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Assessment of Heavy Metal Contamination of the Lower Pra River, Ghana

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ABSTRACT

In this study, surface water and sediments were collected from twenty-four (24) different sites in four (4) different locations along the longitudinal transect of the Lower Pra river and evaluated for their quality using several multivariate statistical methods including Principal Component Analysis and pollution index model. Environmental parameters such as heavy metals, water nutrients and physicochemical parameters were determined in the dry and wet periods. The PCA indicated that heavy metals Fe, Mn, Ni and Zn were from predominantly natural sources, whilst Hg, Cu and Pb were from anthropogenic sources. Fe, Mn, Zn and Ni had an association with TSS whilst Hg, Se and Pb had an association with TDS.

Introduction

Water is man's most important resource and throughout history it has been the key to socioeconomic development. However, human activities have led to the introduction of chemicals which tend to pollute water.

A pollutant is any substance in the environment, which causes objectionable effects, degradation of the environment, reduction in the quality of life and may eventually lead to death. Pollution of water negatively impacts the economy of many developing countries specifically in the area of human health and ecosystem disruption. Heavy metal pollution of water bodies remains a serious environmental concern. This can occur naturally or from anthropogenic activities (Jarup et al., 200). Some trace metals like Zn, Fe, and Cu are essential in many biological processes but at high concentrations, they can be detrimental to human health (Mertz, 1981). It is therefore necessary to assess the levels of these trace metals so as to safeguard the health of the individuals in the catchment area. The Pra River is the longest river in the south western part of Ghana and it is adjoined by two major tributaries i.e., the Birim and the Offin Rivers, with a catchment area of 23188 km^2. Many mining and quarrying units are located along the river basin since this area is rich in mineral deposits. Alluvial gold mining has been predominant around the northern parts of the Pra basin over the years, but illegal gold mining is on the rise in recent times (Donkor et al., 2006). As a consequence of these mining activities, there is the release of pollutants in to the environment. The objective of this study therefore is to determine the levels of these metals in sediments and water from the lower Pra. In addition, Multivariate statistical analyses such Principal Component Analysis (PCA) and models like Pollution Load Index (PLI) will be used to assess the quality of water (Manoj., et al 2012; Nair et al., 2010; Oishlaqi and Moore, 2001).

Materials and Method

Study Area

The study area is situated between latitudes 05˚ 08' - 05˚ 00' N and longitudes 001˚ 39' - 001˚ 37'W covering a distance of 20 km as shown in Figure 1. The study area is located in the south western belt of Ghana with a relative humidity of 60 - 90% (Dickson and Benneh, 2004). Surface water and sediment samples were collected from twenty-four (24) different sites in four (4) different locations along the longitudinal transect in October representing the wet season and in March representing the dry season. Water and sediment samples were collected using the ultra-clean free metal sampling technique as described by Bonzongo et al., 1996 and Warner et al., 2005. Water samples for heavy metal determination were collected into acidified pre-treated Teflon bottles. Prior to sampling, the bottles were rinsed with water and after collection the samples were acidified with concentrated HNO_3 and stored in an ice chest and transported to the laboratory for subsequent analyses. Water samples for Dissolved Oxygen (DO) were collected into 300 ml Biological Oxygen Demand (BOD) bottles with the Winkler reagent fixed on the field prior to analysis. Water samples for nutrients and ion determination were collected into separate acid treated Teflon bottles and stored in an ice chest and transported to the laboratory for subsequent analyses. Physicochemical parameters such as pH, electrical conductivity (EC) and temperature were measured in situ using a Hanna's portable dual purpose pH-conductivity meter. Sediment samples were collected into pre-treated poly-ethylene bags stored in an ice chest and finally transported to the laboratory for subsequent analyses.

Reagents used for the laboratory work were of analytical grade. Analysis for trace metals was done using flame atomic absorption spectrophotometer (FAAS) AGILENT 270 FS, and mercury was analyzed using, cold vapor (CV) AAS. Alkali metals such as Na and K were analyzed using the flame photometric method (APHA, 1998). Water nutrients (NO_3^-, SO_4^{2-} and PO_4^{3-}) were analyzed using various procedures described in APHA, 1998. Sediment quality was evaluated by the use of pollution load index (PLI) (Cabrera et al., 1999; Banu et al., 2013; Iwuoha et al., 2012)

A multivariate statistical analysis, such as the Principal Component Analysis was used to identify the possible sources of heavy metals and their association with physicochemical parameters such as TSS, TDS and some anionic species.

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Figure 1. Map of study area including sampling locations

Results and Discussion

Physicochemical parameters

The results of the physical parameters of water and sediments are shown in Table 1. Water temperature ranged from 27.5 °C to 29.5 °C in the wet season and 30.8 °C to 32.0 °C in the dry season. The mean electrical conductivity of the water samples in the wet season (25850 µS /cm), was higher than the measured value observed for the dry season (2386.13 µS/cm). This could be as a result of run off during the wet season. Dissolved oxygen (DO) levels varied between 6.40 and 6.60 mg/L in the wet season and between 13.11 and 13.22 mg/L for the dry season. The higher dissolved oxygen levels observed in the dry season could be attributed to the higher water temperature in the dry season. In the dry season the pH of river water was neutral and no variation was observed for the two seasons, with a mean value of 7.2 in the wet season and 7.7 in the dry season. The total suspended solids (TSS) measured ranged between 91 and 509 mg/L with an average 322 mg/L for the wet season while that measured for the dry season varied between 14 and 376 mg/L with a mean value of 160 mg/L The difference in the two values can be attributed to the influence of runoff during the rainy season. Mean concentration of total dissolved solids (TDS) measured in the wet season was 1,012 mg/L while the concentration of TDS measured in the dry season was (7527 mg/L). The higher concentration of TDS in the dry season could be as a result of evaporation of water during the dry season.

Table 1: Descriptive statistics of some physicochemical parameters determined

Variable	Units	Mean	SD^e	Min.	Max.
pH^a in sediment	-	5.7	0.2	5.53	6.0
pH^a in water	-	7.2	0.2	6.98	7.38
pH^b in sediment	-	5.1	0.8	4.1	6.1
pH^b in water	-	7.7	0.6	6.73	8.31
Temp^a	°C	28.6	0.9	27.5	29.5
Temp^b	°C	31.3	0.5	30.8	32.0
EC^a	µS/cm	25850	-	36900	11600
EC^b	µS/cm	2385.13	-	3999	152
DO^a	mg/L	-	-	6.40^c	6.60^d
DO^b	mg/L	-	-	13.11^d	13.22^c
TSS^a	mg/L	322	149	91	509
TSS^b	mg/L	160	84	14	376
TDS^a	mg/L	1013	160	757	1164
TDS^b	mg/L	7527	7016	752	20764

^{a} Wet season ^{c} Upstream Daboase ^{e} Standard deviation

^{b} Dry season ^{d} Downstream Shama

Table 2: Descriptive statistics for heavy metals determined in sediments

Parameters	Units	Mean	SD^e	Skew	Min.	Max	Range	Co. V%	TEL^f
Fe^a	mg/Kg	5738	360	1.693	5470	6388	918	6.2	
Fe^b	mg/Kg	773	89	0.407	675	895	220	11.5	
Mn^a	mg/Kg	213	42	0.322	156	274	118	19.6	
Mn^b	mg/Kg	24	7	-0.540	15.2	30	14.8	11	
Pb^a	mg/Kg	14	10	1.868	7	31	24	71.4	
Pb^b	mg/Kg	8	5	0.420	0.9	13.6	12.7	62.5	35^d
Cd^a	mg/Kg	0.8	0.3	-0.355	0.3	1.3	1.0	37.5	0.6^d
Cr^b	mg/Kg	1.9	0.7	1.154	1.2	3	1.8	36.8	37.3^d
Ni^a	mg/Kg	7	1	-0.370	5	8	3	14.3	
Ni^b	mg/Kg	1.6	0.8	1.174	0.9	2.8	1.9	50	18^d
Cu^a	mg/Kg	2.8	0.9	0	2	4	2	30	
Cu^b	mg/Kg	5	1	-0.124	2.6	7	4.4	20	35.7^d
Zn^a	mg/Kg	55	1	1.697	41	82	41	27.2	
Zn^b	mg/Kg	4	2	1.926	3.1	7.4	4.3	40.3	120^d
Se^a	mg/Kg	65	54	1.909	-	70	70	83.4	
Se^b	mg/Kg	0.9	0.5	1.300	0.4	1.8	1.4	55.6	
Hg^a	µg/Kg	205	215	1.602	-	500	500	104.9	
Hg^b	µg/Kg	1111	869	1.999	297	2568	2271	78.1	200^c

^{a} Wet Season ^{c} USEPA (19) ^{e} Standard deviation

^{b} Dry Season ^{d} Interim Sediment Quality Guidelines (ISQG) (20) ^{f} Threshold Effect Level (TEL)

Heavy metals, nutrients and other ions

Heavy Metals

The results for the analysis of heavy metals, in the sediments and water are shown in Table 2 and Table 3 respectively. From Table 2, the mean concentration of Fe in sediments was 5738 mg/Kg and varied from 5470 to 6388 mg/Kg) in the wet season and varied between 675 and 895 mg/Kg with 773 mg/Kg in the dry season.

The overall mean concentration of Mn in sediments in the dry season was found to be 24 mg/Kg, and ranged between 15.2 and 30 mg/Kg which is much lower than what was recorded for the wet season which ranged between 156 and 274 mg/Kg) with an average of 213 mg/Kg. Zn was generally higher in the wet season with mean values of 55 mg/Kg, and ranging between 41 and 82 mg/Kg) than in the dry season with a mean value of 4.0 mg/Kg, ranging from 3.1 to7.4 mg/Kg.

Ni in sediments was generally higher in the wet season than in the dry season with an overall mean concentration of 7 mg/Kg varying from 5 to 8 mg/Kg in the wet season and a mean of 1.6 mg/Kg which ranged between 0.9 and 2.8 mg/Kg in the dry season. Cr and Cd had concentrations below the detection limit in sediments for both the wet and the dry seasons. Generally, the concentrations of the heavy metals measured were higher for the wet season compared to the dry season. Heavy metals distribution in sediments was in the decreasing order of Fe > Mn > Zn > Pb > Ni > Cu > Cd > Cr in the wet season and a decreasing order of Fe > Mn > Pb > Cu > Zn > Ni > Cr > Cd in the dry season.

From Table 3, the concentration of Fe measured were highest in surface waters with a mean concentration of 6 mg/L in the wet season and a mean concentration of 0.7 mg/L in the dry season. Concentrations of Fe were generally higher for the wet season than the dry season for all locations. Maximum average concentration of Mn in the wet season was recorded at Beposo (0.11 mg/L) with a mean of 0.05 mg/L which varied between 0.022 and 0.11 mg/L) in the wet season and a dry season mean concentration of 0.013 mg/L The concentration of. Zn measured had a mean concentration of 0.056 mg/L varying from 0.04 to 0.07 mg/L for the wet season and a mean concentration of 0.014 mg/L and ranged between 0.0095 and 0.0245 mg/L) for the dry season, which is far less than what was recorded for the wet season. Concentrations of Cd and Cr were largely below the detection limits in surface water for both seasons at some selected sites. The levels of heavy metals in the surface water samples was found to be in the decreasing order of Fe > Zn > Mn > Ni≈ Cu > Pb > Cd > Cr in the wet season and for the dry season a decreasing order of Fe > Pb > Cu > Zn > Mn > Ni > Cr > Cd.

Nutrients and other ions

From Table 3, water nutrients and ions determined in surface water were PO_4^{3-} , SO_4^{2-} , NO_3^- , Na^+ and K^+. Four of the ions Na^+, K^+, SO_4^{2-} and NO_3^- had their overall mean concentrations for the study area higher in the dry season than in the wet season. Overall mean concentration of PO_4^{3-} for the dry and wet season were close with values of 0.28 mg/L for the wet season and 0.2 mg/L for the dry season. Mean concentration of NO_3^- in the wet season was 1.1 mg/L varying between 0.509 and .969 mg/L which had increased to 2 mg/L with a range of 0.392 to 4.113 mg/L in the dry season. SO_4^{2-} levels were higher for all four locations in the dry season than in the wet season with mean concentration of 56 mg/L and varied between 11.304 and 121.118 mg/L for the dry season and a mean of 11 mg/L and ranged between BDL and 16.894 mg/L for the wet season. There was a sharp rise in the concentration of Na and K across the sampling sites in Shama. Ions and water nutrients were in the increasing order $PO_4^{3-} < NO_3^- < K^+ < SO_4^{2-} < Na^+$ for the wet season and an increasing order of $PO_4^{3-} < NO_3^- < SO_4^{2-} < K^+ < Na^+$ for the dry season

Pollution Load index (PLI)

Level of contamination of heavy metals in sediments was assessed using the pollution load index (PLI) model. This model is based on the concentration factor (C) of heavy metals in sediments and is expressed as the ratio of the concentration of heavy metals in the sediment to its corresponding background value. The PLI was then calculated as the nth root of the product of the nth contamination factors evaluated. PLI values below the base line of 1 indicate that sediments are in perfect condition. A PLI value above 1 indicates pollution (Cabrera et al., 1999; Banu et al., 2013; Iwuoha et al., 2012). The contamination factor and pollution index are computed as shown in the expression below:

$$(Cf) = \frac{C_m}{C_b}$$

Where C_m is the concentration of heavy metals in sediments and C_b is the corresponding background value. In this study, the average background value of trace metals in soils as proposed by the department of environmental quality of the state of Oregon, USA was used (DEQ, 2013).

$$PLI = (Cf1 \times Cf2 \times Cf3 \times \ldots . \times Cfn)^{(1/n)}$$

Where n is the count of heavy metal species and is the contamination factor of the individual heavy metals present. In computing the PLI of sediments. The of eight heavy metals Cu, Hg, Mn, Zn, Cd, Cr, Ni and Pb were evaluated for both seasons.

The computed values of the various locations for the two seasons are given in Tables 4 and 5. The values of Hg for both seasons for locations which were found to be active in AGM activities were above 1 and this is considered to be moderately contaminated. values of Cd were also above 1 mining locations Daboase and Beposo. The degree of contamination was described as moderate. From Figure 2, the PLI of sediments for the two seasons was below 1 and overall classified as unpolluted. Sediments in Borkokope have the least PLI values along the watercourse for the two seasons and this is because as at the time of the study, this particular location had minimal anthropogenic activities. The PLI for sediments in Daboase and Beposo were high compared to sediments in the other two locations and this is due to illegal gold mining and quarrying activities in these areas.

. Table 4: PLI and Contamination factors of heavy metals in sediments for the Wet Season

Location	Contamination factors (Cf)								PLI
	Mn	Pb	Cu	Cd	Cr	Ni	Zn	Hg	
Daboase	0.108	0.089	0.088	1.250	0.001	0.170	0.261	1.39	0.13
Beposo	0.124	0.139	0.118	0.476	0.001	0.128	0.283	2.174	0.13
Bokorkope	0.086	0.101	0.088	1.510	0.001	0.170	0.227	0.004	0.06
Shama	0.152	0.392	0.059	2.063	0.001	0.106	0.456	0.004	0.08

Table 5: PLI and Contamination factors of heavy metals in sediments for the Dry Season

Location	Contamination factors (Cf)								PLI
	Mn	Pb	Cu	Cd	Cr	Ni	Zn	Hg	
Daboase	0.0116	0.1721	0.024	0.606	0.026	0.0595	0.0172	3.313	0.08
Beposo	0.0161	0.0759	0.205	0.6	0.0394	0.0361	0.018	11.165	0.11
Bokorkope	0.0084	0.0113	0.134	0.63	0.018	0.019	0.02	1.29	0.05
Shama	0.0166	0.1265	0.025	0.6349	0.015	0.023	0.0411	3.69	0.08

Principal Component Analysis (PCA)

Principal component analysis was performed to identify the possible sources of environmental variables (heavy metals, nutrients, and physicochemical parameters) in water and sediments. PCA normally involves auto-scaling of data to better describe the relationship between variables. First, the mean is subtracted from each data dimension to produce a data set whose mean is zero from which the co-variance matrix is extracted. Three principal components were selected, since all the other components with Eigen values less than one are regarded as less significant (Manoj et al., 2012; Oishlaqi and Moore, 2007). The principal components were varimax, rotated with Kaiser-normalization and then three components (factors) were extracted. Based on their absolute values, factors greater than 0.75, between 0.75-0.5, and 0.5-0.3 are classified as strong, moderate and weak respectively. Variables with factor loadings above 0.5 and within the same principal component group (PC1, PC2 or PC3) are said to be associated, and this suggests that they have a similar source (Manoj et al., 2012; Oishlaqi and Moore, 2007). The cumulative variance is the percentage of data variability that was accounted for during the data reduction processes. The rotated factor loadings of the principal component to a descriptor space of three dimensions for environmental variables in sediment and surface water are illustrated in the PCA 1 (figure 2) and the PCA 2 (figure 3) respectively. For sediments, three components extracted accounted for 71% of all data variation with only a 29% loss of information. For water, 70% of all the data variation accounted for 30% loss of data.

The cumulative variance and factor loadings of the three principal components for sediments (PCA 1) are represented in table 6. PC1 with variance of 39% comprising of Ni, Mn, Zn, and Fe. Cu, Hg and Se were the major contributors to PC2 with 17.8% variance. PC3 with a 13.9% variance comprises both Pb and Hg. Hg belonging to both PC2 and PC3 implies that these are coming from similar anthropogenic sources in the study area. Effluents discharged from mining sites into the river are contaminated with Hg from amalgamation and cyanidation practices. Chemicals used in these processes are contaminated with heavy metals like Pb and Cu which cause sediment pollution. Natural and artificial weathering of rocks in the study area accounted for heavy metals such as Ni, Fe, Mn and Zn (PC1) and was released into the aquatic environment through alluvial deposits. Artificial weathering practices such as quarrying and sand winning are other ways in which heavy metals or minerals in their ores are released into the environment.

The cumulative variance and factor loadings of the three principal components for Surface water are represented in table 7. The PC1 with a variance of 34% comprises heavy metals such as Pb, Hg and Se, physicochemical parameter such as TDS, macro elements such as Na, K and ions such SO_4^{2-}. Trace metals such as Fe, Mn, Zn and Ni and physicochemical parameters such as TSS with high factor loadings contributed to PC2. Ni (0.584) and Hg (0.553) with weak factor loadings and water nutrients, NO_3^- (0.862) and PO_4^{3-} (0.613) with stronger factor loadings contributed to PC3. The association between Hg and Se is evident in the PCA1 for sediment and the PCA 2 for surface water. The PCA 2 shows that heavy metals such as Fe, Mn, Zn, and Ni are associated with TSS and these suspended solids are responsible for the distribution of trace metals in the study area. Alkali metals Na and K, SO_4^{2-} and trace elements such as Hg, Pb and Se are associated with the dissolved solids. Water nutrients such as PO_4^{3-} and NO_3^- could be associated with Ni as an insoluble complex in the suspended phase or with Hg as complexes in the dissolved phase

Table 6: Principal Component Analysis (PCA 1) of sediments

Elements	PC1	PC2	PC3
Fe	**.978**	.080	.029
Mn	**.935**	.131	.195
Pb	.244	.011	**.808**
Cu	-.487	**.597**	-.238
Cd	.041	.275	-.047
Zn	**.899**	.032	.347
Ni	**.649**	.382	-.440
Hg	.005	**.670**	**.531**
Se	.387	**.747**	.072
Eigen values	3.763	1.501	1.109
% Total Variance	38.998	17.878	13.945
C. Variance %	38.998	56.866	70.811

Table 7: Principal Component Analysis (PCA 2) of Surface water

Parameters	PC1	PC2	PC3
Fe	-.446	**.744**	-.224
Mn	-.108	**.745**	.212
Pb	**.641**	-.367	-.168
Cu	.164	.059	-.550
Cd	.039	.361	.065
Ni	-.112	**.632**	**.584**
Zn	-.199	**.701**	-.349
Hg	**.705**	.135	**.553**
Se	**.889**	.118	-.175
TSS	.182	**.874**	.143
TDS	**.969**	-.197	.016
Na	**.977**	-.115	-.029
K	**.978**	-.072	-.027
A1-NO_3^-	.228	.185	**.862**
B1-SO_4^{2-}	**.596**	-.576	-.009
C1-PO_4^{3-}	-.516	.443	**.613**
Eigen Values	6.183	3.251	1.813
% Total Variance	33.988	23.024	13.282
% C. Variance	33.988	57.012	70.294

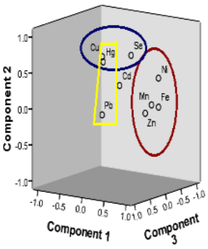

Figure 2: PCA 1 loading plot for the rotated Components for Sediments

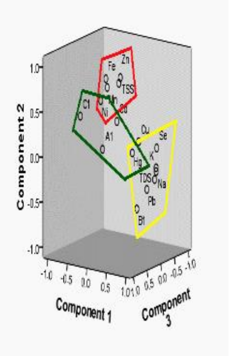

Figure 3: PCA 2 loading plot for the rotated Components for Surface water

Conclusion

Several statistical methods were used to evaluate the water and sediment quality in the study area. The application of PCA was an effective way in the overall assessment of environmental parameters such as heavy metals, water physicochemical parameters and nutrients. The Principal Component Analysis showed the sources of heavy metals and their association with parameters such as TSS or TDS. From PCA 2 it was found that Fe, Mn, Zn, and Ni were associated with suspended solids whilst elements such as K, Pb, Hg, Na and Se were found to be associated with the dissolved solids. Hg had an association with both Cu and Pb for both plots and this was attributed to anthropogenic sources, since illegal miners acquire Hg through illegally means and could be contaminated with these heavy metals prior to or during the amalgamation process. Pollution Index results indicate that the overall sediment quality was below the baseline value of 1 which shows that sediments were not polluted with respect to heavy metals. However, contamination factors () for Hg and Cd were above 1 in illegal gold mining areas, and therefore sediments showed a considerable degree of contamination. Apart from Hg and Cd that had their mean concentrations in the sediment exceeding the USEPA and ISQG threshold effect level respectively. Levels of Ni, Cu, Cr, Se, Mn, and Zn in surface water were all below WHO maximum permissible limits, for drinking water for both seasons (WHO, 2011). The results from this study revealed that illegal gold mining activities affect the quality of water.

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