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Multivariate and spatial assessment of water quality of the Lower Pra basin, Ghana

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Abstract

In this paper, multivariate statistical approaches based on principal component analysis (PCA) coupled with spatial assessment were employed to assess physicochemical parameters (turbidity, pH, electrical conductivity, total dissolved solids, total suspended solids, nitrates, nitrite, phosphate, ammonium, total hardness, total alkalinity, dissolved oxygen, BOD, Na, Cl, Ca, HCO_3, SO_4 and F) and heavy metals (Cu, Cd, Fe, Mn, Pb, Hg and Zn) of more than fifty five (55) water samples from 20 mining and non-communities within the lower Pra basin. The correlation matrix, however, shows significant inter-metal relationships ($p<0.05$ and $p<0.01$). The Fe–Mn correlation is recognized as the weakest with a correlation coefficient $r=0.422$. Also, significant strong correlations ($r>0.5$) were found between Zn – Cd, Pb–Zn, Pb – Cd, Pb – Cu, Cu – Zn, Cu – Cd, Hg – Zn, Hg – Cd, Hg - Cu and two more toxic metals, Hg and Pb. From the results of the principal component analysis on surface water in the study, component model 1 is interpreted to be contaminated water with mercury. This is because Hg has the highest correlation value (0.985). Within the study area, illegal artisanal small scale miners (popularly referred to as galamsey) use mercury extensively in their activities. The mercury is a steady source of contamination of the surface water in the Lower Pra Basin area. The use of mercury in gold mining by the Artisanal Small Scale Miners constitutes a point source of contamination.

Keywords: Multivariate statistical techniques, Principal component analysis, Lower Pra Basin, Heavy Metals

1. Introduction

Toxic chemicals such as heavy metals in urban water bodies are of great environmental concern because of their potential long-term effects on human health particularly in developing countries where remedial techniques do not exist (Armah et al., 2010; Iscen et al., 2008; Obiri et al., 2010). The origin of such metals in the natural environment is either geogenic or anthropogenic. In general, the anthropogenic releases constitute a constant source of pollution, whereas surface runoff is a seasonal phenomenon which is affected by climate within the water system. Many investigations have been conducted on anthropogenic contaminants of ecosystems (Shrestha and Kazama, 2007; Simeonov et al., 2003; Wu and Wang, 2007). The application of multivariate statistical techniques such as principal component analysis (PCA) assists in the interpretation of complex data matrices for a better understanding of water quality and ecological characteristics of a study area. This technique coupled with spatial interpolation (Chehata et al., 2007) provide the identification of possible sources that affect water environmental systems and offer a valuable tool for reliable management of water resources as well as rapid solution for pollution issues (Simeonov et al., 2002).

In Ghana and for that matter the study area, one of the main anthropogenic sources of concern is mining. Gold mining is widespread and according to Naylor (2003), it contributes about 44% of Ghana's export earnings. Large-scale as well as small – scale extraction of gold occurs predominantly along the banks of river Pra in Western, Eastern and Ashanti regions *e.g.* Bibiani and Obuasi, and is accompanied by arsenic, mercury and sulphur contamination to water bodies, soil and even air pollution causing acid rain and degradation to the surrounding environment and impacts on human health (Amonoo-Niezer et al., 1996; Asante et al. 2007).

This study contributes to the burgeoning literature on water quality of the lower Pra basin. Water samples were collected from more than 20 locations in 10 mining and 9 non-mining communities along the banks of the lower Pra basin, in order to assess the water quality. Multivariate statistics and spatial techniques were applied to identify metals influenced by anthropogenic activities and generate metal spatial distribution maps. Specifically, statistical correlation, PCA and water quality index (WQI) interpolation were the tools used in identifying the contamination hotspots and possible sources of heavy metals. Twenty eight water quality indicators including pH, turbidity, electrical conductivity, total dissolved solids, and nitrates, Cd, Fe, Mn, Pb, Hg, Cu and Zn.

2. Materials and Methods

2.1 The study area

The Pra River is the largest of the three principal rivers that drain the area south of the Volta divide. It rises in the Kwahu Plateau near Mpraeso and flowing southward for 240 km through rich cocoa farming areas, valuable forests and gold mining rich areas in the Akan lowlands,the Pra enters the Gulf of Guinea at Shama, east of Takoradi. The main tributaries are the Ofin, Anum and Birim rivers. The northern part of the Pra is worked for artisanal gold with metallic mercury, which has caused some contamination. The Birim river valley is a major source of diamonds. Figure 1 is the location of the Pra River and its tributaries. Water courses have thus been blocked and as a result of the alluvial method of mining, and the water quality has deteriorated to the extent that tons of alum are needed to treat the water for potable use.

2.2 Sampling and Laboratory Analysis

The samples investigated in this work were collected from surface water across Ghana from January to February 2013(see Figure 1). Geo-satellite positioning of all the locations, were determined with a Garmin Etrex GPS. Fifty five (55) samples were collected. Sampling protocol followed acceptable standards (APHA 1989, 2002). Sampling bottles were washed with detergent and rinsed with 10% hydrochloric acid and double-distilled water prior to sampling. At each of the sampling locations, the bottles were rinsed with the distilled water to be collected to reduce or completely eliminate any contaminations that might be introduced. At each location the water was allowed to run for some time to purge the system before being sampled. The collected samples were immediately put into ice-chests containing ice cubes (around 4^oC) and conveyed to the laboratory for analysis.
Methods used in the laboratory are as summarized below:

1. Dissolved oxygen (DO) and biochemical oxygen demand (BOD) – determined by a modification of the Winkler's method (FAO, 1975).
2. Nutrients:
   a. Orthophosphate (PO_4-P) – determined using ammonium molybdate and ascorbic acid method (Mac-kereth*et al*., 1978);
   b. Ammonia-Nitrogen (NH_4-N) – determined by the indophenol blue method (FAO, 1975);
   c. Nitrate-Nitrogen (NO_3-N) – determined by hydrazine reduction followed by diazotization to form an azo-dye which was measured colorimetrically;
   d. Nitrite-Nitrogen (NO_2-N) – determined by N- (1-naphthyl) ethylene diaminedihydrochloride method;
   e. Sulphates (SO_4) – determined by barium chloride method.
3. Chloride (Cl) – argentometric method
4. Magnesium (Mg) – by calculation as (Total hardness – Calcium hardness) x 0.244
5. Conductivity – determined by a conductivity meter (Fisher)
6. Total dissolved solids (TDS) – determined by weighing after evaporating a known volume of sample
7. Total Suspended Solids (TSS) determined by membrane filtration (glass fibre type C) method (dried at 105°C).

8. Turbidity (FTU) – determined by a DRT 100B Turbidimeter.
9. Metals – Atomic Absorption Spectrophotometry

2.3 Data Treatment

All data for this study are the mean data obtained from surface and groundwater. The standardized skewness and standardized kurtosis were determined to assess whether the sample came from a normal distribution. Values of these statistics outside the range of -2 to + 2 indicated significant departures from normality. The statistical analyses of data were carried out on all variables in the original dataset.

2.4 Principal Component Analysis

PCA reduces the dimensionality of a data set consisting of a large number of interrelated variables, while retaining as much of the variability present in a data set as possible (Iscen et al., 2008). This reduction is achieved by transforming the data set into a new set of variables, the principal components (PCs), which are orthogonal (non-correlated) and arranged in decreasing order of importance.

2.5 Water Quality Index (WQI)

The Water Quality Index (WQI) is a classification system that uses an index calculated from selected water quality parameters. The index classifies water quality into one of four categories: good, fairly good, poor, and grossly polluted. Each category describes the state of water quality compared to objectives that usually represent the natural state. The index thus indicates the degree to which the natural water quality is affected by human activity. The index can be used to describe the state of water quality as a whole in a body of water. It also indicates the suitability of water for various uses such as domestic, recreation and agriculture (i.e. irrigation and livestock watering), where such uses are naturally sustainable.

The adapted WQI used in assessing the state of water quality in the lower Pra basin is based on the Solway River Purification Board (RPB) Weighted Water Quality Index developed by Bolton *et al.* (1978), and adopted by WRC (2003). This is the general water quality indices type in which various physical, chemical and microbiological variables are aggregated to produce an overall index of water quality. The parameters that were used to calculate the Water Quality Index for the river basins are: Dissolved Oxygen (% Saturation), Biochemical Oxygen Demand (BOD), Ammonium Nitrogen (NH_4-N), pH, Nitrate as Nitrogen (NO_3-N), Phosphate as Phosphorus (PO_4-P), Total Suspended Solids (TSS), Conductivity and Temperature.

3.0 RESULTS AND DISCUSSION

3.1 Summary statistics of physicochemical parameters and heavy metals

Table 2 presents the descriptive statistics of the selected parameters under study. The mean pH value of the water samples is slightly above neutral, ranging from 5.130 to 8.730. The mean value of turbidity for all locations did not meet the Ghana water standards or World Health Organisation guidelines. All heavy metal concentrations observed were above the recommended values.

Total metal concentrations in the water column are considered as the sum of dissolved and particulate metal concentrations. No strong correlations between the seven trace metals: Hg, Cd, Cu, Zn, Fe, Mn, and Pb are noticeable (Table 3). The correlation matrix, however, shows significant inter-metal relationships ($p<0.05$ and $p<0.01$). The Fe–Mn correlation is recognized as the weakest with a correlation coefficient $r=0.422$. Also, significant strong correlations ($r>0.5$) were found between Zn – Cd, Pb–Zn, Pb – Cd, Pb – Cu, Cu – Zn, Cu – Cd, Hg – Zn, Hg – Cd, Hg - Cu and two more toxic metals, Hg and Pb. In the literature, only a few examples of strong correlations between dissolved trace metals such as in the North Australian coastal zone and in Bynoe River have been reported (Munksgaard and Parry, 2001). To explain the differences in correlations between the trace metals in each of the compartments, physical, chemical and biological processes occurring permanently in an aquatic environment (internal processes) as well as discharging of pollutants and other anthropogenic activities (external processes) and their effects on the partitioning and behaviour of heavy metals in that aquatic system must be taken into consideration (Baeyens et al., 1998; Nguyen et al. 2005).

3.2 Principal Component Analysis

Four principal components (Eigen values >1) were extracted from the water data sets (Table 4). These cumulative explain about 70% of the variance in the data. Group 1 (or factor 1, expressing about 31.028% of the total variance) includes mainly toxic heavy metals in water (Cu, Pb, Hg, Cd and Zn); group 2 (explaining about 15.9% of the total variance) includes mainly hydrochemical properties of water (electrical conductivity, TDS, Na, Ca and Cl) which probably shows the result of mineral water reactions in the area. Group 3, accounts for 13.483% of the total variance, contains high loadings for total alkalinity; temporal hardness and HCO_3 are assumed to be indicative of natural processes and water – rock interactions. Group 4 explains 8.00% of the total variance and includes Fe, TSS and turbidity (Table 5) which is abundant in the Birimian and Tarkwaian rock system in the study area.

3.3 Spatial characteristics of environmental factors

Field data provide information on heavy metal water contamination at the specific sampled sites, but do not provide the same information on other unsampled locations. Therefore, the spatial distribution of the metals across the entire communities in the study area cannot be thoroughly determined. Since it is difficult and expensive to perform field measurements for every location in the study areas, the GIS locations were employed in this study to provide region-wide metal and selected physico – chemicals parameters distribution along the rivers. From the maps of contents of heavy metals and selected physico – chemical parameters, large spatial variability in their distribution has been observed (Figures 2 -12). For instance, in fig. 2.0 below, the highest mercury concentrations were found around Twifo Praso and Akim Kade. These areas have a lot of illegal small – scale miners, who usually uses mercury.

3.4 Water quality classification

The results of water quality classification using Solway River Purification Board (RPB) Weighted Water Quality Index developed by Bolton *et al.* (1978), and adopted by WRC (2003) is presented in fig. 13.0 below.
From fig. 13.0 above, water quality in the lower Pra basin can be classified as follows:

- Muoso, Appiah Nkwanta, Daboase, Adankrono (Kade), Kibi (Anum) Apapam and Kobriso are in class II and the rest of the stations were in either class III or IV, poor quality and grossly polluted.
- The poor quality waters were as a result of mining and domestic activities in the catchment areas of the river basins.
- Antoakrom and Kwahu Praso are in class IV indicating grossly polluted waters. These are as a result of intense galamsey activities in the area.
- The cost of treating such waters for drinking purposes is high and the health and social implications are also enormous.

4.0 Conclusion and recommendation

This study used multivariate statistical techniques to identify the source/genesis of chemical parameters in surface water and ground water systems in the Lower Pra basins. Twenty seven parameters including trace elements (Cu, Mn, Cd, Fe, Pb, Hg and Zn) and physico-chemical parameters (pH, conductivity, turbidity and total dissolved salts) were determined from 55 sampling points within the Lower Pra basin area in Ghana. Data set was analysed using principal component analysis (PCA). PCA identified four factors responsible for data structure explaining 69% of total variance in surface water explaining about 70%, of the selected parameters according to common features.

From the results of the principal component analysis on surface water in the study, component model 1 is interpreted to be contaminated water with mercury. This is because Hg has the highest correlation value (0.985). Within the study area, illegal artisanal small scale miners (popularly referred to as galamsey) use mercury extensively in their activities. The mercury is a steady source of contamination of the surface water in the Lower Pra Basin area. The use of mercury in gold mining by the Artisanal Small Scale Miners constitutes a point source of contamination.

Also, it can be inferred from principal component analysis 1 as well as the Pearson Product Moment correlation coefficients that water samples within the Lower Pra basin are contaminated with toxic heavy metals such as cadmium, copper, zinc and lead (showed significant positive correlation at $P>0.05$).

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Table 1 : Water Quality Index

Class	Range	Description
I	> 80	Good -Unpolluted and/or recovering from pollution
II	> 50 - 80	Fairly good
III	25 - 50	Poor quality
IV	< 25	Grossly polluted

Table 2: Descriptive Statistics of water quality parameters (n=55)

Parameter	Minimum	Maximum	Mean	Std. Deviation	Variance	Skewness	WHO Guideline value
	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic	
pH	5.130	8.370	6.626	0.642	0.413	-0.299	6.5 – 8.5
Colour	2.500	7.5E4	2.189E3	1.059E4	1.122E8	6.423	15
Turbidity	0.60	1324	1.687E2	3.691E2	1.363E5	2.054	5
TSS	1.00	4.74E4	2.548E3	8.167E3	6.669E7	4.153	-
TDS	15.0	2.625E3	4.347E2	5.28E2	2.788E5	2.397	1000
Conductivity	30.0	5.25E3	8.198E2	1.042E3	1.086E6	2.452	-
Sodium	1.80	544	9.103E1	1.292E2	1.67E4	2.134	200
Calcium	0.800	144.0	3.618E1	3.068E1	941.2	1.833	200
Magnesium	0.500	112.0	2.254E1	2.453E1	601.67	1.757	150
Potassium	1.40	75.0	9.256	1.182E1	139.65	4.048	30
Total Alkalinity	8.00	608.0	1.901E2	1.684E2	2.839E4	1.155	-
Temporary hardness	4.00	608.0	167.1	1.525E2	2.324E1	1.334	500
Bicarbonate	9.76	742	2.306E1	2.0839E2	4.343	1.090	-
Sulphate	2.470	909	7.661E1	1.54E2	2.373E4	4.138	250
Chloride	2.98	923	1.068E2	1.854E2	3.440E4	3.248	250
Nitrate	0.001	38.2	4.399	8.727	76.16	2.556	10
Nitrite	0.001	2.320	0.0972	0.324	0.105	6.281	1.0
Ammomium	0.001	0.740	0.0593	0.1603	0.026	3.311	0.00 – 1.5
Phosphate	0.001	0.990	0.2403	0.298	0.089	1.030	-
Fluoride	0.001	2.530	0.2402	0.429	0.184	3.207	1.5
Dissolved Oxygen	0.001	7.640	2.0916	2.637	6.953	0.976	-
BOD	0.000	6.740	1.332	1.880	3.536	1.640	-
Iron	0.004	93.50	6.999	1.748	305.6	3.537	0.3
Manganese	0.005	2.460	0.3101	0.493	0.244	2.586	0.4
Copper	0.000	15.00	0.879	2.772	7.687	4.009	2.0
Lead	0.000	15.00	0.867	2.774	7.696	4.014	0.015
Mercury	0.000	15.00	0.858	2.776	7.710	4.013	0.003
Cadmium	0.000	15.00	0.8548	2.778	7.716	4.011	0.001
Zinc	0.000	15.00	0.919	2.767	7.660	3.987	5

Table 3: Pearson Product-Moment Correlation Coefficients between water quality parameters in Ghana (n=55)

Pearson's Product-Moment Correlation Coefficients

	pH	Cond	TDS	Turb	Nitrate	Zn	Cd	Fe	Mn	Pb	Cu	Hg
pH	1											
Cond	**0.378****	1										
TDS	**0.369****	**0.995****	1									
Turb	-0.216	**-0.294***	**-0.290***	1								
Nitrate	-0.75	-0153	0.183	-0.217	1							
Zn	0.160	0.085	0.087	-0.085	0.166	1						
Cd	0.175	0.100	0.102	-0.115	0.177	**0.996****						
Fe	-0.043	-0.221	-0.228	**0.727****	-0.187	-0.100	-0.121	1				
Mn	-0.111	-0.212	-0.219	**0.426****	-0.256	-0.105	-0.166	**0.422****	1			
Pb	0.173	0.097	0.099	-0.109	0.175	**0.997****	**1.000****	-0.116	-0.156	1		
Cu	0.167	0.095	0.096	-0.098	0.173	**0.999****	**0.999****	-0.110	-0.139	**1.000****	1	
Hg	0.174	0.099	0.101	-0.115	0.176	**0.996****	**1.000****	-0.121	-0.165	**1.000****	**0.999****	1

**. Correlation is significant at the 0.01 level (2-tailed).

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

Table 4: Variance in water quality data explained by the six principals components extracted

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.998	31.028	31.028	8.998	31.028	31.028	5.240	18.068	18.068
2	4.611	15.900	46.928	4.611	15.900	46.928	4.945	17.052	35.120
3	3.910	13.483	60.411	3.910	13.483	60.411	3.765	12.981	48.101
4	2.321	8.003	68.414	2.321	8.003	68.414	3.032	10.454	58.555

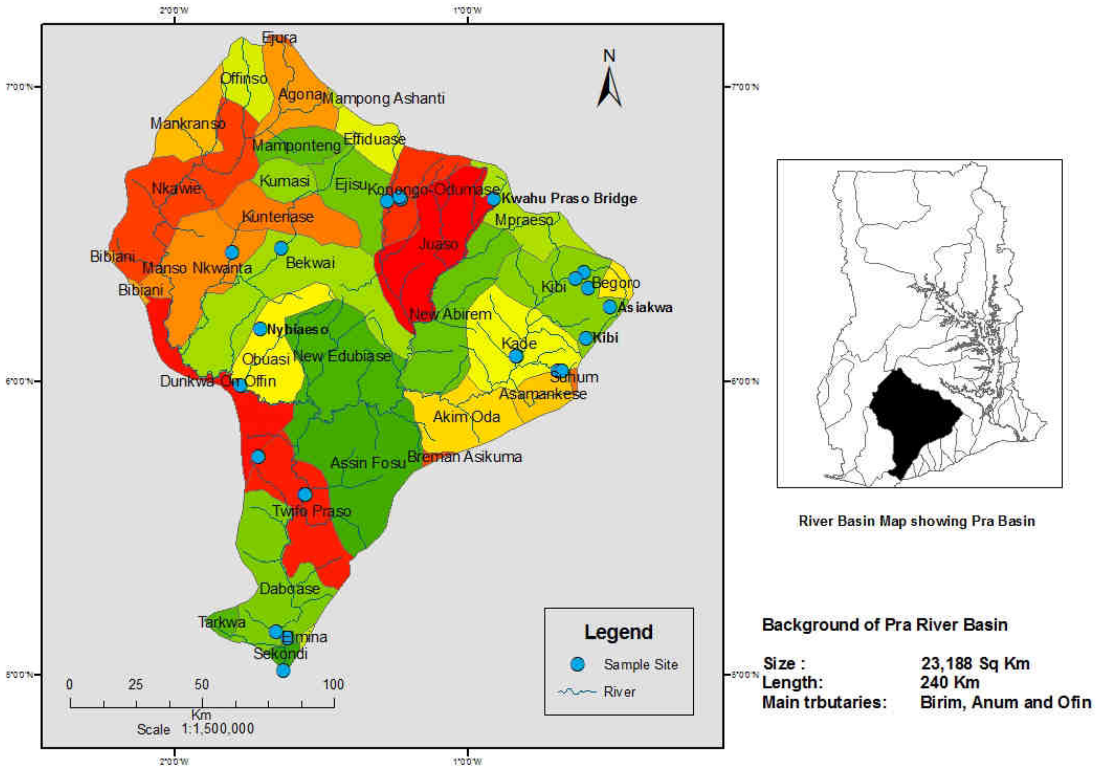
Extraction Method: Principal Component Analysis

Table 5: Matrix of principal components after varimax rotation

	Component						
	1	2	3	4	5	6	7
pH	.125	.296	.455	-.103	-.125	.374	.209
Col	.004	-.117	-.105	.262	.863	-.049	.002
Turb	-.049	-.194	-.165	.794	.229	.081	-.065
TSS	-.031	-.107	-.080	.828	.360	.074	-.016
TDS	.037	.950	.233	-.115	.033	-.030	-.017
Cond	.037	.950	.227	-.110	.039	-.022	.021
Sod	-.007	.917	.268	-.067	.081	-.039	-.025
Ca	.012	.741	.343	-.106	.032	-.289	.124
Mg	.287	.339	.637	-.167	.013	-.117	-.227
K	-.008	.120	-.042	.040	.867	.021	-.002
TAlkalinity	.211	.281	.872	-.122	-.055	-.218	.082
THardness	.190	.236	.888	-.142	-.009	-.208	-.007
HCO3	.207	.279	.872	-.138	-.040	-.221	.081
SO4	-.007	.257	.181	.072	.856	-.037	.006
Cl	-.027	.950	.015	-.098	.045	.016	-.081
NO3	.176	.232	-.167	-.129	-.119	-.502	-.466
NO2	-.048	-.055	-.100	-.067	.038	.617	-.050
NH3	-.109	-.055	-.077	-.162	.022	-.176	.783
PO4	-.081	-.118	-.250	.427	.180	.659	-.224
F	.283	.422	.226	.011	-.158	-.137	.523
DO	-.076	-.055	-.290	.389	-.032	.739	-.134
BOD	-.029	.015	-.244	.468	-.116	.577	-.058
Fe	-.060	-.114	-.105	.901	.034	.198	-.033
Mn	-.068	-.137	-.246	.279	.665	.430	-.037
Cu	.987	.018	.137	-.032	.001	-.052	-.015
Pb	.986	.020	.140	-.039	-.024	-.048	-.015
Hg	.985	.022	.141	-.044	-.035	-.048	-.015
Cd	.985	.022	.141	-.044	-.035	-.049	-.015
Zn	.988	.010	.131	-.025	.033	-.045	-.017

	Component						
	1	2	3	4	5	6	7
pH	.125	.296	.455	-.103	-.125	.374	.209
Col	.004	-.117	-.105	.262	.863	-.049	.002
Turb	-.049	-.194	-.165	.794	.229	.081	-.065
TSS	-.031	-.107	-.080	.828	.360	.074	-.016
TDS	.037	.950	.233	-.115	.033	-.030	-.017
Cond	.037	.950	.227	-.110	.039	-.022	.021
Sod	-.007	.917	.268	-.067	.081	-.039	-.025
Ca	.012	.741	.343	-.106	.032	-.289	.124
Mg	.287	.339	.637	-.167	.013	-.117	-.227
K	-.008	.120	-.042	.040	.867	.021	-.002
TAlkalinity	.211	.281	.872	-.122	-.055	-.218	.082
THardness	.190	.236	.888	-.142	-.009	-.208	-.007
HCO3	.207	.279	.872	-.138	-.040	-.221	.081
SO4	-.007	.257	.181	.072	.856	-.037	.006
Cl	-.027	.950	.015	-.098	.045	.016	-.081
NO3	.176	.232	-.167	-.129	-.119	-.502	-.466
NO2	-.048	-.055	-.100	-.067	.038	.617	-.050
NH3	-.109	-.055	-.077	-.162	.022	-.176	.783
PO4	-.081	-.118	-.250	.427	.180	.659	-.224
F	.283	.422	.226	.011	-.158	-.137	.523
DO	-.076	-.055	-.290	.389	-.032	.739	-.134
BOD	-.029	.015	-.244	.468	-.116	.577	-.058
Fe	-.060	-.114	-.105	.901	.034	.198	-.033
Mn	-.068	-.137	-.246	.279	.665	.430	-.037
Cu	.987	.018	.137	-.032	.001	-.052	-.015
Pb	.986	.020	.140	-.039	-.024	-.048	-.015
Hg	.985	.022	.141	-.044	-.035	-.048	-.015
Cd	.985	.022	.141	-.044	-.035	-.049	-.015
Zn	.988	.010	.131	-.025	.033	-.045	-.017

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.



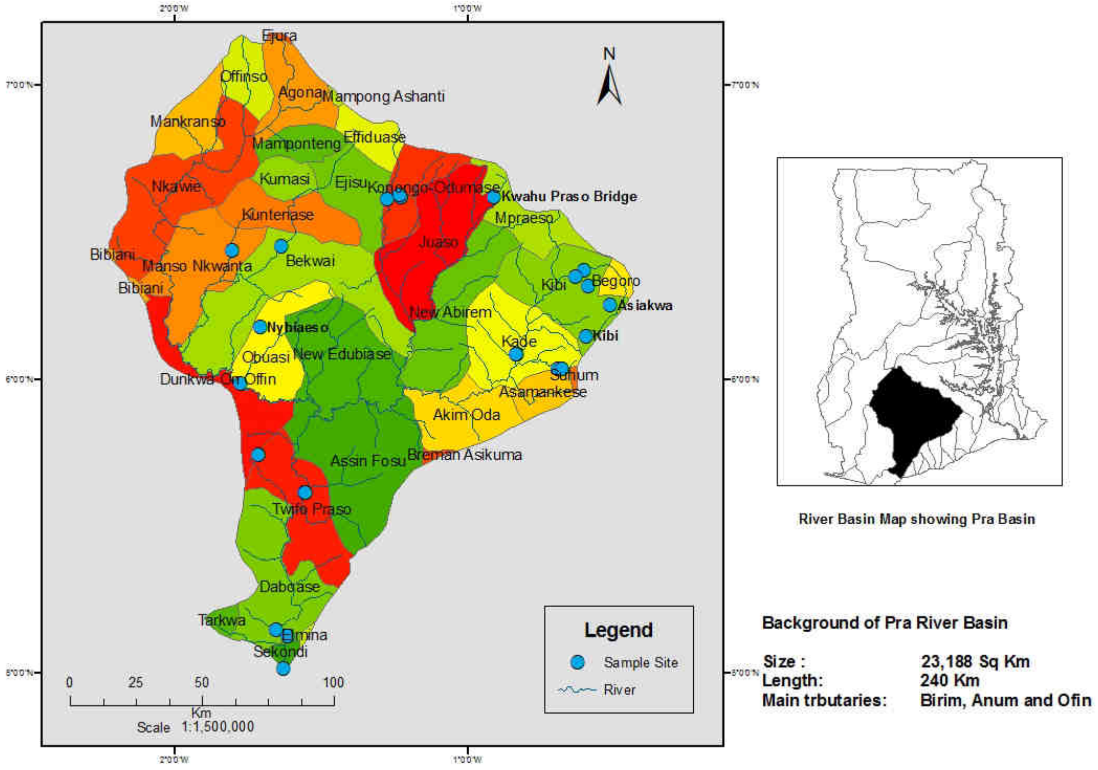


Fig. 1.0 Map of the study area

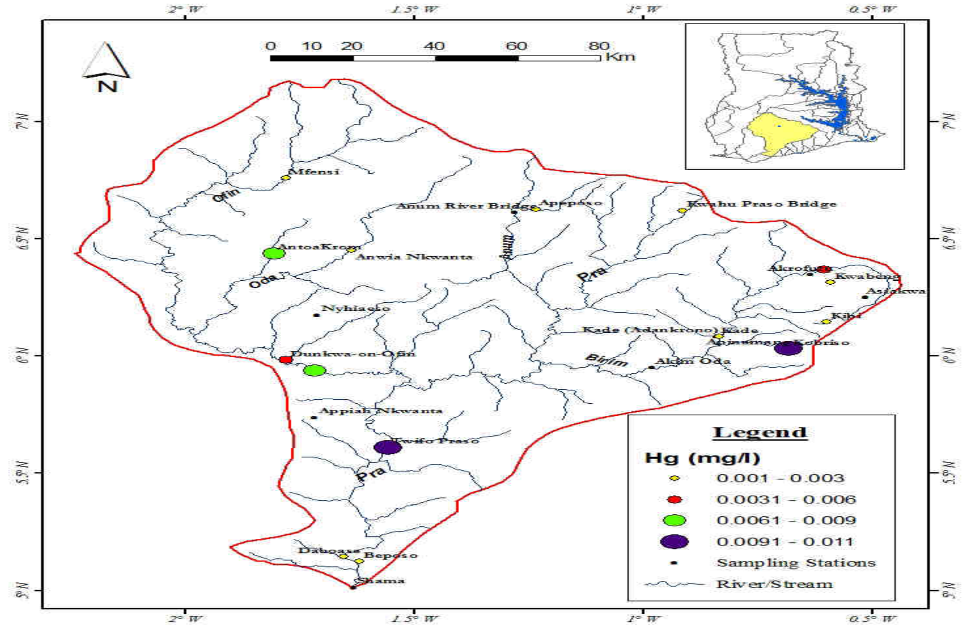


Fig. 2.0 Spatial variation of Hg

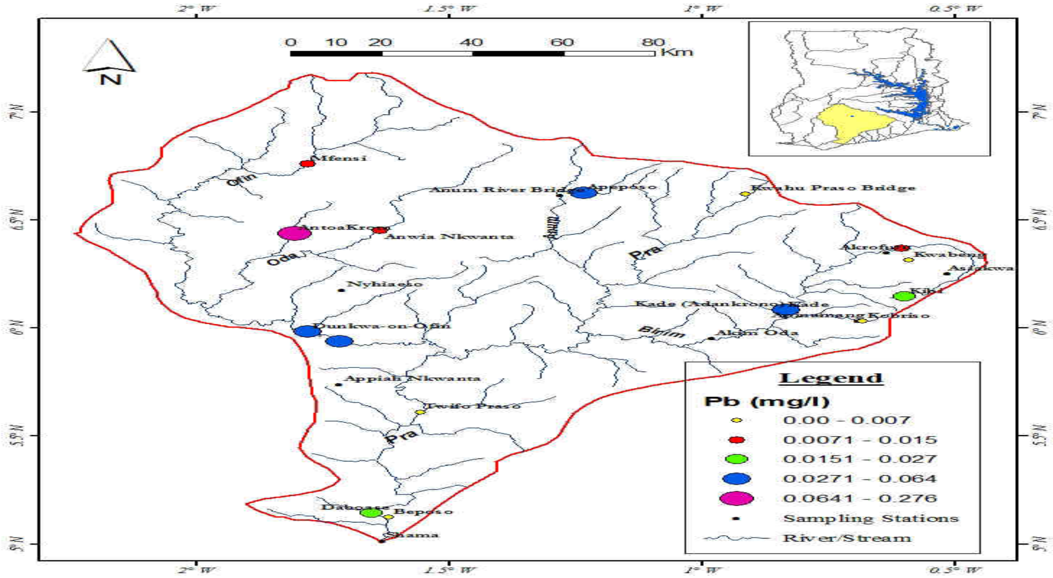


Fig. 3.0 Spatial variation of Pb

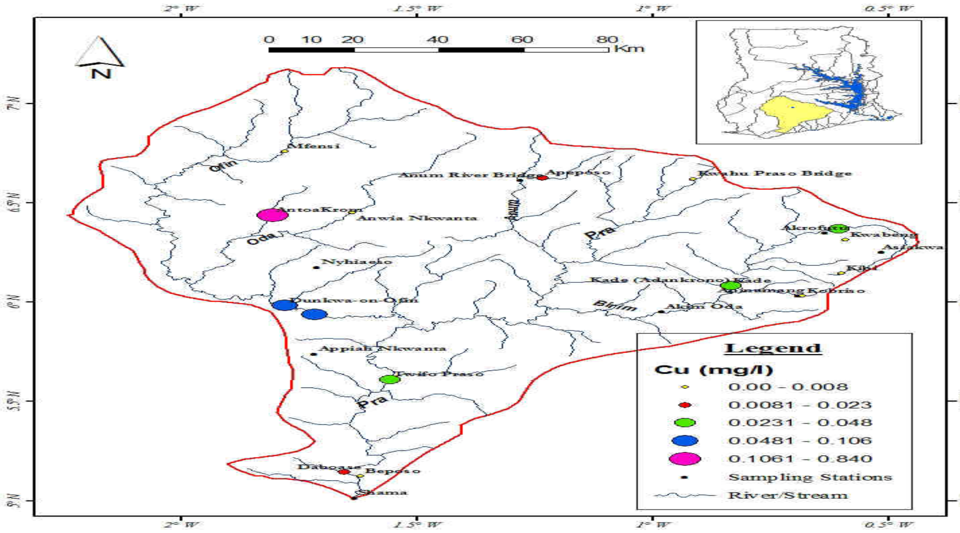


Fig 4.0 Spatial variation of Cu

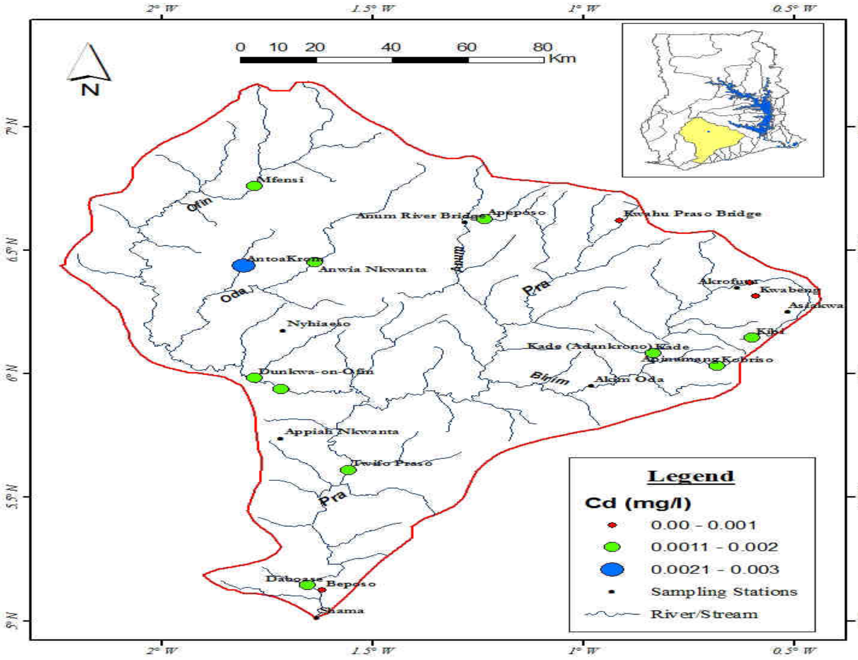


Fig 5.0 Spatial variation for Cd

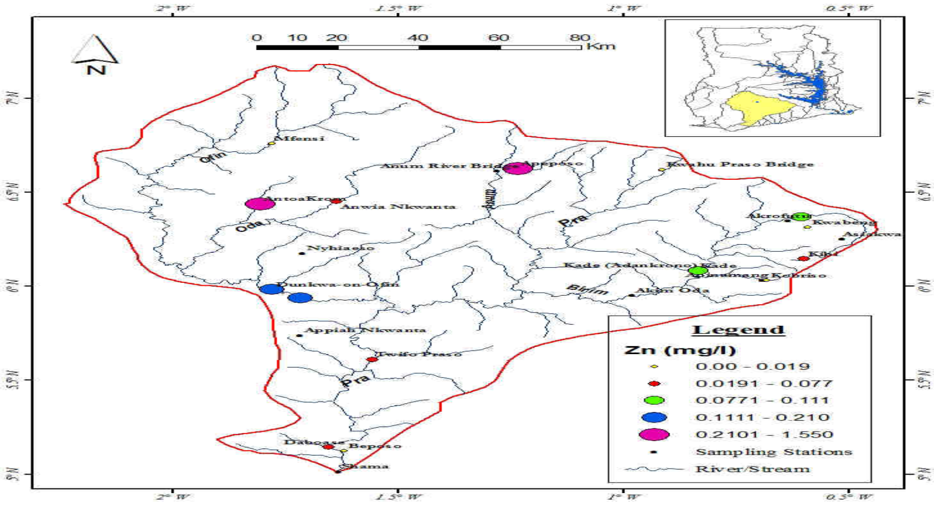


Fig 6.0 Spatial variation of Zn

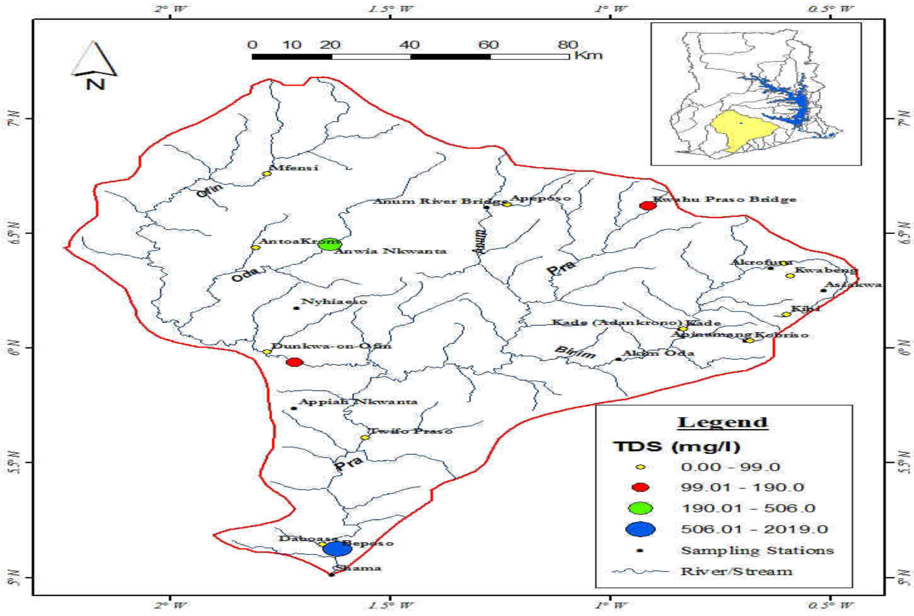


Fig 7.0 Spatial variation of TDS,

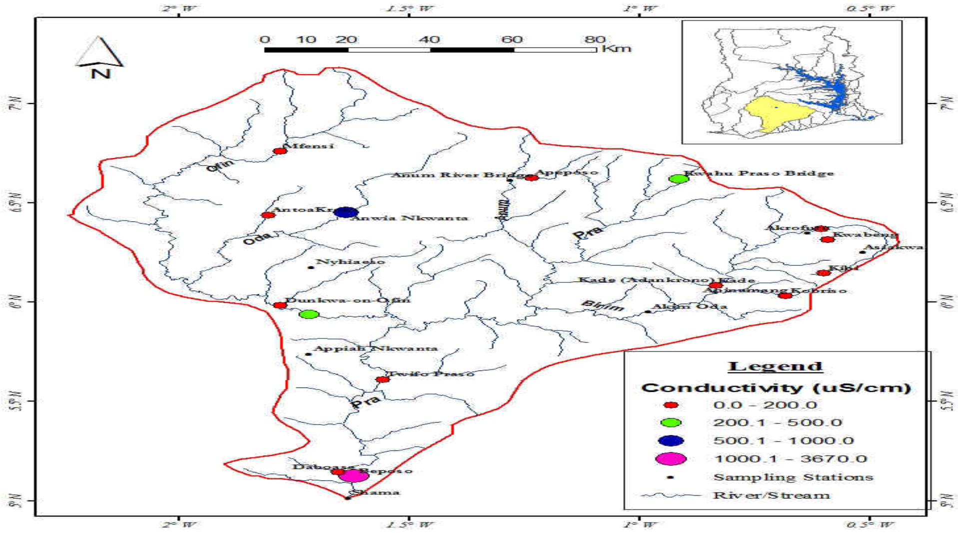


Fig 8.0 Spatial variation of conductivity

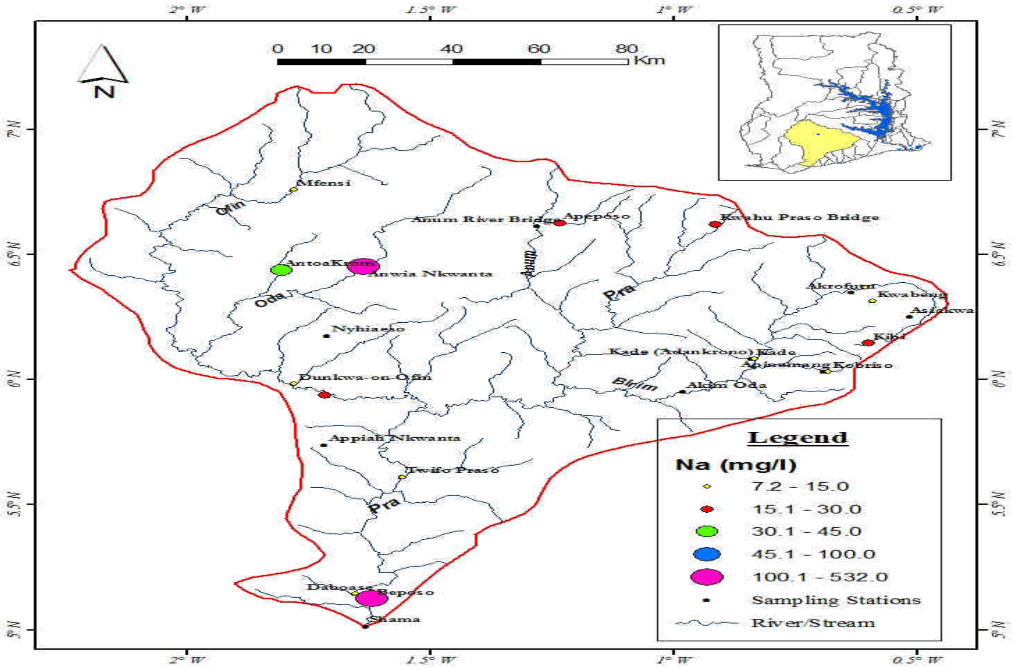


Fig 9.0 Spatial variation of Na

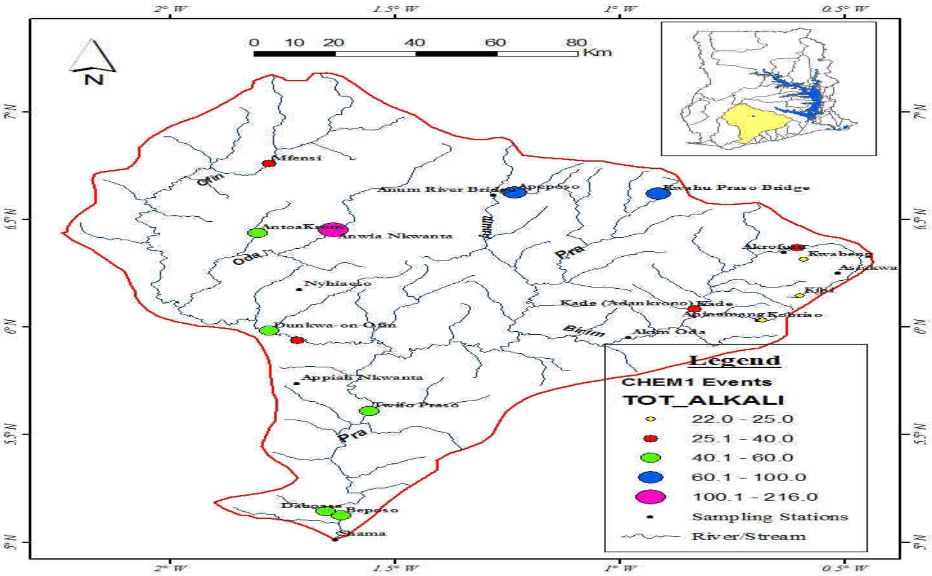


Fig 10 Spatial variation of total alkalinity

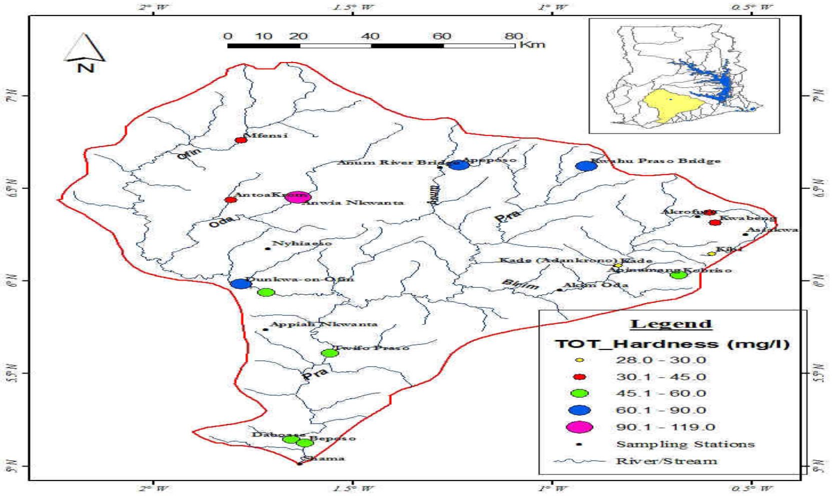


Fig 11 Spatial variation of temporary hardness

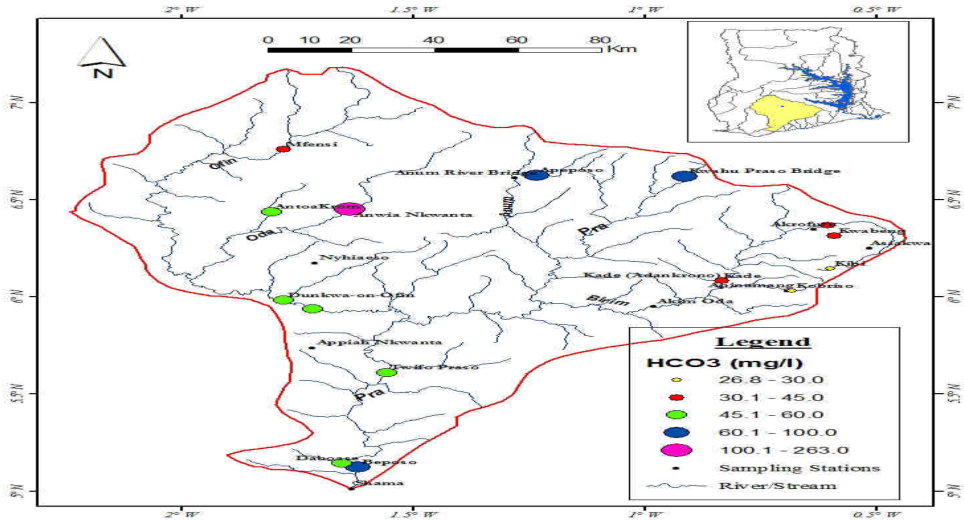


Fig 12 Spatial variation of bicarbonate.

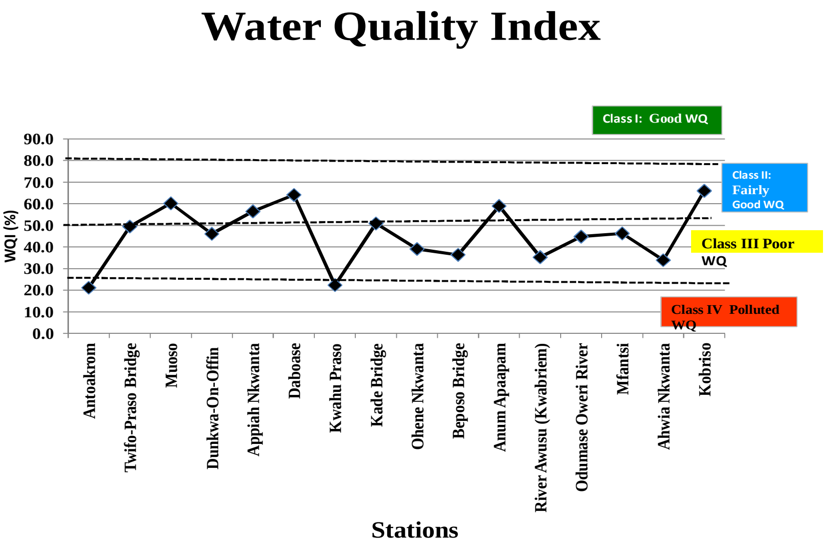


Figure 13.0 : Water quality index of the sampled stations