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Determination of Some Heavy Metals in Selected Vegetable Grown in Ajiwa and Jibia Irrigation Sites of Katsina State, Nigeria

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Abstract
In this study, Micro Plasma Atomic Emission Spectroscopy (MP-AES) was used to determine the concentration of some heavy metals in the selected vegetables (Pepper and Tomato). Zinc, cadmium, copper, nickel, cobalt, lead, manganese and chromium contents were analyzed and compared with WHO/FAO specified maximum limit/levels. The mean concentration (mg/kg) with standard deviations of the heavy metals in the selected vegetable samples (pepper and tomoto) are, Zinc (23.68±0.58, 31.33±0.58, 28.67±1.15 and 25±0.01); Cadmium (ND, 1.00±0.01, 1.00±0.01 and 1.00±0.01); Copper (3.00±0.01, 7.00±0.01, 7.00±0.01, and 7.33±0.58); Nickel (1.00±0.01, 2.00±0.01, 4.00±0.01 and 3.00±0.01); Cobalt (1.00±0.01, 1.00±0.01, 3.67±0.58 and ND); Lead (5.00±0.01, 8.00±0.01, 2.67±0.58 and 1.00±0.01); Manganese (32.33±0.58, 24.00±0.01, 24.00±0.01, and 29.00±0.01); and Chromium (2.67±0.58, 3.33±0.58, 3.33±0.58 and 3.33±0.58) for Ajiwa and Jibia irrigation sites respectively. Concentrations above WHO permissible limits for few metals including cobalt, nickel and manganese were detected in both pepper and tomoto samples cultivated in the two irrigation sites probably due to the use of agro-chemicals containing trace amounts of metals coupled with those metals that may be present in the soil or contaminated dam water. However, most metals (Zn, Cd, Cu and Cr) analyzed are within the permissible limits set by

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standard organizations and therefore the vegetables are safe for human consumption after preparation.

Keywords: Agro-chemicals, Heavy metals, Irrigation sites, Micro Plasma Atomic Emission Spectroscopy (MP-AES), Vegetables

INTRODUCTION

Vegetables constitute an important part of the human diet as they contain carbohydrates, proteins, as well as vitamins, minerals and trace elements (Awode *et al.,* 2008). Vegetables may be contaminated through irrigation by heavy metal contaminated water (Nayek *et al.*, 2010). It is thus desirable to keep irrigation water resources relatively free from such metals. In many countries such as Jordan, Serbia, Nigeria and some parts of India, freshwater resources are limited, and the use of wastewater has become necessary (Surdyk *et al.*, 2010). Heavy metals are also generally present in agricultural soils at low levels. Due to their cumulative behavior and toxicity, however, they have potential hazardous effects not only on crop plants but also on human health (Awode *et al.,* 2008). According to Surdyk *et al.* (2010), there is no risk of heavy metal contamination in vegetables when irrigated with heavy metals contaminated water. However, it was found that irrigating crops with wastewater elevated the health risk (Akbar *et al.,* 2010). Thus, wastewater treatment is a significant yardstick that ensures the safety of the water before irrigation and the quality of dam water should be properly monitored.

In another study conducted in urban areas of Uganda, the researchers reported that crops grown on contaminated soils and treated with heavy metal contaminated water could be consumed provided these vegetables were properly washed before cooking (Nabulo *et al.*, 2010). Although excess levels of essential elements, such as zinc, in vegetables, could help in boosting consumer's immune system, excess levels of cadmium, lead and other dangerous metals may adversely affect the consumer as they bio-accumulate in the body (Maryke, 2012).

It thus become paramount that the vegetables grown through irrigation system be assessed to checkmate any disastrous consequences they stand to pose due to metal accumulation in human system.

The aim of the present research is to assess metal levels in vegetables irrigated at Ajiwa and Jibia dams of Katsina state of Nigeria and compared with acceptable limits established by standard organizations (WHO and FAO). The significance of this research is to provide current information on metal levels in the vegetables irrigated in Ajiwa and Jibia dams to the end users.

MATERIALS AND METHODS

Sampling Area

The two irrigation sites are Ajiwa and Jibia dams of Katsina State. The Ajiwa dam lies on the coordinate 12° 55'51" N 7° 45'31" E in Batagarawa local government area of Katsina state while the Jibia dam lies on the coordinates 13° 04'09" N 7° 13'31" E located in Jibia local government area of Katsina state.

Sample Collection
Vegetable samples (Pepper and tomato) commonly cultivated in the sampling areas were randomly purchased from the rural farmers in the sampling areas and later homogenized to get representative samples.

Sample preparation
The vegetable samples were thoroughly washed with distilled water to remove any soil particles and air-dried for two weeks to remove excess moisture. Samples were then ground in a porcelain mortar with a pestle and passed through a ten-mesh sieve. During digestion, 1 g of each sample was added into a cleaned Pyrex beaker (250 cm^3) followed by 10 cm^3 of tri-acid mixture (HNO_3, $HClO_4$ and H_2SO_4 at 1:1:1 ratio). The mixture was kept for 24 hours and then heated on a hot plate in a fume hood at 95°C until its volume was reduced to 10 cm^3. Another 10 cm^3 of tri-acid mixture was added and heated until the volume was reduced to 4 cm^3. The solution was then diluted with 50 cm^3 deionized water. The digest was finally filtered and made up to 100 cm^3 using deionized water (Afshin *et al.,* 2013).

RESULTS AND DISCUSSION

Table 1: Mean Concentration of heavy metals in vegetable samples (mg/kg)

Sample	Zn	Cd	Cu	Ni	Co	Pb	Mn	Cr
AP	23.68±0.58	ND	3.00±0.01	1.00±0.01	1.00±0.01	5.00±0.01	32.33±0.58	2.67±0.58
AT	28.67±1.15	1.00±0.01	7.00±0.01	4.00±0.01	3.67±0.58	2.67±0.58	24.00±0.01	3.33±0.58
JP	31.33±0.58	1.00±0.01	7.00±0.01	2.00±0.01	1.00±0.01	8.00±0.01	24.00±0.01	3.33±0.58
JT	25.00±0.01	1.00±0.01	7.33±0.58	3.00±0.01	ND	1.00±0.01	29.00±0.01	3.33±0.58

Key: AP = Ajiwa pepper, AT = Ajiwa tomato, JP = Jibia pepper, JT = Jibia tomato and ND = Not Detected.

From Table 1, the amount of chromium found in Ajiwa pepper was 2.67±0.58 mg/kg while a slightly higher concentration of 3.33±0.58 mg/kg was obtained in Jibia pepper. This can be attributed to more human activities in Jibia than in Ajiwa. Bichi & Bello (2013) also reported a higher value of chromium in pepper irrigated along Tatsawarki river in Kano state. Waziri & Adamu (2012) made an intensive investigation on chromium levels in pepper cultivated in North-eastern states and the results obtained were in the range of 3.00±0.05 mg/kg to 3.50±0.10 mg/kg which is in agreement with the result obtained from Jibia pepper samples.
The concentration of chromium found in Ajiwa tomato was 3.33±0.58 mg/kg which is exactly similar to the result obtained for Jibia tomato. Another findings reported by Bassey *et al.* (2014) for tomato samples cultivated in urban fringe in three different sampling sites in Asaba of Delta state, revealed concentrations of 0.01, 0.15 and 0.01 mg/kg respectively which are significantly lower than the WHO/FAO standard values. Also, research conducted in Maiduguri, Borno state by Garba *et al.,* (2018), reported the value of chromium in tomato samples to be 0.571 mg/kg. However, a higher result (146.3 mg/kg) was reported in a tomato sample irrigated in Al-Barada of Damascus (Sumainah and Al-jebah, 2002), while a value of 0.511 mg/kg was reported by Adetogun (2010) for irrigated tomato samples

of Glen valley of Gaborone, Botswana. Also, 9.30 to 55.40 mg/kg of chromium was obtained by Oluyemi & Eyitayo (2013) when they analyzed tomato samples irrigated with waste water in dumpsites in Ekiti state. All these values were above the values obtained in this research and also above the standard limit set by WHO/FAO of 1.3 mg/kg. The higher concentration of chromium in the tomato samples is a great issue of concern and the amounts in the samples is manifested by its presence in the irrigation water. Chromium contaminated vegetables lead to health problems such as kidney and liver damage, skin rashes, stomach upset and ulcer, respiratory problem and lungs cancer and alteration of genetic materials (Moses, 2018).

Results from Table 1 also indicated that, the concentration of manganese in Ajiwa pepper was 32.33±0.58 mg/kg, which is higher than that obtained in Jibia pepper (24.00±0.01 mg/kg). However, the concentration of manganese (24.00±0.01 mg/kg) in tomato from Ajiwa irrigation site was lower than that of Jibia (29.00±0.01 mg/kg). Bassey *et al*. (2014) determined the amount of manganese in tomato samples from three different irrigation sites to be 3.83, 3.01, and 3.05 mg/kg in Peri-urban settlements of Asaba, Delta state, the levels are far lower than the results obtained in the present research possibly due to difference in the sampling sites and less agricultural activities in the Delta site as compared to Katsina. Bichi & Bello (2013) reported the amount of manganese in irrigated crops of Tatsawarki river of Kano state to be higher than the standard limits. Maha (2015) also reported the amount of manganese in tomato samples from selected markets in Khartoum, Sudan, to be about 88.13 mg/kg. Compared to the present findings, the reported value of manganese for tomato from Khartoum is greater the ones obtained in Ajiwa and Jibia, however all are above the WHO/FAO standard limits of 6.61 mg/kg of manganese in vegetables probably because of agricultural and anthropogenic activities taking place around the sites.

It can be also observed from Table 1 that the lead concentration in Ajiwa pepper is 5.00±0.01 mg/kg while that of Jibia is 8.00±0.00 mg/kg. These higher values could be attributed to the discharge of these metallic residues into the tributaries leading to the dams. Waziri & Adamu (2012) reported the concentrations of lead in different pepper samples analyzed using atomic absorption spectroscopy to be in the range 0.1±0.01 – 0.5±0.10 mg/kg in some selected areas of Yobe, Borno and Gombe states, north-eastern Nigeria. These values are lower than the concentration observed from the Jibia and Ajiwa dams of Katsina state likely because the north-eastern states might have less lead content in the soil than the north-western states as geological evidences indicated the presence of abundant lead in Zamfara state which is neighboring Katsina.

Lente *et al.* (2014) reported lead concentration in pepper samples irrigated in Accra, Ghana to be 7.61 mg/kg, which is also higher than 2 mg/kg as recommended by WHO/FAO. Also, Bichi & Bello (2013) analyzed some heavy metals irrigated along Tatsawarki river of Kano state where they observed that the level of lead was higher than the standard values recommended by WHO/FAO thereby unfit for human consumption. Elbagermi *et al.* (2012) reported the concentration of lead in green pepper irrigated in the Misurata area of Libya, to be 0.07±0.01 mg/kg which is lower than the values determined in Ajiwa (5.00±0.01) and Jibia (8.00±0.01) mg/kg, supposedly due geographical conditions and difference in mineral deposits.

Lead concentrations in tomato samples from the two sampling sites were found to be 2.67±0.58 mg/kg and 1.00±0.01 mg/kg for Ajiwa and Jibia dams respectively. These values were found to be higher than (0.50 mg/kg) reported by Adebayo and Raphael (2011). Also, significantly lower lead concentrations were reported by Moses (2018) as 0.35±0 mg/kg when he analyzed tomato samples cultivated from different irrigation dams of Zamfara state.

Other researchers reported their findings on lead concentration for cabbages cultivated at irrigation site close to mining spot of Cape Town, South Africa (Peck & Zinke, 2006). The lead concentrations recorded were unusually high, and this could be due to the anthropogenic activities around the sampling sites, including the application of fertilizers.
The amount of cobalt detected in the analyzed pepper samples irrigated at both Jibia and Ajiwa dams were found to be 1.00±0.01 mg/kg in both the samples. Lente *et al.* (2014) determined the the amount of cobalt in pepper to be below the acceptable limit of WHO/FAO. However, Bichi & Bello (2013) determined the concentration of cobalt to be higher than the recommended value. Elbagermi (2012) also reported the level of cobalt in irrigated pepper samples collected from market to be around 00.34 ± 0.015 mg/kg, which is lower than the value obtained from the two dams analyzed in this research. In another research conducted by Gaya and Ikechukwu (2016), the mean concentration of cobalt in some selected pepper samples from northern Nigeria was 5.550±0.019 mg/kg, which is significantly higher than the mean value obtained in the present research.

The concentration of cobalt recorded for tomato sample irrigated at Ajiwa dam was 3.67±0.58 mg/kg but not detected in the tomato sample irrigated at Jibia dam. Elbagermi (2012) reported the concentration of cobalt in tomato samples to be 0.45 ± 0.011 mg/kg in Misurata irrigated crops market of Libya, which is lower than the concentration obtained from the Ajiwa tomato samples, 3.67±0.58 mg/kg analyzed in this study but still above the maximum allowed limit of 0.1 mg/kg as recommended by WHO/FAO. This could be attributed to the anthropogenic activities exercised close to the water bodies.

The concentration of nickel in pepper sample irrigated at Ajiwa dam is found to be 1.00±0.01 mg/kg while that irrigated at Jibia dam appeared to be 2.00±0.01 mg/kg. The value which is twice that irrigated at Ajiwa dam could be possibly due to domestic activities of the populace in the area. Lente *et al.* (2014) detected the amount of nickel in hot pepper sample irrigated using groundwater in Accra, Ghana, to be to be 4.05 ± 0.01 mg/kg. In another findings, Awode *et al.* (2008) reported similar higher value of nickel in pepper irrigated using bank of river Challawa as 2.73-6.90 mg/kg, which is also higher compared to the value obtained in this research obviously because Chalawa is an industrial area and the irrigation water might have been contaminated by industrial effluents containing nickel. Gaya & Ikechukwu (2016) reported the concentration of nickel in bell pepper samples irrigated in the Kano State, northern Nigeria as 3.417±0.014 mg/kg. However, Elbagermi, (2012) reported the amount of nickel to be 0.19 ± 0.016 mg/kg in pepper sample, which is lower than the value obtained in the present research which could be due to variation in the study areas.

Nickel concentration in Ajiwa irrigated tomato was found to be 4.00±0.01 mg/kg while that irrigated at Jibia was 3.00±0.01 mg/kg. Elbagermi *et al.* (2012) reported the amount of nickel in irrigated tomato samples from Misurata, Libya to be 0.20 ± 0.052 mg/kg. This value is significantly lower compared to the concentration reported in this study. Similarly, Oluyemi & Eyitayo (2013) reported the concentration of nickel in some irrigated tomato samples from Ekiti state as 12.06-46.60 mg/kg, a value which is significantly disastrous upon accumulation in the body.

The concentration of copper in pepper irrigated at Ajiwa dam was found to be 3.00±0.01 mg/kg while that irrigated at Jibia was 7.00±0.01 mg/kg. Gaya & Ikechukwu (2016) reported the concentration of copper in bell pepper to be 5.550±0.019 mg/kg, which is somehow close to the analyzed samples in this research. Another research reported by Makanjuola and Osinfade (2016) obtained values of copper in pepper samples irrigated in Ogun state to be in the range of 0.31 mg/100g - 0.73 mg/100g. Lente *et al.* (2014) reported the concentration of copper in pepper samples irrigated with wastewater in Accra of Ghana as 7.38 ± 2.48 mg/kg. This result is also in agreement with the result obtained in this assessment. Similarly Elbagermi (2012) reported the value of copper in pepper purchased at selected market in Mistura of Libya to be 2.97 ± 0.33 mg/kg.

The concentration of copper found in tomato irrigated at Ajiwa dam was 7.00±0.01 mg/kg while that irrigated at Jibia dam was 7.33±0.58 mg/kg. Bichi & Bello (2013) reported higher value of copper beyond human consumption when they analyzed crops including pepper and tomato irrigated along Tatsawarki river of Kano state. Another research conducted by Oluyemi & Eyitayo (2013) on tomato samples cultivated in Ekiti state, reported a concentration of copper to be 5.18 - 38.15 mg/kg. This shows a significant variation in the concentration of the copper based on location and activities occurring at the irrigation site. A significantly lower value of 2.245±0.050 mg/kg was also reported by Elbagermi (2012). Chaitali (2015) reported the concentration of copper in tomato samples to be 0.045 mg/kg in Amravati city of India while Bassey *et al.* (2014) reported a value of 0.41 mg/kg in tomato samples cultivated in the urban fringe of Asaba of Delta state, Nigeria, which is the lowest observed in recent literature.

The concentration of cadmium was found to be 1.00±0.01 mg/kg in pepper irrigated at Jibia dam while it was not detected in the sample irrigated at Ajiwa dam. Awode *et al.* (2008) reported a value of cadmium in pepper samples irrigated along Challawa river of Kano state as 0.25 - 1.07 mg/kg, and these values were within the determined range of the analyzed Ajiwa and Jibia samples in this work. Gaya & Ikechukwu (2016) reported the value of cadmium in pepper samples irrigated in Kano state to be 6.033±0.013 mg/kg, which is significantly higher than the value (0.01±0.01 mg/kg) reported by Makanjuola & Osinfade, (2016). Lente *et al.* (2014) also reported a concentration of cadmium (less than 0.005 mg/kg) in bell pepper samples irrigated with wastewater in Accra of Ghana. However, majority of these researches indicate significantly higher values of cadmium than the values recommended by WHO/FAO.

The concentration of cadmium in both the Ajiwa and Jibia tomatoes was found to be 1.00±0 .01 mg/kg. Garba *et al.* (2018) reported the concentration of cadmium in tomato samples irrigated in selected areas of Maiduguri of Borno state to be 0.630±0.159 µg/g which is lower than the ones obtained from Ajiwa and Jibia dams in this work. However Moses (2018) reported a value of 0.729±0.003 mg/kg in Sunke irrigated tomato samples of Zamfara State during the dry season and this closely agrees with the cadmium concentration reported in this research. Bichi & Bello (2013) reported 1.7 mg/kg, a significantly higher value than the permissible limit set by WHO/FAO. Oluyemi & Eyitayo (2013) reported a value of cadmium in tomato irrigated in Ekiti state, Nigeria, to be in the range 27.20 - 55.74 mg/kg, which is also higher than the recommended maximum value.

Among all the heavy metals, zinc is the least toxic and an essential element in human diet as it is required for proper maintenance of the body functions. Deficiency of Zn in the diet may be more dangerous to the living organism, including human than its high concentration in the diet. The recommended dietary allowance for zinc is 15 mg/day for men and 12 mg/day for Women (Ogunlesi *et al.,* 2010). It is, therefore, an essential element for plants and animals; however, a small increase in the required level may cause interference with physiological processes.

The concentrations of zinc from Ajiwa and Jibia pepper samples are 23.68±0.58 mg/kg and 31.33±0.58 mg/kg respectively. Elbagermi *et al.* (2012) reported a value of 0.042 − 0.052 mg/kg in selected irrigation and market places of Libya. Lente *et al.* (2014) reported a zinc concentration of 9.29 ± 2.25 mg/kg in some irrigation sites of Accra in Ghana. Gaya & Ikechukwu (2016) determined the amount of zinc in bell pepper in Northern Nigeria to be 3.983±0.013 mg/kg. In similar research conducted by Waziri & Adamu (2012) the concentration of zinc in pepper samples in North-Eastern Nigeria was found to be 3.0±0.05 mg/kg – 3.5±0.10 mg/kg. However, higher concentrations of zinc were reported by Awode *et al.* (2008) to be in the range of 123.30 - 205.00 mg/kg in from pepper samples irrigated along river Challawa of Kano state.

The concentrations of Ajiwa and Jibia tomatoes were found to be 28.67±1.15 mg/kg and 25.00±0.01 mg/kg, respectively. These values are still within the recommended permissible limits of WHO/FAO of 60 mg/kg. Garba *et al.* (2018) were reported to have gotten 2.202±0.086 mg/kg in tomato samples cultivated in Maiduguri of Borno state. Bassey *et al.* (2014) reported a value of 3.33 mg/kg in Asaba of Delta state. These values are in contrast (lower) compared to the ones obtained in this research which can be attributed to the anthropogenic activities, fertilizer applications and soil contributions close to the studied dams. A value of 3.8 mg/kg was also reported by Chaitali (2015) in Amravati city of India. Elbagermi *et al.* (2012) reported a value of zinc to be 8.427±0.635 mg/kg in selected areas of Libya. Oluyemi & Eyitayo (2013) reported zinc concentration in irrigated sites of Ekiti State, Nigeria to be within the range of 7.54-91.10 mg/kg.

CONCLUSION

The levels of some metals in the selected vegetable samples studied fall within the acceptable limits. Metals like cadmium and chromium were found to be at the maximum permissible limit while other metals including cobalt, nickel and manganese were above the permissible limits. This can be related to the agricultural chemicals applied to the vegetable farms in form of fertilizers and other products such as pesticides and insecticides and this must be regulated to ensure healthy vegetables for consumption. Generally, results of this research show that the levels for most metals analyzed are within the permissible limits set by standard organizations and therefore are safe for human consumption after preparation.

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