

Original Research Article

Heavy metal pollution in burnt brick-producing wetland areas of Benue State

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Abstract

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Burnt brick production involves soil excavation and utilises a large volume of fuel wood and takes place mainly along river banks. This study assessed heavy metal pollution (Cadmium, Lead, Chromium, Iron, Manganese and Zinc) resulting from wood-based brick-producing activities in wetland brick-producing areas of Benue State. Eight (8) out of 23 Local Governments Areas (LGAs) were purposively selected for the study. The selected Local Governments are Buruku, Gboko, Gwer West, Konshisha, Kwande, Makurdi, Ushongo and Vandeikya. From each of the selected LGAs, two burnt brick sites were chosen for investigation. Two soil pits were dug at each of the sixteen brick sites selected and samples taken at intervals of 10-15cm, 60-65cm, and 90-95cm. Thus, a total of 96 soil samples were collected from thirty-two soil pits located in sixteen brick sites within the study area. Also four composite soil samples were taken (two each at burnt and unburnt areas of brick sites) that served as control. Collected data were chemically analysed and subjected to descriptive and inferential statistical analyses (means, standard error of the mean, percentages, co-efficient of variation, student T-test, and correlation). The statistical package Genstat Discovery Edition 4 was used for analysis of variance (ANOVA). Results showed that burning of bricks with fuelwood significantly increases the concentrations of heavy metals such as Cd, Pb, Cr, Fe, Mn and Zn, with significant lower concentrations in unburnt soils than ash-rich burnt soils, as well as decreased concentrations with increasing depth. These have very serious environmental (social, economic and physical) implications. The study therefore recommends proper land-use planning in allocation of brick sites, deliberate afforestation and incorporation of appropriate technology in brick making so as to save bodies and rich agricultural lands in the State.

Keywords: Burnt bricks, Burnt and Unburnt soils, Heavy Metals, Mean Concentration, Pollution

INTRODUCTION

Environmental pollution, mainly with heavy toxic metals, is one of the most serious ecological problems presently being faced by man. Heavy metals pollution impacts on flora, fauna and other abiotic components of the ecosystem. Toxic heavy metal pollution alters metabolism in organisms producing unpalatable changes which may have a very high potential for causing severe injury, increased health hazards and even death. Heavy metal

pollution in particular (as well as other closely related anthropogenic influences, such as burnt brick production, agriculture, deforestation, unplanned urbanisation, technological advancement, mining and other profit-oriented economic activities) are the main sources of global pollution.

Heavy metals are generally referred to as the group of metals and metalloids, each with an atomic density

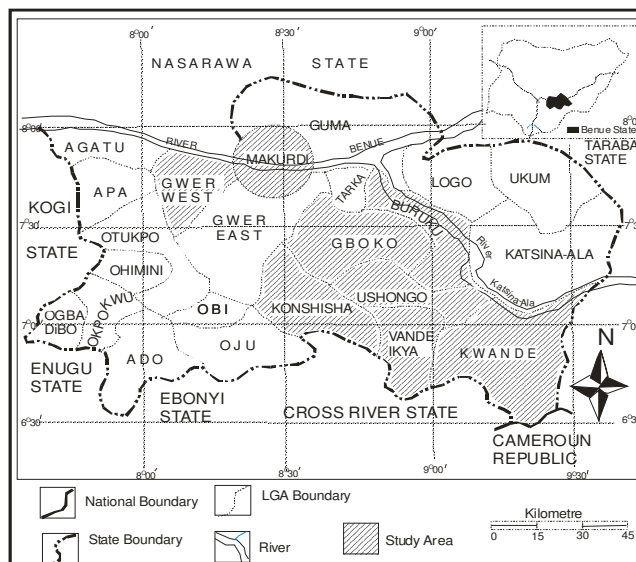


Figure 1. Map of Benue State Showing the Study LGAs

greater than 4g/cm^3 or with densities five times or more, greater than water (Dictionary Thesaurus, 2015). These metallic elements each have a relatively high density and are poisonous or toxic even at low concentrations (Lenntech, 2004). Examples of heavy metals include: Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Mercury (Hg) and Silver (Ag).

Environmental pollution by heavy metals is very prominent in mining areas and old mine sites, and pollution reduces with increasing distance away from mining sites (Peplow, 1999). These metals are leached out along slopes, and are carried by acid water downstream or run-off to the sea. Through mining activities, water bodies are most emphatically polluted (INECAR, 2000).

The potential for contamination is increased when mining exposes metal-bearing ores rather than natural exposure of ore bodies through erosion (Garbarino *et al.*, 1995), and when mined ores are dumped on the earth's surfaces through manual dressing processes. Through rivers and streams, the metals are transported as either dissolved species in water or as an integral part of suspended sediments. They may then be stored in river bed sediments or seep into the underground water thereby contaminating water from underground sources, particularly wells. The extent of contamination will depend on the nearness of the well to the mining site, as wells located near mining sites have been reported to contain toxic heavy metals at levels that exceed drinking water criteria (Peplow, 1999).

Wetlands are saturated with water, either permanently or seasonally, such that it takes on the characteristics of a distinct ecosystem, which makes them susceptible to all manner of contamination and pollution from anthropogenic activities that usually take place there. This study is therefore poised to assess the concentration

of heavy metals in burnt brick producing wetland areas in Benue State, Nigeria.

METHODOLOGY

The Study Area

The study was conducted in Benue State, located along Longitudes $6^{\circ} 35'$ and 10°E and Latitudes $6^{\circ} 30'$ and $8^{\circ} 10'\text{N}$ (figure 1). The state, with a total land mass of $30,955\text{km}^2$, was created by the Murtala Mohammed Military Administration from the defunct Benue-Plateau State in 1976, with Makurdi as the state capital. The State has a population of 4,219, 244 (NPC, 2007). The population has been extrapolated to 5, 505,157 in 2015 given an annual population growth rate of 3%. It is made up of 23 local governments (Figure 1). Benue State is bounded to the north by Nassarawa and Taraba States to the East, Ebonyi and Cross River States and the Republic of Cameroon to the south, as well as Kogi and Enugu States to the west. Burnt brick making is a major livelihood activity of the inhabitants of eight (8) Local Government Areas in the State, namely Buruku, Gboko, Gwer West, Konshisha, Kwande, Makurdi, Ushongo and Vandeikya. The Local Government areas were purposively selected for this study based on their ranking in terms of abundance of clay deposits and massive production of burnt bricks.

Procedures

Soil Sampling

A total of 32 soil pits each measuring $1\text{m} \times 1\text{m} \times 1\text{m}$ were

dug in the eight (8) purposively selected local government areas (LGAs). For each selected LGA, soil samples were collected from four (4) soil pits distributed in two randomly selected brick sites (ie two pits per brick site) at pre-determined depths of 10-15cm, 60-65cm, and 90-95cm. Soil pits of 1m x 1m x 1m is ideal for detailed observation of soil structure, texture, colour, stratification and depth of strata (Rowell, 1994). The effect of soil excavation on chemical soil properties were investigated using standard procedures as outlined by SPAC (1999). Also, four (4) composite soil samples were taken (two each at burnt and unburnt areas of brick-making sites). This helped to serve as control.

Representative soil samples were obtained taking into cognizance the spatial and temporal variability over brick sites. Each soil sample was placed in a separate polythene bag and much of the air expelled before tying the neck (Rowell, 1994). Using indelible ink, each sample was labeled with a number, sampling depth, pit number, location as well as the date on which the sample was collected. Each of the labels was placed into a second polythene bag into which each soil sample was separately placed. The second polythene bag was also labeled before transportation to the laboratory.

Chemical analysis of soil samples

Mehlich 3 extraction method was used for extraction of six heavy metals cadmium (Cd), lead (Pb), chromium (Cr), iron (Fe), manganese (Mn) and zinc (Zn).

Equipment and Apparatus

- Soil scoop calibrated to 2.0 g (1.7 cm³) and levelling rod
- 60 mL extraction bottles
- Automatic solution dispenser
- Reciprocating shaker
- Atomic Absorption Spectrophotometer (AAS), automated Flow Injection Analysis (FIA) if -- - -
- Reciprocating syringe pump calibrated at 20 mL

Reagents

Solutions were made with ASC reagent grade chemicals and distilled water

- Ammonium nitrate (NH₃NO₃)
- Ammonium fluoride (NH₄F)
- Nitric acid (HNO₃), 68-70%,
- Ethylenediaminetetraacetic acid (EDTA)
- Acetic acid, glacial [CH₃COOH]
- Ammonium fluoride-EDTA stock solution (3.75M NH₄F—0.25M EDTA):
- Mehlich-3 extracting solution

Chemical analytical procedure

Extraction

1. Soil samples weighing 3.0± 0.05 g of air dried soil pulverized to pass 10 mesh sieve (< 2.0 mm) were put into a 50-mL glass Erlenmeyer flask.
2. 30 ml of Mehlich 3 extracting solution were then added including a method blank.
3. Extraction flask(s) were placed on reciprocating mechanical shaker for five (5) minutes.
4. Suspension was immediately filtered and the extract collected in 40 mL plastic vials.

Analysis

The plastic vials containing the soil extracts were taken to Zaria for digital determination using an Atomic Absorption Spectrophotometer (AAS)

Analytical methods

Data collected were subjected to descriptive and inferential statistical analyses, which include means, standard error of the mean, percentages, coefficient of variation, student T-test, correlation analysis, and Analysis of Variance (ANOVA) using the Genstat Discovery (Edition 4) statistical package.

RESULTS

Six heavy metals [Cadmium (Cd), Lead (Pb), Chromium (Cr), Iron (Fe), Manganese (Mn) and Zinc (Zn)] were assessed in the soil samples. Their mean concentrations at the various sites and at various depths of excavation are shown in tables 1-8 below.

In Table 3 the concentrations of all the six heavy metals assessed at burnt and unburnt areas of brick sites are compared. The asterisked p-values indicate significant differences between burnt and unburnt areas of brick sites, and they occur in all the L.G.As investigated.

Cadmium (Cd)

From table 1, the mean concentration of cadmium for Gboko, Gwer-West, Konshisha, and Makurdi LGAs varied significantly with those of Buruku Ushongo and Vandeikya as well as Kwande. The highest mean concentration of Cd occurred in Kwande (0.79±149 ppm). The mean Cd concentration for Kwande varied significantly from those of Buruku, Gwer West, Konshisha and Makurdi Local government areas.

Table 1. Mean Concentration of Heavy Metals at Brick Sites in L.G.As

LGA	Cadmium (Cd) (ppm)	Lead (Pb) (ppm)	Chromium (Cr) (ppm)	Iron (Fe) (ppm)	Manganese (Mn) (ppm)	Zinc (Zn) (ppm)
LGAs						
Buruku	0.14±0.025 ^a	3.68±1.04 ^a	2.75±0.46 ^a	436.0±12.30 ^a	13.16±2.12 ^c	0.60±0.05 ^a
Gboko	0.49±0.112 ^b	2.51±0.88 ^a	3.62±0.45 ^{ab}	1395.6±54.0 ^b	6.96±1.25 ^b	2.56±0.29 ^c
Gwer- West	0.40±0.119 ^b	6.59±1.34 ^b	4.85±0.64 ^b	669.0±19.5 ^{ab}	6.30±1.04 ^b	1.41±0.21 ^b
Konshisha	0.52±0.094 ^b	5.94±0.12 ^b	4.24±0.57 ^b	690.0±11.9 ^{ab}	6.55±1.14 ^b	2.62±0.22 ^c
Kwande	0.79±0.149 ^c	4.84±1.43 ^{ab}	3.17±0.87 ^{ab}	949.0±26.7 ^c	2.86±0.62 ^a	1.28±0.25 ^d
Makurdi	0.41±0.108 ^b	5.22±1.50 ^b	1.39±0.40 ^a	1129.0±99.6 ^b	6.78±1.09 ^b	2.81±0.15 ^c
Ushongo	0.19±0.040 ^a	6.76±0.85 ^b	2.17±0.78 ^a	1802±15.29 ^d	4.78±0.85 ^a	0.62±0.09 ^a
Vandeikya	0.18±0.028 ^a	5.27±0.88 ^b	2.42±0.74 ^a	2324±22.9 ^e	2.94±0.67 ^a	0.84±0.09 ^a

Means on the same column with the same superscript are not significantly different ($p>0.05$)
CV=coefficient of variation, LSD=Least Significant Difference

Table 2. Mean Concentration of Heavy Metals at Various Depths of Soil Excavation in the Study Area.

Soil Excavation Depth (Cm)	Cadmium Cd (ppm)	Lead (Pb) (ppm)	Chromium (Cr) (ppm)	Iron (Fe) (ppm)	Manganese (Mn) (ppm)	Zinc (Zn) (ppm)
10-15	0.58±0.09 ^c	7.76±0.72 ^b	4.61±0.40 ^c	548.0±12.5 ^a	9.27±1.08 ^b	2.00±0.27 ^b
60-65	0.39±0.06 ^b	2.22±0.88 ^a	2.96±0.33 ^b	1298.0±55.6 ^b	5.79±0.89 ^{ab}	1.57±0.22 ^{ab}
90-95	0.19±0.03 ^a	2.77±0.37 ^a	1.66±0.27 ^a	1485±85.77 ^c	3.80±0.49 ^a	1.21±0.21 ^a

Means on the same column with the same superscript are not significantly different ($p>0.05$)

Table 3. Mean Concentration of Heavy Metals at the Burnt and Unburnt Areas of Brick Sites

Heavy Metal	Soil Treatment	Buruku (ppm)	Gboko (ppm)	Gwer/west (ppm)	Konshisha (ppm)
Cd	Burnt	0.19±0.007	0.74±0.022	0.81±0.000	0.71±0.102
	Unburnt	0.15±0.004	0.58±0.490	0.65±0.015	0.59±0.545
	<i>P-Value</i>	0.059	0.046*	0.035*	0.027*
Pb	Burnt	4.56±0.78	5.97±2.04	3.90±1.43	7.56±1.83
	Unburnt	1.19±1.04	3.11±2.52	2.17±0.00	3.16±0.00
	<i>P-Value</i>	0.021*	0.034*	0.045*	0.014*
Cr	Burnt	5.51±0.31	4.45±0.59	6.17±0.35	3.17±1.96
	Unburnt	1.76±0.14	2.63±0.73	2.57±0.54	1.39±1.05
	<i>P-Value</i>	0.021*	0.038*	0.020*	0.012*
Fe	Burnt	834.4±19.8	145.1±78.30	770.0±282.30	712.3±19.0
	Unburnt	782.0±30.0	141.50±65.8	743.0±235.0	681.52±6.70
	<i>P-Value</i>	0.045*	0.053	0.124	0.523
Mn	Burnt	18.63±1.52	13.26±0.51	12.01±1.07	13.19±0.68
	Unburnt	14.47±0.59	10.38±0.29	9.04±1.63	10.21±0.40
	<i>P-Value</i>	0.056	0.059	0.069	0.074
Zn	Burnt	1.46±0.76	3.16±2.10	3.91±0.94	3.86±0.57
	Unburnt	1.60±1.03	2.37±1.85	3.78±0.64	3.22±0.67
	<i>P-Value</i>	0.062	0.134	0.174	0.352

Asterisked (*) p-values indicates that there are significant differences between burnt and unburnt areas

In table 4, the mean concentration of Cd in burnt and unburnt areas of brick sites differed significantly from each other for Gboko, Gwer West, Kwande, Konshisha

and Makurdi Local Government Areas; however, the mean values were not significantly different for Buruku, Ushongo and Makurdi Local Government Areas.

Table 3. Mean Concentration of Heavy Metals (Ppm) at Burnt and Unburnt Areas of Brick Sites (Continued)

Heavy Metal	Soil Treatment	Kwande (ppm)	Makurdi (ppm)	Ushongo (ppm)	Vandeikya (ppm)
Cd	Burnt	1.29±0.005	0.45±0.073	0.59±0.000	0.29±0.000
	Unburnt	0.31±0.131	0.18±0.072	0.22±0.073	0.17±0.014
	<i>P-Value</i>	0.017*	0.044*	0.045*	0.061
Pb	Burnt	10.04±5.77	7.46±0.35	5.34±2.17	6.03±0.029
	Unburnt	3.06±0.89	4.45±0.69	2.77±2.17	1.58±1.38
	<i>P-Value</i>	0.006*	0.037*	0.031*	0.021*
Cr	Burnt	5.72±2.74	2.45±1.41	4.67±1.16	4.06±1.08
	Unburnt	2.23±1.56	1.25±0.65	2.42±0.69	1.56±0.88
	<i>P-Value</i>	0.035 *	0.052	0.321	0.041*
Fe	Burnt	937.0±35.90	791.0±42.10	431.0±17.30	336.13±3.72
	Unburnt	903.0±62.10	743.3±85.30	381.0±27.60	308.64±0.85
	<i>P-Value</i>	0.024*	0.049*	0.047*	0.034*
Mn	Burnt	7.67±0.61	14.04±1.14	12.35±0.31	10.26±0.50
	Unburnt	4.48±0.05	9.96±1.24	7.47±0.16	4.80±0.85
	<i>P-Value</i>	0.035*	0.041*	0.053	0.026*
Zn	Burnt	1.02±0.77	1.68±0.96	0.64±0.04	0.34±0.17
	Unburnt	0.46±0.04	1.49±0.49	0.71±0.15	0.59±0.03
	<i>P-Value</i>	0.171	0.139	0.124	0.140

Asterisk (*) p-values indicates that there are significant differences between burnt and unburnt areas

Table 4. Mean Concentration of Cadmium at Burnt and Unburnt Areas of Brick Sites

LGA	Burnt (ppm)	Unburnt (control) (ppm)	Mean±SEM (ppm)
Buruku	0.19±0.007 ^d	0.15±0.004 ^d	0.17±0.021 ^d
Gboko	0.74±0.022 ^b	0.58±0.490 ^b	0.66±0.035 ^{ab}
Gwer	0.81±0.000 ^b	0.65±0.015 ^a	0.73±0.008 ^a
Kwande	1.29±0.005 ^a	0.31±0.131 ^c	0.80±0.021 ^a
Konshisha	0.59±0.545 ^c	0.59±0.545 ^b	0.59±0.362 ^b
Makurdi	0.45±0.073 ^c	0.18±0.072 ^d	0.32±0.025 ^c
Ushongo	0.59±0.000 ^c	0.22±0.073 ^c	0.41±0.041 ^{bc}
Vandeikya	0.29±0.000 ^d	0.17±0.014 ^d	0.23±0.003 ^c

Means on the same column with the same letter are not significantly different (p< 0.05)

Lead (Pb)

In table 1, Buruku and Gboko Local Government Areas had the least mean concentrations of Pb, which did not vary significantly from each other. The mean values of Pb for Gwer-West, Konshisha, Makurdi, Ushongo did not vary significantly even though they varied significantly with Kwande Buruku and Gboko. The mean soil concentration of Pb for Kwande differed significantly with all others.

In table 2, the soil depth of 10-15cm had Pb concentrations that differed significantly from Pb concentrations at soil depths of 60-65cm and 90-95cm. However, the depths 60-65cm and 90-95cm did not exhibit much variation in concentration of Pb.

In table 5, the mean concentration of lead (Pb) at unburnt areas of brick sites were comparatively lower

than the mean concentration at the burnt areas. The Students T-test on Pb concentrations for burnt and unburnt areas of brick sites indicated that the concentration of Pb at burnt sites was higher, even though there were significant differences between the burnt and unburnt areas (P≤0.05).

Chromium (Cr)

From table 1, the mean concentration of Cr for Buruku, Makurdi, Ushongo and Vandeikya LGAs did not differ significantly from each other. However, mean Cr concentrations in soils from Gboko and Kwande LGAs differed significantly from mean Cr concentrations recorded for Buruku, Makurdi, Ushongo and Vandeikya LGAs. Table 1 shows that the soil excavation depths of

Table 5. Mean Concentration of Lead at Burnt and Unburnt Areas of Brick Sites

LGA	Burnt (ppm)	Unburnt (control) (ppm)	Mean±SEM (ppm)
Buruku	4.56±0.78 ^b	1.19±1.04 ^a	2.87±0.26 ^a
Gboko	5.97±2.04 ^c	3.11±2.52 ^e	4.54±1.25 ^c
Gwer	3.90±1.43 ^a	2.17±0.00 ^c	3.04±0.14 ^b
Kwande	7.56±1.83 ^d	3.16±0.00 ^e	5.36±1.69 ^d
Konshisha	10.04±5.77 ^e	3.06±0.89 ^e	6.55±0.54 ^f
Makurdi	7.46±0.35 ^d	4.45±0.69 ^f	5.96±0.78 ^e
Ushongo	5.34±2.17 ^c	2.77±2.17 ^d	4.05±2.33 ^c
Vandeikya	6.03±0.029 ^e	1.58±1.38 ^b	3.81±0.21 ^{bc}

Means on the same column with the same superscript are not significantly different ($p>0.05$)

Table 6. Mean Concentration of Chromium in Soil Samples at Burnt and Unburnt Areas of Brick Sites

LGA	Burnt (ppm)	Unburnt (control) (ppm)	Mean±SEM (ppm)
Buruku	5.51±0.31 ^b	1.76±0.14 ^{ns}	3.64±0.22 ^{bc}
Gboko	4.45±0.59 ^a	2.63±0.73 ^{ns}	3.54±0.65 ^b
Gwer	6.17±0.35 ^b	2.57±0.54 ^{ns}	4.37±0.10 ^c
Kwande	3.17±1.96 ^a	1.39±1.05 ^{ns}	2.29±1.51 ^a
Konshisha	5.72±2.74 ^b	2.23±1.56 ^{ns}	3.98±2.15 ^b
Makurdi	2.45±1.41 ^a	1.25±0.65 ^{ns}	1.85±1.03 ^a
Ushongo	4.67±1.16 ^b	2.42±0.69 ^{ns}	3.54±0.93 ^b
Vandeikya	4.06±1.08 ^a	1.56±0.88 ^{ns}	2.81±0.98 ^a

Means on the same column with the same superscript are not significantly different ($p>0.05$)

Table 7. Mean Concentration of Iron at Burnt and Unburnt Areas of Brick Sites

LGA	Burnt (ppm)	Unburnt (control) (ppm)	Mean±SEM (ppm)
Buruku	834.40±19.8 ^b	782.00±30.0 ^b	808.35±0.23 ^b
Gboko	145.10±78.30 ^f	141.50±65.8 ^e	143.30±0.53 ^g
Gwer	770.00±282.30 ^c	743.00±235.0 ^b	756.50±214.01 ^c
Kwande	937.00±35.90 ^a	903.00±62.10 ^a	920.00±0.42 ^a
Konshisha	712.30±19.0 ^c	681.52±6.70 ^c	696.91±6.21 ^d
Makurdi	791.00±42.10 ^c	743.30±85.30 ^b	767.15±35.12 ^c
Ushongo	431.00±17.30 ^d	381.00±27.60 ^d	406.00±12.24 ^e
Vandeikya	336.13±3.72 ^e	308.64±0.85 ^d	322.39±1.23 ^f

Means on the same column with the same superscript are not significantly different ($p>0.05$)

10-15cm, 60-65cm and 90-95cm the concentration of Cr decreased with increasing depth of excavation.

However, the mean concentrations of Cr at unburnt areas, in table 6, were lower than that of burnt areas of brick sites. The Students t-test results indicated that Buruku, Gboko, Gwer West, Kwande, Konshisha and Vandeikya L.G.As, had mean Cr concentrations from burnt areas that differed significantly from mean concentrations of Cr from unburnt areas.

Iron (Fe)

In table 1, Ushongo and Vandeikya had mean Fe concentrations which were significant from each other, and higher than all the means for the other LGAs sampled. From table 2, the mean concentration of Fe at various soil depths differed significantly from each other and increased with the depth of excavation. The concentration of Fe at burnt areas of brick sites followed a similar pattern with that at unburnt areas. From Table 7,

Table 8. Mean Concentration of Manganese at Burnt and Unburnt Areas of Brick Sites

LGA	Burnt (ppm)	Unburnt (control) (ppm)	Mean±SEM (ppm)
Buruku	18.63±1.52a	14.47±0.59a	16.55±0.74a
Gboko	13.26±0.51b	10.38±0.29b	11.82±0.21b
Gwer	12.01±1.07c	9.04±1.63b	10.53±0.89bc
Kwande	7.67±0.61e	4.48±0.05d	6.08±0.21d
Konshisha	13.19±0.68b	10.21±0.40b	11.70±0.35b
Makurdi	14.04±1.14b	9.96±1.24b	12.00±1.21b
Ushongo	12.35±0.31c	7.47±0.16c	9.91±0.35c
Vandeikya	10.26±0.50d	4.80±0.85d	7.53±0.45d

Means on the same column with the same superscript are not significantly different ($p>0.05$)

the concentration of Fe at burnt areas of brick sites was significantly higher than concentrations of Fe at unburnt areas for five out of eight sampled LGAs. Asterisked p-values indicate a significant difference between burnt and unburnt areas, and are true for Buruku, Kwande, Makurdi, Ushongo and Vandeikya.

Manganese (Mn)

From table 1, the mean concentration of manganese (Mn) in soil samples from Gboko, Gwer West, Konshisha and Makurdi did not vary significantly from each other and were higher than the mean concentrations of Mn for soil samples from Kwande, Vandeikya and Ushongo. The concentration of Mn decreased with the increase in depth of soil excavation (Table 2). Thus, the concentrations of Mn for the various soil depths differed significantly from each other but depth range of 90-95cm was lowest.

The mean concentration of Mn in table 8 indicates that the burnt areas were significantly higher for Buruku compared with all other LGAs. The concentrations of Mn at burnt areas were significantly higher than those of unburnt areas. There were however no significant differences in the concentrations of Mn between burnt and unburnt areas of brick sites for Buruku, Gboko, Gwer- West, Kwande and Ushongo LGAs.

Zinc (Zn)

The mean concentration of zinc (Zn) ranged from 0.60 ± 0.05 ppm, to 2.81 ± 0.15 ppm respectively (Table 1). The mean concentrations of Zn for the entire study area generally decreased with the depth of soil excavation (Table 2), and so differed significantly from each other, but mean values at the excavation depth of 10-15cm were significantly higher than at other depths of soil excavation. The concentration of Zinc did not indicate

any significant difference at burnt and unburnt areas of brick sites for all surveyed LGAs (Table 3).

Correlation matrix of heavy metals at brick sites in the study area based on depth of soil excavation

The correlation matrix of the six heavy metals investigated, ie (cadmium [Cd], lead [Pb], chromium [Cr], zinc [Zn], and iron [Fe]) is presented in Table 9 below. The table highlights the degree of association (negative or positive) between the concentrations of the heavy metals between and within the soil excavation depth ranges of 10-15cm, 60-65cm and 90-95cm.

Within the soil depth range of 10-15cm, Pb was negatively and insignificantly correlated to Cd and Cr, while Pb was negatively and insignificantly correlated to Cr. Mn exhibited a negative and insignificant relationship with Cd, Pb and Cr. Zn correlated positively and significantly ($p=0.0200$) to Cd. Between the soil depth ranges of 10-15cm and 60-65cm, Cd was negatively and insignificantly correlated to Mn ($p>0.05$), however, Fe was positively but insignificantly correlated to Pb, Cr and Zn. Also, Pb was positively and significantly correlated ($p>0.05$) to Pb, but the correlation was insignificant for other heavy metals ($p>0.05$).

Between the soil depth ranges of 60-65cm, and 60-65cm, there was a negative and insignificant relationship between Pb and Cd. Also, Cr, Cd and Pb were positively but insignificantly correlated, ($P>0.05$). However, there were no significant correlations in the concentrations of all the heavy metals examined.

Between the soil excavation depth ranges of 90-95 and 10-15cm, Cd was positively and significantly ($P=0.00$) correlated to Cd and Zn, Also, Cr was positively and significantly correlated to Cr. There was however no significant correlations between other heavy metals at these soil depth ranges. Between the soil depth ranges of 90-95 and 60-65cm, Zn was positively and significantly correlated to Cd, ($p=0.049$). Zn was also positively and significantly correlated to Zn ($p=0.00$).

Table 9. Continue

Cr	0.228	0.217	0.589	0.180	0.321	-0.235	0.083	-	0.830	0.185	0.369	-	0.170	0.107	-			
	0.397	0.419	*	0.505	0.225	0.575	0.760	0.208	*	0.492	0.159	0.342	0.529	0.694				
Mn			0.016					0.440	0.000			0.408						
	-	-	-	0.931	0.020	-0.209	-0.237	-	0.157	0.917*	0.143	-	-0.426	-	0.223	-		
	0.233	0.161	0.074	*	0.942	0.619	0.376	0.264	0.561	0.000	0.596	0.190	0.100	0.310	0.408			
Zn	0.386	0.550	0.785	0.000				0.324				0.653		0.242				
	0.265	0.051	-	0.100	0.875	0.367	0.500	-	-	-0.015	0.901	-	0.053	-	0.180	0.141	-	
	0.322	0.852	0.242	0.713	*	0.372	*	0.357	0.030	0.956	*	0.135	0.844	0.125	0.504	0.603		
Fe			0.367	0.000			0.049	0.174	0.912		0.000	0.745		0.643				
	-	-	-	-	-	-0.351	-0.336	-	-	-0.291	-	-	-0.175	0.059	-	-	-0.221	-
	0.468	0.142	0.013	0.494	0.195	0.394	0.416	0.144	0.380	0.889	0.214	0.306	0.679	0.889	0.317	0.493	0.598	
	0.243	0.738	0.976	0.214	0.643			0.734	0.679		0.444	0.214		0.444	0.214			

* Indicates statistical difference at 0.05%; Cell Contents: Pearson correlation P-Value

DISCUSSION OF RESULTS

The depth of soil excavation was negatively correlated to the concentration of the studied heavy metals (Cr, Pb, Cd, Fe, Mn, and Zn). This could be attributed to decreases in the organic matter content of soils with increasing depth of soil excavation. Organic matter contains a lot of nutrients and other elements which are liberated following organic matter breakdown (Nwoboshi, 2000). Further, soil excavation may increase the surface area of top soil (0-30cm depth), thus correspondingly leading to more exposure of heavy metals within the nutrient-rich top soil depth.

Burning of woody biomass significantly increased the concentrations of the heavy metals chromium (Cr), lead (Pb), cadmium (Cd), iron (Fe), manganese (Mn), and zinc (Zn). Although Fe, Mn and Zn are heavy metals, they are vital in plants as micronutrients, but their soil concentrations above threshold levels can be detrimental to plant growth. The usefulness of Cr, Pb and Cd in plants is scantily documented. Increase in the concentrations of heavy metals occasioned by liberal production of wood ash rich

in heavy metal deposits when added to heavy metal exposures from soil excavation, may have serious deleterious effect on the terrestrial, aerial and aquatic environments. Aluminum (Al) concentration increased significantly within the 10-15cm depth after brick firing. A reduction in the amount of elements available in ash may result due to loss of ash which may occur as a result of both wind and water erosion. The nutrients in ash may be dissolved and readily leached into the mineral soil or lost during run-off several years after a high intensity burn (Brady and Weil, 1999), typical and recurring at burnt brick sites.

The most significant effect of burning on heavy metal capital is the change from organic state of these elements to the inorganic form as ash. Woody biomass ash contains heavy metals and other toxic substances that may cause harm to the environment and human health if indiscriminately released; the ash must be handled carefully to avoid releasing toxic pollutants that might otherwise have been containable (Ljung and Nordin 1997). Although biomass ash is often treated as a hazardous waste, such disposal fails to take advantage of the beneficial components of ash, such as valuable

nutrients. Because these nutrients are vital to long-term forest health, biomass ash holds promise as a soil supplement for harvested forests.

The concentrations of the heavy metals chromium (Cr), lead (Pb), cadmium (Cd), iron (Fe), manganese (Mn), and zinc (Zn), differed significantly between soil samples taken from burnt areas of brick sites and unburnt areas. The concentration was significantly higher in soil samples from burnt areas. Although Fe, Mn and Zn are heavy metals, they are vital in plants as micronutrients, but their soil concentrations above threshold levels can be detrimental to plant growth. The usefulness of Cr, Pb and Cd in plants is scantily documented. Increase in the concentrations of heavy metals occasioned by heavy metal-rich wood ash deposits from woody biomass combustion when added to heavy metal exposures from soil excavation, may have serious deleterious effects on the terrestrial, aerial and aquatic environments. Woody biomass ash produced after brick firing contains heavy metals and other toxic substances that may cause harm to the environment and human health if indiscriminately released. The ash must be hand-

led carefully to avoid releasing toxic pollutants that might otherwise have been contaminated (Ljung and Nordin 1997). Although biomass ash is often treated as a hazardous waste, such disposal fails to take advantage of the beneficial components of ash, such as valuable nutrients. Because these nutrients are vital to long-term flora health, biomass ash holds promise as a soil supplement for harvested forests. Soil mining also exposes metal ores bearing heavy metals. Environmental pollution by heavy metals is very prominent in mining areas and old mine sites, and pollution reduces with increasing distance away from mining sites (Peplow, 1999). Mining and dredging activities, poorly planned stockpiling and uncontrolled dumping of overburden, and chemical/fuel spills reduce water quality for downstream users, increasing cost for downstream water treatment plants and poisoning of aquatic life.

Unlike organic chemicals which are eventually broken down to simple non-toxic compounds, the addition of metals and other potentially toxic elements to soils leaves a residue which is permanent, unless leaching occurs. These chemicals are therefore potentially more damaging to crops, animals and man than are pesticides and herbicides (Rowell, 1994). The potentially toxic elements added to soils (as pollutants) can be divided into two groups (Rowell, 1994) as follows:

- i. Zinc, copper, nickel and boron which can have direct effects on plant growth if the concentrations are high enough.
- ii. Cadmium, lead, mercury, molybdenum, arsenic, selenium, chromium, iron, silver and fluorine which are not normally toxic, but may affect animals (and man) feeding on crops grown on contaminated land. Cadmium can be harmful to crops, but effects on animals occur at smaller concentrations.

Nwoboshi (2000) posits that "over 90 elements have been positively identified in plants... as the analytical methods become more sensitive, virtually every element in the root environment may appear as a plant constituent". Fuel wood burnt to cure bricks has the potential of leaving residues of some constituent elements on the soil that may eventually have immense ecological impacts on flora and fauna.

"Heavy metals" generally refer to the group of metals and metalloids each with an atomic density greater than 4g/cm^3 or with densities five times or more, greater than water (Hawkes, 1997). These metallic elements each have a relatively high density and are poisonous or toxic even at low concentrations (Lenntech, 2004). Cadmium exposures are associated with kidney and bone damage. Cadmium has also been identified as a potential human carcinogen, causing lung cancer (World Health Organisation, 2007).

Surface contamination by lead in air and soil is considered a great problem. Lead does not dissipate biodegrade or decay, therefore, lead pollution deposited into soil and dust remains a potential source of lead

exposure. Children below six years of age are more prone to health deficiencies caused by elevated levels of lead exposure; these health deficiencies include, *inter alia*, delayed puberty in girls, abnormal deliveries in women, low sperm count in men, lowered IQ, reading and learning disabilities in children, impaired hearing, reduced attention span and hyperactivity in children (Kantai, 2004).

Lead exposures have developmental and neuro-behavioural effects on fetuses, infants and children, and elevate blood pressure in adults. Although human body contains sufficiently large amounts of lead, moderately increased Pb concentrations become toxic from health point of view. The large affinity of Pb^{+2} for thiol (-SH) and phosphate-containing legands inhibits the biosynthesis of heme and thereby affects the membrane permeability of kidney, liver and brain cells. These result in either reduced functioning or a complete breakdown of these tissues since Pb is a cumulative poison. A British military unit stationed in Hong Kong, was overtaken by acute lead poisoning and suffered from severe vomiting intestinal cramps and circulatory disorder. The source was traced to lead chromate, which had been used to improve the colouration in curry powder. Analysis revealed a lead content of 1.08% (Duruibe, 2007).

The incubation period for chronic cadmium intoxication may vary considerably usually between 5-10 years, but in some cases up to 30 years. During the first phase of poisoning, a yellow discolouration of teeth, "cadmium ring" is formed, followed by loss of the sense of smell. The mouth becomes dry and gradually, the number of red blood cells is diminishes, resulting in impairment of bone marrow production..

Inhalation of dust containing Cr in high oxidation states (IV) and (VI) is associated with malignant growth in the respiratory tract and painless perforation in nasal septum among trivalent and hexavalent states being the most stable and common in terrestrial environments (Rai and Pal, 2002). Hexavalent chromium is the form considered to be the greatest threat because of its high solubility, its ability to penetrate cell membranes and its strong oxidizing ability. Hence, Cr (+6) is more toxic than Cr (+3) because of its high rate of absorption on living surface.

Lead and cadmium have also been found to have reproductive and endocrine system-disrupting effect. Aluminium has been found to cause Alzheimer's disease in human beings reported from several parts of the world (Rai, and Pal, 2002). Exposure to relatively low levels of these chemicals have been documented to have had catastrophic effect on populations of Beluga whales, alligators, turtles, mink, otters, bald eagles, osprey, cormorants, terns, herring gulls, migratory birds, chickens and lake trout etc. throughout the U.S. and Canada. Animals and human foetal development is dependent on hormonal levels at various phases of development and the endocrine, reproductive, neurological, and immune

systems are all being affected, often seriously or catastrophically. These chemicals are being found to have estrogenic effect and/or anti-androgenic effect on the hormonal/endocrine system.

Environmental pollution by heavy metals is very prominent in mining areas and old mine sites and pollution reduces with increasing distance away from mining sites (Peplow, 1999). Apart from removing nutrients and exposing ores of heavy metals, brick production also results in removal of large volumes of soil; thus soil removal for brick production is analogous to mining operations. These metals are leached out and carried along slopes by acid water downstream runoff into the sea. Through mining activities, water bodies are most emphatically polluted (INECAR, 2000). The potential for contamination is increased when mining exposes metal-bearing ores rather than natural exposure of ore bodies through erosion (Garbarino et al., 1995), and when mined ores are dumped on the earth surfaces in manual dressing processes. Through rivers and streams, the metals are transported as either dissolved species in water or as an integral part of suspended sediments, (dissolved species in water have the greatest potential of causing the most deleterious effects). They may then be stored in river bed sediments or seep into the underground water there by contaminating water from underground sources, particularly wells. The extent of contamination will depend on the nearness of the well to the mining site. Wells located near mining sites have been reported to contain toxic heavy metals at levels that exceed drinking water criteria (Peplow, 1999).

Chromium is a naturally occurring heavy metal that is commonly used in industrial processes and can cause severe health effects in humans. Although it can be released through natural forces, the majority of the environmental releases of chromium are from industrial sources. Chromium released through brick-producing activities can exist in air, water, soil, and food, and common exposure pathways include ingestion, inhalation, or dermal contact. Chromium is commonly found in two forms: trivalent chromium (chromium III) and hexavalent chromium (chromium VI). Chromium III is the most stable form of the element, and occurs naturally in animals, plants, rocks, and soils. Chromium VI rarely occurs in nature, and is usually the product of anthropogenic activities.

The health effects of chromium depend on the route of exposure and the form of the chromium. For example, inhaling chromium can cause damage to the respiratory system, whereas dermal or oral exposures generally do not. Gastrointestinal effects are generally associated with oral exposure, but not with dermal exposure. In addition, chromium VI typically causes greater health risks than chromium III. The reasons for the increased danger of chromium VI versus chromium III are complex, and relate in part to the varied paths of cellular uptake between the two forms.

The primary health impacts from chromium are damage to the gastrointestinal, respiratory, and immunological systems, as well as reproductive and developmental problems. Chromium VI is a known human carcinogen, and depending on the exposure route, can increase the rate of various types of cancers. Occupational exposure to chromium VI, which often occurs through inhalation, has been linked to increased rates of cancer in the respiratory system

CONCLUSION

Burning of bricks using diverse fuel wood tree species significantly increases the concentration of the heavy metals chromium (Cr), lead (Pb), cadmium (Cd), iron (Fe), manganese (Mn), and zinc (Zn). Unburnt soils had significantly lower concentrations of heavy metals compared to ash-rich burnt soil samples. These heavy metals were also present in all the unburnt soil samples taken at varying depths of soil excavation. The soil excavation depth of 10-15 cm had a significantly higher concentration of heavy metals while the soil excavation depth of 90-95cm had the lowest concentration of heavy metals, implying that the top soil (10- 15 cm) has a higher concentration of heavy metals. The exposure of a large surface area of top soil at burnt bricks sites in conjunction with firing of bricks with fuel wood compounds heavy metal pollution problems at brick sites, and these have serious environmental (social, economic and physical) implications.

RECOMMENDATIONS

Based on the result and implications of these findings, this study therefore recommends the followings:

- i. Land-use planning involving all stakeholders in the burnt brick industry is necessary to confine burnt bricks industries to areas where their heavy metal pollution potential on surface and ground water, agricultural and grazing land can be controlled.
- ii. There is need to sensitise brick producers on the need for health safety precautions while they are at work
- iii. Afforestation of burnt brick sites can reduce the concentration of heavy metals since trees absorb some of these heavy metals and immobilise them in tree biomass.
- iv. Greener sources of energy (solar, hydro- and wind) can replace fuel wood use at brick production, and
- v. Bricks production technologies requiring less heating can be adopted to reduce over-dependence on fuel wood.

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