Fluoride and Chloride Ions Concentration and their Health Implications in Groundwater within Bwari Area Council, Abuja, Nigeria

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ABSTRACT: According to the World Health Organization, fluoride in drinking water, either below or above the established permissible range, can adversely affect oral health, including tooth decay and dental fluorosis. The objective of this study was to evaluate fluoride and chloride ion concentration and their health implications in groundwater within Bwari Area Council, Abuja, Nigeria using ion-selective electrode potentiometric titration for fluoride ion and Argentometric titration for chloride ion determinations. The results showed a high fluoride concentration in well water samples ranging from 0.126 mg/L to 0.216 mg/L, compared to borehole water samples ranging from 0.013 mg/mL to 0.052 mg/L. Among the chloride concentrations, the highest levels were observed in the well water sample A (96.09 mg/L), followed by borehole samples, A (63.08 mg/L) and B (49.35 mg/L). The lowest chloride concentration was recorded in the borehole sample H (11.82 mg/L). Notably, both well and borehole water sources in the studied communities had fluoride concentrations below the established minimum WHO standard (0.5 mg/L). The chloride concentrations in the groundwater samples from the study area fell within WHO standards (< 250 mg/L). The results from this study suggest that the continuous consumption of water from these community sources, without additional sources of fluoride, may increase the risk of tooth decay. Therefore, addressing this issue and ensuring appropriate water treatment measures is vital for maintaining optimal oral health in the region.

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Fluorine and chlorine are members of the halogens, which are found in group seven (7) of the periodic table. They are non-metallic elements. Other members of the group include bromine, iodine, and astatine. Chlorine and fluoride can easily bind to other elements due to their high reactivity (Bratovic and Odobasic, 2011; Pradhan et al., 2023; Ning et al., 2023). Fluorine accounts for about 0.3 g/kg of the Earth’s crust. It is known to be a poisonous yellow gas with an irritating smell. It is a strong oxidizing agent (Sunitha et al., 2014). In terms of reactivity, fluorine is the most reactive element found on earth. The high reactivity of fluorine is due to its high electronegative power and relatively low dissociation energy (Deshmukh et al., 1995; Liang et al., 2013). It can react directly with all other non-metals except nitrogen, helium, neon, and argon to form fluorides, for example, phosphorus pentafluoride, PF₅ and sulphur hexafluoride, SF₆.
Fluoride and Chloride Ions Concentration and their Health.

Fluorine can react with any compound containing hydrogen to form hydrogen fluoride (HF). When fluorine (F) reacts with water (H₂O), hydrogen fluoride (HF) and oxygen gas are formed. Fluorine may exist in water, air, and food substances as fluoride ions (F⁻) with an oxidation state of -1 (WHO, 2004; Fuge, 2019; Wang et al., 2023). Fluorides come naturally into water by dissolving minerals that contain fluor, such as fluorite (CaF₂),apatite (Ca₅(PO₄)₃F), cryolite (Na₃AlF₆) and fluorapatite (Ca₅(PO₄)₃F). Again, rocks rich in alkali metals have a larger content of fluoride than other volcanic rocks (Pollick, 2004; Uma et al., 2016). Georgius Agricola, in the year 1530 described fluorite, consisting mainly of calcium fluoride as the major source of fluorine in the form of fluoride ions as cryolite (Na₃AlF₆) until the major deposits in Greenland ran out in 1987 (Sunitha et al., 2014). Fluorides may be found in the environment and constitute 0.06 – 0.09 % of the earth’s crust. They are not found naturally in the air in large quantities.

The average concentration of fluoride in air is in the magnitude of 0.5 mg/m³. Fluoride is found more frequently in different sources of water but with higher concentrations in groundwater due to the presence of fluoride-bearing minerals (Wang et al., 2023). The average fluoride concentrations in seawater are approximately, 1.3 mgL⁻¹ (Fuge, 2019; Wang et al., 2023), in ground waters at concentrations up to 67 mg/L, and in most surface waters at concentrations less than 0.1 mg/L. Fluoride is also found in foods particularly fish and tea (Lennon et al., 2004; Malde et al., 1997; Chowdhury et al., 2018). Chlorine is the most important element in the halogen family. Chlorine was first discovered by Scheele in 1774 when he heated some concentrated hydrochloric acid with manganese (IV) oxide (Lennon et al., 2004; Gray et al., 2007; Chang, 2022). In 1810, Davy named the gas chlorine, which originated from the Greek word “chloros” which means greenish-yellow (Lennon et al., 2004; Gray et al., 2007; Chang, 2022). Chlorine does not occur freely in nature because it is too reactive. It is usually found in a combined state as chlorides, such as sodium chloride (NaCl), and calcium chloride (CaCl₂). Chlorine reacts with water (H₂O) to form hydrochloric acid (HCl) and hypochlorous acid (HOCl) (Gray et al., 2007; Chang, 2022). Sodium chloride is a common constituent of some water sources, especially well water. The concentration of sodium chloride above 140 ppm is considered to be toxic for plants, and a value of 600 mg/L has been set as the tolerance limit for irrigation water (Tattini et al., 1992; Sayyed et al., 2011; Hoque et al., 2018). Chloride occurs in all-natural water in widely varying concentrations. The chloride content in water normally increases as the dissolved minerals containing chloride increase. Upland and mountain supplies usually are quite low in chloride, whereas rivers and groundwaters usually have considerable amounts of chlorides. The occurrence of chloride in groundwater can be from both natural and anthropogenic sources, such as runoff containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas (Vengosh and Pankratov, 1998; Sameer et al., 2011; Khatri and Tyagi, 2015).

Chloride ions in large quantities are present in seawater and sediments of the Earth’s crust where it is associated with ions such as Na⁺, K⁺; and Mg²⁺, and are widely spread in nature as salts of sodium chloride (NaCl), potassium chloride (KCl), and calcium chloride (CaCl₂). Chlorides are leached from various rocks into soil and groundwater by weathering. Man’s exposure to chloride in the air has been reported to be insignificant (Kelly et al., 2012; Sayyed and Bhosle, 2011). Chloride ion (Cl⁻) is generally mobile; chloride concentration in groundwater is consistently increasing, due to the presence of the minerals containing chlorine. Chloride levels in unpolluted waters are generally below 10 mg/litre and sometimes even below 1 mg/L (Sameer et al., 2011; Kelly et al., 2012) Chloride in water may be significantly increased through the treatment processes in which chlorine or chlorides used as a disinfectant. Studies have shown that the level of fluoridation in drinking water can have a great impact on oral health and skeletal formation.

For example, fluoride levels below the minimum WHO standard and Nigerian standard for drinking water quality (NSDWQ) of 0.5mg/L can lead to tooth decay if the water is consumed without any supplementary fluoride intake (Pollick, 2018; Benson et al., 2019). Fluoride levels above the maximum WHO standard (1.5 mg/L) may lead to dental fluorosis, while fluoride levels far above the maximum WHO standard may lead to skeletal fluorosis (Srivastava et al., 2011; Shruithi and Anil, 2018). In the case of chloride, no health-based guideline value is proposed for chloride in drinking water. However, high levels of chloride can corrode and weaken metallic piping and fixtures, give a “salty” taste to the drinking water, damage household appliances, and boilers, and, if the water is being used for irrigation, it may inhibit the growth of vegetation (Cotruvo, 2017). It is therefore important to assess the fluoride and chloride concentrations of any consumable water sources. Hence, the objective of this paper was to evaluate fluoride and chloride ions concentration and their health implications in groundwater within Bwari Area Council, Abuja, Nigeria.

ISAH, S. B; UDOURIOH, G. A; MATTHEWS-AMUNE, C. O; NWEKE, P. I.
MATERIALS AND METHODS

Equipment and Reagents: The following apparatus and instruments were used: pH meter using and burette. The reagents and chemicals used include stock fluoride solution 1000 mg/L, standard fluoride solution, ionic strength adjuster solution TISAB III, potassium chromate indicator (K₂CrO₄), standard silver nitrate solution (AgNO₃), and standard sodium chloride solution (NaCl).

Sample Collection and Preparation: Water samples were collected using clean 1-liter polyethylene plastic bottles. The samples were collected from six (6) wells and eight (8) boreholes from different locations on the same day making a total of fourteen (14) samples. Sample from well A, B, C and D were collected from Gaba I, Gaba II, Zuma II, and Zuma I respectively, while samples from wells E and F were collected from Bwari at different locations. The Borehole water samples were collected in the same order and labelled borehole water samples (BWS) A, B, C, D, E, F plus G and H collected from Veritas University Abuja. All the samples were stored in the refrigerator and later used for the analysis.

Standardization of Fluoride: 30 ml of 1 mg/L and 10 mg/L of standard fluoride solution were collected in each of the two 50 ml polyethylene beakers; 3 ml of ionic strength adjuster solution was added to each of the beakers. 30 ml of distilled water was collected in another beaker and 3 ml of ionic strength adjuster solution was added. The instrument was switched on and the appropriate procedures for operation were followed, the instrument was standardized with the standard solutions, and the slope value was observed.

Fluoride Determination by Ion Selective Meter: After the standardization of the instrument, 30 ml of water samples were taken differently from each of the samples and were all analyzed directly from the ion-selective meter, and the results were recorded accordingly.

\[ \text{Fluoride (mg/L)} = \text{IMR (mg/L)} \times \text{DF} \]

Where IMR = Ion meter reading mg/L; DF = Dilution factor

Chloride Determination by Argentometric Titrations: All glass apparatus to be used were washed and rinsed with distilled water. A solution of 0.01 M silver nitrate was prepared in 500 ml standard volumetric flask. 50 ml burette was clamped on a retort stand, and the solution of 0.01 M silver nitrate was used to fill the burette up to the initial point and was titrated against 100 ml of distilled water (blank), the blank titration was repeated twice and values were recorded. A 100 ml measuring cylinder was used to measure 100 ml of water sample for the first sample into 3 different 250 ml conical flasks. 5 drops of potassium dichromate indicator solution were added to each 250 ml conical flask containing the water samples. A yellow color solution was observed at the initial point. The solution of 0.01 M of silver nitrate was titrated against the solution of 100 ml water sample and the 5 drops of potassium dichromate in the conical flask. A brick-red color was observed at the endpoint. The titration was repeated two times and the average titer value was calculated. The same procedure was used for each sample of water and the average titer value for each sample was recorded.

\[ \text{Chloride (mg/L)} = \frac{T \times M \times \text{MM} \times 1000}{V} \]

Where \( T \) = Average titration volume, \( M \) = Molarity of silver nitrate, \( \text{MM} \) = Molar Mass of Chloride, and \( V \) = Volume of sample used.

RESULTS AND DISCUSSION

The results of the study are presented in Tables 1 and 2, and Figures 1 to 6. Table 1 shows the fluoride and chloride concentrations in well water samples (WWS) while Table 2 presents the fluoride and chloride concentrations for borehole water samples (BWS) obtained at different locations within the study area.

Table 1: Fluoride and Chloride concentrations (mg/L) of Well water samples from Bwari Area Council communities

<table>
<thead>
<tr>
<th>S/N</th>
<th>Well Water Sample (WWS)</th>
<th>Fluoride concentration (mg/L)</th>
<th>Chloride concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WWS A</td>
<td>0.148</td>
<td>30.07</td>
</tr>
<tr>
<td>2</td>
<td>WWS B</td>
<td>0.126</td>
<td>15.37</td>
</tr>
<tr>
<td>3</td>
<td>WWS C</td>
<td>0.216</td>
<td>96.09</td>
</tr>
<tr>
<td>4</td>
<td>WWS D</td>
<td>0.190</td>
<td>21.90</td>
</tr>
<tr>
<td>5</td>
<td>WWS E</td>
<td>0.155</td>
<td>27.79</td>
</tr>
<tr>
<td>6</td>
<td>WWS F</td>
<td>0.186</td>
<td>24.03</td>
</tr>
</tbody>
</table>

Table 2: Fluoride and Chloride concentrations (mg/L) of Borehole water samples from Bwari Area Council communities

<table>
<thead>
<tr>
<th>S/N</th>
<th>Borehole Water Sample (BWS)</th>
<th>Fluoride concentration (mg/L)</th>
<th>Chloride concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BWS A</td>
<td>0.034</td>
<td>63.08</td>
</tr>
<tr>
<td>2</td>
<td>BWS B</td>
<td>0.052</td>
<td>49.35</td>
</tr>
<tr>
<td>3</td>
<td>BWS C</td>
<td>0.019</td>
<td>15.02</td>
</tr>
<tr>
<td>4</td>
<td>BWS D</td>
<td>0.038</td>
<td>13.14</td>
</tr>
<tr>
<td>5</td>
<td>BWS E</td>
<td>0.021</td>
<td>11.96</td>
</tr>
<tr>
<td>6</td>
<td>BWS F</td>
<td>0.013</td>
<td>17.15</td>
</tr>
<tr>
<td>7</td>
<td>BWS G</td>
<td>0.018</td>
<td>19.17</td>
</tr>
<tr>
<td>8</td>
<td>BWS H</td>
<td>0.025</td>
<td>11.82</td>
</tr>
</tbody>
</table>

Figures 1 and 2 compare the fluoride concentrations in well water samples, borehole water samples with the
WHO standard and the Nigerian Standard for Drinking Water Quality (NSDWQ) respectively. Figure 3 compares the fluoride concentrations in well and borehole water samples. Similarly, Figures 4 and 5 compare the chloride concentrations in well water samples, borehole water samples with the WHO standard and the Nigerian Standard for Drinking Water Quality (NSDWQ) respectively while Figure 6 compares the chloride concentrations in well and borehole water samples.

The trends of fluoride concentrations in the well water samples (Fig 1) are WWS C (0.216) > WWS D (0.190) > WWS F (0.186) > WWS E (0.155) > WWS A (0.148) > WWS B (0.126) with WWS C (0.216) recording the highest concentration while the WWS B (0.126) records the lowest concentration of fluoride. The variations observed may be attributed to anthropogenic and industrial contaminations or geological inputs. In any case, the comparison of the fluoride level with the permissible established WHO minimum standard and NSDWQ shows that the well water record fluoride concentrations below the established minimum range of 0.5 – 1.5 mg/L. For the borehole water samples (BWS) the fluoride concentrations (mg/L was in the order BWS B (0.052) > BWS D (0.038) > BWS A (0.034) > BWS H (0.025) > BWS E (0.021) > BWS C (0.019) > BWS G (0.018) > BWS F (0.013) (Fig. 2). The BWS B (0.052) shows the highest concentration of fluoride in the list of boreholes analyzed while BWS F (0.013) shows the lowest concentration. A comparison of the fluoride concentration in well water samples (WWS) with those of borehole water samples (BWS) (Fig. 3) shows clearly that the concentrations of fluoride determined from the water samples are higher in well water samples than the borehole water samples. This may be attributed to the presence of minerals such as fluorite (CaF₂), apatite (Ca₅(PO₄)₃F), cryolite (Na₃AlF₆) and fluorapatite (Ca₅(PO₄)₃F) in a mineable depth of the earth crust in which well water may have direct contact with than the borehole water (Malago et al., 2017; Uriah et al., 2014). The depths of the borehole water are more often deeper than those of wells which may limit the contact with these minerals (Malago et al., 2017; Uriah et al., 2014). Again, the dissolving minerals that contain Fluor and rocks that are rich in alkali metals and often found around the well depths also have a larger content of fluoride than other volcanic rocks (Babu et al., 2016)
In the comparison of the overall fluoride concentration of both the well water samples (WWS) and borehole water samples (BWS) with the WHO standard and Nigerian standard for drinking water quality (NSDWQ) (Figs. 1 and 2), the fluoride concentrations are quite below the minimum permissible limit. When fluoride concentration is very low (<0.5 mg/L) in water and is frequently consumed, it causes tooth decay, and when frequently consumed in higher concentration (>1.5 mg/L), it leads to dental fluorosis or mottled enamel (Bardsen et al., 1999; Kisku and Sahu, 2020). Again, when consumed in extremely high concentration (>3.0 mg/mL), it may lead to skeletal fluorosis. Dental fluorosis is a condition that causes changes in the appearance of tooth enamel. It is characterized by hypo-mineralization of tooth enamel caused by ingestion of excessive fluoride during enamel formation (Bardsen et al., 1999; Kisku and Sahu, 2020). Skeletal fluorosis is a health effect of excessive fluoride in bones leading to changes in bone structure which weaken the bone. It is seen in areas with exceptionally high natural fluoride in drinking water. (Srivastava et al., 2011; Shruthi and Anil, 2018) (See Fig 1). More so, when fluoride concentration in water is between 1.5 and 2.0 mg/L, it leads to dental mottling which is characterized by opaque white patches on the teeth and in advanced stages leads to dental fluorosis. Skeletal fluorosis more often occurs when fluoride concentration exceeds 4 to 8 mg/L (Srivastava et al., 2011; Shruthi and Anil, 2018).

From this present study, the concentration of fluorides in all the samples are below 0.5 mg/L, and this indicates the possibility of tooth decay among the people who are using this water if there is no means of eating or consuming other food substances containing fluorides (such as food from plant source), and brushing the mouth with toothpaste at least twice daily (Srivastava et al., 2011).

Furthermore, for the chloride concentration (mg/L) in the well water samples (WWS), it follows the order WWS C (96.09) > WWS A (30.07) > WWS E (27.79) > WWS F (24.03) > WWS D (21.90) > WWS B (15.37) (Fig. 4). From the trend, WWS C (96.09) shows the highest concentration of chlorides in the water samples while WWS B (15.37) shows the lowest chloride concentration. Similarly, the chloride concentration in the borehole water samples (BWS) followed the order: BWS A (63.08) > BWS B (49.35) > BWS G (19.17) > BWS F (17.15) > BWS C (15.02) > BWS D (13.14) > BWS E (11.96) > BWS H (11.82) (Fig. 5). From the trends of chloride concentrations in each sample, BWS A (63.08) has the highest amount of chloride while BWS H (11.82) gives the lowest concentration of chloride. A snapshot comparison of
the chloride concentrations in the well water samples with those of borehole water samples (BWS) (Fig. 6), showed diverse trends with some samples showing an increased concentration of chloride in well water while some show an increase in borehole water. In comparing the results for the chloride concentrations in both the well water samples (WWS) and borehole water samples (BWS) with the WHO standard and NSDWQ (Figs. 4 and 5), the chloride concentration is within the permissible minimum standard (<250 mg/L). This means that the water sources do not pose a threat related to chloride concentration.

**Conclusion:** Groundwater quality assessment is crucial for ensuring the safety of drinking water. This study focused on determining the concentrations of fluoride and chloride ions in well and borehole water samples within Bwari Area Council, Abuja, Nigeria, with inference to its health implications. All fluoride concentrations were below the standard permissible limit, indicating a potential risk of tooth decay if the water was the primary source of consumption. Public awareness and alternative fluoride sources are essential for maintaining oral health within the area.

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