Occurrence and distribution of fluoride in groundwater of Chad formation aquifers in Borno state, Nigeria

Abstract

Borno State is largely underlain by the Chad Formation, which is the youngest stratigraphic sequence in the Chad Basin and most prolific in terms of groundwater resources. The Formation consists of the three prominent water bearing zones known as the Upper, Middle and Lower zone aquifers. The Middle and Lower zone aquifers are confined while the Upper zone aquifer is unconfined, semi-confined and confined in some places. A total of 175 water samples were collected from boreholes and hand dug wells tapping these aquifers. The samples were collected using plastic bottles and at each sampling point pH, temperature and electrical conductivity were measured using portable pH/EC meter. In the laboratory, samples were analysed for fluoride concentration using Spectrophotometer with detection limit of 0.01mg/l. The Upper zone aquifer has fluoride concentration within the WHO acceptable limit of less than 1.5mg/l, except for a sample in Magumeri which has concentration of 1.8mg/l. The Middle and Lower zone aquifers have relatively higher concentrations, with the highest of 4.6mg/l in Gubio and 9.00mg/l in New Marte respectively. The relatively higher concentrations (above the WHO limit of 1.5mg/l) in these aquifers might be because of leaching from the confining clay layers, enhanced by long residence time and high temperature. The alkaline nature of water in these aquifers and their moderate electrical conductivity favour dissolution of fluoride. In the study area, cases of mild to severe dental fluorosis have been observed in areas with high fluoride concentration – above the WHO limit. In New Marte for instance, where the highest fluoride concentrations was recorded, cases of skeletal fluorosis have been noticed.

Keywords: groundwater, aquifer, Chad formation, fluoride

Introduction

The study area lies within latitude 11.15º and 13.25ºN and longitude 11.45º and 14.00ºE (Figure 1). The area is situated within the semi-arid region of north-eastern Nigeria with an annual rainfall that is generally less than 600mm and evapotranspiration of over 2,000mm. Surface waters are seasonal except for the Lake Chad, therefore, groundwater is the perennial source of water supply for drinking and for other purposes. Groundwater in this part of the State occurs dominantly within the Chad Formation, which is the youngest and the most viable in terms of water resources in the Chad Basin. The Chad Formation comprises of lacustrine sediments that vary in lithology both laterally and vertically. It hosted the three well-defined arenaceous horizons that form the water bearing zones (aquifers). These aquifers are termed the Upper, Middle and the Lower zone aquifers.1 Groundwater always contains dissolved and suspended substances of organic and mineral origin.2 Therefore, assessing the quality of the water in the study becomes necessary as ingestion of high concentration of some these constituents have health implications. Naturally occurring fluorides in groundwater result from the dissolution of fluoride containing rock minerals, while artificially high fluoride levels occur through contamination from phosphate fertilizers, sewage sludge or pesticide.3 Fluoride occurs in three forms, namely, fluoride, apatite or rock phosphate (Ca F(PO4)3) and cryolite (NaAlF3).
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and hydrogeology of the Chad Basin have been described by many authors. Various stratigraphic unit were identified in the basin, these include the Bima Sandstone which is the oldest stratigraphic unit (Table 1). The Formation consists of sequence of red sandstone and mudstone of the Continental Group lying unconformably on the basement complex. The Bima sandstone is overlain by the Gongila Formation and according to Matheis, the age of the Formation is Cenomanian. The Gongila Formation is overlain by Fika Shale which consists mainly of dark-grey to blue-black shale with occasional gypsum, glauconite and fine-grained sandstone in the upper part of the Formation. The Gombe Sandstone is of Maastrichtian age and consists of cross-bedded sandstone and siltstone. The Gombe Sandstone is overlain by the Kerri-Kerri Formation of Palaeocene age and composed of alternating layers of grit and sandstone with well-developed cross bedding. The Chad Formation is the youngest stratigraphic unit in the basin (Table 1) and it covers the entire part of the study area. Groundwater resources in the study area are derived from the three aquifers of the Chad Formation. The aquifers are subdivided into Upper, Middle and the Lower zone aquifers on the basis of prominent sandy zones separated by thick clayey members (Figure 2). The Upper zone aquifer contains water under phreatic condition. It is sandy to clayey in composition and attains a thickness of between 5 and 12 meters. It occurs at an average depth of between 40 and 110 meters below ground surface. The aquifer according to Beacon Services and Consulint Intl. Ltd. is further subdivided into three sub-units known as the A, B and C. These units are unconfined, semi-confined to confined.

Table 1 Generalized stratigraphic column of North eastern Nigeria (Modified from Carter et al., Avbovbo et al.)

| Age            | Formation | Thickness (M) | Description                        |
|----------------|-----------|---------------|------------------------------------|
| Quaternary     | Chad      | 400           | Clay with sand inter-beds          |
| Palaeocene     | Kerri-Kerri | 130          | Predominantly iron-rich sandstone  |
|                |           |               | and clay with plinth of laterite   |

| Unconformity   |                                      |
|----------------|--------------------------------------|
| Maastrichtian  | Gombe                                |
|                | 315                                  |
|                | Sandstone, siltstone and clay beds   |
| Senonian       | Fika                                 |
|                | 430                                  |
|                | Dark grey to black shale, gypiferous with limestone beds |
| Turonian       | Gongila                              |
|                | 420                                  |
|                | Alternating limestone and shale with sand beds |
| Albian to Cenomanian | Bima                      |
|                | 3050                                 |
|                | Poorly sorted, feldspathic sandstone |
| Albian         | Pre-Bima                             |
|                | 800                                  |
|                | Sand/shale succession                |

| Nonconformity  | Basement Complex                     |
|----------------|--------------------------------------|
| Precambrian to Cambrian |                        |

Figure 2 Cross-section of chad formation showing the three aquifer zones (Modified after Miller et al.).

The Middle zone aquifer underlies the entire basin, extending to Niger, Chad and Cameroon. It is separated from the Upper zone aquifer by some thick argillaceous layer. The aquifer consists of sands, sandy clay and clays with extremely variable proportions in different sections. The aquifer has shown some considerable lowering of piezometric head, over the last half a century. The Lower zone aquifer which was previously known to occur only in Maiduguri area has also been found to be extended up to the fringes of the Lake Chad. The aquifer is confined, with variable thickness reaching up to 90m in some places, and occurs at an average depth of 550 to 600m. The aquifer consists of fine to coarse grained sands and gravels. The age of the groundwater in the Middle and Lower zone aquifers have been estimated at 24 and 18.6 thousand years before present respectively prior to the last glacial maximum. The mean annual temperature at this recharge time was at least 6°C cooler than at the present day based on interpretation of noble gas data.

Methodology

A total of 175 samples were collected from boreholes and hand dug wells in the three aquifers of the study area. Samples were collected using plastic bottles, which were initially washed with 10% HNO₃ and rinsed thoroughly with distilled water. The bottles were filled to the brim and sealed by screwing the cap. Samples were stored in frozen box for onward delivery to laboratory. Physical parameters are electrical conductivity, pH and temperature, which were measured at the sampling point using a portable pH/EC meter. Samples were then sent to laboratory for analysis of fluoride concentration using Spectrophotometer (Multiparameter ion specific meter) with a detection limit of 0.001mg/l. In carrying out the analysis, 4ml SPADNS reagent was used to prepare a blank. Contour maps and map showing sampling points were constructed using the Surfer 8.0 version computer software. Microsoft excel was also used for linear plots of fluoride concentrations to pH and EC.

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Results

The results of fluoride concentration and the physical parameters of samples collected measured in the field for the Upper, Middle and Lower aquifers are presented in Tables 2, Table 3 & Table 4 respectively. The fluoride concentration in the Upper zone aquifer varies between 0.01 and 1.8mg/l (Table 2). The highest concentration of 1.8mg/l was recorded at the Magumeri Forestry sample. The pH of the groundwater in the Upper zone aquifer ranges from 6.64 and 8.52 with the highest value obtained at the Kijimatari borehole. The fluoride concentration in the Upper zone aquifer shows wide variation from 110 to 3,754µS/cm. The electrical conductivity is low around Maiduguri and towards the eastern part (along the Benisheikh axis). It increases tremendously towards the northern part of the study area close to the Lake Chad (Figure 3). The highest conductivity of 3,754µS/cm was recorded in Cross Kauwa about 50Km from the Lake Chad (Table 2).

Table 2. Results of fluoride concentrations (mg/l) and physical parameters of groundwater samples from the Upper zone aquifer.

| S/ no | Location | Latitude | Longitude | pH | EC (µS/cm) | T (°C) | F (mg/l) | Depth (m) |
|-------|----------|----------|-----------|----|------------|--------|----------|-----------|
| 1     | Dikwa West | 12.0261' | 13.5436' | 7.41 | 460 | 31.1 | 0.71 | 56.0 |
| 2     | Dikwa Salleke | 12.0213' | 13.5478' | 7.00 | 293 | 30.0 | 1.26 | 53.0 |
| 3     | Garadai | 12.01491' | 13.5291' | 6.91 | 894 | 30.3 | 0.73 | 49.0 |
| 4     | Umarari ll | 11.0526' | 13.0804' | 7.18 | 525 | 31.0 | 0.43 | 61.0 |
| 5     | Low Cost | 11.0516' | 13.0744' | 7.08 | 340 | 31.7 | 0.41 | 72.0 |
| 6     | Polo Road | 11.0873' | 13.0873' | 7.52 | 181 | 29.6 | 0.64 | 94.0 |
| 7     | Circular Road | 11.0853' | 13.0881' | 7 | 208 | 30.8 | 0.59 | 56.0 |
| 8     | 202 estate | 11.0812' | 13.1127' | 7.42 | 255 | 27.7 | 0.30 | 47.0 |
| 9     | Mainok | 11.0969' | 13.3753' | 7 | 161 | 30.8 | 0.58 | 58.0 |
| 10    | Ngamadu | 11.0455' | 13.1538' | 6.66 | 918 | 30.2 | 0.31 | 62.0 |
| 11    | Mainok | 11.04961' | 13.3798' | 6.76 | 267 | 31.0 | 0.53 | 53.0 |
| 12    | Damboa Rd | 11.0861' | 13.0800' | 7.03 | 185 | 33.3 | 0.01 | 92.0 |
| 13    | Kuluri | 11.0839' | 13.0763' | 7.34 | 186 | 32.4 | 0.49 | 89.0 |
| 14    | Kuluri | 11.0834' | 13.0727' | 6.64 | 110 | 31.9 | 0.57 | 40.0 |
| 15    | Masludemami | 11.0804' | 13.0703' | 6.91 | 145 | 32.3 | 0.45 | 42.0 |
| 16    | Tudun Wada | 11.0602' | 13.0668' | 6.82 | 155 | 31.6 | 0.36 | 65.0 |
| 17    | Dala | 11.04942' | 13.0605' | 6.88 | 169 | 33.1 | 0.45 | 96.0 |
| 18    | Umaranri | 11.0525' | 13.0855' | 7.4 | 550 | 31.8 | 0.00 | 85.0 |
| 19    | Ngannamam | 11.0526' | 13.0860' | 7.38 | 513 | 32.0 | 0.45 | 73.0 |
| 20    | Bulabulin. | 11.05318' | 13.0845' | 7.23 | 611 | 31.9 | 0.00 | 78.0 |
| 21    | Bulabulin 2 | 11.05331' | 13.0905' | 7.27 | 410 | 32.1 | 0.20 | 93.0 |
| 22    | Rail Quarters | 11.05246' | 13.0929' | 7.26 | 511 | 31.6 | 0.00 | 47.0 |
| 23    | Bolori Layout | 11.06127' | 13.0707' | 7.28 | 357 | 2.7 | 0.20 | 56.0 |
| 24    | Bolori Bunu | 11.06168' | 13.0788' | 7.06 | 875 | 32.0 | 0.28 | 59.0 |
| 25    | Bolori Cross | 11.06156' | 13.0769' | 7.03 | 668 | 31.8 | 0.10 | 61.0 |
| 26    | Low Cost ll | 11.05158' | 13.0732' | 7.1 | 317 | 33.0 | 0.13 | 68.0 |
| 27    | Kwana Yobe | 11.05044' | 13.1147' | 7.31 | 670 | 32.7 | 0.47 | 72.0 |
| 28    | Jajeri | 11.05225' | 13.0750' | 7.03 | 405 | 31.5 | 0.34 | 95.0 |
| 29    | Alameri | 11.04909' | 13.0401' | 6.89 | 215 | 31.6 | 0.25 | 94.0 |
| 30    | GRA | 11.04810' | 13.0850' | 7.63 | 201 | 30.0 | 0.32 | 96.0 |
| 31    | Gambori | 12.05197' | 12.3324' | 8.02 | 382 | 32.6 | 0.91 | 42.0 |
| 32    | Goni bukarli | 12.04921' | 12.3722' | 7.93 | 431 | 31.4 | 0.82 | 48.0 |
| 33    | Mallumti | 12.04264' | 12.4034' | 8.03 | 851 | 32.0 | 0.00 | 56.0 |

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| S/ no | Location     | Latitude  | Longitude  | pH  | EC (µS/cm) | T (°C) | F (mg/l) | Depth (m) |
|------|--------------|-----------|------------|-----|------------|--------|----------|-----------|
| 34   | Zaimolo      | 12°38.70' | 13°42.69' | 7.71| 1071       | 32.2   | 0.32     | 47        |
| 35   | Kareem       | 12°09.57' | 13°48.39' | 7.94| 217        | 32.0   | 0.38     | NA        |
| 36   | Magumeri F   | 12°06.92' | 13°48.86' | 7.64| 411        | NA     | 1.81     | 96        |
| 37   | Fashar       | 12°06.06' | 13°56.94' | 8.18| 347        | 31.6   | 0.36     | 83        |
| 38   | Gajiganna    | 12°51.44' | 13°06.31' | 7.04| 568        | 32.0   | 0.43     | 105       |
| 39   | Ala          | 12°12.41' | 13°52.66' | 7.07| 756        | 31.1   | 0.11     | 46        |
| 40   | Old marte    | 12°21.68' | 13°49.84' | 8.07| 953        | 31.7   | 0.35     | 56        |
| 41   | Bama         | 11°31.51' | 13°41.16' | 6.78| 470        | 30.5   | 1.25     | 95        |
| 42   | Kawuri       | 11°35.41' | 13°32.12' | 6.81| 841        | 29.3   | 1.32     | 76        |
| 43   | Kinjirin     | 12°21.72' | 13°08.37' | 7.6 | 607        | 31.0   | 0.28     | 54        |
| 44   | Burimari     | 12°34.19' | 13°18.29' | 8.14| 2977       | 31.0   | 0.60     | 49        |
| 45   | Gasarwa      | 12°37.01' | 13°19.82' | 7.94| 3163       | 30.6   | 0.81     | 65        |
| 46   | Aljari       | 12°40.48' | 13°23.74' | 7.88| 2529       | 31.5   | 0.39     | 48        |
| 47   | Alimatari I  | 12°41.03' | 13°33.08' | 8.52| 676        | 29.7   | 0.60     | 38        |
| 48   | Kijimatari II| 12°41.02' | 13°33.07' | 8.39| 752        | 29.2   | 0.33     | 36        |
| 49   | Mile 90      | 12°46.72' | 13°39.86' | 7.97| 1147       | 33.1   | 1.45     | 85        |
| 50   | Dogoshia     | 12°51.67' | 13°40.64' | 8.13| 3238       | 29.5   | 1.01     | 73        |
| 51   | Cross Kauwa  | 12°56.56' | 13°40.37' | 8.14| 3511       | 31.8   | 0.40     | 46        |
| 52   | Cross kauwa  | 12°56.53' | 13°40.32' | 8.47| 3754       | 29.2   | 1.14     | 51        |
| 53   | Garin Giwa   | 13°00.13' | 13°43.59' | 7.84| 1599       | 33.3   | 0.60     | 40.0      |
| 54   | Baga Military| 13°03.64' | 13°45.73' | 8.17| 1269       | 29     | 0.77     | 43.0      |
| 55   | Baga Hausa   | 13°05.81' | 13°49.29' | 8.32| 1511       | 28.8   | 1.01     | 39.0      |
| 56   | Baga Kauwa   | 13°06.02' | 13°49.16' | 7.92| 1726       | 30.2   | 0.66     | 42.0      |
| 57   | Gajagaja I   | 13°05.48' | 13°49.35' | 7.53| 1690       | 30.5   | 0.48     | 37.0      |
| 58   | Gajagaja II  | 13°05.46' | 13°49.34' | 7.5 | 1692       | 30.5   | 0.75     | 38.0      |
| 59   | Gajagaja III | 13°05.44' | 13°49.35' | 7.07| 1351       | 31.0   | 0.77     | 39.0      |
| 60   | Gudunbal     | 12°56.57' | 13°10.80' | 7.61| 1704       | 32.0   | 0.75     | 45.0      |
| 61   | Damasak      | 13°05.93' | 13°30.72' | 7.77| 226        | 32.0   | 0.33     | 45.0      |
| 62   | Damasak Za   | 13°06.00' | 13°30.57' | 7.46| 876        | 29.2   | 0.00     | 39.0      |
| 63   | Damasak I    | 13°06.03' | 13°30.55' | 7.31| 468        | 29.7   | 0.17     | 33.0      |
| 64   | Damasak 2    | 13°05.95' | 13°30.58' | 7.5 | 233        | 29.7   | 0.25     | 31.0      |
| 65   | Damasak Za   | 13°05.90' | 13°30.59' | 7.5 | 197        | 29.9   | 0.30     | 39.0      |
| 66   | Damasak W    | 13°06.33' | 13°30.52' | 7.31| 190        | 29.4   | 0.77     | 47.0      |
| 67   | Damasak N    | 13°05.61' | 13°31.08' | 7.09| 164        | 28.7   | 0.63     | 53.0      |
| 68   | Kinnari      | 13°00.71' | 13°33.91' | 8.01| 291        | 30.8   | 0.33     | 42.0      |
| 69   | Layi I       | 12°55.05' | 13°37.02' | 8.21| 676        | 31.0   | 0.69     | 35.0      |
| 70   | Layi II      | 12°55.04' | 13°37.10' | 8.29| 677        | 30.4   | 0.94     | 33.0      |
| 71   | Gremari      | 12°52.57' | 13°31.82' | 8  | 292        | 30.1   | 0.03     | 46.0      |
| 72   | Bama 2       | 11°32.30' | 13°42.18' | 6.89| 512        | 30.3   | 0.85     | 115       |
| 73   | Kawuri       | 11°34.51' | 13°32.28' | 6.69| 831        | 30.1   | 0.65     | 98        |
| 74   | Kawuri I     | 11°34.59' | 13°32.39' | 6.12| 210        | 30.0   | 0.51     | 89        |

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### Table 3: Results of fluoride concentrations (mg/l) and physical parameters of groundwater samples from the Middle zone aquifer

| S/no | Location        | Latitude (N) | Long. (E) | pH   | EC (µS/cm) | T (°C) | F (mg/l) | Depth (m) |
|------|-----------------|--------------|-----------|------|------------|--------|----------|-----------|
| 1    | Maiwa           | 11°52.93′    | 13°27.11′ | 6.78 | 1080       | 36.4   | 0.97     | 303       |
| 2    | Ngarannam       | 11°52.93′    | 13°34.55′ | 6.66 | 1040       | 36.4   | 0.01     | 318       |
| 3    | Mafa west       | 11°52.93′    | 13°35.75′ | 6.76 | 790        | 36.4   | 0.25     | 336       |
| 4    | Ajiri yoberi    | 11°52.93′    | 13°42.50′ | 6.55 | 840        | 36.4   | 1.08     | 296       |
| 5    | Ajiri           | 11°52.93′    | 13°45.23′ | 6.33 | 869        | 36.4   | 0.17     | 325       |
| 6    | Farjalari       | 11°58.82′    | 13°59.11′ | 6.59 | 829        | 39.4   | 0.03     | 318       |
| 7    | Gajibo          | 12°06.59′    | 13°51.57′ | 6.75 | 939        | 38.3   | 0.03     | 322       |
| 8    | NMarte ISQ      | 12°15.09′    | 13°08.09′ | 7.61 | 581        | 37.3   | 1.4      | 380       |
| 9    | Umarari         | 11°52.46′    | 13°09.05′ | 6.8  | 408        | 38.3   | 1.7      | 273       |
| 10   | Hausari         | 11°50.39′    | 13°09.08′ | 7.36 | 190        | 36.6   | 0.67     | 264       |
| 11   | Hausari Goro    | 11°50.48′    | 13°00.99′ | 6.8  | 390        | 36.4   | 0.29     | 258       |
| 12   | Njimtilo        | 11°54.91′    | 12°29.27′ | 6.87 | 630        | 37     | 0.95     | 279       |
| 13   | Benisheikh      | 11°48.44′    | 12°29.68′ | 6.87 | 233        | 35.3   | 0.08     | 262       |
| 14   | Benisheikh K    | 11°48.63′    | 12°15.76′ | 7.1  | 253        | 35.5   | 0.56     | 253       |
| 15   | Ngamdu Alh      | 11°45.67′    | 12°15.45′ | 7.35 | 225        | 36.6   | 0.19     | 252       |
| 16   | Ngamdu          | 11°45.26′    | 12°16.45′ | 7.91 | 467        | 35.8   | 0.52     | 264       |
| 17   | TC Ngamdu       | 11°46.42′    | 12°37.96′ | 7.25 | 323        | 36     | 0.61     | 257       |
| 18   | Mainok East     | 11°49.78′    | 12°45.51′ | 7.3  | 202        | 35.4   | 0.41     | 253       |
| 19   | Jakana West     | 11°50.26′    | 13°07.74′ | 6.32 | 555        | 36.2   | 0.05     | 215       |
| 20   | Shuwari         | 11°48.35′    | 13°04.91′ | 7.1  | 158        | 36.3   | 0.68     | 282       |
| 21   | Ngomari         | 11°49.87′    | 13°04.82′ | 7.59 | 218        | 35.2   | 0.5      | 278       |
| 22   | Ngomari Bus Stop| 11°49.50′    | 13°08.87′ | 7.16 | 186        | 35.1   | 0.08     | 269       |
| 23   | Bulabulin       | 11°53.52′    | 13°08.92′ | 7.18 | 440        | 38.2   | 0.94     | 253       |
| 24   | UmarariI        | 11°51.17′    | 13°52.76′ | 6.85 | 415        | 37.9   | 0.3      | 263       |
| 25   | Ala             | 12°12.87′    | 1°303.69′ | 7.11 | 588        | 36.7   | 1.1      | 344       |
| 26   | Tungushe        | 12°01.78′    | 14°10.77′ | 7.21 | 650        | 36.1   | 0.06     | 285       |
| 27   | Ngala CBDA      | 12°20.84′    | 13°41.76′ | 8.06 | 693        | 40.2   | 3.2      | 314       |
| 28   | Bundur          | 12°53.47′    | 13°54.66′ | 7.3  | 477        | 41.1   | 0.86     | 390       |
| 29   | Ala             | 12°08.93′    | 13°04.44′ | 6.66 | 950        | 38     | 0.35     | 344       |
| 30   | Suwurmari       | 12°07.65′    | 13°04.45′ | 7.03 | 586        | 40.1   | 1.74     | 360       |
| 31   | Karnowa         | 12°08.35′    | 13°04.67′ | 7.11 | 581        | 39.5   | 0.57     | 345       |
| 32   | Wulomari        | 12°10.64′    | 13°06.57′ | 7.1  | 601        | 38.9   | 0.22     | 328       |
| 33   | Gajiganna       | 12°15.66′    | 13°07.81′ | 7.2  | 615        | 40.1   | 0.3      | 341       |
| 34   | Zindur          | 12°18.76′    | 13°07.81′ | 7.17 | 576        | 40.2   | 0.73     | 354       |
| 35   | Kulu Kawiya     | 12°24.33′    | 13°09.95′ | 7.66 | 616        | 39.2   | 0.47     | 315       |
| 36   | Kote            | 12°26.96′    | 13°11.12′ | 7.37 | 575        | 38.7   | 0.38     | 296       |
| 37   | Kalaa           | 12°27.69′    | 13°11.67′ | 7.08 | 545        | 40.2   | 0.27     | 325       |
| 38   | Gajiram         | 12°29.69′    | 13°12.71′ | 7.67 | 541        | 39.6   | 0.32     | 342       |
| 39   | Ali Gambori     | 12°39.59′    | 13°22.13′ | 7.31 | 406        | 39.8   | 0.5      | 336       |
| 40   | Garu kimeI      | 12°41.14′    | 13°34.97′ | 7.37 | 440        | 39.9   | 0.43     | 358       |

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Table continued...

| S/no | Location       | Latitude (N) | Long. (E) | pH  | EC (µS/cm) | T (°C) | F (mg/l) | Depth (m) |
|------|----------------|--------------|-----------|-----|------------|--------|----------|-----------|
| 41   | Monguno        | 12°56.03     | 13°36.50  | 7.31| 427        | 39.4   | 0.61     | 362       |
| 42   | Monguno        | 12°50.07     | 13°37.16  | 7.28| 386        | 38.2   | 0.39     | 358       |
| 43   | Monguno S      | 12°39.89     | 13°37.17  | 7.26| 433        | 38.8   | 1.17     | 360       |
| 44   | Monguno C      | 12°40.47     | 13°36.35  | 7.33| 415        | 39.9   | 0.54     | 373       |
| 45   | Mile 90        | 12°46.66     | 13°39.74  | 7.31| 372        | 41.6   | 1.39     | 348       |
| 46   | Yoyo           | 12°42.80     | 13°38.24  | 7.31| 378        | 39.6   | 1.19     | 311       |
| 47   | Baga tasha     | 12°05.60     | 13°49.13  | 7.1 | 1337       | 39.2   | 0.68     | 451       |
| 48   | Kukawa I       | 12°55.75     | 13°34.54  | 7.27| 734        | 39.1   | 0         | 325       |
| 49   | Kukawa 2       | 12°55.16     | 13°34.63  | 7.12| 611        | 39.3   | 0.13     | 318       |
| 50   | Kukawa 3       | 12°55.55     | 13°33.77  | 7.35| 382        | 40.3   | 1.58     | 299       |
| 51   | Kukawa 4       | 12°55.43     | 13°33.61  | 7.25| 567        | 35.8   | 0.42     | 321       |
| 52   | Damasak 1      | 12°05.94     | 12°50.92  | 7.73| 184        | 36.1   | 0.35     | 325       |
| 53   | Damasak 2      | 12°06.37     | 12°50.46  | 7.6 | 160        | 39.6   | 0         | 333       |
| 54   | Wakilti        | 12°53.69     | 12°32.53  | 6.87| 1166       | 37.3   | 0.78     | 321       |
| 55   | Kareto         | 12°53.30     | 12°30.48  | 7.21| 1177       | 37.5   | 0.86     | 311       |
| 56   | Gubio park     | 12°59.72     | 12°46.54  | 7.67| 256        | 38.2   | 1.75     | 339       |
| 57   | Gubio kumbu    | 12°30.12     | 12°46.81  | 7.45| 257        | 38.1   | 1.7       | 341       |
| 58   | Gubio Central  | 12°59.89     | 12°46.99  | 7.43| 256        | 39.1   | 1.5       | 344       |
| 59   | Gubio Cross    | 12°59.58     | 12°47.17  | 7.56| 255        | 37.2   | 4.6      | 325       |
| 60   | Golaram        | 12°21.80     | 12°47.78  | 7.36| 394        | 38.4   | 0.64     | 346       |
| 61   | Madamari       | 12°17.33     | 12°47.08  | 7.73| 294        | 38.9   | 1.35     | 327       |
| 62   | Magumeri 1     | 12°06.87     | 12°49.43  | 7.55| 402        | 39.2   | 1.9      | 339       |
| 63   | Magumeri 2     | 12°06.85     | 12°49.57  | 7.51| 339        | 37.8   | 4.5      | 354       |
| 64   | Goniri         | 12°59.49     | 12°57.63  | 7.93| 430        | 38.0   | 0.94     | 298       |
| 65   | Hoyo           | 12°38.41     | 12°58.47  | 8.31| 435        | 37.5   | 0.34     | 313       |
| 66   | Wulgo          | 12°59.32     | 12°10.67  | 6.85| 658        | 38.6   | 0.48     | 341       |
| 67   | Kaje           | 12°08.94     | 13°54.66  | 6.86| 812        | 39.2   | 0.48     | 334       |
| 68   | Wulgo2         | 12°59.65     | 14°10.85  | 6.93| 739        | 38.8   | 0.56     | 325       |
| 69   | Limanti        | 12°22.35     | 11°52.84  | 6.85| 825        | 37.9   | 0.25     | 308       |
| 70   | Kirenowa       | 12°35.70     | 13°55.57  | 6.83| 612        | 38.7   | 0.62     | 296       |
| 71   | Tungushe       | 12°01.65     | 13°53.72  | 6.8 | 637        | 36.1   | 0.33     | 285       |
| 72   | Ngala East     | 12°01.05     | 14°10.93  | 8.01| 701        | 39.5   | 1.95     | 321       |
| 73   | Tungushe 1     | 12°02.33     | 13°04.32  | 6.78| 801        | 36.7   | 0.05     | 264       |
| 74   | Baale          | 12°03.00     | 13°46.00  | 7.23| 573        | 37.1   | 0.15     | 307       |

Figure 3: Distribution of fluoride in the upper aquifer groundwater of the chad formation.

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### Table 4: Results of fluoride concentrations (mg/l) and physical parameters of groundwater samples from the Lower zone aquifer

| S/no | Location               | Latitude (N) | Longitude (E) | pH | EC (µS/cm) | T (°C) | F (mg/l) | Depth (m) |
|------|------------------------|--------------|---------------|----|------------|--------|----------|-----------|
| 1    | Mafa Hausari           | 11°55.15'    | 13°36.15'     | 7.04 | 573 | 44.4 | 1.42 | 575 |
| 2    | Dikwa Ajari            | 12°01.92'    | 13°35.38'     | 6.75 | 791 | 43.3 | 1.05 | 563 |
| 3    | Logomani               | 12°12.11'    | 14°01.08'     | 6.83 | 817 | 44.5 | 0.32 | 590 |
| 4    | Albany                 | 12°07.18'    | 13°35.85'     | 6.84 | 870 | 41.4 | 0.54 | 597 |
| 5    | N/Marte ISQ            | 12°14.72'    | 13°51.97'     | 8.00 | 623 | 43.2 | 9.00 | 589 |
| 6    | N/MarteSSQ             | 12°15.04'    | 13°51.90'     | 7.99 | 522 | 44.5 | 6.00 | 593 |
| 7    | Pomponmari             | 11°51.44'    | 13°06.59'     | 7.52 | 304 | 41.6 | 2.26 | 612 |
| 8    | Boroli                 | 11°51.63'    | 13°06.63'     | 7.48 | 320 | 50.6 | 3.30 | 618 |
| 9    | Bulumkutu              | 11°50.05'    | 13°06.51'     | 7.45 | 282 | 43.6 | 0.77 | 598 |
| 10   | Ngarannam PTF          | 11°52.67'    | 13°09.05'     | 7.48 | 334 | 49.8 | 3.15 | 618 |
| 11   | Old Maidugu            | 11°51.69'    | 13°01.43'     | 7.34 | 276 | 42.6 | 0.63 | 594 |
| 12   | 777 Estate             | 11°49.83'    | 13°03.58'     | 7.53 | 325 | 42.1 | 1.11 | 468 |
| 13   | Kekeno                 | 12°47.46'    | 13°40.30'     | 7.36 | 380 | 41.2 | 0.89 | 563 |
| 14   | Suleimanti F           | 11°47.84'    | 13°37.80'     | 7.49 | 273 | 40.8 | 0.60 | 588 |
| 15   | Cross kauwa            | 12°46.75'    | 13°40.38'     | 7.13 | 700 | 42.9 | 1.13 | 577 |
| 16   | Gajiganna NNPC         | 12°15.19'    | 13°07.11'     | 6.91 | 894 | 41.5 | 0.40 | 610 |
| 17   | Gajiganna              | 12°14.85'    | 13°06.32'     | 7.76 | 393 | 45.7 | 2.10 | 596 |
| 18   | Jigalga                | 12°36.31'    | 13°09.17'     | 7.16 | 412 | 40.6 | 0.43 | 578 |
| 19   | Baga CBDA              | 13°04.00'    | 13°46.25'     | 7.18 | 1050 | 42.9 | 0.30 | 524 |
| 20   | Baga Fishery           | 13°04.79'    | 13°46.92'     | 6.98 | 1418 | 41.1 | 0.19 | 563 |
| 21   | Baga Bud               | 13°05.95'    | 13°49.80'     | 6.95 | 1040 | 42.5 | 0.69 | 571 |
| 22   | Kukawa Gwange          | 12°55.88'    | 13°36.77'     | 7.18 | 576 | 42.1 | 0.08 | 523 |
| 23   | Milei Kukaw            | 12°55.59'    | 13°35.17'     | 7.30 | 360 | 43.7 | 2.90 | 585 |
| 24   | Lawsa Filling Station  | 11°54.29'    | 13°04.25'     | 8.22 | 312 | 43 | 3.80 | 611 |
| 25   | Monguno Irrigation     | 12°41.22'    | 13°37.23'     | 7.28 | 363 | 40.9 | 0.88 | 566 |
| 26   | Madari                 | 12°50.75'    | 13°39.94'     | 7.3 | 436 | 40.9 | 0.19 | 590 |
| 27   | Mairari                | 12°41.02'    | 13°26.33'     | 7.36 | 422 | 40.1 | 4.60 | 388 |
| 28   | Lingir                 | 12°41.29'    | 13°30.59'     | 7.23 | 392 | 40.3 | 0.83 | 596 |
| 29   | Mongunu Forestry       | 12°41.23'    | 13°35.87'     | 7.32 | 408 | 41.3 | 0.97 | 578 |
| 30   | Monguno BHS            | 12°39.81'    | 13°36.62'     | 7.35 | 401 | 40.5 | 0.97 | 568 |
| 31   | Baga Mission           | 13°05.71'    | 13°48.86'     | 6.95 | 1295 | 41.4 | 0.04 | 563 |
| 32   | Sijin                  | 12°55.67'    | 13°32.42'     | 7.24 | 398 | 43 | 0.85 | 578 |
| 33   | Kukawa Garage          | 12°55.59'    | 13°33.58'     | 7.32 | 381 | 42 | 0.26 | 593 |
| 34   | Gudumbali kagunri      | 12°56.34'    | 13°10.98'     | 6.97 | 959 | 43.1 | 1.11 | 603 |
| 35   | Kukawa View Center     | 12°55.47'    | 13°34.01'     | 7.08 | 723 | 40.5 | 0.67 | 611 |
| 36   | Gur Kimel              | 12°40.98'    | 13°34.95'     | 7.63 | 374 | 40.3 | 0.87 | 589 |
| 37   | Wulgo                  | 12°39.15'    | 14°10.65'     | 6.61 | 522 | 41.8 | 0.67 | 593 |
| 38   | Granda                 | 12°39.21'    | 13°00.05'     | 6.51 | 725 | 40.7 | 1.25 | 573 |

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In the Middle zone aquifer, the concentration of fluoride ranges from 0.01 and 4.6mg/l. Nine samples out of the 74 analysed for this aquifer show fluoride concentrations above the WHO permissible limit of 1.5mg/l. About 75% of the samples have fluoride concentration below the permissible limit. Four samples collected within Gubio Town recorded fluoride concentration above 1.5mg/l (Table 3). One well located at Ngala the north-eastern part of the study area showed fluoride concentration up to 3.2mg/l. Figure 4 shows the distribution of fluoride in the Middle zone aquifer across the study area. The pH values of groundwater in the Middle zone aquifer vary from 6.32 to 8.31, with over 70% of the samples having pH values of greater than 7.00. The highest temperature recorded for the Middle zone aquifer groundwater is 41.3ºC at Mile 90. Over 80% of the samples from this aquifer have groundwater temperature greater than 36ºC. The electrical conductivity of groundwater in this zone varies from 158 to 1,337µS/cm. The conductivity is low around Maiduguri just like the Upper zone but further north around Kareto axis (Figure 4) it is as high as 1,166µS/cm.

The Lower zone aquifer recorded the highest concentration of fluoride of about 9.00mg/l at New Marte and a second well in the town equally recorded high fluoride concentrations of 6.00mg/l (Table 4). The corresponding temperatures of these wells are as high as 44.5ºC 43.2ºC and the values of the pH are 8.00 and 7.99 respectively. The high fluoride concentrations are widely distributed across the study area. The fluoride level within Maiduguri, for instances in places like Bolori, Ngarranam, Pompongami, recorded about 3.30, 2.26, 3.15, 3.80mg/l respectively. The maximum temperature of 50.6ºC was recorded at Bolori in Maiduguri, the southern part of the study area (Figure 5). The lowest temperature (40.1ºC) in the zone was obtained at Maiwar Village which recorded fluoride concentration of about 5.0mg/l. The lowest electrical conductivity (273µS/cm) in the Lower zone was also obtained at Maiduguri and the maximum value of about 1,418µS/cm was obtained at Baga extreme northeastern part of the study area. This shows that the distribution of conductivity in all the three aquifers show similar trend; that is, increases towards the northern and NE parts of the study area, close to the Lake Chad. Contour of fluoride concentrations in groundwater from the three aquifers of the study area are plotted in Figure 3, Figure 4 & Figure 5 to show their spatial distribution. A linear plot of electrical conductivity against the concentrations of fluoride for the samples of the study area is carried out in Figure 6 to evaluate their relationship. Figure 7 is a plot of fluoride concentrations to groundwater sample depth from the three aquifers of the Chad Formation. This is to evaluate their depth relationship.

Discussion

The occurrence and distribution of fluoride in the Upper, Middle and Lower zone aquifer across the study area are shown in Figure 3, Figure 4 & Figure 5 respectively. The fluoride contour map for the Upper zone aquifer (Figure 3) shows a low fluoride concentration (less than 1.5mg/l) for most parts, except for a sample at Monguno that is 1.8mg/l, which is slightly above the WHO permissible limit of 1.5mg/l. The low concentration in the Upper zone aquifer could probably be attributed to the shallow phreatic nature of the aquifer with active groundwater recharge. Map of fluoride concentrations to depth (Figure 7) shows that high fluoride concentrations are found in the deeper confined aquifer. The highest concentration of 9mg/l was recorded in a well tapping the Lower zone aquifer at a depth of 589m. The Middle zone aquifer at a depth of between 250m to 400m, also shows high fluoride concentrations, with the highest of...
4.6mg/l at the Gubio Cross borehole. This is consistent with the work of Vasquez et al.,17 that water with higher fluoride content comes from deep aquifers. Vasquez et al.,17 have also mentioned that increased fluoride concentrations is related to longer residence time of water and the deeper Middle and Lower aquifers of the study area do have palaeowaters,19 recharged between 24,000 and 18,400 years before present.15 Similar conclusions were reached by Ramakrishnan18 who added that the longer residence time will give longer reactions time with the aquifer materials and if they contain fluoride will lead to its dissolution.

Leakage of fluoride rich pore fluid from intervening clay rich aquitard layers induced by excessive exploitation of groundwater is also a potential source of the fluoride.20 In the study area, both the Middle and Lower zone aquifers are confined by thick (about 100m) clay layers. Also, in the case of the Middle zone aquifer decline in its piezometric head of over 15 m in the last 50 years has been reported.14 which they attribute to over exploitation. This may explain the source of high fluoride in these aquifers in the line with the position of Gupta.20 From the foregoing, therefore, contact time and leaching from fluoride bearing minerals within the clays may be important factors controlling the occurrence and distribution of fluoride in the study area. The low fluoride concentrations in the Upper aquifer is because of lack of the confining clay layer. Linear plot of fluoride to electrical conductivity (Figure 6) did not show a clear relationship or trend, which indicates that fluoride concentrations does not control the value of the electrical conductivity. The same trend is observed between the pH values and fluoride concentrations. Although, at the boreholes in New Marte where both samples recorded high fluoride concentrations of 9.00 and 6.00 mg/l, their pH values are 8.00 and 7.99 respectively, while their electrical conductivity values are moderate at 623 and 522µS/cm respectively. This is similar to the conclusions of Saxena & Ahmed21 that alkaline pH (7.6 and 8.6) and moderate electrical conductivity are favourable conditions for dissolution of fluoride bearing minerals. The relatively high temperature of the deeper zones also enhances the dissolution. Chandrasekharan & Antu22 have mentioned that water rock interaction is enhanced by elevated temperature. In the study area, the alkaline nature and high temperature of the groundwater in the confined aquifers (Middle and Lower) may have favour the dissolution of fluoride and thus explain its high concentrations in these aquifers.

High fluoride concentrations in groundwater has also been linked to high evapotranspiration in arid regions.23 Although, the study area also falls within the semi-arid and arid region with high evapotranspiration rate, this link has not been observed. Because the aquifer that could have been affected most will be the Upper aquifer in this area, but it is the one with low fluoride concentrations. Normal fluoride content in atmospheric air is reported to be between 0.01-0.4mg/l.24 Average fluoride content of precipitation varies from almost zero to 0.089 mg/l.25 This may contribute some fluoride to the Upper zone aquifer, as it receives present day recharged from rainfall. Fluoride is an indispensable element for the maintenance of dental health.26 It is well known that the excess fluoride intake is responsible for dental and skeletal fluorosis.26 The cases of dental fluorosis have been observed in areas where fluoride concentration is greater than 1.5mg/l. These cases are rampant among children living in the area. The dental fluorosis seen in the study area is mostly characterised by brown to black staining on the surface of the teeth. These types were seen at Bolori and Pompmomari where the fluoride concentration reaches up to 3.30 and 2.26mg/l respectively. Although, the extent of the damage differs from one individual to the other, perhaps due to levels of exposure and varying nutritional status of individual.27 In Gubio area where the two boreholes have fluoride concentrations of 4.6mg/l and 1.7mg/l, the level of dental fluorosis observed is severe with eroded teeth and some have lost their shapes and sizes. Skeletal fluorosis has been seen in New Marte where the two boreholes have fluoride concentrations of 9mg/l and 6.00mg/l.23

**Conclusion**

The occurrence and distribution of fluoride in groundwater of Chad Formation aquifers in Borno State show that fluoride concentrations vary widely, but generally higher in the confined Middle and Lower zone aquifers. The low fluoride concentrations in the Upper aquifer could probably be attributed to the shallow phreatic nature of the aquifer with active groundwater recharge. The high fluoride concentrations in Middle and Lower aquifers result from its dissolution from fluoride bearing minerals probably within the confining clay horizons. This is enhanced by the long residence time of water and high temperature in these aquifers facilitating water-rock interaction. The alkaline nature of water in these aquifers and their moderate electrical conductivity are also favourable conditions for fluoride dissolution. Fluoride concentrations above the WHO permissible limit of 1.5mg/l have been recorded in many places in the study area. In these parts, cases of dental fluorosis have been observed manifested by black staining on the surface of the teeth. In locations where fluoride concentrations are very high eroded teeth and lost in shape and size have been observed. In New Marte town where the concentrations reached 9mg/l cases of skeletal fluorosis have been seen.

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**Conflict of interest**

The authors declare there is no conflict of interest.

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