ASSESSMENT OF SELECTED TRACE ELEMENTS IN SOIL AND
VEGETABLE (Spinaca oleracea) IN RUAI, NAIROBI CITY
COUNTY, KENYA

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DECLARATION

This thesis is my original work and has not been presented for a Degree or Award in any other University.

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DEDICATION

This thesis is dedicated to my wife Jescah Kerubo and children Emmanuela Moraa and Emmanuel Nyandika.
ACKNOWLEDGEMENTS

The successful completion of this thesis is the culmination of intensive efforts of the researcher and the support of many people directly and indirectly to whom the researcher is honestly grateful. Though it may not be possible to mention all people that contributed to these efforts, I mention the following as a representation of these invaluable contributions. I am grateful to the unceasing support and guidance from my supervisors Dr. Esther Kitur and Dr. Julius Nzeve who were readily available despite their extremely tight schedules to provide insightful comments and guidance that shaped the study.

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<thead>
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<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
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<tr>
<td>EDDI</td>
<td>Estimated Daily Dietary Intake</td>
</tr>
<tr>
<td>EVM</td>
<td>Expert Group on Vitamins and Minerals</td>
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<tr>
<td>FAO</td>
<td>Food and Agricultural Organization</td>
</tr>
<tr>
<td>HQ</td>
<td>Hazard Quotient</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>ICRAF</td>
<td>International center for research in Agroforestry</td>
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<tr>
<td>MA</td>
<td>Millennium Assessment</td>
</tr>
<tr>
<td>NGO</td>
<td>Non-Governmental Organization</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>PCF</td>
<td>Plant Concentration Factor</td>
</tr>
<tr>
<td>PMTDI</td>
<td>Provisional Maximum Tolerable Daily Intakes</td>
</tr>
<tr>
<td>PMTWI</td>
<td>Provisional Maximum Tolerable Weekly Intakes</td>
</tr>
<tr>
<td>PXRF</td>
<td>Portable X-ray fluorescence</td>
</tr>
<tr>
<td>SDG</td>
<td>Sustainable Development Goal</td>
</tr>
<tr>
<td>SRM</td>
<td>Standard Reference Material</td>
</tr>
<tr>
<td>TF</td>
<td>Transfer factor</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
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ABSTRACT

Urban farming makes a substantial influence on the household economy of the urban poor especially in developing countries. Urban soil the hot spot of urban farming is a natural sink for contaminants especially the potentially toxic trace elements derived mainly from anthropogenic activities. The sources of trace elements include effluents from sewerage drainage system, unprocessed wastewater from neighboring manufacturing industries in addition to farming activities along polluted rivers and other streams. This study quantified the concentrations of selected potentially toxic trace elements (Cr, Mn, Cu, Ni, and Zn) in top (0-20 cm) and sub (21-50 cm) soils and selected vegetable (Spinacea oleracea) from gardens in Ruai sewage area, Nairobi City, County. Grid soil sampling method was used to collect soil samples while plant samples were sampled randomly in tandem and their total concentrations was determined using a portable X-ray Fluorescence Spectrometer. Data analysis was performed using R version 3.3.3. The study revealed that the topsoil had higher concentration of trace elements than sub soil. The topsoil concentration in mg/kg were; 61.62 ± 6.14, 4042.58 ± 380.45, 30.82 ± 1.21, 43.90 ± 12.05 and 456.43 ± 71.61 for Cr, Mn, Ni, Cu and Zn respectively. The subsoil concentration in mg/kg were; 54.67 ± 5.85, 3791.38 ± 572.11, 30.32 ± 1.37, 27.83 ± 12.54 and 370.32 ± 74.42 for Cr, Mn, Ni, Cu and Zn respectively. It also noted that concentration of the trace elements was higher during dry season than wet season but not significantly different (P ≥ .05) for all the elements. The study also revealed that hazard quotient for all the elements were below 1. Values for Wet season were 0.0012, 0.4929, 0.0552 and 0.1167 for Cr, Mn, Cu and Zn respectively whereas dry season had 0.0013, 0.3552, 0.0627 and 0.0914 for Cr, Mn, Cu and Zn respectively. Calculated Transfer Factor were below 1 for both seasons with a trend order of Zn>Cu>Cr>Mn. The elemental estimation of daily intake rates through consumption of the sampled Spinacea oleracea was within the WHO permissible maximum tolerable daily intake. Thus, there is no imminent health risk in consuming Spinacea oleracea from the study area. However, it recommended that there is need to monitor levels of trace elements in soil and Spinacea oleracea to ensure they do not exceed acceptable levels.
CHAPTER ONE: INTRODUCTION

1.1 Background Information

Consumption of crops grown within urban areas has increased exponentially due to the rise in urban demand. This has resulted unto acceptance of food production in urban areas as a basic urban occupation (Ghosh, 2004). This notwithstanding, crops cultivated in urban areas are usually exposed to a higher concentration of trace elements than those grown in rural areas (Margenat et al., 2019). In Kenya it is reported that 29% of urban households grow crops in towns (Orsini et al., 2013) Some of the Reasons why this practice of urban agriculture is greatly increasing include easy access to markets and transportation of products, a source to increase household income of the urban poor and due to shortage of land hence what is available is utilized (Olowoyo & Lion, 2016).

Soil is a major resource in both rural and urban areas for it serves as the prime nutrient source for plants. Determination of soil quality is unrivaled measure of its fertility which makes it an economical way of maintaining nourished health plant leading to excellent crop productivity (Galuszka et al., 2015). In an urban area this need is necessitated by the fact that rural environments are less polluted than urban areas. Hence crops cultivated in an urban area tend to have a higher exposure to contaminants, like the potentially toxic trace elements, due to emissions from traffic and burning of fossil fuels for energy and manufacturing use (Mielke et al., 2011).
Soil as a constituent of the biosphere, is very important since it is a geochemical sink for pollutants, and it serves as a natural buffer regulating passage of chemical elements and other substances to the atmosphere, hydrosphere, and biota. Also, in food production, soil plays a major role thus making it a very essential component in the survival of humans. Therefore, mankind has a responsibility of maintaining the agricultural and ecological functions of soil (Kabata-Pendias, 2011). Poor soil conditions affect food security and safety directly and indirectly. Direct effects results in poor crop yield and a deprived nutritious standard of crop produce. Nutrient imbalance in soil, caused by shortage of some and toxicity resulting from excess of others, is a primary cause of poor yield in tarnished soils that has strong undesirable influences on crop harvest (Lal, 2009).

In urban areas, soil, a component of the landscape, among other functions, has recreational and esthetical roles in gardens and parks that enhance safeguarding of biodiversity. Unlike other soils, urban soil is prone to be used differently hence making its connection with other compartments of the ecosystem to vary. This is especially common due to presence of anthropogenic supplies that get mixed with it hence altering its functioning (Bhattacharjee et al., 2019). Anthropogenic activities, like industrial activities, traffic emissions, waste disposal and fuel combustion, inevitably result in soil pollution (Ajmone-Marsan & Biasioli, 2010). These anthropogenic doings have caused contamination of the soils with various pollutants. Among the pollutants, potentially toxic elements (PTEs) and heavy elements are a main cause of concern. This concern becomes eminent as a result
of the closeness of soil to humans and the roles soils play (Ajmone-Marsan & Biasioli, 2010).

According to Duzgoren-Aydin et al., (2006), the concentration of energy and matter mostly due to anthropogenic activities in cities, results in buildup of trace elements. As a consequence, urban soils have a possibility of being more polluted than their other counterparts in the rural areas (Johnson & Ander, 2008). Whereas it is hard to list all Trace elements that are potentially toxic in soil, among those that have been identified are; Cr, Mn, Ni, Cu and Zn (Nawar et al, 2019). The danger of high concentrations of PTEs is typically interrelated to their chances to enter the food chain through plant uptake or to percolate to groundwater. Also, toxicity of the potentially toxic trace elements can be through contact with contaminated soil, direct consumption, and breathing of particles (Cheng et al., 2015).

Crops cultivated in soil polluted by heavy metals, assimilate the elements and store them (Khan et al., 2014). Therefore, pollution of toxic metals is a weighty environmental concern because their non-degradable nature that leads to extensive consequences on the biological system like that of a human (Margenat et al., 2019). Some trace elements (Cr, Mn, Ni, Cu and Zn) are vital to human beings hence they are required in minute levels for functions like hemoglobin formation, vitamin synthesis and enzyme systems. Nevertheless, if the heavy metals are in excess, they become disastrous to the metabolic functions of the
body (Hina and Rizwani 2011). Despite the benefits of urban and peri-urban farming such as provision of food urban dwellers (Cheng et al., 2015), if wrongly done, it has health hazards, especially those resulting from exposure to pollutants like trace elements and are prone to be abundant in city soils (Kim et al., 2014).

1.2 Problem Statement and Justification
The urban area is predominantly susceptible to trace elements pollution because of their accumulation in the soil. One such area is Ruai that is heavily under cultivation for food crops especially the land surrounding the sewage treatment plant at the North-Eastern region of the sewage plant. Farmers in the area either use wastewater from the sewerage plant for irrigation or water from nearby Nairobi River. Their source of water for irrigation is irrefutably dirty hence its prone to have toxic trace elements. Also, its location being near Nairobi city, industrial activities and other anthropogenic activities are likely to pollute the area thus making it unsuitable for farming. Vegetables cultivated in the area are: Spinach, kales, Amaranth and Black Nightshade. Also, there are cows, goats and sheep that graze in the area which belongs to the residents and visiting nomadic Maasai (Ongoma et al., 2013). Due to environmental pollution in Nairobi city, urban farming like that in Ruai sewage area poses food safety concerns. The environmental pollution is as a result of its location near to industrial activity and sewage effluents (Oka et al., 2014). These, coupled with other intensive anthropogenic activities in the city, a weighty load on the quality of the soil is
imposed and consequently the quality of vegetables (Zhao et al., 2007). If the quality of vegetables under cultivation is contaminated by toxic trace elements, consumers are likely to be affected, hence a need of doing a study in the area. Therefore, the aim of the study was to find out the concentration of trace elements in soils and spinach vegetables which are grown in Ruai an urban area irrigated with sewage water.

1.3 Research Questions

1. What are the concentration levels of selected trace elements in soil and Spinach vegetable grown in Ruai?

2. What are the concentration levels of selected trace elements in Spinach vegetable grown in Ruai area? Do the trace elements concentration level in soils and crops vary with seasons?

3. What is the risk of consuming vegetables grown in Ruai in relation to metal Transfer factor and Hazard Quotient?

1.4 Research Hypotheses

1. There is no significant difference between the concentration of trace elements (Cr, Mn, Ni, Cu and Zn) in soil and Spinach vegetables grown in Ruai.

2. The relationship between the levels of trace elements (Cr, Mn, Ni, Cu and Zn) in topsoil (0-20 cm) and subsoil (21-50 cm) in Ruai is not significant.
3. The concentration of trace elements in soils and Spinach vegetables do not exhibit any seasonal changes.

4. There is no risk of consuming vegetables grown in Ruai in relation to metal Transfer factor and Hazard quotient.

1.5 Objectives

The general objective of the study was to quantify the concentration of selected trace elements (Cr, Mn, Ni, Cu and Zn) in soils and Spinach vegetable grown in Ruai Nairobi County.

1.5.1 Specific objectives

1. To assess concentration of selected trace elements (Cr, Mn, Ni, Cu and Zn) in topsoil (0-20 cm), sub soil (21-50 cm) and Spinach vegetables grown in Ruai area.

2. To investigate concentration of selected trace elements (Cr, Mn, Ni, Cu and Zn) in Spinach (*Spinaca oleracea*) vegetables grown in Ruai area.

3. To assess seasonal variability in concentration of selected trace elements (Cr, Mn, Ni, Cu and Zn) in soils and Spinach.

4. To determine the potential risk of consuming Spinach vegetables grown in Ruai.
1.6 Significance of the study

Information gathered in the study contributes to the understanding of trace elements contamination in soil and crops grown in an urban area where contaminated (untreated sewage) water is used for irrigation. Also, the information is important for the ministry of Agriculture to give advice on the impacts of using contaminated soils and water in urban food production. This will enable effective monitoring of both environmental quality and sustainable urban food production.

The study will be of importance to policy makers like the Ministry of Environment and Mineral resources, Ministry of Agriculture, livestock and Fisheries, and NGOs among other stakeholders as it provides information that could be used to formulate management strategies for safety of the environment and human health. Finally, information gathered can be used as a literature source for other scholars with interests in trace element contamination in urban farming research.

1.7 Conceptual framework of the study

In an urban setup, Industrial effluents and municipal effluents are likely to be used for irrigation in farming. Typically, this is the experience at Ruai sewage area and these factors were independent factors for our study. These independent factors have an influence on the dependent factors which in the study are soil quality of the area and the quality of vegetables cultivated in the area our study case being
Spinach vegetables (Spinaca oleracea). Intervening factors are efficiency of the Ruai sewage treatment plant and use of contaminated wastewater for irrigation (Figure 1.1)

**Figure 1.1**: Conceptual framework of the study.

**1.8 Scope of the study, Limitations and Assumptions**

The study covered Ruai area as an urban area where a sewage treatment plant for Nairobi city is located. The study did not extend to adjacent urban areas within Nairobi city where gardening is practiced due to logistic constrains and availability of resources. Elements investigated were not exhaustive due to
constrains. It was assumed that the results from the study area represent other areas which use untreated sewage water for irrigation. The vegetable considered in this study is *Spinaca oleracea* due to its availability and high consumption in the city. The study did not consider other vegetables grown in urban gardens and those consumed in the city due to constrains of resources.

1.9 Definition of terms

**Trace elements:** These are chemical elements that are required in minute amounts for biological purposes. Of the 89 naturally occurring elements, only 10 elements (O, Si, Fe, Al, Ca, K, Na, Mg, Ti & H) are not trace elements. These elements together form in excess of 99% of the Earth’s crust by weight. The other 79, are trace elements which account less than 0.5% by weight. Although these elements account for small percentage of the total body weight, their role in the body is inversely related to their weight (Wada, 2004).

**Urban farming:** This is the cultivation of crops and practice of animal husbandry within cities. A noticeable aspect of urban farming is the incorporation of the urban economy. This incorporation involves use of urban occupants as laborers, urban dwellers being consumers of the products and use of organic waste and wastewater for irrigation (Olowoyo & Lion, 2016a).

**Topsoil:** The topmost layer of the soil is called the topsoil. It normally constitutes a blend of decomposing organic matter, silt clay and sand. Although the topsoil is comparatively thin, most of the nutrients are in this layer (Chemistry, 2017).
Subsoil: This is the layer of soil that is immediately below the topsoil. The layer is mostly made up of weathered parent material rocks in as much it may contain organic matter. (Chemistry, 2017).

X-ray fluorescence (XRF): This is a spectroscopic technique of analysis of elemental determination. The main principle of this technique is that when atoms are irradiated with x-rays, they radiate secondary x-rays in a process referred as fluorescence radiation. Fluorescence intensity is used to calculate the elemental concentration whereby each element is associated with specific wavelength and energy of the fluorescence radiation.
CHAPTER TWO: LITERATURE REVIEW

2.1 General Overview

In geochemistry the term “trace elements” is used to refer to those elements present in rocks and soils at a concentration below 1000 mg/kg. In biological field the term is used to refer to elements occurring at low concentrations (typically less than 100 ppm) in the waterless material of living organisms. In nutrition discipline, a trace element is an element whose occurrence is natural with a concentration hardly in excess of 20 ppm in the food consumed (Al-Fartusie and Mohssan, 2017). Nonetheless, some trace elements like Manganese and Zinc can be in excess of this concentration (Kabata-Pendias, 2011). In plant nutrition, essential trace elements are vital to plant growth but are only required in minute amounts and are generally referred to as micronutrients.

Of the eighty-nine naturally occurring elements, only ten elements (O, Si, Fe, Al, Ca, K, Na, Mg, Ti & H) are not trace elements. These elements together form in excess of 99% of the Earth’s crust by weight. The other seventy-nine, are trace elements which account less than 0.5% by weight. They do not play an indispensable role in the face of the Earth’s crust but their importance in ecosystem, farming, medication, toxicology and many more areas have an inverse relationship to their little crustal richness (Al-Fartusie and Mohssan, 2017).

The chief source of trace elements to human beings, animals and plants is soil. Soil vertical variability in trace elements could be as an outcome of the parent
material, climate, time, topography, soil organism and agricultural practices (Bhattacharjee et al., 2019). Leaching and cycling of nutrients due to plants and animal excreta leads to both exhaustion and improvement in specific soil horizons. Also, the soil can increase elements through dust introduced from other areas, by adsorption from water draining into a soil from elsewhere and by contamination as a result of anthropogenic activity (Council, 2013). Urban settings are erratically prone to be polluted with substances such as metals and organic contaminants due to human activities such as mining, traffic, poor agricultural practices, wrong waste dumping, industries and fossil fuel burning (Sun, 2020). Recently, it has been established that a large proportion of lethal trace elements find their way into the human nutrition through intake of contaminated crops and farm produce (Nabulo et al., 2010).

Soils in areas next to industries are predisposed by the injurious effects of a variety of pollutants. To a certain degree, soils can eliminate the toxic effects. However, when contaminants are in excess of this capability, this contaminants can be mobilized, resulting in pollution of cultivated crops (Radziemska et al., 2017). Of these contaminants, trace elements tops in the list. This means that urban soils can be polluted by trace elements in varying levels from moderately to too severely. This extreme levels is dangerous to human health (Radziemska et al., 2017).
Trace element contamination is problematic globally hence it needs much consideration, because of its perennial toxicity, the danger of bioaccumulation in organisms, and the hindrance of ecosystem processes (Drava et al., 2020). This pollution leads to accumulation of trace elements in soils and other surfaces, such as plant shoots and leaves. This causes worries about growing crops in urban areas, which tend to be more polluted than rural areas (Margenat et al., 2019). However, not all trace elements are harmful or toxic. On the contrary, many of these elements if consumed in right quantities, are vital for appropriate operational of the human body (Drava et al., 2020).

Parent material of soil and environmental contamination; greatly contribute to presence of trace elements that are found in all soils (Shao et al., 2018). Exposure to contaminants by farmers can happen in many ways: ingestion of soil unintentionally, breathing polluted dust and through direct skin contact (Pipoyan et al., 2018). Particles on the surface of plants can easily be ingested by those who eat produce that are grown in polluted areas (Morgan and Sonnino, 2010).

Climate and bedrock configuration among other factors, determine soil properties that are different from place to place. As a result, some places may contain elements that exceed the recommended levels for the health of plants, animals and human beings. Occasionally, levels of some trace elements in soil and other substances may surpass recommended levels for the health of crop cultivation, humans or animals (Margenat et al., 2019). The increase in human activities resulting from population explosion over time, coupled with increasing
industrialization amongst others have contributed greatly to global environmental degradation leading to excess levels of recommended trace elements (Onuoha and Felicia, 2014). This is especially, experienced in peri-urban and urban areas that are commonly highly contaminated than rural areas and urban vegetation and farm yields tend to be exposed to high levels of pollution, including trace elements, as a result of traffic emissions and fossil fuels combustion for energy and industrial purposes (Mielke et al., 2011).

Atmospheric fallout of particles is one of the supplier of trace elements contamination in vegetable plants via stomata uptake (Mgbeahuruike, 2011). Thereby, contamination occurs not only through the roots, but also through leaves of the plant whereby absorption of trace elements from the atmosphere, water and soil ultimately accrue in the plant (Margenat et al., 2019). Vegetable quality is greatly affected by surface deposition, particularly when careless washing of the vegetable is done (Liu et al, 2013).

2.2 Urban Farming

Urban farming is the cultivation of plants and animal husbandry in cities for consumption at home and as a means generating income (Orsini et al, 2013). It encompasses all forms of vegetable cultivation and fruit trees, as well as the cultivation of other crops for specialized purposes like medicinal. Also, it captures husbandry of all forms of animals at a small-scale level. Nevertheless, a peculiar and an important feature of urban farming is its increasingly significance
in cities from an environmental and social–economic perspective (Olowoyo and Lion, 2016b).

Urban farming is considered as an significant answer to food safety in the ever increasing developed world (Gelman, 2014). Because current towns rely nearly completely on outside resources especially food; fast urban development might result in food deficiencies and put the health and wellbeing of urban dwellers at a risk (Gelman, 2014). In light of this fast urban growth, there is a concern about urban food safety globally (Morgan and Sonnino, 2010). Notably, this is the very experience in Nairobi the capital city of Kenya.

Urban farming contributes to socio-economic development, eradication of poverty and provision of food to the urban poor. Also it makes it possible for urban wastes to be used productively and it makes the city appear green (Poulsen et al., 2017). Lately, there is a prominence on food production within urban areas that could lead to less dependencies on rural areas for food provisions, mitigation of urban poverty and nutrition problems (Margenat et al., 2019). Outstandingly, this form of food production is being accepted widely all over the globe and its becoming the norm in cities of high population density all over the world (Olowoyo and Lion, 2016a).

Substantial amounts of food get wasted at the consumer level, however, major loses are as a result of spoilage that occurs during transportation, storing, distribution and packaging – loses which can be reduced to minimal levels if food
is consumed in the locality of its production (Gustavsson et al., 2011). Also, if a smaller amount of food is wasted, then it will lead to production of less amount of food, hence reduction to the general environmental impact. Therefore, even though it has been accelerated by economic hardship, farming in an urban set up, leads to reduction of energy cost since the market of the produce is within the same locality (Olowoyo and Lion, 2016a). Due to availability of ready market, a variety of crops are being cultivated in cities just like in rural areas (Orsini et al., 2013).

2.3 Uptake of Trace elements by plants

Plant growth is necessitated by absorption of nutrients from the soil. Their capability to absorb nutrients is dependent on the nature of the soil. Soil generally comprises a mixture of organic matter, clay, sand and silt. The nature of a soil quality and its pH level influences availability of nutrients to plants. Typically metals favorably concentrate highly in the roots, followed by the branches and are less concentrated in the leaves. Several factors influence trace elements bioavailability and accumulation that are linked to type of plant, nature of soil, agronomic management and climatic environments (Kirmani et al., 2011). Supplementary sources of these trace elements for plants are precipitation and dusts from the atmosphere which may perhaps be adsorbed via the blades of the leaf. A significant contamination source, in vegetables, is foliar uptake of atmospheric trace elements discharges (Shahid et al., 2017). Plant absorption of
potentially toxic trace elements is the major pathway through which these elements can enter the food chain (Khan et al., 2015). Plant availability of trace elements varies extensively amongst species of plants and tissues (Nworie et al., 2019). Therefore, the importance of trace elements in health and nutrition of both human and animal requires continuous monitoring of their levels in the environment.

2.4 Trace elements in soils and vegetables

2.4.1 Chromium

Chromium is a trace element present in foodstuffs of animals and plant source. It takes part in a variety of metabolic functions thus it is regarded as an essential element. It occurs in food in form of Cr\(^{3+}\). Chromium(VI) is hardly found in food and it is lethal (Rêczajska et al., 2005). Even though chromium is undeniably recognized as an indispensable nutrient, there is no specific recommended dietary allowance for Cr. The appraised harmless and acceptable daily dietary ingestion of chromium for adults ranges from 50 µg/day to 200 µg/day (Lukaski, 2000; Rêczajska et al., 2005).

The immobility of soil Chromium could be accountable for its insufficient amount to plants. Chromium is an essential trace element because of the role it plays in human and animal nutrition. Readily solvable Chromium (VI) in soil is lethal to animals and plants (Dogo et al., 2011). Presence of Chromium in surface soil tends to be elevated as a result of contamination from numerous sources, of which
the major ones are industrial wastes and municipal sewage sludges. The extra Chromium to soils from these anthropogenic activities is generally accumulated at the top level of soil (Kabata-pendas & Henryk, 2001). Generally, there is enough Chromium in soils, however, its availability to plants is limited. The readily available Chromium to plants is Cr(VI), which is highly uneven under ordinary soil conditions hence making its availability difficult (Kabata-pendas & Henryk, 2001). Nevertheless, addition of Chromium in soil from anthropogenic activities tends to influence the Cr availability of plants, and its uptake by plants is influenced by several plant and soil factors. Typically, less Chromium is detected in leaves than in roots that tend to have high Cr level while grains have the lowest levels of this trace element.

2.4.2 Manganese

Manganese is present in nearly all soils, its worldwide concentration in soils fluctuate from 2 mg/kg to 9200 mg/kg, with a global mean of 437 mg/kg and its highest presence are notable in calcareous soils and loamy soils (Kabata-Pendias, 2011). A concentration mean of 330 mg/kg is estimated to be a background mean for agricultural soils (Eckel et al., 2015). High presence of Manganese is usually notable in soils rich in organic matter, soils over mafic rocks and soils from arid and semi-arid regions. Presence of soil organic matter makes Mn accumulation in topsoil to be higher than sub soil (Avila et al., 2013). In soils Manganese occurs in the forms of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$. However, it is only Mn$^{2+}$ that is absorbed
by plants. Solubility of soil Manganese is very important since its plant availability is dependent on the level soluble in soil. Reduction of soil pH increases Manganese solubility in soil (Kabata-Pendias, 2011).

### 2.4.3 Nickel

Nickel is a transition element whose presence in the environment is at very little levels and is essential in minor amounts. Nickel is carcinogenic if excess levels is consumed hence it is a hazardous trace element when the maximum acceptable levels are surpassed. Its pollution in soil mainly occurs through anthropogenic activities that include sewage and oil burning for power and heat (Khodadoust et al., 2004; Wuana & Okieimen, 2011). Parent material influences highly on Nickel levels of soil (Kabata-Pendias, 2011). However, its concentration in topsoil is influenced by anthropogenic activities. Soils all over the globe contain Nickel with a reported range 0.2–1000 mg/kg (Bradford et al., 1996).

Ni absorption in humans occurs as a result of consumption of plant and animal foodstuffs. Its presence is high in vegetables like legumes, spinach, lettuce and nuts. In plants like corn and potatoes, Ni, like other metals is largely ligated to polysaccharides (Nordberg et al., 2007). The average approximated intake of Nickel is estimates to be in the range of 200–300 μg/day, though its oral intake due to leaching from cooking ware, kitchen utensils, and water piping can feasibly be as high as 1 mg/day (Bencko, 1983).
2.4.4 Copper

Copper is an essential trace element which is a vital part of several enzymes. Its globe mean concentration for uncontaminated soils ranges from 13 mg/kg to 24 mg/kg (Kabata-pendas & Pendias, 2001). Copper tends to be a fixed element in soil thus it shows little variation in various soil (Kabata-Pendias, 2011). However, its accumulation in topsoil is high due to its bioaccumulation and anthropogenic sources (Kabata-Pendias, 2011). The main anthropogenic sources of copper to the soils are wastewater sludge and copper mining (Georgopoulos et al., 2001). Soluble organic chelates are the main form of copper in solution, but its solubility decreases at pH 7 to 8 (Kabata-pendas & Pendias, 2001).

Copper is a component of numerous enzymes and is vital in physiological processes like photosynthesis and respiration (Al-Fartusie & Mohssan, 2017). The daily intake of copper in adults from food generally varies from approximately 1–2.5 mg, corresponding to 15–45 μg/kg body weight in adults (WHO, 1996). WHO, (1996) suggested daily requirements of 1.2 mg Cu/day for adult women and 1.3 mg Cu/day for adults. Intake of a large amount of copper may cause gastrointestinal disturbances (WHO, 1996).

2.4.5 Zinc

Zinc is an essential trace element whose presence in the earth’s crust is roughly 0.02% by weight of (Kumar et al., 2015). An average of 78 mg/kg is reported as the content of Zn in the earth’s crust (Hooda, 2010a). Occurrence of Zn is only in
the divalent state and does not occur as a metal in nature. Content of Zinc in soil and its bioavailability are very critical for growth of plants (Adriano, 2001). Factors that influence availability of Zinc to plants include its total concentration in soils, organic matter, PH level in soil, amount of other micronutrients and macronutrients and soil moisture. Availability of Zinc to plants increases as soil pH decreases and may become lacking in soils with a PH above 6.5. Generally, Soil pH influences Zinc availability more than any other factor (Kanda, Djaneye-boundjou, Wala, & Gnandi, 2012). Enrichment of Zinc in soil occurs through use of chemical fertilizer, industrial discharge and sewage sludge. High acidity increases mobility of Zinc from sludge to soil (Nordberg et al., 2007). An average of 40–90 mg/kg has been reported to be the concentration of Zinc of noncontaminated soil with a range of 1 mg/kg to 200 mg/kg (Adriano, 2001).

2.5 Trace elements transfer factor (TF) from soil to Spinach

Determination of human exposure of metals through food is achieved by soil to plant transfer factor. Normally, the transfer factor expresses the bioavailability of a metal at a position on a species of plant. However, this is dependent on various factors like nature of soil, type of plant and soil acidity or alkalinity. Transfer factor values are used to describe the accumulation of chemicals in organisms, especially those living in contaminated environments. The low the value of TF, the less available the metal is. Hence, the low transfer factor values indicate no risk to human health (Tsafe et al., 2012).
2.6 Risk assessment

To guard human beings from detrimental effects of consuming excess metals, World Health Organization has established similar values for harmfulness, referred as provisional maximum tolerable weekly intakes (PMTWI) and Provisional maximum tolerable daily intakes (PMTDI). PMTDI is the end point for contaminants with no cumulative properties while PMTWI is the end point for food contaminants such as heavy metals with cumulative properties (FAO & WHO, 2011). An element will be detrimental if its estimated daily intake exceeded its provided PMTDI.
CHAPTER THREE: MATERIALS AND METHODS

3.1 Description of the study Area

The study was carried out in Ruai ward, Ruai sewage area, which is located in Nairobi East Kasarani constituency, Kasarani Sub County. The area is approximately 30 km East of Nairobi City Centre off Kangundo road (Figure 3.1). Its geographical coordinates are 1° 18' 0" South, 36° 55' 0" East. (Opiah et al., 2007)

![Figure 3.1: Map of Nairobi showing Location of Ruai Sewage treatment plant the study area. (Source: Author)]
3.1.1 Climate

The rainfall is bimodal with long rains occurring between March and May while the short rains are in August to November. The rainfall ranges between 750 mm to 1500 mm, with a mean annual rainfall of 1125mm. The temperature varies from 17°C to 27°C. June and July are the months with lowest temperature while the hottest months are January and September with temperature ranging from 25°C to 27°C. (Opijah et al., 2007).

3.1.2 Drainage and soil

The area is drained by Nairobi River and its tributaries which flow northeastwards and eastwards. Nairobi River has several seasonal tributaries which have water during the rainy seasons and immediately after, otherwise they are normally dry most part of the year. The geology of the area generally contains Nairobi volcanics sheltered by black cotton clay soils. The area is generally flat with Nairobi River at the north Eastern region of the area (Opijah et al., 2007).

3.1.3 Economic activities in the area

The area is heavily under cultivation for food crops especially the land surrounding the sewage treatment plant at the North-Eastern region of the sewage plant. Some of the farmers use the wastewater for irrigation and the sewerage sludge as fertilizer. The vegetables cultivated are: Spinach, kales, Amaranth and Black Nightshade. Also, there are cows, goats and sheep that graze in the area
which belongs to the residents and visiting nomadic Maasai (Ongoma et al., 2013).

3.2 Research Design

The research study was empirical it involved sample collection in the field, preparation of the samples and laboratory analysis of the samples to obtain data.

3.2.1 Selection of study site and sampling points

Domestic and industrial waste in Nairobi city are transported to Ruai for treatment. These wastes have pollutants from the municipal drainage or the industrial drainage that are either dissolved in sewage water or attached to suspended matter. These pollutants eventually get into the treatment plant and finally to the sludge. Therefore, the area was considered for the study because some potentially toxic trace elements were prone to be in the sewage sludge and consequently into the soil. Close to fifty acres of land sandwiched between the sewage and Nairobi River is under vegetable cultivation. These vegetables find their way into the tables of many Nairobi city county residents.

3.3 Sample Collection

A 50 m by 50 m grid was constructed over the site. 15 sampling points were identified (Table 3.1) within the area using grid soil sampling pattern according to Wollenhaupt & Wolkowski, (1994). At each sampling point topsoil (0-20 cm)
and sub soil (21-50 cm) samples were collected by use of a 3in (76 mm) standard auger from five cores within a 2-meter radius and pooled into two buckets, one for topsoil and the other for subsoil. The samples were then thoroughly mixed in the buckets using a trowel. About 50 g of the sample was subsampled into labeled plastic bags respectively to form a total of thirty soil samples. All the labeled thirty soil samples were individually sealed into polythene bags to avoid cross contamination and thereafter transported to the World Agroforestry (ICRAF) laboratories in Nairobi for preparation and analysis. Sampling and transfer of samples was done on the same day. Sampling was done during the dry and wet season.

Table 3.1: GPS coordinates positions where sampling was done.

<table>
<thead>
<tr>
<th>Sampling Positions</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>2</td>
<td>-1.23653</td>
<td>37.0141</td>
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<tr>
<td>4</td>
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<td>37.01378</td>
</tr>
<tr>
<td>15</td>
<td>-1.23365</td>
<td>37.01389</td>
</tr>
</tbody>
</table>
Vegetable samples were also collected using the grid sampling pattern from the same point the soil samples were collected. A total of 15 samples were collected into porous bags and labelled. The vegetable samples that were picked were the most recent mature leaves. Spatial coordinates were taken at each of the sampling points (Table 3.1) and 15 – 20 leaves were sampled at each grid point. All the labeled 15 vegetable samples were individually sealed into polythene bags to avoid cross contamination and then transported to the World Agroforestry (ICRAF) laboratories in Nairobi for preparation and analysis. Sampling and transfer of the vegetable samples was done on the same day. Sampling was done during the dry and wet season.

3.4 Instrumentation

The elemental concentration of both the vegetable and soil samples was done using Bruker Tracer 5i pXRF instrument (900F4473) with Rhodium tubes. The units had resolutions (full width height maximum, or FWHM) of 135 eV at the Manganese K-alpha line. Vegetable samples were analyzed with a voltage of 35 kV and a current of 35 μA for 90 seconds with filter (Cu 75μm: Ti 25μm: Al 200μm) for Trace elements. Soil samples were analyzed with a voltage of 30 kV and a current of 50 μA for 60 seconds with filter (Ti 25μm: Al 300μm) for Trace elements. X-ray fluorescence is a non-destructive elemental analysis technique for quantification of almost any element from Magnesium to Uranium depending on specific configurations of the spectrometer used. X-ray fluorescence is a well-
established analytical technique used in many industrial and research applications for materials characterizations. Portable X-ray fluorescence (pXRF) spectroscopy is a breakthrough technology that allows quick and cheap determination of elemental composition of soil and plant materials among other samples. XRF method is robust - basically counting atoms (Towett et al., 2016).

The working principle for x-ray fluorescence, is by displacement of electrons from their atomic shells locations, resulting to a release of a burst energy that is distinctive of a precise element (Figure 3.2).

**Figure 3.2**: Image showing how displacement of electrons occurs due to X-ray beam
The X-ray fluorescence technique has numerous advantages in comparison to other multi-element methods of analysis like atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS). The major advantages include: non-destructive analysis, limited preparation time for solid samples, less production of hazardous waste, low start-up and running cost and increased total speed (Parsons et al., 2013).

**Figure 3.3:** A Photo showing Tracer portable X-ray fluorescence spectrometer performing analysis.

### 3.5 Sample Preparation and analysis

Soil samples were air-dried, mechanically crushed using a stainless-steel roller and sieved through 2-mm sieves. About 10 grams was then subsampled by coning and quartering and further milled to attain a particle size of between 20-75 μm.
using a Retsch RM 200 mill (Retsch, Düsseldorf, Germany) automated milling machines. About 3g homogenized sample was loaded into special XRF cups (Figure 3.4) made from 4μm (0.16 mil) polypropylene XRF film free from irregular surfaces and contamination. The loaded XRF cup with a sample was placed on the sample table (Figure 3.3) of the instrument for XRF analysis using Bruker remote control software and later quantified using Buker instrument tool software. This was done for all the samples and the elemental concentrations found in the samples were auto saved. The data acquisition time was 60 seconds per sample. All the samples were analyzed in duplicates.

The vegetable sample were washed with normal tap water and air dried. After the water had evaporated, the vegetable samples were oven-dried at 60°C for 72 hours and then ground into powder to pass a 1-mm sieve using a Cyclotech mill; it was then further milled to fine particles of less than 75 µm sizes using a ball mill. About 3g of the homogenized sample were loaded into XRF cups (Figure 3.4) prepared from 4μm (0.16 mil) polypropylene XRF film which was free from irregular surfaces and contamination. The XRF cup loaded with vegetable sample was then placed on the sample table (Figure 3.3) of the instrument for XRF analysis using Bruker remote control software and later quantified using Buker instrument tool software. This was done for all the samples and the elemental concentration found of the samples was auto saved. All the samples were analyzed in duplicates.
For both soils and plants, measurement was achieved by identifying a descriptive name of the sample being measured (sample ID), selecting a folder where the data could be saved and then clicking save to begin measurement. This was accomplished by use of S1PXRF software that controls the pxrf spectrometer (Figure 3.3).

Figure 3.4: A photo showing XRF Cups with the base sealed with polypropylene XRF film

3.6 Quality assurance

The quality performance of the Tracer 5i XRF spectrometer for the estimation of trace elements was assessed by analysis of Duplex 2205 reference sample
supplied by Bruker. The instrument is deemed fit if average concentration of each element is within the accepted reference values.

3.6.1 Certified Reference Material

To check the quality and reliability of the plant results obtained by this method, NIST SRM 1575a (pine needles), a Certified Reference Material distributed by National Institute of Standards and Technology, was analyzed. Also, for quality assurance purposes of the soil results obtained by this method, SRM SAR-M a certified reference material distributed by United States Geological Survey, was analyzed. All the samples and reference materials were subjected to same technique and measurement settings.

3.7 Transfer factor (TF)

The transfer factor is the metal concentration in plant tissue above the ground divided by the total metal concentration in the soil. It signifies the amount of potentially toxic trace elements in the soil that ended up in the plant. The TF was estimated by dividing the content of trace element in vegetables by the total trace element content in soil (Cui et al., 2004; Kachenko & Singh, 2006)

\[
TF = \frac{C_{plant}}{C_{soil}}
\]

Where, plant \( C_{plant} \): metal concentration in vegetable tissue, mg kg\(^{-1}\) and soil \( C_{soil} \): metal concentration in soil, mg/kg.
3.8 Hazard Quotient (HQ)

Danger of ingestion of vegetables polluted with trace elements was characterized by Hazard Quotient (HQ). This is a ratio of determined dose to the reference dose ($R_f D$). Consumers of the vegetables will be in danger if the calculated HQ is equal or more than one and if the calculated ratio is less than one then consumers will be at no danger. This risk calculation technique has been used by various scholars (Chauhan & Chauhan, 2014; Farooq et al., 2009, 2009; Guerra et al., 2012) and has demonstrated to be effective and accurate. The following equation was used to estimate the Hazard Quotient (HQ);

$$HQ = (\text{Div}) \times (C_{\text{metal}}) \times (C_{\text{factor}}) / R_f D \times Bo$$

Where;

- $\text{Div.}$ is the dry weight of contaminated plant material consumed (kg per day)
- $(C_{\text{Metal}})$ is the concentration of metal in the vegetable (mg/kg)
- $(C_{\text{factor}})$ is the fresh to dry weight conversion factor
- $R_f D$ is the oral reference dose for the metal (mg/kg of body weight per day)
- $Bo$ is the human body mass (kg)

The conversion factor of 0.085 is to convert fresh vegetable weight to dry weight (Bao et al., 2014; Farooq, 2009)
$R_{fD}$ is an estimate of a daily oral exposure for the human population, which does not cause harmful effects during a lifetime. The oral reference dose was taken from FAO/WHO, (2011) (Table 3.2). The average body mass that was considered is 65kg and the daily intake of vegetable was estimated at 300g as per the recommendation of WHO 1989 that set a required range of 300g to 350 g of spinach.
Table 3.2: Reference doses \((R_{DO})\) mg kg\(^{-1}\) day\(^{-1}\) for Trace elements

<table>
<thead>
<tr>
<th>Element</th>
<th>FAO/WHO (2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn</td>
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</tr>
<tr>
<td>Cu</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn</td>
<td>0.3</td>
</tr>
</tbody>
</table>

3.9 Estimation of Daily trace elements intake through consumption of spinach

Estimated daily dietary intake (EDDI) were calculated in this study to ascertain whether the intake of spinach vegetables is safe for the consumers in Ruai region. To ascertain vegetable safety, the estimated EDDI were compared to the PMTDI value provided by WHO. An element is detrimental if its EDDI exceeded its PMTDI.

Calculation of EDDI was achieved by use of the following equation (Farooq et al., 2009)

\[
EDDI = C_{\text{Element}} \times C_{\text{Factor}} \times D_{\text{Vegetable}} / B_o
\]

Where

\(C_{\text{Element}}\) = Trace element concentration in vegetable (mg/kg) metal

\(C_{\text{Factor}}\) = conversion factor

\(D_{\text{Vegetable}}\) = daily intake of vegetables (kg)

\(B_o\) = Average Body weight

The conversion factor of 0.085 is to convert fresh vegetable weight to dry weight.
3.10 Data Analysis

Results obtained were collated and statistically analyzed based on the set objectives using R Version 3.3.3. Soil elemental concentration between the seasons and depths together with the spinach elemental concentration between the seasons were subjected to analysis of variance using R version 3.3.3. Box plots demonstrating variation of elemental concentration due to depth and seasons were generated using R. The variation in elemental concentration due to depth and seasons were subjected to t-test to test the difference between the seasons and depths. The obtained data was presented inform of tables, bar chats and box plots.
CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter gives results on the assessment of selected trace elements (Cr, Mn, Cu, Zn and Ni) in soil and Spinaca oleracea from gardens in areas of Ruai, their discussions of results and comparisons with other previous studies.

4.2 Trace elements concentration in topsoil (0-20cm), sub soil (21-50cm) and Spinach

4.2.1 Trace elements in topsoil (0-20cm)

4.2.1.1 Chromium

The study revealed that the concentration of Chromium in topsoil (0-20 cm) showed variation during the study period (Table 4.1), the concentration ranged from 54 mg/kg to 77.5 mg/kg (Table 4.1). The mean concentration of Chromium in topsoil (0-20 cm) was 61.62 mg/kg (Table 4.1). The highest Cr concentration was revealed in plot 7 whose GPS coordinates are -1.23661 S, 37.01451 E (Table 3.1), whereas the lowest concentration was revealed in plot 13 whose GPS coordinates are -1.23358 S, 37.01378 E (Table 3.1).
Table 4.1: Concentration of the five trace elements of topsoil (0-20 cm), for both season from the fifteen plots.

<table>
<thead>
<tr>
<th>Lab ID</th>
<th>Plot No.</th>
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<th>Mn</th>
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Levels of Chromium in soil has been reported to vary according to area and the degree of contamination from anthropogenic activities (Kabata-pendas & Henryk, 2001; Kamaludeen et al., 2003; ). Another aspect that has been reported to influence level of Chromium in soil, is the amount that has been removed through volatilization, surface runoff, leaching and Phyto-uptake. The sampling site being a place where cultivation is done and irrigation is done, variation of chromium concentration in soil is expected as was revealed in the study (Avudainayagam et al., 2003).

For all the plots sampled, plot 7 reported the highest concentration of Chromium that could be attributed to the position of the plot where sampling was done. Location of plot 7 is very close to the sewage water path that was used for irrigation, being close to the sewage water source might have influenced its high content as this location is prone to receive more than any other location. Also, such a location is favorable for germination of other vegetation leading to high organic matter content which may elevate the content of Cr. The lowest Cr concentration was revealed in plot 13 whose location was a margin to the farm which had poor cultivation leading to low organic content.

The mean concentration of Chromium from the study area (61.62 mg/kg) is slightly below what has been reported on a worldwide basis on Cr concentration in urban soil of 66.08 mg/Kg (Su et al., 2014). A study in Iran, revealed a mean concentration of Chromium of 28.7 mg/kg that was much lower than what was
found in the current study (Maleki et al., 2014). Further, a study in Varanasi, India, reported a mean concentration of 56.3 mg/kg (Mishra & Tripathi, 2008)

4.2.1.2 Manganese

Manganese content of the topsoil (0-20 cm) depicted a concentration range of 3320.00 – 4752.00 mg/kg with a mean concentration of 4042.58 mg/kg (Table 4.1). The highest Manganese concentration was revealed in plot 11 whose GPS coordinates are -1.23363 S, 37.01372 E (Table 3.1), whereas the lowest Manganese concentration was revealed in plot 1 whose GPS coordinates are -1.23668 S, 37.01421 E (Table 3.1).

The total concentration of Manganese in surface soil has been reported to vary greatly ranging from less than 7 mg/kg to more than 9000 mg/kg (Hooda, 2010b). Most of the soil manganese is from the parent material and other minor sources include atmospheric deposition, irrigation water and the use of sewage sludge (Hooda, 2010b). High manganese content is reported for soils over mafic rocks, soils from arid or semiarid regions and soils rich in organic matter (Hooda, 2010b; Kabata-pendias and Henryk, 2001). Fixation of organic matter in top soils is the reason why it tends to accumulate more on top soils (Kabata-pendias and Henryk, 2001).

The observed levels of Manganese could be attributed to Manganese content of the parent material, Fixation of organic matter and anthropogenic activities
around the area that include Irrigation of wastewater and atmospheric deposition. Highest Mn content was revealed in plot 11 which was very close to Nairobi river which was a source of water used for irrigation. Being close to the river, runoff water from other regions of the farm is prone to flow to this location thus organic content is likely to be high in this location. Low Mn content was revealed in plot 1 which was at the edge of the farm with poor cultivation and it served as the main entrance to the farm.

The range of Manganese of 3320.00 – 4752.00 mg/kg is high compared with various ranges that have been reported from similar studies that include; a study on urban soil contamination conducted in the city of Novokuybyshevsk Russia had a range of 125.7 mg/kg to 270.6 mg/kg (Galitskova & Murzayeva, 2016). A study in Penas Albas, Spain, revealed a concentration range of 751 mg/kg to 1850 mg/kg (Couce and Vega, 2015). Further, a study in Manaila, Romania, revealed a concentration range of between 161 mg/kg to 1258 mg/kg (Simona et al., 2015).

4.2.1.3 Nickel

The mean total Ni concentration was 30.82 mg/kg in topsoil (0-20 cm) with a range from 28.50mg/kg to 33.00 mg/kg (Table 4.1). The highest Nickel concentration was revealed in plot 8 whose GPS coordinates are -1.2363 S, 37.01434 E (Table 3.1), whereas the lowest Nickel concentration was revealed in plot 13 whose GPS coordinates are -1.23358 S, 37.01378 E (Table 3.1).
Though the range is within the reported broad world-wide range of 0.2 mg kg\(^{-1}\) to 450 mg kg\(^{-1}\), the concentration mean of top soil was higher than the soil world calculated mean of 22 mg/kg (Kabata-pendias and Henryk, 2001). However, the study location being an urban area that has a high possibility of being contaminated, the concentration mean of Nickel is prone to be higher than its reported world calculated mean. Typically, the mean concentration of Nickel from contaminated urban soil has been reported to be 29.14 mg/kg (Su et al., 2014).

Nickel concentration mean of 30.82 mg/kg for top soil was higher compared to the reported world mean of contaminated urban soils which is 29.14 mg/kg (Su et al., 2014). This shows the location has been highly contaminated in the previous period or the background concentration level of Nickel was higher for the site. The likely sources of pollution could be the sewage sludge and industrial dust to the area. In a similar study done in India, it was observed that constant application of untreated and treated sewage water to the soil led to elevated concentrations of trace elements in the soil (Mishra & Tripathi, 2008).

The highest concentration of Nickel was revealed in plot 8 which could be attributed to the position of the plot where sampling was done. Location of plot 8 was very close to the sewage water path that was used for irrigation, being close to the sewage water source might have influenced its high content as this location is prone to receive more wastewater than any other location. Also, such a location is favorable for germination of other vegetation leading to high organic matter content which may elevate the content of Ni. The lowest Nickel concentration
was revealed in plot 13 whose location was a margin to the farm which had poor cultivation leading to low organic matter.

A similar study on urban soil contamination conducted in the city of Novokuybyshevsk Russia had a range of 16.5 mg/kg to 35.25 mg/kg (Galitskova & Murzayeva, 2016). A study in the city of Tabriz Iran, revealed a concentration range of 2.50 mg/kg to 72.50 with a mean of 38.73 mg/kg (Taghipour et al., 2013).

### 4.2.1.4 Copper

Copper content of the topsoil (0-20 cm) showed a range concentration of 22 mg/kg to 69 mg/kg with a mean concentration of 43.90 mg/kg (Table 4.1). From the study, the highest Cu concentration was revealed in plot 7 whose GPS coordinates are -1.23661 S, 37.01451 E (Table 3.1), whereas the lowest concentration was revealed in plot 8 whose GPS coordinates are -1.23363 S, 37.01372 E (Table 3.1).

Copper typically accrues in the topsoil, a phenomenon explained by the bioaccumulation of the element and existing anthropogenic activities (Kabata-Pendias 2001). Like other elements investigated, variation in total elemental concentrations of copper was revealed. This variation could be attributable to differences in parent materials and to local pedologic and anthropogenic influences (Towett et al., 2015).
The revealed mean concentrations of Copper from the study is above the reported world mean that vary from 13 to 24 mg/kg (Kabata-pendias & Henryk, 2001). Therefore, copper levels were high as per the findings of the study in comparison to other global findings. The high concentration of copper could be attributed to Particulates of copper that are released into the atmosphere by windblown dust and influence of other anthropogenic sources (Nazir et al., 2015).

The highest concentration of Copper was revealed in plot 7, the high level could be attributed to the position of the plot where sampling was done. Location of plot 7 was very close to the sewage water path that was used for irrigation, being close to the sewage water source might have influenced its high content as this location is prone to receive more wastewater than any other location. Also, such a location is favorable for germination of other vegetation leading to high organic matter content which may elevate the content of Copper as was revealed. The lowest Cu was in plot 11 whose location was close to the river. Its low content could be attributed to the parent material of the location as Cu content in soil is more dependent on the parent rock than pedogenic factors.

A similar study on urban soil contamination conducted in the city of Novokuybyshevsk Russia had a range of 4.6 mg/kg to 27.75 mg/kg (Galitskova & Murzayeva, 2016). A study in the city of Tabriz Iran, revealed a concentration range of 13.17 mg/kg to 265.67 with a mean of 101.25 mg/kg (Taghipour et al., 2013). A study in Varanasi India, revealed a concentration range of 32.3 mg/kg
to 123.6 mg/kg with a higher mean concentration of 77.8 mg/kg (Mishra & Tripathi, 2008). A study in China revealed a concentration range of 22.2 mg/kg to 93.0 mg/kg with a slightly lower mean of 42.4 as compared to the present study (Guo et al., 2013).

### 4.2.1.5 Zinc

Concentration of Zinc of the topsoil (0-20 cm) exhibited a concentration range of 363.00 mg/kg to 590.00 mg/kg with a mean concentration of 456.43 mg/kg (Table 4.1). From the study, the highest Zinc concentration was revealed in plot 8 whose GPS coordinates are -1.2363 S, 37.01434 E (Table 4.1), whereas the lowest Zinc concentration was revealed in plot 11 whose GPS coordinates are -1.23363 S, 37.01372 E (Table 4.1).

The overall Zn concentration of soils is reported to vary greatly with a reported range of 10 to 300 mg/kg (Haluschak et al., 1998), while background levels of uncontaminated soils are 17 to 125 mg/kg on a world-wide basis (Kabata-pendias and Henryk, 2001). Anthropogenic sources of zinc are substantial to its elevated levels, that majorly arise from industrial activities, waste combustion and steel processing. The world's Zn production is increasing, and manufacturing applications tend to scatter Zinc extensively in the environment, resulting to concentration levels that are above pre-industrial levels in soil, water and air.
The mean content of Zinc of the site was high compared to concentrations recognized for soils on the globe (Kabata-Pendias and Henryk, 2001) and soils from polluted urban areas (Su et al., 2014). The high Zn content is a typical characteristic of contaminated sites whose Zn level together with other trace elements could be high and has been reported to range from 443 to 1112 mg/kg (Kabata-Pendias and Mukherjee, 2007). In addition, the elevated concentration of Zinc may be due to anthropogenic activities that are prone to influence its level, especially in the top horizon of soil.

The highest concentration of Zinc revealed in plot 8 could be attributed to the position of the plot where sampling was done. Location of plot 8 was very close to the sewage water path that was used for irrigation, being close to the sewage water source might have influenced its high content as this location is prone to receive more wastewater than any other location. Also, such a location is favorable for germination of other vegetation leading to high organic matter content which may elevate the content of Zinc. The lowest Zn was in plot 11 whose location was close to the river. Like Copper, its low content could be attributed to the parent material of the location as Zn content in soil is more dependent on the parent rock than pedogenic factors. A similar study on urban soil contamination conducted in the city of Novokuybeshevsk Russia had a range of 34.75 mg/kg to 73.5 mg/kg (Galitskova & Murzayeva, 2016). A study in the city of Tabriz Iran, revealed a concentration range of 49.80 mg/kg to 163.80 with a mean of 98.27 mg/kg (Taghipour et al., 2013). A study in Varanashi India,
revealed a concentration range of 86.4 mg/kg to 158.3 mg/kg with a mean concentration of 122.3 mg/kg which was lower than the current study. (Mishra & Tripathi, 2008). A study in China revealed a concentration range of 31.2 mg/kg to 213.6 mg/kg with a lower mean of 129.9 as compared to the present study (Guo et al., 2013).

4.2.2 Trace elements in sub soil (21-50cm)

4.2.2.1 Chromium

Chromium concentration of sub soil (21-50 cm) had a concentration mean of 54.67 mg/kg with a range varying from 47 mg/kg to 74 mg/kg (Table 4.2). From a worldwide basis, Cr mean concentration in urban soil has been reported to be 66.08 mg/Kg (Su, Jiang & Zhang, 2014).

A study carried out in Niger Delta; Nigeria reported a mean concentration of Chromium in subsoil to be 23.4 mg/kg with a range of less than 0.002 mg/kg to 34.2 Mg/Kg (Iwegbue & Iwegbue, 2015). A study in Hangzhou, China revealed a mean concentration of Chromium in sub soil of 43.91 mg/kg with a range of 22 mg/kg to 80.4 mg/kg (Ji et al., 2012).

4.2.2.2 Manganese

Sub soil (21-50 cm) concentration of Manganese from the study revealed a concentration range that varied from 2864.00 mg/kg to 4627.00 mg/kg with a concentration mean of 3791.38 mg/kg (Table 4.2). This concentration is low
compared to that of topsoil (Table 4.1). This trend is expected due to fixation of organic matter in top soils that makes it to accumulate more on top soils (Kabata-pendias and Henryk, 2001).

A study carried out in Niger Delta; Nigeria reported a mean concentration of Manganese in subsoil of 169.0 mg/Kg with a range of less than 53.67 mg/kg to 539.4 Mg/Kg (Iwegbue & Iwegbue, 2015). A similar study carried out in Germany, revealed a mean concentration in sub soil of 821 mg/kg with a range that varied from 433 mg/kg to 4501 mg/kg (Reiss & Chifflard, 2015).

### 4.2.2.3 Nickel

Sub soil (21-50 cm) concentration of Nickel had a mean concentration of 30.32 mg/kg with a range that varied from 27.5 mg/kg to 32.50 mg/kg (Table 4.2). Though the range is within the reported broad world-wide range of 0.2 mg kg\(^{-1}\) to 450 mg kg\(^{-1}\), the mean of sub soil was higher than the soil world calculated mean of 22 mg kg\(^{-1}\) (Kabata-pendias & Henryk, 2001). Also, this mean of sub soils was higher compared to the reported world mean of contaminated urban soils which is 29.14 mg/mg (Su et al., 2014).
### Table 4.2: Concentration of the five trace elements of sub soil (21-50 cm), for both season from the fifteen plots.

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<td>mscluk07ogy12</td>
<td>14</td>
<td>51.00</td>
<td>4039.00</td>
<td>30.50</td>
<td>24.00</td>
<td>340.00</td>
</tr>
<tr>
<td>mscznw1spw64</td>
<td>15</td>
<td>51.50</td>
<td>3614.00</td>
<td>29.00</td>
<td>28.00</td>
<td>330.50</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>54.67</td>
<td>3791.38</td>
<td>30.32</td>
<td>27.83</td>
<td>370.32</td>
</tr>
<tr>
<td>Maximum</td>
<td></td>
<td>74.00</td>
<td>4627.00</td>
<td>32.50</td>
<td>68.50</td>
<td>567.50</td>
</tr>
<tr>
<td>Minimum</td>
<td></td>
<td>47.00</td>
<td>2865.00</td>
<td>27.50</td>
<td>9.50</td>
<td>271.50</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>5.85</td>
<td>572.11</td>
<td>1.37</td>
<td>12.54</td>
<td>74.42</td>
</tr>
</tbody>
</table>
The high Nickel mean content from the site as compared to the world mean can be credited to the parent material as Nickel concentration of soils is extremely reliant on its concentration in background material (Kabata-Pendas, 2011). Nevertheless, higher content of Nickel in soils indicates the added impact of anthropogenic factors and soil-forming processes.

A study carried out in Niger Delta; Nigeria reported a mean concentration of Nickel in subsoil to be 26.5 mg/Kg with a range of less than 11.9 Mg/Kg to 37.9Mg/Kg (Iwegbue & Iwegbue, 2015). A study in Hangzhou, China revealed a higher mean concentration of Nickel in sub soil of 32.88 mg/kg with a range of 22.1 mg/kg to 58.6 mg/kg (Ji et al., 2012).

### 4.2.2.4 Copper

Concentration of Copper in subsoil (21-50 cm) revealed a range of between 9.50mg/kg to 68.50 mg/kg with a concentration mean of 27.83 mg/kg (Table 4.2). As expected, this concentration mean was lower compared to that of topsoil (0-20 cm) that was 43.90 mg/kg (Table 4.1). Copper is said to be associated with organic matter (Iwegbue & Iwegbue, 2015), hence, subsoil samples tend to have smaller amounts of Cu in comparison with topsoil samples, perhaps owing to presence of less organic substances in the subsoil and because at the topsoil is where biological activities mainly occur (Abollino et al., 2002).
A study carried out in Niger Delta; Nigeria reported a mean concentration of Copper in subsoil to be 5.50 mg/Kg with a range of less than 0.002 mg/kg to 15.0 mg/kg (Iwegbue & Iwegbue, 2015). A study in Hangzhou, China revealed a higher mean concentration in sub soil of 37.49 mg/kg with a range of 16.7 mg/kg to 70.9 mg/kg (Ji et al., 2012).

4.2.2.5 Zinc

From the study, Zinc concentration in sub soil (21-50 cm) revealed a concentration range of between 271.00 mg/kg to 567.50 mg/kg with a concentration mean of 370.32 mg/kg (Table 4.2). The Zinc concentration in soil is said to be subject to organic matter, the type of parent material, texture, and pH, and its world-wide range is from 10mg/kg to 300 mg/kg with a projected average of 64 mg kg (Kabata-Pendias 2001).

A study carried out in Niger Delta; Nigeria reported a mean concentration of Zinc in subsoil of 30.8 mg/Kg with a range of less than 8.67 mg/kg to 48.0 mg/kg (Iwegbue & Iwegbue, 2015). A study in Hangzhou, China revealed a mean concentration of Zinc in sub soil of 120.90 mg/kg with a range of 72.5 mg/kg to 215.0 mg/kg (Ji et al., 2012).

Like in the top soil (0-20 cm), the mean concentration of Zinc in sub soil (21-50 cm) from the study was high compared to concentrations reported for soils on a world-wide basis (Kabata-pendias & Henryk, 2001) and those from contaminated urban areas (Su et al., 2014). The high Zn content is a distinctive characteristic of
contaminated sites whose Zn level may be quite high, from 443 mg/kg to 1112 mg/kg (Kabata-Pendias & Mukherjee, 2007). In addition, anthropogenic source of Zinc may greatly influence its high contents and are most likely responsible for the observed elevated levels of Zn (Kabata-Pendias & Mukherjee, 2007).

4.2.3 Trace elements in Spinach

The trace elements that were investigated in Spinach were: Cr, Mn, Ni, Cu, and Zn. The results of analysis of the five trace elements in spinach as determined by Tracer 5i XRF spectrometer are presented in table 4.3. Notably, Nickel concentration was not detected. The probable reason is its total concentration was below the detection limit of Tracer 5i which is 7 mg/kg (Bruker, 2017). Reported background mean of Ni in vegetables is 1.3 mg/kg. Therefore, if Nickel was present in the vegetables within this range or even five times higher the reported mean, it could not be detected.

4.2.3.1 Chromium

From the study, Chromium in spinach vegetables revealed a concentration mean of 4.73 mg/kg with a range that varied from 4.00 to 6.00 mg/kg (Table 4.3). Notably, Chromium was below the detection limit for most of the spinach samples (close to 60 %) (Table 4.3). Chromium is a nonessential element to plants and plants don’t have a precise mechanism for its assimilation. Its uptake is
through carriers used for the uptake of essential trace elements for plant metabolism (Shanker et al, 2006).

The Chromium uptake by plants is positively correlated to chromium application as has been found by other researches (Devars et al, 2001) Hence, accumulation of Chromium tends to be high in spinach cultivated in high Cr concentrated soils and it has been found to be an economical way of removing Chromium from contaminated soils (Gangwar, 2009). The mean concentration of 4.73 mg/kg is higher than a concentration mean of 1.46 mg/kg obtained in Accra Ghana (Ackah et al., 2013). Also, it was higher than a mean level of 2.99 mg/kg obtained in areas of Jagjeetpur, Haridwar India (Vinod & Thakur, 2018).

Chromium as a trace element, its content in plants is influenced by various factors that include its concentrations in soils, organic matter content, soil pH, cation exchange capacity, types and varieties of plants. (Naser et al., 2011). The varied concentration level that was revealed could be attributed to these factors dominant of them being its concentration in soil (Adriano, 2001).

### 4.2.3.2 Manganese

Manganese had a mean concentration of 162.33 mg/kg. All the spinach samples had presence of Manganese that ranged from 73.5mg/kg to 436.5 mg/kg (Table 4.3). Of all the elements investigated, Manganese had the highest concentration indicating its uptake from soil to spinach leaves is high compared to the rest. A
similar observation was encountered by (Intawongse et al., 2007) who found that Manganese is easily mobilized from soil to plants.

From a similar study in India, a lower level of 4.25 mg/kg was reported (Vinod & Thakur, 2018). A lower concentration of 52.8 mg/kg was reported in a study carried out in Bangladesh (Naser et al., 2012). Also a mean of 26.53 mg/kg was reported in a study carried out in Saudi Arabia (Ali and Al-qahtani, 2012). However, mean concentration of 162.3 mg/kg though high as compared to similar studies that have been reported, it was found to be within the vegetable permissible level of 500 mg/kg as set by the Codex Alimentarius Commission (FAO/WHO, 1999).

4.2.3.3 Copper

From the study, Spinach revealed an average concentration of 6.15 mg/kg with a range of between 3.5 mg/kg to 9.0 mg/kg (Table 4.3). For all the spinach samples, copper was detected with an exception of two samples whose copper content was below the detection limit of 3.5 mg/kg (Bruker, 2017).

Mean concentration of 6.15 mg/kg is higher compared to a mean level of 4.98 mg/kg obtained in areas of Jagjeetpur, Haridwar India (Vinod & Thakur, 2018). A study in Bangladesh revealed a concentration mean of 10.9 mg/kg which was higher than what was found in the present study (Naser et al., 2012). Also a mean of 11.38 mg/kg was reported in a study carried out in Saudi Arabia (Ali and Al-
qahtani, 2012). A mean concentration of 6.15 mg/kg was found to be within the vegetable permissible level of 73.3 mg/kg as set by the Codex Alimentarius Commission (FAO/WHO, 1999).

4.2.3.4 Zinc

Presence of Zinc was detected in all the spinach samples that revealed a range of between 40.5 mg/kg to 120.50 mg/kg with a mean concentration of 77.17 mg/kg (Table 4.3). Of the elements that were investigated, Zinc was the second highest in concentration indicating its uptake from soil to spinach leaves is high compared to the rest. A similar observation was encountered by (Intawongse et al., 2007) who found that Zinc is easily mobilized from soil to plants and it tends to accumulate more in vegetables with its concentration dependent on its concentration in soil.
Table 4.3: Concentration of the five trace elements of spinach vegetables, for both season from the fifteen plots

<table>
<thead>
<tr>
<th>Lab ID</th>
<th>Cr</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mscdib06khu38</td>
<td>&lt; LOD</td>
<td>373.00</td>
<td>5.00</td>
<td>69.00</td>
</tr>
<tr>
<td>mscdcpq09lwp63</td>
<td>&lt; LOD</td>
<td>436.50</td>
<td>5.50</td>
<td>91.00</td>
</tr>
<tr>
<td>msdcddz06jxh38</td>
<td>&lt; LOD</td>
<td>172.50</td>
<td>7.00</td>
<td>71.00</td>
</tr>
<tr>
<td>mscdzc6wjl54</td>
<td>&lt; LOD</td>
<td>88.50</td>
<td>9.00</td>
<td>63.50</td>
</tr>
<tr>
<td>msdcfifx03oiq48</td>
<td>4.50</td>
<td>287.00</td>
<td>7.00</td>
<td>87.00</td>
</tr>
<tr>
<td>msccgy63mza31</td>
<td>&lt; LOD</td>
<td>131.00</td>
<td>5.00</td>
<td>55.50</td>
</tr>
<tr>
<td>msccjst71vac56</td>
<td>4.00</td>
<td>127.50</td>
<td>4.00</td>
<td>69.50</td>
</tr>
<tr>
<td>mscdcbp90dpq47</td>
<td>&lt; LOD</td>
<td>228.00</td>
<td>5.50</td>
<td>119.00</td>
</tr>
<tr>
<td>mscdclq63fqi81</td>
<td>&lt; LOD</td>
<td>120.50</td>
<td>7.50</td>
<td>72.50</td>
</tr>
<tr>
<td>msckpn76cfn87</td>
<td>&lt; LOD</td>
<td>161.00</td>
<td>6.00</td>
<td>100.50</td>
</tr>
<tr>
<td>mscdlsk03mwpd2</td>
<td>4.50</td>
<td>250.00</td>
<td>&lt; LOD</td>
<td>114.00</td>
</tr>
<tr>
<td>mscnkvb74trq23</td>
<td>5.00</td>
<td>129.00</td>
<td>&lt; LOD</td>
<td>107.50</td>
</tr>
<tr>
<td>mscnca58jagq26</td>
<td>&lt; LOD</td>
<td>177.50</td>
<td>3.50</td>
<td>108.00</td>
</tr>
<tr>
<td>mscnzt71gij83</td>
<td>&lt; LOD</td>
<td>147.50</td>
<td>6.50</td>
<td>59.00</td>
</tr>
<tr>
<td>mscootu83npr64</td>
<td>&lt; LOD</td>
<td>103.50</td>
<td>5.00</td>
<td>73.00</td>
</tr>
<tr>
<td>mscpsds04hyd86</td>
<td>5.50</td>
<td>142.50</td>
<td>5.50</td>
<td>61.50</td>
</tr>
<tr>
<td>msqca60xse14</td>
<td>4.00</td>
<td>123.50</td>
<td>5.50</td>
<td>56.00</td>
</tr>
<tr>
<td>msqcx72squ18</td>
<td>5.00</td>
<td>101.00</td>
<td>5.50</td>
<td>58.00</td>
</tr>
<tr>
<td>mscrw56ehw72</td>
<td>5.00</td>
<td>128.00</td>
<td>6.50</td>
<td>53.00</td>
</tr>
<tr>
<td>mscdsh50uwh41</td>
<td>&lt; LOD</td>
<td>73.50</td>
<td>6.00</td>
<td>40.50</td>
</tr>
<tr>
<td>mscx06rhc21</td>
<td>&lt; LOD</td>
<td>83.00</td>
<td>8.50</td>
<td>56.00</td>
</tr>
<tr>
<td>mscvpq28tye62</td>
<td>&lt; LOD</td>
<td>124.50</td>
<td>5.50</td>
<td>118.00</td>
</tr>
<tr>
<td>mscwcw76fa168</td>
<td>&lt; LOD</td>
<td>108.50</td>
<td>5.50</td>
<td>71.00</td>
</tr>
<tr>
<td>mscwls90rlp56</td>
<td>&lt; LOD</td>
<td>129.00</td>
<td>7.00</td>
<td>74.00</td>
</tr>
<tr>
<td>mscwsv35epj21</td>
<td>&lt; LOD</td>
<td>208.00</td>
<td>6.00</td>
<td>120.50</td>
</tr>
<tr>
<td>msyfh92eqn65</td>
<td>4.00</td>
<td>120.00</td>
<td>7.50</td>
<td>63.50</td>
</tr>
<tr>
<td>msczvb04oqt72</td>
<td>4.50</td>
<td>180.50</td>
<td>5.00</td>
<td>79.50</td>
</tr>
<tr>
<td>msctf05iv23</td>
<td>6.00</td>
<td>136.00</td>
<td>8.50</td>
<td>72.00</td>
</tr>
<tr>
<td>msczu46weu28</td>
<td>&lt; LOD</td>
<td>116.50</td>
<td>7.00</td>
<td>54.50</td>
</tr>
<tr>
<td>Average</td>
<td>4.73</td>
<td>162.33</td>
<td>6.15</td>
<td>77.17</td>
</tr>
<tr>
<td>Maximum</td>
<td>6.00</td>
<td>436.50</td>
<td>9.00</td>
<td>120.50</td>
</tr>
<tr>
<td>Minimum</td>
<td>4.00</td>
<td>73.50</td>
<td>3.50</td>
<td>40.50</td>
</tr>
<tr>
<td>SD</td>
<td>0.65</td>
<td>83.47</td>
<td>1.33</td>
<td>22.96</td>
</tr>
</tbody>
</table>

< LOD indicates less than the limit of detection
ND indicates the element was not detected
The revealed mean of 77.17 mg/kg is higher compared to what was reported by a study in Accra Ghana that showed a mean of 5.38 mg/kg (Ackah et al., 2013). Also, a lower level of 5.6 mg/kg was reported in Haridwar India (Vinod and Thakur, 2018). A study by Naser et al., (2012) carried out in Bangladesh, revealed a concentration mean of 84.4 mg/kg which was higher than what was found in the present study. Also, a mean of 35.54 mg/kg was reported in a study carried out in Saudi Arabia (Ali and Al-qahtani, 2012). However, the mean of 77.17 mg/kg was within the guideline of 100 mg/kg (FAO/WHO, 1999). A higher accumulation of Zinc in spinach has a negative effect as excess of Zinc tends to decrease uptake of other elements like copper, Iron and Magnesium in plants (Alia et al., 2015).

4.3 Elemental concentration in topsoil compared to sub soil

All the elements; Cr, Mn, Ni, Cu and Zn depicted a higher concentration in the topsoil (0-20 cm) than in the sub soil (21-50 cm) for both seasons (Table 4.4). The higher concentrations of these elements in top soil could be due to fixation by soil organic matter (Kabata-pendias, 2011). These observation is similar to what has been reported by other researches who indicated elemental concentration in soil tends to decrease with depth (Adugna, 2015; Jobbágy and Jackson, 2014). Also, it has been reported that the observed elemental differences between soils horizons is due to the influence of predominating pedogenic and anthropogenic processes (Abbaslou et al, 2014).
Table 4.4: Basic statistics of the elemental concentration in topsoil compared to sub soil and P-values

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Topsoil Mean</strong></td>
<td>61.62±6.14</td>
<td>4042.58±380.45</td>
<td>30.82±1.21</td>
<td>43.90±12.05</td>
<td>456.43±71.61</td>
</tr>
<tr>
<td><strong>Topsoil Max</strong></td>
<td>77.5</td>
<td>4752.5</td>
<td>33</td>
<td>69</td>
<td>590</td>
</tr>
<tr>
<td><strong>Topsoil Min</strong></td>
<td>54</td>
<td>3320</td>
<td>28.5</td>
<td>22</td>
<td>363</td>
</tr>
<tr>
<td><strong>Sub soil mean</strong></td>
<td>54.67±5.85</td>
<td>3791.38±572.11</td>
<td>30.32±1.37</td>
<td>27.83±12.54</td>
<td>370.32±74.42</td>
</tr>
<tr>
<td><strong>Sub soil Max</strong></td>
<td>74</td>
<td>4627</td>
<td>32.5</td>
<td>68.5</td>
<td>567.5</td>
</tr>
<tr>
<td><strong>Sub soil Min</strong></td>
<td>47</td>
<td>2865</td>
<td>27.5</td>
<td>9.5</td>
<td>271.5</td>
</tr>
<tr>
<td><strong>P-value</strong></td>
<td>&lt;0.001</td>
<td>0.0518</td>
<td>0.14</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
Figure 4.1: Box plots of soil elemental concentration of top and sub soil during dry season
To establish if the difference of topsoil and sub soil were significant or not, student T-Test were done. Results revealed that P- value for Cr, Cu and Zn were 0.0000313, 0.000004 and 0.0000273 respectively indicating that their differences were significant whereas for Mn and Ni their P- value were 0.0518 and 0.14 respectively indicating that their differences were not significant.
4.4 Trace elements concentration during seasons

4.4.1 Soil Trace elements concentration during seasons

For all the elements investigated (Cr, Mn, Ni, Cu and Zn), their soil mean concentration during dry season was higher than wet season (Table 4.6). Statistically, concentration levels of these elements were found to be of no significant difference between the dry season and wet season (Table 4.6). Other researchers have reported that during wet season trace elements tend to be significantly lower compared to dry season (Osobamiro & Adewuyi, 2015; Teutsch et al., 1999). The differences tend to be as a result of precipitation that has an effect on depletion and enrichment trends of trace elements in soils (Teutsch et al., 1999). Plant uptake, precipitation, discharge and erosion could be responsible for the reduction in trace elements levels in wet season as compared to dry season (Osobamiro and Adewuyi, 2015).

Table 4.5: Mean concentration of Elements in topsoil and Spinach during dry season and wet season

<table>
<thead>
<tr>
<th>Element (mg/kg)</th>
<th>Dry season</th>
<th>Wet season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soil</td>
<td>Spinach</td>
</tr>
<tr>
<td>Cr</td>
<td>62.53±6.78</td>
<td>4.86±0.75</td>
</tr>
<tr>
<td>Mn</td>
<td>4049.40±387.74</td>
<td>126.75±34.07</td>
</tr>
<tr>
<td>Ni</td>
<td>30.73±1.12</td>
<td>ND</td>
</tr>
<tr>
<td>Cu</td>
<td>45.90±12.87</td>
<td>6.39±1.16</td>
</tr>
<tr>
<td>Zn</td>
<td>463.17±71.02</td>
<td>69.86±22.40</td>
</tr>
</tbody>
</table>
Of the elements that were investigated, Cr and Cu exhibited a directly proportional relationship between soil and spinach. Their mean concentration in soil were higher during the dry season corresponding to a higher mean concentration in spinach during the dry season (Table 4.5). The probable reason for this could be during dry season, content of Cr and Cu was high in soil compared to the wet season. Therefore, uptake of these elements by spinach was positively correlated to their concentration in soil like what has been reported by other researchers (Gangwar, 2009; Verma et al, 2005). However, as reported by Verma et al, 2005, this positive correlation has an optimum level beyond which uptake of these elements decreases as their concentration in soil increase.

Manganese and Zinc had an inverse relation in their concentration between soil and spinach. Even though Mn and Zn exhibited a higher concentration during dry season than wet season in soil, their concentration in spinach was higher during the wet season than the dry season (Table 4.5). This is probably due to change in soil Ph that affects availability of these trace elements to plants as reported by (Sillanpää, 1982), plant content for Mn and Zn tend to strongly decrease with rising PH. During dry season, sewage water was used for irrigation whose Ph is high. This is explained by the fact that in as much the decomposition of organic matter could lower the PH, presence of industrial wastewater could produce extreme fluctuations that makes PH of sewage water to be high (Iit and Kharagpur, 2000).
During wet season, rainwater was the main source of water to the farm. Naturally, rainwater is acidic, and it tends to be more acidic in urban areas due to reaction of air pollutants, mainly sulfur oxides and nitrogen oxides resulting into formation of acids like sulfuric and nitic. Sources of these air pollutants are vehicles and industrial & power -generating plants whose presence in Nairobi city is high (Dubey, 2013). Therefore, this explains how availability of Mn and Zn to spinach was much higher during wet season (lower PH season) than dry season (high PH season) (Table 4.5). Nonetheless, statistically, for all the elements investigated, the observed difference in elemental concentration in spinach between the seasons had no significant different except that of Manganese (Table 4.6).

**Table 4.6**: Elemental concentration in soil during wet and dry season.

<table>
<thead>
<tr>
<th>Elements Mg/kg</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet season soil Mean</td>
<td>57.07±6.11</td>
<td>3903.02±500.35</td>
<td>30.50±1.41</td>
<td>33.63±13.46</td>
<td>404.42±83.91</td>
</tr>
<tr>
<td>Wet season soil Max</td>
<td>71</td>
<td>4752.5</td>
<td>33</td>
<td>59.5</td>
<td>590</td>
</tr>
<tr>
<td>Wet season soil Min</td>
<td>49</td>
<td>2865</td>
<td>27.5</td>
<td>9.5</td>
<td>271.5</td>
</tr>
<tr>
<td>Dry season soil Mean</td>
<td>59.22±7.56</td>
<td>3930.95±503.92</td>
<td>30.63±1.22</td>
<td>38.10±15.64</td>
<td>422.33±85.42</td>
</tr>
<tr>
<td>Dry season soil max</td>
<td>77.5</td>
<td>4619</td>
<td>32.5</td>
<td>69</td>
<td>576</td>
</tr>
<tr>
<td>Dry season soil min</td>
<td>47</td>
<td>3008.5</td>
<td>28</td>
<td>14.5</td>
<td>289</td>
</tr>
<tr>
<td>P – value</td>
<td>0.167</td>
<td>0.826</td>
<td>0.373</td>
<td>0.161</td>
<td>0.346</td>
</tr>
</tbody>
</table>
4.4.2 Elements concentration in spinach during dry and wet seasons

The trace elements that were investigated in vegetables were: Cr, Mn, Ni, Cu, and Zn. The Mean, Maximum, minimum, Median and Standard deviation of the five trace elements of wet season and dry season vegetables are presented in Table 4.7. Mean concentration of Copper was 5.96 mg/kg during wet season with a range of between 3.5 – 9.0 mg/kg. Dry season had a mean concentration of 6.30 mg/kg with a range of between 5.0 – 8.5 mg/kg. Zinc concentration during wet season had a mean of 84.79 mg/kg with a range of between 55.5 – 119.0 mg/kg. Dry
season depicted a mean of 70.07 mg/kg with a range of between 40.5 – 120.5 mg/kg. Concentration of both seasons were much above the reported background mean of 27 mg/kg.

**Table 4.7: Wet season and dry season vegetable Trace elements concentration**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cr</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinach wet season Mean</td>
<td>4.50±0.41</td>
<td>202.11±102.28</td>
<td>5.96±1.54</td>
<td>84.79±21.78</td>
</tr>
<tr>
<td>Spinach wet season Max</td>
<td>5</td>
<td>436.5</td>
<td>9</td>
<td>119</td>
</tr>
<tr>
<td>Spinach wet season Min</td>
<td>4</td>
<td>88.5</td>
<td>3.5</td>
<td>55.5</td>
</tr>
<tr>
<td>Spinach dry season Mean</td>
<td>4.86±0.75</td>
<td>125.20±34.07</td>
<td>6.30±1.16</td>
<td>70.07±22.40</td>
</tr>
<tr>
<td>Spinach dry season Max</td>
<td>6</td>
<td>208</td>
<td>8.5</td>
<td>120.5</td>
</tr>
<tr>
<td>Spinach dry season Min</td>
<td>4</td>
<td>73.5</td>
<td>5</td>
<td>40.5</td>
</tr>
<tr>
<td>P - value</td>
<td>0.407</td>
<td>0.0104</td>
<td>0.517</td>
<td>0.0844</td>
</tr>
</tbody>
</table>

Wet season had a mean of 202.11 mg/kg for Manganese with a range of between 88.5 – 436.5 mg/kg. Dry season exhibited a mean of 125.20 mg/kg with a range of between 73.50 – 208.00 mg/kg. Chromium had a concentration mean of 4.5 mg/kg during the wet season and a mean of 4.86 mg/kg during the dry season. A range of between 4.00 – 5.00 mg/kg was depicted during wet season and 4.00 – 6.00 mg/kg during dry season.
The observed elemental concentrations in spinach were high during the dry season for Chromium and copper (Table 4.7). The probable reason for this could be during dry season, content of Cr and Cu were high in soil compared to the wet season (Table 4.4). Therefore, uptake of these elements by spinach was positively correlated to their concentration in soil. Other researches have reported a similar observation (Gangwar, 2009; Verma et al., 2005). However, statistically, these differences had no significant difference based on their P-value from a student T-Test analysis that was carried out that was 0.407 and 0.517 respectively. Manganese and Zinc had a higher concentration during the wet season than dry season which is probably due to change in soil PH that affects availability of these trace elements to plants as reported by (Sillanpää, 1982). Plant content for Mn and Zn tend to strongly decrease with rising PH. Statistically, the differences was significant for Manganese (P-value of 0.0104) that indicates it is highly influenced by the PH changes.

4.5 Risk assessment of consuming Spinach vegetables from Ruai

4.5.1 Trace elements transfer factor from soil to Spinach

Consumption of vegetables is the source through which humans get micronutrients, so the soil-to-plant transfer measure is the major source of human exposure. A suitable method for measuring the comparative variances of bioavailability of trace elements to plants is the transfer factor (Iit & Kharagpur, 2000). The transfer factor measures the comparative variances of bioavailability
of trace elements to vegetables and is influenced by both properties of vegetable and soil. Low transfer coefficient signifies a poor efficiency of vegetable to absorb the trace element. High coefficient indicates a meager retention in soil of the trace element (RC & A, 2015).

The calculated TF of the selected trace elements from soil to vegetable are presented in table 4.8. Low transfer coefficient signifies a poor efficiency of vegetable to absorb the trace element. High coefficient indicates a meager retention in soil of the trace element (RC & A, 2015). The TF or PCF values during dry season were; Cr 0.078, Mn 0.031, Cu 0.139, and Zn 0.151. Transfer factor values for wet season were; Cr 0.074, Mn 0.044, Cu 0.134, and Zn 0.198. Trend of TF for trace elements in vegetable samples studied for both seasons were in the order: Zn>Cu>Cr>Mn.

**Table 4.8**: Transfer factor of elements from soil to Spinach during dry and wet season

<table>
<thead>
<tr>
<th>Element</th>
<th>Dry season</th>
<th>Wet Season</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.078</td>
<td>0.074</td>
</tr>
<tr>
<td>Mn</td>
<td>0.031</td>
<td>0.044</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>0.139</td>
<td>0.134</td>
</tr>
<tr>
<td>Zn</td>
<td>0.151</td>
<td>0.198</td>
</tr>
</tbody>
</table>

The highest TF value found was 0.198 and 0.139 for Zn and Cu respectively. These may be attributed to higher mobility of these trace elements and their poor holding of them in the soil than other trace elements (Alam, et al, 2003; Naser, et
According to the calculated transfer factors for the selected trace elements, it can be resolved that Zn and Cu were high accumulators amid the studied trace elements. All TF values were below 1. This implies that it is very difficult for these trace elements to transfer from the soils to the plant, that is trace element bioavailability to spinach vegetable in the soil is very low. The less the transfer factor value, the less the chances of experiencing trace element contamination by anthropogenic activities (Farooq et al., 2009).

### 4.5.2 Hazard Quotient (HQ)

Danger of ingestion of vegetables polluted with trace elements was estimated by Hazard Quotient (HQ). This is a ratio of determined dose to the reference dose ($R_f$ D). Consumers of the vegetables would be in danger if the calculated HQ is equal or more than one and if the calculated ratio is less than one then consumers will be at no danger. This risk calculation technique has been used by various scholars (Chauhan & Chauhan, 2014; Farooq et al., 2009, 2009; Guerra et al., 2012) and has demonstrated to be effective and accurate.

Table 4.9 has the calculated Hazard quotient for the various trace elements during dry and wet seasons. The HQ ratio for the studied vegetable samples are less than 1 for all the elements, hence the population that consumes spinach from Ruai area has no health risk.
Table 4.9: Hazard quotient for trace elements in Vegetable for Dry and Wet seasons

<table>
<thead>
<tr>
<th>Element</th>
<th>Wet season</th>
<th>Dry Season</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.0012</td>
<td>0.0013</td>
</tr>
<tr>
<td>Mn</td>
<td>0.4929</td>
<td>0.3552</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0552</td>
<td>0.0627</td>
</tr>
<tr>
<td>Zn</td>
<td>0.1167</td>
<td>0.0914</td>
</tr>
</tbody>
</table>

4.5.3 Estimation of Daily trace elements intake through consumption of spinach

Estimated daily dietary intake (EDDI) were calculated in this study to ascertain whether the intake of these vegetables is safe for the consumers in Ruai region (Table 4.11). To ascertain vegetable safety, the estimated EDDI were compared to the PMTDI value provided by WHO. An element will be detrimental if its EDDI exceeded its PMTDI.
Table 4.10: Estimated daily dietary intake of trace elements during wet and dry season and their PMTDI value

<table>
<thead>
<tr>
<th>Element</th>
<th>Wet season (µg/kgbw/day)</th>
<th>Dry Season (µg/kgbw/day)</th>
<th>PMTDI (µg/kgbw/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.7654</td>
<td>1.9066</td>
<td>150*</td>
</tr>
<tr>
<td>Mn</td>
<td>69.0069</td>
<td>49.7250</td>
<td>150*</td>
</tr>
<tr>
<td>Cu</td>
<td>2.2087</td>
<td>2.5068</td>
<td>500</td>
</tr>
<tr>
<td>Zn</td>
<td>35.0135</td>
<td>27.4066</td>
<td>1000</td>
</tr>
</tbody>
</table>

*EVM Values were used in the absence of PMTDI

Zinc is an essential trace element which is involved in various aspects of cellular metabolism and is required for catalytic activity of approximately 100 enzymes (Sandstead et al., 1997) the mean daily intake of zinc by spinach consumers sourced from Ruai is estimated to be 35.0135 µg/kgbw/day during wet season and 27.4066 µg/kgbw/day during dry season. These values may not pose adverse health effects according to PMTDI of 1000 µg/kgbw/day (Electronic & House, 2000; WHO, 1996a). No adverse, health effects are thus expected from Zn as a result of consuming spinach unless other surplus and richer sources of this trace element in the diet contribute considerably to its intake.

Copper is an essential trace element, vital to the healthy life of many animals and plants. The estimated average daily intake of Cu from spinach sourced from Ruai is 2.2087 µg/kgbw/day and 2.5068 µg/kgbw/day during wet season and dry
season respectively. This value is far much below the current PMTDI of Cu of 500 µg/kgbw/day \cite{Electronic, WHO}. Therefore, no adverse health effects are expected from Cu intake from spinach. Chromium is another essential trace element found in spinach. The availability of this trace element in human is important for many biological activities \cite{Manahan}. It regulates blood sugar, therefore reducing medication and insulin needs in diabetic patients \cite{KCS} and also plays a role in the management of heart diseases by regulating fat and cholesterol synthesis in the liver \cite{WHO}. The estimated average daily intake of Cr by spinach consumers is 1.7654 µg/kgbw/day during wet season and 1.9066 µg/kgbw/day during dry season. The WHO has not recommended PMTDI for this element but, EVM has set a limit of 150 µg/kgbw/day. Therefore, no adverse health effects are expected from Cr due to spinach intake.

Manganese is a constituent of many of enzymes and activates a variety of others \cite{EVM}. Therefore, risk assessment associated to intake of this trace element is imperative. The estimated average daily intake of Mn due to spinach consumption is 69.0069 µg/kgbw/day during wet season and 49.7250 µg/kgbw/day during dry season. Even though WHO has not set its PMTDI, EVM has set a limit of 150 µg/kgbw/day. There are no antagonistic health issues expected from Mn as a result of consuming spinach unless other surplus and richer sources of this trace element in the diet contribute considerably to its intake.
CHAPTER FIVE: SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary of Results

The results of elemental concentration in top soil (0-20 cm) and sub soil (21-50 cm) showed that Cr had 61.62 mg/kg in top soil and 54.67 mg/kg in sub soil, Mn had 4042.58 mg/kg in top soil and 3791.38 mg/kg in sub soil, Ni had 30.82 mg/kg in top soil and 30.32 mg/kg in sub soil, Cu had 43.90 mg/kg in top soil and 27.83 mg/kg in sub soil and Zn had 456.43 mg/kg in top soil and 370.32 mg/kg in sub soil. The elemental concentration of spinach was 4.73 mg/kg for Chromium, 163.96 mg/kg for Manganese, 6.12 mg/kg for Copper and 77.98 mg/kg for Zinc.

All elements depicted a higher concentration in topsoil than sub soil probably due to fixation by soil organic matter and influence of pedogenic processes and anthropogenic activities. From T-Test analysis, it was noted that statistically the differences were significant for Cr, Cu and Zn whereas Mn and Ni their differences were not significant statistically.

For all the elements investigated, their soil mean concentration was higher during dry season than wet season. Cr had 57.07 mg/kg during wet season and 59.22 mg/kg during dry season, Mn had 3903.02 mg/kg during wet season and 3930.95 mg/kg during dry season, Ni had 30.50 mg/kg during wet season and 30.63 mg/kg during dry season, Cu had 33.63 Mg/kg during wet season and 38.10 mg/kg during dry season and Zn had 404.42 mg/kg during wet season and 422.33 Mg/kg during dry season.
The observed elemental concentrations in spinach were high during the dry season for Chromium and copper. The probable reason for this could be uptake of these elements had a positive correlation to their concentration in soil. However, statistically, these differences had no significant difference. Manganese and Zinc had a higher concentration during the wet season than dry season which is probably due to change in soil Ph that affects availability of these trace elements to plants in that content for Mn and Zn tend to strongly decrease with rising Ph. Statistically, the difference was significant for Manganese (P-value of 0.0104) that indicates it is highly influenced by the Ph changes.

The risk assessment carried out considered that of Hazard quotient (HQ) and estimation of daily dietary intake of trace element (EDDI). The HQ ratio was less than 1 for all the elements. Cr had a ratio of 0.0012 during wet season and 0.0013 during dry season, Mn was 0.4929 during wet season and 0.3552 during dry season. Cu was 0.0.0552 during wet season and 0.0627 during dry season. Zn was 0.1167 during wet season and 0.0914 during dry season. Therefore, the population that consumes spinach from Ruai area has no health risk. For all the elements, the calculate EDDI did not exceed the PMTDI for the elements under study. Cr had a figure of 1.7654 µg/kgbw/day during wet season and a figure of 1.9066 µg/kgbw/day during dry season against a PMTDI figure of 150 µg/kgbw/day. Mn had a figure of 69.0069 µg/kgbw/day during wet season and a figure of 49.7250 µg/kgbw/day during dry season against a PMTDI figure of 150 µg/kgbw/day. Cu had a figure of 2.2087 µg/kgbw/day during wet season and a figure of 2.5068
µg/kgbw/day during dry season against a PMTDI figure of 500 µg/kgbw/day. Zn had a figure of 35.0135 µg/kgbw/day during wet season and a figure of 27.4066 µg/kgbw/day during dry season against a PMTDI figure of 1000 µg/kgbw/day. Therefore, the results of this study indicate that intakes of the selected trace element due to consumption of spinach, has no health risk since the values are lower than the respective permissible intakes.

5.2 Conclusion

In this study the levels of five trace elements in spinach and soil from Ruai sewage area were analyzed. The result showed that:

Topsoil had higher concentration of elements investigated than the sub soil. This probably is due to anthropogenic activities that have influenced their higher concentration in topsoil.

Trace elements investigated were higher during dry season than wet season with an exception of Ni whose results for both seasons were in the same range.

The hazard quotient (HQ) for all the elements (Cr, Mn, Cu and Zn) were below 1, suggesting that the population is at no health risk in consuming spinach from Ruai.

For all the elements, their estimation of Daily intake through consumption of spinach was within the WHO permissible maximum tolerable daily intake (PMTDI).
5.3 Recommendations from the study

This study covered only five elements. More trace elements other than those considered in this study should be analyzed to provide a comprehensive data on elements profile of soil from an urban area and that of spinach vegetable grown in urban areas.

Anthropogenic activities that tend to increase trace elements in soil should be limited to avoid a continuous increase of these elements in the soil. This is since all the elements investigated were above the reported mean on a worldwide basis except for chromium. This indicates that the site is highly contaminated, a fact that was proved by a decrease of elemental concentration between topsoil and subsoil.

To establish the effect of seasonal variability in trace element intake of the spinach vegetable, a controlled experiment needs to be done that will take account of the effect of other physiochemical factors that influence nutrients uptake by plants.

Although the intakes of the selected trace elements due to consumption of spinach pose no health risk, there is need for continuous monitoring of the levels of trace elements in spinach grown in urban areas to ensure that they do not exceed acceptable levels.
5.4 Recommendations for further work

The available guidelines seem to be insufficient in assessment of soil contamination for farming as they lack site specific factors like bioavailability of the element, plant type and soil properties that have a great influence on phytotoxicity. These findings recommend a further controlled experiment that could take account of specific factors like bioavailability of trace elements, uptake of various species, presence of other trace elements and soil properties. Such a controlled study would aid in the understanding of bioavailability of trace elements from contaminated soil.

Similar studies should be done to other vegetables grown in the area as different plants observe trace elements differently.
REFERENCES


Lukaski, H. C. (2000). Magnesium, zinc, and chromium nutriture and physical activity1,2,3 (Henry C Lukaski ), 72.


APPENDICES

Appendix 1: Quality assurance of results

The validity of the portable X-ray fluorescence (PXRF) results was assessed by using certified reference sample standards which were of known levels and calculating percentage recoveries.

Table 1: Comparison of certified values with the observed values for different elements analyzed by PXRF

<table>
<thead>
<tr>
<th>Element</th>
<th>SAR-M Certified value</th>
<th>SAR-M Observed value</th>
<th>Recovery %</th>
<th>SAR-M Certified value</th>
<th>SAR-M Observed value</th>
<th>Recovery %</th>
<th>NIST 1575a Certified value</th>
<th>NIST 1575a Observed value</th>
<th>NIST 1575a Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>79.7</td>
<td>62.3</td>
<td>78.17</td>
<td>0.4 ± 0.1</td>
<td>ND</td>
<td>ND</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>5220</td>
<td>5071.25</td>
<td>97.15</td>
<td>488 ± 12</td>
<td>525</td>
<td>107.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>331</td>
<td>314.7</td>
<td>95.07</td>
<td>2.8 ± 0.2</td>
<td>3</td>
<td>107.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>930</td>
<td>932.5</td>
<td>100.27</td>
<td>38 ± 2</td>
<td>40.5</td>
<td>106.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>41.5</td>
<td>38</td>
<td>91.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The elemental concentrations determined by PXRF in NIST SRM 1575a (Pine needles) and USGS SRMs-SAR-M along with the certified values are listed in Table 1. An assessment of results of analyzed values with the certified values shows good agreement. Therefore, results of analysis using the PXRF are expected to be correct and accurate.
General performance of the instrument was checked by taking ten measurement of Duplex 2205 sample supplied by Bruker. The instrument is deemed fit if the calculated average measured value is within the acceptance limits provided. Table 2 has the average measured value that were within the accepted limit. Therefore, the quality of the results generated by the instrument were of high accuracy.

Table 2: Average measured value of Duplex 2205 compared to the accepted limit

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acceptance Limit MIN</strong></td>
<td>21.934</td>
<td>1.062</td>
<td>5.413</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Acceptance Limit MAX</strong></td>
<td>22.665</td>
<td>1.626</td>
<td>5.938</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Average Measured Value</strong></td>
<td>22.407</td>
<td>1.329</td>
<td>5.706</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Appendix 2: Box plots indicating soil trace elements concentration variation by depth
Mn variation by depth

Ni variation by depth
Appendix 3: Box plots indicating soil trace elements concentration variation by season

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**Cr variation by season**

---

**Mn variation by season**
Zn variation by season
Appendix 4: Box plots indicating spinach trace elements concentration variation by season

Cr Veg. variation by season

Mn Veg. variation by season
Appendix 5: Sampling location
KENYATTA UNIVERSITY
GRADUATE SCHOOL

E-mail: dean-graduate@ku.ac.ke
Website: www.ku.ac.ke

Internal Memo

FROM: Dean, Graduate School
TO: Mr. Hezekiah Okiom Nyandika
C/o Department of Environmental Science

DATE: 22nd September, 2017
REF: N50/CTY/PT/32733/15

SUBJECT: APPROVAL OF RESEARCH PROPOSAL

This is to inform you that Graduate School Board, at its meeting on 6th September, 2017, approved your Research Proposal for the M.Env. Science Degree entitled, “Assessment of Selected Trace Elements Contamination in Urban Areas of Ruai, Nairobi City County, Kenya.”

You may now proceed with your Data collection, subject to clearance with the Director General, National Commission for Science, Technology & Innovation.

As you embark on your data collection, please note that you will be required to submit to Graduate School completed Supervision Tracking Forms per semester. The form has been developed to replace the Progress Report Forms. The Supervision Tracking Forms are available at the University’s Website under Graduate School webpage downloads.

Thank you.

ELIJAH MUTUA
FOR: DEAN, GRADUATE SCHOOL

CC: Chairman, Environmental Science Department

Supervisors:

1. Dr. Esther Kitur
   C/o Department of Environmental Science
   Kenyatta University

2. Dr. Julius Nzeve
   C/o Department of Environmental Science
   Kenyatta University