



Assessment of Levels of Trace Elements in Sediment and Water in Some Artisanal and Small-Scale Mining Sites at Tarkwa –Nsuaem Municipality in The Western Region of Ghana

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ABSTRACT

Trace metal concentrations in water and sediment samples collected from six rivers in some artisanal and small-scale gold mining sites at Tarkwa-Nsuaem Municipality in the Western Region of Ghana were studied. A total of 70 water and sediment samples were analysed for Mercury (Hg), Arsenic (As) Lead (Pb), Cadmium (Cd), Zinc (Zn), Copper (Cu) and Manganese (Mn) using Atomic Absorption Spectrometry (AAS). Four out of the seven trace metals, namely, Hg, As, Pb and Cd in all the water samples examined exceeded their respective WHO maximum acceptable limit in drinking water. In order of decreasing ecological threat, the trace metals investigated can be arranged in the following order: $Hg > Cd > As > Cu > Pb > Zn > Mn$. The Geo-accumulation index (I_{geo}) and Contamination factor (C_f) values of sediment indicate that all the rivers studied were heavily contaminated ($3 < I_{geo} \leq 4$) and uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$) with Hg and Cd respectively. The strong correlation between Hg, As and Cd concentrations in water and sediment samples showed the possibility of sediment acting as a secondary pollution source. High Potential Ecological Risk (PER) index values ($332.67 \leq RI \leq 649.03$) were recorded for the six rivers studied suggesting possible detrimental effect on the health of inhabitants of the community who depend on the rivers for drinking water without prior treatment.

1. Introduction

In recent times, a lot of attention has been drawn to the mining industry and its adverse impacts on the environment. Notwithstanding the socio-economic benefits of gold mining to the local communities and the country as a whole, a significant amount of stress has been put on the environment and basic life support systems. This poses potential threat to the health of the people [1, 2]. In Ghana, small scale gold mining is reported to be responsible for about 5% of the annual gold production. However, this gold mining of late has become unpopular as it is seen as the source of significant heavy metal contamination of the environment. Some of the impacts associated with small scale gold mining include the destruction of vegetation, land degradation and the pollution of water bodies [3].

Milling operations coupled with grinding, ore concentrations, disposal of tailing and wastewater of mining activities provide obvious sources of trace elements contamination in the environment. These trace elements could cause health problems at higher exposure and destroy aquatic organisms when leached into water bodies. Residues from trace elements in contaminated habitat may accumulate in micro-organisms, aquatic flora and fauna, which in turn may enter the human food chain and result in health problems [2, 4]. Several studies have been conducted in Ghana on the extent of heavy metal pollution in some mining towns or areas [4-7]. Most of these studies have indicated significant levels of heavy metals such as As and Hg in environmental samples collected from these mining areas. According to Ghana Living Standard Statistical Survey [8], more than 40% of Ghanaians in rural areas and pre-urban centres especially children die each year from diseases associated with unsafe drinking water due to pollutants from mining sites.

This study was carried out in Tarkwa –Nsuaem Municipality which has a long history of mining activities where most of the water bodies look turbid and assume to contain elemental contaminants. According to regional employment assessments by Agyapong [9], over 6000 illegal and 117 registered artisanal goldmines are found in the Municipality.

The aim of this research work was to assess the levels of trace elements in sediments and water in some artisanal mining sites at Tarkwa-Nsuaem Municipality in the Western Region of Ghana.

2. Experimental Methods

2.1 Description of Study Area

Tarkwa-Nsuaem Municipality is one of the seventeen districts in the Western Region of Ghana. It is located in the south-western part of the country. It lies between latitudes $4^{\circ} 0' N$ and $5^{\circ} 4' N$ and $1^{\circ} 45' W$ and $2^{\circ} 1' W$ and shares boundaries with Prestea Huni-Valley District to the north, Nzema East District to the West, Ahanta West District to the South and Mponoh District to the East as shown in Fig. 1 [10]. The Municipality has a population of 90,477 and total land area of 978.26 square kilometers [11]. The capital town of the Municipality; Tarkwa is located about 100 km from the regional capital, Sekondi-Takoradi. The study was carried out in the six localities Bedukrom, Effuanta, Bonsawiri, Akyempim and Essamang within Tarkwa- Nsuaem Municipality in the Western region of Ghana along six river courses – rivers Ahomaburo (Ab), Bediabewu (Be), Bonsa (Bo), Bonsawire (Bw), Chifan (Ch) and Nyaani (Ny) respectively.

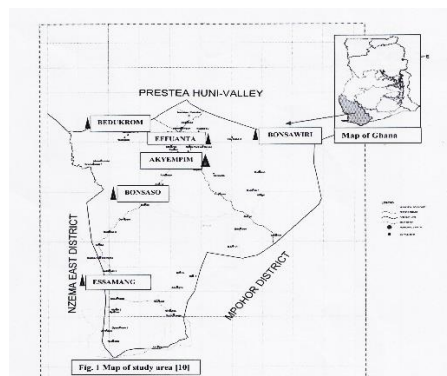


Fig. 1 Map of study area [10]

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2.2 Procedure for Sampling

Both water and sediment samples each were collected at different locations at each of the six river-course sources between October and November 2014. Water samples were collected from the river section downstream of artisanal mining activities. The collection of water samples of the rivers were performed by wearing polyethylene gloves and facing the direction of flow of the rivers. Pre-cleaned acid washed polyethylene bottles were used for sampling. At each sampling point, the bottles were rinsed three times with water before collection of the sample. Each sampling bottle was immersed at 8 cm below the water surface to collect samples of water below the water surface. Sediments were collected from all sampling sites as the water samples. Sediment samples at a depth of about 15 cm from the surface were collected with a pre-cleaned polyethylene shovel. The shovel was used to scoop the sediment. The sediment samples were transferred into pre-cleaned polyethylene bottles. Water and sediment samples from the source of river which has no record of pollution and sprang through the mining area were taken and analysed to serve as reference. Water and sediment samples were collected following the standard procedure described by DWAF [12]. A total of 70 samples consisting 35 water and 35 sediment samples were carefully labelled, kept in ice chest loaded with ice block and transported to the laboratory of the Soil Research Institute at Kwadaso-Kumasi for elemental analysis. Water samples were stored at 4 °C whilst sediment samples were frozen at -18 °C in a refrigerator until analyses.

2.3 Samples Preparation and Analyses

Sediment samples were allowed to defrost, and then air-dried to constant weight to avoid microbial degradation. The sediment samples were sieved mechanically using 2 mm sieve and homogenized. A gram of dried fine sediment sample was weighed and transferred into an acid washed, round bottom flask containing 10 cm³ concentrated nitric acid. The mixture was slowly evaporated over a period of 1 hour on a hot plate. Each of the sediment residue obtained was digested with a 9:4:1 ratio of concentrated HNO₃, H₂SO₄ and HClO₄. Perchloric acid (HClO₄) was used purposely for increasing the efficiency of oxidation of the samples and the rate of digestion of the samples. The digested mixture was placed on a hot plate and heated intermittently to ensure complete evaporation of the fumes of HClO₄. The mixture was allowed to cool at room temperature and filtered using whatman No.1 paper into a 50 cm³ volumetric flask. The filtrate was then stored in pre-cleaned polyethylene storage bottles.

The determination of the trace metals in both water and sediment samples were performed with Varian Spectra AA220 Zeeman Atomic Absorption Spectrophotometer (AAS) (Varian Canada Inc.). The instruments setting and operational conditions were in accordance with the manufacturer's specification.

The accuracy of the analytical method was evaluated using the standard reference materials IAEA 433, IAEA 405, QTM 080MS and QTM 081MS.

Table 1 WHO's permissible limit for trace metals in drinking water and aquatic sediment [13]

Metal	Sediment (mgkg ⁻¹)	Water (mgL ⁻¹)
Cd	0.60	0.003
Pb	31.00	0.01
Zn	120.00	3.00
Mn	460.00	0.40
Hg	0.20	0.01
Cu	16.00	2.00
As	6.00	0.01

2.4 Heavy Metal Indices

2.4.1 Assessment According to Geo-Accumulation Index (*I_{geo}*)

The degree of pollution in sediments can be assessed by determining the geo accumulation index *I_{geo}*, a criterion able to evaluate the heavy metal pollution in sediments [14]. It is mathematically expressed as

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right]$$

where *C_n* is the concentration of element 'n' and *B_n* is the standard geochemical background value (world surface rock average) [15]. The factor '1.5' is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. Table 6 lists the geochemical background values (*B_n*) for each metal tested. The geo-

accumulation index scale consists of seven grades (0–6) defining pollution levels ranging from unpolluted to highly polluted, as given in Table 2. Table 2 gives the calculated *I_{geo}* values for the metals investigated and the class in which they fall.

Table 2 Pollution grades of geo-accumulation index of metals *I_{geo}* class [14]

<i>I_{geo}</i> Class	<i>I_{geo}</i> Class	Sediment Quality
0	<i>I_{geo}</i> ≤ 0	Uncontaminated
1	0 < <i>I_{geo}</i> ≤ 1	Uncontaminated to moderately contaminated
2	1 < <i>I_{geo}</i> ≤ 2	Moderately contaminated
3	2 < <i>I_{geo}</i> ≤ 3	Moderately to heavily contaminated
4	3 < <i>I_{geo}</i> ≤ 4	Heavily contaminated
5	4 < <i>I_{geo}</i> ≤ 5	Heavily to extremely contaminated
6	5 < <i>I_{geo}</i>	Extremely contaminated

2.4.2 Contamination Factor (*C_F*) and Degree of Contamination (*C_d*)

Two useful indicators that reflect the extent of environmental contamination are the contamination factor (*C_F*) and degree of contamination (*C_d*). The contamination factor (*C_F*) is employed to evaluate the possible anthropogenic input of metals to observed sediment. Mathematically, it is expressed as:

$$C_F = \text{Measured Concentration/Background Concentration.}$$

The background concentration value of the metal is the world surface rock average as given by Martin and Meybeck [15]. The degree of contamination (*C_d*) is used to assess the excessive values of monitored elements in soil sediment samples. It is expressed as

$$C_d = \sum C_i^F$$

where *C_F* is the contamination factor for the *i*th element.

The five *C_F* ranges, their pollution grades and corresponding intensities are given in Table 3.

Table 3 *C_F* ranges and their designated pollution grade and intensity

<i>E_F</i>	Grade	Intensity
<i>C_F</i> < 1	I	Low contamination factor
1 ≤ <i>C_F</i> < 3	II	Moderate contamination factor
3 ≤ <i>C_F</i> < 6	III	Considerable contamination factor
<i>C_F</i> ≥ 6	IV	Very high contamination factor

2.4.3 Potential Ecological Risk Index Method

The assessment of the potential risk of the heavy metal contamination was proposed as a diagnostic tool for water pollution control purposes as a result of the increasing content of heavy metals in sediments and their subsequent release into the water, which could threaten ecological health. The potential ecological risk index method is used to assess heavy metal contamination in the soil. In addition, it associates ecological and environmental effects with toxicology, and evaluates pollution using comparable and equivalent property index grading method [16-18].

According to this method, the potential ecological risk coefficient *E_i* of a single element and the potential ecological risk index, RI of the multi-element can be computed via the following equations:

$$C_i^F = C_i^s / C_i^n$$

$$E_i^r = T_i^r \times C_i^F$$

$$RI = \sum_{i=1}^n E_i^r$$

where, *C_F* is the pollution coefficient of a single element of "i"; *C_s* is the measured level of sedimentary heavy metal; *C_n* is the background level of sedimentary heavy metal and *T_r* is the toxic response factor for the given element of "i" which accounts for the toxic and sensitivity requirement (Tables 4 and 5).

The toxic response factors for Hg, Pb, Cd, Cr, Cu, Zn and Mn were 40, 5, 30, 2, 5, 1 and 1, respectively. Average shale values and average crustal abundance were commonly used to provide elemental background concentrations. The average shale background concentration of global sediments is selected as the reference baselines in this study. RI method covers a variety of research domains, i.e., biological toxicology, environmental chemistry as well as ecology, and can evaluate ecological risks caused by heavy metals comprehensively [16, 17].

Table 4 Indices and grades of potential ecological risk factors

Critical Range for i-th Heavy Metal	Grade for Ecological Risk Factor
$E_i < 40$	Low
$40 \leq E_i < 80$	Moderate
$80 \leq E_i < 160$	Considerable
$160 \leq E_i < 320$	High
$E_i \geq 320$	Very high

Table 5 Indices and grades of the potential ecological risk index

RI Class	Critical Range for Heavy Metals	Grade for Ecological Risk Index
A	$R_i < 110$	Low
B	$110 \leq R_i < 220$	Moderate
C	$220 \leq R_i < 440$	High
D	$R_i \geq 440$	Very high

Table 6 Mean concentration (mgkg⁻¹) of trace metals from sediment samples

Name of River	Hg	As	Pb	Cd	Zn	Cu	Mn
Ahumaburo (Ah)	3.09±0.98	1.92±0.61	0.84±0.32	0.14±0.022	22.41±5.21	5.20±0.68	1.54±0.43
Bediabewu (Be)	4.18±0.30	2.48±0.80	1.26±0.8	0.32±0.11	33.6±8.33	6.04±2.42	2.73±0.62
Chifan (Ch)	3.73±0.86	0.97±0.22	0.68±0.16	0.17±0.05	16.27±3.8	4.83±1.35	1.69±0.21
Nyaayi (Ny)	5.53±0.46	3.39±0.73	0.72±0.26	0.51±0.18	28.40±9.1	4.22±0.98	1.78±0.34
Bonsa (Bo)	5.06±0.89	1.46±0.44	1.38±0.81	0.31±0.09	30.41±0.5	5.56±1.81	3.12±0.96
Bonsawiri (Bw)	5.79±0.87	2.56±0.66	3.14±1.1	0.44±0.15	26.72±6.06	6.8±2.82	2.27±0.88
River Source (ref.)	0.09	<0.01	0.2±0.05	<0.01	2.42±0.81	0.25±0.10	0.15±0.03
Bn	0.40	13.0	20.0	0.2	129	32.0	850

Table 7 Mean concentration (mgL⁻¹) of trace metals from water samples

Name of River	Hg	As	Pb	Cd	Zn	Cu	Mn
Ahumaburo (Ah)	1.47±0.45	0.34±0.14	0.162±0.11	0.41±1.21	0.37±0.19	0.98±0.34	0.17±0.10
Bediabawu (Be)	2.08±0.57	1.02±0.32	0.43±0.16	0.82±0.84	0.44±0.22	1.42±0.36	0.11±0.04
Chifan (Ch)	0.49±0.41	0.66±0.24	0.17±0.05	0.61±2.34	0.18±0.11	0.66±0.22	0.25±0.11
Nyaayi (Ny)	1.90±0.66	0.87±0.22	0.23±0.11	0.65±1.12	0.72±0.31	1.68±0.65	0.18±0.07
Bonsa (Bo)	2.38±0.91	0.56±0.18	0.14±0.08	0.49±3.14	1.12±0.44	1.03±0.42	0.16±0.07
Bonsawiri (Bw)	1.78±0.76	0.92±0.34	0.18±0.07	0.73±0.9	0.35±0.17	0.84±0.26	0.14±0.09
River source (ref.)	0.04	0.01	0.03	0.01	0.01	0.02	0.02

Table 8 Correlation matrix of levels of trace metals in sediment samples

	Hg	As	Pb	Cd	Zn	Cu	Mn
Hg	1						
As	0.811*	1					
Pb	0.656	0.448	1				
Cd	0.918**	0.891**	0.583	1			
Zn	0.862**	0.815*	0.508	0.774*	1		
Cu	0.845**	0.652	0.719*	0.624	0.854**	1	
Mn	0.811*	0.539	0.552	0.624	0.914**	0.859**	1

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

Table 9 I_{geo} values and class for trace metals in sediment samples

River	Hg		As		Pb		Cd		Zn		Cu		Mn	
	Value	Class	Value	Class	Value	Class	Value	Class	Value	Class	Value	Class	Value	Class
Ah	2.36	3	-3.35	0	-5.16	0	-1.11	0	-3.11	0	-3.2	0	-4.05	0
Be	2.8	3	-2.98	0	-4.57	0	0.09	1	-2.53	0	-3	0	-3.23	0
Ch	2.63	3	-4.33	0	-5.46	0	-0.82	0	-3.5	0	-3.31	0	-3.92	0
Ny	3.2	4	-2.5	0	-5.38	0	0.77	1	-2.77	0	-3.51	0	-3.84	0
Bo	3.07	4	-3.74	0	-4.44	0	0.05	1	-2.67	0	-3.11	0	-3.04	0
Bw	3.27	4	-2.9	0	-3.25	0	0.55	1	-2.86	0	-2.82	0	-3.5	0
Ref.	-2.73	0	-3.41	0	-7.22	0	-4.91	0	-6.32	0	-7.58	0	-4.95	0

3. Results and Discussion

3.1 Trace Metal Concentration in River Sediments

The mean concentration of the seven monitored trace metals (Hg, As, Pb, Cd, Zn, Cu and Mn) in sediment and water samples from the rivers Ahumaburo (Ah), Bediabewu (Be), Chifan (Ch), Nyaayi (Ny), Bonsa (Bo) and Bonsawiri (Bw) are reported in Tables 6 and 7.

Out of the seven trace elements studied in the sediment samples, only Hg consistently showed higher values than the WHO maximum acceptable level of 0.2 mg/kg (Table 1). The mean Hg concentration in all sediment samples were at least 15 times more than the WHO maximum acceptable level. Conversely, mean concentrations of all other trace elements in sediments recorded in all the rivers were found to be lower than their respective maximum WHO limits. Levels of trace metals recorded for the reference sediment samples were far below those recorded in the six rivers studied (Table 6).

The matrix (Table 8) summarizes the strength of the linear relationships between each pair of variables. There are strong positive correlations between the metals in river sediments as follows:

Hg-Cd (0.918), Hg-Zn (0.862), Hg-Cu (0.845), As-Cd (0.891), Zn-Cu (0.854), Zn-Mn (0.914) and Cu-Mn (0.859) pairs are significantly

positively correlated with each other at the 99% confidence level while significant correlations was also observed for the metal pairs Hg-Mn (0.811), Hg-As (0.811), As-Zn (0.815), Pb-Cu (0.719) and Cd-Zn (0.774) at 95% confidence level.

3.2 Heavy Metal Indices

3.2.1 Assessment According to Geo-Accumulation Index (I_{geo})

Table 9 gives the calculated I_{geo} values for the trace metals monitored and the class in which they fall. It can be deduced from Table 2 that with reference to the Muller scale the sediments in all the rivers studied were heavily contaminated with Hg.

None of the rivers showed signs of sediment contamination for As, Pb, Zn, Cu and Mn ($I_{geo} \leq 0$). For Cd, the sediments were uncontaminated at Ah and Ch but uncontaminated to moderately contaminate at Be, Ny, Bo and Bw.

3.2.2 Assessment according to Contamination Factor (C_f) and Degree of Contamination (C_d)

The C_f results show that all the rivers studied have high levels of Hg in their sediments. Considering the cumulative effect of all the individual

trace elements present in the sediment samples taken from the rivers studied, Bw registered the highest degree of contamination while Ah registered the lowest (Table 10). The increasing order among the sediments with respect to degree of contamination is as follows: Bw > Ny > Bo > Be > Ch > Ah.

Table 10 Contamination factor C_f and degree of contamination (C_d)

River	Hg	As	Pb	Cd	Zn	Cu	Mn	Degree of contamination
Ah	7.725	0.148	0.042	0.700	0.174	0.163	0.002	8.953 (6th)
Be	10.450	0.191	0.063	1.600	0.260	0.189	0.003	12.756 (4th)
Ch	9.325	0.075	0.034	0.850	0.126	0.151	0.002	10.563 (5th)
Ny	13.825	0.261	0.036	2.550	0.220	0.132	0.002	17.026 (2nd)
Bo	12.650	0.112	0.069	1.550	0.236	0.174	0.004	14.794 (3rd)
Bw	14.475	0.197	0.157	2.200	0.207	0.213	0.003	17.451 (1st)
Ref	0.225	0.001	0.010	0.050	0.019	0.008	0.000	0.313

3.2.3 Assessment According to Potential Ecological Risk (PER)

The potential ecological risk of a given contaminant is defined in Tables 4 and 5. The sum of the individual potential risks (R1) is the potential risk for that particular water body. The risk assessment findings are indicated in Table 11. The results suggest that Hg and Cd are the metals present in the rivers studied that needs to be monitored. The calculated PER values for As, Pb, Zn, Cu, Mn (Table 11) suggest that these metals present a low potential ecological risk [17, 19].

Table 11 Potential ecological risk assessment for soil sediments

River	Hg	As	Pb	Cd	Zn	Cu	Mn	RI
Ah	309	1.477	0.21	21	0.174	0.8125	0.0018	332.67
Be	418	1.908	0.315	48	0.260	0.9438	0.0032	469.43
Ch	373	0.746	0.17	25.5	0.126	0.7547	0.0020	400.30
Ny	553	2.608	0.18	76.5	0.220	0.6594	0.0021	633.17
Bo	506	1.123	0.345	46.5	0.236	0.8688	0.0037	555.08
Bw	579	1.969	0.785	66	0.207	1.0625	0.0027	649.03
*Ref.	9	0.008	0.05	1.5	0.019	0.0391	0.0002	10.62
Mean	456	1.64	0.33	47.2	0.20	0.85	0.003	506.61
ER Grade	very high	low	low	moderate	low	low	low	Very high

3.3 Trace Metal Concentration in Water

The mean concentration of the seven monitored trace metals (Hg, As, Pb, Cd, Zn, Cu and Mn) in water samples from Ah, Be, Ch, Ny, Bo and Bw are reported in Table 7.

The mean concentration of Hg, As, Pb and Cd in water samples in all the rivers monitored were found to be higher than the reference samples taken from the river source at Bediabewu and also above the maximum acceptable levels of 0.001, 0.010, 0.010, 0.003 mg/kg respectively for drinking water. The mean concentrations of Zn, Cu and Mn in the rivers studied were however, lower than the acceptable maximum levels in drinking water (Table 1).

Table 12 Correlation matrix of levels of trace metals in water samples

	Hg	As	Pb	Cd	Zn	Cu	Mn
Hg	1						
As	0.660	1					
Pb	0.577	0.807*	1				
Cd	0.661	0.977**	0.815*	1			
Zn	0.834**	0.347	0.202	0.339	1		
Cu	0.811*	0.765*	0.750*	0.761*	0.631	1	
Mn	0.224	0.433	0.184	0.553	0.289	0.429	1

**Correlation is significant at the 0.01 level

*Correlation is significant at the 0.05 level

Significant correlations was observed between the trace metals in water as follows: Hg-Zn (0.834), Hg-Cu (0.811); As-Pb (0.807), As-Cd (0.977) and As-Cu (0.765); Pb-Cd (0.815), and Pb-Cu (0.750) and Cd-Cu (0.761).

Table 13 Correlation matrix between trace metals in water and river sediments

Hg(W,S)	As(W,S)	Pb(W,S)	Cd(W,S)	Zn(W,S)	Cu(W,S)	Mn(W,S)
0.803*	0.805*	0.231	0.756*	0.722	0.618	0.419

*Correlation is significant at the 0.05 level (2-tailed)

The data showed a strong positive correlation between trace metals in water and sediment samples as follows: Hg (0.83), As (0.805) and Cd (0.756) (Table 13). Other studies have also established significant positive correlation in the pollution of river ecosystems [2, 17, 20].

The Hg, As, Pb and Cd levels recorded in all the river water samples exceeded the WHO maximum acceptable levels of these metals in drinking water [13]. The elevated levels of Hg, As, Pb, and Cd in water sample recorded at all the six rivers studied could be due to anthropogenic inputs; both point and non-point sources. Direct and indirect discharge of mine waste into water bodies in the area may be a contributing factor to the higher levels of Hg, As, Pb and Cd observed.

The high mean concentration of Hg in both sediment and water samples recorded in all the rivers studied could be attributed to the numerous artisanal mining activities located along these rivers; with frequent use of Hg to extract gold from the ore [2, 21, 22].

The relatively high mean concentration of Cd in sediment samples recorded at Be, Ny, Bo and Bw rivers may be due to natural occurrence of the metal in sediments and surrounding soils. There is also the possibility of Cd being washed into rivers from agricultural chemicals used by farmers in the study area [2].

In general, the mean concentration of the trace metals in sediments samples (Table 6) were higher than water samples (Table 7) and this might be due to the fact that metals can be transported with the waste or suspended sediments stored within the river bed bottom sediments. Furthermore, suspended sediments and metallic chemical solids are stored in riverbed sediment after they aggregate to form larger denser particles that settle at the bottom of the water [20, 23].

All the trace metal pairs in sediment samples (Table 8) exhibited positive relations: Hg-Cd (0.918), Hg-Zn (0.862), Hg-Cu (0.845), As-Cd (0.891), Zn-Cu (0.854), Zn-Mn (0.914), Cu-Mn (0.859) and Hg-Mn (0.811), Hg-As (0.811), As-Zn (0.815), Pb-Cu (0.719) and Cd-Zn (0.774) pairs were significantly positively correlated with each other at the 99% and 95% confidence levels respectively, which may suggest a common pollution sources or a similar geochemical behaviour for these metals and a similar terrigenous source or a result of similar mechanisms of transport and accumulation within the sediments [24,25]. The significant correlation between all trace metals studied and Hg also suggests higher affinity with oxides associated with these metals [17, 24].

The correlation matrix of the trace metals in water suggest good inter-relationship between two groups of trace metals; Hg-Zn-Cu and As-Pb-Cd-Cu (Table 12). The relationship within the two groups suggests a common source of these metals into the water. The Hg-Zn-Cu is likely to be from anthropogenic source (since Hg is not a common component of the earth crust) resulting from mine waste discharge into the river system and atmospheric depositions. The As-Pb-Cd-Cu group might be from other point, non-point sources and natural sources. Arsenic, in the form of arsenopyrite (FeAsS), occurs as an impurity in gold ore and in many other mineral deposits [6, 26]. Thus As association with other metals in the water may indicate a natural origin probably from parent material of bottom sediments.

The high correlation of Hg, As, and Cd in water-sediment (Table 13) in the rivers studied suggests a strong relationship between water and sediment metal concentrations in these rivers; similar correlation between water and sediment have been reported by Bosompem et al. [2] and Adomako et al. [27]. The strong correlation between Hg, As and Cd concentration in water and sediment indicates the possibility of the sediment acting as a secondary pollution source.

The Geo-accumulation index (Igeo) calculations of the sediment samples indicates that all the six rivers studied were heavily contaminated with Hg. Apart from rivers Be, Ny, Bo and Bw which showed a slight contamination by Cd, none of the rivers indicated signs of sediment pollution for As, Pb, Zn, Cu and Mn.

The C_f and C_d results (Table 10) shows that Bw, Ny, Bo and Be rivers are highly contaminated with Hg and moderately contaminated with Cd. The rivers however, recorded low contamination for As, Pb, Zn, Cu and Mn. The various enrichment of the trace metals studied could be attributed to the rampant and numerous artisanal mining activities and natural sources.

The PER results (Table 11) indicated that the trace metals examined especially Hg and to a lesser extent Cd need to be closely monitored as they registered very high and moderate levels of pollution respectively. In order of decreasing ecological threat, the trace metals investigated can be arranged in the following order: Hg>Cd>As>Cu>Pb>Zn>Mn.

The relatively high levels of trace metals particularly Hg and Cd in the rivers studied is worrying because of their accumulation and toxicity effects on aquatic organisms and the human population. The high concentration of trace metals in the sediments may also serve as secondary pollution source even when the main pollutant is reduced or eliminated [2, 17, 19, 28].

4. Conclusion

The high individual potential risk values (RI) recorded from all the six rivers studied suggests possible detrimental effect on the health of the inhabitants of the community that use the rivers directly without treatment. Contamination levels could increase over time as artisanal mining activities along these rivers are still ongoing. Attention of the public and government should therefore be drawn to the high pollution levels of these rivers as a result of indiscriminate mining activities. There is the need for constant monitoring and education for the local population about the need for environmental protection and the ill effects of indiscriminate and illegal mining activities so as to curb any unanticipated disaster. Based on the study findings, it is recommended that activities of miners should be monitored to ensure that gold extraction and other mining activities do not occur close to drinking water source. Reforestation should be carried out to help reclaim the vegetation cover and elevate the densities of tree species. The government should introduce relevant drinking water treatment technique which can reduce the current levels of trace metals in drinking water. The government, the Minerals Commission, the civil society, and non-governmental organizations should conduct proper campaigns to enhance awareness on the impacts of environmental pollution. The initiative should aim at educating the small scale miners on the impacts of their activities.

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