Effect of Wood Ash Waste from Black Soap-making on Heavy Metals in Leaf Amaranth, Cowpea and Maize

O.J. Ayodele, O. S. Shittu

Abstract— The production of lye needed for black soap-making leaves large quantities of leached wood ash as waste. This waste has piled up on 0.4 ha land during a 50-year period of operation at a facility in Ikere-Ekiti, Nigeria. The impact of this long-term ash deposit on heavy metal content was measured at 0, 15, 30, 60, 75, 105 and 150 m from the waste pile and compared to a control sample. Four-week top-growths of maize, cowpea and leaf amaranth in the soil samples were harvested, oven-dried and analyzed for heavy metals. Fe was the most abundant metal in the soils. Pb, Ni, Co and Cu were highest at 0 m and decreased with distance from the ash waste pile but all metals showed accumulation at the valley bottom (150 m). Enrichment Factor was highest for Cu, Ni and Pb at 0 m and decreased with distance. The Contamination Factor was highest for Co, Cu, Ni and Pb at 0 m and decreased farther from the ash waste pile while the Pollution Load Index exceeded 1.0 at 0 m only. Cowpea shoot Ni and Pb contents increased with distance from the ash waste pile; leaf amaranth Co, Cu and Pb content decreased and Ni increased from 0 to 30 m while maize Co and Cu content increased. Transfer Factors were high for Co at all distances, low for Cu, Ni and Pb at 0 m and high with distance in leaf amaranth; high for Co at all distances, low for Pb at 75 and 150 m in maize; and high for Cu at 15 m and Pb at 0 m in cowpea.

Keywords— Contamination Factor, Heavy metals, Leached wood ash, Pollution Load Index, Transfer Factor

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1 INTRODUCTION

SOAP-MAKING had been natural and in small quantities for rural households through a chemical reaction involving lye (alkaline solution initially got from leaching wood ash) and vegetable oil or animal fats (tallow) which makes soap a salt of fatty acids (Naught and Wilkinson, 1997). This principle has remained unchanged even with inevitable industrialization and commercial-scale soap manufacture that began since the late 19th century in Europe and America (O'Neil, 2013). The outcome is operation in several factories whose processes, equipment and sophistication vary and with different kinds and types of soap produced under censored regulations on raw materials handling, emission and effluent control, by-products and waste disposal which minimize hazards to the environment and human life (US EPA, 1995; Wansbrough, 2002). Nevertheless, hand-made or natural soap are still being produced. Native or African black soap is a hand-made soap produced with natural ingredients and other secret additives such that the colour, texture, odour and lathering quality differ among the various West African tribes (Popovitch, 2013). Traditional black soap-making is devoid of machinery or sophistication and consists of a 3-step process: (1) gathering and burning of wood to obtain wood ash (or kitchen wood ash is collected) which is leached in perforated earthen pots to obtain lye (2) mixing of lye with vegetable oil and (3) stirring the mixture continually in metal or earthen pots with moderate heat from firewood until it solidifies and the brown to black soap is allowed to cool and cut to sizes ready for use or sale.

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Black soap-making is a small-scale localized industry hardly recognised in the current desire to understand the interrelationships between natural resources utilization for economic development, pollution, public health and the enviromental being promoted in the industrial sector (FMI, 2003). Without safety regulations in the production process, waste generation and disposal, pollution of the environment would go on unchecked. The main waste which has not been given consideration but should be of major environmental concern is the leached ash usually discarded on surrounding lands. Afao Quarter, Ikere-Ekiti, Ekiti State is one of the places known for black soap-making in Nigeria and whose leached ash residue from >50 years of operation has piled up and spread on about 0.40 hectares of land. The long-term presence of this pile can be a source of heavy metals as the trees from which the wood burnt was derived would have absorbed these elements during their lifetime.

Heavy metal concentration is used to assess the level of contamination in an enviroment. Wood ash contains typically low amounts of heavy metals (Etiegni *et al.*, 1991; Risse and Harris, 2008) of diverse mobility but which can be of ecotoxical significance when they cause changes in the soil, ground vegetation and ground water chemistry (Campbell, 1990). Land application of wood ash increases the pH of the organic matter-rich surface layer of the soil (Ohno and Erich, 1990; Saarsalmi *et al.*, 2001) which reduces the solubility of heavy metals and so can cause their accumulation in soils. Herein lay the interest in heavy metals which at high concentrations would form complex compounds with the organic and inorganic soil colloids, sorb on clay and sequioxides surfaces or precipitate as hydroxides and carbonates (Ruby, 1999). Thus, the heavy metals may accumulate in the soil and enter the animal system through the food chain such that monitoring the level of bioavailability using

plants has elicited substantial interest. Heavy metals with regards to potential hazards and occurrences in contaminated soils are cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb) and zinc (Zn) (Alloway, 1995; Akoto et al., 2008). The growing trend in nutritional studies worldwide is to assess the essential micronutrients and heavy metals contained in foodstuffs, especially fruits and vegetables and compare with established allowable concentrations. This study assessed the properties and the contents of some heavy metals in the surface layer of soils in the vicinity of a black soap-making facility at Ikere-Ekiti and related these to the concentration in three food crops and with consideration for food safety.

2 MATERIALS AND METHODS

2.1 Study Site

Afao Quarter, Ikere-Ekiti (lat. $7°39'N$, long. $5°33'E$) is renowned for the production of black soap. The study site is a location where black soap-making had taken place for over 50 years before it was abandoned and on which a large quantity of leached ash refuse had piled up. The land slopes northward into a basin formed by natural drainage and was chosen for sampling because of susceptibility to contamination by runoff and other erosion agents from the refuse pile.

2.2 Soil Sample Collection, Preparation and Analysis

Sampling took place at specific distances: 0, 15, 30, 60, 75, 105 and 150 m from the ash refuse pile, and a control location where the influence of the ash was absent and labelled as TP_0, TP_{15}, TP_{30}, TP_{60}, TP_{75}, TP_{105}, TP_{150} and CP, respectively. Surface (0-15 cm) soil samples were taken randomly and bulked to make a composite sample for each location. The soil samples were air-dried, slightly crushed in agate mortar and pestle, and sieved (<2 mm). Particle size distribution, pH, organic matter, total nitrogen, available phosphorus, exchangeable cations and acidity, and available micronutrients were determined using the laboratory analytical procedures described in IITA (1979) Laboratory Manual. One gram (1 g) of each sample was weighed into a digestion tube and 100 ml of a mixture of concentrated nitric acid and perchloric acid (in 2: 1 v/v ratio) were added. The mixture was heated at $150°C$ for 90 minutes on a Tecator Digestor and the temperature increased to $230°C$ for another 30 minutes. The digests were allowed to cool and washed into 50 ml volumetric flask, made up to mark and heavy metals (Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb and Zn) determined on an atomic absorption spectrophotometer (AAS, ALPHA 4 Model).

2.3 Pot Study

Five hundred ml of soil samples were measured into 600 ml plastic cups and watered to near field capacity. Seeds of maize (SUWAN 1-SR-Y), cowpea (IT 84S-2246-4) and leaf amaranth (NHAc 23) were sown in the next day. Seedlings that emerged were thinned to 2, 2 and 10 per cup for maize, cowpea and leaf amaranth, respectively. The plants were watered daily and grown for four weeks. The plants were harvested by cutting the plants at the soil surface, rinsed in distilled water, packed in labelled envelopes, oven-dried at $60°C$ for 48 h and ground into fine powder with mortar and pestle. 250 mg finely-ground plant samples were digested with 5 ml concentrated nitric acid and the digests diluted to 60 ml with demineralized distilled water. Co, Cd, Cr, Cu, Fe, Ni, Zn and Pb were determined with AAS.

The extent of soil pollution was compared to a baseline concentration through the calculation of some indices of heavy metal contamination.

(1) Enrichment factor (EF) was calculated from the relationship used by Liu et al. (2005) as:

$$\frac{C_n \text{ (sample)}/ C_{ref} \text{ (sample)}}{B_n \text{ (background)}/ B_{ref} \text{ (background)}}$$

Where, C_n (sample) = concentration of metals in the sample,

C_{ref} (sample) = concentration of the reference metal in the sample

B_n (background) = concentration of the metal in background environment

B_{ref} (background) = reference metal's concentration in the background.

Iron (Fe), aluminium (Al), manganese (Mn), selenium and titanium are the widely used reference metals (Reinmann et al., 2000; Liu et al., 2005; Fang et al., 2006). Agunbiade and Fawale (2009) had used Fe whose abundance implied its natural occurrence in the soils and was adopted as reference metal in this study. The interpretation is as follows: E.F. <2.0, 2.0-5.0 and >5.0 means deficiency of mineral enrichment, moderate enrichment and high level of enrichment, respectively.

(2) Contamination Factor (CF) = $\dfrac{C_m \text{ sample}}{C_m \text{ background}}$

Where, C_m (sample) = mean of the concentrations of individual metals from all distances

C_m (background) = background or baseline concentration of individual metal

The interpretation is in four categories as follows: CF<1.0 = low contamination; 1<CF<3 = moderate contamination; 3<CF<6= considerable contamination and 6<CF = very high contamination

(3) Pollution Load Index (PLI) = $(C_{F1} \times C_{F2} \times C_{F3}\text{-------}C_{Fn})^{1/n}$

Where, n = number of metals investigated

C_F = Concentration factor, ratio of concentration of each metal in sample to the baseline soil

PLI value below or close to 1 means baseline heavy metal loads while >1 means heavy metal pollution or accumulation at the site

(4) Transfer factor (TF) of the heavy metal into plants, also referred to as the extraction coefficient was determined using the expression C_P/C_s

Where, C_P = concentration of the metal in plant sample

C_s = concentration of the metal in corresponding soil sample

TF>1 means high level of heavy metal contamination in the plant.

3 RESULTS

Table 1 shows the properties of the surface layer (0-15 cm) of

soils in the study area. The soils were slightly alkaline to moderately alkaline compared to the slightly acid control sample. The highest value (pH= 8.3) was obtained at 0 m and the pH decreased with distance from the ash pile. The soils were silt loam at 0 m, sandy loams in the control and at 150 m and sandy clay loams at other distances. The soils contained 1.14-3.37% organic carbon and 0.14-0.43% total N with the highest values at 150 m while the control contained 0.46% soil organic carbon and 0.06% total N. Available P content was 9.4-33.9 mg.kg^{-1} in the study location and 7.9 mg.kg^{-1} in the control.

The highest levels of exchangeable cations were: K at 30 m and 150 m, Ca and Mg at 0 m and Na at 150 m.

The heavy metal contents of the soils are shown in Table 2. Fe was the most abundant heavy metal at 105.7-229.5 mg.kg^{-1} compared to 157.5 mg.kg^{-1} in the control. Mn varied between 1.6 and 2.2 mg.kg^{-1} while Zn was at 11.74-16.68 mg.kg^{-1} over the 0-105 m range compared to 25.1 mg.kg^{-1} at 150 m. Cu varied between 2.7 and 62.5 mg.kg^{-1} with highest value at 0 m and accumulation at 150 m. Ni, Pb and Co had a similar distribution pattern that indicated highest values at 0 m, reduction at 15 m and increases thereafter.

TABLE 1
PROPERTIES OF SOILS AT SPECIFIC DISTANCES FROM ASH REFUSE PILE IN THE BLACK SOAP-MAKING FACILITY

| Property | Distance from ash refuse pile (m) | | | | | | | |
	TP$_0$	TP$_{15}$	TP$_{30}$	TP$_{60}$	TP$_{75}$	TP$_{105}$	TP$_{150}$	CP
pH	8.3	7.6	7.8	7.9	7.4	7.9	7.7	6.4
Sand, %	31.0	55.0	48.0	45.0	59.0	49.0	58.0	63.0
Silt,%	54.0	16.0	20.0	33.0	14.0	22.0	25.0	19.0
Clay, %	15.0	36.0	32.0	22.0	27.0	29.0	17.0	18.0
Textural Class	SiL	SCL	SCL	SCL	SCL	SCL	SL	SL
Organic Carbon, %	2.29	1.14	2.33	1.44	1.98	1.76	3.37	0.46
Total N, %	0.29	0.14	0.30	0.18	0.25	0.22	0.43	0.06
Available P, mg.kg^{-1}	22.5	9.4	28.3	12.3	19.7	19.2	33.9	7.9
Exchangeable Cations, cmol.kg^{-1}								
K	0.78	0.27	1.13	0.39	0.75	0.26	1.96	0.11
Ca	12.90	6.90	7.40	8.00	6.10	8.90	7.00	1.40
Mg	8.90	5.70	5.90	6.50	4.90	6.70	5.10	0.80
Na	0.47	0.31	0.51	0.35	0.46	0.47	0.88	0.27

C = Control site; SiL = Silt loam; SCL = Sandy clay loam; SL = Sandy loam

TABLE 2
EFFECT OF ASH DEPOSIT ON HEAVY METAL CONTENT IN SURFACE LAYER OF SOILS IN A BLACK SOAP-MAKING FACILITY

| Heavy metals | Distance from ash refuse pile (m) | | | | | | | |
	TP$_0$	TP$_{15}$	TP$_{30}$	TP$_{60}$	TP$_{75}$	TP$_{105}$	TP$_{150}$	CP
Mn	2.10	2.05	1.86	1.62	2.15	1.56	1.75	2.20
Zn	12.91	11.74	16.68	15.81	12.36	14.11	25.11	8.64
Pb	27.00	2.80	7.20	10.50	10.40	7.00	23.80	18.25
Ni	32.00	4.20	5.50	6.00	6.00	5.30	7.20	ND
Fe	203.30	119.87	162.28	155.22	174.85	105.67	229.46	157.45
Co	16.00	1.70	4.70	5.10	3.40	4.10	7.40	ND
Cu	62.50	2.70	6.50	10.90	7.60	8.90	22.70	5.60

ND = Not Detected (below detectable level)

The relationships between heavy metals and some soil properties are shown in Table 3. The significant correlations are: soil pH with Ni and Co; clay with Fe and Pb; silt with Co, Cu and Ni; and soil organic matter with Ni and Zn. The heavy metal pairs with significant correlations are: Fe/Pb, Cu/Pb, Cu/Ni, Cu/Co and Ni/Co.

Table 4 shows the heavy metal contents in leaf amaranth, cowpea and maize top-growths. Pb, Ni and Cu were detected in the shoot of cowpea grown in ash-impacted soils while Pb and Ni were not detected in the control sample. Pb content increased from 2.4 mg.kg^{-1} at 0 m to 13.6 mg.kg^{-1} at 150 m, Ni was not detected at 0 m and increased to 24.0 mg.kg^{-1} at 150 m while Cu was highest at 150 m. In leaf amaranth, Co and Cu decreased from 0 m and showed accumulation at 150 m. Ni increased from 0 m to 30 m, decreased till 75 m and increased thereafter to a maximum at 150 m. Ash decreased Pb in leaf amaranth up till 30 m and increased to a maximum at 150 m.

Co and Cu content in maize increased with distance from the ash refuse; Ni increased to the maximum value at 60 m and decreased till 150 m whereas Pb was high and decreased with distance. Pb in the control sample was lower than at 0 m only. Thus, there was enhancement of Ni, Co and Cu compared to the control sample.

TABLE 3
CORRELATION MATRIX OF THE RELATIONSHIPS BE-TWEEN SOIL PROPERTIES AND HEAVY METAL CON-TENT IN SOILS AFFECTED BY LEACHED ASH REFUSE

	pH	Sand	Silt	Clay	OM	Co	Cu	Fe	Mn	Ni	Pb	Zn
pH	-	-0.81	0.59	0.07	0.60	0.73	0.54	0.12	-0.49	0.71	0.04	0.08
Sand		-	-0.37	-0.18	-0.18	-0.01	-0.55	-0.11	0.25	-0.84	-0.26	0.01
Silt			-	-0.39	0.18	0.94	0.92	0.43	-0.12	0.90	0.66	0.08
Clay				-	-0.50	-0.53	-0.65	-0.72	-0.40	-0.47	-0.94	0.20
OM					-	0.59	0.43	0.67	-0.28	0.81	0.39	0.86
Co						-	0.96	0.59	-0.06	0.96	0.67	0.24
Cu							-	0.59	0.12	0.97	0.78	0.13
Fe								-	0.20	0.44	0.83	0.56
Mn									-	0.14	0.12	-0.55
Ni										-	0.61	0.02
Pb											-	0.10
Zn												.

Correlation coefficients, r = 0.71 and 0.83 are significant at 5 and 1% respectively

TABLE 4
HEAVY METAL CONTENTS OF CROPS GROWN IN SOILS AFFECTED BY RESIDUAL ASH FROM A BLACK SOAP-MAKING FACILITY

Treatment	Pb	Ni	Co	Cu
a) Maize				
CP	27.20	7.20	36.00	8.80
TP_0	29.60	11.20	31.20	9.60
TP_{15}	22.40	17.60	28.00	10.40
TP_{30}	13.60	14.40	41.60	15.20
TP_{60}	26.40	24.80	48.80	11.20
TP_{75}	24.80	16.80	46.40	20.00
TP_{105}	20.80	16.60	48.60	20.80
TP_{150}	16.00	14.40	42.40	30.40
b) Leaf Amaranth				
CP	28.80	13.60	51.20	29.60
TP_0	20.00	13.70	60.80	30.40
TP_{15}	20.00	19.20	14.90	32.00
TP_{30}	13.60	20.80	47.20	30.40
TP_{60}	36.80	9.60	20.80	21.60
TP_{75}	36.00	5.60	12.80	16.00
TP_{105}	30.40	16.00	8.00	16.80
TP_{150}	40.00	24.00	14.40	25.60
c) Cowpea				
CP	ND	ND	ND	3.20
TP_0	2.40	ND	ND	5.60
TP_{15}	9.60	8.14	ND	4.01
TP_{30}	8.35	10.40	ND	6.40
TP_{60}	9.60	6.40	ND	4.05
TP_{75}	4.80	16.05	ND	4.80
TP_{105}	10.19	24.03	ND	5.16
TP_{150}	13.60	16.80	ND	8.24

Correlation coefficients, r = 0.71 and 0.83 are significant at 5 and 1% respectively

The correlation coefficients of the relationships between soil properties and heavy metals in the test crops are shown in Table 5. Soil organic matter content showed significant correlation with Cu in cowpea and maize. The correlations between the heavy metals in soil and crops were not significant. Table 6 shows the correlation coefficients among heavy metals in the test crops. The correlations were low in maize and high between the pairs of Cu/Ni and Ni/Pb in cowpea and Co/Cu and Cu/Pb in leaf amaranth but these were not significant.

Table 7 shows the enrichment factors of heavy metals in the study location. The site was not enriched with Fe (EF<2.0) while Mn showed moderate enrichment except at 15 and 105 m where EF exceeded 5.0. Enrichment was high for other heavy metals (EF>5.0) at all the distances. Cu had the highest enrichment at 0 m followed by Pb while the other distances were most enriched with Pb. The trend of enrichment from the ash refuse pile is as follows: (1) Cu and Ni decreased with distance (2) Cu and Pb decreased but with slightly higher values at 150 m and (3) Zn increased to the highest value at 105 m. CF

TABLE 5
CORRELATION COEFFICIENTS OF RELATIONSHIPS BETWEEN SOIL PROPERTIES AND HEAVY METAL CONTENT OF CROPS GROWN ON SOILS AFFECTED BY LEACHED ASH REFUSE FROM BLACK SOAP-MAKING

Soil Properties	Co	Cu	Ni	Pb
a) Leaf Amaranth				
pH	-0.10	-0.09	0.14	-0.18
Sand	-0.41	-0.16	0.04	0.40
Silt	0.53	0.23	-0.08	-0.14
Clay	-0.43	-0.05	-0.68	-0.42
OM	-0.14	-0.11	0.43	0.16
Co	0.40	-	-	-
Cu	-	0.24	-	-
Ni	-	-	-0.08	-
Pb	-	-	-	0.23
b) Maize				
pH	-0.13	-0.09	0.48	-0.13
Sand	-0.04	0.52	-0.16	-0.27
Silt	-0.22	0.23	-0.07	0.46
Clay	-0.19	-0.05	0.38	0.58
OM	-0.14	0.69	0.07	-0.55
Co	0.40	-	-	-
Cu	-	0.24	-	-
Ni	-	-	0.19	-
Pb	-	-	-	0.30
c) Cowpea				
pH	-	0.47	0.23	0.46
Sand	-	-0.13	0.26	0.07
Silt	-	0.17	-0.47	-0.71
Clay	-	-0.20	0.41	0.34
OM	-	0.97	0.41	0.54
Cu	-	0.33	-	-
Ni	-	-	0.27	-
Pb	-	-	-	-0.31

Correlation coefficients, r = 0.71 and 0.83 are significant at 5 and 1% respectively

was highest at 0 m for Co, Cu, Ni and Pb with each element decreasing with distance from the ash refuse pile. The contamination of Co and Ni was moderate ($1 < CF < 3$) at 0 m and decreased to low contamination ($CF < 1.0$) thereafter. Cu contamination was high ($CF > 6.0$) at 0 m and moderate at 75, 105 and 150 m while Pb contamination was high at 0 m, moderate at 30-105 m but considerable ($3 < CF < 6$) at 150 m. Zn contamination was low at 0-15 m and increased to moderate level up till 150 m. Mn and Fe showed low contamination in the study location. PLI exceeded 1.0 at 0 m and the values decreased thereafter.

Table 8 shows the transfer factor of heavy metals in the crops grown in soils affected by ash refuse pile. There was high level Co contamination at all distances in leaf amaranth while Cu, Ni and Pb contamination was low at 0 m but high over the 15-150 m distance. Co contamination occurred at all distances in maize; Pb did not contaminate 75 and 150 m while Cu and Ni did not contaminate 0 m only. Contamination in cowpea is as follows: Cu only at the 15 m distance, Ni at all distances except 0 m and Pb at 15-30 and 105 m.

4 DISCUSSION

The high pH of soils in the location is due to the long-term presence of ash which is alkaline (pH 9.0-13.0) and rich in basic cations (Risse and Harris, 2008). One benefit of the ash left on the soil surface from slash-and-burn bush clearing, the main feature of smallholder traditional crop farming, is that the pH of the top layer of soils rises to a high level during the first year after clearing land from forest re-growth (Lal, 1999). Since the linear increase in soil pH with the amounts of ash added is due to the substantial reduction in soil exchangeable Al (Nottidge *et al.*, 2006), wood ash is a liming material with same efficiency as limestone in neutralizing acidity in soils (Campbell, 1990; Utzinger *et al.*, 2008). Besides, the nutrients absorbed by the trees and used for development are recycled because the ash retains the overall composition and proportions of the mineral nutrients contained in the wood even as their presence as oxides would further explain the alkalinity of wood ash (Hume, 2006; Serafimova *et al.*, 2011). The high level of exchangeable cations caused by the presence of the ash refuse pile is similar to significant increases in exchangeable Ca, K, Na and Mg which maintained effective cation exchange capacity through soil amendment with wood ash (Demeyer *et al.*, 2001; Nottidge *et al.*, 2006).

The total Fe, Mn and Zn contents are very low compared to 0.63-7.6%, 0.02-0.19% and 26-189 mg.kg^{-1}, respectively reported for most upland soils in Nigeria (FMANR, 1990). Awolola *et al.* (2007) obtained 1.01-3.62% total Fe and 19.55-77.60 mg.kg^{-1} total Zn in soils around some villages, factories, highways and solid waste disposal sites at Ibadan. The ash did not affect Mn and Fe contents compared to the control whereas Co, Cu, Ni and Pb varied, indicating increase or decrease, with distance from the ash refuse pile. Long-term application of wood ash caused the reduction of heavy metal concentration and accumulation in soils compared to the control due to ash-induced increase in soil pH which reduces the solubility and availability of the heavy metals (Saarsalmi *et al.*, 2001). Risse and Harris (2008) observed that wood ash and amended soils contain heavy metals but there is little or no crop uptake in soils whose pH exceeds 6.0 as the heavy metals become chemically-bound in the soil.

Heavy metals are environmental pollutants especially in

TABLE 6
CORRELATION MATRIX OF THE RELATIONSHIPS BE-
TWEEN HEAVY METAL CONTENTS OF CROPS IN SOILS
AFFECTED BY LEACHED ASH REFUSE

	Co	Cu	Ni	Pb
a) Leaf Amaranth				
Co	-	0.66	0.02	-0.59
Cu		-	0.46	-0.68
Ni			-	0.06
Pb				-
b) Cowpea				
Co	-	-	-	-
Cu		-	0.67	0.57
Ni			-	0.66
Pb				-
c) Maize				
Co	-	0.51	0.50	-0.25
Cu		-	0.50	0.10
Ni			-	-0.08
Pb				-

Correlation coefficients, r = 0.71 and 0.83 are significant at 5 and 1% respectively
areas with high anthropogenic pressure where the presence and accumulation in the atmosphere, soil and water can cause serious problems to all organisms. Heavy metal accumulation in soils is of particular concern to agricultural production because of the adverse effects it can have on crop growth, food quality (safety and marketability) and environmental health (Islam *et al.*, 2007). The pollution potentials of the heavy metals were assessed by comparing their concentrations in soils with the threshold values determined by the EU, UK, USA and Canada Regulatory Systems (CCME, 2001) and the WHO/FAO maximum permissible limits. Soil threshold for heavy metal toxicity is the highest permissible content in a soil that does not inhibit growth and cause yield reduction in crops (Islam *et al.*, 2007). It affects the soil environmental capacity of heavy metals and determines the cumulative loading limit. Fe, Mn, Cu and Zn are essential micronutrients for plant growth but whose over-abundance can cause displacement of other elements. Cu and Zn are deficient in the upland soils of Nigeria based on the critical levels determined with 0.1M HCl extractant (FMANR, 1990) and the total contents are much below the 63-200 and 200-300 mg.kg⁻¹ threshold limits for soils according to the EU, EK and Canada regulatory systems. The increases in Cu and Zn in ash refuse-impacted soils compared to the control would be an advantage. Pb was lower than 70-300 mg.kg⁻¹ threshold values and the WHO/FAO (2001) maximum permissible limit of 100 mg.kg⁻¹ in soils. Ni was equally below the 50-210 mg.kg⁻¹ thresholds in the regulatory systems and 75 mg.kg⁻¹ maximum permissible limits in soils. The im-

plication of ash refuse pile in raising Zn and Cu levels, especially at 0 m, is probably of agronomic significance while Pb, Ni and Co enrichment may not be of serious environmental concern. Besides, the concentrations of the heavy metals decreased with distance from the ash refuse pile which Ghrefat and Yusuf (2006) attributed to removal by the action of water and translocation elsewhere. Ngole and Ekosse (2012) noted that the direction of water flow down the slope would cause the heavy metals to be dispersed by runoff. Thus, the heavy metals accumulated and attained higher concentrations at the valley bottom than in the control site and nearby soils not impacted by ash refuse pile.

The significant positive correlations of Co and Ni with soil pH

TABLE 7
ENRICHMENT AND CONTAMINATION FACTORS FOR
HEAVY METALS IN SOILS AFFECTED BY LEACHED
WOOD ASH REFUSE PILE

	0	15	30	60	75	105	150 m
a) Enrichment Factors							
Co	37.82	6.83	13.93	15.79	9.35	18.62	15.51
Cu	151.56	11.12	19.77	34.61	21.44	37.26	48.80
Fe	0.26	0.16	0.24	0.26	0.22	0.18	0.35
Mn	3.84	6.35	4.26	3.88	4.57	5.47	2.83
Ni	54.02	12.04	11.64	13.26	11.78	17.18	10.71
Pb	134.75	23.73	45.06	68.62	60.39	67.10	105.29
Zn	19.76	30.51	32.01	31.69	22.01	41.48	34.07
b) Contamination Factors							
Co	1.83	0.20	0.54	0.58	0.39	0.47	0.85
Cu	7.34	0.32	0.76	1.28	0.89	1.05	2.66
Fe	0.05	0.03	0.04	0.04	0.04	0.03	0.06
Mn	0.19	0.18	0.17	0.14	0.19	0.14	0.16
Ni	2.61	0.34	0.45	0.49	0.49	0.43	0.59
Pb	6.52	0.68	1.74	2.54	2.51	1.69	5.75
Zn	0.96	0.87	1.24	1.17	0.92	1.05	1.86
PLI	**1.11**	**0.25**	**0.43**	**0.48**	**0.44**	**0.40**	**0.75**

are unexpected. Heavy metal concentrations reduce with increase in soil pH that will result from long-term ash application, due to lower heavy metal accumulation and decreased solubility in soils compared to controls ((Saarsalmi *et al.*, 2001). The colloidal fraction and exchange complex of mineral soils are dominated by clay and organic matter which retain metals and would continue to contaminate the soil as long as the nearby sources of pollution are active (Mmolawa *et al.*, 2011).

The long-term presence of ash refuse pile and seasonal effect on the surface soil by the attendant movement of runoff down the slope are active sources of heavy metals. This view has not been supported by the negative correlations of Fe and Pb with clay and positive significant correlations of only Ni and Zn with soil organic matter probably due to the greater influence of long-lasting liming effect from the leached ash refuse. The significant positive correlations between Co/Cu, Co/Ni, Cu/Ni, Cu/Pb and Fe/Pb relate to the similar sources of enhancement and mutual existence in the soil, and nature of chemical and physical factors controlling their association in parent materials and in the processes involved in soil formation (Mmolawa *et al.*, 2011).

The total contents only measure the degree of soil exposure to heavy metals but not their mobility and bioavailability as indicated by the poor correlations between the concentrations of the metals in the soils and plants. The metals exist in various fractions, chemical species- soluble, exchangeable, carbonate-, oxide- and organic matter-bound and crystal lattice- such that their availability differs as governed by dynamic equilibrium between the fractions (Islam *et al.*, 2007). Soil pH is one of the factors responsible for heavy metal availability as it controls the extent at which the elements are chemically-bound to the soil components. Risse and Harris (2008) noted that ash and ash-impacted soils contain heavy metals but these are rarely found in the crops because the resultant soil pH will be 6.0 or more.

The capacity of the crops to absorb heavy metals varied. Leaf amaranth and maize contained the highest amounts of Pb, Co, Cu and Ni that exceeded the contents of these elements in the soils. Only cowpea in the control soil contained less Pb than the maximum permissible limits for human health in edible plant parts estimated at 0.2 mg.kg^{-1} (CDPM, 1995) and 0.3 mg.kg^{-1} (WHO/FAO, 2001). The leached ash increased maize Ni content beyond the 10 mg.kg^{-1} limits at all locations, in cowpea at 75-150 m and in amaranth except at 60-75 m. Cu in leaf amaranth exceeded the 10 mg.kg^{-1} maximum permissible limits (CDPM, 2003) but only the control and 0 m contained values lower than this in maize.

The higher concentration of heavy metals in leaf amaranth and maize than the soil suggests their potentials for cleaning up polluted land through bioaccumulation (Tsui *et al*, 2006). Whiting (2000) classified plants into four chemotaxonomic groups based on the heavy metal uptake: excluders transfer negligible amounts of metals; indicators whose shoot content is a good measure of soil pollution; and accumulators and hyper-accumulators with large quantities concentrated in the shoots in relation to environmental factors which make the elements present in available forms. McGrath (1998) observed that shoot heavy metal concentrations in hyper-accumulators exceed the threshold values because they would absorb the less soluble metal fractions which makes them a tool for phytoextraction in metal-polluted soils. Co was not detected which shows that cowpea can be used as an excluder of this heavy metal while the low concentrations would probably make it an indicator plant for Cu, Ni and Pb pollution. Leaf amaranth contains more of the heavy metals; this agrees with the general observation that leaf vegetables have greater po-

tentials for accumulating heavy metals in edible parts within their short growing cycles due to higher transpiration rates. The backyard garden is often used for vegetable production but the food safety concerns means that this agricultural activity would require careful consideration.

TABLE 8
TRANSFER FACTORS OF HEAVY METALS IN CROPS GROWN IN SOILS AFFECTED BY LEACHED WOOD ASH REFUSE

	0	15	30	60	75	105	150 m
a) Leaf Amaranth							
Co	3.80	8.82	10.00	4.06	3.77	1.95	1.95
Cu	0.49	11.85	4.68	1.98	2.11	1.89	1.13
Ni	0.43	4.57	3.78	1.60	0.93	3.02	3.33
Pb	0.74	7.14	1.89	3.51	3.46	4.34	1.68
b) Cowpea							
Cu	0.09	1.48	0.99	0.38	0.63	0.74	0.37
Ni	0.00	1.93	1.89	1.07	2.68	4.53	2.22
Pb	0.09	3.43	1.17	0.91	0.46	1.46	0.57
c) Maize							
Co	1.95	16.47	8.85	9.57	13.65	11.90	5.73
Cu	0.15	3.85	2.34	1.07	2.63	2.34	1.34
Ni	0.35	4.19	2.62	4.13	2.80	3.17	2.00
Pb	1.10	8.00	1.89	1.29	0.40	2.97	0.67

5 CONCLUSION

The leached ash refuse contained high amounts of exchangeable cations whose impacts down the slope included increase in soil pH to alkaline level compared to the slightly acid control sample. The ash increased soil Co, Cu, Fe, Ni and Pb compared to the control while some heavy metals showed accumulation at the valley bottom. The heavy metal contents are lower than the international threshold values while the accumulative factors show variable levels of enrichment from leached ash waste. The ash increased maize Cu and Ni, leaf amaranth Co, Cu and Ni, and cowpea Cu, Ni and Pb but reduced Pb content of maize and leaf amaranth while Co was not detected in cowpea. Transfer factors in maize, leaf amaranth and cowpea grown for a short duration indicate higher levels of heavy metal accumulation closest to the leached ash

waste. The test crops should be grown for a longer duration as part of routine monitoring of the heavy metal status in order to provide data needed for policy recommendations on the appropriate utilization of the soils.

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