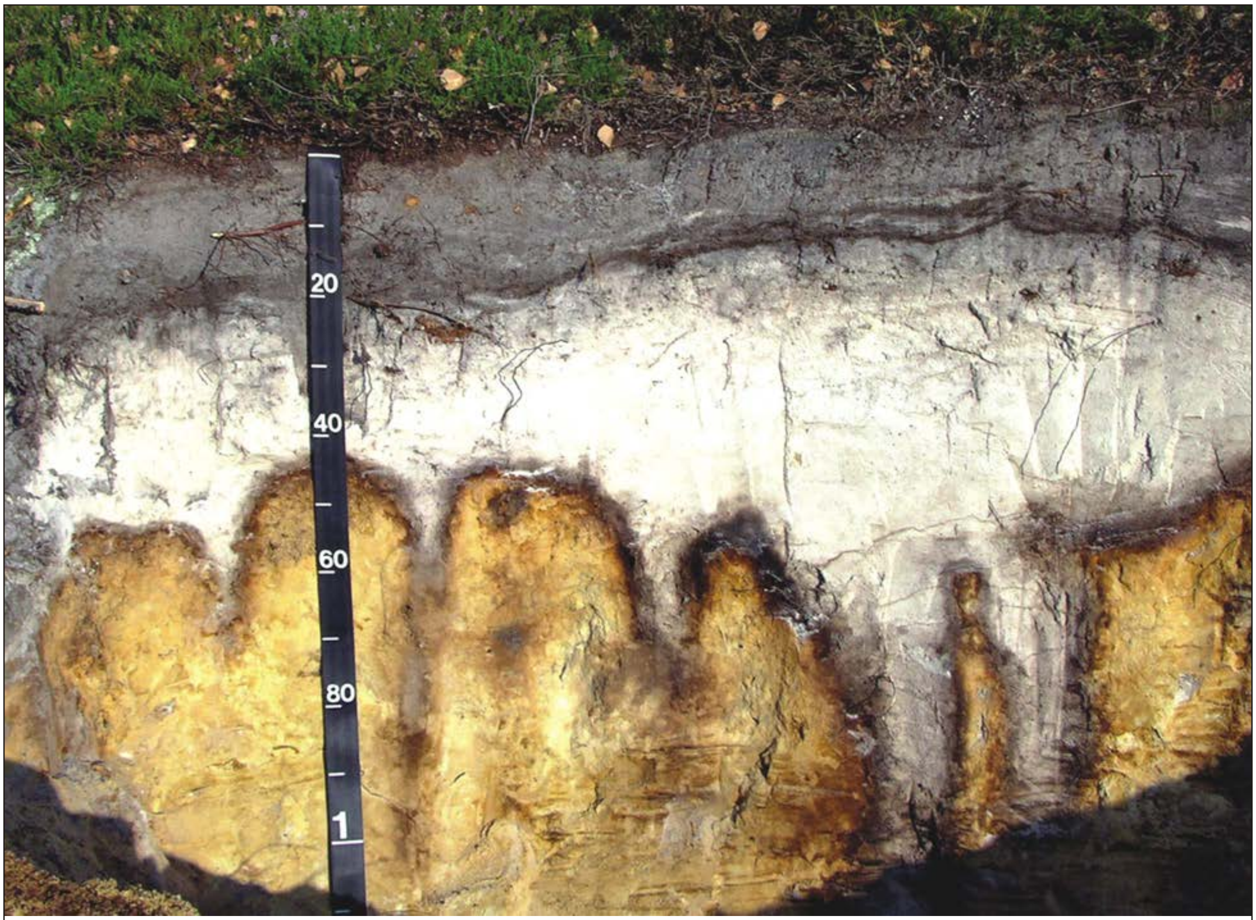

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Lead, Nickel, Vanadium, Cobalt, Copper and Manganese Distributions in Intensely Cultivated Floodplain Ultisol of Cross River, Nigeria

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Abstract: Presently, heavy metal pollution of our cultivable agricultural farmlands is increasing and is often associated with anthropogenic sources. Wetlands contaminated with detectable levels of metal toxicants and other trace macro-elements are frequently used for growing vegetable crops. To assess the impact of floodwater on soil of floodplain wetland of Cross River, soil samples were taken from uppermost 0-30 cm within designated thirty square grids and analytical determinations of cobalt (Co), lead (Pb), manganese (Mn), nickel (Ni), vanadium (V) and copper (Cu) were carried out. The results show high accumulation of Mn (40.22±2.79 μg g^{-1}), Pb (22.47±0.58 μg g^{-1}), Cu (16.17±7.93 μg g^{-1}) and Ni (17.24±4.12 μg g^{-1}) from the wetland. The exploratory data analyses for each of the heavy metals revealed that the concentrations of the metals in the floodplain ultisols were more effectively influenced by environmental and anthropogenic attributes.

Key words: Heavy metals, floodplain soil, soil pollution, Cross river

Introduction

Although some trace metals are considered as essential plant nutrients, most heavy metals are of considerable health and environmental concern because of their toxicity and bioaccumulative behavior (Omgbu and Kokogbo, 1993; Yusuf *et al*., 2003; Ajibola and Ozigis, 2005). Enhanced soil levels can result in increased phytoextraction and assimilation by plants (Numberg, 1984; Yusuf *et al*., 2003; Moreno *et al*., 2005; Benson and Ebong, 2005; Udosen *et al*., 2006), which may inadvertently enter the food chain posing considerable health risks to humans and animals (Numberg, 1984; Banuelos and Mayland, 2000; Ellis and Salt, 2003; Pillay *et al*., 2003; Moreno *et al*., 2005). Recent studies have indicated that crops raised on metal contaminated soil accumulate metals in concentrations excessive enough to cause clinical problems both to humans and animals that consume these metal rich plants (Rattan *et al*., 2005).

The presence and detection of heavy metals in soil are commonly associated with geochemical as well as biological process and are greatly influenced by anthropogenic activities such as industrial activities, waste disposal and agricultural practices (Zauyah *et al*., 2004; Benson and Ebong, 2005; Udosen *et al*., 2006). Due to the non-biodegradability of heavy metals and because emission (partly by leaching) is far less than anthropogenic inputs (cadmium in fertilizers; copper in pig manure; atmospheric dispersal like lead in petrol exhausts of cars, trucks; mercury by volatilization; lead in batteries, etc.) heavy metals steadily accumulate in soils as sinks (Udosen *et al*., 2006).

The ultisols of Cross River State supports more than 40% of Nigeria's population with agricultural produce. The dominant vegetables grown are *Telfairia occidentalis* (fluted pumpkin) and *Hibiscus esculentes* (okra). *Colocasia preussii* (cocoyam) is of increasing importance in Cross River wetland agriculture, with women as the sole farmers. The wetlands of Cross River tributaries between Boki and Bekwara and including Bansara are also dotted with large parcels of rice farms (Inyang and Okoji, 2000). The area has vast freshwater resources that are dotted with floodplain soil and cultivable lowlands. Although the agricultural sector in this part of Nigeria has over the years depended on the availability of water for the thrivability of crops, occasional flooding of rivers onto plain lowlands often provides succors to local farmers. Moreover, finding adequate supplies of unpolluted freshwater especially during the dry season months to meet the ever-increasing agricultural needs is becoming a national problem as most rivers are impacted with toxic contaminants such as heavy metals, aromatic hydrocarbons, pesticides and radioactive substances. These toxicant-laden waters when emptied unto plain lowland soils during intermittent flooding end up being retained in the upper soil layer prior leaching to lower horizons of the soil. The bioaccumulation potential of these pollutants by the soil can lead to harmful effects on crops thereby reducing bioproductivity as well as entering the food chain.

The aim of this study was to investigate the levels of heavy metals of toxicological interest in the cultivated wetlands of Cross River, Nigeria, where varieties of crops are grown during the dry seasons, making use of residual moisture.

Materials and Methods

The study area is a floodplain wetland located along the lower reaches of Cross River in the southeastern part of Nigeria. It is bounded by latitude 04° 45' - 05° 15' N and longitude 08° 00' - 08° 15' E. The fluvial biotope is characterized by relatively flat land bordering the lower reaches of the lotic Cross River system. The floodplain soils must have been formed by the deposition of sediments transported down by the river. As a seasonal fluvial system, water inundates the floodplain and layers of sediment laden with organic and inorganic substances are deposited during each flooding.

Soil samples (0-30 cm) were collected using a stainless steel auger from a well mapped out square grids (Fig. 1) along the cultivated floodplain soils. The ultisol samples were systematically obtained from the investigated area between August 29 and September 6, 2003, into calico bags, zipped and transported to the laboratory for pretreatment before analysis of their heavy metal contents. Ninety soil samples homogenized into thirty composite sub-samples were air-dried and sieved using a 2 mm sieve. Total heavy metal contents in 1.0 g of each sample were extracted using Analytical grade (Aldrich Chemical Company) 1 mL 60% $HClO_4$ (perchloric acid) and 7 mL 40% HF (hydrofluoric acid) (Radojevic and Bashkin, 1999). Residues in platinum crucibles were evaporated to dryness on a hot plate until fumes of $HClO_4$ appear. Resultant contents were taken in 1mL H_2SO_4 and heated

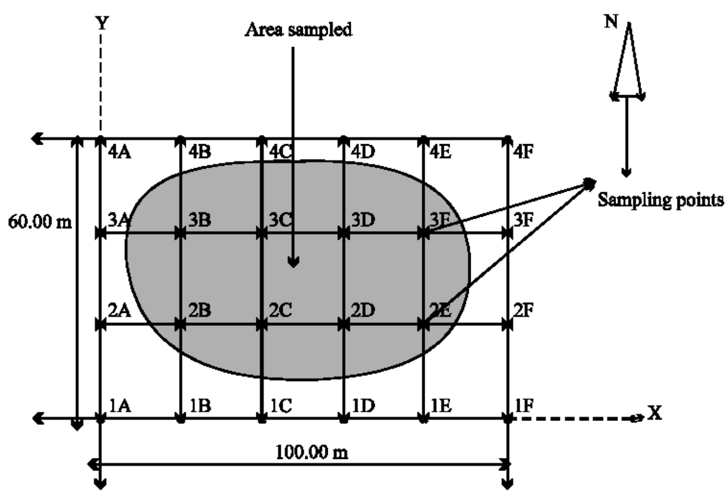

Fig. 1: Square-grid schematic presentation of sampled area along the floodplain ultisol of Cross River, Nigeria

again to drive off $HClO_4$. Cold aliquots were diluted with water and filtered into 100 mL volumetric flask and made up to mark. Blanks were prepared by following the same procedure with all reagents but without the soil samples. The filtrates were analysed for manganese, vanadium, copper, cobalt, lead and nickel using Atomic Absorption Spectrophotometer (AAS). All analysis were performed in duplicates and the data reported in $\mu g\ g^{-1}$ (on dry weight basis). Detection limits for Co, Cu, Mn, Ni, Pb and V were 0.01, 0.01, 0.01, 0.02, 0.05 and 0.2 $\mu g\ g^{-1}$ respectively. Continuous summary descriptives and correlation analysis among extractable heavy metals was also performed using Analyze-It + General 1. 73© statistical software.

Results and Discussion

The computed statistical data on measured heavy metal concentrations (Co, Cu, Pb, Mn, Ni and V) in both floodplain wetland and background soils investigated are presented in Table 1. The levels of these heavy metals are represented in Fig. 2, in to depict the apparent distributions of the metal toxicants in the floodplain soil.

The results show that the floodplain soils contain high concentrations of manganese, lead, copper and nickel. Moreover, considerable differences in the concentrations of these heavy metals were dependent on the site of sampling. Their levels appeared to have followed a distribution pattern down the lower reaches of the river. Remarkably, Co, Ni and V were more absorbed in the soil as evidenced by their relative low concentrations. The heavy metal concentrations in the flood zones (Co, 11.52; Cu, 22. 61; Mn, 43.92; Ni, 22.38; Pb, 23.60 and V, 15.87 $\mu g\ g^{-1}$, respectively) were generally higher than the background values (Co: 0.033; Cu: 1.00; Mn: 4.11; Ni: 0.45; Pb: 1.15 and V: 0.05 $\mu g\ g^{-1}$, respectively). Manganese recorded the highest mean concentration of 40.22±2.79 $\mu g\ g^{-1}$ followed by lead with 22.47±0.58 $\mu g\ g^{-1}$. Vanadium and cobalt recorded very low levels in the floodplain soils investigated with mean concentrations of 8.30±3.51 and 7.92±1.99 $\mu g\ g^{-1}$,. On the whole, the trend in heavy metal levels in the floodplain wetland soils was Mn>Pb>Cu>Ni>V>Co.

The enhanced concentrations of the metals in the floodplain soils when compared with the background values could be attributed to the floodwater of the Cross River System. From the results, Pb and Mn indicated very low mobility potential judging from their low coefficient of variation values (Table 1). Manganese and lead could be assumed to have been adsorbed more strongly to the colloidal minerals of the soil. Vanadium, cobalt and nickel had relatively high coefficients of variation of 42.22, 25.24 and 23.89% respectively, indicating that these metals were highly variable. This implies that they were more weakly held within the soil, making them more labile and bioavailable (Alloway, 1990).

Table 1: Continuous summary descriptives of heavy metals levels in floodplain and background soil. Concentrations in $\mu g\ g^{-1}$

Heavy metal	Mn (FP)	Mn (BG)	Ni (FP)	Ni (BG)	Pb (FP)	Pb (BG)	V (FP)	V (BG)	Co (FP)	Co (BG)	Cu (FP)	Cu (BG)
Arithmetic mean	40.22	2.284	17.24	0.145	22.47	0.550	8.30	0.019	0.009	7.92	16.17	0.419
Median	40.68	2.123	17.65	0.100	22.65	0.425	7.62	0.015	0.005	7.69	19.13	0.380
Standard deviation	2.79	0.981	4.12	0.127	0.58	0.410	351.00	0.021	0.011	1.99	7.93	0.224
Standard error	0.89	0.310	1.30	0.040	0.18	0.129	1.11	0.007	0.004	0.63	2.51	0.071
Min.	33.60	4.11	22.38	0.45	22.60	1.15	15.89	0.050	11.52	0.030	22.61	1.000
Max.	42.92	1.12	10.40	0.00	21.39	0.20	4.38	0.000	5.09	0.000	14.09	0.250
Range	9.32	2.990	11.98	0.450	1.17	1.190	11.57	0.050	0.030	6.430	20.51	0.770
Lower quartile	40.32	1.534	14.77	0.083	22.07	0.235	5.93	0.000	6.93	0.000	14.39	0.278
Upper quartile	41.44	2.740	19.60	0.185	22.78	0.713	8.53	0.033	8.41	0.013	22.24	0.450
95% C.I. of mean	38.22	1.582	14.29	0.054	22.06	0.257	5.79	0.004	0.001	6.49	10.49	0.259
	42.23	2.986	20.19	0.236	22.89	0.843	10.81	0.034	0.017	9.35	21.84	0.579
IQR	1.11	1.203	4.83	0.103	0.71	0.478	2.59	0.033	0.013	1.48	7.85	0.173
CV(%)	7.00	43.00	24.00	87.00	3.08	75.00	42.00	109.00	122.00	25.00	49.00	53.00

FP-Floodplain soil samples; BG-Background soil samples

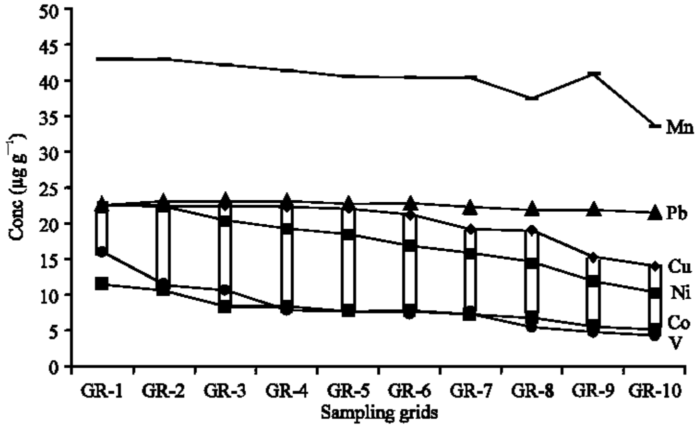

Fig. 2: Concentration of metals in each sampling grids from Cross River floodplain soils

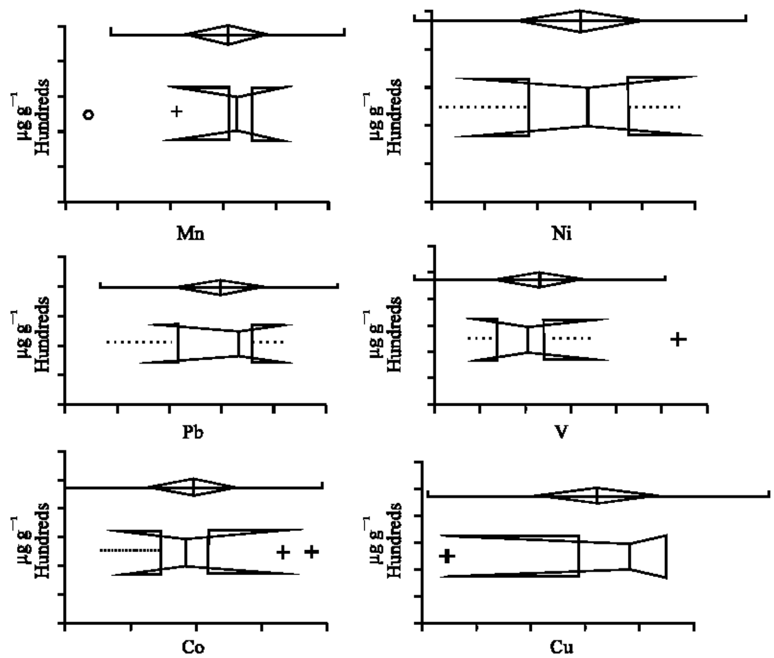

Fig. 3: Multiple Box-and-Whiskers diagram for heavy metals determined in Cross River floodplain ultisols

The area investigated is usually inundated with floodwater at moderate rise in water level. Suspended matter in the floodwater settles considerably on floodplain soils, leaving behind organic and inorganic-laden sediments (Yahya, 1994) which in the short-and long-term, leads to phytoextraction of these noxious substances, especially if the pollutants binding capacity of the soil is exhausted. Moreover, for phytoextraction to occur, metal contaminants must be bioavailable (Lasat, 2000). Soil pH affects not only metal bioavailability, but also the very process of metal uptake into roots (Yahya, 1994; Brown *et al*., 1995; Lasat, 2000). Despite these seemingly inhibiting factors, uptake of heavy metals is generally increased in plants that are grown in areas with increased soil concentrations

(Benson and Ebong, 2005; Udosen *et al*., 2006). Many researchers have shown that common garden vegetables are capable of accumulating high levels of metals from the soil (Garcia *et al*., 1981; Khan and Frankland, 1983; Xiong, 1998; Cobb *et al*., 2000; Yusuf, 2003; Rattan *et al*., 2005; Benson and Ebong, 2005). Cabbage (*Brassica* species) have been reported as hyper-accumulators of heavy metals into the edible tissues of plants (Xiong, 1998) and *Telfairia occidentalis* have been shown to possess High Phytoextraction Preference (HPP) for Pb and Ni (Udosen, 1994; Benson and Ebong, 2005). *Telfairia occidentalis* is a dominant vegetable grown in the floodplain soils of Cross River. Considering the toxicity of the metals investigated, many people could be at long-term risk of adverse health effects from consuming vegetables cultivated in the floodplain soils of the Cross River, owing to continuous deposition of metal-laden sediments from floodwater.

The correlation among heavy metals in the floodplain soil in each grid revealed a very interesting result. The correlation coefficients, r, calculated mostly ranged between 0.64 and 0.95. Also, the coefficients of determination ranged from 40.74% (Pb/V) to 90.27% (Ni, V and Co). Significant ($p>0.05$) and positive relations were found between all metals except between Mn and Ni, which indicated a significantly ($p>0.05$) negative relation ($r=-0.76$). These results indicated that these heavy metals were bound to the sediments, which were subsequently deposited unto the floodplain soil within the same period and could be interpreted as having a common pollution origin (Ho *et al*., 2003).

The Box-and-Whiskers plots for Co, Cu, Pb, Mn, Ni and V (Fig. 3) demonstrate the exploratory data analysis for each heavy metal, thus highlighting possible outliers (Armitage and Berry, 1994; Chmielewska and Medved, 2001). The notched box plots cover the middle 50% of concentrations recorded between 75th and 25th percentiles. The dotted lines in each box are medians. The whiskers extend only to the points which are within 1.5 times of the box length (interquartile range). On the figures, possible outliers are highlighted as single points outside the range of the whiskers. This is suggestive that environmental factors could have influenced the levels of heavy metals in the soil samples where such anomalous values were recorded.

Conclusions

The results of the present investigation show the relatively high heavy metal (Pb, Mn, Co, Co, Ni and V) concentrations in the floodplain ultisol than the background soil. Nevertheless, the results obtained do not provide elaborate information on the various metal bioavailability and mobility. However, it is suggested that metal speciation studies be conducted in order to fully understand this, although the total metal concentrations obtained indicated that a significant deterioration of the integrity of the floodplain wetland is expected with increased deposition of sediments laden with heavy metal and other pollution variables.

References

Ajibola, V.O. and I. Ozigis, 2005. Partitioning of some heavy metals in Kaduna streets soils. J. Chem. Soc. Nigeria, 30: 62-66.

Alloway, B.J., 1990. Sorption of Trace Metals by Humic Materials in Soil. In: Alloway, B.J. (Edn.), Heavy Metals in Soils. Blackie, Glasgow.

Armitage, P. and G. Berry, 1994. Statistical Methods in Medical Research. 3rd Edn., Blackwell Scientific Publications, Oxford, England.

Banuelos, G.S. and H.F. Mayland, 2000. Absorption and distribution of selenium in animals consuming canola grown for selenium phytoextraction. Ecotoxicol. Environ. Safety, 46: 322-328.

Benson, N.U. and G.A. Ebong, 2005. Heavy metals in vegetables commonly grown in a tropical garden ultisol. J. Sustainable Tropic. Agric. Res., 16: 77-80.

Brown, S.L., R.L. Chaney, J.S. Angle and A.M. Baker, 1995. Zinc and cadmium uptake by hyper-accumulator *Thlaspi caerulescens* and metal-tolerant *Silene vulgaris* grown on sludge-amended soils. Environ. Sci. Technol., 29: 1581-1585.

Chmielewska, E. and J. Medved, 2001. Bioaccumulation of heavy metals by green algae *Cladophora gomerata* in a refinery sewage laoon. Croatia Chemica Acta, 74: 135-145.

Cobb, G.P., K. Sands, M. Waters, B.G. Wixson and E. Dorward-King, 2000. Accumulation of heavy metals by vegetables grown in mine wastes. Environ. Toxicol. Chem., 19: 600-607.

Ellis, D.R. and D.E. Salt, 2003. Plants, selenium and human health. Curr. Opin. Plant Biol., 6: 273-279.

Garcia, W.J., C.W. Blessin, G.E. Inglett and W.F. Kwolek, 1981. Metal accumulation and crop yield for a variety of edible crops grown in diverse soil media amended with sewage sludge. Environ. Sci. Technol., 15: 793-804.

Ho, S.T., I.J. Tsai and K.C. Yu, 2003. Correlation among aqua-regia extractable heavy metals in vertical river sediments. Difusse Pollution Conference, Dublin, 14: 12-18.

Inyang, I.B. and M. Okoji, 2000. Southeastern Nigeria: It's Environment. Abaam Publishing Co., Nigeria.

Khan, D.H. and B. Frankland, 1993. Effects of cadmium and lead on raddish plants with particular preference to movement of metals through soil profile and plant. Plant and Soil, 70: 335-345.

Lasat, M.M., 2000. Phytoextraction of metals from contaminated soil: A review of plant/soil/metal interaction and assessment of pertinent agronomic issues. J. Hazardous Substance Res., 2: 1-25.

Moreno, D.A., G. Villora, M.T. Soriano, N. Castilla and L. Romero, 2005. Sulphur, chromium and selenium accumulated in Chinese cabbage under direct covers. J. Environ. Manage., 74: 89-96.

Numberg, H.W., 1984. The Voltametric approach in trace metal chemistry of natural waters and atmospheric precipitation. Anal. Chim. Acta, 164: 1-21.

Omgbu, J.A. and M.A. Kokogbo, 1993. Determination of Zn, Pb, Co and Hg in soils of Ekpan, Nigeria. Environ. Intl., 19: 611-612.

Pillay, A.E., J.R. Williams, M.O. Al-Lawati, S.M.H. Al-Hadabbii, M.H. Al-Hamdi and A. Al-Hamdi, 2003. Risk assessment of chromium and arsenic in date palm leaves used as livestock feed. Environ. Intl., 29: 541-545.

Radojevic, M. and V.N. Baskin, 1999. Practical Environmental Analysis. The Royal Society of Chemistry, UK.

Rattan, R.K., S.P. Datta, P.K. Chhonkar, K. Suribabu and A.K. Singh, 2005. Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater-a case study. Agric. Ecosys. Environ., 109: 310-322.

Udosen, E.D., 1994. Levels of toxic metals in *Telfairia occidentalis* from a paint industry environment. J. Applied Chem. Agric. Res., NRI., 1: 35-42.

Udosen, E.D., N.U. Benson, J.P. Essien and G.A. Ebong, 2006. Relation between aqua-regia extractable heavy metals in soil and *Manihot utilissima* within a municipal dumpsite. Intl. J. Soil Sci., 1: 27-32.

Xiong, Z.T., 1998. Lead uptake and effects on seed germination and plant growth in a Pb hyperaccumulator *Brassica pekinensis*: Rupr. Bull. Environ. Contam. Toxicol., 60: 285-291.

Yahya, A., 1994. Heavy metal concentration in floodplain soils in Le An River Area. China Environ. Sci., 5: 135-139.

Yusuf, A.A., T.A. Arowolo and O. Bamgbose, 2003. Cadmium, copper and nickel levels in vegetables from industrial and residential areas of Lagos City, Nigeria. Food Chem. Toxicol., 41: 375-378.

Zauyah, S., B. Juliana, R. Noorhafizah, C.I. Fauziah and A.B. Rosenani, 2004. Concentration and Speciation of Heavy Metals in Some Cultivated and Uncultivated Ultisols and Inceptisols in Malaysia Peninsular. 3rd Australian New Zealand Soils Conference, University of Sydney, Australia.