HEAVY METALS IN SOIL AND VEGETABLES OF ALLOTMENT GARDENS IN THE CAPE TOWN ENVIRONMENT

BY

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DECLARATION

I, Motuli Kweza, declare that the contents of this dissertation/ thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

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ABSTRACT

This study investigated the concentration of selected heavy metals in soil, water and vegetable crops from selected allotment gardens in Cape Town. Heavy metals occur naturally in the earth's crust, but due to human activities, their biochemical balance and geochemical cycles have been altered. Heavy metals are abundant in air, soil and water due to environmental pollution. It was therefore of interest to conduct this study to determine the levels of heavy metals (Pb, Cd, Mn, Zn, Cr, Cu, Ni, Fe and Co) in soil, water and vegetables such as spinach, cabbages, green peppers, brinjals and leek onions. Soil, water and vegetables were sampled during winter and summer from the allotment gardens of Cape Town environment and were analyzed using Inductively Coupled Plasma (ICP).

The physicochemical parameters of soil and water were determined during both seasons. The average pH of water in winter was 6.53 ± 0.6, while the summer pH was 6.71 ± 0.7. The average soil pH was 6.58 ± 0.2 in winter, while in summer the soil pH was 6.60 ± 0.2. The soil organic matter ranged from 1.7 % to 13.5 % in both seasons.

The heavy metals in water and soil showed seasonal fluctuation ($p < 0.05$). In summer the concentrations in water ranged from 0.062 mg/L to 0.947 mg/L, while in winter it ranged from 0.002 mg/L to 2.347 mg/L. The soil heavy metal concentrations in summer ranged from 0.52 mg/kg to 1127.41 mg/kg, while in winter it ranged from 0.59 mg/kg to 1209.95 mg/kg, Fe having the highest concentrations for both seasons.

The heavy metal concentration in vegetables was generally higher in summer than in winter, although Fe was still the highest in both winter and summer. Fe was particularly high in spinach with a concentration of 144.28 mg/kg in summer, while in winter the concentration was 116.56 mg/kg, followed by leek onion and cabbage.

The results for water and soil showed a decrease and weak correlation with a decreasing order Fe > Cu > Cr > Ni > Pb > Co > Zn > Mn > Cd > and Fe > Zn > Mn > Cu > Pb > Cr > Ni > Co > Cd, respectively. The distribution sequence of the heavy metals in vegetables during winter is in the order; spinach (Fe > Zn > Cr > Mn > Cu > Co> Cd ≥ Pb ≥ Ni); cabbage (Fe > Mn > Cr > Zn > Cu >

Co > Cd ≥ Pb ≥ Ni) and leek onion (Fe > Zn > Mn > Cr ≥ Co > Cu > Cd ≥ Pb ≥ Ni). The corresponding sequence during summer was; spinach (Fe > Zn > Mn > Co > Cr > Cu > Cd ≥ Pb ≥ Ni); cabbage (Fe > Mn > Cr > Zn > Pb > Co > Cu > Cd ≥ Ni) and leek onion (Zn > Fe > Pb ≥ Mn > Cr > Co > Cu > Cd ≥ Ni); brinjal (Fe > Mn > Zn > Cr > Cu > Co > Cd ≥ Pb ≥ Ni) and green peppers (Fe > Zn > Mn > Co > Cu > Cr > Cd ≥ Pb ≥ Ni).

Results showed that concentration levels of all the selected heavy metals were below the permissible limits in soil, water and vegetables set by WHO.

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ABBREVIATIONS

ANOVA : Analysis of variance

AR : Analytical reagent

CCME : Canadian Council of Ministers of the Environment

CSA : Community Supported Agriculture

EMR : Electromagnetic radiation

EU : European Union

FAO : Food and Agriculture Organization

ICP-OES : Inductively coupled plasma- optical emission spectrometry

JCFA : Joint committee on food additives

MAC : Maximum allowed concentration

MCL : Maximum contamination levels

MCLG : Maximum contamination level goals

OM : Organic matter

PCA : Principal component analysis

PTFE : Polytetrafluoroethylene

SAS : Statistical analysis system

SABS : South African Bureau of Standards

SCAGA : Siyazama Community Allotments Garden Association

TT : Treatment technique

WHO : World Health Organization

XRF : X-ray fluorescence

CHAPTER ONE

INTRODUCTION

1.1   Background

Heavy metals are those elements with relatively high atomic numbers, atomic weights and densities > 4.0 g.dm^{-3}. They are naturally present at very low concentrations in the environment, while their levels are exacerbated by release from many different sources. Airborne metal particulates do not remain for long in the atmosphere, hence they are superficially deposited on the plants and soil surfaces, from where they are sorbed, or horizontally/vertically leached, or taken up in soil solution by plants and distributed into different plant tissues.

Heavy metal pollution is a universal issue, although severity and levels of pollution differ from place to place. Heavy metals are not degradable; hence, they have tendency to persist and accumulate in different environmental compartments. Many heavy metals are toxic, and about 20 of them are emitted into the environment at concentrations that may pose great risks to humans and the environment. Elements such as Hg, Cd, Pb, and As have no known benefits and their accumulation over time can cause harmful consequences such as serious illness and early death (Okem et al., 2012), while some referred to as essential minerals are needed for proper metabolism and enzyme function (Schwalfenberg and Genius, 2015). Exposure to certain concentration levels of elements such as Cu, Zn, and Fe have been reported to be dangerous and harmful (Martin and Griswold, 2009; Khaled and Muhammad, 2016). For example, high concentration of toxic metals in plant tissues can have damaging effects on the plants, and where they are stored in food plants, they pose a health hazard to man and animals (Muchie and Akpor, 2010). Alloway (1995) reported that anthropogenic activities, such as agriculture and industry, tend to release heavy metals that cause soil degradation, water contamination and exposure to synthetic products. Industries are a major anthropogenic source of heavy metals. Emissions from stack towers in industries release particulate heavy metals into the atmosphere and this becomes potential sources of water and soil pollution via dry or wet deposition.

Industrial wastewater containing heavy metals and other organic contaminants is also discharged into municipal drains, fresh water, surface water and other drainage systems. Other sources of

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heavy metals into the environment include use of manure and fertilizers on soil, exhaust fumes from automobile and internal combustion engines (burning of fossil fuel and wood), corrosion products (tyres and metal components), etc. (Okem et al., 2012).

Heavy metals may be present in agricultural soil at a level of abundance due to the use of different phosphate fertilizers, organic matter, pesticides and animal residue for soil amendment. The use of wastewater and sewage sludge for irrigation can also increase the amount of heavy metals in agricultural soil (Muchie and Akpor, 2010). Soil therefore acts as a natural receiving sink for heavy metals especially because of its ability to bind various chemicals. These chemical substances are present in distinct forms in soils and kept bonded to soil particles by different forces. An understanding of these correlations is very important because uptake and toxicities of metals depend on the form in which they subsist in the environment. Soil equilibrium may change due to environmental factors caused by climate change, and soil variability. These changes can result in leaching of toxic heavy metals that are loosely or tightly bound to soil particles (Dube et al., 2001; Rajib et al., 2016).

1.2   Problem statement

Plants take up heavy metals either by absorbing air-borne particulates deposited on surface parts of plants exposed to metal-contaminated air or from soil of a polluted environment. The presence of heavy metals in soils can also result in plants growing on such contaminated soils to take up these heavy metals, with the possibility of magnifying to higher concentrations. This bio-magnification may be detrimental to the plants and humans or animals through heterotrophic transfer. These elements can also be trans-located from soil to other environmental matrices where they may cause harm.

Although the maximum concentrations of heavy metals that may occur in plants may not be directly related to the sources of contamination, it is generally assumed that direct uptake of metals from soils around plant roots or aerial deposition of metal particles on leaves and other external plant tissues contribute to heavy metals load in plants. Heavy metals such as Pb, Cd, Ni, and Zn amongst others may accumulate in vegetables through contaminated resources such as

soil, water and crops. The consumption of such foods by living organisms can result in detrimental consequences on the health of living organisms.

Previous studies also revealed the detection of heavy metals in the tissues of plants growing on soil adjacent to roads suggesting that plants could be contaminated by heavy metals as a result of traffic and during long-term road service. Findings from heavy metal studies conducted around industrial sites and agricultural lands in urban metropolis or cities revealed contamination due to well-known sources such as the burning of fossil fuels, traffic and use of fertilizers in agricultural lands.

Less attention has been paid to the accumulation of heavy metals in home gardens, schools, rural areas and small gardens, where many people sustain their lives for both economic benefits and family subsistence. In some of the gardens, fertilizers may pose the risk of containing heavy metals. Meerkotter reported the detection of heavy metals, Cd, Cu, Pb, Mn, Ni, Cr, Fe, Co and Zn at elevated concentrations in soil, water and vegetables in the formal Philippi Horticultural area and Kraaifontein agricultural areas of Cape Town in excess of the limits set by South African regulations and guidelines.

Due to the scarcity of information, this study was intended therefore to investigate the occurrence levels and distribution patterns of heavy metals in allotment gardens within the vicinities of selected schools and communities around informal settlements in the Cape Town environment. This is in order to collect information about general forms of practices in informal agriculture and to raise awareness amongst the farmers of these farming areas, with regard to heavy metal pollution and the cycling of heavy metals in backyard soils used for informal agricultural purposes.

1.3   Objectives of study

- To determine the physicochemical parameters of water and soil in the sampling area.
- To determine the concentration of selected heavy metals in the soil, water and vegetables from the allotment gardens of Cape Town.

- To investigate the spatial distribution of heavy metals in surface soils of the allotment gardens.
- To identify crops that are posing a health risk by means of comparing the determined results to the allowed limits and the possible effect of heavy metals on the environment.

1.4   Research questions

- Is there any significant difference between summer and winter concentration levels and accumulation of heavy metals on soil, water and vegetable crops?
- Is there any evidence that the physicochemical parameters have an influence on metal concentration in the soil and vegetable crops?
- What is the spatial distribution of heavy metals between the various sites?
- How do the heavy metal concentrations in soils, water and vegetable crops relate to the permissible limits?

CHAPTER TWO
LITERATURE REVIEW

2.1   Sources and distribution of heavy metals in the environment

Heavy metals occur naturally in the earth's crust, but due to human activities, their chemical balance and geochemical cycles have been altered. The abundant existence of heavy metals in different environmental matrices and compartments such as air, soil and water is a result of anthropogenic release, leading to contamination or pollution of the media (Suruchi and Khanna, 2011). Natural sources of heavy metals include earthquakes, magma degassing, volcanic activities etc., while typical anthropogenic sources include; traffic (gas exhaust), intensive agriculture, manure, mining, corrosion products (tyres and metal components), leaching of metal ions from the soil into lakes and rivers by acid rain, fertilizers (inorganic), combustion of fossil fuels, municipal wastewater, treatment plants, and manufacturing industries (Koldabadi et al., 2012; Khaled and Muhammad, 2016).

Mining presents two pathways of input i.e. solid waste containing impurities of toxic elements such as arsenic, copper, lead, cadmium, cobalt, chromium, nickel, or titanium from metal ores, and mine tailings and slag (Prabhakaran et al., 2016). Due to the utilization of solid waste and slag for landfill and construction, farming and forestry and roads, the contamination of soil with these materials cannot be avoided. Once in soils, metals are primarily accumulated by a different mechanism of binding including (i) binding to organic matter and sulfides (ii) binding to reducible phases (iii) binding to carbonate phases and (iv) detrital or lattice metals. Heavy metals present in these categories have different remobilization behaviour under changing environmental conditions (Zhi-gang et al., 2014).
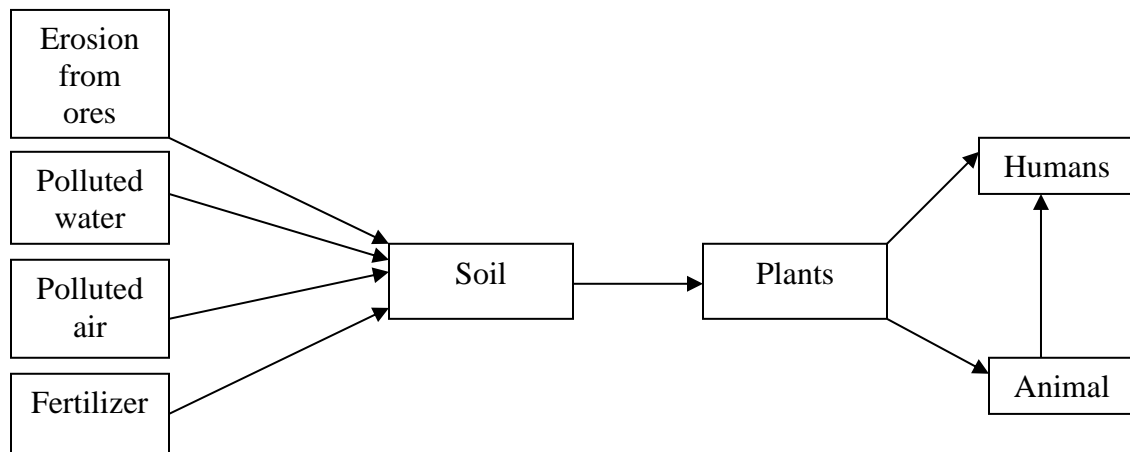
Figure 2.1: Sources and translocation of heavy metals

The bioavailability and remobilization behaviour of the heavy metals in the environment is directly influenced by the geochemical forms of the heavy metals in soil which affects their solubility (Zhi-gang et al., 2014; Prabhakaran et al., 2016). Hence, metals can be transported either as an integral part of fluvial suspended sediments or dissolved species in soil water. They may also be stored in soils or volatilized to the atmosphere. Organisms take up toxic heavy metals; with the metals dissolved in water having the greatest potential of causing the most deleterious effects.

The main concerns about the occurrence of elevated concentrations of heavy metals in soil are the contamination of agricultural soil and that of water resources (Suruchi and Khanna, 2011). This is because soils are the primary sources of nutrients and minerals to plants, especially vegetables and other food crops. Heavy metals, unlike organic pollutants, are not biodegradable; Plants do not have the ability to discriminate metals, although they have been reported to show different tolerance for different metals. Hence, there is a tendency for these metals to accumulate in soil or bio-accumulate in plants in excessive amounts (Ayeni et al., 2010; Wuana and Okieimen, 2011). The consumption of vegetables or food crops with elevated concentrations of accumulated heavy metals could result in detrimental effects on the health of consumers in the long run (Sheldon, 2005; Street, 2012).
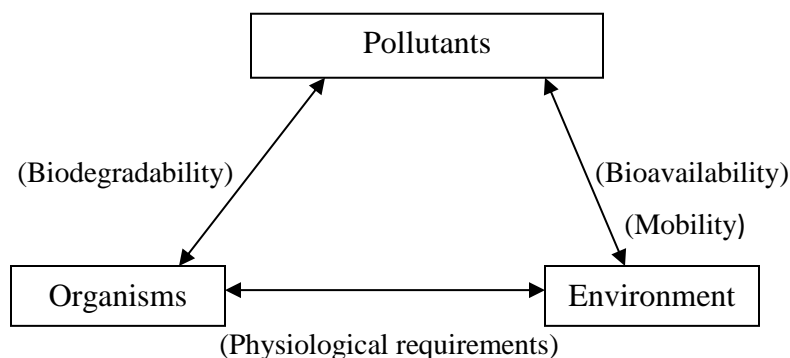
Figure 2.2: Exposure of human to chemical substances

The route of exposure of human to chemical substances occurs in three main ways (WHO, 1995; Jaishankar et al., 2015) namely: inhalation; ingestion and through contact with the skin. Food and drinking water intake are the major sources of exposure of biota and the general population to most chemical substances. These substances accumulate or contaminate vegetables by many routes, with some contaminating it directly while others are during preparation or processing. Others pass via heterotrophic routes from soil to plants and from herbivorous animals to milk or meat (Kienzler et al., 2016).

2.2   Accumulation of heavy metals

The presence and accumulation of heavy metals in soils are dependent on a variety of factors, including soil pH, soil conductivity, heavy metal solubility, etc. Chemical substances enter humans and the environment through complex and inter-related pathways. For example, fertilizers and pesticides enter the environment as a result of direct application (Jung, 2008; Khaled and Muhammad, 2016), while substances such as trace metals and polycyclic aromatic hydrocarbons may result from combustion processes (Saeedi et al., 2012). Waste water/effluent flow is another source of chemical substances released from industries and manufacturing processes that generate unwanted by-products, with air and water-borne wastes that are sometimes more toxic than the raw materials (Abdel-Raouf et al., 2012; Staszewski et al., 2015).

Heavy metals are not degradable; hence, they tend to persist long in soil especially where they are tightly bonded to soil. Soil rich in clay content has been reported to have very high retention capacities for heavy metals, while crystalline sandy soils have the least retention capacity (Silveira et al., 2003; Chibuike and Obiora, 2014). As a consequence, they tend to accumulate with continuous reception and low climatic influence. The presence and or accumulation of heavy metals are generally affected by soil pH, soil type or class, and soil organic matter.

2.2.1 Soil pH

Soil pH is important in assessing the potential availability of valuable nutrients to plants as well as the toxicity of excess levels of essential metals and heavy metals in plants. pH controls nearly all chemical processes in the soil, including hydrolysis, reduction/oxidation, dissolution/ precipitation and adsorption. Generally, metals can occur in various forms in soil, with different interstitial forces keeping them in binding to the soil particles. These interactions are very important because the toxicity of metals and other chemical substances depend on the form in which they exist in the environment (Dube et al., 2001; Caporale and Violante, 2016).

Heavy metals under acidic conditions become extremely mobile, resulting in it being available for uptake. Mobility of metals generally decreases with an increase in pH towards alkalinity. Metal ions can be retained in soil by sorption, precipitation and complexation reactions, depending on pH and can be removed from soil through uptake and leaching. According to Cherameti (2010) and Magdi (2015), the concentration of metals in a soil solution is influenced by the nature of both organic (citrate, oxalate, fulvic, dissolved organic carbon) and inorganic (HPO_4^{2-}, NO_3^-, Cl^- and SO_4^{2-}) ligand ions and soil pH through metal sorption processes.

Soil microbial population is negatively affected by increased heavy metal content and this may affect soil fertility negatively. However, soil characteristics such as pH, clay content and soil organic matter can modify the negative or positive impacts of heavy metals on soil enzymes by improving soil fertility, quality and nutrient causing resistance on mobility of heavy metals in soil (Kelly et al., 2003; Ayansina and Olubukola, 2017).

2.2.2   Soil type

Particle size distribution, soil mineralogy, endogenous metal concentration, and soil processes (mineral weathering, microbial activity) are some of the factors prompting solubility and accessibility of metal species in soil. The kinetics and metal sorption reactions are strongly influenced by particle size distribution of soil, thereby playing a determining role on the forms of metals either as soluble and insoluble chemical species and their resultant concentration in soils (Cataldo and Wildung, 2000). The grain size distribution of gravel, sand, silt and clay provides a basis for classifying soil by texture. Texture and surface area are closely related so that, as particle size decreases, the surface area per unit mass increases, resulting in an increase of adsorption capacity (Sheldon, 2005; Adam et al., 2011).

Different soil classes, for example, sandy, loam, silt or clay possess a heterogeneous collection of adsorption sites when the surface charge is negative. Therefore, there is a greater tendency of adsorption of cationic species such as the heavy metals on clay, compared to other grain types due to their larger surface areas.

2.2.3   Soil organic matter

Organic matter content is essential in soil for appropriate uptake of certain elements that are vital for health and crop development, e.g. Cu and Zn. The retention/mobility of heavy metals is inadvertently affected by the adsorption of heavy metals on soil particles, which is not only partial to the formation of surface complexes but also residency of metals in the interior of soil minerals and organic sequestration (Bruemmer et al., 1986). The relative amount of available soil organic matter thus determines the metal mobility and availability in soil.

However, a decrease in the level of soil organic matter can beneficially influence organic inputs, which can be reduced or lessened by the potential enhancement of the bioavailability of the elements with unknown metabolic function. For instance, cadmium which is a powerful enzyme inhibitor and considered an enormously substantial pollutant may be readily available in soil with low organic carbon content, due to its great solubility in water (Hernandez et al., 2012).

The relative content of organic matter in soil predictates the concentration and speciation of metals in the soil solution or in similar aqueous equilibrium solutions of soil samples and the

removal of metals from solid pools to the liquid phase and vice versa (Adam et al., 2011). Agricultural practices requiring the application of organic amendments or irrigation with wastewater introduce organic compounds in soil, and this affects the reactivity, solubility and bioavailability of metals, although it may also compromise environmental health and crop nutrition.

2.3   Contamination of the environment by heavy metals

Environmental contamination is mostly the result of activities such as mining and smelting operations, industrial production and use, domestic and agricultural use of metals and metal-containing compounds (EEA. 2000; Wuana and Okieimen, 2011). Metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and groundwater also contributes to heavy metals in the environment (Simeonov eds., 2011; Tchounwou et al., 2012). Industrial sources include metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants (Joshia et al., 2016).

2.3.1   Water contamination by heavy metals

Water is a crucial necessity that supports all forms of plants and animals. Two main sources of natural water is obtained from, are surface waters such as freshwater lakes, rivers, streams etc. and groundwater such as borehole and hand-dug well water (Momodu and Anyakora, 2010). Unfortunately, water pollution is a critical problem because various human activities have resulted in the deterioration of water quality. This makes water unhealthy for drinking and other domestic uses. Numerous toxic heavy metals have been discharged in domestic and industrial waste into the environment triggering severe water and soil pollution (Bvenura and Afolayan, 2012; Matthew et al., 2016).

Central to the sources of water pollution are chemical fertilizers and pesticides from untreated sewage, dumping of waste and industrial effluents into rivers and streams traversing through or by urban metropolis and lowlands. Also, rainfall accompanied by flocculation or coagulation may lead to problems such as the formation of large amounts of sediments containing heavy

metal ions, discharge of large magnitude of toxic metals into receiving water systems, and their subsequent transmission into human food chain (Hussein and Sheriff, 2013; Staszewski et al., 2015).

2.3.2 Soil contamination by heavy metals

Soil is a vital component of natural environments extending throughout rural and urban areas. Hence, the retention of soil quality is important; and this can be achieved by sustainable land use and proper land management procedures. Contamination of soils may occur at old landfill sites, predominantly those that accept industrial waste, old orchards that used insecticides containing arsenic as an active ingredient, fields that had past applications of wastewater or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground or in areas down from industrial sites (Wuana and Okieimen, 2011). Heavy metal contamination of urban and agricultural soils may be due to mining, manufacturing and the use of synthetic products e.g. pesticides, paints, batteries, industrial waste and land application of industrial or domestic sludge (Donahue and Auburn, 2000).

2.3.3 Atmospheric contamination by heavy metals

Air pollution arises from several biotic and abiotic processes such as plants and animals, gaseous exchange cycles, radiological decomposition, forest fires and emissions from land and water, causes natural background concentrations. Although this differs according to local sources or specific weather conditions, the spread of poisonous substances released into the atmospheric environment from industries, industrial plants and heavy traffic may be due to the existence of elevated concentration of heavy metals in the atmosphere. Changes in lifestyle may also increase the levels at which trace metals are added to soil, water, plants and air from anthropogenic sources (Chibuike and Obiora, 2014).

2.4   Fate and Toxicity of Heavy metals

Increasing soil heavy metal burden may be due to the continuous contamination from either natural or anthropogenic source input, and this could induce soil enzyme activities, with different metals infracting different fate, depending on the type of metal/metal salt (Zhang et al., 2009).

Chemical substances may also undergo physical and chemical changes in the environment including combination with other chemicals, and this can affect their toxicity (Khaled and Muhammad, 2016). When a relatively harmless chemical has been chemically transformed, it may transform into a toxic by-product in the environment and may further enter the food chain and accumulate in living organisms (Wuana and Okieimen, 2011; Ayeni et al., 2010).

Chemical products such as agrochemicals and petrochemicals have been recognized to have brought valuable effects to man and his environment, while others such as alkylated lead and some other pesticides have brought unprecedented harm (Abdel-Raouf et al., 2012). Significant scientific information is available on the short term effect of some well-known chemicals hazardous to human health or animal species especially domestic animals, where the effect may appear for a long time after exposure, to a high dose over a short period or a low dose over an extended period can be acute i.e. immediate and obvious response to exposure beyond threshold limit or chronic. The effect of human exposure to chemical substances at low concentrations over a lengthy period is not fully known.

The biodiversity of microorganism may be reduced by environmental pressure caused by contamination and may also disturb the ecosystem. Ahmad et al. (2005) and Lenart and Wolny-koladka (2012) reported that even in soils contaminated with toxic heavy metals and other xenobiotics, soil microorganisms might adapt to growth, by developing various mechanisms to resist heavy metal contamination.

Generally, the significance of exposures can be measured in terms of mortality, morbidity and of physiological changes, which are precursors of morbidity (Jaishankar et al., 2015). Chemical mutagenesis induces gene mutations in the protoplasm and they can be permanent. Long-term exposure results to health hazards from toxic substances include the possibilities of carcinogenicity, mutagenicity and teratogenicity (Abdel-Raouf et al., 2012).

2.5   Heavy metal exposure and effect

Although heavy metals in the earth's crust occur naturally, anthropogenic activities such as mining and smelting operations, industrial production and agricultural use of metals and metal-containing compounds result in human and environmental exposure. Environmental contamination can also occur through metal corrosion, atmospheric changes, soil erosion of metal ions and leaching of heavy metals and metal evaporation from water resources to soil and ground-water (Tchounwou et al., 2012; Kamunda, 2017). In spite of the natural occurrence of heavy metals in the soil environment, they do not occur at levels that induce toxicity, except when accumulated.

Hazardous chemicals in food and water comprise a wide range of both inorganic and organic substances. These substances are derived from a variety of sources of which air pollutants (Wei et al., 2017) deposited directly on aerial parts of the food plants, are the most important. This is because they may not partake in plant metabolic activity and or degradation thus accumulating several-fold. They also include pollutants taken up from the soil or irrigation water via the root of food plants (Jung, 2008).

However, the human body has effective mechanisms, both on systemic and cellular levels, to retain homeostasis over a broad exposure range, and beyond given thresholds for different substances, there could be negative responses to toxicity.

2.5.1   Cadmium

Cadmium is bio-persistent and once captured by an organism, it remains inhabitant for a long time (subsisting in humans and animals) (Nordberg, 2010). A major source of Cd in the environment is from the use of fertilizers, and the indiscriminate dumping of wastes containing Cd (Godt et al., 2006). Phosphate fertilizers contain excessive amounts of cadmium as impurities are occasioned by its close characteristics with zinc. However, it is eventually expelled from the body over time. Cadmium enters the human body through leafy vegetables, grains and cereals. High exposure can cause disease associated with lung cancer, renal dysfunction, bone defects in humans and animals.

2.5.2 Chromium

Chromium (Cr^{3+} and Cr^{6+}) is an essential nutrient required in trace levels by plants and animals for proper metabolism. However, when in high concentration, it can be harmful. Chromium is a component useful for cement, paints, paper and other materials. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Sneddon, 2012; Smith et al., 2010). It can cause skin irritation and ulcers on exposure. Long-term exposure can cause damage to the kidney, liver, circulatory tissue and nerve tissue.

2.5.3 Copper

Copper is an important nutrient needed in the human and animal body. Copper usually occurs in drinking water running through copper pipes due to leaching or corrosion of pipes, as well as from additives designed to control algal growth during water treatment (Desai and Kaler, 2008). High concentrations of Cu in humans and animals can cause liver damage, anemia, intestinal irritation and kidney damage. Copper was reported to be the cause of a disease known as Wilson's disease (Wilson, 2011). Copper is also known to be very toxic to sheep hence must not be present in many animal seed.

2.5.4 Lead

Lead (Pb^{2+} and Pb^{4+}) is relatively immobile in soil and occurs naturally in the earth's crust. It is one of the known extremely poisonous elements. Lead from water and airborne sources have been shown to accumulate in agricultural areas and this might lead to increase concentrations in agricultural produce and farm animals (Xintaras, 1992; Tukker et al., 2006).

Children are more vulnerable to the absorption of Pb as it is absorbed more efficiently than in adults. Thus they may exhibit symptoms of the harmful consequences of lead toxicity. Lead affects mental growth of children and their neuropsychological function (Rollin et al., 2008).

2.5.5 Nickel

Nickel may be released into the environment from furnaces used for making alloys or from power plants and trash incinerators. Nickel released via stack emissions from power plants is

associated with particulate substances, which are deposited on soil under gravity, or seeded out of the air during rain or snow. It usually takes many days for nickel to be removed from air due to size dynamics, hence Ni has a longer half-life in air. Significant amounts of nickel released into the environment end up in soil or sediments where it is strongly attached to particles containing iron or manganese. Nickel travels freely in soil under acidic conditions and might seep into groundwater. Studies showed that some plants could absorb and accumulate nickel. Short-term overexposure to nickel is not known to cause any health problems, but long term exposure can cause decreased body weight, heart and liver damage and skin irritation (Das et al., 2008; Sheldon, 2005).

2.5.6 Iron

Iron is an essential component of haemoglobin (the red colouring agent of the blood) which is responsible for oxygen transport in human and animals. Iron can be found in meat, whole meal products, potatoes and vegetables. Exposure to high concentrations of Fe may cause pneumoconiosis, choroiditis, conjunctivitis and retinitis (Wilson, 2011). Iron in soil exists in Fe^{2+} and Fe^{3+} forms and not readily available for plant uptake, but due to poor soil aeration or reduced oxygen level that are caused by flooding or rainfall the Fe minerals become contaminated and are taken up by plants (Chibuike and Obiora, 2014).

2.5.7 Cobalt

Cobalt is useful to humans because it provides an important route in the synthesis of vitamin B12, which is essential for good health in humans and animals. Cobalt stimulates the production of red blood cells; therefore, it is used to treat anaemia in pregnant women. Humans may be exposed by breathing air, drinking water and eating food that contains cobalt. However, high concentrations of cobalt may cause damage to organisms. Health effects of Co may include hair loss, vomiting, bleeding and death (Campbell, 2012). Cobalt occurs naturally in soils through the breakdown of organic matter and the weathering of the minerals into soil particles. Adsorption of cobalt to soil is rapid resulting in easy uptake by plants (Chibuike and Obiora, 2014).

2.5.8 Manganese

Manganese is an essential metal vital for metabolism in the human body. When high concentrations are present in the human body it can be toxic. The uptake of manganese by humans is mainly through food, such as spinach, tea and herbs. Foodstuffs containing a high concentration of Mn include grains and green beans. High concentrations of Mn in humans may result in deleterious toxic effects such as neurological damage, anxiety and insomnia (McAllister, 2011; Rollin et al., 2005). Mn^{2+} ions are released into the soil solution during weathering of silicates which are easily accumulated by plants (Chibuike and Obiora, 2014).

2.5.9 Zinc

Zinc is an essential trace element in human and animal nutrition. Zinc impacts human organs on the cellular level and may be a crucial regulator of apoptosis as well as neuronal death following brain injury (Plum et al., 2010). Consequently, zinc has rather low toxicity; hence a severe impact on human and animal health by intoxication with zinc is a relatively unusual event. Zinc occurs with excess of the sulphate and phosphate content in the soil solution. Zinc can also be found adsorbed onto iron, manganese and aluminum oxides which can be taken up by plants easily (Chibuike and Obiora, 2014).

2.6 Accumulation of heavy metals in vegetables

Plants and vegetables contain vital diet constituents; thus, they are a source of vitamins, proteins, carbohydrates, lipids, essential minerals such as iron, calcium, nickel, and many others, which are required in trace or small amounts. These nutrients act as buffering agents for acidic substances, alkaline substances and free radicals produced during the digestion process. Over an extensive range of concentrations, plants may harbor crucial metals and toxic elements.

Metal buildup in vegetables may pose a direct threat to human health. This is because vegetables absorb heavy metals from metal contaminated soils and from deposits on different aerial parts of the vegetables exposed to air in polluted environments. Islam et al. (2007) reported that almost half of the mean ingestion of lead, cadmium and mercury is through food of plant origin (fruit, vegetables and cereals). Furthermore, some population groups are likely to be at risk of higher

exposure, especially vegetarians, since they absorb more frequently 'tolerable daily doses' (Islam et al., 2007).

The contamination of food by heavy metals depends on their movement in the soil and their bioavailability, although determination of the food risk contamination is tricky (Gergen et al., 2011).

2.7   Effect of heavy metals on exposed living organisms

Toxic levels of heavy metals affect human beings, animals and plants. These metals may be present either as a deposit on the surface of vegetables or taken up by the crop through the roots and enter into the edible part of plant tissues. Heavy metals deposited on plant (vegetable) surface can be eliminated by washing prior to consumption; whereas bio-accumulated metals are difficult to remove and are of major concern (Lente et al., 2012).

Metals such as cobalt, copper, chromium, iron, magnesium, manganese, molybdenum, nickel, selenium and zinc have been reported to form part of the essential nutrients that are required for various biochemical and physiological functions (Tchounwou et al., 2012; Kamunda, 2017). Thus, inadequate supply of these essential micronutrients may results in a variety of deficiency diseases or syndromes, while excess beyond require dose may elicit toxic responses.

Dietary exposure to heavy metals such as Cd, Pb, Zn and Cu has been identified as a risk to human health through the consumption of vegetable crops. Some heavy metals have toxic and mutagenic effects even at very low concentrations. Several cases of human disease, disorders, malfunction and malformation of organs caused by exposure to metals are listed in Table 2.1 (Koldabadi et al., 2012).

Table 2.1: Selected heavy metals and their effect on human health with their permissible limits

	Major sources	Effects on human health	Allowed level for soil (mg/kg)	Allowed levels for plants (mg/kg)	Allowed levels for water (mg/L)
Pb	Paint, smoking, mining and coal	Mental retardation and liver damage	0.1	2	5.0
Cd	Welding, fertilizer and pesticide	Renal dysfunction and lung cancer	0.06	0.02	0.01
Mn	Fuel addition and welding	Nervous damage and inhalation	0.26	10	0.5
Zn	Refineries and plumbing	Zinc fumes and nervous damage	15	2	0.5
Cr	Mines and mineral sources	Nervous system damage	0.05	1.30	0.1
Cu	Mining, pesticide and metal piping	Anemia, liver and kidney damage	0.1	10	0.2
Ni	Soil and underground water	Weight loss, skin irritation and liver damage	0.015	10	0.2
Fe	Metal tonnage, food and rust	Retinitis and pneumoconiosis	20	5	0.01
Co	Air pollution, food and water	Hair loss, vomiting, and death	0.05	0.02	0.01

Source: (Singh et al., 2011)

2.8   Regulations and guidelines concerning heavy metals in the environment

There are several guidelines stipulated for the sustenance and health of the environment, especially where it may have a direct impact and implication on humans and animals. The suggested guideline levels are not the same for all media since metals behave differently in different media.

2.8.1   Soil guidelines

Guideline concentration ranges for the safe limit of heavy metals in soils are important in order to avoid potential health risks to plants, humans and animals. Countries such as United States of America (USA), United Kingdom (UK), the European Union (EU), Poland and many more have suggested variable but close concentration levels that would ensure the protection of the environment (Table 2.2).

Table 2.2: Soil concentration ranges and regulatory guidelines for some heavy metals

Metal	Soil concentration range (mg/kg)	Regulatory limits (mg/kg)
Pb	1.00 – 69 000	600
Cd	0.10 – 345	100
Cr	0.05 – 3 950	100
Hg	<0.01 – 1 800	270
Zn	150 –5000	1500

Where the metal concentration in the soil environment exceeds the recommended threshold, deleterious consequences might be triggered. In order to avoid these deleterious consequences, target concentration levels and intervention are required and have been suggested in Table 2.3.

Table 2.3: Target and intervention values for some metals for a standard soil

Metal	Target value (mg/kg)	Intervention value (mg/kg)
Ni	140.00	720.00
Cu	0.30	10.00
Zn	—	—
Cd	100.00	380.00
Pb	35.00	210.00
As	200	625
Cr	20	240
Hg	85	530

The maximum allowed concentration levels of heavy metals proposed for soil in various countries is suggested in Table 2.4 in order to ensure the protection of the agricultural soils.

Table 2.4: Maximum allowable concentration (mg/kg) (MAC) of trace metals element in agricultural soils proposed or given in the directives in various countries during different years

Element	USA 1993	Germany 1993	UK 1987	Poland 1993	Sweden 1993	Denmark 1993	EU 1993
Cd	20	1.5	3 – 15	1 – 3	1	0.5	1 – 3
Cr	1500	100	-	50 – 80	30	30	100 – 150
Cu	750	60	50	30 – 70	40	40	50 - 140
Mo	8	1	-	10			
Ni	210	50	20	30 – 75	1.5	15	30 - 75
Pb	150	100	500 – 2000	70 – 150	40	40	50 - 300
Zn	1400	200	130	100 – 300	100	100	150 - 300

Source: Adapted from Alloway (1995); Kabata Pendias & Pendias (2000)

The European Union directive on concentrations of heavy metals in soil was based on the general averages of heavy metals in soils of some European countries and widely applicable in many European countries. Table 2.5 shows the maximum allowed concentration (MAC in mg/kg) recommended by the European Union for soil and sludge, and assumed safe for plant growth as well as reduce the risk of human (Kabata-Pendias and Pendias, 2000).

Table 2.5: Environmental quality criteria in the European Union: soil and sludge quality criteria, (maximum admissible concentration mg/kg).

Element	European Union Soil Limit value (mg/kg)	European Union: Sludge for agricultural use Limit value (mg/kg)	Soil concentration for loamy and silty soil (ppm)
Cd	1 – 3	20 – 40	0.08 – 1.61
Co	50 – 140	1000 – 1750	4.0 – 100
Pb	50 – 300	750 – 1200	1.5 – 70
Hg	1 – 1.5	16 – 25	-
Ni	30 – 75	300 – 400	3.0 – 110
Zn	150 – 300	2500 – 4000	9.0 – 362
Cr	-	-	4.0 – 1100
Mn	-	-	45 – 9200
Mo	-	-	0.1 – 7.2

Source: Adapted from Visser (1993); ECE DG XI (1992); Redojevic and Bashkin, 1998; Kabata-Pendias & Pendias (2000)

2.8.2 Guidelines of heavy metals in aqueous matrices

Heavy metals occur largely as dissolved metal in aqueous matrices. Their solubility and resident time differs from one aqueous system to another. Fresh water, surface water, wastewater, water for irrigation, water for recreation, coastal and marine water all have different recommended guideline concentrations. Fresh water maximum contaminant guideline levels and potential consequences at exposure beyond these concentrations are presented in Table 2.6.

Table 2.6: Maximum contaminants levels of selected heavy metals in water, health effect and sources

Conta minant	MCLG (mg/L)	MCL or TT (mg/L)	Potential Health Effects from Long-Term Exposure at > MCL	Sources of Contaminant in Drinking Water
Ni	0.2	0.2	Decrease body weight, heart And liver damage	Released into the environment by power plants, metal factories and waste incinerators, used in fertilizers.
Mn	0.5	0.5	Neurological damage, anxiety and insomnia	Occurs naturally on surface water and ground water and in soils that may erode into water, also human activities are responsible for contamination in water.
Fe	0.01	0.01	Pneumoconiosis, choroiditis, Conjunctivitis and retinitis	Mineral water contains high amounts of iron ions and present in all waste waters.
Co	0.01	0.01	Vomiting, bleeding and hair loss	Exposure through air, drinking water and industrial areas.
Cr	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits.
Cu	1.3	TT; Action Level=1.3	Short term exposure: Gastrointestinal distress Long term exposure: Liver or kidney damage	Corrosion of household plumbing systems; erosion of natural deposits.
Pb	0.0	TT; Action Level=0.0 15	Infants and children: slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits.
Cd	0.01	0.01	Lung cancer, renal dysfunction and bone defects in humans and animals	Occurs naturally in Zn, Pb, Cu and other ores which can serve as sources of ground water and surface water.
Zn	0.5	0.5	Brain injury	Used in fertilizers that may leach into groundwater.

TT- Treatment Technique; MCLG-Maximum contamination level goal; MCL- Maximum contamination level

2.8.3   Food and beverages

The need to regulate the levels of heavy metal in food and beverages is very contingent. This is because they are major routes in nature for heterotrophic transfer process. Therefore imposing regulation on metal levels in food and beverages is necessary. The deleterious effects of heavy metals on biota have led to exigent need for stating reference concentration for safe exposure thus, the importance of acceptable threshold limits and environmental standards set for the protection of the components of the biosphere and the ecosystem against heavy metals exposure (Olatunji et al., 2016). Many developed countries have defined guidelines for many heavy metals and organic pollutants in media including drinking water, arable agricultural soils, food, plant, sediments etc. These limits are set to protect species of organisms within an ecosystem from adverse negative consequences of heavy metals.

The World Health Organization (WHO), Joint Experts Committee on Food Additives (JCFA) and Food and Agriculture Organization (FAO) also recommended a guideline threshold concentration for heavy metals in plants consumed as food. The guideline concentration of heavy metals for normal plants growth as well as the heavy metals phytotoxic levels recommended by Kabata Pendias and Pendias (2000) are presented in Table 2.9.

Table 2.7: Guideline concentration (mg/kg) values for heavy metals in plants

Status	Metal concentration (mg/kg)				
	Pb	Cd	Cr	Ni	Zn
Deficient	-	-	-	-	<10
Normal	0.5 – 10	0.05 – 2.0	0.1 – 0.5	0.1 – 5.0	10 – 150
Phytoxic	30 – 300	5 – 700	1 – 10	10 – 100	>100

Source: Adapted from Kabata-Pendias and Pendias (2000)

The ability of plants to concentrate heavy metals in their tissues is largely a function of their metabolic processes. Uptake and translocation of heavy metals in solution phase are controlled

by either active or passive mechanisms. Ravi et al. (2003) reported that regulatory criteria have been established with limits on environmental and human health.

Kabata-Pendias and Pendias (2000) noted that some plants might appear healthy, growing on contaminated soils whereas they contain unsafe levels of heavy metals. It is, therefore, possible that depending on specific conditions and soil type, significant metal concentrations can be tolerated in some cases without appreciable risk of detriment to plant.

Lower plants such as lichen and moss have been reported to take up heavy metal from soil, hence can be used as an indication of heavy metal contamination (bio-indicator) status of soil environments, while atmospheric contamination status can be assessed using tree barks of plants as indicator (Singh et al., 2007).

2.9   Determination of heavy metals in vegetables and soil: review of analysis methods and procedures for environmental samples

2.9.1   Sample digestion

The decomposition of materials sampled in preparation for analysis is crucial to the accuracy of results. This can be achieved by digestion, which is the breaking down of chemical substances into free ions, atoms or molecules, such that they can be selectively determined by a sensitive and specific analytical technique. Method of digestion varies for different samples and this is clearly a function of the element or elements to be determined; the matrix in which they exist, and the purpose for which the results are needed (Markert, 1995). There exist two procedures (dry and wet) for digestion of samples needed for metal analysis.

2.9.1.1 Dry digestion

Dry digestion is the destruction of (biological) samples from their dry state to ash i.e. total destruction of the organic component of a sample, usually carried out in a furnace at elevated temperatures $(450 - 600\,°C)$ set by the volatility point of the element required for assaying. Dry samples are charred first at temperatures of between $120\,°C - 160\,°C$, before subjecting them to

severe temperatures in highly cleaned porcelain or platinum crucible in a furnace (Hamilton and Mehrle, 1986).

Dry digestion is however linked with some demerits (Hamilton and Mehrle 1986):

i.   Samples are susceptible to contamination by furnace lining materials, which are usually suspended in thermal current (Hamilton and Mehrle 1986).

ii.   Excess of heat i.e. high temperatures of ashing is associated with volatility losses, which negatively affects the results obtained.

iii. Charge losses during material transfer and dissolution must also be considered when preparing for dry ashing.

In the ashing of biological materials, localized sites where exothermic reactions occur, usually give rise to localized spikes where temperatures in excess of those recorded by the furnace thermocouple reading were exceeded (Hamilton and Mehrle 1986). This phenomenon results in volatility losses; thus, the development and use of low-temperature ashing equipment came up as a correction to the problems associated with high-temperature ashing. Sealed quartz containers under vacuum are now available, which greatly reduces sample contaminations and volatility losses from volatile phases. Ashing aid such as sodium pyrosulphate or sodium carbonate may also be employed in order to facilitate dry digestion procedures and to avoid sample contamination.

Adebayo et al. (2005) applied dry digestion technique in the decomposition of fish samples by subjecting homogenized sample of scaled filleted fish to digestion by ashing at 550 ℃ in a muffle furnace. The resulting residue was dissolved in deionised water and made up to standard volume for analysis.

2.9.1.2   Wet digestion

Wet digestion techniques employ the use of reagents to enhance the extraction of metallic elements from their matrices into solution of the digesting reagent under carefully regulated and suitable temperatures. The use of this method is suitable for both biological and environmental

samples and is widely adapted because volatility losses are greatly reduced, and localized spikes are eliminated. However, several modifications and developments to the wet digestion procedure are ongoing (Voegborlo and Adimado, 2010).

Potts (1969), for instance, used digestion bombs made of a screw cap metal lined inside with Teflon (polytetrafluorinated ethylene PTFE material) to decompose biological materials under pressure. This resulted in faster digestion and infinitesimal losses under carefully controlled temperatures. High-temperature digestion in Teflon-lined digestion bombs is also possible because PTFE (polytetrafluorinated ethylene) is heat resistant and can endure high temperatures, where the screw cap enhances the build of pressure and also prevents volatile losses by trapping. However, today the use of microwave-assisted digestion is widely employed for biological materials in acid decomposition in sealed containers.

The wet technique is suitable for many sample types; Bunzl et al. (2001) adopted the method of Schramel et al. (1996) by digesting plant sample grown on slag contaminated soils and soil – slags in supragrade and ultragrade quality concentrated HNO_3/HCl acids in microwave-assisted high-pressure digestion (EPA method 3050). Singh et al. (2000) also applied wet method in the digestion of soil and plant tissue in the plant *Larrea tridentata* using 1:1 nitric acid (HNO_3), and reported very efficient oxidation with minimal volatility losses associated with dry ashing procedures (Singh et al., 2000).

2.9.2   Reagents for wet digestion of samples

The choice of reagents for wet digestion is determined by the ease and effectiveness in extracting the analyte of interest from the matrix of the sample type under consideration. The use of nitric acid is sufficient for most metals; however, the use of many other oxidizing agents such as hydrogen peroxide, sodium peroxide, sulphuric acid, perchloric acid, hydrogen fluoride, etc. for samples that are not easily oxidizable have been reported in various research works (Bunzl, et al., 2001).

The use of divergent reagents for wet digestion such as sodium or ammonium acetate (for carbonate bounded metals) at regulated pH (Tessier, et al., 1979; Markert, 1995); $MgCl_2$ or $CaCl_2$ for exchangeables (Kuo, 1996); Hydroxyl amine hydrochloride for Fe–Mn bounded

metals (Tessier, et al., 1979), and even deionised water for water-soluble metals has been considered effective (Tessier, et al., 1979). Most reports indicate the use of oxidizing acids because a significant proportion of heavy metals exist either as organic bounded or as residues in many biological and geochemical samples (Tessier, et al., 1979; Bunzl, et al., 2001).

Modification of reagents was also considered in evaluating the effectiveness of extraction and oxidation efficiency. Markert (1995) studied the efficiency of extraction using various mixtures of reagents with respect to time and at specific pH, for which some mixtures demonstrated a high extent of extraction of some amount of heavy metals.

The use of combined reagents was also reported to be clearly efficient, for example, aqua regia i.e. a combination of nitric acid and hydrochloric acid in ratio three to one (3:1). This extracts with ease organic bounded and residual heavy metals, which form the bulk in geochemical and biological samples under regulated conditions (Santoro, et al. 2017). The use of a combination of hydrochloric acid and perchloric acid ($HCl/HClO_4$) was also reported by many researchers (White et al., 1977) and $HCl/HNO_3/HF$.

In evaluating total metal in a given matrix and the form in which the metals exist, the use of sequential extraction has been recommended to be particularly effective. Tessier et al., 1979, employed sequential extraction procedures in examining metal distribution in sediment samples, resulting in separation of six fractional extracts including water solubles, exchangeables, carbonates, Fe-Mn bounds, organic bound and residuals.

2.9.3 Determination of heavy metals in environmental samples

The earliest technique for heavy metal determination is the classical methods involving titrimetry and gravimetry. These methods are known to be time-consuming, cumbersome and require skills. However, their merit lies in the method's precision and accuracy. Classical methods are subject to modifications of procedure that aims at improving the quality of analysis results, such as the use of changes in electrical potentials for endpoint determination.

Advancing on the classical methods are voltammetric (anodic stripping voltammetry or analysis and cyclic voltammetry) and polarographic (differential pulse polarography and square-wave polarography) methods, which explores the relationship between current and voltage in

electrochemical processes. Voltammetric and polarographic techniques are very sensitive analytical methods used for trace metal analysis (Rajagopalan and Rajagopalan, 1974).

The development of the use of electromagnetic radiation (EMR) to measure the concentration of metals refers to spectrophotometry.

Strong (1952) reported that Colorimetry was the earliest spectrometric method developed after Beer-Bouguer-Lambert (1729-1760), which selectively utilizes monochromatic wavelength of energy. In this method, sample solutions absorb electromagnetic radiations (EMR) from an appropriate light source, and the quantity absorbed is related to the concentration of the analyte in the solution. Atomic absorption spectrometry developed by Allan Walshin 1948 is one of the rapid methods of metal determination in use today. The method involves the absorption of light by elemental aerosol of atomic species under the influence of thermal energy.

Atomic spectroscopy, therefore, involves sample vaporization at high temperatures and concentrations of the selected atoms are determined by measuring absorption or emission of their characteristics wavelength (Viets and O' Leary, 1992; Harris, 2010). Atomic spectroscopy is however not as accurate as wet classical methods with precision hardly better than 1-2 %.

Atomic spectroscopy can be classified into three; designated as absorption spectroscopy, fluorescence spectroscopy and emission spectroscopy. Atomic absorption spectroscopy can, however, be achieved either by the use of flame or non-flame technique.

Inductively coupled plasma (ICP) technique differs from atomic flame emission spectroscopy in that the operating temperature is much higher than that of normal flame atomic emission spectroscopy making it a useful tool in emission spectroscopy. The plasma at this temperature is very stable, and thus eliminates interferences and other sources of error encountered in convectional flame emission spectroscopy. This feature makes it desirable for analytical work, but it is still relatively more expensive.

X-Ray fluorescence (XRF) spectroscopy is one of the fast analytical techniques, whose development is still undergoing modifications and rapid improvements. The method is rapid and non-destructive of the sample because XRF spectroscopy does not require sample digestion

2.10   Cape Town weather and climate

Cape Town has a Mediterranean climate located between the Indian and Atlantic oceans, sheltering the land. Cape Town has moderate rainfall throughout the year; winter weather conditions are mild and summer conditions are pleasant. Cape Town has moderate temperatures and distinctive seasons. Cape Town rainfall ranges between 550 and 1200 mm per annum, where most rainfall occurs in the winter season. The summer season starts from the month of December and lasts until February and has temperatures ranging from around 15 to 27 ℃. It has dry, warm and hot conditions and strong south-easterly winds are experienced in summer. The winter season starts from the month of June to August with average temperatures between 7 to 20 ℃. Dry, windy and dusty conditions and cold nights are sometimes experienced. The temperature may fluctuate causing dramatic changes in weather conditions. The average seasonal temperature and rainfall of Cape Town are shown in Figure 2.3 and Figure 2.4, respectively.
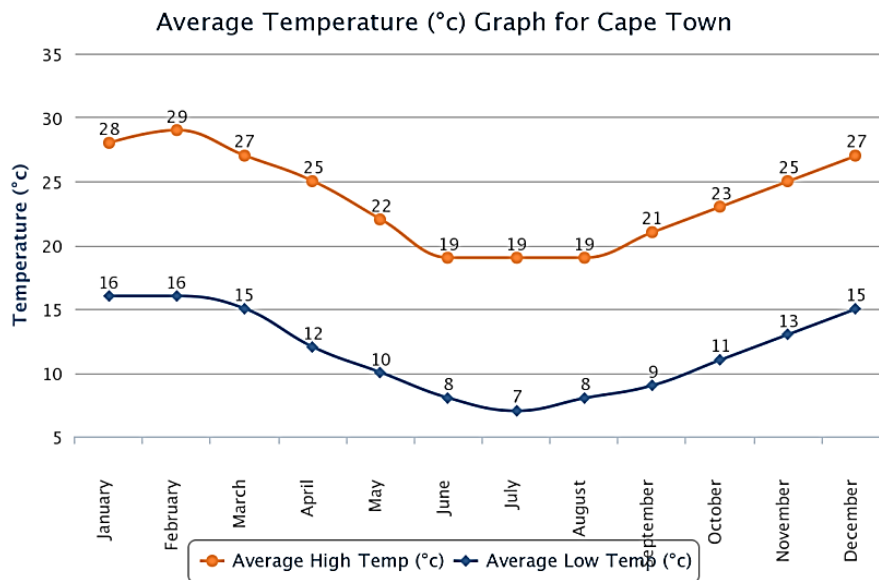
Figure 2.3: Average seasonal temperature for Cape Town, South Africa (van de Velden, 2013)
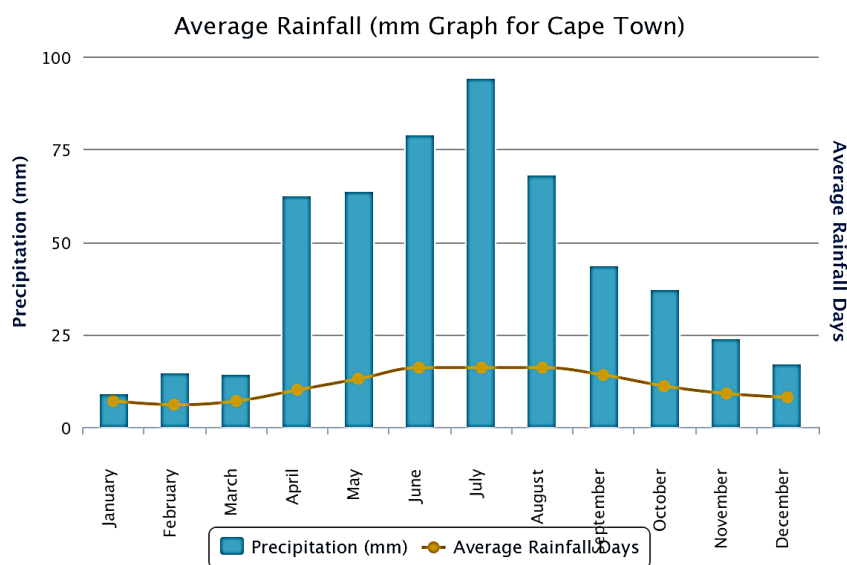
Figure 2.4: Average rainfall for Cape Town, South Africa (van de Velden, 2013)

2.11 Cape Town agricultural production

Cape Town is one of the cities in the Western Cape where urban farming is practiced. Due to population growth, rapid urbanization, scarce food resources and environmental concerns, cities around the world have been forced to think of new ways for better living. Cape Town has a rapidly growing urban farming practice. Many community farms and non-profit projects, such as Phillipi Horticultural farmers and Abalimi centre produce 50 % of the freshly produced crops that are consumed in Cape Town. The farmers provide products such as carrots, tomatoes, lettuce, potatoes and much more (James, 2013; Averbeke, 2007; Megan, 2016).

The Abalimi centre has over 25 years of operation, it is a non-profit project which was established in 1982. Since then, Abalimi centre has developed and provides training, supplies and supports to enable the poor to obtain employment and become self-employed as gardeners and small urban farmers (Spiro, 2018). The Abalimi centre has also partnered with Harvest of Hope which was established as a community support agriculture (CSA) system which connected the Abalimi centre with potential consumers within the Cape flats environment and helps in

maintaining stability income security for these urban farmers. Abalimi centre gardens are based in local communities such as Khayelitsha, Nyanga, Phillipi and Gugulethu within schools and home gardens (Spiro, 2018; Wachholz, 2017).

Abalimi community garden centre provides low cost, subsidized resources such as seedlings, manure, tools and pest control. Various special projects such as 3-day urban organic food garden training workshop are implemented by field workers such as the Young Farmers Training Centre situated at the Siyazama Community Allotments Garden Association (SCAGA) and about 300 people attend these workshops annually. Abalimi centre has helped the communities to start and retain the growing of many thousands of organic vegetable gardens (Wachholz, 2017; Small, 2007). Figure 2.5 shows the provincial number of farming units and average farm size, in South Africa.
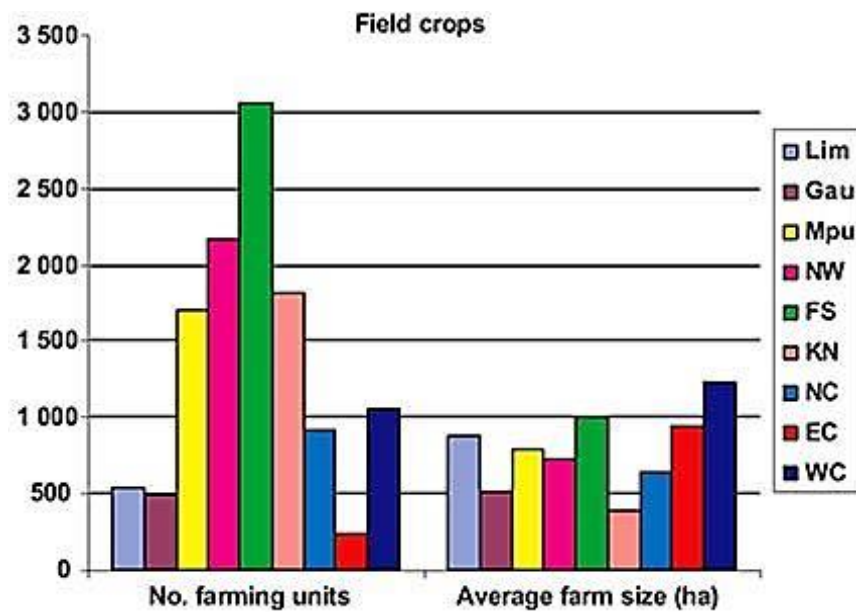
Figure 2.5: Number of farming units and average farm size (Small, 2007)

A provincial land area and field crop for South Africa is shown in Figure 2.6.
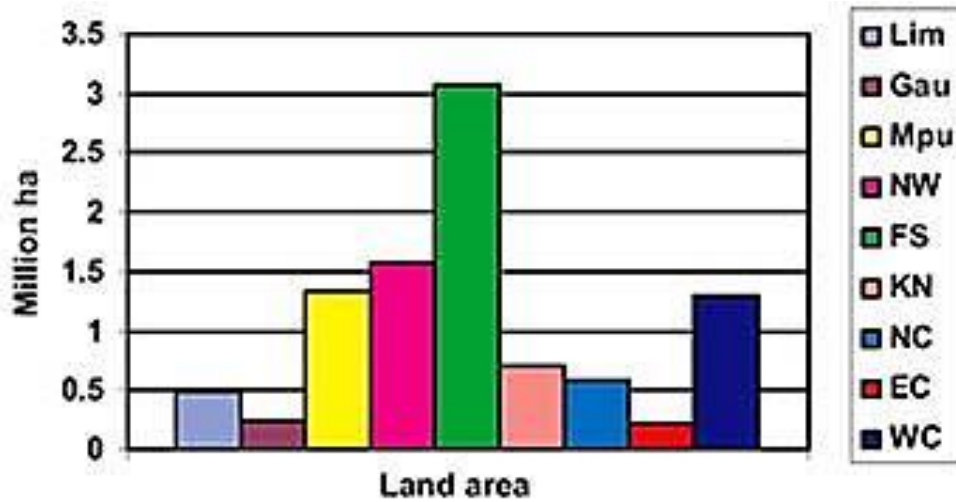
Figure 2.6: Land area and field crops (Small, 2007)

Agriculture is one of the main pillars of the Western Cape economy. It produces about 23 % of the total value of the agricultural sector in South Africa which was R25 billion in 2001. The province contributes about 14 % to the country's gross domestic product. Agriculture accounted for 5.2 % of the Western Cape's gross regional product in 2001 (Vink and Tregurtha, 2005). Figure 2.7 shows the diverse agricultural production in the Western Cape, South Africa.
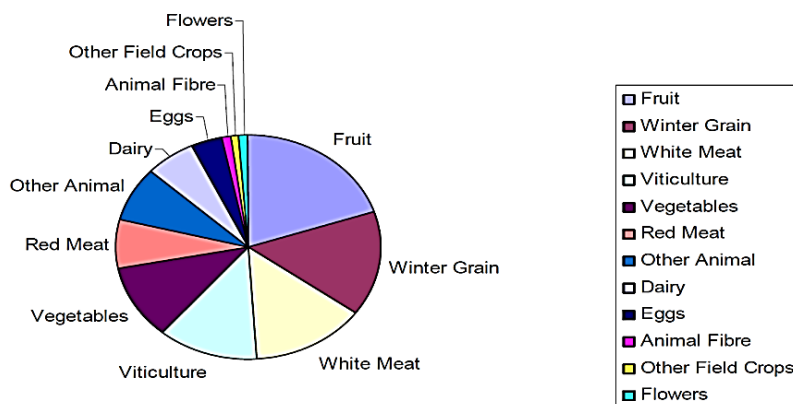
Figure 2.7: Agricultural production in the Western Cape, South Africa (Vink and Tregurtha, 2005)

Agricultural production in the Western Cape is an essential component especially vegetable production, representing about 12 % of total production. Most trade-produced vegetables are through urban fresh produce market; where in 1999 an estimation of 61 260 million tons of fresh vegetables were distributed from Cape Town, although about 50 % of the fresh vegetable production is provided by the informal sector produced under contract for major supermarket chains (Vink and Tregurtha, 2005).

2.12   Informal settlement: pollution, heavy metal status and agricultural practices

Informal settlements are a common reality in cities and urban metropolitan centers in Africa. It is a common view even in clean and eco-cities such as Cape Town and South Africa's urban landscape. The living conditions are the framework for lack of services, like appropriate sanitation and refuse removal, clean water, public health initiatives, adequate safety and access to economic opportunity. A result of backyarders is that they unconsciously contribute towards pollution through the influence on storm-water. These are often the poorest of people who reside on the property of their landlord and construct a dwelling on the property. In most circumstances the backyarders have no direct access to water, electricity and sanitation services as a result of the lack of access to services. A common practice is to deposit waste and contaminated water into rivers and water drainage, thereby posing a threat of contamination to the receiving water resource (Arif et al., 2015). This problem seems to be a fairly common one in most informal settlements across the Western Cape (Bredell and Smith, 2005). These inadequate circumstances are the major sources of soil pollution and vegetable crops due to the usage of contaminated water and soil. As a result accumulation of heavy metals in soil, water and vegetables may be high resulting in high risks of affecting human health (Dixon and Ramutsindela, 2006).

Vegetable crops in home gardens of Alice, a small town in Eastern Cape, were analysed for possible contamination by heavy metals. Elements of interest that were analysed were Pb, Cu, Cd, Mn and Zn. The vegetables analyzed were onions, carrots, cabbage, spinach and tomatoes and were reported to accumulate the heavy metals at high concentrations ranging from 0.01 mg/kg – 1.12 mg/kg. The absolute concentrations of each heavy metal in the vegetables and soils were compared to the concentration of each heavy metal known by FAO (Food and Agriculture

Organization) to ensure their potential health hazard to human health (Bvenura and Afolayan, 2012). Table 2.9 and Table 2.10 shows heavy metal content of soil and vegetables respectively in the Alice environment, Eastern Cape.

Table 2.8: Heavy metal content (mg/kg) of soil in the Alice environment, Eastern Cape

Heavy metal	Maximum permissible limit	Happy Rest	Golf course	Ntselamanzi
Cd	6	0.80 ± 0.01	0.30 ± 0.08	0.10 ± 0.01
Pb	500	10.00 ± 0.02	14.01 ± 0.16	5.15 ± 0.13
Cu	270	5.14 ± 0.03	7.66 ± 0.01	4.95 ± 0.04
Zn	600	53.01 ± 0.01	34.28 ± 0.01	17.58 ± 0.01
Mn	-	377.61 ± 0.09	442.72 ± 0.04	499.68 ± 0.09

Source: (Bvenura and Afolayan, 2012).

Table 2.9: Heavy metal content (mg/kg) in vegetable types grown in the Alice environment, Eastern Cape

Heavy metals	WHO	Site	Cabbage	Carrot	Onion	Spinach	Tomato
Maximum permissible limits (mg/kg)							
Cd	0.3	Happy rest	0.26 ± 0.31	0.94 ± 0.82	0.21 ± 0.19	0.21 ± 0.22	0.50 ± 0.34
		Golf course	0.26 ± 0.38	1.03 ± 0.23	0.19 ± 0.02	0.25 ± 0.22	0.38 ± 0.45
		Ntselamanzi	0.20± 0.16	0.92 ± 0.61	0.21 ± 0.18	1.12 ± 1.32	0.04 ± 0.06
Cu	40	Happy rest	nd	7.06 ± 0.07	9.29 ± 1.02	5.54 ± 3.62	9.60 ± 9.09
		Golf course	0.69 ± 0.99	nd	7.56 ± 5.31	4.40 ± 4.00	4.48 ± 3.88
		Ntselamanzi	1.18 ± 1.07	2.19 ± 3.79	9.24 ± 0.45	10.68 ± 9.53	8.31 ± 1.14
Mn	-	Happy rest	42.59 ± 17.60	13.80±4.85	28.44 ± 0.14	112.38±27.7	28.73±11.96
		Golf course	20.41 ± 7.57	8.25 ± 0.05	23.93 ± 3.51	7165 ± 0.82	7.79 ± 3.15
		Ntselamanzi	23.56 ± 1.85	14.91±11.35	28.90 ± 0.92	nd	11.53 ± 0.21
Zn	60	Happy rest	38.10 ± 22.39	10.02± 13.71	49.68± 5.90	33.75±11.51	61.96±26.81
		Golf course	14.42± 12.49	4.27± 1.38	46.34±40.28	25.28±24.71	8.95± 6.69
		Ntselamanzi	29.62± 3.24	15.52± 26.16	89.88± 2.85	81.56±71.18	15.54± 0.98

Source: (Bvenura and Afolayan, 2012). nd = not detected

A study at a school vegetable garden in Johannesburg was conducted due to the proximity of the school garden to nearby gold-mine tailing dams. Based on the Canadian Council of Ministers of the Environment, the results showed that arsenic exceeded the reference levels for soil by 37.5 % with an average concentration of 30.5 ppm. The vegetable sample percentage that exceeded the recommended limits for lead, zinc and mercury were 91 %, 83 % and 75 %, respectively. The concentration of lead in fruiting vegetables was the highest across all the three sites under investigation and decreased in order: tomatoes (1.91 mg/kg) > peppers (1.85 mg/kg) > butternut (1.09 mg/kg) > pumpkin (0.47 mg/kg). The concentration of rooting and leafy vegetables was particularly high in zinc, the highest concentration of (143 mg/kg) was found in carrots from the private organic garden. The concentration of mercury in fruiting vegetables mainly in the school garden was found highest and decreased in the order: peppers (0.99 mg/kg) > tomatoes (0.76 mg/kg) > butternut (0.21) > pumpkin (0.12 mg/kg) (Kootbodien et al., 2012).

Several researchers (Olade, 1987; Fatoki, 1996; Majer et al., 2002; Muhammad et al., 2011; Casimir et al., 2015) have reported high concentrations of trace metals as far as 250 m from the roadside. Vehicle exhausts, lubricating oils, tyres and plating materials have been found to be the sources of these metals (Fatoki, 1996). The studies showed that roadside vegetation by air-borne zinc have high contamination due to motor vehicle emission. These motor vehicles uses lubricating oils that contains zinc additives which gets emitted to the air and sit on the top surface of soil and vegetables resulting contamination. The contamination of copper on roadside soil and vegetation was reported even though results showed small amounts of copper compared with that of zinc (Odiyo et al., 2005).

The contamination of Cu, Zn, Pb, Cr, Pt, Fe and Pd in roadside soils, vegetation, sewage and river waters in Thohoyandou in Limpopo was investigated. Further studies investigated the correlation between these trace metals in roadside soil and vegetables in order to identify the potential influence of roadside trace metals contamination on vegetables. The collected surface soil and vegetable samples were analyzed using AAS for Pb, Cu, Cr, Zn and Cd, while water samples were analyzed by ICP-OES for Pt, Zn, Fe, Cu and Pd (Odiyo et al., 2005). A linear correlation was observed between soil and vegetable metal concentration, which suggests the same source of metals in the samples except for Cu. The findings also exposed a general decrease in soil and vegetable samples and the mean concentrations were found to follow the

decreasing order Pb > Zn > Cr > Cu > Cd > and Pb > Zn > Cd > Cr > Cu, respectively. The main source of trace metal pollution was found to be the sewage system leaking directly into the rivers. The mean concentrations of trace metals in the water were found to be in the order: Fe > Zn > Pt > Cu > Pb. Synthetic contaminants contained a significant amount of Zn while the majority of Cu and Pb were mostly from soil parent material. Another study reported that motor vehicles emit Pb, cow manure contains Cu and the irrigation with sewage and urban surface water contains Zn (Shi-Bo et al., 2011).

China has experienced rapid urban growth in recent years. The acceleration of urban growth has created opportunity and wealth as well as strengthened environmental and ecological problems, especially soil pollution. The results showed the levels of heavy metals in soil used for vegetable production declined gradually from urban to rural areas. The mean levels of heavy metals, calculated by subtracting the sub-layer 15-30 cm from top layer 0-15 cm were above zero and large in absolute value in urban areas, while the mean levels were above or below zero in suburban and rural areas and small in absolute value as shown in Table 2.13 (Shi-Bo et al., 2011).

Table 2.10: Top-layer soil heavy metal contents

Heavy metals	Location	No. of samples	Conc. Mean (mg/kg)
Pb	Urban	5	65.23
	Suburban	5	36.61
	Rural	4	32.10
Zn	Urban	5	224.75
	Suburban	5	122.11
	Rural	4	144.69
Cr	Urban	5	67.49
	Suburban	5	60.09
	Rural	4	53.98
Cu	Urban	5	50.17
	Suburban	5	29.27
	Rural	4	24.93
Hg	Urban	5	0.494
	Suburban	5	0.176
	Rural	4	0.136

Source: (Shi-Bo: 2011)

Further analyses showed that (urban) heavy metal accumulation depends on how long the vegetable-growing soil was cultivated with vegetables (Rahlao et al., 2007). The top layer heavy metals were accumulating with increasing cultivation time, signifying that long-time vegetable cultivation and corresponding operation could be the cause of urban heavy metals in vegetable-growing soil. The primary pollution sources of heavy metal contaminants in soil are manure, irrigation water and intensified use of fertilizers (Muthuvel et al., 2002).

Investigation of water, soil and vegetable pollution by wastewater showed that at least 20 million hectares of land in North and South Africa, South America, Middle East, Southern Europe, South West America, Mexico and major parts of central and East Asia which are irrigated with raw sewage, mostly used for cultivation of vegetables. This leads to soil contamination and heavy metal accumulation both in soil and plants. The investigation also showed that more than 6 m^{3}s^{-1} water and surface water discharged by the urban conglomerate Tehran through drains and canals which accumulate different urban and industrial wastes are used for the purpose of irrigating fields and farmland located in the South of Tehran (Bigdeli and Seilsepour, 2008). Accumulation of heavy metals in the soil has been due to long-term use of waste-water for cultivation of leafy and other vegetables and their transfer to the various crops under cultivation with levels of contamination that surpassed permissible limits. All the vegetable samples exceeded the maximum allowed concentration for lead, while spinach, raddish and cress were high in cadmium. The concentration of zinc in green pepper and spinach exceeded the allowed Zn level (Awufolu et al., 2005). At present the consumption of most of the metals constitutes less than the theoretical maximum daily intake and hence the minimal health risk; however, if the community increase in vegetable intake the situation could be worsening in the future (Hussain et al., 2001).

CHAPTER THREE
METHODOLOGY

3.1   Introduction

This research project was based on the investigation of heavy metals in soil, water and vegetable crops from selected allotment gardens in the Cape Town environment. The focus was on heavy metals such as Cr, Zn, Mn, Fe, Co, Ni, Cd, Pb and Cu. The study was conducted in 7 areas and 9 communal gardens which included Nyanga, Khayelitsha, Phillipi, Mfuleni, Gugulethu, Bellville and Delft. Water, soil, and vegetable crops were sampled at each site. These sites were located at schools and in small communal gardens in various communities. Figure 3.1 shows the location of the study areas in the Cape Town region.
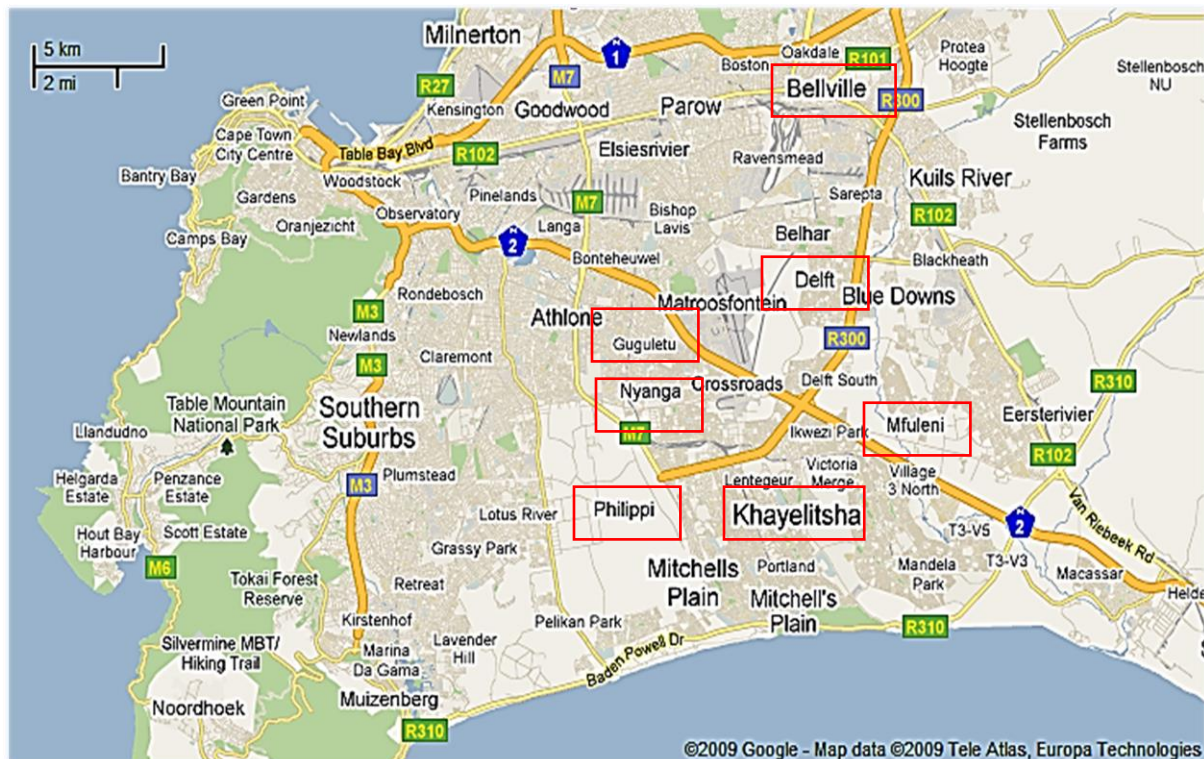
Figure 3.1: Location of the study areas in the Cape Town region

Sampling of the soil, water and vegetable crops was done during winter and summer seasons.

3.2 Site location

Figure 3.2 shows the sites in which the soil, water and vegetables were sampled in each location. In Nyanga sampling was done at the Abalimi centre. Khayelitsha had 3 sampling sites in Kwamfundi, Scaga and Sakhe. Gugulethu, Mfuleni, Delft, Phillipi and Bellville each had 1 sampling site at Fezeka, Mfuleni, Blikkiesdorp, Esam-sakho and Ravensmead, respectively.
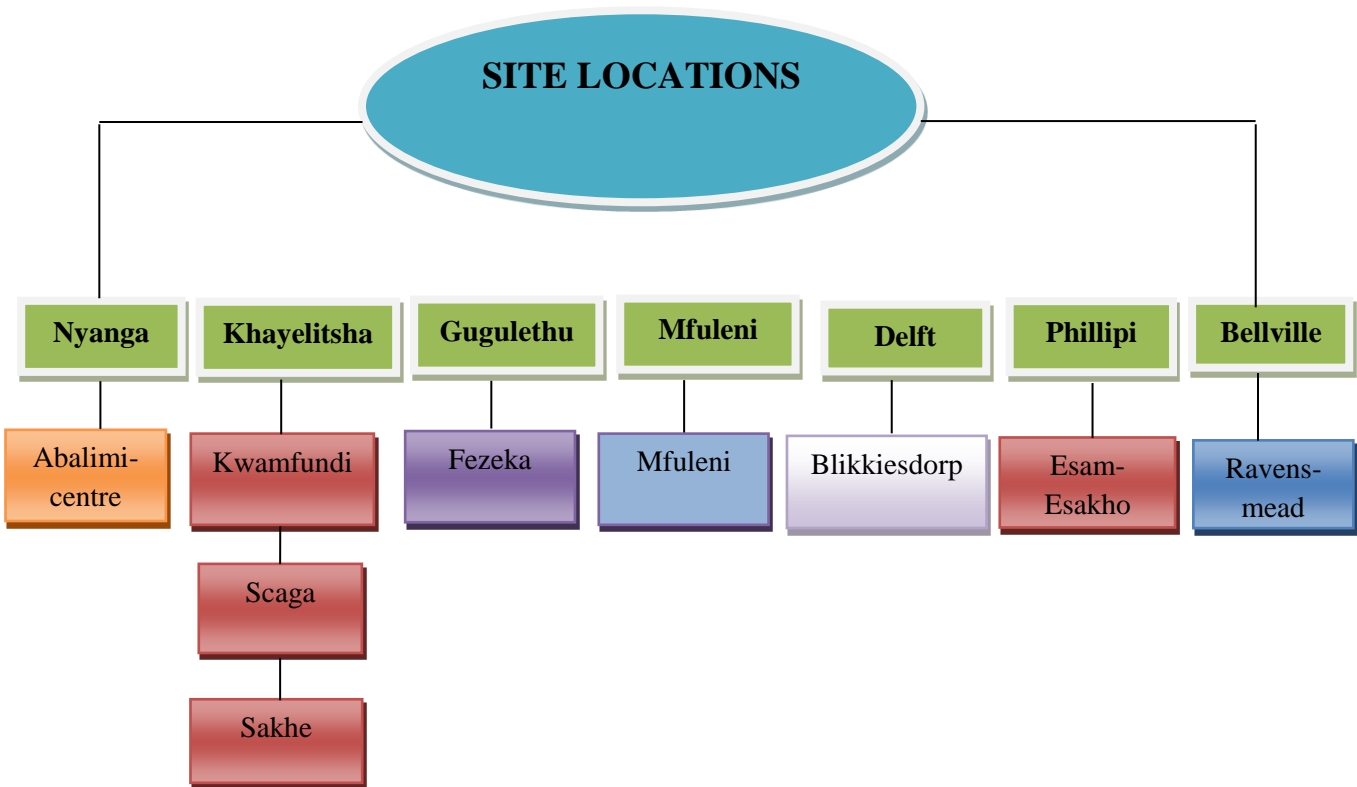
Figure 3.2: Location of sampling sites

The location coordinates for each of the sampling sites of the selected school and small communal gardens were recorded and are shown in Table 3.1.

Table 3.1: Location coordinates of selected allotment gardens in Cape Town environment

Site location	Latitude	Longitude	Site location	Latitude	Longitude
Abalimicentre	33° 59′ S	18° 35′ E	Mfuleni	34° 00′ S	18° 40′ E
Blikkiesdorp	33° 58′ S	18° 37′ E	Ravensmead	33° 58′ S	18° 35′ E
Esam-esakho	34° 02′ S	18° 42′ E	Sakhe	34° 03′ S	18° 41′ E
Fezeka	34° 00' S	18° 33′ E	Scaga	34° 00′ S	18° 35′ E
Kwamfundo	34° 02′ S	18° 39′ E			

3.3   Reagent preparation

3.3.1   Ultra-pure water

Reverse Osmosis technique was used for water purification using a Millipore apparatus.

3.3.2   Standard Stock Solutions

1000 ppm standard stock solutions were used during the preparation of calibration standards. These stock solution solutions were obtained from Saarchem and were all analytical reagent grade.

3.3.3   Mixed Calibration Standards

Mixed calibration standards were prepared by combining appropriate volumes of stock standard solutions in 100 mL volumetric flasks. The standards were grouped into 2 categories (Cd, Zn, Pb and Mn, then Co, Fe and Ni, Cu and Cr) according to the EPA method (EPA Method 2007). 5 % of supra-pure nitric acid was added to the volumetric flasks. The freshly prepared standards were then transferred to the acid cleaned polyethylene bottles for storage.

3.4   Blanks

Three types of blank solutions were prepared and used during analysis.

1. A calibration blank was used in order to establish the analytical calibration curve.
2. A laboratory reagent blank was used to assess possible contamination from the sample preparation procedure.
3. A rinse blank was used to flush out the instrument uptake system and nebulizer between standards and samples in order to reduce memory effects.

3.4.1   Calibration blank

The calibration blank was prepared in a 1000 mL volumetric flask. About 50 mL of 65 % supra-pure nitric acid was diluted with 950 mL of ultra-pure water, making the solution a 5 % solution of supra-pure nitric acid. All calibration blanks were prepared in this manner and were used during sample analysis.

3.4.2   Laboratory reagent blank

The laboratory reagent blank contained all the reagents in the same volumes used in processing the samples. The laboratory reagent blank was carried through the entire preparation procedure and analysis scheme. The final solution contained the same acid concentrations as sample solutions for analysis.

3.4.3   Rinse blank

A rinse blank was prepared as an acid was solution in the same manner as the calibration blank. A 5 % solution of supra-pure nitric acid was used as a rinsing agent.

3.5   Sample Blank

3.5.1   Water blank

Water blank was prepared by adding 10 mL of supra-pure nitric acid into a 50 mL of water in a 150 mL Phillips beaker and digested at 55 °C on a hotplate. After digestion, the solution was

cooled and transferred to a 100 mL volumetric flask and made up to the mark with ultra-pure water.

3.5.2 Soil blank

A soil blank was prepared by transferring 2 mL of hydrochloric acid and 6 mL of supra-pure nitric acid in a 150 mL Phillips beaker. The beaker was covered with a watch glass and the content digested on a hotplate at 55 °C. The solution after digestion was cooled and transferred into a 50 mL volumetric flask and made up to the mark with 5 % nitric acid solution.

3.5.3 Vegetable blank

A vegetable blank was prepared by transferring 2 mL of supra-pure hydrogen peroxide and 5 mL of supra-pure nitric acid into a reaction vessel. The vessel was then placed in the carousel of microwave digester and digested (Stewart, 1989). After digestion, the blank was transferred into a 25 mL volumetric flask and made up to the mark with 5 % nitric acid solution.

3.6 Calibration

Calibration standards were prepared by combining appropriate volumes of the 1000 ppm stock standard solutions in 100 mL volumetric flasks.

3.7 Quality control

Certified reference standard of heavy metal were used in order to determine the accuracy and precision of the total digestion procedure. The reference standards for soil and water were prepared in the same way as the samples.

3.8   Sampling

3.8.1 Water sampling

Water samples were collected in 250 mL polypropylene bottles which were pre-treated by soaking in dilute in 10 % nitric acid and rinsed with ultra-pure water prior to use, to eliminate any possible contamination.

Polypropylene bottles were initially rinsed with borehole water before collection. The pH was measured in the laboratory on the same day of the sampling, by means of a handheld multisystem meter. For calibration, buffers of pH 4.0 and 7.0 were used. The water samples were preserved by acidification with 5 % supra-pure nitric acid (pH < 2) and stored in the refrigerator until analysis (EPA Method 2007).

3.8.2   Soil sampling

Composite samples were collected at each site by combining small portions of soil from various locations within the plot. Soil was sampled at a depth of 15 cm (EPA Method 2007). Polyethylene sampling bags were used for the storage of the soil samples.

3.8.3   Vegetable sampling

Composite samples of vegetables were collected in appropriately labeled brown paper bags at the same locations as soil samples. Vegetables were collected based on availability at the selected sites. The collected vegetables were rinsed thoroughly with ultra-pure water in order to remove all adhered soil and dust particles to ensure that there was no contamination. This was followed by oven drying at a temperature of 75 °C for 3 days.

3.8.4   Compost sampling

Compost samples were collected based on their availability at the selected sampling sites. These samples were collected in appropriately labeled brown paper bags. The samples were then dried in the oven at a temperature of 75 °C for 3 days.

3.9   Sample preparation

3.9.1   Liquid samples

A stock solution for water quality control was prepared by spiking ultra-pure water with 10 ppm standards from the 1000 ppm certified reference standard of heavy metal. The water sample was digested with concentrated supra-pure nitric acid. Approximately 10 mL of supra-pure nitric acid was added to 50 mL of water in a 150 mL Phillips beaker. The mixture was evaporated to half the actual volume on a hot plate, cooled and filtered into a volumetric flask (EPA Method 2007).

3.9.2   Soil samples

Soil samples were sieved with a 2 mm sieve. The soil was carefully mixed to achieve uniformity and then dried in the oven at $75\,°C \pm 5\,°C$ until moisture was removed. Once the soil had been cooled, 1.0 g of the dried soil was accurately weighed using an analytical balance capable of weighing to the nearest 0.0001 g. The soil was transferred to a 150 mL Phillips beaker. To this, 6.0 mL of concentrated supra-pure nitric acid and 2 mL of concentrated hydrochloric acid were added. A watch glass was used to cover the beakers containing the samples. The samples were heated to approximately 55 °C and gently refluxed for approximately 30 minutes. Once again, only slight boiling was allowed. After 30 minutes, the sample was cooled, transferred to a 50 mL volumetric flask and diluted to the mark with 5 % supra-pure nitric acid solution. The sample was ready for analysis (EPA Method 2007).

3.9.3   Vegetable and compost samples

The collected vegetables and compost were dried in the oven at 75 °C for 3 days, until all the moisture was completely removed. After grinding the dried vegetables using a mortar and pestle, 0.1 g of each sample was accurately weighed and transferred into a microwave digestion vessel. 2 ml of 30 % of supra-pure hydrogen peroxide and 5 mL of supra-pure nitric acid were added to the contents of the microwave digestion vessel. The samples were placed in the carousel of microwave digester and digestion was preceded using the microwave programme schedule shown in Table 2.2. The digestion was carried out in a Milestone-MLS 1200 Mega microwave

oven with carousel of 6 digestion vessels. After digestion, the samples were cooled, transferred to a volumetric flask and then made up to the mark with ultra-pure water.

Table 3.2: Programme used for the microwave digestion of vegetable samples

STEP	POWER	DURATION
1	250 W	1 min
2	0 W	2 min
3	250 W	5 min
4	400 W	5 min
5	600 W	5 min

3.9.4   Soil organic matter

The soil samples were dried in the oven at 75 °C, after which about 1 g of each of the soil sample was weighed out accurately into different crucible. A muffle furnace was heated to approximately 500 °C and the crucibles containing the soil samples were placed in the furnace for 2 hours. The samples were allowed to cool in a desiccator for 1 hour and weighed (Storer, 1984). The percentage organic matter was determined by mass difference.

3.9.5   pH of soil and water

The pH of the soil was determined using sieved soil samples. About 10 g of soil samples was weighed into clean 150 mL Phillips beaker. Ultra-pure water of about 100 mL was added to form a slurry solution and pH measurements were made using a pH meter (Kalra, 1995). The pH meter was calibrated with standard buffers of pH solutions of pH 4 and 7 prior to use.

 The pH of the water samples were measured immediately after sample collection in the laboratory by immersing a pre- calibrated pH meter probes into the samples until the readings stabilized. The pH of the soil was potentiometrically measured in the supernatant suspension of a 1:5 soil/liquid mixture. This liquid was 0.01 M $CaCl_2$ solution. 20 g of soil was weighed and to this 100 mL of ultra-pure was added (Kalra, 1995).

3.10   Instrumentation

An ICP-OES was used for the determination of the heavy metals in the soil, water and the vegetable samples. The ICP-OES was chosen for this study because of its multi-element capabilities and effective interference removal. It has the highest matrix tolerance because of its scanning mono-chromator and has the widest usable dynamic range; More also, it has good detection limits and background corrections can readily be made. The wavelengths tabulated in Table 3.3 provided the sensitivity needed to carry out analysis and was corrected for spectral interferences. Suitable wavelengths were used for the selected heavy metals to give accurate concentration levels using ICP-OES as shown in Table 3.3.

Table 3.3: Wavelength selection for metal analytes

Elements	Line selection (nm)
Zn	213.856
Cd	228.802
Pb	220.353
Mn	257.611
Ni	231.604
Cr	267.716
Co	228.616
Fe	256.941
Cu	324.754

ICP-OES generator parameters were set to ensure the instrument provides sensitivity and the ability to perform the analysis. Each parameter is uniquely designed and set to function properly for better analysis of ICP-OE. Table 3.4 shows the suitable parameters used to give accurate concentration levels using ICP-OES.

Table 3.4: ICP-OES generator parameters

Parameters	Units
Plasma power	1400 W
Pump speed	30 rpm
Coolant flow	12.00 L/min
Auxiliary flow	1.00 L/min
Nebulizer flow	1.00 L/min
Add. Flow	None
Oxygen flow	None

The instrumental parameters for element line detection during analysis and the correlation coefficient between the elements analysed are shown in Table 3.5. The distance factor was defined in concentration/concentration.

Table 3.5: ICP-OES instrumental parameters

Parameters	Cr	Cu	Fe	Ni	Cd	Mn	Pb	Zn	Co
Detection Limit, (mg/L)	0.259	0.057	0.014	0.026	0.019	0.023	0.031	0.029	0.068
Correlation Coefficient, (r^2)	0.999	0.999	0.999	0.998	0.999	0.999	0.999	0.999	0.999
Standard error	0.729	0.956	0.822	2.370	1.130	0.824	0.830	0.029	0.815

3.11 Statistical Analysis

Descriptive and multivariate statistical analyses were carried out on the data obtained using SAS statistical software (James et.al, 1976). A number of descriptive and inferential statistical techniques were used to summarise the data and provide information on relationships that exists between variables. A generalized linear model (GML) procedure was performed to eliminate any variables that did not correspond to the even or normalized distribution of data. After performing

the GLM procedure, the 9 sites corresponded to the procedure and were used to perform the statistical analysis. The statistical analysis was performed based on 2 seasons, 2 matrices and 9 sites to determine the inter-relationship between those three factors. After performing the GLM procedure, ad-hoc factorial 3 ANOVA procedure was applied to the data for all the heavy metals as dependent variables.

Another procedure was performed called Duncan's multiple range tests, which was derived from post-hoc ANOVA to compare the mean values between the three factors, the relationship that exists between the matrix, season and sites and to determine if there were any significant differences between the 3 factors. These comparisons were determined by comparing the effect of matrix means and standard deviation, comparing the effect of seasonal means, the effect of site means, effects of seasonal mean versus mean matrix, effect of site means versus matrix means and effect of site means verses seasonal means and matrix means. All these comparisons were performed under post-hoc ANOVA to determine the inter-relationship between the 3 factors. A correlation procedure was also applied to establish significant relationship between the variables at 95 % confidence.

Principal component analysis (PCA) was applied to study/determine variable patterns, sample grouping and trends. PCA is a popular multivariate technique used to reduce the dimensionality of p multi-attributes two or three dimensions. It mainly extracts data that correlate from the uncorrelated components which are estimated from the eigenvectors of the correlation matrix of the variables. Multivariate scree plots and component plots were applied to determine the number of important factors in multivariate settings, such as PCA and factor analysis which assess which factors explain most of the variability in the data. PCA explains the total variance in a variable as possible, while factor analysis explains the correlation of the factors.

The principal component analysis was used to decrease the number of variables comprising a data set while retaining the variability in the data, identifying hidden patterns in the data and classifying them according to how much of the data accounted for. Gabriel introduced PCA in 1971 as a graphical technique for displaying both the samples and variables of multivariate data. In 1966 Cattel introduced scree plots, which are visual tools used to help determine the number of important components in multivariate settings. During the application of PCA, eigenvalue which measures the amount of variation in the components are obtained. These Eigenvalues are

then used to plot a graph producing a scree plot. The scree plots are used to illustrate the rate of change in the magnitude of the eigenvalue for the PCA.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   Introduction

This chapter focuses on the results of the concentrations of the measured heavy metals in water, soil and vegetables collected from the selected allotment gardens, the relationship that exists between soil, water used for irrigation and the vegetables. Physicochemical parameters of soil and water were determined and descriptive statistics were applied to interpret the data. ANOVA and Principal Component Analysis were used to study variable patterns as well as sample grouping and trends.

4.2   pH and OC in soil and water samples

Physicochemical parameters of soil and water can have a pronounced effect on heavy metal mobility and accumulation, and this, in turn, could induce an effect on their availability for plant uptake. Descriptive statistics were applied to the data set to illustrate the range of pH, organic matter and mean measurements of soil and water. Comparisons between soil and water, in summer and winter were made. Table 4.1 shows the physicochemical parameters of soil and water samples.

Table 4.1: Physicochemical measurements of soil and water samples

Matrix	Season	pH	Organic carbon, %
Water	Winter	6.53 ± 0.6	-
	Summer	6.71 ± 0.7	-
Soil	Winter	6.58 ± 0.2	6.8 ± 3.5
	Summer	6.60 ± 0.2	5.6 ± 2.5

The pH of water in winter ranged between 5.80 – 7.24 (6.53 ± 0.6), while in summer it ranged between 5.20 – 7.60 (6.71 ± 0.7). The pH showed no significant seasonal variation ($p > 0.05$). The pH indicates the circum-neutral nature of the water and meets the target range of South African irrigation water (pH 6.5 – 8.4) (Younger, 2007).

The soil pH in winter ranged between 6.29 - 6.84 (6.58 ± 0.2), with corresponding summer values of 6.28 - 6.90 (6.60 ± 0.2). This implies that soils within the study are slightly acidic. The soil pH for both seasons was comparable ($p > 0.05$) and met the targeted pH range of 6.5 to 8.5 for agricultural soils in South Africa (WRC, 1997). The soil pH has a significant influence on metals solubility and soil anion exchange capacity and therefore the availability of heavy metals in soil (Malan et al., 2014). The mean soil organic matter (OM) percentage for the winter and summer sampling periods were 6.8 ± 3.5 % and 5.6 ± 2.5 %, respectively. The organic carbon content for soils in winter was higher than in summer ($p < 0.05$). This could be due to increased use of fertilizers during winter. The sorption of heavy metals to the soil as a result of organic carbon content is probably one of the factors that determine heavy metals concentrations in the soil environment and this depends on soil pH (Kelly et al., 2003; Ayansina and Olubukola, 2017). Sorption to soil affects not only the contaminant level in an ecosystem, but the movement and fate of the contaminant as well.

4.3   Heavy metal in soil and water

The concentration of the selected heavy metals observed in water and soil samples was variable. These concentrations were compared with the allowed limits set by the World Health Organization (WHO, 1995).

4.3.1   Heavy metals in water samples

The mean concentration, with standard deviation of the heavy metals in water during summer and winter, are presented in Table 4.2.

Table 4.2: Mean heavy metal concentrations (mg/L) in water samples obtained from allotment gardens

	Pb	Zn	Cd	Mn	Ni	Cr	Co	Fe	Cu
Summer	0.062± 0.095	0.056± 0.076	0.002± 0.001	0.009± 0.017	0.035± 0.022	0.039± 0.020	0.048± 0.111	0.947± 0.622	0.054± 0.035
Winter	0.041± 0.031	0.002± 0.005	0.005± 0.013	0.007± 0.007	0.106± 0.071	0.088± 0.034	0.024± 0.015	2.347± 4.894	0.096± 0.034
Matrix	0.052± 0.069	0.029± 0.059	0.003± 0.009	0.008± 0.012	0.070± 0.063	0.064± 0.037	0.036± 0.078	1.647± 3.460	0.075± 0.040
Allowed limits (WHO)	2	5	0.03	0.5	0.2	0.1	0.1	3	0.2

The results indicate concentration fluctuation for water during winter and summer, with no definite trend. The concentration of some of the investigated heavy metals appeared to be low during summer with values; Cd, 0.002 ± 0.001 mg/L; Ni, 0.035 ± 0.020 mg/L; Cr, 0.039 ± 0.020 mg/L; Fe, 0.947 ± 0.622 mg/L; and Cu, 0.054 ± 0.035 mg/L, compared with winter concentrations which were, Cd, 0.005 ± 0.013 mg/L; Ni, 0.106 ± 0.071 mg/L; Cr, 0.088 ± 0.034 mg/L; Fe, 2.347 ± 4.894 mg/L and Cu, 0.096 ± 0.034 mg/L. On the other hand, the concentrations of Pb, 0.062 ± 0.095 mg/L; Zn, 0.056 ± 0.076 mg/L; Mn, 0.009 ± 0.017 mg/L; and Co, 0.048 ± 0.111 mg/L appeared to be high during summer compared with winter concentrations of Pb, 0.041 mg/L; Zn, 0.002 mg/L; Mn, 0.007 mg/L and Co, 0.024 mg/L.

These results indicate that there was no significant difference in heavy metal concentration between the two seasons ($p > 0.05$). Fe exhibited the highest concentration variation with respects to season compared to the other heavy metals, with a concentration of 0.947 mg/L during summer and 2.347 mg/L during winter. Cd had the lowest concentration during summer compared to levels of all the other heavy metals, while Zn appeared to be low during summer compared to the rest of the metals. The concentration of the heavy metals in water follow the order Fe > Cu > Cr > Ni > Pb > Co > Zn > Mn > Cd.

All the heavy metals were within the allowed concentration set by WHO (1995).

4.3.2 Heavy metals in soil samples

The mean soil heavy metal concentration with standard deviations collected from different allotment gardens during summer and winter are presented in Table 4.3.

Table 4.3: Mean heavy metal concentrations (mg/kg) in soil samples obtained from allotment gardens

	Cd	Zn	Pb	Mn	Co	Fe	Cr	Cu	Ni
Mean summer	0.52 ± 0.2	30.52 ± 21.2	12.01± 2.1	28.44± 22.3	0.95 ± 0.4	1127.41± 505.3	5.69 ± 5.5	11.42 ± 7.5	3.90 ± 2.9
Mean winter	0.59 ± 0.1	47.41 ± 27.1	16.01± 4.9	43.85 ± 31.4	0.98± 0.4	1292.50± 610.8	7.92± 3.4	18.11± 10.2	7.40 ± 9.0
Mean matrix	0.56 ± 0.2	38.96± 25.1	14.01 ± 4.2	36.14 ± 27.6	0.97 ± 0.4	1209.95± 550.4	6.80 ± 4.6	14.76 ± 9.3	5.65 ± 6.8
Allowed limits (WHO)	10	56	20	-	10	-	10	37	75

The soil heavy metal concentration during summer were: Cd, 0.52 ± 0.2 mg/kg; Zn, 30.52 ± 21.2 mg/kg; Pb, 12.01 ± 2.1 mg/kg and Mn, 28.44 ± 22.3 mg/kg, while levels observed during winter indicated slight elevation, Cd, 0.59 ± 0.1 mg/kg, Zn, 47.41± 27.1 mg/kg, Pb, 16.01 ± 4.9 mg/kg and Mn, 43.85 ± 31.4 mg/kg. However, no significant seasonal variation was observed for the soil heavy metal concentration ($p > 0.05$) of Pb, Zn, Cd and Mn.

The concentrations of Ni, Fe, Co, Cr and Cu in contrast did show a significant seasonal difference at ($p < 0.05$), which were 3.90 ± 2.9 mg/kg; 1127.41 ± 505.3 mg/kg; 0.95 ± 0.4 mg/kg; 5.69 ± 5.5 mg/kg and 11.42 ± 7.47 mg/kg, respectively, during summer, while during winter, levels increased to 7.40 ± 9.0 mg/kg; 1292.50 ± 610.8 mg/kg; 0.98 ± 0.4 mg/kg; 7.92 ± 3.4 mg/kg and 18.11 ± 10.2 mg/kg, respectively.

The soil concentration of Fe appeared to be significantly higher than that for other heavy metals during both seasons. The soil heavy metal concentration decreases in the order Fe > Zn > Mn > Cu > Pb > Cr > Ni > Co > Cd.

The results between water and soil appeared to show a decrease and weak correlation as they were found to follow the decreasing order Fe > Cu > Cr > Ni > Pb > Co > Zn > Mn > Cd and Fe > Zn > Mn > Cu > Pb > Cr > Ni > Co > Cd, respectively. A similar trend was observed in a study conducted by Shi-Bo et al. (2011). The heavy metals in soil were significantly higher ($p <$ 0.05) than in water. Co and Cd appeared to have the lowest concentration for both seasons. Although Cd has no known health benefits to humans, their accumulation at high concentrations can cause deleterious consequences (Page et al., 1987). On the other hand, Fe and Cu are important nutrients needed at low concentrations, when they exceed the allowed concentrations they become toxic and may cause chronic illnesses (Wilson, 2011).

The availability of Fe in the soil is largely determined by the interaction of soil acidity and aeration. Soil pH < 7 and poorly aerated soil result in high Fe availability (Schulte, 2004). The use of fertilizers also affects the availability of Fe because excess use of fertilizers contributes to the formation of Fe complexes that improve Fe availability. Also, when soil oxygen levels are low, which is caused by flooding Fe can reach high toxic levels in the soil solution (Schulte, 2004; Singh et al., 2011).

4.4   Heavy metals in compost

The concentrations of heavy metal in compost collected from different allotment gardens during summer and winter are presented in Table 4.4.

Table 4.4: Average concentrations (mg/kg) of heavy metals in compost used at sites

Sites	Cd	Zn	Pb	Mn	Ni	Cr	Co	Fe	Cu
Abalimi Centre	nd	39.96 ± 0.05	7.48 ± 0.07	107.69 ± 0.04	nd	15.81 ± 0.20	0.43 ± 0.20	981.09 ± 0.40	nd
Fezeka	nd	137.97± 0.06	6.97 ± 0.04	100.57 ± 0.60	nd	26.37 ± 0.02	0.87 ± 0.30	805.47 ± 0.60	nd
Sakhe	nd	89.30 ± 0.02	2.91± 0.40	148.83 ± 0.02	nd	35.59 ± 0.50	1.04 ± 0.40	946.29 ± 0.20	nd

nd = not detected

The Abalimi centre had the highest Fe concentration of 981.09 ± 0.4 mg/kg, followed by Sakhe with a concentration of 946.29 ± 0.2 mg/kg. Compost at Sakhe was high in Mn followed Abalimi centre with concentrations of 148.83 ± 0.02 mg/kg and 107.69 ± 0.04 mg/kg, respectively. Fezeka showed a high concentration of Zn, followed by Sakhe with a concentration of 137.97 ± 0.06 mg/kg and 89.3 ± 0.02 mg/kg, respectively. Cu, Ni and Cd were not detected in compost. The concentration levels of Cd, Ni and Cu observed in soil could be natural or from other sources such as the use of fertilizers. Although the use of compost improves soil physical, chemical and biological properties it can cause significant contamination of the soil by introducing toxic traces of heavy metals (Dumontent et al., 2001; Singh and Kalamdhad, 2013).

4.5 Seasonal effect on heavy metals concentration levels in soil and water

Graphical representations of the mean heavy metals concentration in soil and water samples during summer and winter seasons were used to present trends, and draw comparisons between the two seasonal levels. The charts represented in Figure 4.1 (a) and (b) illustrate the heavy metals concentration in soil and water during summer and winter.

(a)   (b)
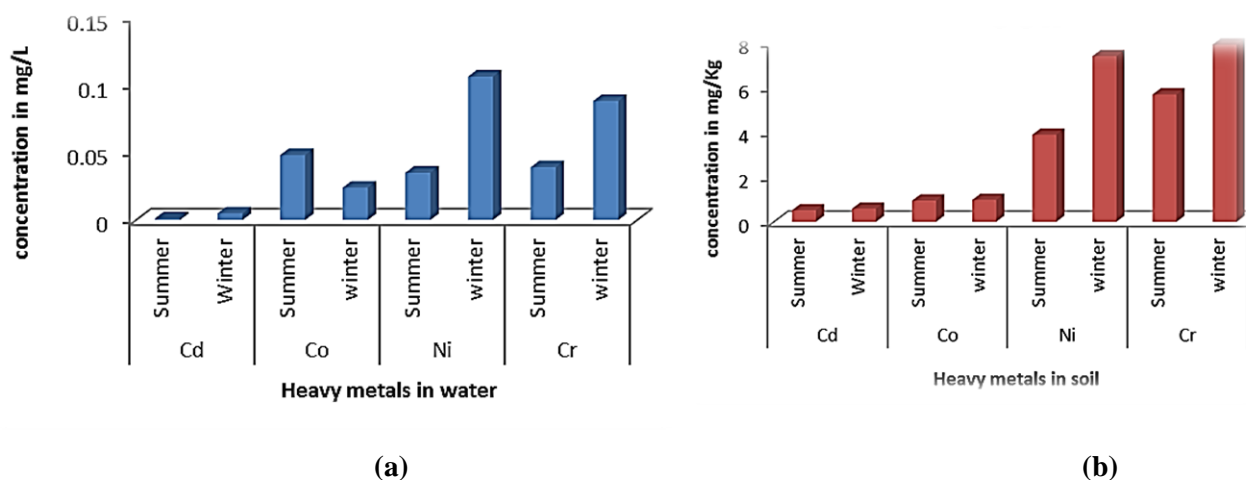
Figure 4.1: Heavy metal concentrations in water (a) and in soil (b) during summer and winter

During winter Ni had the highest concentration at 0.106 ± 0.071 mg/L in water when compared with other heavy metals, followed by Cr in winter with a concentration of 0.088 ± 0.034 mg/L. When comparing the concentration of the heavy metals in soil (Figure 4.1b), the figure shows that Cr followed the trend of having high concentration and then Ni at 7.92 ± 3.4 mg/kg and 7.40 ± 9.0 mg/kg, respectively. This suggests that heavy metals accumulate more in soil than in water, with higher concentrations of Ni and Cr compared with the other heavy metals tested. These low concentrations in water may be due to the fact that the borehole water is stored in irrigation tanks, thus allowing for the possibility of contaminants precipitating and settling out in the tank (Sawere and Ojeba, 2016).

(a)   (b)
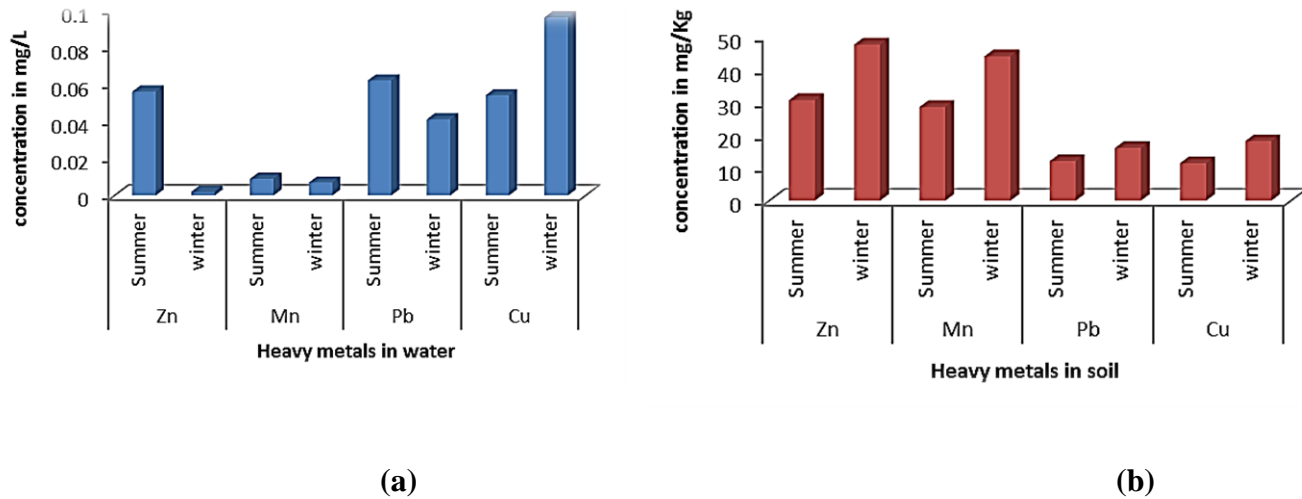
Figure 4.2 Heavy metal concentrations in water (a) and in soil (b) during summer and winter

Figure 4.2a shows that Cu has the highest concentration in water during winter, with concentration of 0.096 ± 0.034 mg/L. Zn and Pb had high concentration in summer when compared to winter, with a concentration of 0.056 ± 0.076 and 0.062 ± 0.095 mg/L, respectively. When the water results were compared with the soil results in Figure 4.2b, a change was observed in heavy metal accumulation. Cu and Pb had the lowest concentrations, while Zn and Mn had the highest concentrations in soil. During winter, Zn and Mn had concentrations of 47.41

± 27.1 mg/kg and 43.85 ± 31.4 mg/kg in soil, respectively. The results showed no significant difference ($p > 0.05$) in the concentration of the measured heavy metals.

(a)   (b)
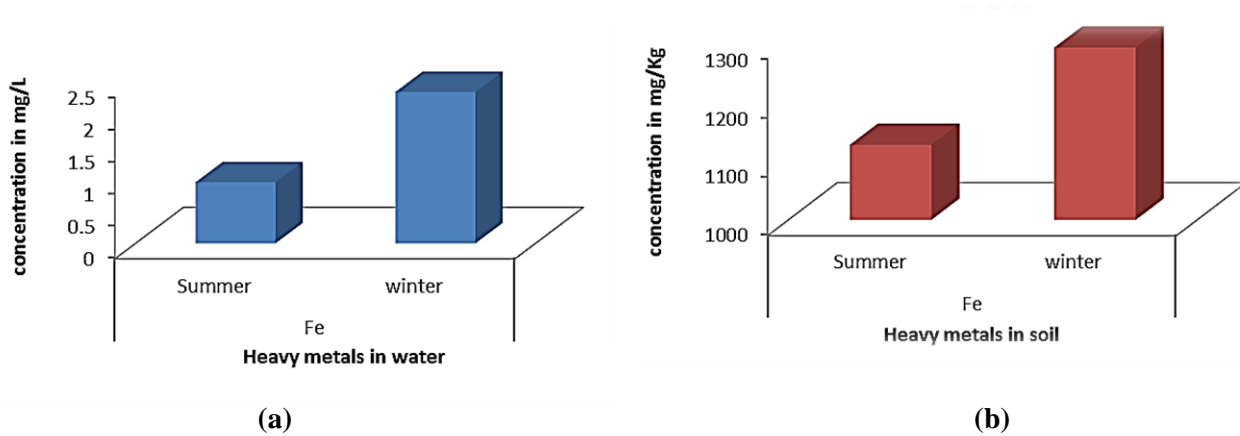
Figure 4.3: Concentrations of Fe in water (a) and in soil (b) during summer and winter

Figure 4.3a illustrates the concentration of Fe in water. The figure shows that Fe had the highest concentration of 2.35 ± 4.89 mg/L in water during winter as compared with a concentration of 0.95 ± 0.62 mg/L in summer, showing a significant seasonal difference at ($p < 0.05$). The results of Fe in soil (Figure 4.3b) were of 1292.50 ± 610.8 mg/kg and 1127.41 ± 505.3 mg/kg in soil for winter and summer, respectively.

There appears to be an increase in the heavy metals concentration of soil during winter, while the results for water fluctuated during both seasons. In a similar study, Saeed et al. (2014) stated that a physicochemical characteristic of water such as pH affects the precipitation of heavy metals.

4.6   Heavy metals at the different sampling sites

The results of the measured heavy metals concentrations in water and soil at the different sampling sites are presented in Figures 4.4a and 4.4b. The mean heavy metal concentration in soil and water at each of the sites was used comparatively to evaluate trends in matrix variations as well as location differences in order to draw inferences between the various sampling sites.
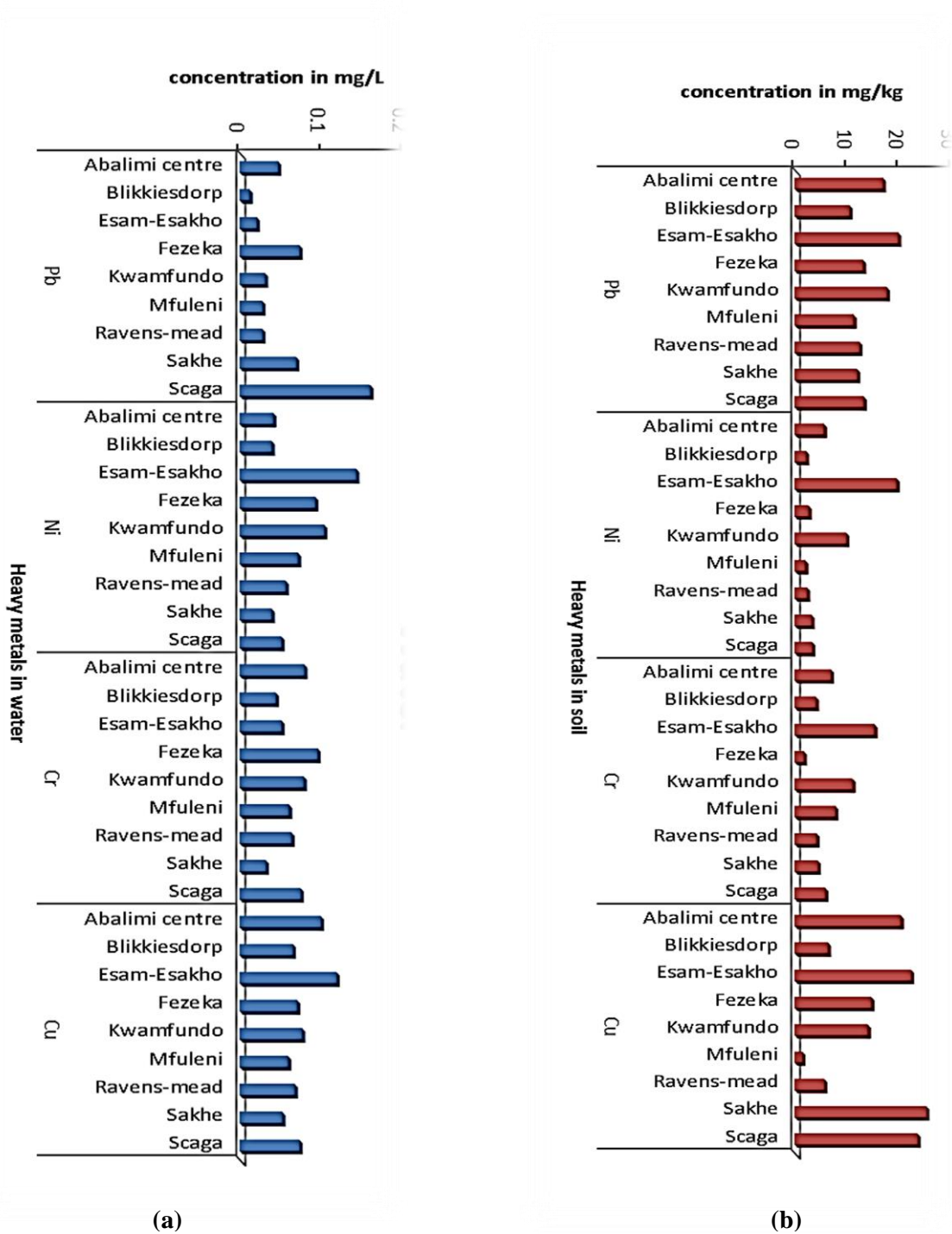
Figure 4.4: Variation in concentration of Pb, Ni, Cr and Cu in water (a) and soil (b) from sampling sites

When results of soil were compared with the results of water shown in Figures 4.4a and 4.4b, the data suggest that Ni, Cr and Cu had relatively high concentrations at most of the sampling sites. Scaga and Esam-esakho showed relatively high concentrations of Pb and Ni in water. In soils, Cu and Pb had the highest concentrations at most of the sampling sites, compared to Ni and Cr content. Sampling sites at Esam-esakho appear to have high levels of Pb, Ni, Cr and Co in soil, compared to the rest of the sampling sites followed by Abalimi Centre.

The 9 sampling sites indicate varying concentrations for the heavy metals. Figure 4.5a and 4.5b represent the mean concentration of Fe in soil at the various sampling sites.

(a)   (b)
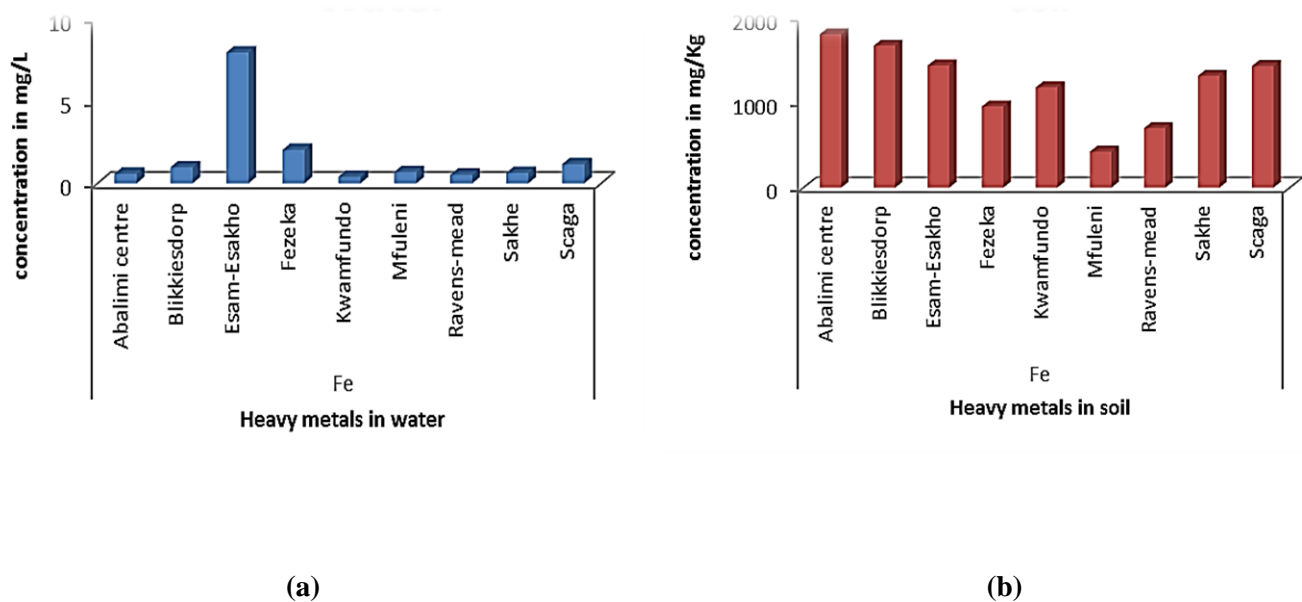
Figure 4.5: Variation in concentration of Fe in water (a) and soil (b) from sampling sites

Figure 4.5a showed low concentration of Fe in water with Esam-esakho being the only site with a concentration of 7.906 mg/L. Figure 4.5b showed high concentrations of Fe in soil at different sampling sites, with most of the sites having Fe concentrations above 1000 mg/kg except for Mfuleni and Ravensmead. Fe in soil has been extremely high when compared to the rest of the heavy metals in soil. High Fe concentration could be due to the fact that soil pH was slightly acid and high in organic content, which probably resulted in retaining heavy metals or enhancement of fertilizers which had a high Fe content (Murray et al., 2014; Chang et al., 2014). Also, Cape Town soils are known to be sandy and known for its relatively high content of Fe (Silveira et al.,

2003; Chibuike and Obiora, 2014). The results clearly indicate that heavy metals in soil and water differ in concentration with sampling site. The rest of the heavy metals such as Co, Mn, Cd and Zn showed higher concentrations in soil than in water, meaning that soil accumulates these heavy metals more rapidly than water. The concentrations of all the heavy metals in the soil and water samples were within the allowed limits set by WHO (1995).

4.7   Multiple linear correlation analysis of heavy metals concentration in soil and water

A Pearson correlation matrix for all parameters was performed on the data. Table 4.5 represents the significant simple linear correlation coefficients between soil heavy metals and soil physicochemical characteristics. The correlation coefficients considered significant were those with a probability level smaller than 1 ($p < 0.05$).

Table 4.5: Pearson correlation matrix for soil heavy metals, organic matter and soil pH

	Cd	Zn	Pb	Mn	Co	Fe	Cr	Cu	Ni	pH	OM
Cd	1										
Zn	0.07	1									
Pb	0.10	0.70	1								
Mn	0.08	0.89	0.54	1							
Co	0.44	0.70	0.39	0.73	1						
Fe	0.01	0.62	0.24	0.68	0.66	1					
Cr	0.31	0.43	0.57	0.44	0.62	0.27	1				
Cu	-0.02	0.81	0.54	0.66	0.48	0.53	0.25	1			
Ni	0.20	0.49	0.78	0.38	0.50	0.23	0.69	0.40	1		
pH	-0.19	0.04	0.31	-0.03	-0.14	-0.14	0.30	-0.09	0.29	1	
OM	0.15	0.69	0.41	0.71	0.65	0.46	0.41	0.39	0.32	0.26	1

Soil pH showed no significant correlation with soil heavy metals. Soil organic matter showed moderate correlation with the micronutrients, Zn, Mn and Co, with a slightly weaker correlation with Fe. The lack of correlation between most of the heavy metals implies that organic matter cannot regulate the availability of heavy metals via complexation of free ions of the heavy metals, with organic material unavailable to plants (Ramachandran and D'Souza, 1998).

It was observed that the correlation among some of the heavy metals was significant ($p < 0.05$). These strong correlations could be due to the fact that cultivated soil was simultaneously contaminated by heavy metals through fertilizers, manures, aerial depositions or borehole water used for irrigation.

Organic matter also has a moderate role in affecting the correlation variation of heavy metals concentration in the soil, as it is affected by factors such as temperature, rainfall and land use which changes the organic matter content as well as the heavy metal concentration in soil (Daka and Sarma, 2012).

The correlation between (Cu and Zn) and (Mn and Zn) in soil was observed to be significant.

These strong correlations serve as a reliable prediction of crop uptake. Studies done in 1992 by Kabata-Pendias showed that the root tissue has a strong capability to hold Cu or Zn against the transport to shoot under conditions of both Cu or Zn deficiency and Cu or Zn excess. This clearly shows that the addition of Zn to soil will result in an increase in Cu uptake by crops.

4.8   Inter-relationships between soil heavy metals, soil pH and Organic matter

4.8.1   Inter-relationship between the heavy metal concentrations in soil

The scree test provides the eigen-value associated with each significant variable. The results showed that the first 3 variables (soil heavy metals, soil pH and Organic matter) explain 77.12 % of the total variability of the data as shown in Table 4.6. Any variable with an eigen-value > 1 is assumed to be meaningful and is retained for rotation; those < 1 are assumed to be unimportant and are not retained.

Table 4.6: Eigen-values for first three variables of PCA

Variable	Eigenvalue	Variance %	Cumulative %
1	5.415	49.23	49.23
2	1.718	15.62	64.85
3	1.350	12.28	77.12
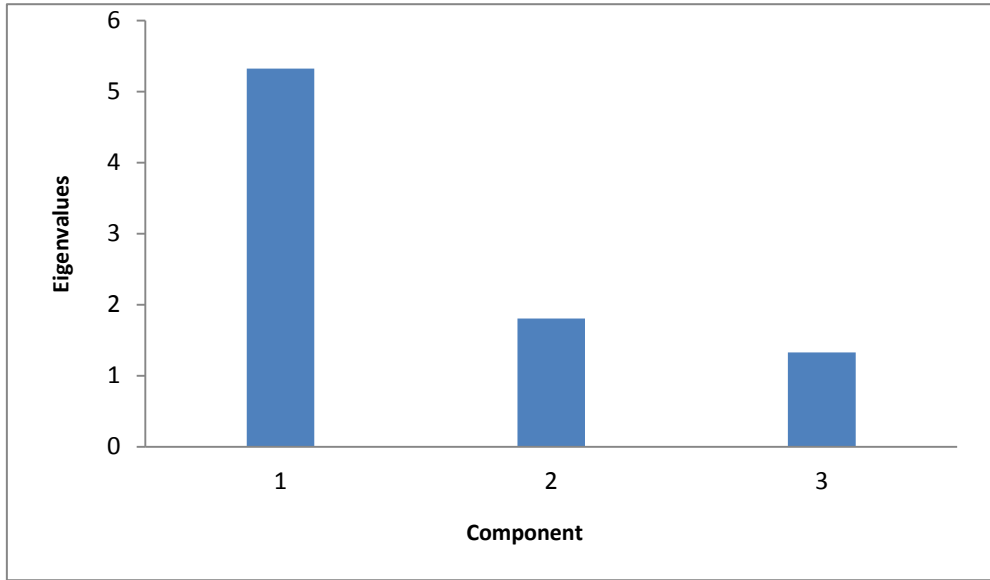
Figure 4.6: Eigen-values for the first three variables

Referring to Table 4.6, principal component 1 comprised 49.23 % of the variance. Component 2 comprised 15.62 % of the variability, while component 3 accounted for the remaining 12.28 %. The 3 components thus describing 77.12 % of the data.

Principal component analysis has been used to assess any trends that might exist among the variables in the data set. Figure 4.7 gives the principal component plot of the soil heavy metals, soil pH and soil organic matter.
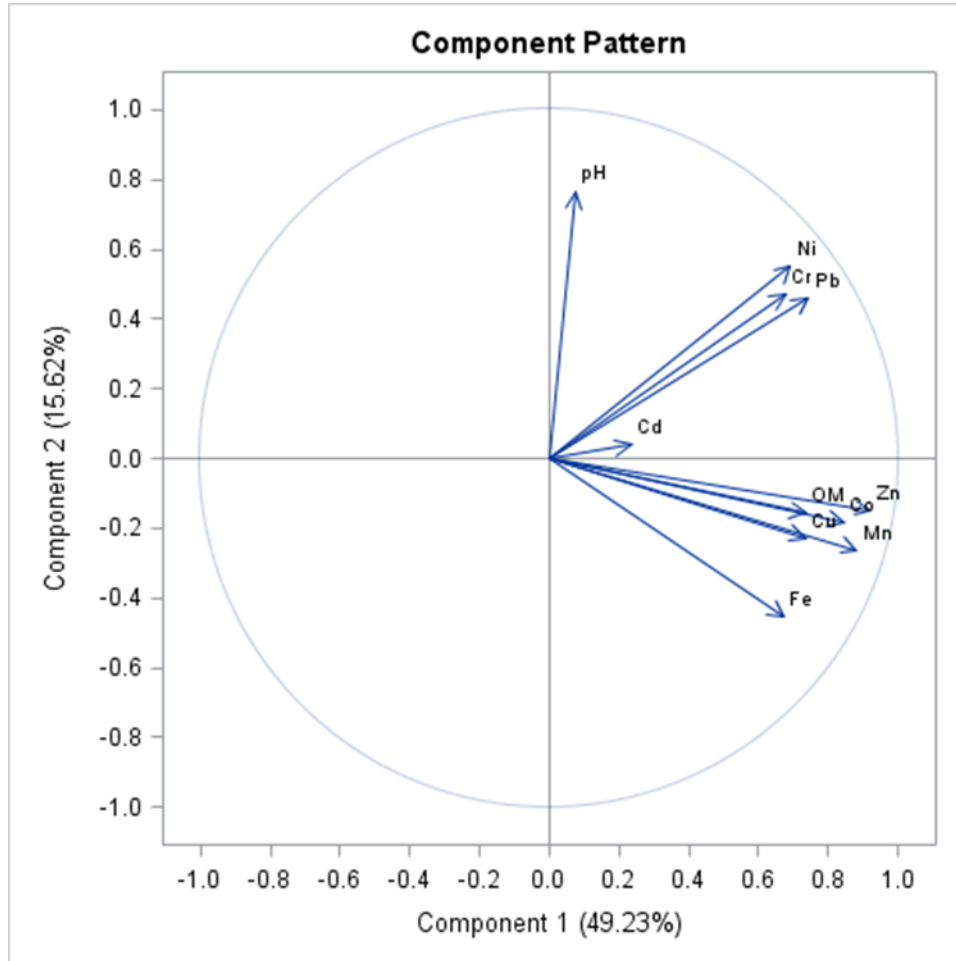
Figure 4.7: Principal component analysis (PCA) for heavy metals in soil

It is clear from the PCA plot that two main groupings exist for the heavy metals, i.e. the clustering of the metals considered as micronutrients (Zn, Mn, Cu, Co and Fe) and that of the non-essential metals (Ni, Pb, Cd and Cr). It is of interest to note that Cr is clustered with the non-essential heavy metals. This could be attributed to the fact that Cr could exist as both Cr^{3+} and Cr^{6+}. The component plot shows that the metals, Zn, Mn, Co, Cu and Fe (to a lesser degree) are influenced to a greater extend by the soil OM compared to Ni, Pb, Cd and Cr. The results also suggest that the concentration of the heavy metals such as Cu, Mn, Co and Fe in soil could be lowered with increasing soil pH which is in agreement with reports by Prescott and Stitt (1976)

4.9 Heavy metals in vegetable samples

Vegetables are an important part of a healthy diet, providing essential nutrients and vitamins for the maintenance of human and animal health. Urban farming has become popular for social, recreational and economic benefits. Among the common vegetable crops grown in home and school gardens are cabbage, spinach, leek onion and green pepper. However, these vegetables may be contaminated either by the use of borehole water for irrigation, or the uptake of bioavailable metals if planted on soils polluted with heavy metals (Saeid, 2012). This can lead to health risks. Furthermore, vegetables can be contaminated with heavy metals due to atmospheric contamination, which might also pose a threat to vegetable quality, animals and human health (Livia et al., 2015; Hang et al., 2016).

The average concentration of heavy metals detected in different vegetables collected from the different sampling sites during summer and winter is presented in Tables 4.7 and 4.8, respectively.

Table 4.7: Average concentrations (mg/kg) of metals in vegetables during summer

	Cd	Zn	Pb	Mn	Ni	Cr	Co	Fe	Cu
Brinjal	nd	5.85 ± 0.6	nd	9.70 ± 4.6	nd	2.16 ± 0.9	1.57 ± 0.8	27.73 ± 22.6	2.10 ± 0.3
Cabbage	nd	1.38 ± 0.9	1.19 ± 0.8	11.01 ± 5.9	nd	1.84 ± 0.3	2.09 ± 0.8	35.63 ± 30.1	1.05 ± 0.7
Spinach	nd	71.17 ± 79.5	nd	9.21 ± 2.4	nd	1.23 ± 0.7	1.24 ± 0.7	126.86 ± 99.6	1.19 ± 0.9
Green pepper	nd	9.73 ± 0.4	nd	8.51 ± 3.3	nd	0.35 ± 0.1	1.39 ± 0.1	63.42 ± 27.3	0.69 ± 0.3
Leek onion	nd	30.77 ± 14.3	10.63 ± 7.4	10.63 ± 4.5	nd	3.85 ± 0.8	1.58 ± 0.2	28.05 ± 22.8	0.9 ± 0.1

nd = not detected

The results show that the average concentration of heavy metals differs for the different types of vegetables sampled during summer. The concentration of Fe was the highest observed in all of the vegetables. Fe levels in spinach were particularly high, with an average concentration of 126.86 ± 99.6 mg/kg. This may be due to easy accumulation of Fe in spinach causing Fe to be rich in spinach (Street, 2012; Jessie, 2015). This was followed by Zn with an average concentration of 71.17 ± 79.5 mg/kg. Cr, Co and Cu, though not significantly different, were 0.35 ± 0.1 mg/kg $-$ 3.85 ± 08 mg/kg; 1.25 ± 0.7 mg/kg $-$ 2.09 ± 0.8 mg/kg; 0.69 ± 0.3 mg/kg $-$ 2.10 ± 0.3 mg/kg, respectively. Cd and Ni did not occur at detectable concentration in all of the vegetables, while Pb was detected in cabbage at 1.19 ± 0.8 mg/kg and leek onion at 10.63 ± 7.4 mg/kg.

When the summer results are compared with that of winter shown in Table 4.8, they showed that spinach was high in Fe, followed by leek onion and cabbage. These vegetables are leafy vegetables that are known to be good accumulators of heavy metals (Thilini and Anil, 2014; Anjula and Sangeeta, 2011). The concentration of heavy metals in vegetables were all within the allowed limits set by (WHO, 1995).

Table 4.8: Average concentrations of metals in vegetables during winter in mg/kg

	Cd	Zn	Pb	Mn	Ni	Cr	Co	Fe	Cu
Cabbage	nd	7.19 ± 5.1	nd	9.19 ± 2.6	nd	7.84 ± 6.9	0.96 ± 1.3	67.14 ± 58.4	1.85 ± 0.6
Spinach	nd	10.69 ± 6.9	nd	6.71 ± 2.2	nd	6.82 ± 4.7	0.38 ± 0.2	92.39 ± 29.9	2.30 ± 0.8
Leek onion	nd	7.17 ± 2.3	nd	4.71 ± 0.8	nd	0.41 ± 0.2	0.41 ± 0.2	62.76 ± 24.9	2.14 ± 0.5

nd = not detected

Similar to the observation for Fe levels in spinach during summer, the concentration of Fe was still highest in most of the vegetables for winter, reaching 92.39 ± 29.9 mg/kg in spinach. This was followed by cabbage and leek onion with concentrations of 67.14 ± 58.4 mg/kg and 62.76 ± 24.9 mg/kg, respectively. The concentration of Cr was 0.41 ± 0.2 mg/kg in leek onion to 7.84 ± 6.9 mg/kg in cabbage; Co, 0.38 ± 0.2 mg/kg in spinach to 0.96 ± 1.3 mg/kg in cabbage and Cu,

1.85 ±0.6 mg/kg in cabbage to 2.30 ± 0.8 mg/kg in spinach. Cd, Pb and Ni were not detected in all vegetables. The average concentration of Mn ranged from 4.71 ± 0.8 - 9.19 ± 2.6 mg/kg, and Zn 7.17 ± 2.32 – 10.69 ± 6.9 mg/kg.

Reports on heavy metal levels in soil in towns in the Eastern Cape Province of South Africa revealed that the concentration of heavy metals in vegetables could occur in the range of 0.01 - 1.12 mg/kg (Fatoki, 1996). Another study conducted showed high levels of Mn in spinach and cabbage, which were beyond toxic levels (Bvenura and Afolayan, 2012).

It has been shown that the uptake of heavy metals by plants is affected by factors such as soil pH, organic matter and soil texture, and this may result in lack of correlation between vegetable and soil concentration of heavy metals in different vegetables (Murray et al., 2014; Chang et al., 2014).

4.10   Comparison of heavy metal in vegetables during summer and winter

A graphical representation of the average heavy metal concentration in the various vegetables was used to illustrate trends and draw comparisons between the various vegetables. Figures 4.8 and 4.9 illustrate average heavy metal concentration levels in vegetables during summer.

The vegetable heavy metal concentration during summer followed the order: spinach (Fe > Zn > Mn > Co > Cr > Cu > Cd ≥ Pb ≥ Ni); cabbage (Fe > Mn > Cr > Zn > Pb > Co > Cu > Cd ≥ Ni) and leek onion (Zn > Fe > Pb ≥ Mn > Cr > Co > Cu > Cd ≥ Ni).
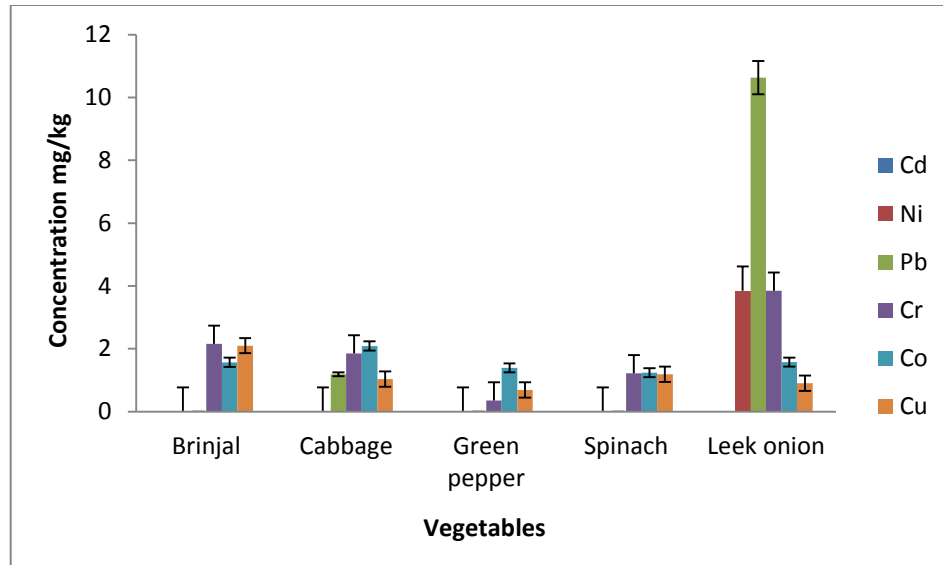
Figure 4.8: Variation in concentration of Cd, Ni, Pb, Cr, Co and Cu in vegetables during summer
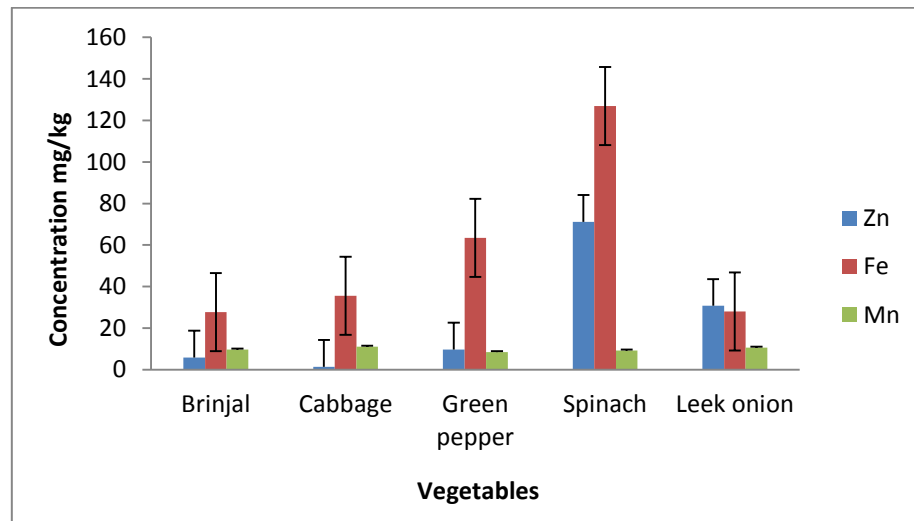
Figure 4.9: Variation in concentration of Zn, Fe and Mn in vegetables during summer

Spinach showed relatively high accumulation tendency for Fe, Zn and Mn, at 126.86 ± 99.6 mg/kg, 71.17 ± 79.5 mg/kg and 9.21 ± 2.4 mg/kg, respectively. A similar trend was observed in a study done by Latit et al 2018, where Fe, Zn and Mn were found to be high in spinach and suggested that the soil type and fertilizers could be responsible factors for the high contents of

these heavy metals in spinach. Zn and Mn are also one of the basic micro-nutrients required for normal plant development (Latit et al., 2018). The levels of Fe, Zn and Mn are low in brinjal and leek onion compared to spinach and cabbage. The level of Cr in leek onion was 3.85 ± 0.8 mg/kg, while Cu in brinjal vegetable was 2.10 ± 0.3 mg/kg. Ni, Pb and Cd were the least accumulated heavy metals by all the vegetables. Figures 4.10 and 4.11 illustrate trends and comparisons of the heavy metals detected in the different vegetable samples during winter.

The vegetable heavy metal concentration during the winter season follows the order: spinach (Fe > Zn > Cr > Mn > Cu > Co > Cd $\geq$ Pb $\geq$ Ni); cabbage (Fe > Mn > Cr > Zn > Cu> Co > Cd $\geq$ Pb $\geq$ Ni) and leek onion (Fe > Zn > Mn > Cr $\geq$ Co > Cu > Cd $\geq$ Pb $\geq$ Ni).
Spinach accumulates Zn at a concentration of 10.69 ± 6.9 mg/kg, followed by leek onion at a concentration of 7.17 ± 2.3 mg/kg. The Mn concentration in cabbage reached 9.19 ± 2.6 mg/kg, followed by spinach at concentration, 6.71 ± 2.2 mg/kg. Cd, Ni and Pb were not at detectable concentrations.
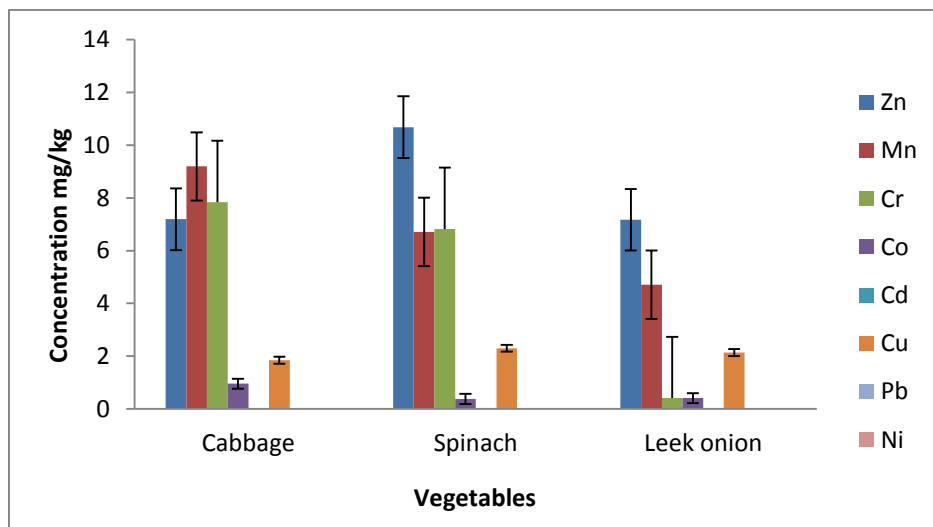
Figure 4.10: Variation in concentration of heavy metals in vegetables during winter

The levels of Fe in Figure 4.11 appear to be the highest in all the vegetables, compared with the other heavy metals.
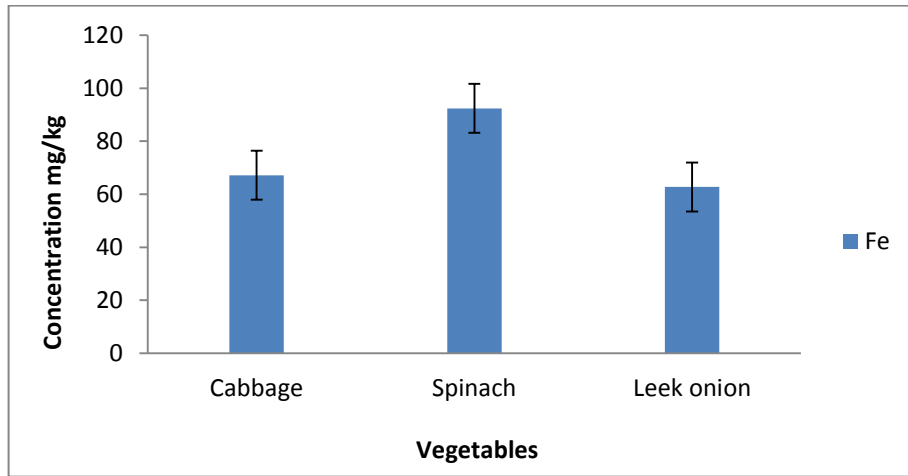
Figure 4.11: Variation in concentration of Fe in vegetables during winter

Spinach had the lowest concentration of Fe in winter than in summer with a concentration of 92.39 ± 29.9 mg/kg, which shows a decrease in Fe concentration, whereas cabbage and leek onion concentration levels of Fe increased in winter by 67.14 ± 58.4 mg/kg and 62.76 ± 24.9 mg/kg, respectively when compared with the summer data.

4.11   Comparison of spatial variation in soil heavy metals between sites location

A non-parametric Mann-Whitney test was performed to assess whether there is any evidence of spatial variation in soil heavy metals level across all sampling sites. A non-parametric test is used to interpret population data that does not have a normal distribution. Non-parametric tests can perform well with non-normal continuous data if the data is sufficiently of large sample size. The statistical parameter P is compared with the critical value. In all cases below the statistical parameter, P exceeds the critical value, implying that no significant difference exists.

Zn: Zn was high in Blikkiesdorp with an average concentration of 38.00 mg/kg, followed by Abalimi with a concentration of 31.00 mg /kg. The sites had no significant difference between Zn concentrations ($P > 0.77$).

Pb: Pb was high in Blikkiesdorp with an average concentration of 41.00 mg.kg, followed by a concentration of 32.00 mg/kg in Scaga. There was no significant difference between the sites ($P > 0.14$).

Mn: Mn was high in Mfuleni, when compared to the rest of the sites with an average concentration of 38.00 mg/kg. Fezeka had the lowest concentration of 12.00 mg/kg of Mn, whereas the observed concentration of Mn for the rest of the sites had no significant difference ($P > 0.05$).

Cr: Ravensmead and Fezeka had the lowest concentration of 7.00 mg/kg and 8.50 mg/kg, respectively when compared with the rest of the sites. Sakhe had the highest average concentration of 34.00 mg/ kg, followed by Esam-esakho site with a concentration of 32.13 mg/kg. This shows that there was no significant difference ($P > 0.15$).

Co: There was no significant difference in the observed concentration levels of Co in all the sites. The lowest concentration of Co was found at Ravensmead and Fezeka (15 mg/kg) with $P > 0.97$.

Fe: Blikkiesdorp had the lowest average concentration of 3.00 mg/kg. The sites had no significant difference in concentration levels with ($P > 0.70$).

Cu: Sakhe had the highest concentration of 36.00 mg/kg, followed by Scaga with a concentration of 34.66 mg/kg when compared with the rest of the sites. Both sites are of the same area, Khayelitsha, which shows no significant difference with the rest of the sites with $P > 0.08$.

The above data showed that, the spatial variation in the concentration distribution of the heavy metals observed or detected in the various sampling sites are not significant.

4.12   Multiple linear correlation analysis for heavy metal concentrations in the vegetables

The Pearson correlation matrix for all parameters was performed to interpret the data. The correlation analysis is a method that is applied to describe the relation between two different parameters. The high correlation coefficient (near $+1$ or -1) means a good relationship between two variables and its correlation around zero means no relationship between them at significant levels of 0.05 % levels. Table 4.9 represents the significant simple linear correlation coefficients between heavy metals and vegetable characteristics. The correlation coefficients considered significant were those with a probability level smaller than 1 ($p < 0.05$). Table 4.9 shows the correlation matrix between heavy metals in vegetables and physicochemical parameters at different sites.

Table 4.9: Pearson correlation matrix of heavy metals in vegetables and physicochemical parameters

	Cd	Zn	Pb	Mn	Co	Fe	Cr	Cu	Ni	OM	pH
Cd	1										
Zn	0.10	1									
Pb	0.13	0.61	1								
Mn	0.17	0.84	0.43	1							
Co	0.49	0.66	0.37	0.69	1						
Fe	0.06	0.55	0.20	0.63	0.68	1					
Cr	0.25	0.39	0.54	0.38	0.53	0.23	1				
Cu	0.02	0.80	0.48	0.69	0.47	0.51	0.26	1			
Ni	0.21	0.43	0.79	0.32	0.50	0.23	0.68	0.39	1		
OM	0.21	0.61	0.28	0.55	0.63	0.45	0.23	0.33	0.20	1	
pH	-0.14	0.02	0.29	0.45	-0.14	-0.13	0.28	0.06	0.29	-0.15	1

Table 4.9 shows the correlation of heavy metals in vegetables at the different sites and soil characteristics. It was observed that the correlation between some of the heavy metals was significant ($p < 0.05$). A strong correlation was observed between (Mn and Zn), (Cu and Zn) and (Ni and Pb). These strong correlations could be due to soil, fertilizers and borehole water impacting plant material in the same way. The accumulation of heavy metals by vegetables depended on the type of vegetables as this kind of trend was observed in this study (South African Bureau Standard, 1984; Ying et al., 2014). In a study reported by Awufolu (2005), it was found that Cd was high in spinach, while Zn concentration was high in spinach and green pepper.

4.13   Bioaccumulation indices of vegetables for the uptake of selected heavy metals

Bioaccumulation factors (BAF) were used to assess the accumulation of heavy metals in vegetables. Bioaccumulation is a process in which certain substances such as heavy metals accumulate in living organisms, posing a threat to health, life and to the environment. If the *BAF* > 1 then the vegetables can be accumulators; *BAF* = 1 is no influence and if the *BAF* < 1 then the vegetables can be an excluder. The bioaccumulation factors of Cd, Zn, Pb, Mn, Co, Fe, Cr, Cu and Ni for vegetables, calculated using Equation 4.1, are given in Table 4.10. The table shows that all the heavy metals have *BAF* < 1.

$$BAF = C_V / C_S$$

 Where: C_V is the mean metal concentration in vegetable samples (mg/kg) and C_S is the mean metal concentration in soil samples (mg/kg).

The ability to accumulate heavy metals varied for the different vegetables. All the vegetables had low uptake for Cd, Ni and Pb, except for spinach and cabbage which showed poor accumulation of 0.11 and 0.06, respectively, during summer (Table 4.10). Cabbage showed greater ability to concentrate Co reaching a maximum accumulation factor of 0.88, followed by Cr with a maximum accumulation factor of 0.82. Of all the vegetables, spinach had the most accumulation of Zn during summer with accumulation factor of 0. 98.

Table 4.10: Bioaccumulation factors for the uptake of heavy metal by the selected vegetables

Vegetables	Bioaccumulation Indices								
	Cd	Zn	Pb	Mn	Co	Fe	Cr	Cu	Ni
Summer									
Brinjal	nd	0.46	nd	0.24	0.74	0.03	0.59	0.15	nd
Cabbage	nd	0.07	0.06	0.29	0.88	0.10	0.82	0.02	nd
Spinach	nd	0.98	0.11	0.58	0.53	0.18	0.79	0.66	nd
Winter									
Spinach	nd	0.25	nd	0.16	0.64	0.46	0.87	0.09	nd
Cabbage	nd	0.21	nd	0.68	0.31	0.03	nd	0.10	nd
Leek onion	nd	0.16	nd	0.22	0.39	0.05	0.52	0.09	nd

nd – not detected

The accumulation factor for brinjal, spinach, and cabbage to hold Zn ranged between nd – 0.46; 0.06 – 0.98; and nd - 0.07, respectively, during summer; while it ranged between 0.03 – 0.25 for spinach, nd - 0.21 for cabbage, and nd - 0.16 for leek onion during winter. The accumulation of Mn in brinjal, cabbage and spinach were; nd – 0.24; 0.23 – 0.29 and 0.22 – 0.58 during summer, while during winter they were; nd – 0.68 for cabbage, 0.07 – 0.16 for spinach and nd – 0.22 for leek onion. The vegetables showed relatively better uptake of Co, with accumulation indices; nd – 0.74 for brinjal, 0.04 – 0.88 for cabbage and nd – 0.53 for spinach during summer.

This trend is similar during winter, although with lower uptake compared with summer (nd – 0.31 for cabbage, 0.13 – 0.64 for spinach and nd – 0.39 for leek onion). Cr was also observed to be fairly bioavailable during summer with brinjal holding between nd – 0.59, spinach, 0.29 – 0.79 and cabbage 0.13 – 0.87. The vegetables showed no particular trend on the uptake of heavy metals with respect to season, as the concentrations varied.

Similar studies recorded that Cr in spinach and cabbage had high bioaccumulation of heavy metals above 1.0 compared to other heavy metals, while Cd was below the detected limit (Lugwisha and Othman; 2016). This trend was also observed in the present study.

The overall vegetables bioaccumulation factors observed for heavy metals were generally below 1.0, indicating a higher proportionate heavy metals concentration in soil in relation to vegetables,

and therefore low vegetable uptake of heavy metals. Significant differences ($p < 0.05$) were found in the bioaccumulation factors of Mn, Zn, Fe, Cu and Cr in the vegetables during both seasons. A similar trend was observed in a study by Zhou et al. (2016). These results also indicate that the ability for heavy metal accumulation in the leafy vegetables was higher than that of the other vegetables.

CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1   Conclusion

The soil pH was generally found to be slightly acidic, while that of water ranged from acidic to neutral. The slight acidity of the soil will imply moderate mobility of the heavy metals. The soil and water pH in winter and summer did not differ significantly ($p > 0.05$).

The soil organic matter ranged from 1.7 % to 13.5 %. Organic matter influences the physical conditions of soil such as increasing the water-holding capacity of soil and regulates heavy metal concentration through complexation. The results indicated that organic matter for soil in winter is higher than in summer ($p < 0.05$).

The water results for all the heavy metals during winter and summer showed variability with no definite trend. Cd, Ni, Cr, Fe and Cu had low concentrations as compared with winter, while in summer Pb, Zn, Co and Mn had higher concentrations as compared with winter. There is no significant difference in heavy metal concentrations between the two seasons ($p > 0.05$). Fe exhibited the greatest concentration increase in comparison to the rest of the heavy metals, showing a significant difference between both seasons. All the heavy metals in water were within the allowed concentration limits set by WHO.

The soil heavy metal concentrations showed a significant difference between both seasons ($p < 0.05$). The soil heavy metal concentrations in winter were higher when compared to summer, indicating that seasonal changes have an effect on the availability of heavy metals in soil and the slight acidity of the soil allowing availability of heavy metals for uptake by plant (vegetables). Fe concentrations were significantly higher when compared to the rest of the heavy metals in soil during both seasons with winter obtaining a greater value of 1292.50 mg/kg. The high Fe concentration in soil during winter could be due to the fact that most seasonal rainfall occurs in winter, resulting in an increase of heavy metals in the soil due to anthropogenic activities.

The data showed a strong correlation between heavy metals in soils ($p < 0.05$), with a moderate correlation of some heavy metals with soil organic matter. There appears to be no significant

correlation between heavy metals and soil pH. These findings suggest that organic matter can regulate the availability of heavy metals via complexation of free ions of the heavy metals, with organic material unavailable to plants. Also, the results suggest that the concentration of some of the heavy metals in soil could be lowered with increasing soil the pH.

There is evidence to suggest that vegetable species vary in their uptake of heavy metals and are independent of site location and seasonality, soil pH and soil organic matter. The results indicate that Fe was of the highest concentration present in all the vegetables during both winter and summer. Fe was particularly high in spinach followed by leek onion and cabbage in summer when compared to that of winter. Zn was also high in spinach in winter than in summer.

In general, leafy vegetables such as cabbage and spinach have better heavy metal uptake than less-leafy vegetables. The Fe level in spinach was higher when compared to all the other vegetables. The heavy metal concentration in vegetables had no correlation between both seasons and the sampling site.

There was a significant difference ($p < 0.05$) found in the bioaccumulation of Mn, Zn, Fe, Cu and Cr during both seasons in the vegetables. The results of this study indicate that the concentration of the heavy metals in soil, water and vegetables were within the allowed limits set by WHO.

5.2 Recommendations

Testing of soil and regular monitoring of toxic heavy metals in soil and vegetables should be practiced to establish the sources of heavy metal contamination to minimize and prevent excess build-up in water and the food chain.

The environmental health officials should put procedures in place for monitoring of heavy metals in vegetables on a more regular basis, which will ensure that no contaminated vegetables reach the public.

Inform the farmers about the results obtained from the study for better farming practices.

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