

# Distribution and Dynamics of toxic heavy metals in cultivated farm produce from Tsumeb, Grootfontein and Otavi localities of, Namibia

Ву

**Joshua Kaviyu Hidinwa** Student no: 215041585

Thesis submitted to the Faculty of Health and Applied Sciences of the Namibia University of Science and Technology in partial fulfillment of the requirements for the award of master's degree in Health Sciences

Supervisors: Professor Omotayo Awofolu Co-Supervisors: Doctor Sylvanus A. Onjefu Doctor Euodia Hess

July 2019

# TABLE OF CONTENTS

Abstract	3
Declaration	5
Retention	5
Acknowledgements	6
Dedication	7
List of abbreviations	8
List of tables	9
Chapter One: Introduction	
1.1 Background of study	
1.2 Statement of the problem	12
1.3 Research question	12
1.4 Aim of study	13
1.5 Objectives	13
1.6 Significance of the study	13
1.7 Limitation	13
1.8 Delimitation	14
1.9 Research outline	14
Chapter Two: Literature Review	16
2.1 Introduction	16
2.2 Cultivated farm soil contamination	17
2.3 Heavy metal contents of soil	
2.4 Sources of heavy metals in soils	19
2.5 Public Health Problem	
2.6 Heavy Metals Analysis Using ICP-OES	20
2.7 Previous researches on distribution	21
Chapter Three research methodology	25
3.1 Sample and sample collection	25
3.2 Selected food samples	25
3.3 Study area	27
3.4 Research design	28
3.5 Quality assurance	

3.6 Data analysis	30
3.7 Research ethics	31
3.8 Statistical Analysis	31
Chapter Four: Results and Discussion	32
4.1 Introduction	32
Chapter Five: Conclusion and Recommendation	53
5.1 Conclusion	53
5.2 References	56
5.4 Appendices	57

#### ABSTRACT

The presence of toxic heavy metals such as Cr, Pb, Ni, As and Hg in foods constitute serious threat to the health of consumers, particularly humans. Continual consumption of foods with high level of toxic metals can lead to bioconcentration and bioaccumulation with long-term health implications. This study was carried out in Tsumeb, Grootfontein and Otavi local municipal areas in the Oshikoto region of Namibia. The focus was to assess the level, distribution and chemical mobility of selected toxic heavy metals in soil and farm produce from agricultural farmlands from these local municipalities. An experimental research design was used in the process of data collection. Soil and food samples from farms were collected over a period of two years. Samples were pre-treated and heavy metals content extracted using mineral acid microwave assisted digestion protocol. Qualitative and quantitative analysis of the metals was by the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

The mean concentration of heavy metals in soil samples across the period ranged from 0.8 mg/kg; 1513.72 mg/kg; 7.97 mg/kg; 1.21 mg/kg; 2.03 mg/kg 13.18 mg/kg and 9.36 mg/kg from Tsumeb. The level in Grootfontein varied from 0.12 mg/kg; 1317.07 mg/kg; 7.97 mg/kg; 0.08 mg/kg; 1.61 mg/kg and 1.35 mg/kg and 8.18 mg/kg, while the concentration from Otavi ranged from 0.41 mg/kg; 1082.9 mg/kg; 7.96 mg/kg; 0.53 mg/kg; 1.75 mg/kg 7.82mg/kg and 8.49 mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The mean concentration of these toxic metals in food samples across the period also ranged from 5.8 mg/kg; 12.49 mg/kg; 0.68 mg/kg; 1.27 mg/kg; ND and ND from Tsumeb. The level in Grootfontein varied from 1.7 mg/kg; 153.5 mg/kg; 0.41 mg/kg; 1.42 mg/kg; 5.13 mg/kg and 13.22 mg/kg 2.06 mg/kg, while the concentration from Otavi ranged from 0.64 mg/kg; mg/kg; 62.3 mg/kg; 0.65 mg/kg; 0.61 mg/kg and 7.33 mg/kg 13.87 mg/kg 4.38 mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. Analyzed metals were widely distributed in both soil and food samples. Metallic accumulation factor (AF) of > 1 was obtained in Manganese, Copper, Nickel and Zinc food samples which revealed chemical mobility of metals from labile metals fractions obtained in soil samples. The mean concentrations of 77.7mg/kg, 60.0 mg/kg, 17.8 mg/kg and 50.4 mg/kg for Manganese, Copper, Nickel and Zinc respectively obtained in food samples were found to be higher than permissible levels in foods.

The presence of analysed metals at this level constitute serious threat to the health of consumers with possible long-term health implications. Comprehensive soil treatment and remediation is recommended for sustainable food production and safety of human health.

Keywords: Heavy metals; Dynamics; Food Produce; Soil; ICP-OES, Namibia

# Retention and use of thesis

I, Joshua Hidinwa, being a candidate for the degree of Master of Health Sciences accept the requirements of the Namibia University of Science and Technology relating to the retention and use of theses deposited in the Library and Information Services.

In terms of these conditions, I agree that the original of my thesis deposited in the Library and Information Services will be accessible for purposes of study and research, in accordance with the normal conditions established by the Librarian for the care, loan or reproduction of theses.

Signed	Date
Joshua Hidinwa	
Signed	Date
Supervisor: Prof. O. Awofolu	
supervisor	
Signed	Date
Co-Supervisor: Dr S. A. Onjefu	
Co-Supervisor: Dr E. Hess	Date
Signed	

## ACKNOWLEDGEMENTS

Firstly, I would like to acknowledge my heavenly Father for giving me strength, wisdom and for blessing me with people in my life who always giving me courage and helping hand. I would like to thank Dundee Precious Metal for financial support. My supervisor Professor Omotayo Awofolu for his wisdom, courage and endless support. I also would like to acknowledge my supervisors Doctor Euodia Hess and Doctor Sylvanus Onjefu for their support. I would also like to acknowledge Dr Julien Lusilao and my friend Shabani Peter for their assistant in the completion of this project. The support received from the Ministry of Agriculture, Tsumeb Municipality and Is acknowledged. Appreciation also goes to the farm managers from Mannhem Research Station, Tsumeb, Otavi fontain Otavi and De Rust, Grootfontein.

# DEDICATION

I would like to dedicate this research to my son Joaquim Panduleni Hidinwa, for always believing in me and reminding me that I need to complete the project.

#### LIST OF ABBREVIATIONS

PM: Particulate Matter HM: Heavy metals WHO: World Health Organisation FAO: Food and Agriculture Organization **RF: Radio Frequency** K: Kelvin SEPI: Single elemental pollution index ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy **BAF: Bioaccumulation Factor** Pb: Lead As: Arsenic Cd: Cadmium Cu: Copper Cr: Chromium Mn: Manganese Ni: Nickel Zn: Zinc Hg: Mercury

# LIST OF TABLES

Table 3. Samples of farm produce collected

Table 3.1 Farm produce collected for sampling purposes

Table 4.1: Maximum Allowable Limits of Heavy Metal in Soils and Vegetables (mg/kg)

Table 4.2: Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 20<sup>th</sup> July 2017.

Table 4.3: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period 20 July 2017.

Table 4.4): Accumulation factors/metal uptake by food samples collected in Tsumeb in Grootfontein and Otavi on the 20th July 2017.

Table 4.5: Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 25th October 2017.

Table 4.6: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period 25 October 2017.

Table 4.7: Accumulation factors/metal uptake by food samples collected in Tsumeb in Grootfontein and Otavi on the 25 July 2017.

Table 4.8): Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on 01 December 2017.

Table 4.9: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period 01 December 2017.

Table 4.10: Accumulation factors/metal uptake by food samples collected in Tsumeb in Grootfontein and Otavi on the 01 December 2017.

Table 4.11: Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 29th March 2018.

Table 4.12: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period of the 29th March 2018.

Table 4.13: Accumulation Factors/metal uptake by food samples collected in Tsumeb in Grootfontein and Otavi on the 29 March 2018.

Table 4.14: Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 13th July 2018.

Table 4.15: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period of the 13th July 2018.

Table 4.16: Accumulation factors of Heavy Metals in food samples collected in Tsumeb, Grootfontein and Otavi on the 13 July 2018.

Table 4.17: Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 14th September 2018.

Table 4.18: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period of the 14th September 2018.

Table 4.19: Accumulation factors of heavy metals in food famples collected in Tsumeb, Grootfontein and Otavi on the 14 September 2018.

Table 4.20: Mean value for SEPI for Tsumeb.

Table 4.21: Mean value for SEPI for Grootfontain.

Table 4.22: Mean value for SEPI for Otavi.

#### **CHAPTER ONE: INTRODUCTION**

#### **1.1** Background of the Study

The ever-growing global concern over the release and subsequent deposition of heavy metals in soils cannot be overemphasised. Alloway (1990), stated that anthropogenic activities, such as mining, agriculture and industrial activities tend to release heavy metals into the soil, water and atmosphere; hence the release of these metals has often been linked to soils in urban areas, and mostly as a result of anthropogenic activities. While justification for research has been fuelled by well-known sources of contamination, such as industrial, petrochemical activities, and automobile emissions around the study area, the interest in the research is premised on the possible effect of these industrial activities on the health human and wildlife. This concern emanates from possible contamination of soil through atmospheric deposition/fallout of elemental contaminants such as lead (Pb), Arsenic (As), Cadmium (Cd), Copper (Cu), Chromium (Cr) and many others.

The study areas are notable for intense commercial agricultural practices as well as many subsistence and communal agricultural cooperative groups. From the former, agricultural produce are cultivated for commercial purposes. Produce are distributed and sold to many other distributors, commercial and retailer stores across the country. The latter also grow agricultural produce for own consumption and for sale at local markets in their respective localities to supplement their incomes. It is generally known that some plants have the potential to take up and sometimes accumulate contaminants. The presence of high level of contaminants in soil may trigger their dynamic transfer from the soil to the plants.

Karagas, Ahsan, Gossai, Pendergrast, Slaughter, Argos, Signes-Pastor and Davis (2017), noted that one of the routes by which toxic trace metals such as copper (Cu), lead (Pb), zinc (Zn) and cadmium (Cd) find their way into human system is through food consumption. This situation may lead to further transfer into human consumers. The consumption of fodders or feedstuff from dried and processed plant shafts e.g. maize shafts that are laden with toxic heavy metals may also lead to transfer to ruminants and eventually human consumers of these animals. Hence, the research is aimed at assessing the distribution and dynamics of toxic heavy metals in cultivated farm produce from three localities namely Tsumeb, Grootfontein and Otavi of Namibia. It is important to provide some information on the three study areas in order to understand their history, nature and some peculiarities.

Tsumeb municipal area is located in the northern central part of Namibia on the edge of the Otavi Mountainland. The major part of the current urban area of Tsumeb is developed on deeply weathered arkosic sandstone and shale of the Tschudi Formation (Mulden Group) and carbonate rocks of the Hüttenberg Formation of the Tsumeb Subgroup. The carbonate rocks of the Hüttenberg Formation are part of the Precambrian platform sedimentation close to the Congo Craton in the northern zones of the Damara Sequence (Schneider, 2004). The dolomites and limestones comprise a thickness of several hundred meters and consist of thin bedded dark dolomite rock with some intercalations of phyllite, limestone, and chert (Schneider, 2004).

Grootfontein: This town is located in the north-east of Namibia in a lush green environment. The district is abundantly endowed with wildlife and game, while the district is well known for its cattle and crop farming. The town still functions as the shipping point for timber products arriving from Kavango-inhabited areas farther to the northeast, while copper and lead mined west of Grootfontein are smelted at Tsumeb.

Otavi town in Namibia, Otjozondjupa region. It is a town of 4,000 inhabitants in the Otjozondjupa Region of central Namibia. It is the district capital of the Otavi electoral constituency. Most of the area is dolomitic (Precambrian) and the district was in the past renowned for its mineral wealth. Most of the deposits have now been exhausted. The towns of Otavi, Tsumeb (to the north) and Grootfontein (to the northeast) define an area known as the "Otavi Triangle", also known as the Otavi Mountainland. This geographical region is sometimes referred to as the "Golden Triangle", or as the "*Mahangu* triangle", owing to the cultivation of *Mahangu* (Pearl Millet) in the area. The three towns that define the triangle are roughly 60 km from each other.

Economy: Much of the town's economy relies on the two grocery stores, a mill, 2 banks, two gas stations, and many surrounding game/cattle farms, as well as a handful of other small business. The owners of most of these businesses are Afrikaners (white Africans of Boer, ultimately Dutch, heritage) or Germans (https://www.namibweb.com/otavi.htm).

11

#### **1.2** Problem Statement

Namibia is endowed with some natural resources including metals such as zinc, uranium and gold. However, during the exploitation of these resources, certain pollutants such as trace metals are generated and released into the environment. Trace metals can find their way into the environment through several routes such as atmospheric deposition as particulate matter (PM), as wastewater and as solid wastes (Benson et al., 2008). Docekalova, Kovarikova and Docekal (2012), states that trace metal mobility across the food chain has been of concern to food experts in view of the health implications. It is upon this background that the researcher carried out this research on the analysis of distribution and dynamic of toxic of heavy metals in cultivated farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia.

Anthropogenic activities such as petrochemical, mining, metal foundries and quarry have been reported as some sources of elemental contaminants in the environment (Bireescu et al., 2014). These contaminants may be distributed widely in the study areas with negative effects on the health of human and wildlife. During metal extraction processes, metals that are of environmental and health significance are released as waste products. Metals such as copper (Cu), zinc (Zn), cadmium (Cd), mercury (Hg) and arsenic (As) can be transported as particulate matter through air and are later deposited on soil surfaces. Cultivated agricultural produce may become contaminated and the consumption of food laden with toxic metals may lead to accumulation in human system with consequential health problems (Afiza et al., 2013). Lead (Pb) for example has been reported to cause brain disorder in children (Canfield et al., 2005). The paucity of information and data on the prevalence and distribution of toxic trace metals in farm produce necessitate this study. The study areas are known for higher agricultural practices compared to some other parts of the country. Research into the possible prevalence of these toxic metals in farm produce is important and significant in view of the health implication across the food chain.

## 1.3 Research questions

The research questions of this research are:

- i. Are the selected toxic heavy metals prevalent in soil and food produce in the agricultural farmlands?
- ii. Are these metals widely distributed in the samples and sampling areas of study?

- iii. Are these metals mobile between the soil and food samples?
- iv. What are the possible health human health implications of consumption of these food samples by humans?

# 1.4 Aim of Research

The main aim of the study was to assess the level, distribution, and dynamics of selected toxic trace metals in the soil and cultivated farm produce from farms around Tsumeb, Grootfontein and Otavi localities of Namibia.

# 1.5 Research objectives

The above research aim will be achieved though the following objectives:

- i. Assess the level of heavy metals in soil and farm produce from the study areas.
- ii. Evaluate the distribution and mobility/transfer of analysed heavy metals from soil to the farm produce.
- iii. Deduce possible human health implications of the level of heavy metals in the farm produce.

# 1.6 Significance of the study

Namibia is endowed with some natural resources such as uranium and gold. Revenues obtained from these are utilized by government to the benefits of all citizens and the country. Although, copper is not mined in Namibia, it is processed and refined in the country. Some gaps however exist in the area of human and environmental protection from exposure to contaminants emanating, purportedly, from anthropogenic activities such as transport, agriculture and industrial activities can be the vehicle of releasing heavy metals in the environment which poses the risk of contaminating the soil and cultivated farm produce.

## 1.7 Limitation

This research was limited to the analysis of the distribution and the dynamics' of toxic heavy metals in soil and cultivated farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia. This means that the research topic is examining the varying occurrence of various farm products like, cabbages, cassava, maize, carrots, spinach, pier melt and sweet potatoes toxic of heavy metals in Tsumeb, Grootfontein and Otavi, in Namibia.

#### 1.8 Delimitation

The delimitations of the study are in light of the sample setting and location, and this reduced the scope of the study also the availability of the farm produce at the different sampling site at the time of sample collection. The target population of the study was farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia.

## 1.9 Research outline

This research is divided into five chapters. The chapters are outlined as follows:

Chapter one covers the research introduction, background of the study, statement of the problem was all explored on the analysis of distribution and dynamics of toxic of heavy metals in cultivated farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia. Research questions and significance of the study are also discussed in this chapter. Finally, the limitations, delimitations and abbreviations were covered in this first chapter.

Chapter two includes the literature review of all the related previous studies concerning the analysis of distribution and dynamics of toxic of heavy metals in cultivated farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia. This chapter discussed different researches and views of different scholars on the analysis of distribution and dynamics of toxic of heavy metals in cultivated farm produce from various farms.

Chapter three outlines the methodology that was used to carry out the research of which the approach was exploratory and experimental. Farm produce that were sampled over the study period include Maize, Pearl Millet, Spinach, Cabbage, Sweet Potato, Carrots and Cassava. Samples were collected based on their availability during the period sample collection which took place once every two months from the three sampling areas of Tsumeb, Grootfontein and Otavi for six periods. Samples were placed in zipper plastic bags, labelled accordingly and transported to Health Sciences laboratory at the Namibia University of Science and Technology for pre-treatment and analysis. Simultaneously, Soil samples were also collected randomly close to the farm produce up to a depth of 15 cm using non-steel scoop sampler. Soil samples were also placed in zipper bags, labelled and take to the laboratory for storage until analysis. This chapter outlines how the data was collected using the ethical considerations of research.

Chapter four is explores the findings and the analysis of data collected, which was based on the soil and agricultural farm produce like, maize, pearl Millet, Spinach, Cabbage, Sweet potato, Carrots, Cassava and of their respective soils were collected from three different locations in Tsumeb, Grootfontein and Otavi. The data collected was analysed and presented in tables, graphs.

Chapter five concentrates on the study's main findings and the recommendations made to the relevant stakeholders. The chapter ends with a conclusion and pointing to further studies followed by appendix A about the granted permission to carry out this research.

#### **CHAPTER TWO: LITERATURE REVIEW**

#### 2.1 Introduction

Heavy metals are natural components of the earth crust and as a result they are found naturally in soils and rocks with a subsequent range of natural concentrations in soils, sediments, waters, and organisms (Hutton and Synmon, 1986). Human activities through industrial, agricultural, traffic, domestic, mining, and other anthropogenic processes have contributed to elevated and toxic levels of these metals when compared to those contributed from geogenic or lithological processes (Pam et al 2013). Traffic associated environmental pollution is one of the most critical or challenging sources, because it is a non-point source and vehicular emissions spread beyond the expected distances polluting the air, land, and water bodies. Onianwa and Fakayode (2000), reported that automobile exhaust accounts for about 80% of the air pollution by heavy metals in Nigeria and this was corroborated by Adriano (2001), who stated that automobile emission is perhaps the greatest single source of contamination.

Onder et al. (2007) reported high content of heavy metals in urban roadside soils and plant samples and attributed it mostly to high density of traffic. Namibia is endowed with some natural resources including metals such as zinc, uranium, and gold. However, during the exploitation of these resources, certain pollutants such as trace metals are generated and released into the environment. Hasheela (2018), states that the contamination of topsoil and crops traces back to both old and recent smelter emissions as well as to windborne dust derived from the tailings and slag dumps of the smelter complex. The concentrations of arsenic lead and cadmium in most of the fruits and vegetables (Marula fruit, pumpkin, chilli, and tomato) correlate with the heavy metal values of the underlying contaminated topsoils.

Mapani et al. (2013) also states, that the topsoils surrounding the smelter, especially in the down wind direction, are highly contaminated with lead, zinc, copper, arsenic, and cadmium. The contamination of the topsoil and crops is a result of historical smelter emissions as well as due to windborne dust derived from the tailings and slag dumps of the smelter complex. Abah et al. (2013) claimed that varying concentrations levels of chromium, cadmium, cobalt, lead, nickel and arsenic in the cabbage and soil obtained from the Bezi bar farm area of Katima Mulilo, Namibia. Trace metals can find their way into the environment through several routes

such as atmospheric deposition as particulate matter (PM), as wastewater and as solid wastes (Benson et al., 2008). According to Ali, Elhagwa, Elfaki, Sulieman (2017), heavy metal inputs into agricultural soils due to atmospheric deposition and application of commercial fertilizers, animal manure, sewage sludge and pesticides take place at rather slow rate, but on large areas. These metals may eventually find their ways into human systems through consumption of these foods (Davis, 2017).

These metals can be deposited on farmlands which are then taken up by plants and agricultural farm produce. Through this route, the metals can find their way into the food chain including humans. There are anthropogenic activities such as mining, quarrying, petrochemical and metal foundry within the study areas whose undertakings may potentially lead to the release of contaminants into the environment. Some studies on the level of heavy metals around Tsumeb were carried out by (Johnson and Myers, 2012; Ellmies et al., 2015). None however, focused on possible distribution and impact outside the vicinity of this area especially in relation to human health. Some of the farm produce, especially fruits, are consumed directly with great implications on human health. In view of this, the project intends to assess the level, distribution, and dynamics of selected toxic trace metals (Cd, Pb, Cu and Zn) in soil and farm produce from selected cultivated sites around Tsumeb, Grootfontein and Otavi localities of Namibia.

#### 2.2 Cultivated farm soil contamination

Soil contamination is any addition of compounds in the soil that results in detectable adverse effect on soil functioning. These also leave elevated levels of heavy metals, hydrocarbons, nutrients, and other compounds on land and possibly in the ground water. Heavy metals constitute an ill-defined group of inorganic chemical hazard. According to Ali, Elhagwa, Elfaki, Sulieman (2017), heavy metal inputs into agricultural soils due to atmospheric deposition and application of commercial fertilizers, animal manure, sewage sludge and pesticides take place at rather slow rate, but on large areas. In addition, Karagas, Ahsan, Gossai, Pendergrast, Slaughter, Argos, Signes-Pastor and Davis (2017), noted that one of the routes by which toxic trace metals such as copper (Cu), lead (Pb), zinc (Zn) and cadmium (Cd) find their way into human system is through food consumption. Trace metal mobility across the food chain has been of concern to food experts in view of the health implications (Docekalova et al., 2012). Metals such as Cd, Pb, Cr, Ni, Zn, Hg and Cu can be deposited on farmlands which may then be taken up by agricultural farm produce. Through this route, the metals can find their way into the food chain including humans. Previous studies on the level of heavy metals around Tsumeb was carried out by (Johnson and Myers, 2012; Ellmies et al., 2015). None however, focused on possible distribution and impact outside the vicinity of this area especially in relation to human health. Some of the farm produce, especially fruits, are consumed directly with great implications on human health. In view of this, the project intends to assess the level, distribution, and dynamics of selected toxic trace metals (Cd, Pb, Cu and Zn) in soil and farm produce from selected cultivated sites around Tsumeb, Grootfontein and Otavi localities of Namibia.

#### 2.3 Heavy metal contents of soil

Soil represents direct sink for contaminants that were released into the atmosphere by anthropogenic polluting activities including mining. Contaminants associated with particulates emitted from mining operations are usually concentrated in the fine fraction (<2 mm), and those from smelting even concentrated in the ultrafine particle fraction (<0.5 mm), which may travel greater distances into the environment (Uzu et al., 2011). Heavy metals can be deposited on soil of farmlands which are then taken up by plants and agricultural farm produce. Some metals like zinc, copper, iron and cadmium are important components of many alloys, wires, tires and many industrial processes and could be released into the roadside soil and plants as a result of mechanical abrasion and wear (Quasar and Kamal, 1999).

Since these metals are not biodegradable, they persist and accumulate over a long time in the soils and vegetation resulting to serious environmental pollution (Mutai et al., 2015). This calls for an increasing concern because the pollution may eventually result in negative influence on plants, animals and humans through food chain (Mtuazi et al., 2015). The determination of metals in soil and vegetation samples is very important in monitoring environmental pollution (Al-Khashman, 2012). Overload of metal ions in soil environment clearly poses a significant risk to the quality of soils, plants, natural waters and human health (Adraino, 2001). The presence of heavy metals in soil could be a double-edged sword ranging from the role in

normal growth of plants and living organisms to toxicity associated with presence of certain metals (Pb, Cd and Hg etc).

## 2.4 Sources of heavy metals in soils

Heavy metals are introduced to the soil environment through a variety of sources such as combustion, extraction processes, agricultural runoff, transportation of dissolved metals etc. (Akhilesh et al., 2009). They further stated that frequent use of heavy metal-contaminated water in agricultural field's leads to soil pollution and gradually enriching the soil. Different studies have revealed that the presence of toxic heavy metals like iron (Fe), lead (Pb), mercury (Hg) reduce soil fertility and agricultural output. Anthropogenic activities, such as mining and industrial processing, were reported as the main sources of heavy metal contamination in the environment (Xilong et al., 2005).

There are different sources of toxic element in urban soils (Thomas et al., 2015). Their loads in and around human settlements are a global problem. Human activities through industrial, agricultural, traffic, domestic, mining and other anthropogenic processes have contributed to elevated and toxic levels of these metals when compared to those contributed from geogenic or lithological processes (Pam et al., 2013).

## 2.5 Public health problem of heavy metals contamination

Some of the farm produce, especially fruits and vegetables, are consumed directly without precooked which can pose great implications on human health. Also as people become health concerned, they consume more fresh fruit and vegetable sometimes direct from the farms which can pose health problems if the soil where the farm produce has been contaminated with heavy metals and a bioaccumulation of the trace metals occurs in the farm produce which in returns end up in the human body when consumed. According to Ali, Elhagwa, Elfaki, Sulieman (2017), heavy metal inputs into agricultural soils due to atmospheric deposition and application of commercial fertilizers, animal manure, sewage sludge and pesticides take place at rather slow rate, but on large areas. In addition to that, Karagas, Ahsan, Gossai, Pendergrast, Slaughter, Argos, Signes-Pastor and Davis (2017) notes that, one of the routes by which toxic trace metals such as copper (Cu), lead (Pb), zinc (Zn) and cadmium (Cd) find their way into human system is through food consumption.

Other researchers also reported on age-related diseases (Prakash, Upadhyay, Gupta, Pushpangadan, & Singh, 2012). According to (Jarup, 2003), some heavy metals (As, Cd, and Pb) have no known beneficial role in human metabolism and are considered as chemical carcinogens even at very low levels of exposure. It has been reported that the dietary intake of lead, copper, and chromium through food is due to plant origin (fruits, vegetables, and cereals) and it is sometimes higher than permissible limits within urban areas (Yebpella et al., 2011). The contamination of farm produces with heavy metals due to soil and atmospheric contamination poses a threat to its quality and safety. High concentrations of heavy metals (Cu, Cd and Pb) in fruits and farm produces were related to high prevalence of upper gastrointestinal cancer (Turkdogan et al., 2002).

Regulations have been set up in many countries and for different industrial set up to control the emission of heavy metals. This research is mainly on the analysis of distribution and dynamic of toxic of heavy metals in cultivated farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia. This means that the research topic is examining the varying occurrence of various farm products like, cabbages, cassava, maize, carrots, spinach, pier melt and sweet potatoes toxic of heavy metals in Tsumeb, Grootfontein and Otavi, in Namibia. According to Ali, Elhagwa, Elfaki, Sulieman (2017), heavy metal inputs into agricultural soils due to atmospheric deposition and application of commercial fertilizers, animal manure, sewage sludge and pesticides take place at rather slow rate, but on large areas. Air pollution may pose a threat to post-harvest farm produces (Agrawal, 2003). Demonstration and determination of trace metals in food are an important task for nutritionists, environmentalists and scientists. Farm produce such as fruits are some of the most common foods of human diet. These are rich sources of vitamins, minerals, fibres and also take on a dependable anti-oxidative effect.

#### 2.6 Heavy metals analysis using ICP-OES

Inductively coupled plasma/optical emission spectrometry (ICP-OES) is a spectroscopic technique suitable for trace elements analysis in several types of samples. The technique is based on the unprompted emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge. Samples are usually introduced into the plasma in liquid

form; thus, solid samples require acid digestion prior to injection, while gas and liquid samples may be injected directly into the instrument. The sample solution is converted to an aerosol then sends into the centre of the plasma which maintains high atomization temperature of around 10,000 K. As the plasma free atoms in the gaseous state are generated and adequate energy is often available to convert the atoms to ions then promote the ions to excited states. The ionic excited state species may then return to the ground state via emission of photons. Specific wavelength of the photons can be used to identify the elements and the number of photons is directly proportional to the concentration of the element. Quantitative determination of As, Cu, Zn, Cd, and Pb in soft drink samples collected from several regions in Turkey was conducted by ICP-OES (Bingöl, Yentür, Er and Öktem, 2010). Also, Raja et al. (2009) reported on Heavy metals concentration in four commercially valuable marine edible fish species from Parangipettai Coast, South East Coast of India using ICP-OES.

#### 2.7 Previous studies on distribution of heavy metals in farm soils

Heavy metal contamination of farm produces cannot be underestimated since human population depended on foodstuff for day to day living. Farm produces are rich sources of essential nutrients to humans and also have beneficial antioxidative effects. However, intake of heavy metal-contaminated farm produces may pose a risk to the human health. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance (Marshall, 2004; Radwan and Salama, 2006; Khan et al., 2008). Rapid and unorganized urban and industrial developments have contributed to the elevated levels of heavy metals in the urban environment of developing countries such as in Egypt by Radwan and Salama (2006). The release of heavy metals from industrial and vehicular active may lead to their deposition on the farm produce surfaces during production processes, transportation of these product and also during their marketing of the farm products.

A study in Saudi Arabia by Al Jassir et al. (2005) reported an elevated concentration of toxic heavy metals in farm produce sold in open markets of the city of Riyadh occasioned by atmospheric deposition. In a recent study by Sharma et al. (2008a, b) reported that atmospheric deposition may results in the elevation of the levels of heavy metals deterioration of farm produce. The study indicated that the ingestion of increase levels of heavy metals through foodstuff pathways may results to disease and damage to the livers and

kidney of human (WHO, 1992; Jarup, 2003). Some heavy metals such as Cu, Zn, Mn, Co and Mo serve as essentials micronutrients and help in the growth of humans and animals only if they are present in trace quantities. On the other hand, other metals such as Cd, As, and Cr are considered carcinogenic (Feig et al., 1994; Trichopoulos, 1997).

The contamination of farm produces with heavy metals due to soil and atmospheric contamination poses harm to its quality and consumption safety. Dietary intake of heavy metals also poses risk to animals and human health. Heavy metals such as Cd and Pb have been shown to have carcinogenic effects (Trichopoulos, 1997). High concentrations of heavy metals (Cu, Cd and Pb) in fruits and farm produces were related to high prevalence of upper gastrointestinal cancer (Turkdogan et al., 2002). Regulations have been set up in many countries and for different industrial set up to control the emission of heavy metals. The uptake of heavy metals in farm produces are influenced by some factors such as climate, atmospheric depositions, the concentrations of heavy metals in soil, the nature of soil on which the farm produces are grown and the degree of maturity of the plants at the time of harvest (Lake et al., 1984; Scott et al., 1996).

Air pollution may pose a threat to post-harvest farm produces during transportation and marketing, causing elevated levels of heavy metals in farm produces (Agrawal, 2003). The mining and smelting of metal ores are one of the important sources of environmental pollution by metals and metalloids (Nriagu, 1996). According to a global inventory by Nriagu and Pacyna (1988) in the late 1980s, about 106kg Pb, and 106 kg Zn were released into the environment annually through mining and smelting activities. More recently, Pirrone et al. (2010) estimated that ore mining and processing is responsible for 13% of global Hg emissions. Despite the fact that Hg, Pb, and Cd emissions from the non-ferrous metal industry decreased in Europe over the last 50 years due to the installation of efficient flue gas cleaning systems (Pacyna et al., 2009), the increasing industrial activities on other continents (Asia, Africa) could significantly affect the global emissions of metals (Pirrone et al., 2010; Zhang et al., 2011).

Zhang et al. (2011) estimated that up to 2007 cumulative emissions from mining, ore dressing, and smelting activities in China were about 1.62 Mt Pb and 3.32 Mt Zn, with the contribution

of the smelting processes accounting for 19% and 27%, respectively. It is known that largescale non-ferrous metal smelters are important local-to-regional sources of pollution. For instance, Li et al. (2011) reported that the largest Pb/Zn smelter in China, located in Zhuzhou (Hunan), emitted 77.82 tonnes of Cd into the atmosphere in the period 1991 to 2000, accounting for 95% of total emissions from the city. Soils represent direct sinks for contaminants emitted to the atmosphere by smelters. Contaminants associated with particulates emitted from mining operations are usually concentrated in the fine fraction (<2 mm), and those from smelting even concentrated in the ultrafine particle fraction (<0.5 mm), which may travel greater distances into the environment (Ettler et al., 2005a; Uzu et al., 2011; Csavina et al., 2011, 2012, 2014; Sorooshian et al., 2012). This was perfectly demonstrated by Hou et al. (2006), who studied Pb concentrations and isotope compositions in soils affected by the Horne copper smelter (Rouyn-Noranda, Canada), and found that the signature of the smelter's emissions was to be found as far as 116 km downwind.

Soils represent direct sinks for contaminants emitted to the atmosphere by smelters. Contaminants associated with particulates emitted from mining operations are usually concentrated in the fine fraction (<2 mm), and those from smelting even concentrated in the ultrafine particle fraction (<0.5 mm), which may travel greater distances into the environment (Ettler et al., 2005a; Uzu et al., 2011; Csavina et al., 2011, 2012, 2014; Sorooshian et al., 2012). This was perfectly demonstrated by Hou et al. (2006), who studied Pb concentrations and isotope compositions in soils affected by the Horne copper smelter (Rouyn-Noranda, Canada), and found that the signature of the smelter's emissions was to be found as far as 116 km downwind.

However, highly volatile contaminants such as Hg can be deposited in soils to lesser extent. Wu et al. (2014) calculated that a large-scale Pb/Zn smelter in Zhuzhou (China) emitted 105t of Hg during the period 1960 to 2011, with only 14% of this amount deposited locally in the soil, with the remainder emitted into the global pool. Historic smelting activities were often responsible for extensive soil contamination having persisted through to modern times. Baron et al. (2006) studied medieval metallurgical sites at the Mont-Lozere Massif (southern France), and estimated from the mass balances and isotope compositions that 95% of Pb in the soils originated from the medieval metallurgical workshops, rendering later pollution sources negligible.

Similarly, Kierczak et al. (2013) found that soils in the areas around historic smelters, which were active between the 14th and 16<sup>th</sup> centuries, are still highly polluted with metal(loids)s (up to 4000 mg/kg Cu, 1500 mg/kg Zn, 300 mg/kg As, and 200 mg/kg Pb) due especially to the centuries-long dissolution of smelter wastes into the soils. They concluded that the legacy of old smelting sites, even those which have not been operational for centuries, must still be considered as a serious environmental problem today. Demonstration and determination of trace metals in food are an important task for nutritionists, environmentalists and scientists. Farm produces and Fruits are some of the most common foods of human diet in all around the humankind. These are rich sources of vitamins, minerals, fibres and also take on a dependable anti-oxidative effect.

# CHAPTER THREE: RESEARCH METHODOLOGY

# 3.1 Sample and sample collection

Soil and agricultural farm produce such as (maize, pearl millet, spinach, cabbage, sweet potato, carrots and cassava). Three samples that are available throughout the year were collected from farm sites in Tsumeb, Grootfontein and Otavi once every two months for six periods. Samples of maize, pearl millet, spinach, cabbage, sweet potato, carrots, cassava and of their respective soils were collected from 3 different locations in Tsumeb, Grootfontein and Otavi. The samples were placed in zipper plastic bags, labelled accordingly and were then transported to Environmental Health Department, Namibia University of Science and Technology for pre-treatment and laboratory for analysis. Simultaneously, soil sample from the same locations of farm produce were collected from a depth of 2 to 15 cm by using a non-steel sampler (scoop sampling).

# 3.2 Selected food samples

To analysis for heavy metals in soil and food sample from the three selected locations, the following food samples presented in table 3.1 were selected.

**Table 3.1:** Farm produce collected for sampling purposes



Spinach (Spinacia Oleracea)	
Cassava	
(Wianinot esculenta)	
Maize	
(Zea mays)	
Pearl Millet (Eleusine Coracana)	
	TE ASTA A STATES I SALE



# 3.3 Study Area

Namibia's population is estimated at 2.1 million according to Namibia Population Census of 2011 (NPS 201). Namibia is one of the least densely populated countries in the world with just 3.13 people per square kilometre. Figure 3.1 show the Map of Namibia with location where samples were collected.

# 3.3.1 Tsumeb

Tsumeb (Otjiherero name: Okavisume) is a city of 15,000 inhabitants according to Namibian Population census of 2011 (NPC, 2011). Tsumeb is the largest town in the Oshikoto region in northern Namibia located at 19<sup>o13</sup>'59.99''S; 17°43'0.01''E. Tsumeb is the "gateway to the north" of Namibia. It is the closest town to the Etosha National Park. Tsumeb used to be the regional capital of Oshikoto until 2008 when Omuthiya was proclaimed a town and the new capital. The area around Tsumeb forms its own electoral constituency and has a population of 44,113. The town is the site of a deep mine (the lower workings now closed), that in its heyday was known simply as "The Tsumeb Mine" but has since been renamed the Ongopolo Mine.

# 3.3.2 Grootfontein

Grootfontein (English: Large Spring after the nearby hot springs) is a city of 23,793 inhabitants in the Otjozondjupa Region of central Namibia (NPC 2011). It is located at 19°34'0.01''S; 18°7'0.01''E. Grootfontein is one of the three towns in the Otavi Triangle, situated on the B8 national road that leads from Otavi to the Caprivi Strip. Grootfontein receives an annual

average rainfall of 557 millimetres (21.9 in), although in the 2010/2011 rainy season 956 millimetres (37.6 in) were measured.

# 3.3.3 Otavi

Otavi is a town of 4,000 inhabitants in the Otjozondjupa Region of central Namibia located in19°65′0.01″S; 17°20′0.01″E. It is the district capital of the Otavi electoral constituency. Most of the area is dolomitic (Precambrian) and the district was in the past renowned for its mineral wealth. Most of the deposits have now been exhausted.



Fig 3.1: Map of Namibia and in-set, the region and areas of sample collection

## 3.4 Research design

Exploratory and experimental research design was adopted in the study. This type of research design is appropriate since determinants on which the evaluation and interpretation of data were based on the investigation for possible presence through scientific laboratory processes. Similar approaches have been used in previous studies (Mohammed and Al-Qahtani, 2012). Purposive sampling for data collection purposes was adopted. One agricultural farmland from each of the study areas (Tsumeb, Grootfontein and Otavi) was selected for this study.

Purposive sampling site selection was carried out based on farm owners' acceptance of collecting samples from the farmland. Samples were collected once every two months for twelve (12) months. Hence, six (6) sets of samples/data were generated from the exercise.

Soil and agricultural farm produce that are commonly cultivated were sampled. These include and Maize, Pearl Millet, Spinach, Cabbage, Sweet potato and Cassava). Food samples were collected based on seasonal availability across the three sampling sites. Three (3) samples were selected from the agricultural farm and collected from the identified sample sites. Hence, a total of nine food samples and three soil samples were collected per sample collection period. Soil samples were collected and analysed with the aim of establishing possible transfer/dynamics of trace metals from the soil to the produce.

#### **3.4.1** Sample preparation

All farm produce samples were thoroughly washed with water and then with distilled water in order to remove any attached soil particles. They were then cut into small pieces, places in clean crucibles and then dried in the oven at 105 °C for a period of 24 hours. Collected soil samples were already dry, however, they were also further air-dried for about 24 hours. Dried food samples were grounded using clean acid-washed mortar and pestle and then sieved using a 0.5 mm sieve, stored in labeled plastic containers until analysis. Dried soil samples were also sieved using 0.2 mm sieve and analysis was based on the fine soil particles obtained from this process.

#### 3.4.2 Experimental

Experimental (qualitative and quantitative) analysis of samples involve sample digestion, preconcentration, extraction, and metal determination was conducted following previously described method (Opaluwa et al., 2012).

#### 3.4.2.1 Metal extraction from food samples

Briefly, the method involves digesting gently on low heat about 2g of food sample with 15 ml of nitric acid, 20 ml of perchloric acid and 15 ml of hydrofluoric acid on hotplate for about 2 hrs in the fume hood. On cooling, the digested sample were filtered into 50 ml standard flask, made up to mark with deionised water and the metallic content determined using Inductively

Coupled-Plasma Optical Emission Spectrophotometer (ICP-OES). For food samples, 2-3 g of dried powdered samples were digested with 10 ml of perchloric acid, 5 ml of nitric acid and 5 ml of sulphuric acid in the fume hood for about 1 hr. At the end, the digest is allowed to cool, filtered into 50 ml standard flask and make up to the mark with deionised water. The metallic content is determined using Inductively Coupled-Plasma Optical Emission Spectrophotometer (ICP-OES). Blank digestion was carried out to check for any background influence. Data obtained were subjected to statistical analysis for proper interpretation and discussion.

#### **3.4.2.2** Metal extraction from soil samples (3-Steps BCR Extraction Process)

A three-step modified BCR sequential extraction procedure was used to obtain exchangeable, reducible-iron/manganese oxides, oxidizable-organic matter and sulphides and residua fractions (Li, 2012).

#### Step 1 (Exchangeable Fractions)

40 cm<sup>3</sup> of acetic acid (0.11 M) was added to 1 g of soil and shaken for 16 hours using mechanical agitator. The extract was separated from the solid residue by centrifugation, filtered with a filter paper (0.45  $\mu$ m) and stored in a polyethylene container at 4°C until needed. The residue was washed with 20 cm3 of deionized water, shaken for 20 minutes, centrifuged and the supernatant discarded ensuring that no solid residue was lost.

#### Step 2 (Reducible-Iron/Manganese Oxides)

40 cm<sup>3</sup> of hydroxyl ammonium chloride solution (0.5 M, pH = 2) was added to the residue obtained in step 1 and extracted using the procedure in step 1.

## Step 3 (Oxidizable-Organic Matter and Sulphides)

10 cm3 of hydrogen peroxide solution (30%) was added to the residue obtained in step 2 and digested at room temperature for 1 hr. The digestion was continued by heating at 85°C in the digestion block for 1 hr to reduce the volume to less than 3 cm3. A second aliquot of hydrogen peroxide solution (30%, 10 cm<sup>3</sup>) was added and the digestion procedure repeated. 50 cm<sup>3</sup> of ammonium acetate (1 M, pH = 2) was added to the cool moist residue. The sample was shaken, centrifuged and the extract separated as described in step 1. The metallic content is determined using Inductively Coupled-Plasma Optical Emission Spectrophotometer (ICP-OES). Blank digestion was carried out to check for any background influence.

## 3.5 Quality Assurance

Quality control tests was carried out on the soil and farm produce samples in order to evaluate the applicability of the experimental process. Standard metal addition method of pre-digested samples of farm produce and soil with 0.5 ppm of analysed metals (Hg, Mn, Ni, Cr, Cu, Pb, and Zn) prepared from 1000µg/g stock standard solution was carried out. The spiked samples were then digested following the same procedure as that of soil and farm produce samples. Detection of analysed metals was conducted using Inductively Coupled-Plasma Emission Spectroscopy (ICP-OES).

## 3.6 Data analysis

Data generated from the instrumental analyses of digested samples were presented in tabular and graphical forms as applicable.

## 3.7 Research ethics

Ethical clearance was obtained from the Faculty of Health and Applied Sciences of the Namibia University of Science and Technology. Additional approval was obtained from the Namibian Ministry of Agriculture, Water & Forestry as well as from the local authorities of Tsumeb, Grootfontein and Otavi.

## 3.8 Statistical Analysis

## 3.8.1 Accumulation Factors (AFs) of Heavy Metals

The processed data provided an indication of possible incidences and level of trace metals in soil and analysed food samples. It revealed possible mobility/distribution of these trace metals among analysed samples as well as potential health implications to consumers. Accumulation factors (AFs) is defined as the ratio of the metal concentrations in plants/the edible parts of the vegetable to the metal concentrations in the soil.

AF can be used to estimate the ability of plants/vegetables to accumulate metals in their edible parts (Kaewtubtim et al., 2018).

# 3.8.2 Single Element Pollution Index (SEPI)

The permissible level of metals in soil suggested by Kabata-Pendias (2004) was used for calculation and each heavy metal was classified as low contamination (SEPI  $\leq$  1), moderate contamination (1<SEPI  $\leq$ 3) or high contamination (SEPI>3) (Chen et al. 2005). The permissible used for the calculation of SPEI are presented in Table 4.1.

## CHAPTER FOUR: RESULTS AND DISCUSSION

## 4.1 Introduction

The previous chapter presented the research design and the methodology used to collect data. In this chapter, the collected data were analysed and presented in tables and graphs and end with a conclusion.

Results of the quality assurance process of applied methods showed Percentage recoveries of standard metal addition of pre-digested samples to be in the range of 90-96% for the analysed metals. This range showed the applicability of the analytical process utilised as well as reliability of the results obtained.

The WHO/FAO Maximum Allowable Limits (MALs) of heavy metals in plants/vegetation and soil is as presented in Table 4 below. This table will be used in evaluating the level of heavy metals obtained in collected samples.

Element		Samples
	Soil	Vegetable
Cr	100	1.30
Mn	2000	500
Hg	0.03	0.03
Ni	50	67.0
Cu	100	73.0
Zn	300	100
Pb	100	0.30

Table 4.1: Maximum Allowable Limits (mg/kg) of Heavy Metal in Soils and Vegetables

Source: (WHO/FAO, Codex Alimentarius, 2002)

# 4.2 Heavy metals in food and soil samples after first sampling

Results of the level of analysed heavy metals in food samples and soil during the first period of sampling (20 July 2017) are as presented in Tables 4.2 and 4.3 respectively. Results of the bioaccumulation factors (BAFs) of the metals are presented in Tables 4.4.

SA	FS	Metals									
Т	SP	Cr	Mn	Hg	Ni	Cu	Zn	Pb			
		7.35	18.8	0.80	0.92	ND	ND	ND			
	CA	4.25	6.17	0.56	1.62	ND	ND	ND			
	Х	5.8±1.6	12.5±6.3	0.68±0.12	1.27±0.4	ND	ND	ND			
G	SN	1.57	389	0.41	ND	6.23	17.7	2.58			
	CR	1.82	30.0	0.40	1.42	4.03	17.6	2.68			
	СВ	ND	41.4	ND	ND	ND	4.35	0.92			
	Х	1.7±0.2	153.5±205	0.405±0.1	1.4	5.13±1.6	13.22±7.7	2.06±1.0			
0	SN	0.23	52.3	0.51	ND	10.6	19.3	3.83			
	CR	1.01	11.5	0.84	0.61	4.06	12.5	5.65			
	СВ	0.67	123	0.59	ND	ND	9.80	3.66			
	Х	0.64±0.4	62.3±56.4	0.65±0.17	0.61	7.33±6.6	13.87±5.0	4.38±2.0			

**Table 4.2:** Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 20<sup>th</sup> July 2017

SP = Sweet Potatoes; CA = Cassava SN = Spinach; CR = Carrot; CB = Cabbage; X = mean T = Tsumeb;
 G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample; ND = Not Detected

The level of toxic heavy metal in food samples from the farmland in Tsumeb were 7.35 mg/kg (Cr) in Sweet Potatoes; 4.25 mg/kg in Cassava; 18.8 mg/kg (Mn) in sweet potatoes; 6.17 mg/kg in cassava; 0.80 mg/kg (Hg) in sweet potatoes; 0.56 mg/kg in cassava; 0.92 mg/kg (Ni) in sweet potatoes; 1.62 mg/kg in cassava; and Cu, Zn and Pb were not detected in both sweet potatoes and cassava. The level of analysed metals in food samples from the farmland in Grootfontein were 1.57 mg/kg (Cr) in spinach; 1.82 mg/kg in carrots; ND in cabbage; 389 mg/kg (Mn) in spinach; 30.0 mg/kg in carrots; 41.4 mg/kg in cabbage; 0.41 mg/kg (Hg) in spinach; 0.40 mg/kg in carrots and ND in cabbage. Nickel was also ND in spinach; 1.42mg/kg was recorded in carrots; 6.23 mg/kg of Cu in spinach; 4.03 mg/kg in carrots and ND in cabbage.

With respect to Zn, 17.7 mg/kg was recorded in spinach; 17.6 mg/kg in carrots; 4.35 mg/kg cabbage; 2.58mg/kg (Pb) in spinach; 2.68 mg/kg in carrots and 0.92 mg/kg in cabbage. And the level of toxic heavy metal in food samples from the farmland in Otavi were 0.23 mg/kg (Cr) in spinach; 1.01mg/kg in carrots; 0.67 mg/kg in cabbage; 52.3 mg/kg (Mn) in spinach; 11.5mg/kg in carrots; 123 mg/kg in cabbage; 0.51 mg/kg (Hg) in spinach; 0.84 mg/kg in carrots and 0.59 mg/kg in cabbage; (Ni) was not detected in both spinach and cabbage; 0.61 mg/kg in carrots; 10.6 mg/kg (Cu) in spinach; 4.06 mg/kg in carrots; cabbage it was not detected 19.3 mg/kg (Zn) in spinach; 12.5 mg/kg in carrots; 9.80 mg/kg in cabbage; 3.83 mg/kg (Pb) in

spinach; 5.65 mg/kg in carrots; 3.66 mg/kg in cabbage for the period of 20th July 2017 respectively.

The permissible limit of Chromium in vegetable 1.30mg/kg as indicated in the recommendation of WHO/FAO. Concentration of chromium were as follow, in Sweet potatoes 7.35 mg/kg, 18.8 mg/kg in Cassava (Tsumeb), 1.57 mg/kg in sweet potatoes, 1.82 mg/kg in Carrots (Grootfontain) farm produce during the first sampling period, which is higher the permissible level. The permissible limit of Nickel in plants recommended by WHO/FAO is 10mg/kg. The level of Nickel (Ni) in farm produce samples ranged between 0.23, 0.61, 0.67, 0.92, 1.01 to 1.62 mg/kg which is below the permissible limit. The permissible limit of copper for plants is 10mg/kg recommended by WHO. Copper in farm produce samples ranged between 4.03, 4.06, 6.23 to 10,6 mg/kg. Most of these farm produces are found to be below the permissible limit in vegetable as recommended by WHO. Lead in farm produce samples ranged between 0.92, 2.58, 2.68, 3.66, 3.83 to 5.65 mg/kg, which is below the permissible limit including Cabbage for the first sampling period (20 July 2017).

	(20 Jul	y 2017)						
SA	SS				Metals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	EXB	0	25.57	11.95	0	0.02	15.90	11.95
	RIM	0	14.75	11.96	0	0	12.28	11.96
	OM	2.4	4500.83	0	3.62	6.07	11.37	4.18
	Х	0.8±1.1	1513.7±259.9	7.97±6.9	1.21±2.1	2.03±3.5	13.18±2.40	9.36±4.49
G	EXB	0	24.26	11.96	0.08	0.08	0.31	11.96
	RIM	0	18.87	11.96	0.03	0	0.56	11.96
	OM	0.36	3908.08	0	1.63	4.74	3.16	0.61
	Х	0.12±0.2	1317.07±2243.9	7.97±6.9	0.08±0.9	1.61±2.7	1.35±1.58	8.18±6.55
0	EXB	0	40.02	11.94	0	0	0	11.94
	RIM	0	13.49	11.94	0	0	11.78	11.94
	OM	1.22	3195.17	0	1.58	5.25	11.68	1.58
	Х	0.41±0.7	1082.9±1829.4	7.96±6.9	0.53±0.9	1.75±3.1	7.82±6.8G	8.49±5.98

**Table 4.3:** Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period

 (20 July 2017)

**EXB** = Exchangeable; **RIM** = Reducible-iron/Maganese Oxides; **OM** = Oxidizable-Organic-Matter; **X** = mean; **SA** = Sampling Area; **SS** = Soil Sample; **T** = Tsumeb; **G** = Grootfontein; **O** = Otavi

The mean concentration of HMs in soil samples from Tsumeb during the first sampling period (20 July 2017) ranged from 0.8mg/kg; 1513.7mg/kg; 7.97mg/kg; 1.21mg/kg; 2.03mg/kg; 13.18 and 9.36mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. While the values in the soil from Grootfontein during the same period of (20 July 2017) varied from 0.12mg/kg; 1317.07mg/kg; 7.97 mg/kg; 0.08mg/kg; 1.61mg/kg; 1.35mg/kg and 8.18mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. As for Otavi the soil samples concentration obtained for the period of (20 July 2017) were 0.41mg/kg; 1082.9; 7.96mg/kg; 0.53mg/kg; 1.75mg/kg; 7.82mg/kg and 8.49mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. For the above results, the levels of HMs found to be lower than the maximum permissible limit in soil, however this showed the availability of the plant to uptake the metals. The source of these metals may include atmospheric particulate matter (PM) deposition from Anthropogenic activities and other natural occurring.

The AFs of HMs were deduced using the metal exchangeable fraction from the Speciation analysis. This is because these are the available metals in the soil for the plant uptake.

				,					
SA	FS		Metals						
		Cr	Mn	Hg	Ni	Cu	Zn	Pb	
Т	SP	-	0.07	0.07	-	-	-	-	
	CA	-	0.2	0.05	-	-	-	-	
G	SN	-	16.03	0.03	-	77.9	60.0	0.2	
	CR	-	1.24	0.03	17.8	50.4	56.8	0.2	
	СВ	-	1.7	-	-	-	14.0	0.08	
0	SN	-	1.3	0.04	-	-	-	0.3	
	CR	-	0.29	0.07	-	-	-	0.47	
	CB	-	3.07	0.05	_	_	-	0.31	

**Table 4.4:** Accumulation factors/metal uptake by food samples collected in Tsumeb inGrootfontein and Otavi on the 20<sup>th</sup> July 2017

SN = Spinach; CR = Carrot; CB = Cabbage; T = Tsumeb; G = Grootfontein; O = Otavi; SA = Sample Area;
FS = Food Sample

The AFs of HMs such as Mn, Ni, Cu and Zn in some food samples during sample collection period of 20 July 2017 recorded values much greater than 1.0 (Table 4a<sub>3</sub>). However, AF values of < 1 were generally recorded for Cr, Pb and Hg across the sampling areas. These generally revealed the accumulation of the metals in the food samples. Higher AFs values such as 16 (Mn), 78 and 50 (Cu), 60 and 57 in Zn showed higher mobility and uptake of the metals by the

food samples. More worryingly is the fact these higher metallic mobilities were obtained in food samples (Spinach, Carrot and Cabbage) that are regarded as common, staple and widely eaten. Bioaccumulation of these metals in consumers is highly possible as a result of longterm consumption with serious health effects. Although these metals were found in soils and plant in both sites, it is worthy of note that they were above WHO permissive levels, is still safe i.e. the values are below the tolerable levels of 90-300mg/kg recommended by European Commission (EC), 1986, but in very high concentrations plants may pose danger to consumers of plants around these areas. However, continuous usage of these farmlands for growing crops could lead to bioaccumulation of these metals and their eventual entry into the food chain with the associated health risks being manifested.

## 4.3 Heavy metals in food and soil samples after second sampling

Results of the level of analysed heavy metals in food samples and soil during the second sampling period (25 July 2017) are as presented in Tables 4.5 and 4.6 respectively. Results of the accumulation factors (AFs) of the metals are presented in Tables 4.7

		itelii ana ot		0000000 201								
SA	FS		Metals									
		Cr	Mn	Hg	Ni	Cu	Zn	Pb				
Т	SN	1.06	151	0.36	1.84	14.9	209	2.17				
	CA	8.37	50.8	1.03	3.76	10.8	22.8	4.24				
	SP	0.63	40.1	0.82	0.27	6.12	0.53	2.97				
_	Х	3.35±4.4	80.6±61.2	0.74±0.3	1.96±1.8	10.61±40	77.4±11.5	3.13±1.0				
G	SN	2.06	635	0.39	ND	7.06	19.7	2.94				
	CR	2.02	18.4	1.49	0.40	ND	19.7	24.8				
	MZ	1.62	6.74	ND	2.06	ND	28.0	ND				
	Х	1.9±0.24	220.5±359.4	0.94±0.9	1.23±1.2	7.06	22.5±4.8	13.87±15.5				
0	SN	6.80	74.0	ND	ND	7.19	19.4	ND				
	CR	1.20	15.0	2.66	1.01	5.32	36.2	6.22				
	СВ	3.13	105	1.36	ND	ND	29.0	ND				
	Х	3.71±2.8	64.5±45.7	2.01±0.9	1.01	6.26±1.3	28.2±8.4	6.2				

**Table 4.5:** Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 25<sup>th</sup> October 2017

SP = Sweet Potatoes; CA = Cassava SN = Spinach; CR = Carrot; CB = Cabbage; X = mean T = Tsumeb;
 G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample

The level of toxic heavy metal in food samples from the farmland in Tsumeb were 1.06 mg/kg (Cr) in Spinach; 8.37 mg/kg in Cassava; 0.63 mg/kg in Sweet Potatoes; 151 mg/kg (Mn) in Spinach; 50.8 mg/kg in cassava; 40.1 mg/kg in Sweet potatoes; 0.36 mg/kg (Hg) in Spinach; 1.03 mg/kg in cassava; 0.82 mg/kg in Sweet Potatoes; 1.84 mg/kg (Ni) in Spinach; 3.76 mg/kg in cassava; 0.27 mg/kg in Sweet Potatoes; 14.9 mg/kg (Cu) in Spinach; 10.8 mg/kg in Cassava; 6.12 mg/kg in Sweet Potatoes; 209 mg/kg (Zn) in Spinach; 22.8 mg/kg in Cassava; 0.53 mg/kg in Sweet Potatoes; 2.17 mg/kg (Pb) in Spinach; 4.24 mg/kg in Cassava; 2.97 mg/kg in Sweet Potatoes. While the level of toxic heavy metal in food samples from the farmland in Grootfontein were 2.06 mg/kg (Cr) in Spinach; 2.02 mg/kg in Carrots; 1.62 mg/kg in Maize; 635 mg/kg (Mn) in Spinach; 18.4 mg/kg in Carrots; 6.74 mg/kg in Maize; 0.39 mg/kg (Hg) in Spinach; 1.49 mg/kg in Carrots; 2.06 mg/kg in Maize; 7.06 mg/kg (Cu) in Spinach; in both Carrots and in Maize it was not detected.

About 19.7 mg/kg of Zn was recorded in Spinach; 19.6 mg/kg in Carrots; 28.0 mg/kg in Maize; 2.94 mg/kg (Pb) in Spinach; 24.8 mg/kg in Carrots and in Maize it was not detected. And the level of toxic heavy metal in food samples from the farmland in Otavi were 6.80 mg/kg (Cr) in Spinach; 1.20 mg/kg in Carrots; 3.13 mg/kg in Cabbage; 74.0 mg/kg (Mn) in Spinach; 15.0 mg/kg in Carrots; 105 mg/kg in Cabbage; (Hg) was not detected in Spinach; 2.66 mg/kg in Carrots; 1.36 mg/kg in Cabbage; (Ni) was not detected in both Spinach and Cabbage; 1.01 mg/kg in Carrots; 7.19 mg/kg (Cu) in Spinach; 5.32 mg/kg in Carrots; cabbage it was not detected; 19.4 mg/kg (Zn) in Spinach; 36.2 mg/kg in Carrots; 29.0 mg/kg in Cabbage; (Pb) was not detected in both Spinach and Cabbage; (Pb) was not detected in both Spinach and Cabbage; 2017 respectively.

Higher concentration of metals was found in Spinach, 15, 40, 635 and 74mg/kg respectively for Cu, Mn, Mn and Mn, followed by the level of Zn in Spinach of 209, 20, and 19 mg/kg. Cassava has higher metal content of 51 mg/kg of Mn, 11mg/kg of Cu and 23mg/kg of Zn, while Carrots have metal content of 20mg/kg of Zn, 25mg/kg of Pb, 15mg/kg of Mn and 36mg/kg of Zn and Cabbage with 105mg/kg of Mn and 29mg/kg of Zn for both sampling areas. All these levels found to be above the permissible limit recommended by WHO, except for Chromium however, the presence of these metals is evidence that the consumption of the farm produce can increase the chance of bioaccumulation of those elements.

	peno		ei 2017)					
SA		SS			Metals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	EXB	ND	17.69	12.00	0.10	ND	2.89	12.00
	RIM	ND	34.16	12.00	0.25	ND	4.00	12.00
	OM	1.63	5764.68	ND	0.05	3.88	12.75	3.47
	Х	0.54±0.9	1938.8±3313.3	8±6.93	0.13	1.3±2.24	6.55±5.40	9.16±4.92
G	EXB	0	29866.74	11.95	0.07	0.08	0.27	11.95
	RIM	0	8.00	11.95	0.05	0	0.15	11.95
	OM	2.04	6407.79	0	0.51	4.28	2.5	-0.36
	Х	0.68±1.2	1209.18±15720.6	7.97±6.9	0.21±0.3	1.5±2.5	0.97±1.3	7.84±7.1
0	EXB	0	24.78	11.98	0	0.17	16.55	11.98
	RIM	0	35.69	11.98	0	0	0	11.98
	OM	8.11	6162.6	0	3.32	7.5	11.27	4.39
	Х	2.7±4.7	2074.36±3540.5	7.99±6.9	1.1±1.92	2.6±4.3	9.3±8.5	9.45±4.4

**Table 4.6:** Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period (25 October 2017)

EXB = Exchangeable; RIM = Reducible-iron/Manganese Oxides; OM = Oxidizable-Organic-Matter; X = mean; SA = Sampling Area; SS = Soil Sample T = Tsumeb; G = Grootfontein; O = Otavi

The mean concentration of HMs in soil samples from Tsumeb during the second sampling period (25 October 2017) were as follow, 0.54mg/kg; 1938.84mg/kg;8mg/kg; 0.13mg/kg; 1.3mg/kg; 6.55mg/kg and 9.16mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The values in the soil samples from Grootfontein during the same period of (25 October 2017) ranged from 0.68mg/kg; 1209.18mg/kg; 7.97mg/kg; 0.21mg/kg; 1.5mg/kg; 0.97mg/kg and 7.84mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The volues in Otavi on the (25 October 2017) the HMs concentration that were obtained are 2.7mg/kg; 2074.36mg/kg; 7.99mg/kg; 1.1mg/kg; 2.6mg/kg; 9.3mg/kg; and 9.45mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. For the second sampling period, the levels of HMs found to be above the maximum permissible limit in soil of 0.01mg/kg. This showed the availability of the plant to uptake the metals. The source of these metals may include atmospheric particulate matter (PM) deposition from Anthropogenic activities and other natural occurring.

The AFs of HMs were deduced using the metal exchangeable fraction from the Speciation analysis. This is because these are the available metals in the soil for the plant uptake

SA	FS			Ν	/letals					
		Cr	Mn	Hg	Ni	Cu	Zn	Pb		
Т	SP	-	2.27	0.07	2.7	-	0.18	0.25		
	CA	-	2.87	0.09	37.6	-	7.89	0.35		
	SN	-	8.54	0.03	18.4	-	72.32	0.18		
G	SN	-	0.02	0.03	-	88.25	72.96	0.25		
	CR	-	0.00	0.12	5.71	-	72.97	2.08		
	MZ	-	0.00	-	29.43	-	103.70	-		
0	SN	-	2.97	-	-	42.29	1.17	-		
	CR	-	0.60	0.22	-	31.29	2.19	0.52		
	СВ	-	4.24	0.11	-	-	-	-		

**Table 4.7:** Accumulation factors/metal uptake by food samples Collected in Tsumeb in

 Grootfontein and Otavi on the 25 October 2017

SN = Spinach; CR = Carrot; CB = Cabbage; MZ; Maize T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample

The AFs of HMs such as Mn, Ni, Cu, Zn and Pb in some food samples during sample collection period of 25 October 2017 recorded values much greater than 1.0 (Table 4d). These generally revealed the bioaccumulation of the metals in the food samples. Higher BAF values such as 8.54, 4.24, 2.97, 2.87 and 2.27 (Mn), 37.6, 29.43, 18.4, 5.71 and 2.7 (Ni), 88.25, 42.29 and 31.29 (Cu), 103.70, 72.97, 72.96, 7.89, 2.19 (Zn) and 2.08 in Pb showed higher mobility and uptake of the metals by the food samples. These higher metallic mobilities were obtained in food samples (Spinach, Carrot, Maize, Cassava and Cabbage) that are regarded as common, staple and widely eaten which can pose health risk to the consumer. Bioaccumulation of these metals in consumers is highly possible as a result of long-term consumption with serious health effects. However, AF values of < 1 were generally recorded for Cr, Pb and Hg across the sampling areas.

#### 4.4 Heavy metals in food and soil samples after third sampling

Results of the level of analysed heavy metals in food samples and soil during the third period of sampling (1st of December 2017) are as presented in Tables 4.8 and 4.9 respectively. Results of the bioaccumulation factors (AFs) of the metals are presented in Tables 4.10.

SA	FS			Metal	S			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	7.35	18.8	0.80	0.92	ND	ND	ND
	CA	4.25	6.17	0.56	1.62	ND	ND	ND
	Х	11.6±2.2	12.49±8.9	0.68±0.2	1.27±0.5	ND	ND	ND
G	SN	1.57	389	0.41	ND	6.23	17.7	2.58
	CR	1.82	30.0	0.40	1.42	4.03	17.6	2.68
	СВ	ND	41.4	ND	ND	ND	4.35	0.92
	Х	1.7±0.2	153.5±204.1	0.41±0.1	1.42	5.13±1.6	13.22±7.7	2.06±1.0
0	SN	0.23	52.3	0.51	ND	10.6	19.3	3.83
	CR	1.01	11.5	0.84	0.61	4.06	12.5	5.65
	СВ	0.67	123	0.59	ND	ND	9.80	3.66
	Х	0.64±0.4	62.27±56.4	0.17	0.61	7.33±0.3	13.87±5.0	4.38±2.0

**Table 4.8:** Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on 01 December 2017

SP = Sweet Potatoes; CA = Cassava SN = Spinach; CR = Carrot; CB = Cabbage; X = mean T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample.

The level of toxic heavy metal in food samples from the farmland in Tsumeb were 7.35 mg/kg (Cr) in Sweet Potatoes; 4.25 mg/kg in Cassava; 18.8 mg/kg (Mn) in Sweet Potatoes; 6.17 mg/kg in Cassava; 0.80 mg/kg (Hg) in Sweet Potatoes; 0.56 mg/kg in Cassava; 0.92 mg/kg (Ni) in Sweet Potatoes; 1.62 mg/kg in Cassava; (Cu) it was not detected in both Sweet Potatoes and Cassava; (Zn) it was not detected in both Sweet Potatoes and Cassava; (Zn) it was not detected in both Sweet Potatoes and Cassava; (Zn) it was not detected in both Sweet Potatoes and Cassava; (Pb) it was not detected in both Sweet Potatoes and Cassava. While the level of toxic heavy metal in food samples from the farmland in Grootfontein were 1.57 mg/kg (Cr) in Spinach; 1.82 mg/kg in Carrots; In Cabbage it was not detected; 389 mg/kg (Mn) in Spinach; 30.0 mg/kg in Carrots; 41.4 mg/kg in Cabbage; 0.41 mg/kg (Hg) in Spinach; 0.40 mg/kg in Carrots and was ND in Cabbage.

Nickel (Ni) was not detected in Spinach and Cabbage while 1.42 mg/kg was recorded in Carrots. 6.23 mg/kg of Cu was detected in Spinach; 4.03 mg/kg in Carrots while it was detected Cabbage. About 17.7 mg/kg of Zn was recorded in Spinach; 17.6 mg/kg in Carrots and 4.35 mg/kg in Cabbage. About 2.58 mg/kg of Pb was detected in Spinach; 2.68 mg/kg in Carrots; 0.92 mg/kg and in Cabbage. The level of toxic heavy metal in food samples from the farmland in Otavi were 0.23 mg/kg (Cr) in Spinach; 1.01 mg/kg in Carrots; 0.67 mg/kg in Cabbage; 52.3 mg/kg (Mn) in Spinach; 11.5 mg/kg in Carrots; 123 mg/kg in Cabbage; 0.51

mg/kg (Hg) in Spinach; 0.84 mg/kg in Carrots; 0.59 mg/kg in Cabbage; (Ni) was not detected in both Spinach and Cabbage; 0.61 mg/kg in Carrots; 10.6 mg/kg (Cu) in Spinach; 4.06 mg/kg in Carrots; cabbage it was not detected; 19.3 mg/kg (Zn) in Spinach; 12.5 mg/kg in Carrots; 9.80 mg/kg in Cabbage; 3.83 mg/kg (Pb) in Spinach; 5.65 mg/kg in Carrots; 3.66 mg/kg in Cabbage for the period of 01 December 2017 respectively. The metal level concentration exceeded the permissible limit recommended by WHO, except Chromium in carrots and cabbage in Otavi sampling area for the period of 01 December 2017.

S				Metals			
	Cr	Mn	Hg	Ni	Cu	Zn	Pb
EXB	ND	18.35	12	0.067	ND	0.415	12
RIM	ND	60.9	12	0.458	ND	3.034	12
OM	7.55	1604.64	ND	0.1	4.9	3.47	2.96
Х	2.52±4.4	561.3±903.8	8±6.9	0.21±0.2	1.63±2.8	2.3±1.7	8.98±5.2
EXB	ND	24.76	11.95	0.073	0.185	0.727	11.95
RIM	ND	17.84	11.95	0.084	ND	0.262	11.95
OM	3.62	1953.1	ND	0.36	4.9	3.88	1.22
Х	1.21±209	665.23±1115.3	7.97±5.6	0.172±0.1	1.70±2.3	1.63±1.6	8.37±5.1
EXB	ND	29.13	11.98	ND	ND	ND	12
RIM	ND	25.98	11.98	ND	ND	2.018	12
OM	2.35	1650.07	ND	1.79	4.13	5.36	6.43
Х	0.78±1.4	568.4±936.8	7.99±6.9	0.6±1.3	1.38±2.4	2.46±2.7	10.14±3.2
	S EXB RIM OM X EXB RIM OM X EXB RIM OM X	S         Cr           EXB         ND           RIM         ND           OM         7.55           X         2.52±4.4           EXB         ND           RIM         ND           OM         3.62           X         1.21±209           EXB         ND           RIM         ND           OM         2.35           X         0.78±1.4	S         Cr         Mn           EXB         ND         18.35           RIM         ND         60.9           OM         7.55         1604.64           X         2.52±4.4         561.3±903.8           EXB         ND         24.76           RIM         ND         17.84           OM         3.62         1953.1           X         1.21±209         665.23±1115.3           EXB         ND         25.98           OM         2.35         1650.07           X         0.78±1.4         568.4±936.8	S         Cr         Mn         Hg           EXB         ND         18.35         12           RIM         ND         60.9         12           OM         7.55         1604.64         ND           X         2.52±4.4         561.3±903.8         8±6.9           EXB         ND         24.76         11.95           RIM         ND         17.84         11.95           OM         3.62         1953.1         ND           X         1.21±209         665.23±1115.3         7.97±5.6           EXB         ND         29.13         11.98           RIM         ND         25.98         11.98           RIM         ND         25.98         11.98           OM         2.35         1650.07         ND           X         0.78±1.4         568.4±936.8         7.99±6.9	S         Metals           Cr         Mn         Hg         Ni           EXB         ND         18.35         12         0.067           RIM         ND         60.9         12         0.458           OM         7.55         1604.64         ND         0.1           X         2.52±4.4         561.3±903.8         8±6.9         0.21±0.2           EXB         ND         24.76         11.95         0.073           RIM         ND         17.84         11.95         0.084           OM         3.62         1953.1         ND         0.36           X         1.21±209         665.23±1115.3         7.97±5.6         0.172±0.1           EXB         ND         25.98         11.98         ND           RIM         ND         25.98         11.98         ND           OM         2.35         1650.07         ND         1.79           X         0.78±1.4         568.4±936.8         7.99±6.9         0.6±1.3	S         Metals           Cr         Mn         Hg         Ni         Cu           EXB         ND         18.35         12         0.067         ND           RIM         ND         60.9         12         0.458         ND           OM         7.55         1604.64         ND         0.1         4.9           X         2.52±4.4         561.3±903.8         8±6.9         0.21±0.2         1.63±2.8           EXB         ND         24.76         11.95         0.073         0.185           RIM         ND         17.84         11.95         0.084         ND           OM         3.62         1953.1         ND         0.36         4.9           X         1.21±209         665.23±1115.3         7.97±5.6         0.172±0.1         1.70±2.3           EXB         ND         29.13         11.98         ND         ND           RIM         ND         25.98         11.98         ND         ND           RIM         ND         25.98         11.98         ND         ND           QM         2.35         1650.07         ND         1.79         4.13           X         0.78±	S         Metals           Cr         Mn         Hg         Ni         Cu         Zn           EXB         ND         18.35         12         0.067         ND         0.415           RIM         ND         60.9         12         0.458         ND         3.034           OM         7.55         1604.64         ND         0.1         4.9         3.47           X         2.52±4.4         561.3±903.8         8±6.9         0.21±0.2         1.63±2.8         2.3±1.7           EXB         ND         24.76         11.95         0.073         0.185         0.727           RIM         ND         17.84         11.95         0.084         ND         0.262           OM         3.62         1953.1         ND         0.36         4.9         3.88           X         1.21±209         665.23±1115.3         7.97±5.6         0.172±0.1         1.70±2.3         1.63±1.6           EXB         ND         29.13         11.98         ND         ND         ND           RIM         ND         25.98         11.98         ND         ND         2.018           GM         2.35         1650.07         ND<

**Table 4.9:** Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period(01 December 2017)

EXB = Exchangeable; RIM = Reducible-iron/Manganese Oxides; OM = Oxidizable-Organic-Matter; X = mean T = Tsumeb; G = Grootfontein; O = Otavi;

Heavy metals concentration in soil samples from Tsumeb during the third sampling period (01 December 2017) were, 2.52mg/kg; 561.3mg/kg; 8mg/kg; 0.21mg/kg; 1.63mg/kg; 2.3mg/kg and 8.98mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The concentration of HMs in the soil samples from Grootfontein for the period of (01December2017) ranged from 1.21mg/kg; 665.23mg/kg; 7.97mg/kg; 0.177mg/kg; 1.70mg/kg; 1.63mg/kg and 8.37mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The values in the soil samples that were collected in Otavi during the sampling period of (01December 2017) are, 0.78mg/kg; 568.4mg/kg; 7.99mg/kg; 0.6mg/kg; 1.38mg/kg; 2.46mg/kg and 10.14mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The levels of HMs found to be above the maximum permissible limit in soil of 0.01mg/kg. This showed the availability of

the plant to uptake the metals. The source of these metals may include atmospheric particulate matter (PM) deposition from anthropogenic activities and other natural occurring. As stated previously the AFs of HMs were deduced using the metal exchangeable fraction from the Speciation analysis. This is because these are the available metals in the soil for the plant uptake.

SA	FS			Μ	etals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	-	1.02	0.07	13.73	-	-	-
	CA	-	0.34	0.05	24.18	-	-	-
G	SN	-	15.71	0.34	-	33.68	24.35	0.22
	CR	-	0.05	0.03	19.45	21.78	24.21	0.22
	СВ	-	1.67	-	-	-	5.98	0.08
0	SN	-	1.80	0.04	-	-	-	0.31
	CR	-	0.39	0.07	-	-	-	0.47
	CB	-	4.22	0.49	-	-	-	0.31

**Table 4.10:** Accumulation factors/metal uptake by food samples collected in Tsumeb inGrootfontein and Otavi on the 01 December 2017

SN = Spinach; CR = Carrot; CB = Cabbage; MZ; Maize T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample.

Following similar pattern during the sample collection period of 01 Dec 2017, higher mobility of metals (BAF > 1) was obtained in most of the food samples. Some metallic transfer was obtained such as 1.02, 15.71, 1.67, 1.80, 4.22 Mn, 13.73, 24.18, 19.45 Ni, 33.68, 21.78 Cu and 24.35, 24.21, and 5.98 for Zn while there was no transfer for Pb, Hg and Cr. Again, this is worrisome the fact these higher metallic mobilities were obtained in food samples (Spinach, Sweet Potatoes, Carrot and Cabbage) that are regarded as common, staple and widely eaten. Bioaccumulation of these metals in consumers is highly possible as a result of long-term consumption with serious health effects. However, AF values of < 1 were generally recorded for Cr, Pb and Hg across the sampling areas.

## 4.6 Heavy metals in food and soil samples after fourth sampling

Results of the level of analysed heavy metals in food samples and soil during the fourth period of sampling (29th March 2018) are as presented in Tables 4.11 and 4.12 respectively. Results of the accumulation factors (AFs) of the metals are presented in Tables 4.13.

SA	FS			Μ	letals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	ND	20.2	1.20	0.11	7.40	7.12	4.96
	CA	ND	10.5	1.24	1.48	ND	11.4	6.46
	PM	ND	47.3	0.41	0.76	11.6	67.7	2.71
	Х	ND	26.0±19.1	0.95±0.5	0.78±0.7	9.5±2.97	28.74±33.8	4.71±1.9
G	SN	1.51	64.1	ND	ND	6.87	30.63	ND
	CR	ND	16.3	ND	ND	0.20	4.76	ND
	СВ	ND	61.3	0.74	ND	021	23.05	ND
	MZ	0.64	42.4	0.10	0.90	10.52	45.61	ND
	Х	1.08±0.6	46.03±22.4	0.42±0.3	0.9	57.8±104.2	26.01±17.0	ND
0	SN	0.19	100	0.98	Nd	13.2	33.7	ND
	MZ	ND	8.9	0.95	0.55	ND	25	3.53
	СВ	0.1	102	0.24	ND	ND	19.2	ND
	Х	0.15±0.6	70.3±53.2	0.72±0.4	0.18±0.3	4.4±7.62	25.97±7.30	1.18±2.4

**Table 4.11:** Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 29<sup>th</sup> March 2018

SP = Sweet Potatoes; CA = Cassava SN = Spinach; CR = Carrot; CB = Cabbage; PM = Pier Melt; X = mean T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample.

The level of toxic heavy metal in food samples from the farmland in Tsumeb were (Cr) was not detected in both Sweet Potatoes, Cassava and Pier Melts; 20.2 mg/kg (Mn) in Sweet Potatoes; 10.5 mg/kg in Cassava; 47.3 mg/kg in Pier Melt; 1.20 mg/kg (Hg) in Sweet Potatoes; 1.24 mg/kg in Cassava; 0.41 mg/kg in Pier Melt; 0.11 mg/kg (Ni) in Sweet Potatoes; 1.48 mg/kg in Cassava; 0.76 mg/kg in Pier Melt; 7.40 mg/kg (Cu) in Sweet Potatoes; in Cassava it was not detected; 11.6 mg/kg in Pier Melt; 7.12 mg/kg (Zn) in Sweet Potatoes; 11.4 mg/kg in Cassava; 67.7 mg/kg in Pier Melt; 4.96 mg/kg (Pb) in Sweet Potatoes; 6.46 mg/kg in Cassava; 2.71 mg/kg in Pier Melt. While the level of toxic heavy metal in food samples from the farmland in Grootfontein were 1.51 mg/kg (Cr) in Spinach; it was not detected in both Carrots and Cabbage while 0.64 mg/kg was detected in Maize. The level of Mn in Spinach was 64.1 mg/kg; 16.3 mg/kg in Carrots; 61.3 mg/kg in Cabbage and 42.4 mg/kg in Maize. Mercury (Hg) was not detected in both Spinach and Carrots.

Chromium was not detected in most food samples for the sampling period of (29 March 2018) however, Maize, Spinach and Cabbage were recorded as 0.64mg/kg, 0.19mg/kg and 0.1mg/kg respectfully with exception of Spinach in Grootfontein which was recorded as 1.51mg/kg higher than the permissible limit. Nickel recorded below the recommended permissible limit of by WHO in both sampling sites for the same period. Copper was also found below the permissible limit as recommended by WHO. Lead were found to be below the recommended limit in Tsumeb and Otavi sampling areas with no detection in Grootfontein area.

SA	FS				Metals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	EXB	0	25.57	11.95	0	0.02	15.90	11.95
	RIM	0	14.75	11.96	0	0	12.28	11.96
	OM	2.4	4500.83	0	3.62	6.07	11.37	4.18
	Х	0.8±1.1	1513.7±259.9	7.97±6.9	1.21±2.1	2.03±3.5	13.18±2.4	9.36±4.5
G	EXB	0	24.26	11.96	0.08	0.08	0.31	11.96
	RIM	0	18.87	11.96	0.03	0	0.56	11.96
	OM	0.36	3908.08	0	1.63	4.74	3.16	0.61
	Х	0.12±0.2	1317.07±2243.9	7.97±6.9	0.08±0.9	1.61±2.7	1.35±1.6	8.18±6.6
0	EXB	0	40.02	11.94	0	0	0	11.94
	RIM	0	13.49	11.94	0	0	11.78	11.94
	OM	1.22	3195.17	0	1.58	5.25	11.68	1.58
	Х	0.41±0.7	1082.9±1829.4	7.96±6.9	0.53±0.9	1.75±3.1	7.82±6.8	8.49±6.0

**Table 4.12:** Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period of the 29th March 2018.

**EXB** = Exchangeable; **RIM** = Reducible-iron/Manganese Oxides; **OM** = Oxidizable-Organic-Matter; **X** = mean **T** = Tsumeb; **G** = Grootfontein; **O** = Otavi

The mean concentration of HMs in soil samples from Tsumeb during the fourth sampling period (29 March 2018) ranged from 0.8mg/kg; 1513.7mg/kg; 7.97mg/kg; 1.21mg/kg; 2.03mg/kg; 13.18mg/kg and 9.36mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. While the values in the soil from Grootfontein during the same period of (29 March 2018) varied from 0.12mg/kg; 1317.07mg/kg; 7.97mg/kg; 0.08mg/kg; 1.61mg/kg; 1.35mg/kg and 8.18mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. As for Otavi the soil samples concentration obtained for the period of (29 March 2018) were 0.41mg/kg; 1082.9mg/kg; 7.96mg/kg; 0.53mg/kg; 1.75mg/kg; 7.82mg/kg and 8.49mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively.

The AFs of HMs were deduced using the metal exchangeable fraction from the Speciation analysis. This is because these are the available metals in the soil for the plant uptake.

				ſ	Vetals			
SA	FS	Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	-	0.99	0.10	1.14	65.49	24.63	0.41
	CA	-	0.52	0.10	15.42	-	24.55	0.54
	PM	-	2.33	0.03	0.08	105.45	233.45	0.23
G	SN	-	2.24	-	-	7.63	40.30	-
	CR	-	0.57	-	-	0.22	6.26	-
	СВ	-	2.14	0.06	-	237.88	30.92	-
	MZ	-	1.48	0.01	18	11.69	60.01	-
0	SN	-	4.43	0.08	-	-	-	-
	MZ	-	0.39	0.08	-	-	-	0.29
	CB	-	4.52	0.02	-	-	-	-

**Table 4.13:** Accumulation Factors/metal uptake by food samples Collected in Tsumeb inGrootfontein and Otavi on the 29 March 2018

SN = Spinach; CR = Carrot; CB = Cabbage; PM = Pier Melt; MZ; Maize T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample

As with the other sampling periods, generally mobilities were recorded as following, 4.52, 4.43, 1.48, 2.14, 2.24 and 2.33 Mn, 1.14, 15.42, and 18 for Ni, 65.49, 105.45, 7.63, 237.88, and 11.69 for Cu, 24.63, 24.55, 233.45, 40.30, 6.26, 30.92 and 60.01 for Zn in most of the food samples across sampling areas. Of particular concern is the high metallic transfer of Zn and Cu in food samples except from those at Otavi. These high metallic transfers are of great concern to consumers of these foods. Although, Zn is regarded as a macronutrient that is utilized by humans, higher level might be dangerous to health.

#### 4.7 Heavy metals in food and soil samples after fifth sampling

Results of the level of analysed heavy metals in food samples and soil during the fifth period of sampling (13th July 2018) are as presented in Tables 4.14 and 4.15 respectively. Results of the bioaccumulation factors (BAFs) of the metals are presented in Tables 4.16.

SA	FS			Me	tals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	CA	7.76	9.16	1.44	5.36	7.09	29.82	1.95
	SP	7.00	73.56	1.87	2.91	9.99	34.50	2.03
	Х	7.38±0.52	41.36±45.5	1.65±0.3	4.14±1.7	8.54±2.1	32.16±3.31	1.99±0.06
G	MZ	3.75	134.40	0.40	1.57	7.42	35.28	0.69
	SP	7.32	31.95	1.20	5.52	9.09	100.69	39.05
	СВ	4.29	0.83	ND	3.15	2.23	5.76	1.21
	Х	5.12±1.9	55.73±69.9	0.05±0.6	3.41±2.0	6.25±3.6	47.24±48.6	13.65±22.0
0	MZ	4.40	21.15	1.14	2.87	4.13	27.87	1.51
	СВ	4.16	17.77	0.95	1.10	10.48	56.18	1.48
	SP	4.44	5.58	1.75	3.04	5.09	25.73	1.40
	Х	4.33±0.2	14.83±8.2	1.28±0.4	2.34±1.1	6.57±3.4	36.6±17.0	1.5±0.5

**Table 4.14:** Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 13<sup>th</sup> July 2018

SP = Sweet Potatoes; CA = Cassava SN = Spinach; CR = Carrot; CB = Cabbage; X = mean T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample.

The level of toxic heavy metal in food samples from the farmland in Tsumeb were 7.00 mg/kg (Cr) in Sweet Potatoes; 7.76 mg/kg in Cassava; 73.56 mg/kg (Mn) in Sweet Potatoes; 9.16 mg/kg in Cassava; 1.87 mg/kg (Hg) in Sweet Potatoes; 1.44 mg/kg in Cassava; 2.91 mg/kg (Ni) in Sweet Potatoes; 5.36 mg/kg in Cassava; 9.99 mg/kg (Cu) in Sweet Potatoes; 7.09 mg/kg in Cassava; 34.50 mg/kg (Zn) in Sweet Potatoes; 29.82 mg/kg in Cassava; 2.03 mg/kg (Pb) in Sweet Potatoes; 1.95 mg/kg in Cassava. While the level of toxic heavy metal in food samples from the farmland in Grootfontein were 7.32 mg/kg (Cr) in Sweet Potatoes; 4.29 mg/kg in Cabbage; 3.75 mg/kg in Maize; 31.95 mg/kg (Mn) in Sweet Potatoes; 0.83 mg/kg in Cabbage; 134.40 mg/kg in Maize; 1.20 mg/kg (Hg) in Sweet Potatoes; 3.15 mg/kg in Cabbage; 0.40 mg/kg in Maize; 5.52 mg/kg (Ni) in Sweet Potatoes; 3.15 mg/kg in Cabbage; 1.57 mg/kg in Maize; 9.09 mg/kg (Cu) in Sweet Potatoes; 5.76 mg/kg in Cabbage; 35.28 mg/kg in Maize; 39.05 mg/kg (Pb) in Sweet Potatoes; 1.21 mg/kg in Cabbage; 0.69 mg/kg in Maize.

The level of toxic heavy metal in food samples from the farmland in Otavi were 4.44 mg/kg (Cr) in Sweet Potatoes; 4.16 mg/kg in Cabbage; 4.40 mg/kg in Maize; 5.58 mg/kg (Mn) in Sweet Potatoes; 17.77 mg/kg in Cabbage; 21.15 mg/kg in Maize; 1.75 mg/kg (Hg) in Sweet

Potatoes; 0.95 mg/kg in Cabbage; 1.14 mg/kg in Maize; 3.04 mg/kg (Ni) in Sweet Potatoes; 1.10mg/kg Cabbage; 2.87 mg/kg in Maize; 5.09 mg/kg (Cu) in Sweet Potatoes; 10.48 mg/kg in Cabbage; 4.13 mg/kg in Maize; 25.73 mg/kg (Zn) in Sweet Potatoes; 56.18 in Cabbage; 27.87 mg/kg in Maize; 1.40 mg/kg (Pb) Sweet Potatoes; 1.45 mg/kg in Cabbage; 1.51 mg/kg in Maize for the period of 13 July 2018 respectively, as mentioned before these farm produces are found to be above the permissible limit in vegetable as recommended by WHO in both sampling area.

SA	FS				Metals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	EXB	ND	25.57	11.95	ND	0.02	15.90	11.95
	RIM	ND	14.75	11.96	ND	ND	12.28	11.96
	OM	2.4	4500.83	ND	3.62	6.07	11.37	4.18
	Х	0.8±1.1	1513.7±259.9	7.97±6.9	1.21±2.1	2.03±3.5	13.18±2.4	9.36±4.9
G	EXB	ND	24.26	11.96	0.08	0.08	0.31	11.96
	RIM	ND	18.87	11.96	0.03	ND	0.56	11.96
	OM	0.36	3908.08	ND	1.63	4.74	3.16	0.61
	х	0.12±0.2	1317.07±2243.9	7.97±6.9	0.08±0.9	1.61±2.7	1.35±1.6	8.18±6.6
0	EXB	ND	40.02	11.94	ND	ND	ND	11.94
	RIM	ND	13.49	11.94	ND	ND	11.78	11.94
	OM	1.22	3195.17	ND	1.58	5.25	11.68	1.58
	Х	0.41±0.7	1082.9±1829.4	7.96±6.9	0.53±0.9	1.75±3.1	7.82±6.8	8.49±6.0

 Table 4.15: Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi during period of the 13th July 2018

EXB = Exchangeable; RIM = Reducible-iron/Maganese Oxides; OM = Oxidizable-Organic-Matter; X = mean T = Tsumeb; G = Grootfontein; O = Otavi

The mean concentration of HMs in soil samples from Tsumeb during the second sampling period (13 July 2018) were as follow, 0.8mg/kg; 1513.7mg/kg; 7.97mg/kg; 1.21mg/kg; 2.03mg/kg; 13.18mg/kg and 9.36mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. While the values in the soil from Grootfontein during the same period of (13 July 2018) varied from 0.12mg/kg; 1317.07mg/kg; 7.97mg/kg; 0.08mg/kg; 1.61mg/kg; 1.35mg/kg and 8.18mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. As for Otavi the soil samples concentration obtained for the period of (13 July 2018) were 0.41mg/kg; 1082.9mg/kg; 7.96mg/kg; 0.53mg/kg; 1.75mg/kg; 7.82mg/kg and 8.49mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. As mospheric particulate matter (PM) deposition from anthropogenic activities and other natural occurring could be the source of pollution. As with the other sampling

period, the AFs of HMs were deduced using the metal exchangeable fraction from the speciation analysis. This is because these are the available metals in the soil for the plant uptake.

SA	FS				Metals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	-	4.68	-	3.46	83.25	23	0.17
	CA	-	0.58	-	63.81	0.59	19.88	0.16
G	SP	-	1.40	-	26.29	77.69	112.25	3.26
	СВ	-	0.04	-	15	19.06	6.42	0.10
	MZ	-	5.88	-	7.48	63.42	39.33	0.06
0	SP	-	0.33	-	-	-	-	0.12
	MZ	-	1.24	-	-	-	-	0.13
	СВ	-	1.04	-	-	-	-	0.12

**Table 4.16:** Accumulation factors of heavy metals in food samples collected in Tsumeb,Grootfontein and Otavi on the 13 July 2018

SN = Spinach; CR = Carrot; CB = Cabbage; PM = Pearl Millet; MZ; Maize T = Tsumeb; G= Grootfontein
 O = Otavi; SA = Sample Area; FS = Food Sample

No metallic transfer was observed for Cr and Hg into food samples during this period of 13 July 2018. However, AFs > 1 were obtained for 4.68, 1.40, 5.88, 1.24 and 1.04 (Mn), 3.46, 63.81, 26.29, 15 and 7.48 (Ni), 83.25, 77.69, 19.06, and 63.42 (Cu), 23, 19.88, 112.25, 6.42 and 39.33 (Zn) and 3.26 (Pb). With the exception of Hg, Ni, Cu, Zn and Pb in food samples at Otavi.

#### 4.8 Heavy metals in food and soil samples after sixth sampling

Results of the level of analysed heavy metals in food samples and soil during the sixth period of sampling (14th September 2018) are as presented in Tables 4.17 and 4.18 respectively. Results of the accumulation factors (AFs) of the metals are presented in Tables 4.19.

SA	FS			Met	als			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	4.01	14.32	11.96	1.62	5.86	9.06	11.97
	CA	3.62	7.84	11.93	1.94	2.02	6.81	11.93
	Х	8.82±0.3	11.08±4.6	11.95±0.2	1.78±0.2	3.94±2.7	7.94±1.6	11.95±0.3
G	SP	3.31	64.15	11.95	1.29	7.08	18.66	11.95
	СВ	3.26	39.80	11.99	1.41	2.34	15.33	11.99
	Х	3.29±0.4	51.98±17.2	11.97±0.3	1.35±0.9	4.71±3.4	17±2.4	11.97±0.3
0	CR	3.76	20.99	11.95	1.97	6.05	10.89	11.95
	СВ	3.49	25.26	11.99	1.51	2.27	15.48	11.99
	SP	1.89	17.13	12.00	0.56	4.33	19.26	12.00
	Х	3.05±1.0	21.13±4.1	11.98±0.3	1.35±0.7	4.22±1.9	15.21±4.2	11.98±0.3

**Table 4.17:** Level of heavy metals (mg/kg) in analysed food samples collected in Tsumeb, Grootfontein and Otavi on the 14<sup>th</sup> September 2018

SP = Sweet Potatoes; CA = Cassava SN = Spinach; CR = Carrot; CB = Cabbage; X = mean T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample

The level of toxic heavy metal in food samples from the farmland in Tsumeb were 4.01 mg/kg (Cr) in Sweet Potatoes; 3.62 mg/kg in Cassava; 14.32 mg/kg (Mn) in Sweet Potatoes; 7.84 mg/kg in Cassava; 11.96 mg/kg (Hg) in Sweet Potatoes; 11.93 mg/kg in Cassava; 1.62 mg/kg (Ni) in Sweet Potatoes; 1.94 mg/kg in Cassava; 5.86 mg/kg (Cu) in Sweet Potatoes; 2.02 mg/kg in Cassava; 9.06 mg/kg (Zn) in Sweet Potatoes; 6.81 mg/kg in Cassava; 11.97 mg/kg (Pb) in Sweet Potatoes; 11.3 mg/kg in Cassava. While the level of toxic heavy metal in food samples from the farmland in Grootfontein were 3.31 mg/kg (Cr) in Sweet Potatoes; 3.26 mg/kg in Cabbage; 64.15 mg/kg (Mn) in Sweet Potatoes; 12.9 mg/kg (Ni) in Sweet Potatoes; 11.95 mg/kg (Hg) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 1.29 mg/kg (Ni) in Sweet Potatoes; 1.41 mg/kg in Cabbage; 7.08 mg/kg (Cu) in Sweet Potatoes; 2.34 mg/kg in Cabbage18.66 mg/kg (Zn) in Sweet Potatoes; 15.33 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage; 11.95 mg/kg (Pb) in Sweet Potatoes; 11.99 mg/kg in Cabbage.

The level of toxic heavy metal in food samples from the farmland in Otavi were 3.76 mg/kg (Cr) in Carrots; 3.49 mg/kg in Cabbage; 1.89 mg/kg in Sweet Potatoes; 20.99 mg/kg (Mn) in Carrots; 25.26 mg/kg in Cabbage; 17.13 mg/kg in Sweet Potatoes; 11.95 mg/kg (Hg) in Carrots; 11.99 mg/kg in Cabbage; 12.00 mg/kg in Sweet Potatoes; 1.97 mg/kg (Ni) in Carrots; 1.51 mg/kg Cabbage; 0.56 mg/kg in Sweet Potatoes; 6.05 mg/kg (Cu) in Carrots; 2.27 mg/kg

in Cabbage; 4.33 mg/kg in Sweet Potatoes; 10.89 mg/kg (Zn) in Carrots; 15.48 in Cabbage; 19.26 mg/kg in Sweet Potatoes; 11.95 mg/kg (Pb) Carrots; 11.99 mg/kg in Cabbage; 12.00 mg/kg in Sweet Potatoes for the period of 14 September 2018 respectively. These farm produces are all found to be above the permissible limit in vegetable as recommended by WHO as shown in (table 4f1) above in both sampling areas. Continue consumption of these farm produce can results in accumulation of these elements which can cause health complications in the future.

SA	FS				Metals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	EXB	ND	25.57	11.95	ND	0.02	15.90	11.95
	RIM	ND	14.75	11.96	ND	ND	12.28	11.96
	OM	2.4	4500.83	ND	3.62	6.07	11.37	4.18
	Х	0.8±1.1	1513.7±259.9	7.97±6.9	1.21±2.1	2.03±3.5	13.18±2.4	9.36±4.5
G	EXB	ND	24.26	11.96	0.08	0.08	0.31	11.96
	RIM	ND	18.87	11.96	0.03	ND	0.56	11.96
	OM	0.36	3908.08	ND	1.63	4.74	3.16	0.61
	Х	0.12±0.2	1317.07±2243.9	7.97±6.9	0.08±0.9	1.61±2.7	1.35±1.6	8.18±6.6
0	EXB	ND	40.02	11.94	ND	ND	ND	11.94
	RIM	ND	13.49	11.94	ND	ND	11.78	11.94
	OM	1.22	3195.17	ND	1.58	5.25	11.68	1.58
	Х	0.41±0.7	1082.9±1829.4	7.96±6.9	0.53±0.9	1.75±3.1	7.82±6.8G	8.49±5.98

**Table 4.18:** Soil metal fraction (BCR) collected in Tsumeb, Grootfontein and Otavi duringperiod of the 14<sup>th</sup> September 2018

EXB = Exchangeable; RIM = Reducible-iron/Manganese Oxides; OM = Oxidizable-Organic-Matter; X = mean T = Tsumeb; G = Grootfontein; O = Otavi

The mean concentration of HMs in soil samples from Tsumeb during the second sampling period (14 September 2018) were as follow, 0.8mg/kg; 1513.7mg/kg; 7.97mg/kg; 1.21mg/kg; 2.03mg/kg; 13.18mg/kg and 9.36mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. While the values in the soil from Grootfontein during the same period of (14 September 2018) varied from 0.12mg/kg; 1317.07mg/kg; 7.97mg/kg; 0.08mg/kg; 1.61mg/kg; 1.35mg/kg and 8.18mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. As for Otavi the soil samples concentration obtained for the period of (14 September 2018) were 0.41mg/kg; 1082.9mg/kg; 7.96mg/kg; 0.53mg/kg; 1.75mg/kg; 7.82mg/kg and 8.49mg/kg for Cr, Mn, Hg, Ni, Cu, Zn and Pb respectively. The source of these metals may include atmospheric particulate matter (PM) deposition from Anthropogenic activities and other natural occurring.

As stated previously the BAFs of HMs were deduced using the metal exchangeable fraction from the Speciation analysis. This is because these are the available metals in the soil for the plant uptake.

SA	FS			ſ	Vetals			
		Cr	Mn	Hg	Ni	Cu	Zn	Pb
Т	SP	-	0.81	0.99	5.51	39.07	5.92	0.99
	CA	-	0.44	0.99	6.60	13.47	4.45	0.99
G	SP	-	3.14	1.00	39.09	101.14	38.08	1.00
	СВ	-	1.95	1.00	42.72	33.42	31.29	1.00
0	CR	-	0.67	1.00	-	-	7.26	1.00
	CB	-	0.80	1.00	-	-	10.32	1.00
	SP	-	0.55	1.00	-	-	12.84	1.00

**Table 4.19:** Accumulation Factors of Heavy Metals in Food Samples Collected in Tsumeb,Grootfontein and Otavi on the 14 September 2018

SN = Spinach; CR = Carrot; CB = Cabbage; PM = Pier Melt; MZ; Maize T = Tsumeb; G= Grootfontein O = Otavi; SA = Sample Area; FS = Food Sample.

General transfer of analysed HMs was obtained for most of the metals in food samples across the sampling areas except for Cr, Ni and Cu in Otavi. Of more concern is the uptake of Hg and Pb by food samples across the sampling areas. Ingestion of food that contain heavy metals such as Hg and Pb over a long period can lead to serious health problems.

In Tsumeb and Grootfontein, (Cr) was not accumulated by the analysed food samples while all other metals showed accumulation in the food samples. Hence all other metals were transferred from the soil to the food samples.

Most concentration levels are found to be above the permissible levels according to WHO's recommendation in both sampling areas.

The prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of heavy metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases (WHO, 1992; Jarup, 2003). Consumption of food laden with these toxic metals may lead to accumulation in human system with consequential health problems (Afiza et al., 2013). Ruminants that also feed on roadside grasses and plants may also accumulate the metals with possible biomagnification in humans across the food chain (Sivaruban et al., 2016).

Agricultural practices and Industrial Regulations have been set up in deferent Nations for the control of emission of heavy metals. This research is mainly on the analysis of distribution and dynamic of toxic of heavy metals in cultivated farm produce from Tsumeb, Grootfontein and Otavi localities in Namibia. This means that the research topic is examining the varying occurrence of various farm products like, cabbages, cassava, maize, carrots, spinach, Pearl Millet and sweet potatoes toxic of heavy metals in Tsumeb, Grootfontein and Otavi, in Namibia.

Similarly, Kierczak et al., (2013) found that soils in the areas around historic smelters, which were active between the 14th and 16<sup>th</sup> centuries, are still highly polluted with metal(loids)s (up to 4000 mg/kg Cu, 1500 mg/kg Zn, 300 mg/kg As, and 200 mg/kg Pb) due especially to the centuries-long dissolution of smelter wastes into the soils. They concluded that the legacy of old smelting sites, even those which have not been operational for centuries, must still be considered as a serious environmental problem today; Arsenic is a metalloid that is distributed widely in rocks, water and soil (Wang and Mulligan., 2006).

#### 4.9 Mean values of Heavy metals across the entire period and the SEPI

The mean values of heavy metals collected throughout the sampling period and the calculated values of SEPI are presented in Table 4.20 to 4.22 for the three sampling locations of Tsumeb, Grootfontain and Otavi respectively.

#### 4.9.1 SEPI values for Tsumeb

The SEPI value for Tsumeb follow the order of Cr<(Ni= Cu)< Zn<Pb<Mn<Hg and varied from 0.01 to 266. Therefore, the results of single elemental pollution index (SEPI) showed low contamination (SEPI  $\leq$  1) for the metals Cr, Mn, Ni, Cu, Zn and Pb respectively. However, the calculated SEPI for Hg indicated high contamination (SEPI > 3). This high contamination with Hg may have come from the use of phenylmercury acetate ethylmercury which are commonly used as fungicides, preservatives, and antiseptics for industrial and agricultural activities (Xilong et al., 2005).

Table 4.2	D: Mean value for SEPI for Tsumeb		
HM	Mean value mg/kg	SEPI	
Cr	1.04±1.62	0.01	
Mn	1425.82±876.1	0.72	
Hg	7.98±6.9	266	
NI	0.86±8.6	0.02	
Cu	2.18±0.84	0.02	
Zn	10.26±2.78	0.03	
Pb	9.12±5.4.99	0.09	

#### 

#### 4.9.2 SEPI values for Grootfontein

The order of single elemental pollution index (SEPI) for Grootfontein follow the trend (Cr=Zn=Ni) <Cu<Mn<Pb<Hg. The calculated values of the SEPI indicated low contamination (SEPI ≤ 1), and high contamination of Hg (SEPI > 3).

Table 4.21: Mean value for SEPI for Grootfontein						
HM	Mean value mg/kg	SEPI				
Cr	0.395±35.2	0.00				
Mn	1190.5±27552.2	0.60				
Hg	7.97±6.7	265.8				
NI	0.01±4.0	0.00				
Cu	1.60±2.6	0.02				
Zn	1.33±1.6	0.00				
Pb	8.16±102.5	0.08				

Table / 21. Mean value for SEPI for Grootfontein

## 4.9.3 SEPI values for Otavi

The values of single elemental index for Otavi follow the order of (Cr= Ni) <(Cu=Zn) <Pb<Mn<Hg. The study showed that the SEPI values calculated indicates low contamination for all elements investigated except Hg which indicated high contamination of soil. We found that the three locations monitored in this study are contaminated with Hg.

Table 4.23: Mean value for SEPI for Otavi					
HM	Mean value mg/kg	SEPI			
Cr	0.85±1.5	0.01			
Mn	1342.88±1965.8	0.67			
Hg	15.97±6.9	532.3			
NI	0.64±1.14	0.01			
Cu	1.83±3.2	0.02			
Zn	7.17±6.42	0.02			
Pb	8.93±0.3	0.09			

#### **CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATION**

#### 5.1 Conclusion

The prevalence of toxic heavy metal in the Tsumeb soil shows that, Chromium (Cr) was 7.35 grams on sweet potatoes, 4.25 grams on cassava, Manganese (Mn) in sweet potatoes 18.8 grams, cassava 6.17 grams, Mercury (Hg) in sweet potatoes 0.80 and in cassava 0.92, Nickel (Ni) in sweet potatoes 0.92 and cassava 1.62grams, Copper (Cu) was not detected in both sweet potatoes and cassava, Zinc (Zn) was not detected in both sweet potatoes and cassava, Lead (Pb) was not detected in both sweet potatoes and cassava.

The prevalence of toxic heavy metal in the Grootfontein soil shows that, Chromium (Cr) was 1.57 grams on spinach, 1.82 grams on carrots, on cabbage it was not detected, Manganese (Mn) in spinach 389 grams, carrots 30.0 grams, cabbage 41.4 grams, Mercury (Hg) in spinach 0.41 grams, carrots 0.40 grams and in cabbage it was not detected, Nickel (Ni) in spinach was not detected, carrots 1.42 grams, Copper (Cu) in spinach 6.23, carrots 4.03 grams and on cabbage it was not detected, Zinc (Zn) in spinach 17.7 grams, carrots 17.6 grams, cabbage 4.35 grams, Lead (Pb) in spinach 2.58, carrots 2.68, cabbage 0.92 grams.

The prevalence of toxic heavy metal in the Otavi soil shows that, Chromium (Cr) was 0.23 grams on spinach, 1.01 grams on carrots, 0.67 grams on cabbage, Manganese (Mn) in spinach 52.3 grams, Carrots 11.5 grams, cabbage 123 grams, Mercury (Hg) in spinach 0.51 grams, carrots 0.84 grams and in cabbage 0.59 grams, Nickel (Ni) was not detected in both spinach and cabbage, carrots 0.61 grams, Copper (Cu) in spinach 10.6 grams, carrots 4.06 grams, cabbage it was not detected, Zinc (Zn) in spinach 19.3, carrots 12.5, cabbage 9.80, Lead (Pb) 3.83 grams in spinach, carrots 5.65 grams, 3.66 grams in cabbage for the period of 20<sup>th</sup> July 2017 respectively.

The single elemental pollution index was also employed to evaluate the degree of contamination of the soil. The study found that all three sites were low in contamination with the elements of Cr, Cu, Zn, Pb, Mn and Ni respectively. However, all three locations recorded high contamination with Hg.

Although some of the metal's concentrations in soils and vegetables was found to be below the permissible levels as recommended by FAO/WHO standards, the fact that they are present its an indication that continuing consumption of those farm produce may results in accumulation of those metals in both humans and animals.

# 5.2 Recommendation

The results of this study have provoked many questions which need further investigations to determine the minimum amount of each source of contamination that will result in the accumulation of heavy metals in farm produce as well as in soils beyond acceptable limits. And to develop appropriate legislation with the relevant permissible levels. No matter how low the levels of heavy metals in both vegetables and soil are, the fact that they are present create a worrisome for the consumer as well as the environment.

#### References

Alloway, B.J., Ed. (1990) Heavy Metals in Soils, Blackie and Son Ltd., Glasgow, 100-124.

- Adriano, D.C. (2001). Trace Elements in the Terrestrial Environment, 2nd edition. Springer-Verlag, New York.
- Abah, J., Mashebe, P. S., Ubwa, S.T., Denuga, D.D. (2014). Some Heavy Metals Content of Cabbage and Soil Cultivated in the Bezi Bar Farm Area of Katima Mulilo, Namibia. American Journal of Chemistry 2014, 4(3): 101-108.
- Akhilesh, J., Savita, D., Suman, M. (2009). Some trace elements investigation in groundwater of Bhopal and Sehore District in Madhya Pradesh, India. J Appl. Sci. Environ. Manag. 13, 4, 47–50.
- Awofolu, O.R. (2005). A survey of Trace Metals in vegetation, soil, and lower animals along some selected major Roads in metropolitan city of Lagos. Environmental monitoring and Assessment, 105, 431-447.
- Agrawal, M. (2003). Enhancing Food Chain Integrity: Quality Assur- ance Mechanism for Air Pollution Impacts on Food and Vegetable System. Final Technical Report (R7530) submitted to Department for International Development, United Kingdom.
- Al Jassir, M. S., Shaker, A and Khaliq, M.A. (2005). Deposition of heavy metals on green leafy vegetables sold on roadsides of Riyadh city, Saudi Arabia. Bulletin of Environment Contamination and Toxicology, 75, 1020-1027.
- Baron, S., Carignan, J and Ploquin A. (2016). Dispersion of heavy metals (metalloids) in soils from 800-year-old pollution (Mont-Lozère, France) Environ. Sci. Technol., 40 (2006), pp. 5319-5326, 10.1021/es0606430.
- Bireescu, L., Bireescu, G., Vincenzo, M.S. (2014). Environmental quality / Qualité de l'Environnement / Qualità ambientale, 13, 01-07.
- BiNgö, M., YeNtür, G., Er, B and ökte, A.B. (2010). Determination of Some Heavy Metal Levels in Soft Drinks from Turkey Using ICP-OES Method. Czech J. Food Sci., 28, 3, 213–216.
- Canfield, D., Minik, E., Rosing, T and Bjerrum, C. (2006). Early anaerobic metabolisms. Biol. Sci., 361, 1474, 1819–1836.
- Craig, H., Benson, E.K and Joseph, S. (2010). Geotextiles and Geomembranes. Geological Engineering, University of Wisconsin, Madison WI 53706, USA Shannon and Wilson, Seattle WA 98103, USA.
- Csavina J., Landázuli, A., Wonaschütz, A., Rine, K., Rheinheimer, P., Barbaris, B., Conant, W., Sáez, A.E and Betterton, E.A. (2011). Metal and metalloid contaminants in atmospheric aerosols from mining operations Water Air Soil Pollut., 221, 145-157, doi: 10.1007/s11270-011-077.
- Csavina, J., Field, J., Taylor, M.P., Gao, S., Landázuli, A., Betterton, E.A., Sáez, A.E. (2012). A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations Sci. Total Environ., 433, 58-73, doi:10.1016/j.scitotenv.2012.06.013
- Csavina J., Taylor, M.P., Félix, O., Rine, K.P., Sáez, A.E and Betterton, E.A. (2014). Size-resolved dust and aerosol contaminants associated with copper and lead smelting emissions:

implications for emission management and human health Sci. Total Environ., 493, 750-756, doi:10.1016/j.scitotenv.2014.06.031

- Davis, M.A, Signes-Pastor, A.J., Argos, M., Slaughter, F., Pendergrast, C., Punshon, T., Gossai,
   A., Ahsan, H and Karagas, M.R. (2017). Assessment of human dietary exposure to arsenic
   through rice. Sci. Total Environ., 586:1237-1244. doi: 10.1016/j.scitotenv.
- Docekalova, H., Kovarikova, V and Docekal, B. (2012). Mobility and bio-accessibility of trace metals in soil assessed by conventional extractions procedure and passive diffusive sampler chem. Speciat. Bioavailability, 24, 4, 261-265.
- Elfaki, J., Ali, M., Elhagwa, M and Sulieman, M. (2017). Influence of the artisanal gold mining on soil contamination with heavy metals: A case study of Dar-Mali Locality, North of Atbara, River Nile State, Sudan. Eurasian Journal of Soil Science, 6, 1, 28-36.
- Feig, D.I., Reid, T.M and Loeb, L.A. (1994). Reactive oxygen species in tumorigenesis. Cancer Research, 54, 1890-1894.
- Hasheela, I. (2018). Contamination mapping and land use categorization for Tsumeb. Communications of the Geological Survey of Namibia, 19, 1-7.
- Hou, X., Parent, M., Savard, M.M., Tassé, N., Bégin, C and Marion, J. (2006). Lead concentrations and isotope ratios in the exchangeable fraction: tracing soil contamination near a copper smelter Geochem. Explor. Environ. Anal., 6, 229-236, doi:10.1144/1467-7873/05-092.
- Hutton, M and Symon, C. (1986). The Quantities of Cadmium, Lead, Mercury, and Arsenic entering the U.K. Environment from human activities Sci. the Total environment, 57: 129-150.
- Jarup, L. (2003). Hazards of heavy metal contamination. Brazilian Medical Bulletin, 68, 425–462.
- Kabata-Pendias, A. (2004). Soil-plant transfer of trace elements-an environmental issue. Geaoderma, 122, 2, 143-149.
- Kaewtubtim, P., Meeinkuirt, W., Seepom, S and Pichtel, J. (2018). Phyto-management of radionuclides and heavy metals in mangrove sediments of Pattani Bay, Thailand using Avicennia marina and Pluchea indica. Mar. Pollut. Bull., 127: 320–333, doi.org/ 10.1016/j.marpolbul.2017.12.021.
- Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z and Zhu, Y.G. (2008). Health risk of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China Environmental Pollution, 152, 3, 686-692.
- Kierczak, J., Potysz, A., Pietranik, A., Tyszka, R., Modelska, M., Néel, C., Ettler, V and Mihaljevič, M. (2013). Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland) Geochem J. Explor., 124, 183-194, doi:10.1016/j.g explo.2012.09.008.
- Lake, D.L., Kirk, P.W.W and Lester, J.N. (1984). The fractionation, characterization, and speciation of heavy metals in sewage sludge and sewage sludge amended soils: a review J Environ. Qual, 13, 175-183.

- Li, Z., Feng, X., Li, G., Bi, X., Sun, G., Zhu, J., Qin, H and Wang, J. (2011). Mercury and other metal and metalloid soil contamination near a Pb/Zn smelter in east Hunan province, China Appl. Geochem., 26, 160-166, doi:10.1016/j.apgeochem.2010.11.014.
- Mapani, B., Ellmies, R., Hahn, I., Schneider, G., Ndalulilwa, K., Leonard, R., Zeeuw, M., Mwananawa, N., Uugulu, S., Namene, E., Amaambo, W., Sibanda, F and Mufenda, M. (2014). Contamination of Agricultural Products in the Surrounding of the Tsumeb Smelter Complex. Communs Geol. Surv. Namibia, 15, 92-110.
- Mohamed H.H.A and Al-Qahtani, K.M. (2012). Assessment of some heavy metals in vegetables, cereals, and fruits in Saudi Arabian markets. Egyptian Journal of Aquatic Research, 38, 31–37.
- Mtunzi, F.M., Dikio, E.D and Moja, S.J. (2015). Evaluation of heavy metal Pollution on soil in Vaderbijlpark, South Africa. Int. J. Environ. Monit. and Analysis, 3, 2, 44-49.
- Al-Khashman, O.A. (2012). Assessment of Heavy Metal Accumulation in Urban Soil around Potash Industrial Site in the East of the Dead Sea and their Environmental Risks, Soil and Sediment Contamination: An International Journal, 21, 2, 276-290.
- Obaidy, A.H.M and A.A. Mashhadi. (2013). Heavy metals contaminations in urban soil within Baghdad city, Iraq. Journal of Environmental Protection, *4*, 72.
- Onder, S., Dursun, S., Gezgin, S. and Demirbas, A. (2007). Determination of heavy metal pollution in grass and soil of City Centre Green areas (Konya, Turkey). Polish J. Environmental Studies, 16, 1, 145 154.
- Onianwa, P.C and Fakayode, S.O (2000). Lead contamination of topsoil and vegetation in the vicinity of a battery factory in Nigeria. Environ. Geochem. Health. 22, 3, 211-218.
- Opaluwa, O.D., Aremu, M.O., Ogbo, L.O, Abiola, K.A., Odiba, I.E., Abubakar, M.M and Nweze, N.O. (2012). Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria. Advances in Applied Science Research, 3, 2, 780-784.
- Pam, A., Rufus, S and John, O. (2013). Evaluation of heavy metals in soils around auto mechanic workshop clusters in Gboko and Makurdi, Central Nigeria. J of Environmental Chemistry and Ecotoxicology, 5, 11, 298-306.
- Pacyna, J.M., Pacyna, E.G and Aas, W. (2009). Changes of emissions and atmospheric deposition of mercury, lead, and cadmium, Fifty Years of Endeavour, Atmos. Environ., 43, 117–127.
- Pirrone, N., Cinnirella, S., Feng, X., Friedli, H.R., Levine, L., Pacyna, J., Pacyna, E.G., Streets, D.G and Sundseth, KH. (2010). Assessment Report – Emissions and Projections, Tech. Rep. Chapter B3, LRTAP – Task Force on Hemispheric Transport of Air Pollutants, http://htap.icg.fz-juelich.de/data/ChapterB3
- Qasem, M.J and Kamal, A.M. (1999). Contamination of roadside soil, plants, and air with heavy metal sin Jordan a comparative study. Turkish Journal of Chemistry, 23, 209-220.
- Radwan, M.A and Salama, A.K. (2006). Market basket survey for some heavy metals in Egyptian fruits and vegetables. Food and Chemical Toxicology, 44, 1273-1278.

- Schreck, E., Yann, S., Sobanska, G., Cécillon, S., Castrec-Rouelle, L., Uzu, M and Camille, D. (2012). Metal and metalloid foliar uptake by various plant species exposed to atmospheric industrial fallout: Mechanisms involved for lead. Sci. The Total Environment, 427-428, 253-262.
- Schneider, G.I. C and Mocke, H. (2015). Communication of the Geological Survey of Namibia, Vol. 16.
- Scott, D., Keoghan, J.M. and Allen, B.E. (1996). Native and Low Input Grasses—A New Zealand High Country Perspective. New Zealand Journal of Agricultural Research, 39, 499-512, doi.org/10.1080/00288233.1996.9513211.
- Sharma, R.K., Agrawal, M. and Marshall, F.M. (2008). Heavy metals (Cu, Cd, Zn and Pb) contamination of vegetables in Urban India: a case Study in Varanasi. Environmental Pollution, 154, 254-263.
- Sorooshian, A., Csavina, J., Shingler, T., Dey, S., Brechtel, F.J., Sáez, A.E and Betterton, E.A. (2012). Hygroscopic and chemical properties of aerosols collected near a copper smelter: implications for public and environmental health. Environ. Sci. Technol., 46, 9473-9480, 10.1021/es302275k.
- Thomas, I.H.L., Francisco, B., Fredy, R.C.R., Maria, D.C.D., Patricia, Q.O., Daniel, A. and Avto, G. (2015). Concentration of toxic elements in topsoils of the metropolitan area of Mexico City: Spatial analysis using ordinary kriging and indicator kriging. Rev. Int. Contam. Ambie. 31, 1, 47-62.
- Trichopoulos, D. (1997). Epidemiology of cancer: DeVita, V.T. (Ed.), Cancer, Principles and Practice of Oncology, Lippincott Company, Philadelphia, pp. 231-258.
- Turkdogan, M.K., Kilicel, F., Kara, K. and Tuncer, I. (2002). Heavy metals in soil, vegetables, and fruits in the endemic upper gastrointestinal cancer region of Turkey Environmental Toxicology and Pharmacology, 13, 175-179.
- WHO, (1992). World Health Organization. Cadmium. Environmental Health Criteria, vol. 134, Geneva.
- WHO, (1994). World Health Organization. Quality Directive of Potable Water, Geneva, second ed., p. 197.
- WHO, (1993). World Health Organization. Evaluation of Certain Food Additives and Contaminants. In: Forty-First Report of the Joint FAO/WHO Expert Committee on Food Additives., WHO, Geneva, Switzerland. (WHO Technical Series, 837).
- WHO/FAO, (2001). Food additives and contaminants. Joint Codex Alimentarius Commission. 2001.
- WHO, (2004). World Health Organization. Evaluation of certain food additives and Contaminants. In: Sixty-First Report of the Joint FAO/WHO Expert Committee on Food Additives. WHO, Geneva, Switzerland. (WHO Technical Series, 922).
- Wu, Q., Wang, S., Wang, L., Liu, F., Che-Jen, L., Zhang, L and Wang, F. (2014). Spatial distribution and accumulation of Hg in soil surrounding a Zn/Pb smelter Sci. Total Environ., 496, 668-677, 10.1016/j.scitotenv.2014.02.067.

- Xilong, W., Sato, T., Baoshan, X. and Tao, S. (2005).Health risk of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. Science of the total Environment 350, 28-37.
- Yebpella, G.G., Magomya, A.M., Udiba, U.U., Gandu, I., Amana, S.M., Ugboaja, V.C. and Usman, N.L. (2011). Assessment of Cd, Cu, Mn and Zn Levels in Soil, Water and Vegetable Grown in Irrigated Farm along River Kubani, Zaria, Nigeria. J. Appl. Environ. Biol. Sci., 1, 5, 84-89.

# APPENDICES Appendix A: Ethical Clearance for the Project

#### FACULTY OF HEALTH AND APPLIED SCIENCES RESEARCH ETHICS COMMITTEE (FHAS-REC) APPLICATION FORM FOR ETHICAL CLEARANCE FOR RESEARCH/DATA COLLECTION

<b>NB:</b> The form should be completed by the principal re	search	er (PI)	or stude	nt researcher (in consultation with the
supervisor /promotor), attach the approved research r	proposa	al by th	ne depar	tment and then submit to the Faculty
Research Ethics Committee.			ie aepai	
Full name of researcher: Mr. Joshua Kaviyu Hidinwa				
Department & Faculty of Researcher: e.g. Health and Ap	plied S	ciences	;	
Title of research project: Distribution and Dynamic of to	xic hea	vy met	als in cult	tivated farm produce from
Grootfontein, Otavi and Tsumeb Localities, Namibia.				
If a registered NUST student, indicate degree programm	ne: Ma	aster of	Health S	ciences
NUST staff or student number: 215041585				
Supervisor/promotor (if applicable): Prof: Omotayo Aw	ofolu			
ETHICAL CONSIDERATIONS (Please indicate with X)	Yes	NS*	No	ACTION REQUIRED
1. Familiarity with ethical codes of conduct				
As researcher, I have familiarised myself with the	٧			If YES: Continue with the checklist.
professional code(s) of ethics and guidelines for ethically				If NS/NO: Researcher must do so
responsible research relevant to my field of study AND				before proceeding.
the policy for the assurance and promotion of ethically				
accountable research at NUST (researchers' obligation).				
2. The proposed research: (Proceed with the whole of Se	ection 2	2)		
a) Involves collection of information directly from	Yes	NS	No**	If YES: Continue with the checklist.
human participants (individuals or groups) (e.g. by				If NO: This checklist process does not
means of questionnaires, interviews, observation of			v	apply to the proposed research,
participants(s) or working with personal data of people).				except if 2 (b) applies.
b) Involves collection of information directly from			V	If YES: Continue with the checklist.
companies, corporations, organisations, NGOs,				If NO: This checklist process does not
government departments etc. that is not available in the				apply to the proposed research.
public domain.				
c 1) Is linked to or part of a bio-medical research project				If YES/NS: FHAS-REC clearance will be
c2) Is linked to or part of nuclear/radio-active research			v	required.
project.				
c3) Is linked to bio-technological research project e.g.				
GMOs, Environmental Nanotech research etc.				
d) Involves collection of information without consent				If YES/NS: FHAS-REC clearance will be
/assent, i.e. will be conducted without the			v	required.
knowledge of the individual/participants in the				
research				
e) Involves collection of identifiable information about				If YES/NS: FHAS-REC clearance will be
people from available records/archival material to			v	required.
be collected on individuals/groups/lists with				
personal information				
f) Involves collection of environmental samples (such as	٧			If YES: provide an indication of no
water, soil, and plant resources etc.				impact on the resources in the
				proposal

#### NB: \* NS = Not sure/Don't know

**\*\* Please note:** If the "No" option is selected; it does not nullify the responsibility of the researcher to ensure that ethical research practices are followed throughout the research process. The onus rests on the researcher to ensure that, should any ethical issues arise in the course of the research, all necessary steps are taken to minimise and report these risks to the supervisor/promotor of the study (where relevant/applicable), the Departmental Head , and the FHAS-REC. **Furthermore:** If the "No" option is chosen it does not absolve the researcher to seriously consider any other possible risk that may emanate and become a disadvantage to research participants and/or stakeholders or deny them fundamental rights.

In the case of \*NS, researcher is expected to seek clarification with the supervisor/promoter or an expert in the field of study prior to completion of the form/indication of NS. This might prevent delays in the ethical clearance process and commencement of the research project.

3. The proposed research involves the collection of informat	ion fr	om pe	ople in	the fo	ollowing categories:
a) Minors (persons under 18 years of age)		-	٧	lf Fl	YES/NS for any of these categories (a-f): HAS-REC clearance will be required. The
b) People with disabilities, orphans			٧	n r	ommittee must screen the proposal and hay seek further external clarification if he ethical risk is assessed as medium or
c) People living with/affected by HIV/AIDS			۷	h	igh.
				lf w	NO for all of these categories: Continue vith the checklist.
d) Prisoners			v		
e) Another category deemed vulnerable; SPECIFY here: [check glossary for definitions]					
f) NUST staff, students, or alumni			٧	lf o si w	<sup>4</sup> YES/NS: FHAS-REC clearance must be btained. Complete the checklist and ubmit to the committee. If NO: Continue vith the checklist.
4. Assessment of risk of potential harm as a result of the rese	arch	(tick C	NE app	oropria	ate YES or NS box)
a) <b>Minimal risk</b> (for a classification of risk types, and definition, see reference below <sup>†</sup> and for Standard Research	Yes	NS	No	) If a	YES/NS: Established ethical standards pply. Proceed to 5, 6 and 7 and
Res Policy) <sup>‡</sup>			v	lf	NO: Proceed to 4b).
b) <b>Low risk</b> (for a classification of risk types, and definition, see reference below <sup>†</sup> and for Standard Research Operation Procedure for research and research ethics (NUST-Res Policy) <sup>‡</sup>	Yes	NS	Nc √	) If a o	YES/NS: Established ethical standards pply; further assessment may be carried ut by FHAS-REC. Proceed to 5, 6 and 7 nd completion of checklist
( oney)				lf	NO: Continue with the checklist.
c) <b>Medium risk</b> ((for a classification of risk types, and definition, see reference below <sup>†</sup> and for Standard Research	Yes	NS	No	) If O	YES/NS: FHAS-REC clearance must be btained; further assessment/
Operation Procedure for research and research ethics (NUST- Res Policy) <sup>‡</sup>			V	cl P cl	larification may be carried out by F-REC. roceed to 5, 6 and 7 and completion of hecklist.
				If	NO: continue with the checklist.
d) <b>High risk</b> (for a classification of risk types, and definition,	Yes	NS	No	) If	YES/NS: FHAS-REC clearance must be
Procedure for research and research ethics (NUST-Res Policy) <sup>‡</sup>			v	a: o	ssessment/clarification may be carried ut by FHAS-REC. Proceed to 5, 6 and 7
				a If	nd complete the checklist. NO: Continue with the checklist.
5. The proposed research involves processes regarding the se	lectio	on of p	articip	ants in	the following categories:
a) Participants that are subordinate to the person doing the	Yes	NS	No	) If	YES: FHAS-REC clearance may be
recruitment for the study			V	re If	equired. NO: Continue with the checklist.
b) Third parties are indirectly involved because of the person	Yes	NS	No	) If	YES: FHAS-REC clearance may be
being studied (e.g. family members of HIV patients, parents or guardians of minors, friends)			v	re If	equired. NO: Continue with the checklist.
		-			
6. Steps to ensure established ethical standards are applied (	rega	rdless	of risk	assess	ment)
a) <b>Informed consent</b> : Appropriate provision has been/will made for this (in writing) or indicated in the research tool.	be	Yes	NS	No	If YES: Provide evidence together with the submitted proposal. Continue with
b) Voluntary participation: Respondents/informants will	be			v √	If NS/NO: Attach/provide justification
unformed, inter alia, they have the right to refuse to answ questions and to withdraw from participation at any time	ver				for further assessment and advice.
c) <b>Privacy</b> : Steps will be taken to ensure personal data informants will be secured from improper access	of	_		V	This should be reflected in the evidence of 'informed consent' or as
d) <b>Confidentiality and anonymity:</b> Confidentiality of informati	on			٧	reflected in the research instrument
unless explicitly waived by respondent.	eu				

e) Training: research assistants/ fieldworkers will be used to			•	V	1	
collect data, and ethics awareness will be included in their training			_			
f) <b>Mitigation of potential risk:</b> Likelihood that mitigation of risk of	Yes	S N	S	No	lt cul	YES/NS: Develop protocols for
appropriate steps have been/will be taken (e.g. referral for				v	ch	ecklist
counselling)				•	If	NO: Proceed with checklist.
g) Access: Institutional permission is required to gain access to	Yes	5 N.	5	No	lf	YES: Develop application for
participants and has been/will be secured. Specify here from					au	thorisation process it accordingly.
whom:				V	Со	ntinue with checklist.
					It I	NS: Refer proposal to departmental
If the permission letter required is available, attach a conv with					an	d advice Continue to 6 (b)
the application. If it is not available, apply for it immediately and					If	NO: Proceed to 6 (h).
indicate when it will be available.						
h) Accountability research*: Institutional permission to gain	Yes	5 N.	S	No	lf	YES/NS: Refer proposal to
access to participants poses an obstacle to conduct the research.					de	partmental research co-ordinator
				v	an	d/HoD for clarification and advice.
					0	ntinue with checklist.
					١f N	NO: continue with checklist.
i) Public availability of instruments to gather data: [When	Yes	5 N.	S	No	١f ١	YES or not applicable: proceed with
applicable] Are the instruments that will be used to gather data					ch	ecklist.
available in the public domain?	v				If N	NS/NO: Obtain permission to use the
					Ins	rmission with the proposal to
					de	partmental research co-ordinator
					an	d/HoD for clarification and advice.
					Со	ntinue with checklist.
j) Use of psychological tests: [When applicable] Are the	Yes	5 N.	5	No	١f ١	YES/NS: Indicate who will administer
instruments that will be used to gather data classified by law as					the	ese tests, and whether they are
psychological tests?				v	ap ad	equately trained to do so. Provide
^May provide brief answer here (where required:				-	reg	gistration number and professional
					bo	dy. Continue with checklist.
					If I	NO or not applicable: Proceed with
k) Protecting data from unputherized access: Are appropriate	Voi	. NI		No	cho	ecklist.
measures in place to protect data from unauthorized access? If	res		5	NO	ch	ecklist.
yes, specify what the measures are:	v				0	
					If	NO/NS: Develop and put in place
^May provide brief answer here (where required:					ар	propriate measures. Continue with
					cn	ecklist.
l) Unexpected information: If unexpected, unsolicited data is reveal	ed	Yes	NS	N	0	If YES: Proceed with checklist.
during the process of research, data will be kept confidential and v	vill					
only be revealed if required by law.		٧				If NO/NS: Consult on this matter
						with FHAS-REC for further
m) Fmergency situations: If an unexpected emergency situation	is	Yes	NS	N	0	If YES: Proceed with checklist
revealed during the research, whether it is caused by my research	or	103			5	
not, it will immediately be reported to my supervisor/promotor a	nd	٧				If NO/NS: Consult on this matter
Departmental Chair for further advice.						with FHAS-REC. Continue with
		V		+		checklist.
<ul> <li>n) rermission to use archival data: [When applicable] is permissi granted from the custodian of the archive to use it</li> </ul>	on	Yes	NS	N	0	IT YES: Proceed with checklist.
Brance wom the custodian of the drenive to use it.		v				If NO/NS: Consult on this matter
						with FHAS-REC. Continue with
						checklist.
o) The archive itself does not pose problems: [When applicable] T	he	Yes	NS	Ν	0	If YES, proceed with checklist.
initial conditions under which the archive originated allow you as	: a	v	l I			It NO/NS' Consult on this matter
third-narty recearcher to use the material in the archive	, u	•				with EHAS_PEC Continue with
third-party researcher to use the material in the archive.	, u	•				with FHAS-REC. Continue with checklist.

7. Conflict of interest				
Is the researcher aware of any actual or potential conflict of interest in	Yes	NS	No	If YES/NS: Identify concerns, attach
his/her proceeding with this research?			v	details of steps to manage them,
				and refer to F-REC for assessment
^If "yes" May provide brief answer here (where required:				and advice.
				If NO: No further actions are
				required, except signing the
				declaration and the checklist, and
				submit to FHAS-REC together with
				supporting documentation where
				required.

#### **DECLARATION BY RESEARCHER:**

I hereby declare that I will conduct my research in compliance with the professional code(s) of ethics and guidelines for ethically responsible research relevant to my field of study as specified in the list herewith attached, AND the 'Framework policy for the assurance and promotion of ethically accountable research at the Namibia University of Science and Technology', even if my research poses minimal or low ethical risk.

Name of Researcher: Joshua Kaviyu Hidinwa	Signature:	Date: 03/05/2017	
---	------------	---------------------	--

Name of Supervisor (if applicable):	Signature:	Date:
Name of co-supervisor(s) (if applicable):	Signature:	Date:
Name of co-supervisor(s) (if applicable):	Signature:	Date:

#### RECOMMENDATION BY THE REVIEWER: PLEASE INDICATE WITH (X) AS APPROPRIATE

i. No ethical issue(s) in the proposal; researcher may proceed with the project

ii. Minor ethical issue(s) in the proposal; researcher may provisionally proceed with the project **BUT** must comply with recommendations below within specified time otherwise provisional consent will be withdrawn

iii. Major ethical issue(s) in the proposal; researcher should not proceed with the project until all recommendation(s) below is/are complied with and application resubmitted for consideration.

Comments by the reviewer (may attach separate page as necessary):

Title, full name of reviewer & (field of specialisation):	
Date:	
Signature:	
Jighatare.	

**Note:** It is the responsibility of the department/supervisor to provide researcher or (PG students) with a list of professional Code(s) of Ethics and Guidelines for ethically responsible research in their specific field of study or refer them to appropriate online site(s) where the information can be accessed.

NB: As a guide, you may read the general guideline for research ethics as well as subject specific guidelines at "The Norwegian National Research Ethics Committee (<u>https://www.etikkom.no/en/In-English/Publications/-</u> accessed: 30-01-2016) \*Classification of risks: Risk classification of research projects (<u>http://mams.rmit.edu.au/zbxuyx1l4zchz.pdf</u>) \*NUST Research Policy: http://staffintranet.nust.na/?q=filedepot

THIS ETHICAL CLEARANCE APPLICATION SHOULD BE PROPERLY FILED AND SEND TO THE FACULTY RESEARCH ETHICS COMMITTEE TOGETHER WITH COPY OF THE RESEARCH PROPOSAL. ON RECEIPT OF THE DOCUMENT, THE RESEARCH ETHICS COMMITTEE WILL PROCESS AND REVERT BACK TO THE RESEARCHER AS SOON AS POSSIBLE.

# Appendix B: Approval letter from the Ministry of Agriculture, Water & Forestry

P.O.Box 40094 Ausspannplatz Namibia

06 September 2017

## **Permanent Secretary**

Ministry of Agriculture, Water & Forestry

Private Bag 13184

Windhoek

Dear Sir/Madam,

# RE: Request for permission / consent to conduct research in Tsumeb, Grootfontein and Otavi District

I am currently registered for the Master of Health Sciences Degree at the Namibia University of Science and Technology (NUST) and one of the requirements is to carry out a research project.

The title of my research is the "Distribution and Dynamics of Heavy Metals in Farm Produce from Farmlands within Tsumeb, Grootfontein and Otavi Local Areas". It involves the collection of farm produce (tomatoes, potatoes, cabbage, carrots maize) from agricultural farms.

It is against this background that I am humbly requesting for permission/consent from your good office to conduct the above-mentioned activity.

I hope my request will find your favourable consideration in this regard.

Yours faithfully

<u>\_\_\_\_</u>

Joshua K. Hidinwa

0812600555

# **Compliance with Ethical Standards**

The authors adhere to all ethical requirements involved in this research project.

**Conflict of interest:** The authors declare that there was no conflict of interest in the implementation of this research.

**Research involving Human Participants and/or Animals:** Research did not involve human and/or animal participants.

Informed consent: All participants were duly informed.