Available online at http://ajol.info/index.php/ijbcs

Int. J. Biol. Chem. Sci. 5(1): 111-122, February 2011

ISSN 1991-8631

International Journal of Biological and Chemical Sciences

Original Paper

http://indexmedicus.afro.who.int

Analysis of Cu and Pb in the sediments of Kakum River, its estuary and tributaries

E.J. KORANTENG–ADDO *, J.K. BENTUM, B. AWUAH and E. OWUSU–ANSAH

School of Physical Sciences, Department of Chemistry, University of Cape Coast, Ghana.
**Corresponding author; E-mail: korantengaddo@yahoo.com*

ABSTRACT

This paper discusses the levels of some heavy metals (Cu and Pb) in the soil sediments of the Kakum River, its estuary and tributaries. Samples were collected at five sites, two at the estuary of River Kakum (MZ and TZ) and the other at confluence of three of its tributaries, namely Nkontro, Kakum and Sruwe. The total Cu concentrations were found to be: Nkontro, 4.656 mg/kg > Kakum, 3.197 > Sruwe 3.16 mg/kg kg > MZ, 1.893 mg/kg > TZ, 1.277 mg. The total lead concentrations were as follows: Nkontro, 6.611 mg/kg > Kakum, 6.063 mg/kg > MZ, 3.983 mg/kg > Sruwe, 3.901 mg/kg > TZ, 3.038 mg/kg. Generally, both Cu and Pb in the sediment (residue) at the five sites follow the trend Sruwe >Kakum > TZ > MZ, while the trend for the leachate was MZ > Kakum > TZ. The levels of both metals in the leachate at site MZ were higher compared to the levels at site TZ. The contamination factors and geo-accumulation index values suggest that the sediments of the river at the selected sites were not polluted with Pb and Cu.

Keywords: River Kakum, soil sediment, Copper and Lead.

INTRODUCTION

River sediments provide foodstuffs for living organisms. They also serve as a sink and reservoir for a variety of environmental contaminants, including heavy metals. Heavy metal concentrations in the water column can be relatively low, but the concentrations in the sediment may be elevated, since aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration. Low level discharges of a contaminant may meet the water quality criteria, but long-term partitioning to the sediments could result in the accumulation of high loads of pollutants. It has been estimated that about 90% of particulate matter carried by rivers settles in estuaries and coastal areas (Vermeulen et al., 1999; Santos Bermejo et al., 2003; Casper et al., 2004; Linnik et al., 2008; Viers et al., 2009). The occurrence of elevated levels of trace metals especially in the sediments can be a good indication of man-induced pollution and high levels of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering (Binning and Baird, 2001; Ukabiala et al., 2010). Heavy metals accumulate in sediments via several pathways, including disposal of liquid effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban,

industrial and agricultural activities, as well as atmospheric deposition (O'Connors et al., 2009).

Diagenetic processes in the sediments can change and redistribute these contaminants between the solid and the dissolved phases, but most of the elemental contaminants are immobilized through sedimentation (Jackson et al., 2005). The effect of heavy metal contaminants in the sediment may be either acute or chronic (cumulative) on benthic organisms (Fianko et al., 2007).

According to Neuberger et al. (2005), estimates of the flux of heavy metals into the sediments (sedimentary flux) of a river estuary and the diffusive flux of metals across the sediment-water interface provide quantitative approximations on the movement of heavy metals from the water column into the sediments, and vice versa.

The objective of this paper was to investigate the distribution and levels of sediment contamination by heavy metals, copper and lead, in the Kakum River, its estuary and tributaries.

MATERIALS AND METHODS

Study area

The sediment samples were collected at five sites along the Kakum River (Figure 1). Three of the sites were at the confluence of the Kakum River and its tributaries namely Kakum River, Sruwe River and Nkontro River. The three rivers were respectively labeled as Kakum, Sruwe and Nkontro. The other two samples were collected along the overlapping zones in Kakum estuary where seawater mixes with fresh water from these rivers. The sample site labeled MZ indicates the middle area where strong salt water and fresh water mix. The other was collected at the tidal river zone where fresh water preponderates and was labelled TZ. Samples were taken over a period of seven weeks, during the dry season in November/ December 2008. Four samples were collected weekly from each site.

Sample analysis

In the laboratory, the four weekly sediment samples were homogenized, air-dried at room temperature (25 ^{0}C) and subsequently kept for 1 h in an oven at 100 °C. The sample was ground in an agate mortal to below 63 mm mesh size and stored at 4 °C. 1 g of dried ground sample was shaken with 10 ml of 1.0 M ammonium acetate (CH_3COONH_4) on the shaker for 2 hours. After shaking, the solution was then filtered through filter paper into a 50 ml volumetric flask and the filtrate (leachate) was made to the mark with distilled water. The residue was washed with distilled water and the concentration of heavy metals in the residue determined by mineralization method described by MAFF (1981), using 1 ml of (5:1:1) 60% perchloric acid, concentrated sulphuric acid and nitric acid. The digest was subsequently diluted to 50 ml mark using ultra pure distilled water. The concentration of Pb and Cu in the solution was determined using Inductively Coupled Plasma Spectrophotometer (HP4500 series ICP/MS Spectrophotometer). All acid used were of analytical grade; quality control was assured by the use of procedural blanks and spikes.

Statistical analysis

The data from this study was subjected to statistical analyses using SPSS software (Version 16). The normality of the data was checked using Shapiro-Wilk procedure. Box plots (box-and-whisker diagrams) and Pearson's correlation methods were used to assess the variation of the examined metals.

One way ANOVA was applied to compare the mean concentrations of Cu and Pb in each sampling site. The critical differences among the different sampling sites were examined using Least Significant Difference (for equal variances assumed variables) and Games-Howell Post-Hoc (for equal variances not assumed variables) multiple comparisons tests.

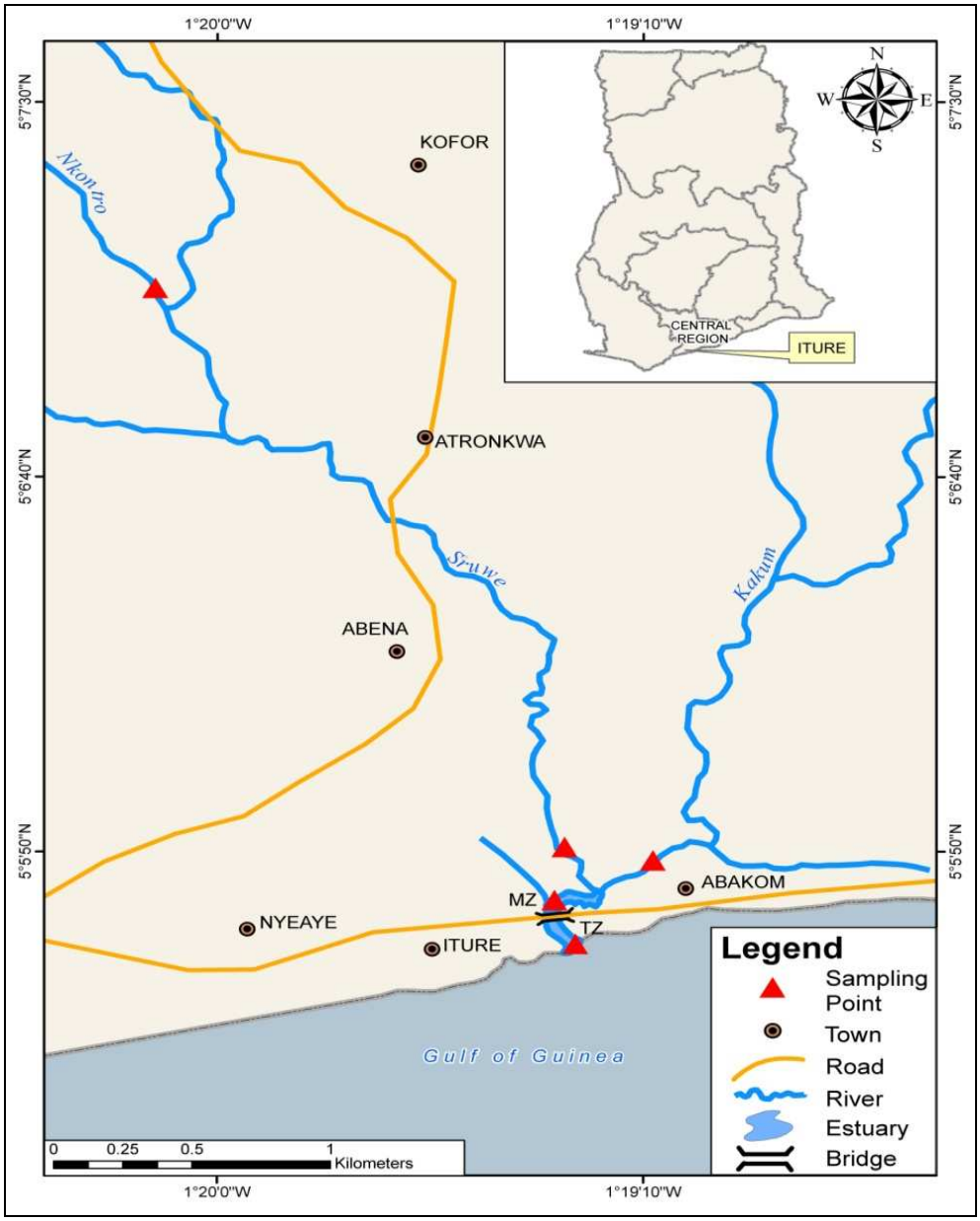

Figure 1: Map of Sampling Site.
Source: University of Cape Coast Geography and Planning Unit.

RESULTS

Copper and lead levels in samples

The results of the analyses of Cu and Pb in the soil sediments are shown in Tables 1 and 2. The variations of Cu and Pb in samples from studied sampling sites are depicted on Figures 2 and 3. The mean concentration of Cu metal in the residue of the soil sediments at the different sites over the seven week period were as follows: Sruwe, 5.778 mg/kg > Kakum, 5.374 mg/kg > Nkontro, 5.343 mg/kg > TZ, 1.81 mg/kg > MZ, 1.37 mg/kg.

For the leachate the Cu concentrations were: Nkontro, 3.97 mg/kg > MZ, 2.416 mg/kg > Kakum, 1.02 mg/kg > TZ, 0.745 mg/kg > Sruwe, 0.542 mg/kg.

The total Cu concentrations were found to be: Nkontro, 4.656 mg/kg > Kakum, 3.197 > Sruwe 3.16 mg/kg kg > MZ, 1.893 mg/kg > TZ, 1.277 mg/kg.

The Pb concentrations in the residue were: Nkontro, 9.778 mg/kg > Kakum, 7.924 mg/kg > Sruwe, 4.432 mg/kg > TZ, 4.293 mg/kg > MZ, 3.784 mg/kg. For the leachate the Pb concentrations were: MZ, 4.183 mg/kg > Kakum, 4.202 mg/kg > Nkontro, 3.445 mg/kg > Sruwe, 3.37 mg/kg > TZ, 1.779 mg/kg. The total lead concentrations were as follows: Nkontro, 6.611 mg/kg > Kakum, 6.063 mg/kg > MZ, 3.983 mg/kg > Sruwe, 3.901 mg/kg > TZ, 3.038 mg/kg. There were variations in the levels of both metals during the seven weeks.

Variations of copper and lead in sediments

Box plots (also called box-and-whisker plots) of Cu and Pb levels in the five sampling sites were examined (Figures 4 and 5). The line across the box represents the median, whereas the bottom and top of the box show the locations of the first and third quartiles (Q_1 and Q_3). The whiskers are the lines that extend from the bottom and top of the box to the lowest and highest observations inside the region defined by $Q_1 + 1.5(Q_3 - Q_1)$ and $Q3+1.5(Q_3 - Q_1)$. Individual points with values outside these limits (outliers) are plotted with small circles (each circle numbered).

According to Vega (1998) and Owusu-Ansah (2010), box plots provide a visual impression of sampling sites and the shape of the underlying data distributions. For example, box plots with long whiskers at the top of the box (such as that for copper concentrations in leachate at Nkontro river sediment samples) indicates that the underlying distribution is skewed toward relative high concentration. Box plots with large spread indicate seasonal variations of the metal concentrations (Mainly Pb concentrations in the samples). By inspecting these plots it was also possible to perceive differences among the five sampling sites.

Sampling sites similarities and differences

One way analysis of variance (One-Way ANOVA) results of the Cu levels in sediment leachate and residue samples showed that the differences in the five sampling sites were statistically significant (F=2.534, df=4, P-value =0.048, n=70). Hence a post-hoc test (multiple comparisons of sampling sites) was done using Games-Howell method. Games-Howell method was appropriate since the test of homogeneity of variances gave a p-value of 0.010 (Wie- Addo et al., 2010). Table 4 presents the multiple comparisons results of Cu concentrations in samples across the sampling sites. Table 4 shows that the difference between the Cu concentrations in the Nkontro river and Kakum river estuary (TZ) samples is statistically significant (P-value=0.014) at the 0.05 level. The results also showed high similarities between the other sampling points in terms of the Cu levels in the leachate and residue sediment samples.

On the other hand, the differences in the Pb concentrations in samples from the five sampling sites were generally not significant at the 0.05 level (F=2.394, df=4, P-value=0.059). However, when the Least Significant Difference (LSD) post hoc test (Table 5) was explored, the differences in the Pb levels in the samples from Nkontro and Sruwe rivers were statistically significant at the 0.05 level (P-value=0.047). The LSD result also showed that the difference in the Pb concentrations in Nkontro river and Kakum river estuary (TZ) was statistically significant (P-value=0.009) at the alpha level of 0.05.

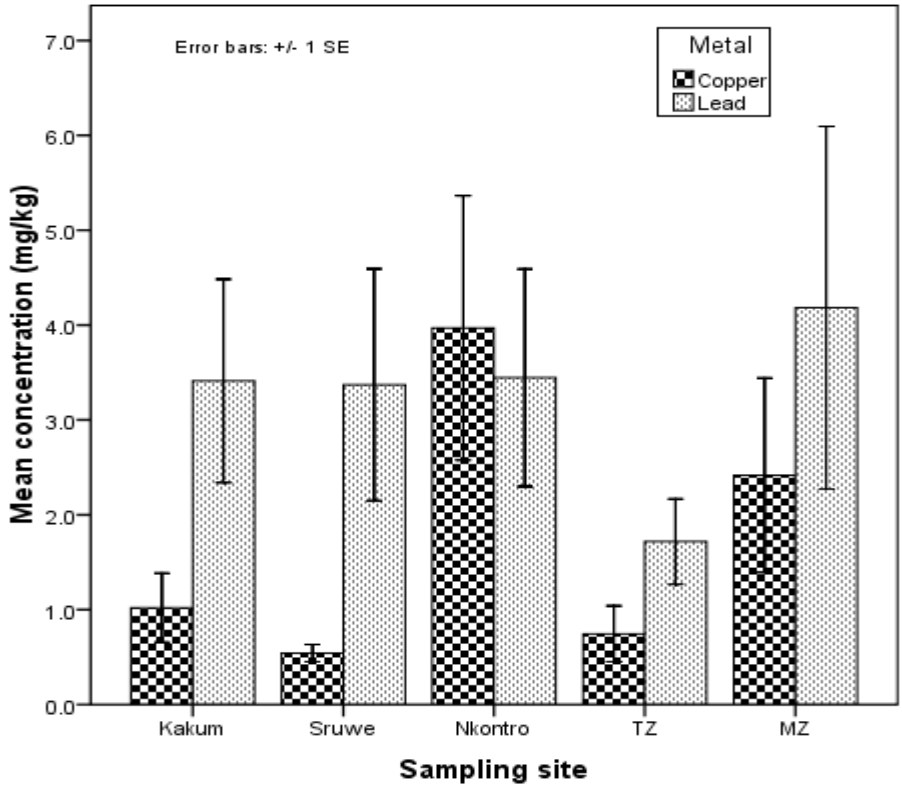

Figure 2: Variation of Cu and Pb concentrations in leachate sediment samples from sampling sites.

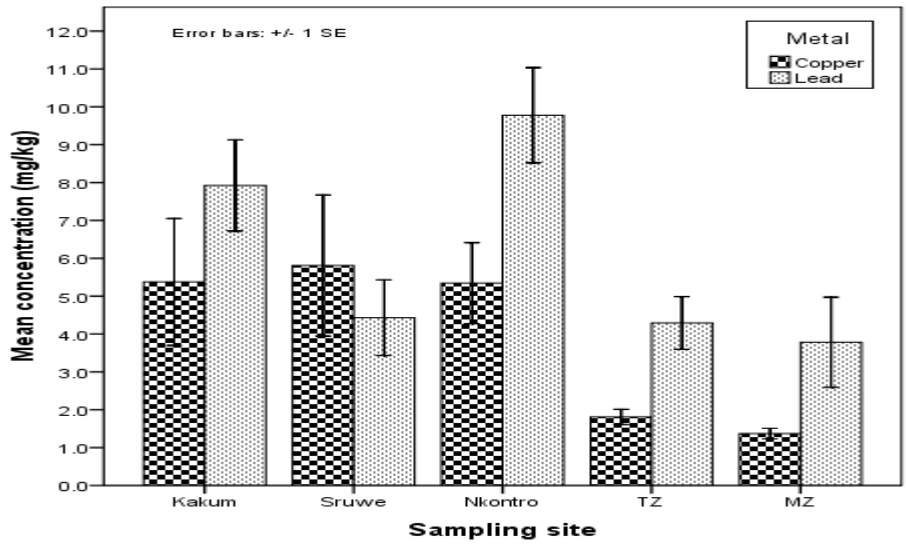

Figure 3: Variation of Cu and Pb concentrations in residue sediment samples from sampling sites.

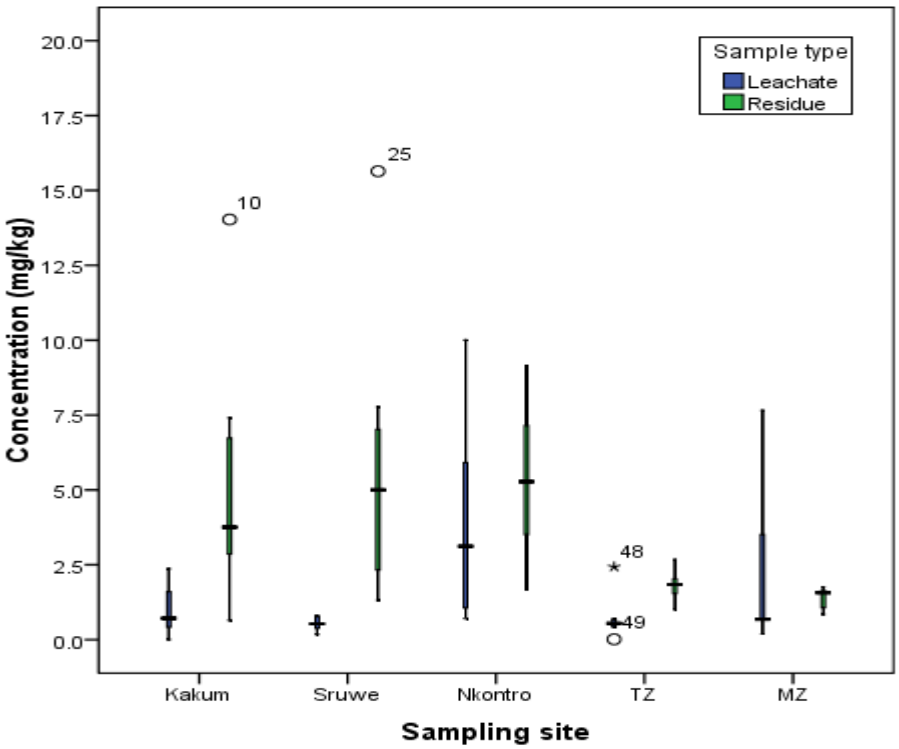

Figure 4: Box plot for copper concentrations in leachate and residue sediment samples.

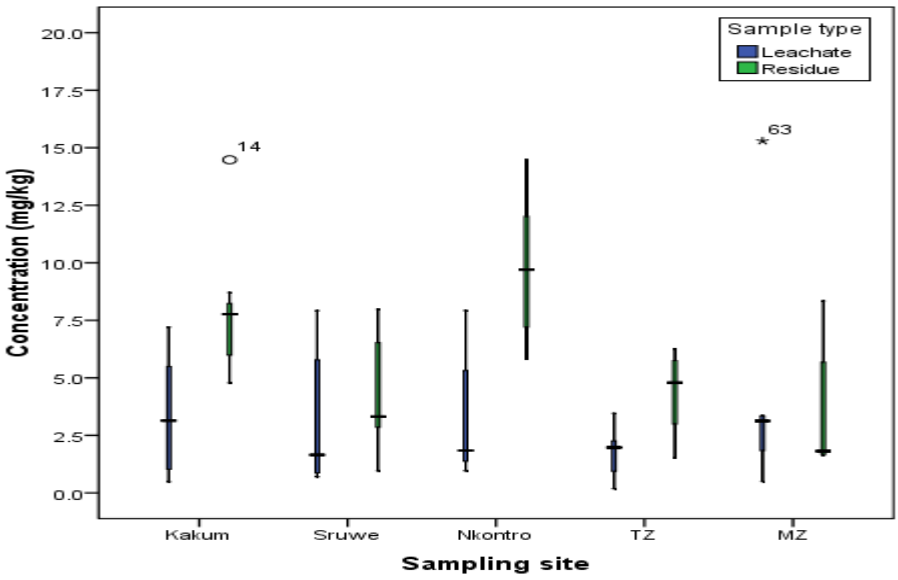

Figure 5: Box plot for lead concentrations in leachate and residue sediment samples.

Table 1 : Mean weekly concentration of Cu in soil sediments from Kakum River, its estuary and tributaries.

Sampling site		**1st week**	**2nd week**	**3rd week**	**4th week**
Kakum	Leachate	0.165±0.002	2.367±0.001	2.35±0.002	0.855±0.000
	Residue	0.648±0.022	3.487±0.001	14.03±0.007	3.755±0.001
Sruwe	Leachate	0.37±0.001	0.73±0.002	0.175±0.002	0.53±0.004
	Residue	2.575±0.001	6.275±0.017	2.085±0.001	15.64±0.001
Nkrotro	Leachate	0.7075±0.001	3.122±0.001	1.105±0.001	3.753±0.002
	Residue	3.444±0.003	1.67±0.001	9.025±0.000	9.13±0.001
TZ	Leachate	0.425±0.002	0.645±0.021	0.44±0.002	0.544±0.000
	Residue	2.13±0.000	1.015±0.001	1.84±0.001	1.73±0.002
MZ	Leachate	3.14±0.001	3.885±0.002	0.685±0.001	0.677±0.002
	Residue	1.58±0.002	1.695±0.002	1.165±0.002	1.76±0.001
		5th week	**6th week**	**7th week**	**mean**
Kakum	Leachate	0.715±0.002	0.01±0.001	0.675±0.001	1.02±0.964
	Residue	2.225±0.001	7.41±0.002	6.06±0.001	5.374±4.43
Sruwe	Leachate	0.805±0.001	0.791±0.001	0.39±0.003	0.542±0.243
	Residue	1.32±0.003	5.00±0.002	7.766±0.001	5.778±4.93
Nkrotro	Leachate	10.006±0.002	8.073±0.003	1.022±0.001	3.97±3.69
	Residue	5.28±0.001	3.57±0.002	5.28±0.002	5.343±2.83
TZ	Leachate	0.71±0.001	2.435±0.002	0.014±0.001	0.745±0.779
	Residue	1.935±0.000	1.35±0.001	2.67±0.001	1.81±0.534
MZ	Leachate	0.19±0.001	7.65±0.001	0.685±0.001	2.416±2.71
	Residue	1.57±0.002	0.975±0.002	0.845±0.001	1.37±0.369

Mean (± Standard Deviation) weekly concentration of Cu in soil sediment (mg/kg)

Table 2: Mean weekly concentration of Pb in soil sediments from Kakum River, its estuary and tributaries.

Sampling site		**1st week**	**2nd week**	**3rd week**	**4th week**
Kakum	Leachate	3.14±0.002	3.885±0.001	7.205±0.002	1.03±0.001
	Residue	5.845±0.001	8.704±0.002	7.766±0.005	6.125±0.002
Sruwe	Leachate	7.92±0.001	3.802±0.002	0.784±0.002	7.766±001
	Residue	7.975±0.005	7.615±0.002	3.32±0.001	2.855±0.006
Nkontro	Leachate	7.925±0.001	7.615±0.002	3.015±0.001	1.74±0.002
	Residue	9.70±0.001	13.535±0.004	14.475±0.001	6.7±0.002
TZ	Leachate	0.185±0.003	1.974±0.031	3.455±0.001	0.1870.002
	Residue	6.27±0.001	5.225±0.001	3.32±0.003	6.27±0.002

MZ	Leachate	0.500±0.001	3.125±0.003	0.655±0.002	3.015±0.002
	Residue	1.665±0.002	1.675±0.002	1.815±0.002	3.03±0.002
		5th week	**6th week**	**7th week**	**mean**
Kakum	Leachate	7.00±0.001	7.105±0.001	0.483±	4.202±2.89
	Residue	4.784±0.001	7.766±0.001	14.475±0.002	7.924±3.19
Sruwe	Leachate	0.965±0.001	0.70±0.001	1.654±0.001	3.37±3.23
	Residue	2.855±0.002	5.44±0.002	0.965±0.001	4.432±2.64
Nkontro	Leachate	0.965±0.003	1.015±0.001	1.84±0.001	3.445±3.033
	Residue	10.515±0.001	5.808±0.001	7.71±0.001	9.778±3.32
TZ	Leachate	2.00±0.002	1.69±0.001	2.53±0.002	1.779±1.19
	Residue	1.51±0.003	2.66±0.002	4.795±0.004	4.293±1.84
MZ	Leachate	3.355±0.002	3.335±0.004	15.295±0.001	4.183±5.06
	Residue	1.63±0.002	8.335±0.003	8.335±0.011	3.784±3.15

Mean (± Standard Deviation) weekly concentration of Pb in soil sediment (mg/kg)

Table 3: Contamination Factors and Igeo values of Cu and Pb.

Sampling Site	**Cu_{CF}**	**Pb_{CF}**	**$Igeo_{Cu}$**	**$Igeo_{Pb}$**
Kakum River	0.071	0.303	-4.4	-2.307
Sruwe River	0.07	0.195	-4.417	-2.943
Nkontro River	0.103	0.331	-3.858	-2.182
Bridge Estuary	0.028	0.152	-5.724	-3.305
Estuary	0.042	0.199	-5.156	-2.913

In environmental pollution studies correlation coefficients (R) indicates the nature of a relationship between two measurable variables. It denotes whether the pollutants move together or in opposite directions. Variables moving together imply they may be from a common source (Boamponsem et al., 2010).

In order to investigate the relationship between the Cu and Pb concentrations in the sampling sites, a correlation analysis was conducted using Pearson's method. Pearson's method was selected for the test since the data was generally normally distributed (parametric data) as indicated by the Shapiro-Wilk test (P>0.05). The result is presented in Table 6. Besides sampling point MZ, the relationship between Cu and Pb was very weak and not statistically significant at the 0.05 level. This may suggest that the sources of these metals at Kakum, Sruwe and Nkontro rivers are different.

Table 4 : Games – Howell's multiple comparisons of Cu concentrations across sampling sites.

Interval				95% Confidence	
(I) Sampling Site	(J) Sampling Site	Mean Difference (I-J)	Sig	Lower Bound	Upper Bound
Kakum	Sruwe	0.018	1.000	-4.371	4.406
	Nkontro	-1.463	0.785	-5.220	2.293
	TZ	1.915	0.329	-1.089	4.920
	MZ	1.300	0.751	-1.919	4.518
Sruwe	Kakum	-0.018	1.000	-4.406	4.371
	Nkontro	-1.481	0.841	-5.735	2.772
	TZ	1.898	0.515	-1.773	5.569
	MZ	1.282	0.846	-2.548	5.112
Nkontro	Kakum	1.463	0.785	-2.293	5.220
	Sruwe	1.481	0.841	-2.772	5.735
	TZ	3.379[a]	0.014	0.611	6.147
	MZ	2.763	0.081	-0.237	5.764
T Z	Kakum	-1.915	0.329	-4.920	1.089
	Sruwe	-1.898	0.515	-5.569	1.773
	Nkontro	-3.379[a]	0.014	-6.147	-0.611
	MZ	-0.616	0.809	-2.325	1.094
M Z	Kakum	-1.300	0.751	-4.518	1.919
	Sruwe	-1.282	0.846	-5.112	2.548
	Nkontro	-2.763	0.081	-5.764	0.237
	TZ	0.616	0.809	-1.094	2.325

[a] The mean difference is significant at the 0.05 level.

Table 5 : LSD's multiple comparisons of Pb concentrations across sampling sites.

Interval				95% Confidence	
(I) Sampling Site	(J) Sampling Site	Mean Difference (I-J)	Sig	Lower Bound	Upper Bound
Kakum	Sruwe	1.766	0.192	-0.909	4.441
	Nkontro	-0.944	0.484	-3.619	1.731
	TZ	2.662	0.051	-0.013	5.337
	MZ	1.684	0.213	-0.991	4.359
Sruwe	Kakum	-1.766	0.192	-4.441	0.909
	Nkontro	-2.710[a]	0.047	-5.385	-0.035
	TZ	0.896	0.506	-1.779	3.571
	MZ	-0.082	0.951	-2.757	2.593
Nkontro	Kakum	0.994	0.484	-1.731	3.619
	Sruwe	2.710[a]	0.047	0.035	5.385
	TZ	3.606[a]	0.009	0.931	6.281
	MZ	2.628	0.054	-0.047	5.303
TZ	Kakum	-2.662	0.051	-5.337	0.013
	Sruwe	-0.896	0.506	-3.571	1.779
	Nkontro	-3.606[a]	0.009	-6.281	-0.931
	MZ	-0.978	0.468	-3.653	1.697
MZ	Kakum	-1.684	0.213	-4.359	0.991
	Sruwe	0.082	0.951	-2.593	2.757
	Nkontro	-2.628	0.054	-5.303	0.047
	TZ	0.978	0.468	-1.697	3.653

[a] The mean difference is significant at the 0.05 level

Table 6 : Correlation matrix of the relationship between Cu and Pb across sampling sites.

	Leachate		Residue	
Sampling Site	**R**	**P - value**	**R**	**P - value**
Kakum River	0.162	0.728	0.282	0.539
Sruwe River	-0.179	0.702	-0.28	0.544
Nkontro	-0.548	0.203	-0.016	0.973
TZ	-0.073	0.876	0.092	0.845
MZ	-0.218	0.639	-0.810[a]	0.027

[a] Correlation is significant at the 0.05 level (2 – tailed).

DISCUSSION

Generally, both Cu and Pb in the sediment (residue) at the five sites follow the trend Sruwe >Kakum, > TZ, > MZ while the trend for the leachate was MZ > Kakum > TZ. The higher level of both metals in the leachate at site MZ compared to the levels at site TZ could be due to the fact that MZ is at middle area of the three overlapping zones in the estuary, where strong salt water and fresh water mix, and therefore are influenced by the metals in the sea water. The mean levels of both Cu and Pb in the leachates of sample MZ were higher than those in the residues. The Pb levels were higher than the Cu at all the sites.

Index of Geo-accumulation for the metals were determined to evaluate the degree of metal contamination or pollution in an aquatic and marine environment (Tijani et al., 2009) using the following expression (Ji et al., 2008):

$$Igeo = \frac{\log_2 Cn}{1.5(Bn)}$$

Where Cn is the concentration of metal examined in soil samples and Bn is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lithospheric effects (Mediola et al., 2008).

The geoaccumulation index consists of seven grades or classes (Huu et al., 2010).

Class 0 (practically uncontaminated): Igeo ≤0; Class 1 (uncontaminated to moderately contaminated): 0<Igeo < 1; Class 2 (moderately contaminated): 0 < Igeo < 2; Class 3 (moderately to heavily contaminated): 2 < Igeo < 3; Class 4 (heavily contaminated): 3 < Igeo < 4;

Class 5 (heavily to extremely contaminated): 4 < Igeo < 5; Class 6 (extremely contaminated): 5 < Igeo.

Class 6 is an open class and comprises all values of the index higher than Class 5. The elemental concentrations in Class 6 may be hundredfold greater than the geochemical background value.

The CF is the ratio obtained by dividing the concentration of each metal in the soil by the baseline or background value (concentration in unpolluted soil):

$$Contamination\ degree\ (CF) = \frac{\text{Concentration of metal in sample}}{\text{Concentration of metal in background}}$$

The contamination levels may be classified based on their intensities on a scale ranging from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) (Huu et al., 2010); the highest number indicates that the metal concentration is 100 times greater than what would be expected in the crust. The contamination factors and the geo-accumulation index for the metals are presented in Table 3.

According to Huu et al. (2010), the results indicated that none of the sediments are polluted with Pb and Cu.

Conclusion

Lead and copper were detected in both leachate and residues of the soil sediments. The results indicated that Pb was in higher concentration than Cu at all the sites.

The contamination factors and geo accumulation index values suggest that the sediments of the river at the selected sites were not polluted with Pb and Cu. It also indicates that the quality of the sediment has not been significantly affected or contaminated by anthropogenic activities.

This research may serve as a reference for future studies on the assessment of the levels of toxic metals in the study sites. It is envisaged that the results of this study will enrich the discussion and understanding of the effects of anthropogenic activities on the environment as well as the health implications of aquatic organisms. It is recommended that bioavailability of Cu and Pb to aquatic organisms involving metal speciation and exposure modeling using the Windermere humic acid aqueous model (WHAM) and Biotic Ligand Models (BLM) are integrated in future studies on metals assessment of the marine environment.

ACKNOWLEDGEMENTS

We wish to thank all those who gave us support during the collection of samples and analysis. We are also grateful to the Tema Oil Refinery (TOR) and Aboadze Thermal Plant Takoradi for their technical support.

REFERENCES

Binning K, Baird D. 2001. Survey of heavy metals in the sediments of the Swartkops River Estuary, Port Elizabeth, South Africa. *Water SA*., **27**(4): 461-468.

Boamponsem LK, Adam JI, Dampare SB, Nyarko BJB, Essumang DK. 2010. Assessment of atmospheric heavy metal deposition in the Tarkwa gold mining area of Ghana using epiphytic lichens. *Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms*, **268**: 1492-1501.

Casper ST, Mehra A, Farago ME, Gill RA. 2004. Contamination of surface soils, river water and sediments by trace metals from copper processing industry in the Churnet River Valley, Staffordshire, U.K. *Environ. Geochemistry and Health*, **26**: 59.

Fianko JR, Osae S. Adomako D, Adotey JK, Serfor- Armah Y. 2007. Assessment of heavy metal pollution of the Iture Estuary in the central region of Ghana. *Environ. Monit. & Assess.*, **131**: 467-473.

Huu HH, Rudy S, Van Damme A. 2010. Distribution and contamination status of heavy metals in estuarine sediments near Cau Ong harbor, Ha Long Bay, Vietnam. *Geology Belgica*, **13**(1-2): 37-47.

Kow A, Wie- Addo, John Blay Jnr., Owusu-Ansah E. 2010. Assessing the effectiveness of the non-polar extract of *Crotalaria retusa i*n the control and management of the flea beetle, *Podagrica uniformis* (L) on okro, *Abelmoschus esculentus* (L) *moench]*. *J. Chem. Pharm. Res*., **2**(4): 387-397.

Jackson RN, Baird D, Els S. 2005. The effect of the heavy metals Pb (2+) and Zinc (2+) on the brood and larval development of the burrowing crustatean *Callianassa kraussi*. *Water SA*, **31**(1): 107-116.

Ji Y, Feng Y, Wu J, Zhu T, Bai, Ding C. 2008. Using geo-accummulation index to study source profiles of soil dust in China. *J. Environ. Sci.*, **20**(5): 571–578.

Linnick PM. 2008. Zinc Lead and Cadmium speciation. Lakes & Reserviours: Research & Managenent. *Wiley Online Library*, **5**(4): 261 – 270.

Mediolla LL, Domingues MCD, Sandoval MRG. 2008. Environmental assessment of and active tailings pile in the State of Mexico (Central Mexico). *Research Journal of Environmental Sciences*, **2**(3): 197–208.

Ministry of Agriculture, Fisheries and Food (MAFF). 1981. Code of good agriculture

practice for the protection of soil. Draft consultation document. *London Academic S.L. Leon*., **221**: 45.

Neuberger – Cywiak L, Achituv Y, Garcia EM. 2005. Sublethal effect of Zn++ and Cd++ on respiration rate ammonia excretion and O:N ratio of *Donas trunchulus* (Bivalria Donacidae). *Bull. Environ. Contam. Toxicol*., **75**(3): 504-514.

O'Connors TP, Kostas D, Daskalais JL, Paul JF, Summers JK. 2009. Environmental toxicology and chemistry. *Wiley online library*, **17**(3): 468-471.

O'Connors TP, Paul JF. 2000. Misfit between sediment toxicity and chemistry. *Marine Pollut. Bull.*, **40**(1): 59-64.

Owusu-Ansah E, Ametepe ON, Boamponsem LK, Asiamah I, Koramteng-Addo JE, Tuffour JK. 2010. Quality evaluation of locally manufactured amodiaquine tablets in Accra, Ghana. *J. Chem. Pharm. Res*., **2**(4): 378-386.

Santos BJC, Beltran R, Gomez Ariza JL. 2003. Spatial variation of heavy metals contamination in sediments from Odiel River (Southwest Spain). *Environ. Int*., **26**: 29.

Tijani MN, Onodera S. 2009. Hydrogeochemical assessment of metals contamination in an urban drainage system: A case study of Osogbo township, SW-Nigeria. *Journal of Water Resource and Protection*, **3**: 164-173.

Ukabiala CO, Nwinyi OC, Abayomi A, Alo BI. 2010. Assessment of heavy metals in urban highway runoff from Ikorodu expressway, Lagos, Nigeria. *J. Environ. Chem. Ecotoxicol*., **2**(3): 34-37.

Vega M, Pardo R, Barrado E, Deban L. 1998. Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Wat Res.*, **32**(12): 3581-3592.

Vermeulen LA, Wepener V. 1999.Spatial and temporal variations of metals in Richards Bay Harbour (RBH), South Africa. *Marine Pollut. Bull*. **39** (1): 304.

Viers J, Dupre B, Gaillardet J. 2009. Chemical composition of suspended sediments in World Rivers: New insights from a new database. *Sci. Total. Environ*., **407**(2): 853-868.