Fluoride Contamination of Shallow Groundwater in Parts of Zango Local Government Area of Katsina State, Northwest Nigeria

Aminu Tukur1, Amadi Akobundu N.2*

1Katsina State Rural Water Supply and Sanitation Agency, Nigeria
2Department of Geology, Federal University of Technology, Minna, Nigeria
*Corresponding author: geoama76@gmail.com

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Abstract
Serious health problems are experienced in many parts of the world due to high concentration of fluoride in drinking water which causes dental and skeletal fluorosis to humans. Zango Local Government Area of Katsina State, Nigeria is one such area where high concentration of fluoride occurs in groundwater. Though there are no major studies with reference to fluoride in the area in the past, the present study was carried out to provide baseline information on groundwater quality in Zango Local Government Area of Katsina State, Nigeria with emphasis on fluoride concentration. A total of 87 groundwater samples each were collected from hand-dug wells and boreholes in the area for both dry and wet seasons, between February 2011 to March 2012 and analyzed for fluoride concentration and other quality parameters at the National Research Institute for Chemical Technology Laboratory Zaria, Nigeria. The fluoride concentration in groundwater of the area ranged between 0.10 to 3.16 mg/l with a mean value of 0.94 mg/l for dry season and between 0.10-1.47 mg/l and an average value of 0.52 mg/l for the rainy season. The low concentration of fluoride in the rainy season is due to the dilution effect of rain-water. The study revealed that about 75% of the groundwater samples in the area that are suitable for human consumption fall within the sedimentary rocks of the Gundumi and Chad Formations as well as the Basement Complex rocks while 25% of the samples with high fluoride concentration above the permissible limit of 1.5 mg/l are from the Younger Granites Suites. Fluorite, a hydrothermal mineral in granite and due to its fast dissolution kinetics, is probably the source of fluoride in the groundwater in the area. The fluoride concentration map developed for the study was in agreement within the interpretation as the area dominated with sedimentary formations show low concentration of fluorite while the region occupy by younger granites show high fluoride concentration. This implies that fluoride-rich groundwater in the area emanates from the granite aquifers and the problem of fluorosis in the area is purely by natural processes. Communities living in the granite/rhyolite dominated region where cases of fluorosis have been observed should discontinue the use of groundwater from the area for domestic and drinking purposes. The Katsina State Government should provide an alternative source of drinking water for the people in the region.

Keywords: Fluoride contamination, groundwater, Zango area, Katsina State, Nigeria


1. Introduction

The chemical composition of groundwater is controlled by many interrelated processes and the understanding of these processes is important for effective groundwater quality assessment and management (Amadi et al., 2013). Fluoride is an electronegative element with dual significance. It helps in the normal mineralization of bones and formation of dental enamel (Chidambaram et al, 2003). Fluoride when consumed in inadequate quantities (<0.5 mg/l) causes health problems like dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially among the children (Fluhler et al, 1982). Also, fluoride when consumed in excess (>1.5 mg/l), it leads to several health complications such as skeletal and or dental fluorosis (Deshmukh et al, 1995). Being a cumulative bone seeking mineral, the resultant skeletal and dental changes/metabolic processes are progressively affected negatively. Fluoride is a typical lithophile element under terrestrial conditions and studies have revealed their association with granitic rocks. It is a major constituent in silicate rocks especially those of late magmatic stages typified in apatite, Fluorspar, Cryolite and Fluorapatite as well as villiaumite and syenites.

According to Omueti (1977), the fixation of the bulk of fluoride as complex hydroxy-silicates and hydroxyalumino-silicates, in which the hydroxyl ions (OH) are largely replaced by fluoride are common in
amphiboles and minerals of the mica family (biotite and muscovite). Fluoride in the groundwater derives from the weathering and subsequent leaching of fluoride-bearing minerals in rocks and soils. A substantial amount of this fluoride is retained in subsoil horizons, where it complexes with Aluminum that is associated with phyllosilicates (Vaish and Vaish, 2002). Larsen and Widdowson (1980) observed that the solubility of fluoride in soils is favoured by pH <5 and >6 values. It appears that the predominant retention mechanism is that of fluoride exchange with the OH group of amorphous materials, such as Al-hydroxides. Studies have shown that weathering of rocks and evaporation of groundwater are responsible for high fluoride concentration in groundwater of an area apart from anthropogenic activities including irrigation which accelerates weathering of rocks (Rao et al, 1993; Murthy et al, 2003; Amadi et al, 2012).

UNICEF estimates that fluorosis is endemic in at least 25 countries across the world including some parts of Northern Nigeria. The difficulties in diagnosing the early stages of fluorosis from the arthritic symptoms results to damage before detectable bone changes are evident (Wagner et al, 1993). The early symptoms are usually misdiagnosed as rheumatoid or osteoarthritis due to similarity in symptoms (Susheela, 1999). Bassin et al, (2006) states that the misdiagnosis of possible skeletal fluorosis, leads to severe disability and damage to the brain resulting in low intelligent quotient. This study examines the fluoride content of well water in different parts of Zango Local Government Area of Katsina, Nigeria with emphasis on the health implications and mitigation techniques. The study is aimed at providing baseline information to stakeholders in the water and health sector, the natural background concentration of fluoride in the groundwater system in the area and the need for government and other stakeholders to take urgent and meaningful steps to reduce the incidence of dental and skeletal fluorosis in the area.

1.1. Study Area Description

![Map of Zango Local Government Area, Katsina State, Nigeria](image)
Katsina State covers an area of about 24,000 km² and located between latitudes 11°08’N and 13°22’N and longitudes 6°52’E and 9°20’E. The state is bounded in the north by Niger Republic, in the east by Jigawa and Kano States, in the south by Kaduna State and in the west by Zamfara State (Figure 1). Katsina State forms part of the extensive plains known as the High Plains of Hausaland. The state is composed of undulating plains which generally rise gently from 360 m around Daura to 600 m around Funtua in the southwest.

Zango Local Government Area (Figure 1) is located at the north-eastern part of Katsina State of North Western Nigeria approximately between latitudes 12°50’N and 13°00’N and between longitudes 8°26’E and 8°44’E. It is located about 100 km east of Katsina town and is accessible through a network of both tarred and untarred roads. It has an area of 601 km² and a population of about 154,743 (Census, 2006). It is bounded in the north by Niger Republic, in the east by Baure Local Government Area, in the south by Jigawa State and in the west by Sandamu Local Government Area. Zango’s uniqueness is extraordinary in the sense that it is the only local government area in Nigeria that is underlain by the following four different lithologies (Older Granites, Younger Granite/Rhyolites, Gundumi Formation and Chad Formation).

1.2. Physiography of the Area

The latitudinal position of Katsina State and its interior location away from the sea determines the climate which is characterized by two main seasons (dry season from November to May and wet season from June to October). Therefore the climate is a hot one with maximum day temperatures reaching 38°C during the peak of the dry season. The area is affected by two wind patterns, the harmattan wind from the Sahara which is responsible for the cool months of December to February (about 24°C) and the Southwest Monsoon Trade Winds blowing across the Atlantic Ocean which is responsible for the rains of June to October (Nigerian Meteorological Agency, 2013). Average relative humidity is put at 42%. Average rainfall is from about 800 mm to 1000 mm (Figure 2).

![Figure 2. Chart of Average Rainfall, Temperature and Relative Humidity from 2003 to 2013 of Zango Local Government Area, Katsina State, Nigeria](image)

1.3. Vegetation

The area is predominantly Sudan Savanna which consists of scattered trees with sparse shrubs and grasses. The trees here grow long tap roots and thick barks that make it possible for them to withstand the long dry season. The grass too has long durable roots which remain underground after stalks are burnt away or wilted in the dry season only to germinate with the first rains. This area has been subjected to many years of bush-burning and over grazing. Trees such as Azadiracha Indica (Neem) and Parkia Biglobosa (Locust Bean) are now being planted to check against desert encroachment and erosion.

1.4. Geological Mapping of the area

Reconnaissance survey was carried out on the study area in order to familiarize the area and identify the sampling points. This was followed by detailed geological investigation of the area in which four main rock types were identified. The lithologies includes: the Gundumi Formation emanating from the Sokoto Basin, the Chad Formation which is part of the Chad basin as well as Granites and Rhyolites from the Basement Complex Rocks and Younger Granites suites (Figure 3).
1.5. Water Sampling

Water samples were collected across the entire local government area. Boreholes, hand-dug wells, and solar powered water schemes were the sources that were sampled for this study. The sampling covers the Gundumi Formation emanating from the Sokoto Basin, the Chad Formation which is part of the Chad basin and the Basement Complex Rocks as well as the Younger Granites suites. A total of 87 water samples each were collected in the dry season and rainy season respectively. The measurement of the following physical parameter such as pH, temperature, conductivity, and turbidity were carried out in-situ (on site) using their appropriate instruments in line with the specified standards (APHA, 1998). Glass and plastic containers were used to collect the samples at each location. Two drops of concentrated
HNO₃ were added to the water samples in the plastic container (Schroll, 1976). The water samples in the plastic containers were used for the determination of major cations and heavy metals while the water samples in the glass container are for the determination of the anions. At each sampling point (Figure 4), the longitude, latitude and elevation were taken with the aid of a global positioning system. All the analysis was analyzed at National Research Institute for Chemical Technology Laboratory Zaria, Nigeria. The determination of the physical parameters was carried out in the field using standard procedures while the analyses of chemical and bacteriological parameters were done in the laboratory. The physical parameters such as pH, electrical conductivity (EC) and temperature were taken in-situ. Anions such as SO₄, PO₄, NO₃, HCO₃, and Cl were determined using titration method while fluoride was determined using colorimetric method. Concentration maps were plotted using the ArcGis version 9.3.

2. Results and Discussion

The result of the water analyses are summarized in Table 1. The pH values ranged between 5.70 to 7.50 with a mean value of 6.45. The values indicate that the water is slightly acidic and this encourages weathering of bedrock and is expected of a basement terrain. The pH value is a good water quality indicator. The conductivity of water is an expression of its ability to conduct an electric current. The concentration of electrical conductivity (EC) ranged from 22.70 to 3050.00 µs/cm with a mean value of 305.04 µs/cm. Temperature is a measure of the degree of hotness or coldness of an area or substance. It is an important water quality parameter that determines the distribution of organism on the environment as well as the solubility of substance in water (Amadi et al., 2012). The temperature value ranged from 28.10°C to 34.50°C with a mean value of 32.32°C. The values ranged between 6.0-126.0 mg/l with a mean value of 23.79 mg/l for dry season. Even though no significant difference was observed between results from the sedimentary and Basement rocks, the results are still higher for samples from the sedimentary terrain. Enrichment of groundwater by bicarbonate is mostly natural via bedrock dissolution due to the contact between groundwater and the host rock. The measured values are within the acceptable limit of WHO, (2006) and NSDWQ, (2007).

The concentration of chloride in the groundwater ranges between 0.0 to 21.62 mg/l with a mean concentration of 7.21 mg/l. These values fall significantly below the permissible limit of 250.0 mg/l (WHO, 2006; NSDWQ, 2007). High chloride content in groundwater may indicate pollution by sewage, effluent or marine source (Amadi et al., 2011; Dan-Hassan et al., 2012). Although the chloride concentrations in the area are within the recommended value, the highest values fall within the granite and rhyolite region, an indication of geogenic source.

The concentration of sulphate varied from 0.06 to 78.65 mg/l with an average value of 11.69 mg/l while the concentration of nitrate ranged between 0.60 to 19.12 mg/l and a mean value of 6.30 mg/l. The value of phosphate for the ranged between 0.01 mg/l to 9.40 mg/l with a mean value of 1.74 mg/l. The concentration of potassium ranged between 0.19 mg/l to 28.22 mg/l while the concentration of sodium varied between 0.07 mg/l to 31.18 mg/l. The concentration of magnesium falls between 0.0 to 3.19 mg/l while calcium has values ranged between 0.03 mg/l to 10.95 mg/l with a mean value of 4.15 mg/l. The concentrations of the cations are within the acceptable limit of Nigerian Standards for Drinking Water Quality. Studies by Amadi et al., (2012) revealed that magnesium in water is better and easily absorbed than dietary magnesium. Calcium is necessary in animals for the formation of strong teeth and bones. There is some evidence to show that the incidence of heart disease is reduced in areas served by a public water supply with a high degree of hardness, the primary constituent of which is calcium (EPA 2001).

Fluoride content in groundwater of the area ranged between 0.10 to 3.16 mg/l with a mean value of 0.94 mg/l for dry season and between 0.10 to 1.47 mg/l and an average value of 0.52 mg/l for the rainy season. The low concentration of fluoride in the rainy season is due to the dilution effect of rain-water. The study revealed that about 75% of the groundwater samples in the area that are dilution effect of rain-water. The study revealed that about 75% of the groundwater samples in the area that are

Table 1. Statistics of the physico-chemical and bacteriological parameters for dry season

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Max.</th>
<th>Min.</th>
<th>Mean</th>
<th>Range</th>
<th>Variance</th>
<th>S.D.</th>
<th>M.D.</th>
<th>Skew</th>
<th>Kurt</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.85</td>
<td>5.15</td>
<td>6.489</td>
<td>2.7</td>
<td>0.373</td>
<td>0.611</td>
<td>0.489</td>
<td>0.238</td>
<td>0.354</td>
</tr>
<tr>
<td>EC (µs/cm)</td>
<td>3050</td>
<td>22.7</td>
<td>305.04</td>
<td>3027.3</td>
<td>22865</td>
<td>473.14</td>
<td>265.8</td>
<td>3.953</td>
<td>18.29</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>34.5</td>
<td>28.1</td>
<td>32.32</td>
<td>6.4</td>
<td>1.467</td>
<td>2.111</td>
<td>0.941</td>
<td>-0.22</td>
<td>0.403</td>
</tr>
<tr>
<td>Cl (mg/l)</td>
<td>21.62</td>
<td>0.0</td>
<td>7.208</td>
<td>21.62</td>
<td>25.599</td>
<td>5.06</td>
<td>4.073</td>
<td>0.557</td>
<td>-0.07</td>
</tr>
<tr>
<td>HCO₃ (mg/l)</td>
<td>126</td>
<td>6.0</td>
<td>23.786</td>
<td>120</td>
<td>389.117</td>
<td>19.726</td>
<td>13.592</td>
<td>2.717</td>
<td>12.06</td>
</tr>
<tr>
<td>F (mg/l)</td>
<td>7.16</td>
<td>0.1</td>
<td>0.806</td>
<td>7.06</td>
<td>0.813</td>
<td>0.902</td>
<td>0.696</td>
<td>1.523</td>
<td>1.261</td>
</tr>
<tr>
<td>Ca (mg/l)</td>
<td>127.82</td>
<td>0.06</td>
<td>5.815</td>
<td>127.76</td>
<td>240.026</td>
<td>15.493</td>
<td>6.712</td>
<td>6.721</td>
<td>51.85</td>
</tr>
<tr>
<td>Mg (mg/l)</td>
<td>3.19</td>
<td>0.0</td>
<td>1.714</td>
<td>3.19</td>
<td>1.44</td>
<td>1.2</td>
<td>1.11</td>
<td>0.229</td>
<td>1.613</td>
</tr>
<tr>
<td>Na (mg/l)</td>
<td>31.18</td>
<td>0.07</td>
<td>6.791</td>
<td>31.11</td>
<td>48.758</td>
<td>5.863</td>
<td>5.832</td>
<td>1.135</td>
<td>0.75</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>28.22</td>
<td>0.19</td>
<td>8.347</td>
<td>28.03</td>
<td>39.376</td>
<td>6.275</td>
<td>5.047</td>
<td>0.996</td>
<td>0.75</td>
</tr>
<tr>
<td>SO₄ (mg/l)</td>
<td>78.65</td>
<td>0.06</td>
<td>11.688</td>
<td>78.59</td>
<td>275.912</td>
<td>16.611</td>
<td>11.021</td>
<td>2.633</td>
<td>7.428</td>
</tr>
<tr>
<td>NO₃ (mg/l)</td>
<td>19.12</td>
<td>0.06</td>
<td>6.279</td>
<td>18.52</td>
<td>21.144</td>
<td>4.598</td>
<td>3.801</td>
<td>0.73</td>
<td>-0.23</td>
</tr>
<tr>
<td>PO₄ (mg/l)</td>
<td>9.4</td>
<td>0.01</td>
<td>1.744</td>
<td>9.39</td>
<td>4.021</td>
<td>2.005</td>
<td>1.564</td>
<td>1.688</td>
<td>2.96</td>
</tr>
</tbody>
</table>

ND- not detected; EC- electrical conductivity; Min- minimum; Max- maximum; SD- standard deviation; MD- mean deviation; Temp- temperature; Kurt- kurtosis; Skew- skewness
area dominated with sedimentary formations show low concentration of fluorite while the region occupy by younger granites show high fluoride concentration. This implies that fluoride-rich groundwater in the area emanates from the granite aquifers and the problem of fluorosis in the area is purely by natural processes.

High concentration of fluoride in groundwater causes a disease known fluorosis which affects mainly the teeth and bones of animals/man (Plates 1-4). These findings suggest that the enrichment factor of the ions on the groundwater is possibly geogenic and related to the local geology of the area. The alkaline pH and high bicarbonate are responsible for release of fluoride-bearing minerals into groundwater. The arid climate of the region, the granitic rocks and the low freshwater exchange due to periodical drought conditions are the factors responsible for the higher incidence of fluorides in the groundwater resources. Apart from these prevailing natural conditions, years of neglect and lack of restoration programs on terrestrial and aquatic environments have led to accumulative impacts on groundwater, soils, plants, and animals including humans. The people dependent on these groundwater resources are prone to dental fluorosis and mild skeletal fluorosis. Table 2 shows the concentration of fluoride and the corresponding health implications. Fluoride is both beneficial in strong teeth and bone formation (<1.5 mg/l) and also damage both the teeth and bone that it helped in their formation if the concentration exceeds 1.5 mg/l (Table 2). The scatter plot of fluorite versus chloride is illustrated in Figure 6. This correlation suggests that as fluorite concentration increases, chlorites content also increases and vice versa.

<table>
<thead>
<tr>
<th>Fluoride Content (mg/l)</th>
<th>Level of Impact on Human Health</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>Safe limit, beneficial in tooth and bone formation</td>
</tr>
<tr>
<td>1≤3</td>
<td>Dental fluorosis</td>
</tr>
<tr>
<td>3≤4</td>
<td>Stiff and brittle bones</td>
</tr>
<tr>
<td>&gt;4</td>
<td>Deformation and crippling of bones, Permanent and irreversible paralysis</td>
</tr>
</tbody>
</table>

Statistical analysis shows that the fluoride has a good positive relation, with pH and bicarbonate. This indicates an alkaline environment, as a dominant controlling mechanism for leaching of fluoride from the source material. Other supplementary factors responsible for the occurrence of fluoride in the groundwater are evapotranspiration, long contact time of water with the aquifer material, and agricultural fertilizers. A lack of correlation between fluoride and chloride, and a high positive correlation between fluoride and bicarbonate indicate recharge of the aquifer by the river water. However, the higher concentration of fluoride observed in the groundwater in some locations indicates insufficient dilution by the river water. That means the natural dilution did not perform more effectively. Hence, the study emphasizes the need for surface water management structures, with people's participation, for getting more effective results.

High fluoride content in groundwater can be attributed to the continuous water-rock interaction during the process of percolation with fluoride-bearing country rocks under arid, low precipitation, and high evapotranspiration conditions. The interpretation of plots for different major ions and molar ratios suggest that weathering of silicate rocks and water-rock interaction is responsible for major ion chemistry of groundwater. The petrographic studies...
revealed that the rocks which are granites, rhyolites and sandstone contain galena-chalcopyrite-sphalerite mineralization (Chae et al. 2007; Amadi, 2009). During weathering processes the fluorite is released and is leached downward via infiltration into the groundwater system.

Mineralogical evaluation of granitic rocks suggests the presence of fluoride bearing minerals such as fluorite, fluor-apatite and apatite as well as nacaphite. Studies have shown that the sodium concentration increases with the solubility of fluoride bearing minerals due to similarity in their charges (Chae et al. 2007). This implies that the high fluoride content observed in the groundwater system in Zango Local Government Area of Katsina, North-western Nigeria is purely geogenic due to weathering and dissolution of fluorite-rich minerals contained in the host-rock. The level of enrichment of any mineral (fluoride) in groundwater is a function of chemistry of the aquifer, well-depth, hydrological conditions, residence time and geological structures.

Figure 6. Concentration of fluorite versus chlorite in Zango LGA, Katsina State

Plate 1. Dental fluorosis observed in the Southern part of Zango LGA (Garni area)

Plate 2. Dental Fluorosis observed in the southern part of Zango LGA (Kasuwayal, Area)

Plate 3. Dental fluorosis observed in the central part of Zango LGA (Jama’ar Malam-Sani Area)

Plate 4. Dental fluorosis observed in the central part of Zango LGA (Dishe Area)
3. Conclusion and Recommendation

An effective groundwater management and quality assessment cannot be made without a comprehensive knowledge of the groundwater chemistry, geology and hydrogeology of the catchment. Petrographic studies revealed that the parent rocks which are granites, rhyolites and sandstone contain galena-chalcopyrite-sphalerite mineralization and these rock contain fluoride-rich minerals. The composition of groundwater is characteristics of the lithologic environment. During weathering processes these metals are released and are leached downward through infiltration to contaminate the groundwater or through surface run-off and pollute surface water.

Because all the investigated sites in Zango Local Government Area of Katsina state, North-western Nigeria showed minimal anthropogenic influence, the observed high fluoride concentration in the groundwater system of the area is purely a natural background concentration from processes such as weathering and dissolution. The study further established that fluoride concentration in groundwater was higher in dry season than in rainy season and it may be attributed to the dilution effect of rainfall. This remarkable finding serves as a geo-reference for identifying natural source of groundwater contamination.

The choice of Zango Local Government area is partly due to the fact that it is the only local government area in Nigeria that has the following rock types: sediments from the Sokoto Basin (Gundumi Formation), sediments from the Chad Basin (Chad Formation) and older granites of the Basement Complex rocks and the Younger Granites (Rhyolites). The study has established the problem of fluorosis in the groundwater in the area. The geochemical evolution of groundwater from the four different aquifer types in the area is quantitatively described by the interaction of the groundwater with minerals present along the flow-path. The observed concentration ranges of major and trace elements is a function of the natural background concentration and can serve as a reference for groundwater from hydrogeologically different environments.

Recommendation

The high fluoride concentration in the groundwater was attributed to weathering and dissolution of the fluoride-rich mineral contained in the host rock. Communities living in the granite/rhyolite dominated region where cases of fluorosis have been observed should discontinue the use of groundwater from the area for drinking purposes. The Federal and State government should provide an alternative source of drinking water for the people.

Reference


