Vol. 13(2), pp. 18-36, July-December 2021
DOI: 10.5897/JTEHS2021.0488
Article Number: C5F142967630
ISSN: 2006-9820

http://www.academicjournals.org/JTEHS

Journal of Toxicology and Environmental Health Sciences

Full Length Research Paper

Evaluation of the levels of selected heavy metals in leafy vegetables from irrigation farming sites in Jos, Plateau, Nigeria

Samuel Y. Gazuwa* and Ochube E. Olotuche

Department of Biochemistry, Faculty of Basic Medical Sciences, College of Health Scieces, University of Jos, Jos Nigeria.

Received 25 May, 2021; Accepted 8 July, 2021

Leafy vegetables are used in making soups, local salads and diverse forms of foods for human consumption is common in Africa. These vegetables include *Brassica oleracea* (cabbage), *Phaseolus vulgaris* (green beans) and *Solanum lycopersicum* (tomatoes). The area of study is famous for agriculture and mining activities; Farmers cultivate them on degraded farmlands polluted with metals; these vegetables absorb these metals thereby making them enter the food chain. During dry season, water from mining ponds is used for irrigation. Industrial waste water is also used. Levels of cadmium (Cd), Arsenic (As), copper (Cu), and lead (Pb), were assessed using Inductively Coupled Plasma Optically Emitting Spectrophotometer (ICP-OES) equipment. Five samples of each vegetable were collected randomly from different irrigation farms situated at *Bassa*, *Bisichi* and *Zaramaganda*. Graph pad prism-7 multiple comparison tests in a one-way ANOVA was used to compare variations in metal concentrations at 95% confidence limit. Pb, As and Cd were not detected in water samples from *Bisichi* but mean level of Cd and Pb in water from *Bassa* and *Zaramaganda* were 0.932 mg/L (P=0.05) and 1.242 mg/L (P=0.05); 0.84 mg/L (P=0.05) and 16.338 mg/L (P=0.05), respectively relative the FAO/WHO safe limits. Water samples from *Bassa* contained Cu whose level was above (P=0.05) safe limits; only one was below the standard (P>0.05). Samples from *Zaramaganda* contained highest levels of the metals. cabbage and green beans from *Zaramaganda* and *Bisichi* contained Pb, Cu above (P=0.05) the FAO/WHO limit. Mean Pb content in cabbage and green beans from *Bisichi* was 2.099 and 0.189 mg/kg respectively. From *Bassa,* Pb content in tomatoes and green beans were 0.086 and 491.31 mg/kg respectively. From *Zaramaganda,* Pb content in green beans and tomatoes were 12.31 and 14.522 mg/kg; level of Cd in green beans 0.481 mg/kg. Considering Cu, tomato from *Bassa* contained highest level, 64.310 mg/kg (P=0.05), green beans from Zarmaganda was 48.251 mg/kg (P=0.05), tomato from *Bisichi* contained 38.541(P=0.05) relative safe limits. In conclusion, the significant concentrations of Cd, Pb and Cu in the vegetables in the area of study, which are routinely used in making soups, portage and local salads, predispose consumers to, cancer, cardiovascular diseases, inhibition of the heme biosynthesis pathway, hemolysis and febrile reactions due to their respective toxicities.

Key words: Cabbage, tomatoes, green beans, cadmium, arsenic, copper, and lead.

INTRODUCTION

Food safety is a major public concern globally, especially in economically weaker countries. The production of safe food is a key factor in food quality and human health. Vegetables are important components of human diets due to their high nutrients content such as vitamins, minerals, folate, dietary fibre, ascorbic acid, carotene and other nutrients. They are useful in managing ailments resulting from micronutrients deficiency such as night blindness and anaemia (Asdeo and Looker, 2011). Reports from various studies have indicated that the consumption of various types of vegetables can significantly prevent chronic heart diseases and some types of cancers especially of the gastrointestinal tract such as colon cancer (Lawal and Audu, 2011; Temple and Schrauzer, 2012).

Heavy metals and their compounds easily contaminate arable farm lands and are a global concern (Laughlin and Agrawal, 2015). They are the most contaminants of soil ecosystems and hence the food chain. For example, lead is a known toxic heavy metal that inhibits the activity of γ –aminolaevolinic acid dehydratase, which catalyses the committed step of heme synthesis (heamatopoietic system). It easily accumulates in the kidney posing danger to human health (Engwa et al., 2019; Patrick, 2006). The sources of heavy metals contamination of vegetables include waste water used for irrigation (Mapanda et al., 2005), pesticides and fertilizers, and industrial emissions. High concentrations of heavy metals were reported in vegetables from untreated waste water irrigated areas (Singh et al., 2010; Sharma et al., 2007). Dry season farmers use contaminated waters to irrigate their farms. Area of study is famous for dry season irrigation farming and the vegetables produced from these farms are sold to consumers in and around the locations. The use of industrial waste water for irrigation is of serious concern in Nigeria because these effluents are highly polluted with heavy metals, chemicals and metabolic compounds (Jarup et al., 1998). Chronic exposure to heavy metals results in the disruption of vital biochemical pathways and could adversely affect vital organs such as the kidneys, and so on. Generally, humans are exposed to heavy metals by consumption of contaminated foodstuffs such as fruits, vegetables and drinking water (Qaisar et al., 2012). Consumption of fruits and vegetables contaminated with Cd, Pb has been reported to cause cancer of the pancreas, urinary bladder or prostate (Turkdogan et al., 2002). This work was designed to assess the levels of selected heavy metals in some vegetables commonly consumed in the study areas, and to compare their concentration with FAO/WHO maximum permissible limits in vegetables.

MATERIALS AND METHODS

Study locations

The area of study encompassed Bassa, *Bisichi* and *Zaramaganda*. *Bisichi* was selected due to abundant mining ponds in the area used by dry season farmers for irrigation. *Zaramaganda* was chosen because of its proximity to the *NASCO* industries where soaps, detergents, cosmetics, foods such as biscuits, flakes of cereals and fibre are manufactured using medley of chemicals and reagents. Similarly, the Jos International Breweries and the *Makery* smelting plant (processing tin and columbite) share a common fence with *NASCO* Industry. Using a GPSMAP 78s GARMIN device, elevation, sampling locations and their surroundings features were determined.

Collection of samples

Samples of vegetables and water were obtained from irrigation farms situated at *Bassa, Bisichi* and *Zarmaganda,* and with coordinates, elevation and location as follows; *Bassa:* elevation = 1271 m*,* location (N): 095°548’.21”; E = 008°48’33.80”. *Bisichi:* elevation =1230 m; location (N): 094°224’13” E = 008°54’50.96” *Zarmaganda:* elevation = 1280 m; location (N): 095°133’.12” E = 008°52’15’.06”

Vegetable samples used were *Brassica oleracea* (cabbage), *Phaseolus vulgaris* (green beans) and *Solanum lycopersicum* (tomatoes). They were randomly collected from different farms in the study locations and kept in properly labeled polythene bags and taken to the laboratory for processing and analysis. Samples were washed with tap water to remove any soil particles and rinsed with distilled water. The edible portions of the vegetable samples were air-dried in the open laboratory for twenty four hours to reduce the water content. Thereafter, all the samples were oven-dried at 70°C for 24 h. The dried samples were then pulverised using a Teflon pestle and mortar, sieved with muslin cloth and stored in airtight containers until required for digestion.

Digestion of samples

1 g each of the pulverized samples from each sampling site was weighed and placed in crucibles. Each sample was digested using a mixture of trioxonitrate (V) acid, (HNO_3) monoxochlorate (I) acid (HOCl) and hydrochloric acid (HCl) in the ratio of 1:6:1 respectively. Hot plates were used in heating the samples with intermittent addition of 3 ml of the digestion mixture until white precipitate was obtained. The digested samples were dissolved in 2 ml of trioxonitrate (V) acid for 10 mins, removed and allowed to cool and then transferred into 100 ml volumetric flask and made up to the mark with distilled water. For water samples, 20 ml of water samples were mixed with 2.5 ml of HNO_3 before analysis.

Analysis of samples

The samples were analysed for Cd, Pb, Cu, As, using Inductively Coupled Plasma Optically Emitting Spectrophotometer (ICP-OES). All reagents used were of analytical grade.

Operating conditions for ICP-OES Machine

Power,1350W, plasma flow, 13.0 L/min, nebulizer flow,1.00 L/min, auxiliary flow,1.25 L/min, sampling depth, 2.0 mm, scanning times, 160 times, exit plate, 0V, pump rate, 20 rpm, rinse time, 10 s, replicates 5, replicate read time, 8 s, instrument stabilization, 8 s,

*Corresponding author E-mail: sygazuwa@gmail.com; gazuwas@unijos.edu.ng. Tel: 08036907936.

Table 1. Mean levels of Pb, Cd, As, Cu, in water used for irrigation in different parts of the area of study.

Location	Metals (mg/L)			
	Pb	Cd	As	Cu
Bassa`1	0.842±0.01[b]	0.932±0.01[b]	ND	1.042±0.01[a]
Bisichi-	ND	ND	ND	0.983±0.01[b]
Zaramaganda	16.338±0.05[b]	1.242±0.001[b]	ND	1.841±0.01[b]
FAO/WHO	0.01	0.003	0.01	1.0

ND=Not detected.
Values are means of three determinations (± SEM); n=5.
[a]below the permissible level of Pb, Cd and Cu stated by FAO/WHO
[b]above the permissible level of Pb, Cd, Cu, Fe, Mn and Cr stated by FAO/WHO.

Table 2. Mean values of Pb, Cd, As and Cu, in vegetables from irrigated farms in different parts of the area of study. Metals (mg/kg).

Location	Crop	Pb	Cd	As	Cu
Bassa	Cabbage	0.001±0.00[a]	0.002±00[a]	ND	31.431±0.001[b]
Green beans	ND	0.001±0.00[a]	ND	34.340±0.001[b]	
Tomato	0.0086±0.002[b]	0.059±0.001[a]	ND	64.310±0.011[b]	
Bisichi	Cabbage	2.099±0.001[b]	0.209±0.001[b]	ND	0.209±0.001[b]
	Green beans	0.189±0.001[b]	0.241±0.001[b]	ND	ND
	Tomato	ND	ND	ND	38.541±0.001[b]
Zaramaganda	Cabbage	12.310±0.015[b]	0.043±0.009[a]	ND	28.331±0.001[b]
	Green beans	14.522±0.001[b]	0.481±0.001[b]	ND	48.251±0.001[b]
	Tomato	13.824±0.199[b]	0.041±0.001[a]	ND	ND
FAO/WHO	Cabbage	0.1	0.05	0.01	0.4
	Green beans	0.1	0.1	0.2	0.4
	Tomato	0.05	0.05	0.2	0.4

ND=Not detected. Values are means of three determinations (± SEM); n=5.
[a]below the permissible level of Pb, Cd and Cu stated by FAO/WHO.
[b]above the permissible level of Pb, Cd, Cu, Fe, Mn and Cr stated by FAO/WHO.

sample delay uptake, 60 s.

Statistical analysis

One-way analysis of variance (ANOVA) was used to compare variations in metal concentrations at 95% level of significance.

RESULTS

Table 1 contains mean levels of Pb, Cd, As, Cu, in water used for irrigation in different parts of area of study. The highest level of the metals was detected in the water sample from *Zaramaganda* while the lowest was detected in the sample from *Bassa*. Table 2 bears the mean levels of Pb, Cd, As and Cu in vegetables from irrigated farms within the area of study. Arsenic was not detected in samples from all the locations. The highest concentration of Pb and Cd were detected in the vegetable samples from *Zaramaganda*, with green beans having the highest level.

Figure 1 shows the comparative concentrations of heavy metals (Pb, Cd and Cu) in selected irrigation water sites in different parts of the area of study. *Zaramaganda* has the highest concentration of lead above (P=0.05) the maximum permissible limit set by FAO/WHO. It was not detected in the irrigation water from *Bisichi*. The mean level of detected cadmium and copper in *Zaramaganda* were above (P=0.05) the maximum permissible limit set by FAO/WHO while that of *Bassa* and *Bisichi* were within maximum permissible limits.

Figure 2 shows the comparative mean levels of Pb (mg/kg) in vegetables from irrigated farms in the area of study. Cabbage, green beans and tomatoes from *Zaramaganda* had the highest levels of Pb while green beans from *Bisichi* had the lowest value. Lead was not detected in all the vegetable samples from *Bisichi.*

Figure 3 shows the comparative mean levels of Cd (mg/kg) in vegetables from irrigated farms in area of study. The detected mean levels of cadmium in cabbage from *Bisichi,* green beans from *Zaramaganda* and *Bisichi* were above the FAO/WHO maximum permissible limit

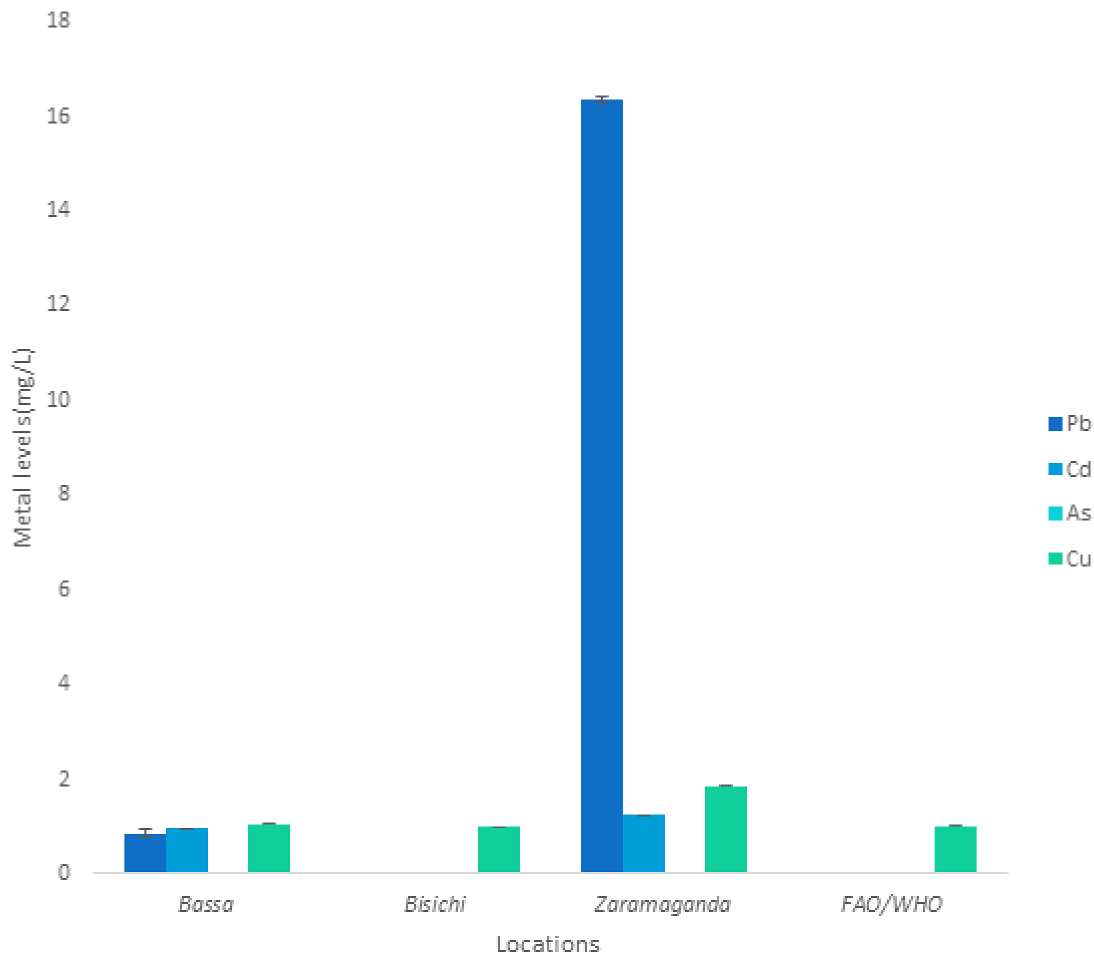

Figure 1. Mean levels of Pb, Cd, As, Cu in water used for irrigation in area of study.

while cadmium was not detected in cabbage from *Bassa* and tomato from *Bisichi.*

DISCUSSION

This work sought to analyze levels of cadmium (Cd), lead (Pb) Copper (Cu) and arsenic (As) in samples of water and vegetables from the area of study (*Bassa, Bisichi* and *Zarmaganda*). Because the area of study is famous for mining tin, columbite, and ores of other metals, numerous mining ponds abound in the milieu. Industries such as *Nasrideen* Company (*NASCO*), Jos International Breweries (JIB), Makeri Smelting Plant (MSP) are situated around *Zarmaganda* area. Hence, industrial effluents are discharged into water bodies. Farmers use water from mining ponds (ponds in *Bassa* and *Bisichi*) which contain heavy metals for dry season irrigation purposes. The levels of these metals in the samples were generally above maximum permissible limits set by WHO/FAO. That being the case, the crucial biological functions of mineral elements such as calcium, phosphorus, zinc and others could negatively. This can be seen in the context of structural analogs; cadmium competes with zinc for binding the active sites of enzymes because it is structurally similar to zinc which is a co-factor of the DNA polymerases I, II, and III. Cabbage and green beans from *Zarmaganda* contained highest Pb level in that order. From *Zarmaganda,* green beans contained 0.481 mg/kg Cd. Cd content in green beans and cabbage from *Bisichi* were 0.241 and 0.20 mg/kg levels respectively and above safe limits (P=0.05). Tomatoes from *Bassa, Zarmaganda* and *Bisichi* contained Cu thus: 64.31, 48.25, and 38 mg/kg in that order. This poses hazard to humans via the food chain (Gazuwa and Timothy, 2019; Alam et al., 2003; Asdeo and Looker, 2011), and (Khan et al., 2011). They reported that the use of waste water generally led to changes in the physicochemical characteristics of soils and consequently heavy metal uptake by vegetables. Similar work done by Patrick (2006) reported high levels of lead in soil and vegetables irrigated with old tin mining ponds water in *Barkin Ladi* local government area of Plateau state, Nigeria. On the other hand, Nimyel et al.

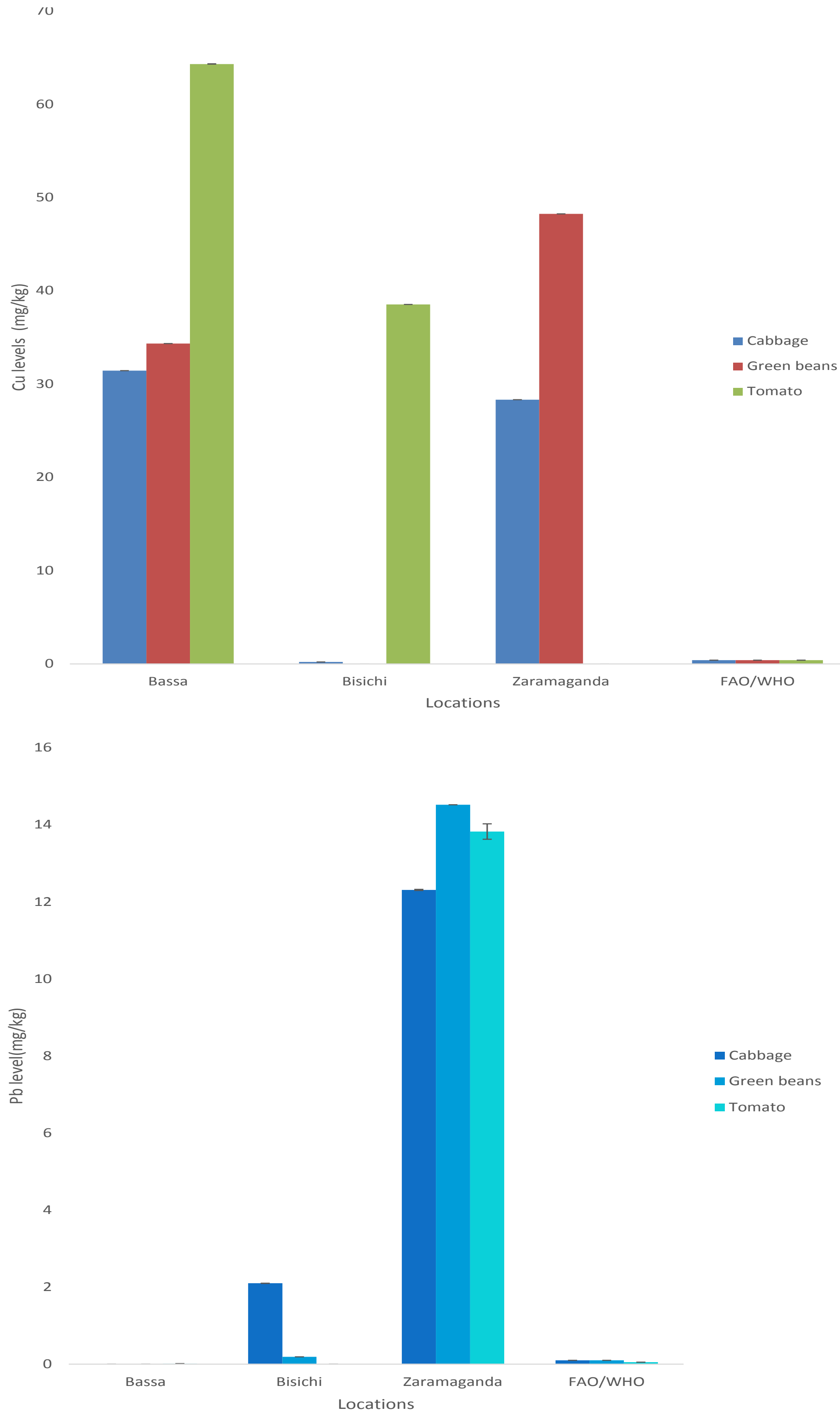

Figure 2. Comparative levels of lead (mg/kg) in vegetables from irrigated farms in area of study.

(2015) have demonstrated that wild vegetables obtained from *Dengi* metropolis contained Cd and Pb at levels below the permissible limits (P>0.5).

Table 1 bears the mean values of selected heavy metals in water used for irrigation in different parts of area of study. Mean levels of Pb, Cd and Cu in water samples

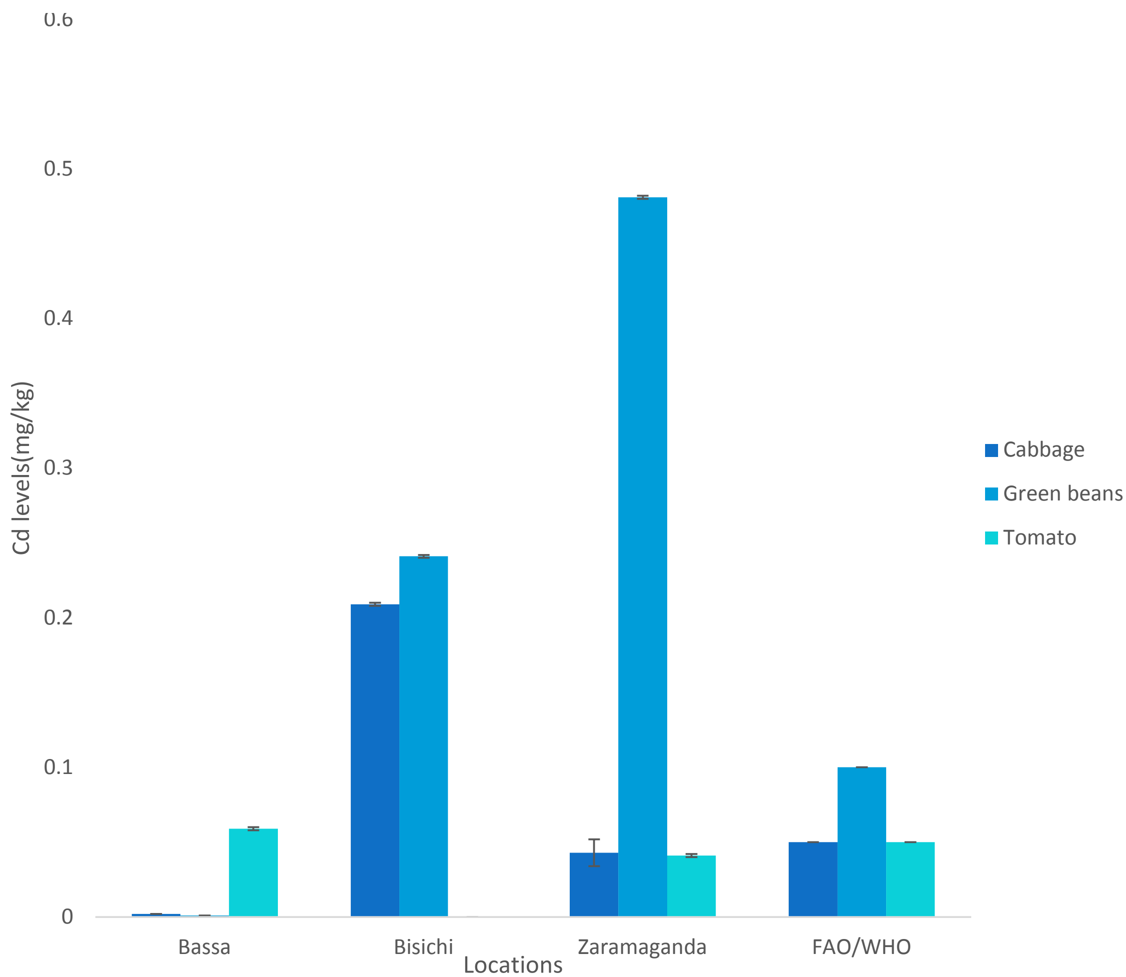

Figure 3. Comparative levels of cadmium (mg/kg) in vegetables from irrigated farms in area of study.

from *Zaramaganda* were above the WHO/FAO maximum permissible limits (P=0.5) in this order: Pb> Cd > Cu. This may be attributed to high industrial activities in the area. This is in agreement with the work done by Laughlin and Agrawal (2015) which showed that heavy metals were among the pollutants in industrial waste water. Also, effluents from a print textile industry and Nigerian breweries that discharge their waste water into the Lagos lagoon have been reported by (Adebayo et al., 2007) to contain high levels of manganese, lead, cadmium, chromium, iron and copper. Orish et al. (2017) reported levels of Pb above WHO/FAO permissible limits in soils and water of *Dilimi* river, *Bukuru* and *Barkin Ladi* Local Government Area of Plateau state. Gazuwa and Timothy (2019) reported significant concentration Pb, Cd and Fe (P = .05) in vegetables and soil samples in *Dengi,* Plateau state. Further, Michael et al. (2018) reported levels of Pb, Cd, and Fe in cabbage cultivated using irrigation water from ex-mining ponds. The presence of these metals in vegetables and water at levels above their permissible limits is a threat to consumers since these metals ultimately enter the food chain and accumulate up to toxic levels (Athar et al., 2019). These heavy metals are not easily excreted from the body and therefore accumulate over time to toxic levels affecting metabolism and absorption of mineral elements and perhaps antioxidant capacities the absorption and metabolism of micronutrient elements with the possibility of losing their other biological functions. Bello et al. (2020) reported low blood iron, zinc and copper levels owing to interaction with cadmium and lead.

Table 2 bears the mean concentration of heavy metals in vegetables obtained from irrigated farms within the area of study. The results revealed mean levels of Pb in all the vegetables from *Zarmaganda,* cabbage from *Bassa,* to be above (P=0.5) the maximum permissible limits set by WHO/FAO. The level of Cd in green beans obtained from *Zarmaganda* and *Bisichi*, cabbage from *Bisichi* were above the safe limits and statistically significant (P=0.05). Comparing these results with the mean levels of these metals in the water samples from the three locations, it can be stated that high levels of these metals in vegetables from *Zarmaganda* was as a result of absorption from the soil and water used for irrigating these crops. These results are similar to that of (Lente et al., 2014) and (Samuel et al., 2008) who reported high levels of heavy metals in vegetables obtained from Accra and Kumasi metropolis of Ghana. Also, Dabak et al. (2013) have reported the presence of heavy metals above WHO maximum permissible limits in vegetables. Green beans from *Bassa* contained 491.31 mg/kg Pb burden; in tomatoes, Pb was 0.086 mg/kg. Level of Cu was 64.31 mg/kg. These values, especially Pb in green beans is alarming because it is above (P=0.05) the safe acceptable limits. The Pb content of green beans, tomatoes were 12.31 and 14.52 mg/kg in samples from *Zarmaganda*; both above (P=0.05) safe limits. The Pb content in samples obtained from *Bisichi* in cabbage and green beans were 2.099 and 0.189 respectively; both of which were higher (P=0.05) safe limits. The level of Cu in tomatoes was 38.54 mg/kg.

From biochemical standpoint, the prime targets to lead toxicity are the heme synthesis enzymes, thiol-containing antioxidants and enzymes superoxide dismutase, catalase, glutathione peroxidase, glucose 6-phosphate dehydrogenase and antioxidant molecules like GSH (Nemsadze et al., 2009). The main sources of lead exposure include drinking water, food, cigarette, and domestic sources. The industrial sources of lead include gasoline, house paint, plumbing pipes, lead bullets, storage batteries, pewter pitchers, toys and faucets (Godwill et al., 2019). Lead is released into the atmosphere from industrial processes as well as from vehicle exhausts. Therefore, it may get into the soil and flow into water bodies which can be taken up by plants and hence human exposure of lead may also be through food or drinking water (Godwill et al., 2019).

Pb interacts in two ways: it binds strongly to sulfhydryl groups and electron donor groups in general, thereby changing the configuration of a wide range of proteins. Because of its similarity to other divalent cations such as calcium and zinc, it interferes with the vast array of cellular mechanisms that are regulated by and mediated by these cations (Lidsky and Schneider, 2003). Because of the ubiquity of electron donor groups and divalent cations throughout the human body, the pathophysiology of lead toxicity is quite complex and involves virtually every organ system.

Lead is thought to undermine the normal synaptic pruning process in young brains, likely underlying the cognitive and behavioral changes seen in young children with excessive lead exposure (Souza et al., 2013). Peripheral neuropathy is a common manifestation of chronic lead toxicity in adults. The most severe neurologic manifestations of lead toxicity such as seizures and coma occur in acute lead encephalopathy, which is thought to be at least in part secondary to lead-induced cerebral microvascular changes leading to cerebral edema and resultant increased intracranial pressure (Souza et al., 2013). Lead causes anemia by being a potent inhibitor of multi-enzyme activities involved in heme synthesis as well as enzymes involved in maintaining erythrocyte cell membrane integrity, which leads to decreased production and increased destruction of erythrocytes, respectively (Lidsky and Schneider, 2003). For example, the classic appearance of basophilic stippling is thought to represent clumps of degraded RNA, which is normally cleared by an enzyme known as pyrimidine-5'-nucleotidase that is inhibited by lead (Valentine et al., 1976).

Studies have shown that cadmium has toxic effects on the human body. For example, cadmium reaches the kidney in form of cadmium-metallothionein (Cd-MT). Cd-MT is filtrated in the glomerulus, and subsequently reabsorbed in the proximal tubules. It then remains in the tubules cells as is not easily excreted from the body. An increasing cadmium load in the kidney is known to cause a higher calcium excretion, thus leading to a higher risk of kidney stones.

The urinary cadmium excretion was shown to correlate with the degree of cadmium induced kidney damage: A urinary excretion of 2.5 µg cadmium per gram creatinine reflects a renal tubular damage degree of 4% (Qaisar et al., 2012). The primary markers of kidney damage however, are the urinarily excreted β2-microglobulin, N-acetyl-α-D-glucosaminidase (NAG), and retinol-binding-protein (RBP) (Bernard, 2004). The China Cad-Study showed significantly higher values for urinary β2-Microglobulin and RBP in people with high blood cadmium concentration than in people with normal values (Qaisar et al., 2012).

Several studies in the 20^{th} Century showed a connection between cadmium intoxication and bone damage, e.g. bone damage and the *itai-itai* disease, under which patients show a wide range of symptoms such as low grade of bone mineralization, high rate of fractures, increased rate of osteoporosis, and intense bone associated pain. Underlying osteoporosis, possibly enhanced by cadmium intoxication, was suggested to be the actual reason for the observed symptoms (Kazantzis, 2004). Cadmium is similar to calcium and replaces calcium in the bone mineral composition.

Cupric and cuprous forms of Cu are implicated in the generation of reactive oxygen species thereby participating in redox reactions. Antioxidants such as glutathione, ascorbate reduce cupric to cuprous form which is capable of catalyzing the decomposition of H_2O_2 to form •OH by the Fenton reaction.

Among the metals essential for diverse biological phenomena is copper (Cu). This metal is a co-factor associated with prosthetic groups or bound to proteins. This metal, through a complex system of transporters and chaperone proteins, is tightly regulated. It is implicated in hepatic disorder and neurodegenerative changes if its homeostasis is perturbed. It has capacity to spark off oxidative damage through Cu-induced cellular toxicity.

Current trends indicate that several factors, including lipid metabolism, gene expression and activation of acidic shingomyelinase, are involved in its toxicity (Lisa et al., 2014). Experimental studies confirmed that copper can induce DNA strand breaks and also oxidation of nitrogenous bases in presence of free oxygen radicals (Godwill et al., 2019). The toxicity of copper induces numerous pathologic phenomena which are deleterious to the well being of humans (Amor and Tariq, 2021). Albeit copper plays critical functions such as being a co-factor in some redox reactions, excess predisposes to cellular components. It can induce not only oxidative stress but DNA damage as well as reduction of cell proliferation Copper metabolism plays an important role in physiologic homeostasis. Copper toxicity, however, induces several pathologic processes that are detrimental to human health. While copper is required as an important catalytic cofactor in redox chemistry for many proteins, when present in excess, free copper ions can cause damage to cellular components.

Conclusion

The study has shown higher levels of the selected heavy metals in vegetables cultivated using industrial waste and mining pond water for irrigation. The significant concentrations of Cd, Pb and Cu in the vegetables in the area of study, which are routinely used in making portage, soups and local salads, predispose consumers to ailments such as cancer, cardiovascular diseases, inhibition of the heme biosynthesis pathway, hemolysis and febrile reactions owing to their respective toxicities. The use of industrial effluents (waste water) and mining ponds water for irrigation purposes by farmers should be banned by Government. This is because consumption of vegetables irrigated on such farmlands with water from mining ponds or industrial effluents puts the consumers at risk of heavy metals poisoning. Crops should not be cultivated on farmlands within the vicinities of mining ponds and industries to check the exposure to these toxic metals. Heavy metals are non biodegradable. They possess long biological half-lives therefore could accumulate to toxic concentrations.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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