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Sequential Extraction of Lead, Copper, Zinc, Cadmium and Chromium in Soil Samples from Dumpsites in Lafia, Nasarawa State Nigeria

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Abstract
Sequential extraction of lead, copper, zinc, cadmium and chromium in soil from Jos road and Emir Palace dumpsites were carried out using Tessier et al (1979) method. The values for these metals varied from 0.02-2.68, 0.01-2.58, 0.03-2.31, 0.18-1.40 and 0.03-0.65mgkg^{-1} for exchangeable, Fe-Mn oxide, organic, carbonate and residual fraction respectively for Jos road dumpsite and 0.13-9.25, 0.34-3.20, 0.31-25.40, 0.85-27.80 and 0.20-4.52 mgkg^{-1} for exchangeable, Fe-Mn oxide, organic, carbonate and residual fraction respectively for Emir Palace dumpsite. For water analysis the values of conductivity varied from 1215-1320uscm^{-1}, TDS from 825-902ppm, lead 0.03-0.04ppm aluminium 0.63-0.82ppm and magnesium 3.88-5.47ppm were above Standard organization of Nigeria requirement for drinking water. Hence dumpsites pollute soil and water.
Keywords:Heavy metal, dumpsite, sequential and extraction.

1.0 INTRODUCTION

Concern over the possible effects of the increasing accumulation of metallic contaminants in the environment is growing (Yahaya et al, 2009). For this reason the investigation of heavy metals in soils is essential since even slight changes in their concentration above the acceptable levels whether due to natural or anthropogenic factors can result in serious environmental and subsequent health problems. (Fangueiro et al, 2002, Saudroni and Smith 2002, Cobelo-Garcia et al 2004).

The occurrence of heavy metals in soil can be of geogenic or natural and anthropogenic origins. The anthropogenic sources include mining, smelting, fusil fuel combustion and various industrial activities (Adekola et al, 2012). Industrial activities are the major source of soil heavy metals contamination (Chandia et al, 2005, Chen et al, 2005, Fayun et al, 2008, Olajire, 2003).

The situation of heavy metal pollution is more worrisome in the developing countries where research efforts towards monitoring the environment have not been given the desired attention by the stakeholder (Yahaya et al, 2009).

The use of dumpsites as a farmland is common practice in urban and sub-urban centers in Nigeria because of the decayed and composted wastes enhances soil fertility (Ogunyemi et al 2003). When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissue (Trueby, 2013). Animals that graze on such contaminated plants and drink from polluted waters as well as marine lives that breed in heavy metal polluted waters also accumulates such metals in their tissue and milk (Garbarino et al, 1995).

Municipal waste contains such heavy metals as Pb, Co, Hg, Mn, As, F and so on which end up in the soil as the sink when the leached out from the dumpsites. Contamination of the environment by heavy metals is viewed as an international problem because of the effects on ecosystem in most countries.

In Nigeria the situation is no better by the activities of most industries and populace towards waste disposal and management which usually lead to increasing levels of population of the environments. Many studies have shown municipal refuse may increase heavy metal contamination in soil and underground water (Okoronkwo et al 2005, Okoronkwo et al, 2006) which may have effects on the host soils, crops and human health (Smith et al, 1996). Thus the environmental impacts of municipal refuse are greatly influenced by their heavy metal contents. However, while total heavy metal contents is a critical measures in assessing risk of refuse dumpsite, total metal content alone does not provide predictive insight on mobility and fate of the heavy metal contaminants (Uba et al, 2008), Thus it is the chemical or species of the heavy metal that is an important factor in assessing their impacts on the environment. This is because it is the chemical form of the heavy metal that controls its mobility (Norvell, 1984).

Heavy metals are reported to remain in soils even after their addition to soils have been stopped. (Lee et al, 2001, Raw et al, 2008).

1.2 DUMPSITE:

Dumpsite is where waste materials are disposed and is the oldest form of waste treatment (Abdul-salam et al, 2011). Historically, dumpsites have been the most method of un-organized waste disposal and remain so in many places around the world. Most dumpsites are located within the vicinity of living communities and wetland (Ibrahim, E.G, 2013).

The dumpsites are not lived or basement prepared for selective adsorption or toxic substances. Therefore it is prone to the release of pollutants to nearby water and to the air through leachates and dumpsites gases respectively.

Industrialization, population growth and unplanned urbanization have partially or totally turned our environment to dumping for waste materials (Alimba et al, 2006). Poor regional and urban planning, lack of enforcement of relevant laws and edicts on waste disposal, lack of organized land fill sites contribute to the presence of dumpsites within living areas in developing nations. This result in the discharge of household swage and refuse into the environment untreated. The surface run-off and leachates from dumpsites are sources of fresh water contamination.

The general belief that wastes are sometimes hazardous to health cannot be over-emphasized. Hazardous waste can cause and has caused pollution, damaged to health and even death. Exposure to multiple chemical combinations in population living near waste dumpsites has lead to series of human health disorder (Palmer et al, 2005).

In Nigeria it is general believed that individual, government and environmental agencies pay little or no attention to the environmental impacts of the waste disposal and management even when it is a statutory responsibility of the parties concerned (Abdul-salam et al, 2011).

Agencies like the Federal Environmental Protection Agency (FEPA), Ministry of Environment and even the local authorities are responsible for planning a defined line of action for disposal and management of waste generated in daily basis in our society. Determining of the potency of the waste and some pollutants effects on soil through soil analysis will go a long way to provide information needs for the development of techniques for tackling the problem of soil pollutants and the effects of solid wastes in the environment. Poor management of dumpsites could create a number of adverse environmental impacts including wind-blow litter, attraction of mice and pollutants such as leachates which can pollute underground soil bed and aquiver (Abdul-salam, 2009).

The disposal of domestic, commercial and industrial garbage is a world-wide problem that a continues to grow with human and no method so far is completely safe. All forms of waste disposal have negative consequences on the environment, public health and local economics. (Adekola et al 2010).

Haven seen this the objective of this study, therefore was to investigate the chemical fractionation of Cd, Cr, Pb, Cu and Zn. Heavy metal in some refuse dumpsites in lafia and determines their mobility and fate in order to assess the human health and ecological risks associated with the refuse dumpsites.

2.0 SAMPLING AND SAMPLE TREATMENT

2.1 **STUDY AREA:** Lafia is the state capital of Nasarawa State as indicated in Fig 1, lies between latitude $8^{o}\,30^{1}\,21^{1}$N and longitude $8^{o}\,30^{1}\,20^{1}$ E and Nasarawa State is located centrally in the middle belt region and lies between latitude 7^{0} and $9^{0}\,37^{1}$E of the Greenwich meridian: it shares boundary with Kaduna state in the North, Plateau state in the east, Taraba and Benue State in the South, which Kogi and Federal Capital Territory flank in the waste (Ibrahim et al 2013).

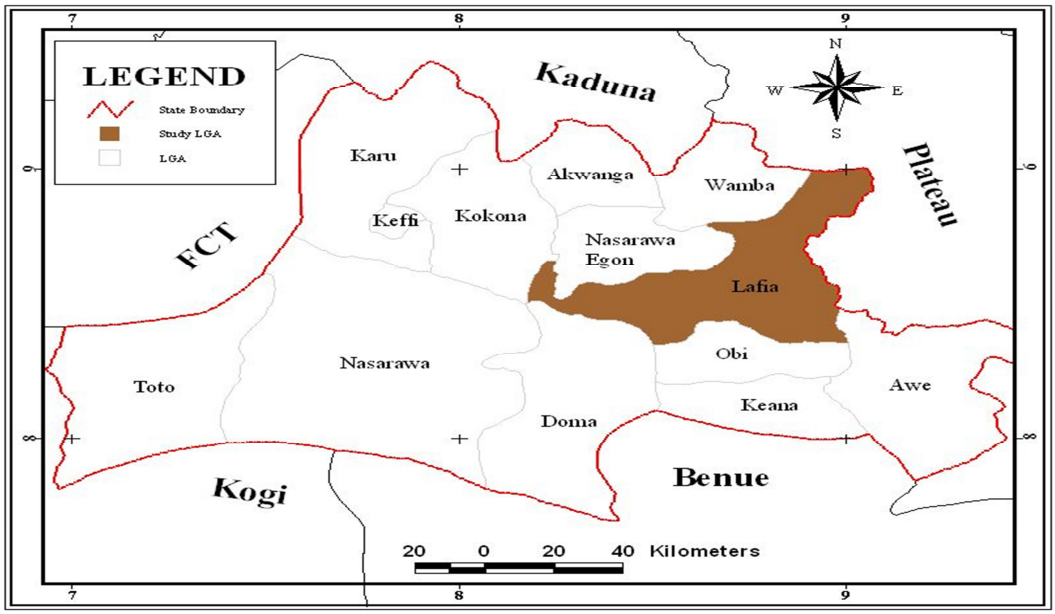

Fig.1showing the study area.

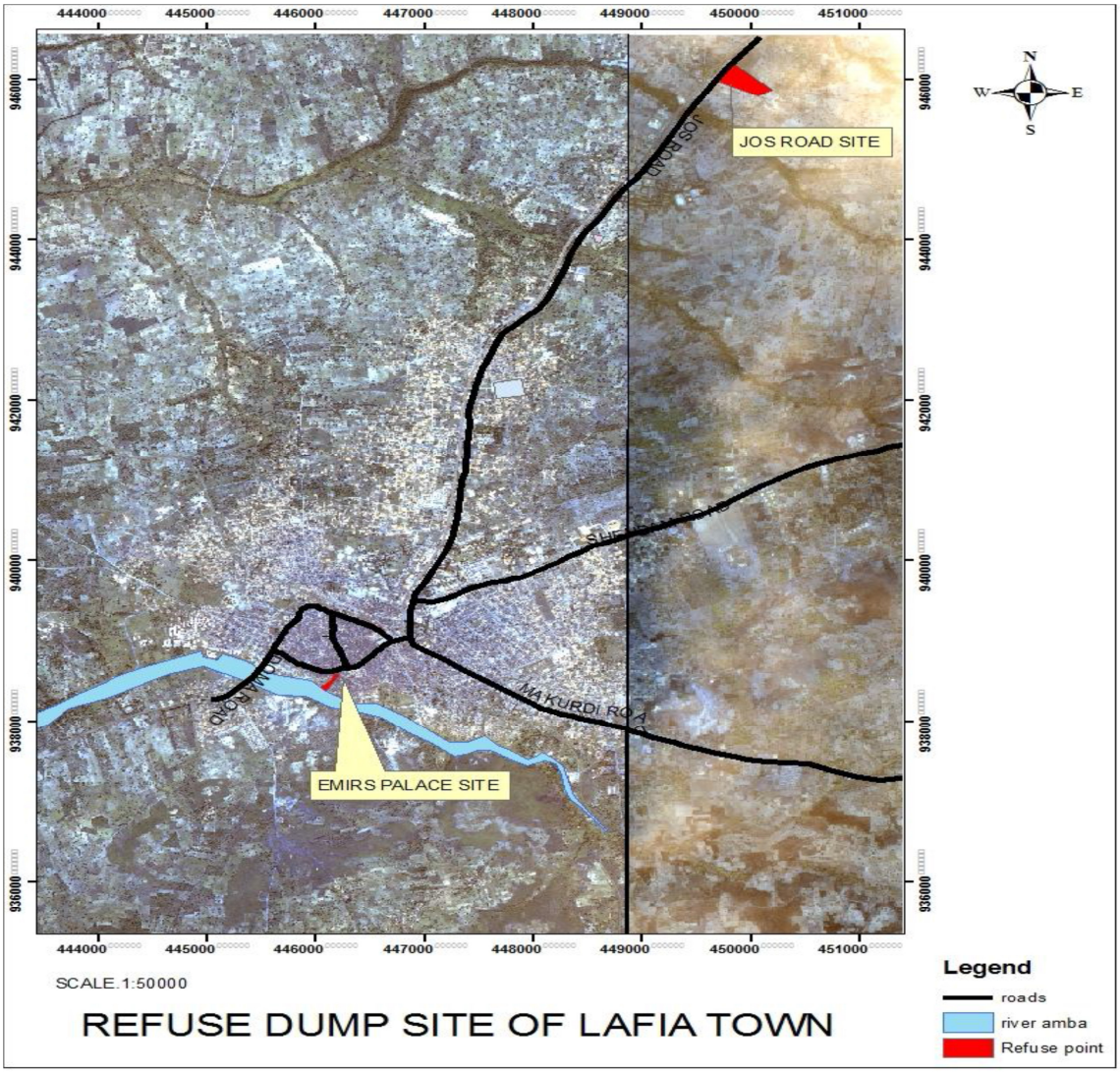

Fig. 2: Topography of the study area showing the two dumpsites

2.2 SAMPLING AND TREATMENT

Soil samples were taken between 0-15un in four different locations of the two dumpsites shown in fig 2. into a pre-washed cleaned polyethylene bags between the month of September and October, these dumpsite are Jos Road dumpsite and Emir Palace dumpsite. Each of the samples from each dumpsite were mixed to obtained a composite sample of two and these two were transported to the laboratory and air dried at room temperature for two weeks, after which it was grinded using mortar and pestle, the grinded samples was sieved using 0.2 mm sieve size and bottled in a polyethylene bottle at room temperature before extraction. Water sample was also collected in three different points in the river located closed to Emir Palace dumpsite as indicated in fig. 2. into a cleaned polyethylene bottle, the PH, conductivity and TDS were determined insitu using Hanna digital PH meter and sprite conductivity meter. While the elemental analysis was carried out in the laboratory using standard methods (APHA 1995).

Fig. 3 Emir Palace dumpsite

Fig. 4 Jos road dumpsite

3 METHODOLOGY

3.1 SOIL ANALYSIS

a. Total metal analysis: Digital weighing balance was used to weighed 1.00g of the sieved dried soil from each of the two dumpsites in triplicate and was digested with a mixture of 15ml HCl and 25ml HNO_3 for 2hrs at 100^0c and allowed to cool, this was then filtered and the filtrate was made up to 50ml and analyzed with AAS model 7000 series east and west analytical instrument and reported in $MgKg^{-)}$

b. Speciation: Tessier et al (1979) method was used for the speciation of metal in the five extractions except the residual fraction which Maina et al (2012) method was used.

i. Exchangeable fraction: 1.00g derived sieved soil sample from the two dumpsite was shaken with 20ml of 1m$Mgcl_2$ at PH 7 in a stoppered polyethylene bottle for one hour on a junior orbit mechanical shaker at room temperature. The mixture was filtered and the filtrate was analyzed.

ii. Carbonate fraction: the residue from fraction 1 was shaken with 20ml 1MCH_3COONa in a stoppered polyethylene bottle at room temperature for five hours; the pH was adjusted with CH_3COOH to pH 5, before shaking. The mixture was filtered and the filtrate analyzed.

iii. Fe-Mn oxide fraction: residue from fraction 2 was digested with a mixture of 10ml 0.04M $NH_2OH.HCl$ and 10ml of 25% CH_3COOH at 96^oC for 6hrs. The mixture was filtered and the filtrate analyzed.

iv. Organic fraction: the residue from fraction 3 was transferred into 250ml beaker (Pyrex) and 9ml of 0.02MHNO_3 and 15ml of H_2O_2 were added. The mixture was heated to 85^oc on a water bath for 5hrs. After two hours heating another 15ml of 30% H_2O_2 was added. The mixture was allowed to cooled and filtered, the filtrate was analyzed.

v. Residue fraction: the residue from fraction 4 was digested with aqua regia (i.e. 7.5ml of 37% HCl and 2.5ml of 65% HNO_3) and heated to 85^0c for 1 hour (Maina et al 2012) on a heating mantle inside a fume cupboard. The mixture was filtered and the filtrate was analyzed.

4 Results: the results o the analysis of water and soil samples from the two dumpsite is shown below

Table 1: Physiochemical analysis of water

Parameter	Point A	Point B	Point C
pH at 25^oC	7.30	7.60	7.80
Conductivity $uscm^{-1}$	1215	1315	1320
TDS (ppm)	825	899	902
Ca (ppm)	12.07	14.60	16.81
Na (ppm)	8.14	7.86	8.10
K (ppm)	2.79	3.74	5.55
As (ppm)	0.08	0.07	0.07
Mg (ppm)	3.88	4.27	5.47
Zn (ppm)	0.09	0.10	0.15
Fe (ppm)	1.88	2.59	3.18
Pb (ppm)	0.03	0.04	0.04
Cd (ppm)	ND	ND	ND
Al (ppm)	0.63	0.70	0.82

Note. Point A= upstream, point B= entrance point and point c= downstream

Table 2. Total metal concentration (mgk^{-1})

Sample	Pb	Cu	Zn	Cd	Cr
Dumpsite A	6.31±0.20	5.07±0.10	5.95±0.30	5.25±0.10	5.37±0.2
Dumpsite B	5.70±0.3	5.21±0.2	8.85±0.40	ND	5.40±0.3

Note: Dumpsite A= Jos road dumpsite
Dumpsite B= Emir Palace dumpsite

Table 3: Concentration ($mgkg^{-1}$) of sequential fractionation of metals in dumpsite A

Fraction	Pb	Cu	Zn	Cd	Cr
Exchangeable	2.68±0.10	0.05±0.01	1.38±0.07	0.02±0.01	0.25±0.01
Fe-Mn Oxide	2.24±0.2	0.42±0.02	2.58±0.02	0.01±0.001	0.70±0.01
Organic	2.31±0.20	0.25±0.01	3.10±0.30	0.03±0.01	0.35±0.02
Carbonate	1.40±0.02	0.35±0.10	0.52±0.20	1.20±0.02	0.18±0.01
Residual	0.45±0.10	0.03±0.01	0.26±0.02	0.65±0.10	0.24±0.02

Table 4: Percentage fractionation of metals in dumpsite A

Fraction	Pb	Cu	Zn	Cd	Cr
Exchangeable	29.50	4.50	17.60	1.04	14.53
Fe-Mn Oxide	24.70	38.20	32.90	0.52	40.70
Organic	25.40	22.70	39.50	1.57	20.35
Carbonate	15.40	31.80	6.60	62.83	10.47
Residual	5.00	2.70	3.30	34.03	13.95

Table 5: Concentration ($mgkg^{-1}$) of sequential fractionation of metals in dumpsite B

Fraction	Pb	Cu	Zn	Cd	Cr
Exchangeable	2.18±0.01	0.13±0.01	9.25±1.00	0.80±0.10	0.74±0.20
Fe-Mn Oxide	1.82±0.10	1.42±0.20	3.20±0.50	0.34±0.01	0.85±0.20
Organic	1.45±0.10	0.85±0.20	25.40±2.0	0.31±0.10	1.41±0.20
Carbonate	19.67±2.50	10.32±2.50	27.80±3.50	0.85±0.20	1.82±0.30
Residual	4.52±1.0	0.30±0.10	2.15±0.30	0.20±0.01	0.75±0.20

Table 6: Percentage fractionation of metals in dumpsite B.

Fraction	Pb	Cu	Zn	Cd	Cr
Exchangeable	7.35	1.00	13.64	32.00	13.29
Fe-Mn Oxide	6.14	10.93	4.72	13.60	15.26
Organic	4.89	6.31	37.46	12.40	25.31
Carbonate	66.36	79.45	41.00	34.00	32.68
Residual	15.25	2.31	3.17	8.00	13.46

4.1 DISCUSSION OF RESULT

The result of physiochemical analysis of water from Emir palace dumpsites river (Amba) is shown in table 1, the pH varied from 7.30-7.80, the conductivity varied from 1215 – 1320 $uscm^{-1}$ and TDS is from 825-902ppm, the pH of the water is within WHO standard for drinking water PH (6.5-8.5) but the conductivity is higher than the WHO standard (1000 $Uscm^{-1}$) for drinking water. This is as a result of presence of ions which increases the conductivity of the water and hence increases the TDS from 825 – 902 ppm above the regulatory standards of WHO, SON and NAFDAC (500ppm) for drinking water. All other parameters analyzed in the water are within the WHO, NAFDAC and SON standard exception of lead, iron, aluminium and magnesium which is a little higher than the maximum allowable limit for drinking water, (0.03 – 0.04ppm, 1.88 – 3.18ppm, 0.63 – 0.82ppm and 3.88-5.47ppm) as against (0.01, 0.3, 0.5 and 2ppm) Cadmium was not detected probably the concentration is below the detection limit of the instrument. It can also be seen that the concentration of these parameter studied increases down the dumpsite (i.e. from upstream to downstream), this may be due to run-off from this dumpsite which lead to translocation of these metals ion in the river.

The result of the concentration of total metals is shown in Table 2. The dumpsite A (Jos road dumpsite) has the highest content of Pb ($6.31mgkg^{-1}$), this may be attributed to exhaust from vehicles since the dumpsite is located along the road, as this is in agreement with the work of other researchers (Joshi et al, 2010). The order of total metal concentration in Jos road dumpsite is PH>Zn>Cr >Cd>Cu_1 but for Emir palace dumpsite zinc has the highest concentration ($8.85mgkg^{-1}$) probably because of a specific waste material that is rich in zinc, and it followed this order Zn>Pb>Cr>Cu and Cadmium was not detected because the concentration is below the instrument detection limit.

4.2 SPECIATION

Table 3 shown the result of sequential fractionation of metals from Jos road dumpsite, the exchangeable fraction has the highest concentration of lead ($2.68mgkg^{-1}$) with a percentage of 29.5% as indicated in Table 3. This agreed with the work of other researchers (Godwin et al, 2012, Joshi et al, 2010). This concentration of metals such as lead, copper, zinc and ion increases due to exhaust from motor vehicles. The concentration of these

metals increases in the order Pb>Zn>Cr>Cu>Cd. In Emir Palace dumpsite zinc has the highest value of 9.25mgkg^{-1} followed by lead and the order is Zn>Pb>Cd>Cr>Cu. From the results it can be seen that lead is commonly associated with the exchangeable as reported by other's work (UBA et al, 2008). The high result of zinc in both dumpsites could be as a result of discharge of waste from the city which agreed with the work of others (costal et al, 1991)

The highest concentration of Zinc is associated to carbonate fraction in the Emir Palace dumpsite with the value of 27.80mgkg^{-1} followed by the organic fraction in the same dumpsite with the value of 25.40mgkg^{-1}, generally Zinc shown appreciable value in the Emir Palace dumpsite, this could be as a result of Waste containing zinc materials are deposited in this dumpsite.

Lead has a higher value in the carbonate fraction in the Emir Palace dumpsite (19.67mgkg^{-1}) copper has the highest value (10.32mgkg^{-1} in the carbonate fraction in the Emir palace dumpsite and has the least value in the residual fraction of the Jos road dumpsite (0.03mgkg^{-1}).

In both dumpsite studied cadmium and chromium has the lowest concentration, this may be as a result of low industrialization in lafia which mean most of the waste that contain higher percentage of cadmium and chromium are absence in this dumpsite.

Cadmium is associated with the carbonate fraction in both dumpsite studied, this agreed with the work of others (Yusuf, K.A, 2007).

5 SUMMARY AND CONCLUSION

The primary objective of this study was to determine the chemical availability of metals in water and soil from the dumpsites in lafia, nasarawa state. The total metal concentration of Pb, Cu, Zn, Cd and Cr were determined. For the water analysis some of the parameters (Pb, Fe, Al, EC and TDS) were above the WHO standard. From the dumpsites studied all the metals investigated were available and varied from the different dumpsite location simply because of the different in nature of the waste as it could be se in the dumpsite picture above.

ABBREVIATION, NOTATION AND SYMBOLIC

WHO	-	World health Organisation
SON	-	Standard Organisation of Nigeria
NAFDAC	-	National Agency for Food Drug Administration and Control.
TDS	-	Total Dissolved Solids
EC	-	Electrical Conductivity

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