

# Distributional Coefficients and Enrichment Studies of Potentially Toxic Heavy Metals in Soils Around Itakpe Iron-Ore Mine, North Central Nigeria

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## Abstract

Soil samples were collected randomly but uniformly distributed around Itakpe iron-ore mines in both dry and wet seasons. Surface soils were collected from 0cm to 10cm using stainless steel augers and located using Global Positioning System (GPS). Soil samples were air-dried, sieved through 500um mesh and 1.0g digested, evaporated and analysed using Atomic Absorption Spectrometer (AAS). Five (5) geo-environmental indices were used to quantitatively evaluate the degree of soil contamination due to iron ore mining. The anthropogenic factor (AF) for both seasons revealed that all heavy metals have greater than 50% AF except for Cd in the dry season. The geo accumulation index (Igeo) for both seasons showed background concentration to unpolluted for Cu and Zn while Fe, Ni, Cd and Pb recorded moderately to very highly polluted. The pollution index (Er<sup>j</sup>), showed tiny hazard level for all the heavy metals in dry season and in wet season, Cd and Ni recorded strong hazard level while tiny hazard level were observed for Cu and Pb. The ecological pollution index for the area is strong (RI=323.25). Dry and wet season enrichment factor (EF) revealed background concentration for all the heavy metals except Fe with EF > 40 (extremely high enrichment). While contamination factor (CF) was very high for Fe in both seasons, Cu and Ni recorded considerable to very high contamination in dry season. The wet season also revealed considerable contamination for Ni and Cd; moderate to considerable contamination for Cu, Zn and Pb. The sites in both seasons have experienced various degrees of deterioration but more significant in wet season. Based on these indices, the soils around Itakpe iron-ore area has suffered significant degrees of contaminations with respect to Fe, Ni, Cd and Pb.

**Keywords:** Itakpe, geo-accumulation index, enrichment factor, contamination factor, pollution index.

## 1. Introduction

The Itakpe iron-ore deposit is mined from ferruginous quartzites. The ferruginous quartzites are metamorphosed iron-rich sediments that occur as bands and lenses within the Precambrian gneisses and migmatites (Olade, 1978 and Odigi, 2002). The Itakpe deposit contains more than 300 million tons of iron-ore, with an average of 40% Fe (Olade, 1978). Iron and steel are the backbone of human civilization and industrialization. Iron ore can be used as a measure of level of industrial development and living standards of nations. If this Itakpe iron-ore deposit is properly harnessed to its logical conclusion, Nigeria could experience rapid industrial and economic developments.

Pollution of the environment due to mining is ubiquitous because these metals are indestructible and most of them have toxic effects on living organisms and man. Heavy metals with potential hazards and occurrences in contaminated soils around iron ore mines include: Cd, Cr, Pb, Zn, Ni, Fe, Cu among others (Akoto *et al.* 2008). This study is to evaluate the spatial distribution of these heavy metal pollutants in soils around Itakpe iron-ore mines using locally determined background values (control values) for metal concentrations, employing in-depth heavy metal analysis using integrated approaches.

The objectives of the present work therefore, include: i) assessment of heavy metal contamination by Cu, Pb, Zn,

Cd, Ni and Fe using control values obtained few kilometers from the mining area and devoid of iron ore deposit; ii) to assess mine site contamination using six of these approaches; a) Enrichment factor (EF); b) Contamination factor (CF), c) Pollution load index (PLI), d) Geo-accumulation index (I<sub>geo</sub>), e) Anthropogenic factor (AF), f) Ecological risk factor and iii) to establish the heavy metals probable sources.

## 2. Geology of Itakpe

Nigeria forms part of the reactivated Precambrian basement of the Dahomeyan shield which lies between the West Africa and Congo Cratons. Almost half of the country is underlain by crystalline rocks of Archean gneisses, Proterozoic metasediments and Pan-African (Late Precambrian) granitoids (Olade, 1978). The Archean, gneiss-migmatite complexes are the most widespread within rejuvenated crystalline basement. They are composed of para-amphibolites and quartzites, which are in places ferruginous (Figure 1). The Proterozoic metasediments and metavolcanics occurs as well defined schist belts steeply infolded into the reactivated basement.

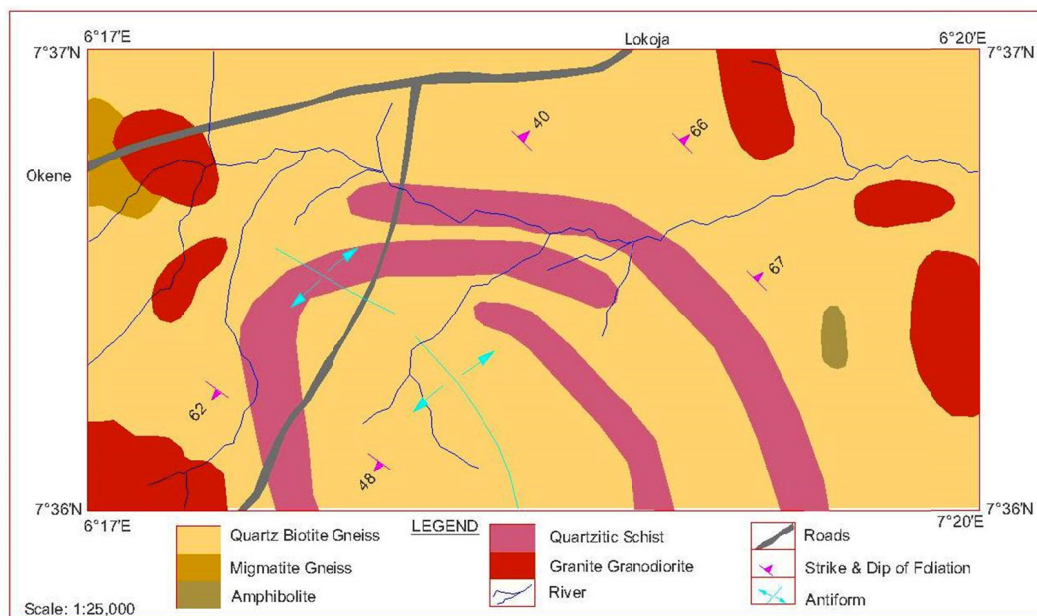


Figure 1. Geology of Itakpe (Odigi, 2002)

The dominant lithologies in the study area are: amphibolites, ultramafic schist, pelitic and semi-pelitic schists and ferruginous quartzites (Olade, 1978).

The ferruginous quartzites consist mainly of iron oxides and quartz gangue. The Itakpe deposits occur as steeply-dipping bands and lenses intercalated within gneisses and quartzites (Olade, 1978). The central body consists of high grade ore lenses of 35m and 15m thick and extending 200m along strike. The northern ore body which occurs at the northern flank thins from 60m in the west to 25m in the east. Petrographic studies have shown that the ores are of three types, massive magnetite ore (4% of reserves), banded or granular hematite-magnetite ore (80% of reserves) and schistose hematite ore (15%). Average ore grade is 40% Fe with values of up to 62% Fe in the massive ore. Metallurgical tests have shown that the ores can be beneficiated by magnetic and gravity methods to yield a concentrate with 65% Fe (Olade, 1978).

## 3. Materials and Methods

### 3.1 Sample Collection, Preparation and Analysis

Soil samples were randomly collected during dry (February, 2012) and wet seasons (July, 2012). The control point was located at least 500m to 1km away from the mine site but with similar geology and little or no influence from the mining activities. All soil samples were obtained at the surface (0 to 10cm depth) using hand driven stainless steel augers. The exact locations of all sampled sites were determined using the global positioning system (Figure 2).

The soil samples collected were air-dried to constant weight and sieved through a 500 um stainless steel mesh wire. Samples of 1.0g were digested in 20ml freshly prepared aqua regia (1:3 HNO<sub>3</sub>: HCl) on a hot plate for

three hours (3hrs), evaporated and analysed for heavy metal concentrations. Standard reference material was prepared using stock solution from SAARCHM and MERCH and used to check the accuracy of the results. The total concentration of heavy metals in the filtrate were then determined using Atomic Absorption Spectrometer (AAS) at the State Key Laboratory for Mineral Deposit Research, Nanjing, University, China.

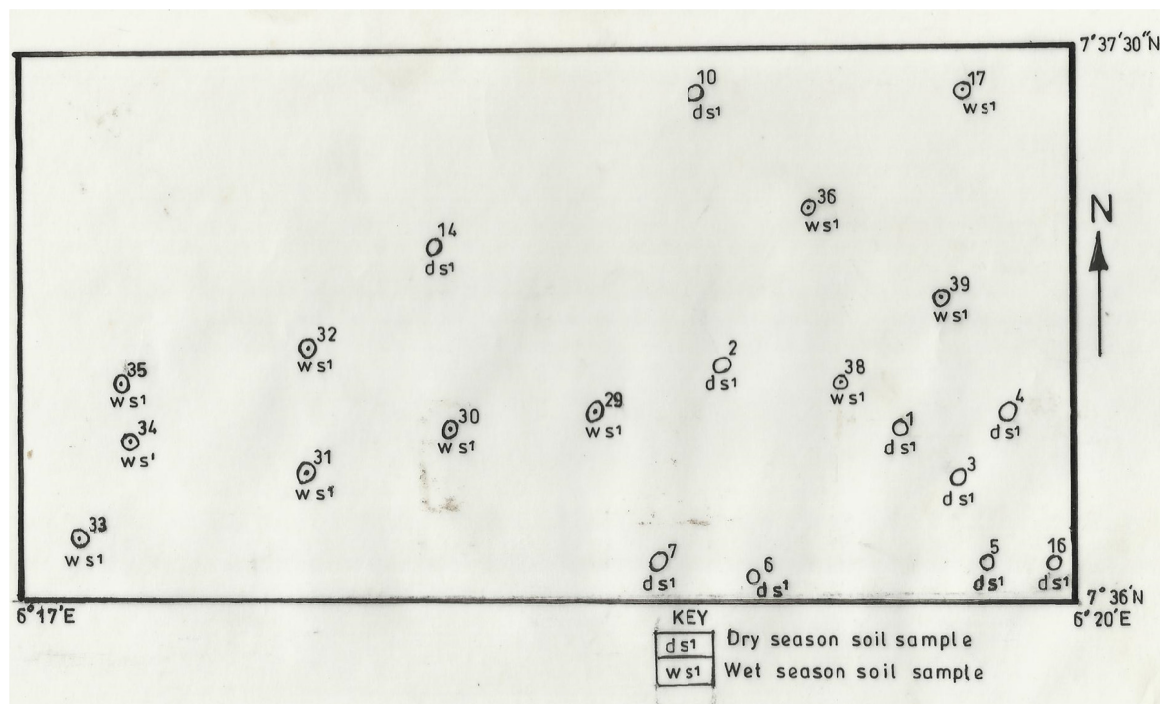


Figure 2. Sample points location map.

### 3.2 Assessment of Heavy Metal Contamination Methods

(i) Enrichment factor (EF): assessment of heavy metal and level of contamination in soils require pre-anthropogenic knowledge of heavy metal concentrations which act as pristine values. In this study, it is the control point values that were used. A number of different enrichment calculation methods and different reference material have been reported (Sutherland, 2000; Chakravarty and Patgiri, 2009; Olade, 1978, Ameh *et al.* 2014.). In this manuscript, the degree of pollution was established by adapting the enrichment factor ratios (EF) used by Sutherland *et al.*, 2000, as follows:

$$\text{The EF} = (C_m/C_{Fe})_{\text{sample}} / (C_m/C_{Fe})_{\text{control/background value}} \quad (1)$$

Where  $(C_m/C_{Fe})_{\text{sample}}$  is the ratio of concentration of heavy metal ( $C_m$ ) to that of Fe ( $C_{Fe}$ ) in the soil sample and  $(C_m/C_{Fe})_{\text{control/background value}}$  is the reference to the ratio in the control/background value. According to Sutherland (2000), five contamination categories are generally recognized on the basis of the enrichment factor:  $EF < 2$ , depletion to minimal enrichment;  $2 \leq EF < 5$ , moderate enrichment;  $5 \leq EF < 20$ , significant enrichment;  $20 \leq EF < 40$ , very high enrichment; and  $EF > 40$ , extremely high enrichment.

The selected reference sample is usually an average crust or local background sample. The immobile element is often taken to be Li, Sc, Zr, Ti and sometimes Fe or Mn has been used (Qingjie *et al.*, 2008). In this study, Fe was used.

The enrichment factor categories for equation (1) are outlined below:

$EF \leq 1$	background concentration
$EF 1-2$	depletion to minimal enrichment
$EF 2-5$	moderate enrichment
$EF 5-20$	significant enrichment
$EF 20-40$	very high enrichment
$EF > 40$	extremely high enrichment

(ii) Contamination factor (CF): The level/degree of soil contamination by heavy metals is expressed in terms of contamination factor (CF) calculated as:

$$CF = C_m \text{ sample} / C_m \text{ control values} \quad (2)$$

Where the contamination factor,  $CF < 1$  refers to low contamination;  $1 < CF < 3$  means moderate contamination;  $3 < CF < 6$  indicates considerable contamination and  $CF > 6$  indicates very high contamination. Each sample location was evaluated for the extent of heavy metal pollution by employing the method of pollution load index (PLI) developed by Thomilson et al., 1980 as follows:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (3)$$

Where  $n$  is the number of metals studied (six in this study) and  $CF$  is the contamination factor calculated (equation 2). The PLI provides simple but comparative means of assessing a site quality, where a value of  $PLI < 1$  denote perfection;  $PLI = 1$  indicate that only baseline levels of pollutants are present and  $PLI > 1$  indicate deterioration of site quality (Thomilson et al. 1980).

This method has been defined in many ways by different authors as numerical sum of eight factors (Hakanson, 1980). Ibrahim (2005) defined site quality as arithmetic mean of analyzing pollutants but in this study, it is appropriate to express the PLI as the geometric mean of the studied pollutants because this method reduces outliers which could bias reported results.

(iii) Geo-accumulation index (Igeo): Heavy metal enrichment above the control point values was evaluated using the geo-accumulation index (Igeo) method proposed by (Muller, 1979). This method assesses the heavy metal pollution in terms of seven (0 to 6) classes of enrichment, ranging from background concentration to very heavily polluted as follows:

$$Igeo = \log_2 [C_m \text{ sample} / 1.5 \times C_m \text{ control}] \quad (4)$$

The factor 1.5 is introduced in this equation to minimize the effect of possible variations in the control values,  $C_m$  control, which is attributed to lithogenic variations in soils. The proposed descriptive classes for Igeo values are in Table 6b (Muller, 1979).

(iv) Anthropogenic factor (AF): This was calculated for the top sediment samples.

$$\text{The AF} = C_s / C_c \quad (5)$$

where  $C_s$  = concentration of heavy metal in sediments;  $C_c$  = concentration of heavy metals in control values. This result indicates the extent of anthropogenic influence on heavy metals in top sediment samples.

(v) Ecological risk factor ( $Er^i$ ): An ecological risk factor ( $Er^i$ ) is used to quantitatively express the potential ecological risk of a given contaminant as suggested by Hakanson, (1980) as follows:

$$Er^i = Tr^i \times C_f^i \quad (6)$$

where  $Tr^i$  is the toxic-response factor for a given substance (Table 1) and  $C_f^i$  is the contamination factor. The following terminologies are used to describe the risk factor:  $Er^i < 40$ , low potential ecological risk;  $40 \leq Er^i < 80$ , moderate potential ecological risk;  $80 \leq Er^i < 160$ , considerable potential ecological risk;  $160 \leq Er^i < 320$ , high potential ecological risk; and  $Er^i \geq 320$ , very high ecological risk.

Table 1. Toxicity factor by Hakanson (1980)

Elements	Cd	Cu	Pb	Ni	Zn
Toxic reference factor	30	5	5	3	1

#### 4. Results and Discussion

Table 2. Itakpe dry and wet seasons soil sample (mg/l) and descriptive statistics

Acv values shifted

	Na	K	Ca	Mg	Fe	Cu	Zn	Pb	Ni	Cd
Min	13.69	22.24	28.75	3.52	11737.5	0.14	0.53	0.05	0.01	0.45
Max	30.82	95.42	751	4.93	142420	0.8	1.63	0.64	6.86	1.89
Mean	19.4	56.27	149.09	4.04	60924.5	0.46	1.17	0.28	1.69	1.24
Std Error	1.79	1.76	7.68	69.66	0.16	10892.02	7.68	10.74	6.38	7.06
T-test	10.85	7.32	2.14	25.47	5.59	5.98	2.54	4.52	2.08	2.18
ACv value 14.52	60.13	37.3	3.41	307.75		0.17	0.83	0.04	0.55	1.68
Std. Dev.	5.65	24.29	220.3	0.5	34443.59	0.24	0.45	0.19	2.26	0.6

Min.	7.24	45.5	22.5	2.5	9158.6	0.39	0.11	0.01	0.07	0.98
Max.	21.62	189.22	139.25	4.5	46900	3.27	1.85	0.16	2.61	1.95
Mean	13.91	73.91	80.91	3.76	27784.82	1.02	0.81	0.09	0.55	1.69
T-test	10.09	6.18	6.04	1.75	7.37	4.76	3.94	2.08	2.85	1.2
ACv value 86.82	13.88	22.57	3.84	81		0.54	0.56	0.03	0.02	0.34
Std. Dev	4.57	39.65	44.44	0.64	12523.03	0.83	0.56	0.06	0.76	0.4

\*ACv = average control value

The control values of all analytes were lower than their respective mean values except for K and Cd whose control values were 60.13mg/l and 1.68mg/l and their mean values were 56.27mg/l and 1.24mg/l respectively. The major and heavy metal concentrations order were Ca> K>Na>Mg for both seasons and Fe>Ni>Cd>Zn>Cu>Pb and Fe>Cu>Cd>Zn>Ni>Pb for dry and wet seasons respectively (Table 2).

Table 3. Correlation matrix of dry season soil samples

	Na	K	Ca	Mg	Fe	Cu	Zn	Pb	Ni	Cd
Na	1	.261	.018	-.039	.033	-.081	-.265	-.058	-.323	.141
K		1	.518	-.017	.210	-.094	-.281	-.166	.235	-.684*
Ca			1	.396	.783**	.325	-.427	.387	.710*	-.356
Mg				1	.225	-.137	-.149	.609	.546	.372
Fe					1	.417	-.333	.643*	.441	-.023
Cu						1	-.594	.339	-.150	-.311
Zn							1	-.470	.154	.286
Pb								1	.211	.393
Ni									1	-.157
Cd										1

\*Correlation is significant at the 0.05 level. \*\* Correlation is significant at the 0.01 level.

Table 4. Correlation matrix of wet season soil samples

	Na	K	Ca	Mg	Fe	Cu	Zn	Pb	Ni	Cd
Na	1.000	.564	.164	.318	.127	-.436	-.164	.490	.064	-.418
K		1.000	.300	.755**	.400	-.645*	.036	.760**	.082	-.300
Ca			1.000	.127	.345	.264	.391	-.027	.191	.000
Mg				1.000	.318	-.473	-.136	.485	.136	.191
Fe					1.000	.173	-.309	.508	.300	.127
Cu						1.000	-.155	-.339	.109	.291
Zn							1.000	-.394	.318	-.036
Pb								1.000	.133	-.330
Ni									1.000	.309
Cd										1.000

\*.Correlation is significant at the 0.05 level.\*\*Correlation is significant at the 0.0 level.

In dry season at  $P < 0.01$ , Fe-Ca displayed strong correlations. At  $P < 0.05$ , Pb-Fe-Ni-Ca-Cd-K also recorded significant correlations (Table 3). During rainy season, at  $P < 0.01$ , Mg-K, Pb-K showed positive and strong correlations (Table 4). Also at  $P < 0.05$ , Cu-K revealed strong relationships. These strong relationships indicate same sources for these elements. The likely sources of these heavy metals from the study area are: mining and processing activities, fuels from automobiles and agricultural sources among others.

Table 5. Anthropogenic factor of heavy metals in dry and wet season soils

Heavy metals (mg/l)	Dry				Wet			
	Mean measured concentration	Control point concentration	Anthropogenic factor (AF) value	% (AF) AF	Mean measured concentration	Control point concentration	Anthropogenic factor (AF) value	% (AF) AF
Fe	60924.50	307.75	197.97	99.00	27784.82	81.00	343.02	99.71
Cu	0.4590	0.17	2.70	73.00	1.02	0.54	1.89	63.38
Zn	1.1660	0.83	1.40	58.00	0.81	0.56	1.45	59.12
Pb	0.2760	0.04	6.90	87.34	0.09	0.034	2.65	72.58
Ni	1.6930	0.55	3.08	75.48	0.55	0.02	27.5	96.49
Cd	1.2400	1.68	0.74	42.47	1.69	0.34	4.97	83.25

AF =  $C_m/C_v$ ;  $C_m$  = mean concentration;  $C_v$  = control concentration

From table 5, it is clear that dilution has reduced the effect of AF between the dry and wet season concentrations. Iron (Fe) was relatively higher during wet season as a result of precipitation and co precipitation of ox hydroxides from solution (Ameh, et al., 2014). The highest AF during dry season was iron (Fe) 99% and the least was Cd (42.47%) while in wet season, Fe recorded the highest AF value of 99.71% and Zinc the least AF of 59.12%.

Table 6a. Igeo of heavy metals in dry season soils

Heavy metals (mg/l)	Sample locations									
	ITK01	ITK02	ITK03	ITK04	ITK05	ITK06	ITK07	ITK10	ITK14	ITK16
Fe	7.46	6.89	6.53	4.95	7.11	4.67	6.63	6.89	7.29	6.45
Cu	0.82	0.79	-0.50	1.21	0.58	-0.50	1.65	1.56	1.42	-0.87
Zn	-0.92	0.15	0.28	0.26	-0.96	-0.62	0.39	0.34	0.20	-1.23
Pb	2.42	3.42	0.74	3.17	1.12	-0.26	1.32	2.12	2.59	1.81
Ni	3.06	2.15	-6.37	-0.46	-6.37	-1.08	-6.37	1.73	1.60	-2.46
Cd	-2.28	-2.49	-1.12	-0.42	-1.28	-0.46	-0.50	-0.52	-0.74	-2.45

The  $I_{geo} = \log_2 [(C_m)/(1.5 * C_v)]$ : Where  $C_m$  = measured concentration;  $C_v$  = control values; 1.5 = a factor for possible variations in reference concentration due to lithologic differences.

Table 6b. Geo-accumulation indices of heavy metal classes (Muller, 1979)

Igeo index	Pollution intensity
0	background concentrations
0-1	unpolluted
1-2	moderately to unpolluted
2-3	moderately polluted
3-4	moderately to highly polluted
4-5	highly polluted
>5	very highly polluted

The dry season Igeo showed that Fe was highly polluted to very highly polluted in all locations while the wet season was very highly polluted for all locations. Except for few locations (which recorded moderately to unpolluted), Cu recorded unpolluted in all locations in both seasons. During both seasons, Zn recorded unpolluted in most locations. Moderately polluted was observed with respect to Pb in the dry season while in wet season, Pb recorded unpolluted in most locations while fewer locations experienced moderately to unpolluted.

During wet season, Ni revealed moderately to very highly polluted in most locations while in dry season, most locations recorded moderately to unpolluted. Cadmium in wet season was moderately to unpolluted in all locations while during the dry season, background concentrations were observed in all locations (Tables 6 & 7). The Igeo index order were Fe > Pb > Ni > Cu > Zn > Cd for dry season and thus Fe > Ni > Cd > Pb > Cu > Zn for wet season (Figure 3).

Table 7. The Igeo of wet season soils

Sample location	Heavy metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
ITK29	7.72	2.01	-0.42	0.45	5.10	1.73
ITK30	7.94	0.43	0.14	1.65	3.42	1.70
ITK31	7.96	0.08	-0.22	-2.35	2.94	1.93
ITK32	6.67	-0.54	1.14	1.56	2.74	1.88
ITK33	8.43	0.15	0.51	1.56	1.42	1.92
ITK34	8.19	1.08	1.03	0.65	6.44	1.46
ITK35	8.08	-0.09	-0.43	0.97	3.22	1.93
ITK36	8.59	-1.06	-2.93	1.46	4.97	2.26
ITK37	8.01	-0.27	-0.62	0.97	2.66	1.51
ITK38	6.40	-0.56	-1.25	-1.36	1.74	1.29
ITK39	6.24	-0.67	-1.64	-2.35	1.22	0.94

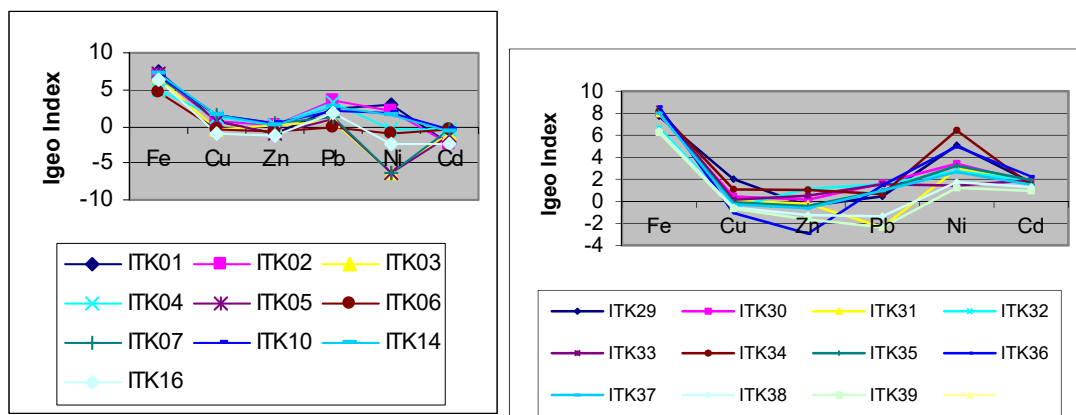


Figure 3. The Igeo index average of heavy metals in dry and wet season soil

Table 8. Grading standard of  $E_r^i$  and RI (Hakanson, 1980)

Pollution coefficient $E_r^i$	Pollution index RI	Pollution level (ecological hazard)
$\leq 40$	$\leq 150$	Tiny
40-79	150- 299	Middle
80-159	300-600	Strong
160-320	> 600	very strong
>320	-	Serious

Table 9. Assessment of potential ecological risk of heavy metals in dry season soil

Elements	Toxicity coefficient	Measured value (mg/l)	Ratio of Cs/Cn (mg/l)	$E_r^i$	Hazard level
Cd	30	1.24	0.74	22.20	Tiny
Cu	5	0.46	2.71	13.55	Tiny
Pb	5	0.28	7.00	35.00	Tiny
Ni	3	1.69	3.07	9.21	Tiny
Zn	1	1.17	1.41	1.41	Tiny
RI	81.37				

Table 10. Assessment of potential ecological risk of heavy metals in wet season soil

Elements	Toxicity coefficient	Measured value (mg/l)	Ratio of Cs/Cn (mg/l)	$E_r^i$	Hazard level
Cd	30	1.69	4.97	149.10	Strong
Cu	5	1.02	1.89	9.45	Tiny
Pb	5	0.09	2.65	13.25	Tiny
Ni	3	0.55	50.0	150	Strong
Zn	1	0.81	1.45	1.45	None
RI	323.25				

Dry soil samples around Itakpe iron-ore showed tiny ecological pollution index ( $RI = 81.37$ ) and all the heavy metals also showed tiny hazard level. Wet season soil samples from the same area revealed strong ecological pollution hazard level ( $RI = 323.25$ ), while Cd and Ni also showed strong hazard levels. Both Cu and Pb recorded tiny hazard levels (Tables 9 and 10).

Table 11a. Enrichment factor (EF) of heavy metals in Itakpe dry season soils

Heavy Metals (mg/l)	Sample locations									
	ITK01	ITK02	ITK03	ITK04	ITK05	ITK06	ITK07	ITK10	ITK14	ITK16
<b>Fe/100</b>	3.31	1.07	3.31	2.58	2.68	0.39	0.76	0.94	1.36	2.05
<b>Cu</b>	0.01	0.01	0.01	0.01	0.01	0.03	0.03	0.02	0.02	0.01
<b>Zn</b>	0.00	0.01	0.01	0.00	0.00	0.03	0.01	0.01	0.01	0.00
<b>Pb</b>	0.03	0.09	0.02	0.03	0.02	0.03	0.03	0.04	0.04	0.04
<b>Ni</b>	0.65	0.51	0.00	0.03	0.00	0.26	0.00	0.38	0.27	0.03
<b>Cd</b>	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.01	0.00	0.00

Table 11b. Enrichment factor of heavy metal classes (Sutherland, 2000)

EF indices	Degree of enrichment
$EF \leq 1$	background concentration
EF 1-2	depletion to minimal enrichment
EF 2- 5	moderate enrichment
EF 5- 20	significant enrichment
EF 20- 40	very high enrichment
EF > 40	extremely high enrichment

Table 12. Enrichment factor (EF) of wet season soils

Sample location	Heavy metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
ITK30	223.94	0.006	0.005	0.013	0.044	0.013
ITK32	46.04	0.007	0.022	0.029	0.065	0.036
ITK33	243.29	0.003	0.004	0.009	0.008	0.011
ITK29	281.49	0.019	0.004	0.007	0.161	0.016
ITK31	289.51	0.004	0.004	0.001	0.031	0.015
ITK34	143.53	0.007	0.007	0.005	0.294	0.009
ITK35	365.90	0.004	0.003	0.007	0.034	0.014
ITK37	392.40	0.003	0.003	0.008	0.024	0.011
ITK38	202.48	0.008	0.005	0.005	0.039	0.029
ITK39	234.52	0.008	0.004	0.003	0.031	0.025
ITK36	2947.76	0.001	0.000	0.007	0.08	0.012



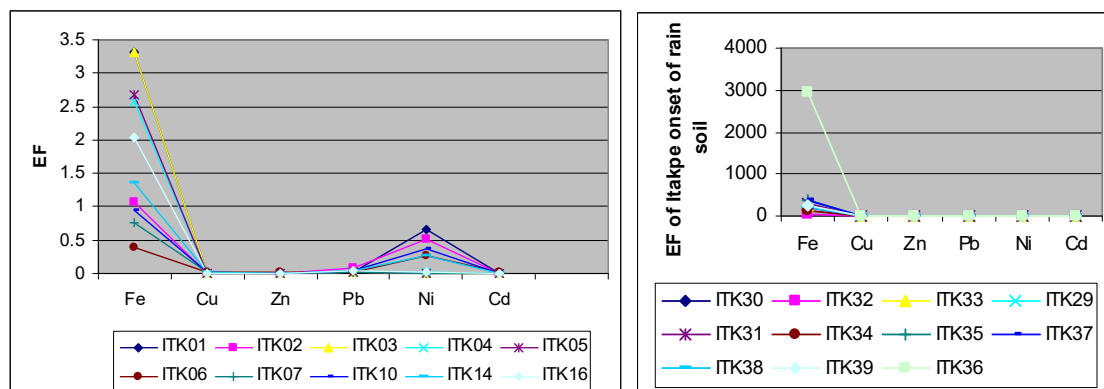


Figure 4. The EF average of dry and wet season soils

For both seasons, the enrichment factor for Fe was extremely high with raining season having higher degree of enrichment. For other heavy metals, background enrichment was recorded in both seasons. All heavy metal's EF were lower during rainy season than dry season (Tables 11 and 12). On the average, order of heavy metal enrichment were  $Fe > Ni > Pb > Cu > Zn > Cd$  for dry season and  $Fe > Ni > Cd > Pb > Cu > Zn$  in wet season (Figure 4).

Table 13a. The CF of heavy metals in dry season soils

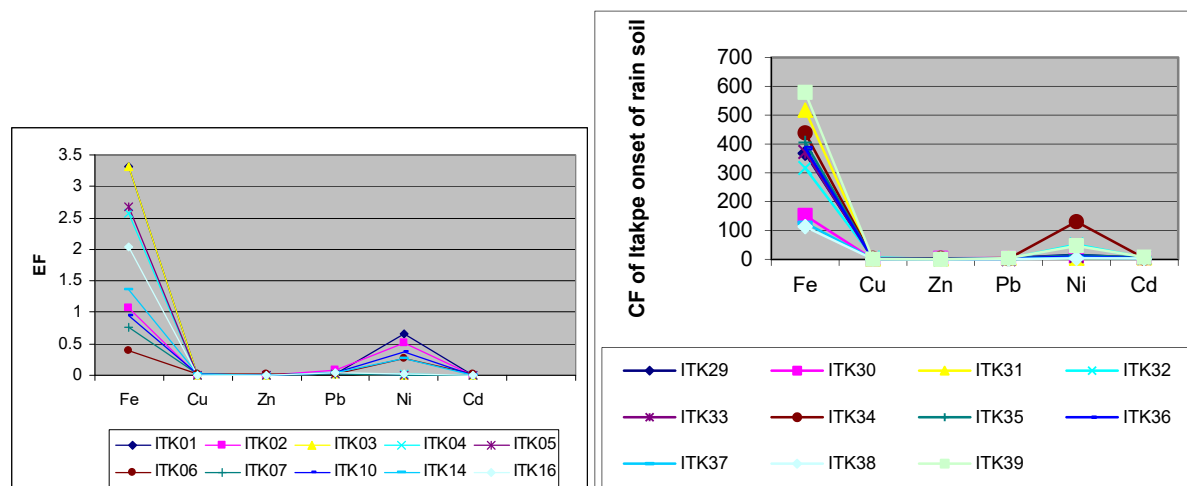
Heavy Metals (mg/l)	Sample locations									
	ITK01	ITK02	ITK03	ITK04	ITK05	ITK06	ITK07	ITK10	ITK14	ITK16
<b>Fe/10</b>	26.32	17.79	13.83	46.28	20.70	3.81	14.82	17.84	23.51	13.07
<b>Cu</b>	2.65	2.59	1.06	3.47	2.24	1.06	4.71	4.41	4.00	0.82
<b>Zn</b>	0.80	1.66	1.82	1.80	0.77	0.98	1.96	1.90	1.72	0.64
<b>Pb</b>	8.00	16.00	2.50	13.5	3.25	1.25	3.75	6.50	9.00	5.25
<b>Ni</b>	12.47	6.65	0.02	1.09	0.02	0.71	0.02	4.98	4.55	0.27
<b>Cd</b>	0.31	0.27	0.69	1.13	1.10	1.10	1.10	1.05	0.90	0.27

Table 13b. Contamination factor of heavy metal classes (Hakanson, 1980)

Contamination factor (CF) indices	Degree of contamination
$CF < 1$	low contamination
$1 \geq CF \geq 3$	moderate contamination
$3 \geq CF \geq 6$	considerable contamination
$CF > 6$	very high contamination

Table 14. Contamination factor (CF) of wet season soils

Sample location	Heavy metals (mg/l)					
	Fe	Cu	Zn	Pb	Ni	Cd
ITK29	367.90	2.02	1.64	4.71	16.00	4.85
ITK30	152.10	1.04	3.30	4.41	10.00	5.50
ITK31	516.98	1.67	2.13	4.41	4.00	5.68
ITK32	316.67	6.06	1.13	2.06	51.50	4.97
ITK33	372.22	1.59	1.29	0.29	11.50	5.71
ITK34	438.27	3.17	3.05	2.35	130.5	4.15
ITK35	405.09	1.41	1.11	2.94	14.00	5.75
ITK36	385.39	1.24	0.98	2.94	9.50	4.26
ITK37	126.55	0.94	0.63	0.59	5.00	3.68
ITK38	113.07	0.93	0.48	0.29	3.50	2.88
ITK39	579.01	0.72	0.20	4.12	47.00	7.21



Figures 5. The CF averages of dry and wet season soil

The contamination factor for Fe was generally lower at dry season than during rainy season. In both seasons, Fe had very high contaminations. The contamination factor for Cu and Zn were moderate for both seasons. Fewer locations showed considerable contamination in dry season for Cu. Dry season CF for Pb revealed very high contamination in most locations while wet season recorded mostly considerable contamination. Nickel in wet season showed higher degree of contamination than in dry season. While Ni recorded very high contamination in wet season, considerable contamination was observed in most locations in dry season. Cadmium revealed considerable contamination in wet season while low to moderate contamination was recorded during dry season (Figure 5). Heavy metals such as Fe, Ni and Cd were relatively higher during wet season than dry season.

Table 15a. The PLI of dry and wet seasons

Dry season		Sample locations									
Heavy metals (mg/l)	ITK01	ITK02	ITK03	ITK04	ITK05	ITK06	ITK07	ITK10	ITK14	ITK16	Average PLI
PLI	5.08	5.29	1.45	6.03	1.72	1.84	2.20	6.09	6.25	1.72	37.65

Wet season		Sample locations										Average PLI
Heavy metals	ITK2	ITK3	ITK3	ITK3	ITK3	ITK3	ITK3	ITK3	ITK3	ITK3	ITK3	
(mg/l)	9	0	1	2	3	4	5	6	7	8	9	
PLI	8.74	7.09	7.54	10.23	2.90	13.24	7.29	6.18	3.06	2.30	6.99	75.56

Table 15b. Pollution load index of heavy metal classes (Thomilson et al., 1980)

PLI indices	Pollution level
0	Perfection
1	Only baseline levels of pollutants present
> 1	Progressive deterioration of the site

While the samples were not exactly from same point in both seasons, dry season PLI were on average lower than in wet season. Both seasons have shown site deterioration but the pollution load for wet season was significantly higher when compared site by site with dry season (Tables 15).

## 5. Discussion

The soil samples around Itakpe showed tiny ( $RI = 81.37$ ) ecological hazard risk level in dry season and strong ecological hazard risk level during the rainy season ( $RI = 323.25$ ). The potential ecological risk was in the order

Ni > Cd > Pb. All the heavy metals indicated tiny hazard level in dry season. While Cd and Ni showed strong hazard level, Cu and Pb showed tiny hazard level and Zn showed none in the rainy season. Sources of Ni in this study area include: both mining and fuel sources. Though Pb sulphides may be present in the area, automobile fuels which have historically contained Pb as additives for value lubrication, chemical fertilizers were the major sources of Pb. Another factor could also be the strongly hydrophobic nature of lead (Akoto, *et al.*, 2008). Cadmium was also strongly enriched and its major sources were pesticides, fertilizer applications as well as mining activities (Akoto *et al.*, 2008).

On the basis of the indices used, Pb was lower in wet season than dry season. This could be due to its immobility, possible dilution due to rainwater and flood water. It's also possible that Pb attached to the soil particles were removed from the soil surfaces and translocated elsewhere by the action of water and wind (Harrison *et al.*, 1981). On the other hand, Fe, Ni and Cd were all higher in rainy season than in dry season. Iron (Fe) is generally present in the secondary oxides due to its mobility and dispersion which may contribute to its higher spatial content (Harrison *et al.*, 1981). Over 75% of Cd is associated with mining ferrous and nonferrous materials. The absorption of Cd on particulate matter and bottom sediments are major factors affecting Cd concentration (Ibrahim, 2005). The hydrous iron and Mn oxides have a large capacity for sorption or co-precipitation with heavy metals such as Ni. This may suggest why Ni was higher in rainy season than in dry season.

These hydrous oxides exist as coatings on the particles, particularly clays and can transport sequestered metals to great distances (Ibrahim, 2005). The Ni may also have been incorporated into solid minerals by nonspecific and specific adsorption, co-precipitation and precipitation of discrete oxides and hydroxides (Ibrahim, 2005). Furthermore, Fe and Mn oxyhydroxides form surface coatings on other mineral surfaces such as clays, carbonates and grains of feldspars and quartz (Ibrahim, 2005). The Cd concentration was also higher during rainy season because of its relative mobility which enables its dispersion/discharge. Besides this, Cd may have been remobilized from commercial fertilizers, pesticides, animal and waste water discharges as a result of runoff arising from rainfall (Ibrahim, 2005).

High PLI suggests appreciable input from anthropogenic sources (Chakravarty and Patgiri, 2009). The higher PLI observed in rainy season can be traced to rainfall discharge and dispersion of metals under tropical conditions where soils are scarcely vegetated and the subsequent severe erosions due to runoff and landscape topography (Chakravarty and Patgiri, 2009).

## References

- Akoto, O., Ephraim, J. H., & Darko, G. (2008). Heavy metal pollution in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghana. *Int. J. Environ. Res.*, 2(4), 359-364.
- Ameh, E. G., Omatola, D. O., & Awulu, T. D. (2014). Utilization of Environ Metric and Index Methods as Water Quality Assessment Tools Focusing on Heavy Metal Content of Water Around Okaba Coal Mines, Kogi state, Nigeria. *Advances in Research*, 2(2), 80-94. Article no. AIR.2014.003.
- Callender, E. (2003). Heavy metals in the environment-Historical trends. In *Environmental Geochemistry* (ed. B.S.Lollar) Vol. 9. Treatise on Geochemistry (Eds. H. D. Holland and K. K. Turekian) Elsevier-
- Chakravarty, M., & Patgiri, A. D. (2009). Metal pollution assessment in sediments of the Dikrong River, N.E. India. *J. Hum. Ecol.*, 27(1), 63-67.
- Gong, Q. J., Deng, J., Xiang, Y. C., Wang, Q. F., & Yang, L. Q. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences*, 19(3), 230-241.
- Hakanson, L. (1980). Ecological Risk Index for Aquatic Pollution Control, a Sedimentological Approach. *Water Res.*, 14, 975-1001.
- Harrison, R. M., Laxen, D. P. H., & Wilson, S. J. (1981). Chemical association of Lead, cadmium, copper and zinc in street Dust and road soils. *Environ. Sci. Tech.*, 15, 1378-1383.
- Ibrahim, G. M. S. (2005). Holocene sediments of Tamaki Estuary: characterization and impact of recent human activity on an urban estuary in Auckland, New Zealand. PhD thesis, University of Auckland, Auckland, New Zealand, p. 36.
- Muller, G. (1979). Schwermetalle in den sediments des Rheins-Veränderungen seit 1971. *Umschau*, 79, 778-783. In Chen, C., Kao, C., Chen, C and Dong, C., 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*, 66, 1431-1440.
- Odigi, M. I. (2002). Geochemistry and geotectonic setting of migmatitic gneisses and amphibolites in the

- Okene-Lokoja area of SW Nigeria. *Journal of Mining and Geology*, 38(2), 81-89.
- Olade, M. A. (1978). General features of a Precambrian iron ore deposit and its environment at Itakpe ridge, Okene, Nigeria. *Applied earth science*, 87, B1-B10. Pergamon, Oxford, 67-107.
- Sutherland, R. A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39, 611-37.
- Thomilson, D. C., Wilson, J. D., Harris, C. R., & Jeffrey, D. W. (1980). Problems in heavy metals in estuaries and the formation of pollution index. *Helgol. Wiss. Meeresunlter*, 33(1-4), 566-575.

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