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Assessment of heavy metals contamination and pollution around mining sites of Anka, north-west Nigeria

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Abstract. Artisanal mining is a common practice in Anka communities, North-West Nigeria, and this has brought about serious environmental and health concerns in the area. This study assessed the concentration of heavy metals in the rocks, soils, sediments and plants in the mining environment of Anka. Thirty two samples were collected and analysed for K, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb using Energy Dispersive X-ray Fluorescence. The results obtained showed the heavy metal concentration in rock > soil > sediment > plant. The evaluation of the contamination factor in soil and sediment revealed that all the samples were severely contaminated. The results of geo-accumulation index revealed that the contamination with heavy metals was generally higher in rock and soil; followed by sediment while plant samples accounted for the least contamination. The result of the contamination factor and pollution index of soil and sediment indicated severe contamination and pollution respectively. The contamination assessment was complemented with the use of contamination degree and the modified contamination degree indices. The assessment of contamination factor and potential ecological risk from heavy metal in both soil and sediment was shown to come majorly from Pb, Ni and Cu. Active mining sites found in Dareta, Daki Takwas, Dan Kamfani and the processing areas of Abare, Dan Kamfani, Dateta and Abare were identified as areas with high heavy metal pollution risk. These results generally show that artisanal mining and processing in the study area pose significant environmental risk to the local population and the environment.

Keywords: Anka; Artisanal mining, Contamination, Concentration, Geo-accumulation index, Heavy metal

Abbreviations: EDXRF - Energy Dispersive X-ray Fluorescence; QXAS - Quantitative Analysis of X-ray Spectroscopy; MTL – Maximum Tolerable Limit; ND – Not Detected; RK – Rock; SL – Soil; SD – Sediment; PT – Plant/Vegetable

1. INTRODUCTION

The Earth environment serves as a reservoir for several resources, which also comes in the form of solid, liquid or gas. The presence of heavy metals in the environment comes from both natural and anthropogenic sources; the natural sources include weathering of metal-containing rocks and volcanic eruptions while anthropogenic sources include agricultural activities, mining, industrial emissions and smelting (Ali et al., 2019; Udiba et al., 2019). The concentration of mineral deposits in the earth varies according to the geological formation, altitude and the anthropogenic activities; this variation is largely responsible for the uneven distribution of elements and other natural resources in the Earth environment (Joshua et al., 2009).

Heavy metal contamination of soil has been identified as a primary origin of metals in plants/vegetables, which finally finds its way into the food chain (Gebeyehu and Bayissa, 2020). This could be as a result of migration and release into the surface and subsequent incorporation into the food chain. Vegetable plants take up these heavy metals by absorbing them from the air, polluted environments and contaminated soils (Kachenko & Singh, 2006). According to Kapile and Matundi (2016), plant uptake of Cu and Zn as essential micronutrients is higher than that of toxic elements such as Cd and Pb. Studies have shown that heavy metals such as Co, Cr, Cu, Fe, Mg, Mn, Mo,

Se and Zn have nutritional value while Cd, Pb, Hg and Ni are said to have no known nutritional value (Kacholi and Sahu, 2018; USEPA, 2009).

In Anka, gold is mined from gold-bearing deposits containing an unusually problematic concentration of lead and other heavy metals. The crushing of rocks in dry running flour mills produces enormous amounts of dust which in some places is highly contaminated with lead and other heavy metals. Hence, mining and ore processing is accompanied by major negative physical, biological, hydrological as well as environmental impacts. Environmental and health problems have been reported in the study area and there are speculations that this could be as a result of local and crude mining activities. According to Udiba et al. (2019), mining generally generates volumes of mineral waste such as waste rocks or tailings, as the materials of interest are often surrounded by other ores and rocks during mining.

Moreover, toxic contamination from the mined ores and the waste arising from the processing mills find their way into the natural environment thereby affecting air, arable land (soil), habitat and water (Merem et al., 2017). As a result of this heavy metal contamination, there have been reported cases of deaths, mostly among children of ages 0 - 5 years (Innocent et al., 2013; Dooyema et al., 2012). The number of fatalities was put at over 400 children (IGF, 2017). These fatalities and other illnesses reported were attributed to heavy metal pollution (Tirima et al., 2016; Kaufman et al., 2012). Acute lead toxicity is also said to be destroying the biodiversity¹³ (Uduma and Jimoh, 2014).

The study of heavy metal contamination is aimed at identifying the particular heavy metals responsible and potential areas of contamination. The study area is an agricultural region of Anka in the present Zamfara State, North-West Nigeria. Over the past years, Anka has been greatly exploited and degraded due to artisanal mining activities. Traditionally, most villagers rely on farming to earn a living, however, some areas are also rich in mineral resources, such as gold hosted in lead-zinc ores. Hence, artisanal mining and crude value addition (processing) is also one of the thriving enterprises in the area.

Therefore, the prime objective of this work to determine the concentration of heavy metal (K, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb) in rock, soil, sediment and plant samples in Anka, North-West Nigeria. This study is also aimed at evaluating the risk of heavy metals in soil and sediments using different contamination, pollution and ecological risk indices. The study will help in understanding the effect of artisanal mining on the environment.

2. MATERIALS AND METHOD

2.1 Study Area

The study was carried out in artisanal mining and mineral processing communities of Anka, North-West Nigeria. Anka lies between latitude 11°51'N and 12°08'N, and longitude 5°51'E and 6°08'E and covers an area of 2,940 km² (Akpanowo et al., 2019). The map of Anka showing the study area is shown in Figure 1. The geology of Anka is characterized by the Anka schist belt that hosts the lead mineralization, and the lead-copper-silver-gold poly-metallic association (Buba, 2016). Anka, like some other similar geological belts in Nigeria, has been the focus of artisanal gold exploitation for several decades. Gold found in Anka is hosted by schists, phyllites and quartzites associated with sub-regional structural elements subsidiary to the Anka fault (Waziri and Andrews, 2013).

2.2 Sampling and Sample Preparation

A total of Thirty Two samples were collected from the study area; the Thirty two samples consisted of 6 rocks, 15 soils, 8 sediments and 3 plants/vegetables. The edible parts of plant leaves were considered and the samples were collected in October 2018 and November 2019, when most of plant/vegetable had reached maturity. Majority of the samples were collected within 200 m of the mining and mineral processing sites in Dareta, Abare, Dan Kamfani and Daki Takwas communities (Figure 1). After collection, all the samples were conveyed to the laboratories at the Centre for Energy Research and Training (CERT) for sample preparation.

Initial sample preparation was carried out at the Material Science laboratory at the Centre for Energy Research and Training, Zaria, Nigeria. The rock, soil and sediment samples were oven- dried between 120 and 150°C, while the plant samples were dried at room temperature of about 22 to 25°C to avoid ashing. The samples were ground into fine powder using agate mortar and pestle, made of 99% silica to avoid contamination. The ground samples were sieved through a Test Sieve through an aperture of 250 µm to achieve the greatest possible homogeneity and to prevent low concentration associated with large samples (Zhu and Shaw, 2000). About 200 g of the dried sample was weighed using the Sartorius (CP622) weighing balance and packaged for onward transfer for laboratory analysis.

Figure 1. A 2-Dimensional Arc-GIS Map of Anka showing studied area (Akpanowo et al., 2019).

2.3 X-Ray Fluorescence (XRF) Elemental Analysis

Thirty-two samples (6 rocks, 15 soils, 8 sediments and 3 plants/vegetables) were analyzed for elemental composition at the Centre for Energy Research and Development (CERD), Ile-Ife, Nigeria. The AMPTEK^(R) Energy Dispersive X-ray Fluorescence (EDXRF) system was employed for the analysis.

Before the analysis, certified Soil-7 reference standards were irradiated for calibration purposes using the following parameters: For potassium (K), the certified and experimental values were the same, 12100 ppm; for iron (Fe), the certified and experimental values were also the same, 25700 ppm; however the certified and experimental values for Zirconium (Zr) were 185 ppm and 184.96 ppm respectively. Sample analysis was done by exposing the samples in the sample holder of the XRF system and bombarded by X-ray fluorescence spectrometer with a silver (Ag) anode at a voltage of 25 kV and current of 50 μ A for 1000 seconds or 16.67 minutes in an external chamber setup (Oyedotun, 2018).

The instrumentation of the EDXRF spectrometry system, the x-ray released from the sample strikes directly on the solid-state lithium floated silicon detector. The detector is capable of discriminating the x-ray spectra tens to thirty elements simultaneously (Oyedotun, 2018); hence, the simultaneous analysis of the elements in the periodic table can be achieved.

Characteristic X-ray of the sample was detected by the solid-state Si-pin detector system and spectrum acquisition was done using an Amptek model multi-channel analyzer while elemental analysis was done using the thick target mode of the International Atomic Energy Agency (IAEA) Quantitative Analysis of X-ray Spectroscopy (QXAS) software. The resolution of the detector system of the EDXRF was 220 eV FWHM for the 5.9 keV peak of ⁵⁵Fe. The detector was attached to a Multichannel Analyzer with model number MCA8000A, which was used to acquire data and process signals.

2.4. Environmental Risk Assessment

This work employed some well-known single and multiple contamination/pollution indices to analyze the concentration of heavy metals in the study area. These include contamination factor (Cf), Contamination degree (C_d), modified Contamination degree (C_d), geo-accumulation index (I_{geo}) and pollution index (PI)

2.4.1. Contamination Factor (Cf)

According to Brady et al. (2015) the application contamination factor (Cf) is the most direct method of determining the sediment or soil quality. It is the ratio of an element in a sampling site to the background value of the element and it is calculated as:

$$Cf = \frac{C_s}{C_b} \quad (1)$$

where C_s is the concentration of the element of interest at a site and C_b is the reference concentration of the same element at a control site.

2.4.2. Geo-accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}) is commonly applied in the evaluation of the extent of contamination or pollution in the terrestrial and marine environment by heavy metals (Okedeyi et al., 2014). The I_{geo} was calculated by Equation 1 following the studies of Santos-Francés et al. (2017); Fosu-Mensah et al. (2017); Okedeyi et al. (2014) and Nowrouzi and Pourkhabbaz, (2014):

$$I_{geo} = \log_2 \left(\frac{C_n}{B_n \times 1.5} \right) \quad (2)$$

where C_n is the measured concentration of the n metal examined in the soil, and B_n is the background level of the n metal. The factor 1.5 was used to correct possible variations in the background values of a particular metal in the environment. The quantity I_{geo} was calculated using the global average shale data reported by Nowrouzi and Pourkhabbaz (2014).

2.4.3. Contamination Degree Index (C_d)

The contamination degree index was proposed by Hakanson (1980) for the quantifying the degree of contamination of elements due to the limitation of single element pollution indices. It is given as the sum of the Cf for each sample:

$$C_d = \sum_{i=1}^n Cf_i \quad (3)$$

where Cf_i is the contamination factor of the *i*th element.

2.4.4. Modified Contamination Degree Index (mC_d)

The Hakanson's contamination degree (C_d) index was modified by Brady et al. (2016) to assess the overall contamination degree at particular site by heavy metal. The modified contamination degree (mC_d) is given as the sum of the contamination factors (Cf) for a particular set of heavy metal divided by the number of heavy metals analyzed. This is given by:

$$mC_d = \frac{\sum_{i=1}^n Cf_i}{n} \quad (4)$$

where *n* is the number of analyzed heavy metals and *i* is the *i*th heavy metal.

2.4.5. Pollution Index (PI)

The pollution index indicates the quality of sediment (soil) and was developed by Nemerow to take into consideration the effect of a single element contamination (Brady et al., 2016; Nemerow, 1991). This is similar to the modified contamination degree index but it is calculated based on the average values of the contamination factors (Cf_{average}) and the maximum contamination factor (Cf_{max}).

$$PI = \sqrt{\frac{(Cf_{average})^2 + (Cf_{max})^2}{2}} \quad (5)$$

The corresponding threshold values of contamination factor (Cf), Contamination degree (C_d), modified Contamination degree (C_d), geo-accumulation index (I_{geo}) and pollution index (PI) are presented in Table 1.

Table 1. Threshold values for Contamination/Pollution Indices in Soil and Sediment

Class	Contamination/ Pollution level	I_{geo}	Cf	C_d	mC_d	PI
0	Unpolluted	≤ 0	$Cf < 1$		$C_d < 1.5$	$PI < 0.7$
1	Slightly	$0 < I_{geo} < 1$		$mC_d < 6$	$1.5 < mC_d < 2$	$0.7 < PI < 1$
2	Moderately	$2 < I_{geo} < 3$	$1 < Cf < 3$	$6 \leq mC_d \leq 12$	$2 \leq mC_d \leq 4$	$1 < PI < 2$
3	Moderately –Strongly	$3 < I_{geo} < 4$			$4 \leq mC_d \leq 8$	
4	Strongly	$4 < I_{geo} < 5$	$3 < Cf < 6$	$12 \leq mC_d \leq 24$	$8 \leq mC_d \leq 16$	$2 < PI < 3$
5	Severely	$4 < I_{geo} < 5$	$Cf > 6$	$mC_d > 24$	$16 \leq mC_d \leq 32$	$PI > 3$
6	Extremely	$I_{geo} \geq 5$			$mC_d > 32$	

Abbreviation: C_d – Contamination degree; PI – Nemerow pollution index; I_{geo} – Geo-accumulation index; Cf – Contamination factor (Adapted from Kolawole et al., 2018; Brady et al., 2015)

2.4.6. Potential Ecological Risk Index

Hakanson proposed Potential Ecological Risk Index (RI) to evaluate the hazard of heavy metal in soil and sediments (Guo et al., 2010; Hakanson, 1980). The primary function of the index is to point out the heavy responsible for the contamination of the environment to allow for streamlined studies (Sivakumar et al., 2016).

Ecological risk factor (E_r) is used to assess the toxicity of individual heavy metals in soils and sediments (Santocs-Francés et al., 2017). The Ecological risk factor (E_r) is expressed as:

$$E_r^i = T_r^i \times C_f \quad (6)$$

where C_f is the contamination factor and T_r^i is the toxic response factor. Hakanson had given a set of values for Cr, Mn, Ni, Cu, Zn and Pb as 2, 1, 5, 5, 1 and 5 respectively (Kolawole et al., 2018; Hakanson, 1980). Therefore, the potential ecological risk index (RI) is expressed:

$$RI = \sum_{i=1}^n E_r^i \quad (7)$$

The classification of potential ecological risk index and ecological risk factor is presented in Table 2.

Table 2. Ecological risk Factor and Potential ecological Risk Index for Pollution Level Assessment

Level of Ecological Risk	Ecological Risk Factor (E_r^i)	General level of Potential Ecological Risk	Potential Ecological Risk Index (RI)
Low	$E_r^i < 40$	Low	$RI < 150$
Moderate	$40 < E_r^i < 80$	Moderate	$150 \leq RI < 300$
Considerable	$80 < E_r^i < 160$	High	$300 \leq RI < 600$
High	$160 < E_r^i < 320$	Very high	$RI \geq 600$
Very High	$E_r^i \geq 320$		

(Adapted from Kolawole et al., 2018; Guo et al., 2010)

3. RESULTS AND DISCUSSION

3.1. Analysis of Elemental Concentration

The results obtained for the various samples are presented in Table 3 for rocks, Table 4 for Soils, Table 5 for Sediments and Table 6 for plant/vegetables.

The samples were collected from Dareta 3 and Dareta 1 respectively. Dareta 1 seemed to present the highest concentrations for most of the elements while Dareta 3 presented the least concentrations as indicated in Table 3. The elemental Fe concentration for rock samples ranged from 750 to 296090 mgkg^{-1} , K ranged from 33290 to 256910 mgkg^{-1} , V ranged 472 to 3125 mgkg^{-1} , Cr ranged 343 to 2548 mgkg^{-1} and Mn ranged from 80 to 11140 mgkg^{-1} . The concentration of Ni ranged from 223 to 394 mgkg^{-1} , Cu ranged from 126 to 8574 mgkg^{-1} and Zn ranged from 59 to 357 mgkg^{-1} . The concentration of lead (Pb) ranged from 7 to 6675 mgkg^{-1} .

The summary of the concentrations for the 15 soil samples is presented in Table 4. From the result of elemental concentration, Fe ranged from 360 to 390090 mgkg^{-1} , K ranged from 20180 to 359810 mgkg^{-1} , V ranged from 201 to 4678 mgkg^{-1} and Cr ranged from 473 to 4955 mgkg^{-1} . The concentration of Mn ranged from 380 to 19380 mgkg^{-1} , Ni ranged from 124 to 255000 mgkg^{-1} , Cu ranged from 130 to 3567 mgkg^{-1} and Zn ranged from 43 to 665. For Pb, the minimum concentration of 16 mgkg^{-1} was measured in Dan Kamfani while the maximum of 2629 mgkg^{-1} was obtained from Dareta 4.

Table 5 summarizes the concentration of elements determined for sediment samples. The Eight (8) sampling sites including Abare (3 locations), Anka town, Anka River, Dan Kamfani and Dareta (2 locations). The values of

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elemental concentration for K ranged from 19200 to 223700 mgkg⁻¹, V ranged from 455 to 5311 mgkg⁻¹, Cr ranged from 381 to 3282 mgkg⁻¹ and Mn ranged between 700 and 18900 mgkg⁻¹. Additionally, the concentration of Fe ranged 26800 to 547900 mgkg⁻¹, Ni ranged from 138 to 302 mgkg⁻¹, Cu from 138 to 970 mgkg⁻¹ and Zn ranged from 55 to 469 138 to 970 mgkg⁻¹.

Table 3. XRF Elemental Concentration in Rock samples (mgkg⁻¹)

Sample ID	K	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
RK 1	39440	564	721	1510	38200	374	126	118	43
RK 2	49990	598	538	4060	57570	253	289	124	64
RK 3	256910	1893	2169	11140	296090	394	8574	248	6675
RK 4	34200	572	343	650	22490	311	132	59	7
RK 5	33290	472	472	80	750	278	136	74	11
RK 6	219510	3125	2548	9640	252410	223	5864	357	4719
Mean	105556.7	1204.0	1131.8	4513.3	111251.7	305.5	2520.2	163.3	31.3
Max	256910	3125	2548	11140	296090	394	8574	357	64
Min	33290	472	343	80	750	223	126	59	7
SD	103601.7	1084.2	965.4	4774.9	128373.2	67.6	3739.7	115.9	27.1

Table 4. XRF Elemental Concentration in Soil Samples (mgkg⁻¹)

Sample ID	K	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
		3301							
SL 1	38390	539	902	8500	223400	338	2563	463	1922
SL 2	31910	3290	1278	500	360	356	288	98	147
SL 3	124230	3849	4955	11900	367500	130	490	485	30
SL 4	114650	3209	964	6380	291600	202	1419	496	990
SL 5	151600	3583	591	12400	340600	282	1627	665	912
SL 6	129580	201	516	1800	90000	3495	1175	479	141
SL 7	29920	478	530	380	23500	23480	130	43	18
SL 8	32650	526	540	740	44800	331	152	62	17
SL 9	37150	2822	473	1040	35900	212	239	200	73
SL 10	136230	638	837	11330	338290	318	615	485	36
SL 11	20180	4029	584	1040	44820	367	188	108	16
SL 12	61790	3543	789	7150	250990	328	1056	567	155
SL 13	359810	4678	3099	19380	390090	124	1694	304	587
SL 14	159610	2420	913	6440	255000	12480	3567	549	2599
SL 15	181910		1421	5840	280860	251	3259	428	2629
Mean	107307.3	2473.7	1226.1	6321.3	198514.0	19014.3	1230.8	362.1	684.8
Min	20180	201	473	380	360	124	130	43	16
Max	359810	4678	4955	19380	390090	23480	3567	665	2629
SD	89552.6	1549.5	1222.1	5643.8	142015.2	6539.5	1135.5	207.2	947.0

Pb recorded the minimum concentration of 7 mgkg⁻¹ at Anka Town while the maximum was recorded at Dan Kamfani 2 with a value of 187 mgkg⁻¹. Generally, the least concentrations per site was recorded against Anka

Town while the highest was recorded Dan Kamfani 2. The elemental concentration for samples collected from Abare 2 and Anka River was low.

The elemental concentrations measured from plant samples are summarized in Table 6. Samples were collected from 3 locations, including Abare, Daki Takwas and Dareta. From the data presented, the minimum concentration of K was 15470 mgkg⁻¹ while the maximum was 87430 mgkg⁻¹. The Concentration of V ranged from 134 to 3672 mgkg⁻¹, Cr ranged from 311 to 1240 mgkg⁻¹, Mn ranged from 380 to 10780 mgkg⁻¹ and Fe ranged from 24450 to 172670 mgkg⁻¹.

Table 5. XRF Elemental Concentration in Sediment Sample (mgkg⁻¹)

Sample ID	K	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
SD 1	176300	3723	1010	18000	426900	217	579	295	102
SD 2	26700	543	381	1500	39700	251	225	55	99
SD 3	215000	5312	916	8700	266800	138	600	279	85
SD 4	23100	563	389	700	33900	302	161	73	7
SD 5	19200	455	435	1600	41400	221	138	65	12
SD 6	180100	3872	964	1500	97600	260	759	332	164
SD 7	223700	3317	3282	18900	547900	239	970	469	187
SD 8	23200	610	386	990	26800	293	186	67	17
Mean	110912.5	2299.4	970.4	6486.3	185125.0	240.1	452.3	204.4	84.1
Min	19200	455	381	700	26800	138	138	55	7
Max	223700	5312	3282	18900	547900	302	970	469	187
SD	95262.9	1962.8	975.5	7827.2	204985.5	51.4	317.6	159.4	68.8

Table 6. XRF Elemental Concentration in Plants (mgkg⁻¹)

Sample ID	K	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
PT 1	15510	134	311	380	24450	241	103	39	12
PT 2	87430	3672	1240	2800	172670	291	979	648	97
PT 3	15470	571	521	10780	74930	226	95	38	15
Mean	39470.0	1459.0	690.7	4653.3	90683.3	252.7	392.3	241.7	41.3
Max	87430	3672	1240	10780	172670	291	979	648	97
Min	15470	134	311	380	24450	226	95	38	12
SD	41534.6	1928.9	487.2	5442.1	75355.3	34.0	508.1	351.9	48.2

Additionally, the concentration of Ni ranged from 226 to 291 mgkg⁻¹, Cu ranged from 95 to 979 mgkg⁻¹ and Zn ranged from 38 to 648 mgkg⁻¹. The range of Pb concentration was recorded as 12 mgkg⁻¹ (Abare) to 97 mgkg⁻¹ (Daki Takwas). Among the sampled location, plant/vegetables from Abare recorded the least elemental concentration while Daki Takwas recorded the highest concentrations. The low concentration in plant in Abare could be as a result of use of natural stream water in the sluicing of the ores, thereby reducing the concentration in soil and possible increasing it in water and sediment. On the other hand, there is no natural stream in Daki Takwas, hence the waste water and mine tailing are dumped on farmland.

Therefore, the variation in concentration could be linked to waste disposal strategy; in areas where there are streams and rivers, the waste generated from the mineral processing is disposed along the streams, which also poses addition problem to the aquatic environment. Where there are no rivers or streams, contaminated waste are disposed on farmlands, thereby polluting the soil and the plants.

As shown in Table 8, the maximum mean concentrations in Cu and Pb with 2520 mgkg⁻¹ and 1920 mgkg⁻¹, were recorded against rock samples while soil samples accounted for the maximum mean concentration in Cr, Mn, Fe, Ni, Zn. On the other hand, the minimum mean concentrations were recorded against plant samples, except for Mn which value was marginally lower in rock samples.

From the mean concentrations of elements for all the samples, there seems to a trend exists; while K and Fe have higher concentrations, the concentrations of Cr, Ni, Cu, Zn, and Pb were observed to be lower. The variation in the concentration of elements in the samples could be due to the distribution of elements in the various media, the geology of the study area, which is dominantly schist, hosting the lead mineralization, and the lead-copper-silver-gold poly-metallic association (Buba, 2016). The high concentration of K could be attributed to the application of fertilizers for agricultural purposes. The elemental concentration could be linked to the disparity in the parent materials at the various sampling sites and other factors such as hydrology and the actual mining and

processing locations, which is in agreement with the argument put forward by Towett et al. (2015) as shown in Table 7.

Table 7. Mean elemental concentration in rock, soil, sediment and plant measured in mg/kg and those of other studies in the world

Description	Mean Elemental Concentration (mg/kg)								
	K	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Rock	105557	1204	1132	4513	111252	305	2520	163	1920
Soil	107307	2470	1401	6321	198514	2846	1231	362	685
Sediment	110913	2299	971	6486	185125	240	452	204	84
Plant	39470	1459	690	4653	90683	253	392	242	42
Okpoko (Nig) ^a				17.1	1437.1	1.52	9	24.55	9.58
Soil (Africa) ^b	15000	100	60	1400	45900	20	30	80	15
Soil (Africa) ^c	10893	37	64	466	27954	19	17	29	37
Ethiopia ^d	-	-	36.23	1763	46426.7	35.38	25.96	98.86	37.92
Tanzania ^e	-	-	-	-	2796.6	-	17.8	307.1	22.4
Bangladesh ^f	9706	2760	874	12236	957533	-	-	11640	-
World Mean ^g	-	60	42	418	-	18	14	62	25
MTL ^h	-	-	400	-	-	-	30	60	100

^a Nwankwoala and Ememu, 2018

^b Towett et al., 2013

^c Towett et al., 2015

^d Gebeyehu and Bayissa, 2020

^e Kacholi and Sahu, 2018

^f Rahman et al., 2015

^g Reported by Towett et al., 2015

^h Reported by Kapile and Makundi, 2016

The concentration of elements in this study for soil was compared with other studies carried out in the world and is presented in Table 7. The trend of elemental concentrations in soil were obtained as Fe > K > Ni > Mn > Cr > V > Cu > Pb > Zn. This does not translate to the fact the concentration of the elements such as Cu, Pb and Zn were low. Kapile and Makundi, (2016) reported the tolerable maximum limits of some chemically toxic elements in soil measured in mgkg⁻¹ as follows: Cu (30), Zn (60), Pb (100) and Cr (400) as shown in Table 6. The results of the study exceed these limits, which suggest very high toxicity levels despite the seemingly low concentration compared to Fe, K and Ni. Exposure to metal/metalloid mixtures of Pb, Cr and Cd have been reported to produce more severe effects at both relatively high dose and low dose levels (Tchounwou et al., 2012). K and a couple of elements are regarded as nutrients to the plants/vegetables and much less toxic.

Furthermore, the results obtained were generally higher than those of other studies. Hence, the results for K, Cr, V, Ni, Zn, and Pb were highest among elements determined and well above the world mean values given in Table 6. The mean concentration of Mn was 6321 mgkg⁻¹ obtained in this study was higher than the world mean of 418 mgkg⁻¹ and the results reported by Towett et al. (2015; 2013) but lower than that reported by Rahman et al. (2015) for Bangladesh. For Cr, the mean concentration in soil was 1401 mgkg⁻¹; the value was many times higher than the MTL of 400 mgkg⁻¹ (Kapile and Makundi, 2016) as well as results reported in Africa by Towett et al. (2015) and in Bangladesh by Rahman et al. (2015).

Pb recorded a mean concentration of 685 mgkg⁻¹ for soil, which is greater than the World mean of 25 mgkg⁻¹ and the maximum tolerable limit of 100 mgkg⁻¹. The mean concentration of Pb presented by Udiba et al. (2019) in Dareta was higher than those obtained in this study; 1404.57±141.00 mgkg⁻¹ and 6724.68±84.00 mgkg⁻¹ obtained from abandoned and active processing mills, respectively. The concentration of Pb obtained from rock in Dareta 1 and Dareta 4 was 6675 and 4719 respectively, which is much similar to the result by Udiba et al. (2019). This is a proof that the mined rock ores contribute significantly to the high concentrations of Pb in Dareta and Anka in general.

Similarly, the mean concentration of Cu obtained in this study (1231 mgkg⁻¹) was higher than the world mean and the maximum tolerable limit (Kapile and Makundi, 2016) as well as those reported by Towett et al. (2015, 2013) as presented in Table 7.

The data obtained from studies conducted by Rahman et al. (2015) in Bangladesh showed that the mean elemental concentrations in soil for Fe (957533 mgkg^{-1}) and Zn (11640 mgkg^{-1}), were higher than other studies, including the present study with 198514 mgkg^{-1} and 362 mgkg^{-1} respectively. Conversely, Ni recorded 19014 mgkg^{-1} as the mean concentration in soil; the world mean and the results presented by Towett et al. (2015, 2013) all ranged between 18 and 20 mgkg^{-1} .

Table 8. Mean Elemental Concentration and Geo-accumulation of heavy metals

Mean Elemental Concentration (mgkg^{-1})							
Sample	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Rock	1132	4513	111252	306	2520	163	1920
Soil	1226	6321	198514	2846	1231	362	685
Sediment	970	6486	185125	240	452	204	84
Plants	691	4653	90683	253	392	242	41

Geo-accumulation Index							
Sample	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Rock	3	2	4	2	5	0.2	6
Soil	3	2	5	5	4	1	5
Sediment	3	2	5	1	3	0.5	1
Plants	2	2	4	1	2	0.8	0.5

The result of Nwankwoala and Ememu, (2018) on Okpoko, Southeastern Nigeria shows the least concentrations of heavy metals in soil when compared to the present study. This is commonly as a result of the difference in geological formation in the study areas. The southeastern region of Nigeria is known to have a sedimentary formation, where sandstone and shale can be found compared to the basement complex formation in North-West Nigeria (Joshua et al., 2009). Moreover, the mining and mining processing activities contribute significantly to the high heavy metal concentration in the study area. This position is supported by Udiba et al. (2019).

The concentrations obtained in this study are well beyond the maximum tolerable limits. Hence, appropriate measures should be taken to create awareness on the hazards of the toxic elements in the mining and processing areas. Measures should be taken in protecting the local population (especially children) from undue contamination from these heavy metals.

3.2. Assessment of Single Element Indices

For single element analysis, the contamination factor (C_f) and the geo-accumulation index (I_{geo}) were employed. The computed contamination factor of different heavy metals analyzed for soil and sediment in the study area is presented in Table 9 and Table 10 respectively. Figure 2 shows that the soil is severely contaminated with Ni (41.86), Pb (34.32), Cu (24.61), Cr (12.26) and Mn (7.43) in their respective order. Only Zn (3.81) is shown to be strongly contamination.

The sediments show severe contamination from Cr, Cu and Mn with C_f of 9.70, 9.05 and 7.63 respectively. Pb (4.21) and Ni (3.53) fell within the category of strongly contaminated and moderately contaminated with Zn.

Generally, the C_f of computed in soil is higher than that of sediments as shown in Figure 3; this is because the enrichment of heavy metal in soil is higher than in sediments. Hence, the enrichment of heavy metals higher in soil is than in sediments.

The geo-accumulation indices of some heavy metals were calculated to assess the level of contamination of the samples and by extension, the artisanal mining environment, the threshold values are presented on Table 1. The extent of metal contamination is assessed in terms of geo-accumulation index; this has been divided into seven classes based on the increasing numerical value of the index according to Kolawole et al. (2018), Brady *et al.* (2015) and Al-Haidarey (2010). The classification of the geo-accumulation index ranges from uncontaminated to very strongly contaminated.

The highest index of 7 was recorded for Ni from soil sample while the least index of 0.2 was recorded for Zn from rock sample. For Cr, the I_{geo} was 3 for rock, soil and sediment samples indicating moderately to strongly contaminated while plant/vegetable returned an index of 2, meaning moderately contaminated. The value of I_{geo} for Mn was 2 for all the samples, it is moderately contaminated. Rock and Plant samples recorded an index of 4 for Fe

signifying strongly to severely contaminated. The I_{geo} for soil and sediment was 5, which means severely contaminated.

Figure 2. Contamination factor of soil and sediment in Anka

Figure 3. Relationship between contamination degree and the modified contamination degree in soil

For Ni, the I_{geo} was 2 for rock (moderately contaminated), 7 for soil (extremely contaminated), 1 for plant/vegetables and sediment (slightly contaminated). The geo-accumulation index for Cu decreased according to the samples; rock (5), soil (4), sediment (3) and plant/vegetable (2). This implies that the level of contamination decrease from extremely contaminated in rock to moderately contaminated in plant/vegetable.

Table 9. Contamination factor (C_f), Contamination Degree (C_d), Modified Contamination Degree (mC_d) and Pollution Index (PI) of Soil in Anka, North West Nigeria

Sample ID	Contamination factor (C_f)						C_d	mC_d	PI
	Cr	Mn	Ni	Cu	Zn	Pb			
SL 1	9.02	10.00	4.97	51.26	4.87	96.10	176.22	29.37	71.06
SL 2	12.78	0.59	5.24	5.76	1.03	7.35	32.75	5.46	9.83
SL 3	49.55	14.00	1.91	9.80	5.11	1.50	81.87	13.64	36.34
SL 4	9.64	7.51	2.97	28.38	5.22	49.50	103.22	17.20	37.06
SL 5	5.91	14.59	4.15	32.54	7.00	45.60	109.79	18.30	34.74
SL 6	5.16	2.12	51.40	23.50	5.04	7.05	94.27	15.71	38.00
SL 7	5.3	0.45	345.29	2.60	0.45	0.90	354.99	59.17	247.72
SL 8	5.4	0.87	4.87	3.04	0.65	0.85	15.68	2.61	4.24
SL 9	4.73	1.22	3.12	4.78	2.11	3.65	19.61	3.27	4.09
SL 10	8.37	13.33	4.68	12.30	5.11	1.80	45.58	7.60	10.85
SL 11	5.84	1.22	5.40	3.76	1.14	0.80	18.16	3.03	4.65
SL 12	7.89	8.41	4.82	21.12	5.97	7.75	55.96	9.33	16.33
SL 13	30.99	22.80	1.82	33.88	3.20	29.35	122.04	20.34	27.94
SL 14	9.13	7.58	183.53	71.34	5.78	129.95	407.30	67.88	138.37
SL 15	14.21	6.87	3.69	65.18	4.51	131.45	225.91	37.65	96.69
Mean	12.26	7.44	41.86	24.62	3.81	34.24	124.22	20.70	51.86
Min	4.73	0.45	1.82	2.60	0.45	0.80	15.68	2.61	4.09
Max	49.55	22.80	345.29	71.34	7.00	131.45	407.30	67.88	247.72
SD	12.22	6.64	96.17	22.71	2.18	47.35	120.41	20.07	66.13

Table 10. Contamination factor (C_f), Contamination Degree (C_d), Modified Contamination Degree (mC_d) and Pollution Index (PI) of Sediment in Anka, North West Nigeria

Sample ID	Contamination factor (C_f)						C_d	mC_d	PI
	Cr	Mn	Ni	Cu	Zn	Pb			
SD 1	10.1	21.18	3.19	11.58	3.11	5.10	54.25	9.04	16.28
SD 2	3.81	1.76	3.69	4.50	0.58	4.95	19.29	3.22	4.17
SD 3	9.16	10.24	2.03	12.00	2.94	4.25	40.61	6.77	9.74
SD 4	3.89	0.82	4.44	3.22	0.77	0.35	13.49	2.25	3.52
SD 5	4.35	1.88	3.25	2.76	0.68	0.60	13.53	2.25	3.46
SD 6	9.64	1.76	3.82	15.18	3.49	8.20	42.10	7.02	11.83
SD 7	32.82	22.24	3.51	19.40	4.94	9.35	92.26	15.38	25.63
SD 8	3.86	1.16	4.31	3.72	0.71	0.85	14.61	2.43	3.50
Mean	9.70	7.63	3.53	9.05	2.15	4.21	36.27	6.04	9.77
Max	32.82	22.24	4.44	19.40	4.94	9.35	92.26	15.38	25.63
Min	3.81	0.82	2.03	2.76	0.58	0.35	13.49	2.25	3.46
SD	9.76	9.21	0.76	6.35	1.68	3.44	27.53	4.59	8.00

Comparatively, the I_{geo} for Zn was low; ranging from slightly contaminated for rock, sediment and plant samples to moderately contaminated in soil. On the other hand, the I_{geo} of Pb was above 5 for rock and soil, signifying extremely contaminated. Sediment was moderately contaminated (1) while plant/vegetable was slightly contaminated with 0.5.

Geo-accumulation index values of Cr, Mn, Fe, Ni, Cu and Pb were all ranged between 2 and 6 for rock samples, indicating that moderately contaminated to very extremely contaminated with these metals. Pb, which is a poisonous contaminant, ranked the highest with 6 while Cu was second with 5; both, however, belong to the most risky group, extremely contaminated. The I_{geo} of Fe (4) > Cr (3) > Mn (2) and Ni (2). The values were generally

higher than those obtained at the Matla power plant by Okedeyi et al., (2014) with Pb (2.32), Fe (0.005) Mn (0.03) and Ni (0.65).

Figure 4. Relationship between contamination degree and the modified contamination degree in Sediment

Table 5. Pollution index in soil sample of Anka

For soil, the I_{geo} for Ni was 7, Fe was 5 and Pb was 5, all belonging to Class 7. The trend from high to low shows that the I_{geo} of $Cu > Cr > Mn > Mn > Zn$; the level of contamination ranged from moderately contaminated to extremely contaminated. In comparison with the studies by Santos-Francés et al. (2014) in Andes Mountain Range, Peru, soils were not included in Classes 3, 4, 5, and 6 (from moderately contaminated to very strongly contaminated). Hence, the risk of heavy metal contamination in the study area is significantly high.

The geo-accumulation index for heavy metals in the sediment samples varied according to the elements. Fe was the highest with I_{geo} of 5 while Zn was the least with I_{geo} of 0.5 according to the classification by Kolawole et al. (2018); Brady et al. (2015) and Al-Haidarey (2010). The trend of I_{geo} was $Fe > Cr$ and $Cu > Mn > Ni$ and $Pb > Zn$. The contamination risk of heavy metals in the sediment samples can be said to be high and as such sediments in the study area can be said to be highly contaminated with heavy metals.

Plant samples were not left out in the contamination by heavy metals; while the I_{geo} of Zn and Pb were classified as uncontaminated to moderately contaminated, Fe recorded the highest I_{geo} for plants with 4 - strongly

contaminated to very strongly contaminated. The level of contamination was however lower than those of rock, soil and sediments.

The single element assessment indices show that heavy metals, which originate from the artisanal mining; the heavy metals present in the ores also find their way into the environment through indiscriminate and unregulated disposal of mine tailing and other waste materials. The implication of this is that the active mining and mineral processing enhance the spread of harmful heavy metal contaminants in the environment to a very high degree.

Table 11. Ecological risk factor (Er) and potential ecological risk index (RI) of soils in Anka

Sample ID	Ecological risk factor (Er)						Mean	RI
	Cr	Mn	Ni	Cu	Zn	Pb		
SL 1	18.04	10.00	24.85	256.30	4.87	480.50	132.43	794.57
SL 2	25.56	0.59	26.18	28.80	1.03	36.75	19.82	118.91
SL 3	99.1	14.00	9.56	49.00	5.11	7.50	30.71	184.26
SL 4	19.28	7.51	14.85	141.90	5.22	247.50	72.71	436.26
SL 5	11.82	14.59	20.74	162.70	7.00	228.00	74.14	444.84
SL 6	10.32	2.12	256.99	117.50	5.04	35.25	71.20	427.22
SL 7	10.6	0.45	1726.47	13.00	0.45	4.50	292.58	1755.47
SL 8	10.8	0.87	24.34	15.20	0.65	4.25	9.35	56.11
SL 9	9.46	1.22	15.59	23.90	2.11	18.25	11.75	70.53
SL 10	16.74	13.33	23.38	61.50	5.11	9.00	21.51	129.06
SL 11	11.68	1.22	26.99	18.80	1.14	4.00	10.64	63.83
SL 12	15.78	8.41	24.12	105.60	5.97	38.75	33.10	198.63
SL 13	61.98	22.80	9.12	169.40	3.20	146.75	68.87	413.25
SL 14	18.26	7.58	917.65	356.70	5.78	649.75	325.95	1955.71
SL 15	28.42	6.87	18.46	325.90	4.51	657.25	173.57	1041.40
Mean	24.52	7.44	209.28	123.08	3.81	171.20	89.89	539.34
Max	99.10	22.80	1726.47	356.70	7.00	657.25	325.95	1955.71
Min	9.46	0.45	9.12	13.00	0.45	4.00	9.35	56.11

Table 12. Ecological risk factor (Er) and potential ecological risk index (RI) of Sediment in Anka

Sample ID	Ecological risk factor						Mean	RI
	Cr	Mn	Ni	Cu	Zn	Pb		
SD 1	20.20	21.18	15.96	57.90	3.11	25.50	23.97	143.84
SD 2	7.62	1.76	18.46	22.50	0.58	24.75	12.61	75.67
SD 3	18.32	10.24	10.15	60.00	2.94	21.25	20.48	122.89
SD 4	7.78	0.82	22.21	16.10	0.77	1.75	8.24	49.43
SD 5	8.70	1.88	16.25	13.80	0.68	3.00	7.39	44.32
SD 6	19.28	1.76	19.12	75.90	3.49	41.00	26.76	160.56
SD 7	65.64	22.24	17.57	97.00	4.94	46.75	42.36	254.14
SD 8	7.72	1.16	21.54	18.60	0.71	4.25	9.00	53.98
Mean	19.41	7.63	17.66	45.23	2.15	21.03	18.85	113.10
Max	65.64	22.24	22.21	97.00	4.94	46.75	42.36	258.77
Min	7.62	0.82	10.15	13.80	0.58	1.75	7.39	34.72

3.3. Assessment of Multi-element Indices

The assessment of multiple elements was carried out by evaluating the contamination degree (C_d), the modified contamination degree (C_d), and the pollution index (PI). The contamination degree of ranged from 15.6 to 407.30. About 80% of the sites fell within the category of extremely contaminated while the remaining 20% were strongly contaminated. In applying the modified contamination degree index, the values ranged from 2.61 to 67.88. 20% of

the sites are extremely contaminated, 27% were severely contaminated, 20% were strongly contaminated. 13 % were moderately to strongly contaminated and the remaining 20% were moderately contaminated. The relationship between the contamination degree and the modified contamination degree in soil is presented in Figure 3

The Pollution index of soil in the study area indicated values from 4.09 to 247.72. Although all the sites fell under the category of severely polluted, with all the sites exceeding Anka Town (SL 7), Dareta 3 (SL 14) and Dareta (SL 15) were ranked highest in that order.

Table 6. Pollution index in soil sample of Anka

As presented in Table 10 for sediments, contamination degree of ranged 13.49 to 92 with 50% of the site indicating severely contaminated and the remaining 50% falling within the category of strongly contaminated. On the other hand, the modified contamination degree index ranged from 2.25 to 15.37. 25% of the site was within the strongly contaminated category, 25% were also moderately to strongly contaminated while 50% were moderately contaminated. Figure 4 shows the variation of C_d and mC_d in sediment samples of the study sites.

The Pollution index for sediment ranged from 3.46 to 25.62 as shown in table 10; this indicates that all the sites are severely contaminated just like in soil. The highest values were found in Dan Kamfani 2 (SD 7), Dan Kamfani 1(SD 6) and Abare BF (SD 3) in corresponding order, as shown in Figure 4.

This results obtained in this study is similar to the earlier studies conducted in industrial area of Southwest Nigeria by Kolawole et al. (2018), where the soil and sediments were described as severely polluted.

3.4. Assessment of Ecological Risk Index

Table 11 and Table 12 summarize the ecological risk factor (E_r) and the potential ecological risk index (RI) of Cr, Mn, Ni, Cu, Zn and Pb in soil and sediment of the study area. For soil, of the 15 sampling sites, the highest mean ecological factor and the highest potential ecological risk index of 325.95 and 1955.71 were recorded at the site of SL14 respectively. These are followed by SL7 and SL 15 with mean E_r of 292.58 and 173.57 respectively, and RI of 1755.47 and 1041.40. The least mean E_r and RI values were obtained in SL8 (9.35 and 56.11), SL11 (9.35 and 63.83) and SL9 (10.63 and 21.51).

Considering the soil pollution level assessment of Cr, Mn, Ni, Cu, Zn and Pb, based on the ecological risk factor presented in Table 2, 47% of the sites can be considered as low, 26.7% is moderate, and 20% is considerable and 6.7% is high. On the other hand, 33.3% of the sites recorded low level of potential ecological risk with heavy metals, 13.3% was moderate, 26.7% was high and 26.7% was very high. The E_r and the RI pollution assessment indices are however not exactly the same based ecological risk. The E_r here seems to be skewed towards low ecological pollution risk while RI gives a wider spread, that is, from low to very high. Hence, the application of only one of the indices might lead to a wrong conclusion. The two indices can best be complementary to each other.

In sediment, the maximum mean of E_r in the 8 sampling sites was 42.36 in Dan Kamfani 2 (SD 7) while the minimum was 7.39 from Anka River (SD5). The ecological risk factor was low for 87.5% of the sites while 12.5 % was moderate. On the other hand, the RI ranged from 44.32 to 160.56. Of the 8 sampling sites, 75% had low

potential ecological risk while 25% has moderate potential ecological risk. The results for Er and RI in sediment agree better than in soil. However, the result further confirms higher potential ecological risk in soil than in sediment.

Figure 7. Average contribution of Heavy Metals to the Ecological Risk of Anka

4. CONCLUSION

This study examined the concentration of heavy metals in rocks, soils, sediments and plants in artisanal mining area of Anka. The estimated mean elemental concentrations of the heavy metals indicate that the values obtained in this study are well beyond the maximum tolerable limits and the world average reported by the World Health Organization. The concentration of Pb was particularly noted to be higher with the analysis of rock and soil samples.

Different contamination, pollution and ecological risk indices have been employed to assess the environmental risk of heavy metals in the study area. The results of I_{geo} revealed that severe heavy metals contamination in rock and soil. This is associated with the geology and the anthropogenic activities in the study area. The contamination of the soil originates from the parent ores (rocks) that are excavated and brought to the surface, which finds its way into the environment and are dispersed in air, absorbed in the soil, deposited in sediments and absorbed by plants. The absorption in plants was found to be least among the sample types. Using the pollution index, the soil and sediments was categorized as severely polluted but the enrichment of heavy metal was observed to be higher in soil than in sediment. The assessment of contamination factor and potential ecological risk from heavy metal in Anka majorly comes from Pb, Ni and Cu. Zn presented the least values. The potential ecological risk is higher soil than in sediments.

The use of single and multiple element indices allowed the assessment of individual heavy metal and the sampling locations. Among the study areas, the active mining sites found in Dareta, Daki Takwas, Dan Kamfani and the processing areas of Abare, Dan Kamfani, Dateta and Abare were identified as areas with high heavy metal pollution risk.

5. RECOMMENDATIONS

With the level of contamination of the various sample types with heavy metals, there is a need to ensure adequate protection of the local populace and the worker as ingestion of contaminated materials or inhalation of dust particles containing these heavy metals poses a significant health risk. The Ministry of Mines and Steel Development and Ministry of Environment should collaborate to educate and create the needed awareness on the risk associated with artisanal mining and processing in the area using crude methods.

Agricultural activities such as crop planting and animal grazing should be restricted, especially in the mining areas where the concentration of heavy metals in soil and plants are beyond recommended levels. This will reduce the risk of consuming vegetables and meat contaminated with heavy metals. It is also recommended further studies should be conducted in the study area to assess the health risk associated with the consumption of water and vegetables in the study area.

Conflict of Interest Statement

The authors declare no conflict of interest.

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