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Levels of heavy metals and their health risk assessment from wastewater irrigated spinach in railway quarters, Bauchi, Bauchi state, Nigeria

RK Adebayo[1], UF Hassan[2*], HM Adamu[3], HF Hassan[4], Haruna Baba[5], DA Ajiya[6]
[1, 2, 3, 6] Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi, Bauchi, Nigeria
[4] Department of Community Medicine, Aminu Kano Teaching Hospital, Kano, Nigeria
[5] Department of Chemistry, College of Education, Minna, Niger, Nigeria

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Abstract
Scarcity of irrigation water can affect human health and economic development. Increase in industrial activities has led to the discharge of wastewater in large quantities which is used for the cultivation of vegetables in urban areas due to unavailability of clean water. Health problems in humans arise as a result of the consumption of vegetables contaminated with heavy metals. The health risk assessment of heavy metals through consumption of contaminated spinach (*Amarantus caudatus*) grown with wastewater of Railway Quarters was evaluated. The results obtained from the study area revealed that the wastewater and spinach respectively collected from Railway Quarters contain some amount of heavy metals. The concentrations (µg/cm^3) of cadmium (0.01), chromium (0.01), manganese (0.05), nickel (0.03) and lead (0.02) in the wastewater studied are within the threshold limits of SON (2002, 2007), Indian standard limits, NAFDAC (2001), WHO (2011) and FAO (1985). The concentration of the observed copper (0.10 µg/cm^3) exceeded the recommended limits set by Indian Standard (0.05 µg/cm^3). The levels (mg/kg or µg/g) of cadmium (1.00), chromium (1.65), copper (7.70), manganese (12.65) and nickel (7.70) in spinach sample are all within the permissible limits set by various standard regulatory organizations, but the level of lead (6.60) assayed is far greater than the permissible and safe limit (2.50) of Indian Standard. The observed Health Risk Index (HRI) of cadmium (0.3000), chromium (0.0003), copper (0.2150), manganese (0.1240), nickel (0.1250) and lead (0.5000) are all less than 1.0000 which signifies that the spinach sample cultivated in Railway irrigation farm are relatively safe for human consumption.

Keywords: *amarantus caudatus*, heavy metals, health risk index, threshold limits

Introduction

Cultivation of vegetables in cities serves as a source of income to farmers and this plays a significant role in the nutritional requirement of the city. Growing of vegetables depend on the availability of ground, surface water or rain. A major restriction to vegetable farmers in Railway Quarters and its surrounding communities is the unavailability of fresh water for agricultural purpose. Vegetables are needed for human nutrition and health, especially as dietary fibre, folic acid, niacin, minerals, pyridoxine, thiamine and vitamin C, their biochemical function and anti-oxidative effects. The most important area of food quality assurance is the adulteration of food items with heavy metals [1]. Vegetables absorb metals from adulterated soils, apart from deposits on the part of vegetables exposed to polluted air [2]. Vegetable roots absorb heavy metals which pile up in their edible parts at high enough concentrations [3]. A major source of heavy metals adulteration is anthropogenic activities which include emission from vehicles, industries and agricultural crop residue. In general, certain quantities of useful nutrients and heavy metals are present in wastewater used for irrigation [4].The consumption of vegetables adulterated with heavy metals may cause health problems to humans. Heavy metals are dangerous due to their non-biodegradable nature, long biological half-lives and their ability to proliferate in various body parts [5]. Long term consumption of food items that are contaminated with heavy metals can lead to accumulation of heavy metals in the kidney and liver of human beings resulting in different disorders in many biochemical processes that could result also in kidney, bone cardiovascular and nervous diseases [6]. The human health risk as a result of the consumption of vegetables is based on the amount of vegetables eaten and the mass of the individual consumers. Long – term consumption of heavy metals with low levels has negative impact on the health of humans. After exposure for many years, the effect becomes visible [7, 8, 9]. Prolonged application of adulterated water for the irrigation of vegetables can facilitate increase in the levels of heavy metals in soils and their consequent transfer to crops under cultivation, with concentrations of adulteration that is greater than the recommended limits [10]. Vegetables grown in soils polluted with venomous heavy metals absorb such metals and store them in their edible and non-edible parts in large quantities that are capable of causing clinical problems to both animals and human beings that eat these contaminated vegetables because there is no means to eliminate them from the human body [11]. Heavy metals aggregation in soil can decrease soil quality, lower crop yield and the quality of agricultural products irrespective of their origin and can also have effects on the health of animals, human and the ecosystem [12]. The aim of this research work is to determine the levels of heavy metals and their risk assessment from wastewater irrigated spinach in Railway Quarters of Bauchi, Bauchi state, Nigeria.

2. Materials and Methods

Chemicals of analytical reagent grade purity and distilled water were used in the preparation of all the solutions. The equipment used for this research work was Bulk Scientific Atomic Absorption Spectrophotometer Model 210 VGP.

2.1 Experimental Site Bauchi State is in North-East geo-political zone of Nigeria and was created in 1976. The State is located between latitudes 9^0 30' and 12^0 30' North of equator and between longitudes $8^0$45' and $11^0$0' East of the Green Wich Meridian. There are 20 Local Government Areas in the State namely: Alkaleri, Bauchi, Bogoro, Dambam, Darazo, Dass, Gamawa, Ganjuwa, Giade, Itas-Gadau, Katagum, Kirfi, Jama'are, Misau, Ningi, Shira, Tafawa Balewa, Toro, Warji and Zaki respectively (*en.m.wikipedia.org/wiki/Bauchi-State).* The study area (Railway Quarters) is located between latitudes $10^0$17'44.8"N and longitudes $9^0$51'02.4"E.

2.2 Sampling Procedure

2.2.1 Sampling of Water

Water samples used for irrigation practices were collected from the site in pre-cleaned polyethylene bottles. The bottles were rinsed earlier with a metal-free soap, soaked in 10.00 % trioxonitrate (V) acid overnight and finally washed with deionised water [13]. The sample was brought into Chemistry laboratory for digestion.

2.2.2 Sampling of Vegetables

African spinach (*Amarantus caudatus*) was collected from an irrigation farm in Railway quarters, Bauchi where they were harvested into edible as well as non-edible parts and washed with tap water to remove some form of depositions like soil particles, debris and dirts. Edible parts of the vegetables were air-dried, ground into powder using ceramic pestle and mortar, passed through a 2 mm sieve and stored at room temperature before the analysis [14].

2.3 Digestion of Samples

2.3.1 Digestion of Vegetable Samples

A 1.00 g of ground vegetable sample (*Amaratuu caudatus*) was digested in 15.00 cm^3 of HNO_3, H_2SO_4 and $HClO_4$ mixture (5:1:1) at a temperature of 80^0C until brown fumes of trioxonitrate (V) acid was observed [15]. The resulting digest was filtered using Whatman filter paper number 1 into a 50 cm^3 volumetric flask and water added to volume.

2.3.2 Digestion of Water Sample

Water sample (50.00 cm^3) was digested with 10.00 cm^3 of concentrated trioxonitrate (V) acid at 80^0C until brown fumes were observed and the solution reduced to 10.00 cm^3 of its initial volume [16]. The digest was filtered through Whatman filter paper number 1 and diluted to 50.00 cm^3 with water. The concentrations of Cd, Mn,Cu, Pb, Ni and Cr in the sample solution were determined using Bulk Scientific Atomic Absorption Spectrophotometer Model 210 VGP at their respective wavelengths.

2.4 Quality Assurance

Chemicals used were of analytical grades and distilled water was used in the preparation of all the solutions. The glass wares used were washed with detergent solution and rinsed thoroughly with 10.00 % trioxonitrate (V) acid. The mixtures of all the reagents used were utilized to auto-zero the machine. Standard errors of the means were evaluated as measures of precision and accuracy of the results were monitored through repeated analyses.

2.5 Environmental Health Risk Assessments

2.5.1 Health Risk Assessment

The health risk of heavy metals through consumption of the vegetable (African spinach) was determined based on Transfer Factor (TF), Daily intake of metals (DIM) and Health Risk Index (HRI).

2.5.2 Transfer Factor (TF)

Transfer factor was evaluated to determine the level of risk due to wastewater irrigation and consequent heavy metal accumulation in edible parts of vegetables [17]. The soil to plants metal transfer was evaluated as transfer factor.$TF = C_{plant} / C_{soil}$,, Where C_{plant} is the concentration (mg/kg) of heavy metals in the plant and C_{soil} is the concentration (mg/kg) of heavy metals in the soil.

2.5.3 Daily Intake of Metals (DIM)

The daily intake of vegetable in adult was determined using the data that was obtained during the survey through questionnaire. The following equation was used to evaluate DIM.
$DIM = C_{metal} \text{ X } C_{factor} D_{food\ intake} / B_{average\ mass.}$ [13], where C_{metal} represents the concentration of heavy metals in the plant (mg/kg), C_{factor} is the conversion factor (0.085), $D_{food\ intake}$ is the daily intake of vegetables (kg/person) and $B_{average\ mass}$ is the average body mass (kg/person).
The average vegetable intake was calculated by conducting a survey where 100 people (male and female) having average body mass of 57.50 kg were asked for their daily intake of African spinach (*Amanrantus caudatus)* from the sampling site.

2.5.4 Health Risk Index (HRI)

To determine the human health risk index of the heavy metals, vegetables cultivated at the irrigation site were collected and analysed for the heavy metals investigated. The concentrations of the metals obtained were therefore used to calculate the health risk index (HRI). The value of health risk index depends on the daily intake of metals (DIM) and oral reference dose (Rf_D) (mg/kg/day). Rf_D is an estimated exposure of metal per day to human body that has no harmful effect during life time [18].
The health risk index of manganese, cadmium, lead, copper nickel and chromium due to eating adulterated vegetable was evaluated using the equation:
$HRI = DIM / Rf_D$ [19].
Where, Rf_D denotes the reference oral dose and DIM is the daily intake of metals. The Rf_D values of Mn, Cd, Pb, Cu, Ni and Cr are 0.033, 0.001, 0.004, 0.04, 0.02 and 1.50 (mg/kg bw/day) respectively [18]. Human beings are considered to be safe if the HRI is less than one (1) [20].

3. Results and Discussion
3.1 Results
Tables 1, 2 and 3 respectively show the levels of some heavy metals (μg/cm^3) in irrigation wastewater of Bauchi Railway Quarters, levels of some heavy metals (mg/ kg) in spinach samples of irrigation farm in Railway Quarters, Bauchi as well as the levels of daily intake of metals (DIM), reference oral dose (Rf_D), health risk index (HRI) and transfer factor (TF).

Table 1: Levels of Some Heavy Metals (μg/cm^3) in Irrigation Wastewater of Railway Quarters, Bauchi

Heavy Metals	Concentration
Cd	0.01 ± 0.00
Cr	0.01 ± 0.00
Cu	0.10 ± 0.00
Mn	0.05 ± 0.00
Ni	0.03 ± 0.00
Pb	0.02 ± 0.00

Values are mean ± standard error of the mean (n = 3)

Table 2: Levels of Some Heavy Metals (mg/kg) in Spinach Sample of Irrigation Farm in Railway Quarters, Bauchi

Heavy Metals	Concentration
Cd	1.00 ± 0.00
Cr	1.65 ± 0.00
Cu	7.70 ± 0.00
Mn	12.65 ± 0.00
Ni	7.70 ± 0.00
Pb	6.60 ± 0.00

Values are mean ± standard error of the mean (n = 3)

Table 3: Levels of Daily Intake of Metals, Reference Oral Dose, Health Risk Index and Transfer Factor

Heavy Metals	DIM	Rf_D	HRI	TF
Cd	0.0003	0.0010	0.3000	1.0100
Cr	0.0005	1.5000	0.0003	0.1500
Cu	0.0086	0.0400	0.2150	0.0300
Mn	0.0041	0.0330	0.1240	0.0800
Ni	0.0025	0.0200	0.1250	0.1100
Pb	0.0020	0.0040	0.5000	0. 2300

3.2 Discussion
3.2.1 Levels of Heavy Metals in Irrigation Wastewater
The levels of heavy metals in irrigation wastewater of Railway Quarters of Bauchi are summarized in Table 1. The observed level of cadmium is 0.01μg/cm^3. This value is lower than literature value of 0.02 mg/dm^3 (0.02 μg/cm^3) reported by Ftsum and Abraha, 2018 [21]. The value is also lower than the permissible limit (0.03 μg/cm^3) of cadmium in water [22], but is in good agreement with the Indian Standard safe limit (0.01 μg/cm^3) of cadmium in water [23]. The concentration (0.01μg/cm^3) of cadmium may be due to the presence of lubricating oils and / or old tyres as well as the rough surfaces of our roads that can increase the wearing of tyres. Chronic exposure of cadmium may lead to renal dysfunction, increasing incidence of some forms of cancer and calcium metabolism disorder [24]. The concentration of chromium in the wastewater sample investigated was found to be 0.01 μg/cm^3. The experimental value is lower than literature values (μg/cm^3) of 0.053 and 0.18 [21, 23]. Comparatively, the observed value of chromium is lower than permissible limits of 0.05 μg/cm^3 in water respectively set by Indian Standard, NAFDAC, 2001; SON, 2002; SON, 2007 and WHO, 2011[22, 23, 25, 26, 27]. The toxic behaviour of chromium in the environment is rare, but it can cause some risks to human health because it can accumulate in lungs, muscle fat, skin, hair, liver, nails, dorsal fin and placenta, where this can be responsible for different health conditions in human beings [28]. The sources of chromium may be from cement, leather, dyes, paints, detergents, water erosion of rocks, municipal waste and wood preservatives [28, 29]. The concentration of copper found in the irrigation wastewater sample of Railway Quarters, Bauchi was 0.10 μg/cm^3. This value is the highest concentration of all heavy metals determined. The level of copper found is greater than 0.07μg/cm^3 [21] as well as 0.05 μg/cm^3 Indian Standard safe limit of copper in water [23]. Too much copper can be life-threatening to both man and other forms of animals since it reduces enzyme activity and when suddenly released from hepatic storage into the blood stream can cause anaemia, hemolysis and icterus [30]. 0.05 μg/cm^{3}of manganese was assayed in the sample. This value compares favourably well with 0.05 μg/cm^{3}manganee value in wastewater of Khaji Wala Kha [31]. The observed value has a very good agreement with the same 0.05 μg/cm^3 [22], but lower than Indian Standard safe limit of 0.10 μg/cm^3 [23] as well as 2.00, 0.20 and 0.40 μg/cm^3 [25, 26, 27]. Manganese occurs naturally in many surface and ground water sources and even in soils that erode into the waters [32]. Manganese is important for the normal physiological functioning of humans as well as animals. Exposure of manganese at low levels in the diet is regarded as nutritionally important in human health [33]. The concentration of nickel determined in wastewater sample of Railway Quarters of Bauchi was 0.03 μg/cm^3. This value is lower than literature value of 0.07 μg/cm^3 determined in wastewater sample of Dinapur Area [34] as well as 0.06 μg/cm^3 found in wastewater irrigated area of Varanasi, India [23]. The observed value of nickel (0.03 μg/cm^3) is lower than the Standard FAO, 1985 nickel value of 0.20 μg/cm^3 [23]. Nickel can cause allergic reactions in humans and in extreme cases this may lead to degenerative respiratory disease that can be fatal [35].The concentration of lead (0.02 μg/cm^3) determined in the study area is less than lead value of 0.03 μg/cm^3 found by Ftsum and Abraha, 2018 [21] and also far less than literature value of 0.09 μg/cm^3 [23]. The value of lead determined in the present study is comparatively far less than the Indian Standard value of 0.10 μg/cm^3 reported by Singh *et al*., 2010 [23]. Lead has negative influence on both children and adults. It can also affect the physical and mental growth of children [36].

3.2.2 Levels of Some Heavy Metals (mg/kg) in Spinach Sample in the Study Area
The levels of some heavy metals (mg/kg) in spinach sample of irrigation farm in Railway Quarters, Bauchi are depicted in Table 2. The concentration of cadmium determined in the study area is 1.00 mg/kg, which is lower than reported literature value of 1.80 mg/kg [21]. The observed value of cadmium is however greater than another literature value of 0.022 mg/kg [37]. This variation may be as a result of increasing use of sewage water for irrigation farming in the study location. The observed value (1.00 mg/kg) is comparatively lower than the Indian standard safe limit of cadmium (1.50 μg/g or 1.50 mg/kg) in plants as reported by Singh *et al*., 2010 [23]. The high level of cadmium in the spinach may be due to the release of wastewater from the bridge in which various

vehicles are washed, improper dumping of domestic wastes and sewage from different houses into the irrigation soil that accumulated in the plant material. Another source of cadmium may be due to the presence of phosphate fertilizers in the wastewater, which consequently accumulated in the soil and plant [38]. Cadmium in small amounts can lead to adverse changes in the arteries of human kidney. It also biochemically replaces zinc and can therefore cause high blood pressure and kidney damage [39]. The level of cadmium assayed in the spinach sample is 1.65 mg/kg. In a similar study, Ftsum and Abraham, 2018 [21] reported a high chromium concentration of 13.50 mg/kg. The observed value of chromium is also comparatively lower than 3.69 µg/g or 3.69 mg/kg found for radish in wastewater irrigated soil [23]. The level of chromium in the present study is far less than the Indian Standard safe limit of chromium in plants (20.00 µg/g or 20.00 mg/kg) reported by Singh *et al*., 2010 [42] as well as the standard limit (2.30 mg/kg) established by FAO/WHO, 2011 [40]. The most common forms of chromium are chromium (III) and (VI). Chromium (III) is an important part of a balanced diet in both animals and human beings and its deficiency can lead to disturbance in lipid and glucose metabolism in human beings, whilst chromium (VI) is said to be carcinogenic [41]. A 7.70 mg/kg copper level was determined in the spinach investigated. The experimental value in the present study is far less than reported literature copper values of 16.70 mg/kg [21] and 13.75 mg/kg or 13.75 µg/g [23]. The observed level of copper is also far less than the Indian Standard safe limit (30.00 µg/g) of copper in plants [23] as well as the Standard safe limit of 70.00 mg/kg (70.00 µg/g) established by FAO/WHO, 2011 [40]. The concentration of copper determined in the spinach has therefore not reached an unacceptable limit that can cause phyto-toxicity. The primary effects of copper on humans are damage to organs and liver [42]. A 12.65 mg/kg manganese concentration was determined in the analyte. It is the highest of all the metals determined in the vegetable sample. In a related research, Rilwan *et al*., 2019 [43] determined the concentrations of manganese in *Allium cepa* of Gwallaga irrigation site (28.80 mg/kg) and that of Gombe road irrigation site (23.30 mg/kg). The determined value of manganese is comparatively much lower than the above two values and that of FAO/WHO, 2007 Standard value of 500.00 mg/kg reported by Rilwan *et al*., 2019 [43]. At higher concentrations, manganese is toxic with some degrees of neurological effects [44]. A 7.70 mg/kg of nickel was found in the spinach sample. The observed value falls within the nickel range of 5.55 to 15.00 µg/g or 5.55 to 15.00 mg/kg [34]. The level of nickel determined (7.70 mg/kg) is far less than the Standard safe limit of 67.00 mg/kg specified by FAO/WHO, 2001[45]. Excess concentrations of nickel can cause lung disease and eventually death in dogs [35]. The level of lead determined in the test sample is 6.60 mg/kg, which is lower than 12.20 µg/g or 12.20 mg/kg lead found in radish [23]. Tsafe *et al*., 2012 [46] determined a higher level (44.5875 mg/kg) of lead. The observed value of lead in the present study is far greater than the Indian Standard safe limit of lead (2.50 µg/g or 2.50 mg/kg) in plants [23]. The toxic effects of lead has multiple biochemical effects such as such as competing with calcium for incorporation into bones and this can interfere with nerve transmission and the Development of the brain [47].

3.2.3 Daily Intake of Metals (DIM)

The daily food intake (0.22 kg/person/day) of the inhabitants/consumers was obtained from the questionnaire given to them. The daily food intake, average body mass (57.50 kg) and conversion factor of 0.085 was used to compute the DIM of the elements. The degree of toxicity of heavy metals to human being is based on their daily intake. A DIM of 0.0086 was found in Cu, followed by Mn (0.0041), Ni (0.0025), Pb (0.0020), Cr (0.0005) and Cd (0.0003). The higher DIM values of Cu, Mn and Ni could be due to the high levels of the metals in the spinach vegetable.

3.2.4 Health Risk Assessment of Irrigation Farm of Railway Quarters

Heavy metals can get into plants when they are in the form of solution. The Transfer Factor (TF), a role of both soil and plant characteristics was used to evaluate the heavy metals transferred from soil to plant. Table 3 shows the Daily Intake of Metals (mg/kg), Health Risk Index (HRI) and Transfer Factor (TF) from soil to spinach. As indicated in Table 3, the trend of TF was Cd > Pb > Cr > Ni > Mn > Cu. The high TF values of Cd and Pb indicated the high metal adulteration of the vegetable by anthropogenic activities such as various metal works and discharge of wastewater from the washings of various vehicles which flows into farmlands [48].

3.2.5 Health Risk Index (HRI)

The harmful effect of heavy metals to the consumers of the vegetable (spinach) which is contaminated with those heavy metals was denoted by HRI. People are considered to be safe to feed on the vegetable if the value of HRI is less than 1. As summarized in Table 3, the HRI values of the metals of interest were all less than 1. The high values of HRI of lead (0.5000) and cadmium (0.3000) obtained in the present study agreed with the HRI of Pb and Cd as reported by Ftsum and Abraha (2008) [21] on the health risk assessment of heavy metals via consumption of spinach grown in Elalla River. Similarly, the HRI of Pb and Cd are higher in comparison with other metals. The spinach samples cultivated in the irrigation farm are therefore safe for human consumption since all the HRI values are less than one (1.00). However, prolong use of the irrigation wastewater for the purpose of irrigation farming may lead to increase in the levels of the metals investigated, consequently an increase in the HRI and this will invariably pose health risk and dangers to the consumers of the vegetables (spinach) with time.

4. Conclusion

The results of this study based on DIM and HRI revealed that consumption of the spinach (vegetable) cultivated in Railway Quarters irrigation farm was risk free for all the heavy metals assayed. Although, the values of all the HRI was below one, the prolong use of the wastewater for irrigation farming may lead to heavy metals contamination that may result in health risk to consumers. Based on the present study, it is therefore evident that consumption of spinach from the Railway Quarters irrigation farm of Bauchi is safe for human consumption.

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