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# Hydrochemical characteristics of surface water and ecological risk assessment of sediments from settlements within the Birim River basin in Ghana

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## Abstract

**Background:** Geogenic and anthropogenic activities such as Artisanal and illegal gold mining continue to have negative impacts on the environment and river basins in Ghana. This work studied the hydrogeochemical characteristics of surface water from the Birim River basin and assess the quality of water for human consumption and agricultural activities. In addition, the ecological risk assessment for Cd, Zn, Pb and As in sediment was evaluated using pollution indices.

**Results:** The results show that the turbidity, temperature, colour and iron concentration in the water samples were above the World Health Organization guidelines. Multivariate analysis explained five components that accounted for 98.15% of the overall hydrogeochemistry and affected by anthropogenic and geogenic impacts. The surface water was observed to range from neutral to mildly acidic, with the dominance of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  in ionic strength. The Piper diagram reveals five major surface water types:  $\text{Na-HCO}_3\text{-Cl}$ ,  $\text{Na-Cl-HCO}_3$ ,  $\text{Na-Ca-Mg-HCO}_3$ ,  $\text{Na-Ca-Mg-HCO}_3$  and  $\text{Ca-Na-Mg-HCO}_3$ . The Gibbs plot showed that the major ion chemistry of surface water was mostly influenced by atmospheric precipitation and the water quality index showed that the majority of the surface water from settlements within the Birim River basin were of poor quality for drinking and other domestic purposes. However, irrigation suitability calculations with reference to sodium adsorption ratio, residual sodium carbonate, and magnesium ratio values, together with Wilcox and USSL models indicated that the surface water within the area under study was suitable for agriculture. The potential ecological risk for single heavy metals pollution and potential toxicity response indices gave low to considerable ecological risks for the sediments, with greater contributions from Cd, Pb and As. Whilst geo-accumulation indices indicated that the sediments ranged from unpolluted to moderately polluted Modified degree of pollution and Nemerow pollution index calculations which incorporate multi-element effects, however, indicated no pollution.

**Conclusion:** There are some levels of both potential ecological risks and health hazards in the study area. Hence continuous monitoring should be undertaken by the relevant agencies and authorities so that various interventions could be put in place to prevent the situation from deteriorating further in order to protect the inhabitants of the settlements within the Birim River basin.

**Keywords:** Ecological risk assessment, Hydrogeochemical, Birim River basin, Water quality index, Multivariate analysis

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## Background

Surface water which is the most significant inland water resource for human consumption, agricultural activities, recreational and industrial purposes (Razmkhah et al. 2010) has always been the end point of wastewater disposal from the adjacent areas. Lithology of river basins, anthropogenic inputs, climatic and atmospheric conditions affects the quality of surface water at any point. A series of organic, inorganic and biological pollutants, such as highly toxic heavy metals (Demirak et al. 2006; Moore and Ramamoorthy 2012) or non-toxic, biodegradable materials, such as faeces, food waste and wastewater can affect the quality of surface water (Bain et al. 2014).

The hydrogeochemical characteristics of surface water rely on the chemical composition of rock-forming minerals, such as sulphide, carbonate and silicate, as well as the physical process of erosion, which generates favourable conditions for mineral dissolution. Consequently, water resources are being enriched with metals, metal-loids or ions, which often tend to be toxic to mankind as well as the natural environment (Lang et al. 2006; Négrel et al. 2006; Robinson and Ayotte 2006). Other geochemical activities, such as sorption, redox reactions, ion exchange, and complexation may alter its hydrogeochemistry and subsequently affect the water quality. The hydrogeochemical characterization may be accomplished via several techniques, and among them are the typical hydrogeochemical ratios, which can evaluate the dominant and origin processes of water resources (Zhu et al. 2007), as well as multivariate statistical analysis (Saleem et al. 2015; Purushothaman et al. 2014). These two techniques may be valuable in identifying the factors that influence surface water chemistry, particularly hydrogeological and complex geological systems.

Information on the physicochemical parameters of water for the endurance of organisms, such as fauna and flora is essential for evaluating the quality and type of water (Liu et al. 2010). Temperature and pH are among essential features of the environment since they affect nutrition, growth, metabolic activity and human reproduction. Heavy metals have been revealed to pose a serious threat to human health due to their toxicity, persistence, bioaccumulation in the food chain and non-destructible nature in the environment (Asare-Donkor et al. 2015; Asefi and Zamani-Ahmadmoodi 2015; Boateng et al. 2015; Bortey-Sam et al. 2015; Singh et al. 2013; Zhang et al. 2014). Essential metals, such as Fe, Mn, Zn and Cu play a vital role in the biological processes but turn to be toxic above certain concentrations. Several studies have revealed that chlorine contents in water are related to senility, heart disease as well as cancer of the urinary tract, pancreas, liver, colon, and osteosarcomas (Kim et al. 2011; Comber et al. 2011).

There are diverse reports in literature which assess the geochemical characteristics of surface water systems, as well as anthropogenic contamination influenced by factors such as agricultural fertilizers, sewage effluents, evapotranspiration, water-rock interactions and ion-exchange in several parts of the world (Abdesselam et al. 2013; Alaya et al. 2014; Iranmanesh et al. 2014; Kim et al. 2015; Khashoggi and El Maghraby 2013; Nandimandalam 2012; Singh et al. 2016). However, in Ghana, there are few such reports (Boateng et al. 2016; Helstrup et al. 2007; Fianko et al. 2010; Yidana et al. 2012). The determination of surface water composition is of extreme significance for the assessment of its suitability for drinking, irrigation and domestic purposes. The primary objective the study has been to evaluate the hydrochemical characteristics of surface water from the Birim River basin assess the ecological risk and the suitability for domestic and irrigation uses.

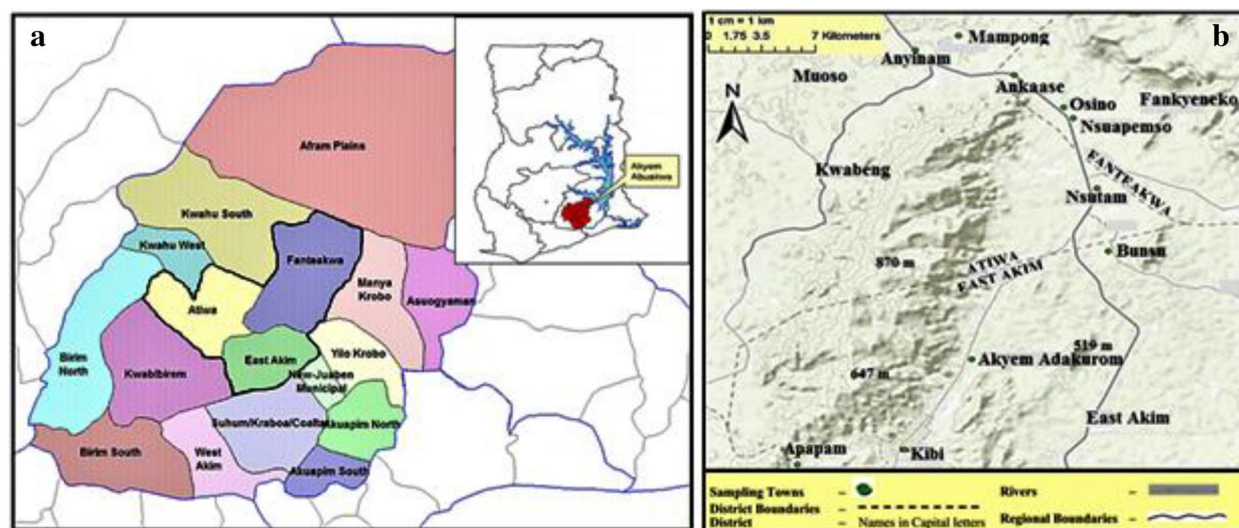
## Methods

### Study area

The Birim River basin is located between latitudes 5°45'N and 6°35'N; and longitudes 0°20'W and 1°15'W. The Birim River takes its source from the Atewa Hills, Eastern Region of Ghana and follows a course of 175 km<sup>2</sup> southwards to join the Pra River. The river drains an area of approximately 3895 km<sup>2</sup> with the major tributaries being Adim, Amaw, Kade and Si. It has an estimated area of 3875 km<sup>2</sup> (Ansah-Asare and Asante 2000). The rainfall pattern in the drainage area varies seasonally with major peaks from June to September and dry spells from December to January. It has a temperature range of 25–30 °C and relative humidity of 70–80% throughout the year. The area is endowed with mineral deposits, such as gold, bauxite, diamond, and others. The main occupations the settlers are farming and small-scale mining activities known as “Galamsey”, mostly along the banks and inside of the Birim River.

### Sampling

Forty-three samples of water and sediment were collected from 10 settlements (Fig. 1) within the Birim River basin. The sampling stations were Apapam (The source of the Birim River), Kibi, Adukrom, Bunso, Nsutam, Nsua-pemso, Osino, Ankaase, Mampong, and Anyinam. Prior to sampling, water sample containers of 500 mL polyethylene bottles were rinsed with detergents and then washed thoroughly several times with distilled water. They were further soaked in 10% (v/v) HNO<sub>3</sub> and left overnight. The surface water samples were collected at the mid-stream at 30 cm depths. Two sets of surface water samples (one for heavy metal and the other for physicochemical parameters) were taken from each sampling point. Electrical



**Fig. 1** Map showing **a** the location of the settlements within the Birim River basin and **b** the sampling stations

conductivity (EC), total dissolved solids (TDS) and pH were measured in situ. The samples for heavy metal analysis were filtered through pre-washed 0.45  $\mu$ m Millipore nitrocellulose filters to remove any suspensions treated with 2 mL of Analar  $\text{HNO}_3$  at  $\text{pH} < 2$  to preserve them. The water samples were appropriately labelled and immediately transported in an ice chest to the laboratory and kept in the refrigerator at  $-4^\circ\text{C}$  prior to analysis.

Sediment samples were taken from the top surface layer of sediment at a depth of 0–6 cm with a plastic trowel into open-mouth plastic containers. Sediment samples were obtained from the same location and at the same point where the water samples were taken. A sediment weight of about 30 g each was collected from each sampling station.

### Sample analysis

#### Physicochemical parameters

Physical parameters, such as EC, pH and TDS were determined using cyberscan PC 650 multimeter series. Turbidity was measured using HANNA HI 93414 turbidity meter while Colour was determined using a spectrophotometer set at 465 nm. The temperature was determined using Mercury in Glass Thermometer and Total alkalinity was measured by the titrimetric method. The carbon dioxide content in the sample was determined by computations from the sample pH and total alkalinity. Total hardness was measured using EDTA titration and thus calculated as  $\text{CaCO}_3$  content (mg/L). Chloride concentration was determined using potentiometric titration with an  $\text{AgNO}_3$  solution with a glass and Ag–AgCl electrode system. The UV technique was used to determine the

nitrogen concentration in the water samples as nitrates at a wavelength of 220 and 275 nm. Magnesium concentration was calculated as the difference between total hardness and calcium hardness multiplied by 0.243. The flame photometric method was used to analyse the potassium and sodium ion concentrations at a wavelength of 766.5 and 589 nm respectively.

#### Heavy metals

Water samples were digested by a method described by Asare-Donkor et al. (2015) and Arnold and Lenore (1989). Briefly, 100 mL of each water sample was transferred into a 250 mL beaker and 5 mL of conc.  $\text{HNO}_3$  was added. The mixture was gently heated on a hot plate after a few boiling chips had been added and evaporated to about 20 mL. Another 5 mL of conc.  $\text{HNO}_3$  was added and then heated for 10 min and allowed to cool. About 5 mL conc.  $\text{HNO}_3$  was used to rinse the sides of the beaker and the solution was quantitatively transferred into a 100 mL volumetric flask and made up to the mark with deionized distilled water.

The sediment samples were initially air-dried and further dried in an oven at  $70^\circ\text{C}$  for 48 h to obtain a constant weight. The sediment was then crushed and ground into fine particles and further passed through a 2 mm sieve. The sediments were digested by a method described by Kouadia and Trefry (1987). About 1.0 g of the finely ground sediment sample was accurately weighed into a beaker and equal amounts of concentrated nitric acid, hydrofluoric acid and perchloric acid were added. The beaker was covered and set aside for several hours and evaporated to a few drops on a hot plate. Then 5 mL of

HClO<sub>4</sub> was added and evaporated to dryness. Conc HCl (10 mL) was added and the mixture was heated until the solution was clear and the fumes had ceased. Deionized distilled water was added and the digested material was filtered into a 100 mL volumetric flask, then the residue was washed several times with deionized distilled water and made to the mark. The heavy metals, such as Fe, Pb, Zn Cd and As were analysed with the VARIAN AA240FS atomic absorption spectrophotometer with an air-acetylene flame. Requisite lamps with appropriate operating absorption wavelength and other operating parameters for each element was employed for the determination. Each of the analysis was done in triplicate, in which the mean values were calculated.

#### Quality assurance

Replicate blanks and Standard Reference Material (SRM) of Fluka Analytical (Sigma-Aldrich Chemie GmbH, Product of Switzerland) were used for the quality control and method validation. Analytical results indicated a good agreement between those reported in this study and the certified value.

#### Statistical analysis

IBM SPSS-20 program was also used to analyse the Pearson correlation, principal component analysis (PCA) and cluster analysis (CA). XLSTAT '2016 statistical software and Origin 2016 Data Analysis and Graphing Software were used for the geochemical analysis.

#### Risk assessment methods

##### Enrichment factor (EF)

The enrichment factor (EF) is a convenient measure of geochemical trends and is used to characterize the degree of anthropogenic pollution through the establishment of enrichment ratios (Zakir et al. 2008). To evaluate the extent of contamination in the environment, the factors EF were computed relative to the abundance of species in the source material and to that found in the Earth's crust (Sinex and Helz 1981).

$$EF = (C_M/C_x \text{ sample}) / (C_M/C_x \text{ Earthcrust}) \quad (1)$$

where  $C_M$  is the content of metal studied and  $C_X$  is the content of the immobile element, immobile elements may be Fe (Zhang et al. 2007). In this study, the background geochemical compositions by Taylor and McLennan (1995) were used as the background values for the calculation. Five classes of enrichment factors have been identified  $EF < 2$ : depletion to mineral,  $2 \leq EF < 5$ : moderate,  $5 \leq EF < 20$ : significant,  $20 \leq EF < 40$ : very high and  $EF > 40$ : extremely high (Sutherland 2000).

##### Index of geo-accumulation ( $I_{geo}$ )

The  $I_{geo}$ , which is the geochemical benchmark to assess heavy metals pollution in sediments was calculated based on Eq. (2):

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 \times B_n} \right) \quad (2)$$

where,  $B_n$  and  $C_n$  represent the geochemical background concentration and the measured concentration of the studied heavy metal  $n$  in the sediment, respectively. Because of the possible dissimilarities in background concentrations of any given heavy metal and anthropogenic influences, a factor value of 1.5 was used.

##### Modified degree of contamination

The modified degree of contamination ( $mC_d$ ) which has an advantage over single element indices since it takes account the synergistic effect of the contaminants at a study site (Brady et al. 2015) was calculated as follows:

$$mC_d = \frac{1}{n} \sum_{i=1}^n C_f^i \quad (3)$$

where  $C_f^i = C^i / C_{ref}^i$ ,  $C^i$  is the heavy metal concentration in sediment samples;  $C_{ref}^i$  the reference value of the element (Turekian and Wedepohl 1961; Hankason 1980) and  $C_f^i$  the contamination factor of each element.

##### Nemerow pollution index

The Nemerow pollution index takes into account the comprehensive effects of heavy metals (Yan et al. 2016) and can be used to interpret heavy metal pollution at particular sites (Duodu et al. 2017). The equation for the calculation is given by Eq. (4).

$$P_N = \sqrt{\frac{\bar{C}_f^2 + C_{fmax}^2}{2}} \quad (4)$$

where  $P_N$  is the Nemerow pollution index,  $\bar{C}_f$ , the arithmetic mean of contamination factors of all heavy metals, and  $C_{fmax}$  the maximum contamination factor among the heavy metals.

##### Potential ecological risk index

The total ecological risk index (RI) for heavy metals in sediments was calculated using Eq. (5)

$$RI = \sum_{i=1}^n E_f^i, \quad \text{where } E_f^i = C_f^i \times T_f^i \quad (5)$$

where  $C_f^i$  is the contamination factor,  $T_f^i$  is the toxicity coefficient of metal  $i$ .



Table 1 shows the classification of heavy metal modified degree of contamination (mCd), Nemerow pollution index ( $P_N$ ), Index of geo-accumulation ( $I_{geo}$ ) and potential ecological risk used for the sediment.

#### Pollution load index

The pollution load index (PLI) was evaluated as the  $n$ th root of  $n$  multiplied contamination factor ( $C_p$ ), as shown in Eq. (6):

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})^{\frac{1}{n}} \quad (6)$$

PLI mainly allows a qualitative comparison between sites. PLI values  $< 1$  signifies no pollution,  $PLI = 1$  signifies baseline levels of pollutants and  $PLI > 1$  signifies progressive site pollution. The pollution load index value of 0.08 indicated no deterioration of the site quality ( $PLI < 1$ ).

#### Water quality index

Water quality index (WQI) was used in the evaluation of the status of water sources from the communities. In this process, each water quality parameter was assigned a specific weight ( $W$ ) based on their relative significance on the water quality and the relative weight ( $W_i$ ) was evaluated based on Eq. (7).

$$w_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (7)$$

where  $w_i$  represent the assigned weight of each parameter,  $W_i$  is the sum of the assigned weights of all the parameters and the number of parameters (Table 2). A maximum weight of five was assigned to  $NO_3^-$  and  $Cl^-$  owing to their significance to water quality, as well as human health.

Water quality index (WQI) allows easier illustrations of complex data to determine the status of water systems. The WQI calculations are depended on significant water quality parameters by providing a specific number to represent the

overall water quality (Pius et al. 2012). According to WHO (2011), the quality rating scale ( $q_i$ ) for each of the water parameter was evaluated following Eq. (8) and finally WQI was calculated using Eqs. (9) and (10):

$$q_i = \frac{C_i}{S_i} \times 100 \quad (8)$$

$$SI_i = W_i \times q_i \quad (9)$$

$$WQI = \sum SI_i \quad (10)$$

where  $C_p$ ,  $q_i$  and  $S_p$  respectively, represent the concentration of each chemical parameter in the water sample, the quality rating and the concentration of each parameter as per the WHO (2011) standard Table 2;  $SI_i$  and  $W_i$  represent the sub-index of the  $i$ th parameter and the sum of the assigned weights of all the parameters (Table 2), respectively.

#### Suitability for irrigation purposes

The suitability of surface water for irrigation purpose was evaluated by calculating the soluble sodium percentage (SSP), sodium adsorption ratio (SAR), Permeability index, Kelly's ratio (KR), residual sodium carbonate (RSC) and magnesium ratio (MR). The SSP, SAR, KR, RSC and MR were calculated using Eqs. (11) to (15) and the values together with the PIs are given in Additional file 1: Table S3.

$$SAR = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}}} \quad (11)$$

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \quad (12)$$

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (13)$$

**Table 1 Classification of heavy metal modified degree of contamination (mCd), nemerow pollution index ( $P_N$ ), index of geo-accumulation ( $I_{geo}$ ) and potential ecological risk**

Class	mCd	Cont deg	$P_N$	Cont deg	$I_{geo}$	Cont deg.	RI	Ecological risk
0	$< 1.5$	Unpolluted	$< 1$	Unpolluted	$< 0$	Unpolluted	$< 110$	Low risk
1	$1.5 \leq Cd < 2$	Slightly polluted	$1 \leq P_N < 2.5$	Slightly polluted	0–1	Slightly to moderately polluted	$110 \leq RI < 200$	Moderate risk
2	$2 \leq Cd < 4$	Moderately polluted	$2.5 \leq P_N < 7$	Moderately polluted	1–2	Moderately polluted	$200 \leq RI < 400$	Considerable risk
3	$4 \leq Cd < 8$	Moderately-heavily polluted	$\geq 7$	Heavily polluted	2–3	Moderately to highly polluted	$\geq 400$	Severe risk
4	$8 \leq Cd < 16$	Heavily polluted			3–4	Highly polluted		
5	$16 \leq Cd < 32$	Severely polluted			4–5	Highly to extremely polluted		
6	$\geq 32$	Extremely polluted			5–6	Extremely polluted		

**Table 2** Weights and relative weights of physiochemical parameters

Parameters	Units	WHO standard (2011)	Weight (wi)	Relative weight $W_i = \frac{w_i}{\sum_{i=1}^n w_i}$
pH		6.5–8.5	4	0.093
TDS	mg/L	500	4	0.093
SO <sub>4</sub> <sup>2-</sup>	mg/L	250	4	0.093
Ca	mg/L	75	2	0.047
Mg	mg/L	50	2	0.047
Total hardness	mg/L	500	3	0.070
NO <sub>3</sub> <sup>-</sup>	mg/L	45	5	0.116
Fe	mg/L	0.3	3	0.070
Zn	mg/L	3.0	3	0.070
Na <sup>+</sup>	mg/L	200	1	0.023
K <sup>+</sup>	mg/L	12	1	0.023
Cl <sup>-</sup>	mg/L	250	5	0.116
HCO <sub>3</sub> <sup>-</sup>	mg/L	300	3	0.070
EC	μS/cm	500	3	0.070
			$\sum w_i = 43$	$\sum W_i = 1$

$$SSP = \frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100 \quad (14)$$

$$MR = \left[ \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \right] \times 100 \quad (15)$$

## Results and discussion

### Physicochemical parameters

Physicochemical parameter values of the surface water samples analysed in the Birim River basin are presented in Table 3. The water temperature ranged between 25.00 and 28.00 °C with a mean value of 26.26 °C. The colour of the water samples ranged from 364.62 to 34615.35 PtCo, with an average 14,583.67 PtCo. The levels of colour in all the surface water samples exceeded the WHO permissible limit of 15 PtCo. Highly collared water may be owned by the decaying vegetation in the water resources (Kari-kari and Ansa-Asare 2006). The pH values of all the surface water samples ranged between 6.36 and 7.02, with a mean pH of 6.68, indicating acidic to neutral to nature of Birim River basin water. The acidic pH was attributable to the naturally occurring silicate minerals. The pH values of all the surface water samples were below the WHO acceptable limits of 6.5–8.5 for drinking and other domestic purposes (WHO 2011). The TDS and EC concentrations in the surface water samples ranged from 29.03 to 64.33 mg/L and 58.03 to 128.97 μS/cm, with a mean of 42.60 mg/L and 25.21 μS/cm, respectively. The

low TDS concentration in the water samples is due to the short residence time of the underground rocks as well as the slow weathering of granitic (Patel et al. 2016). The EC and TDS concentrations of all the river water samples are very much below the WHO acceptable limit of 500 μS/cm and < 600 mg/L, respectively (WHO 2011). Total alkalinity (TA) is a measure of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions. TA refers to the ability of water to neutralise strong acids. The alkalinity of the surface water samples ranged between 20.00 and 161.00 mg/L, with a mean of 79.20 mg/L. The alkalinity of all the surface water samples fell below the WHO permissible limits of 200.00 mg/L. Total hardness (TH) represent alkaline earth elements, such as magnesium and calcium within the water resources. The TH ranged from 51.76 to 168.57 mg/L, with a mean value of 92.31 mg/L. TH concentrations of all the river water samples were below the WHO guideline of 500 mg/L. Turbidity has an average value of 1652.86 NTU that ranges from 31.60 to 3000.00 NTU. All the surface water samples had turbidity concentration above the WHO acceptable limit of 5 NTU. The high turbidity can be ascribed to larger particles, such as dissolved solids and organic matter in the surface water samples (Schafer et al. 2010). The calcium hardness of the sampled surface water varied from 30.74 to 100.26 mg/L, with a mean of 55.15 mg/L, while magnesium hardness ranged between 21.02 and 68.31 mg/L, with a mean of 37.16 mg/L. All the analysed surface water samples were below the WHO permissible limit of 200 mg/L for magnesium hardness. The free and total CO<sub>2</sub> content in the surface water samples ranged from 17.57 to 44.63 and 35.17 to 172.11 mg/L with a mean of 30.02 and 99.24 mg/L, respectively.

### Major ions and heavy metals

The concentrations of major ions, such as K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> are summarised in Table 3. The sources of sodium ion (Na<sup>+</sup>) are from the weathering products of silicate rocks and its movement from the absorbed complex of soil and rocks by magnesium and calcium. The concentrations of Na<sup>+</sup> varied between 2.90 and 5.10 mg/L, with a mean of 3.81 mg/L. The Na<sup>+</sup> concentrations were below the WHO recommended limits of 200 mg/L. The levels of K<sup>+</sup> in the surface water samples ranged between 0.40 and 3.90 mg/L, with a mean value of 1.00 mg/L and the levels were below the permissible limit of 12 mg/L by WHO (2011). The low concentration of K<sup>+</sup> in the surface water samples was due to its affinity to be immobilised by clay minerals to partake in forming secondary minerals. The levels of Ca<sup>2+</sup> ion in the Birim River basin ranged from 12.80 to 41.60 mg/L, with a mean 22.40 mg/L. The levels of Mg<sup>2+</sup> varied between 5.13 and 16.66 mg/L, with a mean level of 8.90 mg/L. The concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup>

**Table 3** Physicochemical parameter of surface water samples collected from settlements within the Birim River basin

	Minimum	Maximum	Mean	Std. deviation	Variance	Skewness	Kurtosis	WHO standard
pH	6.36	7.02	6.68	0.18	0.03	0.27	0.84	6.5–8.5
Conductivity ( $\mu\text{S}/\text{cm}$ )	58.03	128.97	85.37	25.21	635.70	0.65	−0.79	500
Turbidity (NTU)	31.60	3000.00	1652.86	1263.92	1597.38	−0.12	−1.89	5
Alkalinity (mg/L)	20.00	161.00	79.20	42.63	1817.29	0.44	0.14	200
TDS (mg/L)	29.03	64.33	42.60	12.60	158.74	0.64	−0.79	<600
Temperature ( $^{\circ}\text{C}$ )	25.00	28.00	26.26	0.88	0.78	0.95	0.80	<25 $^{\circ}\text{C}$
TH (mg/L)	51.76	168.57	92.31	41.05	1685.14	1.12	0.15	500
Colour (PtCo)	364.62	34,615.35	19,071.33	14,583.67	2126.65	−0.12	−1.89	15
CaH (mg/L)	30.74	100.26	55.15	24.40	595.43	1.09	0.08	–
MgH (mg/L)	21.02	68.31	37.16	16.66	277.41	1.17	0.26	200
$\text{NO}_3^-$ (mg/L)	bd	1.00	0.38	0.31	0.10	0.55	−1.22	45
$\text{K}^+$ (mg/L)	0.40	3.90	1.00	1.07	1.15	2.66	7.50	12
$\text{Na}^+$ (mg/L)	2.90	5.10	3.81	0.79	0.63	0.80	−0.64	200
$\text{Cl}^-$ (mg/L)	11.98	69.96	27.76	19.35	374.46	1.66	1.80	250
$\text{Mg}^{2+}$ (mg/L)	5.13	16.66	8.98	4.04	16.33	1.19	0.30	50
$\text{Ca}^{2+}$ (mg/L)	12.80	41.60	22.40	10.12	102.39	1.19	0.28	75
$\text{SO}_4^{2-}$ (mg/L)	bd	1.00	0.41	0.33	0.11	−0.06	−2.08	250
$\text{CO}_3^{2-}$ (mg/L)	0.01	0.16	0.05	0.05	bd	1.95	4.34	–
$\text{HCO}_3^-$ (mg/L)	19.99	160.84	78.63	43.20	1866.47	0.41	0.02	300
Free $\text{CO}_2$ (mg/L)	17.57	44.63	30.02	9.20	84.63	−0.34	−0.82	–
Total $\text{CO}_2$ (mg/L)	35.17	172.11	99.24	44.21	1954.48	−0.14	−0.72	–
Fe (mg/L)	0.63	6.44	3.41	1.88	3.55	−0.10	−0.95	0.3
Zn (mg/L)	bd	0.02	0.01	0.00	0.00	−0.24	−0.31	3.0

ions, respectively, in all the river water samples, fall below the WHO maximum acceptable limit of 75 and 150 mg/L. Calcium (Ca) and magnesium (Mg) are serious hydrochemical elements in water (Razowska-Jaworek 2014). Ca is a significant ion that affects the hardness of water and has been the most abundant elements found in water resources. The anion chemistry of Birim River basin was dominated by  $\text{HCO}_3^-$  followed by  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ . The  $\text{Cl}^-$  content in the Birim water samples varied from 11.98 to 69.96 mg/L, with a mean of 27.76 mg/L and all the surface water samples were below the acceptable limits of 250 mg/L recommended by the WHO (2011). Sulphate ( $\text{SO}_4^{2-}$ ) ions are limited by  $\text{Ca}^{2+}$  ions in surface water. The major source of sulphate in water resources is sedimentary rock, such as anhydride and gypsum. The sulphate concentration in the Birim River basin ranged between *bd* and 1.00 mg/L, with a mean value of 11.98 mg/L. The  $\text{SO}_4^{2-}$  contents in the Birim River samples were below the acceptable limits of 250 mg/L recommended by WHO. The  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  concentrations ranged from 19.99 to 160.84 mg/L and 0.01 to 0.16 mg/L, with mean values of 78.63 and 0.05 mg/L, respectively. The levels of nitrate ( $\text{NO}_3^-$ ) in surface water can be attributed to the oxidation of nitrogenous waste products in animal and human excreta,

wastewater disposal and agricultural activity. The concentrations of  $\text{NO}_3^-$  in surface water can vary depending on surface runoff of fertiliser, denitrification by bacteria and uptake by phytoplankton. The level of  $\text{NO}_3^-$  in surface water was moderately low, ranged from *bd* to 1.00 mg/L, with a mean value of 0.38 mg/L. The levels of  $\text{NO}_3^-$  were below the acceptable limits of 45 mg/L. The level of iron in the surface water ranged between 0.63 and 6.44 mg/L, with a mean value of 3.41 mg/L. The level of zinc in the surface water ranged between *bd* and 0.02 mg/L, with a mean level of 0.01 mg/L. The levels of zinc were below the acceptable limit of 3 mg/L as per the WHO (2011) standard. The levels of As, Pb and Cd were however observed to be below detection in all the water samples analysed.

#### Correlation of water quality parameters

There was a strong correlation between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with TH indicates that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are the major contributors to water hardness.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  has a significant positive correlation ( $r=1.000$ ,  $p<0.01$ ), indicating the contribution of dolomite to the levels of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the surface water. The positive correlation of  $\text{Cl}^-$  with  $\text{Na}^+$  and  $\text{Ca}^{2+}$  indicates the dominance of soluble salts. High positive correlation of EC with  $\text{CO}_3^{2-}$  and

$\text{HCO}_3^-$  ions signify high mobility of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions in the surface water. In addition, the strong significant correlation between TDS and EC ( $r=1.000$ ,  $p<0.01$ ) might be ascribed to ions in TDS conducting electricity. The strong positive correlation between  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions ( $r=0.703$ ) indicates agricultural activities, such as chemical and organic fertilisers in the study area. The strong correlation between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  signifies the influences of agricultural activities, evaporation, marine sources and poor drainage conditions on the surface water system. Surface water  $\text{HCO}_3^-$  was strongly correlated with pH, EC, alkalinity  $\text{CO}_3^{2-}$  and TDS. Total  $\text{CO}_2$  was strongly correlated with  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and free  $\text{CO}_2$ .

### Hierarchical cluster analysis

The water quality differences between the sampling stations are given by dendrogram as shown in Fig. 2. Cluster 1, representing Adukrom, Nsutam, Osino and Anyinam are areas with high water pollution. Cluster 2 representing Kibi, Nsuapemso and Apapam are areas with moderate water pollution. Cluster 3 representing Ankaase, Mampong and Bunso are areas with lower water pollution.

### Principal component analysis

The physicochemical parameters in the surface water samples were statistically evaluated with R-mode PCA to understand the correlation of the analysed parameters and identify the significant factors influencing the study area. Suitability of components for PCA was tested by performing Kaiser–Meyer–Olkin (KMO) tests. KMO test

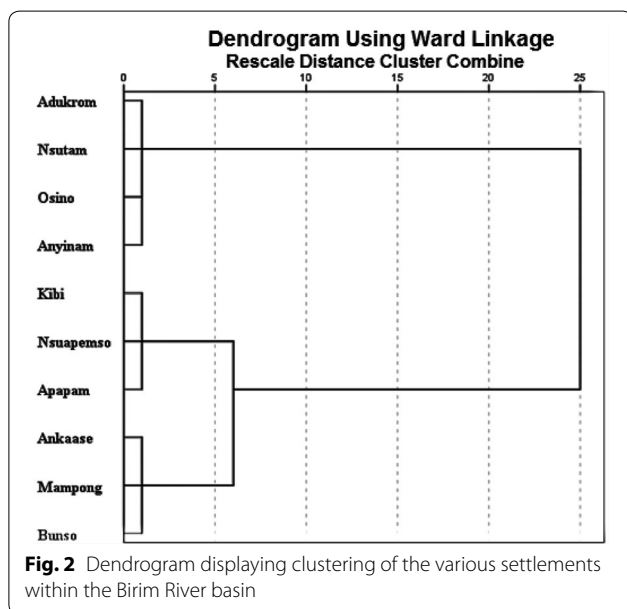
is an index used in relating the magnitude of the observed correlation and partial coefficients with a value of  $>0.5$ . In this study, KMO was 0.83, which indicates the suitability of the physicochemical parameters results for component analysis. The component loadings are classified as strong, moderate and weak with absolute loading values of  $>0.75$ ,  $0.75-0.50$  and  $0.50-0.30$ , respectively. The PCA on the composite data sets extracted five components with eigenvalue  $>1$  and these components explained 98.15% of the total variance as shown in Additional file 1: Table S1.

The first component (PC1) accounted for 49.14% of total variance and includes strong positive loadings of pH, turbidity, alkalinity, total hardness, colour, calcium hardness, magnesium hardness,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^{2-}$  and total  $\text{CO}_2$ ; and moderate positive load of TDS, EC, free  $\text{CO}_2$  and Fe. This component signifies dissolution of carbonate minerals as well as geogenic attributes, such as surface runoff during the rainy season, soil erosion, and weathering of mineral bearing rocks. The second component (PC2) explaining 20.68% of the total variance, have a strong positive loading of temperature; moderate positive loadings of TDS and Fe and weak loadings of EC. The moderate positive load of Fe is influenced by geological activities (Adamu et al. 2015). The third component (PC3) explaining 13.71% of total variance, have a moderate loading of  $\text{SO}_4^{2-}$ , colour, and turbidity, while  $\text{NO}_3^-$  and  $\text{K}^+$  has a weak positive load. The PC3 indicates agriculture practices, such as the use of chemical fertilisers, as well as anthropogenic contaminants induced by domestic wastes (Jalali 2007). The fourth component (PC4) which explained 9.05% of total variance has a moderate positive loading of Zn. The fifth component (PC5) explaining 5.56% of total variance, have a moderate and weak positive loading of  $\text{Cl}^-$  and  $\text{Na}^+$ , respectively.

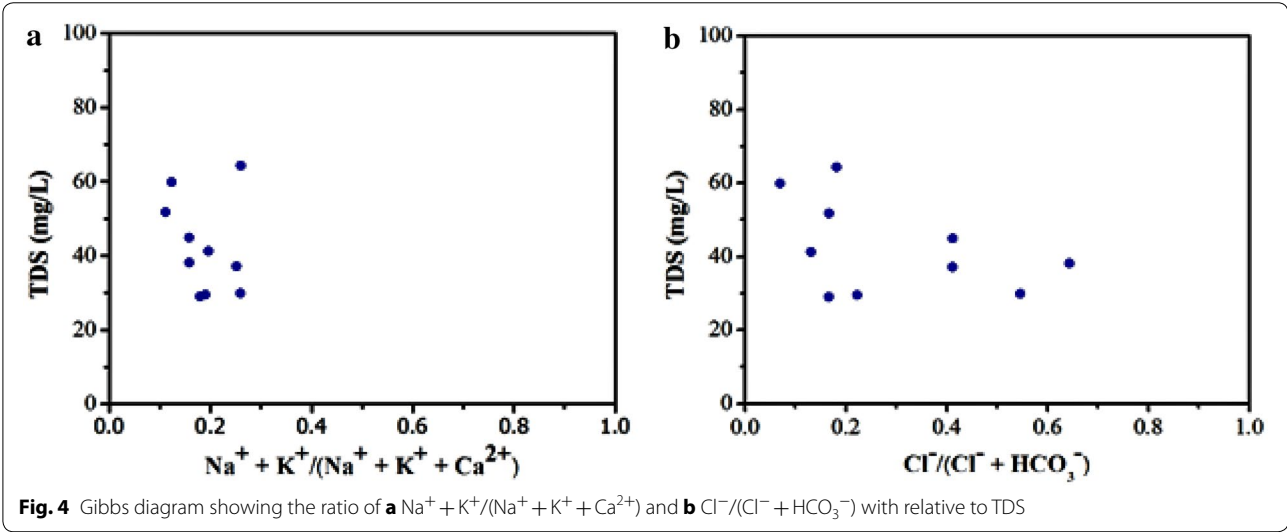
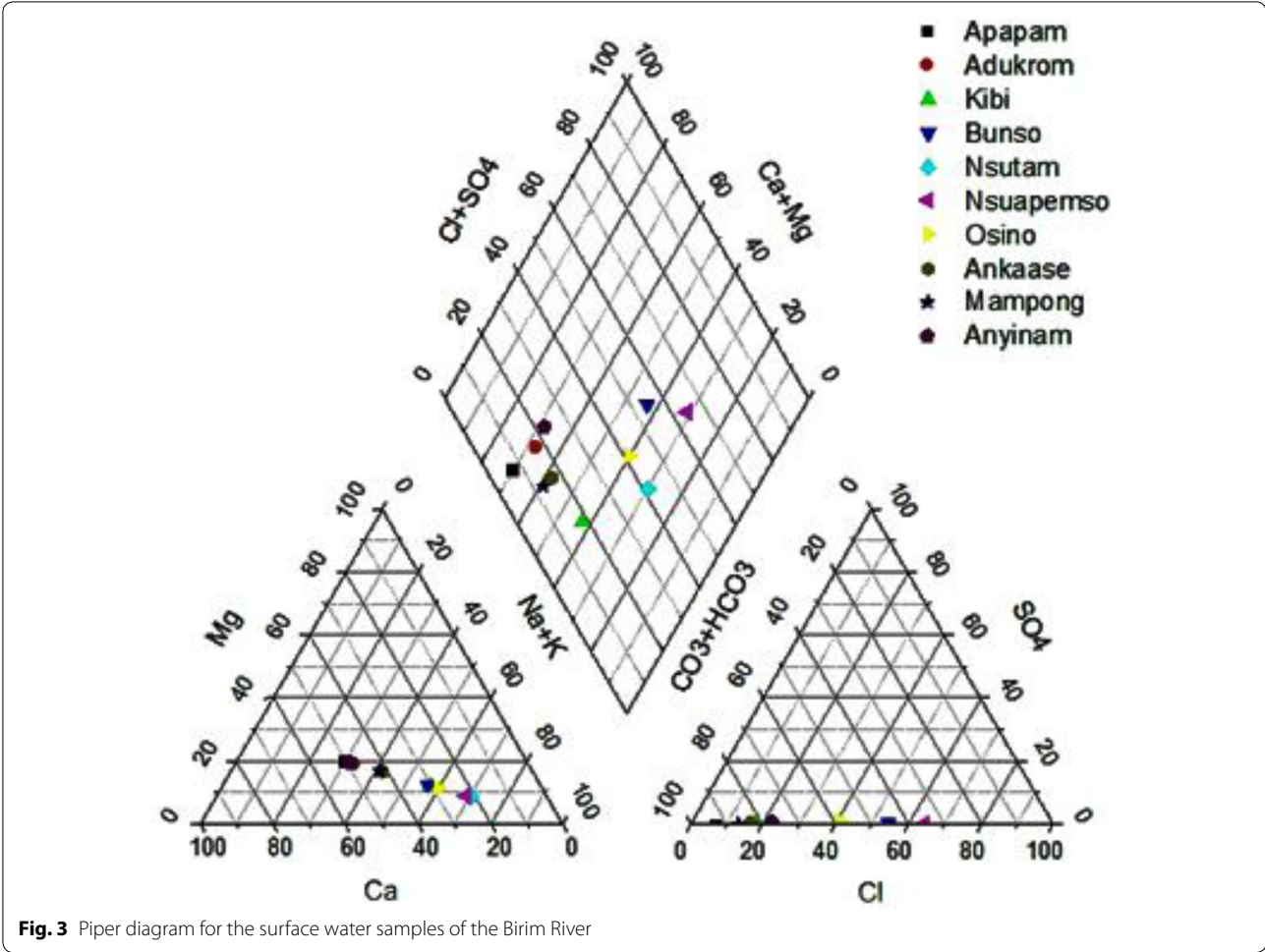
### Surface water evolution mechanisms

The geochemical evolution of surface water was analysed by plotting the levels of major cations and anions in a Piper trilinear diagram. The relative abundance of the anions and cations are shown in Fig. 3. The plot reveals five types of facies Ca–Na–Mg  $\text{HCO}_3$  (39%), Na–Cl– $\text{HCO}_3$  (15%), Na–Ca–Mg– $\text{HCO}_3$  (23%), Na–Ca–Mg– $\text{HCO}_3$  (4%) and Na– $\text{HCO}_3$ –Cl (8%) of which Ca–Na–Mg  $\text{HCO}_3$  is the predominant facies type.

Gibbs plots were used to access the hydrochemical processes, such as evaporation, rock–water interaction and precipitation on surface water chemistry. Gibbs plots have been extensively utilised to evaluate the underlying mechanisms behind water evolution. All the studied water samples are in the lower part of the diagram (Fig. 4), signifying precipitation interactions as the leading factor controlling the surface water chemistry. Thus,





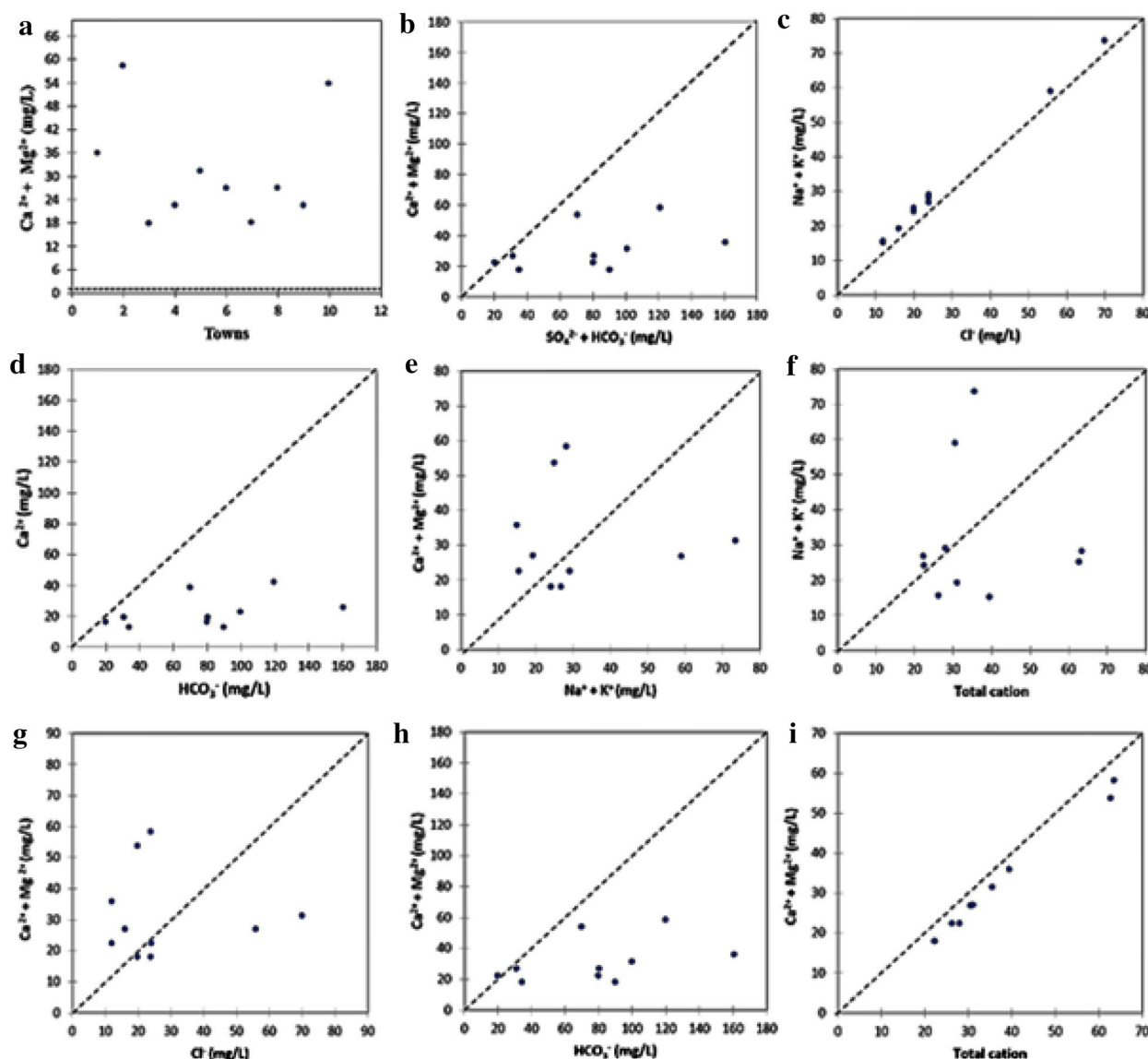


there is a close connection between the surface water chemistry and atmospheric precipitation in the Birim River basin.

### Hydrogeochemical facies

Molar ratios of major ions have been extensively utilised to ascertain the hydrogeochemical formation and process mechanisms of water resources (Murkute 2014; Singh et al. 2013; Marghade et al. 2011).  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio is normally used to evaluate the source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the water systems. The ratio of 1, signifies dissolution of dolomite, a ratio greater than 1 ( $>1$ ), indicates calcite

contribution and a ratio greater than 2 ( $>2$ ), indicates dissolution of silicate minerals (Singh et al. 2013). All the water samples have  $\text{Ca}^{2+} + \text{Mg}^{2+}$  ratio greater than 2 ( $>2$ ) (Fig. 5a), indicating silicate minerals responsible for  $\text{Ca}^{2+}/\text{Mg}^{2+}$  contribution. The bimodal process of Ca enhancement and weathering process (carbonate vs silicate) are shown in Fig. 5b, displaying the ratio of  $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ . If  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  ions are from the dissolution of dolomite, gypsum, and calcite, a 1:1 stoichiometry of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  to  $(\text{HCO}_3^- + \text{SO}_4^{2-})$  might occur (Singh et al. 2014). Most of the water samples, however, deviate from 1:1, which



**Fig. 5** Ionic scatter diagram of surface water in the Birim River: **a**  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs Towns, **b**  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs  $\text{SO}_4^{2-} + \text{HCO}_3^-$ , **c**  $\text{Na}^+ + \text{K}^+$  vs  $\text{Cl}^-$ , **d**  $\text{Ca}^{2+}$  vs  $\text{HCO}_3^-$ , **e**  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs  $\text{Na}^+ + \text{K}^+$ , **f**  $\text{Na}^+ + \text{K}^+$  vs total cation, **g**  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs  $\text{Cl}^-$ , **h**  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs  $\text{HCO}_3^-$ , **i**  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs total cation

indicates that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  primarily occur from the dissolution of gypsum, dolomite, and calcite. The molar ratio also signifies that the sources of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were not only from carbonate since the ratio was not 1:2. The  $(\text{Na}^+ + \text{K}^+)/\text{Cl}^-$  molar ratios in the analysed surface water from the Birim River basin were greater than 1 ( $> 1$ ) (Fig. 5c), indicating that halite, as well as silicate weathering, such as potash plagioclase and sodium plagioclase, was the source  $\text{Na}^+$  and  $\text{K}^+$  ions (Lin et al. 2016a). If  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in the surface water originate mainly from dolomite and calcite, the molar ratio of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions within the surface water will be 1:2 and 1:4, respectively.

In the  $\text{Ca}^{2+}/\text{HCO}_3^-$  plot (Fig. 5d), the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  molar ratio for some of the surface water was between 1:1 and 1:2, signifying that calcite was the only source of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions in the surface water. Nonetheless, most of the surface water samples had a molar ratio less than 1:2 ( $< 1:2$ ), suggesting dolomite as the dominant sources of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions. A high ratio of  $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$  and  $(\text{Na}^+ + \text{K}^+)/\text{total cation}$  demonstrate that the chemical composition of surface water in the Birim River basin was mainly influenced by carbonate weathering with a small contribution of silicate weathering as shown in Fig. 5e, f. The plot of  $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{Cl}^-$  obviously showed that salinity decrease with increase in  $\text{Ca}^{2+} + \text{Mg}^{2+}$ , and this phenomenon can be ascribed to ion exchange (Fig. 5g).  $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$  plot (Fig. 5h) revealed a horizontal trend line, signifying that  $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$  ratio does not alter during the increase of  $\text{HCO}_3^-$ . Thus, the contribution of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  and  $\text{HCO}_3^-$  are from different sources. Enrichment of  $\text{HCO}_3^-$  and depletion of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  may be ascribed to cation exchange. The scatter diagram of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus total cations revealed that the data falls below the 1:1 trend line, which demonstrates an increased contribution of  $\text{Na}^+$  and  $\text{K}^+$  as TDS increases (Fig. 5i).

### Water quality index

According to Sahu and Sikdar (2008), WQI values are grouped into five classifications: excellent ( $< 50$ ), Good (50.1–100), poor (100.1–200), very poor (200.1–300) and unfit for drinking ( $< 300.1$ ).

The observed WQI in analysed surface water samples ranged between 32.80 and 167.71 (Table 4). Based on the surface water quality index, 50% fall under poor type, 20% are the moderate type and 30% shows excellent water type. The WQI results indicate that the majority of the surface water from the Birim River are of poor quality for drinking and other domestic uses and may pose health problems to communities in the area. Generally high values of water quality indices indicate that most

**Table 4 Water quality index values and classification for the individual settlements**

Settlements	WQI values	Classification type
Apapam	32.80	Excellent water
Adukrom	118.77	Poor water
Kibi	38.34	Excellent water
Bunso	69.25	Good water
Nsutam	167.71	Poor water
Nsuapemso	59.59	Excellent water
Osino	126.90	Poor water
Ankaase	92.85	Good water
Mampong	126.04	Poor water
Anyinam	123.21	Poor water

of the study area have excessive levels of one or more water quality parameters. From the sensitivity analysis it was observed that the WQI did not vary much due the removal of an individual parameter with the exception of iron where the variation was very significant. The high WQI values were particularly observed in Nsutam, Osino, Mampong, Anyinam and Adukrom where iron concentrations were observed to be very high and some mining activities have been taking place.

### Heavy metals concentrations in sediments and component analysis

Results of heavy metals concentration in sediments samples at the different sampling sites are presented in Table 6.

From Table 5, heavy metals levels in the sediment samples follow the order:  $\text{Fe} > \text{Zn} > \text{Pb} > \text{Cd} > \text{As}$ . The concentrations of As and Zn in all the sediment samples were below the corresponding values of effect range median (ERM), effect range low (ERL), Interim sediment quality guideline (ISQG) and probable effect level (PEL). Lead contents at all sites, was higher than ERL, ERM, PEL and ISQG guidelines, suggesting that Pb in sediments from the Birim River might be periodically expected to induce adverse biological effects on the biota. Cadmium levels in almost all the communities were higher than the ERM and ISQG guidelines except at Anyinam. Pearson correlation coefficients among the heavy metals in sediments showed significant positive correlations among Zn/As ( $r=0.734$ ,  $p<0.05$ ), Zn/Fe ( $r=0.812$ ,  $p<0.01$ ) and As/Fe ( $r=0.774$ ,  $p<0.01$ ), signifying that these heavy metals were related to each other and could have a common natural or anthropogenic source (Hu et al. 2013). The data were normalised to minimise the grain size effect on the heavy metals. The rotated component matrices are presented in Additional file 1: Table S2. The first two components with eigenvalues  $> 2$  account for 77.77% of the total

**Table 5 Mean Heavy metals concentration (mean  $\pm$  SD) in sediments from settlements within the Birim River basin**

Settlements	Fe	Pb	Cd	Zn	As
Apapam	549.842 $\pm$ 0.003	7.348 $\pm$ 0.001	1.532 $\pm$ 0.001	5.422 $\pm$ 0.002	0.801 $\pm$ 0.001
Adukrom	573.950 $\pm$ 0.014	6.000 $\pm$ 0.004	2.032 $\pm$ 0.001	6.371 $\pm$ 0.001	0.951 $\pm$ 0.001
Kibi	564.975 $\pm$ 0.021	6.857 $\pm$ 0.014	1.582 $\pm$ 0.001	7.471 $\pm$ 0.001	0.851 $\pm$ 0.001
Bunso	582.691 $\pm$ 0.001	7.052 $\pm$ 0.007	1.982 $\pm$ 0.001	9.671 $\pm$ 0.001	1.400 $\pm$ 0.000
Nsutam	563.142 $\pm$ 0.002	8.947 $\pm$ 0.000	1.881 $\pm$ 0.000	4.721 $\pm$ 0.001	0.550 $\pm$ 0.000
Nsuapemso	578.995 $\pm$ 0.007	5.399 $\pm$ 0.002	1.782 $\pm$ 0.001	11.121 $\pm$ 0.001	1.251 $\pm$ 0.001
Osino	548.945 $\pm$ 0.007	5.998 $\pm$ 0.001	1.782 $\pm$ 0.001	5.171 $\pm$ 0.001	0.553 $\pm$ 0.004
Ankaase	578.843 $\pm$ 0.004	7.047 $\pm$ 0.071	1.631 $\pm$ 0.000	12.021 $\pm$ 0.001	1.101 $\pm$ 0.001
Mampong	574.741 $\pm$ 0.001	6.348 $\pm$ 0.001	1.782 $\pm$ 0.001	9.870 $\pm$ 0.000	0.750 $\pm$ 0.000
Anyinam	572.641 $\pm$ 0.001	7.647 $\pm$ 0.000	1.232 $\pm$ 0.001	9.572 $\pm$ 0.002	0.951 $\pm$ 0.001
Mean $\pm$ SD	568.880 $\pm$ 11.900	6.860 $\pm$ 1.010	1.720 $\pm$ 0.240	8.140 $\pm$ 2.640	0.920 $\pm$ 0.280
ERL	–	46.7	1.2	150	8.2
ERM	–	218	9.6	410	70
ISQC	–	30.2	0.68	124	7.24
PEL	–	112	4.21	271	41.6

All results are in mg/kg

ERL effect range low (NOAA), ERM effect range medium (NOAA), ISQC Interim sediment quality guidelines (Environment Canada), PEL probable effect level (Environment Canada)

**Table 6 The computed EF values for heavy metals in sediments samples collected from the Birim River**

Community	Pd	Cd	Zn	As
Apapam	2.34	0.10	0.49	3.40
Adukrom	1.83	0.13	0.55	3.87
Kibi	2.12	0.10	0.65	3.51
Bunso	2.12	0.12	0.82	5.61
Nsutam	2.78	0.12	0.41	2.28
Nsuapemso	1.63	0.11	0.95	5.04
Osino	1.91	0.12	0.46	2.35
Ankaase	2.13	0.10	1.02	4.44
Mampong	1.93	0.11	0.85	3.04
Anyinam	2.34	0.08	0.82	3.88
Mean	2.11	0.11	0.71	3.77

variability. PC1 has very high positive loadings of Zn, Fe, and As. Therefore, this component is supposed to reflect the contribution of natural geological and anthropogenic sources, such as industrial, agricultural and transportation and can originate from similar pollution sources. PC1 results concur with the correlation analysis results. PC2 has very high positive loadings of Cd, which suggested that persistent application of phosphate fertilisers in the study area may have led to an increase in Cd accumulation in the sediments (Guo and He 2013). PCA has been employed to ascertain the hypothetical source of heavy metals (Sun et al. 2010; Yi et al. 2011).

## Heavy metal contamination and its ecological risks in sediments

### Enrichment factor

On the basis of the magnitude of the enrichment factor, five contamination categories have been recognized generally (Sutherland 2000). Additionally, if the EF value of an element is greater than unity it indicates that the metal is more abundant in the sample relative to that found in the Earth's crust. EF values less than 5, though of less significance, are indicative of metal accumulation since such small enrichments may arise from differences in the composition of sample material with respect to the reference Earth's crust ratio values used in the EF calculations. If the EF values are greater than 5, samples are considered contaminated (Atgin et al. 2000). In accordance with the above suppositions, sediments from the Birim River basin (Table 6) are not contaminated with the metals studied ( $EF < 5$ ), but show moderate enrichment ( $2 \leq EF < 5$ ) for only Pb and As. The mean values of EF in the sediments were 2.11, 0.11, 0.71 and 3.77 for Pb, Cd, Zn and As, respectively. These signify the anthropogenic source of Pb and As, which is in agreement with supposition by Zhang and Liu (2002) who stated that EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. It is generally presumed that high EF values are indicative of the anthropogenic source of heavy metals.



**Table 7 Geo-accumulation Index, contamination degree, pollution load index and contamination factor of the surface sediment in the Birim River**

	$I_{geo}$				PLI	$C_f$				Sum $C_f$	$mC_d$	$P_N$
	Pb	Cd	Zn	As		Pb	Cd	Zn	As			
Apapam	-2.07	1.77	-4.51	-4.94	0.07	0.21	0.04	0.15	0.02	0.42	0.105	0.17
Adukrom	-2.36	2.17	-4.28	-4.69	0.08	0.17	0.06	0.18	0.03	0.44	0.110	0.15
Kibi	-2.16	1.81	-4.05	-4.85	0.08	0.19	0.04	0.21	0.02	0.46	0.124	0.17
Bunso	-2.12	2.14	-3.67	-4.13	0.10	0.20	0.06	0.27	0.04	0.52	0.130	0.21
Nsutam	-1.78	2.06	-4.71	-5.48	0.07	0.25	0.05	0.13	0.02	0.45	0.113	0.19
Nsuapemso	-2.51	1.99	-3.47	-4.29	0.10	0.15	0.05	0.31	0.03	0.54	0.135	0.24
Osino	-2.36	1.99	-4.58	-5.47	0.07	0.17	0.05	0.14	0.02	0.38	0.095	0.14
Ankaase	-2.13	1.86	-3.36	-4.48	0.10	0.20	0.05	0.34	0.03	0.62	0.155	0.26
Mampong	-2.28	1.99	-3.64	-5.03	0.08	0.18	0.05	0.28	0.02	0.53	0.133	0.22
Anyinam	-2.01	1.45	-3.69	-4.69	0.09	0.21	0.03	0.27	0.03	0.54	0.235	0.21

**Geo-accumulation and pollution indices**

The  $I_{geo}$ , which is the geochemical benchmark to assess heavy metals pollution in sediments. Because of the possible dissimilarities in background concentrations of any given heavy metal and anthropogenic influences, a factor value of 1.5 was used. The  $I_{geo}$  values of the surface sediments in the Birim river varied from -2.51 to -1.78 (average -2.18) for Pb, 1.45 to 2.17 (average 1.92) for Cd, -4.71 to -3.36 (average -3.99) for Zn, and -5.48 to -4.13 (average -4.81) for As (Table 7). The  $I_{geo}$  index values for Pb, Zn and As were negative and could be included in the unpolluted status (class 0), but pollution from Cd was moderately contaminated in the study area ( $I_{geo}$ : 1–2).  $PLI$  mainly allows a qualitative comparison between sites.  $PLI$  values < 1 signifies no pollution,  $PLI = 1$  signifies baseline levels of pollutants and  $PLI > 1$  signifies progressive site pollution. The pollution load index value of 0.08 indicated no deterioration of the site quality ( $PLI < 1$ ).

**Modified degree of contamination and Nemerow pollution index**

In the environment, heavy metals co-exist together with other organic compounds and their negative effect results from their combined effects. Since the single element indices do not adequately take into account this synergistic effect this study employed the multi-element indices such as the combined degree of contamination and Nemerow pollution indices. The results of both  $mC_d$  and  $P_N$  as shown in Table 7 indicate that they fall within the zero class < 1.5 and < 1 respectively (Table 1). Hence the sediments in the settlements under study are unpolluted.

**Table 8 Potential ecological risk assessment of heavy metals in sediments samples collected from the Birim River**

Community	$E_f^i$				RI
	Pb	Cd	Zn	As	
Apapam	2.62	120.95	0.08	0.80	124.45
Adukrom	2.14	160.42	0.10	0.95	163.61
Kibi	2.45	124.89	0.11	0.85	128.31
Bunso	2.52	156.47	0.14	1.40	160.54
Nsutam	3.20	148.50	0.07	0.55	152.32
Nsuapemso	1.93	140.68	0.17	1.25	144.03
Osino	2.14	140.68	0.08	0.55	143.06
Ankaase	2.52	128.76	0.18	1.10	132.56
Mampong	2.27	140.68	0.15	0.75	143.58
Anyinam	2.73	97.26	0.14	0.95	101.09
Mean	2.45	135.93	0.12	0.92	139.36

**Ecological risk assessment**

The potential ecological risk assessment properly combines the ecological effects and toxicology. This approach was employed to analyse the level of pollution of heavy metals in the surface sediments of Birim River basin. The overall potential ecological index and potential ecological risk from the single metals ( $E_f^i$ ) results are shown in Table 8.

The  $E_f^i$  values range from 1.93 to 3.20 for Pb, 97.26–160.42 for Cd, 0.07–0.18 for Zn, and 0.55–1.40 for As, with mean values of 2.45, 135.93, 0.12 and 0.92, respectively. Based on the  $E_r^i$  results, the ecological risks associated with As, Zn and Pb are generally low whiles that associated with Cd are a considerable risk. The RI values are 101.09–163.61, with an average of 139.36, indicative of a moderate risk. Cd has high (average

97%) contributions to the RI values in the sediments of Birim River basin, and these results are similar to those reported in China (Li et al. 2016; Lin et al. 2016b).

#### Suitability for irrigation purposes

The evaluation of the suitability of surface water for irrigation purpose relies on TDS, EC, and relative concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{HCO}_3^-$  ions. The high content of salts, particularly  $\text{Na}^+$  ion in the irrigation water influences the soil structure, reduces aeration and permeability, as well as resulting in alkaline soil, which can affect plant growth. Sodium adsorption ratio and percent sodium (% Na) is the sodium hazard induced by an excessive  $\text{Na}^+$  ion in the irrigation water (Alam 2014). High  $\text{Na}^+$  ion concentrations in irrigation water can negatively affect soil physical properties, causing soil particle dispersion when large amounts of  $\text{Na}^+$  ion are adsorbed onto the soil particles (Bob et al. 2016; Al-Omran et al. 2016; Arveti et al. 2011). SAR is a measure of the extent to which  $\text{Na}^+$  ion in the water systems might be absorbed by the soil. Generally, the higher the SAR value, the larger the risk of sodium hazard on plant growth. SAR values  $> 2.0$ , signify unsuitability of water for irrigation purpose (Ayuba et al. 2013; Vasanthavigar et al. 2010). The SAR value in the study area ranged between 0.73 and 1.52, with a mean value of 1.01.

The % Na content is also another parameter for evaluating the suitability of water for agriculture purposes. Since the combination of sodium with  $\text{CO}_3^{2-}$  or  $\text{Cl}^-$  results in the formation of alkaline or saline soils. The % Na value ranged between 29.61 and 70.10, with a mean value of 48.91. Hence, virtually all the water samples are suitable for irrigation except at Nsutam and Nsuapemso with % Na values slightly higher than the permitted limit of 60% for irrigation purposes.

KR is the amount of  $\text{Na}^+$  ions measured against  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . A KR greater than unity ( $\text{KR} > 1$ ) is indicative of an excess amount of  $\text{Na}^+$  ions in the water and is considered as of alkali hazard to the soil thereby making the water unsuitable for irrigation. The KR value for all the water samples was above unity, indicating unsuitability of this water for irrigation purpose.

RSC occurs when the excess  $\text{CO}_3^{2-}$  combine with  $\text{Na}^+$  ion to form  $\text{NaHCO}_3$ . RSC shows the potential to eliminate  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from the soil solution. High RSC value in irrigation water can lead to solidification and salinization of agricultural soils (Zaidi et al. 2015). However, as the soil solution becomes more concentrated, there is a high affinity for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to precipitate out as  $\text{CO}_3^{2-}$  which increases the relative proportion of sodium (Ravikumar et al. 2013). According to Li et al. (2016), water for irrigation purposes are classified as suitable, not suitable and marginally suitable

for irrigation when RSC value are  $< 1.25$ ,  $> 2.5$  and  $1.25 - 2.5$  meq/L, respectively. In this study, RSC values ranged between  $-2.42$  and  $125.15$  meq/L, signifying that not almost all the water samples are suitable for irrigation except at Bunso sampling sites.

Magnesium adsorption ratio expresses the relationship between calcium and magnesium concentration in surface water (Ayuba et al. 2013). Moreover, the excess amount of  $\text{Mg}^{2+}$  ion can affect the quality of soil, since high levels of  $\text{Mg}^{2+}$  ions in the soil can cause infiltration problems. MAR value  $> 50$ , represent unsuitable of water for irrigation purposes (Ayuba et al. 2013). The MR value in the surface water samples ranged from 28.53 to 28.77. All the MR in the surface water samples were below the acceptable limit of 50, indicating their suitability for irrigation purpose.

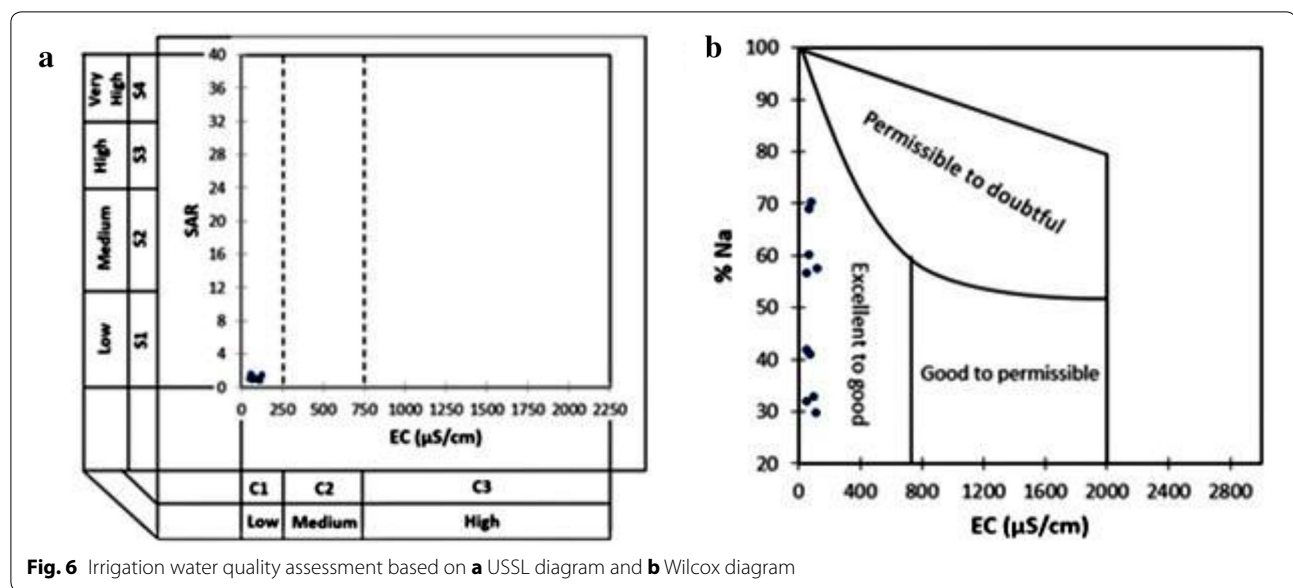
Permeability is greatly affected by  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  contents in the soil. On the basis of PI, water for irrigation purposes can be classified as suitable, marginally suitable and unsuitable for irrigation when the PI values are 100% maximum permeability (class I), 75% maximum permeability (class II) and 25% maximum permeability (class III), respectively. The calculated PI value ranged between 22.88 and 61.65 (Additional file 1: Table S3). According to the classification of PI, almost all the water samples fall under the class II, indicating that they are marginally suitable for irrigation purposes with the exception of those from Adukrom and Anyinam.

This study utilised diagrams established by the United States Salinity Laboratory (USSL) as well as Wilcox to evaluate water quality for irrigation purposes (Fig. 6).

The USSL diagram as shown in Fig. 6a signifies that the alkalinity and salinity values of all the surface water samples were very low (C1–S1), and thus no alkali hazard to crop growth. The Wilcox diagram (Fig. 6b) signifies that all the surface water samples fell under the “Excellent to good” class. Thus both Wilcox and USSL diagrams demonstrated the suitability of all the surface water samples from the Birim River basin for irrigation.

#### Conclusion

The results of this study provided valuable information about the hydrochemistry and water quality of surface water as well as ecological risks of some heavy metal contents of sediment from different settlements within the Birim River basin. The hydrogeochemical analysis of the surface water samples revealed that the water was neutral to mildly acidic and the hydrochemical facies of the area was dominated by the  $\text{Ca-Na-Mg-HCO}_3$  (39%) and  $\text{Na-Ca-Mg-HCO}_3$  (23%) water type. According to the geo-accumulation and Pollution indexes for the studied metals, settlements in the Birim River basin have moderately contaminated sediment. However multi-element



**Fig. 6** Irrigation water quality assessment based on **a** USSL diagram and **b** Wilcox diagram

indices such as the modified degree of contamination and nemerow pollution indices indicate no pollution in the study area so far as the heavy metals studied are concerned. Based on the  $Er^i$  results, the ecological risks associated with As, Zn and Pb are generally low whiles that associated with Cd are a considerable whilst the RI values are indicative of a moderate risk. All these observations notwithstanding a systematic investigation are recommended to monitor the hydrochemistry, metal loading and change in the surface water, as well as sediment quality as both legal and illegal mining activities, is intensifying in the area.

## Additional file

**Additional file 1.** Additional tables.

## Abbreviations

WQI: water quality index; SSP: soluble sodium percentage; SAR: sodium adsorption ratio; KR: Kelly's ratio; RSC: residual sodium carbonate; MR: magnesium ratio; ERM: effect range median; ERL: effect range low; ISQG: interim sediment quality guideline; PEL: probable effect level; PLI: pollution load index; CF: contamination factor; CD: contamination degree;  $I_{geo}$ : Geo-accumulation Index; PERI: potential ecological risk index; ER: ecological risk;  $T_i$ : toxicity coefficient;  $R_i$ : total ecological risk index; USSS: United States Salinity Laboratory; KMO: Kaiser–Meyer–Olkin tests; PCA: principal component analysis.

## Authors' contributions

JOO carried out the sampling, laboratory analyses and participated in the drafting of the manuscript. NKA and AAA conceived the study, participated in its design and coordination, performed the statistical analysis and helped to draft the manuscript. All authors read and approved the final manuscript.

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## Competing interests

The authors declare that they have no competing interests.

## Availability of data and materials

Not applicable.

## Consent for publication

Not applicable.

## Ethics approval and consent to participate

Not applicable.

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