Occurrence of Fluoride and some Heavy Metals in Groundwater from Shallow Aquifers Near Ogbomosho, North-central Nigeria

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Abstract
Groundwater is one of the most important natural resources that when contaminated by either natural or anthropogenic means is difficult and expensive to clean-up. Fluorosis is a disease affecting the bone and teeth of humans due to excessive intake of fluoride either through water or food. Heavy metal pollution is a burning environmental issue due to their toxic, persistent and bio-accumulative nature. The present study evaluates the presence of fluoride and some heavy metals in groundwater from shallow aquifers around Ogbomosho, north-central Nigeria and the result of investigation confirmed their enrichment. The fluoride concentration ranged between 1.35mg/l to 2.75mg/l with a mean value of 2.18mg/l as against the recommended value of 1.50mg/l. This is an indication that continuous use of water from this area may result to colouration of the teeth and deformation of the bone among the people especially children since they are the most vulnerable. 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 study has established that the fluoride-rich groundwater as well as heavy metal contamination in the area may have emanated from geochemical processes of dissolution and weathering of the granite aquifers in the area. The heavy metal enrichment is in the order of: Ni > Mn > Cr > Cd > Fe > Cu > Zn. These findings suggest that the enrichment of the groundwater system is geogenic and related to the local geology of the area. It is recommended that people living in the coarse grained porphyritic biotite granite dominated area should discontinue the use of groundwater for domestic and drinking purposes in order not to experience fluorosis in future. Environmentally friendly techniques such as phyto-remediation and bio-remediation should be employed to monitor and control fluoride and heavy metal content in the groundwater system.

Keywords: Groundwater Quality, Fluorosis, Heavy metals contamination, Shallow Aquifers Ogbomosho and North-central Nigeria

Introduction
According to UNICEF (1999), about 65 million people globally are affected by either skeletal or dental fluorosis. Fluorosis is an abnormal disease of the bone and teeth due to excessive intake of fluoride through water or food. Skeletal fluorosis is a crippling disease with major manifestation of overgrowth or distortion of the bones leading to total deformity of the individual. Dental fluorosis is the damage of the teeth in form of permanent dark-brown colouration. Both skeletal and dental fluorosis are as a result of consumption of water with fluoride concentration greater 1.5mg/l (NSDWQ, 2007; WHO, 2010) while fluoride content below or equal to 1.5mg/l in water is beneficial in building strong bones and tooth (Ahmad et al 2010).

Waters with high levels of fluoride content are mostly found at the foot of high mountains and in areas where the sea has made geological deposits. The known fluoride belt on land include: one that stretches from Syria through Jordan, Egypt, Nigeria, Ghana, Libya, Algeria, Sudan and Kenya, and another that stretches from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China (Figure 1). Long-term ingestion of large amounts of fluoride in the body can lead to potentially severe skeletal problems. The early symptoms of skeletal fluorosis include stiffness and pain in the joints. In severe case, the bone structure may change and ligaments may calcify, with resulting impairment of muscles and pain. Acute high-level exposure to fluoride causes immediate effects of abdominal pain, excessive saliva, nausea and vomiting. Seizures and muscle spasm may also occur (Chae et al, 2007; Aminu and Amadi, 2014).

Studies have shown that about 85% of all communicable diseases affecting human being are either water borne or water related. Fluoride in groundwater in primarily derived from decomposition/dissociation and dissolution of fluoride bearing minerals and secondly by the use of fertilizer containing fluoride impurities (Saxena and Ahmed, 2002). Fluoride contamination in groundwater in parts of northern Nigerian may be attributed to lithogenic interference arising from rock-water interaction as well as pro-longed application of phosphatic fertilizer containing fluoride as impurities (Aminu and Amadi, 2014). Amadi et al., (2015) revealed that lithogenic contamination of groundwater depends on climate of the area, pH, flow pattern and frequency, ionic exchange, resident time, chemistry and mineralogy of the rock. High fluoride concentration in groundwater may persist for years, decades, centuries, and can contaminate the food chain (Chidambaram et al., 2003; McAllister et al., 2005; Chae et al, 2007; Dan-Hassan et al., 2012).
Minerals in rock that contain fluoride include: fluorspar, apatite, fluomica, cryolite, epidote, topaz, phosphorite, tremolite, amphiboles, villauite and clay (Boyle and Chagnon, 1995). Groundwater in contact with any of these minerals can be enriched with fluoride due to rock weathering and dissolution processes. The chemistry of groundwater is modified as it migrates from one area to another due to exchange of ions in the course of its movement. Rock-water interaction allows fluoride rich minerals in bedrock to decompose resulting in enrichment of fluoride in groundwater (Wenzel and Blum, 1992). Investigations have revealed that most fluoride belt in the world are mostly found at the foot of high mountains and in areas where the sea has made geological deposits, though there are few exceptions to this. The level of concentration of fluoride in groundwater depends on the contact time/water-rock-interaction.

Figure 1: Map of Fluoride occurrence in groundwater across (After IGRAC, 2004)

Heavy metals are chemical elements that have relatively high densities (5 times the density of water) and are toxic at low concentrations. From an environmental and health point of view, the elements are carcinogenic and mutagenic (Nikoladis et al., 2008). Heavy metal concentration on the are of great concern because of their toxicity, persistence and bio-accumulative nature as this have serious effects on both plants and animal health through food chain (Amadi et al., 2012). However, some of these elements are beneficial at low concentrations plays some physiological and enzymic functions in plants and animal (USEPA, 1997). Groundwater chemistry is dependent on the mineral composition and lithology through which it migrates as a result of rock-water interaction and the associated resident time (Amadi et al., 2014). This implies that the chemical composition of most groundwater are the imprints of rock-water interaction and other related physico-chemical processes and this is true for areas with no known anthropogenic activity. Studies have shown that hydrogeochemical processes such as dissolution, chemical weathering, decomposition, ionic exchange processes and resident time along flow path controls the chemistry of groundwater in shallow aquifers (Olasehinde et al., 2015; Amadi et al., 2015).

Materials and Methods

Study Area Description
Ogbomoso town lies between 4°10′E to 4°20′E of the Greenwich Meridian and 8°00′N to 8°15′N of the Equator. The geology of this area (Figure 2) has been studied by many workers (Oyawoye, 1964). However some work has been done in recent past on the hydrogeophysics and hydrogeochemistry of the area (Olasehinde et al., 2015). The study area lies within North-central Nigeria which is underlain by the Basement Complex. The study area falls within a tropical rain forest and is characterized by several hills and highlands as well as several rivers (Olarewaju, 2006).

Sampling
Sampling stations were selected, taking into account the direction of groundwater flow, direction of prevailing
winds and the density of the population within the studied area. Glassware and vessels were treated in 10% (v/v) nitric acid solution for 24 h and were washed with distilled and deionized water. The samples for cation determination were collected in polypropylene containers, labeled and immediately few drops of HNO₃ (ultrapure grade) to pH < 2 were added to prevent loss of metals, bacterial and fungal growth and then stored in a refrigerator while samples for anion analysis were collected in glass containers. The physical parameters were determined in situ in the field using appropriate instruments in accordance with APHA (2008) standard. The samples were stored on ice in cooler boxes and transported to the laboratory immediately after sampling was completed.

### Laboratory Analysis

The physical parameters are measured in the field using martini MI 806 with sensitive probe. The cations and heavy metals were determined using ICP-OES method while fluoride was determined using Hana Hatch 83300 Multi-parameter Spectrophotometer. Sulphate was analyzed by colorimetric method while bicarbonate and chloride were determined by titrimetric method. Nitrate determination was by ultra violet visible Spectrophotometer.

### Results and Discussion

The results of the laboratory analyses are summarized in Table 1. The pH value ranged from 6.70 to 7.25 with a mean value of 6.96. The pH values fall within the acceptable limit of 6.50 to 8.50 postulated by Nigerian Standard for Drinking Water Quality (NSDWQ, 2007). The pH is a good water quality parameter indicating the acidity or alkalinity of a medium. The conductivity values ranged between 6.88µs/cm to 1710µs/cm with an average value of 678.65µs/cm. The conductivity values in most locations exceed the WHO acceptable limit of 1000µs/cm. Electrical conductivity is an indication of dissolved materials in water as water in its pure state does not conduct electricity. The concentration of total dissolved solid (TDS) varied from 81.30mg/l to 1108.00mg/l with a mean value of 461.76mg/l. The concentration of TDS in some locations was higher than the recommended value of 500.00mg/l (WHO, 2010; NSDWQ, 2007).

The obtained TDS value in each location is directly proportional to the amount of dissolved ions in groundwater from that location and it is relative (Amadi et al., 2014). Even though no direct health effects is known for TDS, certain components of TDS, such as chlorides, sulphates, bicarbonates, carbonates, magnesium, calcium, sodium and potassium affects corrosion or encrustation in water distribution systems. TDS level (>500mg/l) causes scaling in water pipes which can reduce the lifespan of water heaters, boilers, kettles, pots, and steam irons. Hardness of water is due to the presence of calcium and magnesium ions and it reduces lather formation as well as increases the boiling point of water (Lohani et al., 2008). Hardness of water also leads to the formation of scales in sinks, pipe fittings and cooking utensils (Nwankwoala et al., 2014).

### Table 1: Descriptive Summary of the Physico-chemical Parameters analyzed

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>NSDWQ (2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.70</td>
<td>7.25</td>
<td>6.96</td>
<td>6.50-8.50</td>
</tr>
<tr>
<td>Conductivity</td>
<td>6.88</td>
<td>1710.00</td>
<td>678.65</td>
<td>1000.00</td>
</tr>
<tr>
<td>TDS</td>
<td>81.30</td>
<td>1108.00</td>
<td>466.75</td>
<td>500.00</td>
</tr>
<tr>
<td>Fluoride</td>
<td>1.35</td>
<td>1710.00</td>
<td>2.18</td>
<td>1.50</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.00</td>
<td>0.09</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.01</td>
<td>1.00</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.00</td>
<td>0.01</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Copper</td>
<td>0.10</td>
<td>1.06</td>
<td>0.42</td>
<td>1.00</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.00</td>
<td>0.82</td>
<td>0.34</td>
<td>3.00</td>
</tr>
<tr>
<td>Iron</td>
<td>0.01</td>
<td>0.48</td>
<td>0.22</td>
<td>0.30</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.00</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The concentration of fluoride ranged between 1.35mg/l to 2.70mg/l with an average value of 2.18mg/l. These values imply that the fluoride concentration in groundwater in most locations exceeds the permissible limit of 1.5mg/l (WHO, 2010; NSDWQ, 2007). Since there was no known industry in the area that could have discharged fluoride rich-effluent into the soil or surface water, high fluoride concentration in groundwater of an area may be attributed to weathering and dissolution of rocks as well as irrigation processes which also accelerates weathering of rocks (Murthy et al., 2003; Amadi et al., 2015).

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 (Aminu and Amadi, 2015). According to Omueti (1977), the fixation of the bulk of fluoride as complex hydroxy-silicates and hydroxylumino-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 are 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 Aluminium that is associated with phyllosilicates (Vaish and Vaish, 2002). The result of XRD analyses of the soil sample from the area revealed the presence of nacaphtite, a fluoride rich mineral and the geochemical processes described above may have been responsible for their high concentration in the groundwater system in the area. The concentration of fluoride in most of the location were observed to be higher than the recommended maximum permissible limit of 1.5mg/l (NSDWQ, 2007; WHO, 2010). A mean value of 2.18mg/l (Table 1) calls for urgent attention in terms of remediation before the situation becomes endemic as we have in Zango, Katsina State and Hong in Adamawa State (Aminu and Amadi, 2014).

The concentration of iron varied between 0.01mg/l to 0.48mg/l and an average value of 0.25mg/l as against the permissible limit of 0.30mg/l (WHO, 2010; NSDWQ, 2007). Iron is essential to the human body and its deficiency causes goiter while high intake has no known health effect except reasons of taste and avoidance of staining of sinks and laundered textiles (Amadi et al., 2013). The concentration range of manganese is 0.07mg/l and a mean value of 0.03mg/l. The mean concentration is slightly above the recommended WHO guideline value of 0.02mg/l. Manganese is an important micronutrient for both plants and animals and also plays an important role in enzyme catalysis. However, it can cause damage the liver and other organs at relatively high concentration (Karbassi et al., 2008). Cadmium is a toxic element with no known essential biological function and can travel for long distance from the source of emission by atmospernic transport (WHO, 2007). The average concentration of cadmium is 0.003mg/l from the groundwater analysis. The concentration of zinc in the water sample was below the permissible level of 3.00mg/l (WHO, 2010; NSDWQ, 2007). Zinc is an essential growth element for plants and animals and also plays useful role in a variety of enzyme systems which contribute to energy metabolism, transcription and translation. It leads to phytotoxicity at very high concentration.

The concentration of nickel varied from 0.00-0.09mg/l with a mean value of 0.041mg/l as against the approved limit of 0.02mg/l (WHO, 2010; NSDWQ, 2007). Nickel may be present in groundwater due to chemical weathering and dissolution from nickel ore-bearing rocks. The mean concentration of chromium and copper in the groundwater are 0.04mg/l and 0.42mg/l while their respective permissible limits are 1.00mg/l and 0.05mg/l (WHO, 2010; NSDWQ, 2007). Copper unlike chromium has nutritional value for plants and animals and plays key role in body metabolic processes. Similarly, the presence of these metals in the groundwater system in the area is due to dissolution processes occasioned by rock-water interaction and other favourable geochemical conditions prevalent in area over a period of geological time.

A strong positive correlation with Cu and Ni as well as Cu and Zn as noted at <0.01 level (Table 2) while a low correlation of Cr with Mn and Ni was noted. An excellent relationship of Cu and Fe was established in the study (Table 2). This implies that these metals are released into the groundwater by the same geochemical processes. Also a good relationship exists between TDS and conductivity as well as F and pH. The fluoride and heavy metal are released into the groundwater system at slightly low pH and elevated temperature and their presence in water contribute to TDS content and these makes groundwater conductive.

Table 2: Overall Pearson’s correlation coefficient of the analyzed parameters

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
<th>F</th>
<th>pH</th>
<th>TDS</th>
<th>Cond</th>
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<td>Cd</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.505*</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.207</td>
<td>0.090</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Fe</td>
<td>0.064</td>
<td>-0.271</td>
<td>0.567*</td>
<td>1.000</td>
<td></td>
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<td></td>
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<tr>
<td>Mn</td>
<td>0.089</td>
<td>0.585*</td>
<td>0.213</td>
<td>0.291</td>
<td>1.000</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.012</td>
<td>0.502*</td>
<td>0.623**</td>
<td>0.077</td>
<td>0.231</td>
<td>1.000</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Zn</td>
<td>0.036</td>
<td>0.558*</td>
<td>0.611**</td>
<td>0.342</td>
<td>0.098</td>
<td>0.405</td>
<td>1.000</td>
<td></td>
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<tr>
<td>F</td>
<td>-0.018</td>
<td>0.095</td>
<td>0.498</td>
<td>0.028</td>
<td>0.122</td>
<td>0.082</td>
<td>0.052</td>
<td>1.000</td>
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<tr>
<td>pH</td>
<td>0.169</td>
<td>0.380</td>
<td>0.089</td>
<td>0.365</td>
<td>0.206</td>
<td>0.216</td>
<td>0.278</td>
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</tr>
<tr>
<td>TDS</td>
<td>0.256</td>
<td>0.065</td>
<td>0.221</td>
<td>0.045</td>
<td>0.235</td>
<td>0.346</td>
<td>0.353</td>
<td>0.227</td>
<td>0.335</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Cond</td>
<td>0.167</td>
<td>0.234</td>
<td>0.163</td>
<td>0.202</td>
<td>0.124</td>
<td>0.128</td>
<td>0.054</td>
<td>0.189</td>
<td>0.301</td>
<td>0.652**</td>
<td>1.000</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)
Conclusion and Recommendation

The presence of fluoride and trace elements such as copper, zinc, nickel, manganese, chromium, cadmium, and iron in groundwater around Ogbomosho was investigated in the study and their presence are no longer in doubt. The quality of groundwater depends on the nature of surface run-offs, weathered products and mineralogical composition of the underlying rocks. The geology of an area has a strong influence on the chemistry of groundwater. The natural processes of weathering and dissolution may be responsible for release of fluoride-bearing minerals as well as heavy metals into groundwater system. The enrichment order of the heavy metal are: Ni > Mn > Cr > Cd > Fe > Cu > Zn. People living in the granite dominated region should discontinue the use of groundwater from the area for domestic and drinking purposes in order to avert the problem of fluorosis in the near future. It is suggested that Phyto-remediation, bio-monitoring, bio-mining and bio-remediation techniques be employed to monitor, control and manage the high fluoride content and heavy metal contamination in the groundwater system at this early stage.

Reference


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