



Heavy Metal Pollution of In-situ and Surrounding Soils Profiles at Municipal Solid Waste Dumpsite

Obot E. Essien^{1*} and Rebecca O. Hanson¹

¹Department of Agricultural and Food Engineering, University of Uyo, Uyo, P. O. Box 4309, Uniuyo Post Office, Uyo, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author OEE designed the study, identified the study location and carried out all liaison protocol; analyzed the data; drafted and corrected the manuscript. He also supervised field sampling. Author ROH carried out field sampling. All authors read and approved the final manuscript.

Original Research Article

Received 12th April 2013
Accepted 26th July 2013
Published 15th January 2014

ABSTRACT

Aims: To investigate the levels, variability and degree of heavy metal pollution in in-situ municipal solid waste dumpsite soil (WDS) compared to adjoining area (CS) at 100 – 120m from dumpsite as a contribution to global knowledge of pattern of pollution and data base at dumpsite.

Study Design: Field-scale investigation of nine heavy metals (HM) at source pollution site and surrounding soil.

Place and Duration of Study: Uyo municipal solid waste dumpsite in 2010.

Methodology: Core sampling of soil at solid waste dumpsite and at 100 – 120m away, taken at 0-10cm and 10-20cm profile depths at 4 spatially different points. Acid digestion of HM in soil samples and determination of elemental HM concentration by flame AAS. HM pollution level was assessed using contamination factor, metal pollution index; ANOVA, and covariance for spatial variability.

Results: Mean concentrations of nine heavy metals at municipal waste dumpsite soil were significantly ($P < .01$) higher than the un-dumped surrounding soil, and gave high mean metal pollution index of 5.21 for the overall soil profile. Toxicity was indicated for Fe, Ni, Pb, and B. Correlation between mean HMs at WDS and CS was very low ($R = .488$) but difference was significant ($P = .05$), indicating no lateral transfer to fringe area at

*Corresponding author: E-mail: obotessien@uniuyo.edu.ng;

100 – 120m away.

Conclusion: Heavy metal pollution in municipal solid waste dumpsite soil was higher at all profile depths than in control soil with contamination factors of 3-22 times the control soil values. Pollution was site-specific / anthropogenic (from waste deposition and leachate) rather than terrigenous. Fringe fields at 100-120m from dumpsite, except downslope, were buffered from dumpsite pollution. More research on deeper profile and minimum pollution - free buffer distance are recommended.

Keywords: Heavy-metal contamination; dumpsite soil; anthropogenic source; toxicity; metal pollution index.

1. INTRODUCTION

Heavy metals (HM) create potential concerns for human health when high levels of concentration are encountered in the soil where humans are in close contact. Human beings may be harmed if high levels of HM enter their systems, through such pathways as ingestion of edible plants containing HM through normal food intake, ingestion of plant leaves splashed with contaminated soil, accidental direct swallowing of HM polluted soil such as happened to children or sewer cleaners and pit diggers, and sorters; and, occasionally, by inhaling dust from contaminated soil [1,2]. This is a very serious problem because dietary limitations have favoured daily consumption of fresh vegetables. And vegetables, especially leafy vegetables, grown on soils having heavy metal contaminations, have been found with higher concentrations of heavy metals than crops grown at locations where soils were uncontaminated [3,4]. Consequently, consuming them by humans and livestock can pose serious health hazards [5,6,7,8]. At municipal solid waste dumpsites, human interactions abound, such as researchers, scavengers or sorters, farmers using old dumpsite and periphery of active dumpsite for planting vegetables for city markets obviously because of the expected high nutrient level from composting organic wastes and the possible all year production; and crew men handling waste collection and disposal as well as disposal site management (Plate 1 shows municipal solid waste disposal site with a management staff at Uyo dumpsite). Also, laterite quarrying for buildings or structures were observed close to the dumpsite since it was thought to be a free marginal land.

Unorganized, indiscriminate and unprocessed municipal waste dumping is a common disposal method which is known to adversely impact on the environment [9], such as the soil of the surrounding area of a waste dumpsite. The soil at a distant from open dumpsite can be affected by nonpoint source (NPS) run off that carries pollutants from upstream to the distant field [4,5] or by wind and soil movement such as gathering of humid soil from dumpsite for crop planting, which are all anthropogenic causes. For landfill the protected liners reduces the spreading of pollution in soil except if it is over-flooded or it overflows [10]. For example soils and crops at a downslope farm adjoining an animal market/park which generates mixed wastes at Uyo were found to be polluted to a heavy metal pollution index (HPI) > 2 [4,5]. Yet the peripheral area to a dumpsite is very vital to small-scale farmers' economy, especially in urban supply of green vegetables, which may be affected by the HM of the degraded soil [1,11]. The peripheral soil can also be used for other purposes like foundation to structures. If it is high in organic matter content (O.M.), then the tendency to decompose and develop voids might affect the use of the soil for engineering purpose [12]. Due to the heterogeneity and complexities of the wastes at the dumpsite, a variety of contaminants might affect the immediate and long-term use of the open dumpsite soil for other engineering purposes [13,14]. For instance, the foundation properties in the polluted

soil might be much degraded to the discredit of constructional use of the dumpsite soils, thereby needing time for restoration [15]. The same loss of utility value would affect any surrounding soil that is comparatively contaminated by its proximity to waste dumpsite. The adverse impact in the surrounding soil may capture, to a lower or the same level, the effect at the dumpsite depending on the spreading distance from WDS or any point of pollution.

Heavy metals do not decay generally, but can geo-accumulate on the soil by absorption and precipitation, and may be fixed to anions in in-situ soils thereby creating new chemical compounds in which fixed heavy metals become less available to living things even though they are needed in trace amount only [16]. Soil contamination by HM can be caused by many factors, including metal-enriched parent materials, point source leachate composition, and nonpoint source NPS effluents (such as municipal waste water, runoff, industrial wastewater), municipal solid waste, dumped electronics, other white goods, waste metal and chemical fertilizers [10,17,18,19]. Parent material varies with geographical location and geological formations. Also the composition of mixed waste varies with source from locality residences and regions of the world. The status of the heavy metals and other soil properties at dumpsite depends on the age of the waste dump, the level of leaching and solubility of the metal compounds under pH which controls the metal dynamics of adsorption and precipitation [16,20,21]. The HM effect on soils from different localities are not the same on the scale of magnitude and variability, indicating the need to investigate the specific locality effect on the specific and general pattern of soil degradation under solid waste disposal and effect on adjoining land [1,9,22,23]. The locality features also include the slope and buffer distance of the surrounding soil from the waste dumpsite. Their effect on HM bio-availability at dumpsite should be assessed.

Therefore the objectives of the research was to investigate and contrast the levels, variability and pollution index of heavy metal contamination of soils at municipal solid waste open dumpsite and adjoining land at Uyo, and the spread distance of such pollution, as a contribution to knowledge of the pattern of effect and data base of MSW pollution of soil resources at localities of the world. Due to some physical limitations, the scope of the study was not emphasizing the minimum and maximum pollution spread distance but considers the target distance from the periphery of the dumpsite which urban farming could go on safely.



Plate 1. Showing Solid Wastes at Municipal Solid Waste Dumpsite (WDS), Uyo;
X1 is Foreground, X2 is Dozer spreading the dumped solid waste, X3 is Down slope of dumpsite toward farmland,
X4 is surround fields/OS at a distance from solid waste dumpsite.

2. MATERIALS AND METHODS

2.1 Description of the Study Site

The study site was the municipal solid waste dumpsite and its surrounding area located within Latitudes 5° 2' 0"E – 5° 2' 50"E and Longitudes 7° 55' 15"N – 7° 56' 10"N at the fringe area of Uyo urban on top of a low plateau precipice which outward edge was dissected into two arms sloping steeply into a wide urban ravine which has a lotic perennial spring mixed with the urban drainage water at its bottom (Fig. 1). The leachate effluent from the upslope waste dumpsite directly discharged into the lotic drainage stream in the ravine. The waste dumpsite was about 40m from the upstream of ravine where the effluent cascaded o the bottom stream. The dumpsite occupied an area which landward axis extended directly from the junction of old Stadium road and Eka Street in Uyo Urban to the ravine precipice (Fig. 1). The area was inhabited by civil and public servants, farmers (using the wing and upslope fields of the dumpsite and ravine floodplain for urban green gardening/farming), and forestry Department herbarium. The waste dumpsite is used for municipal solid wastes disposition which were mainly household, domestic and industrial waste from Uyo urban.

The vegetation was fallowed, regenerated bush with evergreen foliage, shrubs and palm trees, forestry cashew plantation and forest trees. The climate was humid tropic with annual temperature between 26 – 27°C, and two distinct seasons, namely, the wet and the dry seasons, from April to October and November to March respectively. The rainy period also had 2-3 weeks of dry spell called August break in August. This marked the end of the rain-fed agricultural season and the beginning of late planting season. Annual rainfall ranged from 2000mm to 3000mm, predominantly in the rainy period. Mean relative humidity was 75%. The geological material in the area was the same Coastal Plain Sands which formed 75% of Akwa Ibom State land where rivers were few and in between. The soil was derived from sandy parent materials and were highly weathered with dominant low-activity clays – it was of inter-fluvial slope with a pattern of increase in clay content down the profile, and generally had low organic matter whereby Uyo was highly subject to gully erosion, hence the wide and long ravine [24].

2.2 Sampling and Analyses

Soil samples were collected using acid-cleaned soil auger and packed in a well-labeled black polythene bag, and transported to the heavy metal analytical laboratory at RUSAL-Aluminum Smelting Plant at Ikot Abasi, Akwa Ibom State. The random core samples were collected from municipal solid waste dumpsite insitu soil (identified as WDS) and from the surrounding area soil (control soil, identified as CS) within 100 – 120m from the waste dumpsite at four spatial points (P1, P2, P3 ,P4 for WDS) at two depths (0 – 10 and 10 – 20 cm) of soil profile, At CS, for comparative and delimiting spread distance purposes, the spatial points were SP1, SP2, SP3, and SP4 (Fig. 1). The samples were dried in an oven at 105^oC overnight; then cooled and pulverized to homogenize and ground to 0.063mm fine powder because metals are known to adhere to fine particles, and sieved mechanically using 0.5mm sieve.

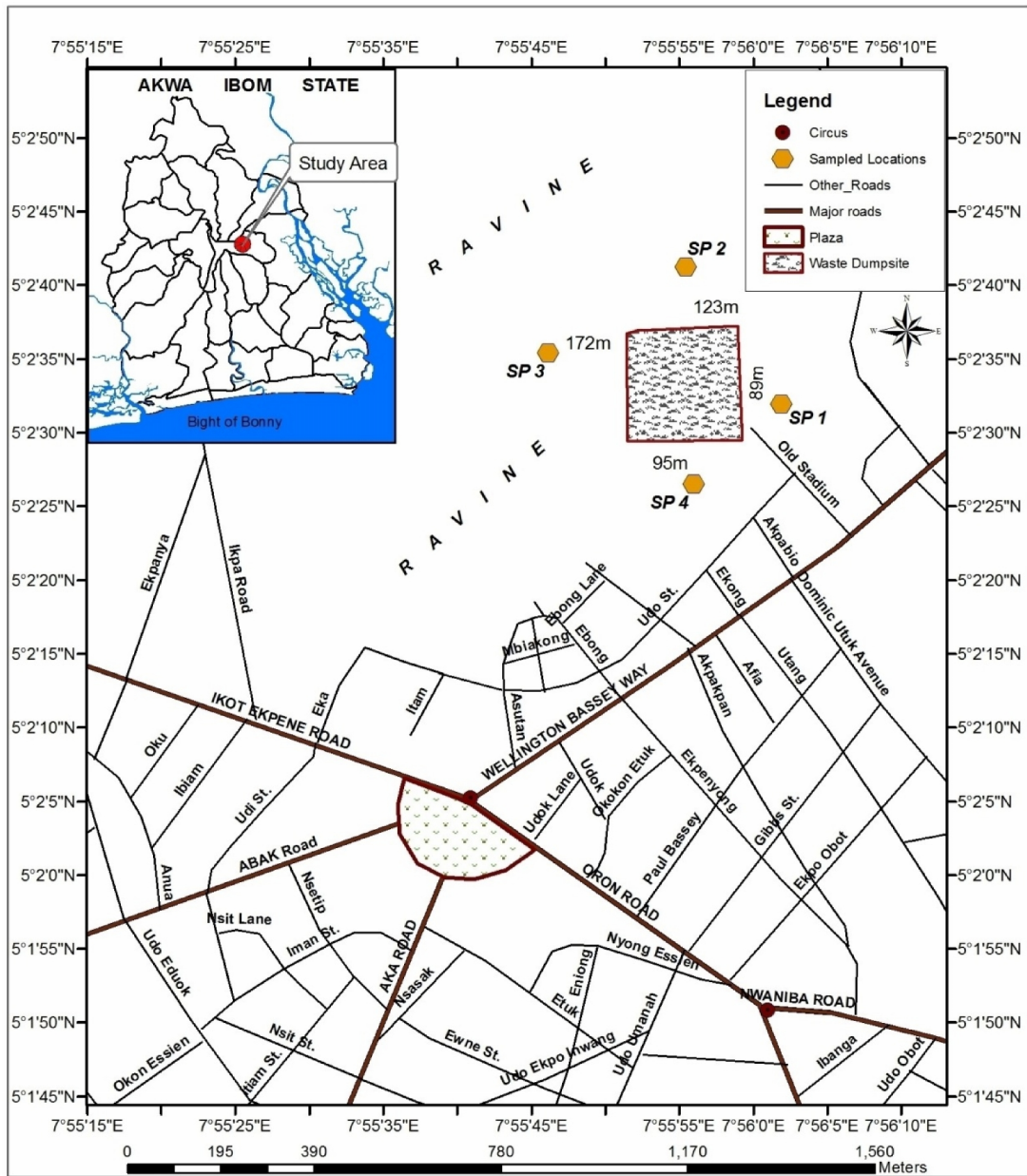


Fig. 1. A cross section of Uyo urban showing waste dumpsite and sampled locations

Afterwards, 1.25g of each sample was digested with 20 ml aqua - regia (HCl/HNO₃ 3:1) in a beaker (for open beaker digestion) on thermostatically controlled hot plate. Each digest was heated to near dryness and cooled to ambient (room) temperature. Then, 5.0ml of perchloric acid was added in parts to complete the digestion and the resulting mixture was heated again to near dryness in a fume cupboard. The beaker walls were washed with 10ml of de-ionized water and 5ml HCl were added, mixed and heated again. The resulting digest was allowed to cool and transferred into a 50 ml standard flask and made up to mark with de-

ionized water. The concentrations of Pb, Cd, Cu, Zn, Mn and Fe elements were then analyzed by direct aspiration of the sample solution into a UNICAM Model 939 A.S. flame atomic absorption spectrophotometer (AAS) as in [25]. For Al, B, Cr, the same aqua-regia wet digestion in open vessel system was used (ISO Standard 11466 [26]). All metals were analyzed using lean blue acetylene flame at different wave lengths: 324.8 nm, slit width 0.2nm for Cu; 228.8 nm, slit width 0.7 nm for Cd; 213.9nm for Zn; 217.0 nm, slit width 0.7mm for Pb; 279.5nm, slit width 0.2nm for Mn and wavelength 510nm for Fe. Procedural blanks and internal standards were also used were appropriate. Before determining any metal sample, a calibration curve of the metal was prepared using aliquot from the standard stock solution of the metal. In addition, the concentration of the metal in sample was related directly to the concentration of the calibration curve [25]. The stock solution was usually of 1000 mg⁻¹. Working standards were stored in plastic bottles or glass ware to prevent contamination.

Since pH and soil texture are relevant contributors to HM presence in soils [21,22], the pH and soil particle size distribution were also determined. The pH was measured from soil solution in place using digital pH meter with glass electrode (HANNA Model 209) while sand, silt and clay particle sizes and properties were determined by mechanical sieving and hydrometer analysis of the dried soil samples (ASTM D422) and using the USDA soil triangle for the texture identification [27].

2.3 Assessment of Heavy Metal (HM) Contamination in Soil Profile

Assessment of heavy metals and contamination levels in soils require pre-anthropogenic pristine values of the heavy metal concentrations. These were obtained from the control soil for use in computing the contamination factor (CF) and heavy metal pollution index (HPI). Contamination factor is the ratio of the concentration of heavy metals in contaminated soil at each depth interval to the concentration of heavy metal in natural local or background soil (i.e. the pristine values) and is calculated as [28,29,30].

$$CF = \frac{HM \text{ concentration found on soil (mgkg}^{-1})}{HM \text{ concentration of natural background soil (mgkg}^{-1})} \quad (1)$$

where CF < 1 means low contamination, 1<CF<3 means moderate contamination; 3< CF < 6 indicates considerable contamination and CF > 6 indicates very high contamination [26]. Also, the overall degree or extent of metal pollution of each layer of soil profile at the dumpsite was evaluated by using HPI [27] as:

$$HPI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \dots \times CF_n)^{1/n} \quad (2)$$

where HPI is the heavy metal pollution indeed; CF is the contamination factor of each pollutant obtained from equation 1; n is the number of heavy metals used. Thus, HPI is also the geometric mean of the studied pollutants contamination factors (CF) and has the following gradation [27,30]:

- HPI < 1.5 is nil to very low degree of contamination
- 1.5 < HPI < 2 is low degree of contamination
- 2 < HPI < 4 is moderate
- 4 < HPI < 8 is high
- 8 < HPI < 16 is very high
- 6 < HPI < 32 is extremely high

HPI > 32 is ultra-high degree of contamination.

Statistical analysis of data of samples for means, variance, coefficient of variation and correlation coefficient using the Words' SPSS software, version 17.

Vertical penetration of profile by pollution is defined by ratio K given as:

$$K = \text{HM concentration in subsoil layer} / \text{HM in surface soil} \quad (3)$$

where $K = 1$ indicates homogenous elemental penetration, $K > 1$ indicates subsoil accumulation, while $K < 1$ indicates superficial distribution.

3. RESULTS AND DISCUSSION

3.1 Heavy Metal (HM) Content of the Soils

The concentrations of the nine heavy metals (Cu, Mn, Ni, Fe, Pb, Al, Cr, Cd and B) studied in the soil at WDS and in the surrounding (control) area are shown in Table 1. Their mean values were in the following increasing order: $\text{Cd} < \text{Cr} < \text{B} < \text{Pb} < \text{Mn} < \text{Al} < \text{Cu} < \text{Ni} < \text{Fe}$ for WDS and CS but mean concentration of Cd was the same (0.16 mgkg^{-1}) in the WDS soil as in the control soil (CS). The concentrations varied from slightly to moderately ($\text{Cv} = 4\text{-}32\%$) in WDS and ($\text{Cv} = 9\text{-}32\%$) in control soil; however while B was homogenous in WDS, it was extremely heterogeneous in CS. For Fe, the variation was high ($\text{Cv} = 48\%$) on WDS but slight ($\text{Cv} = 17\%$) in CS while the reverse was the case for Pb in WDS (slight at $\text{Cv} = 9\%$) and in CS (high variation, $\text{Cv} = 47\%$). It would appear that Pb and Fe were complimentary in quantity.

Also the significant differences in their variability between mean HM in WD and CS were evaluated using t-statistics (Table 2). The concentration of Cu ranged from $536.8 - 1126.0 \text{ mgkg}^{-1}$ in WDS (mean of 809.00 mgkg^{-1}) and was significantly higher than that of CS (268.36 mgkg^{-1}) compared with the undumped soil with the Cu content, it is most likely that the solid waste component was the source of high Cu at WDS.

Hence, solid waste accumulation increased the concentration of Cu in the soils, and the variation in WDS was more homogenous ($\text{Cv} = 28.92\%$) than CS ($\text{Cv} = 31.88\%$).

The variation of individual HM in the two soils are further compared below:

Table 1. Heavy Metal Contents of the Polluted and Control Soils at Old Stadium Road Dumpsite, Uyo

Pro perty	Polluted soil						Control soil						
	0- 10cm	10 –20cm	Mean	Sd	Cv	K2	0- 10cm	10- 20cm	Mean	Sd	Cv	K1	CF
Cu	536.8	1125	809	234.35	28.97	2.1	195.29	346.1	268.36	85.55	31.88	1.8	3.1
Mn	388.5	864.3	681.7	191.8	28.13	2.2	168.19	264.3	215.3	48.86	22.69	1.6	3.1
Ni	1024	1859	1427	368.7	25.84	1.8	163.6	254.5	206.2	49.21	23.87	1.6	7.1
Fe	1043	3534	2027	776.44	38.17	1	93.46	120.5	105.96	10.25	9.67	1.3	19.1
Pb	115	193.64	154	26.66	17.31	1.7	2.45	12.64	6.9	3.25	47.1	5	22.1
Al	634	853	751.9	89.87	11.95	1.3	231.4	483.3	366.6	75.98	20.72	2.1	2.1
Cr	0.14	0.34	0.25	0.08	32	2.4	0.1	0.26	0.19	0.05	26.32	2.6	13.1
Cd	0.12	0.25	0.16	0.04	25	2.1	0.05	0.34	0.16	0.09	56.25	6.8	1.1
B	0.05	0.15	0.1	0.04	4.16	3	0.01	0.08	0.03	0.03	100	8.0	2.1

N/B: Cu: Copper, Mn: Manganese, Ni: Nickel, Fe: Iron, Pd: Lead, Al: Argon, Cr: Chromium, Cd: Cadmium, B: Boron, Unit: mgkg^{-1} , Cv: Coefficient of variability, %; K_1 , K_2 = ratio as in equation 3.

The lower limits of the range are for the 0 – 10cm depth and represent the spatial mean value for the spatial points (P1 – P4) in the respective soils.

Values for Mn with mean of 681.70 mgkg^{-1} in WDS and 215.3 mgkg^{-1} in CS showed variability in the respective 2 layers of the profile depth. Mn in WDS was very significantly different ($P < .01$) from Mn in CS (Table 2). Concentration of Ni in WDS was very high and very significantly ($P < .01$) more than in CS, ranging from $1024.0 - 1859.0 \text{ mg/l}$ with mean 1426.8 mgkg^{-1} in WDS and between 163.6 and 254.5 mgkg^{-1} with mean of 206.18 mgkg^{-1} in CS. Thus, waste accumulation may lead to Ni toxicity in soil. The variation of Ni was not very high both in WDS and CS ($C_v = 25.84$ and 23.8% respectively). Iron (Fe) had higher concentration in WDS than in CS (Table 1); the values in WDS ranged from $1043.0 - 3534.0 \text{ mg/kg}^{-1}$ with mean of 2027.0 mgkg^{-1} and from $93.5 - 120.5 \text{ mgkg}^{-1}$ in CS with mean of 105.96 mgkg^{-1} . The significantly higher Fe in WDS than CS could be attributed to the influence of the wastes on the soil. This could result in Fe toxicity. The C_v was 48.17% in WDS and 9.67% in CS. Comparatively, the soil at CS was more homogenous in terms of Fe content than the soil at WDS. Lead (Pb) with means of 154.0 mgkg^{-1} in WDS and 6.90 mgkg^{-1} in CS was significantly ($P = .05$) higher at WDS than at CS, although the variability from mean showed high variability of HM concentration in CS and homogenous pollution level on WDS. It implies that MSW was a source of constant supply of Pb in the soil, and that such high pollution of Pb at WDS did not affect CS at 100-120m away from WDS. Thus, compared to critical load (31), this implies that waste accumulation could result in Pb toxicity on the WDS soil. Aluminum (Al) content at WDS was significantly ($P = .05$) higher than CS (Tables 1 and 2), with means of 751.90 mgkg^{-1} in WDS and 366.6 mgkg^{-1} in CS showing superiority at WDS over CS in Al content (Table 1).

Variation was low in both WDS ($C_v = 11.95\%$) and CS ($C_v = 20.72\%$). Concentration of Cr in both soils was low, with mean of 0.25 mgkg^{-1} in WDS and between 0.10 and 0.19 mgkg^{-1} in CS. There was no significant difference between its mean concentration in WDS and CS, suggesting that municipal solid waste (MSW) may not significantly affect the Cr content of the soil. Nevertheless, variation of Cr was high at 32.00% and 26.32% in WDS and CS respectively. Cadmium (Cd) concentration also varied with the same mean of 0.16 mgkg^{-1} in WDS and in CS. The variation in CS was wider ($C_v = 56.25\%$) than in WDS ($C_v = 25\%$); making both soils not homogenous in Cd, even though having the same mean (Table 1). Boron (B) which values ranged from $0.05 - 0.15 \text{ mgkg}^{-1}$ with a mean of 0.01 mgkg^{-1} in WDS, and between 0.01 and 0.08 mgkg^{-1} with a mean of 0.03 mgkg^{-1} in CS was significantly ($P < .01$) higher in WDS than in CS (Table 2), suggesting that, in comparison with critical load (31), the B in the waste could cause B toxicity in the soil. The homogenous distribution of boron in WDS, against the highly varied content within the profile in CS, suggests that it has a source of constant supply in the biodegrading MSW from Uyo urban (where the waste emanated). The mean of B in WDS (0.01 mgkg^{-1}) was same as in the lower CS (0.01 mgkg^{-1}).

Fe had the highest variability at WDS but the least at CS (at 100-120m away), while B varied widest at CS but the least at WDS (Table 1).

Table 2. The t-test values for significant difference in heavy metals between WDS and CS at Uyo urban dumpsite, Nigeria

Soil properties	Mean difference	t-value	Significance
Cu	540.63	5.422	**
Mn	466.40	7.064	**
Ni	1220.70	9.391	**
Fe	1921.04	5.547	**
Pb	147.09	14.692	*
Al	385.23	16.210	*
Cr	0.06	1.459	Ns
Cd	0.00	0.093	Ns
B	0.06	3.571	**

3.2 Correlations

Correlations were investigated between: (1) HM and HM and soil particles sizes in the waste dumped soil (Table 3a), (2) between HM and HM and soil particles sizes in the control soil (Table 3b), and (3) between the upper and lower layers of soil profile (Table is not indicated). It was necessary to bring in soil particle sizes since HM are bound up in them.

For the polluted soil (Table 3a), significant correlation ($P = .05$) existed between Cu and Mn Ni, Fe, Pb, Al and B ($R = 0.992 - 0.999$); or B with Mn, Ni, Fe, Pb, others had very high correlations. Although not perfect, Cd correlation was negative with all HMs. However, sand and silt had very high correlations with Cu, Mn, Ni, Fe, and Pb ($R = .910 - .955$); silt correlation varied between good and very high with Cu, Mn, Ni, Fe, Pb, B ($R = .871 - .926$). Sand and silt had no correlation with Cr while clay had only negative, very low-correlation with Cr, but high negative correlation with Cd. All correlations of clay with Cu, Mn, Ni, Fe, Pb, Al were only fair or low. It was observed that (1) HM correlated very highly with themselves (except in the cases of Cd, Cr and Al (except B)), (2) Sand also correlated highly with them (except Cr and Cd), (3) Silt correlation was good with Cu, Mn, Al and Cd, but high with Ni, Fe, Pb, and B and (4) Clay was only negatively high with Cd but fair with others except Cr. This may be attributed to the very small particles proportions in WDS, which were (silt: 6.63% and clay: 16.98%) while sand was quantitatively the highest (76.38%) [32], hence the low correlations with silt and clay (Table 1).

For the control soil (Table 3b), all HM to HM correlations were very high or perfect ($R = .912 - 1.00$) except Cr with Pb and Al ($R = .860 - .892$). Some HMs recorded significant ($P = .05$) correlations with others, namely Cu with Mn and Cd; Mn with Fe, Cd and B; Fe with B, Pb with Al; and Cd with B (Table 3b). Clay in this case had very high to perfect correlation ($R = .951 - 1.00$) with all HMs, but correlated poorly and negatively with sand and silt. Sand and silt had very low and negative correlations with all HMs in CS. Thus, in CS, HM occurred naturally and increased with clay content.

The HMs in the upper and lower soil profiles at WDS and CS also had significant correlations. The lower layer at WDS had significant correlation ($P = .05$) with the lower layer HM values at CS ($R = .695$); it also had significant correlation ($R = .910$) with upper layer HM at WDS and with mean HMs at WDS ($P = < .01$). On the other hand, only fair correlations were observed between HM in upper layer at CS with lower layer at WDS ($R = .601$), and with upper layer at WDS ($R = .325$).

Table 3. Pearson correlation coefficients among heavy metals and with particle sizes at dumpsite soil

Polluted soil (WDS) (a)												
	Cu	Mn	Ni	Fe	Pb	Al	Cr	Cd	B	Sand	Silt	Clay
Cu	1											
Mn	.999*	1										
Ni	.995	.998*	1									
Fe	.992	.996	1.000*	1								
Pb	.995	.998*	1.000**	1.000*	1							
Al	.984	.977	.962	.954	.962	1						
Cr	.501	.468	.413	.387	.413	.647	1					
Cd	-.380	-.415	-.469	-.494	-.470	-.210	1	1				
B	.996	.999*	1.000***	.999*	1.000**	.965	-.458	1	1			
Sand	.910	.925	.947	.955	.947	.822	-.729	.942	1	1		
Silt	.871	.889	.915	.926	.915	.770	-.786	.910	.996	1	1	
Clay	.684	.711	.752	.771	.753	.543	-.935	.744	.925	.954	1	1

Control soil (CS) (b)												
	Cu	Mn	Ni	Fe	Pb	Al	Cr	Cd	B	Sand	Silt	Clay
Cu	1											
Mn	.999*	1										
Ni	.987	.976	1									
Fe	.995	.999*	.966	1								
Pb	.968	.952	.996	.938	1							
Al	.949	.930	.987	.912	.998*	1						
Cr	.977	.987	.930	.993	.892	.860	1					
Cd	1.000*	.999*	.984	.997	.963	.943	.981	1				
B	.996	.999*	.969	1.000**	.941	.917	.992	.997*	1			
Sand	-.469	-.418	-.604	-.377	-.676	-.724	-.269	-.452	-.387	1		
Silt	-.195	-.139	-.349	-.095	-.435	-.494	.020	-.175	-.105	.958	1	
Clay	.998*	1.000**	.976	.999*	.951	.928	.988	.999*	1.000*	-.415	-.135	1

In general, HM in lower profile depth at WDS was not monitoring HM in lower profile at CS, thus pollution at WDS was not related to, or did not affect, any HM level at surrounding soil 100– 120m away from WDS verge. This is significant for the side fields and upslope area and not necessarily for the downward slope, which was observed to have high HM up to 30m reach [33]. Thus, laterally in-soil transportation of HM from WDS to fringe location is limited. The fringe area of WDS is not necessary polluted by HM lateral transfer in soil. Therefore, it can be protected by a verge round the WDS. However, the higher HM pollution at deeper profile at WDS suggests potential vulnerability of deeper and downslope soil by groundwater or lateral flows (sediment and water). This direction requires further research.

3.3 Comparing the Concentrations of Heavy Metals between WDS and CS

Table 2 shows the t-values for significant differences between mean HMs at WDS and CS, with positive very significant ($P < .01$) mean difference obtained in five HMs (namely: Cu, Mn, Ni, Fe and B), significant difference at $P=.05$ for Pb and Al, and no significant difference (at $P= .05$) in Cr and Cd, indicating that mean concentrations of the entire heavy metal, except Cr and Cd, were higher in WDS than CS. The magnitude of the difference showed that the least mean difference was 147.01 mgkg^{-1} obtained in Pb while the highest was $1921.04 \text{ mgkg}^{-1}$ obtained in Fe; Hence, municipal solid waste at dumpsite soil significantly increased the concentration of heavy metals in the in-situ soil. Comparable observations were obtained by researchers in similar circumstance at other places on organic soils in the world [3,34,35,36,37].

Using the ratios K1 and K2, defined in Equation 3 for comparison, the HM in soil surface and bottom layer of top soil also showed profile variation (Table 1). The ratio of HM at bottom layer to the HM concentration at soil surface, which HM concentration showed an increase down the depth, increased in the following order: For WDS soil, K2 increased in the sequence: $B > Cr > Mn > Cu = Cd > Ni > Pb > Al > Fe$. For CS soil, the sequence for K1 was: $B > Cd > Pb > Cr > Al > Cu > Ni = Mn > Fe$ (Table 1). In both cases B gave the highest ratio and Fe the least ratio, while Cu and Cd had equal ratio of 2.1 in WDS, Ni and Mn had equal ratio of 1.6 in CS.

Using t-statistics, significant differences were recorded between the mean HM in control (CS and WDS soils (Table 2). Five heavy metals, Cu, Mn, Ni, Fe and Bo showed very significant difference ($P < .01$) between WDS and CS soil (Table 2) and two HMs, (Pb and Al), showed significant difference at $P = .05$, while the remaining two HM, Cr and Cd, recorded no significant difference at $P = .05$. Also the t-values for the mean HM values between the lower range in WDS and CS were significantly different at $P=.05$ while the HM values between the upper range in WDS and CS (i.e. surface soil layer) were different only at $P=.10$, whereas the overall HM between WDS and CS were significantly different at $P=.05$. Therefore at a distance of 100-120m from WDS, no pollution in the control soil was related to pollution transfer from HM levels at WDS. Thus, the elevated concentration of HM at WDS was most likely caused from location-specific anthropogenic source at WDS (the MSW and leachate composition) rather than terrigenous or parent material.

3.4 Contamination Factor (CF)

The degree of the anthropogenic pollution was differentiated by the overall mean contamination factor (CF) between WDS, as the polluted (treatment) soil, and the hilly terrain soil as the background soil.

The level of soil contamination by each HM pollutant from municipal solid wastes decay and its component leachate infiltration into insitu soil at WDS compared to the background station soil was the contamination factor (Equation 1). The background or pristine HM values for the area were: Pb ($6.90 \pm 3.25 \text{ mg kg}^{-1}$); Cu ($268.36 \pm 85.55 \text{ mg kg}^{-1}$); Ni ($206.20 \pm 48.21 \text{ mg kg}^{-1}$); Mn ($215.30 \pm 48.86 \text{ mg kg}^{-1}$); Cd ($0.16 \pm 0.09 \text{ mg kg}^{-1}$); Cr ($0.19 \pm 0.05 \text{ mg kg}^{-1}$); B ($0.03 \pm 0.03 \text{ mg kg}^{-1}$); Fe ($105.96 \pm 10.25 \text{ mg kg}^{-1}$) [38]. The CF results are shown in Table 4, with values for the overall soil depth studied (0-20cm), for the soil surface (0-10cm) and for the lower layer of root-zone depth (10-20cm).

Table 4. Contamination factor for heavy metal and metal pollution index in municipal solid waste dumpsite soil

HM	0 - 20cm	0- 10cm	10-20cm
Cu	3.02	2.75	3.25
Mn	3.17	2.31	3.27
Ni	6.92	6.26	7.36
Fe	19.13	1.01	1
Pb	22.32	46.88	15.32
Al	2.05	0.27	0.18
Cr	1.32	1.4	1.31
Cd	1	2.5	0.74
B	32	5	1.88
HPI	5.21	2.75	1.94

CF indicator (Table 4) suggests that HM elements in the overall depth of the WDS soil suffered anthropogenic pollution with HM levels in the order: B > Pb > Fe > Ni > Mn > Cu > Al > Cr > Cd. The contamination level varied amongst metals from moderate contamination with Cd, Cr, Al and Cu, to considerable contamination with Mn and Ni and very high contamination with Ni, Fe, Pb and B. The varied levels of different HM contaminations are indicative of the heterogeneous composition of municipal solid wastes at the dumpsite. Many goods like old fridges, generators, plastics, foams, electronics, cans (paint cans and food cans) amongst other items, are usually disposed at the dumpsite to rust and decay along with biodegrading garbage, and the egress leachate is often alkaline ($\text{pH} > 7$) setting off oxidation-reduction reaction in the soil [20,22]. HM toxicity of Bo is very injurious to agricultural production while others would have profound adverse health effect on farmers and urban consumers of crops produced from such a soil [6,7,14].

Fig. 2 shows the graphs with HM toxicity implication at WDS for elements like Fe, Mn, B identified also from their exceedance of critical loads [31]. Thus, bioaccumulation of Fe, B, Mn from HM at WDS has raised toxicity in them which might be of immense risk to vegetables grown there.

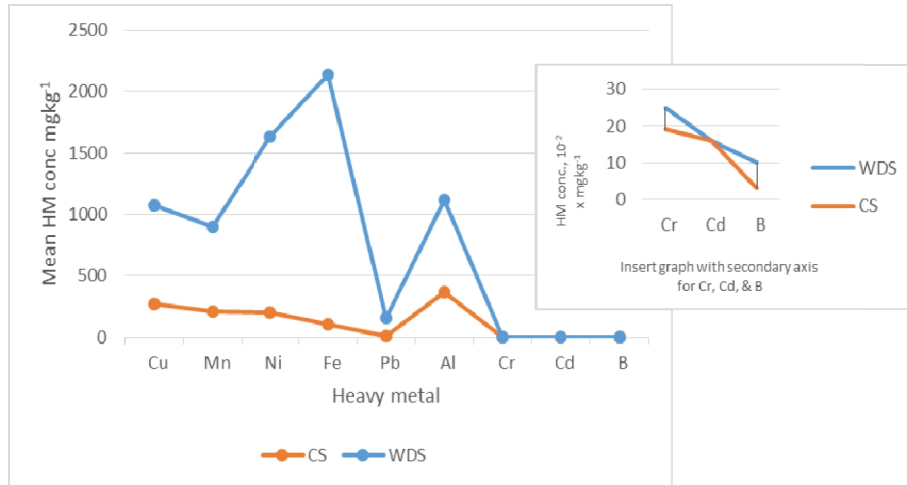


Fig. 2. Comparative graphs of mean heavy metal levels at WDS and CS soils

3.5 Heavy Metal Pollution Index (HPI) and Crop Production

HPI measures the degree of combined HM contamination in the studied soil. The results are shown in Table 4, showing variability in HPI of the combined HM from 2.75 at soil surface (0-10cm) to 1.94 at the lower soil profile (10-20cm), and the higher overall HPI of 5.21 which indicated a synergy effect of the combined or distributed HMs in the overall profile depth. Movement of HMs variously into soil profile to 10-75cm depth at different waste polluted sites is influenced by soil properties and metal [34, 35, 36, 37, and 39]. In this study site, waste deposition and composition, high amount of acidic rainfall, low clay, and low organic matter content, high sand fraction have been observed [32, 33, 38] and might have predisposed WDS soil to HM accumulation in soil profile. The higher concentration of heavy metals in the 10-20 cm profile is the dire field effect and is hazardous if it spreads to nearby farms, because of the ease of HM transfer to dietary vegetables and drainage to ground water.

Heavy metals are important for plant growth although needed in trace amount; those present in the WDS soil are Fe, Mn, B, Cu. Only Fe and B were observed to show prospects of toxicity in WDS due to MSW sustained deposition as compared to their applicable limits to plants [31, 40]. On the other hand, the non-essential elements, Ni and Pb are identified as being toxic level at the dumpsite soil. Al, Mn, Cr and Cd although non-essential, were found in the WDS soil (Table 1).

4. CONCLUSION

Heavy Metal (HM) distribution in municipal solid waste dumpsite soil and adjoining land was investigated. Samples were collected from the soil surface at 0-10cm and sublayer soil at 10-20cm of profile depth. HMs were dissolved from soil samples using acid digestion and flame AAS. Assessment utilized significant differences of mean HM concentrations, contamination factor (CF) and heavy metal pollution index (HPI), and covariance. Significant variations were obtained among HMs, and between HM in the soil surface and sub layer depth indicating profile heterogeneity for most metals. Also, higher concentrations of HMs were recorded at dumpsite soil (WDS) than the control soil, showing that site-specific sources (municipal solid waste and leachate) at dumpsite caused HM profile pollution more

than the status at control soil. The level of HM contamination was significantly high ($P < .01$) for four heavy metals (Ni, Fe, Pb and B) indicating likelihood of toxicity. The degree of (combined HM) pollution indicated by HPI was in reverse order from: higher degree of contamination (2.75) at the soil surface to high degree (1.94) in the sublayer (10-20cm) and highest degree of contamination (5.21) in the overall profile, indicating a higher synergy effect of the combined HM distribution in the studied profile. Correlation coefficient was very significant and very high between four HMs (Fe, Pb, Al, Cr) at $R = 85.0 - 94.9\%$ while negative or no significant relations existed between HMs and grain sizes. Only sand and silt had significant correlation with Al only. These indicated that HM pollution in soil profile stemmed from anthropogenic source at dumpsite and not from parent material of the soil. Landuse (gardening) on fields at 100 – 120 m (points SP1, SP2, Fig. 1 or X4 in Plate 1) from dumpsite, except in the downslope direction (SP3, Fig. 1 or X3 in Plate 1) were safe from dumpsite's HM pollution. The information is good for environmental management; however, the composition of unprocessed dumpsite wastes in relation to high HM profile accumulation in the in-situ soil should be researched into.

COMPETING INTEREST

The authors declare that no competing interests exist. The works were carried out solely by us.

REFERENCES

1. Akan JC, Abdulrahman FI, Sodipo OH, Lang AG. Physiochemical parameters in soil and vegetable samples from Gongulon agricultural site, Maiduguri, Borno state. Nigeria J. of American Science. Accessed 5 July 2011. 2010;6(12):78–85. Available: <http://www.jofamericanscience.org/journals/amsci/am0612>.
2. Martin S, Griswold W. Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens. Centre for Hazardous Substance Research. Manhattan KS 66506: Kansas State University. 2009;15.
3. Sharma RK, Agrawal, Marshall F. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. Ecotoxicol. Environ. Safety 2007; 5.
4. Essien OE, Douglas EE. Heavy metal transfer to vegetables from contaminated farm land adjoining sub-urban animal park/market, Uyo. 2012; 7(8):1268–1275.
5. Cui Y, Zhu Y, Zhao R, Chen D, Huang Y, Qui Y, Liang J. Transfer of metals from soil to vegetables in an area near a smelter in Nanning/China. Environmental International. 2004; 30(August):785-791.
6. Asia VB. Heavy metals in the environ and their health effect. Soil and Environment. Accessed 14 June 2013; 2013. Available:www.soil-environment.blogspot.com/2009/07/heavy-metals-and-their-health-effects.htm.
7. Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environmental Pollut. April 2008;152(3):686–692.
8. Shridhara CN, Kamala CT, Roy D, Samuel S. Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer. Ecotoxicology and Environmental Safety. 2008; 69(3):513–513.
9. Tripathi A, Misra DR. A study of physico-chemical properties 414 and heavy metals in contaminated soils of municipal waste dumpsites at Allahabad, India. International Journal of Environmental sciences. 2012;2(4):2024–2033.

10. IPPTS Associates. How contamination leach out of landfill waste and into leachate. IPPTS Associates. The Leachate Experts Website. Accessed: 26 March 2013; 2011. Available: Leachate.co.uk/main/leachate-chemistry-testing/how-contaminants-leach-out-of-landfill-waste-and-into-leachate/#comment-116.
11. Adjia R, Fezeu NML, Tchatchueng JB, Sorhos EG, Ngassom MB. Long-term effect of municipal solid wastes amendment on soils heavy metal content of sites used for peri-urban agriculture in Ngaoundorc, Cameroun. *Afri. J. Environ. Sci. Technol.* 2008;2(12):412–421.
12. US Department of the Interior. Earth Manual Part 1. 3rd ed. Denver (Colorado): Bureau of Reclamation. US Department of the Interior; 1998.
13. Sukop H, Blume HP, Kunick W. The Soil flora and vegetation of Berlin's waste land, Nature in cities. The natural environment in the design and development of urban green space. Chichester: John Wiley and Sons; 1979.
14. Anikwe MAN, Nwobodo KCA. Long-term effect of municipal solid waste disposal on soil properties and productivity of sites used for urban agriculture in Abakaliki, Nigeria. *Biores. Tech.* 2002;83:241–250.
15. Essien OE. Foundation soil's properties at old dumpsite under short-term restoration effect of municipal solid waste disposal. *International Journal of Engineering Research and Technology.* 2013;2(2):1-6.
16. Nordberg GE, Goyer RA, Clarkson TW. Impact of effects of acids precipitation on toxicity of metals. *Environ Health Perspect.* 1985;63:169-80.
17. Freedman B, Hutchinson TC. Sources of metal and elemental contaminants of terrestrial environments. In: Lepp NW, editor. *Metals in the environment.* London: Applied Sci. Publ. 1981;11:35-74.
18. Alloway BJ. The origins of heavy metals in soil. In: Alloy BJ, editor. *Heavy metals in soils.* 2nd Edition.. Blackie Academic & Professional; Chapman and Hall. 1995;39–57.
19. Ukem EO. Electronic wastes: a growing challenge in Nigeria. *Global Journal of Pure and Applied Sciences.* 2008;14(4):459–462.
20. Salam AK, Helmke PA. The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution. *Geodemia.* 1998; 83:251-291.
21. Wood JM. The role of pH and oxidation-reduction potentials in the mobilization of heavy metals. In: Toribare TY, Miller MW, Morrow PE, editors. *Polluted Rain.* New York: Plenum Press. 1980:223-236.
22. Oyedele DJ, Gasu MB, Awotoye OO. Changes in Soil properties and plant uptake of heavy metals on selected municipal solid waste dumpsites in Ile- Ife, Nigeria. *Afri. J. Environ. Sci. Technol.* 2008; 3(5):107–115.
23. Sayyed MRG, Sayadi MH. Variations in heavy metal accumulations within the surface soils from the Chitgar Industrial area of Tehran. *Proceedings, International Academy of Ecology and Environmental Sciences.* 2011; 1(1):36–46.
24. SLUK – AK. Physical background, soils and landuse and ecological problems. Technical Report of the Task Force on soils and landuse. Uyo: Government Printer; 1989.
25. Siaka M, Owens CM, Birah GF. Evaluation of some methods for the determination of heavy metals in sediment samples by Flame-AAS. *Analytical letters.* 1998; 31(4):703 – 718. DOI: 10.1080/000327/9808001873.
26. Nieuwenhuize J, Poley-Vos CH, van den Akker AH, van Delft W. Comparison of micro-wave and conventional extraction technics for the determination of metals in soils, sediments and sludge samples by atomic spectrometry. *Analyst.* 1991; 116:347 – 351. DOI: 10.1039/AN9911600339.
27. Liu C, Evett JB. Soil properties testing, measurement and evaluation. 4th Edition. Upper Saddle River: Prentice Hall, Inc; 2000.

28. Qingjie G, Yunchuan X, Qingfei W. Calculating pollution indices of heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences*. 2008; 19 (30):230–241.
29. Akoto O, Ephraim JH, Darko G. Heavy metal pollution in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghana. *Int. J. Environ. Res*. 2008; 2(4):359-364.
30. Mmolawa KB, Likuku AS, Gaboutloeloe GK. Reconnaissance 475 of heavy metal distribution and enrichment around Botswana. 5th International Conference of Environmental Science and Technology, Houston, Texas, USA. (July 12-16); 2010.
31. de Vries W, Lofts S, Tipping E, Meili M, Goenenborg JE, Schütze G. impact of soil properties on critical concentrations of cadmium, lead, copper, zinc and mercury in soil and soil solution in view of ecotoxicological effects. *Reviews of Environmental Contamination and Toxicology*. 2007;199:47–89.
32. Essien OE, Hanson OE. Municipal solid waste dumpsite pollution on physico-chemical properties of dumpsite and surrounding soils. *International Journal of Engineering Research & Technology*. 2013;2(4):298–310.
33. Archibong EU, Archibong DB. Field investigation of soil and water characteristics at abandoned municipal dumpsite, Uyo. B. Sc. Project. Faculty of Engineering, University of Uyo, Uyo; 2011.
34. Amusan AA, Ige DV, Olawale R. Characteristics of soil and crop uptake of metals in municipal wastewater dumpsites in Nigeria. *J. Human Ecol. Kamba Rja*. 2005;1(2):167-171.
35. Davis RD, Charton-Smith CH, Stark JH, Campbell JA. Distribution of metals in grassland soils following surface applications of sewage sludge. *Environmental Pollution*. 1998;49:99–115.
36. Schirado T, Vergara I, Schalscha EB, Pratt PF. Evidence for movement of heavy metals in a soil irrigated with untreated wastewater. *Journal of Environmental Quality*. 1986; 15:9–12.
37. Lund IJ, Page AL, Nelson CO. Movement of heavy metals below sewage disposal ponds. *Journal of Environmental Quality*. 1976; 5:330–334.
38. Akwa Ibom Agricultural Development Project (AKADEP). Study of Northern Akwa Ibom swamp resources. Stage 2 Report, Volume 4. Uyo (Nigeria): AKADEP; 1995.
39. Suave S, Henderson W, Allen HE. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden and organic matter. *Env. Sci. Technol*. 2000; 34:1125–1131.
40. FAO. Water quality for agriculture. Irrigation and Drainage Paper 29 Rev. 1. Food and Agriculture Organization (FAO) of UN, Rome; 1985.

© 2014 Essien and Hanson; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sciencedomain.org/review-history.php?iid=408&id=5&aid=3357>