RISK ASSESSMENT OF SELECTED HEAVY METALS IN WASTEWATER SOURCES AND SEDIMENTS FROM ARTISANAL MINING AREAS OF MARU, ANKA AND BUKKUYUM AREAS OF ZAMFARA STATE, NIGERIA.

Kotila, A. A and Koki, F.S.
Department of Physics, Bayero University, Kano.
Correspondence: augustinekotila@gmail.com +2348066707879.

ABSTRACT
Heavy metals are normally exposed to the surface during mining activities. When inhaled (as dust) or ingested (by drinking contaminated water) in significant concentrations, they can lead to health challenges. In this research work, soil and wastewater were collected from gold-mining sites of Anka, Maru and Bukkuyum Local Government Areas of Zamfara State, Nigeria. Heavy metals concentrations were measured using Atomic Absorption Spectrophotometer (AAS) and X-Ray Fluorescence Spectrometer (XRF). The results of heavy metals concentrations (ppm) in the selected areas under study were 2.017 to 2.4781 ppm, 0.6749 to 0.8044 ppm and 0.599 to 0.6029 ppm for Nickel (Ni), Lead (Pb) and Mercury (Hg) respectively, while 0.0202 to 0.0305 ppm, 0.0299 to 0.0512 ppm and 0.0238 to 0.0248 ppm are for Iron (Fe), Copper (Cu) and Cyanide (CN) respectively. The results of the study when compared with the World Health Organization (WHO) standard indicate that most of the samples are contaminated with Ni, Pb and Hg.
Keywords: Risk Assessment, Heavy Metals, Wastewater and Soil.

INTRODUCTION

Human beings have always been exposed to heavy metals for an immeasurable amount of time. These heavy metals are found everywhere because of both natural and anthropogenic activities, and have been some of the most serious problems near mining sites ((Kamunda, 2007). By definition, heavy metals are toxic metals, irrespective of their atomic mass or density. Most of them have a high atomic number, high atomic weight and a specific gravity greater than 5 g/cm^3 (Singh, 2007). This classification includes some metalloids, transition metals, basic metals, lanthanides, actinides and metals of groups III to V of the Periodic Table. Examples include Arsenic (As), Cyanide (CN), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Cobalt (Co), Iron (Fe), Zinc (Zn), Selenium (Se), Aluminum (Al) and Manganese (Mn) (Brandy and Weil, 1999).

While organic pollutants slowly decompose to produce carbon dioxide and water, heavy metals tend to bio-accumulate because they cannot be broken down. They persist in the environment and are transferred from one place to another. They are ingested daily by humans either through air, food, water or soil. Human symptoms and the level of toxicity depend on the type of metal, the dose absorbed, and whether or not the exposure was acute or chronic (CSIR, 2010). Some heavy metals are carcinogenic while others are detrimental to body organs. Even in very small amounts, heavy metals can be toxic to humans and animals (USEPA, 1995). Their effects on humans include increased incidence of tuberculosis, chronic bronchitis, asthma and gastrointestinal diseases. The impacts to aquatic life may range from immediate fish killing to affecting their ability to reproduce. Heavy metals are also considered toxic to plants due to their acute and chronic effect on them. For example, high levels of CN in soils can cause a reduction in photosynthesis, nutrient and water uptake (Kamunda, 2007).

The aim of this study is to evaluate the human risk associated with the exposure to heavy metals in soil, soil water and sediments in the samples collected from Anka, Maru, and Bukunyum Local Government Areas of Zamfara State.

THEORETICAL BACKGROUND

Average Daily Intake (ADI)

The potential exposure pathways for heavy metals in contaminated soils are calculated based on recommendations by several American publications. ADI due to ingestion (mg/kg or mg/L) for the different pathways can be calculated using the following exposure equations as prescribed by (Amos *et al.*, 2021):

$$ADI_{ing} = \frac{Ci \times IR \times ABS_g \times EF \times ED}{AT \times W} \quad (1)$$

$$ADI_{derm} = \frac{Ci \times SA \times Kp \times ABS_d \times ET \times EF \times ED \times CF}{AT \times BW} \quad (2)$$

where ADI_{ing} is the exposure dose through ingestion, ADI_{derm} is the exposure dose through dermal absorption and Ci is the average concentration of heavy metal.

STUDY AREA

The study sites are located in three (3) Local Government Areas of Zamfara State, Northwest Nigeria between 6° 00′ – 7° 00′ E of the Longitude and 12° 00′ – 13° 00′ N of the Latitude.

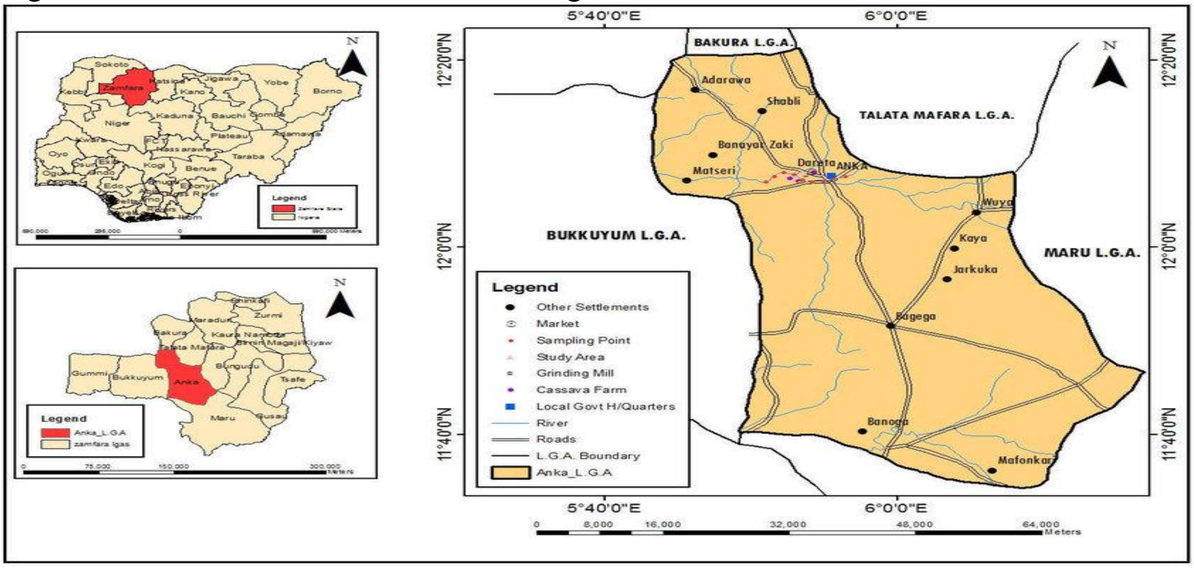


Figure 1: Geological Map of the Study Area.

MATERIALS AND METHOD.

The materials used for this research include, disposable hypodermic syringe (20 ml, 10 ml capacities), digital weighing balance and X-ray Fluorescent (XRF).\

Sampling Procedure

The soil samples were collected by random sampling method from the mine sites at selected locations in three (3) Local Government Areas of the State. The soil samples were packed in air tight polyvinyl chloride (PVC) containers from the areas of surveillance, properly sealed and labeled for easy identification and then transported to the Materials and Science Laboratory at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria.

One liter each of water samples were also collected in washed plastic bottles using standard procedure and used for Atomic Absorption Spectrophotometer (AAS) analysis for metal concentration determination. Stream sediment samples, on the other hand, were collected randomly around each mining site with stainless steel trowel to the depth of 0 to 15 cm stream water and sediment covering both dry and wet seasons. Sediment samples were air dried for four days and kept in labeled polythene bags. They were sieved using a 2 mm mesh to remove large grains, then properly grinded with an agate mortar and made into pellets of 13 mm diameter and 1 mm thickness with a hydraulic pelletizing machine for X-Ray Fluorescence (XRF) analysis.

Sample Analysis

The water samples were analyzed using BUCK Scientific (210) Atomic Absorption Spectrophotometer (AAS). Analysis of sediment samples for metal concentration was carried out with an ECLIPSE III X-Ray Fluorescence Spectrometer (XRF). To ensure quality for the procedure, estuarine standard reference material (SRM 1646a) was irradiated for 1000 s, with the X-ray tube operating at 25 Kv and 50 µA respectively. Seven elements (CN, Pb, Cu, Fe, Mn, Cr and Zn) were detected. Comparison was made between experimental and certified values for the standard reference material used as a measure of quality for the analytical procedures used for stream sediment analysis. Reasonable agreement was observed for the elements with available certified values and this gives a measure of validation for the data generated.

RESULTS AND DISCUSSION

Atomic Absorption Spectrophotometer and X-Ray Fluorescence (XRF) was employed in the analysis of the concentration of heavy metals such as CN, Co, Cu, Fe, Hg, Pb, Ni and Zn in water, soil and rock samples collected at the mining sites selected for this research work. Physicochemical parameters (pH, EC and TDS) were also determined.

The heavy metals in water samples revealed high contamination of metals from the mining area especially with metals like Pb (1.574 mg/l), Hg (0.542 mg/l), CN (0.0484 mg/l), Co (0.1157 mg/l), Cu (0.049 mg/l), Ni (2.404 mg/l) and Fe (19.072±0.45 mg/l). The water analysis also revealed the presence of significant amount of essential metals needed for growth and development of the body such as Ca^{2+} (13.423 mg/l) and Mg (2.417 mg/l). However, emphasis must be drawn to the fact that the excess of these metals beyond the recommended levels could also trigger the negative effects of other toxic metals like Pb (Tsafe *et al.*, 2012).

Physicochemical properties of water like temperature, pH, Electrical Conductivity (EC) and Total Dissolved Solid (TDS) are important properties that determine the mobility of metals in solution and consequently the water quality. Recorded temperature ranged with mean value of 25.0°C. The concentration of pH in the water ranged from 7.39 to 9.82 with mean value of 8.41. While the concentration of electrical conductivity in water samples ranged from 208 to 1638 µs/cm^3 with mean value of 933.25 µs/cm^3. Similarly, the concentration of Total Dissolved Solids (TDS) ranged from 108 to 965 mg/l with mean value of 604.75 mg/l. This shows that the mean value of the recorded pH for the selected area under study is within the range of 6.5 to 9.2 standard set by WHO for domestic purposes. Also, the Electrical Conductivity (EC) is below the standard value set by WHO which is given as $\geq 5000\ \mu scm^{-3}$, which also indicate that it is safe for domestic use, but the TDS mean value is a bit higher than the 500 mg/l limit set by WHO. The table below depicts the concentration of heavy metals from the selected area under study.

Table 1: Heavy Metals Concentration and Physicochemical Parameters of the Area under Study.

Sample ID	PH	TDS (mg/l)	EC (µs/cm^3)	Ni (mg/l))	Cu (mg/l)	Co (mg/l)	Pb (mg/l)	Hg (mg/l)	Zn^{2+} (mg/l)	$Fe3^+$ (mg/l)	CN (mg/l)
A 4	8.05	660	905	0.833	0.029	0.025	0.408	0.993	BDL	BDL	0.030
A 5	9.37	566	806	0.754	0.016	0.054	0.172	0.642	BDL	0.001	0.026
A 6	8.36	672	968	0.993	0.024	0.041	0.493	0.191	BDL	0.000	0.020
A 7	8.48	678	955	1.414	0.025	0.079	0.406	0.636	BDL	BDL	0.025
A 8	8.58	681	966	1.708	0.018	0.065	0.550	0.094	BDL	BDL	0.022
B 10	8.29	899	1240	1.680	0.033	0.040	0.497	0.314	BDL	0.002	0.200
B 11	8.31	926	1278	1.596	0.048	0.006	0.431	0.432	BDL	0.006	0.021
B 12	8.12	344	503	1.643	0.053	0.37	1.133	0.900	BDL	BDL	0.019
C 13	8.20	851	1213	1.672	0.020	0.024	0.596	0.153	BDL	0.004	0.030
D 10	8.18	854	1209	1.753	0.022	0.049	0.666	0.618	BDL	0.000	0.022
D 11	8.07	913	1291	1.649	0.029	0.074	0.747	0.752	BDL	0.006	0.030
D 12	8.59	110	1638	1.738	0.025	0.084	0.825	0.778	BDL	BDL	0.029
F 10	8.48	670	941	1.805	0.033	0.023	0.919	0.268	BDL	0.010	0.033
F 11	9.38	109	1611	2.007	0.030	0.005	1.035	0.691	BDL	0.000	0.022
F 12	8.66	788	1103	2.213	0.031	0.002	1.119	0.940	BDL	BDL	0.023
G 4	8.42	832	1179	2.445	0.047	0.052	1.165	0.731	BDL	BDL	0.026
G 5	8.25	679	964	2.617	0.048	0.010	1.347	0.414	BDL	0.010	0.022
G 6	8.43	671	949	2.387	0.064	0.053	1.606	0.067	BDL	0.000	0.030
E 8	8.52	699	999	2.438	0.043	0.012	1.419	0.638	BDL	0.000	0.27
H 10	8.02	321	471	2.410	0.051	0.147	1.526	0.213	BDL	0.060	0.30
H 11	8.27	221	327	2.464	0.058	0.191	1.562	0.383	BDL	0.011	0.29
I 13	8.34	307	442	2.511	0.046	0.202	1.585	0.319	BDL	BDL	0.020
I 14	9.50	108	161.1	2531	0.051	0.110	1.626	0.126	BDL	0.000	0.020
I 15	8.27	959	1344	2.482	0.076	0.029	2.076	0.183	BDL	BDL	0.020
I 16	8.19	934	1323	2.556	0.072	0.074	2.165	0.606	BDL	BDL	0.023
I 17	7.77	223	327	2.744	0.073	0.083	1.947	0.615	BDL	0.010	0.030
I 18	8.27	802	1160	3.140	0.053	0.087	1.991	0.656	BDL	0.031	0.026
J 7	8.01	677	956	3.243	0.067	0.109	2.062	0.791	BDL	BDL	0.020
J 8	8.79	213	314	3.039	0.061	0.100	2.154	0.023	BDL	0.060	0.021
J 9	7.39	318	469	3.094	0.055	0.133	2.230	0.807	BDL	0.000	0.021
J 10	7.94	882	1258	3.012	0.064	0.135	2.255	0.616	BDL	BDL	0.030
J 19	7.73	319	470	3.154	0.063	0.173	2.314	0.538	BDL	BDL	0.025
K 10	8.09	878	1255	3.098	0.057	0.192	2.322	0.764	BDL	BDL	0.022
K 11	8.44	795	1136	3.052	0.059	0.120	2.433	0.842	BDL	0.006	0.025
L10	8.84	519	851	3.093	0.060	0.144	2.455	0.803	BDL	0.060	0.025
M 10	8.42	671	976	3.135	0.069	0.191	2.790	0.355	BDL	BDL	0.026
M 11	8.48	678	976	3.197	0.075	0.190	3.075	0.443	BDL	BDL	0.018
X 1	9.82	206	208	3.506	0.067	0.221	2.718	0.647	BDL	0.015	0.020
X 2	9.09	592	847	3.708	0.064	0.76	2.731	0.785	BDL	BDL	0.024
X 2b	7.99	965	1341	3.629	0.090	0.167	3.406	0.913	BDL	0.023	0.030

From table 1, the concentration values of Nickel (Ni), Lead (Pb) and Mercury (Hg) were found to be the highest. These highest levels could be linked to alleged sickness in children suffering from diarrheal diseases and chest pains.

Table 2: Mean Values for the three Highest Concentrated Heavy Metals (Ni, Pb & Hg)

Heavy Metals	Ni(mg/l)	Pb(mg/l)	Hg(mg/l)
ANKA	2.1244	0.8044	0.6059
BUKKUYUM	2.0174	0.6749	0.6029
MARU	2.4781	0.7086	0.599

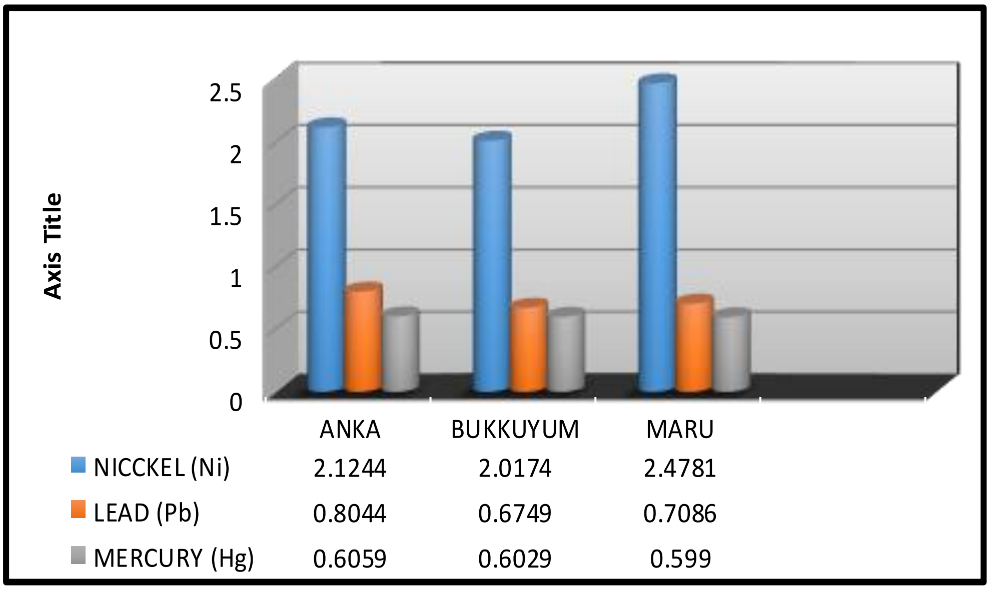


Figure 2: Mean Values for the three Highest Concentrated Heavy Metals (Ni, Pb & Hg).

Table 3: Average Values for the three Least Heavy Metals in the Area under Study.

Heavy Metals	Fe(mg/l)	Cu(mg/l)	CN(mg/l)
ANKA	0.0305	0.0422	0.0243
BUKKUYUM	0.0166	0.0512	0.0238
MARU	0.0202	0.0299	0.0248

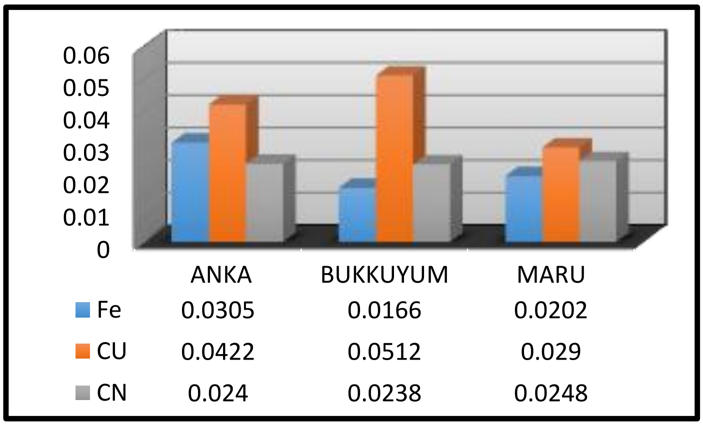


Figure 3: Average Values for the three Least Heavy Metals in the Area under Study.

The quantity of pollutants absorbed by the human body is estimated by the Average Daily Intake (ADI). ADI values for adults and children in both water and soil from the three Local Government Areas selected for this research from Zamfara State were calculated and are presented in table 4.

Table 4: Average Daily Intake (ADI) of Heavy Metals Base on the Exposure Pathways of Ingestion and Dermal Absorption of Water.

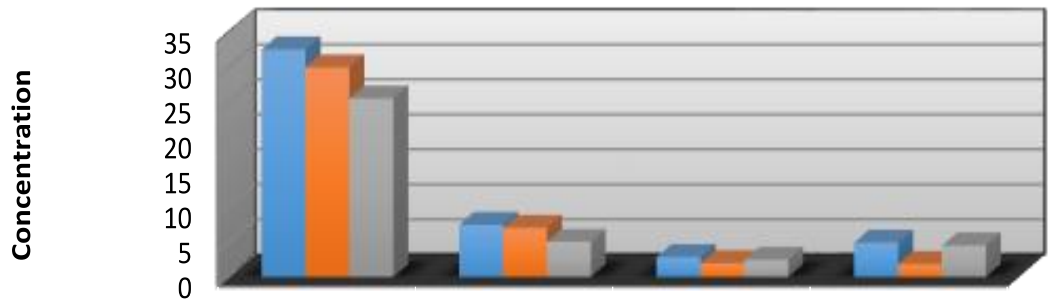
Heavy Metals	**ADI ($Mg^{-1}day^{-1}$) (CHILD)**				**ADI($Mg^{-1}day^{-1}$) (ADULT)**		
	ANKA	**BUKKUYUM**	**MARU**		**ANKA**	**BUKKUYUM**	**MARU**
Ni	3.00×10^{-2}	$2.7\text{X}10^{-2}$	$2.4\text{X}10^{-2}$		$1.2\text{X}10^{-2}$	$1.0\text{X}10^{-2}$	$1.4\text{X}10^{-2}$
Pb	1.5×10^{-2}	$1.3\text{X}10^{-2}$	$1.3\text{X}10^{-2}$		$2.7\text{X}10^{-3}$	$2.3\text{X}10^{-3}$	$2.4\text{X}10^{-3}$
Cu	$2.1\text{X}10^{-3}$	$2.5\text{X}10^{-3}$	$1.5\text{X}10^{-3}$		$3.6\text{X}10^{-4}$	$4.3\text{X}10^{-4}$	$2.6\text{X}10^{-4}$
Hg	$3.00\text{X}10^{-4}$	$3.00\text{X}10^{-4}$	$2.90\text{X}10^{-4}$		$5.20\text{X}10^{-3}$	$5.10\text{X}10^{-4}$	$5.20\text{X}10^{-4}$
CN	$2.00\text{X}10^{-4}$	$1.90\text{X}10^{-4}$	$2.10\text{X}10^{-4}$		$3.50\text{X}10^{-5}$	$3.40\text{X}10^{-5}$	$3.60\text{X}10^{-5}$
CO	$3.00\text{X}10^{-3}$	$3.70\text{X}10^{-3}$	$2.90\text{X}10^{-3}$		$5.20\text{X}10^{-4}$	$6.40\text{X}10^{-4}$	$4.90\text{X}10^{-4}$
Fe	$6.00\text{X}10^{3}$	$5.50\text{X}10^{4}$	$6.70\text{X}10^{-4}$		$1.70\text{X}10^{-4}$	$1.40\text{X}10^{-5}$	$2.80\text{X}10^{-4}$

XRF results for the collected sediment, rock and soil samples evidenced the existence of the following major elements: Ca, Fe, K, Mn, Ti, Cr, Cu, Hg, Ni, Pb and Zn**.** The average concentrations of the heavy metals are shown in table 5.

Table 5: Average Concentration of the Heavy Metals in the Locations under Study.

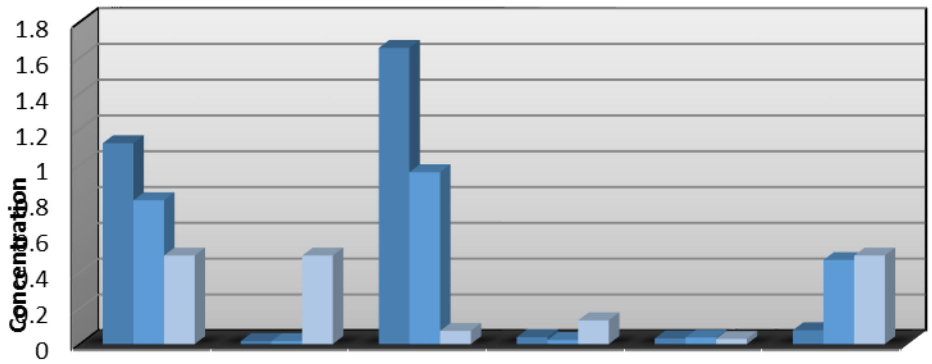
Area	Ca (mg/cm^3	Hg (mg/cm^3)	Hg (mg/cm^3)	Hg (mg/cm^3)	Fe (mg/cm^3)	Cr (mg/cm^3	K (mg/cm^3)	Ti (mg/cm^3)	Al (mg/cm^3)	Si (mg/cm^3)	Mn (mg/cm^3
Anka	1.123	0.017	1.655	0.039	4.899	0.032	2.851	0.774	7.456	32.515	0.081
Maru	0.804	0.017	0.961	0.023	1.846	0.037	1.963	0.470	7.023	29.955	0.031
Bukkuyum	0.495	0.031	0.074	0.133	4.500	0.029	2.452	0.495	5.025	25.505	0.025

From table 5, the concentration of Si, Al, K and Fe are more compared to the concentration of Ca, Hg, Pb, Cu, Cr and Ti. Below are the graphical representations of the heavy metals in the three locations for both the major concentrated elements and the minor concentrated elements:



	Si	Al	K	Fe
ANKA	32.515	7.456	2.851	4.899
MARU	29.955	7.032	1.963	1.846
BUKKUYUM	25.505	5.025	2.452	4.5

Figure 4: Graphical Representation of Major Concentrated Elements in the Locations under Study.



	Ca	Hg	Pb	Cu	Cr	Ti
ANKA	1.123	0.017	1.655	0.039	0.032	0.0774
MARU	0.804	0.017	0.961	0.023	0.037	0.47
BUKKUYUM	0.495	0.495	0.074	0.133	0.029	0.495

Figure 5: Graphical Representation of Minor Concentrated Elements in the Locations under Study.

The assessment of heavy metals showed that the elemental concentrations of Pb, Fe, Si, Cr and Hg were higher than the recommended WHO limits. Heavy metals contamination of water sources in the study area can be said present high carcinogenic and non-carcinogenic risks to the local population who depend largely on streams, rivers and sometimes stagnant ponds for domestic purposes. The risk is not however associated with pipe borne water in the area. The heavy metals contributing to the non-carcinogenic risk were identified as Pb, Hg and Cr, and the major exposure pathway was ingestion. Hence, drinking or domestic use of water from the streams, rivers and surface water from the mining and mineral areas should be discouraged. With the level of heavy metals contaminating water sources especially in Anka, there is need to take adequate protection of the public within the mining sites and the workers as ingestion of contaminated water poses some level of health risks.

CONCLUSION.

Heavy metals assessment has been conducted on soil and soil water sources of artisanal and local mining areas of Anka, Bukkuyum and Maru Local Government Areas of Zamfara State, Northwest Nigeria and the results presented. The assessment showed that the elemental concentrations of Ni, Pb and Hg were higher than the recommended WHO limits. Heavy metals contamination of water sources in the study area can be said present high carcinogenic and non-carcinogenic risks to the local population who depend largely on streams, rivers and sometimes stagnant ponds for domestic purposes. The risk is not however associated with pipe borne water in the area. The heavy metals contributing to the non-carcinogenic risk were identified to be Ni, Pb and Hg, and the major exposure pathway was ingestion. Hence, drinking or domestic use of water from the streams, rivers and surface water from the mining and mineral areas should be discouraged. The study emphasizes the need to continue to monitor concentrations of toxic metals such as Ni, Pb, Hg, Fe, Cu, Co, Cr, Ca, K, Al, Ti, Si and CN in dump sites in order to detect their toxicity on time. There should be proper harnessing and recycling of waste materials. However, their use as manures for gardens requires proper treatment to remove toxic levels of heavy metals accumulation in plants which may subsequently be hazardous to human health when consumed. Proper monitoring and remediation plan should be put in place to reduce the chances of ground water pollution by leaching contaminants.

REFERENCES.

Amos, M. A., Nasiru, A. B., Ibrahim, U., Shekwonyadu, I., Emmanuel, J., Samson, Y and Godwin, B. E. (2021). Assessment of Radioactivity and Heavy Metals in Water Sources from Artisanal Mining Areas of Anka, Northwest Nigeria. *ELSVIER Journal, Scientific Africa, 12 (2021).*

Brandy, N. C and Weil, R. R. (1999). The Nature and Properties of Soils. 12th Edition, Prentice Hall Publishers, London.

Council for Scientific and Industrial Research, (CSIR). A CSIR Perspective on Water in South Africa 2010.

Kamunda, C., Mathuthu, M., Madhuku, M. (2007). Assessment of Radiological Hazards from Gold Mine Tailings in Gauteng Province, South Africa. *Int. J. Environ. Res. Public Health, 13(138).*

Singh, S., Rani, A and Mahajan, R. K. (2007). ^{226}Ra, ^{232}Th and ^{40}K Analysis in Soil Samples from some Areas of Punjab and Himachal Pradesh, India using Gamma Ray Spectrometry. *Radiat. Meas., 39(4): 431-439.*

Tsafe, A. I., Hassan, L. G., Sahabi, D. M., Alhassan, Y and Bala, B. M. (2012). Evaluation of Heavy Metals Uptake and Risk Assessment of Vegetables Grown in Yargalma of Northern Nigeria. *J. Basic. Appl. Sc. Res., 2(7): 6708-6714.*

United States Environmental Protection Agency (USEPA). (1995). Radioactive Equilibrium. Retrieved from http://www.epa.gov/rpdweb00/understand/equilibrium.html on 10/05/2014.