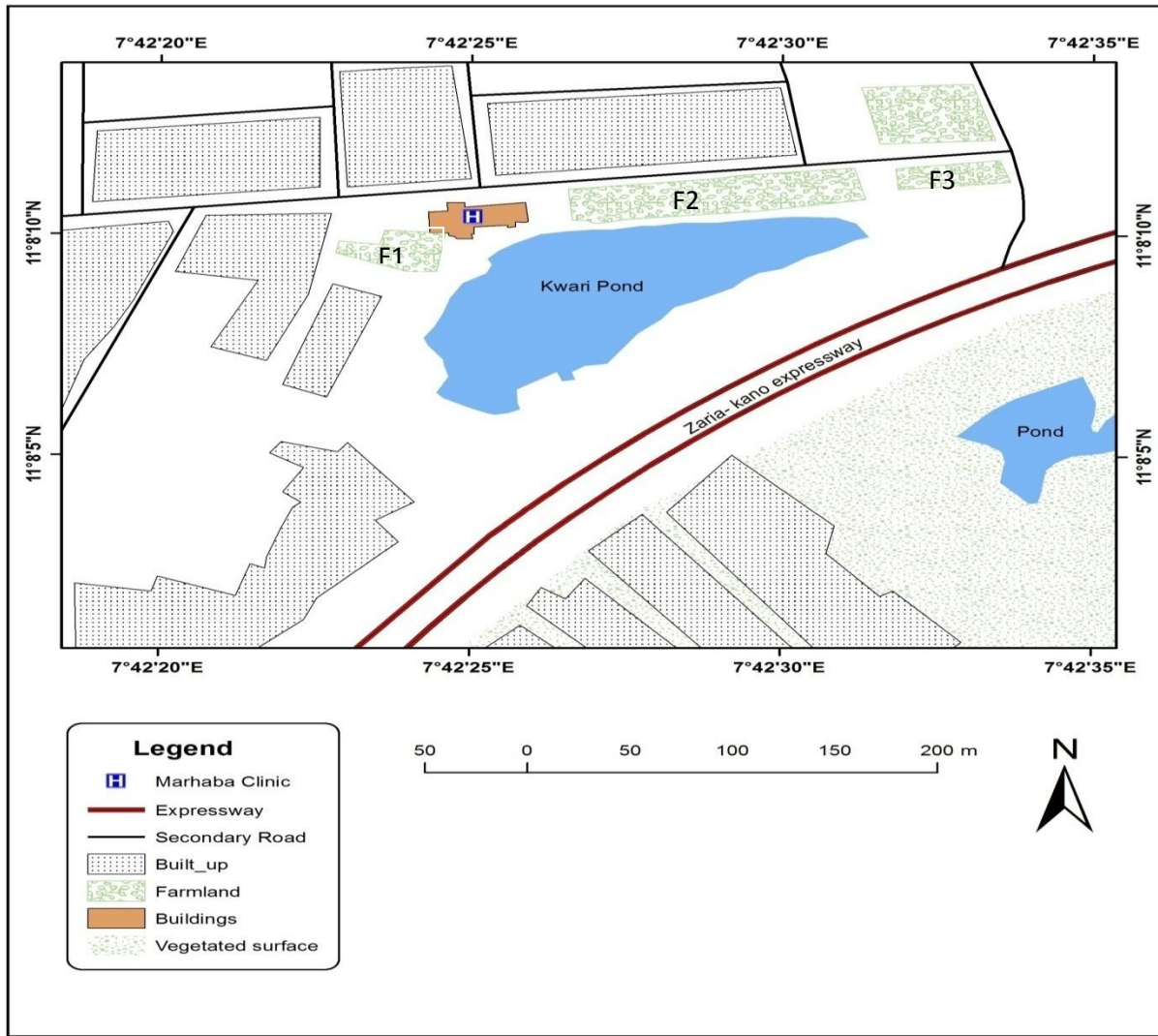


Figure 3.1: Map of Kabama layout: Showing Sample Collection Points F1, F2 and F3 (Adopted and Modified from Google art 2015)



Plate 3.1: Sample Collection Points showing the pond and farms 1



Plate 3.2: Sample Collection Points showing the pond and farm 2



Plate 3.3: Sample Collection Points showing the pond and farm 3

3.2 Samples Collection, Preparation and Analysis

3.2.1 *Water samples*

Samples of water (six) from Kwari pond were collected monthly beginning from February, 2014 to July, 2014 at points near each of the identified possible sources of pollution mentioned in section 3.1 of this work. In the case of agricultural farmlands, collections were made at points where the crop cultivators draw water for irrigation. Water samples were collected in accordance with the technique approved by the Environmental Protection Agency (EPA-600/R-94/111, method 200.9, section 8.0) . On each occasion during the sampling period and at each sampling point 250cm³ of the sample was collected from six point and homogenised by dipping plastic container about 6-10cm below the surface film of the water body as suggested by Clark (1992).

Water samples were collected from six points and mixed into one to give a representative sample;

Point 1: At the point where the pond borders outlet of domestic wastewater.

Point 2: At the border between the pond and the dumpsite.

Point 3: Where effluent from the highway enters the pond.

Point 4: Close to the Maraba Clinic soak away.

Point 5: Near the point of entry of wastewater from hollow block industry.

Point 6: At the point where water is drawn for irrigation.

The EPA guidelines for water, soil and vegetable crops sample preparation were adopted in this work. Water samples (500 cm^3) were filtered using Whatman No. 41 (0.45 mm pore size) filter paper for estimation of dissolved metal content. An aliquot ($\geq 20\text{ cm}^3$) of the filtrate was pipetted and acid preserved into a 50 cm^3 polypropylene centrifuge tube. Then an appropriate volume of (1+1) nitric acid was added to adjust the acid concentration of the aliquot to approximate a 1% (V/V) nitric acid solution, the tube was capped and mixed which rendered the sample ready for analysis.

3.2.2 Soil samples

Composite soil samples were collected from each sampling plot monthly for a period of six months (February, 2014 to July, 2014). Each composite soil samples comprised of soil sub samples obtained from ten places randomly located in each sampling plot Evaristo (2013). The soil sub samples were obtained at the depth of 20 cm below the surface layer using the soil auger. The depth of 20 cm was chosen because that is part of the sub soil used for crop growing and roots penetrate to such depth to extract nutrients and other elements necessary for plant growth (Gupta and Varshney, 1989).

Soil samples were air-dried and grinded into fine powder using pestle and mortar and passed through 1 mm sieve. Well-mixed samples of 2 g each were taken in 250 cm^3 glass beakers and digested with 8 cm^3 of aqua regia on a sand bath for 2 h. After evaporation to near dryness, the samples were dissolved with 10 cm^3 of 2% nitric acid, filtered and then diluted to 50 cm^3 with de-ionized water.

3.2.3 Vegetable crop (spinach) samples

The edible parts of spinach (leaves) (Reuter *et al.*, 1986) were collected randomly from the same plot where the soil samples were collected. Composite samples of spinach were collected from each of the three farmlands surrounding the pond. The samples were collected monthly over a period of six months also.

Spinach samples were thoroughly washed to remove all adhered soil particles. Samples were cut into small pieces, air-dried for 2 days and finally dried at $100 \pm 1^\circ\text{C}$ in a hot-air oven for 3 h. The samples were milled in to powder in warm condition and passed through 1 mm sieve. Digestions of these samples (2 g each) were carried out using 10 cm^3 nitric acid according to the procedure used for soil samples. Well-mixed samples of 2 g each were taken in 250 cm^3 glass beakers for digestion in 24 cm^3 of aquaregia on a sand bath for 3 hours. After evaporation to a lesser volume, the samples were filtered and diluted to 50 cm^3 with de-ionized water for analysis.

3.3 Preparation of Stock Solutions

3.3.1 Stock solutions

1000 mgdm^{-3} lead solution: Prepared by dissolving 1.5990 g $\text{Pb}(\text{NO}_3)_2$ in a 1000cm^3 volumetric flask with distilled deionized water and then making it up to mark. This gives a 1000 ppm solution of Pb.

1000 mgdm^{-3} Cadmium solution: Prepared by dissolving 2.7500 g $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in a 1000 cm^3 volumetric flask with distilled deionized water and then making it up to mark to give the 1000 ppm Cd solution.

1000 mgdm⁻³ Chromium solution: Prepared by dissolving 2.5192 g Na₂Cr₂O₇ in a 1000 cm³ volumetric flask with distilled deionized water and then making it up to mark to give the 1000 ppm Cr solution.

1000 mgdm⁻³ Manganese solution: Prepared by dissolving 1.000g manganese in a minimum volume of 1:1 nitric acid and dilute to 1 litre to give 1000ppm Mn solution.

1000 mgdm⁻³ Zinc solution: Prepared by dissolving 1.000g of Zinc in 40ml 1:1hydrochloric acid and dilute to 1 litre to give 1000ppm Zn solution.

3.3.2 Standard working solutions

Working standards were prepared from the stock solutions using the dilution formula:

$$C_{\text{stock solution}} \times V_{\text{stock solution required}} = C_{\text{standard working solution}} \times V_{\text{standard working solution}}$$

$$V_{\text{stock solution required}} = (C_{\text{standard working solution}} \times V_{\text{standard working solution}}) / C_{\text{stock solution}}$$

Working standard concentrations were prepared from the 1000 mgdm⁻³ solution of each metal stock solution by serial dilution as follows; 1.0, 2.0, 4.0, 5.0 and 10.0 mgdm⁻³ Pb at wavelength 217.0nm, 1.0, 2.0, 3.0, 6.0, 8.0 and 10.0 mgdm⁻³ Cd at wavelength 228.8nm. 5.0, 10.0, 20.0, 40.0 and 80.0mgdm⁻³ Cr. At wavelength 357.9nm. 1.0, 2.0, 3.0, 4.0 and 5.0 mgdm⁻³ Mn at wavelength 279.5nm and 0.01, 0.2, 0.5, 1.0 and 2.0 mgdm⁻³ Zn at wavelength 213.9nm.

3.4. Determination of the metals

As recommended by EPA (1994), levels of Cd, Cr, Mn, Pb and Zn in water, spinach and soil samples were determined using Varian AA240FS Fast Sequential Atomic Absorption Spectrometer available in multi-user laboratory Ahmadu Bello University, Zaria. Also levels of

heavy metals in water, soil and spinach were compared with the maximum allowable limits outlined by relevant agencies (WHO, USEPA, FEPA and FAO) as well as the values obtained from previous studies conducted in Nigeria.

AAS is a standard laboratory analytical technique in which trace metals in solution are detected in elemental form in a flame.

The actual concentration of metals in water, soil and spinach sample was determined using the following formula:

Actual concentration in water sample (mg/l) = AAS result of Digest (mg/l) x Dilution factor (l/l)

Actual concentration in soil and spinach sample (mg/kg) = AAS result of Digest (mg/l) x Dilution factor (l/kg)

Where,

$$\text{Dilution factor} = \frac{\text{Volume of digest used}}{\text{Volume of water and Weight of soil and spinach sample digested}}$$

3.4.1 Transfer factor

The transfer factor was calculated according to Sajjadet.al (2009) who defined it as the relative tendency of a metal to be accumulated by a particular species of plant. Generally, transfer factor expresses the bioavailability of a metal at a particular position on a species of plant. This is however, dependant on factors such as the soil pH and the nature of the plant itself.

This is because different authors have reported different transfer factors for the same metal ions and the same species of plant and across different parts of the plants, such as roots and leafy

parts. The transfer factor calculated in this study was based on the total metal content of the edible part of the plant. The formula used was stated by Cui *et al*, (2004).

TF= concentration of metal in edible part/concentration of metal in soil

3.5 Statistical Analysis

Statistical analysis of the results was done using Microsoft excel, version 2007. The means, standard deviations and actual concentrations were calculated for heavy metals in water, soils and spinach. The results are presented in Tables. In addition, test of dispersion was carried out by the computation of Coefficient of Variation (CV) for each metal in each sample. Statistical significance of the difference of the mean values between different groups was determined by applying the F- test with the level of significance at $P < 0.05$. The correlation between the metals was observed using Pearson correlation analysis. The correlation coefficient 'r' is a measure of linear association between two variables. Values of the correlation coefficient are always between -1 and +1. A correlation coefficient of +1 indicates that two variables are perfectly related in a positive linear sense, a correlation coefficient of -1 indicates that two variables are perfectly related in a negative linear sense, and a correlation coefficient of 0 indicates that there is no linear relationship between the two variables. Analyses of variance ANOVA was employed to test the significance of the difference of the mean values also.

All statistical analyses were performed using computer Microsoft Excel and SPSS package.

CHAPTER FOUR

RESULTS

4.1 Physico-chemical Parameters of the Pond Water (Irrigation Water)

The physico-chemical parameters of the pond water from February to July 2014 are presented in Table 4.1. The temperature ranges from 27.58°C (July) and 32.97°C (May) and the average value was found to be 29.04°C. The pH values varied between 5.80 (May) and 9.17 (February) and the mean concentration recorded was 7.72. Generally the pH of the pond water tended to be alkaline in February, March, June and July except for April and May where the pH were acidic. The conductivity varied between 675.33 µf/cm (July) and 1855.83 µf/cm (May) and the average conductivity was found to be 680.50 µf/cm as shown in Table 4.1. The salinity of the pond ranges from 0.30% to 0.87 % and the mean salinity was found to be 0.44%. The dissolved oxygen values fluctuated between 0.80 mg/L (May) and 2.25 mg/L (June) and the mean concentration was 1.30 mg/L. Turbidity was found to vary between 14.00 NTU (July) and 64.33 NTU (May) and the average turbidity of the pond water was found to be 28.19 NTU. The total dissolved solid concentration in the pond water was found to vary between 309.00 mg/L (June) and 868.33 mg/L (May) and mean concentration was found to be 450.8.

Table 4.1: Physico-chemical parameters of the pond water (irrigation water)

Month	Temp. (°C)	pH	Conductivity (µf/cm)	Salinity (%)	D.O (mg/L)	Turbidity (NTU)	TDS (mg/L)
Feb	28.18	9.17	842.83	0.40	1.43	14.33	381.67
Mar	28.25	8.03	908.17	0.40	1.27	23.00	410.50
Apr	28.82	6.03	791.00	0.40	1.00	21.00	420.33
May	32.97	5.80	1855.83	0.87	0.80	64.33	868.33
Jun	28.42	8.59	680.50	0.30	2.25	32.50	309.00
Jul	27.58	8.72	675.33	0.30	1.03	14.00	311.83
Mean	29.04	7.72	958.94	0.44	1.30	28.19	450.28
SD	±1.968	±1.45	±448.72	±0.21	±0.52	±18.96	±210.28

4.2 Concentration of Heavy Metals (Zn, Cd, Mn, Cr and Pb) in the Water Samples

Monthly variation in the mean concentrations of each metal in the water samples from the pond are shown in Appendix II. As can be observed from Figure 4.1, Zn varied between 0mg/L (April and July) and 2.6 mg/L (May), Cd ranged from 0.02 mg/L (June) to 1.05 mg/L (April), Mn from 0.2 mg/L (July) to 1.58mg/L (April), Cr ranged from 0.95mg/L (February) to 7.26mg/L (May), Pb from 0.16mg/L (June) to 42.02mg/L (May).

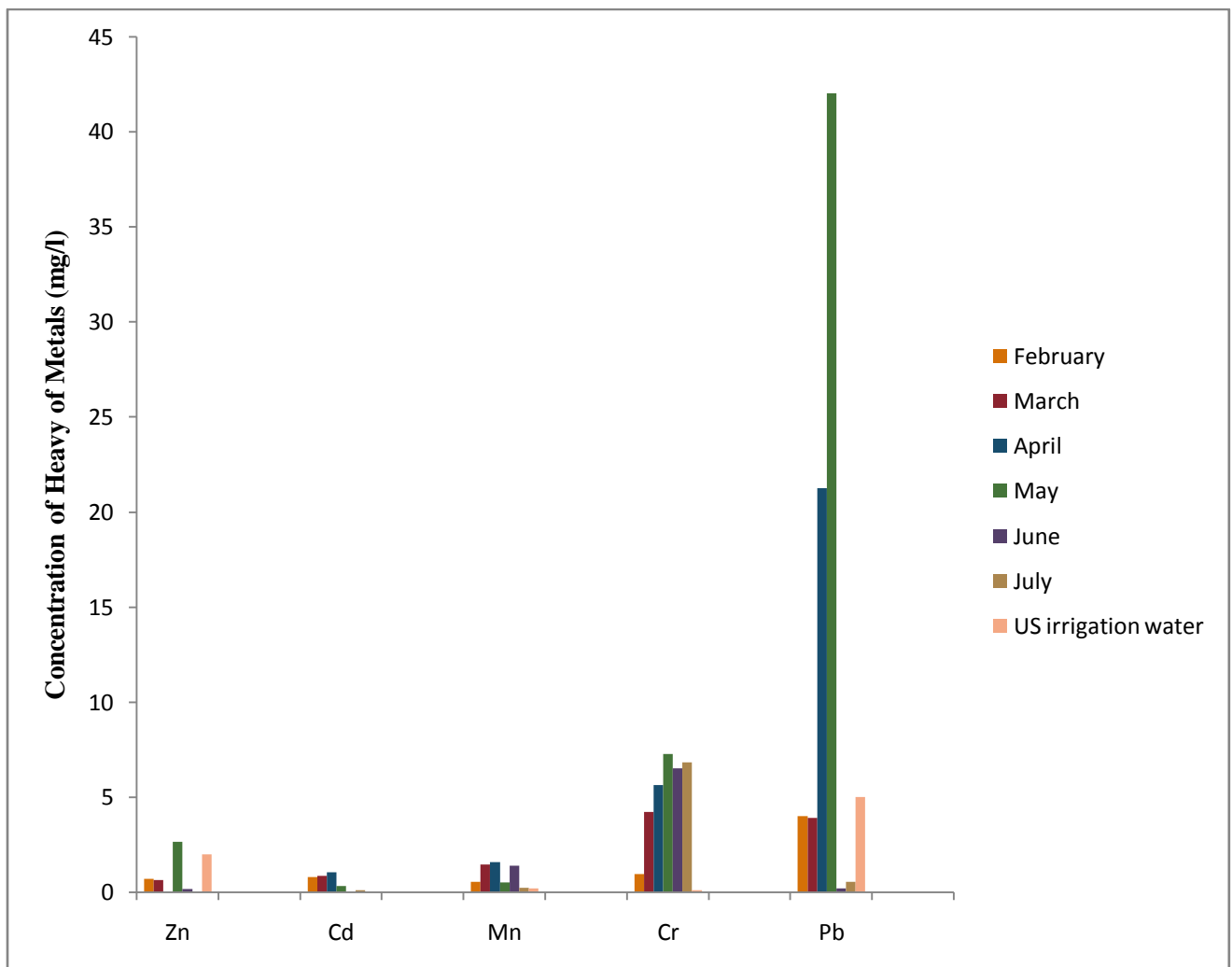


Figure 4.1: Concentrations of Heavy metals (mg/L) in the water samples

4.3 Correlation of Physico-chemical Parameters with the Concentration of Metals in the Pond Water Samples

The correlation coefficients of Physico-chemical parameters and heavy metal concentrations in the pond (irrigation) water are shown in Table 4.2. There was no positive correlation between most of the physico-chemical parameters and Cd except for pH (0.8) which implied that they are from the same point source. No correlation between Mn and all the physico-chemical parameters except for temperature which showed a weak negative correlation (-0.44), Cr showed weak negative correlation with pH (-0.55) and weak positive correlation with turbidity (0.53). Strong positive correlation was observed between Zn and salinity (0.97), Zn and turbidity (0.90) implying a close association between them.

Table 4.2 Correlation coefficients of physico-chemical parameters and heavy metal concentrations in the pond water

	PH	Temp.	Salinity	D.O	Turbidity
Cd	0.806	-0.484	-0.003	-0.359	-0.311
Zn	0.388	0.322	0.973	-0.432	0.903
Mn	0.039	-0.441	-0.278	0.371	-0.085
Cr	-0.554	-0.193	0.267	-0.148	0.53
Pb	0.525	-0.282	0.923	-0.622	0.813

4.4 Correlation Coefficients of Heavy Metals in the Water Samples

The correlation coefficients of the metal pairs in the pond water samples are shown in Table 4.3. Mn and Zn showed high positive correlation (0.95), Mn and Cr showed high positive correlation (0.76), Mn and Pb also showed high positive correlation (0.75). These high positive correlation values indicate that the metals are from the same source (i.e. pollution source). A significant Weak positive correlation between Zn/Cr (0.55) was observed, similar to that between Zn/Pb pair (0.57).

Table 4.3: Pearson Correlation Coefficients of Heavy Metals in the Water Samples

	Cd	Zn	Mn	Cr	Pb
Cd	1				
Zn	0.252	1			
Mn	0.129	0.950*	1		
Cr	-0.108	0.550**	0.763*	1	
Pb	-0.271	0.576**	0.753***	0.765**	1

*** Correlation is significant at 0.05 level (1 tailed)

** Correlation is significant at 0.001 level (1 tailed)

* Correlation is significant at 0.01 level (1 tailed)

4.5 Concentration of Heavy Metals in Soil Samples from Three Farmlands Irrigated with the Pond Water

The mean concentrations of Cd, Zn, Mn, Cr and Pb in soil samples from three farmlands irrigated with water from the pond are shown in Appendix III. As depicted in Figure 4.2 the mean concentrations of Cd in farm 1 ranged from 0.186mg/kg (May) to 4.207 mg/kg (February), in farm 2, it ranged from 0.137 mg/kg (July) to 5.052mg/kg (February), in farm 3, it ranged from 0.071mg/kg (July) to 3.680mg/kg (March). Zn in farm 1 varied between 6.686mg/kg (May) and 35.367mg/kg (February), in farm 2 it varied between 3.752mg/kg (June) and 17.339mg/kg (February), in farm 3 it varied between 3.263mg/kg (July) and 40.334mg/kg (March). Mn concentrations in farm 1 ranged from 75.636mg/kg (July) to 126.164mg/kg (February), in farm 2, it ranged from 69.334mg/kg (March) to 121.389mg/kg (May) while in farm 3, it ranged from 74.571mg/kg (July) to 109.767mg/kg (March). Average concentration of Cr in farm 1 ranged from 20.731mg/kg (April) to 28.906mg/kg (June), in farm 2, it ranged from 24.640mg/kg (February) to 33.633mg/kg (March) and in farm 3, it ranged from 16.852mg/kg (February) to 31.920mg/kg (March). Pb concentration in farm 1 varied between 7.550mg/kg (July) and 39.291mg/kg (March), in farm 2, it varied between 2.703mg/kg (July) and 27.710mg/kg (February), in farm 3, it varied from 2.362mg/kg (July) and 34.783mg/kg (March).

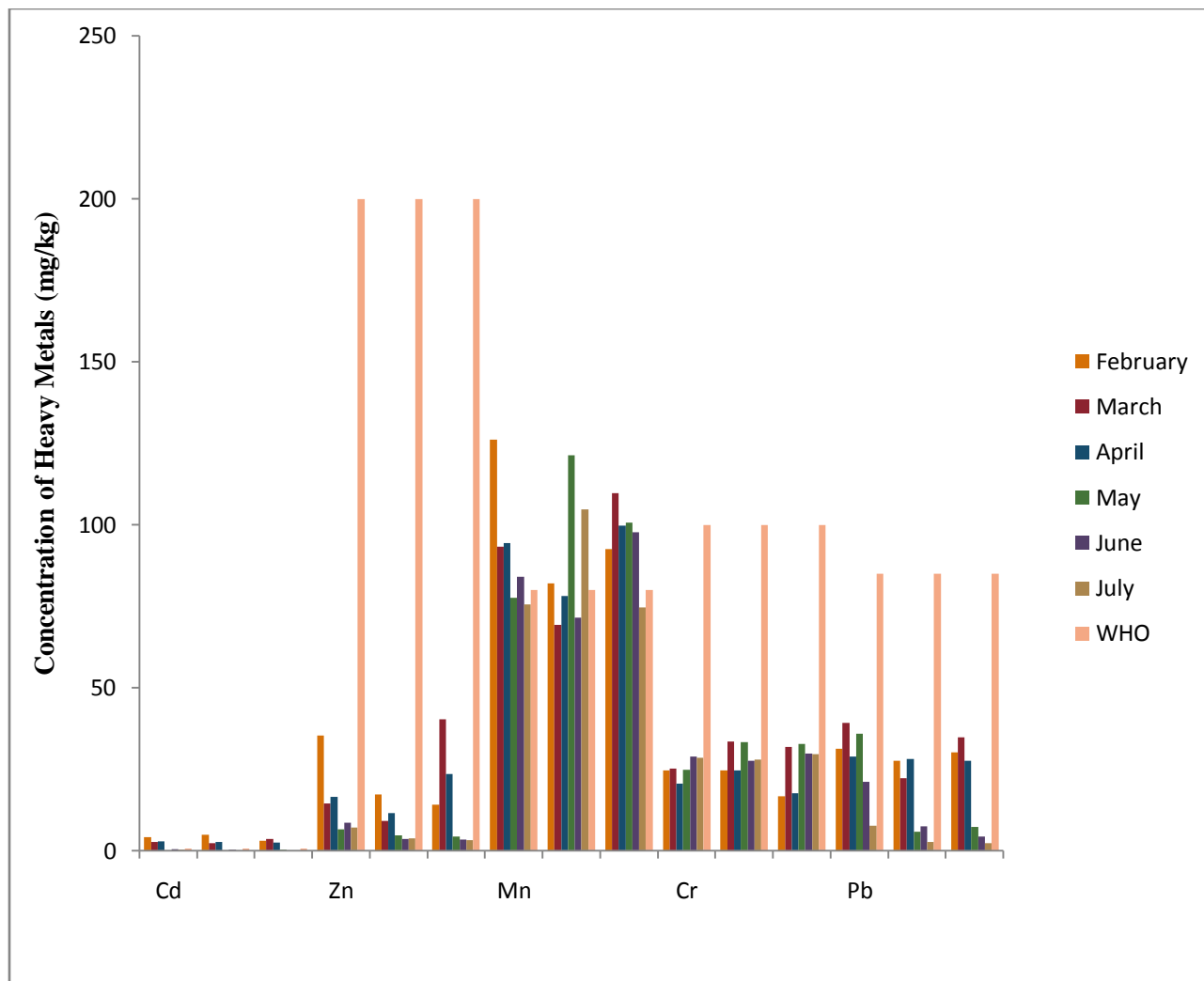


Figure 4.2: Concentrations of Cd, Zn, Mn, Cr and Pb in Soil Samples from three Farmlands Irrigated with Water from the Pond

4.6 Correlation Coefficients of Heavy Metals in the Soil Samples

The correlation coefficients of the metal pairs in the soil samples as presented in Table 4.4 showed a significant negative correlations between Mn/Cd (-0.982), Cr/Zn (-0.953), Pb/Cr (-0.838), Zn/Cd (-0.76), Cr/Mn (-0.679); positive correlations were also observed for Mn/Zn pair (0.87), Pb/Zn(0.63) and Cr/Cd (0.52).

Table 4.4: Pearson Correlation Coefficients of Heavy Metals in the Soil Samples

	Cd	Zn	Mn	Cr	Pb
Cd	1				
Zn	-0.760	1			
Mn	-0.982	0.870**	1		
Cr	0.527	-0.953	-0.679	1	
Pb	0.023	0.632**	0.168	-0.838	1

** Correlation is significant at 0.05 level (1 tailed)

4.7 Concentration of Heavy Metal in Spinach Samples Cultivated at the Farms

The concentrations of Cd, Zn, Mn, Cr and Pb in spinach plant irrigated with the water from the pond are shown in Appendix IV. As can be observed from Figure 4.3, the mean concentrations of Cd in farm 1 ranged from 0mg/kg (May) to 2.979 mg/kg (March), in farm 2, 0.055 mg/kg (June) to 3.323mg/kg (March) and in farm 3 it ranged from 0mg/kg (May) to 3.462mg/kg (April). Zn in farm 1 varied between 1.056mg/kg (July) and 56.359mg/kg (March), in farm 2 it varied between 1.933mg/kg (July) and 45.816mg/kg (March), in farm 3 it varied between 2.536mg/kg (May) and 43.406mg/kg (April). Mn concentrations in farm 1 ranged from 3.395mg/kg (May) to 47.534mg/kg (April), in farm 2, it ranged from 16.186mg/kg (June) to 62.395mg/kg (April), in farm 3, it ranged from 8.702mg/kg (May) to 41.023mg/kg (March). Average concentration of Cr in farm 1 ranged from 12.011mg/kg (February) to 26.342mg/kg (April), in farm 2, it ranged from 7.488mg/kg (February) to 26.342mg/kg (April), in farm 3, it ranged from 15.638mg/kg (July) to 24.695mg/kg (April). Pb concentrations in farm 1 varied between 1.809mg/kg (May) and 24.205mg/kg (April), in farm 2, it varied between 0 mg/kg (June) and 26.332mg/kg (March) while in farm 3, it varied from 1.673mg/kg (June) and 28.894mg/kg (April).

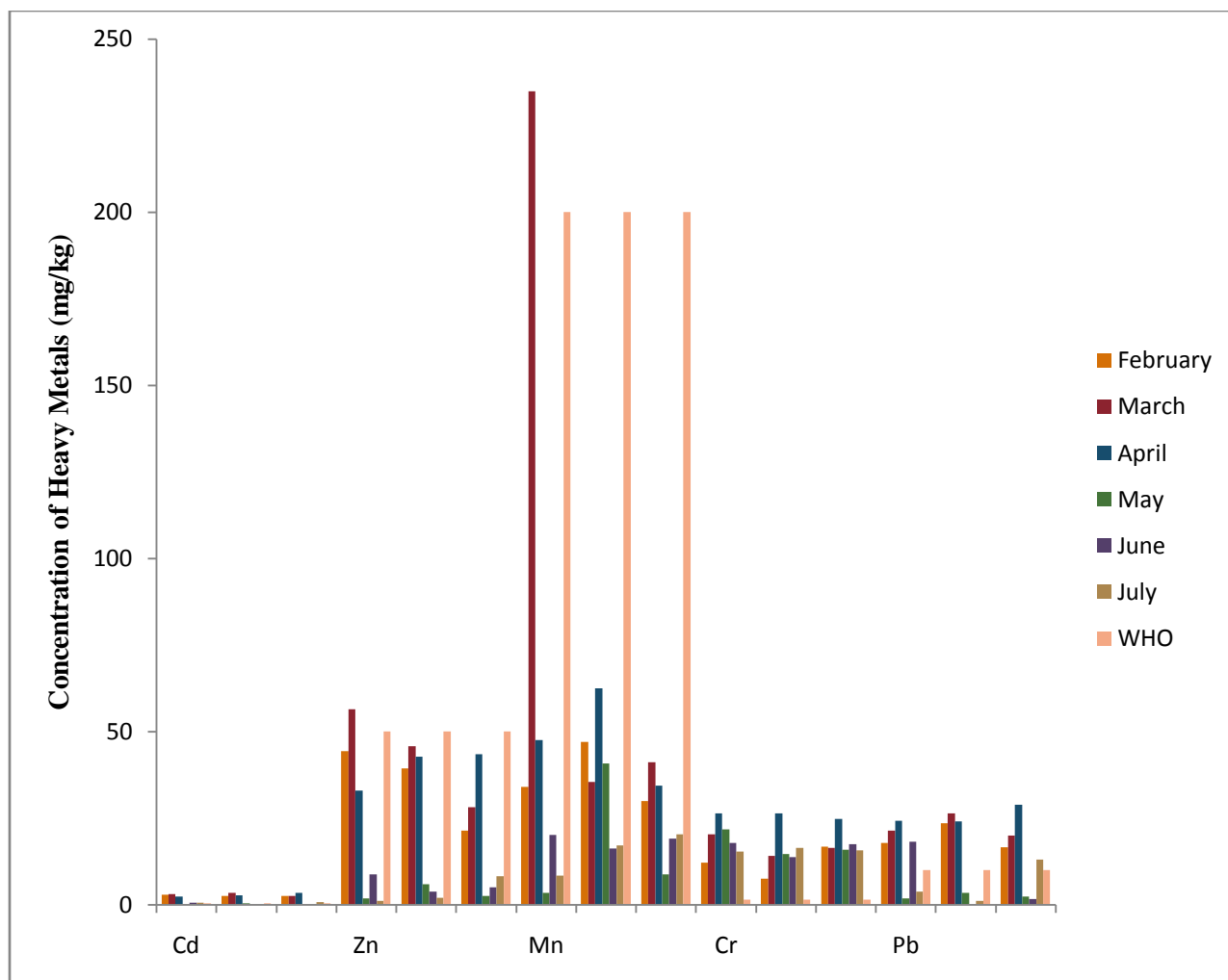


Figure 4.3: Concentrations of Cd, Zn, Mn, Cr and Pb in Spinach Samples from three Farmlands Irrigated with Water from the Pond

4.8 Correlation Coefficients of Heavy Metals in the Spinach Samples

The correlation coefficients of the metal pairs in the spinach samples are shown in Table 4.5. High positive correlations were observed between Mn/Cd (0.917), Mn/Zn (0.844) and Pb/Zn (0.726), strong negative correlations were also observed for Cr/Cd pair(-0.917), Pb/Cd (-0.944), Pb/Cr (0.734).

Table 4.5: Pearson Correlation Coefficients of Heavy Metals in the Spinach Samples

	Cd	Zn	Mn	Cr	Pb
Cd	1				
Zn	-0.457	1			
Mn	0.917**	0.844**	1		
Cr	-0.917	-0.065	0.480	1	
Pb	-0.944	0.726**	0.244	-0.734	1

** Correlation is significant at 0.01 level (1 tailed)

4.9 Soil/ Plant Metal Transfer Factor

The transfer factors of the metals from the soil in the three farms to the spinach plant are shown in Tables 4.6a, 4.6b and 4.6c. In farm 1 Pb has the lowest transfer factor which ranged from 0.050(May) to 0.855(June) while Zn has the highest which ranged from 0.151(July) to 3.867(March). At farm 2 Mn has the lowest metal transfer factor from 0.162(July) to 0.798(April)and Zn has the highest also which ranged from0.514 (July) to 4.932 (March). Whereas at farm 3 the lowest was Mn with 0.086 (May) to 0.374 (March) and Cd has the highest values ranging from 0 (May) to 10.352 (July).

Table 4.6(a) Soil/Spinach Metal Transfer Factor for Farm 1

Months	Transfer Factor				
	Cd	Zn	Mn	Cr	Pb
February	0.673	1.252	0.270	0.486	0.566
March	1.051	3.867	2.515	0.804	0.542
April	0.805	1.972	0.503	1.271	0.833
May	0	0.275	0.044	0.875	0.050
June	1.131	1.014	0.239	0.614	0.855
July	1.822	0.151	0.109	0.534	0.489
Mean	0.914±0.59	1.422±1.37	0.613±0.95	0.764±0.29	0.556±0.29

Table 4.6(b) Soil/Spinach Metal Transfer Factor for Farm 2

Month	Transfer Factor				
	Cd	Zn	Mn	Cr	Pb`
February	0.479	2.268	0.571	0.304	0.845
March	1.339	4.932	0.511	0.417	1.181
April	0.941	3.684	0.798	1.063	0.849
May	1.357	1.227	0.336	0.439	0.587
June	0.140	0.997	0.226	0.498	0
July	0.978	0.514	0.162	0.581	0.350
Mean	0.872±0.48	2.270±1.73	0.434±0.24	0.550±0.27	0.635±0.42

Table 4.6(c) Soil/Spinach Metal Transfer Factor for Farm 3

Month	Transfer Factor				
	Cd	Zn	Mn	Cr	Pb
February	0.803	1.492	0.323	0.990	0.544
March	0.680	0.698	0.374	0.512	0.572
April	1.317	1.843	0.343	1.393	1.047
May	0	0.581	0.086	0.484	0.315
June	0.268	1.412	0.195	0.588	0.385
July	10.352	2.506	0.272	0.530	5.464
Mean	2.237±4.00	1.422±0.72	0.266±0.11	0.749±0.37	1.388±2.01

CHAPTER FIVE

DISCUSSION

5.1 Physico-chemical Parameters and Levels of Heavy Metals in the Pond Water (Irrigation Water)

The mean temperature of the pond throughout the period of the research was 29.04°C with the highest recorded temperature of 32.97°C in the month of May and the least, 27.58°C, in the month of July (Table 4.1). Eneji *et al.*, (2014) reported similar values (29.8°C - 31.0°C) for river Mada Nasarawa Nigeria. Temperature influences the amount of dissolved oxygen in water, the higher the temperature the lower the dissolved oxygen content.

The pH range for the period was 5.80 in May to 9.17 in February with mean pH of 7.72. These values are slightly above the limits of 6.0-9.0 set by FAO (1985) for irrigation water; the values implies that the pond is alkaline in the months of February, March, June and July and acidic in April and May which may likely lead to the high concentration of the metals in the pond. This is higher than the pH of 6.81 reported by Aremu *et al.*, (2010) in the physico-chemical parameters of a pond from derelict udege mines of Nasarawa state, Nigeria. The pH is a function of the dissolved material in water and should be less than 8.5 (USEPA, 2002).

Conductivity range of 675.83µmhos/cm- 1855.83µmhos/cm observed falls within the permissible limits of 750 - 2250µmhos/cm (Camberato, 2001). The higher conductivity recorded from February – May (842.83 - 1855.83µmhos/cm) could be attributed to reduced water volume and high rate of evaporation during the period, while the relatively lower conductivity values (675.33 – 680.50µmhos/cm) might be due to water dilution. These values indicate high salinity level that

may require occasional application of low salinity water for leaching. Enejiet *al.*, (2014) reported lower values in river Mada Nasarawa Nigeria.

Salinity and dissolved oxygen levels ranges from 0.33% – 0.87% and 0.8mg/L – 2.25mg/L respectively over the period of the research with mean values of 0.44% and 1.30mg/L respectively. The dissolved oxygen range of 0.20 – 2.25mg/L recorded is lower than the recommended level of 7.5mg/l for irrigation water (National Guidelines and Standards for Water Quality in Nigeria, 1999). Oils and greases resulting from effluents from block moulding industries and Kaduna - Kano Road formed surface films on the water, thereby inhibiting the transfer of oxygen from the atmosphere to the water. This may have contributed immensely to the low value of dissolved oxygen in the pond. Report by Dike *et al.*, (2013) showed higher dissolved oxygen values (6.57mg/L– 6.63mg/L) in river Jakara Kano Nigeria.

Mean turbidity and total dissolved solids of 28.19NTU and 450.28 mg/L respectively have been observed. The total dissolved solid values observed were within the permissible range of 500 mg/L – 3500 mg/L for irrigation water in Nigeria (National Guidelines and Standards for Water Quality in Nigeria, 1999). The result is in agreement with the 899.00mg/L value reported by Aremu *etal.*, (2010) in a pond from derelict udege mines of Nasarawa state, Nigeria.

With the exception of the month of May, the concentration of Zinc in all the other months (February, March, April, June and July) were well below the 2.0mg/L permissible limit for irrigation water (USEPA, 2011). The high concentration of Zinc (2.62mg/L) recorded in May could have been due to increase in discharge from Maraba Clinic sources owing to massive influx of patients since the month coincided with the government hospitals strike.

Figure 4.1 showed that the concentrations of Cd (0.023 – 1.052mg/L) in all the months are above the 0.01mg/L acceptable limits for irrigation water (USEPA, 2011). The high level of Cd recorded in (February, March and April) might be due to concentration effects.

The concentrations of Mn (0.226 – 1.586mg/L) throughout the period of investigation are above the USEPA (2011) permissible limits of 0.20mg/L for irrigation water. This high concentration may be attributed to the increase waste water discharge from the hospital and block moulding industries nearby. Also, the concentrations of Cr (0.953 – 7.265mg/L) were higher than the 0.10mg/L allowable limits for irrigation water (USEPA, 2011). These high concentrations could be partly attributed to the increased activity at hospital during that period and partly to rainfall and run-off which cause erosion, thereby introducing into the pond soil, silt and even discarded metallic waste besides wastewater from drains nearby.

However, the concentrations of Pb (0.530 – 3.99mg/L) were lower than the 5.0mg/L acceptable limits for irrigation water (USEPA, 2011) in all the months except for the months of April (21.245mg/L) and May (42.02mg/L). Clean-up activities at the hollow block industry near the pond and increased activity at the hospital due to mass influx of patients caused by the strike embarked upon by medics during these periods could have been the reason behind the sharp rise in Pb concentration. There was strong positive correlation between Pb and all the physico-chemical parameters except for temperature which showed a weak negative correlation which implied that they are inter-related and might have emanated from the same source.

As shown in Figure 4.1, the ranges of concentration of metals in the pond water samples were Cd 0.023 - 1.052 (mean 0.53 ± 0.43), Mn 0.226 – 1.586 (mean 0.944 ± 0.59), Cr 0.953 - 7.265 (mean 5.22 ± 2.35), Zn BDL – 2.62 (mean 0.69 ± 0.99) and Pb 0.165 to 42.022 mg/L (mean

11.98 ± 16.66). Based on the result, the trend in metal concentration in the pond is Pb>Cr>M>Zn>Cd. The mean values of Zn, Mn, and Pb are much higher than those reported by Odoh and Kolawole (2011) as 0.0024, 0.0022 and 0.0010µg/ml respectively in irrigation water from river Benue within Makurdi Metropolis, Benue State Nigeria. Muhammad *et al.* (2011) reported a lower mean concentration of Cd (0.010mg/L) and Cr (0.122mg/L) in irrigation waste water. The high levels of these metals indicate that the pond water used on the farm lands around the pond for irrigation is polluted. Therefore, crops cultivated on those farms may be harmful for consumption.

Strong positive correlation coefficients were observed for the metal pairs Zn/Mn (r=0.950, at P<0.01), Cr/Pb (r=0.765, at P<0.001), Mn/Cr (r=0.763, at P<0.01), Mn/Pb (r=0.753 at P<0.05), Zn/Pb (r=0.576 at P<0.001) and Zn/Cr (r=0.550 at P<0.01). These high positive correlation values indicate the metals are likely from the same pollution source. Weak negative correlation coefficients was observed for Cd/Pb and Cd/Cr pairs with coefficients -0.271 and -0.1108 respectively while weak positive correlation was observed for Cd/Mn and Cd/Zn pairs with 0.129 and 0.252 respectively.

Positive linear correlation was observed between pH and Cd, Pb (0.806 and 0.554) while weak positive linear relationship was observed for pH/Zn and PH/Mn (0.30 and 0.039). Negative linear relationship was observed between pH and Cr metal concentration in the pond water, between temperature of the pond water and the concentrations of Cd, Mn, Cr and Pb (-0.484, -0.441, -0.193 and -0.282 respectively) while a positive linear relationship was observed between temperature and Zn metal concentration in the pond water as well as that between pond water salinity and Zn, Cr and Pb concentrations in the pond water (0.973, 0.267 and 0.923

respectively). A weak negative correlation was observed between the salinity of the pond water and Mn concentration (-0.278) and an almost zero correlation between salinity and Cd metal concentration. Strong negative correlation was observed between dissolved oxygen and Pb concentration (-0.622) while weak negative correlation values were observed between dissolved oxygen and Cd, Zn and Cr (-0.359, -0.432 and -0.148 respectively). A very strong positive linear relationship was observed between turbidity and Zn, Pb concentrations (0.903 and 0.813). This high positive correlation coefficient implies they are inter-related and are from the same source.

5.2 Levels of Heavy Metals in the Soil Samples

The results of heavy metals present in soils were shown in Figure 4.2. The results at farm 1 indicated that levels of heavy metals in soil was highest for Mn which ranged from 75.636 to 126.164 (91.914 ± 18.483), followed by Pb 7.550 to 39.291 (27.438 ± 11.543), Zn 6.686 to 35.367 (14.837 ± 10.866), Cr 20.731 to 28.906 (25.485 ± 2.992) and Cd 0.186 to 4.207 (1.807 ± 1.714).

At farm 2, the concentration of heavy metals in soil was highest for Mn which ranged from 69.334 to 121.389 (87.883 ± 20.697), followed by Cr 24.64 to 33.633 (28.694 ± 3.994), Pb 2.703 to 28.202 (15.710 ± 11.639), Zn 3.752 to 17.339 (8.433 ± 5.417) and Cd 0.137 to 5.052 (1.857 ± 1.961).

The concentration of heavy metals in soil at farm 3 was also highest for Mn which ranged from 74.571 to 109.767 (95.908 ± 11.835), followed by Zn 3.263 to 40.334 (14.887 ± 14.817), Pb 2.362 to 34.783 (17.791 ± 14.620), Cr 16.852 to 32.88 (26.458 ± 7.216) and Cd 0.071 to 3.680 (1.713 ± 1.630).

The concentrations of the metals in the soil samples from the three farmlands were generally of the order Mn>Cr>Pb>Zn>Cd except in farm 1 where the concentration of Pb was slightly higher than that of Cr. The concentrations of Cr, Pb and Zn were below the WHO/FAO (2005) recommended maximum limits of 100, 85 and 200mg/kg respectively. However, the concentrations of Mn (91.9mg/kg) and Cd (1.8mg/kg) were above the acceptable limits of 80 and 0.8 mg/kg respectively. Moreover, the concentrations of Zn, Mn and Cr all through the months were not significantly different from one another ($P>0.05$) while the concentration of Cd throughout the months of February, March and April were significantly higher than in the months of May, June and July ($P<0.001$), probably due to dilution effect of rainfall. Likewise, the concentrations of Pb were significantly the same all through the months ($P>0.05$) except in July when significant difference was observed ($P<0.05$).

The levels of Mn in the soil samples from the farms was within the range 69.334 – 126.164 mg/kg with a mean concentration of 91.90 ± 4.01 mg/kg, Cr 16.852 – 33.633 mg/kg, Pb 2.362 – 39.291 mg/kg with mean concentrations of 26.88 ± 1.65 mg/kg and 20.31 ± 6.26 mg/kg respectively. Zn and Cd were within ranges 3.263 – 40.334 and 0.071 – 5.052 mg/kg respectively with mean concentrations of 12.72 ± 3.71 and 1.79 ± 0.07 mg/kg. The high level of the metals in the soil samples compared to irrigation water indicates possible contributions from other anthropogenic sources which are likely vehicular emission and exhaust dust since all farms are situated by express highways; this could be the reason for the observed high concentration of the metals in the farms. High concentrations of heavy metals have been reported for soil samples from farm lands irrigated with polluted water (Olatunji *et al.*, 2013, Hariprasad and Dayananda, 2013 and Lente *et al.*, 2014) ,Dadi-Mamud *et al* (2012) reported high concentration of heavy

metals in soil samples around Makera drain in Kaduna, Nigeria, translating into high metal concentration in crops irrigated with water from the drain. Tsafe *et al* (2012) reported high levels of Mn (142.91), Zn (68.91), Pb (29.66), Cd (0.965) and Cr (16.73) mg/kg in soil and vegetable grown in Yargalma of Northern Nigeria. The high concentrations of Mn over other metals agree with report by Tsafe *et al* (2012) where Mn and Pb were found to be high in soils irrigated with polluted water.

Strong positive correlation coefficients of 0.87, 0.632 and 0.527 were observed for Zn/Mn, Zn/Pb and Cd/Cr pairs respectively indicating the metal pairs are related in a positive linear sense, while weak positive correlations were observed for Cd/Pb and Mn/Pb pairs (0.023 and 0.168) suggesting virtually no linear relation between the two metal pairs. However, Cd/Mn, Zn/Cr, Cr/Pb, Cd/Zn and Mn/Cr pairs had strong negative correlation coefficients of -0.982, -0.953, -0.838, -0.760 and -0.679 respectively, suggesting a strong negative linear relationship between the metal pairs which indicate the metals are very likely to have originated from the same pollution source. The result of the metal concentration in the soil further agrees with reports that farms irrigated with polluted water of any sort are very likely to accumulate the heavy metals from the polluted water and be made available for plant uptake (Sing *et al.*, 2010, Khan *et al.*, 2011 and Ashraf *et al.*, 2010).

5.3 Levels of the Metals in Edible Parts of Spinach

The level of the heavy metals present in spinach were shown in Figure 4.3. At farm 1, Mn has the highest concentration with values from 3.395 to 234.811 mg/kg (58.029 ± 88.131), followed by Zn 1.056 to 56.359 (24.210 ± 23.603), Cr 12.011 to 26.342 (18.891 ± 5.049), Pb 1.809 to 24.205 (14.496 ± 9.411) and Cd 0 to 2.979 (1.523 ± 1.329). The result showed the order of relative concentration as Mn > Zn > Cr > Pb > Cd.

Also, at farm 2 (Figure 4.3), the concentration of Mn was highest ranging from 16.186 to 62.395 (36.455 ± 17.847), followed by Zn 1.933 to 45.816 (23.255 ± 21.370), Cr 7.488 to 26.342 (15.428 ± 6.136), Pb 0 to 26.332 (13.012 ± 12.744) and Cd 0.055 to 3.323 (1.489 ± 1.471). The order of the metals contamination at farm 2 was Mn > Zn > Cr > Pb > Cd.

At farm 3 (Figure 4.3), Zn ranked highest with concentration range from 2.536 to 43.406 (18.096 ± 15.903), followed by Mn 8.702 to 41.023 (25.547 ± 11.737), Pb 1.673 to 28.894 (13.693 ± 10.503), Cr 15.638 to 24.695 (17.805 ± 3.441) and Cd 0 to 3.462 (1.555 ± 1.472). The order of availability of metals in different fractions followed the pattern Zn > Mn > Pb > Cr > Cd.

Mn was observed to have the highest concentration in the spinach samples from all the three farms cultivated with the polluted pond water. The concentrations of Mn was not significantly different all through the period of the research ($P > 0.05$). The concentrations of Cd, Cr and Pb were only significantly different in the months of May ($P < 0.001$) and April ($P < 0.01$, $P < 0.05$) respectively. The general trend of the metals in the spinach samples was observed to be Mn > Zn > Cr > Pb > Cd. This trend shows a high accumulation of these metals by the spinach plant. Cd metal had a concentration range of BDL – 3.462 mg/kg in the spinach samples from the three

farms with a mean of about 1.52 ± 0.03 mg/kg, Zn had a range 1.056 – 56.359 mg/kg with a mean concentration of 21.853 ± 3.29 mg/kg. Mn, Cr and Pb had concentration ranges of 3.395 – 234.811, 7.488- 26.342 and BDL – 28.894 mg/kg respectively with mean values of 40.01 ± 16.53 , 17.375 ± 1.77 , 13.734 ± 0.74 mg/kg respectively.

The mean concentrations of all the metals except Zn and Mn were higher than the WHO/FAO permissible limits of 0.3, 50, 200, 1.50 and 10 mg/kg for Cd, Zn, Mn, Cr and Pb in vegetables respectively, (WHO/FAO, 2005), high positive correlations were observed between Mn/Cd (0.917), Mn/Zn (0.844) and Pb/Zn (0.726), These high correlation values indicate that the availability of the metals are related and the metals are likely to have the same pollution source. Uwah *et al.* (2011) reported equally high levels of Cd ($0.34\mu\text{gg}^{-1}$), Mn($11.75\mu\text{gg}^{-1}$), Pb($4.67\mu\text{gg}^{-1}$) and Zn ($6.35\mu\text{gg}^{-1}$) in spinach samples cultivated (irrigated) with polluted water. Spinach has been reported to have a high uptake of heavy metals from polluted soils (Akan *et al.*, 2013 and Sani *et al.*, 2011). Cd concentration (3.462 mg/kg) compares well with the 3.2 mg/kg value reported by Lone *et al.*, (2003) for spinach irrigated with sewage water. In the months of February, March and April, concentration of metals (Cr.>Pb>Cd) in the spinach vegetable are higher than the WHO permissible limits, this implies that consumption over time might present problems as the tendency for the soil to accumulate and transfer metals to the spinach cultivated increases. And so does the continuous consumption since the metals can also be accumulated in the human body over a long period of time. The high concentrations might be due to concentration effect, atmospheric deposition from urban and agricultural areas and also the use of fertilizers and metal based pesticides in agriculture.

5.4 Transfer Factors of Metals from Soil to Spinach

Transfer factor of the metals from the soil to the spinach plant as can be seen in Tables 4.6a, b, c show farm 1 to have an order Zn (1.42) >Cd (0.91) >Cr (0.76) >Mn (0.61) >Pb (0.55) while orders of Zn (2.27) >Cd (0.87) >Pb (0.63) >Cr (0.55) >Mn (0.43) and Cd (2.23) >Zn (1.42) >Pb (1.38) >Cr (0.73) >Mn (0.26) were observed for farms 2 and 3 respectively. It was observed that Zn and Cd had high transfer factors implying a high mobility of the metals from the soil to the plant while Mn and Cr generally had low transfer factors in the three farms. The pattern of transfer of the metals from soil to the plant can be very useful in bio-monitoring of heavy metal contamination of soil, it also helps in choosing the right bio-index for assessing the accumulation of the metals. Similar transfer factors of Cu (1.03) > Ni (0.96) > Mn (0.85) > Zn (0.67) >Pb (0.58) > Cd (0.50) > Fe (0.48) were reported by Singh *et al.*, (2010) in accumulation and translocation of heavy metals in soil and plants from fly ash contaminated area in India.

CHAPTER SIX

SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

Levels of Cd, Zn, Mn, Cr and Pb were investigated in spinach plant irrigated with pond water using Atomic Absorption Spectroscopy. The physico-chemical parameters and the levels of the metals in the pond water samples were analyzed also. The temperature, salinity, conductivity and dissolved oxygen of the pond water were within permissible limits; however, the pH was slightly above the permissible limit which leads to the high concentration of the metals in the pond. The values of 0.53, 0.94 and 5.22mg/L for Cd, Mn and Cr respectively (all through the months) in the pond water were higher than the US permissible limits for irrigation water (0.01, 0.2 and 0.1mg/L respectively), while the levels of Zn was higher in the month of May only and Pb was higher in the months of May and April. The trend in metal concentration in the pond water is $Pb > Cr > Mn > Zn > Cd$. The high levels of these metals is a clear indication that the pond water used on farm lands around the pond for irrigation is polluted and crops cultivated on those farms may be harmful for human consumption. The high levels of these metals in the pond water is likely due to waste water discharge from a clinic nearby. A similar report was been made (Sunday and Agbaji, 2012). A block moulding industry whose source of water is the pond where and all washings of tools and equipment is done in the pond is a possible source of the metals. Runoffs from the farmlands and a dumpsite close to the pond may have also significantly contributed to these metals which is in agreement with earlier reports (Suhendan *et al.*, 2010; Tulay, 2010).

The concentrations of the metals in the soil samples from the three farmlands were generally of the order Mn>Cr>Pb>Zn>Cd and the mean concentrations of Cr (26.8mg/kg), Pb (20.3mg/kg) and Zn (12.7mg/kg) were below the WHO/FAO recommended maximum limits of 100, 85 and 200mg/kg respectively except for Mn(91.9mg/kg) and Cd(1.7mg/kg) with allowable limits of 80 and 0.8mg/kg. The general trend of the metals in the spinach samples was observed to be Mn>Zn>Cr>Pb>Cd, the mean concentrations of Cd(1.52mg/kg), Cr (17.37mg/kg) and Pb (13.73mg/kg) were higher than the WHO/FAO allowable limits of 0.30mg/kg, 1.50mg/kg and 10.0mg/kg for Cd, Cr and Pb respectively. These high concentrations might be due to concentration effect, atmospheric deposition from urban and agricultural areas and also the use of fertilizers and metal based pesticides in agriculture.

On the other hand, the mean concentrations of Zn (21.8mg/kg) and Mn (40.0mg/kg) were below the WHO permissible limits (50.0, 200.0mg/kg). Transfer factor of the metals from the soil to the spinach plant in farm 1 followed the order Zn>Cd>Cr>Mn>Pb while orders of Zn>Cd>Pb>Cr>Mn and Cd>Zn>Pb>Cr>Mn were observed for farms 2 and 3 respectively. Since the metals in the spinach were higher than permissible limits, consumption over time might present problems as the tendency for the soil to accumulate and transfer metals to the spinach cultivated increases which will subsequently get to man through the food chain.

6.2 Conclusion

The following conclusions were arrived at based on this research:

- (i) The Water, spinach and soils contained variable levels of heavy metals (Cr, Cd, Mn, Pb and Zn).

(ii) Agronomic practices such as application of fertilizers and use of waste water can affect bioavailability and crop accumulations of heavy metals.

(iii) Consumption of these vegetables as food may constitute possible health hazards to humans at the time of the study.

(iv) The results obtained in this study would go a long way in providing a baseline data for the assessment of the distribution of these metals in spinach grown in the surrounding of Kwari pond Kwangila, Zaria.

(v) Since in this research the mean concentrations of most metals were above the WHO permissible thresholds, they pose serious health threat as consumption over time could accumulate the metals in the human body. Consumers of vegetables irrigated with polluted water are at a very high risk of poisoning by these toxic metals over time.

6.3 Recommendation

(i) As much as possible, polluted water should be avoided for use as irrigation water. Where necessary, some form of treatment could be introduced before being used for irrigation.

(ii) Continuous monitoring is very important to ascertain the safety of consumption of such irrigated crops.

(iii) Farmers should be educated on the problems associated with excessive usage of fertilizers and other chemicals, as well as irrigating the crops with waste polluted water and the need to grow crops with safe levels of heavy metals and the adverse health implications in consuming polluted crops.

(iv) Consumers of the spinach and other crops cultivated via irrigation with polluted water should be monitored to assess the bioaccumulation of the metals in their body over time.

(v) Fish and sediment should be analyzed for heavy metals.

(vi) Occasional application of low salinity water is required for leaching

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APPENDICES

Appendix I

List of Reagents and Equipment

Reagents (all reagents are analytical grade)

1. Conc. Nitric acid
2. Perchloric acid
3. Distilled water
4. Conc. Hydrochloric acid

Equipments

1. soil auger
2. plastic container
3. Whatman Filter paper no. 42 grades
4. Pipette
5. Glass rod
6. Hot plate
7. Thermometer
8. Analytical balance
9. Oven
10. Atomic Absorption Spectrometer
11. Beaker – 50ml, 100ml
12. Conical flask – 50ml, 100ml, 250ml
13. Funnel

14. Hot plate
15. Masking tape
16. Measuring cylinder – 5ml, 10ml, 100ml
17. Polyethylene tubes
18. Pyrex flask
19. Spatula
20. Volumetric flask – 10ml, 50ml, 100ml
21. Wash Bottles

Appendix II

Table 4.2: Concentrations of the metals in the water samples

Metals	Concentration of the metals (mg/l)						
	February	March	April	May	June	July	US irrigation water
Zn	0.696	0.634	BDL	2.625	0.157	BDL	2.000
	±0.430	±0.259	0	±1.379	±0.064	0	
Cd	0.794	0.863	1.052	0.317	0.023	0.109	0.010
	±0.298	±0.043	±0.069	±0.276	±0.016	±0.063	
Mn	0.520	1.432	1.586	0.513	1.387	0.226	0.200
	±0.499	±0.521	±1.151	±0.757	±2.781	±0.168	
Cr	0.953	4.202	5.613	7.265	6.485	6.813	0.100
	±0.147	±2.867	±1.826	±10.848	±1.966	±2.115	
Pb	3.999	3.906	21.245	42.021	0.165	0.530	5.000
	±1.991	±0.849	±38.470	±93.984	±0.086	±0.333	

Appendix III

Table 4.5: Concentrations of Cd, Zn, Mn, Cr and Pb in Soil Samples from three Farmlands Irrigated with Water from the Pond

METALS CONC. OF HEAVY METALS (mg/kg)								
	Farms	February	March	April	May	June	July	WHO
Cd	1	4.207	2.835	2.863	0.186	0.512	0.241	0.8
	2	5.052	2.482	2.830	0.249	0.393	0.137	
	3	3.187	3.680	2.628	0.444	0.265	0.071	
Zn	1	35.367	14.573	16.686	6.686	8.697	7.014	200
	2	17.339	9.289	11.611	4.845	3.752	3.763	
	3	14.279	40.334	23.551	4.363	3.533	3.263	
Mn	1	126.164	93.378	94.449	77.766	84.088	75.636	80
	2	82.192	69.334	78.195	121.389	71.530	104.659	
	3	92.668	109.767	99.873	100.697	97.873	74.571	
Cr	1	24.695	25.203	20.731	24.831	28.906	28.541	100
	2	24.640	33.633	24.776	33.397	27.688	28.029	
	3	16.852	31.920	17.730	32.880	29.841	29.523	
Pb	1	31.380	39.291	29.042	36.063	21.303	7.550	85
	2	27.710	22.297	28.202	5.841	7.509	2.703	
	3	30.283	34.783	27.608	7.366	4.346	2.362	

Farm 1: Before Maraba Clinic, Farm 2: After Maraba Clinic and Farm 3: Near A B C Block Moulding Industry.

Appendix IV

Table 4.7: Concentrations of Cd, Zn, Mn, Cr and Pb in Spinach Samples from three Farmlands Irrigated with Water from the Pond

Metal	CONC. OF HEAVY METALS (mg/kg)							
	Farms	February	March	April	May	June	July	WHO
Cd	1	2.832	2.979	2.306	BDL	0.579	0.439	0.3
	2	2.418	3.323	2.663	0.338	0.055	0.134	
	3	2.558	2.504	3.462	BDL	0.071	0.735	
Zn	1	44.280	56.359	32.908	1.836	8.819	1.056	50
	2	39.324	45.816	42.774	5.945	3.740	1.933	
	3	21.309	28.157	43.406	2.536	4.989	8.176	
Mn	1	34.040	234.811	47.534	3.395	20.135	8.258	200
	2	46.911	35.451	62.395	40.812	16.186	16.973	
	3	29.961	41.023	34.268	8.702	19.060	20.266	
Cr	1	12.011	20.264	26.342	21.734	17.756	15.239	1.5
	2	7.488	14.010	26.342	14.649	13.785	16.296	
	3	16.687	16.345	24.695	15.910	17.553	15.638	
Pb	1	17.746	21.307	24.205	1.809	18.218	3.690	10
	2	23.414	26.332	23.949	3.429	BDL	0.945	
	3	16.470	19.890	28.894	2.321	1.673	12.907	

Farm 1: Before Maraba Clinic, Farm 2: After Maraba Clinic and Farm 3: Near A B C Block Moulding Industry