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Information

The Nigerian Mining and Geosciences Society (NMGS) succeeded in 1977, The Nigerian Mining, Geological and Metallurgical Society (NMGMS) which was founded on 15 January, 1961, and officially inaugurated on 17 December, 1962. among its objectives, are the advancement of the study and practice of mining, geological sciences and metallurgy, and promotion of the acquisition and dissemination of scientific contributions and knowledge in the relevant fields. The Society also ensures the protection of the ethics of the respective professions, and has statutory representation in the Council of Nigerian Mining Engineers and Geoscientists (COMEG) enacted into law by the Federal Republic of Nigeria Decree No. 40 of 1990. The categories of membership are Student, Graduate, Corporate, Fellow, Institutional, Affiliate and Honourary member/Fellow, and the current strenght of ca.3500 includes Nigerian and foreign professionals and practicians working or have worked within the country.

This multi-disciplinary publication was initiated in 1963, and to 1965 titled the Journal of the Nigerian Mining Geological and Metallurgical Society. Its current title, Journal of Mining and Geology adopted from the edition of 1966, was modified between 1982 and 1987, as the Nigerian Journal of Mining and Geology. The production of the Journal is normally biannual (2 issues per volume) in March and September, and from Volume 35 No. 1 1999, has been under the aegies of the Petroleum Technology Development Fund (PTDF). The publication has international contributorship, circulation and citation. All contacts including correspondence on advertisement and back numbers, should be directed to the Editor-in-Chief.

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Stream Sediment as Pollution Indicator within Shikira Gold Mining Site, Niger State, North-central Nigeria

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Abstract
The quality of stream sediment within Shikira gold mining sites was investigated in this study as they provide good information on the impact of anthropogenic activities in the area. Lithological mapping of the area revealed schist and granites while the structural analyses indicate NE-SW fracture trend. The results of the laboratory analyses showed that the mean concentration of mercury, cadmium, lead and arsenic were above the respective crustal abundance of the elements thereby signifying pollution. Further application of pollution indices such as geo-accumulation index, contamination factor, degree of contamination, elemental contamination index and metal pollution index on the data further confirmed that the sediment in Shikira gold mining sites are seriously polluted with mercury, cadmium and lead, moderately polluted with arsenic, lightly polluted with iron and copper and very lightly polluted with manganese, zinc, nickel and cobalt in the order of: Hg > Cd >Pb> As > Fe > Cu > Mn > Zn > Ni > Co. The study recommends that washing of gold along the river channel should discontinue and the miners should be trained on modern mining techniques which are environmental friendly. Water from the stream within the mining area should not be used for domestic or drinking purposes including livestock in the present condition except after remediation, due to health implications of the identified metals. Regular monitoring of the sediment quality in the area is advocated.

Keywords: *Stream Sediment, Pollution Indices, Shikira Gold Field, Niger State, North-central Nigeria*

Introduction

Water is an essential requirement for human, industrial and agricultural development. It is the most delicate part of the environment. The increase in water demand for domestic, irrigational and industrial purposes has made it indispensable and most critical natural resources (Amadi *et al*., 2017). Interestingly, the use of water for domestic, industrial and irrigational purposes depends on its quality which is determined in terms of physical, chemical, microbial and radiological characteristics. Water quality is largely influenced by geogenic and or anthropogenic factors. Artisanal mining which is the use of rudimentary methods to extract and process mineral ores has led to environmental degradation. It is a subsistent type of mining which is largely driven by low income and plays an important role in boosting the economic base of the poor rural communities. According to Adekoya (2003), artisanal mining has caused a lot of negative impacts on several communities of the world. It was estimated that about thirteen million people across thirty countries are directly involved in artisanal mining out of which a significant number of are women and children (Garba, 2000; Adler and Rascher, 2007).

Sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants (Saeed and Shaker, 2008, Amadi *et al*., 2017). Sediment represents one of ultimate sinks for heavy metals discharged into aquatic environment and it is an important source for the assessment of an anthropogenic contamination in rivers (Amadi *et al.,* 2016). In river system, sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities (Ali and Fishar, 2005; Aboud and Nandini, 2009). As important component of water environment, river sediment is not only the place where pollutants accumulate from the water body, but also it is a secondary pollution source which has a potential impact on water quality (Anglin-Brown *et al*., 1995). Therefore, sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants (Saeed and Shaker, 2008). Ankley *et al.* (1992) pointed out that heavy metals accumulate in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds. In aquatic ecosystems heavy metals are accumulated in sediments, where it may reach concentrations several orders of magnitude greater than in the overlying water (Adams *et al*., 2008). The presence of metals in marine ecosystem in excess of natural background loads has become a problem of increasing concern with respect to water quality and human health (Liu *et al*., 2009; Aktar *et al*., 2010; Amadi *et al*., 2014; Amadi *et al*., 2015).

Amadi, (2011) noted that under natural condition, the concentrations of metals in sediments reflect the occurrence and abundance of a mixture of material in puts from different sources including eroded rocks and soils, swage and soil waste particles, atmospheric fallout and autochthons formation in the catchment area of the relevant rivers. Due to the ecological importance and the persistence of pollutants in the aquatic ecosystem, sediments are more appropriate to be monitored in environmental evaluations and to understand their potential risk factor (Gorenc *et al*., 2004; Caeiro *et al*., 2005). Sediment pollution, especially from heavy metals, has an important impact on water environment and a direct potential threat on human and aquatic lives (Lin *et al*., 2002). These metals can accumulate to toxic levels in sediments without visible signs, hence the need for the present study. Sediment quality determines the sustainability and productivity of agro-business of any nation. The use of agro-chemical in agriculture as well as artisanal mining coupled with intensive run-off are potential pathways through which stream sediments are enriched with heavy metal and these reduces the soil cohesiveness leading to an increase of erosion. The enrichment of soil and sediment by these metals is a function of soil pH, grain size, organic matter, cation exchange capacity and hydraulic conductivity (Kwon and Lee, 2001; Nachtergaele *et al.,* 2002; Amadi *et al*, 2013).

Pollution indices are useful tools for the assessment of sediment quality. In recent decades, different sediment metal assessment indices applied to marine and fresh water environments have been developed. Okunlola *et al*., (2016) mentioned that sediment quality values are a useful to screen the potential for contaminants within sediment to induce biological effects and compare sediment contaminant concentration with the corresponding quality guideline. The pollution indexes evaluate the degree to which the effect an aquatic organisms and are mangers responsible for the interpretation of sediment quality (Grosheva *et al*., 2000). The pollution indexes evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality. Several numerical sediment quality indexes were recently developed to provide interpretative tools for assessing chemical pollution. The most used approaches are geo-accumulation index, contamination factor, degree of contamination, elemental contamination index and metal pollution index. The research is aimed at determining the pollution level in stream sediments around Shikira mining sites in Rafi Local Government Area of Niger State, North-central Nigeria.

Problem Statement and Justification of the Study

According to the Guardian Newspaper of 14th May, 2015, the death of 28 children below the age five (17 female and 11 male) in Shikira area of Niger State, which were attributed to lead poisoning arising from artisanal gold mining in the area was a monumental loss to the community and a wake-up call for stakeholders in the water sector to ascertain the real cost of death of these children. Unlike the Zamfara lead episode, it was reported in the news that livestock such as cows, goat and ram in the community were affected in the disaster as they animals were restless and misbehaving. During the fieldwork, the villagers and cattle owners showed us the plants species in the vicinity of the mining sites, which the animals ate and started behaving abnormally.

The need to ascertain the level of pollution in stream sediments around Shikira mining sites in Rafi Local Government Area of Niger State, North-Central Nigeria cannot be overemphasized owing to the 14th May, 2015 episode. The investigation of the stream sediments within the study area is necessary because panning, washing and other gold processing activities takes place along the river channels. Livestock such as cow, ram and goat drank these water in the course of grazing. Therefore, analysis of the stream sediment will provide useful information on the level of pollution in the streams within the study area.

Materials and Methods

Study Area Description

The study area is part of Tegina Sheet 142SE and Alawa sheet 143SE. It lies between latitudes N10º00' to N10º04' of the Equator and longitudes E06º26' to E06º34' of the Greenwich Meridian (Fig.1). The study area is drained by River Kaduna and its tributaries (Ajibade and Wright, 1988). The study area is accessible through Minna-Kagara road and other minor roads.

Climate and Vegetation

The study area is characterized by two distinct seasons: the dry and rainy season. The mean annual rainfall in the area is 1200 mm while the minimum and maximum temperatures are 26 ºC and 34 ºC respectively. The vegetation of the study area is typical Guinea savannah which comprises tall grasses with series of tall trees

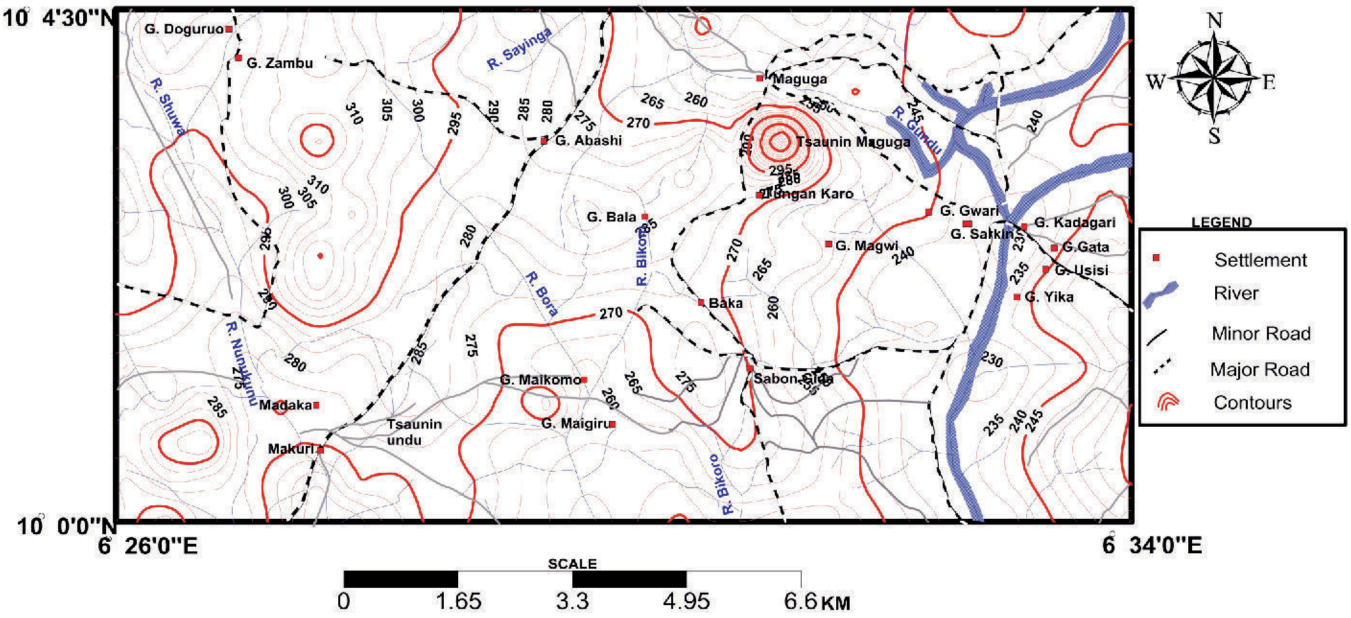


Fig. 1: Topo map of Shikira and Environs

within the vegetation. The trees become more populated along river channels (Federal Meteorological Agency, Minna, 2011; Ajibade, 1982).

Geology of the Study Area

The geological mapping of the study area shows two major rock types: schist and granite (Fig. 2). The granite outcrops are common and well exposed in the area, light-coloured and generally fine to medium grained. The schist shows a strike direction of NE–SW and dip 45°W along stream channels, which is an indication that the streams in the area are structurally controlled. The schist are well foliated are largely deformed and weathered. They are potential sites for gold mineralization based on the structural configuration while the granite is characterized by dominant pegmatitic and quartz vein in granites. Gold mining occurs on the foliations within the schist and along the pegmatitic vein within the granitic rock.

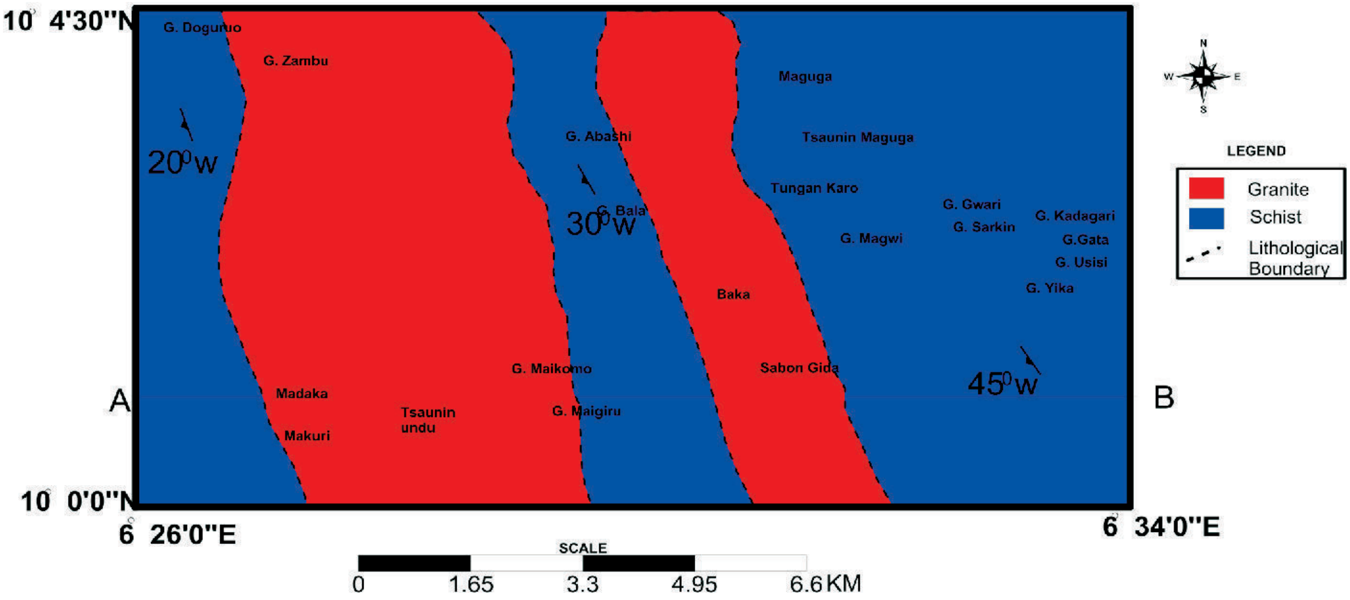


Fig. 2: Geology Map of Shikira and Environs

Sample Collection, Preparation and Analysis

A total of thirty five sediment samples were collected in polythene bags for the present study. Thirty samples were collected within the vicinity of the mining sites while five samples were collected far away from the mining sites which serve as control samples. The sediments samples were air-dried under shade and ground to pass through a 0.5 mm sieve and 2 mm mesh sieve before digestion. 2 g of pulverized sample was put in a digestion tube of 50 cm^3 volume and 10 cm^3 of aqua regia (400 cm^3 of HCl and 133 cm^3 of HNO_3) was added and swirled. A programmable controller of digestion block was set up before the commencement of digestion at the following temperature and time range: temperature step up to 75 °C, held and heated for 30 minutes; temperature step up to 100 °C, held and heated to for 30 minutes; temperature step up to 110 °C, held and heated for 60 minutes and finally step up to 140 °C, and heated for 400 minutes. Within these temperature and time range of digestion, the process was checked for 20 minutes to ensure smooth proceeding of the digestion processes. After the digestion, tubes were removed from the block and allowed to cool at room temperature. 25 cm^3 of 0.1 % of HNO_3 were mixed with a vortex stirrer and transferred to 50 cm^3 centrifuge tube and caped, it was centrifuged for 15 minutes at 1500 revolution per minute. 10 cm^3 of digested solution was decanted as suited for Inductively Coupled Plasma Mass Spectrometry analysis. The analysis was carried out at ALS Geochemical Laboratory, Czech Republic with Agilent 7700X analytical machine and ALS Laboratory Code W-METMSFXI. The samples were prepared in accordance with Czech and USEPA standard for analysis of metals (USEPA, 2001).

The results of the laboratory analyses were further interpreted using Index of Geo-accumulation, Contamination Factor, Degree of Contamination, Metal Pollution Index, Elemental Pollution Index and Correlation Analysis. The results of sediment analysis were further compared with Wedepohl, (1995) as well as Taylor and Mclaennan, (1995) recommended elemental average background values.

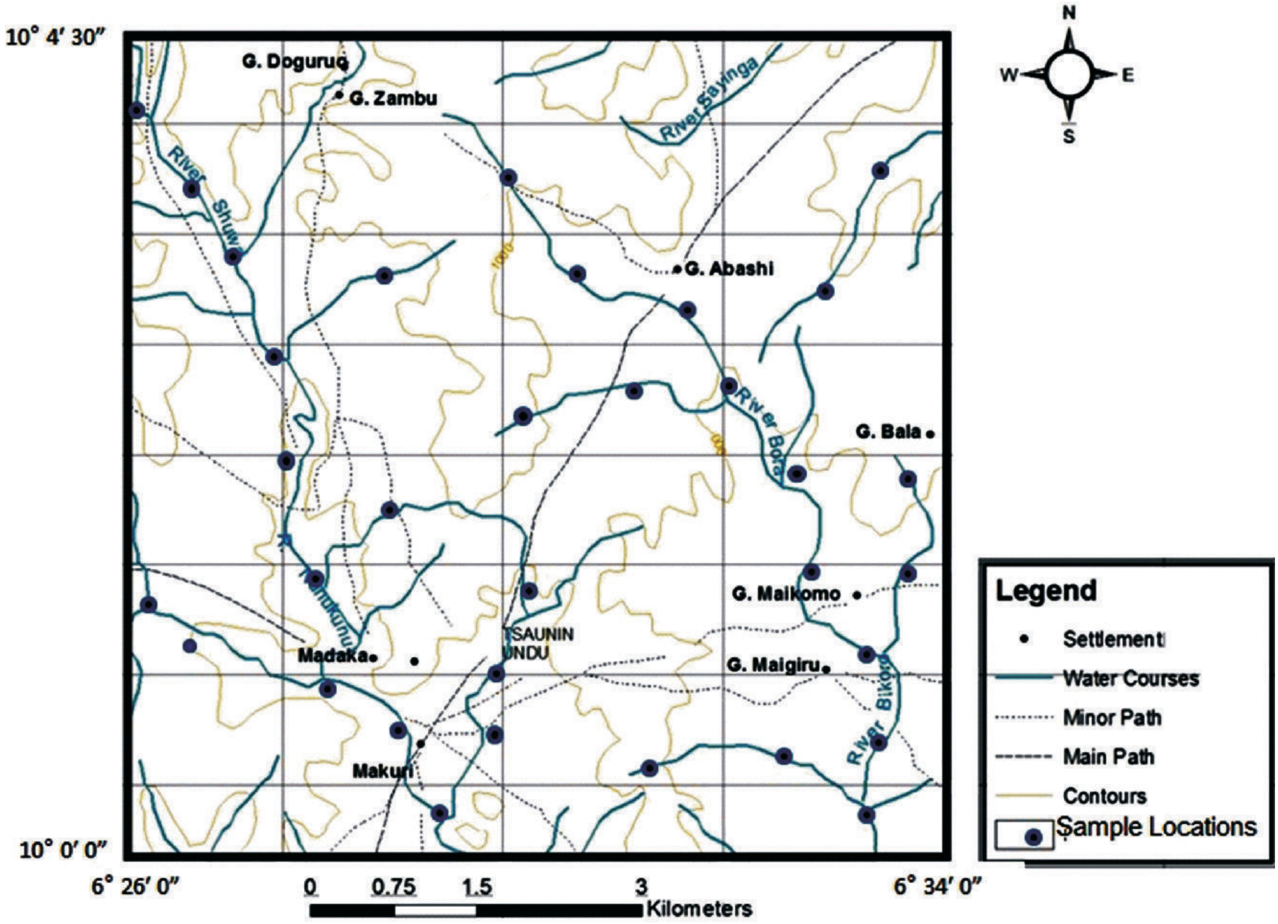


Fig. 3: Drainage Map of Shikira and Environs showing the Sample locations

Results and Discussion

Heavy metals associated with gold mining are of particular interest due to their accumulation effects and biodegradable nature, they tend to remain in sediments for a very long time. A total of 10 heavy metals (Mn, Cd, Hg, Pb, Cu, Zn, Co, Ni, As and Fe) were analyzed in the present study. The mean concentration of the 10 metals used for the study (Table 1) was compared with maximum allowable limit in upper continental crust classification by Wedepohl, (1995), Taylor and McLennan (1995) contained in Table 2. Pollution indices such as geo-accumulation index, contamination factor, degree of contamination, elemental contamination index and metal pollution index were also applied on that data in order to unravel the pollution status of the sediments. Run-off and particle-size plays important role in the mobility of metals in sediments. The mining activities in the area have led to less competent top soil, thereby enhancing infiltration into the subsurface as well as run-off at the surface. Depending on either influent or effluent stream, sediment can be polluted by both natural processes (Amadi *et al*., 2017). The pH of the sediments ranged from 4.6 to 8.0 with a mean value of 5.5 indicating that the sediments are slightly acidic. The low pH in water increases the sorption and mobility rate in metals (Amadi *et al*., 2016). That is, the lower the pH value the more metal that can be found in solution and thus more metals is mobilized. The sediment organic matter is important for the retention of metals by soil solids, thus decreasing mobility, however at higher pH metals tend to be more soluble hence enhancing the formation of organic matter metal complexes (Nachtergaele *et al.,* 2002; Nwankwoala *et al.,* 2017).

Table 1: Statistical Summary of Metal Concentrations in Sediment from Shikira Gold Field

Parameters (ppm)	Minimum	Maximum	Mean	Std. Deviation
pH	4.60	8.00	5.50	6.15
Manganese	79.42	271.11	145.93	75.17
Cadmium	53.34	94.48	78.32	16.06
Mercury	26.50	62.64	44.95	15.59
Lead	3.77	402.97	119.31	166.76
Copper	0.00	203.97	42.87	90.10
Zinc	21.63	119.81	42.45	43.26
Cobalt	0.00	0.10	0.02	0.05
Nickel	1.80	30.50	7.40	16.17
Arsenic	0.00	1.05	0.25	0.46
Iron	114.56	1258.60	402.52	587.95

The concentration of manganese in the stream sediments varied from 79.42 – 271.11 ppm with an average value of 145.93 ppm (Table 1). The concentrations of manganese in stream sediments were lower than the recommended standard of 527 ppm given by Wedepohl (1995) and 600 ppm given by Taylor & Mclenna (1995), an indication of no contamination in the sampled locations. Manganese is an essential element for plant and animal growth and development. Manganese can be adsorbed by sediment, the extent of adsorption depending on the organic content, cation exchange capacity, pH and temperature of the river.

Table 2: Statistical Summary of mean concentration of elements in sediment from Shikira Gold Field compared with average crustal abundance (Wedepohl, 1995; Taylor and Mclenan, 1995)

Parameters	Mean conc. (ppm)	Guideline for maximum allowable limit in upper continental crust			
		Wedepohl, (1995)	*Status*	*Taylor and Mclenan (1995)*	*Status*
Mn	245.93	527 ppm	Low	600 ppm	Low
Cd	89.32	0.102 ppm	High	0.098 ppm	High
Hg	44.95	0.056 ppm	High	0.040 ppm	High
Pb	119.31	17 ppm	High	20 ppm	High
Cu	42.87	14.3 ppm	High	25 ppm	High
Zn	42.45	52 ppm	Low	71 ppm	Low
Co	0.02	11.6 ppm	Low	10 ppm	Low
Ni	7.40	18.6 ppm	Low	20 ppm	Low
As	0.25	0.055 ppm	High	0.050 ppm	High
Fe	402.52	30890ppm	Low	7.07ppm	Low

The concentration of cadmium in the sediments ranged from 52.34 – 94.48 ppm with a mean value of 78.32 ppm (Table 1). Cadmium is a relatively rare metal and is the 67th most abundant elements in the earth crust with crustal abundance of 0.15 ppm in soils. The result of the analyses revealed that the stream sediments are highly contaminated with cadmium with many locations having concentrations above the referenced standard. Artisanal mining exposes the heavy metals contained in the rock into the environment. The study revealed that the concentration of cadmium decreases away from the mining sites (Fig. 4), which is an indication that the anthropogenic activities in the area are responsible for high cadmium concentration in sediment in the area. Cadmium solubility increases under low pH and forms soluble complexes which greatly increase its mobility and very little adsorption of Cd by sediment colloids, hydrous oxides, and organic matter takes place. At higher pH values greater than 6, cadmium is absorbed by sediment solid phase or is precipitated, and the solution concentrations of Cd are greatly reduced (Che *et al*. 2003; Amadi *et al*., 2015).

The concentration of lead in the stream sediments (Fig. 5) varied from 3.77 – 402.97 ppm with an average value of 119.31 ppm (Table 1). The concentration of lead was found to be high in locations 1, 2, 3, 4, 5, 6, 7, 8 and 11.

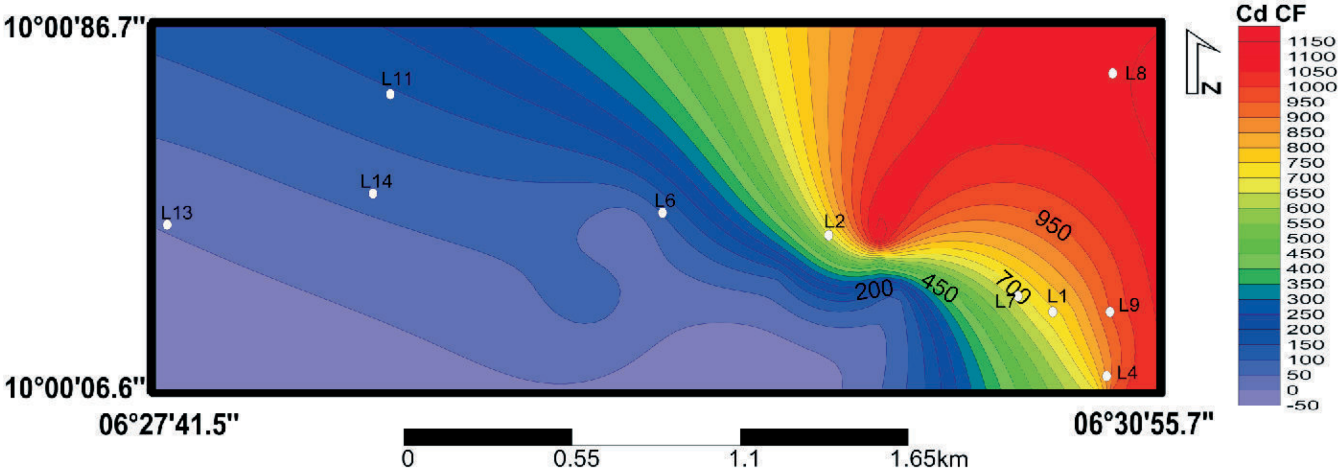


Fig. 4: Concentration Map of Cadmium in Stream Sediment from Shikira gold mining sites

There values are above the specification of 17 ppm of Wedepohl (1995) and 20 ppm given by Taylor & Mclenna (1995). The high contamination of the soil in the area by lead can be linked to the gold mining in the area. Galena (PbS) is the ore hosting the gold in the area. It is most often discarded by the miners on the surrounding soils where they are weathered and subsequently leached into the subsurface. Lead toxicity leads to anaemia both by impairment of haemo-biosynthesis and acceleration of red blood cell destruction. The solubility of Pb in soil solution is strongly determined by the pH. At pH values above 6, Pb is either adsorbed on clay surfaces or forms lead carbonate. At near neutral pH range, higher organic matter promotes the formation of organo-lead complexes thereby increasing lead solubility.

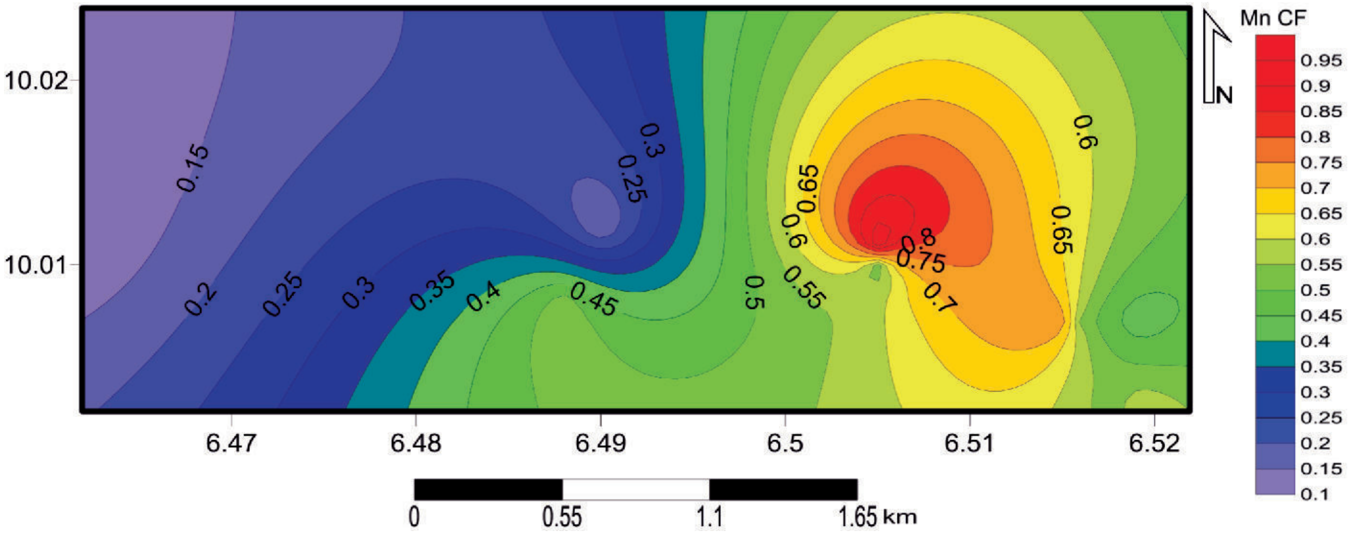


Fig. 5: Concentration Map of Lead in Stream Sediment from Shikira gold mining sites

Concentration of copper in stream sediments (Fig. 6) ranged between 0.00 – 203.97 ppm with a mean value of 42.87 ppm. Samples from locations 3, 4, 6, 7 and 8 are contaminated with copper. Samples from locations 3, 4 and 7 exceed Taylor and Mclenna (1995) acceptable value of 25 ppm while locations 6 and 8 exceed Wedepohl (1995) acceptable value of 14.3. Copper contamination in soils could result from weathering of copper-rich rocks discarded on the environment in the course of gold mining. Exposure to high concentration of copper can lead to health problems such as pulmonary oedema, lung carcinoma and transitory fever (Pascual *et* *al.,* 2004). Gabbro and basalt have the higher concentration of copper while granodiorite and granite have the least copper contents. This implies that soils derived from mafic rocks would have higher natural copper contents than those from felsic varieties (Pascual *et al.,* 2004; Okunlola *et al.* 2016).

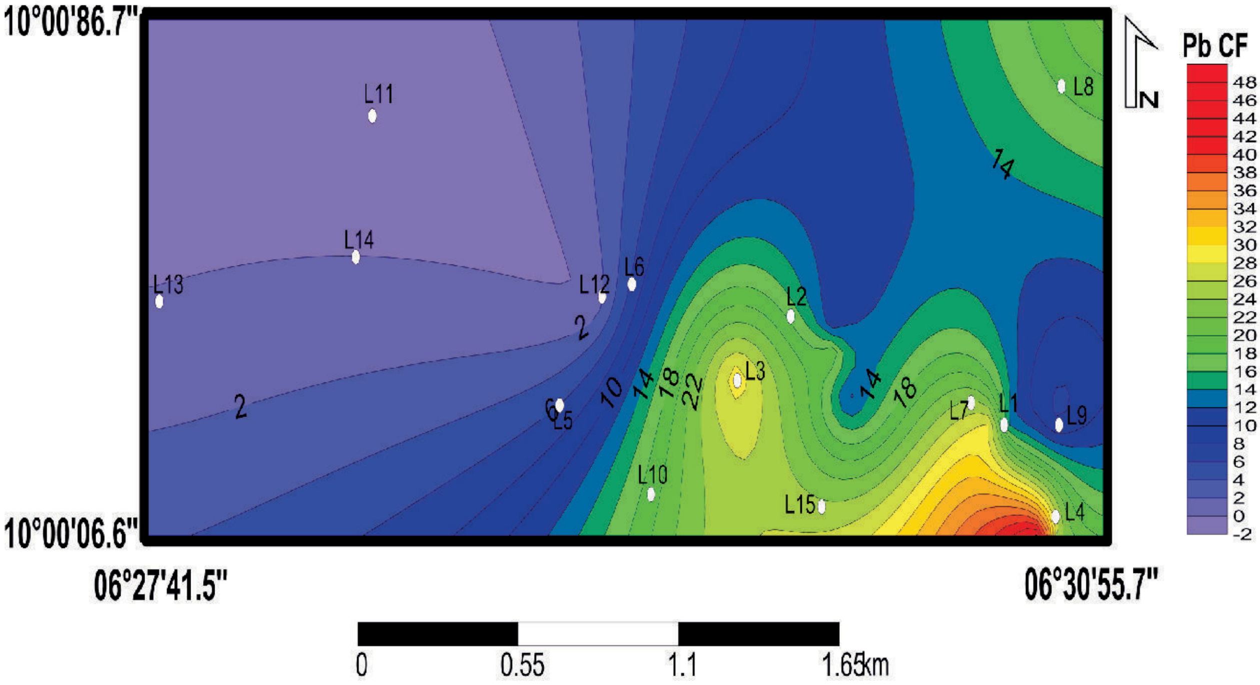


Fig. 6: Concentration Map of Copper in Sediment from Shikira gold mining sites

The concentration of mercury in sediment (Fig. 7) varied from 26.50 – 62.64 ppm with an average value of 44.95 ppm. The area is highly polluted with mercury as all the samples from all the locations were above the acceptable limits of both Wedepohl (1995) of 0.056 ppm and the Taylor and Mclenna (1995) of 0.040 ppm (Table 1). The use mercury by the miners in processing of gold may be responsible for the high content in sediments.

Mercury is a chemical element with atomic number 80 and a silvery-white metal which is liquid at ordinary temperature. It is a rare element with a crustal abundance of 0.08 ppm. It is found either as a native metal (rare) or in cinnabar (HgS) and corderoite. The mobility of mercury increased with pH making mercury more soluble in water.

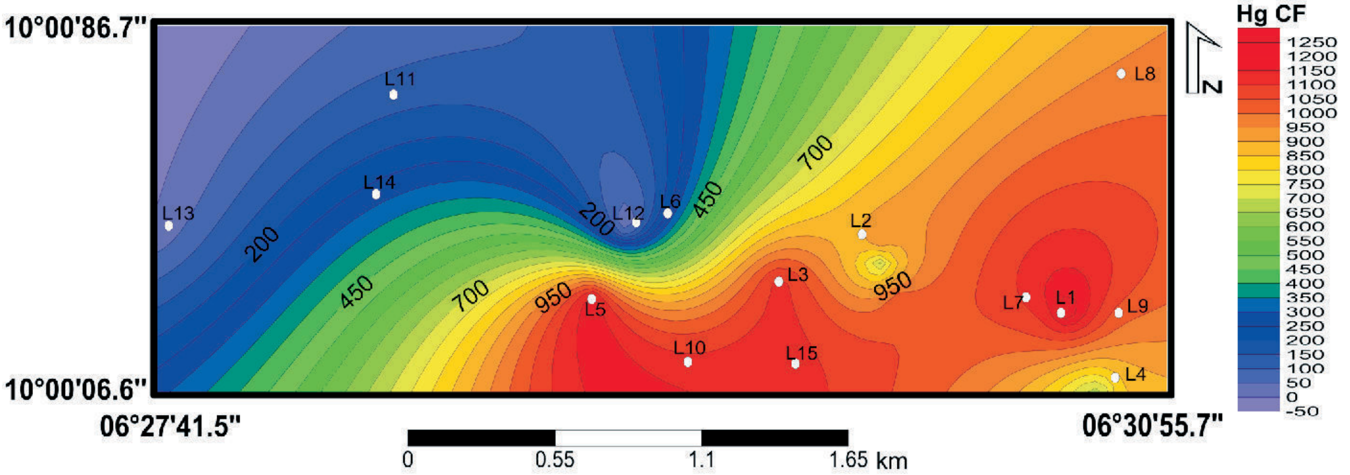


Fig. 7: Concentration map of Mercury in Stream Sediments from Shikira gold mining sites

The concentration of zinc in stream sediment in the study area ranged from 21.63 – 119.81 ppm and an average value of 42.45 ppm. Sample from locations 3 and 10 are found to exceed the acceptable limit of 52 ppm of Wedepohl (1995), while only location 3 exceeds 71 ppm of Taylor and Mclennan (1995). Zinc is an essential element for plants, animals and human beings with a specific gravity of 7.14, a melting of 420 °C and boiling points and 907 °C with an average concentration of 132 ppm in an uncontaminated soil (Alloway, 1990). Zinc concentration in sediments is a function of the composition of parent rock, as well as anthropogenic activities such as mining. The concentration of nickel in sediment varied from 1.80 – 30.50 ppm with a mean value of 7.40 ppm (Table 4.8). These values are below the average crustal abundance of 80.00 ppm for uncontaminated sediments postulated by Dineley *et al.* (1976), which implies that the soil from the area is uncontaminated with respect to nickel.

The concentration of arsenic in stream sediment (Fig. 8) varied from 0.00 – 1.05 ppm with an average value of 0.25 ppm. Samples from locations 1, 3 and 5 have concentration exceeding the acceptable standard. Arsenic is found to be above the acceptable limit of 0.055 ppm and 0.050 ppm of both Wedepohl (1995) and Taylor and Mclennan (1995) and this signifies pollution by arsenic in those locations. Arsenic has a crustal abundance of 5.00 ppm (Prasad and Kumari, 2008). Studies have shown that sediment overlying sulphide deposits and those in which pesticides have been applied can have chances of having high arsenic concentration Anthropogenic source of arsenic in the environment include the use of phosphatic fertilizers in farming as well as artisanal mining. Arsenic occurs as pathfinder element to gold and makes it present in most gold fields. Both pH and ionic exchange are important in determining the mobility of arsenic in sediments. At high redox levels As(V) predominates and arsenic mobility is low, and as the pH increases and redox level reduces As(III) becomes predominant thereby increasing its mobility because of its high solubility (Amadi and Nwankwoala, 2013).

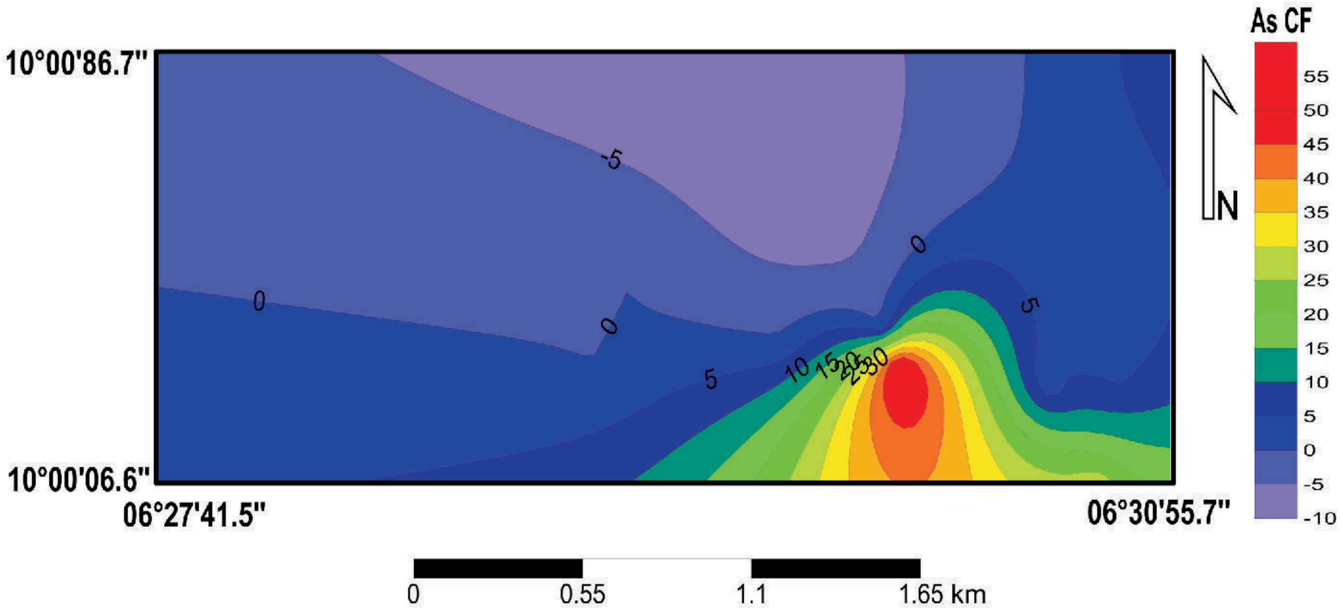


Fig. 8: Concentration map of Arsenic in Stream Sediments from Shikira gold mining sites

The concentration of cobalt in stream sediment varied from 0.00 – 0.10 ppm with an average value of 0.02 ppm. There is no pollution by cobalt from all the sampled locations. Concentrations of cobalt in all the locations are below the 11.6 ppm of Wedepohl (1995) and 10 ppm of Taylor and Mclennan (1995). The concentration of iron in stream sediment varied between 114.56 – 1,258.60 ppm with a mean value of 402.52 ppm. The concentration of iron in sediments depends upon the source rocks from which the soil was derived, transport mechanisms, and overall geochemical history. This is particularly true in stream sediments and groundwater systems that have been environmentally impacted by mining. Iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{+2}) or oxidized insoluble trivalent ferric iron (Fe^{+3}). It has been observed that the high iron value in sediment from the area may be due to the infiltration and run-off of iron stained soil in the course of water movement.

Pollution Indices

In order to determine the level and extent of metal pollution in the stream sediments around the vicinity of Shikira gold mining sites, pollution indices such as geo-accumulation index, contamination factor, degree of contamination and elemental contamination index were applied on the data. The relationship among the metals was also revealed using Pearson's correlation analysis.

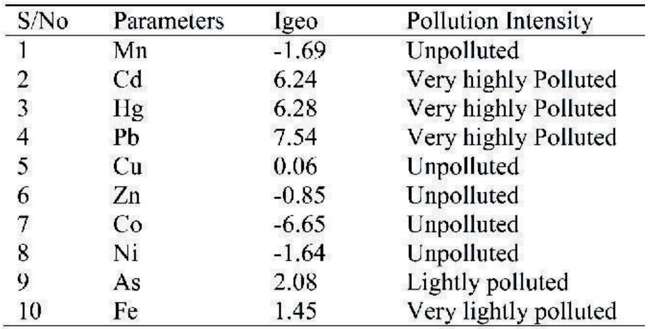
Index of Geo-accumulation (Igeo)

The geo-accumulation index is quantitative check used to describe the concentration trend of metals in soils, sediments and rocks. It was proposed by Mueller (1979) and cited by Lokeshwari and Chandrappa, (2006). It has been widely used to evaluate the degree of metal contamination in terrestrial and aquatic environments. Mathematically, it is expressed as:

$$GeoI \geq \ln [C_m / 1.5 * B_m) \text{ ....(i)}$$

Where: $C_m \geq$ measured concentration of heavy metal in the stream sediment; $B_m \geq$ geochemical background value/Crustal abundance in the upper crust; The factor 1.5 accounts for the possible variation in the background data due to lithologic variation. The result of the Igeo (Table 3) revealed that stream sediment from the Shikira gold mining sites were highly polluted with cadmium, mercury and lead, lightly polluted with arsenic, very lightly polluted with iron and unpolluted with copper, manganese, zinc, cobalt and nickel. The enrichment of the stream sediments by cadmium, mercury, lead and arsenic can be attributed to the artisanal mining going on in the area as subsequent run-off downstream. They miners use mercury as to concentrate gold in the course of panning and at various level of gold processing, while lead, cadmium and arsenic are pathfinder elements to gold and are often discarded into the surrounding streams as gangue. This may explain why the concentrations of the metals are high in stream sediment in the order of: Hg > Cd >Pb> As > Fe > Cu > Zn Ni >Mn> Co. Geological phenomenon such as weathering, bedrock dissolution as well as surface run-off releases these metals from their host rock into the nearby stream sediment. The consistency in the computed heavy metals in the above order across pollution indices is a testimony on the efficacy of pollution indices in assessment of stream sediment quality.

Table 3: Computed Geo-accumulation Index values for sediment from Shikira Mining Sites



S/No	Parameters	Igeo	Pollution Intensity
1	Mn	-1.69	Unpolluted
2	Cd	6.24	Very highly Polluted
3	Hg	6.28	Very highly Polluted
4	Pb	7.54	Very highly Polluted
5	Cu	0.06	Unpolluted
6	Zn	-0.85	Unpolluted
7	Co	-6.65	Unpolluted
8	Ni	-1.64	Unpolluted
9	As	2.08	Lightly polluted
10	Fe	1.45	Very lightly polluted

< 1 ≥ Unpolluted; Igeo>1 - ≥ 2 ≥Very Lightly Polluted; 2 <Igeo ≥ 3 ≥ Lightly Polluted; 3 <Igeo ≥ 4 ≥ Moderately Polluted; 4 <Igeo ≥ 5 ≥ Highly Polluted; Igeo> 5 ≥ Very highly Polluted.

Contamination Factor (CF)

The Contamination factor is used to describe the intensity of contamination in soils and sediments. It is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area (Tijani *et al.*, 2004). It is expressed as:

$$CF \geq C_m / B_m \text{ ....(ii)}$$

Where: C_m is the mean concentration of metal m in soil/sediment and B_m is the background concentration (value) of metal m, either taken from the literature (average crustal abundance) or directly determined from a geologically similar material. The contamination factor (CF) is used to determine the contamination status of the soil and sediment around a mining site in the present study. The result of the contamination factor for stream sediment is shown in Table 4. The results revealed that the stream sediments in the vicinity of Shikira gold mining sites are highly contaminated with cadmium, mercury and lead, considerably contaminated with arsenic and iron, while the intensity of contamination by copper, manganese, zinc, cobalt and nickel were low. The contamination intensity of the analyzed heavy metals decreases in the following order: Hg > Cd >Pb> As > Fe > Cu > Zn > Ni >Mn> Co. The enrichment of these metals in the stream sediment may be attributed to the anthropogenic activities such as mining in the area as well as natural processes such as bedrock dissolution and chemical weathering. Majority of the observed elements are contained in the minerals that make up the rocks in the area and are exposed and subsequently released into the stream sediment through run-off and other human activities such as gold mining. The similarity in the results of pollution intensity as observed in geo-accumulation index and contamination factor confirmed the fact that stream sediment in the area has been polluted by mining activities in the area.

Table 4: Calculated Contamination Factor values for stream sediment from the area

S/N	Parameters	CF	Contamination Factor
1	Mn	0.28	Low Contamination
2	Cd	7.68	Very High Contamination
3	Hg	8.02	Very High Contamination
4	Pb	7.02	Very High Contamination
5	Cu	1.59	Moderate Contamination
6	Zn	0.62	Low Contamination
7	Co	0.29	Low Contamination
8	Ni	0.02	Low Contamination
9	As	3.47	Considerable Contamination
10	Fe	1.26	Moderate Contamination

CF < 1 ≥ Low Contamination Factor;
1 ≥ CF < 3 ≥ Moderate Contamination Factor
3 ≥ CF < 6 ≥ Considerable Contamination Factor;
CF ≥ 6 ≥ Very High Contamination Factor

Degree of Contamination

The degree of contamination (Cd) is the summation of all contamination factors.
Mathematically,

$$Cd = \Sigma\,(CF) \qquad \text{(iii)}$$

Where: Cd ≥ Degree of contamination
CF ≥ Contamination factor

The summation of contamination factors from Table 4 gave corresponding values of 30.25. These values fall in the class of very high degree of contamination under Table 5. The degree of contamination of the metals confirms that sediment around Shikira gold mining sites are highly contaminated with metals due gold mining activities in the area.

Table 5: Degree of Contamination

S/N	Cd	Degree of Contamination
1	Cd < 6	Low degree of contamination
2	6 = Cd < 12	Moderate degree of contamination
3	12 = Cd < 24	Considerable degree of contamination
4	Cd ≥ 24	Very high degree of contamination

Metal Pollution Index

Metal Pollution index (MPI) is a method of rating that shows the composite influence of individual parameters on the overall quality of sediment, soil or water. The rating is a value between zero and one. The higher the concentration of a metal compared to its maximum allowable concentration, the worse the quality of the soil, water or sediment (Amadi, 2011; Tamasi and Cini, 2004). It is expressed as:

$$MPI = \sum_{i=1}^{n} \left[\frac{Ci}{(MAC)i}\right] \qquad \text{(iv)}$$

Where: C_i: mean concentration
MAC: maximum allowable concentration

According to Amadi *et* al., (2013), metal pollution index is an effective means of communicating soil, sediment and water quality to stakeholders in the environmental sector.

The results of the metal pollution index on stream sediments are shown in Table 6. It can be further observed that the degree of metal pollution in the sediment around Shikira gold mining sites ranged from strongly polluted (mercury, lead and cadmium), through slightly polluted (arsenic, copper and iron) to unpolluted (manganese, zinc, cobalt and nickel). Similar results are obtained in other gold field around the world (Che *et al.* 2003; Cesar *et al.,* 2006; Ghrefat and Yusuf, 2006). The subsurface leachate and surface run-off from the various human activities in the area is potential pathway for the contamination of sediment.

Table 6: Calculated Heavy Metal Pollution Index for stream sediments in the Area

Parameters (ppm)	HMPI Value	Rating
Mn	-0.89	Unpolluted
Cd	15.90	Strongly Polluted
Hg	26.30	Strongly Polluted
Pb	22.70	Strongly Polluted
Cu	1.01	Slightly Polluted
Zn	0.98	Unpolluted
Co	0.67	Unpolluted
Ni	0.85	Unpolluted
As	1.12	Slightly Polluted
Fe	1.08	Slightly Polluted

<1≥ Unpolluted; 1 – 4.99 ≥ Slightly polluted;
5 – 19.99 ≥ Moderately polluted;
20 – 40 ≥ Strongly polluted;
> 40 ≥ Very strongly polluted

Elemental Contamination Index

Elemental contamination index is used for the expressions of a single metal contamination within a sample or combined metal contamination for a sample comparative to the background values of the individual metal and it is expressed as:

$ECI \geq (Cn - Bn)/Bn$ ....(v)

Where Cn is the concentration of metal in sample
Bn is the background concentration of the metal.

The outcome of the elemental contamination index (ECI) for stream sediments is contained in Table 7. Interestingly, the outcome is very similar with those of index of geo-accumulation, contamination factor, degree of contamination and metal pollution index. This confirms the utility of pollution indices in geochemical studies.

Table 7: Calculated Elemental Pollution Index for stream sediments in Shikira Area

Parameters (ppm)	ECI Value	Rating
Mn	0.17	Very Low Contamination
Cd	48.40	Very High Contamination
Hg	59.00	Very High Contamination
Pb	73.90	Very High Contamination
Cu	0.55	Very Low Contamination
Zn	0.45	Very Low Contamination
Co	0.11	Very Low Contamination
Ni	0.04	Very Low Contamination
As	5.02	Moderate Contamination
Fe	2.58	Very Low Contamination

< 5 ≥ very low contamination; 5 – 9.99 ≥ low contamination;
10 – 24.99 ≥ medium contamination;
25 – 49.99 ≥ high contamination;
50 – 100 ≥ very high contamination;
> 100 ≥ extremely high contamination

Conclusion

The present study clearly established that gold mining constitute a major source of pollution in the Shikira gold mining sites especially the stream sediment which serves as accumulation points for pollutants in surface water regime. It should be noted that the concentration of the metals decreased away from the mining sites along stream channels. The concentration maps of the analyzed metal in sediments also validate the decrease in concentration away from the mining sites towards the community. Natural attenuation mechanism such as ionic exchange, adsorption, absorption and dilution help in the reduction process of the pollutants. Pollution indices have proved to be effective and efficient the determination of pollution status of an area. The geo-accumulation index, contamination factor, degree of contamination, elemental contamination index and metal pollution index revealed that the sediment in the area are highly polluted with mercury, cadmium and lead, moderately polluted with arsenic, lightly polluted with iron and copper and unpolluted with manganese, zinc, cobalt and nickel in the order of: Hg > Cd > Pb > As > Fe > Cu > Mn > Zn > Co > Ni. Among significant variables that control the distribution and enrichment of heavy metals in sediment are water pH, sediment grain size, run-off, slope, organic matter content and the cation exchange capacity, porosity and permeability of the soil. The use of modern mining equipment that are environmentally friendly are recommended.

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1. **Plot of specific capacity (m^2/day) versus the borehole discharge/yield of studied boreholes in parts of Ibadan, SW, Nigeria.**
2. **Agro-mineral resources sample locations within the framework of geology of Nigeria (modified after Obaje, 2009)**
3. **Part of the Maijuju Younger granite ring complex showing Lineation on the rock, NC, Nigeria.**