MERIT RESEARCH JOURNALS
www.meritresearchjournals.org

Merit Research Journal of Environmental Science and Toxicology (ISSN: 2350-2266) Vol. 4(5) pp. 037-048, July, 2016
Available online http://meritresearchjournals.org/est/index.htm

Original Research Article

Analysis of Some Chemical Pollutants in Vegetable Samples from Sakwa, Thila and Marama in Hawul Local Government Area, Borno State, Nigeria

***Usman Y. B., Kolo B. G., Yakubu J. and Usman B.**

Department of Chemistry, University of Maiduguri, Borno State, Nigeria

***Corresponding Author's Email: yaksonelder@gmail.com**

Abstract

This study is aimed at ascertaining the levels of pollutants in some selected vegetables samples from three agricultural areas in Hawul Local Government Area, Borno state, Nigeria. Vegetables samples from Sakwa, Thila and Marama agricultural Areas of Hawul Local government were collected and analysed for Zn, Pb, Co, Cu, Fe, Ag, Ni, Mn Cr and Cd using Atomic Absorption Spectrophotometric techniques. Results showed varying concentrations based on different parts of the vegetables from root, stem and leaves. High concentration of these metal pollutants were observed in the leaves of the vegetables samples as a result of transpiration process and with Fe having the highest value of 10.37±2.68 µg/g observed in the leaves of Okra Nitrate levels ranged from 11.23±6.72 to 19.66±8.20 (µg/g) in Okra; 1.17±1.04 to 2.52±1.40 (µg/g) in pepper; 2.37±1.35 to 4.03±1.11 (µg/g) in sorrel; sulphate ranged from 9.27±1.77 to 11.99±0.88 (µg/g) in Okra; 7.90±4.38 to 10.77±1.34 (µg/g) in sorrel and 6.54±0.71 to 11.76±2.45 (µg/g) in pepper. The concentrations of some cations analysed in vegetable samples revealed that calcium ion ranged from 11.23±6.72 to 19.66^{c}±8.20 (µg/g) in Okra; 8.37±4.82 to 14.10±4.90 (µg/g) in sorrel; 2.03±1.34 to 3.33±2.52 (µg/g) in pepper while Sodium ion ranged from 3.90±0.86 to 13.16±1.67 (µg/g) in okra; 9.35±2.87 to 12.34±0.32 (µg/g) in sorrel; 2.62±3.42 to 11.94±1.41 (µg/g) in pepper and potassium ion ranged from 8.21±1.7 to 20.12±1.15 (µg/g) in okra; 8.37±4.82 to 14.10±4.90 (µg/g) in sorrel and 2.03±1.34 to 3.33±2.52 (µg/g) in pepper ($p<0.05$). High levels of Fe and other metals is said to be associated with the level of mechanical activities, high vehicle exhaust. The results indicate that some of the vegetables were contaminated with abnormal levels of Pb, Cr, Ag and Ni capable of causing health hazards to the consumers nationwide.

Keywords: Agrochemicals, Concentration, Heavy Metals, Pollutants, Pollution, Vegetables

INTRODUCTION

Vegetables constitute an important part of the human diet since they contain carbohydrates, proteins, as well as vitamins, minerals and heavy metals. Heavy metals are one of a range of important types of contaminants that can be found on the surface and in the tissue of fresh vegetables (Bigdeli and Seilsepour, 2008). A number of elements, such as lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), chromium (Cr), Copper (Cu) and Selenium

(Se) (IV) can be harmful to plants and humans even at quite low concentrations (Usman and Kolo, 2015). Soil pollution is caused by misuse of the soil, such as poor agricultural practices, disposal of industrial and urban wastes, etc. (Usman et al., 2015). Soil is also polluted through application of chemical fertilizers (like phosphate and Zn fertilizers), and herbicides (Demi˙rezen and Aksoy, 2004). Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality, crop growth (Akan et al., 2013) and environmental health. Plant species have a variety of capacities in removing and accumulating heavy metals. So there are reports indicating that some plant species may accumulate specific heavy metals (Santamaria, 2006). The uptake of metals from the soil depends on different factors, such as their soluble content in it, soil pH, plant species, fertilizers, and soil type (Yusuf and Oluwole, 2009). Vegetables, especially leafy vegetables, accumulate higher amounts of heavy metals (Uwah et al., 2009). Roots and leaves of herbaceous plants retain higher concentration of heavy metal than stems and fruits (Yargholi and Azimi, 2008). There are limited studies on heavy metal content at different growth stages of vegetables, the most studies focused on the status of metal content in edible parts of vegetables. And an investigation of the literature also shows a scarcity of data on comparison of metal content at different leafy vegetable species in Hawul (Usman and Kolo, 2015). Potentially harmful metal contents in soils may come not only from the bedrock itself, but also from anthropogenic sources like solid or liquid waste deposits, agricultural inputs, and fallout of industrial and urban emissions (Wilson and Pyatt, 2007). Excessive accumulation in agricultural soils may result not only in soil contamination, but has also consequences for food quality and safety. So, it is essential to monitor food quality, given that plant uptake is one of the main pathways through which heavy metals (HMs) enter the food chain (Antonious and Kochhar, 2009). Vegetables take up HMs and accumulate them in their edible and non-edible parts at quantities high enough to cause clinical problems to both animals and human beings. As an example, the consumption of contaminated food can seriously deplete some essential nutrients in the body causing a decrease of immunological defenses, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer (Oliver, 1997). A study reported that soil and vegetables contaminated with Pb and Cd in Copsa Mica and Baia Mare, Romania, significantly contributed to decrease human life expectancy (9-10 years) within the affected areas. Cadmium and Pb are the most toxic elements for man (Volpe et al., 2009). In terms of environmental concentration, Pb is the HM closest to the level in which toxic signs manifest than any other substance (Baird, 2002). Others elements such as Cr, Co and Ni, although essential for men, at concentrations higher than those recommended, may cause metabolic disorders. Moreover, an increasing awareness in terms of the importance of vegetables and fruits to human diet suggests that the monitoring of HMs in food crops should be carried out frequently, however information concerning this issue is scarce, especially in Brazil. Most major cities have been concerned with HM contents in vegetables (Ferré-Huguet et al., 2008). Absorption and accumulation of heavy metals in vegetables and fruits are influenced by many factors, including: concentration of heavy metals in soil, composition and intensity of atmospheric deposition, including precipitations, phase of plant vegetation (Vontsa et al., 1996). To all of these, can be added other sources generated by agricultural technologies such as: irrigation with wastewater, the administration of organic and mineral fertilizers with the load of heavy metals, or application of pesticides, which contain in their structure such chemical elements (Singh et al., 2004; Sharma et al., 2006). Urban, industrial and household activities, traffic, contribute significantly to increasing the load degree with heavy metals containing particles of inferior atmosphere (Lacatusu et al., 2008), from where these particles will settle own on the plants foliage system and soil. Many times, the plants foliage system is representing the edible part of vegetables (lettuce, parsley, dill, lovage etc.). The heavy metals are overtaking in the edible parts of vegetables and fruits by physiological path, either from soil, from leaves surface or with these kinds of chemicals loaded irrigation water. The intake of heavy metals can lead to altering of humans and animals healthiness state. Thus, the carcinogenic effects generated by continuous consumption of fruits and vegetables loaded with heavy metals such as Cd, Pb or even Cu and Zn are known. There are already published works related to the incidence of gastrointestinal cancer (Tricopoulas, 1997; Turkdogan et al., 2002), and cancer of the pancreas, urinary bladder or prostate (Waalkes and Rehm, 1994). There are, in Romania, three areas (Copşa Mică-Sibiu County, Zlatna – Alba County and Baia Mare – Maramures County) very strongly polluted with heavy metals, caused by nonferrous ores extraction and metallurgical processing. The contents of Cd, Cu, Pb and Zn in the soils around these localities are up to sometime higher than the maximum allowable limits. As a result, the plants, inclusive vegetables, accumulated high quantities of such chemical elements (Usman and Kolo, 2015).

MATERIALS AND METHODS

Sample Collection

Vegetable samples were collected from three agricultural locations (Saakwa, Thila and Marama) within Hawul Local Government Area, Borno State, Nigeria. At each sample location, vegetable samples were collected from three different locations from June to September 2014 to provide replicate samples of each plant. Vegetable samples were divided into fruit, leaf, stem and root. Vegetable samples include Okra, Sorrel and pepper.

Preparation and digestion of samples for heavy metal analysis

Vegetables samples collected were thoroughly washed with water, cut and separated into different parts (root, stem, leave and fruits) and dried in an oven at 80°C for 72 hours. The dried samples were crushed in a mortar and the resulting powder was digested by weighing 1.0 g of the dried grounded sample into 250 mL beaker. 20 mL of HNO_3 was added and heated on a hot plate until no brown fumes was giving off. 10 mL of H_2O_2 was added in small portions to avoid any possible overflow leading to loss of material and the heating continue until the volume was reduced. 10 mL of HCl was finally added and evaporated to dryness. The mixture was cooled and then filtered through a Whatman No. 41 filter paper into a 100 mL volumetric flask and made up to mark with distilled water (USEPA 3050b) (Radojevic and Bashkin, 1999).

Elemental Analysis of Samples

Determination of Pb, Fe, Cu, Zn, Cd, Ni, Mn and Cr as well as were made directly on each final solution using Perkin-Elmer Analyst 300 Atomic Absorption Spectroscopy (AAS).

Determination of Ions in Soil, Fruit and Vegetable Samples

The digested samples prepared were used to determine the concentration of some ions (Ca^{2+}, K^+ and Na^+) using Uv-visible Smart Spectrophotometer (La Motte 2000). Absorbances of these samples were measured at their specific wavelengths. From the standard calibration curve (Beer Lambert's law), absorbance of the unknown were measured at their specific wavelength of their absorption and read out from the graph.

Determination of Nitrate and Sulphate in Vegetable Samples

Levels of nitrate in the vegetable samples solutions were prepared by chopping each sample into smaller sizes. A known amount (1g) of the chopped sample was transferred into 100ml flask and soaked with 50ml of distilled water. The flask was capped and shaken for 30 minutes, then filtered into another 100ml volumetric flask and the volume made to the mark with distilled water (Radojevic and Bashkin, 1999). Nitrate was determined spetrophotometrically using standard cadmium reduction method 3649 – SC (Lamottee, 2000).

For sulphate extermination, 5ml of magnesium nitrate solutions were added to each of the ground and sieved samples in the crucibles. These were then heated to180°C on a hot plate. The heating process was allowed to continue until the colour of the samples changed from brown to yellow (Radojevic and Bashkin, 1999). The samples were then transferred to the furnace at a temperature of 500°C for four hours. Magnesium nitrate was added to prevent loss of sulphur. The contents of each crucible were carefully transferred to different evaporating basins. 10ml of concentrated HCl were added to each of them and covered with watch glasses. They were boiled on a steam bath for 3 minutes. On cooling, 10ml of distilled water were added to each of the basins and the contents of each were filtered into 50ml volumetric flasks and the volumes made up to the marks with distilled water (Radojevic and Bashkin, 1999). Sulphate was determined using Smart Spectrophotometer (2000).

RESULTS AND DISCUSSION

Figure 1 presents the mean concentration of anions and some cations in some vegetables grown in the farms of Sakwa, Thila and Marama within Hawul Local Government Area of Borno State from June to September 2014 for Sakwa with Sodium ion (Na^+) ranging between 9.35±2.87 to 113.90±0.86 (µg/g), Potassium ion (K^+) varied between 9.13±2.84 to 20.12±1.15 (µg/g), calcium ion (Ca^{2+}) ranged between 2.03±1.34 to 19.66±8.20 (µg/g), while nitrate ion varied between 1.07±0.71 to 4.03±8.20 (µg/g) and sulphate ion ranged between 7.90±4.38 to 11.99±0.88 (µg/g).

Figure 2 presents the mean concentration of some anions and cations in some vegetable samples from Thila in which Sodium ion (Na^+) ranged between 12.20±0.52 to 16.71±4.48 (µg/g), Potassium ion (K^+) varied between 10.28±4.97 to 15.78±2.38 (µg/g), calcium ion (Ca^{2+}) ranged between 2.57±1.06 to 14.81±15.91 (µg/g), while nitrate ion (NO_3^-) varied between 1.92±1.14 to 5.39±3.25 (µg/g) and sulphate ion (SO_4^{2-}) ranged between 9.03±1.35 to 12.06±0.49 (µg/g).

Figure 3 present the mean concentration of some anions and cations in some vegetable samples from Thila in which Sodium ion (Na^+) ranged between 11.35±0.84 to 17.67±7.85 (µg/g), Potassium ion (K^+) varied between 14.34±3.28 to 20.04±5.77 (µg/g), calcium ion (Ca^{2+}) ranged between 5.61±7.72 to 13.38±1.57 (µg/g), while nitrate ion (NO_3^-) varied between 0.94±0.38 to 4.06±5.51 (µg/g) and sulphate ion (SO_4^{2-}) ranged between 11.61±2.13 to 13.15±0.45 (µg/g). The statistical analyses of these variations using ANOVA to determine the significance of the variations of the paired means

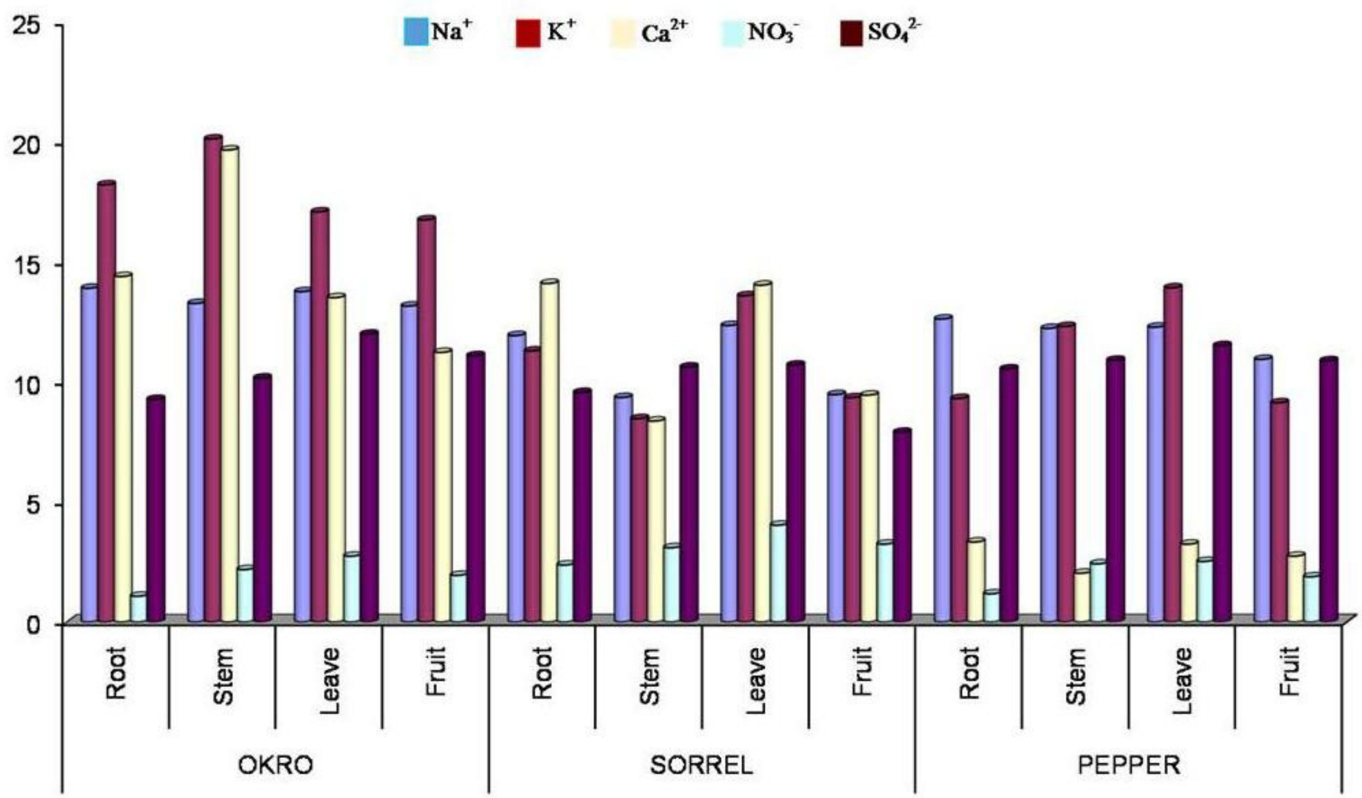

Figure 1. Mean Concentration (µg/g) of Some Anions and Cations in Vegetable Samples from Sakwa Agricultural

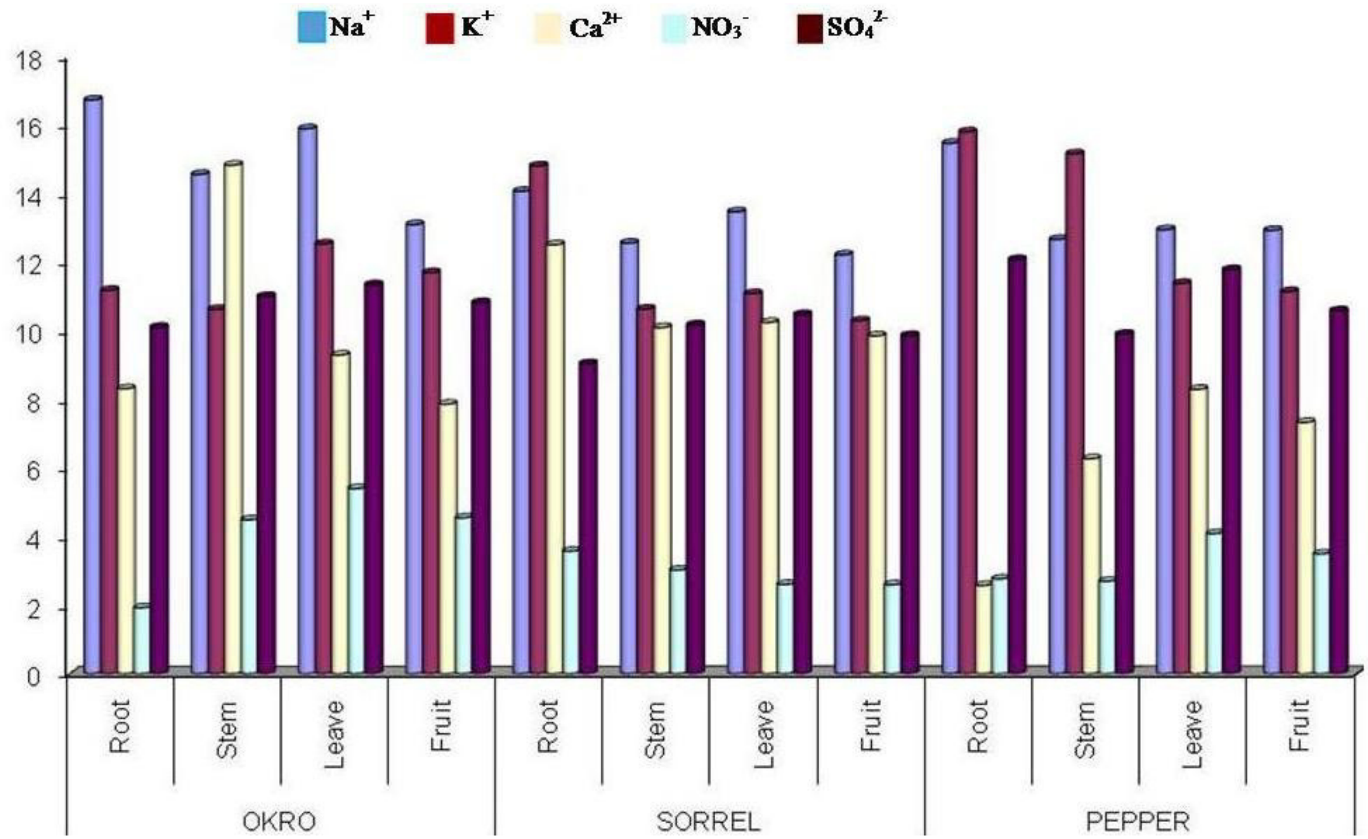

Figure 2. Mean Concentration (µg/g) of Some Anions and Cations in Vegetable Samples from Thila Agricultural

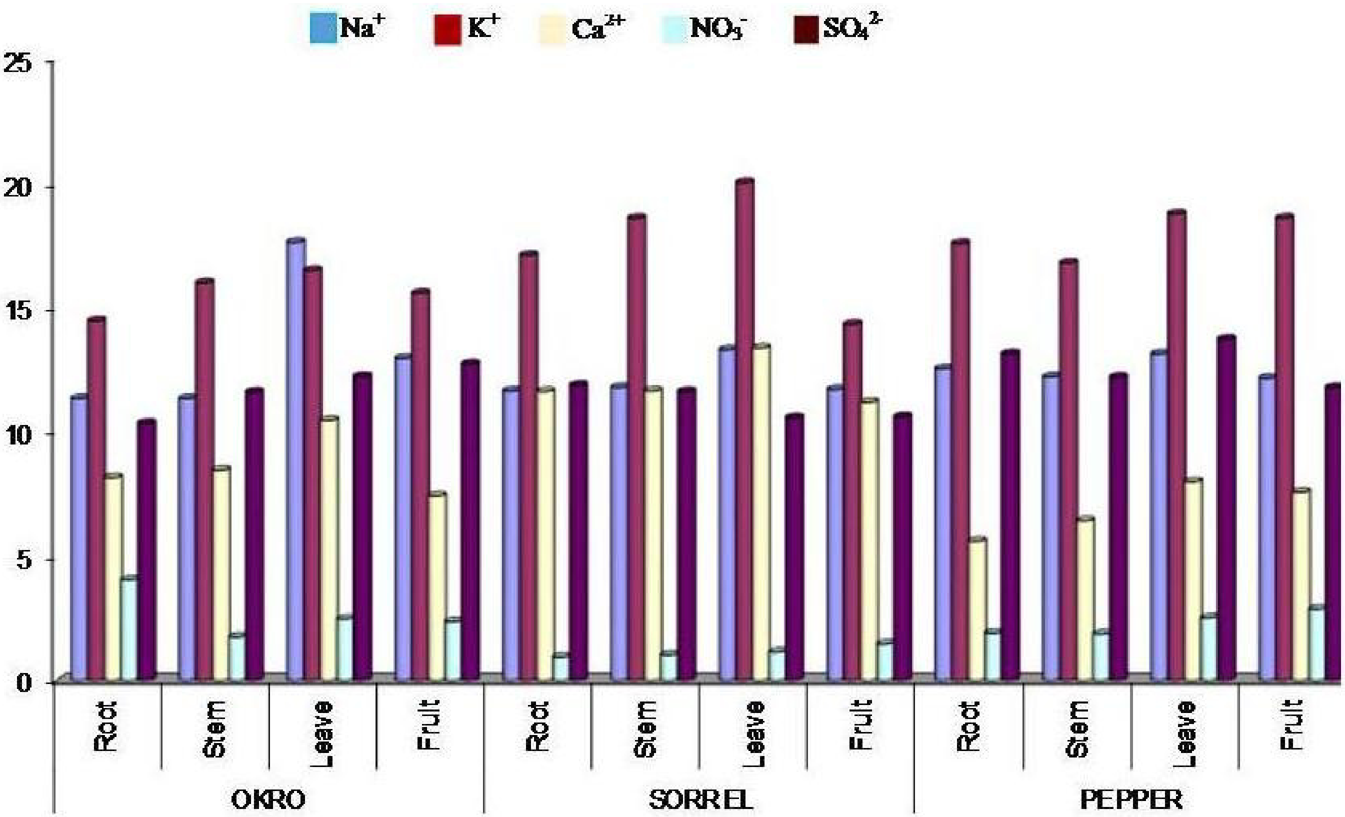

Figure 3. Mean Concentration (µg/g) of Some Anions and Cations in Vegetable Samples from Marama Agricultural Area.

between the concentrations of anions and cations in fruit and vegetable samples from the three Local Government Areas of study are statistically significant ($p < 0.05$).

Table 1 presents the mean concentration (µg/g) of heavy metals in some selected vegetable samples from Sakwa study area within Hawul Local Government of Borno State revealed the variation of these pollutants from the root – stem – leave – fruit. It was observed that the concentration of Lead (Pb) ranged between 0.50±0.13 to 0.69±0.13 (µg/g), copper (Cu) between 0.28±0.03 to 0.43±0.34 (µg/g), Nickel (Ni) varied between 0.18±0.21 to 0.36±0.33 (µg/g), Cadmium (Cd) between 0.18±0.06 to 0.41±0.37 (µg/g), Cobalt (Co) between 0.26±0.09 to 0.46±0.21 (µg/g), Chromium ranged between 0.64±0.98 to 2.36±2.22 (µg/g), Iron (Fe) between 3.45±3.93 to 13.74±2.66 (µg/g) while Manganese (Mn) ranged between 0.26±0.29 to 1.87±0.17 (µg/g) and Zinc (Zn) between 0.08±0.08 to 0.70±0.26 (µg/g).

Table 2, presents the mean concentration (µg/g) of heavy metals in some selected vegetable samples from Thila study area within Hawul Local Government Area of Borno State revealed the variation of these pollutants from the root – stem – leave – fruit. It was observed that the concentration of Lead (Pb) ranged between 0.34±0.11 to 1.24±0.44 (µg/g), copper (Cu)

Table 1. Mean Concentration (µg/g) of Heavy Metals in Some Selected Vegetables Samples from Sakwa, Hawul Local Government, Borno State.

Samples	Pb	Cu	Ni	Cd	Co	Cr	Fe	Mn	Zn
OKRA									
Root	$0.53^{a}\pm0.04$	0.33 ± 0.13	$0.18^{a}\pm0.21$	$0.19^{a}\pm0.07$	$0.26^{a}\pm0.09$	$0.64^{a}\pm0.98$	$9.01^{a}\pm3.44$	$0.71^{a}\pm0.34$	$0.08^{a}\pm0.08$
Stem	$0.54^{b}\pm0.08$	0.35 ± 0.16	$0.19^{b}\pm0.24$	$0.18^{b}\pm0.06$	$0.32^{b}\pm0.06$	$1.47^{b}\pm1.11$	$7.18^{b}\pm3.38$	$0.48^{b}\pm0.19$	$0.30^{b}\pm0.11$
Leaves	$0.52^{c}\pm0.07$	0.37 ± 0.22	$0.30^{c}\pm0.25$	$0.33^{c}\pm0.34$	$0.34^{c}\pm0.10$	$2.36^{c}\pm2.22$	$8.95^{c}\pm2.89$	$1.72^{c}\pm0.62$	$0.39^{c}\pm0.22$
Fruit	$0.54^{d}\pm0.16$	0.38 ± 0.20	$0.14^{d}\pm0.17$	$0.33^{d}\pm0.35$	$0.37^{d}\pm0.07$	$1.95^{d}\pm1.73$	$3.45^{d}\pm3.93$	$1.03^{d}\pm0.55$	$0.23^{d}\pm0.36$
SORREL									
Root	$0.52^{a}\pm0.12$	$0.34^{a}\pm0.12$	$0.27^{a}\pm0.21$	$0.22^{a}\pm0.10$	$0.43^{a}\pm0.29$	$0.95^{a}\pm0.28$	$8.03^{a}\pm2.84$	$1.06^{a}\pm0.51$	$0.29^{a}\pm0.20$
Stem	$0.51^{b}\pm0.12$	$0.39^{b}\pm0.20$	$0.23^{b}\pm0.30$	$0.30^{b}\pm0.26$	$0.44^{b}\pm0.33$	$0.66^{b}\pm0.35$	$7.32^{b}\pm1.79$	$0.45^{b}\pm0.35$	$0.47^{b}\pm0.28$
Leaves	$0.54^{c}\pm0.11$	$0.43^{c}\pm0.21$	$0.21^{c}\pm0.18$	$0.32^{c}\pm0.31$	$0.44^{c}\pm0.37$	$1.18^{c}\pm0.60$	$8.15^{c}\pm0.58$	$1.41^{c}\pm0.095$	$0.44^{c}\pm0.36$
Fruit	$0.50^{d}\pm0.13$	$0.38^{d}\pm0.19$	$0.23^{d}\pm0.29$	$0.37^{d}\pm0.23$	$0.42^{d}\pm0.34$	$0.66^{d}\pm0.37$	$6.82^{d}\pm1.53$	$0.57^{d}\pm0.27$	$0.47^{d}\pm0.37$
PEPPER									
Root	$0.61^{a}\pm0.17$	$0.28^{a}\pm0.03$	$0.36^{a}\pm0.33$	$0.35^{a}\pm0.35$	$0.36^{a}\pm0.06$	$1.34^{a}\pm0.611$	$3.74^{a}\pm2.66$	$1.87^{a}\pm0.17$	$0.38^{a}\pm0.10$
Stem	$0.65^{b}\pm0.16$	$0.43^{b}\pm0.34$	$0.26^{b}\pm0.43$	$0.41^{b}\pm0.37$	$0.43^{b}\pm0.08$	$0.89^{b}\pm0.18$	$4.22^{b}\pm3.80$	$0.66^{b}\pm0.81$	$0.70^{b}\pm0.26$
Leaves	$0.69^{c}\pm0.13$	$0.38^{c}\pm0.27$	$0.33^{c}\pm0.45$	$0.35^{c}\pm0.37$	$0.42^{c}\pm0.13$	$0.94^{c}\pm0.33$	$10.01^{c}\pm3.23$	$0.68^{c}\pm0.48$	$0.47^{c}\pm0.36$
Fruit	$0.66^{d}\pm0.23$	$0.42^{d}\pm0.29$	$0.31^{d}\pm0.46$	$0.37^{d}\pm0.40$	$0.46^{d}\pm0.21$	$0.93^{d}\pm0.48$	$5.97^{d}\pm3.12$	$0.26^{d}\pm0.29$	$0.53^{d}\pm0.31$

Values presented are Mean ± SD of replicate data (n = 4), within columns, Paired means values with different alphabets are statistically significant ($p<0.05$).
Key: SD = Standa

Table 2. Mean Concentration (µg/g) of Heavy Metals in Some Selected Vegetable Samples from Thila Hawul Local Government, Borno State.

Samples	Pb	Cu	Ni	Cd	Co	Cr	Fe	Mn	Zn
OKRA									
Root	0.41^{a}±0.12	0.37^{a}±0.22	0.12^{a}±0.06	0.21^{a}±0.07	0.44^{a}±0.05	1.27^{a}±0.43	6.03^{a}±2.84	0.12^{a}±0.05	0.47^{a}±0.05
Stem	0.54^{b}±0.21	0.40^{b}±0.14	0.15^{b}±0.06	0.25^{b}±0.11	0.41^{b}±0.07	0.58^{b}±0.20	3.89^{b}±3.37	0.12^{b}±0.06	0.44^{b}±0.27
Leaves	0.65^{c}±0.29	0.38^{c}±0.14	0.16^{c}±0.08	0.20^{c}±0.07	0.49^{c}±0.14	1.80^{c}±1.06	6.80^{c}±2.17	0.76^{c}± 0.66	0.48^{c}±0.44
Fruit	0.63^{d}±0.26	0.49^{d}±0.19	0.17^{d}±0.08	0.23^{d}±0.13	0.44^{d}±0.06	1.57^{d}±1.02	4.94^{d}±3.68	0.37^{d}±0.21	0.44^{d}±0.45
SORREL									
Root	0.47^{a}±0.11	0.26±0.05	0.13^{a}±0.06	0.20^{a}±0.09	0.41^{a}±0.08	0.28^{a}±0.36	5.70^{a}±2.14	1.31^{a}±0.81	0.64^{a}±0.45
Stem	0.46^{b}±0.11	0.31±0.05	0.19^{b}±0.13	0.31^{b}±0.21	0.39^{b}±0.10	0.50^{b}±0.27	6.51^{b}±0.34	1.62^{b}±0.45	0.43^{b}±0.36
Leaves	0.52^{c}±0.10	0.40±0.03	0.21^{c}±0.06	0.33^{c}±0.25	0.45^{b}±0.21	0.44^{c}±0.28	9.03^{c}±4.31	1.79^{c}±0.33	0.49^{c}±0.45
Fruit	0.46^{d}±0.097	0.34±0.08	0.31^{d}±0.20	0.25^{d}±0.13	0.28^{d}±0.25	0.39^{d}±0.046	6.34^{d}±0.42	1.23^{d}±0.71	0.49^{d}±0.30
PEPPER									
Root	0.34^{a}±0.11	0.47^{a}±0.12	0.03^{a}±0.03	0.18^{a}±0.06	0.45^{a}±0.21	0.97^{a}±0.621	1.63^{a}±5.48	1.28^{a}±0.82	1.45^{a}±0.88
Stem	0.42^{b}±0.23	0.43^{b}±0.05	0.13^{b}±0.05	0.20^{b}±0.08	0.48^{b}±0.20	1.51^{b}±0.72	8.12^{b}±3.56	1.02^{b}±0.96	1.43^{b}±0.83
Leaves	1.24^{c}±0.44	1.49^{c}±0.42	1.78^{c}±1.15	0.52^{c}±0.27	0.84^{c}±0.15	2.79^{c}±0.49	15.50^{c}±4.93	5.81^{c}±3.98	2.00^{c}±0.86
Fruit	0.85^{d}±0.09	0.91^{d}±0.40	1.27^{d}±1.00	0.25^{d}±0.21	0.62^{d}±0.11	2.17^{d}±0.35	12.74^{d}±7.01	3.12^{d}±3.57	1.44^{d}±0.81

Values presented are Mean ± SD of replicate data (n = 4), within columns, Paired means values with different alphabets are statistically significant (p<0.05).
Key: SD = Standa

Table 3. Mean Concentration (µg/g) of Heavy Metals in Some Selected Vegetable Samples from Marama, Hawul Local Government, Borno State.

Samples	Pb	Cu	Ni	Cd	Co	Cr	Fe	Mn	Zn
OKRA									
Root	0.58^{a}±0.12	0.47^{a}±0.13	0.08^{a}±0.01	0.26^{a}±0.13	0.34^{a}±0.07	0.87^{a}±0.52	10.37^{a}±2.68	0.74^{a}±0.38	0.34^{a}±0.06
Stem	0.60^{b}±0.07	0.55^{b}±0.19	0.12^{b}±0.07	0.29^{b}±0.15	0.33^{b}±0.09	0.71^{b}±0.52	7.91^{b}±4.47	0.61^{b}±0.47	0.25^{b}±0.22
Leaves	0.57^{c}±0.19	0.47^{c}±0.27	0.16^{c}±0.10	0.34^{c}±0.18	0.40^{c}±0.15	0.89^{c}±0.951	0.95^{c}±2.58	1.24^{c}±0.52	0.38^{c}±0.22
Fruit	0.57^{d}±0.23	0.45^{d}±0.26	0.12^{d}±0.07	0.33^{d}±0.15	0.37^{d}±0.06	0.81^{d}±0.56	6.83^{d}±6.38	1.03^{d}±0.49	0.28^{d}±0.25
SORREL									
Root	0.49^{a}±0.15	0.23^{a}±0.08	0.27^{a}±0.38	0.30^{a}±0.13	0.44^{a}±0.15	0.71^{a}±0.84	9.39^{a}±4.54	0.16^{a}±0.06	0.14^{a}±0.07
Stem	0.53^{b}±0.14	0.31^{b}±0.088	0.22^{b}±0.28	0.32^{b}±0.14	0.45^{b}±0.16	0.89^{b}±1.08	6.06^{b}±4.32	0.26^{b}±0.21	0.20^{b}±0.12
Leaves	0.57^{c}±0.12	0.43^{c}±0.05	0.28^{c}±0.16	0.31^{c}±0.17	0.43^{c}±0.24	1.05^{c}±1.07	10.22^{c}±4.51	0.80^{c}±0.60	0.39^{c}±0.42
Fruit	0.51^{d}±0.13	0.36^{d}±0.05	0.22^{d}±0.09	0.31^{d}±0.13	0.43^{d}±0.21	0.46^{d}±0.38	6.68^{d}±4.09	0.54^{d}±0.33	0.38^{d}±0.17
PEPPER									
Root	0.57^{a}±0.11	0.38^{a}±0.10	0.07^{a}±0.06	0.29^{a}±0.14	0.46^{a}±0.11	2.36^{a}±0.79	15.03^{a}±2.09	2.16^{a}±1.16	0.29^{a}±0.18
Stem	0.55^{b}±0.12	0.34^{b}±0.17	0.08^{b}±0.08	0.31^{b}±0.14	0.44^{b}±0.20	1.78^{b}±1.43	6.20^{b}±3.34	0.40^{b}±0.22	0.28^{b}±0.21
Leaves	0.88^{c}±0.25	1.01^{c}±0.55	0.41^{c}±0.37	0.36^{c}±0.18	0.94^{c}±0.39	1.96^{c}±1.40	11.33^{c}±3.01	1.62^{c}±0.98	0.53^{c}±0.32
Fruit	0.66^{d}±0.23	0.63^{d}±0.39	0.19^{d}±0.17	0.31^{d}±0.20	0.63^{d}±0.24	1.56^{d}±1.71	9.16^{d}±1.49	0.77^{d}±0.19	0.30^{d}±0.21

Values presented are Mean ± SD of replicate data (n = 4), within columns, Paired means values with different are statistically significant ($p<0.05$).
Key: SD = Standard deviation.

between 0.26±0.05 to 1.49±0.42 (µg/g), Nickel (Ni) varied between 0.03±0.03 to 1.78±1.15 (µg/g), Cadmium (Cd) between 0.18±0.06 to 0.54±0.27 (µg/g), Cobalt (Co) between 0.28±0.25 to 0.84±0.15 (µg/g), Chromium ranged between 0.28±0.36 to 2.79±0.49 (µg/g), Iron (Fe) between 3.89±3.37 to 15.50±4.93 (µg/g) while Manganese (Mn) ranged between 0.12±0.05 to 5.81±3.98 (µg/g) and Zinc (Zn) between 0.43±0.36 to 2.00±0.86 (µg/g).

Table 3, presents the concentration (µg/g) of heavy metals in some selected vegetable samples from Marama study area within Hawul Local Government Area of Borno State revealed the variation of these pollutants from the root – stem – leave – fruit. It was observed that the concentration of Lead (Pb) ranged between 0.49±0.15 to 0.88±0.25 (µg/g), copper (Cu) between 0.23±0.08 to 1.01±0.55 (µg/g), Nickel (Ni) varied between 0.07±0.06 to 0.41±0.37 (µg/g), Cadmium (Cd) between 0.26±0.13 to 0.36±0.18 (µg/g), Cobalt (Co) between 0.33±0.09 to 0.94±0.39 (µg/g), Chromium (Cr) ranged between 0.46±0.38 to 1.96±1.40 (µg/g), Iron (Fe) between 6.06±4.32 to 15.03±2.09 (µg/g) while Manganese (Mn) ranged between 0.16±0.06 to 2.16±1.16 (µg/g) and Zinc (Zn) between 0.14±0.07 to 0.53±0.32 (µg/g).

Vegetable (Sorrel, Pepper and Okra) samples analyzed within Sakwa, Thila and Marama In Hawul Local Government Area revealed that the variation in the concentration of anions and cations in some selected vegetable samples from these study areas are in the order root>leave>stem>fruit. In Sakwa, the order of the level of concentration is $K^+ > Ca^{2+} > Na^+ > SO_4^{2-} > NO_3^-$ where in okra vegetable, K^+ showed the highest concentration in stem and NO_3^- showed the least concentration in root. Sorrel has Ca^{2+} with the highest concentration in leaves and NO_3^- showed the least concentration in root. Pepper also revealed high concentration of K^+ in leave and NO_3^- showed the least concentration in root. The finding from Thila study area revealed the pattern as $Na^+ > K^+ > Ca^{2+} > SO_4^{2-} > NO_3^-$ with the high concentrations of these ions in leaves and the fruits having the least concentrations. The variation was in the order root>leaves>stem>fruit. While in Marama similar pattern was observed as in Sakwa except the change in concentration of sodium ion (Na^+) and is in the order $K^+ > Ca^{2+} > Na^+ > SO_4^{2-} > NO_3^-$ and the path of mineral intake as root>leaves>stem>fruit, this is justified by the findings reported by some researchers (Jerry, 2011; Akan et al., 2013; Abah et al., 2014).

Heavy metals analyzed from the vegetable samples obtained from Hawul Local Government Areas was observed that, Sakwa study area revealed the variation of these pollutants from the root – stem – leave – fruit. It was observed in Table 1 that the concentration of Lead (Pb) ranged between 0.50±0.13 to 0.69±0.13, copper (Cu) between 0.28±0.03 to 0.43±0.34, Nickel (Ni) varied between 0.18±0.21 to 0.36±0.33, Cadmium (Cd) between 0.18±0.06 to 0.41±0.37, Cobalt (Co) between 0.26±0.09 to 0.46±0.21, Chromium ranged between 0.64±0.98 to 2.36±2.22, Iron (Fe) between 3.45±3.93 to 13.74±2.66 while Manganese (Mn) ranged between 0.26±0.29 to 1.87±0.17 and Zinc (Zn) between 0.08±0.08 to 0.70±0.26. The concentration (µg/g) of heavy metals in some selected vegetable samples from Thila study area was observed in Table 2 that the concentration of Lead (Pb) ranged between 0.34±0.11 to 1.24±0.44, copper (Cu) between 0.26±0.05 to 1.49±0.42, Nickel (Ni) varied between 0.03±0.03 to 1.78±1.15, Cadmium (Cd) between 0.18±0.06 to 0.54±0.27, Cobalt (Co) between 0.28±0.25 to 0.84±0.15, Chromium ranged between 0.28±0.36 to 2.79±0.49, Iron (Fe) between 3.89±3.37 to 15.50±4.93 while Manganese (Mn) ranged between 0.12±0.05 to 5.81±3.98 and Zinc (Zn) between 0.43±0.36 to 2.00±0.86. While Table 3, revealed that the concentration (µg/g) of heavy metals in the selected vegetable samples from Marama study indicated similar trend as in the case of Sakwa and Thila in which Lead (Pb) ranged from 0.49±0.15 to 0.88±0.25; copper (Cu) from 0.23±0.08 to 1.01±0.55, Nickel (Ni) varied between 0.07±0.06 to 0.41±0.37, Cadmium (Cd) between 0.26±0.13 to 0.36±0.18, Cobalt (Co) between 0.33±0.09 to 0.94±0.39, Chromium (Cr) ranged between 0.46±0.38 to 1.96±1.40, Iron (Fe) between 6.06±4.32 to 15.03±2.09 while Manganese (Mn) ranged between 0.16±0.06 to 2.16±1.16 and Zinc (Zn) between 0.14±0.07 to 0.53±0.32. The path was in the order root>leave>stem>fruit from Sakwa, Thila and Marama study areas in Hawul local government area of Borno state.

This is as a result of the transpiration processes that occur in plants. As plant take up minerals from the soil, some of these toxic pollutants are also absorbed which are deposited in various parts of the plants. The leaves being the most active agent of transpiration, was observed to accumulate high levels of these contaminants. Therefore, the path of the concentration of heavy metals in the studied vegetables was observed to be in the order root>leave>stem>fruit.

The results obtained corroborate with the report of Abdullateef (Abdullateef, 2014) (Leaves>root> Stem>Fruits in Neem tree) and also in line with Hussain et al. (2006) (leaves>root>stem> fruits in *withania somnifera*). Abah et al. (2014), also reported the part taken by minerals as Soil>root>stem>leaves. Lead is a trace element in soil and there has been concern about its toxicity to plants and animals. It has been used in leaded petrol, diesel oil and there have been concerns that it is the main pollutant from auto mobile activities (Radwan and Salama, 2006). The pollution of lead from fertilizer was minor when compared to the atmospheric depositions (De-Vries et al., 2002).

The concentration of copper in Sorrel was in the order Sakwa>Thila>Marama in root, Sakwa>Thila>Marama in stem, Marama> Sakwa>Thila in leaves and Sakwa> Marama>Thila in fruit. Similar pattern was observed in Pepper whose order of copper concentration was Thila>Marama>Sakwa in root, Thila>Sakwa>Marama in stem, Thila> Marama> Sakwa in leaves and Thila>Marama>Sakwa in fruit. Which also shows that the order of the path of motion of mineral was leave>root>stem>fruit. This result was supported by the reports of some researchers (Mahwash et al., 2011; Radwan and Salama, 2006; Abdullateef, 2014) in the order of (root>leave>stem>fruit in *Achyranthes aspera, Azadirachta indica* and *Neem tree* respectively). Copper is a trace element in most soils. It is an essential element for plants and animals but it is also a toxic element when it is in high concentration, which is our major concern. Copper normally finds its way in to the drinking water from copper pipes, as well as additives design for the crop yields improvement. Lots of literatures showed strong evidence that use of farm machineries and agrochemicals are vital sources of copper in the agricultural areas (De-Vries et al., 2002).

CONCLUSION

In the whole plants studied from the three agricultural locations, leaf contained higher concentrations of heavy metals than roots and stems. The results also indicate that all the vegetable samples analyzed in this study had high levels of heavy metals, cations and anions. The levels of all the metals studied were relatively higher than those recommended by Food and Agricultural Organization (FAO) and the WHO/EU joint limits of 0.1-0.2 µg/g Cr, 0.3 µg/g Fe; 0.1 µg/g Pb; 0.1 µg/g Cu; 0.1 µg/g Zn; 0.1 µg/g Ni; 0.02 µg/g Cd and 0.3 µg/g Mn.The high levels of these heavy metals place the consumers of these vegetable crops grown within the study area at health risk with time unless an urgent step is taken by relevant agencies in address this issue.

REFERENCES

Abah J, Mashebe P, Ubwa ST, Denuga DD (2014). Some heavy metals content of Cabbage and soil cultivated in the Bezi Bar farm area of Katima Mulilo, Namibia. *Am. J. Chem.* 4(3): 101-108.

Abdullateef B (2014). Levels of heavy metals in Neem Tree as indicator of environmental pollution in Maiduguri, Borno State, Nigeria. (unpublished) pp 22-88.

Akan JC, Kolo BG, Yikala BS, Chellube ZM (2013). Levels of Some Agricultural pollutants in soil samples from Biu Local Government Area of Borno state, Nigeria. *J. Envi. Sci. Tox.* **1**(3) pp 71-81

Antonious G, Kochhar T (2009). Mobility of heavy metals from soil into hot pepper fruits: a field study. Bulletin of Environmental Contamination and Toxicology 82: 59-63.

Baird C (2002). Environmental Chemistry. Bookman, Porto Alegre, RS, Brazil (in Portuguese).

Bigdeli M, Seilsepour M (2008). Investigation of metals accumulation in some vegetables irrigated with waste water in Shahre Rey-Iran and toxicological implications. *American- Eurasian J. Agric. Environ.* Sci.4 (1): 86–92.

Demi˙rezen D, Aksoy A (2004). Accumulation of heavy metals in *Typha angustifolia* (L.) and *Potamogeton pectinatus* (L.) Living in Sultan Marsh (Kayseri, Turkey). Chemosphere 56: 685–696.

De-Vries W, Romkens PFAM, Van LT, Brodwijk JJB (2002). Heavy metals in Agriculture, hydrology and water quality. P.M. Haygarth and S.C. Jarvis eds. CAB int.: 107 – 132.

Ferré-Huguet N, Marti-Cid R, Schuhmacher M, Domingo JL (2008). Risk assessment of metals from consuming vegetables, fruits and rice grown on soils irrigated with waters of the Ebro River in Catalonia, Spain. Biological Trace Element Research 123: 66-79.

Hussain I, Khan F, Khan I, Wali-Ullah (2006). Determination of Heavy Metals in Medicinal Plants in Pakistan. *J. Chem. Soc. Pak.* **28** (4): 347 – 351.

in different parts of some vegetables. *American-Eurasian J. Agric.*

Jerry W (2011). "The Pursuit of Happiness ". The Science Creative Quarterly, *University of British Columbia*. pp. 4.

Lăcătuşu R, Lăcătuşu Anca-Rovena, Lungu Mihaela, Breaban Iuliana Gabriela, (2008). Macro- and microelements abundance in some urban soils from Romania, Carpth. J. of Earth and Environmental Sciences, 3,1,75-83;

Lamottee AE (2000). Smart Spectro water and waste water analysis test procedure manual. LaMottee Inc.USA. pp 68 - 71, 178 -180.

Mahwash ZK, Sheikh M, Farah N, Iftikhar IN, Erum Z (2011). Determination of some toxic and essential Trace Metels in some Medicinal and Edible Plants of Karachi City. *J. B. Appl. Sci.* **79** (2) 89-95.

Oliver MA (1997). Soil and human health: a review. European Journal of Soil Science 48: 573-592.

Radojevic M, Bashkin NV (1999). Practical Environmental analysis. *Royal Society of Chemistry and Thoma Graham House, Cambridge,* U.K. pp 356-377, 400-408.

Radwan MA, Salama AK (2006). Market based survey for some heavy metals in Egyptian fruits and vegetables. *Food Chem.Toxicol.* **44**: 1273-1278

Santamaria P (2006). Nitrate in vegetables: Toxicity content, intake and Ec regulation. *J. Sci. Food Agr.* 86: 10-17.

Sharma RK, Agrawal M, Marshall FM (2006). Heavy metals contamination in vegetables grown in wastewater irrigation areas of Varanasi, India, Bulletin of Environmental Contamination and Toxicology 77, 311-318

Singh KP, Mohou D, Dalwani R (2004). Impact assessment of treated/untreated wastewater toxicants discharged by sewage treatments plants on health, agricultural, and environmental quality in wastewater disposal area. Chemosphere 55, 227-255;

Tricopoulas D (1997). Epidemiology of cancer. In: De Vita, V.T. (Ed) Cancer: Principles and Practice of Oncology. Lippincott Company, Philadelphia, p 231-258

Turkdogan MK, Kilicel F, Kara K, Tuncer I (2002). Heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey, Environmental Toxicology and Pharmacology, 13, 175-179

Usman B, Kolo BG, Lawan M and Usman YB (2015). Determination of heavy metals and ions in vegetable samples from Wawah and Yimir-dhalang agricultural areas, Kwaya Kusar Local Government, Borno State. Ew J Anal and Environ Chem1(1): 14 - 19.

Usman YB, Kolo BG (2015). Assessment of some pollutants in soils of Sakwa, Thila and Marama in Hawul Local Government Area, Borno State, Nigeria. Ew J Anal & Environ Chem1(1): 20 - 24.

Uwah EI, Ndahi NP, Ogugbuaja VO (2009). Study of the levels of some Agricultural Pollutants in Soils and water leaf (*Talinum triangulare)* obtained in Maiduguri, Nigeria. J. Appl. Sci. Environ. Sanita. **4**(2): 71 – 78

Volpe MG, La Cara F, Volpe F, De Mattia A, Serino V, Pettito F, Zavalloni C, Limone F, Pellecchia R, De Prisco PP, Di Stasio M (2009). Heavy metal uptake in the enological food chain. Food Chemistry 117: 553-560.

Vontsa D, Grimanis A, Samara C (1996). Trace elements in vegetables grown in industrial areas in relation to soil and air particulate matter, Environmental Sollution, 94, 325-335;

Waalkes MP, Rehm S (1994). Cadmium and prostate cancer, J. Toxicol. Environ. Health, 43, 251-269

Wilson B, Pyatt FB (2007). Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey, UK. Ecotoxicology and Environmental Safety 66: 224-231.

Yargholi B, Azimi AA (2008). Investigation of Cadmium absorption and accumulation

Yusuf KA, Oluwole SO (2009). “Heavy metal (Cu, Zn, Pb) contamination of vegetables in urban city: A case study in Lagos,” Res. *J. Environ. Sci.* **30**: 292-298.