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Physicochemical, Spectroscopic and Bacteriological Analyses of Surface and Ground Water in Epenti-Ekori, Yakurr Local Government Area, Cross River State- Nigeria

Bassey S. Okori[1]*, Akanimo N. Ekanem[2]

[1] Department of Chemical Sciences, Clifford University, Owerrinta, Abia State, Nigeria
[2]Department of Chemistry, Akwa Ibom State University, Mkpat Enin, Akwa Ibom State, Nigeria

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Abstract

A total of seven water samples, four ground and three surfaces were collected from Epenti-Ekori in Yakurr local government area for analysis. Metals (Fe, K, Mn, Pb, Cr, Cu, Zn, Ni, and Co) and nutrients (sulfate, chloride, nitrate, fluoride, and phosphate) were determined using the UV-VIS spectrophotometric method of analysis while bacteriological parameters were determined using the membrane filtration technique. The mean of the results of the physicochemical parameters of the waters was the temperature (28.33 °C), pH (6.05), TDS (248.98 mg/L), total hardness (119.70 mg/L), electrical conductivity (474.97 mg/L), and turbidity (5.57 NTU). The mean of the nutrient parameters were chloride (22.91 mg/L), fluoride (0.03 mg/L), nitrate (5.50 mg/L), sulphate (2.00 mg/L) and phosphate (0.54 mg/L). The mean of the metals were manganese (0.18 mg/L), iron (0.52 mg/L), zinc (0.12 mg/L), copper (0.09 mg/L), lead (0.03 mg/L), chromium (0.04 mg/L), potassium (2.31 mg/L), nickel (0.09 mg/L) and cobalt (0.07 mg/L). The overall mean concentrations of Fe (0.52 mg/L), Pb (0.03 mg/L), and K (2.31 mg/L) were particularly high as compared to World Health Organization and Nigeria Standard for Drinking Water Quality. In addition, the TCC values were too high indicating a poorly sanitized environment. Pearson's correlations matrix showed positive correlations between most of the parameters. One-way ANOVA revealed that the water samples were significant of similar quality.

Keywords: Water, Heavy metals, Nutrients, Physicochemical, Bacteriological

1 Introduction

The origin of water preceded the evolution of life. The reactions that makeup life such as the synthesis of proteins and nucleotides occurred in the aqueous medium. It is for this reason that water forms a part of biological structures. An adult person consumes about two and a half liters of water a day and loses an equal amount. The high dielectric constant of water makes it an excellent solvent, it is often referred to as the universal solvent and for that reason, water is never pure but a solution of substances that come into contact with it [1]. When the number and or concentration of the chemicals entering a water source become so large that the natural qualities of water are altered, we say that the water has become either polluted or contaminated [2]. Water pollutants are classified into four broad categories; chemical, physical, physicochemical, and biological. Chemical contaminants are sub-divided into organic and inorganic pollutants. The importance of water has been a subject of serious academic attention reflected in the measurement of human development as water is the basic resource essential to man and plants. Without water, life on earth would have been impossible and the increasing demand for potable water has necessitated the inevitable use of groundwater along with other sources like surface water [3]. Good water quality is that which is convenient safe to use and potable for drinking, cooking, washing, bathing, and other domestic purposes [2]. Water should therefore be clean, tasteless, colorless, odorless, not salty, and free from poisonous corroding and staining substances as well as diseases carrying organisms.

The Federal Ministry of Water Resources through its state and local government institutions is entrusted with the responsibility of ensuring the provision of water for all citizens, especially among the rural dwellers. Through institutions like Rural Water Supply and Sanitation Agency (RUWATSSA), Cross River State Water Board Agency (CRSWBA), and the rest, various water facilities have been constructed in most rural areas of the country. Moreover, since most of the inhabitants in most rural communities do not have access to modern facilities, some communities that are located along streams and rivers discharge their waste directly into such water bodies. Others construct open toilets on the drainage channel. Such practices promote fecal contamination of water bodies [4]. The introduction of agricultural inputs to local dwellers has made water contamination an issue of serious concern. These inputs such as fertilizer which contains nitrates and Sulphates have greatly affected water quality especially as all life forms depend on water. These fertilizers are finally washed or leached into surface or groundwater, therefore making these water bodies

* **Corresponding author:** Bassey S. Okori, Department of Chemical sciences, Clifford University, Owerrinta, Abia State, Nigeria. e-mail: sambassey28@gmail.com

contaminated [5]. Recent activities show that man's insatiability has led him into different forms of conflicts and wars where different weapons and ammunitions are used for the conflict. Also, cultural displays which use ammunition and gun powders to show the significance of tradition have left soil and water contaminated. The chemicals in these ammunitions such as sulfur, nitrates and lead all end up not broken down, from where they get into plants, animals, and water bodies [6]. Water, our most precious natural resource is being threatened by a multitude of contaminants, resulting in an unprecedented crisis with local and national implications. Many communities have been told that their water is unsafe to drink, and there is a serious need to clean up their water supplies. Water contamination occurs when contaminants are discharged either directly or indirectly into water bodies without adequate treatment to remove harmful compounds [7]. Water contamination affects plants and organisms, water contamination is a major global problem that requires ongoing evaluation and revision of water resource policy at all levels [8]. Groundwater and surface water interact complexly, consequently leading to contamination. A spill or ongoing releases of chemicals or radionuclide contaminants into soils may contaminate borehole water [7]. The various forms of contaminants which may contaminate drinking water include micro-organisms, disinfectants, disinfectant by-products, inorganic chemicals, organic chemicals, and radionuclide. The micro-organisms may include; *Legionella*, *Salmonella*, *Parasitic worms*, *Burkholderia pseudomallei*, *Giardia lamblia*, *E.coli*, *Total coliform*, etc. The disinfectants may include; Chloramines, Chlorine, Chlorine dioxide, etc. The disinfectant by-product may include; Bromate, Chlorite, Halo acetic acid, Trihalomethanes. The inorganic chemicals may include; Arsenic, Asbestos, Barium, Beryllium, Cadmium, Copper, Antimony, Fluoride, Lead, Mercury, Nitrate, Nitrite, Selenium, Thallium, etc. The organic chemicals may include Acrylamine, Atrazine, Benzene, Benzo[a]pyrene, Carbofuran, Carbon tetrachloride, Chlorobenzenes, P-dichlorobenzene, 1,2-dibromo-3-chloroprocaine, etc. The Radionuclide may include Alpha particles, Beta particles, Photon emitters, Radium 226, Radium 228, Uranium etc [7], [9], [10].

This study aims to evaluate the surface and groundwater quality of the area under study. To determine the extent to which agricultural practices have affected the surface and groundwater quality in the area to know if it conforms to national and international drinking water quality standards.

2 Materials and Methods

2.1 Materials

The materials used in this include sterile 1-liter plastic water bottles, Spectro 22RS, CE1011, 1000 series spectrophotometer, HANNA digital thermometer, HANNA digital pH meter, Buffer solutions, Autoclave (BICASA ISO9061), incubator, beakers, conical flask, syringes, measuring cylinder, Petri-dishes, Cellotape, METTLER TOLEDO conductivity meter, HACH 2100N Turbidity meter, STUART scientific colony counter, UNISCOPE SM9082 oven, Reagent powder pillows(for each test), HACH TDS meter model 50150**,** Hardness test kit model HA-4P-MG-L.

2.2 Methods

2.2.1 Sample Locations and Study Area

Table 1 and Figure 1 show the sample locations and study area.

Table 1: Location of Sampling Points

S/N	Latitude	Longitude	Name of location
1	5.9292832	8.1028831	SW3: Epenti Beach
2	5.8871276	8.1224993	GW1: Lepakem (HP)
3	5.8867541	8.1229874	GW4: Akugum (W)
4	5.8871036	8.1216129	GW2: Beneni (HP)
5	5.8903773	8.1219521	GW3: Beneni Ext (HP)
6	5.8911532	8.1212638	SW1: Kesephagh
7	5.8911532	8.1205664	SW2: Ejom

HP = Hand pump, W = Well

2.2.2 Sample Collection and Preservation

The surface and groundwater samples were collected using sterile plastic containers. One liter of sample each from the various sample sources was collected while some physical parameters were determined in situ. The collected samples were properly labeled and stored in an ice-packed container (cooler) to ensure that the sample temperature does not exceed 4^oC during transportation to the laboratory.

2.2.3 Sample Analysis

The samples were analyzed appropriately in the Cross River State Water Board Laboratory immediately after collection following appropriate standard methods. Temperature (using HANNA digital thermometer), turbidity (displayed in NTU), color (using Spectro 22RS, CE1011, 1000 series spectrophotometer), total dissolved solids (TDS) (using TDS meter, model 50150 from HACH company), conductivity (using METTLER TOLEDO conductivity meter), pH (using pH meter from HANNA company), total hardness (using hardness test kit model HA-4P-MG-L), total iron (using ferrover powder pillow method), Zinc (using zircon method), chromium (using 1,5-diphenylcarbohydrazine method), copper (using Bicinchoninate method), manganese (using periodate oxidation method), nitrate (using Nitriver 5 (powder pillow) method), sulfate (using sulfaver 4 method), phosphate (using phosver 3 method), fluoride (using SPADNS method), lead, potassium, cobalt, arsenic, nickel, chloride concentrations were determined using their different methods. The membrane filtration technique was used for the determination of Coliform.

3 Results and Discussion

3.1 Results

The results of the physicochemical analyses of both groundwater and surface water in the study are presented in figures and tables. These results are in Table 2, Figures 2 – 6. The graphs show the results of samples in Epenti-Ekori, Yakurr Local Government Area, Cross River State. The physical parameters (pH, turbidity, conductivity, biochemical oxygen demand (BOD), total dissolved solids (TDS), temperature, and total hardness) are presented in Figure 2. The chemical parameters (Mn, Fe, Zn, Cu, Pb, Cr, K, Ni, and Co) are presented in Figures 3 and 4. The concentrations of nutrients (chloride, fluoride, nitrate, sulfate, phosphate) are presented in Figure 5 while Figures 6 show the result of the bacteriological analysis (total coliform count and mean fecal coliform count). Table 3 is the Pearson Correlation table. Table 4 is the table for water quality standards by Nigeria Standard for Drinking Water Quality (NSDWQ) and World Health Organization (WHO).

3.2 Discussion

3.2.1 Physicochemical Parameters

The physicochemical parameters are presented in Table 2.

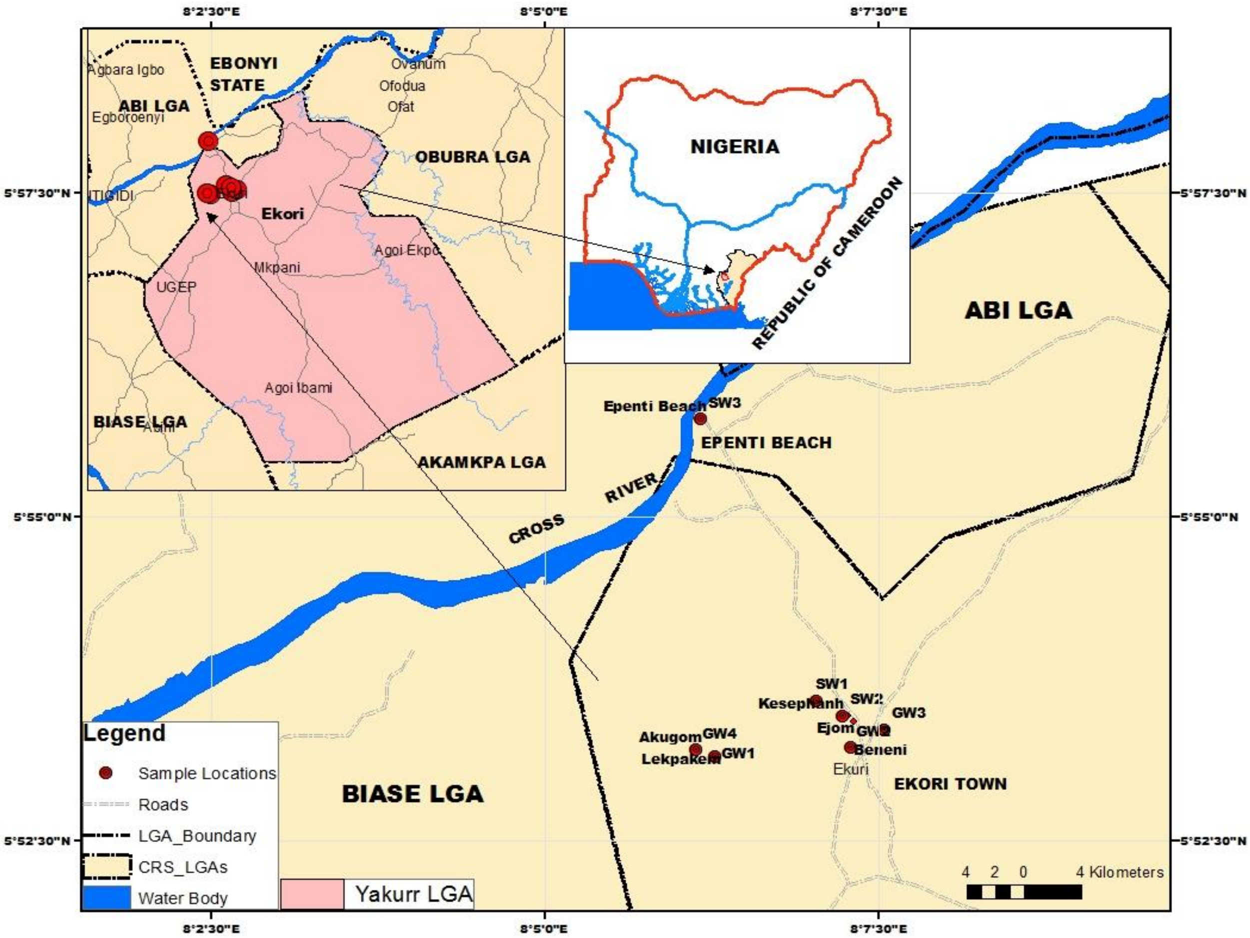

Figure 1: Map of the Study Area

Table 2: Mean Physicochemical and Bacteriological Parameter Concentrations for Water Samples in Epenti-Ekori, Yakurr L.G.A

Parameter/unit	GW1	GW2	GW3	GW4	SW1	SW2	SW3	Mean
Taste	Unobj	Unobj	Unobj	Unobj	Unobj	Obj	Obj	
Appearance	Clear	Clear	Clear	Clear	Unclear	Unclear	Unclear	
Colour	<5	10	<5	<5	<5	<5	15	
pH	6.25	5.89	6.63	6.15	5.10	6.05	6.25	6.05
Turbidity, NTU	0.323	0.873	0.573	2.24	2.79	13.70	18.50	5.57
Conductivity(μs/cm)	1057.0	740.00	497.00	884.00	43.00	58.80	45.00	474.97
BOD (mg/L)	4.80	5.66	4.72	6.19	6.29	7.05	6.12	5.83
TDS (mg/L)	634.20	444.00	298.20	530.40	25.80	35.28	27.00	284.98
Temperature °C	28.10	28.50	28.50	27.90	28.60	28.30	28.40	28.33
Tot.hardness (mg/L)	222.30	153.90	256.50	153.90	17.10	17.10	17.10	119.70
Chloride (mg/L)	16.00	18.00	21.10	20.00	29.20	31.00	25.10	22.91
Fluoride (mg/L)	0.02	0.02	0.03	0.01	0.03	0.06	0.06	0.03
Nitrate (mg/L)	5.22	5.18	4.23	5.49	6.01	4.33	8.01	5.50
Sulphate (mg/L)	1.27	1.31	1.10	1.21	3.46	2.96	2.68	2.00
Phosphate (mg/L)	0.31	0.38	0.40	0.33	0.81	0.77	0.80	0.54
Manganese (mg/L)	0.10	0.06	0.10	0.08	0.25	0.36	0.30	0.18
Iron (mg/L)	0.36	0.29	0.54	0.29	0.67	0.81	0.65	0.52
Zinc (mg/L)	0.08	0.12	0.10	0.05	0.16	0.13	0.19	0.12
Copper (mg/L)	0.088	0.091	0.085	0.081	0.11	0.10	0.09	0.09
Lead (mg/L)	0.01	0.00	0.01	0.01	0.05	0.08	0.03	0.03
Chromium (mg/L)	0.02	0.05	0.03	0.05	0.013	0.09	0.011	0.04
Arsenic (mg/L)	ND	ND	ND	ND	ND	ND	ND	
Potassium (mg/L)	1.70	1.90	1.60	1.90	3.10	2.90	3.10	2.31
Nickel (mg/L)	0.12	0.10	0.13	0.10	0.06	0.08	0.04	0.09
Cobalt (mg/L)	0.05	0.30	ND	0.06	0.022	0.018	0.016	0.07
TCC (CFU/L)	108.00	113.00	72.00	TNTC	TNTC	TNTC	TNTC	
FCC (CFU/L)	51	65	48	TNTC	TNTC	TNTC	TNTC	

TNTC: Too Numerous to Count, ND: Not detected, Obj: Objectionable, Unobj: Unobjectionable, GW1: Lepakem (HP), GW2: Beneni (HP), GW3: Beneni Ext (HP), GW4: Akugum (W), SW1: Kesephagh, SW2: Ejom, SW3: Epenti Beach

Table 3: Pearson Correlation Matrix of Physicochemical Parameters and Metals in Surface and Ground Water from Epenti-Ekori

	Col	pH	Turb	Cond	BOD	TDS	Temp	T.H	Cl^-	F^-	NO_3^-	SO_4^{2-}	PO_3^-	Mn^{2+}	Fe^{2+}	Zn^{2+}	Cu^{2+}	Pb^{2+}	Cr^{6+}	K^+	Ni^{2+}
pH	0.113																				
Turb	0.607	0.081																			
Cond	-0.291	0.367	-0.706																		
BOD	0.101	-0.487	0.617	-0.621																	
TDS	-0.291	0.367	-0.706	1.000	-.0621																
Temp	0.327	0.871	0.201	0.335	-0.267	0.335															
T.H	-0.353	0.598	-0.742	0.815	-0.876	0.815	0.418														
Cl^-	-0.017	-0.461	0.620	-0.921	0.784	-0.921	-0.436	-0.840													
F^-	0.444	0.065	0.912	-0.820	0.502	-0.820	0.154	-0.675	0.723												
NO_3^-	0.784	-0.200	0.548	-0.331	0.200	-0.331	-0.176	-0.515	0.119	0.308											
SO_4^{2-}	-0.232	0.125	-0.259	0.518	-0.482	0.518	0.024	0.356	-0.456	-0.225	-0.058										
PO_3^-	0.315	-0.485	0.749	-0.961	0.691	-0.961	-0.425	-0.916	0.915	0.811	0.452	-0.345									
Mn^{2+}	-0.076	-0.798	0.284	-0.762	0.533	-0.762	-0.845	-0.754	0.806	0.392	0.287	-0.175	0.832								
Fe^{2+}	0.044	-0.210	0.680	-0.914	0.538	-0.914	-0.251	-0.692	0.917	0.866	0.101	-0.255	0.889	0.703							
Zn^{2+}	0.645	-0.575	0.676	-0.845	0.373	-0.845	-0.247	-0.738	0.621	0.752	0.612	-0.288	0.863	0.640	0.683						
Cu^{2+}	-0..242	-0.289	0.471	-0.593	0.705	-0.593	-0.124	-0.610	0.786	0.634	-0.304	-0.136	0.618	0.487	0.754	0.306					
Pb^{2+}	-0.158	-0.390	0.601	-0.774	0.767	-0.774	-0.336	-0.774	0.933	0.722	-0.035	-0.181	0.819	0.711	0.893	0.474	0.927				
Cr^{6+}	-0.310	0.117	0.146	-0.025	0.521	-0.025	0.364	-0.123	0.265	0.173	-0.607	-0.288	-0.025	-0.203	0.144	-0.292	0.669	0.416			
K^+	0.358	-0.565	0.755	-0.887	0.769	-0.887	-0.465	-0.974	0.867	0.736	0.556	-0.306	0.974	0.824	0.785	0.823	0.572	0.783	-0.031		
Ni^{2+}	-0.593	0.514	0.760	0.764	-0.703	0.764	0.380	0.933	-0.675	-0.630	0.780	0.336	-0.868	-0.679	-0.566	-0.820	-0.308	-0.542	0.177	-0.940	
Co^{2+}	0.269	-0.159	-0.340	0.401	-0.086	0.401	0.237	0.181	-0.467	-0.403	-0.098	-0.110	-0.397	-0.387	-0.602	-0.112	-0.221	-0.472	0.198	-0.324	0.171

Table 4: Nigeria Standard for Drinking Water Quality (NSDWQ) and World Health Organization (WHO) Drinking Water Quality Standard for the Parameters

Parameter/unit	NSDWQ, 2017	WHO, 2017
pH	6.5-8.5	6.5-8.5
Turbidity(NTU)	5.0	
Conductivity(µS/cm)	1000	
TDS (mg/L)	500	
Temperature °C	Ambient	Ambient
Tot. hardness (mg/L)	150	100
Chloride (mg/L)	100	250
Fluoride (mg/L)	1.0	1.5
Nitrate (mg/L)	10	50
Sulphate (mg/L)	100	200
Manganese (mg/L)	0.1	0.05
Iron (mg/L)	0.3	0.05-0.3
Zinc (mg/L)	5.0	3.0
Copper (mg/L)	1.0	2.0
Lead (mg/L)	0.01	0.01
Chromium (mg/L)	0.01	0.05
Arsenic (mg/L)	0.01	0.01
Potassium (mg/L)	1.0	1-2
Nickel (mg/L)	0.01	0.07
TCC (CFU/L)	0	0
FCC(CFU/L)	0	0

Sources: (a) NSDWQ(2007): Nigerian Standard for Drinking Water Quality. Nigerian Industrial Standard. NIS:554:13-14, and (b) WHO(2017) Guideline for Drinking Water Quality: the fourth edition incorporating the first addendum.

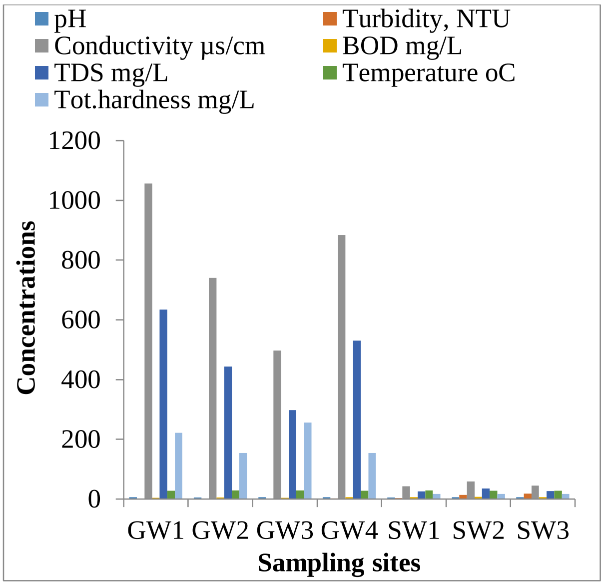

Figure 2: Mean concentrations of physical parameters in water samples from Epenti-Ekori, Yakurr L.G.A

3.2.1.1 Temperature

The ambient temperatures range from 27.90 °C to 28.60 °C with mean value of 28.33 °C (Table 2 and Figure 2). Water for drinking purposes has a better fresh taste at lower temperature of about 15°C, but higher temperatures do not imply impurities [10]. Pearson correlation matrix (Table 3) indicates that low positive correlation existed between temperature and total hardness (r =0.418), fluoride (r =0.154), sulphate (r =0.024), chromium (r=0.364), nickel (r =0.380), cobalt (r =0.237), turbidity (r =0.201), conductivity (r =0.335), TDS (r =0.335). Significant positive correlation existed between temperature and pH (r =0.871).

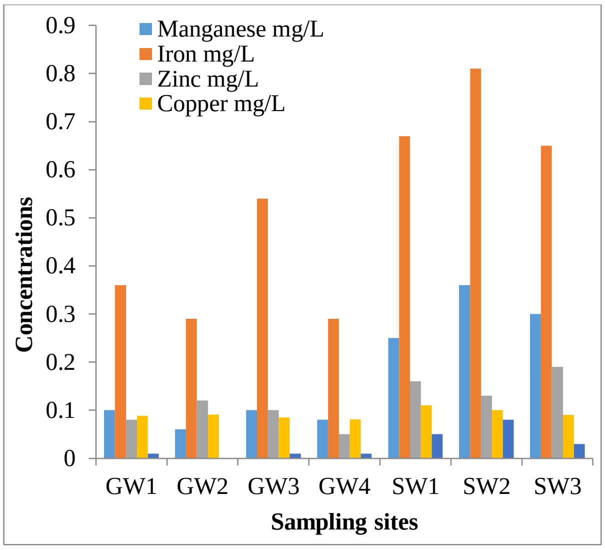

Figure 3: Mean concentrations of some chemical parameters in water samples from Epenti-Ekori, Yakurr L.G.A

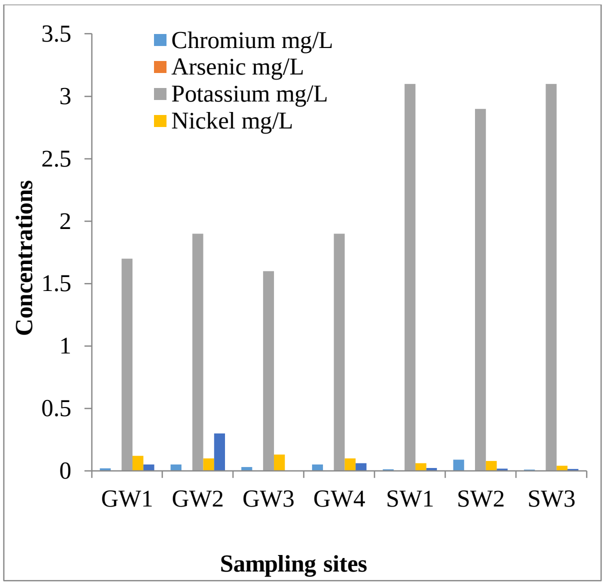

Figure 4: Mean concentrations of some chemical parameters in water samples from Epenti-Ekori, Yakurr L.G.A

3.2.1.2 pH

pH is a measure of acidity or alkalinity of an environment or substance. the pH of water varies naturally within water bodies as a result of the geology and nature of the soil. The pH values for the water sample range from 5.10 to 6.63 with a mean value of 6.05 (Table 2 and Figure 2). These values are lower than the WHO and NSDWQ permissible limits of 6.5 to 8.5 (Table 4). The low pH may be due to soil formation and composition or the formation of tannic acids by decaying plants. High acidity may lead to acidosis and promote disease conditions. Pearson correlation matrix (table 3) indicates that low positive correlations exist between pH and turbidity (r =0.081), conductivity (r =0.0367), TDS (r= 0.367), fluoride (r =0.065), sulphate (r =0.125), chromium (r =0.117), colour (r =0.113). Significant correlation was found between pH and temperature (r =0.8710, total hardness (r =0.598), nickel (r =0.514).

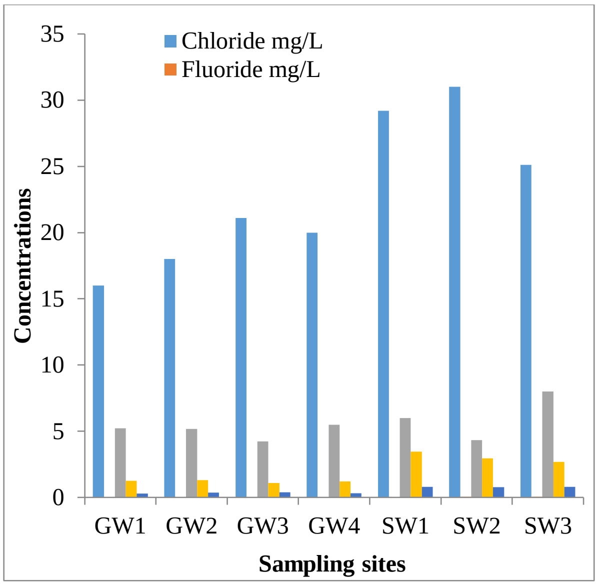

Figure 5: Mean concentrations of nutrients in water samples from Epenti-Ekori, Yakurr L.G.A

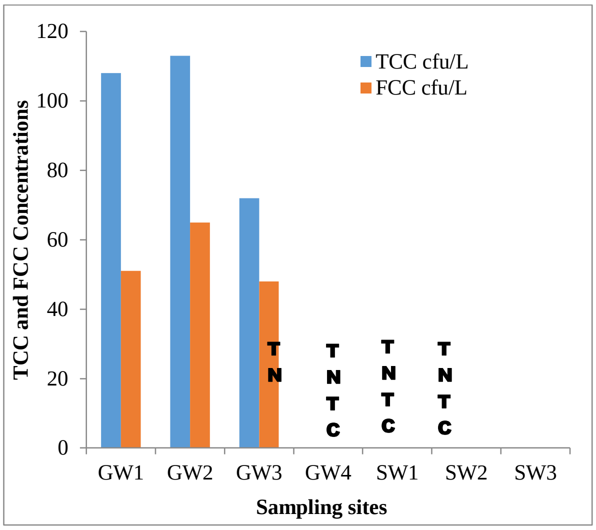

Figure 6: Mean concentrations of TCC and FCC values in water samples from Epenti-Ekori, Yakurr L.G.A. TNTC - Too Numerous to Count

3.2.1.3 Total Dissolved Solids

The total dissolved solids (TDS) recommended by the WHO and NSDWQ for freshwater is between (0 – 1000) mg/L. The water samples have TDS values ranging from 25.80 mg/L to 634.20 mg/L with a mean of 284.98 mg/L (Table 2 and Figure 2). These values are below the WHO allowable limit of 1000 mg/L (Table 4). Pearson correlation matrix (Table 3) indicates that TDS had low positive correlations with temperature (r =0.335), cobalt (r =0.401), pH (r =0.367). Strong positive was observed between TDS and conductivity (r =1.000), total hardness (r =0.815), sulphate (r =0.518), nickel (r =0.764). Positive correlations with metals indicate lithogenic inputs.

3.2.1.4 Total Hardness

The value of total hardness range from 17.10 mg/L to 256.50 mg/L with a mean value of 119.70 mg/L (Table 2 and Figure 2). All the underground water had hardness values above the WHO and NSDWQ permissible limits of 100 mg/L and 150 mg/L (Table 4) respectively. This implies that these areas have hard water. Hardness is beneficial in drinking water despite the problem it creates for the piping system and laundry activities. People who live in the hard water area suffer less from heart diseases than those who live in soft water areas [11]. Pearson correlation matrix (Table 3) indicates that significant positive correlations occurred between total hardness and nickel (r =0.933), pH (r =0.598), conductivity (r =0.815), TDS (r =0.815) while low positive correlations occurred between total hardness and sulphate (r =0.356), cobalt (r =0.181), temperature (r =0.418).

3.2.1.5 Conductivity

Conductivity in water is due to dissolved solutes. The conductivity values range from 43.0 µS/cm to 1057 µS/cm with a mean value of 474.97 µS/cm (Table 2 and Figure 2). These values except for GW1 (Table 4) are below the permissible limit of 1000 µS/cm of NSDWQ but the closeness of the values to the limits calls for concern. The Pearson correlations (Table 3) show that strong positive correlation existed between conductivity and TDS (r =1.000), total hardness (r = 0.815), sulphate (r =0.518), nickel (r =0.764).

3.2.1.6 Turbidity

Turbidity is the degree of cloudiness in water caused by both dissolved and suspended solids. The turbidity values range from 0.323 NTU to 18.50 NTU with mean value of 5.57 NTU (Table 2 and Figure 2). Pearson correlation matrix (Table 3) indicate that low positive correlations occurred between turbidity and temperature (r =0.201), manganese (r =0.284), copper (r =0.471), chromium (r =0.146), pH (r =0.081) while significant positive correlation existed with BOD (r =0.617), chloride (r =0.620), fluoride (r =0.912), nitrate (r =0.548), phosphate (r =0.749), iron (r =0.680), zinc (r =0.676), lead (r =0.601), potassium (r =0.755), colour (r =0.607).

3.2.2 Chemical Parameters

The chemical parameters are presented in Table 2.

3.2.2.1 Potassium (K)

The potassium concentrations were relatively stable. Potassium concentrations range from 1.60 mg/L to 3.10 mg/L with mean concentration of 2.31 mg/L (Table 2 and Figure 4). The highest value (3.10 mg/L) was recorded in SWI and SW3 sampling sites (Table 2). The low concentration of potassium can be attributed to the shallowness of the surface and underground water sources because the concentration of potassium increases with depth due to infiltration, it might also be attributed to the low rate of soil reaction, ion exchange, oxidation and reduction, The low concentration might also be caused by the paucity of soluble material in the bedrock of the formation and the overlying soil [12]. Pearson correlation matrix (Table 3) indicates that potassium had low positive correlation with colour (r =0.358) while positive correlation occurred with turbidity (r =0.755), BOD (r =0.769), chloride (r =0.867), fluoride (r =0.736), nitrate (r =0.556), phosphate (r =0.974), manganese (r =0.824), iron (r =0.785), zinc (r =0.823), copper (r =0.572), lead (r =0.783).

3.2.2.2 Iron (Fe)

The common form of iron in groundwater is the soluble ferrous ion Fe^{2+}. When exposed Fe^{2+} is oxidized to the ferric state Fe^{3+}, which is soluble and precipitates as ferric hydroxide, causing a brown discoloration of the water and the characteristic brown stains in sinks and laundered textiles, metal pipes for reticulation and scaling in pipes [12]. Iron is essential for biological systems. Iron concentrations ranged from 0.29 mg/L to 0.81 mg/L with mean concentration of 0.52 mg/L (Table 2 and Figure 3). However, the highest value recorded was 0.81 mg/L in the SW2 sampling site (Table 2). The iron availability within the area covered was generally high compared to the WHO and NSDWQ allowable limit of 0.3 mg/L (Table 4). Iron is widely distributed in the earth's crust occurring in several ferromagnesian minerals. Pyrite is a common form of iron in sedimentary materials, whereas ferric oxides and hydroxides are important iron-bearing minerals. Corrosion of borehole casing and other pipes may also contribute iron to borehole water. Bacterial activity can decrease or increase iron concentration in ground and surface water. Pearson correlation matrix (Table 3) indicates that significant positive correlation occurred between iron and zinc (r =0.683), copper (r =0.754), lead (r =0.893), potassium (r =0.785), turbidity (r =0.680), BOD (r =0.538) chloride (r =0.917), fluoride (r =0.866), phosphate (r =0.889), manganese (r =0.703) while low positive correlations was observed with chromium (r =0.144), colour (r =0.044), nitrate (r =0.101).

3.2.2.3 Manganese (Mn)

High concentration of manganese slightly above the WHO and NSDWQ maximum permissible limit causes neurological and gastrointestinal disorder [13]. The concentrations of manganese range from 0.06 mg/L to 0.36 mg/L with mean concentration of 0.18 mg/L for (Table 2 and Figure 3). Some of these values were above the permissible limit of 0.2 mg/L of WHO and NSDWQ (Table 4). The presence of iron, copper and manganese can give undesirable taste. Pearson correlation matrix (Table 3) indicates that low positive correlations occurred between manganese and copper (r = 0.487), turbidity (r = 0.284), fluoride (r = 0.392), nitrate (r = 0.287) while significant positive correlations occurred with iron (r = 0.703), zinc (r =0.640), lead (r = 0.711), potassium (r = 0.824), BOD (r = 0.533) chloride (r = 0.806), phosphate (r = 0.832).

3.2.2.4 Lead (Pb)

The primary sources of lead are household plumbing, lead paints used in homes, and lead ammunition used during communal conflicts. The concentrations of lead recorded were significantly higher. The concentrations of lead ranged from 0.00 mg/L to 0.08 mg/L with mean concentration of 0.03 mg/L (Table 2 and Figure 3). However higher levels of lead (0.08 mg/L) were recorded in SW2 water. This value was high compared to the WHO and NSDWQ permissible limit of 0.01 mg/L (Table 4). A high dose of lead causes damage to the central nervous system impairs intelligence and causes attention deficiency. Lead also causes cancer, interferes with vitamin D metabolism, and affects mental development in infants [13] and [18]. Pearson correlation matrix (Table 3) indicates that low correlations existed with chromium (r =0.416), zinc (r =0.474) while strong positive correlations occurred with potassium (r =0.783), turbidity (r =0.601), BOD (r = 0.767), chloride (r =0.933), fluoride (r =0.722), phosphate (r =0.819), manganese (r =0.771), iron (r =0.893), copper (r =0.927).

3.2.2.5 Chromium

Chromium is found naturally in rocks, plants, soil, and volcanic dust, it gets into ground and surface water due to improper disposal of mining tools and manufacturing equipment. The concentration of chromium ranged from 0.011 mg/L to 0.09 mg/L with mean concentration of 0.04 mg/L (Table 2 and Figure 4). These values were very close and some were above WHO and NSDWQ standard of 0.05 mg/L (Table 4). The highest value (0.05 mg/L) was recorded in GW2 and GW4 groundwater. Chromium causes cancer (WHO, 2017). Pearson correlation matrix for the wet season (Table 3) indicate that low positive correlations occurred between chromium and nickel (r =0.117), cobalt (r =0.198), pH (r =0.117), turbidity (r =0.146), temperature (r =0.364), chloride (r =0.265), fluoride (r =0.173), iron (r =0.144), lead (r =0.416) while significant positive correlations occurred with BOD (r =0.521), copper (r =0.669).

3.2.2.6 Copper (Cu)

Mining operations, geological deposits, weathering and erosion of rocks are the major sources of copper in water. The concentrations of copper for the wet season in the study area range from 0.081 mg/L to 0.11 mg/L with mean concentration of 0.09 mg/L (Table 2 and Figure 3). Chronic exposure to copper leads to alteration of brain functions and gastrointestinal disorders [15]and [13]. Pearson correlation matrix (Table 3) indicate that copper had low positive correlations with turbidity (r =0.471), zinc (r =0.306), manganese (r =0.487). Significant positive correlations occurred with lead (r =0.927), chromium (r =0.669), potassium (r =0.572), BOD (r =0.705), chloride (r =0.786), fluoride (r =0.634), phosphate (r =0.618), iron (r =0.754).

3.2.2.7 Zinc (Zn)

High natural levels of zinc are associated with high concentrations of metals such as lead and cadmium. Anthropogenic sources are related to mining and metallurgic operations. The concentration of zinc ranges from 0.05 mg/L to 0.19 mg/L with mean concentration of 0.12 mg/L (Table 2 and Figure 3). These values are below the acceptable limit of NSDWQ set at 3.00 mg/L (Table 4). Zinc is an essential nutrient for bone development, metabolism and wound healing. High zinc level in blood may cause a mental illness called metal fume fever [16]. Pearson correlation matrix (Table 3) indicate that low positive correlations occurred between zinc and copper (r =0.306), lead (r =0.474), BOD (r =0.373) while significant correlation occurred with potassium (r =0.823), colour (r =0.645), turbidity (r =0.676), chloride (r =0.621), fluoride 9r =0.752), nitrate (r =0.612), phosphate (r =0.474), manganese (r =0.640), iron (r =0.683).

3.2.2.8 Nickel (Ni)

Nickel is added to water by leaching from metals in contact with water, usually found with iron, improper disposal of nickel-plated material. It is also found in laterite. The concentrations range from 0.04 mg/L to 0.13 mg/L with mean concentration of 0.09 mg/L (Table 2 and Figure 4). The highest value (0.13 mg/l) of nickel was recorded in GW3 groundwater. These values are significantly higher than the WHO and NSDWQ allowable limit of 0.02mg/L (Table 4). Nickel is possibly carcinogenic [13]. Pearson correlation matrix (Table 3) indicate that low positive correlations occurred between nickel and cobalt (r =0.171), temperature (r =0.380), sulphate (r =0.336), chromium (r =0.177) while significant correlations occurred with pH (r =0.514), conductivity (r =0.764), TDS (r =0.764), total hardness (r =0.933), nitrate (r =0.780).

3.2.2.9 Cobalt (Co)

Cobalt occurs in association with copper, nickel, manganese, and arsenic, its natural sources include soil, dust and forest fires, rock, plants, etc. Its natural occurrence is due to geology rather than anthropogenic. The concentrations of cobalt varied with season. The concentrations range from 0.016 mg/L to 0.05 mg/L with mean concentration of 0.07 mg/L (Table 2 and Figure 4). The highest value (0.30 mg/L) was recorded was in GW2 groundwater. Cobalt in form of vitamin B_{12} is essential to biological life [4]. Pearson correlation matrix

(Table 3) indicate that cobalt had low positive correlations with colour (r =0.267), conductivity (r =0.401), TDS (r =0.401), temperature (r =0.233), total hardness (r =0.181), lead (r =0.198), nickel (r =0.171).

3.2.2.10 Sulphate (SO_4^{2-})

Sulfates may be leached from the soil into water bodies. The sulfate concentrations range from 1.10 mg/L to 3.46 mg/L with a mean concentration of 2.00 mg/L (Table 2 and Figure 5). These values are below WHO's maximum permissible limit of 200 mg/L. Pearson correlation matrix (Table 3) indicate that low positive correlation occurred between sulphate and nickel (r =0.336), pH (r =0.125), temperature (r =0.024), total hardness (r =0.356) while significant correlations occurred with conductivity r =0.518), TDS (r =0.518).

3.2.2.11 Chloride (Cl^-)

Chloride enters water from rock weathering, salt-bearing geological formation, intrusion of salty ocean water into fresh ground water sources. The chloride concentrations range from 16.00 mg/L to 31.00 mg/L with mean concentration of 22.91 mg/L (Table 2 and Figure 5). These values are below the maximum permissible limit of 250 mg/L by NSDWQ and WHO (Table 4). Pearson correlation matrix (Table 4) indicate that low positive correlations occurred between chloride and nitrate (r =0.119), chromium (r =0.265) while significant correlations occurred with fluoride (r =0.723), phosphate (r =0.915), manganese (r =0.806), iron (r =0.917), zinc (r =0.621), copper (r =0.786), lead (r =0.933), potassium (r =0.867), turbidity (r =0.620), BOD (r =0.784).

3.2.2.12 Nitrate (NO_3^{2-})

Nitrates in water are from fertilizers, agricultural run-off and gunpowder . The concentrations of nitrate range from 4.23 mg/L to 8.01 mg/L with mean concentration of 5.50 mg/L (Table 2 and Figure 5). The values were below the NSDWQ recommended value of 50 mg/L. High nitrate doses cause cyanosis and asphyxia (blue baby syndrome) in infants [13]. Pearson correlation matrix (Table 3) indicate that low positive correlations occurred between nitrate and phosphate (r =0.452), manganese (r =0.287), iron (r =0.101), BOD (r =0.200), chloride (r =0.119), fluoride (r =0. 308) while significant correlations occurred with zinc (r =0.612), potassium (r =0.556), nickel (r =0.780), colour (r =0.784), turbidity (r =0.548).

3.2.2.13 Fluoride (F^-)

Fluoride is found in hard rocks as mineral and the hydrogeological conditions contribute more to the mobilization of fluoride in ground water. It main sources are geogenic in nature. The fluoride concentrations range from 0.01 mg/L to 0.06 mg/L with mean concentration of 0.03 mg/L (Table 2 and Figure 5). These values are below permissible limits of 1.50 mg/L by WHO and NSDWQ (Table 4). High fluoride dose cause fluorosis and skeletal tissue morbidity [13]. Pearson correlation matrix (Table 3) indicates that low positive correlations occurred between fluoride and nitrate (r =0.308), manganese (r =0.392), chromium (r =0.173), colour (r =0.444), pH (r =0.065), temperature (r =0.154) while significant correlation occurred with phosphate (r =0.811), iron (r =0.866), zinc (r =0.752), copper (r =0.6340, lead (r =0.722), potassium (r =0.736), turbidity (r =0.912), BOD (r =0.502), chloride (r =0.723).

3.2.2.14 Phosphate (PO_4^{2-})

Phosphate is an essential compound for plant growth, but too much of it can speed up eutrophication of water bodies. The phosphate concentrations in the water samples range from 0.31 mg/L to 0.81 mg/L with mean concentration of 0.54 mg/L (Table 2 and Figure 5). Soil erosion is the major contributor of phosphate to water bodies [18]. Pearson correlation matrix (Table 3) indicates that low positive correlations occurred between phosphate and colour (r =0.315), nitrate (r =0.452) while significant correlations occurred with manganese (r =0.8320, iron (r =0.889), zinc (r =0.863), copper (r =0.618), lead (r =0.819), potassium (r =0.974), turbidity (r =0.749), BOD (r =0.691), chloride (r =0.915), fluoride (r =0.811).

3.2.3 Bacteriological Parameters

The standard water test to determine the microbial quality of water is for total coliform bacteria. The total coliform count ranges from 72 cfu/L to 113 cfu/L while fecal coliform count ranges from 48 cfu/L to 65 cfu/L (Table 2, Figure 6). GW4, SW1, SW2, SW3 sampling sites had coliform concentrations that are too numerous to count. These values were above the maximum permissible limit of 0.00 cfu/L by WHO and NSDWQ (Table 4). This is an indication that fecal contamination by animals and human is at its highest level in the area covered. This also implies a very poor sanitary condition and practice in the area, shallowness of the borehole water sources [18]. The principal risk associated with water is that of infectious disease and is related to fecal contamination, majority of the water-borne diseases are caused by pathogenic bacteria, viruses, and protozoa contained in the human and animal feces [7].

4 Conclusion

Summarily, the study presented an evaluation of surface and underground water quality in Epenti-Ekori in Yakurr local government area of Cross River State using mostly UV-VIS spectrophotometric method of analysis. The study also provided a powerful tool for studying, analyzing, and comparing water quality data for decision-making processes and management of water resources. The concentrations of metals (Mn, Fe, Cu, Pb, Zn, Cr, K, Ni, and Co) and nutrients (chloride, fluoride, nitrate, sulfate, and phosphate) in the surface and groundwater indicated that there were significant variations amongst these parameters, as Pearson's correlation matrix has shown. The dissolution of heavy metals was greatly influenced by physicochemical parameters such as pH and temperature. Agricultural and other anthropogenic activities greatly affected the water quality of the area. The infectious diseases may be due to the poor sanitary condition of the area which was indicated by the high total coliform count (TCC) and fecal coliform count (FCC). Although some tested parameters were within acceptable limits, others were not hence the need to treat the waters before consumption.

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Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

Bassey S. Okori perform the experimental design, prepared the manuscript text, and compiled the data. Akanimo N. Ekanem performed the literature review and manuscript edition.

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