

Original Research Paper

# Pollution Risk Analysis of Heavy Metals at Illegal Mining Sites at Atiwa East District, Ghana

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## Article history

Received: 09-02-2022

Revised: 22-03-2022

Accepted: 11-05-2022

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**Abstract:** This study aims at determining the level of pollution of heavy metals (Cr, Cu and Hg) in the soils of illegal mining sites in Atiwa East District of Ghana. The concentrations of Copper (Cu), Chromium (Cr), and Mercury (Hg) in the soils were determined using Atomic Absorption Spectrometry (AAS). The extent of heavy metal pollution and pollution risk assessment was analyzed at the study site. Thirty (30) soil samples were collected from three (3) illegal mining sites within the district. The average levels of Cu, Cr, and Hg in the soil were 8.8, 6.75, and 3.19 mgkg<sup>-1</sup> respectively, and were all above the WHO threshold. The geo accumulation indices (Igeo) of Cu, Cr, and Hg obtained were 1.92, 3.8, and 6.5 respectively, indicating moderately to extremely polluted soil at the study sites. The research has helped to establish the local Geochemical Baseline Concentrations (GBCs) of heavy metals in the study area so that an appropriate remediation method could be employed.

**Keywords:** Risk Assessment, Contamination, Geochemical Index, Heavy Metal

## Introduction

In the past two decades, there has been a continual demand for gold in the international market, resulting in an astronomical increase in gold prices. The increase in the demand for gold has increased the production of gold globally (USGS, 2014). This development has awakened the drive for the extraction of gold ore from areas that were hitherto not noted for gold mining (Swenson *et al.*, 2011). The cumulative effect of the rise in the demand for gold has resulted in the proliferation of gold mining activities across the world, particularly, in Ghana (Bury, 2004). Most of these mining activities are carried out through small-scale mining as well as illegal mining (Alvarez-Berriós and Aide, 2015). In the rural settings where the geology is rich in mineral resources, small-scale mining is pivotal in employment creation (Hilson and Banchirigah, 2009). Poor mining regulation capacities and weak institutions in developing countries have further accelerated illegal mining activities (Creek, 2009). This arises from the fact that there are limited well-paid jobs for the teeming youth (Amponsah-Tawiah and Darteh-Baah, 2011). Current records indicate that 85% of the one million people involved in small-scale mining activities in Ghana are illegal mining (Ofosu-Mensah, 2010; Akabzaa and Darimani, 2001).

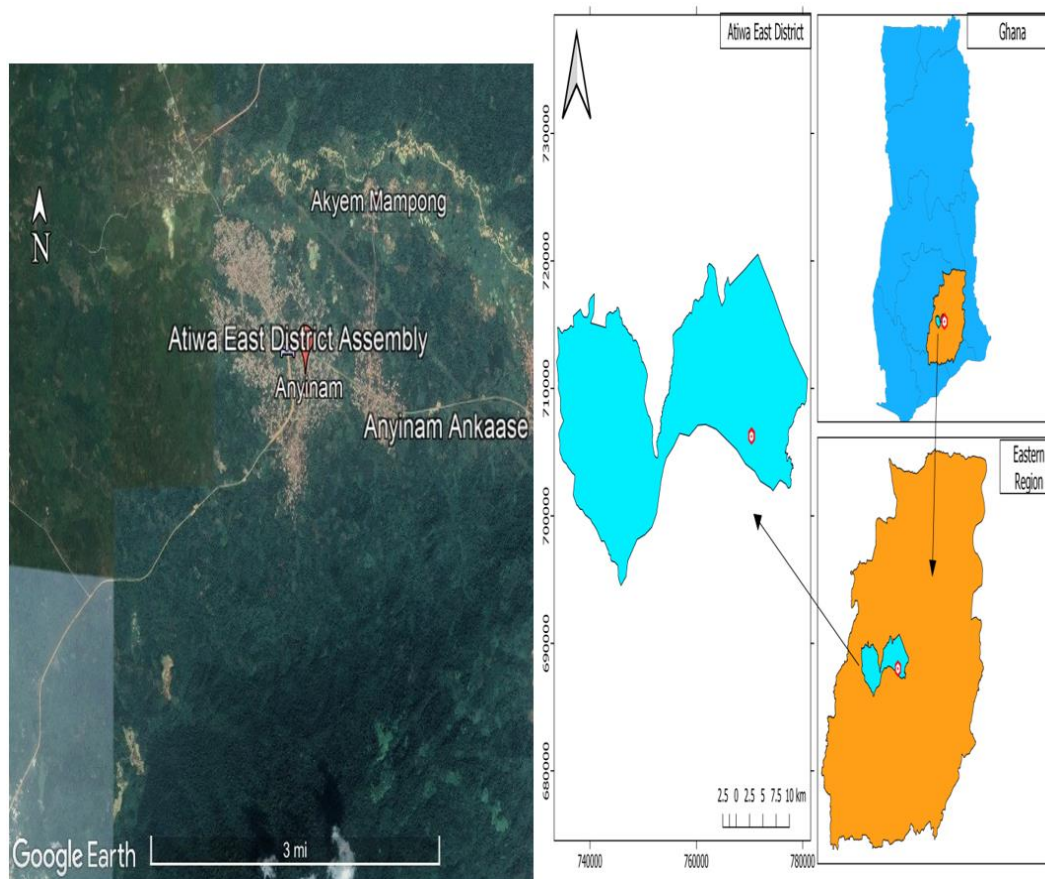
The activities of illegal mining operations have been characterized by incessant destruction of the environment (Villegas *et al.*, 2012). The devastating effect of illegal mining includes deforestation of natural reserves, siltation, and diversions of the natural watercourse as well as the intrusion of contaminants in both soil and water bodies (Opoku-Ware, 2010). Some of these contaminants released from the activities of small-scale mining are heavy metals. The incessant accumulation of heavy metals in the soil and water bodies (Kumari and Tripathi, 2015) eventually affects the food chain through the soil and sediments of water bodies, which serve as a sink to these metals (Rice *et al.*, 2014). The threat of heavy metal contamination in the environment has been prevalent worldwide, due to their bioaccumulation and toxicity. Elevated levels of heavy metals such as Hg, Cd, As, Cr, etc., upon consumption, affects negatively, the immunological and dermatological systems, respiratory, nervous, hepatic, cardiovascular, gastrointestinal, renal, and hematopoietic systems (Shrivastava *et al.*, 2002). There is a need to conduct a risk assessment at the contaminated sites to ascertain the extent of heavy

metal pollution in the affected catchment. A lot of studies have been conducted in this regard at various sites in different parts of the world.

Akoto *et al.* (2018) conducted a risk assessment of heavy metal pollution in the surface soil of Obuasi, Ghana. Their study was premised on the possible heavy metal (Pb, Cd, Hg, Cu, Zn, Co, Cr, Ni, and As) contamination from mining activities in Obuasi. Their results showed that soils in about 41% of the entire community possess a high risk to the surrounding ecological system, as a result of the elevated levels of heavy metals within the study sites. Onysoya *et al.* (2018) carried out a risk assessment of heavy metal contamination in the soil of an artisanal gold mining site at Anka Local Government area in Northwestern Nigeria. Their study was based on the exposure parameters of heavy metals in estimating human carcinogenic and non-carcinogenic risk. The results of their study revealed that 21 out of 23 locations pose a non-cancer risk for children. Their study further showed that both adults and children are at high cancer risk in all locations as the total cancer risk exceeded  $1 \times 10^{-6}$  (Lower limit CTR value). Fagbenro *et al.*

(2021) also researched the concentration of heavy metal contamination in the Igun, Ijana-Gada, and Igbadae gold mining sites using Particle Induced X-ray Emission technique. Their study was premised on ascertaining the background levels of the heavy metals as well as the source of contamination and pollution load on the study sites. Their research revealed that all the heavy metals (Fe, Ti, Mn, Cr, Zn, Pb, Cu) were at elevated levels above the WHO threshold. Also, all the heavy metals within the study sites were classified as moderately-extremely polluted.

In Ghana, not much research on the comprehensive ecological risk assessment has been carried out, especially at the Artisanal Small Scale Gold Miners (ASGM). This research helps to establish local Geochemical Baseline Concentrations (GBCs) due to the lack or inapplicability of background values in the study area. Atiwa east district of Ghana is well noted for its illegal mining activities. Studies conducted by Boakye *et al.* (2022) on the emerging diseases associated with mining, using the Atiwa east district as one of the case studies, revealed that about 39.2% of the population leaving in the mining towns suffer from skin diseases. The results further revealed that 34.2% of the population also suffer from the numbness of the palm, and 18.1% have respiratory problems.



**Fig. 1:** Atiwa east district in the eastern region, Ghana

This research aims to determine the level of pollution of Cr, Cu, and Hg within the catchment of Atiwa east district of Ghana, as a result of small-scale mining operations. To realize the aim of the study, the research is anchored on the following two objectives; 1. To determine the concentration of heavy metals in the soil and the Physico-Chemical properties of the soil and 2. To evaluate the levels of soil and soil toxicity and the environmental risk of heavy metals within the catchment of small-scale mining sites of Atiwa East district using various geochemical indices. The outcome of this study would assist in determining the remedial technique to be implemented to restore the integrity of the environment.

### Study Area

The study was conducted at Akyem Anyinam, Akyem Mampong, and Akyem Ankaase artisanal gold mining sites within the Atiwa East District in the Eastern Region of Ghana (Fig. 1).

Atiwa East District is one of the thirty-three districts in the Eastern Region of Ghana surrounded by green forest reserves. Geographically, the Atiwa East District lies at latitude 6°22' 12.72"N and longitude 0°32' 24"W. The district is covered with an area of 490.1 km<sup>2</sup>, a population density of 127.6/km<sup>2</sup>, and an annual population growth rate of 2.3%. The District is situated in the midst of a very green-covered forest reserve with a lot of tree species such as Odum, mahogany, Wawa, and others within and around its surroundings. On the other hand, the illegal chainsaw operators' activities and small-scale mining keep on destroying the very green cover of the forest reserves as well as the entire environment. There are averagely eighteen illegal small-scale mining sites scattered all over the three study sites.

### Materials and Methods

A total of thirty (30) soil samples, ten (10) each from Akyem Anyinam, Akyem Mampong, and Akyem Ankaase were studied between February and October 2021. The levels of three (3) heavy metals; Chromium (Cr), Copper (Cu), and Mercury (Hg) in the soil samples from the selected research area were studied. The selection of these heavy metals was based on their prevalence and toxicity. Ten spot points each of a defined area (50 × 50 m) on a section of each of the three catchment sites (AM, AA, and AN) were coordinated using a handheld GPS (Garmin-etrex 10) and mapped out (Fig. 2).

### Sampling and Sample Treatment

Thirty (30) soil samples, ten (10) each from Akyem Anyinam (AN), Akyem Mampong (AM), and Akyem Ankaase (AA) were studied. Using a Push Probes and the Veen Van Grab Sampler, 250 g of soil samples were scooped at a depth of 17 cm. The soil samples were placed in a clean and brand new Ziplock bag and well labeled. The procedure was repeated for the rest of the sampled locations. Triplicate sampling was collected at all sampling sites. The samples were then sent to the University of Ghana Ecological

laboratory for analysis. GARMIN GPS was used to obtain the coordinate of all the sampled locations. The soil samples were ground into powder using a mortar and a pestle after they have been air-dried. In determining the physicochemical parameters of the soil samples, the powdered samples were then sieved using a <2 mm sieve. The digestion of the sample (0.5 g) was carried out using 15 mL of nitric acid; HNO<sub>3</sub> (65%; EMSURE) and HCl (36% EMSURE) in the ratio of 3:1 as described by Maiti and Nandhini (2006) over a temperature of 95°C. This temperature is maintained until the solution becomes clearer after the escape of NO<sub>2</sub> fumes. 1% of the nitric acid (HNO<sub>3</sub>) was afterward added to the digested sample mass in a volumetric bottle up to 50 mL and then filtered using a Whatman grade 40 filter with a 2.5 μm pore size. The content of the heavy metals (Cr, Cu, As, and Hg) was achieved by putting the sample in a refrigerator and then using Flame Atomic Absorption Spectrometer (FAAS-AELABAA4530F). The pH and conductivity of the soil were measured using a pH meter (O<sub>2</sub>-Lumitrode-913) by the soil-water suspension. The Kjeldahl Nitrogen Analyzer, Walkey-Black Chromic acid method, and weight loss by oven-dried soil sample through spectrometry were used in determining the total Nitrogen, Organic Carbon, and Organic matter respectively.

The extent of pollution was determined using various geochemical indices such as Contamination Factor ( $C_f$ ), Degree of Contamination ( $C_d$ ), Modified Degree of Contamination ( $mCd$ ), Pollution Load Index (PLI), and geoaccumulation index (Igeo).

### Contamination Factor ( $C_f$ )

The contamination factor ( $C_f$ ) for Cu, As, Cr, and Hg metals were calculated by the equation as described by (Hakanson, 1980):

$$C_f = \frac{C_{metal}}{C_{background}} \quad (1)$$

where,  $C_{metal}$  is the total metal concentration in the soil (mg/kg) and  $C_{background}$  = concentration of background metals in unpolluted soil (mg/kg).

### Degree of Contamination ( $C_d$ )

The degree of contamination was calculated by the equation described by Hakanson (1980):

$$C_d = \sum_{i=1}^n (C_f^i) \quad (2)$$

Then:

$C_f$  and  $C_d$  were classified into four classes as indicated in Table 1 (Vaezi *et al.*, 2015).

### Modified Degree of Contamination ( $mCd$ )

This is described by Abraham and Parker (2008) as in the following equation:

$$mCd = \frac{\sum_{i=1}^n (C_f^i)}{n} \quad (3)$$

where,  $n$  = total quantity of metals taken into consideration, the  $mCd$  is described under seven (7) categories (Table 2).

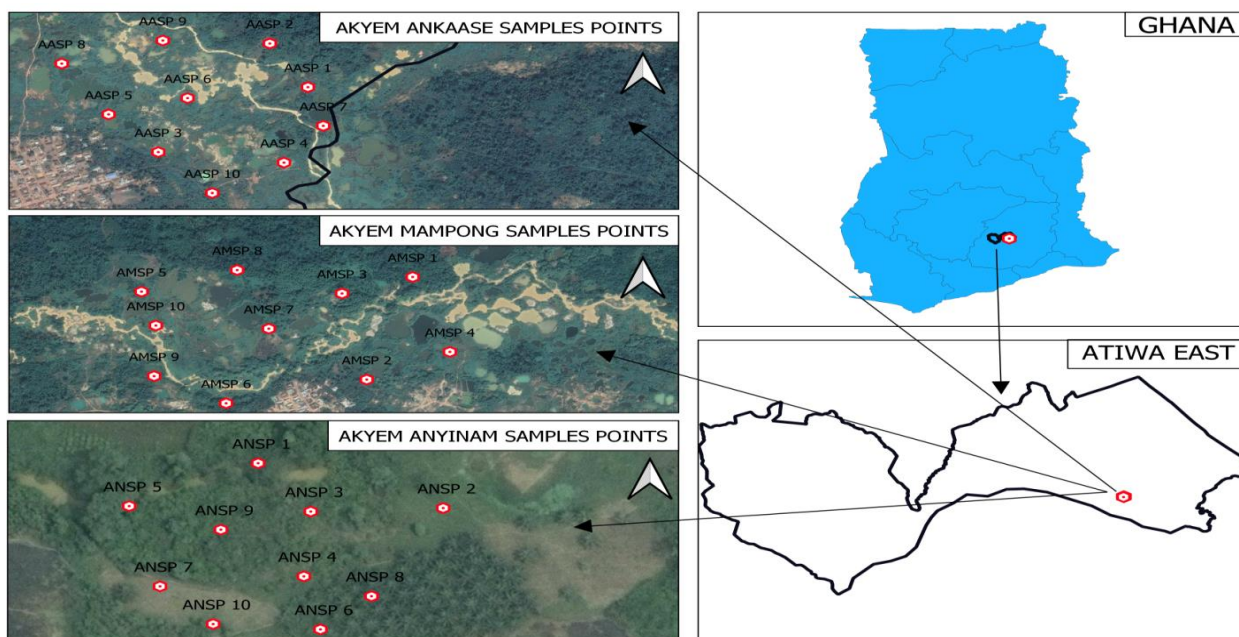
### Pollution Load Index (PLI)

The pollution load index was used to determine the level of metal pollution in the mine site soils as described

by (Tomlinson *et al.*, 1980). Each of the contamination factors ( $C_{fi}$ ) of the three catchment sites was multiplied and increased by a fraction of the total quantity of metals considered in the study. It is given by the equation:

$$PLI = (C_{f1} * C_{f2} * C_{f3} * \dots * C_{fn})^{(1/n)} \quad (4)$$

$C_f$  is the contamination factor and  $n$  is the number of metals.  $PLI > 1$  means the soil is contaminated and  $PLI < 1$ , means the soil is not contaminated.



**Fig. 2:** Spatial locations of sampled sites within the research catchment

**Table 1:** Contamination categories based on the values of  $C_f$  and  $C_d$

$C_f$	$C_d$	Description
$C_f < 1$	$C_d < 7$	Low
$1 < C_f < 3$	$7 < C_d < 14$	Moderate
$3 < C_f < 6$	$14 < C_d < 28$	Considerable
$C_f > 3$	$C_d > 14$	Very high

**Table 2:** Contamination categories based on  $mCd$  values

$mCd$	Description
$mCd < 1.5$	Zero to the low degree of contamination
$1.5 < mCd < 2$	Low degree of contamination
$2 < mCd < 4$	Moderate degree of contamination
$4 < mCd < 8$	High degree of contamination
$8 < mCd < 16$	Very high degree of contamination
$16 < mCd < 32$	Extremely high degree of contamination
$mCd \geq 32$	Ultra high degree of contamination

**Table 3:** Contamination categories based on Igeo values as described by.

Igeo	Description
>5	Extremely polluted
4-5	Strongly to extremely polluted
3-4	Strongly polluted
2-3	Moderately to strongly polluted
1-2	Moderately polluted
0-1	Unpolluted to moderately polluted
≤ 0	Unpolluted

**Table 4:** Two -way analysis of variance tests between-subjects' effects

Source	dependent variables	SS	DF	MS	F	P-Value
Site	Cu	3.690	1	3.690	5.740	0.024*
	Cr	10.995	1	10.995	4.868	0.037*
	Hg	0.341	1	0.341	9.380	0.005**
	Ca	0.273	1	0.273	1.992	0.170
	Mg	0.037	1	0.037	0.346	0.562
	Na	6.921E-09	1	6.921E-09	0.188	0.668
	K	0.000	1	0.000	0.128	0.723
	TN	0.000	1	0.000	1.441	0.241
	OM	1.217	1	1.217	1.358	0.255
	OC	0.380	1	0.380	1.273	0.270
	EC	0.000	1	0.000	0.082	0.777
	Ph	0.292	1	0.292	4.379	0.047
	TEMP	0.150	1	0.150	5.441	0.028*
	Soil Type	Cu	0.318	1	0.318	0.495
Cr		5.448	1	5.448	2.412	0.133
Hg		0.448	1	0.448	12.315	0.002**
Ca		0.063	1	0.063	0.459	0.504
Mg		0.006	1	0.006	0.054	0.819
Na		3.137E-08	1	3.137E-08	0.854	0.364
K		0.004	1	0.004	4.454	0.045*
TN		0.000	1	0.000	0.461	0.503
OM		0.896	1	0.896	1.000	0.327
OC		0.290	1	0.290	0.973	0.333
EC		0.002	1	0.002	0.446	0.511
Ph		0.339	1	0.339	5.086	0.033*
TEMP		0.276	1	0.276	10.021	0.004**
Soil Properties		Cu	0.473	2	0.237	0.368
	Cr	4.533	2	2.266	1.003	0.381
	Hg	0.027	2	0.013	0.365	0.698
	Ca	0.372	2	0.186	1.357	0.276
	Mg	0.488	2	0.244	2.264	0.125
	Na	3.202E-08	2	1.601E-08	0.436	0.652
	K	0.005	2	0.003	2.759	0.083
	TN	0.001	2	0.000	1.537	0.235
	OM	2.807	2	1.403	1.566	0.229
	OC	0.916	2	0.458	1.535	0.235
	EC	0.009	2	0.005	0.824	0.450
	Ph	0.021	2	0.010	0.154	0.858
	TEMP	0.021	2	0.011	0.387	0.683

\*P = 0.005 (2-tailed)

\*\*P = 0.01 (2-tailed)

### Geo-Accumulation Index (Igeo)

The extent of pollution in the mine site soils was evaluated by the geo-accumulation index as described by (Vaezi *et al.*, 2015).

For the geo-accumulation index determination, the values of Cu, Cr, and Hg metal content obtained in each of the three catchment site areas were divided by the heavy metal standards for soil, multiplied by a factor of 1.5, and the logarithm function of the answers was determined.

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \quad (5)$$

where:

$C_n$  = The concentration of metals in the soil

$B_n$  = The geochemical background concentration of the heavy metals

1.5 constant value = Soil lithological variability (Abraham and Parker, 2008).

The results are classified into seven groups (Table 3).

### Data Analysis

To determine the significant difference between the mean metal content and the physicochemical properties in the three sites, a Two-Way Analysis of Variance (ANOVA) was conducted with the significance level of 5 and 1% ( $P \leq 0.050$ ;  $P \leq 0.001$ ) using SPSS software. Pearson correlation analysis in SPSS on the mean physicochemical properties and heavy metal content in the study area soils was also performed.

## Results and Discussion

### Heavy Metal and Physico-Chemical Concentrations

The mean levels of Cu at AMSP, AASP, and ANSP are 8.87, 8.38, and 9.22  $\text{mgkg}^{-1}$  respectively. Whilst that of Cr are 6.42, 6.76, and 7.08  $\text{mgkg}^{-1}$  respectively. Average concentration levels of mercury (Hg) are 3.03, 2.54, and 4.02  $\text{mgkg}^{-1}$  at AMSP, AASP, and ANSP respectively. The levels of the three heavy metals (Cu, Cr, and Hg) in each of the three study sites were found to be above the WHO threshold. This is an indication that the soils in this catchment are contaminated from the incessant leaching of these heavy metals into the environment. The two-way analysis of variance between groups (three sites) (Table 4) indicates that there are no

significant variations between the means of the heavy metals (Cu, Cr, and Hg) between the three study sites. The results give credence to the fact that the extent of small-scale mining activities in each of the sites is similar. Similar work carried out by (Jerome *et al.*, 2014) at Dunkwa-On-Offin came out with findings of elevated levels of Hg and Cu in the soils of the illegal mining catchment area. They attributed the elevated levels of the heavy metals to the indiscriminate and persistent activities of illegal mining at their study sites. A study conducted by (Duncan *et al.*, 2018) on the pollution levels of heavy metals within the catchment of Pra River and its tributaries where the activities of illegal mining are prevalent. Their findings also showed higher levels of Cu, Cr, and Hg in both the soil/sediment and water bodies of the site.

At the three study sites Akyem Anyinam (AN), Akyem Mampong (AM), and Akyem Ankaase (AA) have been suffering from illegal mining activities since there are no major economic activities to engage the teeming youth. Hence, the practice of illegal mining has become an important source for living and investment. However, their activities continuously endanger the environment.

The physicochemical properties of the soil play a major role in the mobility of heavy metals. The pH of the soil in each of the study sites (AM, AA, and AN) are respectively 5.4, 5.3, and 4.8, indicating the acidic nature of the soil in all cases. The soil texture is Sandy-loamy for AM and AA and loamy for AN. High soil acidity affects fertility, and biological and plant productivity. The high acidity of the soil at the study sites will make it very difficult to support agricultural activities in the area. The high acidity of the soil might result from the leaching of heavy metals into the soil from the activities of illegal mining. High soil acidity releases heavy metals and therefore increases their mobility (Young, 1990). This will cause the heavy metals to leach into both groundwater and other adjoining areas which hitherto were not affected by illegal mining.



Fig. 3: Geo-accumulation index of the metals for the three sites

**Table 5:** Metal contamination factors for all the sites (AMSP, AASP and ANSP)

Site Code	Average metal concentration (mgkg <sup>-1</sup> )			Background metal concentration (mgkg <sup>-1</sup> )			Contamination factors (C <sub>f</sub> )			Who standards for rating	
	Cu	Cr	Hg	Cu	Cr	Hg	Cu	Cr	Hg	C <sub>f</sub>	Description
AMSP	8.87	6.42	3.03	3.5	3.8	0.3	0.25*	0.06*	10.10**	C <sub>f</sub> < 1	Low
AASP	8.38	6.76	2.54	3.5	3.8	0.3	0.23*	0.07*	8.46**	1 < C <sub>f</sub> < 3	Moderate
ANSP	9.22	7.08	4.02	3.5	3.8	0.3	0.26*	0.07*	13.39**	3 < C <sub>f</sub> < 6 C <sub>f</sub> > 6	Considerable Very high

\* C<sub>f</sub> = low, \*\*C<sub>f</sub> = very high

**Table 6:** Degree of contamination for all the sites (AMSP, AASP and ANSP)

Site code	Average metal concentration (mgkg <sup>-1</sup> )			Background metal concentration (mgkg <sup>-1</sup> )			Contamination factors (C <sub>f</sub> )			Degree of contamination C <sub>d</sub>	Who standards for rating C <sub>d</sub>	Description
	Cu	Cr	Hg	Cu	Cr	Hg	Cu	Cr	Hg			
AMSP	8.87	6.42	3.03	3.5	3.8	0.3	0.25*	0.06*	10.10**	10.41 <sup>a</sup>	C <sub>d</sub> < 7	Low
AASP	8.38	6.76	2.54	3.5	3.8	0.3	0.23*	0.07*	8.46**	8.76 <sup>a</sup>	7 < C <sub>d</sub> < 14	Moderate
ANSP	9.22	7.08	4.02	3.5	3.8	0.3	0.26*	0.07*	13.39**	13.71 <sup>a</sup>	14 < C <sub>d</sub> < 28 C <sub>d</sub> > 28	Considerable Very high

\* C<sub>f</sub> = low, \*\*C<sub>f</sub> = very high, aC<sub>d</sub> = moderate

**Table 7:** Modified degree of contamination for all the sites (AMSP, AASP and ANSP)

Site Code	Average metal concentration (mgkg <sup>-1</sup> )			Background metal concentration (mgkg <sup>-1</sup> )			Contamination Factors (C <sub>f</sub> )			Modified Degree of Contamination mC <sub>d</sub>	Who standards for rating mC <sub>d</sub>	Description
	Cu	Cr	Hg	Cu	Cr	Hg	Cu	Cr	Hg			
AMSP	8.87	6.42	3.03	3.5	3.8	0.3	0.25*	0.06*	10.10**	3.47 <sup>b</sup>	mC <sub>d</sub> < 1.5	Zero to very low C <sub>d</sub>
AASP	8.38	6.76	2.54	3.5	3.8	0.3	0.23*	0.07*	8.46**	2.92 <sup>b</sup>	1.5 < mC <sub>d</sub> < 2	low C <sub>d</sub>
ANSP	9.22	7.08	4.02	3.5	3.8	0.3	0.26*	0.07*	13.39**	4.57 <sup>bb</sup>	2 < mC <sub>d</sub> < 4 4 < mC <sub>d</sub> < 8 8 < mC <sub>d</sub> < 16 16 < mC <sub>d</sub> < 32 mC <sub>d</sub> ≥ 32	Moderate C <sub>d</sub> High C <sub>d</sub> Very high C <sub>d</sub> Extremely high C <sub>d</sub> Ultra high C <sub>d</sub>

\* C<sub>f</sub> = low, \*\*C<sub>f</sub> = very high, aC<sub>d</sub> = moderate, b mC<sub>d</sub> = moderate C<sub>d</sub>, bb mC<sub>d</sub> = high C<sub>d</sub>

**Table 8:** Pollution index for all the sites (AMSP, AASP and ANSP)

Site Code	Average Metal Concentration (mgkg <sup>-1</sup> )			Background Metal Concentration (mgkg <sup>-1</sup> )			Contamination Factors (C <sub>f</sub> )			Pollution Index (PLI)	Who standards for rating	Description
	Cu	Cr	Hg	Cu	Cr	Hg	Cu	Cr	Hg		PLI	
AMSP	8.87	6.40	3.020	3.5	3.8	0.3	0.25*	0.06*	10.10**	0.54 <sup>c</sup>	PLI < 1	No Pollution
AASP	8.38	6.76	2.539	3.5	3.8	0.3	0.23*	0.07*	8.46**	0.51 <sup>c</sup>	PLI > 1	Pollution
ANSP	9.22	7.10	4.000	3.5	3.8	0.3	0.26*	0.07*	13.39**	0.62 <sup>c</sup>		

\* C<sub>f</sub> = low, \*\*C<sub>f</sub> = very high, <sup>a</sup>C<sub>d</sub> = moderate, <sup>b</sup>mC<sub>d</sub> = moderate C<sub>d</sub>, <sup>bb</sup>mC<sub>d</sub> = high C<sub>d</sub>, <sup>c</sup>PLI = no polluted

**Table 9:** Geoaccumulation Index of the metals for the three sites (AMSP, AASP and ANSP)

Site code	Average metal Concentration (mgkg <sup>-1</sup> )			Geochemical Background of metal Concentration (mgkg <sup>-1</sup> )			Geo Accumulation Index (I <sub>geo</sub> )			Who standards for rating	
	Cu	Cr	Hg	Cu	Cr	Hg	Cu	Cr	Hg	I <sub>geo</sub>	Description
AMSP	8.87	6.4	3.03	22.5	67.0	0.02	1.93*	3.97*	6.66**	> 5	Extremely polluted
AASP	8.38	6.8	2.54	22.5	67.0	0.02	2.01*	3.90*	6.40**	4-5	Strongly to extremely/ strongly polluted
ANSP	9.22	7.1	4.02	22.5	67.0	0.02	1.87*	3.83*	7.06**	3-4 2-3	Strongly polluted Moderately to strongly polluted
										1-2 0-1 0-2 0.3	Moderately Unpolluted to moderately strongly polluted ≤ 0 Unpolluted

\*\*I<sub>geo</sub> = unpolluted to moderately polluted, \*I<sub>geo</sub> = Extremely polluted

The organic matter content of the study sites (AM, AA, and AN) was average 2.09 Cmol (+) kg<sup>-1</sup>. Stefanowicz *et al.* (2020), posited that high levels of heavy metals affect (reduce) the organic matter content of the soil. This is because they could slow the rate of mineralization of the soil. Thus, the low level of the soil organic matter recorded might be a result of the high levels of heavy metals in the soil. Aside from temperature, whose value changes significantly within the study sites, none of the measured physicochemical properties varies significantly.

#### *Ecological Risk Assessment of Metal Contamination within the Catchment Area Soils*

Geochemical indices such as contamination factor, degree of contamination index, Modified degree of contamination, Pollution load index and Geoaccumulation index have been computed to determine the extent of pollution as discussed below.

#### *Geoaccumulation Index (Igeo)*

The geoaccumulation results indicates that all the study sites were uncontaminated with Cu and Cr as their Igeo values were less than zero. However, the Igeo values for Hg high which can be classified as extremely polluted (Fig. 3). This can be attributed to the fact that Hg is mixed with gold-containing materials, forming a mercury-gold amalgam which is then heated, vaporizing the Hg to obtain the gold. This results in the leaching of the Hg into both soil and water within the enclave of artisanal gold mining.

#### *Contamination Factors (C<sub>f</sub>)*

The contamination factors (C<sub>f</sub>) of the soils of the three sites (AMSP, AASP, and ANSP) assessed ranged from low (C<sub>f</sub><1) to very high (C<sub>f</sub>> 6) (Table 5). The mean C<sub>f</sub> of the three soils evaluated (AMSP, AASP, and ANSP) were (0.25, 0.23, and 0.26) for Cu, (0.06, 0.07, and 0.07) for Cr, and (10.10, 8.46, and 13.39) for Hg respectively.

The contamination factor values recorded on the three sites (AMSP, AASP, and ANSP) for Cu and Cr were less than one (C<sub>f</sub>< 1), indicating low levels of Cu and Cr metal contamination at the three sites. Though the C<sub>f</sub> of Cu and Cr were low, the levels recorded at the sites were all above the background concentrations. This is an indication that certain anthropogenic activities have contributed to the rise in Cu and Cr levels at the study sites. The contamination factor for Hg was more than six (C<sub>f</sub>> 6) at all the study sites, indicating very high levels of Hg metal contamination at the three sites. The high contamination factor of Hg can be attributed to the frequent use of Hg in amalgamating the gold which is discharged into the water bodies and the open environment and eventually leached into the soil and to groundwater. The intriguing situation is that most of

the farmers use contaminated water for irrigation. It is, therefore, possible for the Hg to be absorbed by the crops and later ingested by both man and animals which would adversely affect their health.

#### *Degree of Contamination Factors*

The degree of contamination (C<sub>d</sub>) of the three sites' soils (AMSP, AASP, and ANSP) was 10.41, 8.76, and 13.71 for Cu, Cr, and Hg respectively (Table 6). The degree of contamination (C<sub>d</sub>) at site AN was considerably high while at sites AM and AA was detected to be moderately high.

The degree of heavy metal contamination at the three sites is in the order of AN>AM>AA, thus the rate of contamination of the heavy metals is higher at AN, followed by AM and then AA. These results could be attributed to the extent of small-scale mining and other anthropogenic activities at the affected sites. The deterioration of the soil characteristics and water bodies could be increasing rapidly due to the degree of contamination.

#### *Modified Degree of Contamination Factors*

The modified degree of contamination (mC<sub>d</sub>) of Cu, Cr and Hg assessed were 3.47, 2.92, and 4.57 for the three illegal mining sites; AMSP, AASP, and ANSP respectively. The modified degree of contamination (mC<sub>d</sub>) for the three sites was in the order of AN>AM>AA. The mC<sub>d</sub> were high for the site at AN and moderate for the AM and AA respectively (Table 7).

The effective contamination index is high at site AN than at the other three sites, that is, the intensity of contamination as a result of small-scale mining at AN is assuming alarming proportions. Methylmercury is the type of Hg commonly found at mining sites. This state of Hg is easily dissolved in water and soils and consequently enters the food chain, and affects the health of both man and animals.

#### *Pollution Index*

Mercury exhibited Igeo values of 7.06, 6.66, and 6.40 at the AN, AM, and AA respectively (Table 9). These values indicate the extreme pollution of Hg at the three mining sites. The Igeo values of Cu and Cr are all below zero at the three mining sites. Again, the Pollution Load Index (PLI) for Cu, Cr, and Hg are all below one (Table 8). From the foregoing, the contamination factor, degree of contamination, and modified degree of contamination give credence to the extent of pollution of the heavy metals in all three mining sites. Among the three heavy metals, Hg exhibited moderately high contamination in all three mining sites. The geo-accumulation index indicates extreme pollution of Hg at the three mining sites especially site AN. The main



reason for the extreme pollution of Hg at the three mining sites is the excessive use of Hg in concentrating the mined gold. The extreme Hg pollution demands immediate remediation measures to be implemented to redeem the polluted soils and water bodies.

## Conclusion

This research aimed to determine the level of pollution of Cr, Cu, As, and Hg within the catchments of Akyem Anyinam, Akyem Mampong, and Akyem Ankaase in the Atiwa District, Ghana, as a result of small scale and illegal mining operations. The study was anchored on the following two objectives; to characterize and map out the prevalence of heavy metal contamination in the study area, and to evaluate soil toxicity and environmental risk of heavy metals within the catchment of small-scale mining sites.

The Pollution Load Index (PLI) for Cu, Cr, and Hg were 0.24, 0.07, and 10.7, indicating extreme pollution of Hg at the sites. The geo accumulation indices (Igeo) of Cu, Cr, and Hg were 1.92, 3.8, and 6.5 respectively, indicating moderately to extremely polluted soil. An increase in the pollution levels was also observed as a result of the continuous discharge of Hg at the sites. High levels of Heavy metal contamination were observed at Akyem Anyinam (AN). The possible reason for high metal contamination at Akyem Anyinam would be the high number of illegal mining activities and the incessant use of Hg in amalgamating the gold concentrates. The study, therefore, enhances our knowledge about the levels and sources of the three heavy metals in the soils of illegal mining sites and allows water and soil managers to find and implement remedial measures for restricting the release of heavy metals into the environment.

## Availability of Data and Materials

The dataset generated during and/or analyzed during the current study is available from the corresponding author upon reasonable request.

## Acknowledgment

We acknowledge the immense contribution by the Regional Water and Environmental Sanitation Centre, Kumasi (RWESCK) for making available to us all necessary resources and permit rendered to us to carry out this essential research.

## Author's Contributions

**Samuel Wiafe:** Conceptualized the research topic, formulated the objectives and methodology of the research and participated in the data collection and analysis.

**Sarah Fanny Hackman Duncan:** She participated in the writing of the manuscript (Original Draft Preparation) as well as reviewed and edited the manuscript.

**Boakye Ebenezer:** He carried out laboratory work and assisted in the writing of the manuscript

**Samuel Yeboah Baako:** He carried out both the laboratory and Field Investigation as well as the Data Curation of the research work.

## Competing Interests/Conflict of Interest

The authors declare that they have no conflict of interest either directly or indirectly relating to the work submitted within the last three years of beginning the work and outside three years after the work.

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