



SURVEY OF SOME HEAVY METAL CONCENTRATIONS IN SELECTED SOILS IN SOUTH EASTERN PARTS OF NIGERIA

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UDOUSORO¹, I. I., UMOREN, I. U.
AND ASUQUO, E. D.

*Analytical Chemistry Unit, Department of Chemistry,
University of Uyo, P. M. B. 1017 Uyo,
Akwa Ibom State, Nigeria.*

¹Corresponding author: E-mail: imaobong2i@yahoo.com +2348028416551

ABSTRACT: A survey of heavy metal concentrations in some selected soils in Akwa Ibom State was carried out using UNICAM 939/969 Atomic Absorption Spectrophotometer. Results from the analysis of ten soil samples in different locations showed varying levels of Ni, Cd, Zn, Pb and Fe higher than the recommended levels for soils in developing countries for majority of samples. Samples, located in the vicinity of automobile repair workshops had the highest concentrations of Ni and Pb. The soils had a pH range of 5.8-9.3, while the percentage organic matter ranged from 2.70-6.22. These results suggest that the soils investigated are contaminated with heavy metals and may not be suitable for crop cultivation.

INTRODUCTION

Soil is an important habitat for both producers (green plants) and decomposers (bacteria and fungi). While air and water are both self-purifying systems with regard to most inorganic contaminants, soil is a sink - receiving fall-out from the atmosphere which it absorbs or filters, and could retain materials from infiltrating natural waters (Karlen *et al.*, 1997).

Soils perform a number of functions some of which include supporting the growth of plants by providing a medium for plant roots, supplying the nutrient elements that are essential for the plant and control of the fate of water in the hydrological system. Soil also serves as nature's recycling system, it provides habitat for a myriad of living organisms and in human built ecosystems, it serves as an engineering medium (Karlen *et al.*, 1997; Brady and Weil, 1990). The soil ecosystem is usually inundated by heavy metals due to a wide range of activities by man as a consequence of industrialization.

These heavy metals present in the mobile forms in soils could be available for uptake by different parts of plants (Umoren and Udousoro, 2009; Umoren *et al.*, 2007). Heavy metals released into the soil environment have, thus, increasingly and continuously been posing significant threat to the environment and public health because of their ability to accumulate and persist in the food chain (Ceribas and Yetis, 2001; Onianwa and Fakayode, 2001).

Anthropogenic sources of heavy metals include waste from the electroplating, metallurgical, battery manufacturing, mining and chemical manufacturing industries. Also, the manufacture and application of fertilizers increase the environmental load of heavy metals in the soil (Okieimen *et al.*, 1991). However, most soils have a considerable buffering capacity (Karlen *et al.*, 1997) with respect to contaminants and may themselves be self-purifying systems, but the timelines could be long for when pollution of soil environment occurs, it often takes many years to correct. This has stimulated considerable interest on the nature and quality of the soil ecosystem that supports crop production activities (Stewart *et al.*, 2003; Rodrigues *et al.*, 2009;

Hassan *et al.*, 2010). It has also been of interest to the public to know whether vegetables, fruits and food crops cultivated in polluted soils are safe for human consumption. Although, some heavy metals such as Cu, Zn, Mn and Fe are essential in plant nutrition, many others do not play significant role in plant physiology (Okoronkwo *et al.*, 2005). Plants growing in a polluted environment can accumulate the toxic metals at high concentrations causing serious risk to human health when consumed (Vousta *et al.*, 1996; Collins *et al.*, 2006; Sjöström *et al.*, 2008). In addition, majority of the heavy metal ions are toxic to soil microorganisms and this is of grave concern for environmentalists and soil conservationists (Giller *et al.*, 1998; Giller *et al.*, 2009). The uncontrolled input of these heavy metals in soils is undesirable because once accumulated in the soil, the metals are generally very difficult to remove (Smith *et al.*, 1996). Furthermore, the biomagnifications of the metals increases along the food chain, posing great danger to man at the receiving end of the chain. This is because heavy metal pollution of soil enhances plant uptake of the metal ion causing accumulation in plant tissues and eventual phytotoxicity and change in plant community (Zayed *et al.*, 1998).

Thus, this study was carried out to determine the concentrations of some heavy metals in relation to their safety levels in some arable soils in various locations in Akwa Ibom State, Nigeria.

MATERIALS AND METHODS

Study Area

Akwa Ibom State is located within the Niger-Delta Region, in South-south Nigeria, on latitude 4°32' and 5°53' North and longitude 7°25' and 8°25' East, with a land area of 8,412 square kilometers. The State is divided into three Senatorial (Political) Districts – Uyo, Eket and Ikot Ekpene. The Districts together accommodate thirty-one administrative units (called Local Government Areas). Four sampling stations were established within the state in Uruan, Etinan, Ibesikpo-Asutan and Uyo Local Government Areas (Figure 1).

Sampling

Samples were collected from ten locations chosen from the four Local Government Areas of interest as follows: sampling stations SSA to SSC - a newly opened up area for urbanization and industrialization; SSD - an industrial area; SSF and SSI -mechanic village and workshop respectively; SSH - a ravine used as waste dump site and SSE, SSG and SSJ-low/high traffic areas (Table 1 and Figure 1). From each location a total of three samples were collected.

Table 1: Sampling identification and stations.

Sample ID	Sampling location (LGA)	Sampling station
SSA	Uruan	Nwaniba village
SSB	Uruan	Mbiakong
SSC	Uruan	Mbakara village
SSD	Etinan	Ikot Ekan (near a paint factory)
SSE	Ibesikpo Asutan	Ikot Udo Ekpo village
SSF	Uyo	Mechanic village, Abak Road
SSG	Uyo	Urua Ekpa road
SSH	Uyo	University of Uyo (Uniuyo), ravine area
SSI	Uyo	Eka street (near an auto-mechanic workshop)
SSJ	Uyo	Ikpa road

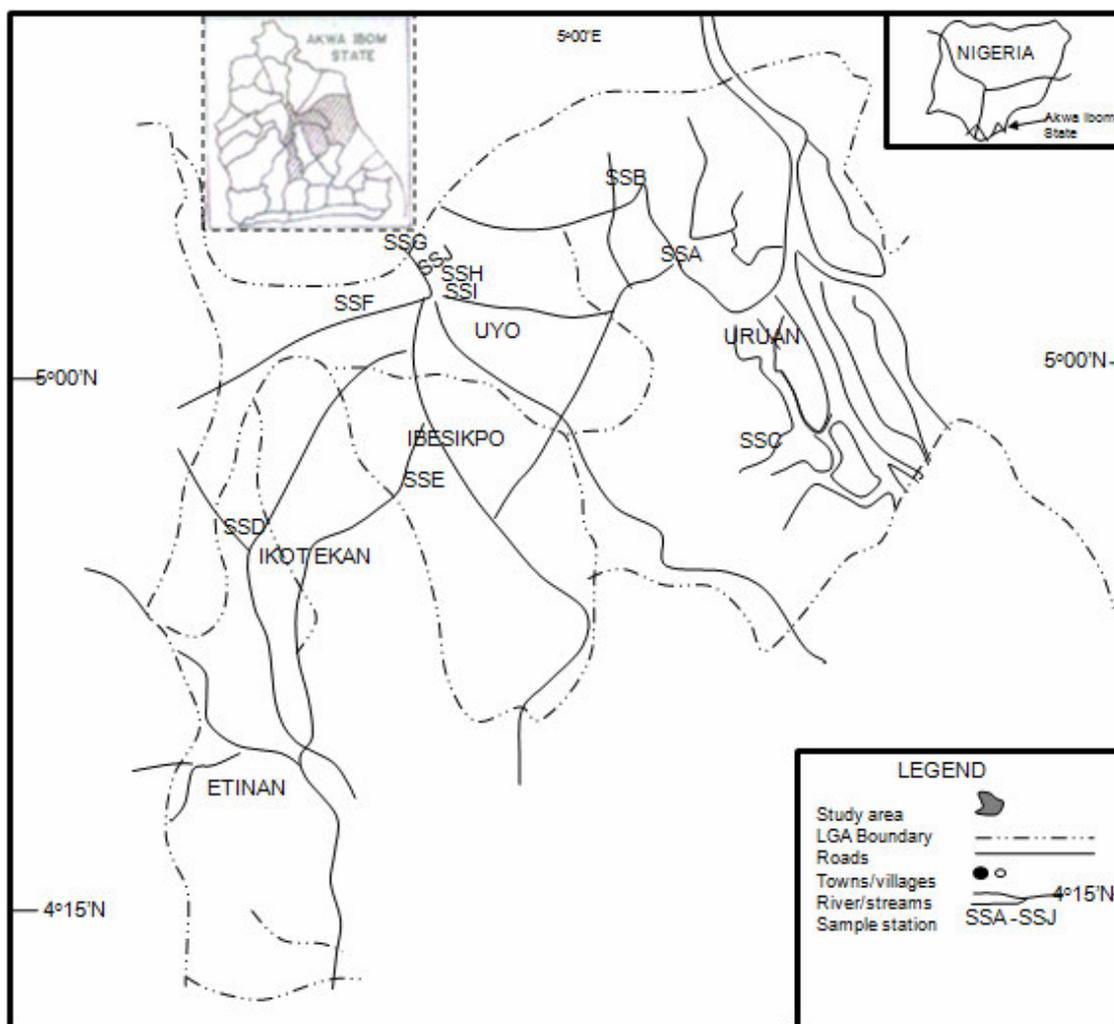


Fig. 1: Map of study area showing sampling stations.

The vegetation cover was removed at each study site. A plastic trowel was then used to take soil samples between 0-15 cm depths and stored in well-labeled polyethylene bags, and preserved in an ice-chest box before being taken to the laboratory.

Sample preparation and chemical analysis

The soil samples were air-dried in the laboratory at room temperature after manual removal of debris. The samples were disaggregated by gently grinding in an agate mortar and pestle and sieved through a 0.5mm nylon sieve. The sieved soil samples were stored in well-labeled polyethylene bags for analysis.

Heavy metals determination

One gram of the 0.5mm soil sample was digested with an acid mixture of concentrated HNO_3 (15 cm^3) and HCl (5 cm^3). The digests were analyzed for Ni, Zn, Cd, Fe and Pb using a UNICAM 939/969 Atomic Absorption Spectrophotometer. The concentrations of the elements were obtained by reference to standard calibration curves.

Soil properties

The basic soil properties, pH, organic matter (OM) and moisture content (of field samples) were obtained by routine methods.

RESULTS AND DISCUSSION

The mean values of pH, organic matter and percentage (%) moisture content for all the soil samples are presented in Table 2.

Table 2: Soil properties for the studied samples.

Site identification	Soil pH	% Moisture content (of field sample)	Organic matter
SSA	6.24	12.9	3.35
SSB	5.88	16.0	2.98
SSC	5.90	22.7	3.66
SSD	8.72	16.4	5.24
SSE	6.02	13.6	2.70
SSF	9.31	11.2	5.45
SSG	6.11	28.1	3.02
SSH	6.13	13.9	3.12
SSI	8.97	7.8	6.22
SSJ	7.35	15.7	2.84

Soil pH is the most widely accepted parameter which exerts a controlling influence on the availability of micro-nutrients in the soil to plants (Sanders, 1982). Also, no other single characteristic is more important in determining the chemical environment of higher plants and soil microbes than the pH (Igwe *et al.*, 2005). Banjoko and Sobulo, 1994 reported that some Nigerian soils especially in the forest and savannah regions are within a pH range of 5.70 – 6.50. This was taken as the normal pH range for ordinary soils that favour plant and micro-organisms. The mean values of soil pH ranged from 5.88 to 9.31. Soil samples SSA, SSB, SSC, SSE, SSG, and SSH were acidic, but sample SSB was the most acidic. Samples SSD, SSF, SSI and SSJ were basic with sample SSF being the most basic. Thus, it can be said that soil samples SSA, SSB, SSC, SSE, SSG and SSH may support crop cultivation.

The organic matter content of the soils is as presented in Table 2. Organic matter content in soils is composed of decomposed plants and animals which result from the activities of innumerable micro-organisms particularly bacteria (Igwe *et al.*, 2005). Sample SSI had the highest organic matter (6.22%), while sample SSE had the least (2.70%). Generally, a good forest top soil should contain between 3 – 4% organic carbons. On this basis the soil samples are rich in organic matter and have the potential to bind toxic metal ions.

Table 3 shows summary of statistics for each of the data variables and UNEP standards for developing countries with regards to health of vegetation, livestock and man.

The concentration of Ni in the soil samples ranged between 8.78 and 512.06 μ g/g (Table 3) Though Ni was present in all samples, higher concentrations of Ni were found in samples SSF and SSI (soils close to mechanic repair workshops), and SSD (soil from the vicinity of a paint factory), while sample SSE, obtained from a rural community, recorded the lowest Ni concentration. The high Ni content at sample stations SSF, SSD and SSI were attributable to human activities such as the disposal of spent automobile batteries from the nearby auto battery charger and various paint wastes and pigments which may have contributed to the

contamination of the different soil samples. Though Ni is a micro-nutrient, excessive level of the metal in the soil may be toxic to some soil fauna like earthworms, which are adjuncts to the micro flora in organic matter decomposition and may also reduce heterotrophic activity of the micro flora (Osuji *et al.*, 2002).

Table 3: Mean concentrations of heavy metal in selected soil samples

Code*	Ni	Zn	Cd	Fe	Pb
SSA*	65.09±0.11	266.49± 1.30	29.00 ± 0.88	18009 ± 149	305.50 ± 8.92
SSB*	45.36 ± 1.59	160.06 ± 0.87	26.64 ± 0.56	6855 ± 394	669.10 ± 49.37
SSC*	17.28 ± 0.19	161.57 ± 1.39	ND	7304 ± 295	385.78 ± 18.35
SSD*	377.10 ± 0.18	381.82 ± 1.21	1.51 ± 0.04	26714 ± 287	665.71 ± 56.30
SSE*	8.79 ± 0.19	312.91 ± 1.09	7.99 ± 0.19	1646 ± 236	448.78 ± 19.78
SSF*	512.06 ± 1.18	249.34 ± 0.73	24.62 ± 0.49	20249 ± 516	735.70 ± 40.75
SSG*	59.04 ± 0.98	351.22 ± 1.61	3.96 ± 0.07	109952 ± 738	662.0 ± 49.35
SSH*	36.72 ± 1.08	392.76 ± 2.02	8.71 ± 0.67	5760 ± 225	412.78 ± 30.01
SSI*	152.14 ± 2.82	311.04 ± 0.95	ND	15291 ± 438	259.10 ± 44.47
SSJ*	30.24 ± 0.44	231.12 ± 0.95	18.72 ± 0.24	12260 ± 461	511.34 ± 16.85
Mean	126.38	128.83	12.12	23404	501.58
SD	167.2	83.06	11.54	31115	165.24
CV (%)	132.3	29.5	95.21	133	32.94
Minimum	8.78	160.06	ND	5760	259.1
Maximum	512.06	392.76	29.02	109952	735.7
Std.	2.34	-0.30	0.55	3.75	-0.02
Skewness					
Std. Kurtosis	1.64	-0.69	-1.11	5.67	-0.93
Standard limit**	10 – 50	10 - 50	5 - 20	3.8 x 10⁴***	0.1 - 2

* n = 3 samples for each site ** UNEP and BMFT (1983) *** UNEP (1998)

Zinc (Zn) was detected in all the soil samples and the concentration ranged from 160 to 392µg/g (Table 3). Sample SSH (obtained from a ravine behind University of Uyo where refuse are being dumped) had the highest Zn concentration while the lowest concentration was obtained for SSB (a rural community newly opened up for urbanisation). The high concentration of Zn at site SSH may be attributed to the dumping of zinc containing solid waste materials near that sampling location as well as the high vehicular traffic. Although zinc is found useful as a metabolic antagonist of metals such as Cu, Fe and Cd, zinc is also known to induce vomiting, dehydration, abdominal pain, nausea, lethargy and lack of muscular co-ordination in man when taken in excess (WHO, 1984). High concentration of zinc was observed to kill and stunt plant growth (Okoronkwo *et al.*, 2005). This metal should therefore not be introduced into the environment indiscriminately (Udosen *et al.*,1990).

Cadmium is a very toxic heavy metal that has no beneficial function in the human body. Cadmium, unlike most heavy metals, can be taken up by several plants such as wheat, maize, rice, spinach or tobacco. It is capable of accumulating in food chains and the accumulation depends on factors such as pH and high temperature (Voogt *et al.*, 1980). Cadmium (Table 3) was detected in all the soil samples with the exception of SSI and SSC. Sample SSA had the highest Cd concentration of 29.02µg/g, while a concentration of 1.51µg/g was found for site SSD. The high Cd concentration at site SSA may be due to human activities in the area. Site SSA is adjacent to a warehouse used for storage of petroleum products. In addition, the presence of Cd in the samples could be attributed to the use of pigments containing cadmium such as Cd/Se as well as from the application of superphosphate fertilizers (Bohn *et al.*, 1979). The soil samples that contain Cd are, therefore, not safe for crop cultivation as any food crop

will certainly contain Cd by the transport of its ions from the soil into the plants. Voogt *et al.*, 1980 showed that 'Itai-itai' disease resulted from the cultivation of rice in fields where Cd ion concentration was about 2 – 3 µg/g. This situation is made worse since Cd ion is relatively soluble and capable of being retained in the soil at any pH (Bohn *et al.*, 1979).

The concentration of Fe in the different soil samples was high ranging from 5759.93 to 26713.87µg/g (Table 3). Sample SSD had the highest concentration of Fe, while sample SSH had the least. This may be attributed to the industrial activity (paints production) carried out within that area. Iron is an essential element that plays a very vital role in the human body as a vital component of proteins such as haemoglobin and cytochromes. However, ingestion of large quantities may cause a condition known as hemochromatosis which causes damage to tissue as a result of iron accumulation (Shils *et al.*, 2007).

Lead was present in all the soil samples (Table 3). Lead is a toxic heavy metal ion that affects blood transport and composition. Lead (Pb) is ubiquitous in the environment as a result of its natural occurrence and industrial use (Klaassen, 2001). The highest concentration of Pb was seen in sample SSF, with a concentration of 735.70µg/g, while the least concentration occurred in sample SSI with a value of 259.10µg/g. The high concentration of Pb in samples SSB, SSF, SSG and SSD may be attributed to anthropogenic factors. In most of these sites, automobile mechanic/repair workshops or paint factory (as in the case of sample SSD) are located. In addition, lead is generally added to the environment by aerial deposition along the highways in proportion with the density of traffic and distance from the road side (Ahmet and Ugur, 1999).

The major concern of environmentalists and nutritionists is often on the ecological magnification of heavy metal ions along the food chain and its possible health implications. A comparison of the concentration of Ni and Zn for all the different soil samples (table 3) showed that sample SSF had the highest concentration of Ni. The concentration of Zn was higher than Ni(II) ion for samples SSA, SSG, SSB, SSH, SSI, SSJ, SSE and SSC, while for site SSD, the concentration of Ni was slightly higher than that of zinc.

In all the sites and LGA's (Figs. 2 a and b) the concentrations of Fe, Pb and Zn were high with Fe having the highest. The mean concentrations of these heavy metal ions in soils in the sample areas indicate a high concentration of heavy metal ions in cultivated soils. The accumulation of heavy metals by plant roots stems and leaves grown in polluted soils have variously been reported. Anikwe and Nwobodo, 2002 reported high levels of heavy metals (Pb, Fe, Cu and Zn) in their study on long term effect of municipal waste disposal on soil properties and productivity of sites used for urban agriculture in Abakaliki. A similar work by Ademoroti, 1996) showed that vegetables accumulate considerable amounts of heavy metals (Pb, Cr, Cu and Zn) in roots and leaves.

The strength of linear relationship between each pair of variables using Pearson moment correlations at 95% confidence level are summarized in Tables 4 (a-c). The following pairs of variables indicated statistically significant non-zero correlations: % moisture and Fe, organic matter and pH, organic matter and Ni, pH and Ni for all location (Table 4a); pH and Zn, pH and Fe, Zn and Fe for Uruan LGA (Table 4b); and % moisture and Fe, organic matter and pH for Uyo LGA (Table 4b).

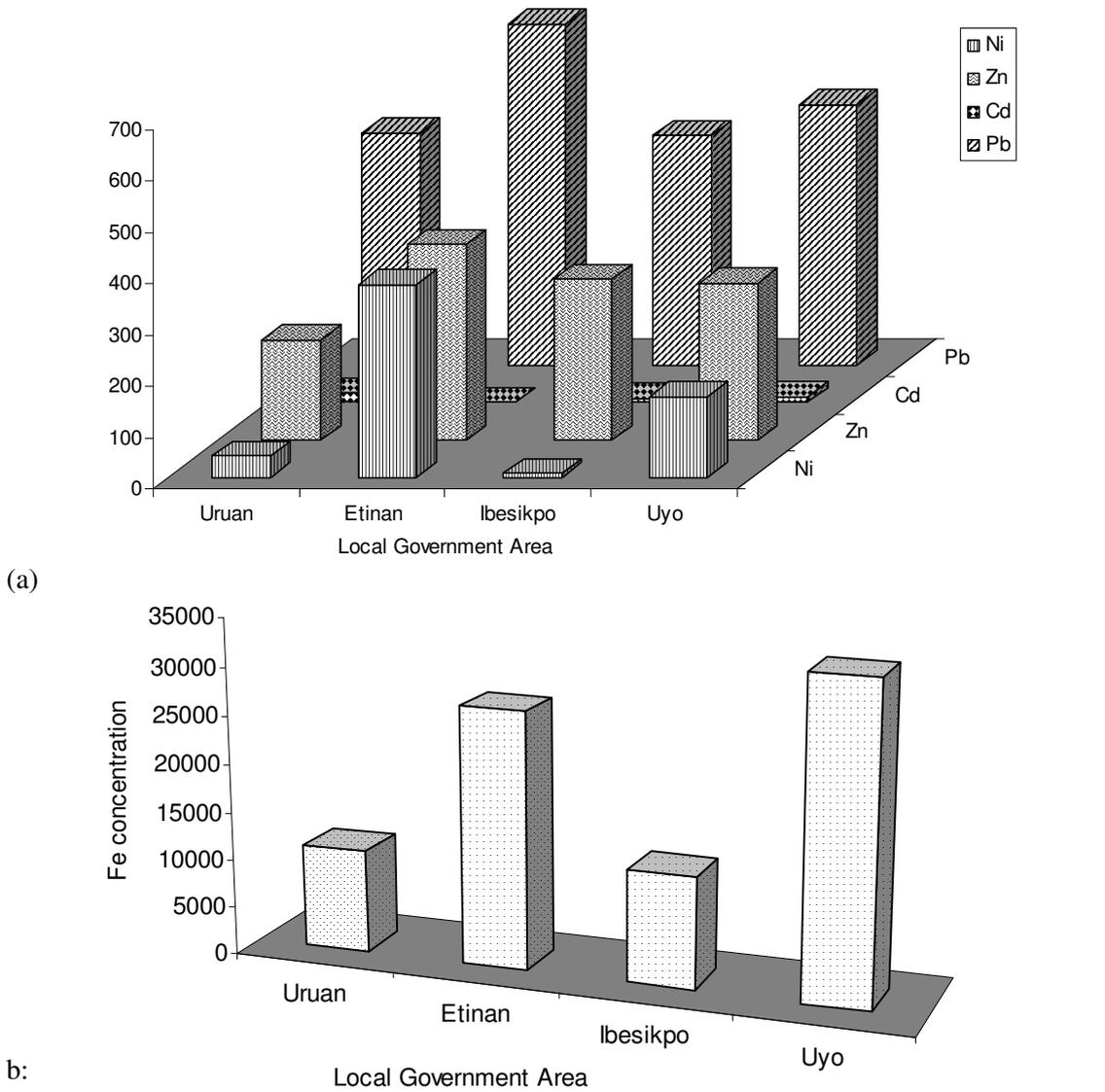


Fig. 2 (a and b): Variations in metal concentrations in study areas

Table 4: Pearson moment correlations

(a) Relationship between variables in all locations.

	% Moisture	OM	pH	Ni	Zn	Cd	Fe	Pb
% Moisture		-0.4763	-0.5209	-0.3255	-0.0588	-0.3031	0.6836*	0.2940
OM	-0.4763		0.8933*	0.7517*	0.1774	-0.2629	-0.0941	0.0095
pH	-0.5209	0.8933*		0.8412*	0.2171	-0.0851	-0.0794	0.2196
Ni	-0.3255	0.7517*	0.8412*		0.1586	0.1203	0.0194	0.5422
Zn	-0.0588	0.1774	0.2171	0.1586		-0.4405	0.3645	-0.0435
Cd	-0.3031	-0.2629	-0.0851	0.1203	-0.4405		-0.2426	0.2476
Fe	0.6836*	-0.0941	-0.0794	0.0194	0.3645	-0.2426		0.3117
Pb	0.2940	0.0095	0.2196	0.5422	-0.0435	0.2476	0.3117	

* Significant at 95% confidence level. n=10

(b) Relationship between variables in Uruan LGA

	% Moisture	OM	pH	Ni	Zn	Cd	Fe	Pb
% Moisture		0.6301	-0.7095	-0.9941	-0.7351	-0.9712	0.7192	0.0027
OM	0.6301		0.1002	-0.5423	0.0632	-0.7970	0.0864	-0.7748
pH	-0.7095	0.1002		0.7816	0.9993*	0.5210	0.9999*	-0.7067
Ni	-0.9941	-0.5423	0.7816		0.8042	0.9397	-0.7902	-0.1110
Zn	-0.7351	0.0632	0.9993*	0.8042		0.5523	0.9997*	-0.6799
Cd	-0.9712	-0.7970	0.5210	0.9397	0.5523		0.5328	0.2357
Fe	0.7192	0.0864	0.9999*	-0.7902	0.9997*	0.5328		-0.6968
Pb	0.0027	-0.7748	-0.7067	-0.1110	-0.6799	0.2357	-0.6968	

* Significant at 95% confidence level. n=3

(c) Relationship between variables in Uyo LGA

	% Moisture	OM	pH	Ni	Zn	Cd	Fe	Pb
% Moisture		-0.7026	-0.7318	-0.4055	0.2964	-0.1804	0.8921*	0.4435
OM	-0.7026		0.8915*	0.6602	-0.2455	-0.0746	-0.3085	-0.2179
pH	-0.7318	0.8915*		0.7706	-0.6450	0.3235	-0.4368	0.0158
Ni	-0.4055	0.6602	0.7706		-0.4614	0.5830	-0.1712	0.5451
Zn	0.2964	-0.2455	-0.6450	-0.4614		-0.6911	0.2799	-0.3502
Cd	-0.1804	-0.0746	0.3235	0.5830	-0.6911		-0.3463	0.6984
Fe	0.8921*	-0.3085	-0.4368	-0.1712	0.2799	-0.3463		0.3992
Pb	0.4435	-0.2179	0.0158	0.5451	-0.3502	0.6984	0.3992	

* Significant at 95% confidence level. n=5

CONCLUSION

In this study, the assessment of the concentration of some heavy metal ions in some cultivated soils in Akwa Ibom State, Nigeria shows that soils investigated are contaminated with the toxic heavy metals Ni, Zn, Cd and Pb with concentrations higher than recommended levels. The bioaccumulations tendency of heavy metals and their non-biodegradable nature render these soils a health risk to man. The developing brain and IQ of children are especially vulnerable to toxic metals, especially lead.

Thus cropping of this heavy metal contaminated soils should be avoided to guard against incidence of heavy metal toxicity.

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