Surface water quality status and chemical speciation of Qua Iboe River system, Niger-Delta, Nigeria

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ARTICLE INFO

ABSTRACT

This study assessed the surface water quality of Qua Iboe River system in the coastal Niger Delta, Nigeria. A total of 7 sampling stations were selected for the study and results obtained using FAAS revealed the following mean trace element concentrations (molar): 3.65×10^{-7} for Cd, 1.50×10^{-7} for Pb, 3.89×10^{-7} for Cr, 1.10×10^{-6} for Cu, 2.50×10^{-6} for Zn, 1.06×10^{-6} for Ni and 9.34×10^{-7} for Co. The ion association model based on Debye-Hückel theory using the llnl.dat database of the PHREEQCI computer program as well as the thermodynamic data was used for the chemical speciation studies. The distribution of solution species for the trace elements using the PHREEQCI model revealed that the predominant species in the river system was the free ions of Ni^{2+}(97.6%), Co^{2+}(97.7%), Zn^{2+}(92.6%), Cu^{2+}(70.2%), Cu^+(81.2%) and Pb^{2+}(62.0%) as well as the hydroxy species, $CrOH_2^+$(58.7%) and chloride species, $CdCl_2^+$(82.3%). From the model calculations, atacamite, $CdCr_2O_7$, $CuCr_2O_7$, $PbHPO_4$, ternorite and pyromorphite solubility showed positive values of the saturation indices (SI), indicating supersaturation which led to mineral precipitation condition of water.

Introduction

Over the past years, the Nigerian coastal environment - which consists of rich and diverse ecosystems, natural resources and increased human population, has been subjected to erosion and different forms of anthropogenic pollution. The pollution of surface water bodies, especially with toxic trace metals, has attracted considerable public attention the past few decades (Suthar et al. 2009). The input of environmental pollutants into the aquatic systems is a common phenomenon in Nigeria (Abu and Egenonu 2008). Industrialization and urbanization is one of the main indices of national and global development, but sometimes, while it enhances the quality of life, it also poses serious threats to the management of the natural ecosystem and public health (Umoren and Udousoro 2009).

Different sources of surface water pollution in the region include crude oil spills, refined oil pipeline leakages, solid wastes, garbage disposal, industrial wastes, municipal sewage, non-point pollutants - runoff from agricultural farmlands, industrial effluents (heavy metals, phosphorus), urban runoff (oils, salts, various chemicals) and atmospheric fallouts of airborne pollution (Otokunefor and Obiukwu 2005; Rim-Rukeh et al. 2006; Abu and Egenonu 2008; Nduka et al. 2008; Umoren and Udousoro 2009). Typically, water quality criteria are defined based on the measurements of metal concentrations and the increasing release of heavy metals into the aquatic environment. This has posed serious threats to the environment and public health due to its accumulation and persistence in the food chain (Onianwa and Fakayode 2001). In order to assess possible effects on the biota, both the total trace element concentrations as well as their chemical speciation have to be determined, because of the increased toxicity and bioavailability of some metal species (Tepavitcharova et al. 2011).

Speciation modeling uses a chemical analysis of water to calculate the distribution of aqueous species using an ion-association aqueous model. The analysis of chemical species of trace metals in surface and ground water using the PHREEQC computer program allowed for the determination of the distribution of the metal species and the calculation of saturation indices to determine the saturation state of the water body with respect to different associated mineral phases (Parkhurst and Appelo 1999; Bhattacharya et al. 2006; Parello et al. 2008; Obiefuna and Orazulike 2010; Zhang et al. 2010; Tepavitcharova et al. 2010; Bouragba et al. 2011; Tepavitcharova et al. 2011). Normally, speciation modeling requires only a SOLUTION (or SOLUTION_SPREAD) data block for each water analysis for which saturation indices are to be calculated (Parkhurst and Apello 1999).

Sequel to the recent interest in massive infrastructural and industrial development of the region by government, which tends to suggest an imminent environmental issues, there is therefore, need for continuous assessment of the pollution status of the region. This study, however, seeks to examine the water quality status of Qua Iboe River system, assess the distribution of solution species (speciation) and to calculate the saturation indices of selected mineral species using the PHREEQCI computer model. Results obtained will be used to predict the pollution status of the river for sustainable monitoring and management of the coastal waters in the area.

Materials and Methods

The study area and design

The study area, Eket and Ibeno communities of the coastal South-eastern part of the Niger Delta region, Nigeria lies between latitude 4°40′ North and longitude 7°55′ East (Eket), and latitude 4°30′ North and longitude 8°00′ East (Ibeno). The Qua Iboe River is a confluence of rivers from different sources

flowing through Eket and Ibeno communities of Akwa Ibom State into the Gulf of Guinea (Atlantic Ocean). The river mainly receives municipal wastes, municipal/urban runoff, untreated industrial discharges from food processing industries, as well as other solid wastes (garbage's, metal scraps, etc.) mainly at Atabong, Marina and Iwuochang stations of the river. The river system serves as a major source of water for the predominantly rural population of the area whose major occupation is commercial fish farming, noting that fish growth depends largely on the quality of the culture medium and other agricultural practices.

Sampling and preparation of samples

Sampling was carried out between June 2009 and May 2010 from seven stations (Figure 1) during the wet and dry season from the two communities located along the river system.

Figure 1. Map of study area showing sampling stations

The sampling stations were chosen to include the likely anthropogenic pollution sources and the affected locations upstream and downstream. The profile of the different stations and the description of activities near sampling stations are shown below:

Sampling Station	Latitude	Longitude	Description of anthropogenic activities at sites
1.Iwuokpom 1 (SQ-1)	4º 32′ N	7º 59′ E	Fishing, wood industry and market wastes.
2.Iwuokpom 2 (SQ-2)	4º 32′ N	7º 59′ E	Fishing, market wastes, boat park, fuel and lubricating oil leakages from boat-engines.
3.QIT (SQ-3)	4º 32′ N	8º 00′ E	Exxon/Mobil-QIT terminal, recreational.
4.Iwuochang (SQ-4)	4º 33′ N	7º 58′ E	Fishing, market/domestic wastes isposal, boatyard, open defecation.
5.Eketai (SQ-5)	4º 37′ N	7º 55′ E	Agricultural farmlands, laundry and commercial car wash activities.
6.Atabong (SQ-6)	4º 38′ N	7º 55′ E	Urban/drainage discharge, abattoir, effluents from fuel stations, auto-mechanic workshop, car-wash activities.
7.Marina (SQ-7)	4º 36′ N	7º 54′ E	Urban/drainage discharge.

A total of 77 samples of surface water were collected. Two surface water samples (one for trace elements and the other for physicochemical and other chemical analysis) were collected in 1000 mL polyethylene sample bottles, previously washed with detergent, soaked overnight with 10% (v/v) M HNO_3 and rinsed with deionised water. Before filling with the sample, the sample bottle was rinsed twice with water resource.

At each sampling site, temperature, pH, EC, DO and TDS were measured in-situ using portable pH/EC/TDS/Temperature combined HANNA, HI 991301 Model instrument. The two separate water samples were taken to the laboratory for analysis.

Water analysis

Trace metal concentration

In the laboratory, the water samples for trace element analysis were immediately filtered using Whatman No.1 filter paper and acidified with 2.0 mL of 10% HNO_3 (AR grade) to a pH < 2, to preserve samples for later analysis and stored at 4^oC in a refrigerator until time for trace metal (Cd, Pb, Cr, Cu, Zn, Ni and Co) analysis using Flame Atomic Absorption Spectrophotometer (model UNICAM SOLAR 939/59) equipped with air-acetylene flame.
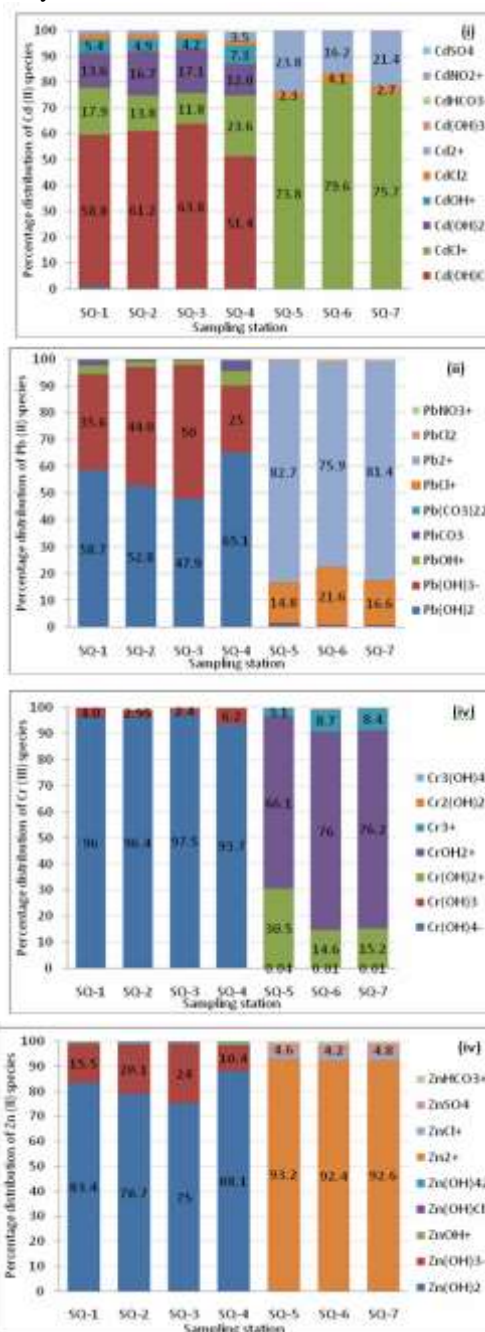

Fig.2(a). Percentage distribution of Cd (II), Pb (II), Cr (III) and Zn (II) species in surface water systems

Determination of nutrients

Nutrient and other water quality parameters - NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}, were measured using spectrophotometer model HACH DR 3800 SC; Turbidity was determined using HACH model 2100P Portable Turbidimeter, chloride (Cl^-) (Mohr method), alkalinity (titration method) and hardness (EDTA titration method using Erio T indicator) according to standard procedures (APHA 2005).
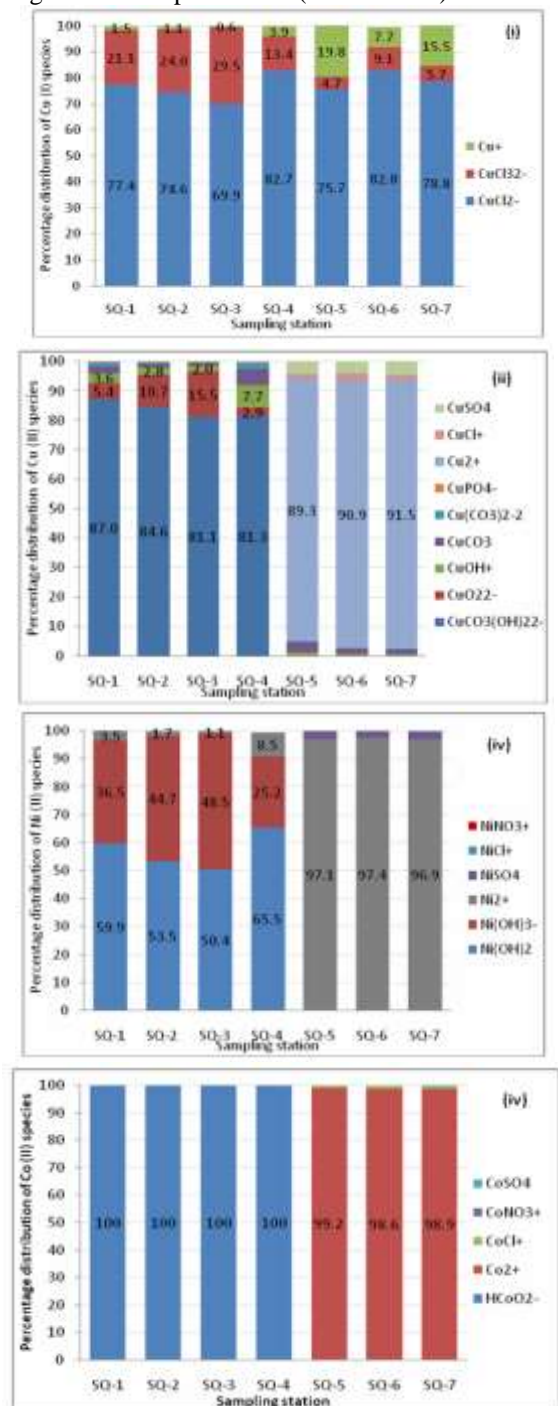

Fig. 2(b). Percentage distribution of Cu(I), Cu (II), Ni(II) and Co (II) species in surface water system

Modeling of surface water using PHREEQC

PHREEQC is a geochemical modeling program designed by the United States Geological Survey (USGS) developed by Parkhurst and Appelo (1999). Geochemical modeling enables quantitative speciation of elements based on species stability constants. PHREEQC is based on the equilibrium chemistry of aqueous solutions with other components, such as minerals, gases, solid solutions, and sorbing surfaces. The PHREEQC model is used to bring the observed water chemistry to thermodynamic equilibrium with the sediments and is designed to perform a wide variety of low temperature aqueous geochemical calculations, **speciation and saturation-index calculations.**

In speciation modeling, analytical data for solution composition (SOLUTION keyword) is needed to calculate the distribution of aqueous species by using ion-association aqueous model to obtain the saturation indices for minerals, which indicate whether a mineral should dissolve or precipitate. Several thermodynamic databases are provided with PHREEQCI version 2.18.5134 (released April 09, 2011 by USGS). The thermodynamic databases include iso.dat, llnl.dat, minteq.dat, minteq.v4.dat, phreeqc.dat, pitzer.dat, sit.dat, and wateq4f.dat. The phreeqc.dat is the smallest, wateq4f.dat has additional data for heavy metals, the minteq.dat and minteq.v4.dat files have a few more organic chemicals, pitzer.dat is for modeling highly saline and SO_4^{2-} rich solutions and the **llnl.dat** is a huge database with many minerals and large-range, temperature dependent equilibrium constants. Therefore, the **llnl.dat** (Lawrence Livermore National Library database) as a chemical speciation code for natural waters finds application in this study. It uses field measurements of some parameters such as temperature, pH, dissolved oxygen and alkalinity, and the chemical analysis of water sample as input and calculates the distribution of aqueous species, ion activities, and mineral saturation indices that indicate the tendency of a water to dissolve or precipitate a set of minerals (Drever 1988; Nordstrom and Munoz 1986).

According to Zhang et al. (2010), the saturation index (SI) for a certain mineral phase, MX, is calculated using the equation below:

$$SI_{MX} = \log\left(\frac{IAP}{K_{SP}}\right) = \log\left[\left(C_{M^{n+}} f_1\right)\left(C_{X^{n-}} f_2\right)\right] - \log K_{SP}$$

where: $C_{M^{n+}}$ and $C_{X^{n-}}$ are the molal concentration of the metal cation and the anion respectively and f_1, f_2 are the ionic activity coefficient (read from the simulation results).

Results

The results of surface water quality (physicochemical characteristics and trace metals) are presented in Table 1. The mean summary of trace metals - Cd, Pb, Cr, Cu, Zn, Ni and Co levels in surface water (μgL^{-1}) samples obtained are given as: 41 ± 49, 31 ± 30, 45 ± 39, 70 ± 71, 163 ± 89, 62 ± 82 and 55 ± 48. The highest metal concentration was recorded at station SQ-6 (Atabong) indicating point sources of anthropogenic pollution while station SQ-5 (Eketai) showed the least concentration.

The correlation matrix analysis (Pearson correlation coefficient, r) of physicochemical characteristics and trace metals are shown in Tables 2 and 3 respectively.

The distribution of species shows the concentration of possible species in the solution (Table 5). For example, the total Cd concentration (in molar) was about 3.65×10^{-7} and there are several dissolved species present including $CdCl^+$ (3.00×10^{-7}), Cd^{2+} (3.88×10^{-8}), $CdCl_2$ (2.49×10^{-8}) and $CdHCO_3^+$ (9.46×10^{-10}) with percentage distribution of 82.3% for $CdCl^+$, 6.8% for $CdCl_2$ and 10.3 % for Cd^{2+}, 0.3% for $CdHCO_3^+$ etc. The distribution of chemical species in all the seven studied stations

is shown in Figure 2(a) and 2(b) and Table 6 shows the saturation indices of the various selected mineral phase.

Discussions

Nutrients and other anions

Higher chloride levels were recorded at the downstream stations with significant influence of sea waters. QIT station (SQ-3) recorded the highest mean value of 1694 ± 342 mgL^{-1}, far above the WHO permissible levels of 250 mgL^{-1} for drinking water quality (WHO 2008). The chemical behavior of the metals and their species in water systems depends on the anion concentrations, e.g., OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-, and on the metal ability to coordinate predominantly with some of the anions. The low concentrations of NH_4^+ and NO_2^- indicate that there is no significant urban pollution. The main nitrogen form is NO_3^-, but the mean concentration in all sampling stations (4.63 ± 2.88mgL^{-1}) was quite below the maximum permissible level (50 mgL^{-1}) for drinking water (WHO 2008). The highest nutrient concentrations (NO_2^-, NO_3^-, NH_4^+, and PO_4^{3-}) were determined in the upstream stations located within the urban (Table 1). Mean sulphate level (36.2 ± 9.8mgL^{-1}) was quite high compared with values reported by Tepavitcharova et al. (2010) for natural waters but below the WHO maximum limit for drinking water quality.

Trace metals in surface water

Cadmium: Cadmium level in surface water was found to be high (Cd $\geq$ 60 μgL^{-1}) with values of 105, 100 and 60 μgL^{-1} recorded for stations SQ-6, SQ-4 and SQ-7, respectively. The least Cd value of $3\pm1\mu$gL^{-1} was obtained from station SQ-1. Cadmium (Cd) level at Iwuochang (SQ-4) could be related to the detritus materials originating from the different kinds of wastes dumped at the bank of the river, while levels recorded at Atabong (SQ-6) were attributable to the day-to-day burning of automobile tyres used by butchers for roasting animals and automobile tyre wear from the high traffic highway leading into Eket urban which are carried by surface runoff into the river. Mean Cd values in the river system far exceeded the WHO acceptable standard guidelines of 3 μgL^{-1} for potable water. Cadmium is known for showing very high toxicity to both aquatic and terrestrial organisms even at low concentrations (Kennish 1992).

Lead: The highest mean Pb value of 79 ± 53 μgL^{-1} obtained for station SQ-6 was attributed to effluents from different fuel stations located around the river and also due to the cumulative effect of exhaust emissions from automobiles which finds way by surface runoff into the lagoon. Results obtained in this study were far lower than 850 μgL^{-1} reported by Wegwu and Akininwor (2006) for New Calabar River, Port Harcout. However, the result compared favourably with River Ijana, Ekpan (25-58 μgL^{-1}) and Esi River (39 μgL^{-1}) reported by Emoyan et al. (2005) and Akporido (2010) respectively. However, the mean total results for all stations in the system was lower than values reported for Lagos Lagoon by Aderinola et al. (2009) and exceeded the WHO guidelines value (10 μgL^{-1}) for drinking water (WHO 2008).

Chromium: The Cr concentration ranged from 9 – 345 (45 ± 31) μgL^{-1}. The highest mean Cr value of 110 ± 35 μgL^{-1} was recorded at Atabong station (SQ-6) and values obtained from stations SQ-4 and SQ-6 exceeded the maximum allowable concentration for

potable water (WHO 2008). Mean results obtained exceeded values (20 μgL^{-1}) reported by Essien et al. (2009) for asphyxiated mangrove ecosystem of Qua Iboe River estuary, and was comparable with those reported for River Ijana (37-67 μgL^{-1}) by Emoyan et al. (2005), Esi River (42 μgL^{-1}) by Akporido (2010) and Lagos Lagoon (60 μgL^{-1}) by Aderinola et al. (2009).

Copper: The highest mean Cu concentration of 210 ± 85 μgL^{-1} in surface water was recorded at station SQ-6, however, station SQ-5 recorded the least Cu level (19 ± 7 μgL^{-1}) in the area. The highest Cu value recorded at station SQ-6 was indicative of high input of organic matter whose source was traceable to municipal/domestic sewage as previously reported by Khan and Khan (2003). However, concentration values compared favourably with values reported for Okirika River (Nduka and Orisakwe 2010) and Lagos Lagoon (Aderinola et al. 2009). However, results obtained were quite below the maximum permissible limit of 2000 μgL^{-1} recommended for drinking water (WHO 2008).

Zinc: The highest mean value (250 ± 81 μgL^{-1}) was recorded at station SQ-6, followed by station SQ-7 (223 ± 80 μgL^{-1}) located about 3km downstream of SQ-6 within Eket urban. According to Muniz et al. (2004), Zn is frequently associated with sewage and perhaps the increased precipitation in the winter months leads to an overflow of local sewage pipes and increased input. The high Zn levels at Ibeno stations of the system was attributed to materials originating from the natural mineral composition of the coastal areas which is rich in sulphide as previously reported by Prieto et al. (2008). However, Zn level in this study did not exceed the WHO maximum allowable concentration of 3000 μgL^{-1} for drinking water quality (WHO 2008).

Nickel: The range of nickel levels in surface water samples was 2 to 311 μgL^{-1} (Table 1) with a relatively high concentration (200 ± 57 μgL^{-1}) recorded at stations SQ-6 which might be related to point source of contamination ascribed to the cumulative effect of petroleum substances (petrol, diesel, kerosene and engine oil) from filling stations and auto-mechanic workshops sited around the river which are washed into the receiving river as previously reported by Udousoro et al. (2010). The results obtained showed higher values when compared with values reported by Abu and Egenonu (2008) for New Calabar River, but was lower than values reported by Nduka and Orisakwe (2010) for Ubeji River.

Cobalt: The range (total mean value in parenthesis) of Co in surface water samples was 3–195 (55 ± 48) μgL^{-1}. Among the seven stations sampled, station SQ-6 and SQ-7 recorded higher levels of Co with mean values of 126 ± 42 μgL^{-1} 104 ± 36 μgL^{-1} respectively. These two stations are located within the urban and it is expected that the stations acts as a sink for polluted runoffs from the fuel stations and auto-mechanic workshops sited around the river.

Statistical Analysis

Correlation Analysis (Pearson Correlation Coefficient)

The correlation matrix for the physicochemical parameters of surface water showed strong positive correlations ($r\geq0.850$, $P<0.05$, df=75) between the pairs alkalinity versus TDS ($r = 0.864$), EC ($r = 0.905$), Cl^{-1} ($r = 0.883$); TDS versus EC ($r = 0.982$) and Cl^{-1} ($r = 0.892$); and EC versus Cl^{-1} ($r = 0.926$) (Table 2). The inter-elemental correlation matrix analyses of trace element concentrations in surface water are shown in Table 3. The trace metal analysis of surface water showed some strong positive correlations ($r\geq0.800$, $P<0.05$, df=64) between the pairs – Pb/Cu ($r = 0.880$), Cu/Co ($r = 0.889$), Cu/Ni ($r = 0.865$),

Zn/Co (r = 0.831) indicating a common source of contamination. But, few cases showed moderately positive correlations (r<0.700), these include the pairs Cd/Pb (0.528), Cd/Cr (0.675), Cd/Cu (0.672), Cd/Ni (0.605), Cd/Co (0.528); Pb/Ni (0.695), Cr/Zn (0.524) and Ni/Zn (0.685) with Pb/Ni showing the highest relationship (Table 3).

Speciation of trace metals in surface water using PHREEQC computer model

The PHREEQC Interactive version 2.18.0.5134 computer geochemical model with the Lawrence Livermore National Library (LLNL) thermodynamic database was applied to show what complexes and species are present in water and the saturation states of various minerals. The chemical speciation of trace metals (Fig. 2) was calculated using the PHREEQCI model. The chemical behaviour of the metals and their species in water systems depends on the anion concentrations, e.g., CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-, and on the metal ability to coordinate predominantly with some of the anions. The differences in chemical speciation distribution were due to the different stabilities of the species in different water systems (Tepavitcharova et al. 2010).

Therefore, the distribution of aqueous species shows the concentration of possible species in solution (Table 5). The speciation and distribution of the trace metals ions in the river system revealed that the metals were found to exist mostly as free and complex species. Results obtained showed that the predominant species in surface water were the free ions of Zn^{2+} (92.6%), Ni^{2+} (97.6%), Co^{2+} (97.7%), Pb^{2+} (62.0%) and Cu^{2+} (70.2%) as well as the chloride species $CdCl^+$ (82.3%), $CuCl_2^-$ (81.2%), $PbCl^+$ (27.1%) and the hydroxy species of $CrOH^{2+}$ (58.7%) and $Cr(OH)_2^+$ (40.2%) (Table 5). The mean distribution of species in all stations is presented in Figures 2(a) and 2(b).

Distribution of Cd and Pb

The mean total Cd concentration (in molar) in surface water sample from the river system was 3.65×10^{-7} molar and several dissolved species present including $CdCl^+$ (3.00×10^{-7}), Cd^{2+} (3.88×10^{-8}), $CdCl_2$ (2.49×10^{-8}) and $CdHCO_3^+$ (9.46×10^{-10}). Dissolved Cd in natural water system occurs in the +2 oxidation state. The model results indicated that the most soluble Cd species was $CdCl^+$ (82.3%) and the other chemical species in solution are Cd^{2+} (10.6%), $CdCl_2$ (6.8%) and $CdHCO_3^+$ (0.3%). Stations SQ-1 – SQ-4 recorded higher values, ranging between 51.4 – 63.8% for Cd(OH)Cl specie, while stations SQ-5 – SQ-7 recorded higher values ranging between 73.8 – 79.6% for $CdCl^+$ specie [Fig. 2(a (i)]. Dissolved Pb in natural water system occurs in the +2 oxidation state, Pb(II), with the free Pb^{2+} being the most soluble form of Pb in surface water. The mean total Pb concentration was 1.50×10^{-7} molar with the most soluble chemical specie being Pb^{2+} representing about 62.0% of total Pb in the system. Complexed species indicates that about 27.1% occurs as $PbCl^+$, 0.2% as $PbNO_3^+$ and 0.1 as $PbOH^+$, about 7.8% occurs as $PbCO_3$ and only 2.0% occur as $PbCl_2$. Results from different stations shows that the hydroxide species $Pb(OH)_2$ and $Pb(OH)_3^-$ were predominant at stations SQ-1 – SQ-4 (downstream stations with significant seawater intrusion) while the free ion Pb^{2+} and $PbCl^+$ specie were predominant at stations SQ-5 – SQ-7 with maximum level of freshness (I=0.01) were recorded.

Distribution of Cr and Cu

From the model, only Cr(III) dominated the Cr species in the solution. About 58.7% occurs as $CrOH^{2+}$, 40.2% as $Cr(OH)_2^+$ and 0.3 % as $Cr(OH)_3$. Only about 0.6% of Cr^{3+} existed as the free Cr specie in the river systems. The complexed species dominates the solution system. Dissolved Cu in natural water system occurs in two oxidation states, i.e. Cu(I) and Cu(II). The model, indicated that out of the total Cu concentration of 11.03×10^{-6} molar, about 51.0% (5.63×10^{-7}) total Cu dominated as Cu(I) while 49.0% (5.40×10^{-7}) occurs as Cu(II). The two complexed species of Cu(I) - $CuCl_2^-$ (81.2%) and $CuCl_3^{2-}$ (16.0%) dominated the solution with free ionic species, Cu^+ (2.7%) as the least in solution. The Cu(II) species revealed about 70.2% of free ionic species being the most soluble chemical species of Cu(II) in surface water and about 21.6% as $CuCO_3$, 2.4% as $CuSO_4$ and the complexed species revealed only 3.0% as $CuCl^+$ and 2.7% as hydroxides ($CuOH^+$).

Distribution of Ni, Zn and Co

Nickel in surface water has only one significant oxidation state of +2 (i.e. Ni (II) and the most soluble chemical species in the sample representing about 97.5% of total Ni. The complexed chemical species indicates that only 2.0% occurs as $NiSO_4$, 0.2% as $NiCl^+$ and 0.1% as $NiNO_3^+$. Stations SQ-1 – SQ-4 recorded significant distribution of the chemical species ranging from 50.4 – 65.5% for $Ni(OH)_2$, 25.2 – 48.5% for $Ni(OH)_3^-$, while the upstream stations (SQ-5 – SQ-7) recorded higher values (about 97%) of Ni^{2+} as shown in Fig. 2(b).

Zinc, like Ni, has only one significant oxidation state, Zn (II), and the most soluble chemical specie in surface water is the free Zn^{2+} ion recording about 92.5% of total Zn in solution. The other chemical species in solution with their corresponding percentage distribution are $ZnSO_4$ (2.9%), $ZnCl^+$ (2.4%), $ZnHCO_3^+$ (1.9%) and $ZnCl_2$ (0.1%) and $ZnOH^+$ (0.1%).

Cobalt may occur in solution both in the +2 (Co^{2+}) and +3 (Co^{3+}) oxidation states. The model results indicates that the free Co^{2+} ion dominated completely representing about 97.7% of total Co^{2+} concentration for the entire river system. The complexed species indicated only about 2.2% as $CoCl^+$, 0.05% as $HCoO_2^-$, 0.03% as $CoNO_3^+$ and 0.02% as $CoSO_4$ for the river system.

Saturation Indices

The saturation state of minerals in the water can be expressed by the saturation index (SI). The surface water chemistry exchanges matter with the various minerals and gases within any system resulting in a dissolution or precipitation of minerals. Under low pH conditions (3-4), water remains undersaturated (dissolved), and it is unlikely that trace elements will precipitate therefore the trace elements will be transported farther downstream (Bhattacharya et al. 2006).

The results of partial pressure of carbon dioxide (P_{CO_2}) and saturation indices of some of the various mineral phases calculations using the PHREEQCI computer model with llnl.dat database (Table 5) revealed that most stations recorded negative saturation indices, indicating simple dissolution of the mineral phases in solution. Generally, cerrusite ($PbCO_3$) shows moderate undersaturation (SI = −0.94), while pyromorphite ($Pb_5(PO_4)_3Cl$) (SI = 7.69), $CuCr_2O_4$ (SI = 7.25) and $PbHPO_4$ (SI = 1.69) are highly supersaturated, with very high tendency to precipitate out of solution. The downstream stations located in Ibeno area (SQ-1 – SQ-4, with seawater intrusion) exhibited some degrees of supersaturation (precipitation) with respect to the mineral phases- atacamite (2.42 – 3.09), $Ni(OH)_2$ (0.64 – 0.89), tenorite (2.77 − 2.92), tsumebite (0.08 − 0.65) and zincite (0.52 − 0.75). On the other hand, some few mineral phases including $CdCr_2O_4$,

$CuCr_2O_4$ and $PbHPO_4$ also exhibited some degrees of precipitation at the upstream stations, SQ-5 (SI = 4.15 – 5.09), SQ-6 (3.93 – 5.13) and SQ-7 (1.06 − 1.41) respectively (Table 6). Significantly, the mineral, pyromorphite ($Pb_5(PO_4)_3Cl$), recorded positive saturation indices values (1.45 − 5.96) in all the stations indicating absolute precipitation of the mineral out of solution in the river system.

Conclusion

Rivers in the coastal Niger Delta environment are often exposed to pollution from different sources such as petroleum industries, manufacturing industries, erosion and natural processes (such as weathering and flooding). This study however gives an assessment of the pollution status of Qua Iboe River system, considering the influence of rapid population in the region and increased agricultural activities (fish farming) along the coast of the river system. However, the study revealed that Atabong (SQ-6) station (located within Eket urban) acting as a sink to different sources of pollution – domestic wastes, municipal runoff, effluents from fuel stations and auto-mechanic workshops, garbage and metal scraps, etc. was remarkably outstanding as the most contaminated station along the river system due to point source pollution. This was however followed by Marina station (SQ-7), located downstream (about 3 km) of Atabong while the least contaminated station was Eketai station (SQ-5).

However, the magnitude of pollution of Qua Iboe River is not comparable to some other polluted rivers of the Niger Delta region as most parameters did not exceed the WHO maximum permissible levels for drinking water. Particular attention should be given to the Atabong and Marina stations, which supports the highest pollution levels among the studied stations of the river due to the anthropogenic activities which influences the pollution pattern of the river system.

The results of calculation of saturation index by the PHREEQC computer program shows that most of the stations recorded negative saturation indices indicating simple dissolution of the mineral phases in solution except those of atacamite, pyromorphite, $CuCr_2O_4$, $CdCr_2O_4$ and $PbHPO_4$ which showed high tendency to precipitate out of solution.

Acknowledgements

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Table 1. Mean physicochemical characteristics and trace metal concentrations (n = 77) of surface water samples from Qua Iboe River system

Parameters	Sampling stations							Mean from all stations
	Iwuokpom 1 (SQ-1)	Iwuokpom 2 (SQ-2)	QIT (SQ-3)	Iwuoachang (SQ-4)	Eketai (SQ-5)	Atabong (SQ-6)	Marina (SQ-7)	
Temp. ^{o}C	28.9 ± 2.8	29.2± 2.9	29.7±3.0	29.8±3.0	29.5±2.7	30.1±3.2	30.1±3.11	29.6±2.9
pH	7.17±0.09	7.09± 0.10	7.06±0.20	6.97±0.17	6.63±0.09	6.70±0.13	6.74±0.10	6.91±0.24
Alkalinity (mgL^{-1})	81.0±15.4	92.9±17.0	111.0±14.7	57.5±22.3	25.0±9.6	33.4±13.8	28.3±8.8	61.3±35.1
Turbidity (NTU)	40.01±4.85	37.73±5.29	67.55±9.51	56.18±5.16	32.21±4.20	70.42±10.91	52.70±5.02	50.5±15.8
TDS (mgL^{-1})	668±94	833±147	956±168	390±87	154±26	264±81	202±28	495±315
E. Cond. (μScm^{-1})	1628±189	1990±217	2296±368	972±214	385±66	661±61	504±78	1205±737
Hardness (mgL^{-1})	27.4±9.9	24.4±5.3	25.2±4.2	21.0±2.4	241.6±78.7	669.3±204.4	579.1±255.1	221.6±290.7
DO (mgL^{-1})	6.97±1.35	7.27±1.47	6.38±1.00	5.78±1.50	6.89±0.86	5.29±0.40	6.33±0.88	6.42±1.27
COD (mgL^{-1})	25.25±1.71	20.51±1.31	26.45±3.32	19.22±1.50	24.64±2.71	18.87±1.55	18.15±1.86	21.9±3.8
BOD$_5$ (mgL^{-1})	2.94±0.40	2.81±0.44	3.31±0.54	2.76±0.52	3.25±0.67	2.76±0.48	2.78±0.63	2.80±0.73
Chloride (mgL^{-1})	1149±277	1334±334	1694±342	714±189	292±92	498±149	338±73	860±547
NH_4^+ (mgL^{-1})	0.36±0.29	0.34±0.25	0.32±0.25	0.49±0.26	0.64±0.33	0.61±0.29	0.47±0.24	0.46±0.29
NO_3^- (mgL^{-1})	1.89±0.67	2.97±0.84	2.60±1.02	4.46±1.43	4.57±1.09	9.77±2.69	6.13±1.77	4.63±2.88
NO_2^- (mgL^{-1})	0.05±0.03	0.05±0.02	0.06±0.04	0.09±0.02	0.10±0.03	0.17±0.03	0.10±0.03	0.09±0.05
PO_4^{3-} (mgL^{-1})	0.11±0.04	0.07±0.02	0.09±0.03	0.07±0.02	0.13±0.02	0.11±0.02	0.12±0.02	0.10±0.03
SO_4^{2-} (mgL^{-1})	33.2±11.0	30.7±12.7	37.2±13.8	32.4±9.8	38.1 ± 4.2	40.0±4.0	41.8±4.4	36.2±9.8
Trace metals								
Cd (μgL^{-1})	3 ±1	4±4	8±3	100±32	6±3	105±43	60±26	41±49
Pb (μgL^{-1})	27±9	19±6	35±13	14±7	11±14	79±53	30±11	31±30
Cr (μgL^{-1})	17±6	18±8	23±10	40±14	51±50	110±35	55±22	45±39
Cu (μgL^{-1})	48±15	35±12	49±16	34±14	19±7	210±85	97±29	70±71
Zn (μgL^{-1})	205±89	141±73	149±50	104±36	68±26	250±81	223±83	163±89
Ni (μgL^{-1})	26±10	16±5	21±7	12±4	8±5	200±57	169±69	62±82
Co (μgL^{-1})	46±18	32±12	50±17	18±27	7±3	126±42	104±36	55±48

Table 2: Correlation matrix (Pearson correlation coefficient, r) of physicochemical properties of QIR system

Parameters	Pearson Correlation Coefficient (r)															
	Temp	pH	Alkalinity	Turbidity	TDS	E. Cond.	Hardness	DO	COD	BOD_5	Cl^-	NH_4^+	NO_3^-	NO_2^-	PO_4^{3-}	SO_4^{2-}
Temp.	--															
pH	- 0.020	-														
Alkalinity	0.264	0.696[a]	-													
Turbidity	0.189	- 0.077	0.108	-												
TDS	- 0.073	0.676[a]	0.864[a]	0.032	-											
E. Cond.	- 0.073	0.676[a]	0.905[a]	0.046	0.982[a]	-										
Hardness	- 0.111	- 0.588	- 0.680[a]	0.243	- 0.598[a]	- 0.611[a]	-									
DO	0.601[a]	0.288	0.397	0.395	0.178	0.257	- 0.381	-								
COD	0.192	0.210	0.442	- 0.180	0.400	0.449	- 0.435	0.394	-							
BOD_5	0.605[a]	- 0.039	0.307	0.086	0.075	0.133	- 0.280	0.517	0.337	-						
Cl^-	0.063	0.600[a]	0.883[a]	0.094	0.892[a]	0.926[a]	- 0.583[a]	0.258	0.484	0.171	-					
NH_4^+	0.564[a]	- 0.268	- 0.160	- 0.011	- 0.362	- 0.294	0.187	0.350	0.140	0.431	- 0.242	-				
NO_3^-	0.118	- 0.570	- 0.571	0.395	- 0.559	- 0.574	0.655[a]	- 0.327	- 0.497	0.019	- 0.544	0.544	-			
NO_2^-	0.481	- 0.596[a]	- 0.431	0.407	- 0.543	- 0.495	0.562[a]	- 0.067	- 0.158	0.135	- 0.424	0.424	0.750[a]	-		
PO_4^{3-}	0.548[a]	- 0.343	- 0.237	- 0.087	- 0.393	- 0.328	0.304	0.430	0.359	0.298	- 0.263	- 0.263	0.149	0.496	-	
SO_4^{2-}	0.544[a]	- 0.280	- 0.061	0.161	- 0.261	- 0.147	0.280	0.439	0.129	0.376	- 0.021	- 0.021	0.194	0.480	0.582[a]	-

[a] *Critical value of |r| at 95% confidence level (P<0.05) for degree of freedom (df) = 75 is 0.224*

Table 3. Correlation matrix (Pearson Correlation coefficient) of trace metals in surface water

	Pearson Correlation Coefficient (r)						
	Cd	Pb	Cr	Cu	Zn	Ni	Co
Surface water (n=77)							
Cd	-						
Pb	0.528[a]	-					
Cr	0.675[a]	0.711[a]	-				
Cu	0.672[a]	0.880[a]	0.794[a]	-			
Zn	0.414	0.703[a]	0.524[a]	0.729[a]	-		
Ni	0.605[a]	0.695[a]	0.715[a]	0.865[a]	0.685[a]	-	
Co	0.528[a]	0.764[a]	0.647[a]	0.889[a]	0.831[a]	0.882[a]	-

[a]*Critical value of |r| for degree of freedom (df)) = 34 is 0.329 at 95% confidence level (P<0.05)*

Table 4. Comparison of metal concentrations of surface water with other rivers in the Niger Delta region and Lagos Lagoon, Nigeria

Study areas/Rivers	Trace metals concentration (mgL^{-1})								Reference
	Cd	Pb	As	Cr	Cu	Zn	Ni	Co	
Asphyxiated mangrove swamp, Qua Iboe River	-	0.01± 0.006	-	0.02± 0.001	0.036± 0.015	0.03± 0.001	0.013± 0.005	-	Essien *et al.* (2009b)
Ubeji Creek, Delta	0.70 (0.64)	0.30 (0.22)	-	ND	5.20 (4.30)	0.78 (0.68)	0.10 (0.08)	-	Nduka and Orisakwe (2010)
New Calabar River, PH	-	0.85	-	0.50	2.08	0.07	-	-	Wegwu and Akininwor (2006)
Iko River, Akwa Ibom	0.04	`0.004	-	0.01	0.13	0.35	0.42	-	Benson and Etesin (2008)
River Ijana, Ekpan	0.010-0.100	0.025-0.058	-	0.037-0.067	0.020-0.050	0.088-0.122	0.030-0.080	-	Emoyan *et al.* (2005)
Esi River, Delta State	0.0024	0.039	-	0.042	0.0161	0.107	0.012	-	Akporido (2010)
Okirika River, PH	0.16±0.04	0.59±0.03	-	0.23±0.02	0.08±0.01	0.02±0.00	0.65±0.01	-	Nduka and Orisakwe (2010)
Abuloma River, Rivers State	0.15±0.02 (0.13±0.00)	0.41±0.03 (0.39±0.01)	-	ND	0.05±0.01 (0.04±0.01)	0.03±0.01 (0.02±0.01)	0.52±0.03 0.47±0.01	-	Nduka and Orisakwe (2010)
Lagos Lagoon, Nigeria	0.354	0.263	0.01	0.06	0.197	0.53	0.140	-	Aderinola *et al.* (2009)
Hindon River, India	0.0024 -0.0241	0.030-0.9021	-	0.0312-0.3309	BDL - 4.3725	0.0005-0.8364	-	-	Suthar *et al.* (2009)
[a]Qua Iboe River, Akwa Ibom	41±49	31±30	3±2	45±39	70±71	163±89	62±82	55±48	Present study

Table 5. The percentage distribution of trace metals species using PHREEQCI model for the river system

Metal species	conc (m)	% dist.		Metal species	conc (m)	% dist.
Cd (II)	3.65E-07			Cr (III)	3.89E-07	
$CdCl^+$	3.00E-07	82.3		$Cr(OH)_3$	1.06E-09	0.3
$CdCl_2$	2.49E-08	6.8		$Cr(OH)_2{}^+$	1.56E-07	40.2
Cd^{2+}	3.88E-08	10.6		$CrOH^{2+}$	2.28E-07	58.7
$CdHCO_3{}^+$	9.46E-10	0.3		Cr^{3+}	2.36E-09	0.6
$CdCl_3{}^-$	1.54E-10	0.04				
Pb(II)	1.50E-07			Zn (II)	2.50E-06	
$PbOH^+$	1.37E-10	0.1		$ZnOH^+$	1.90E-09	0.1
$PbCO_3$	1.17E-08	7.8		Zn^{2+}	2.31E-06	92.6
$PbCl^+$	4.06E-08	27.1		$ZnCl^+$	6.01E-08	2.4
Pb^{2+}	9.28E-08	62.0		$ZnSO_4$	7.27E-08	2.9
$PbCl_2$	2.95E-09	2.0		$ZnHCO_3{}^+$	4.66E-08	1.9
$PbNO_3{}^+$	3.23E-10	0.2		$ZnCl_2$	1.34E-09	0.1
As (V)	4.01E-08			Co (II)	9.34E-07	
AsO_3F^{2-}	2.68E-08	66.7		$HCoO_2{}^-$	4.24E-10	0.0
$HAsO_3F^-$	1.33E-08	33.2		Co^{2+}	9.12E-07	97.7
				$CoCl^+$	2.12E-08	2.3
Ni (II)	1.06E-06			Cu (II)	5.40E-07	
Ni^{2+}	1.03E-06	97.6		$CuOH^+$	1.47E-08	2.7
$NiSO_4$	2.13E-08	2.0		$CuCO_3$	1.17E-07	21.6
$NiCl^+$	1.70E-09	0.2		Cu^{2+}	3.79E-07	70.2
$NiNO_3{}^+$	5.48E-10	0.05		$CuCl^+$	1.61E-08	3.0
				$CuSO_4$	1.30E-08	2.4
Cu (I)	5.63E-07					
$CuCl_2{}^-$	4.57E-07	81.2				
$CuCl_3{}^{2-}$	9.03E-08	16.0				
Cu^+	1.50E-08	2.7				

Table 6. Saturation Indices of some mineral phases at some stations in Qua Iboe River system

Phase	Saturation Indices (SI)							SI_{tot}	log Ksp	Formula
	SQ-1	SQ-2	SQ-3	SQ-4	SQ-5	SQ-6	SQ-7			
Anglesite	-7.28	-7.80	-7.70	-7.12	-3.15	-2.38	-2.70	-2.96	-7.91	$PbSO_4$
Atacamite	3.04	2.42	2.87	3.09	12.55	10.53	11.79	-7.96	14.26	$Cu_2(OH)_3Cl$
Cd(OH)$_2$	-1.64	-1.41	-1.07	-0.13	10.61	10.25	10.35	-9.31	13.73	$Cd(OH)_2$
CdCr$_2$O$_4$	-4.00	-5.22	-5.84	-0.14	5.09	4.82	4.15	7.48	15.00	$CdCr_2O_4$
Cerrusite	-1.62	-2.13	-2.09	-1.63	-2.16	-1.61	-2.05	-0.94	-3.24	$PbCO_3$
CO$_2$	-6.95	-7.25	-7.43	-6.70	-0.94	-0.46	-0.53	-1.15	-7.83	CO_2
Cotunnite	-9.77	10.12	-9.89	10.04	-6.95	-5.72	-6.41	-5.72	-4.85	$PbCl_2$
CuCr$_2$O$_4$	-6.71	-8.27	-9.09	-4.31	5.13	4.73	3.93	7.25	16.22	$CuCr_2O_4$
Cuprite	-1.23	-1.74	-1.72	-0.84	-3.22	-2.09	-2.56	-1.81	-1.91	Cu_2O
Hydrocerrusite	-1.52	-2.74	-2.43	-1.77	-9.14	-7.95	-9.19	-5.41	1.85	$Pb_3(OH)_2(CO_3)_2$
Malachite	0.25	-0.30	-0.25	0.53	-6.23	-5.32	-5.85	-4.04	5.90	$Cu_2(OH)_2CO_3$
Nantokite	-7.13	-7.47	-7.46	-6.96	-3.45	-2.32	-2.71	-2.78	-6.77	$CuCl$
Ni(OH)$_2$	0.89	0.64	0.74	0.64	-8.58	-7.88	-7.94	-6.89	12.75	$Ni(OH)_2$
NiCO$_3$	-4.90	-5.47	-5.57	-4.95	-8.39	-7.26	-7.38	-6.64	3.51	$NiCO_3$
O$_2$	-0.74	-0.72	-0.77	-0.82	-0.74	-0.85	-0.78	-0.80	-2.89	O_2
Otavite	-1.13	-1.22	-1.09	0.58	-4.13	-3.32	-3.49	-2.79	-1.77	$CdCO_3$
Paralaurionite	-2.51	-2.79	-2.56	-2.76	-4.37	-3.71	-4.24	-3.08	0.20	$PbClOH$
PbHPO$_4$	-1.45	-2.16	-2.02	-1.49	1.06	1.41	1.07	1.69	-15.73	$PbHPO_4$
Phosgenite	-9.85	10.71	10.45	10.11	-7.57	-5.80	-6.93	-5.10	-9.65	$Pb_2(CO_3)Cl_2$
Pyromorphite	4.04	1.45	2.31	3.44	3.19	4.96	3.06	7.69	-47.90	$Pb_5(PO_4)_3Cl$
Smithsonite	-3.43	-3.92	-4.09	-3.44	-4.38	-4.07	-4.16	-3.22	0.44	$ZnCO_3$
Sphlaerocobaltite	10.12	10.71	10.79	10.01	-4.59	-3.59	-3.72	-2.92	-0.26	$CoCO_3$
Tenorite	2.89	2.77	2.89	2.92	-3.34	-3.12	-3.35	-2.23	7.65	CuO
Tsumebite	0.65	-0.38	0.08	0.37	-9.62	-9.00	-9.94	-6.35	2.53	$Pb_2CuPO_4(OH)_3$:$3H_2O$
Zincite	0.75	0.58	0.60	0.52	-6.18	-6.33	-6.36	-4.99	11.20	ZnO
ZnCO$_3$:H$_2$O	-3.19	-3.69	-3.87	-3.22	-4.16	-3.86	-3.95	-2.92	0.14	$ZnCO_3:H_2O$