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Hydrochemical Characteristics of Surface Waters and their Suitability for Irrigation in the Artisanal Mining Environment in Ghana

Anthony A. Duah, Anthony Y. Karikari, Bismark A. Akurugu and Humphrey F. Darko.
CSIR Water Research Institute, P. O. Box M.32, Accra, Ghana.

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ABSTRACT

Surface water resources play a crucial role in potable water delivery to many communities in Ghana. They support recreational, agricultural and industrial water needs. However, several interrelated factors of spatial and temporal variation impact on and control the quality of these water bodies. Due to lack of protection, surface water bodies are highly vulnerable to the impacts of climate change and anthropogenic activities. This study sought to evaluate the main factors influencing the hydrochemistry of the Pra, Ankobra and Tano rivers of the south-western rivers system using statistical, spatial and conventional hydrochemical plots. The results revealed high turbidity and TSS levels in the rivers reaching values of 4 645 NTU and 3 615 mg/l, respectively. Significant levels of Fe exceeding recommended WHO guideline level were also identified. The main hydrochemical facies in the rivers were Ca-HCO_3 (47%) and Mg-HCO_3 (44%), with relative abundance of the order Ca > Mg > Na > K for the cations and HCO_3 > Cl > SO_4 for anions. Precipitation, mineral dissolution in the soil zone and anthropogenic activities, particularly artisanal mining, were identified as the main factors influencing the quality of these rivers. However, irrigation assessment shows that the rivers are of excellent quality for irrigation.

Introduction

In Ghana, surface water resources play a very crucial role in the delivery of potable water to most urban and some rural communities. They also support recreational, agricultural and industrial water needs, especially the manufacturing and construction industry, hydroelectric power plants, tourism, and irrigated agriculture (Venkatramanan et al. 2014; Dunca 2018). Most rivers in the country dry up during the long dry season when the rains cease, leaving a few perennial rivers. Most of these rivers which traverse diverse environments, especially mining communities have been reported to be heavily polluted (Boamponsem et al. 2010) and, in some instances, led to the closure of water treatment plants that rely on these rivers for their 'raw' water supply.

Several interrelated and complex factors with spatial and temporal variation impact on and control the quality of surface water bodies. Due to their exposure and lack of protection, surface water bodies are highly vulnerable to the impacts of climate change, runoff from farmlands containing agrochemicals, domestic and industrial effluents etc. However, pollution of rivers is usually not localized, and could be transboundary even, such as in the case of Ghana and Cote d'Ivoire where pollution of the Tano and Bia rivers in Ghana impacted negatively on the surface water supply needs of the former (Asamoah 2017). Most studies on surface water bodies in Ghana focus mainly on the suitability of the water for domestic purposes, and adopt methods such as the water quality index, pollution index and some statistical techniques in these assessments (Boamponsem et al. 2010; Adiyiah et al. 2013; Attua et al. 2014; Humphrey and Ansa-Asare 2014; Afum and Owusu 2016; Asare-Donkor et al. 2018).

Studies focusing on the sources of variation in river water chemistry and the main factors controlling the quality of the rivers in Ghana, as well as studies on the suitability of these rivers for irrigation purposes are very limited. This study adopts similar approaches, with particular focus of the main factors influencing the hydrochemistry of rivers in southwestern Ghana, adopting statistical and conventional hydrochemical plots, coupled with model irrigation water quality assessment diagrams. It further attempts to assess the spatial character of water quality parameters, which could help determine major pollution sources that contribute to the deterioration of these rivers and for a better understanding and management of water resources, which could aid water resources management decisions.

Study Area

This study was conducted in Pra, Tano and Ankobra Rivers of the Southwestern Rivers System of Ghana, and covers a land area of about 47 780 km^2, which translates into about 20% of the entire land area of the country. It lies between the boundaries of longitudes 3°7' and 0°25' west, and latitudes 4°53' and 7°39' north. The study area is bordered to the east by Afram, Densu, Ayensu, Nakwa and Amisa River basins, to the west by Cote d'Ivoire, Black Volta and Pru River basins to the north and the Gulf of Guinea to the south (Fig. 1). Among rivers of the Southwestern River System, the longest and largest is the Pra River, which stretches a course of about 240 km from source to mouth.

Headwater of the Pra River is located in the Kwahu Plateau in the Eastern Region. It flows southwards, meandering through several communities, and finally discharges into the Gulf of Guinea in the Western Region through a small village called Krobo. The study area traverses several administrative regions;

Central, Bono, Bono East, Ahafo, Western North, Western, Eastern, Central and Ashanti. It has a population of approximately 8 790 421 people, with the densest city being Kumasi, which has a population density of 5,419 persons per kilometre square, compared to a national average of 103 persons per square kilometre (Ghana Statistical Service 2012).

In most of the communities in the study area, illegal and artisanal small-scale mining of bauxite and gold is highly endemic. Conventional mining techniques in the area include panning, open pit mining and direct dredging (Adiyiah et al. 2013; Afum and Owusu 2016). Well-established and popular mining sites in the study area include the gold mines at Konongo, Dunkwa, Kenyase, Akwatia, and the AngloGold Ashanti mine in Obuasi, one of the largest mines in Africa (WRC, 2012). Agricultural activities, mainly farming of food and cash crops such as oil palm, rubber, cocoa, cassava, citrus, timber, coffee, maize and vegetables are other socio-economic activities and livelihood supporting activities in the study area.

Towards the coast in the south, the topography of the study area appears relatively flat, with a few mountains in the east close to the Kibi area. Similarly, a few mountaintops can be located in the central parts around Bekwai and Obuasi, and towards the northern parts, in Ashanti Mampong area (Fig. 1). The topography seems to have an overall downward slope, trending in the north - south direction. In the southern parts of the study area, elevations range between 0 – 50 m towards the coast, and gradually reaching 800 m in the northern and central parts which are characterised by mountaintops. The study area falls in the sub-equatorial wet climate, characterized by a two rainfall peaks regime. The major rainy season occurs between May and July, and the minor September and November. The annual rainfall amount varies between 1300 and 2000 mm, with a mean of about 1500 mm. The amount of rainfall in the study area shows an increasing westward trend (WRC, 2012). The air is usually humid during the rainy season. Relative humidity in the area varies between 70% – 85%, and declines steadily during the dry season to about 41%. The peak of the dry season, which is around March, records the maximum temperatures of up to 30 ^{o}C, which steadily falls to a minimum of about 23 ^{o}C when the harmattan sets in around December (Adomako et al. 2011; WRC 2012).

In the coastal parts of the study area, the vegetation is mainly savannah and shrub forest due to the low rainfall regime characteristic of such locations. It is characterized by bush and grassland as well as mangrove swamps particularly where saline water dominates (Yidana et al. 2014). However, the middle and northern parts are dominated by tropical rain forest vegetation, which is characteristically rich in undergrowth of climbers and shrubs of varying heights. As a result of mining activities, and felling of trees for timber, there has been a rapid reduction in the density of trees. In such places, where mining activities have affected the vegetation, ferns and shrubs dominate mostly on hilly slopes. However, in virgin lands where mining activities have not taken place yet, trees reaching heights of about 15 to 45 m dominate, mostly at the summit of hills (Boamponsem et al. 2010).

Geology

The geology of the study area is dominated by Crystalline Precambrian rocks of the Birimian Supergroup (about 70%). These rocks occur almost throughout the study area, intruded by granitoids of the Eburnean and Tamnean Plutonic Suites (Figure 2). The Tamnean and Eburnean Plutonic Suites appear most as remote patches all over the area, but prominent in the northern, southern and central parts of the study area. Common rock types associated with the Birimian Supergroup are phyllite, quartzite, granite-gneiss, gneiss, migmatite and schist composed of basaltic flows, cherts, hornblende, dykes and volcano-clastics (Gyau-Boakye and Tumbulto 2006). The Eburnean and Tamnean granitoid intrusions are K-feldspar-rich, composed mainly of granite and monzonite. The Tamnean and Eburnean Plutonic Suite are thought to be of uncertain age, but believed to be post-Birimian and Pre-Tarkwaian age (Kesse 1985; Abdul-Ganiyu and Gbedzi 2015).

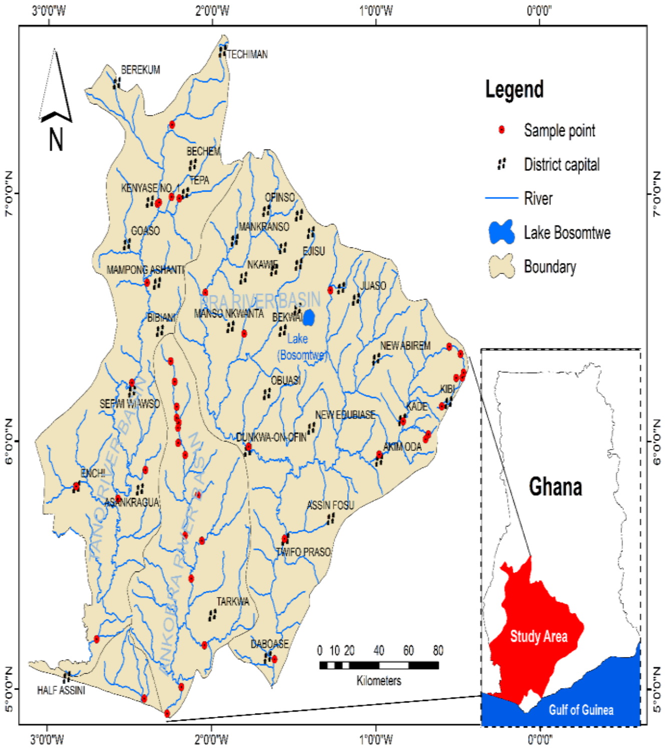


Figure 1. Map of the study area showing sampled locations.

Furthermore, the Tarkwaian Group also underlie eastern sections of the study area, and trends towards the south, in a north-east south-west direction. The rock types identified within this formation are tuff, sandstone, argillite, conglomerate and siltstone. The Late Cretaceous Apollonian Group also underlie the extreme southwestern corner of the study area. The Apollonian Group is one of the most recent rock units in the country, usually linked to marine, lagoon and riverine sedimentary rocks. It is composed of loose sediments that cover a large part of the country and form soils. Common rock types in the Apollonian Group include limestone, marl and mudstone with intercalated sandy beds. Mafic dykes, dolerite of pre-Mesozoic age occur throughout the area.

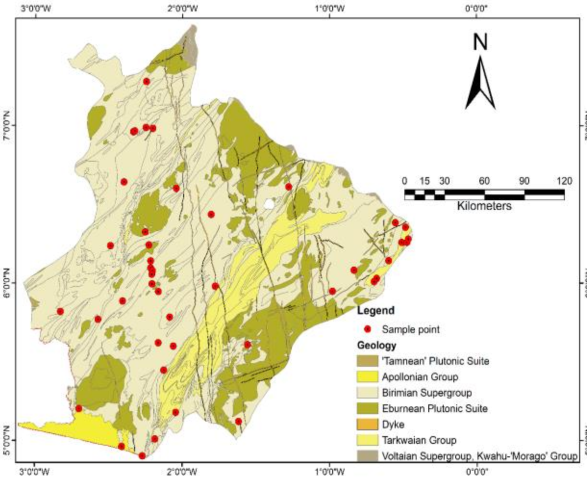


Figure 2. Geology map of the study area

Materials and Methods

Sampling and analysis

A field expedition was conducted between 9th and 21st July, 2018, for the collection of water samples from various segments of the Pra, Tano and Ankobra rivers, and some of their tributaries. Water samples for physico-chemical analyses determination were sampled into pre-cleaned 1000 ml polyethylene bottles. Samples for biochemical oxygen demand (BOD_5) analysis were collected into dark glass bottles and incubated at 20 ºC for 5 days for subsequent DO determination. Also, dissolved oxygen (DO) samples were collected differently in plain glass bottles and fixed with Winkler I and Winkler II Reagents, for subsequent acidification and titration. Water for trace metals (Fe, Mn, Cu, Zn, Cd, Hg) analyses were sampled with 50 ml pre-cleaned polyethylene bottles and further preserved with concentrated nitric acid to avoid further reactions while being stored and transported to the laboratory for analyses. All the samples were preserved in an ice chest conditioned at a temperature of about 3 ºC with ice and sent to the CSIR-WRI Laboratories in Accra for analysis. The filed and laboratory analyses adopted the standard protocols as prescribed by APHA (2012). Electrical conductivity (EC) and total dissolved solids (TDS) were measured *in situ* using HACH HQ14D Portable Conductivity & TDS Meter, while water temperature and pH were determined *in situ* using portable HACH HQ40D pH/Temp field meter. Fe, Mn, Cu, Cd, Zn, Pb and Hg were analysed using Atomic Absorption Spectrometry (AAS), alkalinity, total hardness (TH) and F were analysed using strong acid titrimetric, EDTA titrimetric and SPADNS methods respectively. The other parameters were also analysed using the azide modification of Winkler method for Dissolved Oxygen (DO), HACH DR900 Spectrophotometer for total suspended solids (TSS), 5-day incubation Method for biochemical oxygen demand (BOD5), Diazotization Method for nitrite-nitrogen (NO2-N), Hydrazine Reduction Method for nitrate-nitrogen (NO3-N), Direct Nesslerisation Method for ammonia nitrogen (NH3–N), Stannous Chloride Method for orthophosphates (PO4–P) and Nephelometric Method (Hach 2100P Turbidimeter) for turbidity.

3.2 Statistical tools and analysis

This study adopted both univariate and multivariate statistical techniques in establishing relationships and drawing inferences in an attempt to unearth the underlying factors influencing the chemistry of surface water bodies in the study area. The IBM SPSS ver. 20, Golden Software Surfer ver. 11 and Microsoft Office Excel 2016 were used for all statistical analysis.

The data was subjected to geostatistical techniques such as hierarchical cluster analysis (HCA) and correlation analysis. Prior to running the statistical analysis, the dataset was subjected to normality test using histograms, since most statistical analysis assume Gaussian distribution for optimal statistical analysis. Parameters that were not normally distributed were log-transformed and/or standardized to their corresponding z score values (equation 1).

$$z = \frac{x-\mu}{s} \qquad (1)$$

Where x, μ and s are the measured value, mean and standard deviation of the parameter respectively.

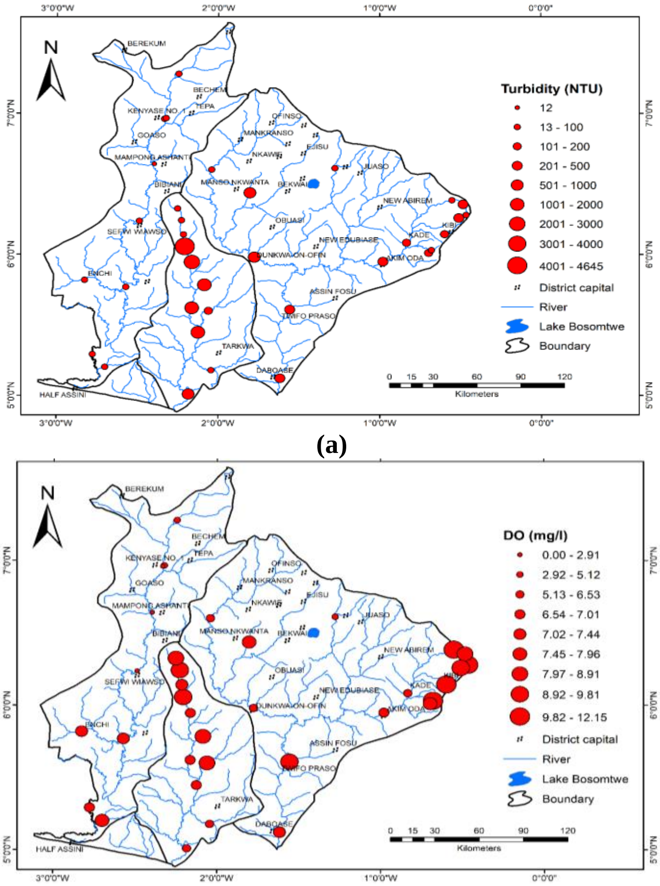
The standardized datasets were then subjected to correlation analysis and R-mode HCA. HCA orders rows and/or columns of data into groups based on similarity, making it easier to see correlations in data. The Q-mode HCA is used to categorize the spatial associations or evolution of the river water into various types in space and/or time, whereas R-mode is used to determine and rank the causes of dissimilarities in the water chemistry. While several similarity/dissimilarity and agglomerative techniques are available in HCA, the squared Euclidean distance and Ward's agglomeration method have been adopted in this study, since a blend of these two techniques have been identified to produce the best results in HCA (Yidana et al. 2010; Loh et al. 2019). Claims and inferences made in relation to the principal factors and processes influencing the rivers' chemistry based on the geostatistical methods were reinforced by employing conventional hydrochemical plots to further establish and reveal the main controls on the chemistry of rivers in the study area. The suitability of the rivers' water for irrigation purposes was assessed using conventional ternary diagrams and water quality classification plots such as Piper, Schoeller, Wilcox and the United States Salinity Laboratory (USSL) combined with the Sodium Adsorption Ratio (SAR) to characterize and classify river water quality and interaction with the underlying geology and surrounding.

Results and Discussions

Summary statistics and hydrochemistry

Table 1 presents summary of the hydrochemical parameters of samples from the rivers in the study area. pH of the rivers varies from slightly neutral to alkaline, with values ranging between 6.96 and 8.18, with an average of 7.6 pH units. It displayed the least variation among the major water quality parameters, with a standard deviation of ± 0.35 pH units, which suggest similar factors or processes influence pH levels of the rivers in the study area. The Ankobra and Tano rivers recorded the highest pH values of 7.5 - 8.18 pH units which occurred around Juakwa, Elubo, Asawinso, Ayiem and Sefwi-Ahwiaso. Li et al (2013), indicate that high pH values in water influence the release of phosphorus in solution, which impacts negatively on the quality of the water. The dissolution of solutes in solution is also greatly influenced by the temperature of the water. Temperatures of the rivers in the study area were largely within the temperatures of natural water bodies, which is usually influenced by the surrounding atmospheric temperature (approximately 25°C). The temperatures of the rivers ranged between 25 and 28.5 °C, with a mean of 26.7 °C and a standard deviation of ± 0.9 °C.

The levels of major ions and TDS in general for surface waterbodies are usually relatively low compared to groundwater mainly due to the limited time such waters interact with solutes/rock material before discharging into the sea. Hence all the major ions in the rivers were relatively low, except for a sample from the Ankobra River at Ayiem which recorded 55.1 mg/l for calcium. Regarding metals on the Offin and Birim Rivers at Antoakrom and Akim-Oda, high levels of Cd and Pb were detected, exceeding the 0.003 and 0.01 mg/l thresholds respectively. Also, Fe exceeded the background value of 0.3 mg/l for freshwater in all cases (Table 1), ranging between 0.63 and 30.2, with an average and standards deviation of 7.28 and ± 7.06 mg/l, respectively. High levels of Fe in the basins could result from geogenic and anthropogenic sources such as runoff from mining activities, farmlands, weathering of iron-rich minerals, etc. DO and turbidity in the rivers also showed some inverse relationship, with the sections of the rivers which recorded high turbidity having low DO levels and vice versa (Fig. 3). High turbidity (12 - 4645 NTU) in the rivers suggest an increase in the level of particles and nutrients load, which can lead to decreases in DO levels (2.56 - 12.15 mg/l) as a result of the increased microbial activity during the degradation of organic matter. Therefore, DO may be used to assess the degree of pollution by organic matter. Four sampled stations, Sefwi-Denyasi, Nobekaw, Tanoso, all on the Tano river and Konongo-Odumasi on the Anum river had DO values below the WRC (2003) guideline of 5 mg/l for fresh water bodies. DO levels below 5 mg/l has been reported to adversely affect the functioning and survival of biological communities, and below 2 mg/l may lead to the death of most fish (Chapman, 1996). Turbidity in all the rivers exceeded the background level of 5 NTU for surface water bodies WRC (2003), which suggested a great influence from anthropogenic activities in the study area. The high turbidity levels were particularly dominant in the small-scale mining endemic communities



(b)

Figure 3. Spatial distribution of (a) turbidity and (b) DO in the study area.

Table 1. Summary statistics of physical and chemical water parameters in the rivers

Parameter	N	Minimum	Maximum	Mean	Std. Deviation (±)
Temp (°C)	35	25.0	28.5	26.7	0.9
pH (pH units)	35	6.96	8.18	7.6	0.35
TDS	35	14	205	61	36
EC (µS/cm)	35	30	425	125	71
TSS	35	4	3615	382	737
Turbidity (NTU)	35	12	4645	488	940
BOD	32	1.39	8.46	4.58	1.78
DO	34	2.56	12.15	7.49	2.53
Alkalinity	35	10.4	92.6	43.8	22.23
Total hardness (TH)	35	12.2	93.8	46	20.2
Ca^{2+}	35	3.7	55.1	15.03	10.66
Mg^{2+}	35	0.8	19.7	7.56	4.16
Na^{+}	35	3.2	19	8.71	3.93
K^{+}	35	1.2	6.1	3.36	1.3
Cl^{-}	35	<0.01	16.2	7.07	3.85
SiO_2	35	3.31	17	10.78	3.08
F	35	<0.005	0.688	0.037	0.153
HCO_3^-	35	12.7	113	53.4	27.1
NO_2-N	35	<0.001	0.188	0.0506	0.039
NO_3-N	35	0.017	1.11	0.173	0.181
NH_3-N	35	0.076	2.223	0.748	0.585
PO_4-P	35	0.021	0.269	0.133	0.064
SO_4^{2-}	35	1.1	13.4	7.87	2.85
Fe	35	0.63	30.2	7.28	7.06
Mn	35	<0.005	0.73	0.142	0.147
Cu	35	<0.020	0.07	0.009	0.017
Zn	35	0.006	0.181	0.038	0.033
Cd	35	<0.002	0.017	0.001	0.003
Pb	35	<0.005	1.64	0.047	0.277
Hg	35	<0.001	0.005	0.001	0.001

*Unless otherwise stated, all parameters were measured in mg/l

Table 2. Correlation analysis of physicochemical parameters

	pH	TDS	TSS	BOD	NO_2-N	DO	Turbidity	Colour (Hz)	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	SiO_2	TH	Alkalinity	HCO_3	Fe	Cu
pH	1.00																			
TDS	0.53	1.00																		
TSS	0.05	-0.29	1.00																	
BOD	0.36	-0.19	0.28	1.00																
NO2_N	-0.05	-0.12	0.30	0.25	1.00															
DO	-0.08	-0.53	0.15	0.58	0.26	1.00														
Turbidity	0.05	-0.29	1.00	0.28	0.31	0.15	1.00													
Colour (Hz)	0.08	-0.25	0.96	0.31	0.27	0.17	0.96	1.00												
Ca^{2+}	0.42	0.32	0.31	0.11	0.00	-0.25	0.32	0.45	1.00											
Mg^{2+}	-0.14	-0.07	0.02	0.19	-0.17	-0.09	0.01	-0.02	-0.16	1.00										
Na^+	0.43	0.81	-0.29	-0.21	-0.26	-0.53	-0.29	-0.28	0.34	-0.05	1.00									
K^+	0.44	0.79	-0.37	-0.17	-0.34	-0.53	-0.37	-0.32	0.39	-0.04	0.93	1.00								
Cl^-	0.18	0.27	-0.02	-0.01	0.06	-0.08	-0.01	0.01	0.28	0.24	0.41	0.23	1.00							
SO_4^{2-}	0.15	0.47	-0.45	-0.13	-0.07	-0.46	-0.46	-0.47	-0.07	0.14	0.46	0.57	-0.16	1.00						
SiO_2	-0.28	0.03	-0.21	-0.03	0.36	0.00	-0.21	-0.28	-0.22	-0.09	-0.07	-0.14	0.06	0.22	1.00					
TH	0.52	0.67	-0.35	0.13	-0.20	-0.33	-0.35	-0.31	0.41	0.08	0.74	0.81	0.42	0.52	-0.01	1.00				
Alkalinity	0.54	0.79	-0.33	0.03	-0.28	-0.41	-0.34	-0.28	0.47	-0.01	0.86	0.91	0.37	0.47	-0.06	0.95	1.00			
HCO_3	0.54	0.79	-0.33	0.03	-0.28	-0.41	-0.34	-0.28	0.47	-0.01	0.86	0.91	0.37	0.47	-0.06	0.95	1.00	1.00		
Fe	-0.10	-0.35	0.79	0.32	0.55	0.28	0.79	0.73	0.04	0.08	-0.37	-0.51	0.02	-0.32	0.17	-0.42	-0.45	-0.45	1.00	
Cu	0.06	-0.23	0.79	0.30	0.33	0.04	0.78	0.76	0.22	0.11	-0.35	-0.32	-0.21	-0.18	-0.15	-0.30	-0.31	-0.31	0.67	1.00

Factors influencing the hydrochemistry of the rivers

Correlation analysis

Results of the correlation analysis in this study suggests that Na, K and HCO_3 are the main contributors to TDS in the rivers, since these parameters have significant positive correlation with TDS (Table 2). pH also appears to influence TDS in the rivers (r = 0.53), probably by causing the dissolution or dissociation of certain ions such as HCO_3, Ca, Na and K in the rivers. Fe and Cu on the other hand appear to occur together, and load significantly with each other and with colour and TSS (Table 2). Fe and Cu are known to strongly influence the colour of water, which explains the significant correlation. The dissolution of iron-rich mineral such as pyrite, marcasite, ankerite, hematite and/or siderite are common sources of Fe in the rivers and constituents of the rock types in the study area. Fe in the study area also correlate significantly with NO_2-N, TSS, K, turbidity and colour, which suggest Fe in the rivers may be of anthropogenic origin, probably from industrial effluents rather than dissolution of rock minerals. Similarly, SO_4, NO_2-N and K also showed some level of linear relationship (Table 2), reinforcing anthropogenic activities in the study area as a dominant hydrochemical process driving the chemistry of the rivers. The application of inorganic fertilizers and manure in agricultural lands and domestic waste waters pose a threat to surface water bodies in the study area since runoff after precipitation events end up in these water bodies. HCO_3, the most dominant anion correlates significantly with Na and K, the most dominant cations in the rivers, which suggest that waters from the rivers are of meteoric origin (Loh et al. 2019).

Hydrochemical facies

In this study, a Piper (1944) trilinear diagram was used to identify and group the main hydrochemical facies in the rivers. Facies characterisation reveals the dominant ions in solution, and provides a general overview of the principal factors controlling the hydrochemistry of the rivers. The plot revealed the rivers are a mixed cation system dominated by Ca-HCO_3 (47%) and Mg-HCO_3 (44%) (Fig. 4). The mixing is probably influenced by baseflow, since most of these rivers are perennial rivers. The Ca and Mg levels are probably from the dissolution of silicate minerals such as mica, quartz, amphibole, feldspar, pyroxene and a variation of clay minerals, as the rivers flow through various geological formations in the weathered zone. This assertion is consistent with the geology of the study area which is underlain mainly by granites and granitoids of the Birimian Supergroup, Eburnean and Tamnean Plutonic Suites. Ion exchange processes may also be playing a role in the hydrochemistry of these rivers. In all, the rivers show characteristics associated with precipitation water dominated by HCO_3, and having slightly acidic to alkaline pH probably influenced by anthropogenic activities.

Similarly, a Shoeller diagram was used to distinguish the relative abundance of the various ions in the rivers, usually in milliequivalents (meq) (Fig. 5). The cations are in the order of Ca > Mg > Na > K and the anions HCO_3 > Cl > SO_4. The dominance of these ions in solution form the bases for the water types identified by the Piper (1944) plot (Fig. 4). Notwithstanding, most of the samples overlapped (Fig. 5), suggesting they may have evolved from a common source, obviously precipitation, amid some form of mixing or evolution (Sunkari et al. 2019).

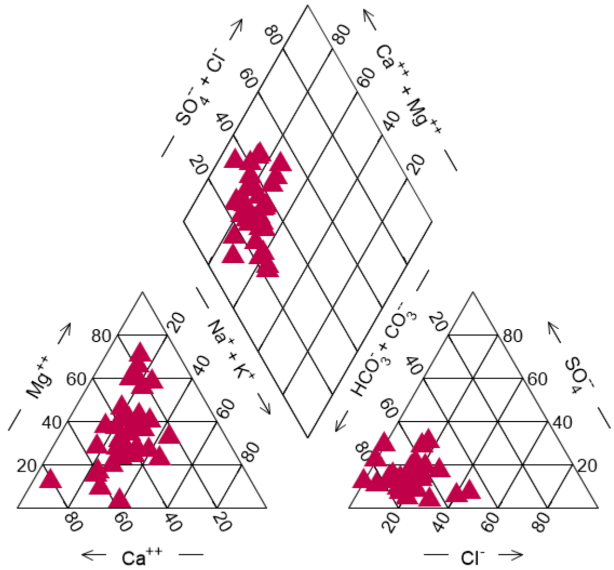


Figure 4. Piper plot showing hydrochemical facies of the rivers.

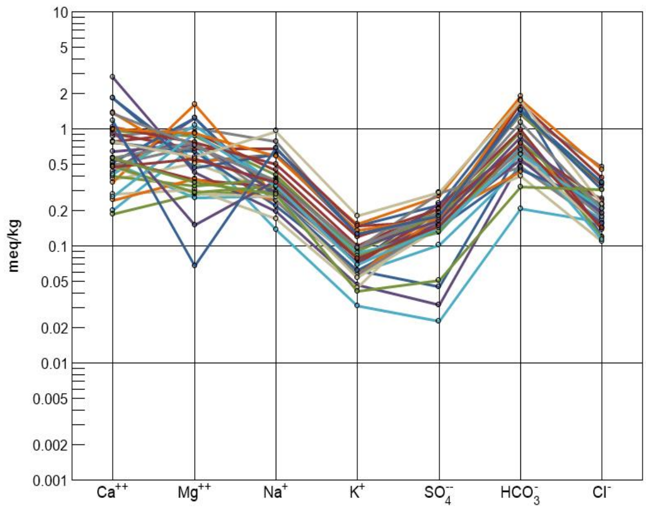


Figure 5. Schoeller diagram showing relative ionic distribution.

Principal controls on river water chemistry

Gibbs (1970) diagram provides general overview of the principal controls on water samples by categorising them into regions of precipitation, rock and evaporation/crystallization dominance (Fig. 6). It has been widely employed in hydrochemical studies to determine the main factors controlling water chemistry at various locations (Fianko et al. 2010; Loh et al. 2019; Sunkari et al. 2019). Precipitation dominance has been revealed as the main factor controlling the chemistry of the rivers in the study area, for the obvious reason that rivers are usually mainly recharged by rain. Precipitation dominance is closed marked by rock dominance in the study area (Fig. 6), suggesting the influence of the dissolution of minerals in the soil zone. Although evaporation/crystallisation appear not to play a significant role in the hydrochemistry of the rivers, probably as a result of the rainy season within which period sampling for this study was conducted, it does not mean evaporation/crystallisation does not play a role, but relative to the other two factors, it is not significant enough. This probably is one of the weaknesses of the Gibb (1970) plots; restricting the factors of influence to only three, eliminating the contributions of other factors.

The controls on the rivers' chemistry in the study area has been further distinguished using R-mode hierarchical cluster analysis (HCA). Figure 7 is a dendrogram showing the visual relationships amongst the 20 physicochemical parameters used in the analysis, with a phenon line drawn at a linkage distance of 11, showing two main clusters. Defining the number of clusters based on the distance of the phenon line is subjective, though its guided by an objective to not generate too many or too few clusters, for adequate interpretation of the main hydrochemical processes in the rivers, as well as the researcher's understanding of the major hydrochemical process prevalent in the study location.

Two clusters were produced from this method which represent two main hydrochemical associations and/or processes in the rivers. Cluster 1 is representing dissolution of minerals in the soil zone, influence by precipitation as seen in the sub-clusters 1a and 1b, link by HCO_3, alkalinity, TH, Na, K, TDS, and SO_4, pH, Ca, respectively. Cluster two on the other hand represents the impacts of anthropogenic activities, dominated by illegal small-scale mining, runoff from mined areas and farmlands. Which explains the clustering of turbidity, TSS, colour, Cu and Fe in sub-cluster 2a (Fig. 7). Turbidity, Cu and Fe are high influencers of the colour of water, whereas turbidity and TSS are highly detrimental to the quality of water, especially in terms of cost of treatment and impacts on equipment used for such waters. As stated above, these parameters also impact negatively on aquatic life, reducing the life supporting capacity of the rivers, and cluster together in sub-cluster 2b (Fig. 7), suggesting a common source of such parameters in the rivers.

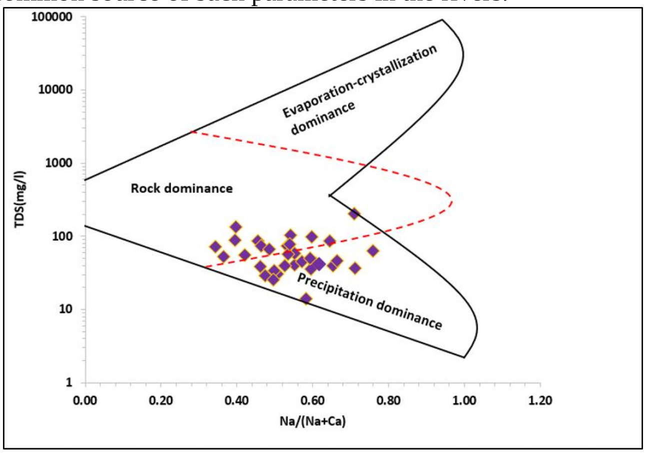


Figure 6. Gibbs diagram showing the main influence on rivers' hydrochemistry

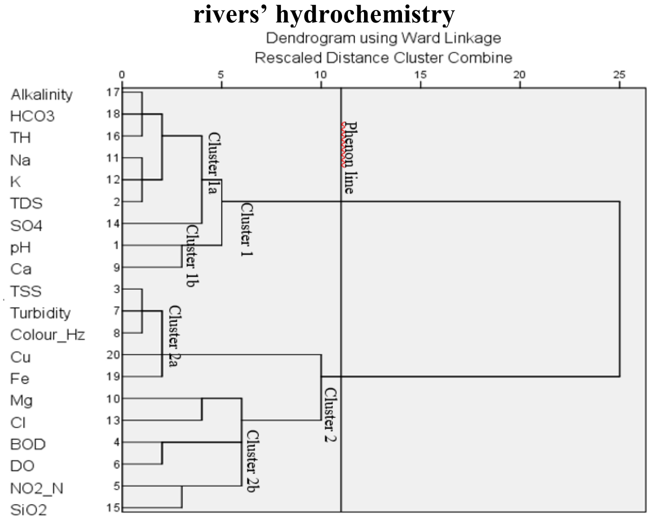


Figure 7. Dendogram from R-mode hierarchical cluster analysis

Irrigation quality assessment of the rivers

The quality of the rivers has also been assessed to examine their suitability for irrigated agriculture which is practiced on a small-scale level in these areas, and augments the predominantly rain-fed agriculture. Different crops have a variety of tolerance levels for the various hydrochemical parameters in the water. Similarly, the various chemical parameters affect various crops differently at different concentrations and conditions. Some of the water quality parameters such as Na is known to affect the structure and permeability of soils at some concentrations, which eventually affects its productivity and yield, and by extension the quality and yield of crops (Loh et al. 2019). As such, an evaluation of river water quality for irrigation purposes which estimates chemical parameters and indices of chemicals which are likely to have detrimental impacts on the soil and crops when found in water used for crop irrigation is vital for healthy and productive irrigated agriculture. It is worth mentioning that at certain levels, physical parameters such as turbidity could also impact negatively on irrigation quality of rivers, since such waters could impair the functions of irrigation equipment, as well as block the stomata of plant leaves, leading to impaired growth and productivity. Sodium based/related assessments have been adopted in determining the suitability of the rivers in this study for irrigation – conventionally, these methods compare the concentration of Na^+ to other ions in the water. High ratios of Na^+ to other cations such as Mg^{2+} and Ca^{2+} tend to impact negatively on soil permeability, resulting in poor soil since through ion exchange, Na^+ tend to get absorbed unto surfaces of clay materials and displace Ca^{2+} and Mg^{2+} in solution. These conditions lead to a soil type that is unsuitable for optimal crop growth and production (Yidana et al. 2011).

The Wilcox (1955) diagram is one of such approaches for irrigation quality assessment. This method plots the fraction of sodium in the water versus EC (salinity). The ratio of Na^+ is computed as a fraction of the concentration of the sum total of the major cations in the water (equation 2). The various categories of water types in the study area based on this classification scheme is presented in Fig. 2 based on this assessment. All samples in the rivers fell within the "excellent" category. While the rivers display rather significant sodium levels, their salinity hazard appear to be generally low, with EC values less than 500 µS/cm corroborating the origin of the rivers as precipitation. Generally, Fig. 8 suggests rivers in the study area are of excellent chemical quality for irrigation, although the turbidity levels might suggest the contrary.

$$\text{Na\%} = \frac{\text{Na}}{\text{Na+Ca+Mg+K}} \times 100 \qquad (2)$$

where concentrations of all ions are in meq/l

Similarly, sodium adsorption ratio (SAR), which is a measure of Na^+ relative to Ca^{2+} and Mg^{2+} in the rivers has also been used for irrigation water quality assessment (equation 3). The United States Salinity Laboratory (USSL) diagram plots SAR versus EC, where EC is used as a measure of salinity hazard of the water.

$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca+Mg})/2}} \qquad (3)$$

where concentrations of all ions are in meq/l.

The USSL diagram classifies irrigation water in the ranges of "low" to "very high" sodicity on the SAR axis and "low" to "very high" salinity hazard in the EC axis. Using this classification, all the rivers in the study area fell in the C1-S1, "low" salinity – "low" sodicity category, except a lone sample which fell in the C2-S1, "medium" salinity – "low" sodicity category (Fig. 9)

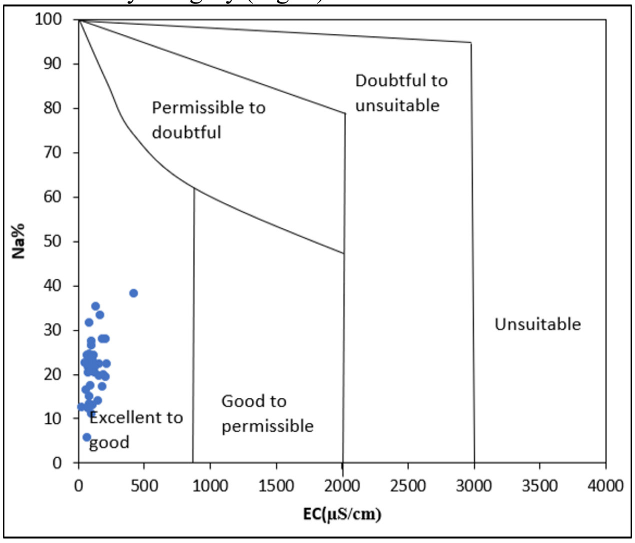
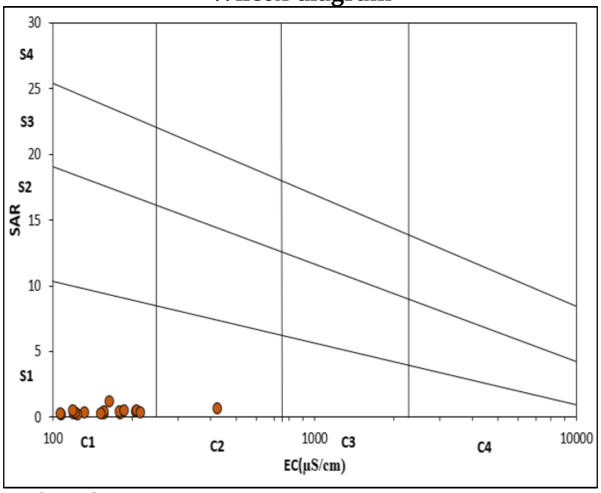


Figure 8. Irrigation quality assessment of rivers using Wilcox diagram



Salinity hazard
C1: Low
C2: Medium
C3: High
C4: Very high
Sodicity
S1: Low
S2: Medium
S3: High
S4: Very high

Figure 9. Water quality classification for irrigation using United State Salinity Laboratory

The Doneen (1954) diagram has been used to assess the long-term impact of using these rivers for irrigation on the permeability of the soils. The long-term impacts of irrigation water on soil permeability is largely influenced by the levels of Na^+, Ca^{2+}, HCO_3^- and Mg^{2+} in the water (Venkateswaran 2013). As such the permeability index (PI) which measures the relative concentrations of sodium and bicarbonate to calcium, magnesium and sodium can be computed (equation 4).

The results from this computation revealed waters from the rivers belong to Class I and Class II water types (Fig. 10), with none falling within Class III; where Class I and Class II are respectively excellent and good permeability for irrigation purposes. Majority of the samples (97%) fell within Class II, "good" permeability category, mainly due to the high levels of Na^+ in the rivers.

$$PI = \frac{Na + \sqrt{HCO_3}}{Na + Ca + Mg} \times 100 \quad (4)$$

where ion concentrations are all in meq/l

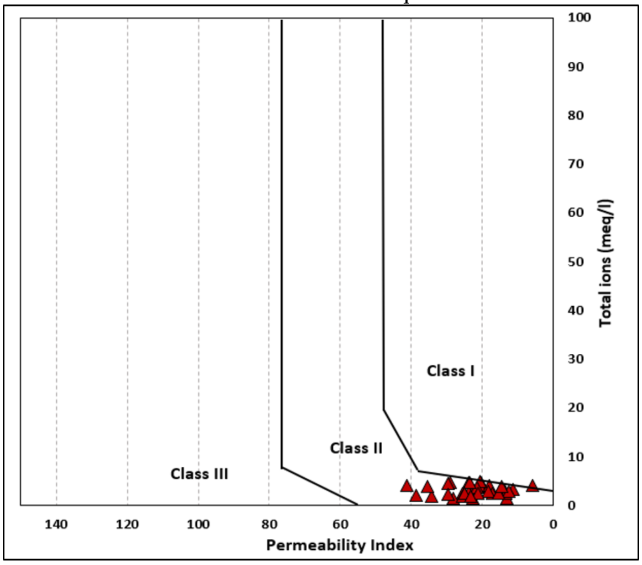


Figure 10. Permeability impact assessment using Doneen diagram

5. Conclusion

The hydrochemistry of the Southwestern Rivers System, Pra, Ankobra and Tano rivers, has been assessed using statistical, spatial and conventional hydrochemical plots to ascertain the main factors controlling the chemistry of these rivers and their suitability for irrigation. The results revealed that turbidity and total suspended solids were relatively high, exceeding the WRC (2003) upper limits of 5 NTU and 100 mg/l, respectively, and reaching maximum values of 4 645 NTU and 3 615 mg/l, respectively. Significant levels of Fe were also identified in the rivers, exceeding the recommended level of 0.3 mg/l in all sampled locations, and may have originated from anthropogenic, rather than geogenic sources. The main hydrochemical facies in the rivers were Ca-HCO_3 (47%) and Mg-HCO_3 (44%), with relative abundance of the order Ca > Mg > Na > K for the cations and HCO_3 > Cl > SO_4 for the anions. Precipitation, mineral dissolution in the soil zone and anthropogenic activities, particularly illegal small-scale mining and agricultural activities have been identified as the main factors influencing the quality of the rivers in the study area. In spite of the anthropogenic pollution levels, irrigation quality assessments revealed that the rivers are of excellent quality for irrigation and good long-term permeability impacts when used for irrigation.

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