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Water Quality Assessment (Physicochemical Parameters). A Case Study of Certain Streams and Boreholes in Abi Local Government Area of Cross River State. Southern Nigeria.

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ABSTRACT

Sustainable access to safe drinking water remains a global concern as many people in the world today still consume water from untreated and unimproved sources. This study was carried out to evaluate the quality of eight (8) streams and two (2) boreholes (underground water) sources used by selected communities in Abi Local Government Area of central Cross River Region in Southern Nigeria to access the suitability for drinking, domestic, industrial and agricultural purposes. Water quality parameters analyzed include: conductivity, temperature, Colour, PH, Dissolve Oxygen (DO), Biological Oxygen Demand (BOD), K^+, Mg^{2+}, Na^+, Fe^{2+}, Cl^-, Nitrate, Ammonium ion, Sulphate, Hardness, Sodium Adsorption Ratio (SAR). The total hardness was used to evaluate the sodium adsorption ratio. The mean value of SAR is within the range of World Health Organization (WHO) acceptability. The mean values of the major cations and anions were all within WHO standard. Several methods employed for these analyses include: Spectrophotometric, turbidimetric, gravimetric and titrimetric techniques. Multi-functonal Probe (Searchtech E-201-E model) methods were also used for most of the physico-chemical parameters. Statistical analysis used for this study was measures of central tendency. This was used to determine the mean values of the various samples and to note the possible outliers. The study results show that water samples were acidic (ST3: PH=5.1) to slightly alkaline (ST8: pH=8.3). SAR in all the samples were less than 6, WHO guideline for SAR suitable for irrigation.

INTRODUCTION

The demand for water for human consumption, domestic, industrial and agricultural purposes has grown considerably over the years and the supply by water board is grossly inadequate. Some people have therefore sort of other alternatives of water supply. This sorting to construction of boreholes (underground water) and the excessive use of surface water . Since streams, and boreholes are for human consumption, there is need for this water to be assessed for quality and to know how extend a particular stream or borehole is good for human consumption, domestic, industrial and agricultural uses. Though, the borehole is significantly protected from surface pollutants as the earth media is composed of different surface layers as a natural filters. Supply of drinking water should be as pleasant as circumstances permit, coolness, absence of turbidity and colour and any other disagreeable taste or smell are of the utmost importance in public supply of drinking water. The construction situation, operation and its distribution system must be such as exclude any possible pollution of the water (WHO, 2011). Water provides energy in form of hydroelectricity and certain countries like Nigeria are nearly 97% dependent on hydro power for their electricity production. Even for thermal and nuclear power station. Substantial amount of cooling water is necessary to dissipate heat. Industry cannot function without water, and water is invariably the focal point for many types of reactions and recreations. (Lohair & Thanh, 1978) The study of environmental water pollution in particular has therefore been of considerable importance not only to water analytical chemist, but also to engineers, hydrologist, toxicologist and pathologist since most of these determinants pose danger threat to man's life including other living organisms. Thus, it is very essential to analyze any water pose to human consumption, either to increase the need parameters or reduce to the required dose to avoid endangering the consumers and render is aesthetically suitable. Unlike oil and most other strategic resources, fresh water has no substitute in most of its uses. It is essential for growing food crops, manufacturing goods and safeguarding human health. Therefore, the development of groundwater or surface water constitute a viable supplement to the earth concrete dam. Fresh water is suitable for human, industrial, domestic and agricultural uses.

MATERIALS AND METHODS

Descriptive research approach was employed in this study. The data for this research study were obtained from samples collected from eight (8) streams from different locations and two (2) boreholes also from different locations as shown in table 1 for the purpose of this study and for easy characterization. The sampling points are given designations as ST and BH, meaning streams and boreholes respectively presented in table 2. The monitoring was carried

out during rainy season. For all the samples, some physical parameters were determined at the field using standard field equipments like Thermometer, PH meter, Conductivity meter and multi-functional probe.

Samples collection

Streams and boreholes were collected in sterile bottles, properly corked to avoid incoming air into the bottles containing the samples and transported in ice pack to the laboratory within twelve hours from the time of collection. The sampling site were randomly chosen within Abi Communities in Central Cross River State of Nigeria. The Cross River State Water Board (CRSWB) laboratory was used for this Analysis.

Study area description

The study area is Abi Local Government Area 0f Cross River State, Southern Nigeria. Geographically, it is situated between latitude 50 30 and 600 North and longitude 80 35 and 850 East. It occupies a land mass of 662.871Km². The area is in the Eastern Niger Delta of Nigeria. Two seasons by fluctuation of precipitation predominate in the area are dry and wet seasons from April to October (wet season) and November to March (dry season). The area is characterized by humid tropical climate (high temperature, humidity and precipitation).

Population of the study area

The study area (Abi Local Government Area) is one of the oldest local government areas in Cross River State. The area though, due to her large land mass, it is not densely populated but witness a serious population explosion, industrial and agricultural growth. It has 352,416 people as at (2000) extrapolated from 2006 National population census. The population rate and the agricultural activities directly deteriorate the quality of groundwater resources.

Selection of sites for sampling

Abi Local Government Area is in the Central part of Cross River State. It comprises of many major communities among which are Itigidi, Ekureku, Imabana, Adadama and Bahumono. Due to the geographical location of many of the communities, many streams in some of these communities do not survive the dry season and as such, samples were not collected in these areas. Samples were only collected in the areas that have the representative or average characteristics of other sources. However, certain criteria were applied in selecting sample sites as follows:

i. Sampling sites were selected such that the samples taken are representative of the different sources from which water enters in the streams.

Ii. Sampling sites were considered in such a way to take account of the number of inhabitants served by each source.

III. Sampling sites were of more interest considering the agricultural activities in the locations

TABLE 1: Showing sample locations including source and designations in Abi Local Government Area Cross River State of Nigeria.

S/N	COMMUNITY	LOCATION	SOURCE	SAMPLE CODE
1	Ekureku	Akarefor	Stream	ST1
2	Ekureku	Ekurekube	Stream	ST2
3	Itigidi	Ikamine	Stream	ST3
4	Bahumono	Ediba	Stream	ST4
5	Itigidi	Eminebol	Stream	ST5
6	Bahumono	Isumutong	Stream	ST6
7	Ekureku	Anong	Stream	ST7
8	Ekureku	Akpoha	Borehole	BH1
9	Imabana	Ileke	Borehole	BH2

Sampling size

The maximum sampling size varies widely depending on the range of variation to be considered and the analytical methods to be employed. The volume required for the individual analysis are summarized in table 3 (WHO, 2017)

Sampling procedure:

sampling from boreholes:

Several procedures were followed to ensure a more precise results.

I. The tap outlet was thoroughly clean by wiping the outlet with clean cloth to remove any dirt attachment that could cause contamination of the water quality.

Ii. The tap was turn on to maximum and allowed to run for 1-2 minutes and then turn off.

III. It was sterilized for 1-2 minutes with a flame (from cigarette).

iv. The water was then turn on and allowed to run at medium rate for 1-2 minutes.

v. The bottles were immediately filled with the sample, taken care to prevent entry of dust and air.

Samples from streams:

i. The sample cups and bottles were sterilized.

ii. The water samples were filled into the bottles using the sample cups.

III. The samples after collection are packed in a cooler containing ice bags.

iv. The samples were then taken to the laboratory within the shortest time.

Data analysis

TABLE 2: Sample volumes required for individual analysis

ANALYSIS	SAMPLE VOLUME (ml)
BOD	1000
Calcium	50
Chloride	100
Iron	50
Nitrate	50
Sodium	100
Magnesium	50
Sulphate	200
DO	1000
Ammonia	400

Conductivity

Probe method was used. The electrode or probe was thoroughly rainsed with deionized water and then plugged into the water sample. The value was recorded in us/cm (micro Siemen per centimeter).

TEMPERATURE

The temperature was determined by dipping the mercury in glass thermometer into the sample and the reading taken as the mercury thread rise to a steady point.

pH

pH meter PHS-25, E-201-E (Searchtech) was used. The meter was set on and adjusted to zero and then dipped into the sample and the reading was recorded.

DISSOLVED OXYGEN

Dissolved oxygen meter was used. The equipment was placed in such a way that it was not exposed directly to heat radiation from the sun. The switch was turned to the normal percentage saturation position,and the display allowed to show a stable value. The display was the adjusted by turning the small screw on the upper right corner until the display showed the ro, the meter was then ready for measuring both saturation as well as part per million (PPM) mg/l. The probe was dipped into the water sample covering about 2/3 of its length. The switch was again turned to the ppm-mg/l position, the result was then recorded in mg/l at a stable value of the display.

BIOLOGICAL OXYGEN DEMAND (BOD)

The biological oxygen dissolved in sample was determined by dissolved oxygen meter. The probe was dipped into the sample to cover the probe to about 2/3 at length. The switch was turned to the ppm-mg/l position. The display was allowed to show a stable value and the result was taken and recorded in mg/l. The sample was incubated for 5 days at 20°C and the dissolved oxygen content remeasured.

Calculation

BOD = (a-b) mg/l. Where, a = Initial dissolved oxygen in the sample and b = Final dissolved oxygen in the sample.

Calcium (Ca^{+2}) mg/l

Calcium dissolves out of almost all rocks and is consequently detected in many water. Water associated with granite or siliceous sand will contain less than 10mg/l of calcium. Many waters from limestone areas may contain 30-100mg/l and those associated with gypsiferous shade may contain several hundred milligrams per liter. Calcium contributes to the total hardness of water. On heating, calcium salts precipitate to cause boiler scale. Some calcium carbonate is desirable for domestic water because it provides a coating in the pipes which protect them against corrosion.

EDTA titrimetric method was used for this Analysis. When EDTA was added to water containing calcium and magnesium ions, it reacts with the calcium before the magnesium. Calcium can be determined in the presence of magnesium by EDTA titration. The indicator used is one that reacts with calcium only. Murexide indicator gives a colour change when all of the calcium has been complexes by EDTA at a PH of 12-13 (Balance, 1990).

The following materials and reagents were used: porcelain dishes 100ml capacity, Burette 50ml, Pipette 25ml, Stirring rod, Graduated Cylinder, 100ml. Sodium Hydroxide (NaOH) 1mol, Murexide Indicator. The colour change from pink to purple at the end-point.

Potassium ion (K^+)

Method: Spectrophotometric techniques.

Reagents: Potassium (K-1) pillow, (K-2) pillow and (K-3) pillow.

Procedure: The K-1 and the K-2 reagents pillow were added to the water sample in 25ml graduated cylinder and swirled to mix. After sometime, when sediment may have occured, the K-3 reagents pillow was added the mixture was agitated for 30 seconds. White precipitate indicating the presence of potassium was observed. A sample bottle was filled to the 25ml mark with the original sample and placed in one bottle holder of the Spectrophotometer and the light shield close and the value of potassium was read in mg/l

Sodium (Na^+)

Method: Gravimetric/Photometric

Procedure: The analysis of sodium sometime can be used as an indication of purity of water for example, in stream condensation, the sodium concentration can be used to indicate water carrying over for boiler system into the stream. Sodium determination will indicate the completeness of cation exchange. The sodium concentration of a typical water sample can be estimated by subtracting the sum of cations ($Mg2+$, $K+$, $Ca2+$) earlier determined from the sum of anions ($Cl-$, $SO²4$) in milli equivalent (mg/l) obtained by dividing their concentration in mg/l by their respective atomic weight. The corresponding difference of value obtained from subtraction was multiplied by the atomic weight of the sodium obtained.

Magnesium (Mg^{2+})

Titan yellow reagent was used for the determination of magnesium, unsatisfactory by many investigation, magnesium which amount up to 180 mg/l has been determined spectrophotometrically using P-Nitro phenylazo-1-nphthol, this reagent form a colour complex with magnesium having absorption band at 405 and 480um (American Society for Testing and Materials, 2009). Magnesium ion was achieved by subtracting from the total hardness of the sample, the original value of calcium in mg/l of each water sample which was multiplied by the atomic weight of calcium 20g prior to the subtraction.

Iron (Fe^{2+})

Method: Phenanthroline Method.

Principle: Sample is boiled with acid and hydroxyl amine to reduce iron to the ferrous state. Ferrous iron obtained is treated with 1,10-phenanthroline at pH 3.1 to 3.3. Three molecules of Phenanthroline chelate on each atom of ferrous iron to form an arrange red complex is read calorimetrically , interfering substances may be present in individual waste water (ISO, 2015)

Material: Calorimetric equipment, Spectrophotometer, for use at 510nm, provide a light path of 1cm of longer wavelength.

Reagents: 1,10-phenanthroline solution. Range: 0-3mg/l(ppm)

Procedure:

1. A clean sample cell was filled to the 25ml mark.

2. A ferrous ion reagent powder pillow was then added to the same and worked to mix.

3. An orange colour was form indicating the presence of ferrous ion which was allowed to settle for 3 minutes to develop fully.

4. To the second bottle, the original sample and made to the 25ml mark and placed in the bottle holder (the blank sample)

5. When the equipment read zero, the blank sample bottle without the reagent was inserted into the cell holder.

6. The shield was closed, and the value of Fe2+ in mg/l read, as the total ion from the screen.

Chloride (Cl^-)

Method: Silver nitrate Method.

Principle/ Theory: Chloride is determined in a natural or slightly alkaline solution by titration with standard silver nitrate using potassium chromate as indicator. Silver chloride is quantitatively precipitated before red silver chromate is formed (ISO, 2015)

Materials: Burette 50ml, Conical flask 250ml, Stirring rod

Reagents: Silver nitrate standard solution, 0.1Mol. potassium chromate indicator, 10%.

Procedure:

1. 100mls of the sample was filtered into a conical flask

2. Three (3) drops of 10% potassium chromate indicator solution was added and then stirred. A redish colour was obtained.

3. The resulting solution was then titrated with silver nitrate solution with constant stirring until only the slightest perceptible redish colour obtained.

4. Steps 1 and 3 was repeated on a 100ml distilled water blank (without the indicator) to allow for the presence of chloride in any of the reagents and for the solubility of silver chromate.

Calculation:

Chloride as Cl^- = V_1-V_2 / Vol. of sample (mg/l)

Where V_1 = Volume of silver nitrate required by the sample (ml)

V_2= Volume of silver nitrate required by the blank (ml).

Nitrate (NO_3^-)

Nitrate the most highly oxidized form of nitrogen compounds, is commonly present in surface and ground waters, because it is the end product of the aerobic decomposition organic nitrogenous matter. Significant sources of nitrate are chemical fertilizers from cultivated lands and drainage from livestock feedlots, as well as domestic and some industrial waters.

Unpolluted natural water usually contain only minute amount of nitrate. In surface water, nitrate is a nutrient taken up by plants and assimilated into cell protein, stimulation of plant growth especially of algae, may cause water quality problems associated with europhication. The subsequent death and decay of algae produces secondary effects in water quality, which may also be undesirable. High concentration of nitrate in drinking water may present a risk to bottle fed babies under three (3) months of age because the low acidity of their stomach favour the reduction of nitrates to nitrites by microbial action. Nitrite is readily absorbed into the bloodstream where it combines irreversibly with haemoglobin to form methaemoglobin, which is ineffective as an oxygen carrier in the blood. In severe cases, a condition known as infantile methaemogloninaemia may occur which can be fatal for young babies (Abouelezz, 2021).

Method: Cadmium reduction method

Principle/Theory: Nitrate is reduced to nitrite when a sample is pass through a column containing amalgamated Cadmium fillings. Nitrate, that originally present plus that reduced from nitrate, is then determined.

Materials: Cadmium Reduction column, Calorimetric equipment, Spectrophotometer (540nm)

Reagents:

Tetraoxosulphate (vi) acid, 10g, hot distilled water 700ml, Conc. Hydrochloric acid, 100ml distilled water, 1000ml, ammonium chloride solution, stock nitrate solution, 7.218g of potassium nitrate, standard nitrate solution, Copper sulphate solution.

Procedure:

1. The reactor was filled with:

(I) Granulated Cadmium (40-60 mesh)

(iii) Copper sulphate solution, copper sulphate pentahydrate, 10ml, distilled water, 1000ml

(iii) Ammonium chloride of pH 8.5, 1.5ml

2. (i) The Cadmium was agitated several times in copper sulphate solution.

(Ii) glass wool plug was used to pack the column while the column was being washed with ammonium chloride buffer several times.

3. The column was the drained and about 1000ml sample was allowed to pass through the column while about 25-30ml was discarded. 50ml of the solution was collected from the column and used for analysis.

4. 2ml sulphuric acid was the added to the 50ml of sample and thoroughly mixed, the allowed to stand for five (5) minutes. The concentration was measured after 20 minutes in Spectrophotometer at 50nm against a blank.

Sulphate (SO_4^{2-})

Sulphate is an abundant ion in the Earth's crust and its concentration in water can range from a few milligrams to several thousands milligrams per litre. Industrial waste and mine drainage may contain high concentration of sulphate. Sulphate also results from the break down of sulphur containing organic compounds.

Sulphate is one of the least toxic anions and WHO does not recommend any guideline value for it in drinking water. However, catharsis, dehydration and gastro intestinal irritation have been observed at high concentration in drinking water and WHO therefore suggests that health authorities should be notified when concentration in drinking water exceed 500mg/l (WHO,1988).

Principle/Theory: The sulphate in water reacts with barium chloride to form insoluble barium sulphate which is measure by increased turbidity of the water.

Reagents: (a) Conditioning reagent 50ml of glycerol was added with a solution of 30ml distilled water, 100ml of 97% ethyl or propyl alcohol and 75g NaCl.

(b) Barium chloride crystals.

Equipment: Spectrophotometer (240nm)

Materials: 5ml graduated pipette, spatula and aspirator bulb.

Procedure:

1. To 5mlnof water sample in a conical flask, a spatula tip of barium chloride crystal and 2.5mls conditioning reagent were added and mixed thoroughly on a magnetic stirrer.

2. The mixture was then allowed to stand for an hour and a colour change observed.

3. Following step 1 and 2 above, a blank sample or solution was also prepared.

4. The concentration of both the sample solution and that of the blank was read through the aid of Spectrophotometer.

Calculation:

SO_4^{2-} =. $MgSO_4$ x 1000/ml of sample

Ammonium (NH_4^+)

When nitrogenous organic matter is decomposed by microbiological activities, ammonia is produced and is therefore found in many surface and ground waters. Higher concentration accurs in water polluted sewage fertilizers, agricultural waste or industrial waste containing nitrogen, free ammonia or ammonium salts.

Method: Direct Nesslerization.

Principle:

In the presence of ammonia Nessler's reagent (alkaline potassium iodomercurate) is decomposed with the formation of dimercuriammonium iodide. The ammonium is then determined calorimetrically at a wavelength of 420um or with colour standard.

Equipment: Spectrophotometer, 425um, Nessler's tube

Reagents: Nessler's reagent, EDTA solution

Procedure:

(a) To 50ml of sample in a Nessler's tube, a drop of EDTA solution was added.

(2) 2ml Nessler's reagent was then added

(c) The tube was then capped with clean rubber stopper and then mixed thoroughly by inverting the tube (at least six times).

Sodium adsorption ratio (SAR). The SAR was calculated using the formula

%Sodium. =. $Na^+/Na^+ + Ca^{2+} + Mg^{2+} + K^+ \times$ 100/1

TATBLE 3. PHYSICOCHEMICAL PARAMETERS

The physicochemical values of the area analyzed are shown in the table below.

S/N	PARAMETER	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	BH1	BH2	RANGE	MEAN	WHO
1	Temperature (ºC)	23	24	23	25	26	24	25	25	24	23	3	24.2	
2	pH	6.3	6.6	5.1	7.2	6.3	6.1	6.5	8.3	7.5	7.1	3.2	6.6	6.5-8.5
3	Conductivit	78	86	78	99	96	79	97	94	58	61	21	82.6	>1000
4	Dissolved Oxygen	7.8	8.5	8.2	8.8	8.6	8.9	8.1	8.2	6.4	6.6	2.5	7.9	6.5-8

5	Na^{2+}(mg/l)	20	16	19	10	20	17	23	14	21	25	15	18.5	<200
6	Ca^{2+}(mg/l)	40	76	48	75	50	79	78	59	50	48	38	79	<75
7	Mg^{2+}(mg/l)	18	22	17	21	26	22	31	20	12	19	19	20.7	450-500
8	Total Hardness (mg/l)	58	93	66	97	71	105	90	70	60	100	47	80.4	>500
9	Chloride (mg/l)	1.6	1.2	2.0	2.1	2.0	1.3	1.4	1.2	2.0	ND	0.8	1.6	<250
10	Nitrate (mg/l)	10	10	15	25	25	27	30	18	12	23	20	19.5	<45
11	$NH4^+$(mg/l)	15	20	21	20	17	19	30	18	16	15	15	19	<35
12	Fe^{2+} (mg/l)	0.04	ND	0.03	ND	0.02	0.01	0.01	ND	ND	0.01	0.03	0.02	0.10
13	TDS (mg/l)	78	91	62	58	92	101	93	68	64	58	43	77	>500
14	SAR	3.7	2.4	3.3	1.4	3.4	2.4	3.3	2.1	3.6	4.4	3.0	3.0	3-6

CONCLUSION

The analyses indicate that the waters are slightly acidic (5.1 to 7.2) in the P^H range, soft (total ardness <500mg/l) and fresh as conductivity is also (<500 us/cm). On the basis of of alkaline hazard, Fe^{2+} is <0.1mg/l. The waters are regarded excellent for irrigation, and most classes of livestock, poultry and fisheries cultivation. With the exception of Ca^{2+}, the mean values of all the parameters analysed were within the international standard for drinking, domestic and agricultural purposes. The quality evaluation scheme as shown in table 4 indicates that water bodyies are generally good except Ca^{2+} which is slightly greater than WHO standard. The boreholes results in terms of conductivity and total dissolve solids (TDS) indicate a high degree of excellent quality for drinking and other domestic uses.

RECOMMENDATION

The surface water is extremely good for irrigation, this is because the sodium adsorption ratio is relatively low. Some streams like ST4, ST8, ST2 and ST6 have SAR of 1.4, 2.1, 2.4 and 2.4 respectively which indicates low SAR content. The lower the SAR the better the water for irrigation. Therefore, the surface water should be used for agricultural purposes.

The surface water P^H shows that the surface water is slightly acidic, addition of calculated amount of calcium hydroxide would be required during irrigation process in order to balance the P^H.

Unwanted materials be recycled more often instead of being dumped into water bodies, as this may lead to sewage.

Filtration should be carried out after pre- treatment to remove sediment which may gives taste, colour and odour to the water.

The boreholes water has lower conductivity as compared to the surface water, this is because, the underground has impervious layers of natural filters. Therefore, the boreholes are better for drinking and other domestic purposes.

Finally, routine assessment of physico-chemical analysis of water be carried out frequently on seasonal basis as means of controlling the hygienic safety streams and boreholes of supply of water.

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