Hydrochemistry of the near shore marine bay, Calabar river (South-eastern, Nigeria)

Hidrokemične razmere v priobalni vodi morskega zaliva ob izlivu reke Calabar v jugovzhodni Nigeriji

Ekwere, A. S.^{1, *}, Edet, A.¹ & Ukpong, A. J^1

¹University of Calabar, Department of Geology, Nigeria

*Corresponding author. E-mail: zerratta77@yahoo.com

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- **Abstract:** A study to assess the current hydrochemical status of the rapid developing marine bay of the Calabar River, south-eastern Nigeria, was carried out. The waters have pH values ranging from slightly acidic to slightly alkaline and defined as generally fresh based on TDS values (<1000 mg/L). Analysis reveals an abundance sequence of Na>Ca>Mg>K and Cl>SO₄>HCO₂>NO₂ for cations and anions respectively. Averages were Ca²⁺ (15.15 mg/L), Mg²⁺ (2.93 mg/L), Na⁺ (21.27 mg/L) and K⁺ (2.86 mg/L) while for the anions it was Cl⁻ (156.99 mg/L), SO_4^{2-} (27.85 mg/L), HCO_3^{-} (14.98 mg/L) and NO_3 (0.551 mg/L). The waters belong to the Na-Ca-Cl field on the Piper diagram plot, indicating influence of atmospheric precipitation. Trace elements Fe, Mn, Pb, Zn, Cu, Cd, Cr, Ni and Co show levels within world averages and acceptable limits. Hydrochemical modelling shows heavy metals to exist mainly in free mobile states, chlorides, sulphates, carbonates and hydroxides bound under prevailing pH-Eh conditions at unsaturated levels. Chemical contents and mineral phases are adjudged to be sourced from mineral dissolution, salinization and minimal anthropogenic input.
- Izvleček: Raziskava je bila opravljena z namenom oceniti sedanje hidrokemične razmere v naglo spreminjajočem se okolju morskega zaliva ob izlivu reke Calabar v jugovzhodni Nigeriji. Vrednosti pH vode nihajo med rahlo kislimi do rahlo alkalnimi. Vodo je mogoče splošno oceniti za sladko glede na vrednosti TDS (celotna raztopljena snov <1000 mg/L). Analiza razkriva naslednji zaporedji kationov in anionov:

Na>Ca>Mg>K in Cl>SO₄>HCO₃>NO₃. Povprečna koncentracija Ca²⁺ je 15,15 mg/L, Mg²⁺ 2,93 mg/L, Na⁺ 21,27 mg/L in K⁺ 2,86 mg/L in anionov Cl⁻ 156,99 mg/L, SO₄²⁻ 27,85 mg/L, HCO₃⁻ 14,98 mg/L in NO₃ 0,551 mg/L. Vode pripadajo Na-Ca-Cl-polju v Piperjevem diagramu, kar nakazuje vpliv atmosfernih padavin. Sledne prvine Fe, Mn, Pb, Zn, Cu, Cd, Cr, Ni in Co so na ravni svetovnih povprečij in v sprejemljivih koncentracijah. Hidrokemijsko modeliranje kaže, da so težke kovine navzoče pretežno v prostih mobilnih specijah kot kloridi, sulfati, karbonati in hidroksidi, ki so v sedanjih razmerah pH-Eh v nezasičenih koncentracijah. Vir raztopljenih snovi in mineralnih faz so raztapljanje mineralov, salinizacija in minimalen antropogeni vpliv.

Key words: river, trace element, mineral species, geogenic, Calabar, Nigeria Ključne besede: reka, sledne prvine, mineralne specije, geogeno, reka Calabar, Nigerija

INTRODUCTION

Rivers transport more than just water from land to sea as river basins are not inert. River chemistry and particulate load reflect natural and human processes within the watershed. The progression of a river along its course leads to interaction with a variety of geological types and it may have input from aquifers not visible on the surface anywhere in the locality.

In most developing communities, increase in human population geared by the quest for good water supply, irrigation, fish production, recreation and navigation has resulted in enormous pressure and stress on reservoirs. This is readily identified by variation of the natural chemistries of reservoirs as well as heavy metal contamination. However two major sources have been identified as possible sources of metal loads in rivers in proximity to urbanised areas. These are natural sources from rock weathering within the catchment and anthropogenic sources derived from human activities (ABRAHIM & PARKER, 2002). MUSTAPHA (2008), reckon water quality deterioration in reservoirs as related to excessive nutrient inputs, eutrophication, acidification, heavy metal contamination, organic pollution and obnoxious fishing practices.

Indiscriminate disposal of industrial and urban waste into river catchment plays a major role in most environmental problems. Associated presence of nutrients and heavy metals especially at elevated levels, leads to accumulation in tissues of organisms. These metals are not readily assimilated for growth or excreted, resulting in amplifications of their concentrations along the food chain and exposure of humans at the apex to the risk of metal poisoning (AKPAN et al., 2002).

Physico-chemical properties have been used to assess water quality in reservoirs (DJUKIC et al., 1994). This gives a good impression of the status, productivity and sustainability of such water bodies.

The estuarine Marine Bay of the Calabar River, south-eastern Nigeria, has experienced a significant increase in activities in recent times. These human perturbations include fishing, shipping, recreation, aquaculture etc. Discharge of effluents into the river basin has been recognized as an integral part of these operations. These apparently will culminate into stresses on the status of the water quality with time. The present study aims to ascertain the potability of the near-shore waters of this marine bay and provide data set for future environmental and resource management issues.

Description of study area

The study area belongs to what has been described as Calabar urban (EDET et al, 2003), situated between latitude 4°15'–5°15' North and longitude 8°15'–8°25' East (Figure 1). The study area receives

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an average rainfall of about 254 mm annually within two distinct seasons; dry and wet seasons. Mean annual air temperature and relative humidity are 26.8 °C and 84.6 % respectively. Geologically the study area is composed of Tertiary and Quaternary sediments referred to as Coastal Plain Sands of the broader Niger Delta basin (SHORT & STAUBLE, 1967). This formation consists of alternating sequence of gravel, sand, silt, clay and alluvium which are derived from the adjoining Precambrian Basement and Cretaceous rocks.

The Precambrian basement (Oban Massif) complex is made up of migmatitesgneisses, granites, schists, para-schists, pegmatites and a host of other ultramafic rock suites (EKWUEME, 2003).

The Cretaceous sedimentary geologic unit is known as the Calabar Flank and is built up of limestones, sandstones, shales and marls (REIJERS, 1996).

Geomorphologically, the study area is of a coastal setting with surface elevations ranging from less than 10 m in the southern part to about 80 m in the north.

MATERIAL AND METHODS

A total of twenty (20) water samples were collected from locations along the near shore of the marine bay. The sampling locations included but were not limited to sites in proximity to marine related human activities within the study area (Table 1). This was to assess possible impacts of anthropogenic activities on water chemistry. The sampling period was June–July 2009 at the peak of the wet season.

Physical parameters (pH, temperature, TDS, Eh and conductivity) were measured in the field using standard equipment: PHT-027 multi-parameter water quality probe. Major and trace element contents were determined by atomic absorption spectrophotometer (AAS), model UNICAM 939. The anion contents of samples were determined by colorimetric method using UNICAM UV2 spectrophotometer. All instrumental analyses were carried out in the quality control laboratory of the Aluminium Smelter Company of Nigeria (ALSCON), Ikot Abasi, Nigeria.

Saturation indices and mineral phases were determined using the VISUAL MINTEQ computer program. The em-



Figure 1. Map of Calabar and environs including sampled river. [*A*] Index map of Nigeria, [*B*] geologic map, [C] Calabar River; modified after EDET & WORDEN (2009)

Location	Surrounding Activities
Henshaw town beach	Sand mining, wood processing, domestic waste disposal
Esuk Ifia (marina)	Boat jetty, wood processing, out-board engine repairs, abandoned boats
Marina Resort	Tourist/leisure park, boating, food waste and effluent disposal
Inland Water Authority	Jetty, boat repairs
UNICEM jetty	Jetty, hauling of cement, boating
Esuk Utan	Sand mining, boating, domestic waste disposal, wood processing
Tinapa	Jetty, boating, waste disposal, oil/crude carrying vessels
Adiabo bridge	Boating, domestic waste disposal
Ibonda (NPA Port)	Boating and boat repairs, shipping, waste disposal
Creek Town beach	Boating, domestic waste disposal, wood processing

ployment of VISUAL-MINTEQ as modelling tool was due to its extensive database of mineral and aqueous species for interpretation purposes.

RESULTS AND DISCUSSION

Table 2 outlines the descriptive statistics for physico-chemical and trace elements contents of samples in comparison to world averages and acceptable standards. Table 3 shows the correlations between major cations and anions as a means of establishing probable controls of chemical characteristics.

Physical properties

The temperature of the sampled waters ranged from 27–29 °C with a mean of 28.5 °C (Table 2). These values are consistent with mean air temperatures as they coincide with period of sampling and diurnal temperature variations within the locality (EDET & WORDEN, 2009).

The pH values ranged from 3.48–7.60 with an average of 6.27. The lowest pH of 3.48 was recorded at one of the most active sites (Esuk Utan) along the shore with great potency for pollution. The rest of the locations revealed pH values of slightly acidic – slightly alkaline with a greater percentage within the 6.5–8.5 WHO recommended standard.

Electrical conductivity (EC) data showed a range of 460–2,240 μ S/cm with an average of 1 080 μ S/cm. the values were generally below the 1,400 μ S/cm WHO limit, except for the site with the maximum value. Comparison of EC data from EDET & WORDEN (2009) shows the values are within background levels, reflecting minimal or absence of pollution effects. Total dissolved solids (TDS) ranged from $320-1140 \times 10^{-6}$ with an average value of 745×10^{-6} . With reference to quality, about 60 % of the sampled waters are freshwater with TDS values <1,000 mg/L (FREEZE & CHERRY, 1979). The rest of the waters were within the lower limits of brackish water (TDS 1,000–10,000 mg/L). There was an observed direct relationship between TDS and EC data, reflecting equilibrium of abundance of free ions in water relative to soluble content (HEM, 1986).

The redox potential values (Eh), ranged from 9–97 mV with a mean of 42 mV. These values are well within the baseline data as reported by EDET et al. (2003) and significant variation in future may indicate pollution effects.

Chemical characteristics

As revealed from mean values, the relative abundance sequence of the major cations was Na > Ca > Mg > K. Sodium concentration varied from 4.65-33.16 mg/L with a mean of 21.27 mg/L. From observations all the values were within the baseline data as reported by EDET et al. (2003), below world average and within the WHO limits.

Calcium had concentrations of 7.07–22.46 mg/L and a mean of 15.15 mg/L. The mean value is in proximity to world average of 15.0 mg/L (TUREKIAN, 1977) and all values were below the WHO limits.

Magnesium and potassium exhibited ranges of values within local baseline data, global averages and below WHO standards with means of 2.93 mg/L and 2.86 mg/L respectively (Table 2).

The relative dominance of Na reflects the mixing of seawater with the freshwater within the estuarine coastal area. Ion exchange processes for seawater cations (especially Na and Mg) for Ca are prevalent at exchange sites with Ca²⁺ going into solution (EDET & WORDEN, 2009). The effect of this would probably be more defined with an assessment based on tidal regimes within the study area.

Sources of Ca and Mg are attributed to the weathering of anorthite, pyroxene and amphibole from the overlying Oban massif in the northern parts of the study area (EDET et al., 2003, EKWERE, 2010). Mineral dissolution incepted by precipitation and weathering of hydroxyl-apatite, fluorite, dolomite, calcite, sylvite, epsomite, mirabilite and halite (which are present in the catchment geology) are also probable sources of these cations (EKWERE 2010).

However, the contributions of rainfall through marine input of sea salts (BERNER & BERNER, 1996) cannot be ruled out as high precipitation levels is characteristic of this marine coastal setting.

of anion Assessment concentrations shows that chloride varied from 118.10-234.10 mg/L with a mean of 156.99 mg/L. All the concentration values of Cl were above the baseline data of EDET et al., (2003) but below the WHO limit of 250 mg/L. The Cl contents in the waters are attributable to seawater incursion into the fresh coastal waters as well as precipitation influence. River runoff dominated by precipitation is proportionally high in Cl (recycled salt) and low in total concentration

Sulphate concentration ranged between 12.10–52.40 mg/L with an average value of 27.88 mg/L. the concentration levels were within the local baseline and below the WHO limit (table 2). Sulphate concentrations are attributed to natural accentuation from pyrite (FeS) within this estuarine setting (EDET & WORDEN, 2009).

The bicarbonate (HCO₃) concentration levels varied from 10.56-24.32 mg/L with a mean value of 14.98 mg/L. The concentrations were within the local baseline and below world average value (Table 2). The dominant source of HCO₃ is the dissolution of carbonate rocks within the Cretaceous sediments which forms part of the catchment geology of the study area.

Nitrate had concentration values ranging from 0.298–0.862 mg/L with a mean of 0.551 mg/L. This shows that all values were below the WHO maximum permissible limit of 10 mg/L. The main source of nitrate in the water is the use of nitrogenous fertilizers for agricultural purposes as well as the indiscriminate dumping of human and animal waste into the environment. These are anthropogenic and though not posing any threat to health status, monitoring is duly advised.

Ammonium concentration ranged from 1.12–3.73 mg/L with a mean of 2.54 mg/L. These concentration levels are the result of agricultural land scrubbing, human and animal waste disposal into the environment.

Heavy metal trend

Assessment of heavy metal data (Table 2) shows that iron and manganese had mean values of 0.95 mg/L and 0.16 mg/L respectively with ranges within world average (TUREKIAN, 1977) but slightly above WHO limits. The relatively more toxic elements; Pb, Zn, Cu, Cd, Cr, Co and Ni, had mean values of 0.004, 0.054, 0.051, 0.004, 0.071, 0.004 and 0.026 mg/L respectively. These values were within world averages and WHO limits.

Contents of trace elements reflect a dominant influence of rock weathering processes, as mineral phases laden with these elements constitute the rocks within the overlying basement and Cretaceous sediments (EKWERE, 2010). However, though minimal, the effects of anthropogenic activities can contribute to concentration levels of these potentially toxic elements.

Hydrochemical facies and variable projections

A plot of the data for the major cations and anions on the PIPER (1944) diagram (Figure 2) shows that the waters fall within the Na – Ca - (Mg) – Cl field. This is in line with relative abundance sequence as revealed from the data set. The recognized water type is defined to be a major constituent of atmospheric precipitation (DAVIS & DE WEIST, 1966).

Bivariate correlation analysis was also employed to assess relations between variables. From the correlation matrix (Table 3), Ca^{2+} exhibits a strong positive correlation with Mg²⁺ and Na⁺ (r > 0.70) and moderate correlation with NO_3^- (r = 0.50-0.70). Magnesium (Mg²⁺) has a strong positive correlation with Na⁺. These relationships between the major exchangeable cations Ca-Mg-Na represent effects of dissolution and precipitation reactions and concentration effects (Ekwere, 2010). Moderate correlation between Na⁺, K⁺ and Cl⁻ suggests evaporite dissolution and seawater mixing effects with the coastal freshwaters. The entire scenario reflects a dominance of geogenic influence over water chemistry than anthropogenic.

Two factorial axes *F1* and *F2* (Table 4) were determined through factor analysis using the STATISTICA computer program, extracting 31.22 % and 17.13 % respectively of total data variance and accumulating to 48.35 %. Classification of factor loadings is described as 'strong', 'moderate' and 'weak', corresponding to absolute values of >0.75, 0.75–0.50 and 0.50–0.30, respectively (LIU et al., 2003). However for this study, factor loadings greater than 0.60, were considered significant.

Factor 1 (Ca, Mg, Na, Cl, SO₄ and Mn) projected a maximum of variables and defined by the majority of parameters that describe water quality. These are contents in calcium (0.676), magnesium (0.906), sodium (0.876), chloride (0.750) and on the negative pole sulphate (-0.805) and manganese (-0.662). This axis defines water of strong salinities and charged in suspended matter (BEN GARALI et al., 2011). The composition of this factor reflects natural weathering from waterrock interactions in geo-matrix of the basement and inputs from primitive saline waters of Cretaceous limestones of the Calabar Flank (EKWERE, 2010).

Factor 2 (HCO₃, Cr, K and Zn) appears erratic in composition but apparently indicates dissolution effects of mineral phases that constitute the rocks of the catchment geology. The dissolution of carbonate rocks from the Calabar Flank

Stat	Temp	E	С	TDS	pН	Eh	C	a	Mg		Na		K
Mean Min Max SD	28.75 28 29 0.42	108 46 224 578	80 50 40 .90	745 320 1140 340.63	6.27 3.48 7.60 1.21	42 9.0 97 29.80	15. 7.0 22.4 4.9	15 07 46 94	2.93 0.78 4.02 1.01	3 3 2	21.27 4.65 33.16 9.45		2.86 1.08 6.11 1.47
BLD		41-2	264		4.0-6.0	31-143	1.73-	4.76	0.51–6	.10	9.05–48.	2	1.3-3.6
WA				120ª			13.	.4 ^b	3.4 ^b	,	5.2 ^b		1.3 ^b
SW				35,000			41	2	1,28	0	10.780		399
WHO		1,4	00	1000	6.5-8.5		20	00	100)	250		12
Stat	C	1		SO_4	HCO ₃	NO		N	H ₄		Fe		Mn
Mean Min Max SD	156 118 234 40.3	.9 .1 .1 34		27.85 12.10 52.40 11.51	14.98 10.56 24.32 4.05	0.55 0.30 0.86 0.21		2. 1. 3. 0.	54 12 73 92		0.95 0.13 2.19 0.60		0.16 0.003 0.712 0.25
BLD	0.78-	69.9		0.18	12.2-18.3	3 1.3-2	.7						
WA	5.8	8 ^b		8.3 ^b	52 ^b						100 ^a		15 ^a
SW	19,3	50		2,710	123								
WHO	25	0		400		50					0.3		0.1
Stat	Pt)		Zn	Cu	Ni		C	d		Cr		Со
Mean Min Max SD	0.00 0.00 0.00 0.00	04 02 07 02		0.054 0.023 0.104 0.023	0.051 0.014 0.086 0.036	0.020 0.001 0.083 0.021	6 3 3 3	0.0 0.0 0.0 0.0	004 001 016 003	(((0.071 0.006 0.211 0.052		0.004 0.001 0.007 0.002
BLD													
WA	3.0)a		20ª	3.0ª	1.5ª		0.0)3ª		1.0 ^a		0.1ª
SW													
WHO	0.0	5		5.0				0.0	005		0.05		

Table 2. Comparison of physico-chemical parameters with baseline data, world average and WHO (2001) standards

Temp (°C), EC (μ s/cm), Eh (mV), TDS (× 10⁻⁶), cations, anions and heavy metals (mg/L) *BLD*-Baseline data (EDET et al., 2003)

WA-World Averages ^a (TUREKIAN, 1977)

^b (Meybeck, 1979)

SW-Sea Water (MILLERO, 1996) WHO-World Health Organization (2001)

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and ultra-mafic rocks from the basement are visible in this factor loading.

Hydrochemical modelling

The modelling package VISUAL-MINTEQ was used to calculate distributions of aqueous species and mineral saturation indices using the measured water compositions. The employment of VISUAL-MINTEQ as a complimentary interpretation tool was to assess chemical species of dissolved component, saturation indices and hazard prognosis. Results for selected parameters for the sampled waters are presented in Table 5.

Mineral equilibrium calculations for water are useful in predicting the presence of reactive minerals in water sys-



Figure 2. Piper trilinear diagram of sampled waters

tem and estimating mineral activity; (TAYLOR et al, 1996; DEUTSCH, 1997 and ZHU et al. 2008). The solution is considered to be in equilibrium with regards to a particular mineral if the saturation index (SI) = 0. It is considered to be undersaturated if SI < 1 and oversaturated if the SI > 1.

Metals can exist in water as many aqueous species and the type(s) of species can affect mineral solubility, adsorption/desorption behaviour and possibly

bioavailability. The predicted predominant aqueous species from hydrochemical modelling are given below for the metals measured and detected in the water samples.

Iron

Iron existed as Fe²⁺, FeOH⁺, FeCl⁺, FeSO_{4(aq)} and FeHCO₃. Despite the many possible aqueous species for iron, the predominant ones were invariably predicted to be Fe^{2+} and $FeSO_{4(aq)}$ (melanterite) constituting 86 % and 8

	Ca	Mg	Na	Κ	HCO ₃	Cl	SO_4	NO_3	NH_4
Ca	1	0.74	0.83	0.44	0.23	0.28	-0.56	0.50	-0.29
Mg		1	0.90	0.52	0.18	0.62	-0.76	0.46	-0.48
Na			1	0.61	0.17	0.58	-0.63	0.40	-0.25
K				1	0.45	0.70	-0.24	-0.16	-0.07
HCO ₃					1	0.09	-0.45	-0.17	-0.49
Cl						1	-0.44	0.31	-0.05
SO_4							1	-0.55	0.62
NO ₃								1	-0.21
NH_{4}									1

 Table 3. Correlation matrix for major constituents of water

	Factor 1	Factor 2
	$\begin{array}{cccc} Ca & 0.676 \\ Mg & 0.906 \\ Na & 0.876 \\ Cl & 0.750 \\ SO_4 & -0.805 \\ Mn & -0.662 \end{array}$	HCO ₃ -0.648 Cr -0.851 K -0.713 Zn -0.674
Eigenvalue	5.619	3.082
% total variance	31.22	17.13
Cumul. Eigenval Cumul. %	5.619 31.22	8.701 48.35

Element	Dominant species	mass fraction, w/%
Fe	${ m Fe^{2+}}\ { m FeSO}_{4(aq)}$	86.0 8.0
Mn	$\frac{Mn^{2+}}{MnSO_{4(aq)}}$	92.0 3.0
Ni	Ni ²⁺ NiSO _{4(aq)} NiHCO ₃	88.0 6.0 3.0
Рb	Pb ²⁺ PbCl ⁻ PbSO ₄	64.0 9.0 6.0
Zn	Zn^{2+} $ZnSO_{4(aq)}$	95.0 3.0
Cu	Cu^{2+} $CuOH^+$ $CuCO_{3(aq)}$	86.0 5.0 4.0
Cd	Cd ²⁺ CdCl ⁻	71.0 23.0
Cr	CrOH ⁻	92.0
Со	Co ²⁺	90.0

 Table. 5 Major chemical species of trace elements.

% respectively of the species. Under the prevailing Eh-pH condition, Fe^{2+} is immobile. Its mobility will further be hindered in the area by precipitation as Fe oxides (hematite, magnetite), oxyhydroxides (goethite) and other coprecipitating metal phases (EDET et al, 2004).

Manganese

Manganese exhibited various species in the water including, Mn^{2+} , $MnCO_{3(aq)}$, MnCl-, $MnSO_{4(aq)}$ and $MnHCO_{3}$. Mn is non-toxic and the dominant phase was the ionic Mn^{2+} accounting for over 92 % in the waters. Lesser to this was $MnSO_{4(aq)}$ constituting about 3 %. Under the present pH- Eh of the waters, Mn^{2+} is immobile posing no problem in the area.

Nickel

The following species of Ni were identified through modelling, Ni²⁺, NiOH⁺, NiCl⁺, NiSO_{4(aq)}, NiCO_{3(aq)} and Ni-HCO₃⁺. Ni²⁺ was the most dominant constituting 88 %, NiSO_{4(aq)} (retgersite) about 6 % and NiHCO₃⁺3 %. Ni²⁺ compounds are non-toxic (REIMANN & CARITAT, 1998) and its immobility under the present pH-Eh condition, Ni does not pose any threat to the waters in the study area.

Lead

Species of lead (Pb) included, Pb^{2+} , PbOH⁺, PbCl⁺, PbCl_(aq), PbSO_{4(aq)}, PbCO_{3(aq)} and PbHCO₃⁺. Though aqueous lead is predicted to be distributed amongst several species Pb²⁺ made up about 64 %, PbCl⁻9 %, while PbSO_{4(aq)} (anglesite) and PbH-CO₃ were 6 % each. The distributions of the species show no marked difference for the different locations. Pb²⁺ appears to be mobile but however poses no problem of contamination as Pb is low (mean 0.004 mg/L) and PbCO₃ will restrict its mobility (EDET et al, 2004).

Zinc

Species of zinc included Zn^{2+} , $ZnOH^+$, ZnCl⁺, ZnSO_{4(aq)}, ZnCO_{3(aq)} and Zn-HCO₃⁺. Zn²⁺ made up about 95 % of the species. Far less but next to this was ZnSO_{4(aq)} (bianchite) constituting only about 3 %.

Copper

Various species of copper were revealed and included Cu^{2+} (86 %), $CuOH^+$ (5 %), $CuCO_{3(aq)}$ (4 %), $CuSO_{4(aq)}$ (3 %) and $Cu(OH)_2^{2+}$, $Cu(OH)_{2(aq)}$, $CuCl^+$, $CuNH_3^{2+}$ and $CuHCO_3^+$. The speciation of copper is controlled by pH, redox, chlorinity, sulphate and total copper concentrations.

Cadmium

Cadmium existed as various species but major constituents included, Cd^{2+} , $CdCl^+$, CdOH, $CdCl_{2(aq)}$, $CdSO_{4(aq)}$, $Cd-HCO_3^+$ and $CdCO_{3(aq)}$. The speciation of cadmium is dependent on pH, chlorinity, sulphate and total cadmium concentrations. However Cd^{2+} was dominant with 71 % and $CdCl^-$ with 23 %. At present pH-Eh condition, Cd^{2+} which is toxic and carcinogenic is immobile and if present in high concentrations may be precipitated, thus reducing its danger potential.

Chromium

Chromium with minimal concentrations in most samples, exhibited a predominance predicted to be CrOH⁻ with about 92 % of total composition. The only other specie was Cr^{2+} . This potentially toxic element is immobile posing no threat to water quality as its content was low at a mean of 0.071 mg/L.

Cobalt

Cobalt (Co^{2+}) , $CoOH^+$, $CoCl^-$, $CoSO_{4(aq)}$, $CoCO_{3(aq)}$ and $CoHCO_3^+$ were the species of cobalt identified. Co^{2+} predominated with over 90 % of total composition.

Mineral saturation states were calculated as part of the output from the modelling program as a means of indicating what minerals might be dissolving or precipitating into or from the water and controlling its composition. The cal-

Mineral species	Chemical composition	Saturation index
Brochantite	CuSO _{4(aq)}	1.423
Malachite	CuCO _{3(aq)}	1.449
Ni-hydroxide	Ni(OH) ₂	1.413
Tenorite	Cu.H ⁺ (H ₂ O)	2.302

Table 6. Oversaturated mineral species

culations are based on an equilibrium model, so the results are only an indication, as kinetic factors may inhibit approach to equilibrium.

The modelling reveals that majority of the species of the metals (hydroxides, carbonates, sulphates, chlorides and bicarbonates) were under-saturated. However a few species were above equilibrium at very low levels of oversaturation (Table 6). These include aqueous Cusulphate (brochantite), Cu-carbonate (malachite), hydrous copper (tenorite) and hydroxides of Ni and Fe.

Free metal species are the most bioavailable and toxic form of trace elements that exist in natural water (APTE et al., 1995). Considered metals exist as free ions and are relatively mobile under prevailing Eh-pH conditions. However their low concentrations in addition to the presence of limiting mineral phases (carbonates and sulphates) reduce the risk of their contamination to the waters.

CONCLUSION

The waters of the marine bay of the Calabar River exhibit a comabundance positional sequence of Na>Ca>Mg>K for cations and Cl>SO₄>HCO₃>NO₃ for anions. The waters are characterised as Na-Ca-Cl, indicating influence of saline water incursion and lesser effects of atmospheric precipitation. The water characteristics also reflect mixing of waters of multiple geogenic origin; Ca-Mg-HCO₂ and Ca-Na-Cl waters from the basement and Cretaceous geologic units north of the study area (Ekwere, 2010). Heavy metals (Fe, Mn, Pb, Zn, Cu, Cd, Cr, Ni and Co) generally show ranges within world averages and acceptable limits. Speciation modelling shows that metals exist as ions, chlorides, sulphates, carbonates and hydroxides, largely at unsaturated levels. Mineral dissolution and salinization are the main controls of water chemistry.

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