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Titanium, Zinc, Lead, Chromium, Cadmium, Cobalt and Copper Concentrations in Vegetables Produced using Wastewater in Urban and Peri-Urban Areas of Nairobi City County, Kenya

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Authors' contributions

This work was carried out in collaboration between both authors. Author DKR designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author JWW managed the analyses of the study as well as the literature searches. Both authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Vegetables are rich sources of vitamins, minerals and fibres. Ingestion of vegetables contaminated with heavy metals is one of the main routes through which heavy metals enter the human body and may cause diseases. In this study we investigated the concentrations of titanium, zinc, lead, chromium, cadmium, cobalt and copper in the commonly produced vegetables viz. *Brassica* sp.,*Spinacia oleracea, Amaranthus* sp. and *Solanum* sp. using wastewater in Ruai ward, Nairobi City County, Kenya. Atomic absorption spectrometry (AAS) was used to estimate the levels of these metals in vegetables sampled from five plots in the study area. The concentration status for each heavy metal in the samples was compared with the permissible levels for corresponding heavy metals set by the Food and Agriculture Organization and World Health Organization. Our findings

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indicated the presence of Ti, Zn, Cr and Cu in all the vegetable samples and their concentrations varied considerably, while Pb, Cd and Co were not detected in most samples. The presence of heavy metals in vegetables was in the order of Pb > Cd > Co > Cu > Cr > Zn > Ti. We concluded that vegetables produced using wastewater had elevated levels of the investigated heavy metals at the time of analysis beyond FAO/ WHO safe limits for corresponding metals in leafy vegetables.

Keywords: Heavy metals; contaminants; bio-accumulate; risks.

1. INTRODUCTION

Upsurge in urban agriculture popularity has been due to concerns about climate change and sustaining food security in urban areas. However, the major challenges in urban agriculture are determining how to monitor, control and reduce risks in the physical, economic and social environment; and understanding how it can be a sustainable component of the global urban food systems [1].

The volume of wastewater generated by domestic, industrial and commercial sources has increased with population, urbanization. improved living conditions and economic development. The productive use of wastewater has also increased, as millions of small- scale farmers in urban and peri- urban areas of developing countries depend on wastewater or wastewater-polluted water sources to irrigate high- value edible crops for urban markets, often as they have no alternative sources of irrigation water. Undesirable constituents in wastewater can harm human health and the environment. Hence, wastewater irrigation is an issue of concern to public agencies responsible for maintaining public health and environmental quality [2].

The use of urban wastewater in farming has been practiced for close to a century and its recognition is brought about by dwindling freshwater resources particularly in most arid and semi-arid areas. In several developing nations for instance, potential areas for production of various agricultural products like vegetables that are in high demand by urban dwellers, include non-built up urban lands situated along the courses of urban drainage systems. Generally, the critical exposure route for urban population is the consumption of uncooked urban wastewater irrigated vegetable produce. In many developing areas, non-built up urban lands, especially those lying along the courses of urban drainage systems, are sometimes seen as locations for production of some agricultural products such as vegetables that are in high demand by urban dwellers [3].

Wastewater composition [4], varies widely and may contain organic particles; pathogens like viruses, bacteria and parasitic worms; organic particles such as faeces, hair, food, plant material; inorganic materials like salts, sand, grit, heavy metals, metal particles and ceramics; and pesticides and other toxins.

Wastewater can be considered as both a resource and a problem. Wastewater and its nutrient content can be used extensively for irrigation and other ecosystem services such as watering lawns and recreational parks. Its re-use can deliver positive benefits to the farming community, society, and municipalities. However, reusing wastewater also impacts negatively humans and ecological systems, which need to be identified and assessed [5].

Wastewater in several developed and middleincome nations such as France, the United States of America, Spain, Tunisia, Jordan and Israel is applied to agricultural fields after it is fully treated. The practice is recognized, wellregulated and controlled by agencies that are well-established. In most developing countries large volumes of urban wastewater generated remain untreated due to inadequate resources for effective wastewater treatment facilities [6].

Vegetables are rich sources of vitamins, minerals and fibres. Ingestion of vegetables containing heavy metals forms one of the main routes through which these elements enter human body with deleterious effects. Heavy metal contamination of food is one of the key aspects of food quality assurance. They rank high among the chief food contaminants of leafy vegetables. Intake of heavy metal contaminated vegetables may pose a risk to human health. Thus, prolonged human consumption of unsafe concentrations of heavy metals in foodstuffs may lead to the disruption of many biological and biochemical processes in the human body. Dietary intake of heavy metals through contaminated vegetables may cause various chronic diseases. Regular monitoring of these metals in vegetables is essential for averting excessive buildup of the metals in the food chain [7].

A survey conducted between 2006 and 2007 by Kaluli, et al. [8], showed nearly half of the wastewater generated in Nairobi ended being treated in the treatment facilities, while raw sewage was used for irrigating more than 720 hectares of cropland. The crops grown included vegetables such as *Brassica* sp., *Spinacia* sp. and the African vegetables like *Amaranthus* sp. Approximately 75% of the vegetables produced was sold for income, while the rest was consumed at the household level.

1.1 Problem Statement

Since the untreated wastewater is discharged into the environment most of the freshwater resources in Nairobi City are heavily polluted. The raw municipal and industrial effluent is conveyed into rivers through natural drainage channels, thus contributing towards pollution of freshwater sources. Urban and peri-urban farmers in the City use the untreated wastewater for irrigation of vegetables [9]. Negative aspects related to wastewater reuse according to Kanyoka & Eshtawi [10], include soil salinity, health of farmers and consumers, public acceptability, marketability of produce, and economic feasibility and sustainability of wastewater irrigation.

The wastewater generated in Nairobi [8], is within the National Environment Management Authority (NEMA) quality guidelines except biological oxygen demand (BOD) and coliform bacteria in raw sewage. Biological oxygen demand is an important water quality parameter used for assessing the effect discharged wastewater will have on the receiving environment. The higher the BOD value, the greater the amount of organic matter available for oxygen consuming bacteria. Nairobi City's untreated wastewater [9], is discharged through natural drainage waterways, hence most freshwater resources are polluted to varying degrees. Urban and peri-urban farmers in the City irrigate their vegetables with the untreated wastewater.

Sewage water farming is associated with too much buildup of heavy metals in the soil that result in increased heavy metal uptake by crops, which affects food safety. Kale (*Brassica* sp.) popularly known as 'sukuma wiki' is one of the most preferred green leafy vegetables that is consumed by most households in Nairobi. Unfortunately, a reasonably large proportion of this vegetable retailed in urban areas pose several food safety risks to consumers. Some of the potential risks are contamination by microbial pathogens, heavy metals, pesticides and residues of chemical fertilizer. Some retailers do sprinkle the vegetables with unclean and often polluted water to maintain freshness and make it look attractive to the customers' eyes [11].

Apart from potential benefits as a valuable resource [5], wastewater can also have harmful effects in agriculture, with potential cost accompanying its use. For instance, its use in agriculture is likely to increase exposure of farmers, farm workers, consumers and people neighbouring wastewater irrigated farmlands to infectious diseases. It is also potential of causing groundwater contamination; impacting the soil negatively through accumulation of salts and heavy metals if used for considerably long time; having negative impacts on value of neighbouring properties; as well as having other negative impacts on socio-ecological systems.

Some farmers in the study area produce vegetables using wastewater of unknown quality standard thus putting themselves and consumers of vegetables produced in this pathway to health risks. The study objective therefore was to establish the levels of selected heavy metals in vegetables produced using wastewater in Ruai ward. Nairobi City County. Kenya and their status compared with the FAO/ WHO safe limits for corresponding heavy metals in leafy vegetables. The research question was: what is the concentration levels of Ti, Zn, Pb, Cr, Cd, Co and Cu in wastewater used for vegetable production in Ruai ward, Njiru Sub County, Nairobi city county, Kenya? The intention of the paper is to raise awareness on health implication of wastewater use in vegetable production in urban and peri-urban setting. The study is expected to create an impact on policy makers and agencies responsible for health and environment sectors.

2. LITERATURE REVIEW

Heavy metals [12], naturally occur in the environment and their exposure to human beings is through various anthropogenic activities. They reach the soils and water bodies through erosion, run-off and acid rain. Metals such as lead (Pb), cadmium (Cd) and manganese (Mn) enter human body via gastrointestinal route when eating food, fruits, vegetables or drinking water or other beverages. It can also be through inhalation, while others such as Pb can be absorbed through the skin. Sources of some heavy metals are given in Table 1. Natural and anthropogenic sources are responsible for increasing levels of heavy metals in the environment. Examples of natural sources are parent geologic rock material, volcanic outcropping, spontaneous contributions or forest fires. Anthropogenic sources include sewage sludge, pesticides, organic matter, compost, fertilizer supplements, industrial waste, smelting and metallurgical industries, and use of treated or untreated industrial and municipal effluents for irrigation purposes. All these sources contribute heavy metals to the soil from where they are translocated into different plant parts via root uptake. Accumulation of heavy metals and their uptake by different plant parts depend on the concentrations of available heavy metals in the soil and form of metals [13].

Soil acts as a medium for plant growth which can recycle nutrient and resources that plants need. It will absorb heavy metals in the polluted river as well as ground water causing side effect for vegetable growth. As roots grow in the soil, they will absorb water and nutrients in solution. Heavy metals that are attached with soil water and soil particles will be absorbed by plant roots and accumulated in vegetables. Using water which is contaminated by heavy metals for irrigation is another pathway through which heavy metals get into vegetables [14]. Heavy metal depositions of agricultural soils [15], could be contributed by several sources such as small scale industries and vehicular emissions.

Vegetables may also get exposed during transportation and marketing to contamination by polluted air, which is potential of increasing levels of heavy metals in the vegetable produce. Heavy metals also enter into vegetables through manure, sewage sludge, fertilizers and pesticides [16]. Although vegetables form an important part of human diet, they contain both essential and toxic elements at varying concentrations on the surface and in the tissue of fresh vegetable [17]. Heavy metals that are essential plant nutrients include copper (Cu), zinc (Zn), Mn and iron (Fe), while some like Cd and Pb do not play any major role in plant physiology and are often found as contaminants in vegetables [18]. Transfer of heavy metals from water to soil and finally uptake from soil and accumulation in edible parts of vegetative tissue [19], represents a direct pathway through which they get incorporated into the human food chain.

Vegetable plants growing on a medium contaminated with heavy metal have the potential to accumulate trace elements in high concentration to cause health risk to consumers [20]. Heavy metals such as Cr, Zn and Cu [21], though essential for biological activities in the body, their presence in high concentrations can be a health risk.

Leafy vegetables [22], are capable of accumulating heavy metals than other vegetables. Assessment of leafy vegetables viz. Amaranthus sp. and Solanum villosum grown in Thika town, Kenya showed the two vegetable species accumulated Pb in their stems and edible leaves but the stems accumulated the highest concentration [23]. The concentration of heavy metals on the surface and within plants are influenced by several factors including climatic conditions, atmospheric deposition, application of fertilizers, type of soil on which the plant is grown, and irrigation with wastewater [21]. The study only investigated selected heavy metals in common leafy vegetables and therefore did not compare metal accumulation in leafy and non-leafy vegetables.

Table 1. Main	toxic metals	in industrial	effluents
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Heavy Metal Cadmium	Source Emitted through industrial processes(e.g. paints, batteries and plastics) into sewage sludge, fertilizers and groundwater and taken up by plants. Human exposure can be by ingesting contaminated leafy vegetables.
Chromium	Present in petroleum, chromium steel, fertilizers, and metal plating. Used in wood preservation.
Copper	Used in production of copper pipes, cables, wires, copper cookware etc. It can accumulate in the soil and up taken by plants.
Lead	Released into the atmosphere from industrial processes and vehicle exhausts and may eventually get into the soil and flow into waterbodies, which can then be taken up by plants, hence human exposure through food or drinking water.
Zinc	Plating, galvanizing, iron and steel

Source: Engwa et al., [12]

All living organisms accumulate in their system substantial amount of Zn without any damaging effect as it is essential for carbohydrate metabolism, protein synthesis and inter nodal elongation. Zinc deficiency causes loss of appetite, growth retardation and immunological abnormalities. However, Zn can be toxic when exposures exceed physiological requirements [21].

Lead is a toxic element that can be harmful to plants, although plants usually show ability to accumulate large amounts of Pb without visible change in their visible appearance or yield [18]. Leafy vegetables are likely to absorb more Pb than fruiting crops such as tomatoes. Excessive accumulation in plant tissue impairs various morphological, physiological and biochemical functions in plants often with deleterious effects. Elevated levels of Pb in the blood is potential of causing kidney dysfunction and brain damage [7]. There is a relationship between Pb in the human body and the increase of blood pressure of adults as pointed out in Ametepey et al. [24]. Lead also causes mental retardation in young children [25].

Cadmium is non-essential and has no nutritional value to plants, animals and human beings because it is toxic, while Cu is an essential micronutrient which functions as a biocatalyst required for body pigmentation [26]. Copper [15] works with many enzymes like those involved in protein metabolism and hormone synthesis. Excessive intake can cause vomiting and nervous system disorder, while its deficiency causes low white blood cell count and poor growth.

Cobalt [27], is essential to human because it forms part of vitamin B_{12} but exposure to elevated levels results in lung and heart diseases, and dermatitis. Symptoms of Co deficiency according to Gezahegn et al. [15], include loss of appetite, emaciation, weakness and anemia. Chromium [24], is crucial for insulin activity and deoxyribonucleic acid transcription in living organism particularly human beings. However, an intake less than 0.02 mg per day could lower cellular responses to insulin.

Human beings get exposed to heavy metals like arsenic (As), Cd, Pb and mercury (Hg), which are linked to several health effects through prolonged consumption of contaminated foodstuff or inhalation of irrigated soil. For instance, exposure to Cd may cause renal damage and osteoporosis in children [28]. Apart from toxicity, deficiencies of heavy metals may also occur and hence, knowledge about their concentration in vegetables for dietary supply is vital [25].

According to Engwa et al. [12], heavy metals naturally occur in the environment and their exposure to human beings is through various anthropogenic activities. Heavy metals reach the soils and water bodies via erosion, run-off and acid rain. Metals such as Pb, Cd and Mn enter human body through gastrointestinal route when eating food, fruits, vegetables or drinking water or other beverages. It can also be through inhalation, while others such as Pb can be absorbed through the skin.

The uptake of heavy metals by leafy vegetables [29], is an avenue of their entry into the human food chain with deleterious effects on health. Examples of heavy metals that are essential plant nutrients [18], are Cu, Zn, Mn and Fe, while those which do not play any major role in plant physiology and are often found as contaminants in vegetables include Cd and Pb.

Soil as a supporting layer for all organisms acts as a medium for plant growth which can recycle nutrient and resources that plants need. Soil will absorb heavy metals in the polluted river as well as ground water and these will cause side effect for vegetable growth. As roots grow in the soil, they will absorb water and nutrients in solution. Heavy metals that are attached with soil water and soil particles will be absorbed by plant roots and accumulated in vegetables. Another pathway for heavy metals to get into vegetables is via irrigation water which is contaminated by heavy metals [14]. Plants growing in metal-polluted environments often do not show visible signs of intoxication even if they contained elevated concentrations of toxic metals [30].

2.1 Model/ Theory Relevant to the Current Study

In countries devoid of adequate resources and technology to effectively operate wastewater treatment facilities, the WHO guidelines [31], for safe wastewater irrigation recommends a 'multiple-barrier' approach (Fig. 1) for health risk reduction. The guidelines' salient features are good agricultural, manufacturing and hygienic practices as a cost effective approaches of enhancing food safety at all stages of food chain where wastewater is used for irrigation [6].



Good practices for risk reduction

Fig. 1. Multi-barrier approach in wastewater food chain Source: Modified from Drechsel et al. [6]

Vegetables often act as a media for carrying poisonous materials like heavy metals and other toxicants from either irrigation water or from land where they are grown. Contamination can be factors like caused by irrigation water contaminated by effluents waste, or contaminated soil. inorganic fertilizers or pesticides. Vegetables tend to absorb and accumulate higher concentration of heavy metals when grown on metal contaminated soils than those grown on uncontaminated soil. The heavy metals are absorbed alongside other plant nutrients. Contamination of soils and crops with the heavy metals may have adverse effects on soil, plants, animals and human beings [32]. Long-term use of vegetables contaminated with heavy metals can cause toxic metals accumulation in the body organs such as the liver and kidneys [33].

The 'multi-barrier' approach for health-risk reduction in the wastewater food chain is relevant to the current study because it presents the exposure routes in the food chain through which consumers of foodstuff including vegetables produced using partially treated or untreated wastewater are exposed to health risks posed by potentially toxic elements. The approach's good practices for risk reduction, which is aimed at enhancing food safety is a clear demonstration of allocating responsibility of risk reduction to various players starting with the farmer followed by the handlers and finally the consumers.

The authors are of the view that such an approach calls for commitment among relevant players. It also requires an obligation among agencies responsible for law enforcement.

3. METHODOLOGY

3.1 Description of Study Area

The study was conducted in Ruai ward, Njiru sub- County, Nairobi City County, Kenya (Fig. 2). The exact location of the study area lies between coordinates X: 36.936, Y: -1.233 (upper left) and X: 36.998, Y: -1.264 (lower right) and it was selected because farmers produce vegetables using wastewater.





Fig. 2. Map of Kenya showing the study area Source: GeoEye-1 [34]

3.2 Sampling of Vegetables and Preparation of Samples

True experimentation was not used in the study because the vegetable samples were not subjected to any control of conditions that would potentially affect the parameters of interest. Thus, four most common types of vegetables viz. Brassica sp., Spinacia oleracea, Amaranthus sp. and Solanum sp. produced using wastewater in the study area were randomly picked at their five from vegetative stage different georeferenced plots. The samples were then pretreated and transported to the laboratory for analysis of selected heavy metals. Selection of plots where samples were collected was informed by sources of wastewater used for irrigation. Thus, plot 1- treated effluent irrigated,

plot 2-discharge point irrigated, plot 3- upstream Nairobi River irrigated, plot 4- raw influent irrigated, and plot 5- downstream Nairobi River irrigated.

One sample each was randomly picked from each of the four vegetable types (in total 20 samples were collected from the same plot) the same day with the permission of plot owners. In picking the samples representativeness of the samples was taken into account by picking them randomly from across the plot. Samples from the same plot were then separately wrapped together in an old newspaper and packed in five separate biodegradable bags marked sample 1 to 5 to avoid mix-up during handling and subsequent preparation before delivering to the laboratory for further treatment and analysis. They were later unwrapped, clearly marked and spread on a clean surface for moisture loss overnight.

The following day the samples were placed separately in between old newspaper and pressed using a plant press. They were regularly turned to ensure all the samples more or less received the same treatment. It was also meant to ensure the samples dried separately to eliminate excess moisture. Dried samples were removed from the plant press, packed in clearly marked paper bags and delivered to the laboratory where they were further treated and analysed using standard methods described in Eaton [35], for titanium (Ti), Zn, Pb, Cr, Cd, Co and Cu concentrations.

Samples of individual vegetable type viz. Brassica sp., Spinacia oleracea, Solanum sp. and Amaranthus sp. were separately sliced in the laboratory into small pieces and oven dried at 100°C for two hours. After cooling, each sample was pounded into a homogenous mass using a porcelain and a mortar. Approximately 2.5 g of each sample was then separated out and transferred into a 100 ml. Pyrex beaker followed by adding 10 ml. of concentrated nitric acid and left to stand for at least 40 minutes. Finally, the beaker was heated at 95°C on a hot plate to evaporate the contents to 10 ml. Using Whatman No. 42 filter paper, the resultant concentrate was filtered and the filtrate maintained to 50 ml. with distilled water. Subsequently the samples were analyzed for Ti, Zn, Pb, Cr, Cd, Co and Cu with Atomic absorption spectrometry (AAS) model Varian Spectr AA- 10 using air-acetylene flame. The instrument was fitted with specific lamp of particular metal and calibrated using manually prepared standard solution of respective heavy metal as well as drift blanks. The samples were read one at a time, while recording the amount of the elements present in the sample displayed in part per million (ppm). What was read from the AAS was then converted into grams per kilogram (g/Kg) to represent the amount of specific heavy metal in grams present in a kilogram of the sample.

4. RESULTS AND DISCUSSION

4.1 Concentrations of Selected Heavy Metals in Treated Effluent-Irrigated Vegetables

Concentrations in g/kg of Ti, Zn, Pb, Cr, Cd, Co and Cu in the treated effluent-irrigated vegetables are given in Fig.3 for *Brassica* sp., *Solanum* sp., *Amaranthus* sp. and *Spinacia oleracea* samples. Titanium concentration was highest (143 g/kg) in *Amaranthus* sp. and lowest (58 g/kg) in *Brassica* sp., while it was 126 and 115 g/kg in *Spinacia oleracea* and *Solanum* sp., respectively. Zinc concentration was highest (167 g/kg) in *Amaranthus* sp. and lowest (16.00 g/kg) in *Brassica* sp. sample.

The rest of the samples recorded Zn concentration of 34 g/kg for *Solanum* sp. and 68 g/kg for *Spinacia oleracea*. Lead was detected only in *Brassica* sp. and *Amaranthus* sp., each recorded 0.05 g/kg. Chromium concentration was highest (19 g/kg) in *Amaranthus* sp. followed by 11 g/kg in both *Brassica* sp. and *Solanum* sp., while *Spinacia oleracea* recorded lowest Cr concentration (0.27 g/kg) was detected in *Spinacia oleracea*, followed by 0.13 g/kg in *Brassica* sp., 0.07 g/kg in of *Solanum* sp. and 0.05 g/kg as the lowest Cd concentration was detected in *Amaranthus* sp.

Cobalt, which was detected only in two out of four samples of vegetables, ranged in concentration between 4 g/kg as the highest recorded in the *Brassica* sp. sample and 3 g/kg as the lowest detected in the *Amaranthus* sp. sample. The highest concentration of Cu (9.00 g/kg) was detected in the *Spinacia oleracea* sample followed by 8 g/kg in the *Solanum* sp. sample, 7 g/kg in the sample of *Amaranthus* sp., while the *Brassica* sp. sample recorded the lowest Cu concentration of 4 g/kg.

4.2 Concentrations of Selected Heavy Metals in the Nairobi River Discharge Point-Irrigated Vegetables

The concentrations of Ti, Zn, Pb, Cr, Cd, Co and Cu in the samples of *Brassica* sp., *Solanum* sp., *Amaranthus* sp. and *Spinacia* oleracea vegetables produced using wastewater from the Nairobi River discharge point are shown in Fig. 4. Titanium concentration was highest (113 g/kg) in the *Spinacia* oleracea sample and lowest (91 g/kg) in the *Brassica* sp. sample. The *Amaranthus* sp.and *Solanum* sp. samples recorded Ti concentration of 101 and 97 g/kg, respectively.

The *Spinacia oleracea* sample recorded the highest (48 g/kg) concentration of Zn, while the *Amaranthus* sp. sample registered the lowest (21 g/kg) Zn concentration. Zinc concentration in the

rest of the samples was 27 and 30 g/kg for *Solanum* sp. and *Brassica* sp. samples, respectively. The samples of *Spinacia oleracea* and *Amaranthus* sp. both recorded the same Cr concentrations of 16 g/kg, being the highest, followed by *Solanum* sp. sample with 5 g/kg, while *Brassica* sp. sample recorded the lowest concentration at 2 g/kg. Both *Spinacia oleracea* and *Solanum* sp. samples recorded the same Cu concentration of 6 g/kg, while *Brassica* sp. and *Amaranthus* sp. samples had Cu concentration of 1 and 3 g/kg, respectively. Lead, Cd and Co were not detected in the samples.

4.3 Concentrations of Selected Heavy Metals in Upstream Nairobi River-Irrigated Vegetables

Concentrations of Ti, Zn, Pb, Cr, Cd, Co and Cu in the samples of vegetables produced using wastewater from upstream of Nairobi River are presented in Fig. 5. The concentration of Ti in the samples from upstream Nairobi River- irrigated vegetables was highest (238 g/kg) in the *Amaranthus* sp. sample followed 171 g/kg detected in the *Spinacia oleracea* sample, 165 g/kg recorded in the *Brassicasp*. sample, while the lowest (90 g/kg) concentration was recorded in the *Solanum* sp. sample.

The *Spinacia oleracea* sample recorded the highest (41g/kg) concentration of Zn, followed by the *Solanum* sp. sample with 32 g/kg, *Amaranthus* sp. sample with 31 g/kg, while the *Brassica* sp. sample recorded the lowest (29 g/kg) Zn concentration. Lead with a concentration of 0.06 g/kg against FAO/ WHO maximum permissible value of 0.0003 g/kgwas detected only in the *Amaranthus* sp. sample.

The Spinacia oleracea sample recorded the highest (19 g/kg) Cr concentration followed by the Solanum sp. sample with 11 g/kg, Brassica sp. sample with 6 g/kg, and 3 g/kg being lowest recorded in the Amaranthus sp. sample. Cadmium was not detected in any of the four vegetable samples. Cobalt concentration was highest (4 g/kg) in the Solanum sp. sample and lowest (3 g/kg) in both Brassica sp. and Spinacia oleracea samples. Copper was detected in all the upstream Nairobi River-irrigated vegetable samples where concentration ranged from 4 g/kg in the Brassica sp. sample, 5 g/kg recorded in the Solanum sp. sample, 6 g/kg in the Amaranthus sp. sample, to 8 g/kg in the Spinacia oleracea sample.

4.4 Concentrations of Selected Heavy Metals in Raw Influent-Irrigated Vegetables

Concentrations (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the samples of raw influentirrigated Brassica sp., Solanum sp., Amaranthus SD.. Spinacia oleracea vegetables are presented in Fig. 6. The results showed the sample of Solanum sp. recorded the highest (216.00 g/kg) concentration of Ti, while the sample of Brassica sp. recorded the lowest (105 g/kg). The Amaranthus sp. and Spinacia oleracea samples recorded Ti concentrations of 172 g/kg and 108 g/kg, respectively.

The concentration of Zn in all the samples varied. Thus, the sample of *Spinacia oleracea*recorded maximum (50 g/kg) concentration, while the *Solanum* sp. sample recorded minimum at 30 g/kg. The *Brassica* sp. and *Amaranthus* sp. samples each recorded Zn concentration of 46 g/kg. Lead with a concentration of 0.06 g/kg was detected only in the *Amaranthus* sp. sample.

The maximum (16 g/kg) and minimum (8 g/kg) concentrations of Cr were detected in the *Spinacia oleracea* and *Amaranthus* sp. samples, respectively. Chromium concentration in the rest of the samples was 14 g/kg for *Brassica* sp. and 13 g/kg for *Solanum* sp. samples. Cadmium concentration in the samples ranged from 0.01 g/kg in the *Spinacia oleracea* sample, 0.04 g/kg in the *Brassica* sp. sample, to 0.23 g/kg in the *Amaranthus* sp. sample. It was not detected in the *Solanum* sp. sample.

Cobalt concentrations in the samples ranged between 3 g/kg in the Solanum sp. sample, 4 g/kg recorded in the Spinacia oleracea and 5 g/kg sample, detected in the Brassica sp. sample. It was not detected in the Amaranthus sp. samplethereby suggesting that of all the samples of vegetables in the category only Amaranthus sp. sample was within the FAO/ WHO maximum permissible value of 0.005 g/kg for cobalt. The maximum Cu concentration of 6 g/kgwas recorded in the Amaranthus sp. sample, while Brassica sp. and Spinacia oleracea samples each recorded 3 g/kg being minimum Cu concentration. The Solanum sp. sample had Cu concentration of 5 g/kg.

4.5 Concentrations of Selected Heavy Metals in the Downstream Nairobi River-Irrigated Vegetables

The concentrations (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the samples of downstream Nairobi River-irrigated *Brassica* sp., *Spinacia oleracea*, *Amaranthus* sp. and *Solanum* sp. vegetables are presented in Fig. 7. Titanium content in the samples was maximum (150 g/kg) and minimum (65 g/kg) in *Solanum* sp. and *Amaranthus* sp. samples, respectively. The *Spinacia oleracea* and *Brassica* sp. samples had Ti concentration of 115 and 85 g/kg, respectively. These values exceeded the FAO/ WHO safe limit of 0 g/kg for Ti in green leafy vegetables.The highest (202 g/kg) and lowest (29 g/kg) Zn concentration were detected in *Spinacia oleracea* and *Brassica* sp. samples, respectively.

The Amaranthus sp. and Solanum sp. samples registered Zn concentration of 49 and 33 g/kg, respectively. Lead was not detected in the samples which suggests Pb in the downstream Nairobi River-irrigated vegetables was within the FAO/ WHO maximum permissible values. Chromium concentration in the samples was 9 g/kg being the lowest concentration in the *Amaranthus* sp. sample, 14 g/kg in the *Brassica* sp. sample, 15 g/kg in the *Solanum* sp. sample, and 27 g/kg as the highest concentration in the *Spinacia oleracea* sample.

Maximum Cd concentration (0.2 g/kg) was detected in the sample of Spinacia oleracea, while minimum concentration (0.02 g/kg) was recorded in the Brassica sp. sample. The Solanum SD. and Amaranthus SD. samplesrecorded Cd concentration of 0.14 and 0.11 g/kg, respectively. Cobalt was not detected in any of the four vegetable samples, which implies Co in the downstream Nairobi Riverirrigated vegetables was within the FAO/ WHO maximum permissible value of 0.005 g/kg. The concentration of Cu was maximum (11 g/kg) in the Spinacia oleracea sample and minimum (1 g/kg) in the Brassica sp. sample. The samples of Solanum sp.and Amaranthus sp. recorded Cu concentrations of 7 and 2 g/kg, respectively.

The findings show the treated effluent-irrigated vegetables recorded maximum and minimum Ti concentration. Thus, the *Amaranthus* sp. sample recorded maximum (238 g/kg) Ti concentration, while the *Brassica* sp. sample recorded minimum (58 g/kg)Ti concentration. Zinc concentration was highest (202 g/kg) in the sample of downstream

Nairobi River-irrigated *Spinacia oleracea* and minimum (16 g/kg) in the sample of treated effluent-irrigated *Brassica* sp. Maximum Zn concentration detected in the *Spinacia oleracea* sampleis in concurrence with the findings of Gupta et al. [7].

The mean concentration of Zn in the vegetable samples viz. 100.8 g/kg for *Brassica* sp., 126.6 g/kg for *Spinacia oleracea*, 58.8 g/kg in the *Amaranthus* sp. and 31.2 g/kgin the *Solanum* sp. sample conflict with the findings of Mutune et al [25]. The values also exceed the FAO/ WHO safe limit of 0.099 g/kg for Zn in green leafy vegetables. Although Zn is essential for biological activities in the body, its presence in high concentration can be a health risk [21].

Lead was detected in the samples of treated effluent-irrigated *Brassica* sp. and *Amaranthus* sp., each recorded 0.05 g/kg. It was also detected in the samples of upstream Nairobi River and raw influent-irrigated *Amaranthus* sp., with similar concentration of 0.06 g/kg. It was not detected in the rest of the samples thereby suggesting either concentrations were far below detectable limit or absent altogether. The presence of Pb in the sample of *Amaranthus* sp. is in concurrence with Inoti et al. [23]. The recorded Pb values, however exceed the FAO/ WHO safe limit of 0.0003 g/kg for Pb in green leafy vegetables.

Excessive accumulation of Pb in plant tissue impairs various morphological, physiological and biochemical functions with deleterious effects. In turn elevated levels of Pb in the blood is potential of causing kidney dysfunction and brain damage [7]. Lead causes mental retardation in young children [25]. Increase of blood pressure in adults is also related to Pb in the human body as pointed out in Ametepey et al. [24].

The concentration of Cr in the samples was minimum (2 g/kg) in the sample of discharge point-irrigated *Brassica* sp. and maximum (27 g/kg) in the sample of downstream Nairobi Riverirrigated *Spinacia oleracea*. The mean concentration of Cr in the samples, which was 9.4 g/kgin *Brassica* sp., 17 g/kgin *Spinacia oleracea*, 12.8 g/kgin *Amaranthus* sp. and 11 g/kgin *Solanum* sp. surpassed the FAO/ WHO safe limit of 0.0023 g/kg for Cr in green leafy vegetables.

Cadmium was not detected in all samples from the discharge point and upstream Nairobi Riverirrigated vegetables. However, it was detected in all the samples from treated effluent and downstream Nairobi River-irrigated vegetables. It was further detected in three out of four samples from raw influent-irrigated vegetables. Thus, maximum (0.27 g/kg) Cd concentration was recorded in the sample of treated effluentirrigated Spinacia oleracea, while the sample of raw influent-irrigated Spinacia oleracea recorded minimum (0.01 g/kg) concentration. In comparison with the FAO/ WHO safe limit of 0.0002 g/kg for Cd in green leafy vegetables, the two values were higher. Due to its nature, Cd is non-essential and has no nutritional value to plants, animals and human beings [26].

Cobalt, which was detected in more than half of the samples, varied in concentration from 3 g/kg, each in the samples of treated effluent-irrigated *Amaranthus* sp., upstream Nairobi Riverirrigated *Brassica* sp. and *Spinacia oleracea* and raw influent-irrigated *Solanum* sp., 4 g/kg each, in the treated effluent *Brassica* sp., upstream Nairobi River-irrigated *Solanum* sp., and raw influent-irrigated *Spinacia oleracea*, to 5 g/kg as the maximum Co value in the raw influentirrigated *Brassica* sp. Cobalt is essential to human beings because it forms part of vitamin B₁₂ also known as cobalamin. However, exposure to elevated levels results in lung and heart diseases and dermatitis [27]. Symptoms of Co deficiency [15] include loss of appetite, emaciation, weakness and anemia.

Copper concentration in all the vegetable samples ranged from 1 g/kg both in the discharge point and downstream Nairobi Riverirrigated *Brassica* sp. samples to 11 g/kg in the downstream Nairobi River- irrigated *Spinacia oleracea* sample. The mean Cu concentration in the samples of 2.6 g/kg for *Brassica* sp., 7.4 g/kgfor *Spinacia oleracea*, 4.8 g/kgfor *Amaranthus* sp. and 6 g/kgfor *Solanum* sp. surpassed the FAO/ WHO safe limit of 0.073 g/kg for Cu in green leafy vegetables.

The vegetables under study viz.*Brassica* sp., *Spinacia oleracea, Amaranthus* sp. and *Solanum* sp. differ in their respective potential to bioaccumulate the investigated heavy metals viz. Ti, Zn, Pb, Cr, Cd, Co and Cu. In addition, the targeted heavy metals in the samples of vegetables produced using wastewater varied in their concentrations from below the detection limit to above the FAO/ WHO safe limits for corresponding heavy metals in leafy vegetables, depending upon the source of wastewaterused in their production. The order of metal contents was found to be Pb > Cd > Co > Cu > Cr > Zn > Ti.



Fig. 3. Concentration (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the treated effluent- irrigated vegetables in Ruai ward, Nairobi City County, Kenya

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Fig. 4. Concentration (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the discharge point- irrigated vegetables in Ruai ward, Nairobi City County, Kenya



Fig. 5. Concentration (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the upstream Nairobi Riverirrigated vegetables in Ruai ward, Nairobi City County, Kenya



Fig. 6. Concentration (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the rawinfluent- irrigated vegetables in Ruia ward, Nairobi City County, Kenya



Fig. 7. Concentration (g/kg) of Ti, Zn, Pb, Cr, Cd, Co and Cu in the downstream Nairobi Riverirrigated vegetables in Ruai ward, Nairobi city county, Kenya

5. CONCLUSIONS

The concentrations of investigated heavy metals in the samples of vegetables produced using wastewater from different sources in the study area varied among different vegetable types. The differences in heavy metal concentrations in the vegetable samples from the same site can be attributed to differences in their morphology and physiology for heavy metal uptake, exclusion, accumulation and retention [7].

Additionally, the concentrations of nearly all the heavy metals in the samples of vegetables exceeded respective FAO/ WHO safe limits for corresponding heavy metals in leafy vegetables and therefore posed potential risk to the consumers of such vegetable produce. The findings also concur with [15], that continuous application of municipal or industrial wastewater for irrigation can cause accumulation of trace elements like Cd, Cu, Zn, Cr and Pb in surface soil. Excessive buildup of such elements in cultivated soils contaminates the soil thereby compromising the quality and safety of food. Heavy metals are translocated into different plant parts via root uptake [13].

From this study, titanium and zinc metals were most elevated in all the vegetables with a mean of 126.2 and 51.45 g/kg, respectively. Lead and Co were not detected in the discharge point and downstream Nairobi River irrigated vegetables. It was also discovered Cd was not detected in the discharge point and upstream Nairobi River irrigated vegetables, while Co was not detected in the discharge point and downstream Nairobi River-irrigated vegetables.

Long-term heavy metal exposure as a result of regular consumption of vegetables containing heavy metals beyond safe limits poses potential health risks [7]. The study therefore recommends consistent monitoring of heavy metals in vegetables to avert their excessive accumulation in the food chain.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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