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Assessment of Cd, Cu, Mn and Zn Levels in Soil, Water and Vegetable Grown in Irrigated Farm along River Kubani, Zaria, Nigeria

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ABSTRACT

Contamination of plants and plant products with toxic chemical elements due to contaminated soil and water has been observed as a result of the release of these toxicants into the sea, rivers, lakes and even into irrigation channels. These toxicants accumulate and constitute an important threat to the life of plants, animals and man through food chain. Therefore investigation into heavy metals level in vegetable, soil and water used for irrigation is apparent. The analysis was carried out using Atomic Absorption Spectrophotometer (AAS) while method validation was achieved using reference material, Lichen (IAEA-336). The research result revealed Cd, Cu, Mn and Zn to be present in the respective samples as follows: Vegetable1.53±0.67ppm Cd, 7.85±1.73ppm Cu, 17.07±6.61ppm Mn, 26.66±12.16ppm Zn; Soil 1.69±0.65ppm Cd, 4.83±1.53ppm Cu, 34.34±6.75ppm Mn, 29.85±11.68ppm Zn and Water 1.30±0.32ppm Cd, 1.55±0.47ppm Cu, 12.67±1.17ppm Mn, 1.98±0.89ppm Zn. The High transfer factor observed between 0.497-0.957 revealed the susceptibility of vegetables to metal contamination by anthropogenic activities, hence routine monitoring of our environment will do us good.

INTRODUCTION

High demands of perishable food stuffs triggered by awareness on the food value of vegetables, exposure to other cultures and acquisition of proper education [1] has greatly influence the practise of irrigation system of farming in developing countries. Vegetables constitute essential diet component by contributing protein, vitamins, iron, calcium and other nutrients, which are usually in short supply [2]. They are also buffering agents for acidic substances produced during the digestion process. However, they contain both essential and toxic elements over a wide range of concentrations.

Research results have recognised heavy metals to be potentially toxic to crops, animals and humans when contaminated soils and water are used for crop production [3,4]. In a literature [5], it was concluded that soil, irrigation water and some vegetables from peri-urban sites were significantly contaminated by Cu, Cd, Pb and Zn, although Cd and Pb were of more concern than Cu and Zn.

The crazy rat race in civilization, industrialization, agricultural technology and urbanization coupled with improper environmental planning has left man with no other choice but indiscriminate dumping and discharge of domestic and industrial waste into our land and water bodies. Indiscriminate handling and disposal of waste from various industrial and domestic activities are major contributors of environmental pollutants that pose risks to human health [6]. Although globally, the problem of waste disposal is more pronounced in the developing nations and the socially-economically underprivileged are most vulnerable.

The wide spread heavy metals contamination in the last decades has raised public and scientific interest hence special attention is given to them throughout the world due to their toxic effects even at very low concentrations [7,8]. Rivers, streams, lakes, water from ponds and ground water are used to irrigate crops and for households and industrial uses. In Nigeria, the use of polluted water in the immediate surroundings of big cities for growing of vegetables is a common practice. Although this water is considered to be a rich source of organic matter and plant nutrients, it also contains sufficient amounts of soluble salts and heavy metals like Fe, Mn, Cu, Zn, Pb, Ni, Sn, Hg, Cr, As, Al [9]. When such water is used for cultivation of crops for a long period, these heavy metals may accumulate in soil and may be toxic to the plants and also cause deterioration of soil [10].

Heavy metals are generally present in agricultural soils at low levels. The input of heavy metals to soil from various sources may prove detrimental to plant through its uptake to toxic limit, thereby facilitating its entry into food the chain.

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There is possibility of biomagnification of toxins as it travels up in the food web. The transfer factor of heavy metals from soil-plant may be an indicator of the plant accumulation behaviour [11]. Large difference in the transfer of Cd, Zn, Ni, Cu, Pb and Cr from soil to different plant parts was observed in previous work [12]. The lowest transfer factors of Cd were found for grains of maize, peas, oats and wheat, whereas the highest values were reported for leaves of spinach and lettuce and the roots of various plants. Low transfer factors of Zn were reported for carrot and grains of maize and pea, whereas the highest were found for leaves of spinach and roots of radish and other plants. The transfer factors in the investigated plants were reported to be similar also for Cu, Cr and Pb.

Numerous studies have linked excessive accumulation of heavy metals to development of health abnormalities which include: cardiovascular kidney, nervous and bone diseases, impairment of reproductive function of males, spontaneous abortion, still birth, blue line on gum, mottling of teeth, low birth weight and abnormal pregnancy, gastrointestinal morbidity, language delay etc [13,14,15,16 &17]. Children are particularly vulnerable to lead and other heavy metal exposure due to high gastrointestinal uptake and the permeable blood-brain barrier [18].

With the increasing awareness of risk assessment of heavy metal in food crops, monitoring of heavy metals in vegetables is therefore critical as it gives information in nutritional planning and provides data for epidemiological studies [19]. The aim of this work is to study heavy metals load in river Kubani and irrigated land along its course. River Kubani is a receptacle where wastes are dumped indiscriminately. The study also aims at assessing the contribution of soil and water to heavy metal load in vegetables grown around Gangare area of the river and also to conduct risk assessment of heavy metals.

MATERIALS AND METHODS

Sampling

The procedure for sampling was adopted from Prabu [20]. A total of ten (10) grab water samples were collected in polyethylene cans and transported to the industrial chemical division, National Research Institute for Chemical Technology, Zaria-Nigeria for further characterization. Vegetable samples were collected in polyethylene bags during the harvest time. Soil samples at surface level (0-15 cm in depth) were collected from the same locations where the vegetable crops were grown.

Sample preparation

Each water sample collected was preserved with 4ml concentrated nitric acid to prevent the precipitation and adsorption of metals and stored in freezer at $4^{o}C$. Soil samples were air dried and ground into fine powder using agate mortar and passed through 2 mm sieve. Well mixed samples of 1 g each were taken in 250 ml glass beakers covered with watch glass and digested with a mixture of nitric acid and perchloric acid in a ratio of 3:1 on hotplate for 2 hours to ensure complete digestion. After evaporation to near dryness, 5ml of ultrapure water was added to the content of the beaker, filtered while hot into volumetric flask and then diluted to 50 ml with ultrapure water. Vegetable samples were thoroughly washed to remove all adhered soil particles. Samples were cut into small pieces, air dried for 5 days in the laboratory. The samples were pulverised and passed through 1 mm sieve. Digestion of these samples (1g each) was carried out using 5 ml of concentrated nitric acid, according to Awofolu [21] with modification.

Analysis

Heavy metal analyses were carried out using flame atomic absorption spectrophotometer AA-6800 (Shimadzu, Japan) at National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria. The calibration curves were prepared separately for all the metals by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination and were subjected to statistical analysis. The chemical composition of water was determined at NARICT and the elements determined included Cd, Cu, Mn and Zn. Transfer factor was calculated for each metal according to the following formula

TF = *Ps* (μg g-1 dry wt) / *St* (μg g-1 dry wt), Where *Ps* is the plant metal content. *St* is the total metal content in the soil [25].

Data analysis

Data collected were subjected to statistical tests of significance using the Multivariate tests ($p<0.05$) to assess significant variation in the concentration levels of the heavy metals in the vegetable, water as well as in soils. Probabilities less than 0.05 ($p < 0.05$) were considered statistically significant. Correlation coefficient was used to determine the association between the heavy metals in vegetable, water and soil at $p = 0.05$. All statistical analyses were done by SPSS software 17.0 for windows.

Validation of analytical method

In order to check the reliability of the analytical methods employed for trace metals determination, Lichens coded IAEA-336 was also digested and then analyzed following the same procedure.

RESULTS AND DISCUSSION

To evaluate the accuracy and precision of our analytical procedure, a standard reference material of lichen coded IAEA-336 was analyzed in like manner to our samples. The values determined and the certified values of the six (6) elements determined were very close suggesting the reliability of the method employed.

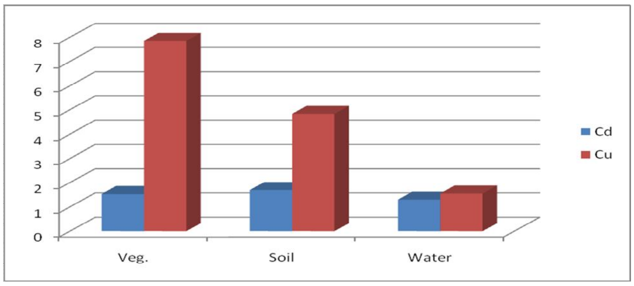
Higher soil trace metals content can result in higher levels of uptake by plants. In this study ten each of vegetable, soil and water samples were distinctly collected from irrigated land where vegetables were grown and analysed for the presence of trace metals of interest (Cd, Cu, Mn, Zn). The mean levels of triplicate measurement of the total trace metal concentration of individual sample (vegetable, soil and water) are presented in Table 2. The range and mean concentrations of elements in the total vegetable, soil and water samples from the study site are shown in Table 3. The order of their detection in each sample analysed where as follows: Zn > Mn > Cu >Cd in vegetable and Mn > Zn > Cu > Cd in soil and water (Fig 1).

Table 1 shows the results of analysis of reference material (Lichen IAEA-359) compare to the reference value

Elements (mg/L)	Cd	Cu	Pb	Mn	Zn
A Value	0.140	4.00	5.25	55.78	29.18
R Value	0.1-1.34	3.1-4.1	4.3-5.5	56-70	27-33.8

A Value = Analysed value R Value = Reference value.

Fig 1 Distribution of concentration of Cd and Cu in vegetable, soil and water



The concentration of Cd in the vegetable, soil and water samples ranged from 0.55-2.41ppm, 0.76-2.55ppm and 0.83-1.72ppm respectively. In vegetables, three out of ten samples analysed had Cd concentration less than 1.00ppm while the rest had Cd levels above 1.00ppm. Only one of the soil samples had Cd levels of 0.76ppm while the rest had Cd concentrations above 1 ppm. For water samples, eight out of the ten samples analysed had Cd levels above 1ppm but less than 2ppm while the remaining two had Cd levels below 1ppm.The highest concentration of trace metals in the soil and water samples was that of Mn of which the lowest and highest concentrations were 24.40 and 47.40 ppm; 11.45 and 14.51ppm respectively with a mean concentration and standard deviation of 34.34±6.75 and 12.67±1.17ppm (Table 3, Fig 3). Mn normally act as metal scavengers, due to their tendency to form colloidal particulate hydrous oxides which have strong adsorption affinities for certain metals like Pd and Cd [22]. Zn mean concentration (26.66±12.16) was observed to be highest in vegetable samples with the lowest and highest concentrations of 14.25 and 49.08ppm respectively.

For all the trace metals determined in this study, the values were observed to be higher in soil than in vegetable and water except for Cu which was higher in vegetable (Table 3). These metals are identified among the wide range of heavy metals found in fossil fuels. They are emitted into the environment as particles during combustion, accumulate in ash, be transported in air and contaminate soils [23]. The observation that soil level of the heavy metals were of higher magnitude than those of water (Table 3, Fig. 3) suggested soil as sink for heavy metals. Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments. The observed higher levels of trace metals in vegetable than in water (Fig. 3) used for irrigation indicate upward mobility of metal pollutants from the soil as earlier reported [24].

Table 2 showing Mean±SD concentration of individual vegetable (V), soil (S) and water (W) sample

Samples	Cd	Cu	Mn	Zn
V1	1.38±0.10	6.03±0.03	26.56±0.14	49.08±0.02
V2	1.58±0.04	7.61±0.08	24.50±0.14	25.45±0.02
V3	2.41±0.07	7.46±0.02	5.92±0.04	20.46±0.05
V4	1.58±0.09	8.89±0.10	8.49±0.19	25.02±0.08
V5	0.55±0.14	6.46±0.07	20.08±0.03	46.28±0.03
V6	1.51±0.04	7.69±0.02	14.31±0.04	25.2±0.02
V7	0.83±0.05	6.41±0.02	17.52±0.12	14.25±0.06
V8	2.48±0.05	11.31±0.02	20.43±0.14	25.29±0.04
V9	0.83±0.10	6.63±0.07	13.18±0.15	11.29±0.04
V10	2.13±0.06	10.02±0.07	19.68±0.04	24.29±0.04
S1	1.24±0.06	4.52±0.02	29.47±0.10	23.72±0.05
S2	2.34±0.01	3.17±0.08	24.40±0.19	10.90±0.01
S3	0.76±0.10	6.86±0.04	47.40±0.11	35.24±0.03
S4	2.55±0.03	7.39±0.02	38.16±0.06	34.53±0.04
S5	1.58±0.04	5.73±0.10	33.09±0.08	39.35±0.05
S6	1.45±0.06	3.92±0.03	30.09±0.17	14.52±0.05
S7	2.55±0.09	4.60±0.05	42.78±0.21	20.90±0.02
S8	1.10±0.13	2.41±0.07	33.24±0.02	19.91±0.05
S9	1.17±0.07	4.90±0.08	31.28±0.23	47.49±0.07
S10	2.13±0.06	4.82±0.04	33.44±0.09	31.96±0.08
W1	0.83±0.09	1.36±0.03	11.60±0.10	1.71±0.07
W2	0.83±0.04	2.19±0.05	12.00±0.15	2.05±0.02
W3	1.45±0.08	1.81±0.05	12.10±0.03	3.13±0.04
W4	1.38±0.06	2.34±0.04	11.45±0.25	3.75±0.03
W5	1.51±0.07	1.43±0.03	11.45±0.11	0.95±9.01
W6	1.72±0.04	1.58±0.01	14.16±0.15	1.98±0.07
W7	1.31±0.05	1.06±0.04	13 .31±0.11	1.28±0.02
W8	1.24±0.09	1.51±0.05	13.81±0.2	1.91±0.01
W9	1.72±0.10	0.83±0.06	14.51±0.10	1.88±0.02
W10	1.03±0.02	1.36±0.08	12.30±0.07	1.13±0.02

V = vegetable S = soil W = water

The levels of heavy metals obtained in this study were compared with values recorded earlier in the literatures. Cadmium (Cd), copper (Cu), manganese (Mn) and zinc (Zn) values in vegetables were higher than findings in Alau Dam and Gongulon in Maiduguri [9] and bank of River Challawa, Kano-Nigeria [25]. Cu, Mn and Zn were found to be lower in this work compare to the findings in Ethiopia [20] while Cd was higher in this work. Generally Cd contents in many crops is categorised as beyond the limits at levels > 1.5ppm dry weight [26]. This value is slightly lower than Cd level obtained in this work. The result obtained for vegetable in this work was also compared to the guideline for maximum allowable limits of metals in vegetable [20]. Cu, Mn and Zn were found to be lower than the maximum allowable limit while Cd was higher than 0.2ppm maximum limit.

WHO reported the average daily consumption of Mn to range from 2.0 to 8.8 mg/kg/day [27]. Vegetables constitute essential diet component by contributing protein, vitamins, iron, calcium and other nutrients, which are usually in short supply [2]. The UK Food Standard Agency's Experts Group on vitamins and Minerals concluded that supplementary intake of up to 4mg/day in addition to the diet would likely produce adverse effects in the general population [28]. Though Mn absorbed, is excreted largely through the bile and is eliminated in the faeces yet it can accumulate in the brain at high intake levels [29]. The level obtained in this work is a cause for concern. Cu is readily absorbed following oral ingestion, absorption being greatest for the most soluble salts. The Joint Committee on Food Additives has recommended a provisional maximum tolerable daily intake (PMTDI) of 0.5mg/kg/day. Zn is a known cofactor of the superoxide dismutase enzymes, stabilise phosphate group and co-ordinate with organic bases. Yet elevated level of dietary Zn intake can have negative effect on Cu balance. WHO propose a PMTDI of 0.3-1.0 mg/kg [29].

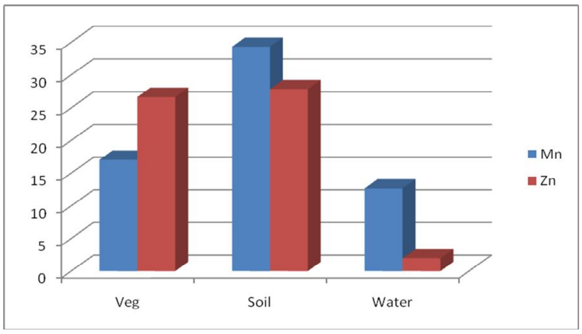
Table 3 showing Mean±SD and range of heavy metals in vegetable, soil and water samples

Element	Sample	Mean±SD	Range
Cd	Vegetable	1.53±0 .67	0.55-2.41
	Soil	1.69±0 .65	0.76-2.55
	Water	1.30±0 .32	0.83-1.72
Cu	Vegetable	7.85± 1.73	6.03-11.31
	Soil	4.83± 1.53	2.41-7.39
	Water	1.55±0 .47	0.83-2.34
Mn	Vegetable	17.07± 6.61	5.92-26.56
	Soil	34.34± 6.75	24.40-47.40
	water	12.67± 1.17	11.45-14.51
Zn	Vegetable	26.66± 12.16	14.25-49.08
	Soil	27.85± 11.68	10.90-47.49
	water	1.98±0 .87	0.95-3.75

Soil heavy metals concentration in this work was found to be higher than the values reported for Alau Dam and Gongulon [9]. This could be attributed to application of compost collected from dumpsite to boost yield. Another reason could be emission of these metals from fossil fuels and dumpsite into the environment as particles during combustion followed by accumulation in ash, transportation in air and deposition. Zn reported for Challawa soil used for irrigation farming was about five times higher compared to our findings. Cd (27-53ppm), Cu (BDL-198ppm), Mn (3000-6600ppm), and Zn (175-1150ppm) reported for Dandora/Korogocho soil in Kenya [6] was far higher than our findings (Table 3). The level of Cd, Cu and Zn determine in this work were compare to elemental concentration in a typical soil in Yauri Nigeria [24]. Cu and Zn values were lower than 25ppm and 60ppm respectively while Cd was about six times higher than 0.3ppm reported for the typical soil. This revealed that the soil used for irrigation is not polluted by these metals except for Cd.

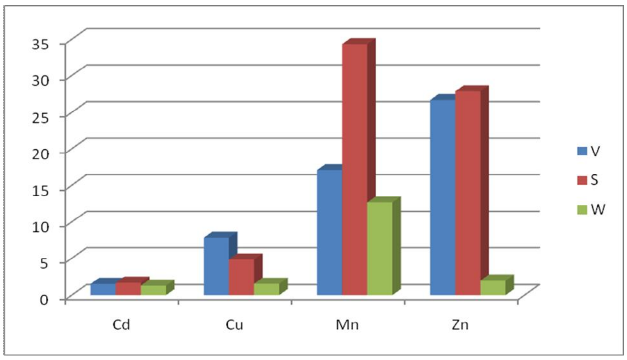
Generally Cd, Cu, Mn and Zn levels in water were lower than soil and vegetable in this work. This correlate the findings of other researchers who reported lower Zn level in water than vegetable [20], lower Cd and Mn levels in water than soil [6]. The result of water analysis was also compared to WHO limits for substances affecting the acceptability of water for domestic purposes [30]. All metals determined in this work were found to be higher than the acceptable limits. These findings could be link to indiscriminate dumping of refuse by the bank and inside the river, washing of cars and discharged of waste water from surrounding compounds.

Fig 2 Distribution of concentration of Mn and Zn in vegetable, soil and water



The result of statistical analysis revealed positive correlation between Cd and Mn, Cd and Zn in water samples though the correlation was not significant at $\alpha = 0.05$. The correlation between Zn and Cu was positive and significant at $\alpha = 0.05$. From the above it could be inferred that Cd source in water could be responsible for the presence of Mn and Zn. Negative correlation was observed between Cd and Cu, Mn and Cu, Zn and Mn indicating different source of these metals in water samples.

Fig 1 Distribution of concentration of Cd, Cu, Mn and Zn in vegetable (V), soil (S) and water (W) samples



Statistical data generated from soil revealed positive correlation between Cd and Cu, Mn and Cu, Zn and Mn as well Zn and Cu. Although the correlations were not significant at $\alpha = 0.05$ except between Zn and Cu. This shows that the metals could likely originate from similar source. The negative correlations observed between Cd and Mn, Cd and Zn, Ni and Zn in soils could indicate different source of these metals in soils of the study area. In vegetable the positive correlation revealed between Cd and Cu was significant at $\alpha = 0.05$ while that found between Mn and Zn was insignificant. Negative correlation was shown between Cd and Mn, Cd and Zn, Cu and Mn, Cu and Zn. The positive correlation between metals in vegetable could indicate similar sources of metals while negative correlation observed among the metals in vegetable could indicate different sources of these metals. The result of statistical analysis revealed positive correlation between Cd and Cu, Zn and Mn in soil and vegetable, this may suggests a possible source relationship between these metals in soil and vegetable. Strong correlation was also observed for Zn and Cu in soil and water indicating source relationship.

Transfer Factor (TF)

Most of the heavy metals are natural constituents of the earth's crust and from there they are taken by plants and thus transferred to food chain. From this study, transfer factor of 0.91, 1.63, 0.50 and 0.96 was observed for Cd, Cu, Mn and Zn in that order. Highest transfer factor was obtained for Cu in vegetable followed by Zn and Cd with Mn being the least. Base on the suggestion that the greater the transfer coefficient value than 0.50, the greater the chances of vegetables for metal contamination by anthropogenic activities [31], the elevated levels of the contaminants heavy metals observed in this study could be linked to emission from anthropogenic activities. Though the suggestion was solely based on the root uptake of metal ignoring the potentials of leafy vegetable to accumulate higher metals compare to other vegetable. All the values are below one (1) with exception of Cu which was found above one.

Conclusion

Four trace metals were determined in this study and their concentrations were found to be higher in soil than in vegetable and water except for Cu which was higher in vegetable. The above observation could be attributed to application of compost collected from dumpsite by the farmers to boost yield. Also the higher levels of trace metals in vegetable than in water used for irrigation indicate upward mobility of these metals from the soil.

REFERENCES

1. Fisseha, I., 2002. Metals in leafy vegetables grown in Addis Ababa and toxicological implications. Ethiop J. Health Dev., 16: 295-302.
2. Thompson, H.C., and Kelly, W.C. (1999). Vegetable crops. 5th ed., New Publishing Company Ltd, London.
3. Xian, X. (1989) Response of Kidney bean to concentration and chemical form of cadmium, zinc and lead in polluted soils. Environ. Poll., 57: 127-137
4. Cambra, K., T. Martinez, A. Urzelai and E. Alonso (1999). Risk analysis of farm area near a lead and cadmium contaminated industrial sit. J. Soil. Contam., 8: 527-540.
5. Singh, S. and M. Kumar, 2006. Heavy metal load of soil, water and vegetables in peri-urban Delhi. Environ. Monit. And Assessm., 120: 79-91.
6. Kimani N.G. (2007) Environmental Pollution and Impact to Public Health; Implication of the Dandora Municipal Dumping Site in Nairobi, Kenya. a pilot study report In cooperation with The United Nations Environment Programme (UNEP)
7. Kumar, A., (2004) Environmental Biotechnology. 1st Ed., Daya,Vedams eBooks (Pvt) Ltd., New Delhi India, ISBN:817035336X.
8. Islam, E., Y. Xiao-E., H. Zhen-li and M. Qaisar. (2007). Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. J. Zhejiang Univ. Sci., 8: 1-13
9. Uwah, E.I., N. P. Ndahi and V. O. Ogugbuaja, 2009. Study of the Levels of Some Agricultural Pollutants in Soils, and Water Leaf (Talinum triangulare) Obtained in Maiduguri, Nigeria. Journal of Applied Sciences in Environmental Sanitation, 4 (2): 71-78.
10. Kirkhan, M. B, 1983. Study on accumulation of Heavy Metals in Soil receiving sewage and Effluent water. Agric. Ecosystem. Environment, 9: 251.
11. Kabata-Pendias A., Pendias H. (1992): Trace elements in soils and plants. 2nd ed. CRC Press, Boca Raton.
12. Lubben 1993 In Puschenreiter, M., O. Horak, W. Friesl, W. Hartl (2005) Low-cost agricultural measures to reduce heavy metal transfer into the food chain – a review plant soil environ., *51*, (1): 1–11
13. Thakur,J.S., S. Prinja, D. Singh, A. Rajwanshi, R. Prasad, H.K. Parwana, R. Kumar (2009). Adverse reproductive and child health outcomes among people living near highly toxic waste water drains in Punjab, India. JECH Online First, published on October 19, 2009 as 10.1136/jech.2008.078568
14. Telisman S, Cvitkovic P, Jurasovic J. (2000) Semen quality and reproductive endocrine function in relation to biomarkers of lead, cadmium, zinc and copper in man. Environ Health Persp. 108: 45.
15. Herz-Picciotto I. (2000). The evidence that lead increases risk of spontaneous abortion. Am J Ind Med. 38: 300-

16. Fagher U, Ladauski T, Schutz A. (1993) Relationship between cadmium and lead burdens and preterm labour. Int J Gynecol Obstet. 1993; 40: 109.
17. WHO 1992. Cadmium. Environmental Health Criteria,Geneva. Vol., 134 and 165.
18. Jarup L. Hazards of heavy metal contamination. Br Med Bull. 2003; 68: 167-82.
19. Bruce, A. and L. Bergstrom, (1983). User requirement for data bases and applications in nutritional research. Food Nutr. Bull., 5: 24-29
20. Prabu, P.C. (2009). Impact of heavy metals contamination of Akaki River of Ethiopia on soil and metal toxicity on cultivated vegetable crops. *EJEAFChe, 8 (9), (*818-827)
21. Awofolu, O.R., 2005. A survey of Trace metals in vegetation, soil and lower animals along some selected major and Roads in metropolitan city of Lagos. Environmental monitoring and Assessment, 105: 431-447.
22. Mill AJ (1980). Colloidal and macromolecular forms of iron in natural waters. A review. Environ. Technol. Lett. 1:97-108.
23. Yahaya, M. I. G. C. Ezeh, Y. F Musa and S. Y. Mohammad (2010). Analysis of heavy metals concentration in road sides soil in Yauri, NigeriaAfrican Journal of Pure and Applied Chemistry Vol. 4(3), pp. 022-030, March 2010
24. Dzoma, B.M., R.A. Moralo, L.E. Motsei, R.V. Ndou and F.R. Bakunzi (2010). Preliminary findings on the levels of five heavy metals in water, sediment, grass and various specimens from cattle grazing adn watering in potentially heavy metal polluted are of the North west province of South Africa. J.Anim.Vet.Adv. 9 (24): 3026-3033.
25. Awode, U.A., A. Uzairu, M.L. Balarabe, G.F.S. Harrison and O.J. Okunola (2008). Assessement of peppers and soil for some heavy metals from irrigated farmlands on the bank of River Challawa, Northern Nigeria. Pakistant Journal of Nutrition.. 7(2): 244-248.
26. Lokeshwari, H., and Chandrappa, G.T. (2006) Imapct of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. Current Science, 91(5), pp.622-27.
27. WHO (World Health Organisation). 1973. Trace Elements in Human Nutrition: Manganese. Report of a WHO Expert Committee. Technical Report Service, 532, WHO, Geneva, Switzerland. pp. 34-36.
28. FSA. 2003. Safe Upper Levels for Vitamins and Minerals. Expert group on Vitamins and Minerals. Food Standards Agency, May 2003. ISBN 1-904026-11-7.
29. EMEA (2008) European Medicines Agency. Guideline on the specification limits for residues of metal catalysts or metal reagents. Doc. Ref. EMEA/CHMP/SWP/4446/2000. HTTP://www.emea.europa.eu.
30. FEPA (1991) Guidelines and Standards for Environmental Pollution Control in Nigeria.
31. Kloke, A., D.R. Sauerbeck and H. Vetter, (1984). The contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chains. In ‘Changing metal cycles and human health: report of the Dahlem Workshop on Changing Metals Cycles and Human Health, Berlin, Germany’. Ed J.O Nriagu Springer-Verlag: Berlin, pp: 113-141.