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Assessment of Fluoride Levels in Groundwater: A Case Study of Ovia North-East, Edo State

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Abstract

Water is essential for human survival, yet over 1.1 billion people, primarily in low and middle-income countries, lack access to safe drinking water. Fluoride, a natural element in groundwater, is beneficial at low concentrations but toxic at higher levels, causing conditions like dental and skeletal fluorosis. Excessive fluoride, a result of natural geological processes, poses significant public health risks, particularly in developing regions. Technologies like adsorption offer potential solutions to mitigate fluoride contamination, though cost and accessibility remain barriers. Addressing these challenges requires comprehensive policies, innovative treatment methods, and community education. This study highlights the importance of safeguarding water quality to promote public health and sustainable development. This study assessed groundwater quality in Ovia North-East, focusing on fluoride levels and other physicochemical parameters. Analysis of borehole water samples revealed that less than 50% met World Health Organization (WHO) standards for fluoride in drinking water (0.5-1.5 mg/l). Some samples exhibited insufficient fluoride, requiring supplementation, while others exceeded the WHO limit, necessitating defluoridation. Activated carbon (palm kernel) was explored as a potential defluoridation method. Additionally, all samples showed pH values outside the WHO recommended range (6.5-8.5), indicating slight acidity and potential heavy metal contamination. Total dissolved solids (TDS) were also generally low, suggesting the need for water treatment. These findings emphasize the importance of monitoring and treating groundwater in Ovia North-East to ensure safe and balanced fluoride intake and address other water quality issues before human consumption. The study underscores the need for appropriate fluoride levels as an essential dietary element.

Keywords: *Fluoride, Groundwater, Adsorption, Contamination.*

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Introduction

Water quality is crucial for health, with fluoride having both beneficial and harmful effects depending on its concentration. At concentrations below 0.5 mg/L, fluoride helps prevent dental caries, while levels exceeding 1.5 mg/L lead to dental and skeletal fluorosis due to its strong affinity for calcium-based structures in bones and teeth [1]. The World Health Organization (WHO) sets a permissible fluoride limit of 1.5 mg/L in drinking water [2], although national authorities are encouraged to adapt standards based on local conditions, such as climate and water intake [3]. Fluoride contamination, mainly in groundwater, occurs due to the weathering and leaching of fluoride-rich minerals from rocks, particularly in sodium bicarbonate-type, calcium-deficient waters, where alkalinity enhances fluoride mobilization [1].

Around 200 million people in 25 countries are at risk of fluorosis due to high fluoride levels in groundwater [4]. Fluoride naturally occurs in all water sources, especially groundwater, with its concentration determined by the geological composition of rocks and fluoride-bearing minerals. In calcium-deficient water, fluoride concentrations remain high, posing significant health risks [7][8]. Fluoride's health benefits in preventing dental caries have been recognized since the 1930s [9], and it plays a role in enhancing enamel structure and inhibiting bacterial acid production, reducing the incidence of dental caries [9][10]. Despite these benefits, dental caries remain widespread, affecting 60-90% of schoolchildren in developed nations, with Latin America and Asia having the highest rates [9].

Water, essential for survival, supports vital biological functions, such as transporting nutrients and removing metabolic wastes [9]. The average daily water intake is about four liters per person, and this requirement doubles in hot, arid climates [12]. Availability of clean water is vital for public health and economic sustainability.

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Contaminated water causes widespread diseases, with the United Nations estimating that 4,400 children under five die daily from waterborne illnesses [14]. Access to clean water is crucial for both health and economic development, with water playing a key role in industrial, agricultural, and recreational activities [14].

The WHO reports that 1.1 billion people in low and middle-income countries lack access to clean water, a challenge that disproportionately affects Asia and sub-Saharan Africa [14]. Meeting the Millennium Development Goal for water supply by 2015 required an additional 260,000 people gaining access to improved water daily [14]. This demonstrates the growing need for effective water supply systems to ensure public health and development.

The aim of this study is to determine the concentration and the remedial action of fluoride level in borehole water. In other to achieve the aim, the following objectives were considered;

i. investigate the physico-chemical and microbiological characteristics of borehole water around the study area
ii. determine the fluoride concentration in selected borehole water samples around the study area
iii. Study the health implications of the amount of fluorine in drinking water on people living within and beyond the study area
iv. Analyse and compare the results of the water quality parameters to notable water standards such as WHO and NSDWQ.
v. Adopt adequate preventive measures in order to reduce fluorine in cases of excessive dosage in drinking water.

Health Effects of Fluoride

Fluoride has both positive and negative health effects, depending on the amount.

Potential benefits:

1. It helps prevent tooth decay
2. May help with bone density and reduce fracture risk
3. Slows down bacterial growth and plaque formation

Potential risks & side effects:

1. Dental fluorosis
2. Skeletal fluorosis
3. People with kidney disease may have difficulty processing excess fluoride, leading to accumulation in the body
4. Some studies suggest potential links to cognitive effects, but research is ongoing

De-fluoridation

Continued consumption of water with fluoride levels above 1.5 mg/l. can result in fluoride related diseases such as fluorosis. Therefore, there is dire need to control intake of fluorides. In order to remove excess fluoride in water, it is essential to determine and monitor the causal factors of enrichment of fluoride concentration in water (Ahmed et al., 2003). The removal of fluoride from potable water has seen many attempts over the years, using a wide variety of materials giving various efficiencies. De-fluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes (Bulusu, 1979). Adsorption is the most popular method for treatment of fluoride polluted water. However, commercial adsorbents which are expensive and require frequent regeneration, limits application of the technology in most developing countries (Haron& Yunus, 2001). Thus, more affordable and easy-to-use de-fluoridating media is therefore desired. The most commonly used method is Nalgonda technique, where alum is mixed with lime at the ratio 700/300 mg/L, it was a test at a research station in Arusha, Tanzania and reduced fluoride concentration from 21 to 5 mg/L at pH 6.9 (Bregnhoj, 1995). Clays, ion exchange resins, activated carbons, sulphonated coals, magnesium compounds, serpentine, iron and aluminium salts have also been applied (Bulusu, 1979). The use of cartridge filter which is packed with bone char has been found to have, efficiency of about 99.5% (Mavura et al., 2004). The bone char method has not been accepted by some communities and use of natural plant materials have been tried such as Moringa Oleifera seeds and rice husks (Vivek et al., 2011). Moringaoleifera seed consists chemical compounds like 4-(4-O-acetyl- a-l-rhamnopyranosyloxy)benzyl isothiocyanate,4 (arhamnopyranosyloxy)benzyisothiocyanate, niazimicin, pterygospermin benzylisothiocyanate, and 4-(a-L-rhamnopyranosyloxy)benzyl glucosinolate and several studies reported on the performance of Moringaoleifera seeds as a primary coagulant, coagulant aid and conjunctive with alum (Jed & Fahey, 2005). Studies conducted in India, have further demonstrated Moringaoleifera seeds to have remarkable de-fluoridation efficiency, even better than that of activated alumina (Subramanian et al., 1992, Ranjan et al., 2009). Desirable characteristics of de- fluoridation processes include cost effectiveness, easiness to be operated (by local population), independent of influences of such factors as fluoride concentration, pH (acidity/alkalinity) and temperature, no effect on taste of water, and not requiring the inclusion of other undesirable substances (e.g.. aluminum) for treatment of water (Hardman et al., 2005).

2.7 The Remedial Action in Normalizing Borehole Water that Contains High or Low Level of Fluoride

In drinking waters with high concentrations of fluoride, treatment of these waters is necessary in order to eliminate any negative effects on the mass population. Three specific treatments have been deemed successful in the removal of fluoride from drinking borehole water.

2.7.1 Coagulation

Coagulation Chemical coagulation is a treatment process commonly used for surface waters. In this process, the chemical coagulant which is usually aluminum or iron salts, are placed in the raw water under specific dosages and conditions to form a solid Blocculent or flukes that may be easily filtered from the water (Fawell et al., 2006). The precipitated floc removes the dissolved fluoride contaminant by charge neutralization, adsorption and entrapment. This process is also known as the Nalgonda process that was developed for low-income African households (Fawell et al., 2006).

This process will remove fluoride up to 50% and possibly in ore depending on the nature and degree of the fluoride content in the water (Fuwell et al, 2006).

2.7.2 Activated Alumina

Activated alumina is used in a treatment process to filter fluoride in drinking water. It is made of aluminum oxide and has a very high surface area to weight ratio allowing it to have many small pores that run through it (Fawell et al, 2006). This process will have a success rate of up to 80% removal of fluoride with less than 1 mg/l, of fluoride content left in the water (Fawell et al, 2006).

De-fluoridation

Continued consumption of water with fluoride levels above 1.5 mg/l. can result in fluoride related diseases such as fluorosis. Therefore, there is dire need to control intake of fluorides. In order to remove excess fluoride in water, it is essential to determine and monitor the causal factors of enrichment of fluoride concentration in water (Ahmed et al., 2003). The removal of fluoride from potable water has seen many attempts over the years, using a wide variety of materials giving various efficiencies. De-fluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes (Bulusu, 1979). Adsorption is the most popular method for treatment of fluoride polluted water. However, commercial adsorbents which are expensive and require frequent regeneration, limits application of the technology in most developing countries (Haron& Yunus, 2001). Thus, more affordable and easy-to-use de-fluoridating media is therefore desired. The most commonly used method is Nalgonda technique, where alum is mixed with lime at the ratio 700/300 mg/L, it was a test at a research station in Arusha, Tanzania and reduced fluoride concentration from 21 to 5 mg/L at pH 6.9 (Bregnhoj, 1995). Clays, ion exchange resins, activated carbons, sulphonated coals, magnesium compounds, serpentine, iron and aluminium salts have also been applied (Bulusu, 1979). The use of cartridge filter which is packed with bone char has been found to have, efficiency of about 99.5% (Mavura et al., 2004). The bone char method has not been accepted by some communities and use of natural plant materials have been tried such as Moringa Oleifera seeds and rice husks (Vivek et al., 2011). Moringaoleifera seed consists chemical compounds like 4-(4-O-acetyl- a-l-rhamnopyranosyloxy)benzyl isothiocyanate,4 (arhamnopyranosyloxy)benzyisothiocyanate, niazimicin, pterygospermin benzylisothiocyanate, and 4-(a-L-rhamnopyranosyloxy)benzyl glucosinolate and several studies reported on the performance of Moringaoleifera seeds as a primary coagulant, coagulant aid and conjunctive with alum (Jed & Fahey, 2005). Studies conducted in India, have further demonstrated Moringaoleifera seeds to have remarkable de-fluoridation efficiency, even better than that of activated alumina (Subramanian et al., 1992, Ranjan et al., 2009). Desirable characteristics of de- fluoridation processes include cost effectiveness, easiness to be operated (by local population), independent of influences of such factors as fluoride concentration, pH (acidity/alkalinity) and temperature, no effect on taste of water, and not requiring the inclusion of other undesirable substances (e.g.. aluminum) for treatment of water (Hardman et al., 2005).

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Specific Treatments:

1. coagulation
2. Activated Alumina
3. membrane ptocess

Coagulation

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Membrane Process

The most significant processes in water treatment for membrane processes include reverse osmosis, ultra-filtration, micro-filtration, and nano-filtration (Fawell et al., 2006). These processes are now recently being applied to the treatment of drinking water. Membrane operations generally utilize artificial membranes to separate the mixtures and Capture the undesired material. This process is successful in fluoride removal from drinking water up to 80% or more, leaving the water with a fluoride content of less than 1 mg/L (Fawell et al., 2006).

2.8 Treatment of Low Concentrations of Water Fluoridation

Water fluoridation is the process of adding fluoride to drinking water to help reduce the risk of tooth decay in the population. The World Health Organization (WHO) recommends fluoride levels in drinking water within the range of 0.5–1.5 mg/L, depending on climate and water consumption patterns. The addition of fluoride typically occurs within the range of 0.7–1.2 mg/L, but the recommended value for artificial fluoridation is 0.5–1.0 mg/L (Murray, 1986). In the United States, the U.S. Public Health Service (PHS) currently recommends an optimal fluoride concentration of 0.7 mg/L to balance the benefits of preventing dental caries while minimizing the risk of dental fluorosis. Fluoride is commonly added in the form of sodium hexafluorosilicate (Na_2SiF_6) or hexafluorosilicic acid (H_2SiF_6).

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2.8 Treatment of Low Concentrations of Water Fluoridation

Water fluoridation is a process of adding fluoride to the drinking water in order to eliminate or reduce the Chances of tooth decay in the population. Minimum recommended values of fluoride within the drinking water to reduce tooth decay. have been denied by both WHO and EPA to be 0.5 mg/L. The addition of fluoride typically occurs within the range of 0.7-1.2 mg/L in the form of sodium hexa- fluorosilicate or hexa-fluorosilicic acid, however the recommended value for artificial fluoridation is 0.5-1.0 mg/L by WHO (Murray, 1986).

Materials and Method

Description of the Study Area

Ovia North-East LGA, headquartered in Okada, spans 2,301 km² in Edo State's central province, between longitudes 5° 45'–6° 15' E and latitudes 5° 15'–6° 45' N. The Ovia River traverses its communities. Benin City, within the rainforest zone, receives 1,500–2,500 mm annual rainfall, with temperatures averaging 25–28°C. The area lies on the Benin Formation, featuring porous sand and clay/shale interbeds with high groundwater retention. Benin City experiences a rainy season (March–October) and a dry season (November–February) with harmattan winds. Global warming has caused irregular rainfall, with peaks in July and September. Its population is approximately 1.75 million (2015 projection).

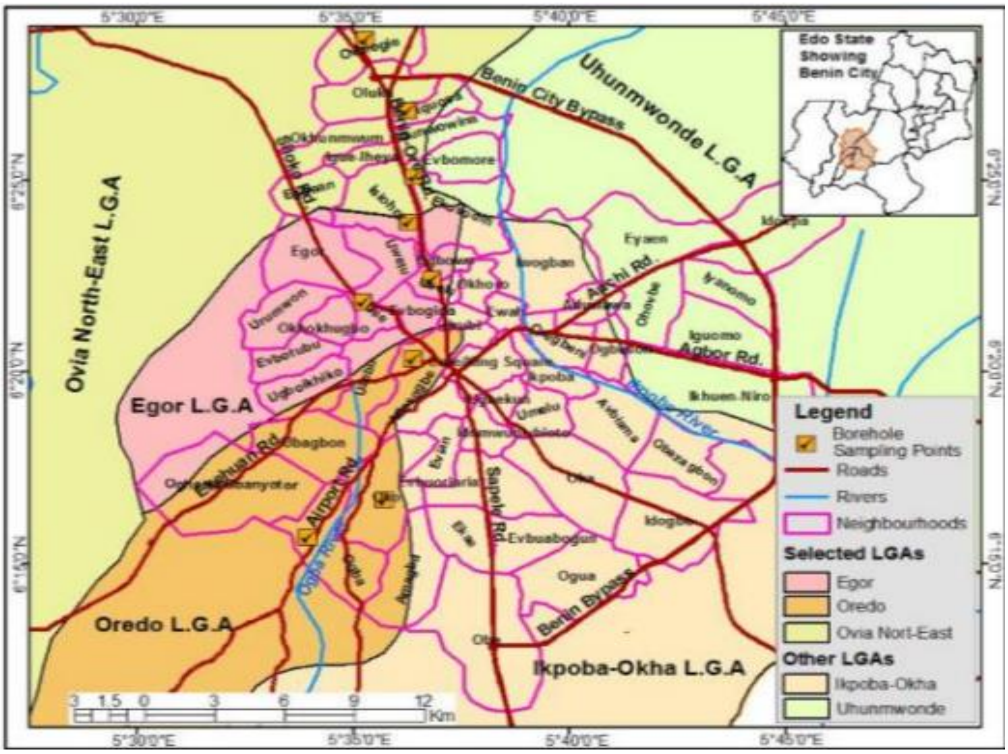

Figure 1: Map of Benin City showing Ovia North-East LGA and other Local Government Areas

The population development of Ovia North East as well as related information and services (Wikipedia, Google, images).

Name	Status	Population Census 1991-11-26	Population Census 2006-03-21	Population Projection 2022-03-21
Ovia North East	Local Government Area	121,769	155,344	229,500
Nigeria	**Federal Republic**	**88,992,220**	**140,431,790**	**216,783,400**

Source: National Population Commission of Nigeria (web), National Bureau of Statistics (web).

Water Sample Collection

Water samples were collected in sterilized 150 cl bottles from ten locations: Okada, Uhen, Oluku, Iguoshodin, Utoka, Oghede, Utese, Ogbese, Isiuwa, and Ora. Groundwater taps ran for 5 minutes before sampling to ensure representativeness. Bottles were filled, tightly sealed, labeled, and accompanied by an information form. Samples were promptly transported to the laboratory for analysis, with all bottles properly cleaned and sterilized beforehand.

The "Manual Borehole Sample Collector" method was used, collecting water samples from frequently used supplies near residents. Samples were transported to the laboratory within 1 to 30 days for fluoride testing, as no special preservation is required. A chain-of-custody form documented relevant details;

- **a.** Sampling location
- **b.** Sample identification number
- **c.** Type of test or analytical procedure
- **d.** The name of the person who handed over the sample.
- **e.** The date and time of both sample collection
- **f.** Sample relinquishment.

Estimation of Fluoride in Groundwater by Spectrophotometric Technique

A sensitive spectrophotometric method was developed to determine fluoride in groundwater using an aluminium-resorcin blue complex. Fluoride reacts with the colored complex to form a colorless aluminium fluoride complex, releasing a free ligand. This approach utilizes fluoride's interaction with colored metal-chelate complexes, resulting in either mixed-ligand complexes or colorless metal fluoride complexes with distinct free ligand colors.

Chemical Reagents

- **a.** Aluminium Nitrate ($Al(No_3)_3.9H_2O$) AR grade
- **b.** Eriochrome Black T
- **c.** Sodium Fluoride (NaF)

Instruments

- **a.** UV/VIS spectrophotometer (Searchtech 7215)
- **b.** 100ml measuring cylinder
- **c.** 250ml beaker
- **d.** 100ml and 1000ml volumetric flask
- **e.** Test tubes and test tube rack

Preparation of Solutions

Stock NaF Solution (1000 mg/L): A stock solution was prepared by dissolving 0.221 g of NaF in 100 mL of distilled water. It was stored in plastic bottles in a refrigerator until use. Calibration standards were created through serial dilution for fluoride level measurements during parameter optimization.

Al-EBT Complex Formation: $1x10^{-3}$ M solutions of $Al(NO_3)_3$ and EBT were prepared using 0.1 g of $Al(NO_3)_3 \cdot 9H_2O$ and 0.12 g of EBT, respectively. Mixing equal volumes of both solutions formed an Al-EBT complex with a concentration of $1x10^{-5}$ M.

Analytical Procedure

Fluoride concentration was measured using a UV-VIS spectrophotometer at 450 nm. A 2 mL stock solution of Al-EBT complex was mixed with 0.2–1 mL of fluoride solution, and the absorbance change was recorded. A standard curve, plotting absorbance against fluoride concentration, determined the molar extinction coefficient. For water samples, 2 mL of the sample was combined with 2 mL of the Al-EBT complex, and absorbance at 450 nm was measured. Fluoride concentration was calculated using the formula: Fluoride Concentration = (1/Slope) x Absorbance.

Treatment of Water Using Activated Carbon

Activated carbon adsorbents were prepared from palm kernel shells. The shells were carbonized in a pyrolysis reactor at 500°C to remove moisture, hydrocarbons, and other gases. The resulting char was then activated with steam at 900°C for 2 hours, with temperatures monitored using a k-type thermocouple. For treatment, varying amounts of activated carbon (1g, 2g, 3g, 4g, and 5g) were added to separate 100 ml plastic bottles. Each bottle received 100 ml of a high-fluoride water sample. The mixtures were agitated on a rotary shaker for 60 minutes, allowed to settle, and then filtered using Whatman No. 42 filter paper. The residual fluoride concentrations in the filtered solutions were subsequently measured using a UV/VIS spectrophotometer.

Results and Discussion

Fluoride in drinking water has significant implications for public health, with both deficiency and excess posing risks. This study investigates groundwater quality in Ovia North-East, focusing on fluoride concentrations and their adherence to World Health Organization (WHO) guidelines. The presence of other physicochemical parameters and their impact on potability are also assessed.

Sources of Water: Bore-hole
Time of Collection: 4:00pm to 6:05pm
Date of Collection: 18th February, 2024.
Local Government: Ovia North-East, Edo State.
Table 1 shows the fluoride levels of each sample, the results were gotten from the laboratory tests.

Table 1: Analysis of Fluoride levels of Groundwater

Sample ID	Abs	F (mg/l)
Iguoshodin	0.016	0.777
Isiuwa	0.001	0.049
Oghede	0.016	0.777
Okada	0.003	0.146
Oluku	0.002	0.097
Ora	0.033	1.602
Uhen	0.002	0.097
Uhiere	0.001	0.049
Utese	0.022	1.068
Utoka	0.034	1.650

Table 2 shows the removal of fluoride from raw water using different grams of activated carbon

Table 2: Analysis of defluoridation using activated carbon Calculations

Sample ID	Abs	F (mg/l)
Raw	0.038	1.845
1g	0.025	1.214
2g	0.019	0.922
3g	0.016	0.777
4g	0.014	0.680
5g	0.012	0.583

F (mg/l) = SR x Abs
(Eq.1)
Where; F = Concentration; SR = Slope reciprocal; Abs = Absorbance

Table 3: Calibration

F (mg/l)	Abs
0.0	0.000
1.0	0.020
2.0	0.039
3.0	0.061
4.0	0.083
5.0	0.106
$\sum x = 15$	$\sum y = 0.309$
SR =($\sum x/\sum y$)	SR = 48.54369

Figure 2 shows the graph of absorbance against concentration. it shows the curve for the behavioural pattern of when activated carbon is added at different amounts

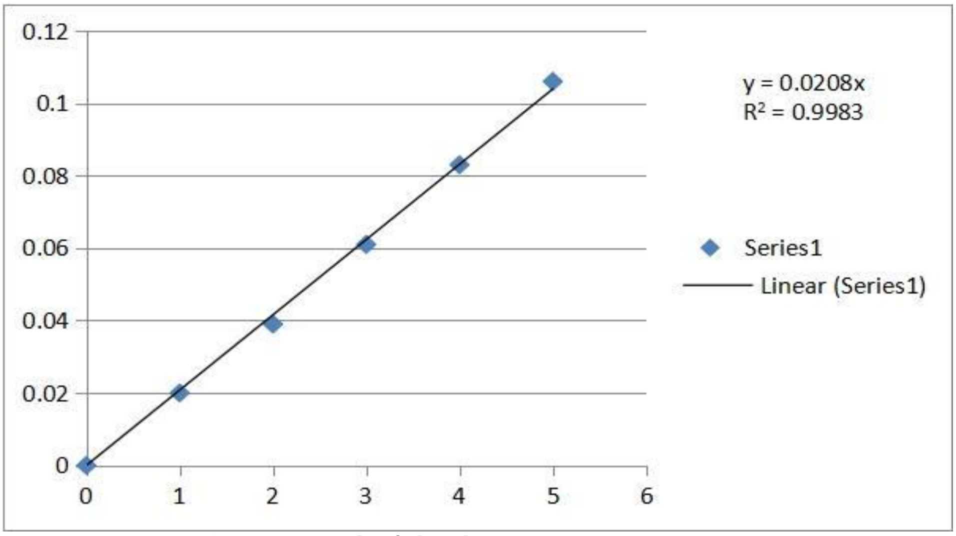

Figure 2: Graph of absorbance against concentration

Table 4 shows some of the physiochemical parameters of groundwater analysis such as Fluoride (fl), potential of hydrogen (pH), Electrical conductivity (EC) and the total dissolved Oxygen(TDS)

Table 4: Physiochemical parameter analysis of groundwater quality in Ovia-North East LGA

SAMPLE ID	F (mg/l)	pH	EC	TDS
Iguoshodin	0.777	5.9	22	11
Isiuwa	0.049	6.5	28	14
Oghede	0.777	5.5	28	13
Okada	0.146	5.6	18	18
Oluku	0.097	5.9	24	12
Ora	1.602	7.5	376	188
Uhen	0.097	6.1	24	13
Uhiere	0.049	6.0	8	4
Utese	1.068	5.4	36	18
Utoka	1.650	5.6	20	10

F = Fluoride
EC = Electrical Conductivity
TDS = Total Dissolved Oxygen

Groundwater samples were analyzed for fluoride, pH, electrical conductivity (EC), and total dissolved solids (TDS). Fluoride levels ranged from 0.5 to 1.5 mg/L, with only four of ten samples meeting the WHO standard (0.5–1.5 mg/L). Five samples required fluoride supplementation, while one exceeded the maximum limit and needed defluoridation, achieved using activated carbon from palm kernel (Table 3).

pH levels for all samples were outside the WHO acceptable range (6.5–8.5), indicating slight acidity potentially linked to anthropogenic activities. This acidity could increase heavy metal solubility and toxicity, affecting taste and water quality. TDS values were mostly low, with only one sample within the WHO preferred range (50–300 mg/L), emphasizing the need for further treatment.

Conclusion

Analysis of borehole water samples revealed that less than half of the study area's water sources are suitable for consumption due to either insufficient or excessive fluoride levels. This highlights the importance of fluoride as an essential dietary element, requiring appropriate concentrations in both food and water. Consequently, the study recommends that drinking water from Ovia North-East be treated before human consumption to ensure safe and balanced fluoride intake.

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