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Assessing the Potential Ecological Risks of a 12-Year Old Reclaimed Post-Mined Site for Agricultural Land-Use

Nat Owusu-Prempeh[1*], Daniel E. K. A. Siaw[1] and Osei Owusu Antobre[1]

[1]Department of Land Reclamation and Rehabilitation, Kwame Nkrumah University of Science and Technology, PMB University Post Office, Kumasi, Ghana.

Authors' contributions

This work was carried out in collaboration between all authors. Author NOP designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author DEKAS managed the analyses of the study. Author OOA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Mining is a crucial component of local and global economies, but it inevitably leads to substantial environmental disturbance. Reclamation ensures that a disturbed land is rehabilitated for a specified end land-use. The study examined the nutrient levels and risks status of a twelve-year old reclaimed site to ascertain its suitability for agricultural land-use. Twenty subplots of dimensions of 10m x 10m were laid within the reclaimed plots whereas 10 subplots where laid within adjacent undisturbed cocoa farm as control plots. Generally, the concentrations of all heavy metals and exchangeable cations of the reclaimed site's soil were significantly higher than the control plots and so were their respective cumulative potential ecological risk (PERI). The level of heavy metals contamination followed the order: Fe > As > Ni > Cu > Zn > Pb. Among the observed cations, only Magnesium (Mg) had the highest correlation with 60% of the variables of the study. The geostatistical analysis obtained by interpolation of risk values of the respective sites and classification into the risk categories revealed that the reclaimed area poses a "considerable ecological risk" (approximately 59% of the study area) due to the heavy metals' contamination.

**Corresponding author: E-mail: nowusu-prempeh@knust.edu.gh;*

Thus, whiles the exchangeable cations concentrations favour agriculture, the potential ecological risks of the reclaimed site due to heavy metals' contamination made it unsuitable for agricultural land-use. The study has provided empirical evidence that would guide policy on decommissioning and release of post-mined reclaimed lands to communities for a specified end land-use in support of their livelihoods.

Keywords: Heavy metals; Potential Ecological Risk (PERI); reclaimed site; land-use; Principal Component Analysis (PCA); Ghana.

1. INTRODUCTION

Mining is considered as one of the most important extractive industries and land-uses competing with agriculture for land in most developing countries. The sector plays a significant role in the development process of Ghana [1]. It contributes approximately US $796 million to Ghana's economy, 3.2 percent to gross domestic product and almost US $4 billion in foreign direct investment to Ghana [2,3]. Despite being a crucial component of local and even global economies, gold mining inevitably leads to substantial environmental damage such as land cover loss, pollution, and deformed landscape including biodiversity loss [4,5]. Consequently, reclamation bonds often require that disturbed landscapes must be rehabilitated for ecologically or socio-economically beneficial end land-use based on local community needs before mined sites are closed [6].

Although many studies have reported successful reclamation activities of post-mined sites through the application of sound and sustainable reclamation strategies and practices, often the concentration of heavy metals in the reclaimed sites do not conform to the acceptable range of standards, a prerequisite for the final release of land back to the community. Agriculture has been the most preferred end land-use for most reclaimed sites. Yet, many mining companies fail to assess the ecological risks their reclaimed soil media pose, although this is important in guiding management decisions. For instance, in China, Brian et al. [7] reported that over 70% of reclaimed mining lands were used for agricultural purposes. Similarly, in Ghana, reclaimed land is mostly returned to landowners/communities mainly for agriculture which is the prime land-use accounting for the livelihood of over 60 percent of the population. Shan et al. [8] used multivariate statistics and Geographic Information System (GIS) to analyse agricultural soils for potentially toxic trace elements (PTEs) such as Fe, Mn, Pb, Zn, Cd, and Co. Collectively, these explained 40.1% of the total variance, which were identified to have originated from farming practices. Kabata-Pendias and Pendias [9] also observed that agricultural soils near mining areas were contaminated by heavy metals. Additionally, Owusu-Prempeh and Asare [10] studied the enrichment of some selected heavy metals in Anglogold concession in Ghana and found that the selected metals accounted for approximately 55% of the variations in the sites.

Despite the wealth of knowledge on heavy metals and their associated risks assessment, there is a limited study on the potential ecological risks of post-mined reclaimed sites in Ghana. Usually, researchers mostly target soil degradation and the presence or absence of ecosystem functions and services in assessing the effectiveness of reclamation activities. Generally, the success of a post-mined land reclamation activity may not only be associated with the recolonization of the area by floral species but also the reduction of PTEs concentration to the permissible level for the end land-use. Often, a way to obtain deeper insight into the risk status of a site is to periodically assess the suitability of the area for the intended end land-use. Therefore, for an informed decision regarding the end land-use options and subsequent decommissioning of mined site, knowledge on the accumulated metals distribution, relationships and the associated potential ecological risks of the site is pertinent. This would guide policies on releasing post-mined lands to communities to support their livelihoods.

Mostly, indicators such as geo-accumulation index and enrichment factors are used to assess the anthropogenic input of elements and estimate their contamination not toxicity [11]. Metal contamination ensues when the metals (mostly toxic trace elements) occur in inappropriate locations within a site and more importantly at concentrations above the respective background levels [12]. The contamination situation is often observed as having potential adverse biological effects on the natural biotic communities. In this perspective, many studies in addition to quantifying the accumulated trace elements in soils have used tools such as Potential Ecological Risk Index (PERI) to establish the potential ecological risks to the local ecosystem [13,14]. The PERI model is an integrated index system which could be applied to assess the ecological risk of trace element pollutants in soils. The model provides more valuable insights into the eco-toxicological effects of elements polluting soils, particularly sediments [11]. Numerous authors have used the PERI model to ascertain the ecological implications of heavy metals at diverse temporal and spatial scales [11,15-19]. Even though the PERI model has been widely used in different regions in Africa, such studies are still lacking in local areas, particularly at post-mined reclaimed sites to help local government and non-government organisations to design appropriate management strategies particularly for decommissioning of post-mined sites.

In this regard, the study assessed the macronutrients status, concentrations of accumulated heavy metals and potential ecological risks of soils from a 12-year old reclaimed mined site. Specifically, the objectives of the study were: (i) to compare the concentrations of heavy metals (i.e. As, Cu, Fe, Ni, Pb, and Zn), and exchangeable cations (i.e. N, P, K, and Mg) distributions, relationships and mobility in the reclaimed mined site and an adjacent cocoa (*Theobroma cacao*) farm, (ii) assess the ecological risk induced by As, Cu, Fe, Ni, Pb, and Zn, and (iii) to model the spatial risk density of the sites.

2. MATERIALS AND METHODS

2.1 Study Area Description

The study was conducted at a reclaimed site at Adubirem near Obuasi within the AngloGold Ashanti (AGA), mine concession. The AGA is involved in the exploration, development, and mining of gold. The area is located between latitude 6º 20′ 34.6″ N and longitude 1º 36′31″ W. The reclamation work commenced in 2006. The post-mined site was reclaimed following standard reclamation procedures including backfilling the pit and spreading with topsoil (20cm), slope buttressing (about 30°) and finally revegetation. Adjacent to the reclaimed site is a large tract of cocoa farm with annual shrubs, which was used as the control site. The area lies within the Moist Semi-deciduous vegetation zone of Ghana. It is characterised by high rainfall amount (1250-1700mm per annum), bimodal rainfall pattern and relatively shorter dry season. This gives farmers the opportunity to farm twice in the year; the major and minor seasons respectively. The relative humidity of the site is always high and rarely falls below 85% [20] and an average temperature of about 26°C.

The area is underlain by Birimian sedimentary rocks comprising mainly of phyllites, schist, and tuff and greywacke sediments. These were laid down in early geological times and consist mainly of clay deposits, which have subsequently been hardened and altered. The Tarkwaian rocks made up of sedimentary units and recent alluvial deposits overlie the Birimian sedimentary rocks [21]. A cross-section of the hills along the roads reveals the presence of an uneven distribution of quartz veins injected into the phyllites, which break upon weathering to give rise to stones and gravel. The dominant soil types within the study area are the Ferric Acrisol, Haplic Acrisol and Dystric Gleysol [22]. Locally, the soils belong to the Bekwai-Nzima/Oda compound association [14]. Typically, in a toposequence, Bekwai series occupies the summit and upper slope sites followed by Nzima series on the upper to middle slopes, whiles Kokofu series follows on the middle to lower slope sites. The narrow valley bottoms are occupied by alluvial soils of Oda series. Both Bekwai and Nzima series are developed in-situ. They are well-drained with few angular quartz gravel and common manganese dioxide concentrations below the topsoil [23]. However, the Kokofu series is a colluvial material from slope wash. The soils are also very deep, imperfectly drained, yellowish brown topsoil over strong brown to brownish yellow subsoil free from gravel and concentrations. The valley bottom soils are deep, grey to yellowish brown, mottled, imperfectly to poorly-drained with varying texture from sandy loam to sandy clay loam [23].

The topography of Obuasi and its environs varies from gently undulating to hilly. There are moderately high-elevated lands with lowlands and valleys lying between them. The highlands are plateau, trending in different directions, with flat tops and amorphous shapes.

2.2 Experimental Procedures

On the field, twenty 10m x 10m subplots were laid within the reclaimed site whereas 10 subplots of dimensions 10m x 10m were laid randomly across the entire half-hectare control site. With the help of a soil auger, soil samples were collected to a depth of 0 to 5 cm. Before laboratory analysis, the soil samples were air-dried, sieve (2mm nylon) and stored in plastic bags. The concentrations of metals, including As, Pb, Zn, Cu, Fe, Ni, and Hg, were analysed after complete dissolving in a mixture of HNO_3-$HCLO_4$ and heated in a microwave digestion system. The analysis followed the atomic absorption spectrometric techniques [24].

2.3 Data Analysis

2.3.1 Ecological risk assessment

The risk of heavy metal of the reclaimed site was ascertained using Potential Ecological Risk Index (PERI). Initially, the contamination factor was combined with risk index (RI) to assess the ecological risk of metals of the reclaimed and control sites. The contamination factor (C_f) is defined as the concentration of heavy metals in the soil relative to the background value. Thus, C_f may be defined mathematically as;

$$\mathbf{C}_f^i = \frac{\mathbf{C}_i}{\mathbf{B}_\mathbf{n}} \tag{1}$$

Where;

C_f^i is the contamination factor of metal species *i*; C_i is the concentration of heavy metals '*i*' in soils; B_n is the background values. The contamination levels were classified by their intensities, ranging from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderate to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) [25]. The Nemerow Synthetic Pollution Index was estimated using equation two as follows:

$$\mathbf{P_N} = \left\{\sqrt{[(\frac{\mathbf{C}_i}{\mathbf{B}_i})_{\mathbf{max}})^2 + (\frac{\mathbf{C}_i}{\mathbf{B}_i})_{\mathbf{ave}})^2}\right\} \tag{2}$$

Where:

C_i and B_i are the concentration and the Background value of *i*-th element.

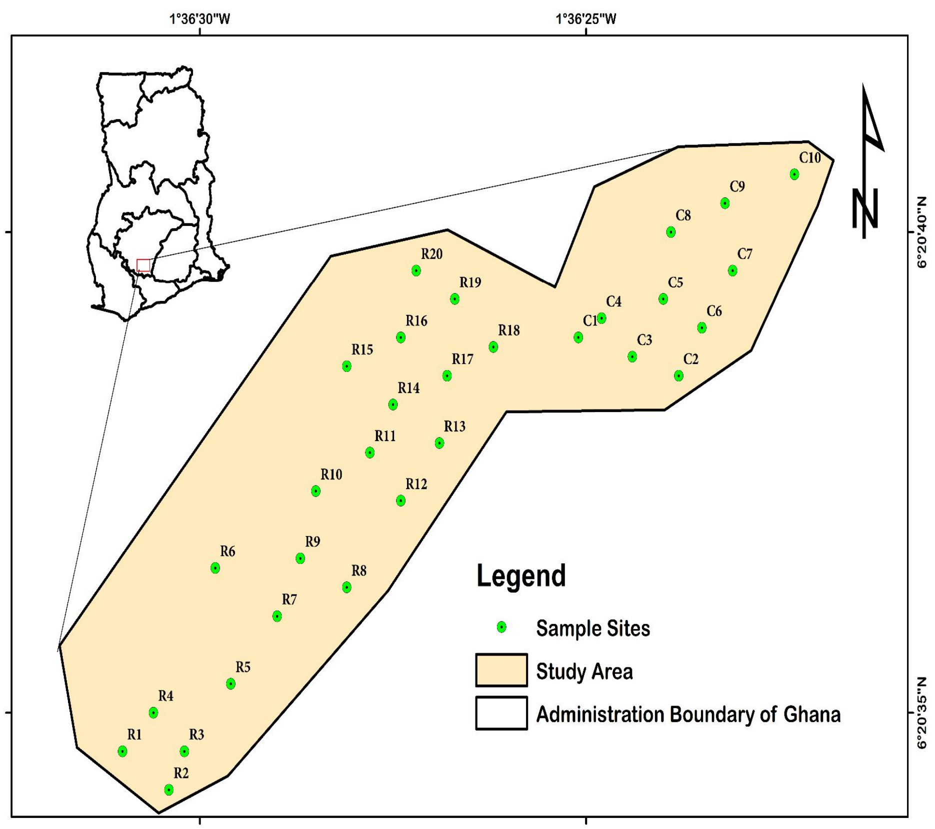

Fig. 1. Map of Ghana showing location of Adubirem, the study area

2.3.2 Statistical analyses

Data from field survey were analysed to obtain meaningful information pertaining to the concentration and variations of the heavy metal and exchangeable cations in the reclaimed site. Moreover, the mean concentrations were compared to the baseline values for agriculture land use and the acceptable word ranges to ascertain their variation and the status of the reclamation activities. Additionally, T-test statistical analysis was used to determine the significant level of probability values at 99% confidence ($p<0.01$). The statistical parameters such as mean, the coefficient of variation (percent of CV) and correlation of determination were used to compare the concentration levels, their variations and magnitude of dependence, respectively. All statistical analyses and graphing were performed using the Microsoft Excel (Microsoft Office Suite 2016 Edition) and Minitab Statistical Tool (v17).

The studied heavy metals were classified into clusters based on similitude within a group and unlikeness between different groups. The Cluster Analysis (CA) was performed on the data using Ward method and squared Euclidean distance.

The Principal Component Analysis (PCA) was used to reduce the original multidimensional space occupied by heavy metals to a new lower component(s), in order to explain the relationships and associations among the heavy metals and cations. This type of multivariate analysis depicts effectively the sources and pathways of heavy metals. Mostly, in the principal component analysis, the extraction of components to reduce the factor loadings is compared to a default Eigenvalue of one. In this study, the Oblimin Rotation Method with Kaiser Normalisation was used to ascertain the loadings of the PCs. The method normalises the factor loadings before rotating them and then denormalising them after rotation [26].

Additionally, the Kriging Method of the Geostatistical Wizard of the PC version of ArcGIS (v10.4) was used to interpolate the ecological risk values obtained for the respective sample sites. The areas of high, medium and low risks were computed as a percentage of the total study area. A normal Quantile-Quantile plot was constructed to check the normal distribution of the variables and add further explanation to the behaviour of the model.

3. RESULTS AND DISCUSSION

3.1 Comparative Analyses of Heavy Metals and Exchangeable Cations at the Reclaimed and Control Sites

Table 1 shows the concentrations of heavy metals and cations obtained from the survey conducted at the Adubirem reclaimed site. The major heavy metals recorded were Arsenic (As), Iron (Fe), Copper (Cu), Lead (Pb), Zinc (Zn), and Nickle (Ni). Generally, the concentrations of all heavy metals at the reclaimed mine site were considerably higher than at the control site. With the exception of Zn and Fe, whose individual values were widely dispersed thus having a higher percent Correlation Variation (CV) at the control site relative to the reclaimed site, all the other heavy metals recorded a higher percent CV at the reclaimed site. Authors like Li et al. [27] and Li et al. [28] demonstrated the use of coefficients of variation to identify the heavy metals pollution sources from natural or anthropogenic activities. Specifically, the concentration of Arsenic of 79.0 mg/kg at the reclaimed site was significantly higher than the concentration of 38.7 mg/kg recorded at the control site at a probability value less than 0.01. Also, within both sites, the concentration of Arsenic was significantly higher than the world limit (1 – 15 mg/kg) and Canadian Soil Quality Guidelines (CSQG) (12 mg/kg) limit for agricultural purpose [29]. Similarly, iron was highly and significantly concentrated in the reclaimed site compared to the control site at 12000 mg/kg at probability value less than 0.01. The concentration of Copper (31.6 mg/kg) recorded at the reclaimed site was significantly higher than that of the control site (23.5 mg/kg) but slightly less than the world standard of 35 mg/kg. The concentrations of Lead (Pb) at the reclaimed site (2.25 mg/kg) and at the control site (1.40 mg/kg) were both lower than the background value of 20.0 mg/kg. Moreover, Pb was lower than the lower limits of the World Grade I range of 10 – 70 mg/kg for non-polluted soils, and CSQG limits of 70 mg/kg for agriculture purposes [29]. This implies that Pb contamination was minimal at the sites. The respective concentrations of Zinc at the reclaimed and control sites were 25.65 mg/kg and 13.00 mg/kg. However, its mean concentration (13.00 mg/kg) at the control site was less than the minimum limit of the world range of 17 mg/kg for agricultural land-use.

The results imply that the impacts of the mining activities on soil quality still prevail, although the concentrations of most of the PTEs were below toxic levels. In a similar research, higher levels of As, Pb, and Zn in soils surrounding an abandoned mercury mine at levels above international standards were found [30]. More so, the findings indicated that undisturbed sites adjacent to mine sites could equally be contaminated by heavy metals due in part to soil water movement and runoffs, particularly where the sites have slopping terrains. For instance, Liu et al. [15] found Lead contamination of an adjacent agricultural ecosystem while assessing the ecological risk of heavy metal pollution of the agricultural ecosystem due to its proximate location to a lead-acid battery factory. Chen et al. [31] and Santos-Francés et al. [32] went further to explore the spatial patterns and risk of heavy metals in soils adjacent mine sites by applying the Nemerow synthetic pollution index and the improved Nemerow synthetic pollution index respectively. Additionally, the ores containing Fe, As, Zn, Cu, and Pb, and chemical weathering process and leaching as exacerbated by the mining activity could be contributing enormously to the contamination of the reclaimed site as opposed to the control sites.

Apart from heavy metals, the five exchangeable cations investigated in the study were Nitrogen (N), Phosphorous (P), Potassium (K), Calcium (Ca), and Magnesium (Mg). Unlike the heavy metals, all exchangeable cations followed a consistent trend of having significantly lower concentrations at the reclaimed site compared to the control ($p>.001$). However, the lower mean concentrations at the reclaimed site witnessed a significantly higher percent correlation variation (CV). Specifically, the mean concentration of N (1.59 mg/kg) was lower than that at the control site (5.10 mg/kg). Moreover, the reclaimed site recorded 126.0 mg/kg of phosphorous relative to 163.2 mg/kg at the control site. The concentration of Potassium (K) at control site (110.8 mg/kg) was significantly higher compared to the concentration of K recorded at the reclaimed site (61.75 mg/kg). Additionally, Calcium was only 57.1 mg/kg at the reclaimed site as opposed to a higher concentration of 73.9 mg/kg at the control site. Similarly, the concentration of Magnesium recorded at the control site (161.6 mg/kg) was significantly higher than that recorded at the reclaimed site (48.1 mg/kg) at 1% level of significance. The higher concentrations of the exchangeable cations (N, P, K, Ca, and Mg) within control plots might be

Table 1. Variation of heavy metals and exchangeable cations at the Adubirem reclaimed site

Metals and Cations	Area	Mean	CV (%)	P-value	Limits		Background value
					CSQG agriculture	World range	
As	CTL	38.7	5.32	0.000	12	1 – 15	13
	RC	79.0	34.34				
Fe	CTL	8700.0	12.18	0.000	-	-	500
	RC	12000.0	11.23				
Cu	CTL	23.5	6.73	0.000	63	6 – 60	32
	RC	31.6	13.98				
Pb	CTL	1.40	36.89	0.004	70	10 – 70	20
	RC	2.25	42.96				
Zn	CTL	13.00	22.06	0.000	200	17 – 125	129
	RC	25.65	15.81				
Ni	CTL	2.34	15.10	0.000	50	-	2
	RC	5.07	22.65				
N	CTL	5.10	16.35	0.000	-	-	-
	RC	1.59	57.64				
P	CTL	163.2	8.45	0.001	-	-	-
	RC	126.0	32.74				
K	CTL	110.8	8.88	0.000	-	-	-
	RC	61.75	32.37				
Ca	CTL	73.9	9.91	0.001	-	-	-
	RC	57.1	31.90				
Mg	CTL	161.6	17.45	0.000	-	-	-
	RC	48.1	32.40				

RC: Reclaimed mined site, CTL: Control site attributed to the use of inorganic fertilisers on cocoa farms. Charkhabi et al. [33] reports that the agriculture use of mineral fertiliser was responsible for a higher ecological risk of metals and cation pollution within the lower reaches of Siarhroud River.

3.2 Source, Distribution and Relationships of Heavy Metals

3.2.1 Cluster analysis (CA)

The results of the cluster analysis produced two major clusters: (i) As-Zn-Ni-Fe-Cu-Pb (heavy metals) and Mg-N-K-Ca-P (exchangeable cations) as shown in shown in Fig. 2. These two major groupings indicated that the heavy metals and exchangeable cations were of entirely different sources. Within the heavy metal clusters, Pb had an entirely different characteristics compared to the other heavy metals such as Zinc, Copper, Arsenic, and Nickel. The most noticeable associations within the heavy metal cluster included As-Zn-Ni, Fe-Cu and Pb. This was an indication that the former group of heavy metals might be of similar sources. Similarly, the Potassium of the exchangeable cations had a different behaviour as opposed to the behaviours of the other cations. The Principal Component Analysis (PCA) analysis performed on these elements confirmed these associations.

3.2.2 Correlation matrix

The relationships, distributions and sources of heavy metals and exchangeable cations are important to establish, particularly whiles comparing to the control. The correlation analysis was used to identify the factors and sources of variables [15]. Thus, the correlation of heavy metals in soils reflects the association between elements and the similarities of their pollution sources. The Pearson Moment Correlation coefficient (r) of variables revealed the closeness and degree of linear association between the measured parameters. Overall, Mg was highly correlated with the about 60% of the elements measured in this study (Table 2). Thus, Mg/N (r = 0.865) > Mg/Zn (r = -0.821) > Mg/Ni (r = -0.790) > Mg/Fe (r = -745) > Mg/Cu (r = -0.733) > Mg/K (r = 0.720).

3.2.3 Principal Components Analysis (PCA)

Multivariate analysis has been proven effective tool for providing suggestive information regarding heavy metal sources and pathways [18]. Worldwide, the PCA has been widely used in several environmental studies relating to metals concentrations in soils due to its capability to characterise the distribution and variability of heavy metals in soils at the study sites [8,10,31, 32]. Two principal components were obtained, which collectively accounted for 68.67% of the

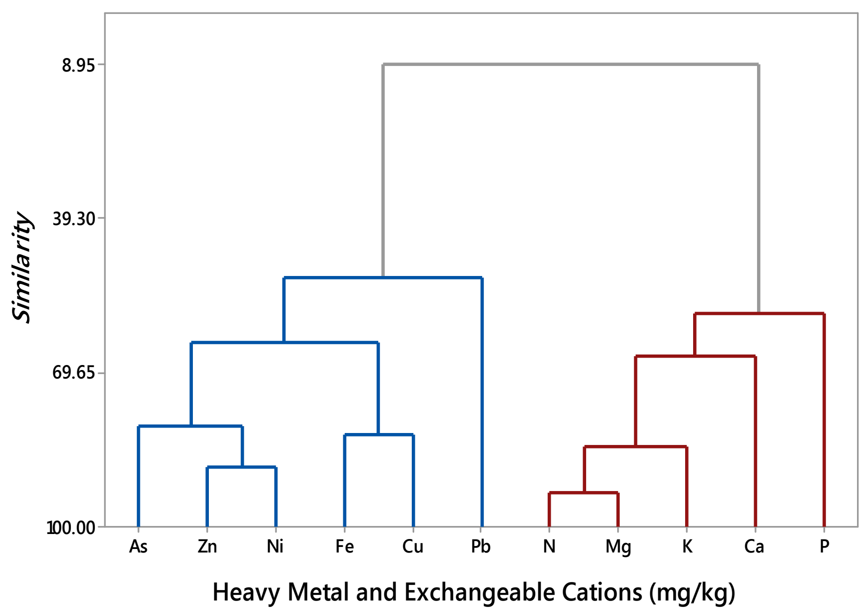

Fig. 2. Dendrogram of the hierarchical clustering of heavy metals and exchangeable cations in the soil samples analysed

Table 2. A matrix constructed for the Pearson Moment Correlation of the relationships between the respective heavy metals and exchangeable cations

	Heavy metals						Exchangeable cations			
	As	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**N**	**P**	**K**	**Ca**
Fe	0.592*									
Cu	0.274	0.637*								
Pb	0.017	0.137	0.291							
Zn	0.605*	0.674*	0.443*	0.396*						
Ni	0.601*	0.522*	0.388*	0.371*	**0.764***					
N	-0.646*	**-0.807***	**-0.734***	-0.279	-0.734*	-0.657*				
P	-0.525*	-0.383*	-0.091	0.083	-0.435*	-0.601*	0.400*			
K	-0.300	-0.621*	-0.633*	-0.454*	**-0.755***	-0.491*	0.685*	0.322		
Ca	-0.447*	-0.202	-0.338	-0.224	-0.355	-0.225	0.449*	0.161	0.326	
Mg	-0.620*	**-0.745***	**-0.733***	-0.490*	**-0.821***	**-0.790***	**0.865***	0.395*	**0.720***	0.431*

**Correlation significant (α level = 0.01)*

total variation (Table 3). The first principal component (PC-1) is strongly correlated with eight of the original variables. The PC-1 varies with increasing Pb, Ni, Ca, Fe, and Zn and decreasing K, N, and Mg. This implies that the former set of elements vary together. Thus, if one increases, the remaining tends to increase as well. Similarly, if an element in the later set decreases, the others tend to decrease as well. Collectively, the eight elements explained about 55.696% of the total variation. The higher correlation of the first principal component with Mg (i.e. correlation of 0.957) could be interpreted as primarily measuring Mg (Table 4). All the sample plots with higher values were inclined to have many compounds associated with Mg^{2+} cations, whereas sample sites with smaller values were inclined toward a relatively fewer Mg^{2+} compounds association. This explained why Mg was highly correlated with 60% of the measured variables.

Similarly, the second principal component is strongly correlated with two of the original variables (i.e. As and P). The PC-2 increases with decreasing Arsenic (As) and increasing Phosphorous (P). The element of the PC-2 collectively explained only 12.978% of the variance. The PC-2 can be viewed as having poor amounts of As and a considerable amount of P at the respective sample stations. The score of the elements of PC-1 and PC-2 are plotted in Fig. 3. Although within the same principal component, the Pb and Cu portrayed an entirely different distribution pattern compared to the other elements in the same principal component.

The correlation analysis, principal component analysis and spatial distribution analysis of heavy metals in soil can at least partially reflect the source of the metals. Copper (Cu) and Zn in the natural soil are known to exhibit similar geochemical affinities as iron family elements [34], but this has not been shown in this study area.

3.3 Ecological Risk Assessment

3.3.1 Statistic of risk indices

In this study, Specific Contamination Factor (C_f), and Nemerow Synthetic Pollution Index (P_N) were used to assess the contamination of specific metal species and the ecological risks, respectively. The t-test indicated that risk at the reclaimed site was significantly higher than the control site (Table 5). The specific contamination factor could also be used to refer to the hazard level of metal species [35]. Specifically, whereas Iron (Fe) registered a “very high” contamination factor, Pb had “very low” contamination factor. Based on the mean C_f values, pollution levels of the heavy metals investigated at the reclaimed site followed the order: Fe > As > Ni > Cu > Zn > Pb. Whiles our study found minimal Lead (Pb) hazard levels, several studies have reported higher lead risks owing to industrial land use. For instance, Akoto et al. [36] found higher hazard levels of Pb at their study area due to mining and fuel sources. Al-momani [37] reported that higher hazard levels of Pb mainly from vehicular emission, previous usage and leakage of leaded gasoline contaminated their study sites. Moreover, Faiz et al. [38] also found that Pb was strongly associated with emission from fossil fuels, brick kilns and industrial activities. Fig. 4 is a line graph that illustrates the variation of the ecological risks at the respective sample plots. The reclaimed site three (R_3) registered the highest degree of contamination, while R_{20} had the lowest. The following is the increasing order with respect to the degree of contamination observed at the reclaimed sites: $R_3 > R_8 > R_2 > R_6 > R_8 > R_{12} > R_{16} > R_{17} > R_5 > R_{18} > R_{11} > R_1 > R_{15} > R_{20} > R_{19} > R_{13} > R_{14} > R_7 > R_{10} > R_4$. With the exception of station C_3, all the control sites had lower risk values compared to the reclaimed sites. The higher risk at the site (C_3) may be attributable to the larger contamination of Iron (Fe) and Arsenic (As). Ameh et al. [35] also found a higher iron content influencing the overall hazard risks of the study sites.

The mean P_N at the reclaimed site (P_N = 620.91) was significantly higher relative to the control site at P_N = 323.56 (t = 7.10; p > 0.01). The four categories established for the Nemerow Synthetic Index (P_N) which included the risk indices were as follows; a low ecological risk of potential contamination (P_N < 150), moderate ecological risk 150 ≤ P_N < 300), considerable ecological risk (300 ≤ P_N < 600) and very high ecological risk (P_N > 600). A larger percentage of the soil samples from the reclaimed site (55%) had "high potential ecological risk", whereas 45% posing a considerable risk of heavy metal contamination. A smaller proportion (40%) of the sample sites had a considerable ecological risk, whereas 60% had a "moderate ecological risk". This corroborates Duan et al. [39] which observed that areas affected by industrial and vehicular emissions have "considerable" ecological risk of Hg, Cd, Cr, Cu, and Zn.

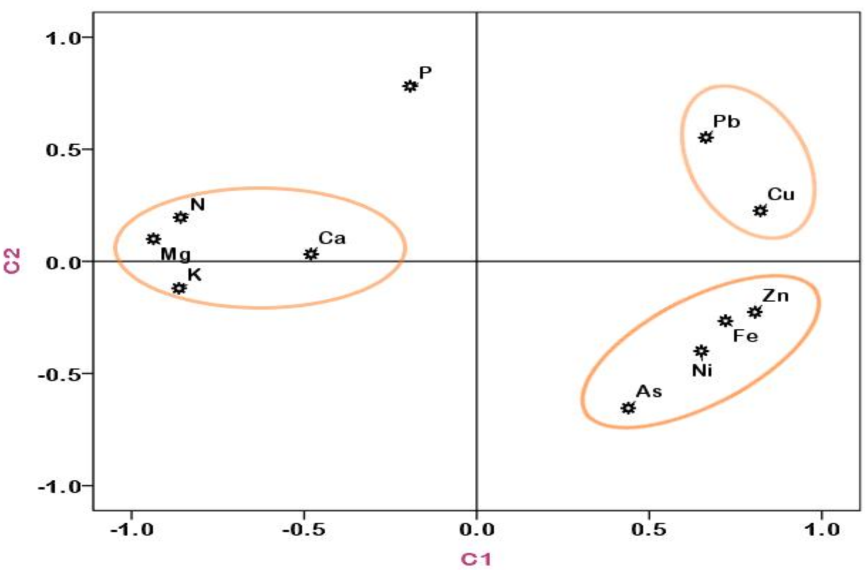

Fig. 3. PCA Score plot showing the distribution of heavy metals and exchangeable cations

Table 3. Total variance explained and factor loadings

Component	**Initial eigenvalues**			**Extraction sums of squared loadings**		
	Total	**% of variance**	**Cumulative %**	**Total**	**% of variance**	**Cumulative %**
1	6.127	55.696	55.696	6.127	55.696	55.696
2	1.428	12.978	68.674	1.428	12.978	68.674
3	0.950	8.633	77.307			
4	0.908	8.258	85.565			
5	0.511	4.647	90.212			
6	0.413	3.750	93.962			
7	0.262	2.379	96.342			
8	0.158	1.434	97.776			
9	0.121	1.103	98.879			
10	0.070	0.632	99.511			
11	0.054	0.489	100.000			

Table 4. Component matrix based on Kaiser Normalisation

Elements	Principal component	
	PC-1	PC-2
As	0.574	**-0.745**
Fe	**0.776**	-0.414
Cu	**0.775**	0.056
Pb	**0.550**	0.415
Zn	**0.853**	-0.393
Ni	**0.733**	-0.534
N	**-0.898**	0.373
P	-0.355	**0.821**
K	**-0.838**	0.058
Mg	**-0.957**	0.294

Although the heavy metals could remain in the soil for a very long time, some steps could be taken to reduce the level of risk they pose. In some cases, heavy metal concentrations can be 'diluted' with deep tillage; for example, to distribute contaminated surface sediments that were deposited by flooding. In garden plots, dilution can be achieved by the addition of uncontaminated soil. Adding organic matter to the soil can help 'tie up' heavy metals chemically, reducing their availability for potential plant uptake. Similarly, liming to a neutral pH and maintaining optimal soil phosphorus levels can reduce heavy metal availability to plants. For some heavy metals, such as lead, there is little evidence that it could be accumulated within crops; the main health hazard is through soil ingestion and inhalation. Soils high containing heavy metals pose a greater health risk to children than to adults because children are more likely to ingest soil directly.

3.3.2 Geostatistically based risk assessment

Using the Kriging Method of the Geostatistical Wizard of ArcGIS (v10.4) the ecological risk values obtained for the respective sample sites were analysed spatially by interpolation. The exponential model that was employed gave a root mean square error (RMSE) of 134.57, a nugget of 3963.56 and a partial till of 52129.71 (Table 6). The areas of high, medium and low risks were computed as a percentage of the total study area. A normal Quantile-Quantile plot was constructed to check the normal distribution of the variables and add further explanation to the behaviour of the model.

Table 5. Comparison of pollution loads and the potential ecological risk at the reclaimed site

Treatments		Min	Max	Mean	Std. error	t-stats	P-value
P_N	RC	446.48	1077.95	620.91	32.79	7.10	0.000
	CTL	270.13	508.06	323.56	26.04		

RC is Reclaimed site, and CTL is the control Site

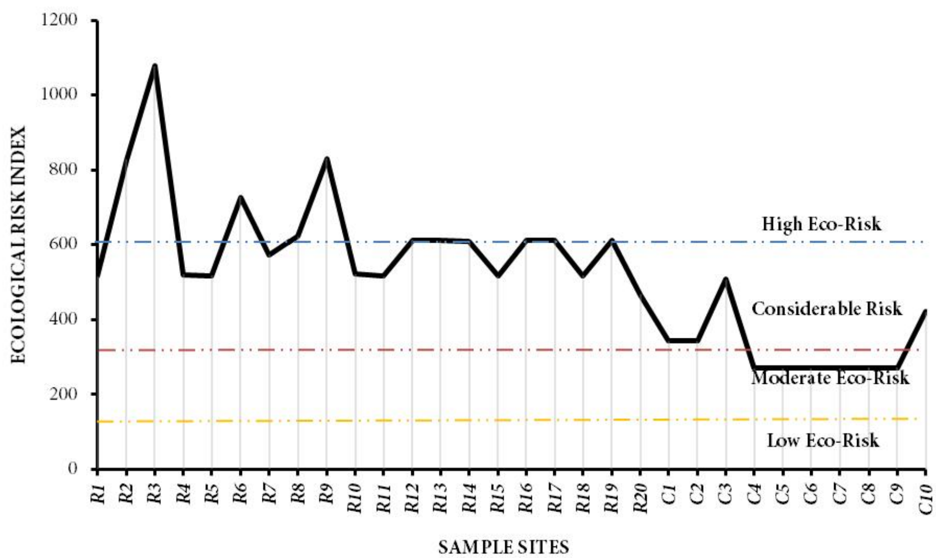

Fig. 4. Specific risk factor of reclaimed and control plots

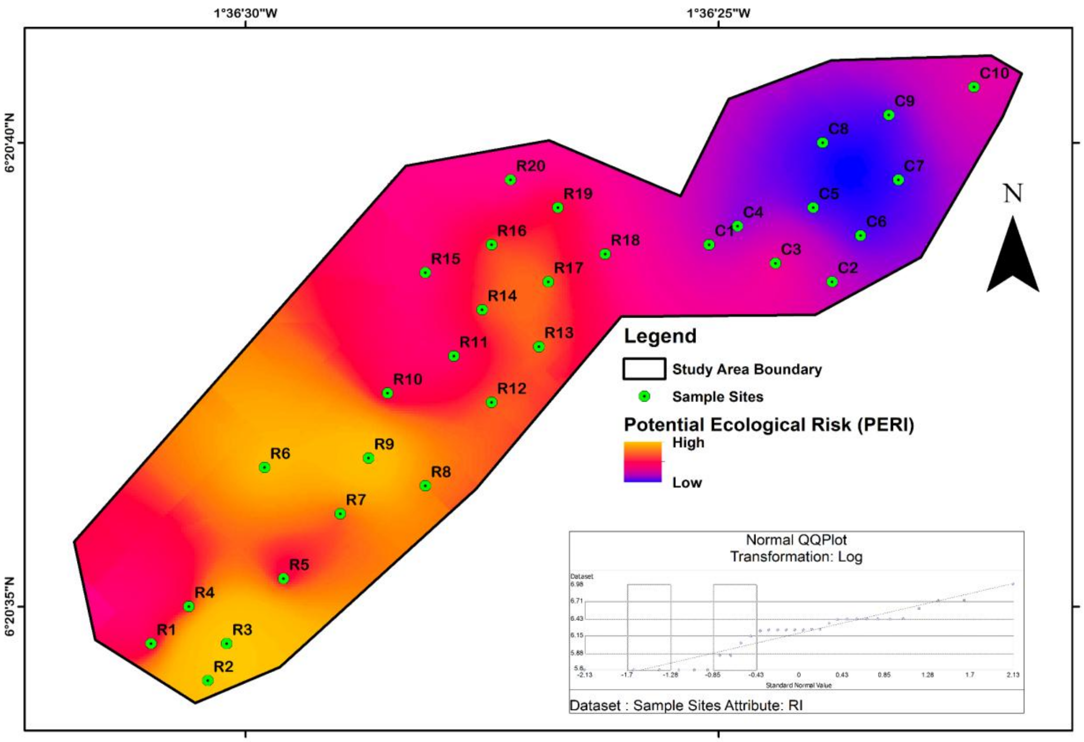

Fig. 5. Spatial presentation of the potential ecological risk of heavy metal pollution

Table 6. Model parameters for ordinary kriging interpolation

Risk parameter	Parameters of semi Variogram analysis					Normality test	
	Model	RMSE*	Nugget	Partial sill	Range (m)	Statistic	P-value
PERI	Gaussian	142.14	-	-	-	0.167	0.033
	Exponential	**134.57***	**3963.56**	**52129.71**	**331.84**		
	Spherical	137.98	-	-	-		
	Linear	142.14	-	-	-		

Fig. 5 shows the spatial representation of the Nemerow Synthetic Pollution Index (P_N), depicting the Potential Ecological Risk (PERI) of heavy metals at the study area. The interpolation was computed and map produced by using the Ordinary Kriging of the Geostatistical Wizard of ArcGIS software (v10.4). The PERI ranged from moderate eco-risk (266.55) to high eco-risk (939.26). The mean PERI of 522.77 estimated for the area, implies that averagely, the area poses a considerable ecological risk. Nonetheless, in percentages, approximately 59% of the study area is estimated to have a considerable ecological risk of heavy metal pollution, while 33% and 9% are estimated to be having a high risk and moderate risk respectively.

4. CONCLUSION

The present study ascertained and compared the concentrations of heavy metals and exchangeable cations bearing in mind their distributions, relationships, and mobility in a reclaimed land and an adjacent cocoa farm (control site), while estimating their cumulative potential ecological risk (PERI). The concentrations of elements of the anthropogenically altered areas (reclaimed and control) varied markedly and so are their cumulative potential ecological risk. The trend of heavy metals achieved based on their specific contamination factor is as follow: Fe > As > Ni > Cu > Zn > Pb. A similar trend was observed at the control site, although they had lower values compared to the remaining site. In all, only Magnesium (Mg^{2+}) had a higher correlation with 60% of the elements and cations investigated in this study. A mean PERI of 522.77 was obtained, which implies that the area has a considerable ecological risk (approximately 59 % of the study area) due to heavy metal contamination. Thus whilst the exchangeable cations concentrations favour agriculture, the potential ecological risks of the reclaimed site due to heavy metals contamination render it unsuitable for agricultural land use particularly for cropping purposes. The study has provided empirical evidence that will guide major stakeholders on the decision to release post-mined reclaimed land back to communities for a specified end land-use to support their livelihoods.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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