Determination of Heavy Metals in Selected Vegetables Obtained from Some Irrigation Areas in Katsina State, Nigeria

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Abstract
The study is aimed at measuring the concentration of Cd, Fe, Ni and Cu in some vegetables obtained from K/Durbi, K/Sauri and Rafukka irrigation areas in Katsina metropolis using the atomic absorption spectrometer. The samples were collected using standard procedures. The results showed high levels of Cu in all the three locations in spinach with a value of 2.103±0.364 mg/g in K/Sauri, 1.785±0.528 mg/g in K/Durbi and 0.220±0.014 mg/g in Rafukka. Cu values in cabbage were 1.409±0.251 mg/g in K/Sauri, 0.261±0.036 mg/g in K/Durbi and 0.018±0.0091 mg/g in Rafukka. Cd level in spinach was 1.677±0.079 mg/g in K/Sauri, 1.067±0.916 mg/g in K/Durbi and 0.070±0.010 mg/g in Rafukka. In cabbage, Cd values were 0.620±0.020 mg/g in K/Sauri, 0.563±0.060 mg/g in K/Durbi and 0.036±0.0021 mg/g in Rafukka. The levels of Fe in spinach were 1.080±0.013 mg/g, 1.022±0.0077 mg/g and 0.017±0.0056 mg/g in K/Sauri, K/Durbi, and Rafukka respectively. K/Sauri had 0.491±0.313 mg/g, K/Durbi 0.431±0.007 mg/g and Rafukka 0.029±0.0097 mg/g in cabbage. Ni level in spinach was 0.951±0.066 mg/g in K/Sauri, 0.713±0.061 mg/g in K/Durbi and 0.077±0.0023 mg/g in Rafukka. Cabbage had 0.746±0.043 mg/g in K/Durbi, 0.113±0.019 mg/g in K/Sauri and 0.038±0.0076 mg/g in Rafukka. Rafukka had lower values of all the metals than the other two sites in both cabbage and spinach which may be an indication that the activities taking place around the areas are responsible for the high levels. All the values were above the WHO/FAO tolerable limits except Cu in cabbage and Fe in spinach obtained from Rafukka.

Keywords: Heavy Metal, Irrigation, Vegetables, Determination

Introduction
The environment is a natural system that encompasses the relationship between relief, vegetation, plant, animal, man and the physical world (Robinson, 1998). Konz-Lisi and Frieble (1998) observed that the environment is constantly being spoiled and rendered very unsafe for human habitation and other organism. This unhealthy environment is brought about through the various activities of man such as mineral exploitation, agricultural practices, industrial production, and food processing, social, domestic and commercial activities. However, the misleading of these activities result in environmental pollution (Robinson, 1998). Advance in technology has led to high levels of industrialization and urban migration leading to the discharge of effluents containing heavy metals in our environment. The various activities of man in recent years have increased the quantity and distribution of heavy metals in the atmosphere, land and water bodies (Zurera-cosano, 2008). Heavy metals are usually present at levels as low as part per billion (ppb) in a polluted or moderately polluted natural source, but biological system accumulate these metals by factor as high as 1000times more (Ademorati, 1996). This accumulation is passed on to the food chain in part per million(ppm) or higher concentration in soil, absorbed by plants, consumed by man in very much.
accumulated amounts and will continue to buildup. The most dangerous and serious implication of these bioaccumulation is that symptoms of heavy metals poisoning may not appear or may not be identified until several years of continuous exposures and intake (Edward and Kuo, 2006). On appearance of these symptoms, they will not be traced back to the correct original cause or source. The said source may have been a regular and delicious diet such as fruits and vegetables, fish or drinking water. Therefore communities relying greatly on a contaminated diet become particularly exposed to the danger of long term chronic heavy metal poisoning (Edward and Kuo, 2006).

In fact humans and many animals have become dependent on vegetables as a source of food (Sobukola, et al., 2007). Leafy vegetables occupy a very important place in the human diet and act as neutralizing agents for acidic substances formed during digestion (Thompson and Kelly, 2000). Vegetables used as food include those used in making soup or served as integral parts of the main sources of a meal (Ihekeronye, 2008). Vegetables constitute an essential dietary component by contributing protein, vitamins, iron, calcium, and other nutrients which are usually in short supply (Thompson and Kelly, 2000). When vegetables are included in the diet, there is found to be a reduction in the incidence of cancer, stroke, cardiovascular disease and other chronic ailments (Yusuf and Oluwale, 2009). Research has shown that, compared with individuals who eat less than three (3) servings vegetables each day, those that eat more than five servings have an approximately 20% lower risk of developing coronary heart disease or stroke (Thompson and Kelly, 2000). As human activities increases, especially with the application of modern technologies, pollution and contamination of the human food chain has become inevitable (Yusuf and Oluwale, 2009).

Heavy metals contamination of the food items is one of the most important aspects of food quality assurance (Radwan and Salama, 2006). Water contamination by heavy metals in some areas is practically inevitable due to natural process (weathering of rocks) and anthropogenic activities (industrial, agricultural and domestic effluents) (Radwan and Salama, 2006).

Materials and Method
Wastewater from the industries of mining, electroplating, paint, or chemical laboratories, often contains high concentrations of heavy metals, including cadmium (Cd), copper (Cu), and lead (Pb). These elements, at concentrations exceeding the physiological demand of fruits and vegetables, not only could administer toxic effect in them, but also could enter food chains, get biomagnified and pose a potential threat to human health (Sharma, et al., 2010). Heavy metals contamination in agricultural soils from wastewater irrigation is of serious concern due to its implications on human health (Sharma, et al., 2010). Fruits and vegetable can absorb metals from soil as well as from deposits on the parts of the plants exposed to the air from polluted environment (Sharma, et al., 2010).

This study aims to determine the levels of some metals in selected vegetables (spinach, cabbage) samples from K/Durbi, K/Sauri and Rafukka area of Katsina metropolis, Katsina state. Samples of spinach and cabbage, sample bottles, measuring cylinder, funnel, volumetric flask, beakers, Whatmans Filter Paper, Masking Tape, Hot Plate, Beam Balance Electrical and AAS, Machine.

Study Sites
The study areas covered in this study were Kofar Durbi, Kofar Sauri and Rafukka quarters in Katsina metropolis, Katsina state, Nigeria. Katsina is a city in northwestern Nigeria. It is the capital of Katsina state one of Nigerians’ 36 states (Nkromah, 2007). The global location of the state is between Latitude 12°15' north of the equator and Longitude 07°30' east of the Greenwich Meridian with a total area of 24,192 km². Katsina has a semi-arid climate (Nkromah, 2007). The town has a lot of registered and unregistered small and large scale industries, companies, and business organizations which includes milling and processing, steel rolling, block industries, sells of cement/depot, bakeries, printing press, filling stations, private and public hospitals, abattoir, motor vehicle repairs and blacksmith operations.
Random sampling technique was used in obtaining the fruit and vegetable samples from the selected irrigation areas. The sampling was conducted by handpicking the representative samples randomly from different location within each sampling area and were then thoroughly mixed to get homogeneous representative samples, then stored in a plastic container, labeled and transported immediately to the laboratory for processing.

Sample Preparation
In the laboratory, each of the fruit and vegetable samples were washed with tap water and thereafter with distilled water. The samples were then cut into nearly uniform size. The cut pieces were placed in a clean acid washed porcelain crucible according to label and oven dried at 105°C for 24hr until they were brittle and crisp. All samples in labeled crucible were grinded according to label using acid washed mortar and pestle and sieved to obtain fine powder.

Digestion
10.0g of the powdered samples in crucibles were placed into muffle furnace heated at 500°C for four (4) hours. The samples were removed and allowed to cool. 10ml of 3 M HCl was added to 0.5g of the resulting ash in a beaker, covered and heated on a steam bath for 15minutes. 1ml of concentrated HNO₃ was added and evaporated to dryness by continuous heating for 1hour. Finally 5ml of 6 M HCl and 10ml of distilled water were then added and the mixture was heated on a steam bath to complete dissolution. It was cooled and filtered into 50ml volumetric flask made up to the mark with distilled water, and then transferred into the sample bottles of 60ml sizes prior to elemental analysis (Akan, et al., 2013).

Preparation of Calibration Curve
Standard working solutions ranging from 0.1 to 10 mgdm⁻³ were each prepared from the Cd, Fe, Ni and Cu stock solutions of 1000mgdm⁻³ by further dilution using deionized water. Each standard solutions and blank were directly aspirated into the flame. The absorbencies’ were recorded and plotted against the concentrations. The nebulizer, atomizer, and burner were flushed each time with distilled water after each sample solutions were aspirated before the next. The element selection on the A.A.S, machine in the drop down box (cathode lamp) was continuously changed before measurement of the next element (Akan, et al., 2013).

Elemental Analysis of the Vegetable Samples
Determination of Cd, Fe, Ni, and Cu were carried out directly on each final solution in the sample bottles using VGP210 Atomic Absorption Spectrophotometer Machine (A.A.S). The metal absorbance’s were recorded and converted to concentration in mg/g by using the Beers Lambert Laws relationship of linear equation Y = mx.

Result
The metal contents obtained from the three (3) irrigation sampling sites are shown in Figure 2 and 3.

![Figure 2: Average concentration of Cd, Cu, Fe and Ni in Spinach Sample obtained from K/Durbi, K/Sauri and Rafukka irrigation sites of Katsina Metropolis, Nigeria.](image-url)
Figure 3: Average concentration of Cd, Cu, Fe and Ni in Cabbage Sample obtained from K/Durbi, K/Sauri and Rafukka irrigation sites of Katsina Metropolis, Nigeria.

Discussion

Cadmium

The average Cadmium levels in spinach was highest in samples collected from K/Sauri with a value of (1.677±0.079 mg/g), K/Durbi had (1.067±0.916 mg/g), and the lowest value of (0.070±0.010mg/g), was obtained in samples collected from Rafukka. The values obtained for cabbage are lower than those of spinach with (0.620±0.020 mg/g), in K/Sauri, (0.563±0.060mg/g) in K/Durbi and (0.036±0.0021mg/g) in Rafukka. All the values obtained are higher than the 0.010 mg/g set by WHO/FAO. The values for both vegetables are lowest in the samples obtained from Rafukka. This may be an indication that the activities such as car repairs, metal works, carried out in K/Durbi and K/Sauri may have contributed to the concentration of the metals since such activities are nonexistence in Rafukka. ANOVA indicated as significant difference between the values obtained in the different sites (P<0.05). The values were however lower than those obtained by Farooq, et al., (2008) in spinach and cabbage with values 35 mg/g and 73 mg/g respectively. Cadmium is a non-essential element in foods and natural waters and it contributes principally in the kidneys and liver (Divrikli, 2006). High levels of cadmium could be due to the application of municipal solid wastes in farmlands as well as the use of other agrochemicals and high levels of cadmium in the soil within the sampling points could pose serious health risk in the environment. Long-term toxicity can cause kidney diseases (Waziri., 2013).

Copper

The highest average amount of copper metal was found in spinach from K/Sauri (2.103±0.364mg/g), followed by K/Durbi (1.785±0.528mg/g) and then that of Rafukka (0.220±0.014 mg/g). The values obtained for cabbages are lower than those of spinach with (1.409±0.251 mg/g) in K/Sauri. K/Durbi (0.261±0.036mg/g) and Rafukka (0.018±0.0091 mg/g). ANOVA indicated as significant difference between the values obtained in the different sites (P<0.05). On comparing with the recommended level of copper 0.130 mg/g by WHO/FAO, (2010) and copper level in spinach (1.90 mg/g) obtained in the literature by Omotayo, et al., (2014). It was indicated that the samples analyzed in this study have greater amount of copper. Copper is an essential micronutrient which functions as biocatalyst, required for body pigmentation in addition to iron, maintain a healthy central nervous system, prevents anemia and interrelated with the function of zinc and iron in the body (Divrikli, 2006). Copper toxicity induces iron deficiency, lipid peroxidation and destruction of membrane (Zaidi, et al, 2005). High concentration of copper in spinach from K/Sauri can be attributed with addition of pollutant like the waste from the industrial mining, steel rolling company, urban waste, motor worn out parts in custom’s barrack, motor vehicle repairs waste that are being discharged into the environment with little or no treatment which may have impact on the vegetables as well as uses of such water.

Iron

The highest average amount of iron metal was observed to be in spinach from K/Sauri (1.080±0.013 mg/g) which is slightly greater than K/Durbi (1.022±0.0077 mg/g) and widely greater than that of Rafukka (0.017±0.0056mg/g). The values obtained for cabbage are lower than those of spinach with K/Sauri (0.491±0.313 mg), KDurbi (0.431±0.007 mg/g) and Rafukka (0.029±0.0097mg/g). ANOVA indicated as significant difference between the values obtained in the different sites (P<0.05). On comparing the high spinach value of Iron (1.080±0.013 mg/g) in this study and the iron contents 3.73 mg/g in spinach obtained by Funtua, et al., (2008), the vegetable samples have a low level of Iron. The values are however higher than the Iron recommended limit of 0.026 mg/g by WHO/FAO, 2010. Iron is an essential element for human life; it is a
component for haemoglobin in blood. Overdoses of ingested iron can cause excessive levels of free iron in the blood. Ferrous iron react with peroxides to produce highly free radicals that can easily damage DNA, proteins, lipids and other cellular components, causing adverse effects which include coma, metabolic acidosis, shock and even death (Kikuchi, 2005). The high concentrations of iron recorded by all the samples analyzed, could be attributed to its role in chlorophylls synthesis in plants in addition to its relative abundance in the each (Audu, et al., 2005).

Nickel

The spinach that was obtained from K/Sauri (0.951±0.066 mg/g) has the highest average amount of nickel metal compared to K/Durbi (0.713±0.061 mg/g) followed by Rafukka (0.077±0.023 mg/g). The values obtained for cabbage are lower than those of spinach with (0.746+ 0.043 mg/g) in K/Durbi, K/Sauri (0.113±0.019 mg/g) and Rafukka (0.038±0.0076 mg/g). ANOVA indicated as significant difference between the values obtained in the different sites (P<0.05). On comparing the nickel levels 0.020 mg/g recommended by WHO/FAO., (2010) and the value obtained by Sobukola, et al., (2010) in the literature 130 mg/g in cabbage, it was observed that the samples from K/Durbi, K/Sauri and vegetables from Rafukka have higher nickel contents than that of WHO, (2010) and having lower than that obtained by Sobukola, et al., (2010). Nickel also plays some role in body functions including enzyme functions. It is valuable in modern times chiefly in alloys and is widely used in coins and jewelry (Das, et al., 2008). It occurs naturally more in plants than in animal flesh. It activates some enzyme systems in trace amount but its toxicity of high levels is more prominent (Divrikli, 2006). The high level of nickel could be attributed with usage of wastewater for irrigation in K/Durbi and K/Sauri areas.

Conclusion

The spinach and cabbage are very important part of a diet. With increasing health consciousness and the growing number of vegetarians nowadays, environmental safety is a very important issue. The metals (Cd, Ni, Cu and Fe) analyzed in the vegetables obtained from K/Durbi, K/Sauri and Rafukka were all analyzed and detected. The result of this study indicates the pollution tendencies of spinach, cabbage and perhaps other growing vegetables crops within the same vicinity. The values obtained in samples collected from Rafukka are lower than those of K/Sauri and K/Durbi in both spinach and cabbage. This may be attributed to the use of hand-dug well for irrigation in Rafukka unlike K/Sauri and K/Durbi were waste water is used in irrigation. The activities carried out around the areas might also have contributed to the values obtained. All the values obtained are higher than the WHO/FAO values. The results further indicate that continued discharge of domestic waste and other effluents into the river following through the K/Durbi and K/Sauri irrigation areas may enter into food chain putting consumers of these vegetables at risk from ingestion of these toxic metals at unacceptable level.

RECOMMENDATION

- Researches on remediation studies of soil samples in the irrigation areas should be encouraged.
- It is recommended that government should provide alternative source of water to the affected irrigation areas.
- There should be proper monitoring and evaluation of environmental health more especially with regards to municipal sewage by the authorities concerned.

REFERENCES


