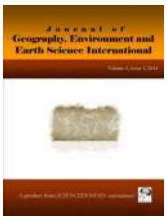

Journal of Geography, Environment and Earth Science International
5(4): 1-13, 2016; Article no.JGEESI.24908
ISSN: 2454-7352

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Use of Enrichment, Ecological Risk and Contamination Factors with Geoaccumulation Indexes to Evaluate Heavy Metal Contents in the Soils around Ameka Mining Area, South of Abakaliki, Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Author MON designed the study, wrote the protocol and wrote the first draft of the manuscript. Author MON managed the literature searches and analyses of the study performed the spectroscopy analysis. Author SNU managed the experimental process. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JGEESI/2016/24908
Editor(s):
(1) Iovine Giulio, CNR-IRPI (National Research Council-Institute of Research for the Geo-hydrologic Protection) of Cosenza, Italy.
Reviewers:
(1) Eleonora Deschamps, FUMEC University, Brazil.
(2) Tariq Hasan Al-Najjar, The University of Jordan, Jordan.
Complete Peer review History: http://sciencedomain.org/review-history/13979

Original Research Article

Received 7th February 2016
Accepted 21st March 2016
Published 1st April 2016

ABSTRACT

Use of enrichment, ecological risk and contamination factors with geo-accumulation indexes were employed to evaluate the Content of Cd, Cu, and Ni in the soils around Ameka mining area, South of Abakaliki, Nigeria. Ecological risk indices and contamination indexes namely, enrichment factor, geo-accumulation index, degree of contamination, contamination factor and pollution load index were used in the assessment of level of metal contamination in the soils around Ameka mining area, Southern Benue Trough Nigeria. Fifteen (15) soil samples were collected at the depth of 5 cm from various locations for laboratory analysis. From the results, the variation of Cu, Zn and Cd concentrations is controlled by anthropogenic intense agriculture activities. For all sites, concentrations of heavy metal in the soils do not exceed the permissible US EPA standard. From

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the results the pollution load index values ranged from 0.19 to 0.86 indicating that the soils were moderately contaminated. As for the single-factor pollution, the average values ranging from 0.25 to 6.52 indicate that the potential ecological risk of the metals in the three sampling sites all has low ecological risk level. The ecological risk assessment revealed the possibility of soils being not polluted. The significant spatial variation recorded in the concentrations of some parameters used in characterizing the sediment quality is a reflection of impacts of anthropogenic activity on quality of the mining area. The geo-accumulation index also revealed that the sediments at all stations were practically uncontaminated by heavy metals. The results of all the contamination indexes used agreed well in explaining the contaminated levels and possible sources of the metals present in the mining area samples. This study recommends an immediate plan for analysis of the quality of drinking water and some staple crops grown in the area to determine the levels of these noxious metals and uptake by plants, to be followed by a comprehensive mitigation plan.

Keywords: Abakaliki; enrichment factor; geo-accumulation index; pollution load index; Southern Benue Trough.

1. INTRODUCTION

The environmental problem of soil and sediment pollution associated with heavy metals according to [1] has received increasing attention in the last few decades in both developing and developed countries. According to [2], environmental issues that pose a threat to soil health include erosion, contamination, sealing, compaction, salinization, landslides, a decline in organic matter content and biodiversity. Pollution of the natural environment by heavy metals is a universal problem because metals are indestructible and most of them have toxic effects on living organisms, when permissible concentration levels are exceeded. Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment. Soil heavy metal contents are not only the serious environmental issue but also frequently related to agricultural soil utilization problems. Soil heavy metals could be beneficial to plants at certain levels but toxic when exceeding specific threshold. If these elements are absorbed by the plants through the root system, they may enter the food chain and become toxic to humans and animals. The ecological importance of soil heavy metals is closely related to human health due to their high ecological transference potential. Researchers such as [3] and [4] have carried out extensive studies on the trace elements in soils from varieties of environments throughout the world, including industrialized cities, highway road sides [5] and rural areas in old mining regions [6]. [7,8] agreed that contamination and subsequent pollution of the environment by toxic heavy metals have become an issue of global concern due to their sources, widespread distribution and multiple effects on the ecosystem. Other studies [9-12] showed that the concentration of heavy metals in soils may vary depending on the intensity of numerous factors of anthropogenic and natural origin.

The people of Ameka are known producers of rice and cassava in Ebonyi State, Southeastern Nigeria. A management plan against the transfer of metals into the ecosystem is needed in order to alleviate existing metal-related health problems. This can be done by reducing the solubility and concentration of metals in the soil to reduce metal intake through the consumption of contaminated forages and soil. Mining is considered to be one of the most dangerous anthropogenic activities affecting soil quality. Uncontrolled mining activities in developing countries have left a lot of environmental hazards, enormous amount of wastes and different types of pollutants on the mining communities. In Nigeria over 75% of solid mineral production is done by artisan and small scale miners, who are frequently challenged by lack of appropriate mining exploitation methods and limited knowledge of mineral processing techniques. Mining activities are being carried out in Ameka, southern Benue Trough Nigeria because of the large deposit of lead and zinc. There are currently wide varieties of methods used to evaluate soil contamination. Most commonly used quantitative methods are the contamination factor (CF), degree of contamination (Dc), enrichment factor (EF) and geo-accumulation index (I_{-geo}). The CF, defined by [13], enables an assessment of soil contamination through the use of concentrations in the surface layer of bottom sediments to preindustrial levels as a reference. Ecological risk assessment of heavy metals in polluted soils has been gaining more attention in recent years. The ecological risk assessment can reveal the

possibility of soil being polluted and even for the ecological function to be harmed by concerned heavy metals. [14] in their work noted that a great deal of data related to soil pollution load by heavy metals can possibly be measured to access the quality of ecological chemistry. The pollution load index provides a simple and comparative means for assessing the level of heavy metal pollution. The potential ecological risk index was proposed by [13] based on elemental abundance and release capacity. The potential ecological risk index shows the differences in bioavailability, relative contribution ratio and geographical space, which is a comprehensive index to reflect the effects of heavy metals on the ecological environment [15]. Though there are some published literatures on heavy metal pollution most particularly in the lead-zinc mining district of Abakaliki, southeastern Nigeria [16,17], the impact and concentrations of the metals have not been discussed extensively using most of the above mentioned contamination indices. However, the overall objective of the present study is to assess the heavy metal contamination using different pollution indices. As a matter of fact, contamination factor and degree of contamination means that a first step towards a diagnostic tool to assess the level of anthropogenic sources, risk factors and risk indices were used as a second step to establish ecological adverse effects. The justification for the work is the fact that Ameka area is well positioned to receive effluents from the various agricultural, mining and quarrying activities which flourish within the neighborhood cities in Ebonyi State, Nigeria.

2. PHYSIOGRAPHY AND GEOLOGY

2.1 Physiography of the Area

The relief of Ameka area is generally undulating and no location exceeds 400 m above-sea-level. The predominant shale within the study area has favored the low erodability of the lithology, resulting in absence or near absence of deep cut valleys and erosion channels. The major river that drains the area is the Ebonyi River and its tributaries, Iyiokwu, Ameka and Amana Rivers. The Ameka area experiences two distinct climates, referred to as the dry and wet (rainy) seasons. The wet season begins in March and ends in October and is characterized by frequent, high volume rainfall, relatively low temperature, and high relative humidity. The dry season begins in October and ends in February and is characterized by infrequent rainfall, high temperature, and low relative humidity. Temperature in the dry season ranges from 20 to 38℃ and during the rainy season, 16 to 28℃. The average monthly rainfall ranges from 3.1 mm in January to 270 mm in July. Average annual rainfall varies from 1,500 to 1,650 mm. The Ameka area lies within one of the four vegetation zones in Nigeria. Regionally the vegetation type is derived savanna. According to [18], topography, drainage and rainfall control the vegetation. The vegetation type of the Ameka area is parkland; this is characterized by stunt trees and pockets of derelict woodland and secondary forest consisting of few shrubs with dispersed large trees and climbers. Its vegetation in most locations is densely populated with grasses and trees of different sizes. The area is marked by undulated range of shale outcrops which are either greyish or reddish brown in colour depending on the shale contents and degree of weathering. The vegetation has largely been modified by farming, mining and construction practices of the people in the study area.

2.2 Geology of the Area

Tectonism in southern Nigeria probably started in early Cretaceous with the separation of Africa from South America and the opening of the south Atlantic. The Benue Rift (see Fig. 1) is generally believed to be an intracontinental rift valley formed during this separation and referred to as aulacogen [19]. The first marine transgression took place in Albian or Aptian time and resulted in the deposition of the Asu River Group in the Abakaliki area. This was followed by the Cenomanian period in which there was virtually no deposition in the Southern Benue Trough except the Odukpani Formation in the Calabar Flank [20]. Further transgression and regression according to [20] took place during Turonian period which deposited the Eze-Aku Formation and the Awgu Shale in the Coniacian. Ameka mining area is located in the southern part of the Benue Trough in Ebonyi State (Fig. 1), Southeastern Nigeria, covering an area of 64 km^2. The geology of the area comprises of sequences of sandy shales, with fine grained micaceous sandstones, mudstones, limestones and volcanic rocks are Albian in age belonging to the Asu River Group as described by authors such as [19] and [20]. The sedimentary rocks are predominantly black carbonaceous shale with intercalation of thin calcareous matter and pyritic with lenses of sandstone and limestone. The rocks are extensively fractured, folded and

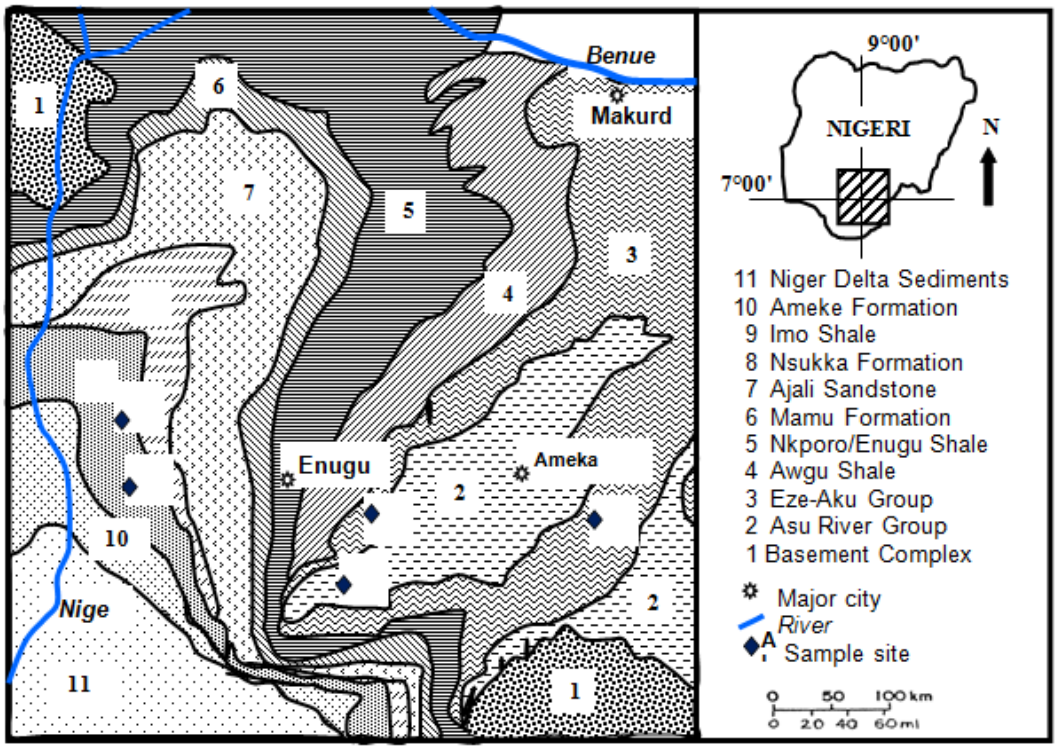

Fig. 1. Geological map of southern Benue Trough showing Ameka mining area (Modified from [21]

faulted. In the Enyigba, Ameri and Ameka areas which are all near Abakaliki area, according to [19] there is incontrovertible evidence of post-mineralization deformation. Although the age of mineralization is not precisely known there is general suggestion that the lodes were developed at the end of Santonian folding [18,19]. [20] postulated a volcanic source for the ore-forming fluids, due to the volcanic activity in Abakaliki area based on the close proximity of few of the deposits. The Benue Trough Pb-Zn mineralization occupies a 600 km stretch of highly deformed Albian sediments from Abakaliki- Ishiagu (Ebonyi State) to Gwana (Gombe State). The mineralization consists of a few occurrences of telethermal Mississippi valley-type Pb-Zn deposits, localized as open space fillings within steeply dipping fractures. The deposits have been mined on and off for several decades. Ameka host massive deposit of the mineralization but of a shallow deposit with a low grade compared to Enyigba and Ameri area.

3. MATERIALS AND METHODS

Fifteen (15) samples were collected at the depth of 5 cm from various locations within the Ameka mining area for laboratory analysis. Fig. 2 shows the accessibility map of Ameka area, southern Benue Trough Nigeria [21,22] indicating the locations where soil samples were collected. The soil samples are herein coded Q1 to Q15 with Q1 to Q5 representing sampling site A, Q6 to Q10 represent sampling site B and Q11 to Q15 represent sampling site C. Soil samples were air-dried, sieved, and analyzed in the laboratory using standard techniques. Procedure for collection and preparation of the samples were in accordance to the method adopted by Abida and outlined in [23]. The collected samples from each point were air – dried and impurities such as clods and crumbs were removed. The dried soil was passed through a 2 mm sieve to remove coarse particles; the soil was then sub-sampled and ground to fine powder using laboratory mortar and pestle in preparation for chemical analysis. A sample of 1.25 g of air – dried ground soil was digested in aqua regia, a mixture of 25% of HNO_3 and 75% of HCl. The resulting solution was analyzed for heavy metals using flame atomic absorption spectrophotometer (SOLAAR 9 SERIES) model AA 6800 equipped with Zeaman background correction and graphite

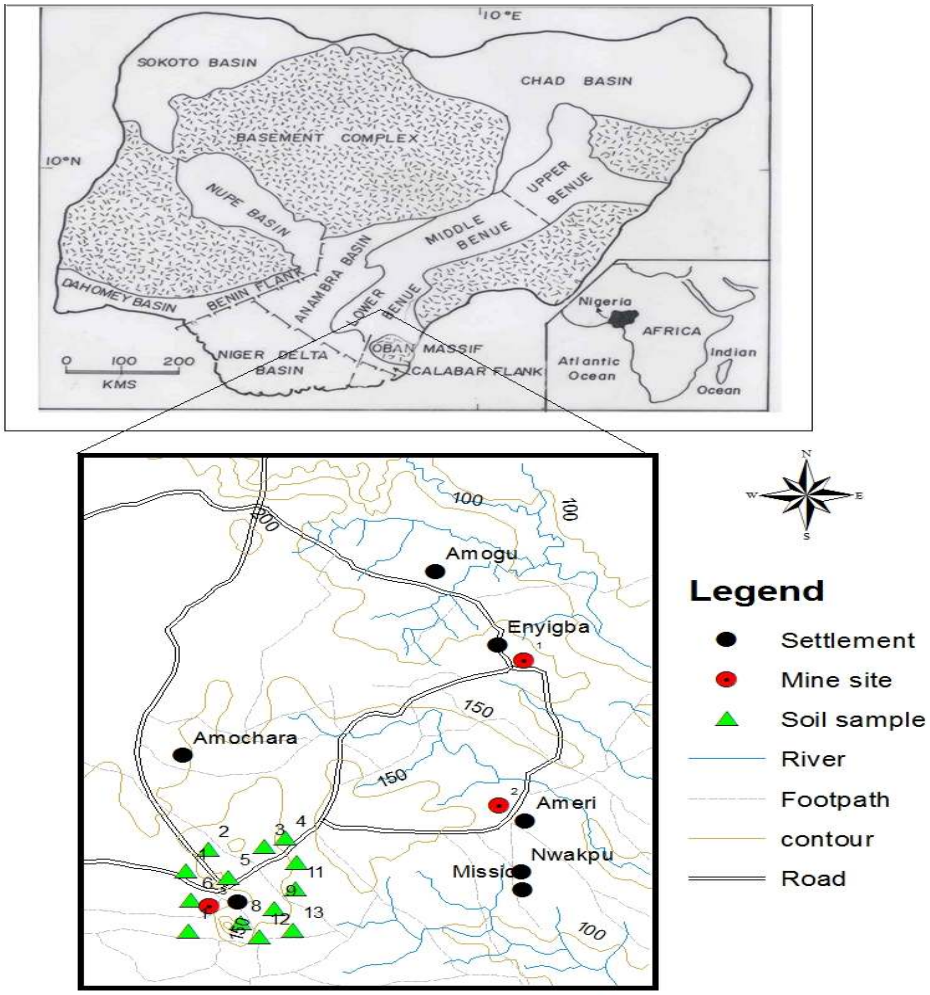

Fig. 2. Accessibility map of Ameka, the study area superimposed by Geologic map of Nigeria (Modified after [21])

furnace. Standard solutions of each of the metals were aspirated to calibrate the atomic absorption spectrophotometer before aspiration of the samples. The Heavy metal concentrations were determined using an atomic absorption spectrophotometer at the National Research Institute for Chemical Technology, Kaduna. The instrument settings and operational conditions were in accordance with the manufacturer's specifications.

3.1 Pollution Indices

This Research adopted the pollution indices classified into three types: (i) contamination indices, (ii) background enrichment indices, and (iii) ecological risk indices as contained in the works of [24] to assess heavy metal contamination.

3.1.1 Pollution load index

Pollution severity and its variation were determined with the use of pollution load index. The Pollution load index is obtained as concentration factor. This concentration factor is the quotient obtained by dividing the concentration of each metal. The pollution load indexes of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. Pollution load index developed by [25] are shown in equations 1 & 2 as follows:

$$PLI=n\sqrt{(C_f^i 1x\, C_f^i 2x\, C_f^i 3x\ldots x\, C_f^i n)} \quad (1)$$

Where

C_f^i = contamination factor,
n = number of metals.

Here, contamination factor (C_f^i) was expanded to be defined as

$$C_f^i = C_i / C_{ri} \quad (2)$$

which is also called concentration factor [26], where C_i is the content of metal *i* instead of mean content from at least 5 sample sites; C_{ri} is the reference value, baseline level of metal *i*. The pre-industrial reference level C_{ri} of Cu, Zn, Cd and Pb is 50, 175, 1.0 and 70 (*μg/g*) according to [13]. The following terminologies are used to describe the contamination factor: $C_f^i<1$, low contamination factor; $1\leq C_f^i<3$, moderate contamination factors; $3\leq C_f^i<6$, considerable contamination factors; and $C_f^i\geq 6$, very high contamination factor.

The degree of contamination is defined as the sum of all contamination factors. According to [25], the following terminologies are used to describe the degree of contamination; Dc<6, low degree of contamination; 6≤Dc<12, moderate degree of contamination; 12≤Dc<24, considerable degree of contamination; Dc≥24, very high degree of contamination. The pollution load index is a potent tool in heavy metal pollution evaluation that provides a simple and comparative means for assessing the level of heavy metal pollution. The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The PLI value of > 1 is polluted, <1 indicates no pollution whereas values of PLI =1 indicate heavy metal loads close to the background level [26].

3.1.2 Ecological risk factor

The potential ecological risk index method proposed by [13] to evaluate heavy metal contamination from the perspective sedimentology reflected in equation 3 was adopted to evaluate the heavy metal pollution in the soils and also to associate ecological and environmental effects with their toxicology and the toxic-response factor T_{ri} of Cu, Zn, Cd, Cr, Ni and Pb is 5, 1, 30, 2, 5 and 5 (*μg/g*), respectively as given by [13]. An ecological risk factor (Er^i) quantitatively expressed as the potential ecological risk of a given contaminant are given by [13] in equation 3 as

$$Er^i = Tr^i \cdot C_f^i \quad (3)$$

Where Tr^i is the toxic-response factor for a given substance, and C_f^i is the contamination factor. The following terminologies are used to describe the ecological risk factor: $Er^i<40$, low potential ecological risk; $40\leq Er^i<80$, moderate potential ecological risk; $80\leq Er^i<160$, considerable potential ecological risk; $160\leq Er^i<320$, high potential ecological risk; and $Er^i\geq 320$, very high ecological risk. The potential ecological risk index (RI) was in the same manner as degree of contamination defined as the sum of the risk factors.

$$RI = \sum_{i=1}^{m} E_r^i \quad (4)$$

Where E_r^i is the single index of ecological risk factor, and m is the count of the heavy metal species. The following terminologies are used for the potential ecological risk index as given by [13]: *RI<150*, low ecological risk; *150≤RI<300*, moderate ecological risk; and *RI>600*, very high ecological risk.

3.1.3 Index of geo-accumulation

The geo-accumulation index (I-geo) as defined by equation (5) was used to quantify the extent of heavy metal contamination associating with the soils. Geo-accumulation index was determined by the following equation according to [27] interpretation which was described by [28].

$$\text{I-geo} = \log 2\ (Ci / 1.5\ Cri) \quad (5)$$

where C_i is the measured concentration of the examined metal *i* in the sediment, and C_{ri} is the geochemical background concentration or reference value of the metal *i*. Factor 1.5 is used because of possible variations in background

values for a given metal in the environment as well as very small anthropogenic influences. The geo-accumulation index was distinguished into seven classes by Müller [29]: $I_{geo} \leq 0$, class 0, unpolluted; $0 < I_{geo} \leq 1$, class 1, from unpolluted to moderately polluted; $1 < I_{geo} \leq 2$, class 2, moderately polluted; $2 < I_{geo} \leq 3$, class 3, from moderately to strongly polluted; $3 < I_{geo} \leq 4$, class 4, strongly polluted; $4 < I_{geo} \leq 5$, class 5, from strongly to extremely polluted; and $I_{geo} > 5$, class 6, extremely polluted.

3.1.4 Enrichment factor

The extent of soils contamination was also assessed using the enrichment factor which was initially developed to speculate on the origin of elements in the atmosphere, precipitation, or seawater [30], but it was progressively extended to the study of soils, lake sediments, peat, tailings, and other environmental materials [31]. Enrichment Factors among other things were used to assess the relative contributions of natural and anthropogenic heavy metal inputs to soils. According to this technique metal concentrations were normalized to the textural characteristic of soils. An equation as proposed by [32] was employed by [33] and [34] to assess degree of enrichment and understand the distribution of elements of anthropogenic origin. Most commonly used reference elements include Sc, Mn, Al and Fe. In this study, Fe was chosen as the geochemical normalizer because of its conservative nature during diagenesis. Moreover, soils in Nigeria have been reported to be rich in Fe [35]. Fe is selected as reference element because Fe has relatively high concentration in the tropics. The redox sensitive iron-hydroxides and oxides constitute significant sink for heavy metals and is one of the widely used reference elements [36,37,34]. Based on [34], EF is defined as:

$$EF = (X/Fe)_{soil} / (X/Fe)_{background} \quad (6)$$

Where $(X/Fe)_{soil}$ is the ratio of heavy metal (X) to Fe in the soil samples from mining sites and $X/Fe)_{background}$ is the natural background value of the metal-Fe ratio. Normalizing element, Fe, with natural background value of 232.7 ug/g was used in the study. The EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas EF>1.0 indicates that the element is of anthropogenic origin [38]. According to [39], five contamination categories are generally recognized on the basis of the enrichment factor: EF<2, depletion to mineral enrichment; 2≤EF<5, moderate enrichment; 5≤EF<20, significant enrichment; 20≤EF<40, very high enrichment; and EF>40, extremely high enrichment.

4. RESULTS AND DISCUSSION

4.1 Hazard Assessment of Heavy Metal

The results for the determination of heavy metals as well as the statistical analysis of heavy metal concentrations of soils are presented in Table 1. The order of occurrence of heavy metals measured in study soils followed the sequence of Fe>Cu> Pb>Si> Zn> Cr>Hg>Ag>Cd lower than the background values and indicating that the soils are not polluted. The result suggests that Due to the influence of mining activities in the study area, Fe, Zn and Cu inputs to the soil in the study area may be attributable to anthropogenic sources. However, high level pollution of Hg and Cd is a serious threat in future because of their accumulation and toxicity effects on marine organisms and the human population. Heavy metals such as Pb and Cd have been implicated in many studies as a threat to vegetation and animals and ultimately affecting the quality of human life through food chain. The significant spatial variation recorded in the concentrations of some parameters used in characterizing the sediment quality is a reflection of impacts of anthropogenic activity on quality of this river. Variation of Cu, Zn, and Cd concentrations is controlled by anthropogenic intense mining activities. The pH values of the soils of Enyigba and Ameka mining areas ranged from 6.4 to 7. 0 according to [40], indicating acidic to neutral. Table 2 shows the average concentrations of the heavy metals in the study area when compared with sediment quality guidelines and background value to assess contamination degree and adverse biological effect. The New York Sediment Criteria and Provincial Sediment Quality Guidelines for metals are divided into low range effect (ISQG-Low) and high effect range (ISQG-High). ISQG-L level indicates the sediment contaminants would not have adverse effects on aquatic organisms in sediment. ISQG-H level indicates that the sediment contaminant certainly have adverse effects on organisms that live in the sediment. Also the level of sediment contamination that is between ISOG-L and ISQG-H shows that the contaminants probably have adverse effects. According to this

comparison, the levels of all the metals are below sediment background values and ISQG-L level. Moderately high concentrations of Fe, Pb, Zn and Cd show evidence of leaching of mine wastes under acidic conditions. For all sites, concentrations of heavy metal in the soils do not exceed the permissible US EPA standard. However, the heavy metals are within US Environmental Protection Agency (EPA) for heavy metal. The results of sediment quality assessment are good evidence to confirm that the surface sediment of the West Port is highly polluted by Cd, Hg and As and it is moderately contaminated with Pb (Table 2); the concentrations of these metals are significantly higher than ISQG-L and their sediment background values.

4.2 Pollution Indices

4.2.1 Contamination and pollution load indices

The calculated values of CF are shown in Table 3. From the results, the values varied from 0.08 to 1.29. Several studies described Cd, Pb, Hg and As originate mainly derived from industrial processes including mining, burning of fossil fuels, waste recycling, cement manufacturing, as well as paper and glass production [42]. Metals like Zn, Cd and Cr have lower (<1) values which according to [13], indicate low contamination factor and Cu which showed values higher (>1) values due to the influence of external discrete sources like industrial activities, agricultural runoff and other anthropogenic inputs, according to [13] indicate moderate contamination factor. According to [43], CF values between 0.5 and 1.5 indicate that the metal is entirely from crust materials or natural processes; whereas CF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. The CF values for Cu, Cr, and Zn were lower than 1 and were found at an unpolluted level at all stations, suggesting these metals may have entirely originated from natural processes or crustal materials. Also, the degrees of contamination values ranging from 1.99 to 2.64 obtained from the metals in Ameka area indicate low degree of contamination (see Table 3). The results of the computed PLI values for soil samples are also presented in Table 3. From the results, PLI values ranged from 0.19 to 0.86 indicates that the soils were moderately contaminated.

The values of PLI (Table 3) were found to be generally low (<1) in all the studied sites. The Pollution Load Index provides a simple, comparative means for assessing a site or estuarine quality: a value of zero (0.0) indicates perfection, values of one (1.0) indicate only baseline levels of pollutants present and values above one > 1.0 indicate progressive deterioration of the site and estuarine quality [25]. Indication from both data sets is that sediments from the soils are unpolluted.

Table 1. Heavy metal concentration in soils of Ameka and environs in (µg/g)

Site	Samples	Si	Zn	Cu	Pb	Cd	Cr	Hg	Ag	Fe
A	Q1	54.88	60.28	86.00	31.67	0.25	0.00	39.3	1.89	157
A	Q2	76.13	72.56	73.13	36.32	0.16	0.00	5.42	1.78	16.2
A	Q3	54.13	21.73	63.12	49.83	0.05	14.92	1.36	0.74	77.7
A	Q4	42.89	67.17	50.15	54.37	0.11	13.21	0.00	0.84	278
A	Q5	38.35	57.30	57.57	97.95	0.11	0.00	0.00	0.74	118
B	Q6	47.71	34.15	114.4	28.49	0.00	7.28	1.36	0.53	279
B	Q7	39.74	26.77	90.56	33.48	0.03	24.48	0.00	1.06	296
B	Q8	25.61	19.74	1.08	33.03	0.00	17.06	0.00	0.74	311
B	Q9	58.20	16.12	23.78	87.51	0.00	37.06	0.00	1.05	275
B	Q10	70.37	36.00	35.85	84.10	0.05	18.28	1.36	0.63	193
C	Q11	38.60	64.40	57.60	97.90	0.14	0.00	0.00	0.74	121
C	Q12	70.30	35.90	36.80	84.10	0.05	18.30	1.36	0.63	192
C	Q13	76.10	72.40	73.10	36.30	0.16	0.00	5.42	1.79	165
C	Q14	44.60	26.80	90.30	33.50	0.03	23.5	6.77	1.06	324
C	Q15	52.50	34.20	114.4	28.50	0.00	10.14	1.36	0.95	294
Minimum		25.61	16.12	1.08	28.49	0.03	7.28	1.36	0.53	16.2
Maximum		76.30	72.56	114.4	97.95	0.25	37.06	39.3	1.89	311
Average		52.67	43.03	64.52	54.47	0.08	12.28	4.25	1.01	206
EPA		Nil	364	310	183	1.00	-	-	-	Nil

Note: EPA- US Environmental Protection Agency for metal

Table 2. Concentrations of heavy metals in this study with sediment quality guidelines in µg/g (Modified after [41])

Subject	Zn	Pb	Cu	Cd	Ni	As	Hg	Cr
New York sediment criteria								
lowest effects range	120	32	16	0.6	16	6	0.15	26
severe effects range	270	110	110	9.0	50	33	1.30	110
Sediment quality criteria								
lowest effects range (ISQG-low)	120	31	16	0.6	16	6	0.2	26
high effects range (ISQG-high)	220	250	110	10	75	33	2	110
Present study (Average values)	43.03	54.47	64.52	0.08	-	-	4.25	12.28

Table 3. Results of contamination indices and pollution load index

Site	Contamination factor of single metal				Degree of contamination by [25]		PLI
	Zn	Cu	Cd	Pb			
A (n=5)	0.32	1.32	0.14	0.77	2.55	Low degree	0.86
B(n=5)	0.15	1.06	0.02	0.76	1.99	Low degree	0.19
C(n=5)	0.27	1.49	0.08	0.8	2.64	Low degree	0.69
Ave.	0.25	1.29	0.08	0.78	2.39	Low degree	

N= number of samples collected from each site

The difference in indices results due to the difference in sensitivity of these indices towards the sediment pollutants. Different heavy metal concentrations of PLI values are in an order of Cd>Zn>Cu>Pb. The values of PLI were found to be very low, and varied between 0.19-0.86, indicating that the Ameka mining areas were unpolluted by total of studied heavy metals using the above index parameters.

4.2.2 Ecological risk analysis

Potential ecological risk indices of Cu, Zn, Cd and Pb in three sampling sites are also shown in Table 4 with the detailed grade recommended by [13]. As for the single-factor pollution, the average values ranging from 0.25 to 6.52 indicate that the potential ecological risk of the metals in the three sampling sites all has low ecological risk level. The comprehensive potential ecological risk had the highest value of 14.97 in sampling site A, so the ecological risk level is not very serious. The main donation of the potential ecological RIs comes from Cd, Cu and Pb. The input of Cd into the soils of the study area is of great concern because of its high toxic-response factor. The potential ecological RIs of all the three sampling sites in Ameka area are far less than the maximum value, so the ecological risk level is not serious within the study area. The main donation of the potential ecological RIs comes from Cd, Cu and Pb, especially Cd. The value of the comprehensive potential ecological risk index ranged from 13.85 to 14.97 indicating an overall (highly-strong potential) posed by the heavy metals, which was the translation of the high Nemerow composite index recorded due to the various operations/activities at this area.

4.2.3 Geo-accumulation and enrichment factor analysis

The results of the $I_{\text{-geo}}$ of the metals investigated in the study are presented in Table 5. The $I_{\text{-geo}}$ scale consists of seven grades (0 - 6) ranging from uncontaminated to very highly contaminated. The mean $I_{\text{-geo}}$ values for all trace elements were lower than 0 (ranged from 0.018 to 0.23), suggesting a lack of soil contamination. The $I_{\text{-geo}}$ values are generally low (< 2) in all cases. In all the soils, the six metals fall within two *I*-geo class based on Muller's interpretation [29,44]; moderate contamination (Pb and Cd) and uncontaminated to moderate contamination (Cu, Cr and Zn). This contamination can only result from anthropogenic activities considered to emanate from mining activities. The risk of Hg and Cd accumulation requires further attention and monitoring.

The descriptive statistics of EF corresponding to the trace elements measured in the study area are given in Table 6. The mean EF calculation results ranged from 0.94 to 1.23 indicating that soils samples were in the category of depletion to mineral enrichment. The application of contamination and EFs reveal considerable contamination and enrichment of Pb and Cd while Zn shows moderate contamination and enrichment. These elevated amounts may enter

Table 4. Result of ecological risk of the samples

	Potential ecological risk				Comprehensive ecological risk [13] Grade	
A (n=5)	0.32	6.6	4.2	3.85	14.97	Low ecological risk
B(n=5)	0.15	5.5	0.6	3.8	13.85	Low ecological risk
C(n=5)	0.27	7.45	2.4	4	14.12	Low ecological risk
Ave.	0.25	6.52	2.4	3.88	14.31	Low ecological risk

Table 5. Results of Index of geo-accumulation

Site	Zn	Cu	Cd	Pb
Site A	0.06	0.13	0.030	0.15
Site B	0.03	0.11	0.004	0.15
Site C	0.05	0.45	0.020	0.16
Average	0.05	0.23	0.018	0.15

Table 6. Results of enrichment factor

Site	Si	Zn	Cu	Pb	Cr	Cd
Site A	1.78	1.79	1.82	1.83	2.00	1.67
Site B	0.86	0.82	0.83	0.82	0.89	0.78
Site C	0.88	0.22	1.06	1.03	1.00	1.00
Average	1.17	0.94	1.24	1.23	1.30	1.15

into the food chain and thus pose a hazard to human and animal health. Basically, as the EF values increase the contribution of anthropogenic origins also increase. According to [2], the EF value between 0.5-1.5 indicate the metal is entirely from crusted material or natural processes, whereas EF greater than 1.5 suggest the source is more likely to be anthropogenic. The results of enrichment factor show that using Fe concentration in the background value, Zn, Cu, Cd and Pb have moderate enrichment. Thus, based on [45] interpretation, the EFs for Cu, Cr and Zn indicated no enrichment which suggested a possible mobilization of metals. Though, according to [44], high EFs do not provide a reliable indication of the degree of human interference with the global environment. The strong association of elements such as Zn, Cd, Pb and Cu in most of the soil samples metals are influenced by anthropogenic activities suggest a similar source. Contamination levels of most metals (except Hg, As and Cd) from unpolluted to slightly polluted to close to container terminal in Ameka area. The heavy metal accumulation within Ameka mining areas based on geo-accumulation index, contamination factor and degree of contamination, pollution index, and enrichment factor as collectively indicate uncontaminated to moderately contaminated. The ubiquitous mining activities characterized by indiscriminate dumping of mine wastes, tailings and other foreign materials, coupled with the intense weathering in the area (which predisposes the minerals hosting the trace elements), have contributed to the re-mobilization and redistribution of the heavy metals into the surrounding soil and sediments.

5. CONCLUSIONS

Statistical Index analysis using Geo-accumulation index, contamination factor and degree of contamination, Metal pollution index, Enrichment factor and Ecological risk were successfully applied for the assessment of heavy metal contamination of Ameka sediments. The mean values of Zn, Ni, Pb, Cr, Hg and Cd in the analyzed soils do not exceed the limited second grade criteria environmental quality standard for soils in the New York Sediment Criteria and Provincial Sediment Quality Guidelines for metals, which means that the soil in this area is not polluted. The concentrations of Pb, Zn and Cd showed evidence of leaching of mine wastes under acidic conditions. The mean values of single pollution index and integrated pollution index are less than 1 in the area. Calculated Pollution Load Index and geo-accumulation index revealed that the sediments at all stations were practically uncontaminated by heavy metals. The significant spatial variation recorded in the concentrations of some parameters used in characterizing the sediment quality is a reflection of impacts of anthropogenic activity on quality of this river. This study would recommend an immediate plan for analysis of the quality of drinking water and some staple crops grown in the area to determine the levels of these noxious

metals and uptake by plants, to be followed by a comprehensive mitigation or remediation plan.

ACKNOWLEDGEMENTS

The authors are highly thankful to the anonymous reviewers for their helpful comments and suggestions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/13979