

## **LEVELS OF HEAVY METALS AND CONTAMINATION STATUS OF A DECOMMISSIONED TAILINGS DAM IN GHANA**

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### **Abstract**

Heavy metal pollution from tailings has become a major global concern due to its toxicity, persistence and accumulative potential with detrimental effects on public health and environmental receptors. In a bid to determine the contamination status of a decommissioned tailings storage facility (TSF 2) from the Chirano Gold Mine Limited (CGML), scoop of mine tailings samples were collected down to a depth of 20 cm from nine sampling sites within a 8100 m<sup>2</sup> grid. Concentrations of As (0.7 to 3.3), Pb (1.3 to 2.2), Cr (0.9 to 1.9), Cd (2.0 to 2.6), Cu (5.5 to 6.5), Zn (2.4 to 3.6) and Fe (4.5 to 12) mg/kg were below FAO/WHO permissible limits. Concentration of heavy metals statistically varied between sampling sites ( $p < 0.05$ ). The geoaccumulation index and contamination factor revealed that, TSF 2 is uncontaminated with As, Pb, Cr, Cu, Zn and Fe. However, mine tailings were significantly enriched with Cd, and thus likely to pose ecological risk to the surrounding environment. In general, the tailings dam is not progressively deteriorating in accordance to pollution load index. Findings of this study would contribute to the environmental database of gold mine tailings at CGM to assist future remediation of the tailings storage facility.

### **Introduction**

Mining forms an important component of global economy growth. Mining of precious metals is one of the important sources of foreign exchange in most developing countries. In Ghana, total earnings from mineral export in 2015 amounted to US\$ 3,322.61 million (GIPC, 2017). In terms of direct domestic revenue, the mining sector contributed US\$ 269,821,500 (GBN, 2017). However, the extraction and processing of the precious metal usually comes with a great cost to the environment and on public health. For example, mine tailings generated from ore processing serves as a source of contamination to the environment (Roussel et al., 2000). The predominant contaminants mostly found in these tailings are heavy metals and residual reagents such as cyanide. The heavy metals are naturally occurring element with density greater than of 6 g/cm<sup>3</sup> (Thornton *et al.*, 1995). As

a result of physical and chemical property changes associated with the lithosphere, these contaminants in mine tailings can be carried, spread to and accumulated in animals and plants, up into the food chain to man as the ultimate consumer (Kim et al., 2000). Also, heavy metals primarily liberated by mining operations ends up in the component of the earth surface layers persisting for years (Gosar, 2004). Thus, due to their soluble and mobile nature, they may be released into surface and ground water systems as well as other geological environment (Jang et al., 2005). Again, heavy metals in mine tailing have tendency to cause terminal disease when accumulated in human internal organs through water and crops in take (Lee et al., 2007). The presence of high levels of Cu in the human body may cause vomiting and damage the liver (Vick, 1990). Cd is said to be highly poisonous and carcinogenic with ability to accumulate in the kidney and liver. According to the WHO, Pb exposes adults to increase risk of high blood pressure, anaemia, damage to kidney and birth problems such as miscarriage. However, according to Bempah *et al.* (2013) heavy metals research in Ghana mostly focus on environmental receptors, consumables (vegetables and fruits) with dearth research of heavy metals in gold mine tailing. Also, with an engineered active Tailings Storage Facilities (TSF), in the assessment of heavy metals, much emphasis is placed on the water (decant pond) on the surface of the TSF whilst limited analysis of heavy metals is periodically conducted on the sediments (consolidated tailings). For these soil tailings dams to be put into productive use, the levels of heavy metals must be assessed. Therefore, this study seeks to investigate the presence of As, Pb, Cr, Cd, Cu, Zn and Fe in gold mine tailings and the contamination status of a decommissioned tailings dam from the CGM in Ghana.

**Keywords:** *Contamination factor, Geoaccumulation Index (Igeo), Enrichment Factor (EF), Contamination factor (Cf), pollution Load Index (PLI), Ecological risk factor (Er)*

## **Materials and Methods**

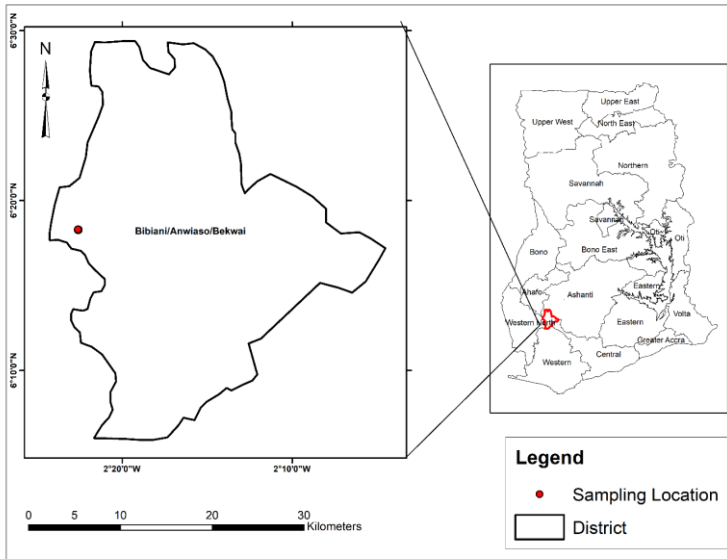
### **Study site**

Chirano Gold Mines Limited (CGML) is a major mining company located in the Western North Region of Ghana specifically between Bibiani-Anhwiaso-Bekwai and Sefwi-Wiawso Districts (Figure 1). It is situated at Latitude 6°00'00'' N and 6°24'75'' N and Longitude 2°21'33'' W and 2°24'33'' W and about 100 km south-west of the city of Kumasi, 15 km south-southwest of the township of Bibiani. The concessional area is 45 km<sup>2</sup>. Gold deposits lie close to a splay off the main Bibiani shear zone known as the Chirano Shear. The capacity of the firm's mill is about 3.5 million ton/annum (Mtpa). The annual rainfall ranges from 1056.2 to 1929.0 mm with a mean rainfall of 1472.7 mm but varies annually.

### **Sampling design**

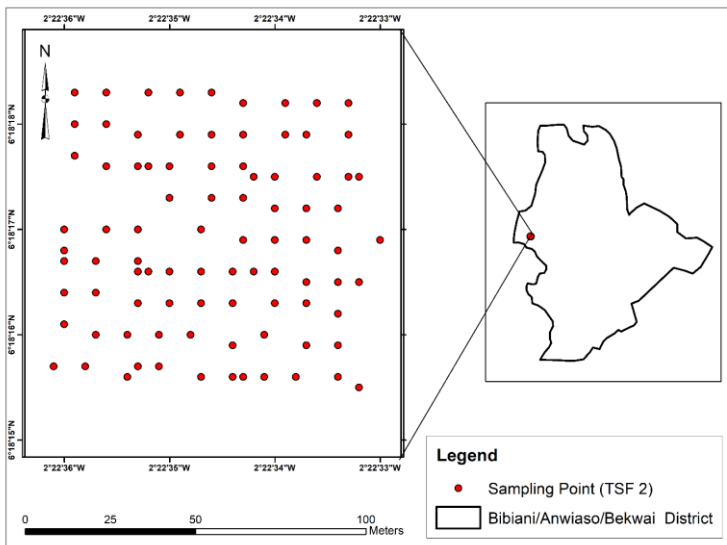
Tailings samples were collected from a decommissioned Tailings Storage Facility (TSF 2) (Figure 2). Samples were collected from a 90 m x 90 m square grid using

systematic composite sampling technique. Three separate sub-plots P1, P2, P3 (90 m x 30 m each) were demarcated within the main plot.



**Figure 1**  
*Study site*

Nine 30 m x 30 m sampling sites (P1S1, P1S2, P1S3, P2S1, P2S2, P2S3, P3S1, P3S2 and P3S3) were demarcated along the sub-plots.



**Figure 2**  
*Sampling location with sampling points*

At each demarcated sampling site, scoop of soil samples were collected down to a depth of 20 cm with hand trowel from nine different sampling points at 10 m apart. Sets of three samples along a column, from the nine sampling points, within each

sampling sites were composited and placed into a well labelled ziploc bag. Each sampling site had three replicates of composited soil samples. Thus, each sampling site was composed of 9 sampling points, giving a total of 81 sampling points and 27 replicate samples. All sampling points were recorded using hand-held GPS on site. Soil samples were transported to Materials and Civil Engineering Laboratory, Kwame Nkrumah University Science and Technology (KNUST) for further treatment and analysis.

### **Sample preparation and analytical methods**

***Determination of pH, EC and particle sizes of tailings samples.*** Samples were air dried for 7 days in the laboratory, passed through a 0.2 mm sieve, homogenized and stored in ziploc bags for subsequent analysis. Soil pH and EC were determined using glass electrode (PC 300 series - Cyberscan) in a soil-water ratio 1:2.5 (Rhoades, 1982). Particle size analysis was carried out using the standard procedures outlined in BS 1377 (1990). The mass percentage of particles sizes or cumulative percentages by mass of the sample passing each of the sieves was plotted on a semi-logarithmic scale using the general relationship, equation [1];

$$\% \text{ passing this sieve} = (\% \text{ passing previous sieve}) - (\% \text{ retained on this sieve}) \quad [1]$$

***Determination of Mineralogical Composition.*** About 10 g of dried samples in a well labelled sterile ziploc bags were taken for XRD analysis at the Department of Physics, University of Ghana. Samples were further grounded into powdered form with the aid of a pestle in a ceramic bowl and homogenized. The homogenized powdered samples were placed into the XRD machine (PAN analytical Empyrean Series 2 X-Ray Diffraction XRD). The XRD analysis was then carried out with Cu K-alpha radiations, 45 kV and 40 mA  $2\theta$  range scanned from  $5-89^\circ$ , step 0.0400 and counting time of 60 sec. Identification of mineral phase was done with Jade software package coupled with diffraction data bases.

***Determination of heavy metals.*** Soil sample (1 g) was weighed into 250 ml digestion flask. The sample was dissolved using Tri-Acid Mixture [ $\text{H}_2\text{SO}_4$ :  $\text{HNO}_3$ :  $\text{HClO}_4 = 5:1:1$  (10 ml)] (Twyman, 2005). Digestion was subsequently carried out on a hot plate for 10 minutes under fumes chamber until dense fumes evolved. Digested samples were cooled and the solution was filtered through a Whatman 1 filter paper into 50 ml volumetric flask. The volume was made to the 50 ml mark by adding distilled water. To ensure quality assurance of digested samples, blank was prepared to check for background contamination introduced by reagents used. The blank sample contained { $\text{H}_2\text{SO}_4$ :  $\text{HNO}_3$ :  $\text{HClO}_4 = 5:1:1$  (10 ml)} which was heated for 10 minutes under fumes chamber, and volume made to the 50 ml mark by adding distilled water.

Instrumental calibration was prepared according to Knödel et al. (2007). As, Cd, Pb, Cr, Zn, Fe, and Cu concentrations were determined using Atomic Absorption Spectrometer (SPECTRA AA 220 Air-acetylene Flame).

## **Contamination Assessment Methods**

**Geoaccumulation Index.** Geoaccumulation Index (Igeo) for tailing samples were computed using the Igeo formula [2] introduced by Müller (1969):

$$I_{geo} = \log_2 (C_n/1.5B_n) \quad [2]$$

Where  $C_n$  is the measured concentration of the element in the samples.  $B_n$  is the geochemical background or pristine value of the element directly measured in pre-civilization or taken from literature (Ephraim and Ajayi, 2014; Mohiuddin et al., 2010). The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Stoffers et al., 1986).

Igeo values were compared to the seven contamination categories or enrichment classes as classified by Müller (1969):

Class 0 : ( $I_{geo} \leq 0$ ); uncontaminated

Class 1: ( $0 < I_{geo} \leq 1$ ); uncontaminated to moderately contaminated

Class 2: ( $1 < I_{geo} \leq 2$ ); moderately contaminated

Class 3: ( $2 < I_{geo} \leq 3$ ); moderately to heavily contaminated

Class 4: ( $3 < I_{geo} \leq 4$ ); strongly contaminated

Class 5 : ( $4 < I_{geo} \leq 5$ ); strongly to extremely contaminated

Class 6 : ( $I_{geo} > 5$ ); extremely contaminated

**Enrichment Factor.** Enrichment factor establish how much soil is unnaturally affected by a metal above background levels mainly through anthropogenic activities (Ho *et al.*, 2010). Accordingly, the anthropogenic impact on tailing samples were computed using EF as proposed by Solomons and Förstner (1984):

$$\text{Enrichment factor (EF)} = M_x \times Fe_b / M_b \times Fe_x \quad [3]$$

where,  $M_x$  and  $Fe_x$  are respective concentrations of the heavy metal and Fe in the sample material;  $M_b$  and  $Fe_b$  are their respective concentrations in a suitable baseline reference material. The reference metal used to normalize the measured heavy metal concentration was Fe. EF values of the samples were separated into different contamination categories as classified by Yongming et al. (2006):

Enrichment factor	Description
EF < 1	Background concentration
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

**Contamination Factor.** Contamination factor necessitates that samples in minimum of five are combined to generate a mean pollutant concentration which is then matched to the background concentration (Abraham and Packer, 2008), according to the equation [4] introduced by Hakanson (1980):

$$\text{Contamination factor (C}_f\text{)} = M_x / M_b \quad [4]$$

where  $M_x$  is the mean concentration of heavy metal in sediment sample.  $M_b$  is the pre-industrial baseline/background reference value for the metal.

Hakanson (1980) separated  $C_f$  into:  $C_f < 1$  signifies low contamination;  $1 \leq C_f < 3$  signifies moderate contamination;  $3 \leq C_f$  signifies considerable contamination;  $C_f > 6$  signifies very high contamination status of a metal.

**Pollution Load Index.** The pollution load index (PLI) as proposed by Tomlinson et al. (1980) was used in this study. The PLI for a single site is the  $n$ th root of  $n$  number multiplying the contamination factors together:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \dots \times CF_n} \quad [5]$$

where CF = Contamination factor,  $n$  = number of metals to the  $n$ th root

According to Tomlinson *et al.* (1980) computed PLI value of 0.0 indicates perfection, a value of 1.0 indicate only baseline levels of pollutants present and values  $> 1.0$  indicate progressive deterioration of the site quality. Numerical indices values were computed using background levels of metals in the upper continental crust: Pb (20 mg/kg), Cu (25 mg/kg), Zn (71 mg/kg), As (1.5 mg/kg), Cd (0.098 mg/kg), Cr (35 mg/kg) and Fe (4.49 mg/kg) described by Taylor and McLeenan (1985).

**Ecological Risk Factor.** The Ecological risk factor (Er) proposed by Tomlinson et al. (1980) was used in this study. The ecological risk of each metal was calculated as follows, equation [6]:

$$Er = Tr \times C_f^i \quad [6]$$

where: Tr = Toxic response factor of a given element,  $C_f^i$  = Contamination factor .

The following expressions is used to define the ecological risk index as categorized by Hakanson (1980),  $Er < 40$  indicate low potential ecological risk,  $40 < Er < 80$  moderate potential ecological risk,  $80 < Er < 160$  considerable potential ecological risk,  $160 < Er < 320$  high potential ecological risk,  $\geq 320$  very high potential ecological risk.

## Data analysis

Data obtained from the study was expressed as mean and standard deviation using Statistical Package for Social Sciences (SPSS) version 20. Subsequently, one-way analysis of variance (ANOVA) was use to rank and compare means at 5% level of significance. Geoaccumulation Index (Igeo), enrichment Factor (EF) contamination degree (Cd), modified degree of contamination (mCd), pollution Load Index (PLI), ecological risk factor (Er) were calculated using Microsoft Excel 2013.

## Results and Discussion

### Physico-chemical properties of tailing samplings in TSF 2

The tailing samples were alkaline with pH value ranging from 8.5 to 8.8 (Table 1). Similar range of pH value (7.1-9.4) of tailings was reported by Singo (2013) in

Musina, South Africa. Previous study conducted by Remy (2013) revealed that, soils at Chirano are neutral in nature. The alkaline nature of the tailing samples could be attributed to the basic chemical (lime) used during ore beneficiation at CGML. The alkaline nature of the samples also suggest that, tailings in CGM is not acid generating (less occurrence of sulphide minerals) as compared to tailings around Incheon Au-Ag mine in Korea, having a pH of 1.9 - 7.4 (Jung, 2001; Enkhzaya et al., 2016). Bempah et al. (2013) observed that, the mobility of As in tailings mud was greatly affected in slightly alkaline condition. Also, most mobile heavy metals such as Cd and Zn in neutral and alkaline soils become immobile in comparison to highly acidic soil medium (Sherene, 2010; Fijalkowski et al., 2012; Nkansah, 2016). Consequently, the alkaline nature of tailings could restrict/decrease the mobility of such metals (As, Cd, Zn) in TSF2. The electrical conductivity ranged from 280 to 2570  $\mu\text{S}/\text{cm}$  reflecting high salinity levels in TSF2. The high salinity levels of mine tailing samples is basically attributed to the presence of soluble salts (calcium, sodium, magnesium, carbonate) in the tailings as indicated by the XRD results (Fig. 1). In terms of metal behaviour, the high pH and high salinity could facilitate the mobility of Cd (Micó et al., 2006; Peris et al., 2007; Tian et al., 2017). There were statistically differences ( $p < 0.05$ ) in the levels of pH and EC between plots at TSF 2. The differences may possibly be due to the fact that, ore from which the tailings were produced were not necessarily sourced from the same pit and each pit has its own geochemical features (Jeleni *et al.*, 2012).

Site	pH	EC ( $\mu\text{S}/\text{cm}$ )	Table 1 <i>Physicochemical properties of tailing</i>
PIS1	8.5 <sup>a</sup>	358 <sup>b</sup>	
P1S2	8.6 <sup>bc</sup>	534 <sup>d</sup>	
PIS3	8.7 <sup>bcd</sup>	435.3 <sup>c</sup>	
P2S1	8.7 <sup>cde</sup>	913 <sup>f</sup>	
P2S2	8.8 <sup>e</sup>	1507 <sup>g</sup>	
P2S3	8.6 <sup>cde</sup>	2570 <sup>h</sup>	
P3S1	8.6 <sup>ab</sup>	280 <sup>a</sup>	
P3S2	8.5 <sup>a</sup>	620 <sup>e</sup>	
P3S3	8.8 <sup>de</sup>	1524 <sup>g</sup>	

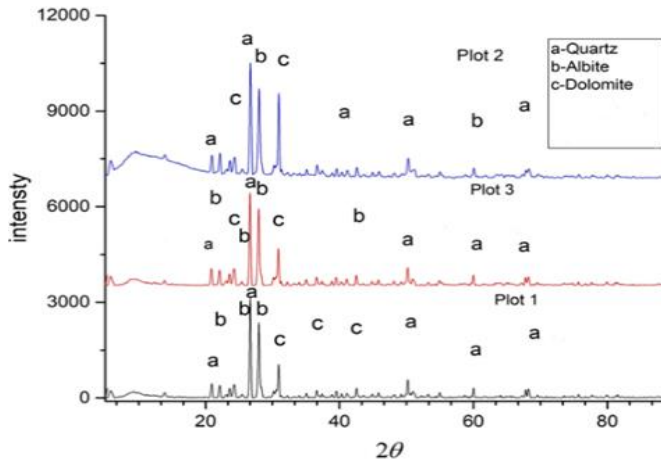
Mean in the same column with different superscript differs significantly ( $p < 0.05$ )

### Mineralogical composition of tailings

The XRD analysis revealed 3 dominant phases of minerals namely the oxide group, silicate group and the carbonate group. In Plot 1, 2 and 3 the mineral phases were Quartz ( $\text{SiO}_2$ ), Dolomite  $\text{CaMg}(\text{CO}_3)_2$  and Albite ( $\text{NaAlSi}_3\text{O}_8$ ) (Fig. 3).

Quartz ( $\text{SiO}_2$ ) recorded the highest compound phase with a value of 61, 56, and 64 for Plot 1, Plot 2 and Plot 3 respectively. Similar findings about the dominance of

quartz than other minerals in tailings were also reported in studies conducted by Novhe et al. (2014) and Munyai et al. (2016).

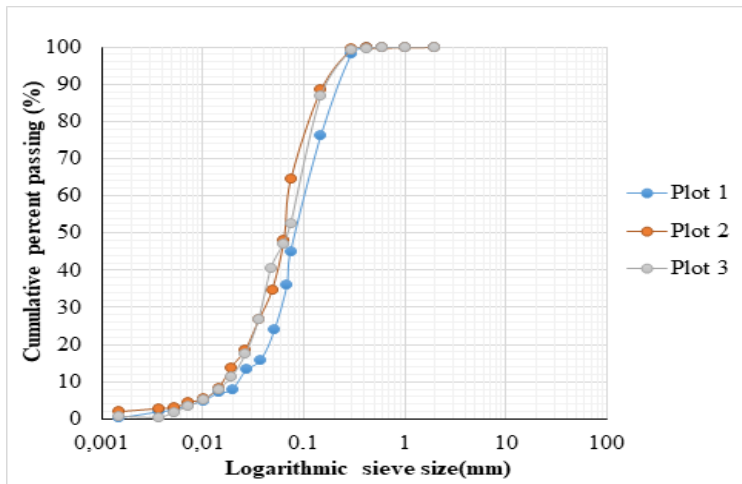


**Figure 3**  
*Mineralogical composition*

The low concentration or percentage of acid forming sulphidic minerals in all mine tailings samples indicates that, the generation of Acid Mine Drainage (AMD) is unlikely in TSF 2. Therefore, there is a very low possibility of contamination of surrounding water bodies as a result of AMD. Eriksson (2002) stated that with time, the presence of Acid Neutralizing Minerals (Dolomite) in mining waste (tailings) maintains a neutral pH and enhance the precipitation of dissolve metals..

**Particle size distribution and texture of the tailings**

The texture of the tailing samples in TSF 2 for Plot1, Plot2 and Plot3 were silty sand with particle size ranging from 0.0015 to 2.0 mm (Fig. 4).



**Figure 4**  
*Particle size distribution curves for tailing samples*

Similar particle size of tailing was reported by Foli (2017), in a decommissioned tailings dam at AngloGold-Ashanti, Obuasi Mine. Plot1, Plot2, Plot3 contained 0.34% 1,95% 0.61% clay, 36.02% 48.17% 47.06% silt and 63.64% 49.88%



52.33% sand fractions, respectively. Indication is that, Plot 1 had lesser proportion of the small particle sizes compared to Plot2 and Plot3 respectively. Also, the deficiency of clay materials in the tailing could be a risk to ground water resources, as according to Boateng et al. (2012) the surface of clay materials greatly adsorb trace metals under appropriate geochemical condition and with high levels of Fe in the medium. Thus, the texture of tailings may enhance the permeability of toxic substances to ground water resources.

### **Concentration of arsenic and heavy metals for various sampling sites**

Due to the toxicity of Arsenic (As), it is considered as one of the most dangerous metals with serious environmental concerns (Choudhury et al., 2011). Exposure to As causes cancer of the lungs, urinary bladder and kidney damage (Abdul-Wahab and Marikar, 2012). Concentration of As for all sampling sites ranged from 0.7 mg/kg in P1S1 to 3.3 mg/kg in P2S3 and were below FAO/WHO (2001), maximum permissible limit of 20 mg/kg (Table 2). Contrary to this finding, higher concentration (1752 mg/kg) in gold mine tailings was observed by Bempah et al. (2013) in AngloGold-Ashanti, Obuasi Mine. In gold ore bodies, As occurs in sulphide minerals such arsenopyrite (FeAsS) Nriagu et al. (2007), hence, the low levels of As in TSF 2 could be attributed to the absence or low concentration of arsenopyrite (FeAsS) in the tailings samples. There were significant difference ( $p < 0.05$ ) in the concentration of As between the means of P2S3 and P3S3 with all other treatment means.

Lead (Pb) is another metal of great concern because it is a metal that can cause genetic mutation. The concentration of Pb for all sampling sites ranged from 1.3 mg/kg in P2S2 to 2.2 mg/kg in P2S1 and were below FAO/WHO (2001), maximum permissible limit of 50 mg/kg (Table 2). Generally, there were significant difference ( $p < 0.05$ ) in the concentration of Pb between sampling sites. According to Matocha et al. (2001) in gold ore, Pb occurs in the form of galena (PbS) with elevated levels determined by high concentration of sulphide, hence the low levels of Pb in all sampling sites could be attributed to the absence of PbS in the tailings.

Chromium (Cr) concentration for all sampling sites were below FAO/WHO (2001), maximum permissible limit of 100 mg/kg ranging from 0.9 mg/kg in P3S3 to 1.9 mg/kg in P2S1 (Table 2). Generally, there were significant difference ( $p < 0.05$ ) in the concentration of Cr between sampling sites.

Due to the high stability and toxicity of cadmium (Cd), it is considered as the most dangerous metal ion (Kermani et al., 2010). The concentration of Cd for all sampling sites were below FAO/WHO (2001), maximum permissible limit of 3 mg/kg ranging from 2.0 mg/kg in P1S3 to 2.9 mg/kg in P1S1 (Table 2). Generally, there were significant difference in the concentration of Cd between sampling sites.

Copper (Cu) concentration for all sampling sites ranged from 5.5 mg/kg in P1S3 to 6.5 mg/kg in P2S3, and were below FAO/WHO (2001), maximum permissible

limit of 100 mg/kg (Table 2). Comparatively similar lower concentration (92.17 mg/kg) in tailings below the FAO/WHO (2001) maximum permissible limit was observed by Bempah et al. (2013) in Obuasi. Generally, there were significant difference in the concentration of Cu between sampling sites.

Zinc (Zn) concentration for all sampling sites ranged from 2.4 mg/kg in P1S3 to 3.6 mg/kg in P3S1 and were below FAO/WHO (2001), maximum permissible limit of 300 mg/kg (Table 2). Generally, there were significant difference in the concentration of Zn between sampling sites. Comparatively similar much lower concentration (2.8 mg/kg) in tailings below the FAO/WHO (2001) maximum permissible limit was also observed by Belford and Nkansah (2017) in CGML. In ore bodies, zinc occurs in the form of sphalerite (ZnS) which is regularly allied with galena Fashola et al. (2016), hence, the low levels of Zn in all samplings sites could be attributed to the absence or low concentration of (ZnS) in the tailings samples.

The concentration of iron (Fe) was the highest for all sampling sites but were below FAO/WHO (2001), maximum permissible limit of 50,000 mg/kg ranging from 4.5 mg/kg in P1S3 to 12.0 mg/kg in P3S3 (Table 2). As such, the order of abundance of metals in TSF 2 was Fe > Cu > Zn > Cd > Pb > Cr > As. Generally, there is relatively high natural deposit of Fe in the earth crust (Abraham and Parker 2008). This could explain the high levels of Fe in all analysed tailings samples. There was significant difference ( $p < 0.05$ ) in the concentration of Fe between the mean of P1S3 with the means of P1S1, P1S2, P3S1, P3S2 and P3S3.

**Table 2.** Mean concentration of arsenic and heavy metals at various sampling sites

Plot	Site	Mean Concentration of Heavy Metal in Tailings (mg/kg)						
		As	Pb	Cr	Cd	Cu	Zn	Fe
1	P1S1	0.7±0.1 <sup>a</sup>	1.6±0.1 <sup>b</sup>	1.4±0.1 <sup>bc</sup>	2.9±0.1 <sup>f</sup>	5.7±0.1 <sup>ab</sup>	2.6±0.1 <sup>b</sup>	10.9±0.1 <sup>b</sup>
	P1S2	0.9±0.1 <sup>abc</sup>	1.8±0.1 <sup>bc</sup>	1.5±0.1 <sup>c</sup>	2.1±0.1 <sup>ab</sup>	5.9±0.1 <sup>bc</sup>	2.9±0.1 <sup>c</sup>	11.2±0.1 <sup>b</sup>
	P1S3	1.2±0.1 <sup>cd</sup>	1.9±0.1 <sup>cd</sup>	1.8±0.1 <sup>ef</sup>	2.0±0.1 <sup>a</sup>	5.5±0.1 <sup>a</sup>	2.4±0.1 <sup>a</sup>	4.5±5.8 <sup>a</sup>
2	P2S1	1.1±0.1 <sup>bc</sup>	2.2±0.1 <sup>e</sup>	1.9±0.1 <sup>f</sup>	2.2±0.0 <sup>bc</sup>	6.3±0.1 <sup>ef</sup>	3.4±0.1 <sup>ef</sup>	8.5±0.1 <sup>ab</sup>
	P2S2	1.5±0.1 <sup>d</sup>	1.3±0.1 <sup>a</sup>	1.8±0.1 <sup>ef</sup>	2.4±0.1 <sup>de</sup>	6.2±0.1 <sup>de</sup>	2.9±0.1 <sup>cd</sup>	8.8±0.1 <sup>ab</sup>
	P2S3	3.3±0.1 <sup>f</sup>	1.4±0.1 <sup>a</sup>	1.7±0.1 <sup>de</sup>	2.6±0.1 <sup>e</sup>	6.5±0.01 <sup>f</sup>	3.2±0.1 <sup>de</sup>	8.9±0.1 <sup>ab</sup>
3	P3S1	0.9±0.1 <sup>ab</sup>	2.2±0.1 <sup>e</sup>	1.6±0.1 <sup>cd</sup>	2.4±0.1 <sup>de</sup>	6.0±0.1 <sup>cd</sup>	3.6±0.1 <sup>f</sup>	11.7±0.1 <sup>b</sup>
	P3S2	0.9±0.1 <sup>ab</sup>	2.1±0.1 <sup>de</sup>	1.3±0.1 <sup>b</sup>	2.1±0.1 <sup>ab</sup>	5.8±0.1 <sup>bc</sup>	3.0±0.1 <sup>cd</sup>	11.7±0.1 <sup>b</sup>
	P3S3	2.4±0.1 <sup>e</sup>	1.8±0.1 <sup>bc</sup>	0.9±0.01 <sup>a</sup>	2.3±0.1 <sup>cd</sup>	6.1±0.1 <sup>de</sup>	3.1±0.1 <sup>cd</sup>	12.0±0.1 <sup>b</sup>
FAO/WHO guideline		<b>20</b>	<b>50</b>	<b>100</b>	<b>3</b>	<b>100</b>	<b>300</b>	<b>50000</b>

Means ±SD in the same column with different letters in superscripts differs significantly ( $p < 0.05$ )

In principal, the observed statistical differences in the distribution of heavy metals between sampling sites could be ascribed to variations in the physicochemical parameters (pH, EC, soil textural class) in the mine tailings samples. The variations also affirm the heterogeneous nature of tailings and significant non-uniform distribution of heavy metals in TSF 2 (Table 1). In terms of distribution of heavy metals according to plots, the order of abundance was Plot 2 > Plot 3 > Plot 1. The relatively high levels of metals in Plot 2 and Plot 3 comparative to Plot 1 may be

due to lesser proportion of the small particle size in Plot 1. According to Munyai et al. (2016) smaller particles have a large surface area and thus likely to liberate metals in high concentrations. It is therefore likely that, metals will be easily leached from Plot 2 and Plot 3 compared to Plot 1.

### Contamination Status of Arsenic and Heavy Metals

**Geoaccumulation index.** Negative Igeo values were recorded for Pb, Cr, Cu, Zn, and Fe for all sampling sites (Table 3). Clearly, there was practically uncontaminated state of Pb, Cr, Cu, Zn and Fe in the tailings samples. In the case of As, there was uncontaminated to moderate contamination with Igeo value of 0.5 at P2S3 and 0.1 at P3S3. Conversely, the Igeo index for Cd in all sampling site was in class 4 indicating strong Cd contamination. On the basis of the mean Igeo value mine, tailings in TSF 2 are enriched with metals in a decreasing order: Cd > As > Cu > Pb > Cr > Zn > Fe.

Site	As	Pb	Cr	Cd	Cu	Fe	Zn	Table 3 Geoaccumulation Index values for tailing samples
P1S1	-1.7	-4.2	-5.3	<b>4.3</b>	-2.7	-12.2	-5.3	
P1S2	-1.2	-4.1	-5.1	<b>3.8</b>	-2.7	-12.2	-5.2	
P1S3	-0.9	-3.9	-4.9	<b>3.8</b>	-2.8	-13.5	-5.5	
P2S1	-1.0	-3.8	-4.7	<b>3.9</b>	-2.6	-12.6	-4.9	
P2S2	-0.6	-4.5	-4.9	<b>4.0</b>	-2.6	-12.6	-5.2	
P2S3	<b>0.5</b>	-4.4	-4.9	<b>4.1</b>	-2.5	-12.5	-5.1	
P3S1	-1.3	-3.8	-5.1	<b>4.0</b>	-2.6	-12.1	-4.9	
P3S2	-1.3	-3.9	-5.4	<b>3.8</b>	-2.7	-12.1	-5.2	
P3S3	<b>0.1</b>	-4.1	-5.7	<b>3.9</b>	-2.6	-12.1	-5.1	
Mean	-0.8	-4.1	-5.1	<b>3.9</b>	-2.6	-12.4	-5.2	

Note: Bold type means Igeo value within class 1-3

**Enrichment Factor.** The EF values for As, Pb, Cd, Cu, Zn and Fe were observed in the ranges of 0.2 to 1.1, 0.0 to 0.1, 0.0 to 0.1, 0.1 to 0.2, 0.0 to 0.0 and 1.0 to 1.0 indicating that, the principal source of these metals were mainly from crust material signifying background metal concentration levels (Table 4).

Site	As	Pb	Cr	Cd	Cu	Fe	Zn	Table 4 Enrichment factor values for tailing samples
P1S1	0.2	0.0	0.0	<b>11.9</b>	0.1	1.0	0.0	
P1S2	0.3	0.0	0.0	<b>8.5</b>	0.1	1.0	0.0	
P1S3	0.8	0.1	0.1	<b>20.5</b>	0.2	1.0	0.0	
P2S1	0.4	0.1	0.0	<b>11.9</b>	0.1	1.0	0.0	
P2S2	0.5	0.0	0.0	<b>12.6</b>	0.1	1.0	0.0	
P2S3	1.1	0.0	0.0	<b>13.1</b>	0.1	1.0	0.0	
P3S1	0.2	0.0	0.0	<b>9.5</b>	0.1	1.0	0.0	
P3S2	0.2	0.0	0.0	<b>8.2</b>	0.1	1.0	0.0	
P3S3	0.6	0.03	0.0	<b>8.6</b>	0.1	1.0	0.0	
Mean	0.5	0.02	0.1	<b>11.6</b>	0.1	1.0	0.0	

Conversely,  $EF > 2$  were recorded for Cd in all tailing samples indicating significant enrichment of Cd in TSF 2. According to Enkhzaya et al. (2016) high EF value of heavy metal in tailing sample point to contribution of anthropogenic sources, indicating mine tailings enrichment by heavy metals during gold extraction process. Again, high concentration of heavy metals in a sample compared to continental crust can be major contamination source for soils and sediments (Levei et al., 2013). Hence, Cd which is carcinogenic could be transported into adjacent soils through moisture movement or wind erosion of dried tailings.

The order of heavy metal enrichment in the tailing samples are as follows: Cd>Fe>As>Cu>Cr>Pb>Zn.

**Contamination Factor.** Contamination factor ( $C_f$ ) for sampling sites for As, Pb, Cr, Cd, Cu, Zn and Fe were observed in the ranges of 0.5 to 2.2, 0.1 to 0.1, 0.0 to 0.0, 20.4 to 29.1, 0.2 to 0.3, 0.0 to 0.1 and 0.00 to 0.00 respectively (Table 5). Accordingly, tailing samples can be classified as exhibiting low contamination status with respect to Pb, Cr, Cu, Zn and Fe for all sampling sites. However, As exhibited low contamination for all sampling sites with the exception of sampling site P2S3 and P3S3 which exhibited moderate contamination. The low contamination status of Pb, Cr, Cu, Zn and Fe in all sampling site may be attributed to the alkaline nature of tailing samples. With respect to Cd, a very high contamination status was observed in all mine tailing samples.

Plot	Site	Contamination Factor ( $C_f$ )						
		As	Pb	Cr	Cd	Cu	Zn	Fe
1	P1S1	0.5	0.1	0.0	<b>29.1</b>	0.2	0.0	0.0
	P1S2	0.7	0.1	0.0	<b>21.2</b>	0.2	0.0	0.0
	P1S3	0.8	0.1	0.1	<b>20.4</b>	0.2	0.0	0.0
2	P2S1	0.7	0.1	0.1	<b>22.8</b>	0.3	0.0	0.0
	P2S2	0.9	0.1	0.1	<b>24.5</b>	0.3	0.0	0.0
	P2S3	<b>2.2</b>	0.1	0.1	<b>26.0</b>	0.3	0.1	0.0
3	P3S1	0.6	0.1	0.0	<b>24.7</b>	0.2	0.1	0.0
	P3S2	0.6	0.1	0.0	<b>21.4</b>	0.2	0.0	0.0
	P3S3	<b>1.7</b>	0.1	0.0	<b>23.2</b>	0.3	0.0	0.0
	Mean	<b>0.9</b>	<b>0.1</b>	<b>0.04</b>	<b>23.7</b>	<b>0.2</b>	<b>0.04</b>	<b>0.00</b>

**Table 5**  
*Contamination factor values of arsenic and heavy metals for tailings samples*

**Pollution Load Index and Potential Ecological Risk Factor of Arsenic and Heavy Metals.** Pollution index is a powerful tool for processing, analysing and conveying raw environmental information to decision makers, managers, technicians and the public (Caeiro et al., 2005). PLI values for the nine sampling sites P1S1, P1S2, P1S3, P2S1, P2S2, P2S3, P3S1, P3S2 and P3S3 ranged from 0.09 to 0.13 with the mean PLI of 0.11 (Table 6). Indication from dataset from the nine sampling site is that, even though tailing samples contain some level of heavy metals, the nine sampling site is not progressively deteriorating.

According to Angula (1996), the PLI is able to give an estimate of the metal contamination status and the necessary action that should be taken. Therefore, considering the relatively low metal concentration and the non-deteriorating nature

of the sampling sites in TSF 2, drastic rectification measures may necessary not be required. However, the detection of all metals (Pb, As, Cd, Cr, Cu, Zn and Fe) in mine tailing samples still require that critical attention must be given to TSF 2.

Site	PLI	As	Pb	Cr	Cd	Cu	Zn	<b>Table 6</b>
P1S1	0.10	4.7	0.4	0.1	872	1.2	0.0	<i>PLI and potential ecological risk factor of heavy metals in mine tailings</i>
P1S2	0.11	6.5	0.5	0.1	637	1.2	0.0	
P1S3	0.09	8.1	0.5	0.1	612	1.1	0.0	
P2S1	0.12	7.3	0.6	0.1	683	1.3	0.1	
P2S2	0.11	9.7	0.4	0.1	735	1.3	0.0	
P2S3	0.13	21.7	0.4	0.1	781	1.3	0.1	
P3S1	0.12	6.0	0.6	0.1	741	1.2	0.1	
P3S2	0.11	6.1	0.5	0.1	643	1.2	0.1	
P3S3	0.12	16.5	0.5	0.1	695	1.2	0.0	
Mean	<b>0.11</b>	<b>9.6</b>	<b>0.5</b>	<b>0.1</b>	<b>711</b>	<b>1.2</b>	<b>0.04</b>	

With respect to the toxicity of each metals, the ecological risk factor (Er) for As was observed in the range of 4.7 to 16.5, that of Pb was in the range of 0.4 to 0.6, that of Cr was observed in the range of 0.1 to 0.1, that of Cu was observed in the range of 1.1 to 1.3, that of Zn was observed in the range of 0.0 to 0.1 (Table 6). Accordingly, As, Pb, Cr, Cu, Zn has low potential ecological risk factor in all sampling sites. Hence, these heavy metals were not likely to pose harm or ecological risk to the environment. However, higher Er value (612 to 872) were recorded for Cd in all sampling sites and likely to pose harm or ecological risk to the environment.

### **Conclusions**

An investigation of arsenic and heavy metals pollution in gold mine tailing soils were conducted in this study. All heavy metals under study were detected in all mine tailing samples. The mean concentration of As, Pb, Cr, Cd, Cu, Zn and Fe for all sampling sites were below FAO/WHO (2001) maximum permissible limits. Results also indicates that, there is a heterogeneous concentration of arsenic and heavy metals in tailings as the levels varied between sampling sites. Tailings samples were silty sand hence, may have low capacity to adsorb contaminants (trace metals) on its surface. The dominant mineral phase in the tailings samples were Quartz (SiO<sub>2</sub>), Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) and Albite (NaAlSi<sub>3</sub>O<sub>8</sub>), the production of AMD in TSF 2 is unlikely.

Based on geoaccumulation indices and contamination factor computed, TSF 2 can be generally described as uncontaminated with As, Pb, Cr, Cu, Zn and Fe. However, there was moderate contamination of As in sampling site P2S3 and P3S3. The enrichment factor revealed background concentration of As, Pb, Cr, Cu, Zn and Fe. In contrast, TSF 2 is highly contaminated with Cd. Also, mine tailings was significantly enriched with Cd and likely to pose ecological risk or harm to the

environment. Hence, Cd should be a major priority in rehabilitation actions. In totality, the nine sampling site is not progressively deteriorating in accordance to PLI values. Findings of this study may provide information and references for present and future management decisions regarding productive use of TSF 2.

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## NIVEAUX DE MÉTAUX LOURDS ET ÉTAT DE CONTAMINATION D'UN BARRAGE DE RÉSIDUS MINIERES DÉCLASSÉ AU GHANA

### Résumé

La pollution par les métaux lourds provenant des résidus miniers est devenue une préoccupation mondiale majeure en raison de sa toxicité, de sa persistance et de son potentiel accumulateur ayant des effets néfastes sur la santé publique et les récepteurs de l'environnement. Dans le but de déterminer l'état de contamination d'une installation de stockage de résidus (TSF 2) désaffectée provenant de la mine d'or Chirano (CGM), neuf échantillons de carottes de résidus miniers ont été recueillis à une profondeur de 20 cm sur une grille de 8100 m<sup>2</sup>. Concentrations d'As (0,7 à 3,3), de Pb (1,3 à 2,2), de Cr (0,9 à 1,9), de Cd (2,0 à 2,6), de Cu (5,5 à 6,5), de Zn (2,4 à 3,6) et de Fe (4,5 à 12) mg / kg étaient inférieures aux limites permises FAO / OMS. La concentration de métaux lourds variait statistiquement entre les sites d'échantillonnage ( $p < 0,05$ ). L'indice de géoaccumulation et le facteur de contamination ont révélé que le TSF 2 n'est pas contaminé par l'As, le Pb, le Cr, le Cu, le Zn et le Fe. Cependant, les résidus miniers étaient considérablement enrichis en cadmium et donc susceptibles de présenter un risque écologique pour l'environnement. En général, la digue à stériles ne se détériore pas progressivement en fonction de l'indice de charge de pollution. Les résultats de cette étude contribueraient à la base de données environnementale des résidus miniers de la mine d'or à CGM afin de faciliter la restauration future de l'installation de stockage des résidus.

**Mots-clés:** Facteur de contamination, indice de géo-accumulation, facteur d'enrichissement, indice de charge de pollution, facteur de risque écologique.

## LIVELLI DI METALLI PESANTI E STATO DI CONTAMINAZIONE DI UNA DIGA DI DECANTAZIONE DISMESSA IN GHANA

### Riassunto

L'inquinamento da metalli pesanti degli sterili è diventato una delle principali preoccupazioni a livello mondiale a causa della sua tossicità, persistenza e potenziale accumulativo con effetti dannosi sulla salute pubblica e sui recettori ambientali. Nel tentativo di determinare lo stato di contaminazione di un impianto di stoccaggio degli sterili dismesso (TSF 2) dalla Chirano Gold Mine (CGM), nove campioni di base di residui di miniere sono stati raccolti fino a una profondità di 20 cm all'interno di una griglia di 8100 m<sup>2</sup>. Concentrazioni di As (da 0,7 a 3,3), Pb (da 1,3 a 2,2), Cr (da 0,9 a 1,9), Cd (da 2,0 a 2,6), Cu (da 5,5 a 6,5), Zn (da 2,4 a 3,6) e Fe (da 4,5 a 12) mg / kg erano inferiori ai limiti consentiti dalla FAO / OMS. La concentrazione di metalli pesanti variava statisticamente tra i siti di campionamento ( $p < 0,05$ ). L'indice di geoaccumulo e il fattore di contaminazione hanno rivelato che, il TSF 2 è incontaminato con As, Pb, Cr, Cu, Zn e Fe. Tuttavia, le operazioni di sminamento sono state significativamente arricchite con Cd, e quindi potrebbero rappresentare un rischio ecologico per l'ambiente circostante. In generale, la diga di sterilizzazione non si deteriora progressivamente in base all'indice del carico inquinante. I risultati di questo studio contribuirebbero alla banca dati ambientale del tailing delle miniere d'oro presso la CGM per assistere il futuro risanamento della struttura di stoccaggio del tailing.

**Parole chiave:** *fattore di contaminazione, indice di geoaccumulo, fattore di arricchimento, indice del carico di inquinamento, fattore di rischio ecologico.*