



ASSESSMENT OF ELEMENTAL COMPOSITION OF KAOLIN FROM KANKARA AND DUTSINMA MINE SITES, KATSINA STATE, NIGERIA

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ABSTRACT

This research aimed to assess the health hazards associated with heavy metals contamination around Kankara and Dutsinma Kaolin mining sites. The analysis was done by using Energy Dispersive X-ray Fluorescence (EDXRF) at the Central Laboratory, Umaru Musa Yar-adua University, Katsina. In which health hazards were evaluated. using numerous Statistical and United States Environmental Protection Agency (USEPA) models. Thirty nine (39) different elements were analyzed using the most associated environmental and health risk of priority in which seven (07) of them are heavy metals of interest; Among them are: Nickel (Ni), Copper (Cu), Zink (Zn), Thallium (Ti), Chromium (Cr), Lead (Pb), and Arsenic (As), with an average concentrations of 20.02, 12.59, 54.03, 1344.4, 21.94, 140.00, and Not Available Value (NA) in the studied area. The Values obtained for overall hazard index (HI) are within the accepted values by (USEPA) which indicates no cancer risk for both adults and Children. While the overall excess lifetime cancer risk for a heavy metal was $8.5555E-06$ (a maximum of 9 people per 1 million may be affected) for children and $7.5773E-05$ (a maximum of 8 people per 1 million may be affected) for adults.

INTRODUCTION

Human health is continuously affected by the sweeping distribution of heavy metals in our environment, emanating from natural sources or as a result of artificial human activities. These activities contaminate the surrounding air, drinking water and the food we eat, and in turn affect the overall human health. Although mining as a business is lucrative in nature, mining of mineral resources is a major source of exposure of toxic metals and a concern for radiation dose to the surrounding populace, especially to the immediate miners. In several countries, despite the availability of adequate protection policies on exposure to radiation and heavy metals, these policies are not strictly adhered to by miners, thus endangering their overall health status.

Furthermore, Heavy Metals are expose to the people leaving within the mining sites as a result of food consumption and bio-accumulating factor

Heavy Metals component of different mining sites have been investigated and reported to assess the health hazard possibilities from the sites (Wei et al., 2018). It should be noted further that, while heavy metals are natural part of the geologic formation of most mining sites, there are two main contributors to natural radiation exposure, namely; high-energy cosmic ray particles incident on the earth's atmosphere originating from the earth crust which are present everywhere in the environment, including the human body (UNSCEAR, 2000). It is further noted that kaolin and other clay minerals contains quartz, long-term exposure to which may result in silicosis, lung cancer, chronic bronchitis and pulmonary emphysema in humans but these are found to be less toxic to aquatic organisms. While report on the effects of extensive use of kaolin in cosmetics and toothpastes is not conclusive, justified serious concerns forms a basis for repeated investigation especially for heavy metal since the level of long-term occasional exposure from dust in mines, processing plants and industries have been known to lead to benign pneumoconiosis known as kaolinos (Zoltan & Williams, 2005).

METHOD

An overview of the materials, equipment and methods used for the research study is presented with emphasis placed on the technically required ingredients and processes to achieve the different objectives set for the study. The method for the study captures the procedure for sample collection, sample preparation and data analysis for (EDXRF). The procedures are mostly captured as steps

in chronological sequential order so as to present a clear idea of how the study objectives were achieved in sequence with respect to achieving the overall aim of the study.

The selection of the sampling locations and collections was purposively carried out based on the accessibility to the public and proximity to the mine. The sampling strategy adopted for the samples collection was however random in line with (ASTM 1983, 1986; IAEA 2004 and USEPA 1989).



Fig1: Map of Katsina state, showing Dutsinma and Kankara Local Government Areas in Relation to the Scope of the Study (Terdoo and Adekola 2014).

The nine Kaolin samples ere collected from three different locations were by three samples are from one particular sampling point with respect to the depth of 5, 15 and 25metres at the mine sites. The specific sample locations are Sambisa-Danmarke and DajinGwamna-Yar’goje in Kankara Local; FararKasarBoto - Garfi/Haukan Zama in Dutsinma Local Government Area of Katsina State. Such locations are coordinated using Global Positioning System (GPS) at altitude 168m (1978ft), (Latitude 11°53’42’’N and Longitude 7°36’31’’E), (Latitude 11°52’37’’N and Longitude 7°26’27’’E) of Yargoje and Danmarke Villages; Kankara LGA; While Altitude 51.2m

(1102ft), (Latitude 12°24'15''N and Longitude 7°26'46''E) is Garhi/Haukan Zama in Dutsinma LGA respectively.

The sampling method adopted is such that at each sampling point, a sample of about 1kg was collected and put in well labeled polythene bag, consistent with procedure adopted in (Kolo et al., 2014). Nine (9) samples were collected and bagged in these areas, with a set designated and labeled for Elemental analysis using EDXRF. Each sample was sealed in a polyethylene bag, firmly tied to avoid cross contamination before labelling. The samples were carried to the Advanced Research Laboratory at the Umaru Musa Yar'adua University Katsina.

Table 1: Sample ID, collection point and depth of mines

S/N	ID	LOCATION	DEPTH (M)
1	Y01	Yar'goje village, Kankara L. G.	5
2	Y02	Yar'goje village, Kankara L. G.	15
3	Y03	Yar'goje village, Kankara L. G.	25
4	S01	Sambisa village, Kankara L. G.	5
5	S02	Sambisa village, Kankara L. G.	15
6	S03	Sambisa village, Kankara L. G.	25
7	G01	Garfi village, Dutsinma, L. G.	5
8	G02	Garfi village, Dutsinma, L. G.	15
9	G03	Garfi village, Dutsinma, L. G.	25

An overview of the materials, equipment and methods used for the research study is presented in table 2 below, with emphasis placed on the technically required ingredients and processes to achieve the different objectives set for the study.

Table 2: presents the material and method used for the different stages of the study in respects to the different stages of the research effort.

SAMPLE ID	MATERIAL	DETAILS/ FUNCTION
SAMPLE COLLECTION	Extractor	Digging Kaolin Sample from the earth crust

FROM MINING SITES	Global Positioning System (GPS)	Locating point and taking coordinate at the sampling location
	Shovel	Collection of dug samples
	Polythene bag	Packaging collected sample at the collection point
	Plastic bucket	Packaging the whole sample at one point for easy movement
	Measuring Tape up-to 100ft (30m)	Measuring the depth of each sampling point
	Touch light	Providing illumination inside the dug mining well
SAMPLE PREPARATION FOR EDXRF	Electronic balance/Digital Scale	Sample weighing for accurate measurement
	Crusher	Grinding of sample into smaller particles
	Mesh (2mm)	Measuring the sample to ensure right size
ELEMENTAL ANALYSIS	Sample Holders	White Plastic container for holding a sample in preparation for analysis
	Polythene Holder Seal	A transparent polythene used for sealing a sample Holder for running the sample
	ARL QUANT'X Machine and Software	Spectrum acquisition machine and software used to read and display the spectrum from EDXRF on the Monitor
	EDXRF Machine	Quantitative and Qualitative elemental analysis of material.
	Computer System	Host of the AARL QUANT'X software system set for display and acquisition of result
	Lead shield	Pre-World War Lead limiting detection of background radiation and noise
DATA ANALYSIS	MS Office Excel	Used in statistical and theoretical analysis of acquired data

RESULTS AND DISCUSSION

The result of the elemental composition of mined Kaolin using EDXRF spectroscopy which provide quantitative details of the elements of the different Kaolin samples are presented in Table 2, which provides the EDXRF spectroscopy concentration in ppm for each elements detected and records for Elements (ELE) present but below detectable limit or NA for elements not present at all. Here, the Concentration of the elements is recorded for the different sampling locations Yargoje (Y), Sambisa (S) and Garfi (G). At the first stage (01) of (Y01, S01 and G01) implies samples collected at 5 m. Also a second stage (02) of (Y02, S02 and G02) implies samples collected at 15 m and final stage (03) of (Y03, S03 and G03) implies samples collected at 25 m depths.

Table 2: Elemental Composition of Mined Kaolin Sample

CONCENTRATION (ppm)									
ELE	YAR'GOJE			SAMBISA			GARFI		
	Y01	Y01	Y03	S01	S02	S03	G01	G02	G03
Fe	17424.00	10401.00	6036.00	13113.00	9531.00	1269.20	19856.00	9606.00	16909.00
Ni	24.70	15.20	18.70	18.80	11.60	12.34	44.10	33.60	55.10
Cu	10.50	13.30	0.28	10.78	12.30	3.70	30.40	12.62	19.40
Zn	40.10	56.50	54.20	69.50	42.20	21.39	56.60	51.30	94.50
Ga	11.94	67.40	37.63	27.10	49.80	30.38	33.75	25.66	34.77
Ge	1.57	1.71	2.08	1.81	3.88	2.28	NA	2.50	1.85
Ta	2.00	142.00	50.00	46.00	103.00	63.00	17.00	60.00	52.00
W	NA	549.00	383.00	237.00	192.00	NA	NA	155.00	425.00
Mg	8900.00	48000.00	14200.00	22500.00	13700.00	17100.00	15900.00	19400.00	18300.00
Al	88330.00	133780.00	149730.00	132480.00	169300.00	149090.00	176090.00	149090.00	171860.00
Si	316540.00	165250.00	322690.00	275850.00	225270.00	243470.00	249570.00	189920.00	248560.00
P	1519.00	180.00	814.00	614.00	546.00	696.00	663.00	447.00	377.00
S	447.00	702.00	233.00	646.00	534.00	312.00	633.00	198.00	691.00
Cl	593.00	497.00	315.00	789.00	397.00	386.00	601.00	634.00	1124.00
K	9975.00	8622.00	25576.00	22853.00	27372.00	50326.00	16228.00	11237.00	25655.00
Ca	1045.00	655.00	422.00	602.00	591.00	203.20	219.00	136.50	205.00
Ti	3957.00	492.00	367.40	2156.20	804.00	689.90	1392.20	759.70	1481.20
V	16.30	NA	NA	NA	NA	NA	NA	NA	NA
Cr	25.10	10.60	8.70	23.30	NA	NA	64.10	18.20	3.60
Mn	229.00	722.40	162.90	612.50	1120.20	29.70	1081.70	128.20	173.20
La	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ce	NA	62.60	54.90	74.60	NA	NA	126.00	103.10	NA

As	3.00	NA	NA	NA	NA	NA	NA	NA	NA
Br	1.80	NA	NA	1.29	NA	NA	NA	NA	NA
Rb	72.40	101.40	190.40	245.10	232.80	372.00	142.30	141.70	225.00
Sr	661.00	629.00	1026.00	1378.00	1314.00	2946.00	2577.00	3529.00	4284.00
Y	22.06	81.60	17.39	25.90	22.10	13.90	16.51	17.20	16.42
Zr	2277.00	NA	NA	1943.00	NA	113.00	292.00	NA	NA
Nb	13.96	13.83	14.02	13.93	13.97	13.64	13.57	13.47	13.60
Sn	NA	NA	100.00	800.00	NA	NA	NA	NA	NA
Pb	67.00	81.40	405.00	127.30	131.00	88.50	111.80	107.30	149.30
Bi	62.00	16.00	28.00	47.00	48.00	61.00	11.00	29.00	45.00
Th	NA	14.70	NA	NA	10.10	NA	18.50	30.90	14.40
U	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ag	95.00	4.80	5.70	9.70	7.60	5.60	4.70	6.10	5.80
Sb	NA	NA	NA	NA	450.00	460.00	NA	NA	NA
I	58.60	5.22	5.74	5.63	5.35	5.42	5.29	5.46	5.09
Cs	270.00	120.00	190.00	NA	130.00	310.00	NA	NA	NA p;
Ba	NA	NA	NA	NA	NA	NA	NA	NA	NA

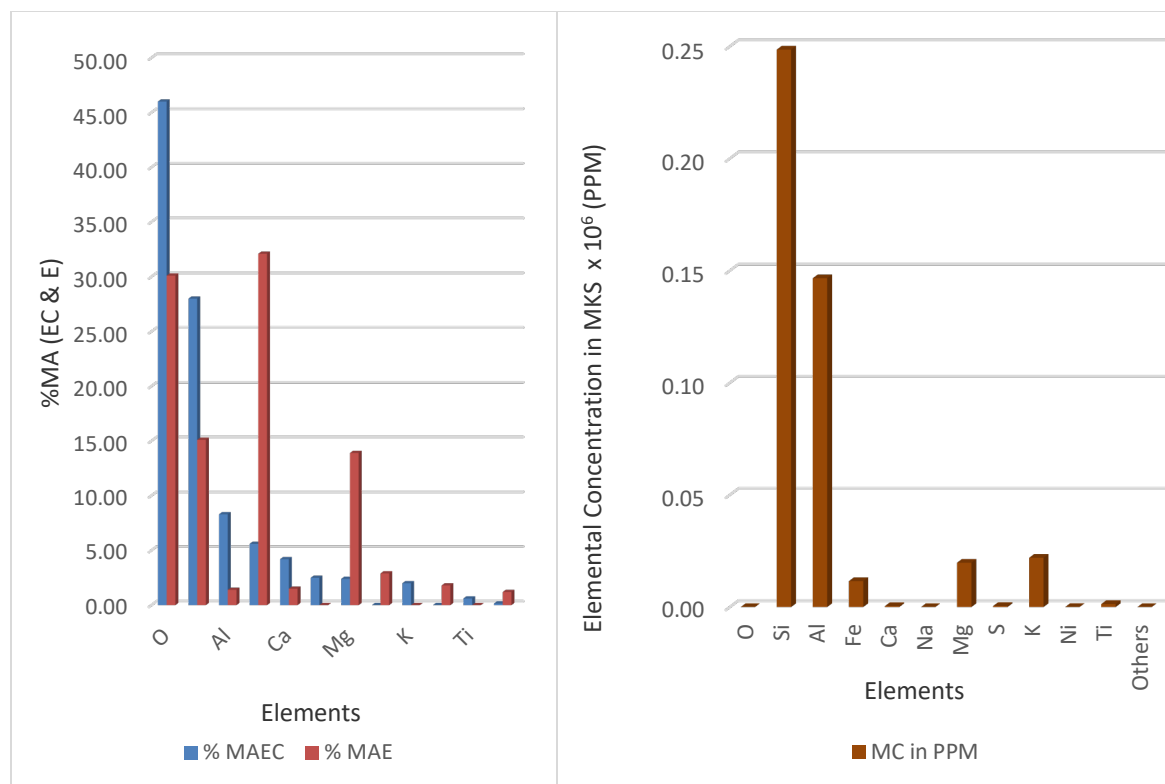
In Table 3 Statistical Analysis of the obtained data has been presented to include the Minimum (Min), Maximum (Max) and Range (R) concentration of all elements in ppm. The Mean Concentration (M), the standard Deviation (SD) and the Standard Error (SE) have also been determined for each Element (ELE).

Table 3: Statistical Analysis of the Elemental Composition of Mined Kaolin Sample

ELE	MIN	MAX	M	SD	SE
Fe	1269.20	19856.00	11571.69	5915.30	1971.77
Ni	11.60	55.10	26.02	15.21	5.07
Cu	0.28	30.40	12.59	8.68	2.89
Zn	21.39	94.50	54.03	20.30	6.77
Ga	11.94	67.40	35.38	15.73	5.24
Ge	1.57	3.88	2.21	0.74	0.25
Ta	2.00	142.00	59.44	42.06	14.02
W	155.00	549.00	323.50	153.53	51.18
Mg	8900.00	48000.00	19777.78	11262.86	3754.29
Al	88330.00	176090.00	146638.89	26935.85	8978.62
Si	165250.00	322690.00	248568.89	52213.31	17404.44
P	180.00	1519.00	650.67	376.35	125.45
S	198.00	702.00	488.44	199.03	66.34
Cl	315.00	1124.00	592.89	247.46	82.49
K	8622.00	50326.00	21982.67	12897.78	4299.26
Ca	136.50	1045.00	453.19	298.39	99.46
Ti	367.40	3957.00	1344.40	1131.87	377.29
V	-	-	-	-	-
Cr	3.60	64.10	21.94	20.18	6.73
Mn	29.70	1120.20	473.31	423.09	141.03
La	ND	ND	ND	ND	ND
Ce	54.90	126.00	84.24	29.67	9.89
As	-	NA	NA	NA	NA
Br	NA	NA	1.55	NA	NA
Rb	72.40	372.00	191.46	90.48	30.16

Sr	629.00	4284.00	2038.22	1334.54	444.85
Y	13.90	81.60	25.90	21.22	7.07
Zr	-	-	1156.25	-	-
Nb	13.47	14.02	13.78	0.21	0.07
Sn	-	-	NA	-	-
Pb	67.00	405.00	140.96	102.36	34.12
Bi	11.00	62.00	38.56	18.46	6.15
Th	-	-	-	-	-
U	-	-	-	-	-
Ag	4.70	95.00	16.11	29.62	9.87
Sb	-	-	-	-	-
I	5.09	58.60	11.31	17.73	5.91
Cs	-	-	-	-	-
Ba	-	-	-	-	-

From fig2 (a) and (b), the elemental abundance of the most important elements of the Earth Crust and the entire Earth can be comparatively analyzed.



(a)

(b)

Fig 2: Elemental Abundance (a) of the Earth Crust (EC) and the Earth (E) in % (Morgan & Anders, 1980) and that of the Mined Kaolin Sample (MKS) in (PPM)

From Fig 2, the elemental compositions of the most important elements in the Mined Kaolin Samples (MKS) are shown to be unique from the known elemental abundance of the Earth and the Earth Crust which are also in variance. While Fe is shown to be the most abundant element in the entire Earth with 32.1% abundance, which is just a little more than O with 30.1% abundance; it is only the fourth most abundant element with about 5.6% of the overall mass of the Earth crust, because a significant portion of it is located in the Earth's outer and inner core, where it is concentrated (Morgan and Anders, 1980; Kong et al., 2012; Gaminchev and Chamati, 2014). In the Earth Crust, Fe is preceded by O (46%), Si (28%), and Al (8.3%). However, considering the bulk mass of the entire Earth (%MA_E) with mass 5.98×10^{24} Kg; after Fe and O, Si contributes 15.1%, Mg 13.9%, S 2.9%, Ni 1.8%, Ca 1.5%, Al with 1.4% while other trace materials consist 1.2% ; Meanwhile, considering the Mass Abundance with respect to the entire Earth Crust (%MA_{EC}), the nine most abundant elements are O with 46% abundance, Si with 28%, Al with

8.3%, Fe with 5.6%, Ca with 4.2%, Na with 2.5%, Mg with 2.4%, K with 2.0%, Ti with 0.61% and other elements occurring at less than 0.15% (Morgan and Anders, 1980).

Thus, from the Elemental Concentration in ppm in Fig 4(b), O is absent due to non-detection by the EDXRF system. In the absence of O data, the abundance of Si is noted as highest in agreement with the MA_{EC} data followed by Al and then Fe. It can thus be concluded that the Elemental Composition measured for this works using the EDXRF is in agreement with the Known Percentage Mass Abundance of the different element in the Earth Crust (MA_{EC}) and not that of the Earth (MA_E). Hence, there is no significance variation between the general composition of the Earth Crust and the composition of Kaolin mines as a result of geophysical processes or anthropogenic activities.

Meanwhile, Heavy metal of interest to Nigeria agricultural and mining soil species has been suggested by (Adamu 2010; Musa 2017 and Nkwunonwo 2020) to include Fe, Ni, Cu, Zn, Cr, Mn, As, Hg, Cd, Co and Pb. Table 4, presents the Concentration (ppm) and Statistical Analysis of data for the heavy metal of interest to Nigeria. In the table, the Concentration of the heavy Metals of consequence is recorded for the different sampling locations such as Yargoje (Y), Sambisa (S) and Garfi (G). Here, as noted earlier, Y01, S01, G01 implies samples collected at 5m, Y01, S02, G02 implies samples collected at 15m and Y03, S03, G03 implies samples collected at 25m.

Furthermore, the Elemental Mean and Standard Deviation for all the sample of a particular Heavy Metal collected throughout the 3 different locations of Yar’goje, Sambisa and Garfi at the same depth is denoted M_e±SD_e. Similarly, Mean and Standard Deviation for a particular Heavy Metal collected at the different depths at the same location is denoted M_d±SD_d. It is also noted that the Elemental Concentration of Heavy metal is a function of both depth and location of mining as seen in the significant SD_e and SD_d computed.

Table 4: Concentration in ppm and Statistical Analysis for Most Important Heavy Metal Identified in Kaolin Sample

ELE	Concentration (PPM)						M _e ±SD _e
Fe	Y01	17424.00	S01	13113.00	G01	19856.00	16797.67±2788.22
	Y02	10401.00	S01	9531.00	G02	9606.00	9846.00±393.64
	Y03	6036.00	S03	1269.00	G03	16909.00	8071.33±6545.19

M_d±SD_d		11287.00±4691.15		7971±4959.52		15457.00±4308.66	
Ni	Y01	24.70	S01	18.80	G01	44.10	29.20±10.81
	Y02	15.20	S01	11.60	G02	33.60	20.13±9.64
	Y03	18.70	S03	12.34	G03	55.10	28.71±18.84
M_d±SD_d		19.53±3.92		14.25±3.32		44.27±8.78	
Cu	Y01	10.50	S01	10.78	G01	30.40	17.23±9.32
	Y02	13.30	S01	3.70	G02	12.64	9.88±4.38
	Y03	0.28	S03	30.40	G03	19.40	16.69±12.44
M_d±SD_d		8.03±5.60		14.96±11.92		20.81±7.32	
Zn	Y01	40.10	S01	69.50	G01	56.60	55.40±12.03
	Y02	56.50	S01	42.20	G02	51.30	50.00±5.91
	Y03	54.20	S03	21.39	G03	94.50	56.70±29.90
M_d±SD_d		50.27±7.25		44.36±19.70		67.47±19.24	
Cr	Y01	25.10	S01	23.30	G01	64.10	37.50±18.82
	Y02	10.60	S01	0.00	G02	18.20	9.60±7.46
	Y03	8.70	S03	0.00	G03	3.60	4.10±3.57
M_d±SD_d		14.80±7.32		7.77±10.98		28.63±25.78	
Mn	Y01	229.00	S01	612.50	G01	1081.70	641.07±348.70
	Y02	722.40	S01	1120.00	G02	128.20	656.07±407.54
	Y03	162.90	S03	29.70	G03	173.30	121.97±65.38
M_d±SD_d		371.43±249.63		587.40±445.47		461.07±439.24	
As	Y01	3.00	S01	0.00	G01	0.00	1.00±1.41
	Y02	0.00	S01	0.00	G02	0.00	0.00±0.00
	Y03	0.00	S03	0.00	G03	0.00	0.00±0.00
M_d±SD_d		1.00±1.41		0.00±0.00		0.00±0.00	
Pb	Y01	67.00	S01	127.30	G01	111.80	102.03±25.57
	Y02	81.40	S01	131.00	G02	107.30	106.57±20.26

	Y03	405.00	S03	88.50	G03	149.30	214.27±137.13
M_d±SD_d		184.47±156.05		115.60±19.22		122.80±18.83	

In the table, of all the heavy metals of serious consequences suggested, data for Co, Cd and Hg are not included because the EDXRF spectroscopy did not provide any data for these elements for any of the 9 samples despite that they fall within the range of detectable element given as $11 \geq A \leq 92$ where A is the Mass Number. It is recalled that, for EDXRF measurement systems, the SiLi detector used for detection of characteristics X-rays of the elements is limited to elements from Na to U. In this case the element below Na cannot be detected as the characteristic X-ray from these elements gets absorbed. For Co, Cd and Hg which fall within this window therefore, the other reason that may be adduced for non-detection is that the concentration of the element is small enough not to be detectable. In this case, Co, Cd and Hg can be considered insignificant contributors to the Heavy Metal profile in Mined Kaolin from the Kankara and Dutsinma LGAs in Katsina State. Of note is the fact that Hg and Cd, which are considered notoriously toxic heavy metals in elemental, compound or oxide forms, are not detectable from the Mined Kaolin Sample at any location or depth (Tchounwou, Yedjou, Patlolla and Sutton, 2012).

The Deduction from Table 4 provides insight to the concentration of different heavy metals of consequence, their distribution across the different locations and their depth distribution. The comparative characterization of their concentrations in mined Kaolin sample is also investigated from the data.

Analysis of the Different Consequential Heavy Metal With Respect to Locations and Depth

Figure 3; presents stacked bar chart of the contribution of different consequential heavy metal with respect to location and depth of the collection of Kaolin samples from the surface of the mine.

The figure shows that Fe has the most significant contribution to the heavy metal profile of mined Kaolin with respect to either location or depth of samples collected while As has the least. The order of significance of the heavy metals reported in the samples with respect to location is therefore presented for the Yargoje, Sambisa and Garfi Kaolin mines as Fe > Mn > Pb > Zn > Ni > Cr > As.

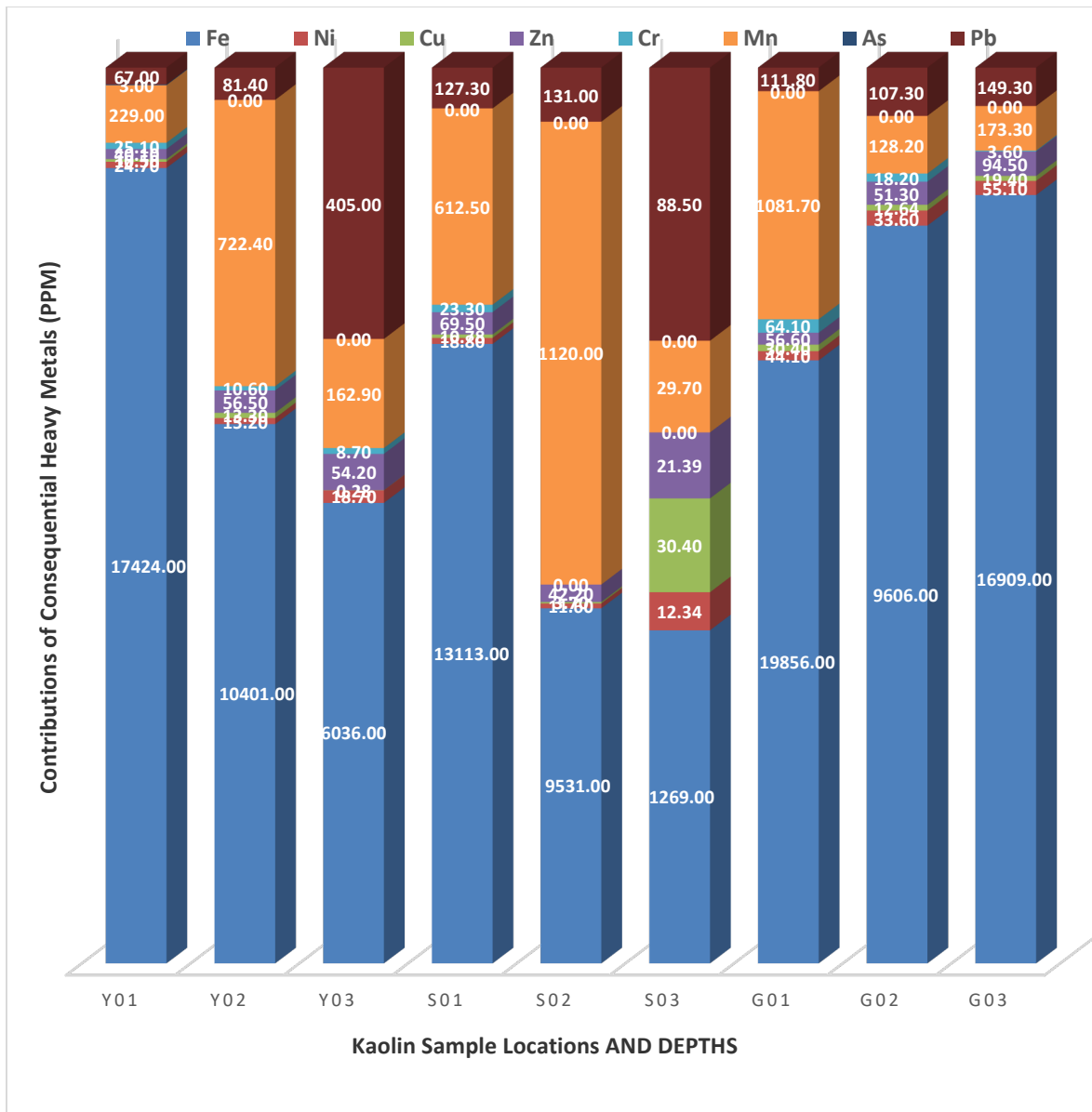


Fig 3: Contribution of Consequential Heavy Metals for Different Kaolin Sampling Location and Depth

Meanwhile, with respect to depth of collection of samples, it is observed as shown in Fig 3; that while the Elemental Concentration decreases with increasing depth for Fe and Cr, it increases with increasing depth for Pb, decreases and then increases for Ni, Cu and Zn and increases and then decreases for Mn. At increasing depth, the elemental concentration of As reduces to zero from 1 PPM within the first 10m depth.

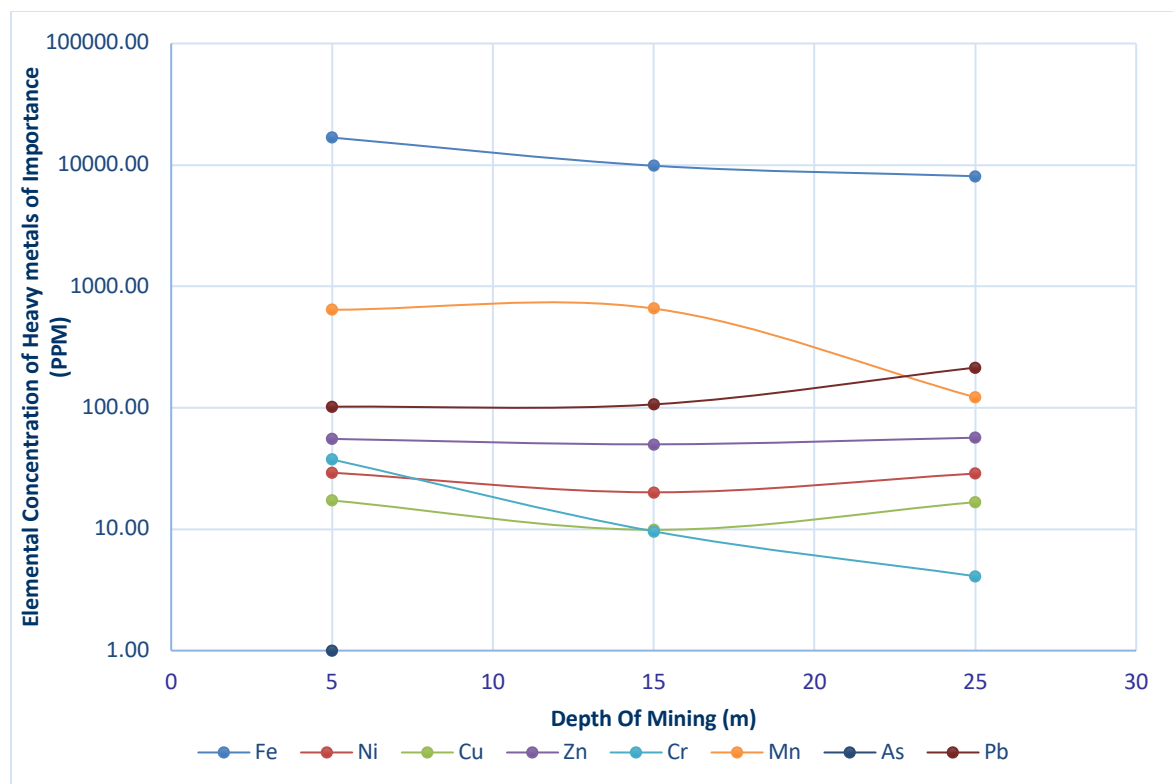


Fig 4: Variation of Elemental Concentration in ppm with Depth of Mining

Thus, the spatial depth dependence of the different heavy metals is seen not to be a function of the geochemical and geophysical properties of the mining sites alone.

The variation may further be influenced by characteristic intrinsic to the different heavy metal especially migration characteristics of the different metal.

Determination of Environmental and Health Hazard Indices from Heavy Metals

Estimation of the health and environmental risk assessment from heavy metal has been carried out including the determination of the effects of exposure to carcinogenic and non-carcinogenic chemicals. The assessments involved Hazard Identification, Exposure Assessment, Toxicity (Dose-Response) Assessment and Risk Characterization. The indices considered include Ingestion of Heavy Metals through Soil (ADI_{ING}), Inhalation of Heavy Metals via Soil Particulates (ADI_{INH}), Dermal Contact with Soil (ADI_{DERM}) for children and adults and for the different heavy metal of interest. The Non-Carcinogenic Hazards Assessment characterized with Hazard Quotient (HQ) were then determined for these categories of indices. Carcinogenic Risks Assessment

characterized by the Excess Lifetime Cancer Risk (ADI_K) were also determined. The equations for this analysis, which have been given in Equation 2.23 – 2.28 are implemented for this study in Microsoft Office Excel.

Table 5 (a) and (b) to 6 (a) and (b) presents the Indices of Ingestion of Heavy Metal through Soil (ADI_{ING}), of Inhalation of Heavy Metals via Soil Particulate (ADI_{INH}) and of Dermal Contact with Soil (ADI_{DERM}) and their corresponding Non-Carcinogenic Hazard Quotient (HQ_{ING} , HQ_{INH} and HQ_{DERM}) in children and in adults for Ni, Cu, Zn, Cr, As and Pb which are considered as Non-Carcinogen Heavy Metals. The values of ADI_{ING} , ADI_{INH} , ADI_{DERM} and HQs were determined respectively using equation 2.23, 2.24, 2.25 and 2.26 as implemented using Microsoft Office Excel.

Table 5: Calculated Result of Indices of Heavy Metal Ingestion (ADI_{ING}) through Soil and Corresponding Hazard Quotient (HQ_{ING}) as a Result of Non-Carcinogenic Heavy Metals (a) In Children

		HEAVY METALS					
Sample ID		Ni	Cu	Zn	Cr	As	Pb
Y01	ADI_{ING}	3.16E-04	1.34E-04	5.13E-04	3.21E-04	3.84E-05	8.57E-04
	HQ_{ING}	1.58E-02	3.63E-03	1.71E-03	1.07E-01	9.59E-02	2.38E-01
Y02	ADI_{ING}	1.94E-04	1.70E-04	7.22E-04	1.36E-04	0.00E+00	1.04E-03
	HQ_{ING}	9.72E-03	4.60E-03	2.41E-03	4.52E-02	0.00E+00	2.89E-01
Y03	ADI_{ING}	2.39E-04	3.58E-06	6.93E-04	1.11E-04	0.00E+00	5.18E-03
	HQ_{ING}	1.20E-02	9.68E-05	2.31E-03	3.71E-02	0.00E+00	1.44E+00
S01	ADI_{ING}	2.40E-04	1.38E-04	8.89E-04	2.98E-04	0.00E+00	1.63E-03
	HQ_{ING}	1.20E-02	3.73E-03	2.96E-03	9.93E-02	0.00E+00	4.52E-01
S02	ADI_{ING}	1.48E-04	1.57E-04	5.40E-04	0.00E+00	0.00E+00	1.67E-03
	HQ_{ING}	7.42E-03	4.25E-03	1.80E-03	0.00E+00	0.00E+00	4.65E-01
S03	ADI_{ING}	1.58E-04	4.73E-05	2.73E-04	0.00E+00	0.00E+00	1.13E-03
	HQ_{ING}	7.89E-03	1.28E-03	9.12E-04	0.00E+00	0.00E+00	3.14E-01
G01	ADI_{ING}	5.64E-04	3.89E-04	7.24E-04	8.20E-04	0.00E+00	1.43E-03
	HQ_{ING}	2.82E-02	1.05E-02	2.41E-03	2.73E-01	0.00E+00	3.97E-01

G02	ADI_{ING}	4.30E-04	1.61E-04	6.56E-04	2.33E-04	0.00E+00	1.37E-03
	HQ_{ING}	2.15E-02	4.36E-03	2.19E-03	7.76E-02	0.00E+00	3.81E-01
G03	ADI_{ING}	7.04E-04	2.48E-04	1.21E-03	4.60E-05	0.00E+00	1.91E-03
	HQ_{ING}	3.52E-02	6.70E-03	4.03E-03	1.53E-02	0.00E+00	5.30E-01

(b) In Adults

HEAVY METALS

Sample ID		Ni	Cu	Zn	Cr	As	Pb
Y01	ADI_{ING}	1.69E-04	7.19E-05	2.75E-04	1.72E-04	2.05E-05	4.59E-04
	HQ_{ING}	8.46E-03	1.94E-03	9.16E-04	5.73E-02	5.14E-02	1.27E-01
Y02	ADI_{ING}	1.04E-04	9.11E-05	3.87E-04	7.26E-05	0.00E+00	5.58E-04
	HQ_{ING}	5.21E-03	2.46E-03	1.29E-03	2.42E-02	0.00E+00	1.55E-01
Y03	ADI_{ING}	1.28E-04	1.92E-06	3.71E-04	5.96E-05	0.00E+00	2.77E-03
	HQ_{ING}	6.40E-03	5.18E-05	1.24E-03	1.99E-02	0.00E+00	7.71E-01
S01	ADI_{ING}	1.29E-04	7.38E-05	4.76E-04	1.60E-04	0.00E+00	8.72E-04
	HQ_{ING}	6.44E-03	2.00E-03	1.59E-03	5.32E-02	0.00E+00	2.42E-01
S02	ADI_{ING}	7.95E-05	8.42E-05	2.89E-04	0.00E+00	0.00E+00	8.97E-04
	HQ_{ING}	3.97E-03	2.28E-03	9.63E-04	0.00E+00	0.00E+00	2.49E-01
S03	ADI_{ING}	8.45E-05	2.53E-05	1.47E-04	0.00E+00	0.00E+00	6.06E-04
	HQ_{ING}	4.23E-03	6.85E-04	4.88E-04	0.00E+00	0.00E+00	1.68E-01
G01	ADI_{ING}	3.02E-04	2.08E-04	3.88E-04	4.39E-04	0.00E+00	7.66E-04
	HQ_{ING}	1.51E-02	5.63E-03	1.29E-03	1.46E-01	0.00E+00	2.13E-01
G02	ADI_{ING}	2.30E-04	8.64E-05	3.51E-04	1.25E-04	0.00E+00	7.35E-04
	HQ_{ING}	1.15E-02	2.34E-03	1.17E-03	4.16E-02	0.00E+00	2.04E-01

G03	ADI_{ING}	3.77E-04	1.33E-04	6.47E-04	2.47E-05	0.00E+00	1.02E-03
	HQ_{ING}	1.89E-02	3.59E-03	2.16E-03	8.22E-03	0.00E+00	2.84E-01

Table 6: Calculated Result of Indices of Heavy Metal Inhalation (ADI_{INH}) via Soil Particulate and Corresponding Hazard Quotient (HQ_{INH}) as a Result of Non-Carcinogenic Heavy Metals

(a) In Children

		HEAVY METALS					
Sample ID		Ni	Cu	Zn	Cr	As	Pb
Y01	ADI _{INH}	1.21E-08	5.16E-09	1.97E-08	1.23E-08	1.48E-09	3.29E-08
	H						
	HQ _{INH}				4.11E-04	4.92E-06	
Y02	ADI _{INH}	7.47E-09	6.54E-09	2.78E-08	5.21E-09	0.00E+00	4.00E-08
	H						
	HQ _{INH}				1.74E-04	0.00E+00	
Y03	ADI _{INH}	9.20E-09	1.38E-10	2.67E-08	4.28E-09	0.00E+00	1.99E-07
	H						
	HQ _{INH}				1.43E-04	0.00E+00	
S01	ADI _{INH}	9.24E-09	5.30E-09	3.42E-08	1.15E-08	0.00E+00	6.26E-08
	H						
	HQ _{INH}				3.82E-04	0.00E+00	
S02	ADI _{INH}	5.70E-09	6.05E-09	2.08E-08	0.00E+00	0.00E+00	6.44E-08
	H						
	HQ _{INH}				0.00E+00	0.00E+00	
S03	ADI _{INH}	6.07E-09	1.82E-09	1.05E-08	0.00E+00	0.00E+00	4.35E-08
	H						
	HQ _{INH}				0.00E+00	0.00E+00	
G01	ADI _{INH}	2.17E-08	1.49E-08	2.78E-08	3.15E-08	0.00E+00	5.50E-08
	H						
	HQ _{INH}				1.05E-03	0.00E+00	
G02	ADI _{INH}	1.65E-08	6.21E-09	2.52E-08	8.95E-09	0.00E+00	5.28E-08
	H						

	HQ _{INH}				2.98E-04	0.00E+00	
G03	ADI _{IN}	2.71E-08	9.54E-09	4.65E-08	1.77E-09	0.00E+00	7.34E-08
	H						
	HQ _{INH}				0.00E+00	0.00E+00	

For Adults

HEAVY METALS

Sample ID		Ni	Cu	Zn	Cr	As	Pb
Y01	ADI _{IN}	5.21E-15	2.21E-15	8.45E-15	5.29E-15	6.32E-16	1.41E-14
	H						
	HQ _{INH}				1.76E-10	2.11E-12	
Y02	ADI _{IN}	3.20E-15	2.80E-15	1.19E-14	2.23E-15	0.00E+00	1.72E-14
	H						
	HQ _{INH}				7.45E-11	0.00E+00	
Y03	ADI _{IN}	3.94E-15	5.90E-17	1.14E-14	1.83E-15	0.00E+00	8.54E-14
	H						
	HQ _{INH}				6.11E-11	0.00E+00	
S01	ADI _{IN}	2.44E-15	2.59E-15	8.89E-15	0.00E+00	0.00E+00	2.76E-14
	H						
	HQ _{INH}				1.64E-10	0.00E+00	
S02	ADI _{IN}	5.70E-09	6.05E-09	2.08E-08	0.00E+00	0.00E+00	6.44E-08
	H						
	HQ _{INH}				0.00E+00	0.00E+00	
S03	ADI _{IN}	6.07E-09	1.82E-09	1.05E-08	0.00E+00	0.00E+00	4.35E-08
	H						
	HQ _{INH}				0.00E+00	0.00E+00	
G01	ADI _{IN}	9.29E-15	6.41E-15	1.19E-14	1.35E-14	0.00E+00	2.36E-14
	H						
	HQ _{INH}				4.50E-10	0.00E+00	
G02	ADI _{IN}	7.08E-15	2.66E-15	1.08E-14	3.84E-15	0.00E+00	2.26E-14
	H						
	HQ _{INH}				1.28E-10	0.00E+00	

G03	ADI _{INH}	1.16E-14	4.09E-15	1.99E-14	7.59E-16	0.00E+00	3.15E-14
	HQ _{INH}				2.53E-11	0.00E+00	

Table 7: Calculated Result of Indices of Dermal Contact with Soil (ADI_{DERM}) and Corresponding Hazard Quotient (HQ_{DERM}) as a Result of Non-Carcinogenic Heavy Metals (a) In Children

HEAVY METALS							
Sample ID		Ni	Cu	Zn	Cr	As	Pb
Y01	ADI _{DERM}	4.05E-05	1.72E-05	6.57E-05	4.11E-05	4.91E-06	1.10E-04
	HQ _{DERM}	7.22E-03	7.17E-04	8.76E-04		1.64E-02	
Y02	ADI _{DERM}	2.49E-05	2.18E-05	9.25E-05	1.74E-05	0.00E+00	1.33E-04
	HQ _{DERM}	4.45E-03	9.08E-04	1.23E-03		0.00E+00	
Y03	ADI _{DERM}	3.06E-05	4.59E-07	8.88E-05	1.42E-05	0.00E+00	6.63E-04
	HQ _{DERM}	5.47E-03	1.91E-05	1.18E-03		0.00E+00	
S01	ADI _{DERM}	3.08E-05	1.77E-05	1.14E-04	3.82E-05	0.00E+00	2.08E-04
	HQ _{DERM}	5.50E-03	7.36E-04	1.52E-03		0.00E+00	
S02	ADI _{DERM}	1.90E-05	2.01E-05	6.91E-05	0.00E+00	0.00E+00	2.15E-04
	HQ _{DERM}	3.39E-03	8.39E-04	9.22E-04		0.00E+00	
S03	ADI _{DERM}	2.02E-05	6.06E-06	3.50E-05	0.00E+00	0.00E+00	1.45E-04
	HQ _{DERM}	3.61E-03	2.52E-04	4.67E-04		0.00E+00	
G01	ADI _{DERM}	7.22E-05	4.98E-05	9.27E-05	1.05E-04	0.00E+00	1.83E-04
	HQ _{DERM}	1.29E-02	2.07E-03	1.24E-03		0.00E+00	
G02	ADI _{DERM}	5.50E-05	2.07E-05	8.40E-05	2.98E-05	0.00E+00	1.76E-04
	HQ _{DERM}	9.83E-03	8.61E-04	1.12E-03		0.00E+00	

G03	ADI _{DERM}	9.02E-05	3.18E-05	1.55E-04	5.90E-06	0.00E+00	2.45E-04
	HQ _{DERM}	0.016115	0.001324	0.002064		0.00E+00	

(b) In Adult

HEAVY METALS

Sample ID		Ni	Cu	Zn	Cr	As	Pb
Y01	ADI _{DERM}	8.38E-06	3.56E-06	1.36E-05	8.52E-06	1.02E-06	2.27E-05
	HQ _{DERM}	1.50E-03	1.48E-04	1.81E-04	NA	3.39E-03	
Y02	ADI _{DERM}	5.16E-06	4.51E-06	1.92E-05	3.60E-06	0.00E+00	2.76E-05
	HQ _{DERM}	9.21E-04	1.88E-04	2.56E-04		0.00E+00	
Y03	ADI _{DERM}	6.34E-06	9.50E-08	1.84E-05	2.95E-06	0.00E+00	1.37E-04
	HQ _{DERM}	1.13E-03	3.96E-06	2.45E-04		0.00E+00	
S01	ADI _{DERM}	6.38E-06	3.66E-06	2.36E-05	7.90E-06	0.00E+00	4.32E-05
	HQ _{DERM}	1.14E-03	1.52E-04	3.14E-04		0.00E+00	
S02	ADI _{DERM}	3.94E-06	4.17E-06	1.43E-05	0.00E+00	0.00E+00	4.44E-05
	HQ _{DERM}	7.03E-04	1.74E-04	1.91E-04		0.00E+00	
S03	ADI _{DERM}	4.19E-06	1.26E-06	7.26E-06	0.00E+00	0.00E+00	3.00E-05
	HQ _{DERM}	7.48E-04	5.23E-05	9.68E-05		0.00E+00	
G01	ADI _{DERM}	1.50E-05	1.03E-05	1.92E-05	2.17E-05	0.00E+00	3.79E-05
	HQ _{DERM}	2.67E-03	4.30E-04	2.56E-04		0.00E+00	
G02	ADI _{DERM}	1.14E-05	4.28E-06	1.74E-05	6.17E-06	0.00E+00	3.64E-05
	HQ _{DERM}	2.04E-03	1.78E-04	2.32E-04		0.00E+00	
G03	ADI _{DERM}	1.87E-05	6.58E-06	3.21E-05	1.22E-06	0.00E+00	5.07E-05
	HQ _{DERM}	3.34E-03	2.74E-04	4.27E-04		0.00E+00	

Furthermore, consideration has been made to determine the carcinogenic impact of the heavy metal concentration from the different samples for both children and adult. As, Cd, Cr and Pb have been classified as Group 1 carcinogens by the International Agency for Research on Cancer (Hyun, Yeo and Young, 2015).

Table 8: Calculated Result of the Indices of Ingestion (ADI^*_{ING}), Inhalation (ADI^*_{INH}) and Dermal Contact with Soil (ADI^*_{DERM}) and Corresponding Carcinogenic Risks (CR_{ING} , CR_{INH} and CR_{DERM}) including the Total for Children and Adult ($CR_{ING-C(T)}$, $CR_{INH-A(T)}$) as a Result of Carcinogenic Heavy Metals Cr, As and Pb.

(a) Inhalation

Sample ID		CHILDREN				ADULT			
		Cr	As	Pb	$CR_{ING-C(T)}$	Cr	As	Pb	$CR_{ING-A(T)}$
Y01	ADI^*_{ING}	2.75E-05	3.29E-06	7.34E-05		1.47E-05	1.76E-06	3.93E-05	
	CR_{ING}	1.38E-05	4.93E-06	6.24E-07	1.93E-05	7.37E-06	2.64E-06	3.34E-07	1.03E-05
Y02	ADI^*_{ING}	1.16E-05	0.00E+00	8.92E-05		6.22E-06	0.00E+00	4.78E-05	
	CR_{ING}	5.81E-06	0.00E+00	7.58E-07	6.57E-06	3.11E-06	0.00E+00	4.06E-07	3.52E-06
Y03	ADI^*_{ING}	9.53E-06	0.00E+00	4.44E-04		5.11E-06	0.00E+00	2.38E-04	
	CR_{ING}	4.77E-06	0.00E+00	3.77E-06	8.54E-06	2.55E-06	0.00E+00	2.02E-06	4.57E-06
S01	ADI^*_{ING}	2.55E-05	0.00E+00	1.40E-04		1.37E-05	0.00E+00	7.47E-05	
	CR_{ING}	1.28E-05	0.00E+00	1.19E-06	1.40E-05	6.84E-06	0.00E+00	6.35E-07	7.47E-06
S02	ADI^*_{ING}	0.00E+00	0.00E+00	1.44E-04		0.00E+00	0.00E+00	7.69E-05	
	CR_{ING}	0.00E+00	0.00E+00	1.22E-06	1.22E-06	0.00E+00	0.00E+00	6.54E-07	6.54E-07
S03	ADI^*_{ING}	0.00E+00	0.00E+00	9.70E-05		0.00E+00	0.00E+00	5.2E-05	
	CR_{ING}	0.00E+00	0.00E+00	8.24E-07	8.24E-07	0.00E+00	0.00E+00	4.42E-07	4.42E-07
G01	ADI^*_{ING}	7.02E-05	0.00E+00	1.23E-04		3.76E-05	0.00E+00	6.56E-05	
	CR_{ING}	3.51E-05	0.00E+00	1.04E-06	3.62E-05	1.88E-05	0.00E+00	5.58E-07	1.94E-05
G02	ADI^*_{ING}	1.99E-05	0.00E+00	1.18E-04		1.07E-05	0.00E+00	6.3E-05	
	CR_{ING}	9.97E-06	0.00E+00	1.00E-06	1.10E-05	5.34E-06	0.00E+00	5.35E-07	5.88E-06
G03	ADI^*_{ING}	3.95E-06	0.00E+00	1.64E-04		2.11E-06	0.00E+00	8.77E-05	
	CR_{ING}	1.97E-06	0.00E+00	1.39E-06	3.36E-06	1.06E-06	0.00E+00	7.45E-07	1.80E-06

(b) Ingestion

Sample ID		CHILDREN				ADULT			
		Cr	As	Pb	CR _{INH-C(T)}	Cr	As	Pb	CR _{INH-A(T)}
Y01	ADI* _{INH}	1.06E-09	1.26E-10	2.82E-09		2.27E-15	2.71E-16	6.05E-15	
	CR _{INH}	4.34E-08	1.90E-08	1.19E-10	6.25E-08	9.29E-14	4.06E-14	2.54E-16	1.34E-13
Y02	ADI* _{INH}	4.47E-10	0.00E+00	3.43E-09		9.57E-16	0.00E+00	7.35E-15	
	CR _{INH}	1.83E-08	0.00E+00	1.44E-10	1.85E-08	3.93E-14	0.00E+00	3.09E-16	3.96E-14
Y03	ADI* _{INH}	3.67E-10	0.00E+00	1.71E-08		7.86E-16	0.00E+00	3.66E-14	
	CR _{INH}	1.50E-08	0.00E+00	7.17E-10	1.58E-08	3.22E-14	0.00E+00	1.54E-15	3.38E-14
S01	ADI* _{INH}	9.82E-10	0.00E+00	5.37E-09		2.1E-15	0.00E+00	1.15E-14	
	CR _{INH}	1.28E-05	0.00E+00	1.19E-06	1.40E-05	8.63E-14	0.00E+00	4.83E-16	8.68E-14
S02	ADI* _{INH}	0.00E+00	0.00E+00	5.52E-09		0.00E+00	0.00E+00	1.18E-14	
	CR _{INH}	4.03E-08	0.00E+00	2.25E-10	4.05E-08	0.00E+00	0.00E+00	4.97E-16	4.97E-16
S03	ADI* _{INH}	0.00E+00	0.00E+00	3.73E-09		0.00E+00	0.00E+00	7.99E-15	
	CR _{INH}	0.00E+00	0.00E+00	1.57E-10	1.57E-10	0.00E+00	0.00E+00	3.36E-16	3.36E-16
G01	ADI* _{INH}	2.70E-09	0.00E+00	4.71E-09		5.79E-15	0.00E+00	1.01E-14	
	CR _{INH}	1.11E-07	0.00E+00	1.98E-10	1.11E-07	2.37E-13	0.00E+00	4.24E-16	2.38E-13
G02	ADI* _{INH}	7.67E-10	0.00E+00	4.52E-09		1.64E-15	0.00E+00	9.69E-15	
	CR _{INH}	3.15E-08	0.00E+00	1.90E-10	3.16E-08	6.74E-14	0.00E+00	4.07E-16	6.78E-14
G03	ADI* _{INH}	1.52E-10	0.00E+00	6.29E-09		3.25E-16	0.00E+00	1.35E-14	
	CR _{INH}	6.22E-09	0.00E+00	2.64E-10	6.49E-09	1.33E-14	0.00E+00	5.66E-16	1.39E-14

(c) Dermal Contact

Sample ID		CHILDREN		ADULT	
		As	CR _{DERM-C(T)}	As	CR _{DERM-C(T)}
Y01	ADI* _{DERM}	4.21E-07		4.36E-07	
	CR _{DERM}	6.32E-07	6.32E-07	6.54E-05	6.54E-05
Y02	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Y03	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
S01	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
S02	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
S03	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
G01	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
G02	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00
G03	ADI* _{DERM}	0.00E+00		0.00E+00	
	CR _{DERM}	0.00E+00	0.00E+00	0.00E+00	0.00E+00

CONCLUSION

The Calculated values obtained of a seven (07) heavy Metals of interest of which they are Nickel (Ni), Copper (Cu), Zinc (Zn), Thallium (Ti), Chromium (Cr), Lead (Pb), and Arsenic (As); brings the average concentrations are 20.02, 12.59, 54.03, 1344.4, 21.94, 140.00, and an unidentified value of Arsenic in the studied area. All calculated values of the hazard index (HI) were within the range of the (USEPA) threshold limit of 1.0 indicating that the exposed population ages are unlikely to experience any Cancer risks. But the overall excess lifetime cancer risk for a heavy metal was $8.5555E-06$ (a maximum of 9 people per 1 million may be affected) for children and $7.5773E-05$ (a maximum of 8 people per 1 million may be affected) for adults; Further studies need to be carried out on other sites of Kaolin mining in Nigeria, for cosmetic, medicinal and construction materials made from Kaolin.

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