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Chemical Speciation of Some Metal Ions in Surface Water Samples of Itu River, Akwa Ibom State, Nigeria

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ABSTRACT
In this research work, Chemical speciation of some metal ions in surface water of Itu River in Akwa Ibom state was carried out using PHREEQC geochemical model. This area is widely polluted by trading, fishing and agricultural activities. The study findings based on the model calculations strongly indicated that Na^+, Ca^+, Mg^+, and K^+ are greatly soluble and the consequential bioavailability ranges are 99% to 99.8% at p^H ranges of 6.1 to 7.8 for surface water system. Fe^{2+}, Pb^{2+} and Zn^{2+} are also bio available; their values 62-99% for Zn, 62-92% for Pb and 95-97% for Fe are connected to the organic complexation of the ions. The model calculation shows that greater percentage of Pb, Zn, and Fe exists in hydrated ion form and fewer carbonates, sulphates, phosphate and chlorides. With this findings Fe, Zn, and Pb levels present deleterious health risks in the water samples and the environment .The result also indicate that the concentration of Na^+, Ca^+, Mg^+, and K^+, at such intensity would be obtainable for uptake by plants and animals, consequently resulting in negative impact on the aquatic organisms, inhabitants and the surrounding environment.

Keywords: Metal ions, speciation, modeling, Itu River, PHREEQ C, Nigeria

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1.0 INTRODUCTION

Water is a major constituent of all living matter, comprising up to two third of the human body. Water is one of the component of total environment which we dwell other components are soil and air [1]. All metals including heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are predominantly low [2].The solubility of metals in surface water system is predominantly regulated by the water pH level, the nature and concentration of liquids on which the metal could absorb the redox environment of the system and the oxidation state of the mineral components [3].Surface and ground water are mostly used domestically for cooking, drinking and laundry activities.

Today, most urban areas of developing countries like Nigeria remain exposed to untreated sewage, and intolerable solid and liquid waste disposal. This presents serious threat to the environment including health risk. Commonly cited effects of industrial effluents on the receiving waters are high turbidity, reduced transparency, increase suspended solids and oxygen depletion [4, 5] To check the toxic effect of heavy metals and their complexity in mobilization, it is highly imperative to understand the various forms of the element (toxic or essential)) present in biota under various conditions [6 - 9].Chemical speciation refers to the form of ions in solution and their interaction with other constituent in both aqueous and solid form [10].In a more elaborate form, speciation deals with the species or the physiochemical forms of an element which together encompass its total concentration in a given sample [11]. More recently, chemical speciation has been described as the identification and quantification of the different species, forms, or phases present in a material [12, 7].The metals selected for this study are of high significance, and forms major components of surface water system. They include K, Na, Mg, Zn, Fe, Ca, Pb. The PHREEQC speciation model was used to calculate the ion activities. PHREEQC is the equilibrium thermodynamic model supported by the United State Geological Survey (USGS) [13, 17]. PHREEQC is computer software which is based on an ion-association aqueous model and has the capabilities for accurately determining the speciation and saturation index of metal ions in surface water system [13]. The aim of this study is to ascertain the extent of surface water pollution by ionic species of Zn, Ca, Mg, Na, Pb, Fe using PHREEQC geochemical models from the determined ion concentration.

2.0 MATERIALS AND METHOD

2.1 Description of study area

Okopedi, Ukumbain and Clark quarters are in Itu Local Government Area of Akwa Ibom State. Located in the south-eastern part of Nigeria which lies between latitude 5.10^{O} North and Longitude 7.59^{O} East and is located within the Niger Delta region of Nigeria. Itu is bounded in the North-East by Odukpani in Cross River State and Arochukwu in Abia State, in the West by Ibiono Ibom and Ini Local Government Areas, in the South and south-east by Uyo and Uruan Local Government Areas respectively. There are few residences around the water bodies and the area is well known for human activities such as trading, fishing and frequent agricultural activities. There is a big market and a motor park located by the river bank in Okopedi for easy loading and transportation of agricultural goods from the other riverside communities.

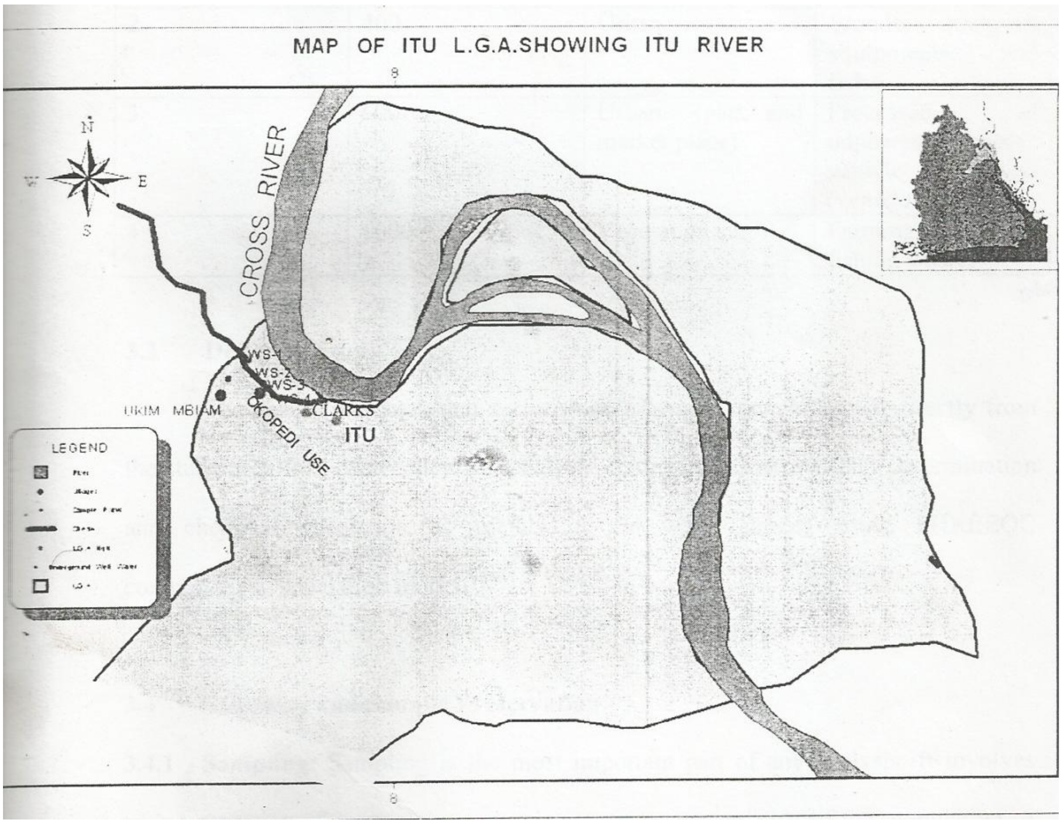

Fig.1 Map of sampling sites

2.2 Characteristics of sampling sites

The first sampling station (SW1) is 250m away from the river mouth. It is mainly characterise by rural, domestic and agricultural activities. Possible waste discharge from this sampling station includes food items, agricultural waste and machine scraps. The second sampling station (SW2) is 400m away from the river mouth and is mainly characterise by urban activities which result in the dumping of woods, transport equipments and fish bones in this area. The third sampling station (SW3) is located 600m away from the river mouth and is dominated by large urban market, the possible waste discharge from this station include processed and unprocessed woods, vehicle pollution(lead from vehicles) and the fourth sampling station (SW4) is characterise by a huge vegetation, and possible waste from this station is farming and fishing waste.

2.3 Samples collection

Water samples were collected in four different locations in the study area in a wide polyethylene and BOD bottles and stored in an ice box for further analysis. The temperature was determined insitu with the aid of a temperature meter (Suntex-TS-2 model), the pH was determined with a pH meter (Suntex-TS-2 model), the Redox potential was determined with potential meter (Suntex-TS-2 model), the electrical conductivity was also determined with a conductivity meter, model HI-98128 by HANNA and the dissolved oxygen was determined appropriately at the site with the aid of dissolve oxygen meter (DO_2) Jenway-9071 model. The essence of collecting samples in different locations was to ensure accurate determination of the spread of pollution in the area. The bottles were washed with 3M HNO_3 and rinsed with distilled water prior to collections. All the Procedures were based on standard methods approved by APHA (American Public Health Agency) [14]. In each case the bottles were carefully filled without trapping air bubbles. Sample for BOD was kept in a dark cupboard for 5 days before analysis. The bottles were washed with 3M HNO_3 and rinsed with distilled water prior to collections. All the Procedures were based on standard methods provided by APHA (American Public Health Agency) [14]. In each case the bottles were carefully filled without trapping air bubbles. Sample for BOD was kept in a dark cupboard for 5 days before analysis.

Since the sample collected contained impurities which could present erroneous analytical result, each of the samples for trace metal determination collected at each location were acidified with 1ml concentrated trioxonitrate (v) acid to preserve the chemical and pathological changes that could unavoidably occur once it has been removed from the water source.

2.4 Determination of physicochemical parameters

In this work, various methods were employed in the determination of range of physico-chemical parameters like pH, dissolve O_2, Redox potential, electrical conductivity, Turbidity, Salinity, total alkalinity, and Acidity which is in accordance with standard methods for the examination of water and Waste Water, America Public Health Association [14]. Anions such as Sulphate, Chloride, Nitrate, and Phosphate in the sample of water were determined with Hach Spectro Dr3800 Model Spectrophotometer.

The heavy metals (Cu, Fe, Zn) concentration in the sample was determined using the UNICAM SOLAR 969 Model atomic absorption spectrophotometer.

The concentration of other metallic elements (K, Mg, Na, Ca) in the sample with low ionization energy was determined using UV/visible spectro-photometer model (UN-2500).

2.5 Computer Speciation Modelling

The speciation of each metal in water was predicted using the AQUACHEM software application with the built in interface to the United State Geological Survey geochemical modelling program PHREEQC [15]. With modified Lawrence Livermore National Library (LLNL) thermodynamic database using the hydro-chemical data for both the inorganic contaminants in surface water samples from selected portion of the study area. The input data to the modelling programs are presented in Table 2.

3.0 Results and Discussions

The results obtained from this study are as presented in Tables 1 to 4. Table 1 showed the physico-chemical parameters of water samples. Table 2 shows the Metal levels, table 3 shows the anion level and table 4 shows the result of the speciation studies.

Table 1: The Physicochemical Parameters of the Water Samples

Parameters	Sampling Sites				
	SW1	**SW2**	**SW3**	**SW4**	**WHO**
Temperature	28.7	29.3	29.2	29.4	27-28
pH	6.35	6.16	7.93	7.35	6.5-8.5
Redox potential	39	89	-82	-37	
EC (us/cm)	28	25	25	25	1000
DO(mg/L)	5.4	6.8	5.1	4.4	
BOD(mg/L)	0.2	0.7	0.8	0.4	
Turbidity(NTU)	5.63	5.18	3.66	9	5
Salinity	0.8	0.6	0.7	0.6	100
Total alkalinity (mg/L)	3.5	6.2	4.1	3.2	100
TDS (mg/L)	<0.1	<0.1	<0.1	<0.1	<0.1
Acidity (mg/L)	3.0	4.2	3.3	2.8	
COD*mg/L)	0.3	1.2	1.2	0.7	

Table 2: Some Metal Levels (mg/l) in the Water Samples

Metals	Sampling sites				
	SW1	**SW3**	**SW3**	**SW4**	**WHO**
Copper	ND	ND	ND	ND	1
Zinc	1.08	0.83	0.71	0.52	3
Lead	1.37	0.00	1.18	<0.00	0.01
Cadmium	ND	1.44	0.64	ND	
Magnesium	2.11	7.49	3.54	2.65	200
Calcium	11.90	8.13	10.46	5.06	200
Sodium	8.90	18.43	2.33		200
Potassium	3.44	5.71	5.79	5.17	

Table 3: Some Anion Levels (mg/l) in the Water Samples

Anions	Sampling sites				
	SW1	SW2	SW3	SW4	WHO
Chloride (mg/l)	28.4	21.7	24.9	21.3	250
Sulphate (mg/l)	3.1	1.9	1.6	2.7	250
Nitrate (mg/l)	2.3	0.5	2.5	2.8	50
Phosphate (mg/l)	0.00	0.18	0.03	0.05	5
Nitrite (mg/l)	0.01	0.02	0.01	0.03	20

SW_1 = Sampling station 1 at Okpedi; SW_2 = Sampling Station 2 at Ukimbian; SW_3 = Sampling Station 3 at Clarke quarters; SW4 = Sampling Station 4 at Clarke quarters; COD = Chemical oxygen demand; ND = Not detected

From the results presented in Table 1, the temperature value for the analysed water samples ranged from (28.7-29.4)^{o}C which were above the WHO standards[15]. The pH values ranged from 6.35 – 7.35. In table 2, the analysed concentration of lead, sodium, calcium, iron, potassium, zinc and magnesium ranged from (0-1.37) mg/L for lead, (2.33-18.43) mg/L for sodium, (2.33 – 8.90) mg/L for Calcium.(0- 1.01) mg/L for Iron, (3.44-5.79) mg/L for potassium, (5.06 – 11.90) mg/L for Zinc, and 2.65 – 7.49) mg/L for magnesium in the surface water from the study area.The determined concentrations of the cations and anions were used to model their speciation in the study environment.

Table 4: Range of highest percentages of speciated forms of metals in water Samples from Itu River

Elements	Species	%	Element	Species	%
Ca	Ca^{2+}	99-99.80	Pb	Pb^{2+}	62-92
	$CaSO_4$	0.01		$PbOH^+$	4-25
	$CaHCO_3$	0.1-03		PbCO	2-12
	$CaNO_3^+$	0.01-0.02		$PbCl^+$	0.9-2
	$CaCl^+$	0.01-0.01		$PbNO_3^+$	0.1-0.2
	$CaCO_3$	0.1-0.3		$Pb(OH)_2$	0.01-0.02
				$PbHPO_4$	0.01-0.2
Fe	Fe^{2+}	96-97	Zn	Zn^{2+}	62-99
	$FeHCO_{3+}$	3-5		$ZnSO_4$	0.01-0.04
	$FeSO_4$	0.01-0.03		$ZnOH^+$	2-10
	$FeCl^+$	0.01-0.02		$ZnHCO_3^+$	0.02-0.04
	$FeCO_3$	0.02-0.05		$ZnCl^+$	0.1-0.3
	$FeOH^+$	0.1-0.2		$ZnHPO_4$	0.01-0.01
	$FeHPO_4$	0.03-0.2		$Zn (OH)_2$	1-3
				$ZnPO_4$	0.02-0.03
	Fe^{3+}	95-97			
	$Fe (OH)_3$	39-50	Mg	Mg^{2+}	99.50-99.80
	$Fe (OH)_2^+$	50-61		$MgSO_4$	0.01-0.03
	$Fe (OH)_4$	0.1-0.15		$MgHCO_3^+$	0.03-0.04

				$MgCl^+$	0.1-0.2
K	K^+	99-99.8		$MgHPO_4$	0.001-0.002
	KSO_4	0.02-0.05			
	KCl	0.01-0.02	Na	Na^+	99.0-99.8
				$NaHCO_3$	0.01-0.03
				NaCl	0.01-0.02
				Na_2SO_4	0.01-0.2

The data presented in Table 4 indicates the speciation and distribution of the metals ions from water samples from the study area, which was predicted using the PHREEQC geochemical modelling software [15]. The application computes and reports the speciation of metals in terms of their free aquo ions and inorganic complexes.

3.1 Chemical Speciation of the selected Metals

In the surface water system, dissolved sodium occurs in +1 oxidation state. The results indicate that Na^+ is the most soluble chemical species of sodium and correspond to about 99% of the sodium in the four sampling sites. Results of the complexed species revealed that 0.01 -0.03% occurs as carbonates ($NaHCO_3$), 0.01-0.2% as sulphates ($NaSO_4$) and 0.01-0.02% as chlorides. Calcium like magnesium has only one oxidation state Ca^{2+} and is chiefly soluble in nearly all types of natural waters. Chemical speciation of calcium showed that 99-99.8% exist as free ions (Ca^{2+}) and for the complexed inorganic minerals, 0.02-0.03% exist as sulphate ($CaSO_4$), 0.1-3%, exist as carbonates ($CaHCO_3$, $CaCO_3$) and 0.01% exist as chlorides ($CaCl^+$).

Iron may possibly occur in solution as Fe^{+2} or Fe^{+3} oxidation state. The redox specification in oxygenated water favours the more oxidized form (Fe^{3+}). Ferrous ions (Fe^{2+}) form complexes with a number of ligands, $FeHCO_3$ and $FeCO_3$ appears likely to be the foremost form in natural water containing dissolved CO_2. Chemical speciation of iron from the study area indicates that 95-97% occurs as free aqua ions (Fe^{+2}) and (Fe^{+3}), 3-5% occurs as $FeHCO_3^+$, 39-50 % occurs as $Fe(OH)_3$, and less than 1% occurs as sulphates, phosphate, sulphides and bicarbonates.

Potassium akin to sodium has only one major oxidation state K^+ and it tends to be soluble in most types of natural water as sodium. Chemical speciation of potassium in surface water indicate the 99-99% of potassium exists as free (K^+) about 0.02-0.05% as sulphate (K_2SO_4) and about 0.01-0.02% as KCl. In natural water system dissolved magnesium occurs in +2 oxidation state. Chemical speciation of magnesium from the study area indicates that 99.5-99.8% occurs as free aqua ions (Mg^{2+}). While 0.01-0.03% occurs as sulphate ($MgSO_4$) and 0.03-0.04% also occurs as carbonate ($MgHCO_3$).

Additionally 001% occurs as phosphate ($MgHPO_4$) and 0.2% exists as chlorides ($MgCl^+$). Low solubility compounds are produced by complexation with inorganic Cl^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}. In natural water system dissolved lead (Pb) occurs in +2 oxidation state. Chemical speciation of lead from the study area showed that 62-92% of lead exist as free aquo ions (Pb^{2+}), 4-25% is complexed as hydroxide $(PbOH)^+$, 2-12 % occurs as carbonate, 0.9-2% occurs as chlorides (PbCl) $^{+}$ and less than 1% occurs as phosphate ($PbHPO_3$).

Zinc which is comparable to Ni has only one significant oxidation state, Zn^{2+}.The result of modelling indicates that Zn^{2+} is also one of the most soluble chemical species of Zn in surface water representing about 62-99% of the total Zn. The Complexed Zn species indicates that about 2-10 % occurs as soluble hydroxide (ZnOH), 1-3% occurs as $Zn(OH)_2$, less than 1% occurs as sulphates ($ZnSO_4$) and phosphates ($ZnPO_4$).

The adverse effects of highly soluble free Fe^{2+} (95-97) %, Pb^{2+}, and Zn^{2+} is significant to surface water chemistry, for the reason that their intrinsic or inherent toxicity is associated to their bioavailability and in surface water, the toxicity of metal ions or species is the hydrated metal ion [10].

4.0 CONCLUSION

For so long, PHREEQC have revealed great efficiency in calculating saturation indices, the distribution of aqueous species, the density and detailed conductance of a specified solution composition [13]. PHREEQC posses the capability of simulating large number of low-temperature geochemical reactions in oil, surface water and ground water systems, as well as interactions with minerals, gases, solid solutions, exchangers, and sorption surfaces, based on mixed equilibrium-kinetic reactions [16].This model consequently can be used to replicate reactive transport during steady-state flow, together with a broad variety of geochemical reactions. However, the model cannot deal with solute transport during transient water flow circumstances. PHREEQC is a universal geochemical program and is applicable to numerous hydrogeochemical environments, but it lacks internal consistency in the data in the databases.

The result shows that the speciated metal ions Na+, Ca^{2+}, Mg^{2+}, K^{+} , Fe^{2+}, Pb^{2+}, and Zn^{2+} at such high level would be available for uptake by plants, animals and humans. It is also highly possible that such conditions may constitute a negative health impact. Greater percentage of Pb, Zn and Fe exist in the hydrated ion variety and smaller amount as carbonates and sulphates. Based on the findings, Fe, Zn and Pb levels represent a health risks in the study area.

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