

Assessing the Physicochemical properties and heavy metal content of surface and groundwater in areas prone to pollution in Cross River State, Nigeria

ABSTRACT

Aims: To assess the level of contamination and quality of the groundwater from boreholes close to dumpsites and slaughterhouse in six L.G.A in Cross River State.

Study design: The study was a Completely Randomized Design (CRD), 3x6 factorial experimental design.

Place and Duration of Study: Cross River State Water Board Laboratory for analysis, between September and October 2023 (8 weeks).

Methodology: Standard laboratory procedures were carried out to determine, total dissolved solids (TDS), heavy metals (nitrate, chloride, copper, zinc, aluminium, Fluoride, and ammonia). Physical analysis of water samples for temperature, pH, conductivity, and BOD, were determined using thermometer, pH meter, Conductivity meter, BOD meter, respectively.

Results: The results revealed that the pH for the ground water samples ranged from 4.26 – 7.0 indicating acidity in some of the water samples. The value for conductivity ranged between 31.33 – 603.67 $\mu\text{s}/\text{cm}$ and was above the WHO standard for drinking water, fluoride ranged between 0.10 – 0.68mg/L and calcium with a range of 11.13 – 2.1.17mg/L which was within the WHO and NIS permissible limits. Standard BOD values were higher than all the controls.

Conclusion: Evidence from BOD values, suggest there is high level of contamination of groundwater sources within the study area. This calls for urgent policy and health interventions.

Key words: Physiochemical, Contamination, Groundwater, Dumpsites, Pollution-prone, Heavy metals

1. INTRODUCTION

Cross River State, known for its diverse ecosystems and significant water resources, faces increasing challenges due to urbanization, industrial activities, and agricultural practices that contribute to water pollution. The knowledge of areas where pollution levels exceed safe limits is invaluable and necessary information for requisite actions aimed at reducing incidence of contaminating water bodies. This study aimed at investigating the quality of surface and groundwater resources for possible pollution, by determining the physicochemical properties, and the heavy metal content of samples, in pollution-prone areas in Cross River State, Nigeria.

1.1 Physicochemical properties

The physicochemical properties of water, including pH, electrical conductivity (EC), total dissolved solids (TDS), turbidity, dissolved oxygen (DO), and chemical oxygen demand (COD), are essential parameters for evaluating water quality. These properties are influenced by both natural factors (such as geological formations) and anthropogenic activities (such as industrial discharges and agricultural runoff). The pH of water as a critical parameter, affects the solubility and toxicity of heavy metals and other pollutants. Water with a pH outside the neutral range (6.5-8.5) can indicate contamination from acidic or alkaline pollutants. For instance, studies in industrial areas have reported deviations from the neutral pH range due to the discharge of acidic industrial effluents [1].

1.2 Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

The study by [2] focuses on the salinization of groundwater and its implications for drinking water quality in the southwestern coast of Bangladesh. The study provides significant insights into the role of Electrical Conductivity (EC) and Total Dissolved Solids (TDS) as key indicators of groundwater salinization and pollution. EC was used in the study to assess the extent of groundwater salinization. The elevated EC levels in the groundwater samples from the region are indicative of high salinity, primarily due to the intrusion of seawater into the aquifers. Authors [2] highlights that EC measurements provide a quick and reliable assessment of the ionic content of groundwater, which directly relates to the presence of dissolved salts and minerals. Elevated EC values in the study area suggested that the groundwater is not only saline but also potentially contaminated with other dissolved substances, posing a risk to drinking water quality. [3] emphasized the importance of EC and TDS as critical parameters for assessing the

salinity and overall quality of water resources, arguing that the characteristics of water resources in Uzbekistan are analyzed through the measurement EC as an indicator of water quality.

Turbidity: Turbidity refers to the cloudiness or haziness of a fluid caused by large numbers of individual particles that are generally invisible to the naked eye, similar to smoke in the air. It is an important indicator of water quality, particularly in effluents, as it can affect the penetration of light into the water, which in turn affects aquatic life. [4], evaluated turbidity as one of the key parameters in assessing the quality of industrial effluents discharged into the environment in Jos metropolis, Plateau State, Nigeria. The study found that the turbidity levels in the sampled industrial effluents varied significantly across different industries. High turbidity values were noted in effluents from certain industries, indicating the presence of suspended particles and possibly contaminants that contribute to the water's cloudiness. These high turbidity levels could have adverse effects on receiving water bodies by reducing the clarity of the water, which can hinder photosynthesis in aquatic plants and disrupt the habitat of aquatic organisms.

Similarly, a recent research [5] found that turbidity levels varied across different sampling sites in the Mnasra region. Elevated turbidity values in certain areas indicated potential contamination, which could be attributed to agricultural runoff, improper waste disposal, or infiltration of surface water into the groundwater system. The researchers noted that high turbidity levels could impair the aesthetic and portability of groundwater, as well as interfere with water treatment processes. Authors believe the presence of high turbidity in groundwater is a concern for both environmental and public health. It can harbor pathogens, reduce the effectiveness of disinfection processes, and make the water less suitable for consumption and irrigation.

Dissolved Oxygen (DO) and Chemical Oxygen Demand (COD): the level of environmental water pollution can be seen by knowing the dissolved oxygen content in the water. Dissolved oxygen is a basic requirement for plant and animal life in water. Water is categorized as polluted water if the dissolved oxygen concentration falls below the limit required for biota [6]. The main cause of reduced dissolved oxygen in water is the presence of waste materials that consume oxygen. These materials consist of materials that are easily decomposed by bacteria in the presence of oxygen. The oxygen available in water is consumed by bacteria that actively break down these materials [7].

DO represents the amount of oxygen that is present in a body of water, which is necessary for the survival of aquatic life [8, 4]. It is among the crucial parameters used in assessing the quality of water bodies and wastewater. [8] found that the wastewater discharge from selected paint industries in Lagos, Nigeria, exhibited low levels of DO. This indicates that the oxygen available in the wastewater is insufficient to support aquatic life, which can lead to hypoxic conditions. Such low DO levels are often a result of the decomposition of organic matter, which consumes oxygen in the process.

COD measures the total quantity of oxygen required to oxidize both organic and inorganic compounds in water. It is an indicator of the amount of pollution in the water, specifically from organic pollutants. The COD values in the wastewater from the paint industries were found to be high, suggesting a significant presence of organic pollutants. High COD levels indicate that a large amount of oxygen would be needed to break down the organic material present in the wastewater. This high organic load can lead to oxygen depletion in receiving water bodies, adversely affecting water quality and aquatic life [8].

Heavy metals are a class of inherently dense and toxic elements, which have become pervasive contaminants of serious concern within the environmental landscape worldwide [9]. A study [10] focused on assessing the quality of groundwater in Karu, Central Nigeria revealed that the concentrations of heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) in the groundwater samples were generally within the permissible limits set by the World Health Organization (WHO). However, certain locations exhibited elevated levels of lead and nickel, which pose significant health risks due to their toxicity and potential to cause long-term health effects such as kidney damage and neurological disorders.

In another instance, [11], investigated the human health risks associated with heavy metal contamination in ground and surface water, in Maharashtra, India. The study found that the concentrations of heavy metals like arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg) in some water samples exceeded the WHO guidelines, indicating potential health risks, including cancer, neurological damage, and developmental issues in children.

In consideration of the broader impact of heavy metal contamination in water on living organisms, [12] correlated the non-biodegradable nature of heavy metals with the propensity of their accumulation in aquatic ecosystems, leading to bioaccumulation in organisms. This bioaccumulation can cause a range of toxic effects, including carcinogenicity, neurotoxicity, and damage to vital organs such as the liver and kidneys in humans and animals.

2. MATERIALS AND METHODS

2.1 Study area

Groundwater samples for the study were collected from diverse sources within six Local Government Areas (LGA) in Cross River State. These locations varied, including rural villages, urban centers, and border areas. The sampling sites including dumpsites and slaughterhouse were located at various village settlements within Yakurr (Latitude 5°45'34" N to 5°48.682' N, Longitude: 8°5'18" E to 8°5'23" E), and Ikom LGA (Latitude 5.9667° N to 6.2000° N, Longitude 8.6000° E to 8.8000° E), situated in the Central Senatorial District, featured village settlements and diverse occupations, including farming and civil service. Despite potential concerns about water quality, the residents of these areas relied heavily on groundwater sources for everyday use.

The Southern Senatorial District, home to Akamkpa (Latitude 5.2500° N to 5.4500° N, Longitude: 8.2500° E to 8.4500° E) and Calabar Municipality (Calabar Municipality: Latitude 4.9200° N to 4.9900° N, Longitude 8.3000° E to 8.3800° E), presented an interesting contrast with its urban features and surrounding rural areas. Yala and Ogoja are located in the Northern Senatorial District of the State. Ogoja lies between Latitude 6.5500° N to 6.7500° N, and Longitude: 8.6500° E to 8.8500° E, while Yala lies between Latitude 6.5000° N to 7.0000° N, and Longitude: 8.5000° E to 9.0000° E.

2.2 Ground water sample collection from boreholes

Groundwater samples for physicochemical and heavy metal analysis were collected from boreholes across six Local Government Areas (Akamkpa, Calabar Municipality, Ikom, Ogoja, Yakurr, and Yala) in the state. In total, 54 water samples were gathered and immediately placed in sterile, acidified bottles to preclude contamination. The bottles were covered, placed in an ice pack, and conveyed to the Cross River State Water Board Laboratory for analysis. During sample collection, the mouth of the tap was sterilized using methylated spirit and the water was allowed to flow for two minutes at maximum flow before being collected in the bottles.

2.3 Experimental design

The study was a Completely Randomized Design (CRD), 3x6 factorial experimental design.

Factor 1: Sources (Control, Dumpsite and Abattoir).

Factor 2: Six Local government Area (Akamkpa, Calabar Municipality, Ikom, Ogoja, Yakurr, and Yala).

2.4 Physical analysis of water samples

Temperature

This was determined with the thermometer. The thermometer was inserted into the water sample in a beaker and the reading was noted [13, 14].

pH

The pH was determined with a pH meter (Model Hach Sension +). The pH meter probe was inserted into the water sample in a beaker, the read key was pressed and the pH reading was taken [13, 14].

Conductivity

Conductivity meter (Model: Orion 3 Star) was used. The conductivity meter probe was rinsed with distilled water and inserted into the sample in a beaker, the conductivity reading was displayed [13, 14].

BOD

BOD meter (Model: HACH HQ40D) was used to determine this parameter. The meter probe was rinsed with distilled water and inserted into the sample. BOD reading was displayed on activation of the read key [13, 14].

2.5 Chemical analysis of water sample

Total iron

The multi-cell adapter with the I-inch square cell holder was inserted into the electronic device after the “total iron” test was selected from a button on the electronic device. Then a clean square sample cell was filled with 10ml of the sample. Contents of one ferrower iron reagent powder pillow was added to the sample cell and swirled to mix. An orange colour was formed indicating the presence of iron [13, 15].

Manganese

The multi-cell adapter with I-inch square cell holder was inserted in the electronic device after the “manganese” test was selected from a button. Then a square sample cell was filled with 10ml of the sample. Contents of one buffer powder pillow, citrate type of manganese stopper was

added. Then contents of one sodium periodate powder pillow was added to the sample cell stopper and inverted to mix. A violet colour indicated the presence of manganese [13, 15].

Copper

A square sample cell was filled with 10 ml of the sample. The blank was inserted into the cell holder with the fill line facing the user. Zero was pressed on the timer with the display showing 0.00 mg/l Cu. Within 30 minutes after the timer expired, prepared samples were inserted into the cell holder with the fill line facing the user. Then results were taken in mg/l Cu [13, 15].

Nitrate

The “nitrate” test was selected from a button on the electronic device, and then the multi cell adapter with 1-inch square cell holder was inserted facing the user. The square sample cell was filled with 10 ml of the sample. Contents of one Nitra Ver 5 nitrate reagent powder pillow were added. Then OK was pressed on the timer. A one-minute reaction period began, and then the cell was shaken vigorously until the time expired. The timer “OK” was pressed again. Then a five-minute reaction period began. An amber colour developed showing the presence of nitrate [13].

Phosphorus

A square sample cell was filled with 10 ml of the sample. The blank was inserted into the cell holder. The ZERO was pressed on the button, with the display showing 0.00 mg/l PO_4^{3-} . The prepared sample was wiped and inserted into the cell holder with the fill line facing the user. Then results were taken in mg/l PO_4^{3-} [13, 14].

Ammonia

The “ammonia” test was selected from a button on the electronic device and the multi cell adapter with one-inch square holder was inserted. The square sample cell was filled with 10ml of the sample. Contents of one ammonia salicylate powder pillow were added to each cell stopper and then shake to dissolve. Then the OK button was pressed, a 15-minute reaction period began. A green color developed showing the presence of ammonia-nitrogen. When the timer expired, the blank was inserted into the cell holder with the fill line facing the user. Zero was pressed on the timer with the display showing 0.00 mg/l NH₃-N. The sample was wiped and inserted into the cell holder and results were taken in mg/l NH₃ [13].

Zinc

Ten millilitres of the sample solution was poured into a square sample cell. With the use of a plastic dropper, 0.5 ml of cyclohexanone was added to the solution in the graduated cylinder. Then OK was pressed on the timer. A 30 second reaction period began, during the period the prepared sample in the cylinder was shaken vigorously. A colour change was observed, which depending on the zinc concentration could be reddish orange, brown or blue [13, 15].

Chromium

Multi-cell Adapter was inserted with the 1-inch square cell holder facing the user and the required test selected. A square sample cell was filled with 10ml of sample. The contents of one ChromaVer® 3 Reagent Powder Pillow was added to the sample cell and swirled to mix. TIMER>OK button was pressed for a five-minute reaction period will begin. A purple color was formed to indicate the presence of hexavalent chromium. When the timer expired, a second

square sample cell was filled with 10ml of sample, the blank was inserted into the cell holder with the fill line facing the user. ZERO button was pressed, the display showed 0.000 mg/L Cr⁶⁺

2.6 Statistical analysis

The collected data were subjected to a two-way Analysis of Variance (ANOVA) while significant means were separated using Least Significant Difference (LSD) test at 5% and 1% probability level.

3. RESULTS

Physicochemical properties of ground water

pH

The result as presented on Table 1 show that the borehole located in the non-pollution prone area in Yala LGA had the highest pH value and significantly higher ($P < 0.05$) than the value obtained from other sources. This was followed by the pH obtained from Akamkpa (control, dumpsite), Calabar Municipality (control), Ikom (control, dumpsite), Ogoja (control, dumpsites, slaughterhouse), Yala (dumpsite, slaughterhouse) with no significant difference ($P > 0.05$) in mean, the pH values obtained from these areas appears to be slightly acidic, which further reduces in areas like Akamkpa and Ikom (slaughterhouse), Yakurr (control, dumpsite, slaughterhouse) (Table 1).

The result revealed that the pH value in Calabar Municipality both in the dumpsite and slaughterhouse areas was the lowest; meaning the boreholes in those areas had a strong acidic content. However, while comparing the pH in the borehole water samples from the different LGAs, excluding the source of collection, it was observed that the pH value from Yala and Ogoja

was the highest, followed by Akamkpa and Ikom, also followed by the pH value from Yakurr while Calabar Municipality had the lowest pH value (Table 2). This result implies that the borehole water samples from the pollution prone areas were acidic.

Electrical conductivity

The borehole located at Ikom (control), Ogoja and Yakurr (control, dumpsite) and Yala (control, slaughter) had significantly high level of conductivity than the mean values obtained from Akamkpa (control), Cal. M (control), Ikom (dumpsite, slaughterhouse), Yakurr (slaughterhouse) and Yala (dumpsite) with no significant difference ($P>0.05$). This was followed by the conductivity value obtained from Calabar Municipality (dumpsite), Akamkpa (dumpsite), Ogoja (slaughterhouse) while, Cal. Slaughterhouse had lower conductivity level (Table 1). Table 2 shows that the boreholes from Yakurr and Yala had the highest conductivity level, followed by Ikom. The conductivity level from Akamkpa and Calabar Municipality was the lowest. This result implies that the conductivity levels in the borehole water samples from the different locations were lower than the WHO standard for drinking water and that the ionic concentration of the water was low.

Total Dissolved Solid (TDS)

The result as presented on Table 1 indicates that the TDS in borehole located at Ogoja (dumpsite), had the highest TDS value than other boreholes. This was followed by the TDS values from Ikom and Yakurr (dumpsite), Yala (control) with no significant difference ($P>0.05$) in mean. While, the TDS value from Akamkpa and Calabar municipal (control, dumpsite, slaughterhouse), Ikom, Yakurr and Ogoja (control, slaughterhouse), Yala (dumpsite and slaughterhouse) was the lowest with no significant variation in mean. However, Table 2 show that the TDS value from borehole water samples was the highest, followed by the TDS in

boreholes from Ikom and Yakurr that shows no significant differences ($P > 0.05$) in mean values, while Akamkpa and Calabar Municipality had the lowest TDS in their borehole water. This result based on the WHO standard for drinking water implies that the level of TDS was below the WHO recommended standard.

Turbidity

The result obtained show that water samples from Ikom (dumpsite) had the highest turbidity level, followed by the turbidity level in borehole water samples from Ikom (slaughterhouse), Ogoja (dumpsite), and Yala (control) with no significant difference ($P > 0.05$). This was also followed by the turbidity level in borehole water samples in Akamkpa, Ikom and Ogoja (control) with no significant difference ($P > 0.05$) in the mean but significantly higher than the turbidity level Akamkpa (slaughterhouse), Calabar Municipality and Yakurr (control), and Yala (dumpsite) while the lowest turbidity level was obtained from borehole water samples from Calabar Municipality (dumpsite, slaughterhouse), and Yakurr (slaughterhouse) with no significant variation in the mean values (Table 1). It was observed that the turbidity of borehole water in Ogoja and Yala was the highest, followed by the values obtained from Akamkpa, also followed by the value obtained from Yakurr while the lowest turbidity value was obtained from the borehole water situated in Ikom (Table 2).

Aluminum

The result show that high Al was detected in Akamkpa (dumpsite), followed by the Al content obtained from Calabar Municipality (dumpsite, slaughterhouse) with no significant difference ($P > 0.05$) in mean, but significantly higher than the mean Al content found in other

locations and sources (Table 1). However, the Al content in Akamkpa, Calabar Municipality was higher than the Al content Ikom, while Al content in the borehole water from Ogoja, Yakurr and Yala was observed to be the lowest. This result implies that Akamkpa and Calabar Municipality had the highest Al content in their boreholes.

Ammonia and biochemical oxygen demand

The result as presented on Figure 1, 2 and 3 signified that the ammonia, BOD level, and temperature in the borehole water samples from the different locations and sources showed no significant difference ($P>0.05$) in the mean values obtained.

Calcium

The result as presented on Table 1 show that Akamkpa and Ikom (dumpsite), Calabar Municipality (control, dumpsite), Ogoja and Yala (slaughterhouse), had significantly high ($P>0.05$) levels of calcium in the borehole water, higher than the calcium level in other borehole water samples. Table 2 show that the calcium levels in the borehole water from Calabar Municipality was the highest, followed by the Ca level in Ogoja boreholes, followed by the Ca levels in Akamkpa and Ikom borehole with no significant difference ($P>0.05$) in mean while the Ca level in Yakurr was the lowest.

Phosphate

It was observed from the result that the phosphate in boreholes from Ogoja (dumpsite) was the highest, significantly higher ($P<0.05$) than the PO_4^{2-} in Akamkpa and Ikom (dumpsite) with no significant difference in mean but significantly higher ($P<0.05$) than the PO_4^{2-} in Calabar Municipality (slaughterhouse) and Yala (dumpsite) boreholes. The lowest PO_4^{2-} value was obtained in Akamkpa and Ogoja (control) boreholes. Table 2 show that the PO_4^{2-} content in

Ogoja boreholes was the highest, followed by the PO_4^{2+} content in Ikom boreholes while Akamkpa and Calabar Municipality boreholes was the lowest.

Fluoride

The availability of fluoride in borehole water from Akamkpa (dumpsite), Calabar Municipality (dumpsite, slaughterhouse), Ikom (dumpsite), Ogoja (dumpsite, slaughterhouse) and Yala (dumpsite) was the highest, with no significant difference ($P>0.05$) in the mean values obtained. This was followed by the fluoride content in boreholes water from Calabar Municipality (control), significantly higher than the fluoride content in other boreholes water samples, which equally showed no significant difference ($P>0.05$) in mean Table 1. The comparison between the fluoride levels among the different borehole locations show that Akamkpa, Calabar Municipality Ikom, Ogoja, Yala had the highest fluoride content, while, Yakurr had the lowest (Table 2).

Nitrate

The result as presented on Table 1 show that Akamkpa and Yakurr (dumpsites) had the highest nitrate levels in their boreholes. This was followed by the nitrate levels in Calabar Municipality (dumpsite, slaughterhouse) and Yala (dumpsite) with no significant difference ($P>0.05$) in the mean values obtained but significantly higher than the nitrate content in the boreholes situated at Akamkpa, Yala and Yakurr (control and slaughterhouse), Calabar Municipality (control), Ikom and Ogoja (control, dumpsite, slaughterhouse) with no significant difference ($P>0.05$) in the mean values. It was also observed that the nitrate level in Calabar Municipality borehole was the highest, followed by the nitrate level in borehole water in Akamkpa and Yakurr that show no

difference ($P>0.05$) in means while the nitrate level in Ogoja borehole had the lowest nitrate level (Table 2).

Heavy metal content in groundwater

Iron (Fe)

The result as presented on Table 3 show that the iron level in Calabar Municipality (dumpsite) borehole was the highest, followed by Akamkpa and Yala (dumpsite) boreholes with no significant difference ($P>0.05$) in the mean values. This was followed by the iron content in other borehole water samples in different locations and sources during the research. Table 4 show that the iron content in Akamkpa borehole was the highest, followed by the iron content in borehole water from Calabar Municipality and Yala while, Ikom, Ogoja and Yakurr boreholes had the lowest iron content with no significant difference ($P>0.05$) in mean.

Zinc (Zn) content

It was observed from Table 3 that the zinc level in Ogoja (slaughterhouse) ground water was significantly low. While borehole water samples from other sources and locations were significantly high in zinc. Table 4 revealed that the zinc in Akamkpa and Ogoja water samples was significantly higher ($P<0.05$) than the zinc level in Calabar Municipality and Yala boreholes water samples, this was followed by the zinc level in Ikom borehole while, Yakurr had the lowest zinc.

Chromium (Cr) content

The chromium level in Ogoja (slaughterhouse) was significantly higher ($P<0.05$) than the Cr level in borehole water samples from other locations and sources that appears to be significantly

low with no variation in mean (Table 3). The result as presented on Table 4 show that the chromium content in Ikom and Yakurr boreholes was the highest with no significant difference ($P>0.05$) in the mean values. This was followed by the chromium content in borehole water from Akamkpa, Ogoja, Yala with no variation in means. While the chromium content in Calabar Municipality was the lowest.

Copper and manganese

The results as presented on Tables 3 and 4 show that the copper and manganese content in ground water samples from the different locations and sources were not significantly different ($P>0.05$).

UNDER PEER REVIEW

Table 1

Physicochemical properties of underground water in polluted soil prone areas

Location	Source	pH	Conductivity	TDS	Turbidity	AL	Calcium	Phosphate	Fluoride	Nitrate
Akamkpa	Control	6.70 ^b ±0.12	203.33 ^b ±7.17	64.33 ^c ±4.26	7.33 ^c ±0.38	0.09 ^c ±0.01	14.43 ^b ±1.35	5.90 ^h ±0.78	0.26 ^c ±0.04	5.04 ^c ±0.20
	Dumpsite	6.23 ^b ±0.20	139.67 ^c ±7.13	71.0 ^c ±4.36	3.31 ^f ±0.44	0.46 ^a ±0.02	18.57 ^a ±0.80	24.49 ^b ±2.73	0.62 ^a ±0.09	17.73 ^a ±0.90
	Slaughterhouse	5.60 ^c ±0.13	39.0 ^d ±14.64	14.0 ^c ±4.58	5.28 ^d ±0.24	0.081 ^c ±0.004	12.5 ^b ±1.00	9.13 ^g ±0.61	0.35 ^c ±0.05	7.35 ^c ±1.59
	Control	6.23 ^b ±0.12	241.0 ^b ±4.93	85.67 ^c ±3.84	5.70 ^d ±0.07	0.08 ^c ±0.02	20.93 ^a ±0.81	8.02 ^g ±1.34	0.45 ^b ±0.03	7.03 ^c ±0.07
Cal. M	Dumpsite	4.26 ^e ±0.09	117.0 ^c ±13.05	57.67 ^c ±6.39	1.58 ^h ±0.07	0.40 ^b ±0.09	20.73 ^a ±0.82	12.18 ^f ±3.34	0.58 ^a ±0.02	12.96 ^b ±2.43
	Slaughterhouse	4.83 ^d ±0.18	31.33 ^d ±6.76	16.00 ^c ±3.61	1.93 ^h ±0.23	0.39 ^b ±0.08	16.35 ^b ±0.10	20.16 ^c ±4.64	0.68 ^a ±0.09	14.04 ^b ±0.77

Ikom	Control	6.50 ^b ±0.	603.67 ^a ±51.	157.0 ^c ±12.7	7.10 ^c ±0.	0.063 ^c ±0.	11.67 ^b ±0.	9.06 ^g ±0.58	0.21 ^c ±0.	3.97 ^c ±0.4
		12	33	4	12	01	18		06	4
	Dumpsite	6.03 ^b ±0.	286.67 ^b ±35.	225.0 ^b ±13.6	8.94 ^a ±1.	0.16 ^c ±0.0	18.07 ^a ±1.	23.43 ^b ±0.9	0.54 ^a ±0.	5.85 ^c ±0.3
		09	67	1	06	3	61	4	01	1
	Slaughterhouse	5.50 ^c ±0.	283.33 ^b ±29.	113.0 ^c ±47.7	8.15 ^b ±1.	0.16 ^c ±0.0	16.37 ^b ±0.	15.85 ^e ±5.4	0.36 ^c ±0.	6.08 ^c ±0.0
		02	87	0	19	5	67	7	10	7
Ogoja	Control	6.70 ^b ±0.	501.33 ^a ±44.	161.67 ^c ±3.8	7.28 ^c ±0.	0.02 ^c ±0.0	13.57 ^b ±0.	4.59 ^h ±0.69	0.22 ^c ±0.	1.34 ^c ±0.2
		12	82	4	14	02	41		01	8
	Dumpsite	6.43 ^b ±0.	486.67 ^a ±29.	336.0 ^a ±73.7	8.20 ^b ±0.	0.08 ^c ±0.0	15.1 ^b ±1.6	27.73 ^a ±11.	0.55 ^a ±0.	7.37 ^c ±2.8
		20	81	6	09	1	6	42	07	7
	Slaughterhouse	6.47 ^b ±0.	144.33 ^c ±7.8	69.00 ^e ±2.08	3.30 ^f ±0.	0.07 ^c ±0.0	21.17 ^a ±1.	18.17 ^d ±0.4	0.74 ^a ±0.	2.78 ^c ±0.6
		20	8		7	2	39	3	04	2
Yakurr	Control	5.67 ^c ±0.	420.67 ^a ±41.	152.67 ^c ±20.	5.45 ^d ±0.	0.07 ^c ±0.0	9.97 ^b ±0.2	8.30 ^g ±0.03	0.10 ^c ±0.	5.24 ^c ±0.4
		23	95	03	25	3	7		00	4
	Dumpsite	5.27 ^c ±0.	578.67 ^a ±84.	272.67 ^b ±10.	2.79 ^g ±0.	0.12 ^c ±0.0	19.18 ^a ±0.	18.17 ^d ±0.7	0.19 ^c ±0.	17.31 ^a ±2.
		23	23	17	23	2	48	8	01	89

	Slaughterho	5.13 ^c ±0.	217.00 ^b ±45.	68.33 ^c ±0.88	2.02 ^h ±0.	0.06 ^c ±0.0	12.80 ^b ±0.	13.70 ^f ±2.3	0.14 ^c ±0.	7.64 ^c ±0.3
	use	09	79		16	1	91	0	03	3
Yala	Control	7.00 ^a ±0.	541.0 ^a ±10.6	223.67 ^b ±11.	7.97 ^b ±0.	0.03 ^c ±0.0	11.13 ^b ±0.	8.63 ^g ±0.26	0.20 ^c ±0.	3.11 ^c ±0.1
		15	9	70	49	01	85		01	7
	Dumpsite	6.37 ^b ±0.	232.0 ^b ±5.51	105.33 ^c ±10.	5.26 ^d ±0.	0.09 ^c ±0.0	12.73 ^b ±0.	20.89 ^c ±2.6	0.61 ^a ±0.	12.27 ^b ±0.
		60		41	31	2	69	2	03	32
	Slaughterho	6.30 ^b ±0.	469.33 ^a ±60.	139.0 ^c ±44.1	4.80 ^e ±0.	0.05 ^c ±0.0	20.10 ^a ±1.	15.50 ^e ±1.2	0.29 ^c ±0.	2.98 ^c ±1.1
	use	12	76	9	15	1	00	6	04	6
LSD		0.23	56.80	46.86	0.43	0.04	1.26	1.64	0.07	1.85
WHO		6.5-8.5	500	250		0.02	0.1	5.0		
NIS		6.5-8.5	1000	500		0.2	50		1.0	15

TABLE 2

Physicochemical Properties of ground water collected from different Local Government Area in CRS

Location	pH	Conductivity	TDS	Turbidity	AL	Ammonia	Calcium	Phosphate	Floride	Nitrate
Akamkpa	6.18 ^b ±0.18	127.33 ^d ±24.46	49.78 ^d ±9.26	5.31 ^c ±0.61	0.209 ^a ±0.06	0.023±0.001	15.17 ^c ±3.15	13.17 ^d ±8.96	0.41 ^a ±0.19	10.04 ^b ±6.0
Calabar	5.11 ^d ±0.30	129.78 ^d ±30.76	53.11 ^d ±10.40	3.07 ^c ±0.66	0.289 ^a ±0.06	0.02±0.001	19.34 ^a ±2.46	13.45 ^d ±0.08	0.57 ^a ±0.13	11.33 ^a ±3.9
Municipal										
Ikom	6.01 ^b ±0.15	391.22 ^b ±68.18	165.0 ^b ±21.97	0.07 ^f ±0.53	0.13 ^b ±0.02	0.02±0.001	15.37 ^c ±3.25	16.11 ^b ±2.01	0.37 ^a ±0.17	5.29 ^c ±1.10
Ogoja	6.53 ^a ±0.10	377.44 ^c ±89.30	188.89 ^a ±44.57	6.26 ^a ±0.75	0.06 ^c ±0.01	0.02±0.01	16.61 ^b ±3.97	16.83 ^a ±0.89	0.50 ^a ±0.24	3.83 ^d ±0.74
Yakurr	5.36 ^c ±0.11	405.44 ^a ±76.74	164.5 ^b ±42.12	3.42 ^d ±0.53	0.09 ^c ±0.01	0.01±0.001	13.98 ^e ±0.19	13.39 ^d ±0.76	0.14 ^b ±0.05	10.06 ^b ±0.0
Yala	6.56 ^a ±0.21	415.11 ^a ±60.76	156.0 ^c ±22.20	6.01 ^a ±0.52	0.06 ^c ±0.01	0.02±0.01	14.66 ^d ±0.33	15.01 ^c ±0.89	0.36 ^a ±0.19	6.12 ^c ±0.72
LSD	0.17	10.57	6.78	0.27	0.05	NS	0.21	0.38	0.09	0.93

Mean with the same superscript along the vertical arrays indicates no significant difference (P>0.05).

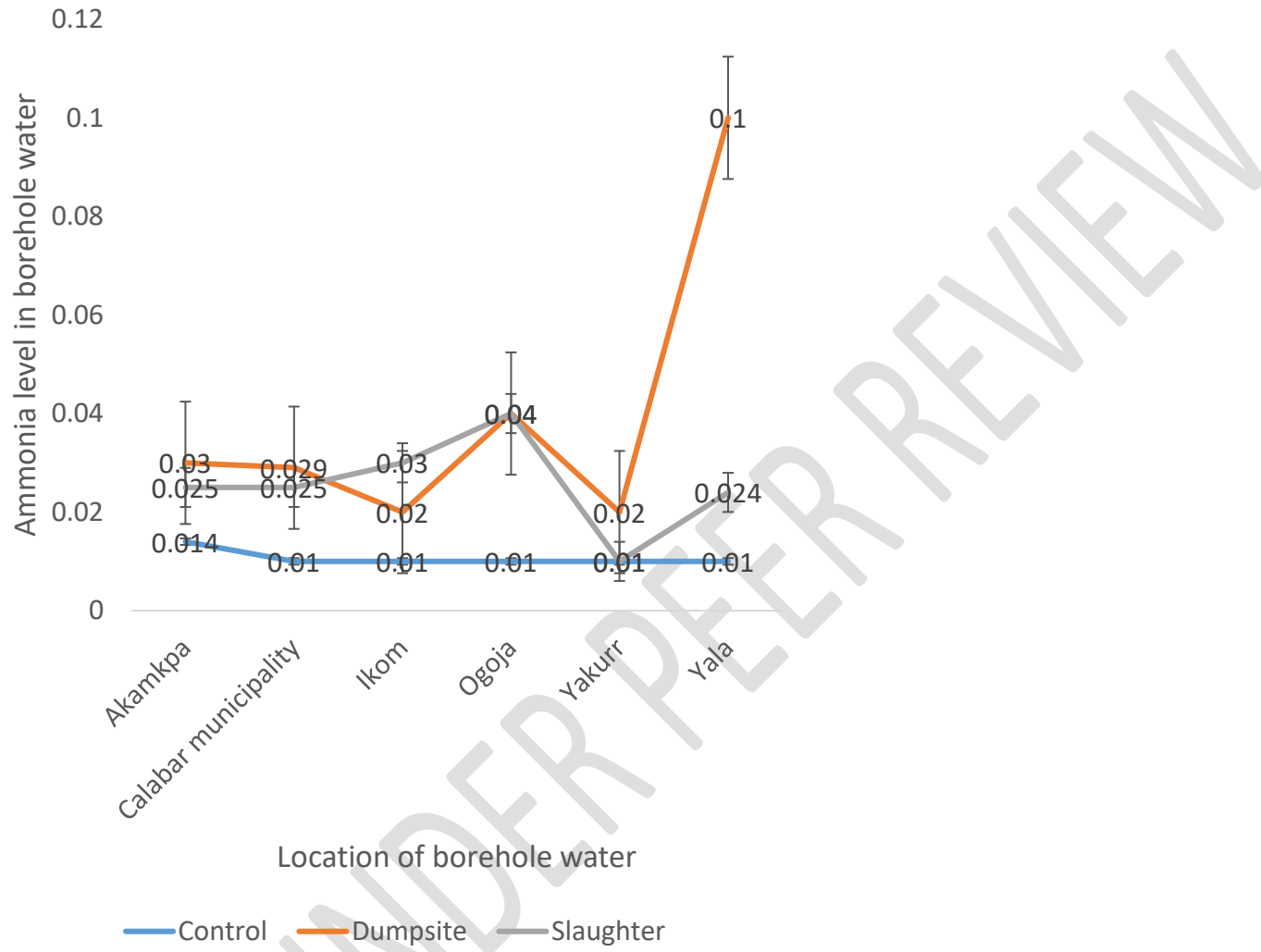


Figure 1: Ammonia content in the borehole water samples

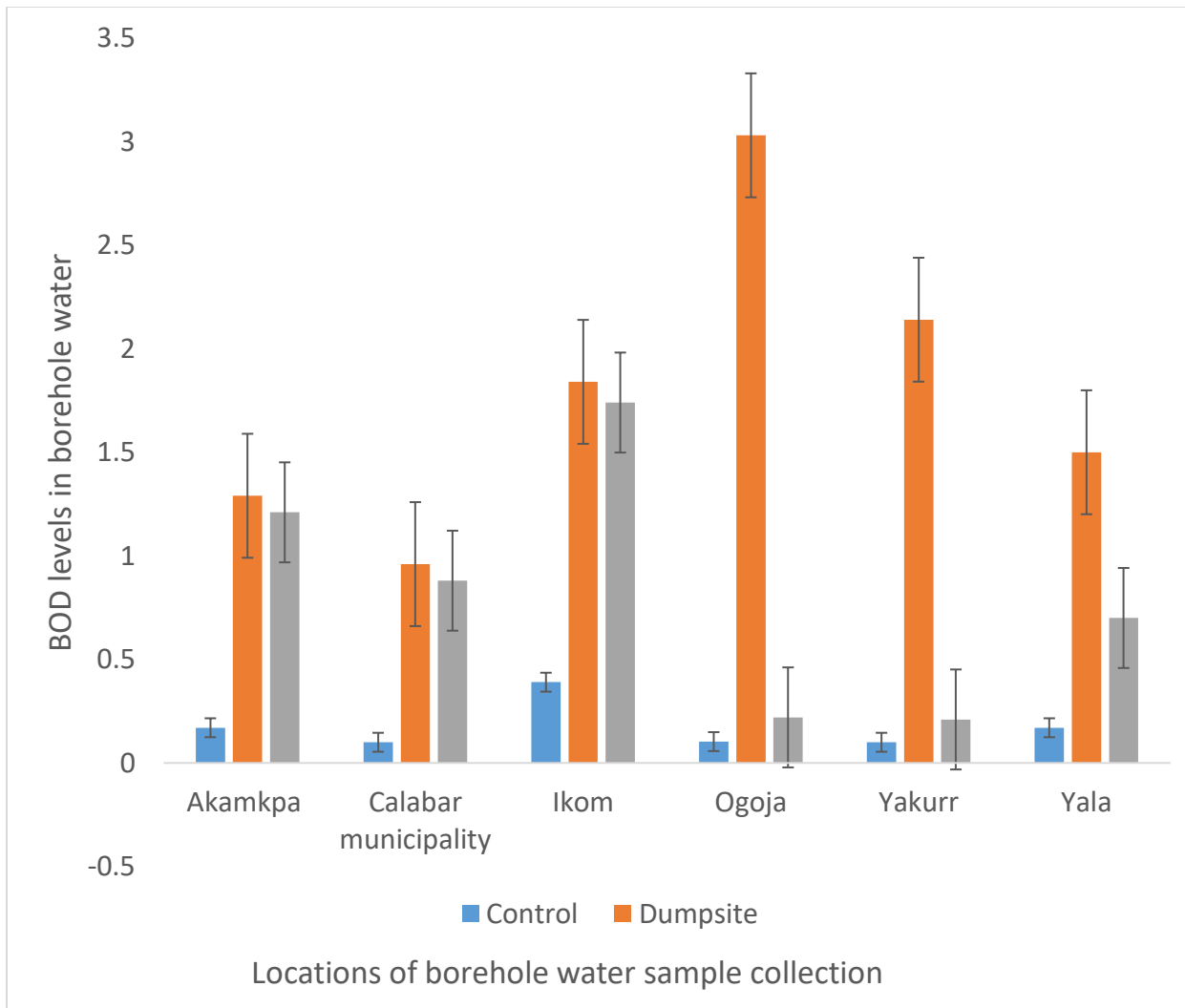


Figure 2: Biochemical oxygen demand in the borehole water

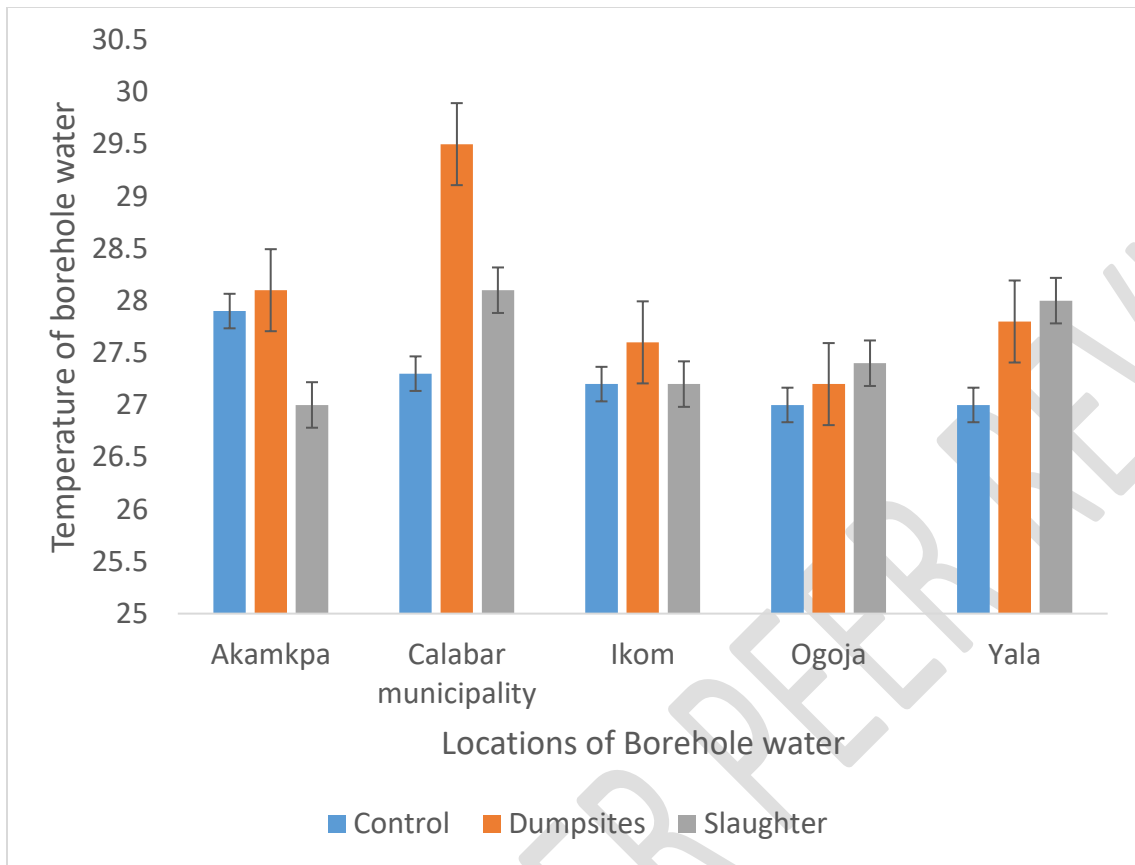


Figure 3: Temperature in the borehole water

TABLE 3

Heavy metal content of underground water in polluted soil prone areas

Location	Source	Fe	Zinc	Chromium	Copper	Manganese
Akamkpa	Control	0.02 ^c ±0.01	1.10 ^a ±0.06	0.01 ^b ±0.01	0.007±0.003	0.003±0.003
	Dumpsite	0.48 ^b ±0.02	1.19 ^a ±0.01	0.10 ^b ±0.01	0.127±0.02	0.01±0.01
	Slaughterhouse	0.07 ^c ±0.02	1.30 ^a ±0.02	0.01 ^b ±0.03	0.007±0.003	0.003±0.003
Calabar municipal	Control	0.02 ^c ±0.01	0.76 ^a ±0.04	0.003 ^b ±0.003	0.01±0.00	0.01±0.003
	Dumpsite	0.99 ^a ±0.39	1.22 ^a ±0.22	0.047 ^b ±0.04	0.07±0.03	0.073±0.04
	Slaughterhouse	0.09 ^c ±0.01	0.99 ^a ±0.08	0.001 ^b ±0.00	0.243±0.05	0.100±0.01
Ikom	Control	0.01 ^c ±0.003	0.47 ^a ±0.09	0.01 ^b ±0.00	-	-
	Dumpsite	0.01 ^c ±0.003	1.44 ^a ±0.38	0.04 ^b ±0.03	0.003±0.003	0.14±0.04
	Slaughterhouse	0.18 ^c ±0.08	0.20 ^a ±0.06	0.16 ^b ±0.08	-	0.07±0.03
Ogoja	Control	0.007 ^c ±0.003	0.43 ^a ±0.15	0.003 ^b ±0.003	0.0067±0.003	0.003±0.003
	Dumpsite	0.04 ^c ±0.01	0.94 ^a ±0.13	0.05 ^b ±0.04	0.11±0.001	0.0067±0.003
	Slaughterhouse	0.031 ^c ±0.003	0.013 ^b ±0.003	2.20 ^a ±0.06	0.003±0.001	0.0067±0.003
Yakurr	Control	0.017 ^c ±0.01	0.30 ^a ±0.12	0.013 ^b ±0.003	-	0.013±0.003

	Dumpsite	0.043 ^c ±0.003	0.88 ^a ±0.21	0.12 ^b ±0.004	0.06±0.03	0.16±0.03
	Slaughterhouse	0.03 ^c ±0.01	0.47 ^a ±0.19	0.14 ^b ±0.02	0.01±0.003	0.013±0.003
Yala	Control	0.017 ^c ±0.01	0.56 ^a ±0.08	0.007 ^b ±0.003	0.003±0.001	-
	Dumpsite	0.49 ^b ±0.01	0.56 ^a ±0.21	0.01 ^b ±0.00	0.044±0.04	0.16±0.06
	Slaughterhouse	0.06 ^c ±0.01	0.93 ^a ±0.08	0.08 ^b ±0.01	0.007±0.003	0.10±0.001
	LSD	0.05	0.17	0.04	NS	NS

Mean with the same superscript along the vertical arrays indicates no significant difference (P>0.05)

TABLE 4**Heavy metal content of ground water collected from different Location Government Area in CRS**

Location	Fe (mg/ml)	Zinc	Chromium	Copper	Manganese
Akamkpa	0.91 ^a ±0.07	1.20 ^a ±0.03	0.04 ^b ±0.02	0.05 ^b ±0.02	0.006±0.002
Calabar municipal	0.37 ^b ±0.19	0.99 ^b ±0.08	0.0001 ^c ±0.00	0.243 ^a ±0.06	0.10±0.001
Ikom	0.07 ^c ±0.04	0.70 ^c ±0.22	0.07 ^a ±0.03	0.001 ^b ±0.001	0.07±0.02
Ogoja	0.02 ^c ±0.01	1.19 ^a ±0.27	0.02 ^b ±0.01	0.04 ^b ±0.02	0.006±0.001
Yakurr	0.03 ^c ±0.004	0.55 ^d ±0.12	0.09 ^a ±0.02	0.02 ^b ±0.01	0.06±0.03
Yala	0.19 ^b ±0.08	0.89 ^b ±0.07	0.04 ^b ±0.01	0.04 ^b ±0.01	0.05±0.001
LSD	0.05	0.18	0.02	0.04	NS

Mean with the same superscript along the vertical arrays indicates no significant difference (P>0.05)

Discussion

Effect of pollutants on the physicochemical properties of groundwater

The temperature values were within the range for a tropical aquatic system ($<40^{\circ}\text{C}$). The pH quantifies the level of acidity and alkalinity of particular substance or solution. The acidic pH values recorded from most of the dumpsites falls outside the recommended range suitable for drinking. This aligns with [1], who reported pH deviation from the neutral range due to the discharge of acidic industrial effluents. The observed acidity maybe as a result of humic acid formed from decaying organic matter from leachate. Ground water pH has also been known to influence the dissolution of minerals in a groundwater system as well as affects the quality for various purposes. This is in line with reports from [16] and [17], that decaying organic matter contributes to humic acid formation and leaching into groundwater with a resultant increased acidity or alkalinity of the groundwater.

The present study revealed that fluoride which is distributed in the lithosphere and hydrosphere varied significantly among the dumpsites and abattoirs in Yakurr and Calabar Municipality. The concentration of fluoride in the water samples studied falls short of the [18] guideline value for fluoride concentration. This could be attributed to high amount of total dissolved solids in the groundwater in the study area with high volume of cations which combine with fluoride to form complexes, thus making fluoride unavailable in free form. This agrees with the position of [19].

Biochemical oxygen demand (BOD) of dissolved oxygen concentration in natural waters depends on the physical, chemical and biochemical activities in the water body. BOD values obtained from the polluted sites across the study area were lower than the [20] water quality standards but the values were higher than all the control. This could be attributed to the high levels of nutrients, organic loads and total solids content of effluents from these dumpsites and abattoirs. BOD is very

crucial for the survival of aquatic organisms [21]. The depletion of BOD at this discharge points (DP) may also be attributed to the enormous amount of organic loads which required high levels of oxygen for chemical oxidation, decomposition of nutrients or break down thereby depleting available oxygen required for respiration. Similar findings have been reported from abattoir effluent by [22, 23].

The electrical conductivity was recorded in high levels at very few discharge points from the study area. The observed values could be attributed to the high levels of conducting elements such as aluminum, fluoride and phosphate. [24], reported also that conducting elements contributed to the high electrical conductivity in a studied dumpsite.

Phosphates can get into water through anthropogenic sources, animal waste, phosphorus rich bedrock, laundry, cleaning, industrial effluents and fertilizer runoff. The present study showed the presence of high levels of phosphates in the dumpsites and abattoirs. The high level of phosphate in the water samples could be due to the leaching of fertilizer residues from agricultural farm lands along the pathways and water bodies, as well as soap and detergent used for washing by slaughterhouse people. This is in line with [24, 25] who recorded other sources of phosphate to include detergents used by the abattoir workers to wash roasted slaughtered animals, and laundry activities of surrounding residents which run-off into the river.

Effect of pollutants on heavy metals contamination of ground water

The relatively high concentrations of heavy metals may be attributed to the salt contaminating nature in some of these locations like Akamkpa with limestone which easily dissolves in water affects ground water. The concentration of the studied heavy metals, iron, zinc, chromium, manganese and aluminum in ground water in all six locations are not above the typical

international standards limits for drinking water. [10] corroborates this in an investigation focused on the quality of groundwater in Karu, Central Nigeria, which revealed that the concentrations of heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) in the groundwater samples were generally within the permissible limits set by the WHO. In contrast, [11], found that the concentrations of heavy metals like arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg) in some water samples exceeded the WHO guidelines, indicating potential health risks.

Iron remains the most abundant element by weight in the earth's crust and the second most abundant metal in the earth crust. The iron concentrations estimated in the groundwater sample collected from the dumpsites and abattoirs are more or less within the range of 0.3 mg/l with exceptions from Akamkpa, Calabar Municipality and Yala dumpsites, which showed iron contents of relatively higher concentrations above the NIS regulation. This finding is in agreement with the reports of [26].

Conclusion

Unhygienic water is detrimental to human health and affects the physiological features of humans. The result of this investigation shows clearly that the physical, chemical, and heavy metal of the water in the different local government areas examined were high and could be injurious to human health. Therefore, Abattoirs and dumpsites should be sited in distance areas away from residential areas.

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