

Heavy Metal Loading in Surface Sediments along the Kawere Stream, Tarkwa, Ghana*

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Abstract

Sediment contamination by heavy metals resulting from anthropogenic activities is increasingly becoming a global concern due to the risk it poses to human well-being and ecological integrity at large. The purpose of this study was to assess the heavy metals loading in sediment along the Kawere stream. Ten sediment samples were collected, acid digested and analysed for copper (Cu), lead (Pb), cadmium (Cd), manganese (Mn), zinc (Zn), nickel (Ni), chromium (Cr), cobalt (Co) and iron (Fe) using a Varian AA240FS Atomic Absorption Spectrometer (AAS). The Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for freshwater sediment quality was used as the benchmark against which the measured metal concentrations were compared. Nemerow's pollution and potential ecological risk indices were used to evaluate the pollution status and ecological risk levels of the heavy metals in the stream. The results obtained indicated that, except Cu which exceeded the ANZECC trigger value of 65 mg/kg at three sampling sites (K01=171.29 mg/kg, K05=170.83 mg/kg and K07=113.31 mg/kg), all other measured heavy metals concentrations were below their corresponding ANZECC values. Heavy metal pollution assessment showed that three samples (K01, K05 and K07) were slightly polluted, suggesting the likelihood of posing a health threat to the aquatic organisms and humans. Calculated Ecological Risk Index (RI) ranged from 3.229 to 19.750 (RI < 150), representing a low ecological risk. As such, the metals, Cu, Ni, Cd, Pb, Cr, and Zn pose a low ecological risk to the aquatic ecosystem. Although the ecological risk is low based on the current results, constant monitoring of the stream quality is recommended due to the increasing human activities along the stream as well as the sediments ability to accumulate and remobilise heavy metals back into the water column and possibly transferring them through the food chain.

Keywords: Heavy Metals, Sediment, Ecological Risk Assessment, Pollution, Stream

1 Introduction

Streams are vital in sustaining human and animal life. Streams are used for numerous purposes including urban and industrial water supply, irrigation, and commercial navigation. In recent times, contamination of these aquatic ecosystems by heavy metals have received much attention due to the quantity released into the ecosystem, its toxicity and bioaccumulative nature (Budiawan *et al*, 2018; Zahran *et al*, 2015; Kanchana *et al*, 2014; Osmar *et al*, 2013; Qu *et al*, 2012).

Generally, heavy metal refers to any naturally-occurring metallic chemical or element characterised by high atomic mass and density which is five times greater than that of water (Tchounwou *et al*, 2012). They are often introduced into aquatic systems via natural and/or anthropogenic sources. Natural sources include atmospheric deposition, mineral weathering, volcanic activities, urban run-offs and natural soil erosion whilst anthropogenic origin include urban and industrial wastewater, pesticides and fertilizers, electroplating processes and, mining and mineral extraction operations (Pawar and Bhosale, 2018; Kanchana *et al*, 2014; Guo *et al*, 2010).

Irrespective of their source, accumulation of heavy metals in aquatic systems can deteriorate water and

sediment quality. Thus, elevated uptake by aquatic biota may affect food quality and safety, posing a health threat to human and animals in the wider ecosystem (Capangpangan *et al*, 2016, Kanchana *et al*, 2014; Nagajyoti *et al* 2010, Fagbote and Olanipekun 2010). Notably, in small quantities, some heavy metals such as copper (Cu), zinc (Zn), iron (Fe), chromium (Cr) and manganese (Mn) are nutritionally essential for maintaining various biochemical and physiological functions in living organisms. However, these metals pose risk to human health when concentrations exceed certain permissible limits (Pawar and Bhosale, 2018; Manahan, 2005).

Some studies have highlighted the effects of heavy metals on flora and fauna; notable amongst them are genetic modification, growth retardation and ultimately loss of species, leading to extinction (Uaboi-Egbenni *et al*, 2010; Davies *et al*, 2006). Moreover, Shah (2017) and Kanchana *et al* (2014) revealed that exposure to higher concentrations of heavy metals may lead to death or reduced energy levels and interfere with normal brain processes.

Sediments, which are the layers of relatively finely divided matter covering the bottom of water bodies are noted to be the ultimate sinks for various contaminants including heavy metals (Manahan, 2005). Thus, for a given water body, about 90% of

the heavy metal loadings are known to be bounded to bottom sediments, especially fine-grained sediments which have higher adsorption capabilities (El-Madani and Hacht, 2017). Studies conducted by Rodrigue *et al* (2016) and Akcay *et al* (2003) indicated that heavy metals could be released to water bodies from sediments through a series of biological, physical and chemical processes when the sedimentary and environmental conditions are altered. This would increase the potential ecological risk and toxicity to aquatic biota as well as organisms at higher trophic levels. Thus, the concentration of heavy metals in sediments is one of the important indices to determine the quality of aquatic ecosystems (Attri and Kerka, 2011). Also, recent studies have shown that the levels of these heavy metals in some of the aquatic ecosystems (reservoirs, lagoons, streams and rivers) in Ghana is on the rise prompting urgent attention to avert the situation due to the health dangers heavy metals pose to human (Afum and Owusu, 2016; Ansah *et al*, 2018; Asare *et al*, 2018).

The Kawere stream originates from Abosso in the Prestea Huni-Valley District and flows through New Atuabo and Kawerekwano, suburbs of Tarkwa. It then extends to Tarkwa Bansa and finally discharges into River Bonsa, from which water is abstracted, treated to potable standard and distributed to inhabitants within the Tarkwa Nsuaem Municipality by the Ghana Water Company Limited. Along its path, the stream receives a copious amount of untreated municipal liquid waste and leachates from dumpsites, which are often rich in heavy metals and other potentially dangerous substances. In addition, economic activities such as illegal mining, farming (both animal and crop), and steel fabrication have been observed along the stretch of the stream, all of which serve as possible sources of heavy metals to the stream. For example, some of the fertilizers and pesticides used for the agricultural activities are known to contain some heavy metals and other dangerous chemicals which often gets washed into the stream through runoffs during precipitation events.

The people of Aboso, New Atuabo, Kawerekwano and Tarkwa Bansa depend on the stream as their main source of water for domestic purposes, fishing and irrigation. Knowledge on the quality of the stream is therefore important due to the detrimental effects of heavy metals on human health. Presently, no studies have been conducted to evaluate the pollution status and ecological risk of heavy metals in the Kawere Stream.

Therefore, the present study was conducted to assess the levels of heavy metal loadings in the Kawere stream sediments, the pollution status of the stream as well as the ecological risk levels of the heavy

metals. The findings of this study may serve as a baseline for future studies and may also be useful for formulating management strategies to mitigate heavy-metal pollution in the study area and other areas.

2 Resources and Methods Used

2.1 Study Area

The Kawere Stream is located at Tarkwa, a mining town in the Western Region of Ghana. Tarkwa is the capital of the Tarkwa Nsuaem Municipal and shares a boundary with Prestea Huni-Valley District to the north, the south with Ahanta West District, the West with Nzema East Municipal and the East with Mpohor and Wassa East. Tarkwa is approximately located on longitude 2°59'45" W and latitude 5°17'42" N (Seidu, 2004).

Geologically, the Municipality lies within the Birimian and Tarkwaian geological formations. The Birimian rocks are the most economical due to their mineral potentials. There are currently, two (2) large-scale gold mining companies and a manganese mining company within the Municipality (Kuma and Younger, 2001).

2.2 Survey and Selection of Sampling Sites

Prior to the collection of sediment samples, a survey was conducted along the stretch of the Kawere stream to identify the study boundary and suitable sampling sites. Some factors including accessibility and activities (such as farming, illegal mining popularly known as 'galamsey', waste discharge, and construction) around the vicinity influenced the selection of these sampling sites as most of these activities present possible sources of heavy metals into the stream.

2.3 Sampling

Due to poor accessibility to the stream bed, 10 sediment samples were taken along approximately 200 m stretch of the stream using a Petersen grab sampler. The samples were immediately transferred into labelled, clean plastic Ziploc bags. A Garmin GPSMAP 62s handheld Global Positioning System (GPS) was used to indicate sampling locations. At the end of the sampling, the samples were transported to the Minerals Laboratory of the University of Mines and Technology (UMaT) for analyses. Sampling points description and locations along the Kawere stream are presented in Table 1 and Fig. 1, respectively.

Table 1 Sample Points Description and Locations

Sample ID	Physical Locations (Activity/Establishment)	Lat. (N)	Long. (E)
K01	Residential Settlement	588473	613454
K02	Residential Settlement, Salon, Steel Fabricators	588313	613624
K03	Galamsey Washing Shed close to Residential Settlement	588114	613513
K04	Farming Area	587734	613633
K05	Residential Settlement	587420	613449
K06	New settlement Development and farming Area	587246	613296
K07	Farming Area	586712	613084
K08	Poultry Farm	586355	612904
K09	Municipal Waste Discharge	585755	612637
K10	New settlement Development	585466	612711

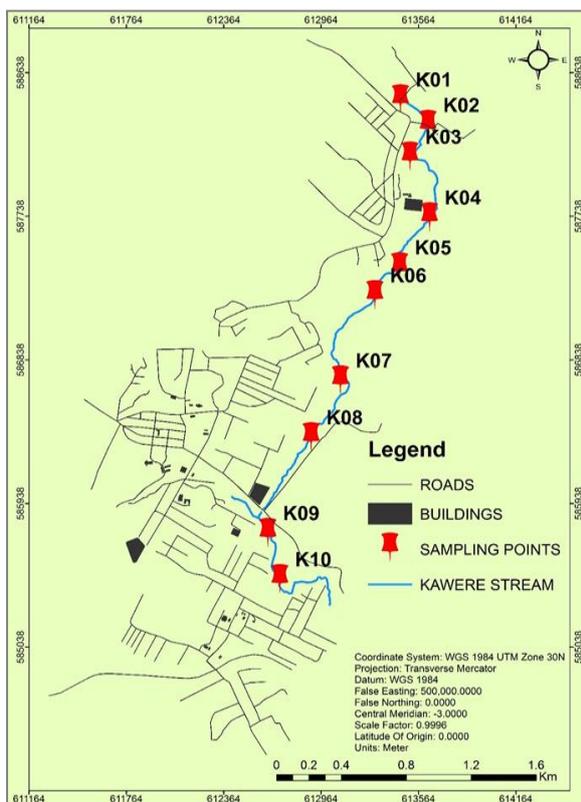


Fig. 1 Sampling Points along the Stream

2.4 Sample Preparation and Analyses

The samples were oven-dried (110 °C), cooled under ambient temperature, and acid-digested using aqua regia (HNO₃ and HCl) in the ratio 1:2. The digests were filtered through 0.45 µm Whatman

filter paper into a 50 mL volumetric flask and made to the mark with distilled water. Heavy metals (Cu, Pb, Cd, Mn, Zn, Ni, Cr, Co and Fe) concentrations in the filtrates were analysed on a Varian AA240FS Fast Sequential Atomic Absorption Spectrometer at the UMaT Minerals Laboratory.

2.5 Heavy Metal Pollution Assessment

To assess the overall heavy metal pollution status of sediments along the Kawere Stream, Nemerow's Pollution index (Pn) was used (Cheng *et al* 2007; Gong *et al* 2010) according to equations (1) and (2) as follows:

$$P_n = \sqrt{\frac{\text{Max } P_i^2 + \text{Ave } P_i^2}{2}} \quad (1)$$

$$P_i = \frac{C_i}{S_i} \quad (2)$$

where, Pn: Nemerow's pollution index, Pi: pollution index for the *i*th heavy metal, Ci: measured concentration of the *i*th heavy metal and Si: required standard of the *i*th heavy metal. In this study, the trigger values of the Australian and New Zealand Environment and Conservation Council (ANZECC) Guidelines for freshwater sediment quality were used as the required standards (Table 2). AvePi and MaxPi are the averages and maximum values of the pollution indices of all the heavy metals, respectively.

The calculated Nemerow's pollution index (Pn) denotes the degree of pollution; the higher the value, the more serious the pollution level. Table 3 represents the pollution level classification criteria based on the Nemerow's pollution index.

2.6 Ecological Risk Assessment

The ecological Risk Index (RI) was evaluated using equation 3 (Hakanson, 1980).

$$RI = \sum E_r^i = \sum T_f^i C_f^i = \sum T_f^i \times \frac{C_m^i}{C_n^i} \quad (3)$$

where, E_rⁱ is the potential ecological risk coefficient of a single element, T_fⁱ is the toxic-response factor for the *i*th heavy metal (Cd=30, Ni=5, Cu=5, Pb=5, Cr=2, Zn=1), which accounts for the toxic requirement and the sensitivity requirement. C_fⁱ is the accumulating coefficient of the *i*th heavy metal, C_mⁱ is the measured concentration of the *i*th heavy metal and C_nⁱ is the background concentration of the *i*th heavy metal in the sediment. The ecological risk levels of heavy metals were classified into five categories based on the values of E_rⁱ and RI (Table 4) (Hakanson, 1980).

Table 2 ANZECC Guidelines for Fresh Water Sediment Quality

Element	Cu	Pb	Cd	Mn	Zn	Ni	Cr	Co	Fe
ISQG-Low (Trigger Value) (mg/kg)*	65	50	1.5	-	200	21	80	-	-
ISQG-High (mg/kg)**	270	220	10	-	410	50	370	-	-

* Limit below which the likelihood of adverse effect is very low or negligible
** Limit beyond which the heavy metal become bioavailable.

Table 3 Classification Criteria Based on Nemerow's Pollution Index

Class	Nemerow's Pollution Index	Interpretation
1	$0 < P_n \leq 0.7$	Unpolluted
2	$0.7 < P_n \leq 1.0$	Marginally polluted
3	$1.0 < P_n \leq 2.0$	Slightly polluted
4	$2.0 < P_n \leq 3.0$	Moderately polluted
5	$P_n > 3.0$	Severely polluted

Table 4 Criteria for Degrees of Ecological Risk Caused by Heavy Metals in Sediments

E_r^i or RI	Ecological Risk
$E_r^i < 40$ or $RI < 150$	Low ecological risk for the water body
$40 \leq E_r^i < 80$ or $150 \leq RI < 300$	Moderate ecological risk for the water body
$80 \leq E_r^i < 160$ or $300 \leq RI < 600$	Considerable ecological risk for the water body
$160 \leq E_r^i < 320$ or $600 \leq RI$	Very high ecological risk for the water body

3 Results and Discussion

3.1 Concentrations of Heavy Metals

Results from the heavy metal concentration analyses are presented in Table 5. Where possible, these results have been compared with the ANZECC guidelines for freshwater sediment quality. Comparatively, the measured concentrations of Cr, Ni, Zn, Cd and Pb in all ten sediment samples were below their corresponding ANZECC lower limits, suggesting little or no threats to the aquatic ecosystem and surrounding environment at these concentrations (Table 5).

In terms of Cu concentration, Table 5 shows that the Cu concentrations for the sediment samples ranged from 7.01 to 171.29 mg/kg. Whilst the Cu concentrations of samples K01, K05 and K07 exceeded the ANZECC trigger value of 65 mg/kg, those of samples K02, K03, K04, K06, K08, K09 and K10 were below the limit. However, the samples that exceeded the trigger value were still below the ANZECC high limit of 270 mg/kg (Table 5). In general, the average concentration of the Cu in the samples is 58.4 mg/kg, which is below the

ANZECC trigger value of 65 mg/kg. This suggests that adverse effects are expected to occur rarely.

The Co concentrations recorded for the samples ranged from 1.13 and 8.69 mg/kg. Unfortunately, the ANZECC guideline has no standard value(s) for Co concentrations in freshwater sediments. However, the Co concentrations recorded in this study seemed slightly higher relative to those reported by Essumang *et al* (2013) and Donkor *et al* (2005) in their work on freshwater sediment for a typical stream in Ghana (0.66 – 3.34 mg/kg; 0.023 – 0.517 mg/kg). Due to the nature of the activities around the study area, it can be suggested that the Co in the sediment may be from natural sources.

Table 5 Concentrations of Heavy Metals in Sediment Samples

Sample ID	Cu	Pb	Cd	Mn	Zn	Ni	Cr	Co	Fe
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
K01	171.29*	15.1	0.07	1048.6	187.41	9.35	20.02	4.35	526140
K02	31.08	13.13	0.04	508.2	83.52	5.24	14.05	3.17	142300
K03	34.71	17.14	0.11	477	96.01	4.51	14.53	3.01	45700
K04	7.01	7.81	0.03	334.8	33.97	4.18	5.74	2.44	32520
K05	170.83*	12.39	0.05	201.4	77.47	5.85	15.79	3.03	36300
K06	13.4	8.13	0.02	183.4	40.22	2.91	9.96	1.13	58560
K07	115.31*	16.66	0.07	382.4	72.22	4.54	11.15	8.69	54040
K08	8.62	8.34	0.06	283.87	34.91	2.8	9.21	4.47	76180
K09	9.95	13.2	0.07	1158	36.52	3.44	12.71	2.71	18440
K10	22.08	10.77	0.06	546.6	34.72	4.32	8.99	4.42	43340
ISQG-Low	65	50	1.5	-	200	21	80	-	-
ISQG-High	270	220	10	-	410	50	370	-	-

* Metal concentration exceeding corresponding ANZECC Standard

The Fe concentration levels ranged from 18440 to 526140 mg/kg (Table 5). The ANZECC guideline does not specify any limits for Fe in freshwater sediments. However, the measured Fe concentrations are relatively higher than similar studies conducted by Afum and Owusu (2016) on the Birim river of Ghana (1064.29 – 13554.2 mg/kg). These elevated levels could be as a result of the commercial sale of iron rods for construction activities and discharge of mining waste generated from illegal mining activities within the catchment area. Thus, the study area lies within the Birimian and Tarkwaian geological formations, which are rich in iron-rich minerals (such as hematite and magnetite) (Kuma and Younger, 2001; Milesi *et al* 1991). The weathering of these iron-rich minerals may have contributed to the higher concentrations of Fe observed (Survey *et al* 1996). Notably, the Fe is an essential dietary mineral for the development and survival of almost all living creatures (Valko *et al* 2005). It helps metabolise proteins and play an important role in the production of haemoglobin and red blood cells, which is responsible for transporting oxygen (O₂) to tissues within the human body. However, like many other essential elements, Fe is harmful (toxic) when overloaded. The Fe overload occurs as a result of the body's inability to maintain normal iron levels, leading to the build-up of excess iron. It is clear that the release of Fe stored in the sediment may be detrimental to human health and aquatic life.

The Mn concentration in sediment samples measured ranged from 183.4 to 1158 mg/kg.

Although there is no ANZECC guideline on Mn concentration in freshwater sediments, the results obtained in this study are as expected due to the presence of Mn-rich minerals around the catchment of the sampled sites. This is evidenced by the presence of a manganese mining company, Ghana Manganese Ltd., in the area.

3.2 Heavy Metal Pollution Index Assessment

Table 6 summarises the heavy metal pollution assessment results. The results for Co, Fe and Mn have not been reported here because the ANZECC standard which was used as the basis for calculation does not specify any values for these elements. From Table 6, the Pi values on average decreased in the order of Cu > Zn > Pb > Ni > Cr > Cd. The calculated Pn values for the ten (10) samples ranged from 0.153 to 1.941 (mean = 0.696). The results showed that 70% of the samples (K02, K03, K04, K06, K08, K09, and K10) had Pn values < 0.7, suggesting unpolluted sediments (Table 3). The remaining 30% samples K01, K05 and K07 yielded Pn values of 1.941, 1.911 and 1.299, respectively. These Pn values classify the samples in the slightly polluted zone according to the criteria in Table 3, suggesting a potential threat to the aquatic organisms and a possible transfer to higher trophic levels.

3.3 Ecological Risk Index Assessment

Ecological risk assessment of each heavy metals are presented in Table 7. Once again, the results for Co, Fe and Mn have not been reported because the

ANZECC standard which was used as the basis for calculation does not specify any values for these elements. The potential ecological risk indices of Cu, Pb, Cd, Zn, Ni and Cr in all studied samples were lower (< 40), which suggests low ecological risk of the corresponding metals in the stream. The E_r^i values on average declined in the order of Cu > Pb > Cd > Ni > Zn > Cr. The RI of sediment samples ranged from 3.229 to 19.750

(Table 7). All RI values in the sediments were less than 150, indicating a low ecological risk of heavy metal to the stream. The risk posed by heavy metals at different sampling sites decreased in the order of K01 > K05 > K07 > K03 > K02 > K10 > K09 > K08 > K06 > K04, based on the values of RI. In a nutshell, the heavy metals under investigation in this study reflected a low ecological risk to the water body.

Table 6 Heavy Metal Pollution Assessment Results

Sample ID	Pi						Max pi	Ave Pi	Pn
	Cu	Pb	Cd	Zn	Ni	Cr			
K01	2.635	0.302	0.047	0.937	0.445	0.250	2.635	0.769	1.9
K02	0.478	0.263	0.027	0.418	0.250	0.176	0.478	0.268	0.4
K03	0.534	0.343	0.073	0.480	0.215	0.182	0.534	0.304	0.4
K04	0.108	0.156	0.020	0.170	0.199	0.072	0.199	0.121	0.2
K05	2.628	0.248	0.033	0.387	0.279	0.197	2.628	0.629	1.9
K06	0.206	0.163	0.013	0.201	0.139	0.125	0.206	0.141	0.2
K07	1.774	0.333	0.047	0.361	0.216	0.139	1.774	0.478	1.3
K08	0.133	0.167	0.040	0.175	0.133	0.115	0.175	0.127	0.2
K09	0.153	0.264	0.047	0.183	0.164	0.159	0.264	0.162	0.2
K10	0.340	0.215	0.040	0.174	0.206	0.112	0.340	0.181	0.3
Mean	0.899	0.245	0.039	0.348	0.224	0.153	0.923	0.318	0.696

Table 7 Ecological Risk Assessment Results

Sample Point	E_r^i						Ri
	Cu	Pb	Cd	Zn	Ni	Cr	
K01	13.176	1.510	1.400	0.937	2.226	0.501	19.750
K02	2.391	1.313	0.800	0.418	1.248	0.351	6.520
K03	2.670	1.714	2.200	0.480	1.074	0.363	8.501
K04	0.539	0.781	0.600	0.170	0.995	0.144	3.229
K05	13.141	1.239	1.000	0.387	1.393	0.395	17.555
K06	1.031	0.813	0.400	0.201	0.693	0.249	3.387
K07	8.870	1.666	1.400	0.361	1.081	0.279	13.657
K08	0.663	0.834	1.200	0.175	0.667	0.230	3.769
K09	0.765	1.320	1.400	0.183	0.819	0.318	4.805
K10	1.698	1.077	1.200	0.174	1.029	0.225	5.402
Mean	4.494	1.227	1.160	0.348	1.122	0.305	8.657

4 Conclusions

The aim of this study was to assess the level of heavy metals loading in surface sediments along the Kawere Stream. Particularly, the pollution status of the stream was examined using Nemerow's pollution and potential ecological risk indices.

Based on the results of this study, it can be concluded that:

- (i) Heavy metals (Cu, Pb, Cd, Mn, Zn, Ni, Cr, Co and Fe) were present in the sediment along the Kawere Stream;
- (ii) With the exception of Cu which exceeded the ANZECC lower limit (65 mg/kg) at sample points K01, K05, and K07, all other heavy metals were below their corresponding ANZECC trigger values;
- (iii) The Nemerow's pollution index (Pn) estimation showed that sediment samples K01, K05 and K07 were slightly polluted with heavy metals based on the pollution criteria.
- (iv) The ecological risk assessment indicated that the heavy metals (Cu, Cd, Ni, Pb, Cr, and Zn) present at the current concentrations and environmental conditions pose a low ecological risk to the aquatic ecosystem.

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