Investigation of Heavy metals Concentration at Some Undesignated Dumpsites within Akungb Akoko,Ondo State, Nigeria

Ebenezer O. Oniya

Abstract— The concentration of heavy metals was studied in soil samples collected from eight (8) undesignated waste dumpsites in Akoko region of Ondo State, southwestern Nigeria with corresponding control samples. The concentrations of heavy metals, lead (Pb), iron (Fe), zinc (Zn), copper (Cu), cobalt (Co), manganese (Mn), nickel (Ni) and chromium (Cr) in the soil samples were determined using Atomic Absorption Spectrometry (AAS). In all the analyzed soil samples, the results reveal that the concentration of Fe, an essential heavy metal was found to be very high while Pb and Co were not detected in all the samples. Over all, the concentration level of the heavy metals were found in decreasing order as Fe>Mn>Ni>Cr>Zn>Cu. The level of pollution and contamination was assessed by estimating Pollution Load Index (PLI), Enrichment factor (EF) and geoaccumulation factor (*Igeo*). The act of uncontrolled refuse dumping has been established to contribute significantly to the heavy metal contaminations in majority of the sites with Fe taking the lead. Therefore, the indiscriminate dumping of refuse at undesignated dumpsites needs be addressed and discouraged. Pollution of soil at the sites was observed to be generally moderate as at the time of the study.

Index Terms— Heavy metals, concentration, undesignated dumpsites, enrichment factor (EF), contamination factor (CF), pollution load index (PLI) Southwestern Nigeria,

1 Introduction

THE presence of heavy metals in the environment beyond acceptable limits calls for concern because of the harmful and damaging effects of toxic metals on humans, animals and plants. Waste dumpsites are of particular importance in this regard as controlled and uncontrolled wastes contribute to the toxicity of the soils directly associated with the dumpsites. The soils become enriched after the bioaccumulation of metallic elements in the soil as several physico-chemical factors condition the transfer of each heavy metal from the solid to the liquid soil phase, causing differences in the availability and, finally, the toxicity of elements such as lead (Pb), iron (Fe), zinc (Zn), copper (Cu), cobalt (Co), manganese (Mn), nickel (Ni), molybdenum (Mo), cadmium (Cd) and chromium (Cr) among others [1]. Often times, the burning of theses wastes in a bid to get rid of organic materials leads to oxidation of metals and hence leaving the ash rich in metal content. Plants take up these metals by absorbing them in soluble form from contaminated soils as well as from deposits on different parts of the plants exposed to the air from polluted environment. Other implications may arise as a result of leaching which leads some of these heavy migrating to groundwater aquifer [2].

Concentrations of heavy metals in soil around dumpsites are influenced by types of wastes, topography, run-off and level of scavenging [3], [4]. Some of these metals such as Mn, Cu, Zn, Mo and Ni, are essential or beneficial micronutrients for microorganisms, plants and animals. Their absence may cause deficiency diseases but at high concentrations all have strong toxic effects and pose environmental threat [5].The heavy metals that most commonly cause problems in human are lead, mercury, cadmium, arsenic, nickel and aluminum. These metals tend to accumulate in the brain, kidneys and immune system where they can severely disrupt normal function [6], [7]. Excessive content of metals beyond Maximum Permissible level (MPL) leads to number of nervous, cardiovascular, renal, neurological impairment as well as bone diseases and several other health disorders [8], [9], [10].

Many cities in Nigeria have developed without proper planning and it has led to the presence of undesignated open dumps within built-up areas inhabited by thousands of people. The use of dumpsites as farm land is also a common practice in urban and sub-urban centers in Nigeria because of the fact that decayed and composted wastes enhance soil fertility. These wastes often contain heavy metals in various forms and at different contamination levels. Consequently, such waste dumps become point source for soil pollution as they serve as host for leachate from dumpsites. Heavy metal assessment of soils may therefore be an important parameter for evaluating risk posed to the environment by refuse dumpsites.

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2 Material and Methods

2.1 Study Location

This investigation was carried out in eight (8) dumpsites in four towns within Akoko region, located in the northern geographical district of Ondo State, southwestern Nigeria. The towns are Akungba-Akoko, Oka-Akoko, Epinmi-Akoko and Oka-Akoko. The Akoko area lies within longitude 5°31′ E to 6°06′ E and latitude 7°18′ to 7°45′ N andis underlain by rock of

- *Dr. E.O. Oniya is an Assistant Professor in the Physics and Electronics Department and the current Sub-Dean of Faculty of Science, Adekunle Ajasin University Akungba Akoko, Nigeria. E-mail: ebenezer.oniya@aaua.edu.ng*

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the precambrian basement complex of the south-western Nigeria [11]. The major lithological units include the granite gneiss. The rocks from icebergs, an isolated or residual hill and continuous ridges. The area exhibits varieties of structural settings such as foliation, fold, faults, joints and fracture. The foliation trends of the area are NNW-SSE. The lineament of the rock in the area is E-W [11]. Akoko experiences annual rainfall with a mean of 1333.2m, the vegetation is green, the outer crops of the solid rock are granite gneiss hills and low lying bounded gneiss are common in some part of the area. However in some part of the basement rocks are concealed. The area is drained by the Ose River and their tributaries and the drainage pattern is dendrite. The dumpsites range from 10 to 20 ft in height and 0.8-1 acre in width with an average lifetime of more than 10 years. The dumpsites are more or less abandoned landfills within and in the outskirts of town.

2.2 Sample Collection

Eight (8) samples (two each) were collected from four (4) different dump waste sites alongside their control samples. About 1 kg each of composite soil samples at a depth of 0 - 15cm from the soil surface were collected with the aid of a shovel. The control samples were taken 50 meters away from the dumpsites. These samples were kept in a clean airtight polythene bag immediately after collection and transported to the laboratory for further analysis using atomic absorption spectrometer.

2.3 Sample Analysis

One gram powdered dry samples were weighed into digestion flask; 3mL of 35% H2O was added to the samples and allowed to react overnight. The following morning the digested flask were placed into a digestion block and carefully heated at 4500C until clear solutions were obtained. Care was taken to ensure that the samples did not dry. A mixture of 3mL of 65% HNO_3 and 9mL of 37% HCl was added and gently heated until a small volume of acid remained. The residue was filtered and the solutions were precisely transferred to 100mL Pyrex standard flasks and made to volume with distilled de-ionized water. Various element concentrations were analyzed with an Atomic Absorption Spectrophotometer manufactured by Buck Scientific model 210 VGP.

3 Result and Discussion

3.1 Heavy Metal Dection

Tables 1. shows the Elemental Composition Analysis of the dumpsites and control soils taken 50 metres away. The sites in Oka-Akoko have been coded A1 and A2, those of Supare-Akoko B1 and B2, Epinmi-Akoko C1 and C2 and Akungba-Akoko D1 and D2.

The distribution pattern of heavy metals in the soiled samples is also shown in Figure 1. Across all the sampling locations, Fe showed the highest concentration across all sampled sites with its highest being 47250 mg/kg in site B2 in Supare. Its mean concentration is highest in the same community with a value of 35525 mg/kg. Soils in Nigeria have been known to be rich in Fe [12]. Cu registered the lowest concentration of 1 mg/kg on site D2 in Akungba.

The lowest mean concentration was recorded by Ni within the same community. Pb and Co were below detection limit in all dumpsite and control soils of all dumpsites which is a likely indication that less industrial and hazardous wastes were dumped in the sites. Zn, Mn, Ni and Cr showed their highest mean concentrations (281, 432, 874, 368 mg/kg) respectively at Epinmi while Fe and Cu showed their highest mean concentraions at Supare (35525 and 97 mg/kg respectively). In nearly all cases, there are sharp differences between the conscentration of the heavy metals at the control and dumpsite soil values in most of the sites with those at the dumpsite taking the lead (Figure 1). This is with an exemption of Oka 1 for Zn, the two Supare sites for Cu and Oka 2 for Cr. These observations are indications that these metal have contributed significantly to the enrichment of the heavy metals in the dumpsite soils. The plants growing on and around the dumpsite at Oka sites are suspected to have taken up large amounts of Cu leading to lower values in the soil.

In table 2, the mean concentration of detected heavy metals based on the communities from which the samples were collected is shown.

3.2 Polution Indices

In this study, the enrichment factor (EF), contamination factor (CF) and pollution load index (PLI) was applied to assess heavy metal contamination in soils at the dumpsites.

3.2.1 Polution Load Indices (PLI)

According to Tomlinson's method [13], the PLI was estimated from the contamination factor (CF) using equations (1) and (2) below

$$CF = \frac{C_{sample}}{C_{background}} \quad (1)$$

$$PLI = [CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n]^{\frac{1}{n}} \quad (2)$$

where C_{sample} is the mean metal concentrate on in polluted soils

$C_{background}$ is the mean natural background value of that metal

n = number of metals = 6

The control samples were taken to represent natural background.

The PLI represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. [14]. It is able to give an estimate the metal contamination status and the necessary action that should be taken [15].

TABLE 1

Research sites and their metallic composition and concentration

Location	Samples	Elements (mg/kg)							
		Pb	Fe	Zn	Cu	Co	Mn	Ni	Cr

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Oka	**Site A1**	BDL*	27650	144	10	BDL	669	53	305
	Control A1	BDL	19900	254	13	BDL	325	43	167
	Site A2	BDL	27250	34	BDL	BDL	87	38	191
	Control A2	BDL	12950	21	BDL	BDL	99	45	210
Supare	**Site B1**	BDL	23800	92	144	BDL	151	7	153
	Control B1	BDL	13250	76	380	BDL	119	7	108
	Site B2	BDL	47250	186	50	BDL	237	14	119
	Control B2	BDL	13350	136	660	BDL	184	14	117
Epinmi	**Site C**	BDL	16750	244	73	BDL	156	933	389
	Control C1	BDL	5150	21	20	BDL	71	824	318
	Site C2	BDL	27650	318	37	BDL	707	815	347
	Control C2	BDL	27200	261	30	BDL	176	749	337
Akungba	**Site D1**	BDL	11200	258	6	BDL	138	6	29
	Control D1	BDL	4300	19	1	BDL	58	2	17
	Site D2	BDL	5100	72	4	BDL	119	5	28
	Control D2	BDL	5050	29	BDL	BDL	101	6	26

*BDL- Below detection limit

Table 2 Mean concentration (mg/kg) of detected heavy metals by location.

Element	Oka (A1 and A2)		Supare (B1 and B2)		Epinmi (C1 and C2)		Akungba (D1 and D2)	
	Mean	Control	Mean	Control	Mean	Control	Mean	Control
Fe	27450	16425	35525	13300	22200	16175	8150	4675
Zn	89	138	139	106	281	141	165	24
Cu	5	7	97	520	55	25	5	1
Mn	378	185	194	152	432	124	129	80
Ni	46	123	11	11	874	787	6	4
Cr	248	96	136	113	368	328	29	22

Table 4 shows the contamination factor and pollution load index. The CF ranged from 0.57 to a highest value of 13.38 both occurring with Zn.The contamination factor of most of the metals are below 6 (CF<6) showing low, moderate and considerable contamination. A few cases however have CFs ≥ 6; Zn in sites C1 and D1 indicating contamination. All the PLIs estimated except for that of site B2 (0.89) are all >1 showing that soils around the dumpsites have been polluted.

3.2.1 Enrichment factor (EF) and geo-accumulation index (Igeo)

The extent to which the soils have been contaminated was assessed using the two indices; enrichment factor (EF) and geo-accumulation index (I_{geo}). The two indices help with a better estimation of anthropogenic input

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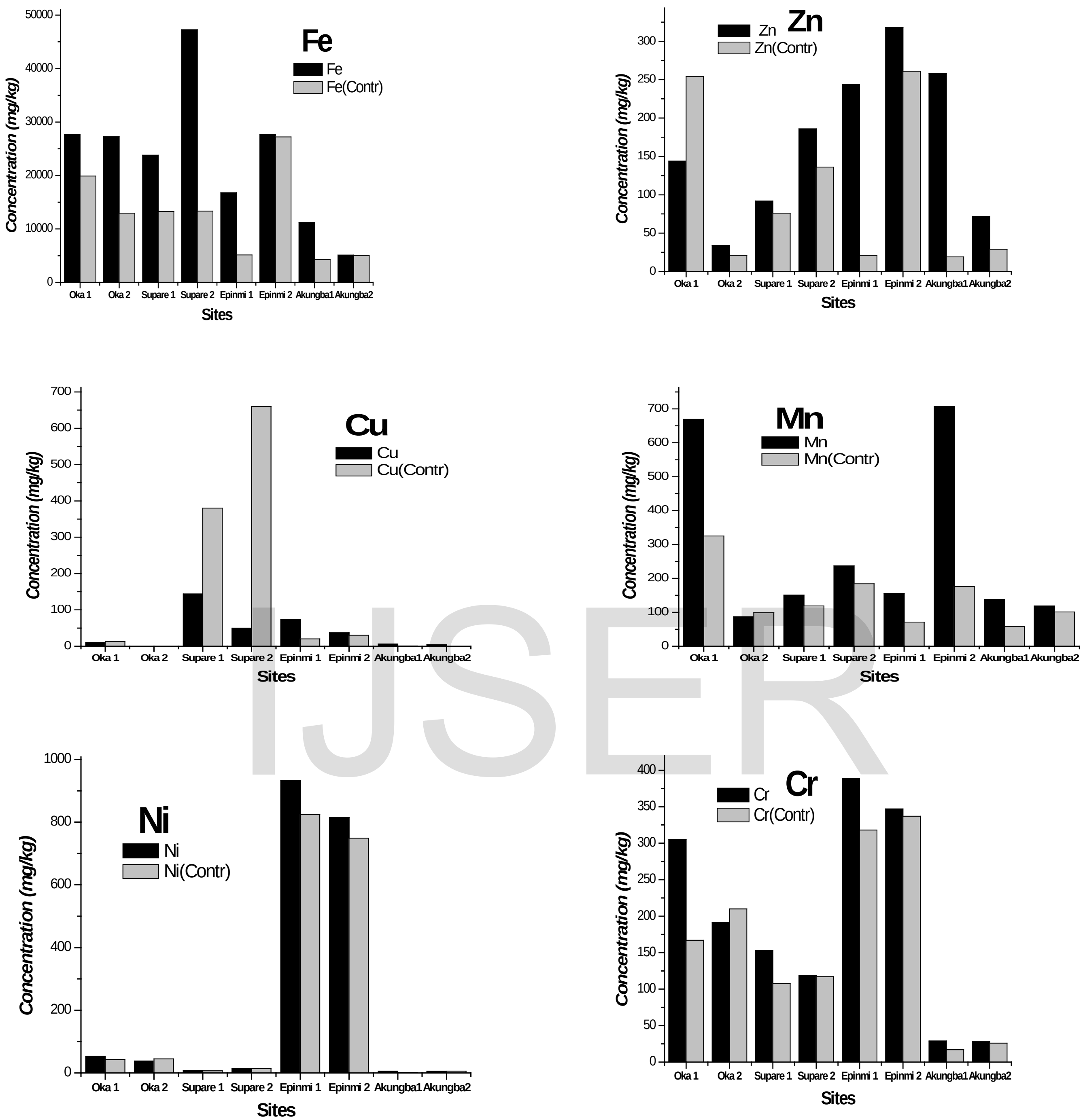

Figure 1. Contributions of refuse dumping to the heavy metal contamination at each site for each of the elements. ‘gray’ is the control in all.

Table 3 Contamination Factors (CFs) of soils and Pollution Load Index (PLI) in the soils

Location	Sample	Contamination Factor (CF)						
		Fe	Zn	Cu	Mn	Ni	Cr	PLI
Oka	Site A1	1.39	0.57	0.76	2.06	1.23	1.83	1.19
	Site A2	2.10	1.62	-[a]	0.88	0.84	0.91	1.18
Supare	Site B1	1.80	1.21	0.38	1.27	1.00	1.42	1.07
	Site B2	3.54	1.37	0.08	1.29	1.00	1.02	0.89
Epinmi	Site C1	3.25	11.6	3.65	2.19	1.13	1.22	2.74
	Site C2	1.02	1.22	1.23	4.02	1.09	1.03	1.38
Akungba	Site D1	2.60	13.58	6.00	2.38	3.00	1.71	3.70
	Site D2	1.01	2.48	-[a]	1.18	0.83	1.08	1.22

*In estimation of PLI, these cases were excluded as a result of the metal concentration or controlvalues being below detection level

Table 4 Enrichment factor of heavy metals in dumpsite soils

Heavy metal	A1	A2	B1	B2	C1	C2	D1	D2	Mean
			Enrichment Factor (EF)						
Zn	0.41	0.77	0.67	0.39	3.57	1.20	5.21	2.46	1.84
Cu	0.01	-[a]	0.21	0.02	1.12	1.21	2.3	-[a]	0.70
Mn	0.02	0.42	0.71	0.36	0.68	3.95	0.91	1.17	1.03
Ni	0.01	0.40	0.51	0.28	0.35	1.07	1.15	0.83	0.58
Cr	0.07	0.43	0.79	0.29	0.38	1.01	0.65	1.07	0.59

[a]The metal was below detection limit at these sites

[15 (Barakat et al., 2012). In order to identify anomalous metal concentration, geochemical normalization of heavy metal data to a conservative element, such as Al, Fe and Si were employed. Several authors have successfully used Fe to normalize heavy metals contaminants [15], [12] because of its conservative nature during diagenesis. The Enrichment Factor (EF) is defined as [16]

$$EF = \frac{(M/Fe)_{sample}}{(M/Fe)} \quad (3)$$

Where $\left(\frac{M}{Fe}\right)$ is the ratio of heavy metal to Fe in the sample and $\left(\frac{M}{Fe}\right)$.

EF values smaller than 1.5 suggest natural source of heavy metal enrichment while EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. The contamination could be divided into different categories based on EF values. If EF<2, it suggests deficiency to minimal metal enrichment. If EF>2, it suggests various degrees of metal enrichment. Table 4 shows the enrichment factor estimated for the metals in the soil samples collected at the different dumpsites. Almost of the metals showed EF estimate lower than 1.5 except Zn (0.39-3.57) in C1 and D1, Cu (0.01-2.3) in D1 and Mn (0.02-3.95) in C2.

From table 4, in terms of source of enrichment, the three metals listed above have been probably enriched due to heavy and indiscriminate dumping of domestic and metallic waste as Akungba-Akoko where sample D2 was collected is a university town and has increased in population so rapidly since the university's establishment over 15 years ago.The mean EF of the metals increased in the order; Ni <Cr < Cu <Mn<Zn. In general, none of the average enrichment factors were >2, which suggests no varying degree of metal enrichment, according to Han et al. (2006). In contrast, the average EF values of all the metals are < 2 suggesting deficiency to minimal metal enrichment.

The I_{geo} index is used to determine metal contamination in soil. It is expressed as

$$I_{geo} = \log_2\left(\frac{C_m}{1.5B_n}\right) \quad (4)$$

where C_m= measured total concentration of metals in soils (mg/kg); B_n= geochemical background values of metals (mg/kg); 1.5 is the background matrix correction factor due to lithogenic effects.

According to Müller [17], $I_{geo} < 0$ indicates 'unpolluted', $0 < I_{geo} < 1$ indicates 'unpolluted to moderately polluted', $1 < I_{geo} < 2$ indicates 'moderately polluted', $2 < I_{geo} < 3$ indicates 'moderately to strongly polluted', $3 < I_{geo} < 4$ indicates 'strongly polluted', $4 < I_{geo} < 5$ indicates 'strongly to very strongly polluted', $I_{geo} > 5$ indicates 'very strongly polluted'.

From table 5, the I_{geo} most of the metals is < 2 which indicates moderate pollution. However, Zn (3.18) in D1 indicates moderate pollution to strong pollution of the soil by the metal

Table 5 Geoaccumulation index (I_{geo}) of the metals in the soil samples

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I_{geo}

Heavy metal	A1	A2	B1	B2	C1	C2	D1	D2
Fe	-0.11	0.49	0.26	1.24	1.17	-0.56	0.80	-0.57
Zn	-1.40	0.11	-0.31	-0.13	2.95	-0.30	3.18	0.72
Cu	-0.96	-[b]	-1.98	-4.31	1.28	-0.28	2.00	-[b]
Mn	0.46	-0.77	-0.24	-0.22	0.55	1.42	0.67	-0.35
Ni	-0.28	-0.83	-0.58	-0.58	-0.41	-0.46	1.00	-0.85
Cr	0.28	-0.72	-0.08	-0.56	-0.29	-0.54	0.19	-0.48

[b]The metal was below detection limit at these sites

[17]. Anthropogenic activities may have contributed well to this.

4.0 Conclusion

The study has evaluated the heavy metal contamination of soil samples collected at eight dumpsites in Akoko region of Ondo state, Nigeria. Soil sample from Akungba –Akoko. The act of uncontrolled refuse dumping has been established to contribute significantly to the heavy metal contaminations in majority of the sites with Fe taking the lead. Therefore, the indiscriminate dumping of refuse at undesignated dumpsites needs be addressed and discouraged. Though the study of the metals have not shown extreme cases of contamination, studies at these sites nevertheless, caution should be taken at intervals at dumpsites to monitor the level of contamination with the passage of time.

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