

## Chapter

# Effect of Mining on Heavy Metals Toxicity and Health Risk in Selected Rivers of Ghana

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## Abstract

Heavy metal contamination of selected rivers in the mining areas of Ghana was studied. In the study, 44 composite water samples were collected, digested, and analyzed for selected metals using ICP-MS. The average concentrations (mg/L) of heavy metals from the pristine sites ranged from 0.003 (As) to 0.929 (Fe), and the mining sites ranged from 0.002 (Pb) to 20.355 (Fe). Generally, the metals were within the WHO and USEPA acceptable limits except Al, Fe, As, Cr, and Mn. Hazard quotients for ingestion (HQing) and dermal contact from pristine and mining sites ranged from 0.838 (Cr) to  $3.00 \times 10^{-4}$  (Cu) and from 0.181 (As) to  $2.40 \times 10^{-6}$  (Cu), respectively. The carcinogenic risks (CRs) for ingestion were within standard limit ( $10^{-6}$  to  $10^{-4}$ ). However, Arsenic showed high CRing above the acceptable limit ( $1.83 \times 10^{-2}$ ). The CRs for dermal contact range from  $4.22 \times 10^{-8}$  to  $1.44 \times 10^{-9}$  (Cr) and from  $7.34 \times 10^{-8}$  to  $5.65 \times 10^{-9}$  (Pb). Carcinogenic risk values for As in the mining areas raise carcinogenic concerns for the residents in the studied areas. PROMETHEE and GAIA indicate major contribution of the metals from the mining. Multivariate PCA and cluster analysis suggest anthropogenic activities as the major source of the metal toxicity of the mine rivers.

**Keywords:** surface water, pristine, mining, heavy metal, contamination, toxicity, health risk

## 1. Introduction

The issues of heavy metals contamination of local, regional, and global environment emanate directly from natural sources and indirectly from anthropogenic activities such as mining, rapid industrialization, urbanization, improper waste management, and other local and regional man-made activities [1].

Substantial quantities of heavy metals are released from different anthropogenic sources into the atmosphere from where they are deposited in soils and aquatic ecosystem through dry and wet deposition processes.

Anthropogenic inputs of heavy metals are currently getting higher and in some areas exceeding natural inputs where human activities are predominant [2, 3]. The metals accumulation and distribution in soil, water, and environment are increasing at a faster rate causing deposition and sedimentation in water reservoirs and affecting

aquatic organisms [4, 5]. High levels of Cd, Cu, Pb, and Fe can act as ecological toxins in aquatic and terrestrial ecosystems [6].

Heavy metals are potentially harmful to humans and various ecological receptors due to their toxicity, persistence, bio-accumulative characteristics, and their nonbiodegradable nature. Toxic metals can cause different health problems depending on the type of the metal concerned, its concentration, and oxidation state. They are among the most toxic and persistent pollutants in freshwater systems [4, 5]. Certain heavy metals and metalloids are toxic and can cause adverse effects and severe problems such as oxidative stress by formation of free radicals even at low concentrations [7, 8].

Heavy metals contamination can result in several diseases and deformities; for instance, in the 1950s, an advanced country such as Japan was devastated by heavy metal poisoning known as the Fetal Minamata Disease, which resulted from contamination of fishes by organic mercury. The situation led to severe nerve damage of newborn babies from pregnant women [9].

In Iraq, babies walked at later age due to consumption of organic mercury contaminated grains by pregnant mothers. Similar incidence occurred in Faroe Islands where school children scored lower grades on brain function test due to consumption of mercury-contaminated whale meat by pregnant women [10].

A third world country such as Bangladesh in recent years has become vulnerable to heavy metal contamination of groundwater [11] and heavy metals contamination of drinking water sources by Cd, Pb, Cu, and Zn in Bolivia, Hong Kong, and Berlin [12, 13].

Efforts were made in both research and monitoring to establish sources, transport, and fate of these metals in the aquatic environment. However, studies have shown that contamination artifacts have seriously compromised the reliability of many past and current analyses and under certain circumstances, metal concentrations have been measured 100 times the true concentrations [14]. These errors are of great concern, since contaminant-free data are necessary to detect trends and to identify factors that control the transport and fate of toxic metals in water bodies.

Many mineral resources including gold represent significant material basis for socioeconomic development, justifying the exploitation and utilization of mineral resources essential to national development. Nonetheless, despite the importance of mineral resources, mineral extraction with its associated release of heavy metals has caused serious environmental damage in many developing and developed countries [15, 16].

As gold mineral is being mined actively in many developing countries, there are fears that the mining activity may be causing serious metal pollution to water resources. Disused and closed mines with huge mine waste materials including tailings were left from the extraction processes without adequate treatment, and as a result, soils, plants, water bodies, and sediments in the vicinity of mines were contaminated by potentially toxic metals from tailings through wind and Acid-Mine-Drainage [17, 18]. Reports from earlier studies have shown that metal levels of surface and groundwater exceeded World Health Organization (WHO)'s acceptable limits for drinking water around Tarkwa mining area [19]. Huge deposits of mine wastes as well as ore stockpiles and waste rocks are usually seen in large piles around both large- and small-scale mining areas. These deposits are gradually washed through weathering and leaching into far and near water bodies, thereby releasing toxic substances into water bodies [20].

Metals associated with gold mines, including Cd, Cu, Pb, and Zn, may be dispersed downstream due to the weathering process of tailings. Thus, the extent and degree of heavy metal contamination around mines may vary depending on geochemical characteristics and mineralization of tailings [21].

Mine tailings may result in the influx of metals and toxic chemicals into the environment. Waste rocks are known to contain arsenic (As), mercury (Hg), cadmium (Cd), lead (Pb), and other toxic metals, which are extensively dispersed into the environment [22]. According to the recent World Health Organization (WHO) report on arsenic, it was recognized that at least 140 million people in 50 countries have been drinking water containing arsenic at levels above the WHO provisional guideline value of 10 µg/L [22, 23]. In the evaluation conclusions, arsenic and other heavy metals exposure through drinking water is causally related to cancer in the lungs, kidney, bladder, and skin. There is also an increased risk of skin cancer and other skin lesions, such as hyperkeratosis and pigmentation changes. Ingestion of inorganic arsenic may induce peripheral vascular disease, which leads to black foot disease [24, 25].

It is therefore imperative to continually assess and monitor the concentration of heavy metals in water bodies in the environment due to anthropogenic activities, including gold mining, for evaluation of human exposure and for sustainable environment [26, 27].

This study investigated the extent of contamination by heavy metals of selected water bodies in the vicinity of gold mines and further compared the metal levels with those from the pristine sites to assess the possibility of mining activities causing toxicity (contamination) of the water bodies.

## **2. Materials and method**

### **2.1 The study area**

Samples were collected in eight regions of Ghana with the land cover ranging from 138 to 2950 km<sup>2</sup>. The rivers that were sampled in the mining areas are Nyam river, Subri river, Birim river, and river Bonsa. The nature and the location of the rivers demonstrate the presence of metal contamination due to mining activities. The rivers from the pristine areas are Oda river, Bosomkese forest river, Ankasa river, Atewa forest river, Kalakpa river, Kakum river, and Mole river. The pristine rivers were used as background checks in order to assess the extent of metal contamination.

### **2.2 Sampling and sample collection**

Water samples were collected from four selected rivers around the gold mining areas and seven rivers from the pristine areas. Sample collection was undertaken from January 2015 to January 2016. A total of 44 composite samples of water were collected from both mining and pristine areas. The rivers were sampled 100 m apart at four different points. 1.5 L plastic bottles that had been prewashed with detergent and 1:1 concentrated nitric acid/distilled water solution and eventually rinsed with only distilled water were used. The samples for metal analysis were acidified to a pH of 2 at site using concentrated HNO<sub>3</sub> before they were transported to the Chemistry Department laboratory of University of Cape Coast. The samples were kept in refrigerator at a temperature of 4°C for further analysis [28].

### **2.3 Digestion and analysis of water samples**

Chemicals and reagents for analysis were acquired from the Central Analytical Facility of Queensland University of Science and Technology. 70% Nitric acid ( $\text{HNO}_3$ ) was further distilled twice in Analab Sub-Boiling Distillation system. Water for the analysis was acquired from MilliQ water purification system (Millipore, Billerica, MA, USA). Water samples were analyzed in triplicates to check the efficiency of the analytical instrument. Centrifuge tubes were washed by rinsing three times in ultrapure water. They were then soaked in 3% analytical grade HCl and left on a hot plate for two days. The operating conditions for the instrument were the following parameters: Cell Gas flow rates: 5 ml/min; Carrier Gas Flow: 1.05 l/min; KED Voltage: 5 V; ICP RF Power: 1550 W; Octopole bias (V):  $-18$ , Octopole RF (V); 190: Spray Chamber t (C); 2: Sample depth (mm); 8.

The samples were digested by acidifying with 1 mL  $\text{NH}_3$ . They were later centrifuged at 3500 rpm for 15 min. The samples were then filtered through 0.45  $\mu\text{m}$  pore size cellulose acetate filters.

They were then analyzed with Agilent 8800 Triple Quadrupole Inductively Coupled Plasma Emission Spectrometer (ICP-QQQMS) in the Central Analytical Research Facility (CARF) laboratory of Queensland University of Technology, Australia. The same digestion procedure was applied to the Quality Control (QC) samples and the blank. The analytes were acquired using He mode, and those elements that do not suffer from polyatomic interferences were acquired in no gas mode.

Some physicochemical parameters such as pH, conductivity, and turbidity were also determined. The pH was determined alongside the temperature using a pre-calibrated JENWAY 3310 and JENWAY 3510 pH meter. Conductivity was measured using a pre-calibrated PHYWE 13701.93 and WAGTECH 4510 conductivity meter. The turbidity was measured with a Hachturbidimeter.

### **2.4 Recovery and reproducibility studies**

Calibration solution was prepared by using Choice Analytical ICV-1 Solution and a Standard Agilent Technologies Multi Element Reference Standard 2A. The Agilent Standard was analyzed as unknown to monitor the accuracy of analytic process. The percent recovery was computed to range from 99.5% to 103.8% with the relative standard deviation ranging between 0.38 and 2.23. The recovery results indicate that the error associated with the determination of concentrations of the metals was negligible.

### **2.5 Data and statistical analysis**

IBM SPSS Statistics version 22 and the Excel Analysis ToolPak were used to analyze the data from the study. Basic statistics such as mean and standard deviation were computed along the multivariate statistics. Relationships associated with the variables were tested using correlation analysis with statistical significance at  $p < 0.05$ . Hierarchical Cluster analysis (HCA) was also employed to provide a visual summary of the clustering process unsupervised pattern recognition technique. Factor analysis (FA) and principal component analysis (PCA) were computed to identify significant principal components in the data. The PCA was carried out by the Promax normalized rotation method for the results [29, 30]. PROMETHEE, a multicriteria outranking method, was employed to rank objects on the basis of range of variables and GAIA to add descriptive complement to the PROMETHEE rankings.

## 2.6 Human health risk assessment

The risk estimation was based on the United States Environmental Protection Agency (USEPA) risk assessment method for ingestion and dermal contact [29, 31].

The average daily dose (ADD) for the heavy metals (Eq. 1) was calculated using the following modified equations from USEPA protocol 1989 and 2004.

$$ADD_{ing} = \frac{C_x \times I_r \times E_f \times E_d}{Bwt \times A_t \times 365} \quad (1)$$

where  $C_x$  is the concentration of the metals in the drinking water (mg/L),  $I_r$  is the ingestion rate per unit time (L/day),  $E_d$  is the exposure duration (years),  $E_f$  is the exposure frequency (days/year),  $Bwt$  is the body weight of receptor (kg), and  $A_t$  is the average lifetime (years), which is equal to the life expectancy of a resident Ghanaian. In addition,  $ADD_{ing}$  is the quantity of heavy metals ingested per kilogram of body weight.

In this study, surface water ingestion is assumed to be the main pathway for risk assessment because the rivers are potential sources of drinking water. However, dermal contact is another important pathway, because residents sometimes swim in these rivers and thus may come into contact with the toxic metals through body contact.

Average daily dose for dermal contact was calculated using the formula in Eq. 2 below:

$$ADD_{derm} = \frac{C_x \times S_a \times P_c \times E_t \times E_f \times E_d \times C_f}{Bwt \times A_t \times 365} \quad (2)$$

where  $S_a$  is the total skin surface area ( $\text{cm}^2$ ),  $C_f$  is the volumetric conversion factor for water (1 L/1000  $\text{cm}^3$ ),  $P_c$  is the chemical-specific dermal permeability constant ( $\text{cm/h}$ ).

The hazard for the metals was estimated as the ratio of the calculated dose to the reference dose (RfD) (mg/L/day) using Eq. 3 below:

$$HQ = \frac{ADD}{RfD} \quad (3)$$

The chronic daily intake (CDI) of the metal was calculated using the Eq. 4 below:

$$CDI = C \frac{DI_{ing}}{Bwt} \quad (4)$$

where  $C$  is the concentration of heavy metal in water,  $DI$  is the average daily intake rate (2 L).

The carcinogenic risks (CRs) of the metals were calculated using Eq. 5 and 6 below for ingestion and dermal contact, respectively. The carcinogenic risk acceptable by USEPA ranges from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$ .

$$CR_{ing} = \frac{ADD_{ing}}{SF_{ing}} \quad (5)$$

$$CR_{derm} = \frac{ADD_{derm}}{SF_{ing}} \quad (6)$$

where  $SF$  is the slope factor (mg/kg)/day. For As, Cd, and Cr, the slope factor values are 1.5,  $6.1 \times 10^2$ , and  $5.0 \times 10^2$  (mg/kg)/day, respectively.

### 3. Results and discussion

#### 3.1 Analysis of physical and chemical parameters

Even though people may not be affected directly by some of these parameters, elevated levels can cause unfavorable conditions and discomfort. For instance, drinking water with elevated pH will taste bitter [32]. Parameters such as electrical conductivity, pH, turbidity, and temperature as shown in (Table 1) were measured in this study. Water samples from the mining sites were acidic with pH values of some of the sites recording as low as 3.51. The pH of the pristine samples was, however, within the normal WHO’s range of 6.5–8.5. The low pH values for mine samples might be responsible for the high metal levels measured.

The electrical conductivity values measured for the water samples were below the WHO normal range (400–600  $\mu\text{S}/\text{cm}$ ) [33]. The temperature values for the samples were below the recommended WHO’s value of 29°C. Turbidity values for the mine samples were higher than those measured for the pristine samples due to activity of mining in those rivers. Other measured parameters such as salinity and total dissolved solids were relatively low. Low turbidity of the pristine samples indicates the absence of disease-causing organisms such as bacteria, viruses, and parasites that cause symptoms such as nausea, cramps, diarrhea, and associated headaches [34].

#### 3.2 Concentration of heavy metals in water

The mean concentrations of the heavy metals obtained from ICP/MS instruments were presented in the attached Table 2. The mean concentrations were compared with the threshold/permmissible values as shown in Table 3. The concentrations of Fe and Al especially from the mining sites were higher than the permmissible values [35].

Sites	pH Range	Cond. ( $\mu\text{S}/\text{cm}$ ) Range	Salinity Range	Turbidity Range	Temp. Range	TDS Range
AOBW	3.45–3.56	64.4–65.6	34.78–35.42	9–22	28.1–28.5	38.6–39.1
BAMW	5.34–5.86	2.98–3.19	1.64–1.72	3–21	28.6–28.9	6.06–6.35
EAMW	5.32–5.44	11.33–11.46	6.12–6.19	12–27	28.0–28.7	5.67–5.90
WTBW	5.10–5.41	9.54–10.05	5.15–5.41	5–15	28.3–28.6	2.70–2.71
EAW	6.20–6.09	4.46–4.89	2.41–2.64	1–6	28.0–28.2	1.96–1.99
WAW	6.14–6.41	0.52–0.54	0.28–0.29	0–4	28.6–28.9	0.31–0.32
BBW	6.38–6.48	1.65–1.66	0.89–0.90	3–9	27.4–27.9	0.98–0.99
AOD	6.24–6.33	2.11–2.19	1.14–1.18	5–7	28.2–28.4	1.64–1.66
VKPW	6.34–6.41	0.53–0.59	0.29–0.32	1–6	28.5–28.7	0.54–0.58
NM	6.06–6.99	0.66–0.73	0.36–0.39	2–9	28.0–28.1	0.40–0.44
CK	6.55–6.77	0.41–0.47	0.22–0.25	0–1	28.0–28.3	0.70–0.76

**Table 1.** Physical and chemical parameters for the water samples from the sites.

Sites	ICP/MS										
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Pb
	<b>Mines</b>										
<b>AOBW</b>	2.453 ± 0.83	0.080 ± 0.00	0.006 ± 0.00	1.827 ± 1.48	3.862 ± 1.55	0.008 ± 0.01	0.011 ± 0.00	0.016 ± 0.01	0.078 ± 0.02	0.226 ± 0.03	0.002 ± 0.00
<b>BAMW</b>	0.684 ± 0.24	0.006 ± 0.01	0.003 ± 0.01	2.667 ± 1.29	6.758 ± 1.76	0.006 ± 0.01	0.005 ± 0.00	0.004 ± 0.01	0.043 ± 0.02	0.010 ± 0.01	0.002 ± 0.00
<b>EAMW</b>	13.847 ± 4.57	0.077 ± 0.02	0.088 ± 0.03	1.213 ± 0.03	20.355 ± 5.60	0.044 ± 0.00	0.024 ± 0.00	0.092 ± 0.02	0.111 ± 0.01	0.007 ± .00	0.024 ± 0.00
<b>WTBW</b>	1.922 ± 0.65	0.003 ± 0.00	0.014 ± 0.01	0.230 ± 0.00	2.371 ± 1.16	0.003 ± 0.00	0.005 ± 0.00	0.245 ± 0.18	0.053 ± 0.03	0.006 ± 0.00	0.026 ± 0.05
	<b>Pristine</b>										
<b>EAW</b>	0.067 ± 0.01	—	—	0.064 ± 0.03	0.463 ± 0.02	—	—	—	0.044 ± 0.02	0.007 ± 0.00	—
<b>WAW</b>	0.111 ± 0.00	—	—	0.019 ± 0.02	0.715 ± 0.00	—	—	0.008 ± 0.02	0.037 ± 0.01	0.005 ± 0.00	—
<b>BBW</b>	0.142 ± 0.02	—	—	0.042 ± 0.01	0.929 ± 0.06	—	—	0.089 ± 0.03	0.044 ± 0.01	0.003 ± 0.00	0.010 ± 0.02
<b>AODW</b>	0.038 ± 0.03	0.010 ± 0.00	—	0.016 ± 0.02	0.157 ± 0.07	—	0.004 ± 0.00	0.006 ± 0.00	0.029 ± 0.01	—	—
<b>VKW</b>	0.030 ± 0.02	—	—	—	0.594 ± 0.18	—	—	0.004 ± 0.00	0.006 ± 0.01	—	—
<b>NMW</b>	0.047 ± 0.02	—	—	—	0.371 ± 0.28	—	—	—	0.021 ± 0.02	—	—
<b>CKW</b>	0.022 ± 0.01	—	—	0.010 ± 0.01	0.074 ± 0.01	—	—	—	0.006 ± 0.01	—	—

The dash (—) means below detection limit.

**Table 2.**  
 Mean concentrations (mg/L) of heavy metals in the rivers from pristine and mining areas (Hadzi et al., 2018).

Water Quality Guideline	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Co
Drinking Water Quality									
EC(1998)	0.01	0.05	2	0.2	0.05	0.02	0.01	0.1	—
WHO (2004)	0.01	0.05	2	—	0.4	0.07	0.01	—	—
USEPA (2009)	0.01	0.1	1.3	0.3	0.05	—	0.015	5	0.11
USEPA (2006)	0.34	—	0.013	1	—	0.47	—	0.12	—

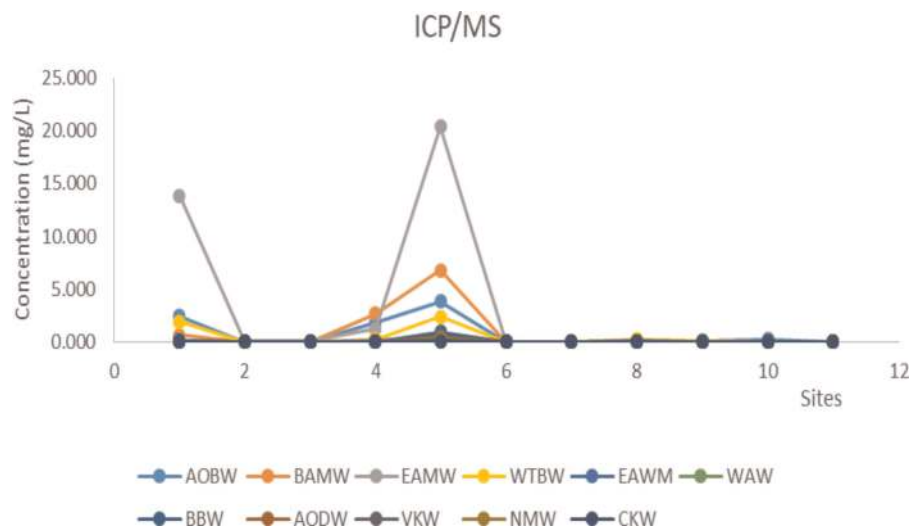
**Table 3.** Maximum permitted heavy metal concentrations (mg/L) for drinking water quality and protection of freshwater aquatic life.

Metal concentrations from this study were safe for aquatic life. Hg and Cd were below detection limit. In general, higher concentrations of heavy metals were measured in mine sample with maximum concentrations of 13.847, 20.355, 2.667, 0.088, 0.245, 0.111, 0.226, and 0.026 mg/l for Al, Fe, Mn, Cr, Cu, Zn, As, and Pb, respectively. The concentrations of most metals in the pristine samples were either below their permissible limits or far below levels obtained from the mining sites, which suggests less anthropogenic activity in the pristine sites. Distribution of Al, Fe, and Zn is the same at the pristine and the mining sites. In assessing the heavy metal contaminations of the various sites, the levels were compared with previous studies from the same sampling sites and other natural rivers, and it was realized that the metal concentrations in this study are lower [36, 37]. A study conducted by Hadzi et al., in 2015 on the same rivers indicated a low metal input. However, similar low concentrations of Cd, Hg, As, Mn, Cu, and Zn in river Samre in the Wassa Amenfi West District in the Western region and Nangodi and Tinga drinking water sources in the Northern region of Ghana were reported. In a separate study in 2013, Cobbina et al., found relatively low concentrations of heavy metals in surface water and boreholes at Tinga in the Bole-Bamboi District of Ghana. According to Bowen [38], freshwater contains 0.1, 3.0, 3.0, and 15 mg/l of Cd, Cu, Pb, and Zn, respectively. However, the concentrations of metals reported at the pristine sites of this study are far less than those reported in freshwater bodies. Aladesanmi et al., in a similar study in Nigeria, 2014 [39], reported concentrations of Cd and As below detection limits and levels of Pb, Cr, Co, and Cu ranging from 0.003 to 0.009 mg/L.

### 3.3 Statistical analysis of data

Possible correlations and variability checks were conducted on the metal concentrations. The cluster analysis, as shown in **Figure 1 (attached)**, indicates two main groups of metals. Cluster 1 comprised V, Co, Cr, Ni, Pb, Cu, Zn, and As with some association with Mn. Cluster 2 comprised Fe and Al with some association with Mn. The measurement of metals such as Pb, Co, Zn, Cu, As, and Cr indicates anthropogenic sources such as mining around the study sites. The PCA analysis identified two components that were significant with eigenvalues greater than 1 and were extracted accounting for total percent variance of 88.6% as shown in **Table 4**. Component 1 accounted for 74.1% of the total variance, and Component 2, 14.5% of the total variance. This association of the metals into components as shown in **Figure 2** was confirmed by the correlation results in which As and Mn correlated





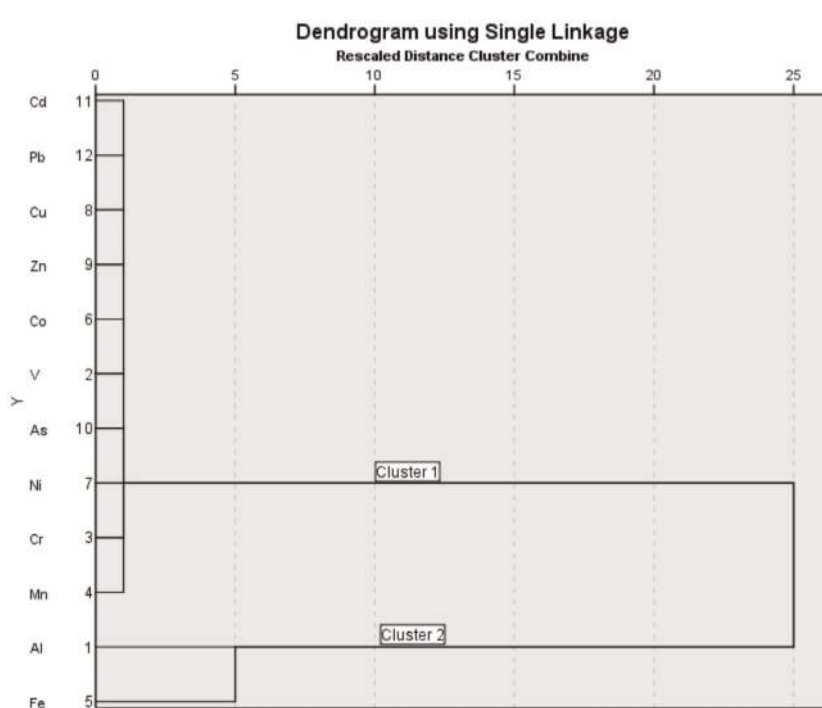
**Figure 1.**  
 A plot of concentration against sampling sites from ICP/MS results source: [12].

	PCA1	PCA2
Co	0.99	
Cu	0.98	
V	0.98	
Al	0.97	
Pb	0.97	
Cr	0.96	
Fe	0.95	
Zn	0.85	
Ni	0.77	
As		0.87
Mn		0.77
Eigenvalues	8.151	1.59
% total Variance	74.10	14.50
% cumulative variance	74.10	88.60

**Table 4.**  
 Factor loading for select heavy metals in water from mining and pristine sites.

weakly with all metals except Mn and Fe (0.76) as shown in **Table 5**. Manganese and As co-precipitate when Mn hydroxide and oxides in clay minerals act as nucleation sites for adsorption of As [40]. There was strong correlation between Pb and Cu, Co, V and Al. Lead was not detected in the pristine samples; therefore, the metal occurrence in the mining samples may be due to anthropogenic activities of mining.

Component 1, which explains majority of the total variance (74.1%), had strong loadings on Fe, Al, Pb, V, Cu, Zn, Co, Ni, and Cr. The presence of metals such as Pb, Cu, Co, Ni, Zn, and Cr suggests that mining might have contributed to metal



**Figure 2.** Dendrogram showing clustering of metals in rivers from pristine and mining sites.

Correlations											
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Pb
Al	1										
V	.921	1									
Cr	-.053	-.074	1								
Mn	.244	.429	-.063	1							
Fe	.740	.832	-.058	.755	1						
Co	.943	.953	-.063	.490	.847	1					
Ni	.498	.529	-.110	.437	.543	.558	1				
Cu	.965	.936	-.055	.259	.709	.957	.510	1			
Zn	.553	.418	-.041	.010	.331	.415	.272	.441	1		
As	-.042	-.039	-.050	.348	.052	.123	.156	.073	-.088	1	
Pb	.967	.896	-.058	.159	.658	.929	.446	.984	.440	.040	1

**Table 5.** Correlation matrix of select heavy metals in water samples from pristine and mining sites,  $n = 44$ .

contamination of the rivers [41]. Component 2 had strong loading on As and moderate loading on Mn suggesting that these two metals may be coming from different pollution sources. The ANOVA two-way computed indicates significant difference in metal concentrations since the probability associated with the p-value (0.005) is less than 0.05 ( $F = 2.89$ ,  $F_{crit} = 1.99$ ). The p value (0.015) for the site study indicates significant

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Rows	112.047	10	11.2047	2.372162	0.015297	1.937567
Columns	122.8127	9	13.64586	2.888984	2.888984	1.985595
Error	425.107	90	4.723411			

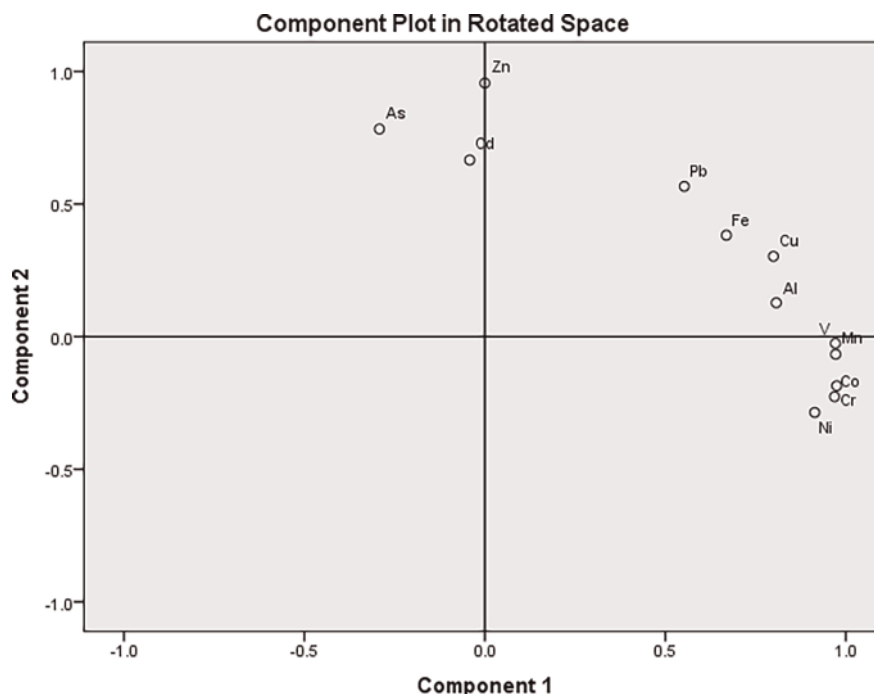
**Table 6.**  
 Two-way ANOVA showing differences between sites and metals.

differences in site concentrations ( $F = 2.37$ ,  $F_{crit} = 1.94$ ) as shown in **Table 6**. These differences were confirmed by PCA, cluster analysis, and the correlation results. The study identifies anthropogenic activities as a major source of metal contamination of the rivers especially from the mining areas.

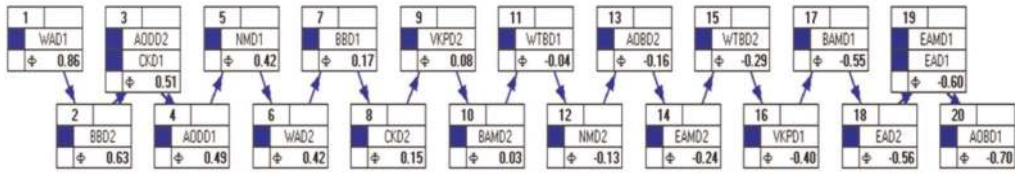
### 3.4 PROMETHEE and GAIA analysis of the heavy metals

Contamination of the rivers by heavy metals was ranked and recognized from site to site by simultaneously and systematically subjecting the concentrations to PROMETHEE and GAIA analysis. PROMETHEE II complete ranking of the sites (**Figure 3**) from least polluted to the highest polluted is shown as follows: CK > AOD > NM > EA > VKP > WA > BB > WTB > AOB > BAM > EAM.

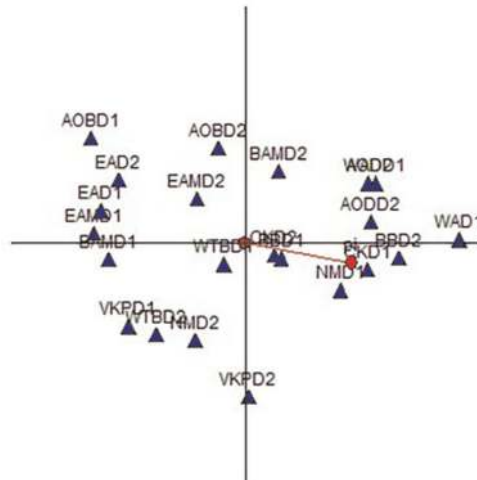
The ranking shows that the pristine sites are less contaminated by the metals compared with the mining sites. The site with the least metal contamination is Kakum River (pristine site), and the highest contaminated river is the Birim River (mining site). GAIA, which is a pattern recognition tool, indicates that approximately 81.90% of the variance is explained by the first two principal components (PCs). The GAIA plot



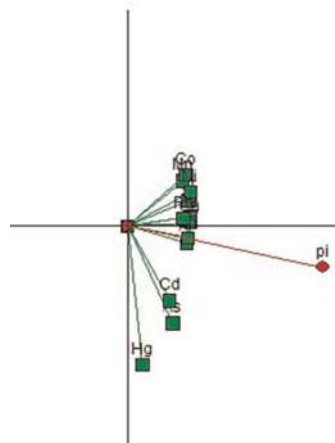
**Figure 3.**  
 Component plot showing metal loadings on components from pristine and mining sites.



**Figure 4.** PROMETHEE 2 outflow ranking of sampling sites based on heavy metals concentration in water samples from mine sites.



**Figure 5.** GAIA plot of site distribution of metals in water samples from pristine and mine sites.



**Figure 6.** GAIA plot showing heavy metals deviation from the decision axis (pristine and mining sites).

(**Figure 4**) identified similar groupings and trend as obtained from the PCA analysis. GAIA plot of the sampling sites (**Figures 5 and 6**) showed the decision axis (Pi) pointing toward the pristine sites. The PROMETHEE and GAIA analysis clearly indicates that the pristine sites are the least contaminated, while the mining sites are the most contaminated with the metals. The results also showed that anthropogenic activities such as mining may be impacting heavily on heavy metal contamination of the rivers.

Oral intake	Cr	Mn	Fe	Cu	Zn	As	Pb
ADD Range	2.5E-03 - 8.57E-05	0.076- 1.14E-04	0.582- 2.11E-03	0.007- 1.14E-05	0.003- 1.71E-04	0.006- 2.86E-05	0.001- 5.71E-05
CDI Range	0.0025- 8.571E-05	0.0762- 1.14E-04	0.5816- 2.114E-03	7.00E-03 - 1.14E-05	0.0032- 1.714E-04	6.50E-03 - 2.86E-05	7.00E-04 - 5.71E-05
CR Range	5.03E-06 - 1.71E-07					4.31E-03 - 1.91E-05	8.74E-05 - 6.72E-06
HQ Range	0.838- 0.0285	3.175- 0.005	0.831- 0.003	0.175- 0.0003	0.011- 0.0005	21.52- 0.095	0.743- 0.057
<b>Dermal Contact</b>							
ADD Range	2.12E-05 - 7.20E-07	6.40E-04 - 9.60E-08	4.89E-03 - 1.77E-05	5.88E-05 - 9.60E-08	1.44E-05 - 8.64E-7	5.42E-05 - 2.40E-07	6.24E-07 - 4.80E-08
CR Range	4.22E-08 - 1.44E-09					3.62E-05 - 1.60E-07	7.34E-08 - 5.65E-09
HQ Range	7.04E-03 - 2.40E-04	2.67E-02 - 4.00E-05	6.98E-03 - 2.54E-05	1.47E-03 - 2.40E-06	4.79E-05 - 2.90E-06	0.18- 8.00E-04	6.24E-04 - 4.80E-05
<b>References</b>							
RfDo, USEPA, 2004, 2013	0.003	0.024	0.7	0.04	0.3	0.0003	0.001
SF (DWSHA), 2012	500					1.5	8.5

**Table 7.**  
*Carcinogenic and non-carcinogenic assessment.*

### 3.5 Carcinogenic risk assessment

Using the Central Tendency Exposure scenario (CTE) for child and adults, carcinogenic risks associated with ingestion and dermal contact with heavy metals (As, Cr, Ni, and Pb) were determined. For ingestion of water, the highest cancer risks for child and adult were measured from river EAM, a mining site for Cr as  $3.45 \times 10^{-1}$  and  $3.70 \times 10^{-1}$ , respectively. The highest cancer risks were measured for child and adult residents from river WA for Cr as  $2.19 \times 10^{-2}$  and  $2.35 \times 10^{-2}$ , respectively. Chromium posed the highest cancer risks in river EAM and WA for adult and child residents (**Table 7**). Chromium concentration from all the sites posed serious carcinogenic risk to both adult and child residents ranging from  $9.39 \times 10^{-2}$  to  $1.35 \times 10^{-1}$  and  $8.77 \times 10^{-2}$  to  $1.26 \times 10^{-1}$ , respectively. The carcinogenic risks for Ni, As, and Pb are within the USEPA risk limit ( $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$ ) [30, 31] except for As ( $3.35 \times 10^{-3}$  and  $3.12 \times 10^{-3}$ ) at site AOB and Pb ( $2.10 \times 10^{-3}$  and  $1.96 \times 10^{-3}$ ) at site EAM for resident adult and child, respectively. This implies that for As and Pb, there is a likelihood that up to 2–3 adults, out of 1000 and 1–3 children out of 1000 respectively if equally exposed continuously for 70 years would contract cancer. The carcinogenic risk via dermal contact (**Table 7**) or As, Ni, and Pb in the pristine and mining sites for adult and child is almost within the USEPA risk assessment guideline limit. However, the carcinogenic risks for Cr from all rivers in the mining sites were higher, ranging from  $7.37 \times 10^{-3}$  to  $1.31 \times 10^{-2}$  and  $3.90 \times 10^{-3}$  to  $1.07 \times 10^{-2}$  for child and adult residents,

respectively. The risk values in this study are comparable with values obtained by other researchers [19, 32, 42]. The high carcinogenic risk values for As and Cr raise carcinogenic concerns for the local residents in the catchment areas. The method of risk estimation employed in this study provides ways to screen those pollutants that are of public health concern in order to prioritize research and policy interventions.

#### **4. Conclusion**

Rivers from pristine sites are less contaminated of heavy metals and are therefore safe for consumption. However, continual anthropogenic deposition of metals in the pristine rivers could accumulate with time and rise beyond acceptable limits resulting in human health risk. It was observed that the average concentrations of some of the toxic metals were low; however, direct consumption of water from these rivers could be harmful to residents since the concentrations of metals from the mining sites were far above the USEPA and WHO drinking water guideline limits. Though alternative sources of metal deposition could be accounting for high heavy metals presence in some of the rivers, anthropogenic activities, possibly mining, are suspected to be the major contributor. The first four most contaminated sites were all from the mining sites linking metal availability to mining activities.

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#### **Conflicts of interest**

The authors have declared that they have no conflict of interest.


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