

Hydrochemical studies of Cross River Basin (southeastern Nigeria) river systems using cross plots, statistics and water quality index

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Received: 1 October 2012 / Accepted: 28 February 2013 / Published online: 31 March 2013
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Abstract Water quality assessment study of the three major rivers within the Cross River Basin have been carried out using cross plots, ionic ratio, correlation analysis, factor analysis and water quality index (WQI) based on the World Health Organization and world average data guidelines. The primary aim was to determine their suitability for domestic and irrigation uses, while the secondary aim was to determine the sources of the ions in the river water. The results showed that the water samples from the Cross River estuary generally had elevated values of dissolved ions as compared to the Calabar and Great Kwa Rivers. Cross plots, ionic ratios, correlation and factor analyses showed tidal influence, silicate weathering, nitrate pollution and dissolution of carbonate minerals from soil CO₂ as the origin of the variables. Chemical indices including sodium adsorption ratio and residual sodium carbonate indicate that the river water of the study area are suitable for domestic and irrigation, while sodium percentage (Na %) indicate unsuitability for irrigation applications. The WQI values on the average indicate water of very poor to excellent quality. Generally in terms of quality for the different rivers, the Great Kwa River is best as compared to the Calabar River and Cross River estuary for domestic and irrigation purposes.

Keywords Cross River · Water quality · Multivariate statistics · Index · Nigeria

Introduction

The rapid economic development and urbanization in many countries of the world has resulted in water pollution and degradation of aquatic ecosystem which in turn have caused massive damage to the functions and integrity of water resources (Song et al. 2011). This thus makes rivers highly vulnerable to pollution due to their role in carrying municipal and industrial waste. Hence, it is essential to assess the quality of river water on a regular basis for the development of environmental strategies and future economic development. The present study therefore examines the various physicochemical characteristics of the major rivers (Cross River estuary, CRE; Calabar River, CR; Great Kwa River, GKR) in Cross River Basin in relation to drinking, domestic and irrigational use based on the existing national and international standards and a water quality index (WQI). Secondly, the study involved the examination of the seasonal and spatial variations of the physicochemical parameters in the different river water systems and also applied multivariate statistics, cross plots and ionic ratios to identify the sources and factors controlling the river water chemistry.

Previous studies on these river systems focused mainly on the effects of season and tidal changes on the quality of the Cross River (Akpan and Offem 1993) and on the concentration and distribution of some heavy metals in the sediments of the Cross River Estuary (Azumatullah and Ekwere 1981). The work of Asuquo (1989), Akpan (2000) and Akpan et al. (2002, 2003a, b) on the Calabar River focused on its baseline characteristics; water quality scheme; influence of tide and coastal activities on the water

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quality; and the processes controlling heavy metal distribution. Other studies on the Calabar River included an evaluation of the effects of industrial, urban and agricultural wastes discharged into the river (Ntekim et al. 1993; Ekpo and Ibok 1998). Study on the Great Kwa River assessed the heavy metal contamination of the Great Kwa River estuary using the I-geo index (Ogri et al. 2009). This study on the GKR concluded that cadmium, zinc and nickel were potential risks in the sediments of the river. In summary, these studies on the rivers were mostly disjointed without any relationship or differences between the different river water bodies. The present study, therefore, is the first attempt to assess the quality and evolution of water from the Cross River Basin river systems as an entity.

Study area

The Cross River Basin river system encompasses three major rivers, including the Cross River Estuary, Calabar River and the Great Kwa River. The basin is situated between latitude $4^{\circ}15'$ and $5^{\circ}15'N$ and longitude $8^{\circ}15'$ and $8^{\circ}25'E$ (Fig. 1). The area is characterized by a tropical climate with two seasons: wet and dry, having an average annual precipitation and average annual air temperature of 2,508.11 mm and $27.07^{\circ}C$, respectively. The Calabar River flows westwards through a vast stretch with numerous streams and forms a network of large and small rivers before joining the Cross River estuary in the southwest. The bank of the CR is characterized by major industries such as markets, holiday

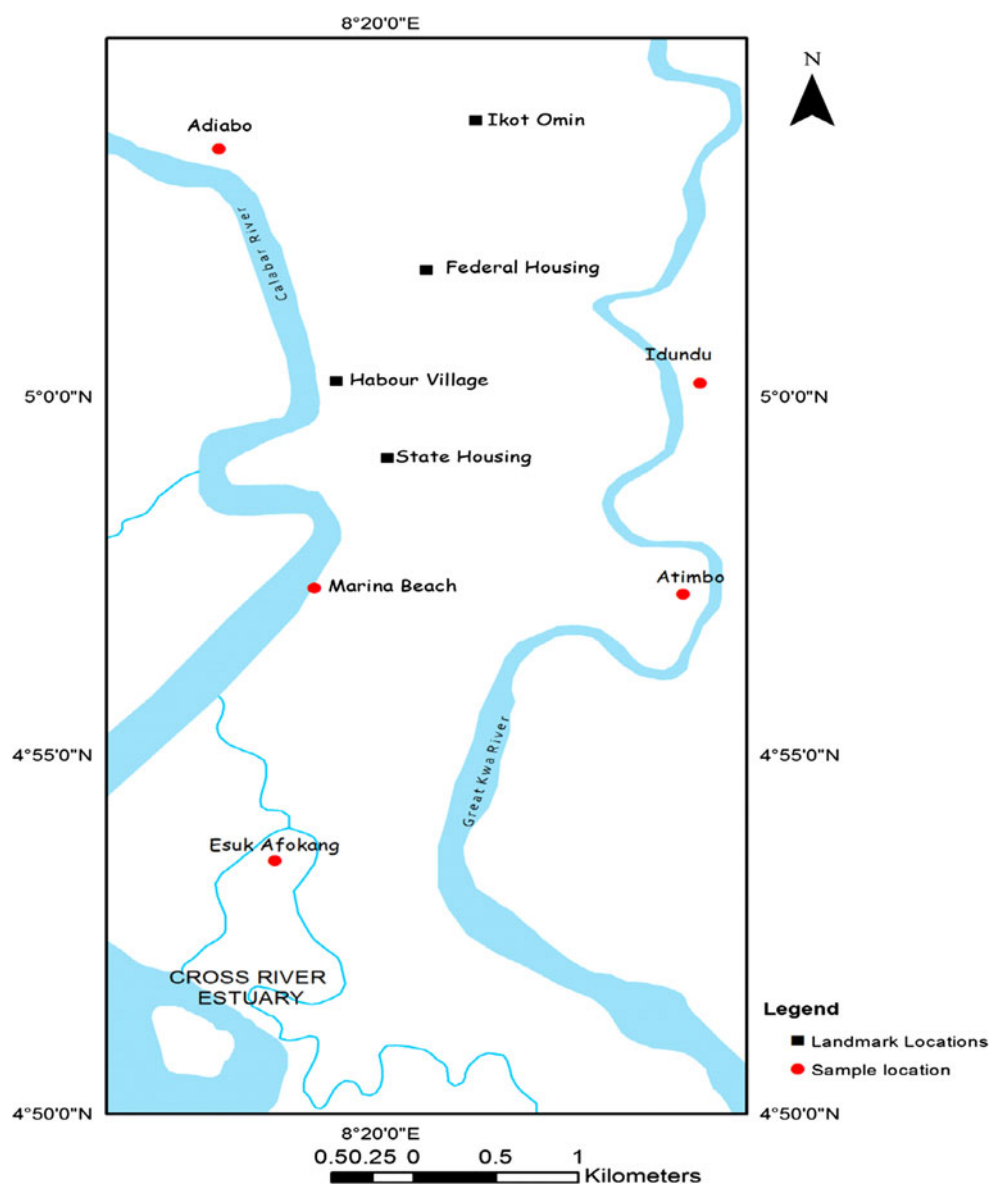


Fig. 1 Map of Calabar (Nigeria) and environs showing the Cross River Estuary, Calabar and Great Kwa Rivers and sample locations

Table 1 River sample locations and characteristics

River name	Location name	Coordinates		Description
		N	E	
Cross River Estuary	Esuk Afokang	4° 53.610	7° 08.672	The sampling location is near a timber market The main activity observed in the estuary is fishing, lumbering, navigation and because of the tidal influence the estuary is salty and not used for domestic purposes. Also observed is the discharge of domestic and human waste into the estuary
Calabar River	Marina Beach	4° 57.307	8° 18.691	This is the downstream sampling point of CR 2 Sampling point is behind the Volvo market. The main activity observed during sampling is marketing, fishing, navigation and sand mining. The water from the river is also used for domestic activities such washing and cleaning
Calabar River	Adiabo	5° 03.316	8° 18.443	This is the upstream sampling point of CR 1 Sampling point is near the Adiabo-Ikoneto bridge The main activity observed is fishing and sand mining
Great Kwa River	Atimbo	4° 56.916	8° 23.788	This is the downstream sampling point of GKR 2 Sampling point is near the Atimbo bridge The main activity observed is fishing and sand mining
Great Kwa River	Idundu	5° 00.938	8° 23.469	This is the upstream sampling point of GKR 1 Sampling point is near the Idundu bridge The main activity observed is fishing and sand mining The intake of the Calabar ADB Water scheme is further north of this location at about 5° 02.015N, 8° 21.828E

resorts, fuel tank farm, export processing zone, sea port, etc. The Great Kwa River (GKR) flows in the eastern part of Calabar from the north to the south, also joining the Cross River estuary in the southeast. The major activities in the GKR include fishing and sand mining. The discharge of the Cross River varies between 38.18 and 2533 m³/s (Lowenberg and Kunzel 1991; Ewa-Oboho 2006), while, that of the Calabar River averaged 1,449.23 m³/s. The Great Kwa River has the lowest average discharge of 90.07 m³/s (Ewa-Oboho 2006). The details of water sampling locations and activities in the river systems are presented in Table 1.

Geomorphologically, the area is underlain by alluvial complexes which pass northwards into loose coastal sands. Heavily dissected narrow fringe of outcropping Cretaceous shales, marls, limestones and thin indurated sandstones mark the northern limits of the study environment (Petters 1989). The area lies within the Niger Delta sedimentary basin. The basin consists of three geologic formations: the Akata, Agbada and Benin. The Benin Formation of Oligocene to recent age underlies the area. It is composed of medium- to coarse sandstones, sands, shales and gravel (Webber and Daukoru 1975).

Data acquisition and analysis

A total of 55 river water samples from 5 monitoring stations (Fig. 1) were collected for the study. Of the 55

samples, 32 samples were collected during the wet season, while 23 samples were collected during the dry season. The river water samples were collected from surface at a depth of 0.3 m in polyethylene bottles rinsed three times with the water sample before filling it to capacity and labeled accordingly. The river water temperature, electrical conductivity (EC), pH, and dissolved oxygen (DO) were measured on site using standard field equipment. Alkalinity was determined by titration with hydrochloric acid at the Institute of Oceanography, University of Calabar (Nigeria) Laboratory shortly after sampling.

The cations were analysed with Flame photometer (Na, K) and Atomic Absorption Spectrophotometer Perkin Elmer 2380 (Ca, Mg). Analyses of the anions (Cl, SO₄, and NO₃) were with ion chromatography Dionex 2000i with Na₂CO₃/NaHCO₃ eluent. These analyses were carried out at the Department of Earth and Ocean Sciences, University of Liverpool (UK). The details of the analyses are contained in Edet and Worden (2009) and Edet et al. (2012). Descriptive and multivariate statistics were performed using the statistical package STATISTICA (Pilz 1993), while cross plots and ionic ratios were done with Microsoft Excel spread sheet.

The river water quality was based on a comparison with the maximum admissible value of WHO (1984, 1993) for domestic purposes and also with the world average values. Total hardness (TH) was based on the scale of Sawyer et al. (2003). The suitability of the river water for irrigation was

assessed by means of sodium adsorption ratio (SAR) (Richards 1954), percent sodium, %Na (Todd 1980) and the excess sum of carbonate and bicarbonate in water over the sum of calcium and magnesium, RSC (Ragunath (1987).

The SAR was estimated using Eq. 1 (Richards 1954):

$$\text{SAR} = \frac{\text{Na}}{[(\text{Ca} + \text{Mg})/2]^{0.5}} \quad (1)$$

The sodium percentage (Na %) was calculated using Eq. 2 (Todd 1980):

$$\text{Na \%} = \frac{(\text{Na}^+ + \text{K}^+) * 100}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \quad (2)$$

where all concentrations are expressed in meq/l.

The residual sodium carbonate (RSC), calculated according to Eq. 3 of Ragunath (1987):

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (3)$$

where all concentrations are expressed in meq/l.

To assess the overall quality of the river water samples a WQI scheme was developed and applied. The WQI is defined as a rating that reflects the composite influence of different water quality parameters (Sahu and Sikdar 2008). The WQI was developed to assess the overall quality of the river water using some variables (TDS, pH, Hardness, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- and HCO_3^-). WQI was computed following the method of Yidana and Yidana (2010). In this approach, weights (W) were assigned to the variables used in assessing water quality based on their importance on water quality (Table 2). Next was the computation of the relative weight (W_r) of each variable using the equation, $W_r = W/\sum W$, where W is the weight assigned to each variable and $\sum W$ the sum of the weights

of all the variables. Finally, a quality scale Q was computed for each parameter as follows:

$$Q = (C_i/S_i) \quad (4)$$

where C_i and S_i represent the concentration for each parameter and the WHO standard/World average for that parameter.

The WQI was calculated as:

$$\sum (C_i/S_i) * W_r \quad (5)$$

for all the variables and the computed WQI were classified as follows: Excellent, E (WQI < 25); Good, G (WQI, 25–50); Moderate, M (51–75); Poor, P (76–100) and Very Poor, VP (>100).

Result

A statistical summary of the results of physicochemical parameters for the different river water samples, including the World Health Standard (WHO 1993) and world averages are presented in Table 3.

Physical characteristics of river waters

The river water temperature varied from 20.90 °C for the GKR to 31.50 °C for the CR. The mean values of pH varied between 6.51 and 6.69 for the different river waters. Generally, 50, 45 and 55 % of all the pH values for CRE, CR and GKR, respectively were not within the WHO (1993) maximum permissible value (MAV) of between 6.5 and 8.5. However, the pH values for the entire study period fell within the pH range of 4.5–9.0 for natural water (Langmuir 1997).

Twenty-five percent of the 12 samples considered for CRE had electrical conductivity (EC) and total dissolved solids (TDS) values higher than the MAV of 1,400 $\mu\text{S}/\text{cm}$ and 1,000 mg/l, respectively. For the samples from CR, 23.8 % had EC and TDS values higher than the MAV. The EC and TDS values for the Great Kwa River water samples were lower in comparison to the CRE and the CR with only 9.1 % of the 22 samples exceeding the WHO (1993) MAV. High variability of EC and TDS shown from the standard deviation values (Table 2) were attributed to tidal flushing (Edet and Worden 2009; Edet et al. 2012). The WHO (1993) stipulates minimum of 5.0 mg/l as the guideline value for DO. The average values of DO from this study indicate that 50, 33.3 and 31.8 % of the water samples for the different rivers (CRE, CR, GKR) had DO values <5.0 mg/l. The standard deviations values for water temperature of between 1.85 and 2.30 (Table 2) indicate uniform temperature for the studied rivers while, the pH values indicate that the river waters are more of acidic than alkaline.

Table 2 Standards and weights used in the study

Parameters	WHO (1984, 1993)	World average (Turekian 1977)	Assigned weight	Relative weight
TDS	1,000		3	0.12
pH	7.5		4	0.16
Hardness	75		2	0.08
Na	200	5.20	1	0.04
K	12	1.30	1	0.04
Ca	100	13.40	2	0.08
Mg	30	3.40	1	0.04
Cl	250	5.80	5	0.20
NO_3	50		4	0.16
SO_4	250	8.30	3	0.12
HCO_3		52.00	2	0.08
Total			25	1.00

Table 3 Summary of physicochemical variables for the different river systems in Calabar

River name	Statistics/standards	Temp (°C)	EC (µS/cm)	TDS (mg/l)	pH	DO (mg/l)	Alkalinity (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	Cl ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)
Cross River Estuary	Mean	27.47	1,834.81	1,318.29	6.69	5.46	33.67	419.53	16.93	13.80	32.44	650.28	23.66	111.19	40.40
	Median	28.00	351.50	189.21	6.55	5.00	19.00	28.92	4.04	3.45	1.89	37.79	22.46	3.21	22.80
	Minimum	21.90	77.10	42.90	5.30	3.60	10.00	10.22	0.61	0.23	0.09	11.50	0.67	0.00	12.00
	Maximum	30.60	10,940.00	7,934.72	7.69	9.20	75.00	2,814.41	81.31	81.36	193.13	4,368.17	51.85	834.21	90.00
	SD	2.13	3,414.23	2,588.59	0.69	1.74	24.57	889.17	25.11	23.73	68.21	1,373.55	18.20	256.15	29.48
	WHO (1993)		1,400	1,000	6.5-8.5	5 min									
WA								5.2	1.3	13.4	3.4	5.8	8.3	52	
SW				35,000				10,780	399	412	1,280	19,350		2,710	123
% Above WHO			25					25	33.3	0	16.7	25	66.7	16.7	
% Above WA								100	91.7	25	33	100		25	33.3
% Above SW								0	0	0	0	0		0	0
Calabar River	Mean	27.95	1,458.26	767.38	6.58	5.80	34.65	255.70	5.82	4.32	10.86	397.37	2.07	44.19	41.58
	Median	27.80	141.40	61.73	6.42	5.60	28.00	9.89	1.66	0.94	0.72	4.01	0.94	1.92	33.60
	Minimum	24.40	32.60	18.43	5.60	3.00	8.60	3.23	0.48	0.00	0.01	0.01	0.00	0.00	10.32
	Maximum	31.50	1,2450.00	6,433.96	7.46	8.50	87.91	2,111.20	35.14	43.66	85.62	3,564.55	12.09	487.78	105.49
	Std.Dev.	1.85	3,052.93	1,618.03	0.54	1.49	25.43	542.93	9.25	9.62	25.45	900.04	2.88	112.40	30.52
	% Above WHO		23.8		23.8				23.8	19	0	0	23.8	0	4.8
% Above WA								81	81	4.8	19	38.1		23.8	23.8
% Above SW								0	0	0	0	0		0	0
Great Kwa River	Mean	27.40	261.81	130.77	6.51	5.80	29.27	35.39	1.17	0.47	0.49	41.02	1.17	8.41	35.13
	Median	27.35	78.05	39.83	6.43	5.85	17.85	5.48	1.06	0.47	0.35	1.10	1.37	0.00	21.42
	Minimum	20.90	40.60	22.97	5.27	3.10	6.10	2.82	0.14	0.04	0.02	0.00	0.00	0.00	7.32
	Maximum	30.80	1,820.00	964.82	7.40	7.80	115.00	360.90	3.62	1.16	2.90	359.94	3.18	98.27	138.00
	Std.Dev.	2.30	474.79	236.11	0.60	1.39	31.30	88.21	0.74	0.25	0.61	97.03	0.94	24.85	37.57
	% Above WHO		9.1						13.6			4.5			
% Above WA								63.6	22.7	0	0	22.7		13.6	13.6
% Above SW								0	0	0	0	0		0	0

WHO World Health Organisation (1993), WA World average (after Turekain 1977), SW seawater (after Drever 2002)

Chemical characteristics of river waters

Twenty-five percent of the samples from the CRE had sodium (Na) concentration higher than the MAV of 200 mg/l (WHO 1993) while, all the samples had concentration of Na higher than the world average value of 5.2 mg/l for concentration in fresh water. For the same CRE samples, the concentration of potassium (K) in 91.7 % of the samples was higher than the MAV WHO (1993) of 10 mg/l and the world average concentration of 1.3 mg/l (Table 2). In the case of CR, 23.8 and 81 % of the samples had Na concentrations higher than MAV and world average values, respectively. The CR samples also had 19 and 81 % of K higher than the MAV and the world average. The GKR data showed lower concentrations compared to the CRE and the CR water samples. In respect of Na, 13.6 % of the samples had values higher than MAV with 63.6 % higher than the world average. For potassium, 22.7 % of the values were higher than the world average. Although the main source of Na and K in the study area are probably from the sea, the values were however, lower than typical concentrations as presented in Table 2. Twenty-five percent of all the samples considered had Ca concentration higher than the world average of 13.4 mg/l for CRE. The concentration of Mg showed that 16.7 and 33.0 % of the water samples from CRE was higher than the MAV value of 100 mg/l and world average of 3.4 mg/l. The concentrations of Ca and Mg in the river water samples from the CR were higher than the world average by 4.8 % (Ca) and 19 % (Mg), respectively. The Ca and Mg concentrations for all the samples in respect of the GKR were within the MAV and world average stipulated values (Table 2).

Twenty-five (25) and 100 % of all the water samples from CRE had Cl values higher than the MAV of 250 mg/l and world average of 5.8 mg/l, respectively, while 33.3 % of the HCO_3^- concentration were higher than the world average of 52 mg/l. The Cl concentration for Calabar River samples was higher than the MAV of 250 mg/l and world average of 5.8 mg/l by 23.8 and 38.1 %, respectively. However, only 23.8 % of bicarbonate concentration was higher than the world average of 52 mg/l. The Cl concentration of water samples from GKR was higher than higher than the MAV and world average by 4.5 and 22.7 %, respectively. The concentration of HCO_3^- was higher than the world average by 13.6 % for samples from GKR.

The concentrations of sulphate (SO_4^{2-}) for the CRE samples were higher than MAV of 250 mg/l and world average of 8.3 mg/l, respectively, by 16.7 and 25 %. The same water samples showed that the concentration of nitrate were higher than the MAV of 50 mg/l by 66.7 %. This is probably due to the poor environmental conditions especially, dumping of domestic and human waste into the

estuary. Besides, the CRE is the receiving water body for the CR and GKR waters (Fig. 1). In the case of the CR, the concentration of sulphate for the samples showed that 4.8 and 23.8 % was higher than the MAV and world average value, respectively. The concentration of sulphate for the GKR samples was higher than the world average by 13.6 %.

The rivers can be described hydrochemically as follows:

- (i) The Cross River estuary is characterized by high ionic concentration, which is attributed to tidal influence and anthropogenic effects from the feeding rivers, including the Calabar and Great Kwa Rivers.
- (ii) The Calabar River runs through a rich industrial and human settlement thus receiving high domestic and industrial loads and
- (iii) The Great Kwa River relative to the CRE and CR is characterized by low ionic concentration as the catchment area is devoid of major industrial and human activities.

Discussion

Seasonal and spatial assessment

The concentrations of all the variables were higher in the dry season as compared to the wet season (Fig. 2). The lower values of ions in the wet season were attributed to dilution effect. The low ionic concentration may also be due to diluting and concentrating effects of feeding river inflows, change in catchment lithology and anthropogenic input (Singh et al. 2005). However, the increase in ionic concentrations during the dry season is due to evaporation effect during the low water level aided by elevated temperature in the area. In addition, as compared to GKR, the

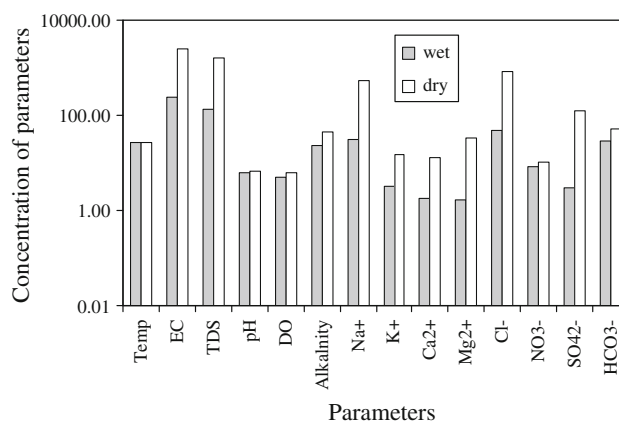
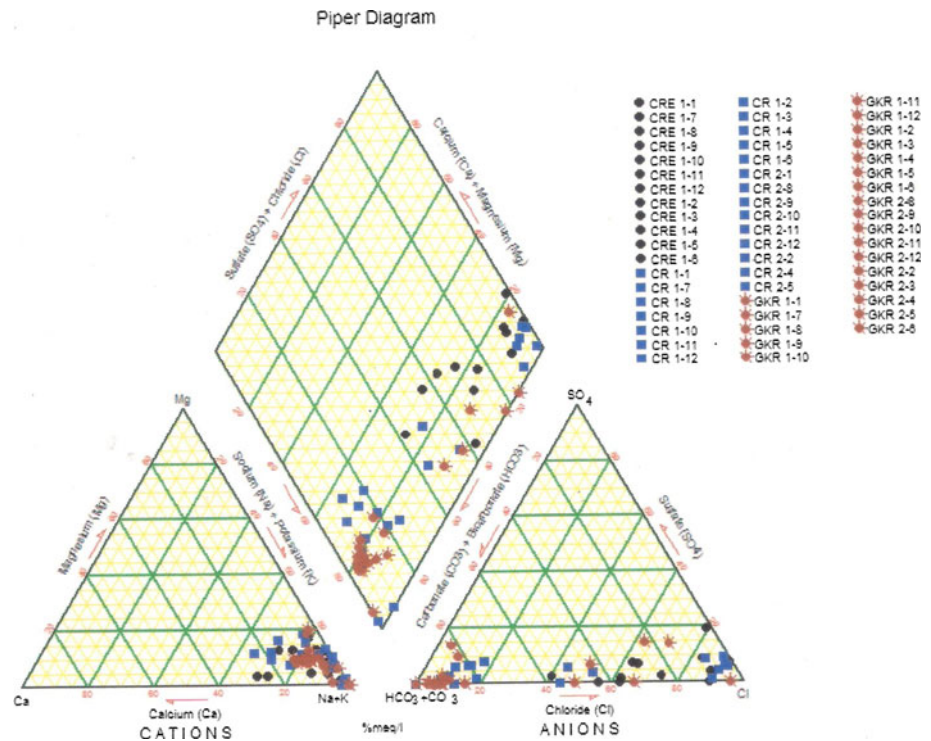


Fig. 2 Comparison of average concentration of parameters in the different seasons for the three rivers. (Units Temperature in °C; EC in $\mu\text{S}/\text{cm}$; TDS, DO, Alkalinity and ions in mg/l)

Fig. 3 Piper diagram plot for the different river water samples. *CRE* Cross River Estuary, *CR* Calabar River, *GKR* Great Kwa River. The nos 1–12 represents sampling between October 2004 (no. 1) and September 2005 (no. 12) (Edet and Worden 2009; Edet et al. 2012)



banks of CR are characterized by many industrial activities resulting in waste disposal into the river. However, the mean concentration for temperature, pH, DO and HCO_3^- were not significantly different for all the river systems.

Evolution of river water chemistry

The evolution of the river water and relationship between rock types and water composition can be evaluated by trilinear diagram (Piper 1944). The piper diagram consists of two triangular diagrams at lower left and lower right describing the relative composition of cations and anions. The plot of the river water chemical data on the piper diagram reveals that majority of the river water samples fall in areas of Na + K, HCO_3^- and Cl suggesting that alkalis exceeds alkaline earth and weak acids exceeds strong acids (Fig. 3). The variations and distributions of hydrochemical facies of the river water show that Na– HCO_3^- , Na– HCO_3^- –Cl and Na–Cl are the dominant facies.

Three major sources of dissolved ions into inland waters are (1) atmospheric deposition of salts (2) weathering of rocks forming minerals and (3) anthropogenic input

(Berner and Berner 1987; Zhang et al. 1995; Sarin and Krishnaswamy 1984; Singh and Hasnain 1998, 1999, 2002). An estimate of the atmospheric contribution to the aquatic system can be assessed by comparing the chemical composition of the river water with that of the local rain water. In this study, the local rain water collected from Calabar (Fig. 1) has been used to derive the atmospheric contributions (Table 4). The assessment shows high concentration (>5 mg/l) atmospheric contribution of Ca^{2+} and NO_3^- and low concentration (<5 mg/l) for Na^+ , K^+ , Mg^{2+} , Cl^- , HCO_3^- and SO_4^{2+} . This indicates weathering of the basin, seawater and anthropogenic sources for these ions. The relative high contribution of Ca^{2+} is due to dust from nearby limestone quarries. NO_3^- may be due to atmospheric and pollution sources (Jeong 2001).

In the studied rivers, sodium and potassium together constitutes more than 80 % of the total cations, while bicarbonate and chloride contribute 49 and 40 %, respectively of the total anions. Atmospheric deposition, seawater intrusion/tidal flushing and silicate weathering can supply sodium and potassium in river water. The plot of Na^+ vs. Cl^- (Fig. 4a) points evolved along the 1:1 line for samples

Table 4 Estimated atmospheric contributions to the river water chemistry

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-
Rain-Calabar	1.51	0.26	1.83	0.16	0.27	1.04	0.74	0.76
Mean-CRE, CR, GKR	203.32	6.39	4.85	11.42	310.01	6.42	44.50	38.74
% Rain contribution	0.74	4.10	37.85	1.43	0.09	16.15	1.66	1.96

from the CRE and for some samples from CR and GKR indicating river water is controlled by tidal flushing (Edet and Worden 2009; Edet et al. 2012). Some samples from CR and GKR show excess of Na over Cl suggesting other sources of Na such as silicate weathering and ion exchange process.

The $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ marks the upper limit of bicarbonate input from carbonate rock weathering (Stallard and Edmond 1983). The variation diagram between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs. $(\text{HCO}_3^- + \text{SO}_4^{2-})$ show that most of the samples fall below the 1:1 trend requiring a portion of the $\text{HCO}_3^- + \text{SO}_4^{2-}$ be

balanced by the alkalis ($\text{Na}^+ + \text{K}^+$), Fig. 4b and c, probably because the catchment area is composed of less reactive rocks. According to Ettazarini (2005), ion exchange process is characterized by an $\text{HCO}_3^- + \text{SO}_4^{2-}$ excess over $(\text{Ca}^{2+} + \text{Mg}^{2+})$. This tends to support the fact that ion exchange might also contribute to the chemistry of the river water. In addition, the plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{total cations}$ (TC) shows the plotted points fall below the equiline reflecting increasing contribution of Na and K (Fig. 4d). On the other hand, the plot of $(\text{Na}^+ + \text{K}^+)/\text{total cations}$ (TC), Fig. 4e show the points are on the 1:1 line indicating contributions sodium and potassium from by tidal flushing.

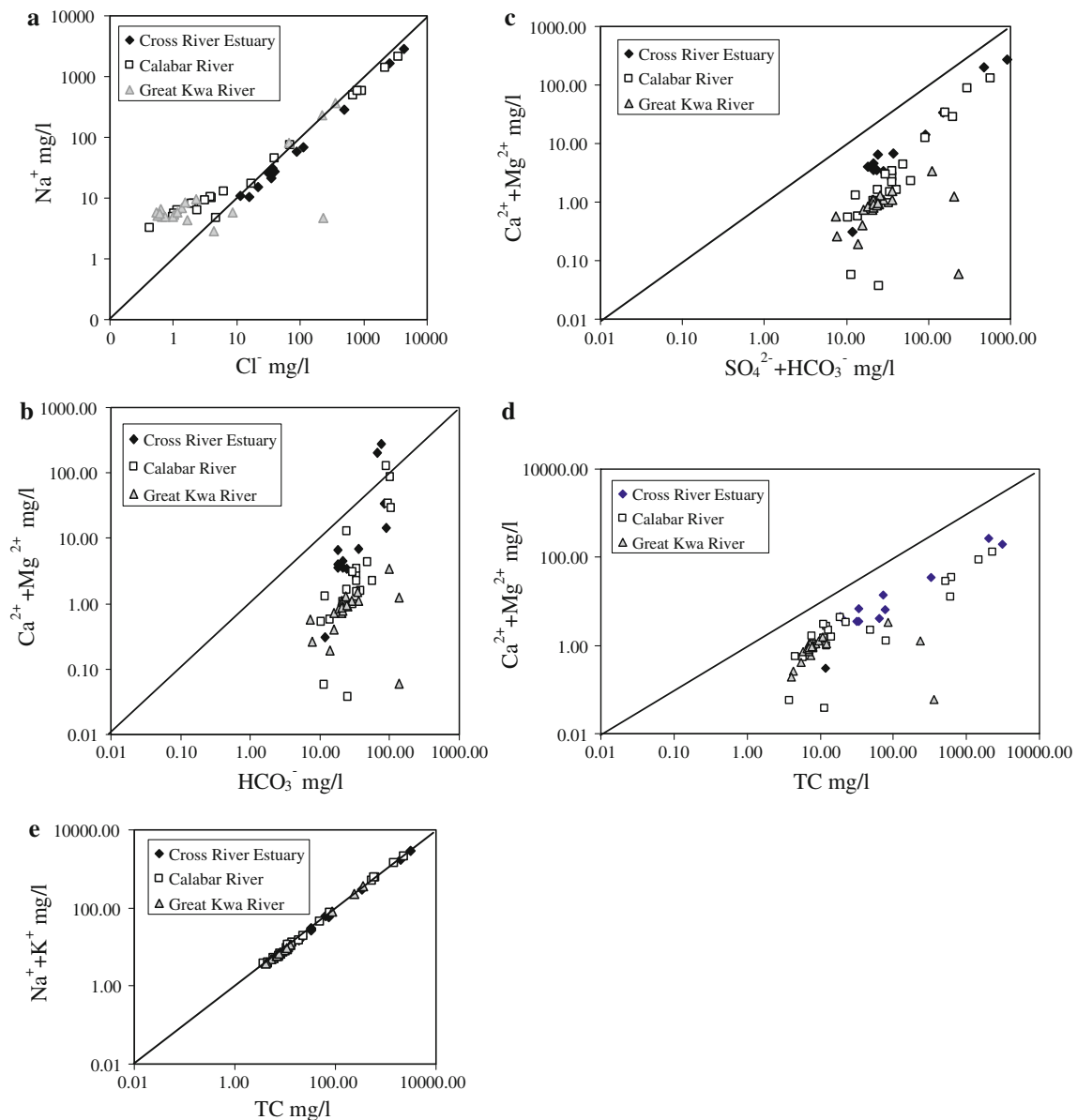


Fig. 4 Cross plots showing the main processes controlling the river water chemistry. **a** Na^+ vs. Cl^- . **b** $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^- . **c** $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. $\text{HCO}_3^- + \text{SO}_4^{2-}$. **d** $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. TC. **e** $\text{Na}^+ + \text{K}^+$ vs. TC

Table 5 Ionic ratios of river waters in the study area

River and ratio	HCO ₃ ⁻ /Cl ⁻	Na ⁺ /Cl ⁻	Ca ²⁺ /Cl ⁻	Mg ²⁺ /Cl ⁻	K ⁺ /Cl ⁻	SO ₄ ²⁻ /Cl ⁻	Ca ²⁺ /Mg ²⁺	Ca ²⁺ /SO ₄ ²⁻	Ca ²⁺ /HCO ₃ ⁻	Na ⁺ /Ca ²⁺	Ca ²⁺ /Na ⁺	Mg ²⁺ /Na ⁺	HCO ₃ ⁻ /Na ⁺	(Ca ²⁺ + Mg ²⁺)/ (Na ⁺ + K ⁺)
Cross River estuary	0.7169	0.6952	0.0911	0.0409	0.1382	0.0890	3.1321	1.2166	0.2341	23.7615	0.1280	0.0600	0.9800	0.1500
Calabar	63.1251	17.8245	0.3127	0.4351	2.8824	0.2272	2.0096	0.6207	0.0798	98.0132	0.0870	0.0650	2.5700	0.1300
Great Kwa	20.2179	5.1649	0.4698	0.3740	1.0000	0.3638	2.0997	0.2640	0.0204	428.5998	0.0730	0.0600	3.3300	0.1100
Seawater	0.0075	0.5526	0.0211	0.0711	0.0200	0.1421	0.2963	0.1481	2.8169	26.2500	0.0381	0.1286	0.0135	0.1608
Carbonate weathering											50.0000	10.0000		
Silicate weathering											0.3500	0.2400		1.0000

Ionic ratios have often been applied to evaluate the extent of seawater effect on the freshwater system (Lee and Song 2007). Table 5 shows some selected ratio of ions for the river water. Values of HCO₃⁻/Cl⁻, indicative of fresh water are all greater than the ratio for seawater of 0.0075. The ratio is highest for CR (63.1252) and lowest for CRE (0.7169) indicating that the influence of seawater through tidal flushing is a major factor in the CRE as compared to CR and GKR. The ratio, Na⁺/Ca²⁺ for CRE is similar to that seawater but does not show any significant relation with TDS indicating that the ratio is not a good indicator of seawater (Lee and Song 2007). The ratios Na⁺/Cl⁻, K⁺/Cl⁻, Ca²⁺/Cl⁻ and Mg²⁺/Cl⁻ exhibited negative correlation with TDS. These ratios decreased as TDS increased, which was derived from chloride enrichment of the rivers due to tidal flushing especially, for Cross River estuary. Thus the lower the values of these ratios, the greater the influence of seawater as reflected in the case of CRE (Table 5). This supports the fact that seawater is a major contributor to the river water chemistry.

The average ratio of (Ca²⁺ + Mg²⁺)/(Na⁺ + K⁺) was 0.1500, 0.1300 and 0.1100, respectively, for CRE, CR and GKR. These values are close to that of seawater (0.1608) but lower than for silicate weathering (1.000). The lower values thus indicate the effect of seawater. The range of ratios of Ca²⁺/Na⁺ (0.0730–0.1280), Mg²⁺/Na⁺ (0.0600–0.0650) and HCO₃⁻/Na⁺ (0.9800–3.3300), Table 5 are much lower than the water that drains carbonate weathering environment but slightly closer to that of silicate weathering and more closer to that of seawater. The order being seawater > silicate weathering > carbonate weathering. Thus the major contributor to the river water chemistry is tidal flushing and silicate weathering. Our estimates show that the river water chemistry is controlled by 73.03, 26.56 and 0.40 % by tidal flushing, silicate weathering and carbonate dissolution respectively.

Multivariate statistical analysis

Pearson’s Correlation coefficient is commonly used to assess the relationship between two variables. It is a simple measure to exhibit how well one variable predicts the other (Bahar and Reza 2010). The correlation matrix for the different variables is shown in Table 6. The data illustrate that EC and TDS show statistically high positive correlation at 95 % confidence limit with Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻ and SO₄²⁻. These correlations indicate that the ions are derived from the same source of seawater due to tidal flushing. In addition, the high positive correlation between Na⁺–Ca²⁺, Mg²⁺–SO₄²⁻ and Ca²⁺–SO₄²⁻ may represent ion exchange and gypsum dissolution and to an extent the relation between Ca²⁺–HCO₃⁻ and Ca²⁺–Na⁺ vs. HCO₃⁻–SO₄²⁻ may represent contributions from silicate

Table 6 Correlation matrix of water quality variables ($n = 55$)

	EC	TDS	pH	DO	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
EC	1.00											
TDS	0.98	1.00										
pH	0.53	0.53	1.00									
DO	0.52	0.52	0.40	1.00								
Na ⁺	0.98	1.00	0.52	0.51	1.00							
K ⁺	0.80	0.87	0.47	0.41	0.84	1.00						
Ca ²⁺	0.76	0.82	0.43	0.42	0.79	0.95	1.00					
Mg ²⁺	0.85	0.93	0.48	0.47	0.91	0.95	0.90	1.00				
Cl ⁻	0.98	1.00	0.51	0.51	1.00	0.84	0.78	0.90	1.00			
NO ₃ ⁻	-0.05	-0.06	-0.02	-0.19	-0.07	0.07	0.04	-0.06	-0.06	1.00		
SO ₄ ²⁻	0.83	0.89	0.48	0.52	0.86	0.94	0.96	0.95	0.85	-0.08	1.00	
HCO ₃ ⁻	0.52	0.48	0.53	0.42	0.47	0.43	0.35	0.38	0.45	0.05	0.43	1.00

and carbonate weathering as reported in the work of Edet and Worden (2009) and Edet et al. (2012).

Factor analysis is a multivariate statistical method which yields the general relationship between measured chemical variables by showing multivariate patterns that may help to classify the original data. The geological interpretation of factors gives an insight into the main processes, which may govern the distribution of hydrochemical variables. Factor analysis can identify several pollution factors reasonably but the interpretation of these factors in terms of actual controlling sources and processes is highly subjective (Matalas and Reihner 1967; Bahar and Reza 2010). R-mode factor analysis on the combined data sets provided three factors with eigenvalue >1 that explained approximately 86.13 % of the variability of the data (Table 7). Factor 1 has an eigenvalue of 8.15 and explains 67.88 % of the total variance and shows high loadings on EC, TDS, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻ and SO₄²⁻. The high loading for EC, TDS, Na⁺ and Cl⁻ indicates high salinity due to seawater influence accelerated by tidal flushing (Edet and Worden 2009; Edet et al. 2012).

The Na⁺, K⁺, Ca²⁺ and Mg²⁺ and SO₄²⁻ may also reflect the contributions of other hydrochemical processes (ion exchange, gypsum dissolution, silicate and carbonate weathering). Factor 2 has an eigenvalue of 1.13 and explains 9.45 % of the total variance with high loading on NO₃⁻. This reveals atmospheric and pollution sources (Jeong 2001). This pollution source is attributed to the dumping of domestic, human and industrial wastes into the river systems. Factor 3 has an eigenvalue of 1.056 and explains 8.80 % of the total variance. It shows high loadings on pH and HCO₃⁻. The HCO₃⁻ can come from the dissolution of carbonate minerals, soil CO₂ or from bacterial degradation as reported in the work of Bahar and Reza (2010). These processes also affect the pH of water (Rao et al. 2001).

Table 7 R-mode varimax rotated factor analysis for the river water variables

Variables	Factors		
	1	2	3
EC	0.87	0.07	0.36
TDS	0.93	0.07	0.30
pH	0.36	-0.01	0.73
DO	0.39	0.38	0.56
Na ⁺	0.91	0.09	0.30
K ⁺	0.94	-0.11	0.16
Ca ²⁺	0.93	-0.08	0.10
Mg ²⁺	0.96	0.05	0.15
Cl ⁻	0.92	0.09	0.28
NO ₃ ⁻	-0.01	-0.96	0.03
SO ₄ ²⁻	0.94	0.06	0.19
HCO ₃ ⁻	0.27	-0.10	0.83
Eigenvalue	8.15	1.13	1.06
% Total variance	67.88	9.45	8.80
Cumul. Eigenvalue	8.15	9.28	10.34
% Cumul. Eigenvalue	67.88	77.33	86.13

Bold values indicate statistical significance ($p < 0.05$)

River water quality

Domestic and irrigation water quality

The results of physicochemical parameters of the river water samples (Table 2) shows the percentages of the variables that exceeds the MAV and world averages for the different river water samples. In all cases, most of the variables exceeded the MAV and world averages especially, for the CRE and CR relative to GKR. The classification of the river water based on total hardness (TH) showed that more than 70.0 % of the samples from the three river systems were soft (Table 8).

Table 8 Suitability of the different river waters for irrigation

Quality parameter	Reference	Range	Classification	No of samples			% of samples		
				CRE	CR	GKR	CRE	CR	GKR
Total Hardness as CaCO ₃ (mg/l)	Sawyer and McMcarty (1967)	<75	Soft	9	17	22	75.0	81.0	100.0
		75–150	Moderately hard		2			9.5	
		150–300	Hard	1			8.3		
		>300	Very Hard	2	2		16.7	9.5	
EC (μS/cm)	Ragunath (1987)	<250	Excellent	9	15	18	75.0	71.4	81.8
		250–750	Good		1	2		4.8	9.1
		750–2,000	Permissible	1		2	8.3		9.1
		2,000–3,000	Doubtful		1			4.8	
SAR	Richards (1954)	<10	Excellent	9	15	20	75.0	71.4	90.9
		10–18	Good	1	1		8.3	4.8	
		18–26	Doubtful	1	2		8.3	9.5	
		>26	Unsuitable	1	3	2	8.3	14.3	9.1
Na (%)	Ragunath (1987)	<20	Excellent						
		20–40	Good						
		40–60	Permissible						
		60–80	Doubtful	5	7	4	41.7	33.3	18.2
RSC	Ragunath (1987)	<1.25	None	12	21	21	100.0	100.0	95.5
		1.25–2.5	Slight-moderate			1			
		>2.5	Severe						

The suitability of the river water for irrigation is based on the effect of mineral constituents of water on both plant and soil (Bahar and Reza 2010). Excessive amount of dissolved ions in water affects plants and soil resulting in decrease in productivity. Thus, electrical conductivity is a good measure of salinity hazard as it reflects the TDS in water. Table 8 shows that more than 70 % of the all water samples from CRE, CR and GKR are excellent for use as irrigation water. Excess salinity may harm plant growth by limiting the uptake of water and nutrients through modification of the osmotic process (Todd 1980; Saleh et al. 1999) and chemically metabolic reactions such as those caused by toxic constituents (Todd 1980). This phenomenon was assessed by means of SAR (Richards 1954). The SAR data show that more than 70 % of the samples are excellent for irrigation purposes (Table 8). This implies that no alkali hazard is anticipated from the water to affect crops.

If water used for irrigation is high in Na⁺ and low in Ca²⁺, the ion exchange complex may become saturated with Na⁺, which destroys soil structure due to dispersion of clay particles (Rao 2006). Sodium concentration plays an important role in evaluating the groundwater quality for irrigation because when the concentration of sodium is

high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing magnesium and calcium ions. The exchange process of sodium in water for magnesium and calcium in soil reduces permeability and eventually results in soil with poor drainage. Hence air and water circulation is restricted during wet conditions and such soils are usually hard when dry (Collins and Jenkins 1996; Saleh et al. 1999; Subramani et al. 2005). Thus the high Na % (Table 8), from this study does not support the use of this water for irrigation.

In addition to the SAR and Na %, the excess sum of carbonate and bicarbonate in water over the sum of calcium and magnesium also affect the suitability of water for irrigation purposes. This is evaluated by using the RSC, Ragunath (1987). The usability of the river waters for irrigation purposes were based on the calculated RSC values (Table 8) indicated that the river waters are safe from bicarbonate hazard.

Overall assessment of river water quality

Assessment of the river water quality for the present study (Table 9) was based on the computed WQI using the WHO (1984, 1993) maximum admissible values and the world

Table 9 Classification of water samples from the different river water bodies for the based on average WQI values

River name	Sample location	Season	WQI WHO	WQI WA	Class WHO	Class WA
Cross River estuary	Esuk Afokang	Wet	3.21	20.98	E	E
	Esuk Afokang	Dry	27.82	535.80	G	VP
Calabar river	Marina Beach	Wet	3.89	53.78	E	M
	Marina Beach	Dry	19.79	426.43	E	VP
	Adiabo	Wet	1.73	5.60	E	E
	Adiabo	Dry	4.59	92.19	E	P
Great Kwa river	Atimbo	Wet	1.60	9.30	E	E
	Atimbo	Dry	4.43	57.35	E	M
	Idundu	Wet	1.45	3.29	E	E
	Idundu	Dry	1.71	4.28	E	E

WQI Water quality index, WHO World Health Organization, WA World average

average (Table 2). The detailed data for all the samples show that WQI based on the WHO standard has 92 % of all the river water samples in the class designated as excellent (E), while 4 % were in the class of good (G) and moderate (M). For the individual rivers, 83, 90 and 100 % representing samples from CRE, CR and GKR belong to the E class, while 17 and 10 % of CRE and CR samples belonged to the M and G classes, respectively.

Using the world average criteria, 75, 7, 2 and 16 % for all the 55 river samples covering the wet and dry seasons were in the class of excellent (E), moderate (M), poor (P) and very poor (VP). When considering the different rivers, 50, 76 and 85 % of samples from CRE, CR and GKR belonged to the E class. The good (G) category had 25 % each for the CRE and GKR, while 17 % of the CRE samples belong to the M class. The very poor category (VP) had 25 % of the samples from the CRE and GKR and only 25 % of the GKR samples fell in the poor quality class.

On seasonal basis, the river water showed better quality in the wet season compared to the dry season. The data also showed that in terms of overall quality, the Great Kwa River is the best followed by the Calabar River and the Cross River estuary. The data also showed that in the wet season, all the river water samples for the three rivers and all the samples for Great Kwa River in the dry season are described as excellent in terms of the overall quality. In the dry season, the samples from the Cross River estuary and the Calabar River are of moderate-good quality.

Conclusions

The levels of some parameters (temperature, pH, DO and HCO_3^-) were not significantly different for the three river while higher concentration were recorded for dry season as

compared to the wet season due mainly to dilution during the wet season and evaporation in the dry season.

Cross plots and ionic ratio show that tidal flushing is the main factor controlling the river water chemistry with little or no contribution from silicate and carbonate weathering. In addition, correlation coefficient data indicate that the ions are derived from the same source while R-mode factor analysis provided three significant factors attributed to tidal influence (factor 1), dumping of domestic and human waste into the river systems (factor 2) and dissolution of carbonate minerals, soil CO_2 or from bacterial degradation (factor 3). Total hardness (TH), sodium adsorption ratio (SAR) and residual carbonate (RSC) data indicate the river waters are good for irrigation purposes, while the percent sodium (Na %) data for the river water indicates unsuitability.

An overall assessment based on a quality index scheme indicates that relatively, the Great Kwa River is the best as compared to the Calabar River and Cross River estuary for domestic and irrigation purposes. The world average tend to be a better tool for assessment as the WHO standard were developed in countries with different environmental conditions compared to the Nigerian and other developing countries environment.

Acknowledgments The first author is grateful to DAAD and Alexander von Humboldt (AvH) for providing field equipment during the field study and the Commonwealth for financial support during the period of analyses at the University of Liverpool, UK. Prof Richard Henry Worden, my host at the University of Liverpool for putting the facilities of the Institute of Earth and Ocean Sciences at my disposal.

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