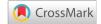


Research Article

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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 the 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 11.15° and 13.25°N and longitude 11.45° and 14.00°E (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, fluorite, apatite or rock phosphate $(Ca_{A}F(PO_{A})_{A})$ and cryolite (NaAlF_)

Volume 2 Issue 4 - 2018

Bura B,¹ Goni IB,² Sheriff BM,² Gazali AK³ ¹Chad Basin Development Authority, Maiduguri, Borno State, Nigeria

²PTDF Centre for Basinal Studies, Department of Geology, University of Maiduguri, Nigeria ³Department of Geology, University of Maiduguri, Nigeria

Correspondence: Goni IB, PTDF Centre for Basinal Studies, Department of Geology, University of Maiduguri, Nigeria, Email ibgoni@yahoo.com

Received: May 14, 2018 | Published: August 31, 2018

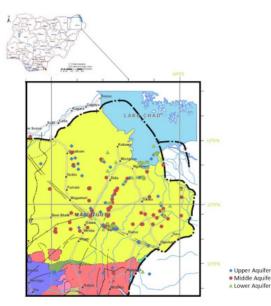


Figure I Map of the study area showing the sampling points.

Geology and hydrogeology of the study area

The area under study area is located within the Nigerian sector of the Chad Basin and is underlain by the Chad Formation. The geology

Int J Hydro. 2018;2(4):528-537.



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and hydrogeology of the Chad Basin have been described by many authors.^{1,4-6} 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.⁷ The Bima sandstone is overlain by the Gongila Formation and according to Matheis,⁶ 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.⁴ The Gombe Sandstone is of Maastrichtian age and consists of cross-bedded sandstone and siltstone.⁸ 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.⁶ 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.⁹ is further subdivided into three sub-units known as the A, B and C. These units are unconfined, semi-confined to confined.

Table I Generalized stratigraphic column of North eastern Nigeria (Modified from Carter et al.,⁴ Avbovbo et al.,²⁸)

Age	Formation	Thickness (M)	Description		
Quaternary	Chad	400	Clay with sand interbeds		
Palaeocene	Kerri-Kerri	130	Predominantly iron-		
			rich sandstone and clay with plinth of laterite		
Uncomformity					
Maastrichtian	Gombe	315	Sandstone, siltstone		
			and clay beds		
Senonian	Fika	430	Dark grey to black shale, gypsiferous 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					
Precambrian to Cambrian	Basement Complex				

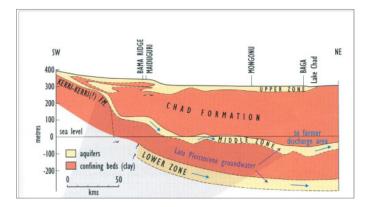


Figure 2 Cross-section of chad formation showing the three aquifer zones (Modified after Miller et al 5).

The Middle zone aquifer underlies the entire basin, extending to Niger, Chad and Cameroon.¹⁰ It is separated from the Upper zone aquifer by some thick argillaceous layer.¹¹ The aquifer consists of sands, sandy clay and clays with extremely variable proportions in different sections.⁵ The aquifer has shown some considerable lowering of piezometric head.^{12–14} over the last half a centuary. 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.¹² The aquifer is confined, with variable thickness

reaching up to 90m in some places.¹⁰ 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 respectively¹⁵ 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.

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

temperature of the water in the Upper zone aquifer ranges from 27.7°C to 33.3°C. There is no wide variation observed in temperature of the Upper zone aquifer. The electrical conductivity in the Upper zone aquifer shows wide variation from 110 to 3,754 μ S/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 3,754 μ S/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	рΗ	EC (μS/ cm)	Т (°С)	F (mg/l)	Depth (m)
I	Dikwa West	12 ⁰ 02.61 [°]	13 ⁰ 54.36 [°]	7.41	460	31.1	0.71	56.0
2	Dikwa Salleke	12 ⁰ 02.13 [°]	13 ⁰ 54.78 [°]	7,00	293	30.0	1.26	53.0
3	Garadai	12 ⁰ 14.91 [°]	13 ⁰ 52.91 ¹ '	6.91	894	30.3	0.73	49.0
4	Umarari II	11 ⁰ 52.66 [°]	13 ⁰ 08.04 ¹ '	7.18	525	31.0	0.43	61.0
5	Low Cost	11 ⁰ 51.66 [°]	13 ⁰ 07.44 ¹ '	7.08	340	31.7	0.41	72.0
6	Polo Road	، ۱۱ ⁰ 08.73	13 ⁰ 08.73 ¹ '	7.52	181	29.6	0.64	94.0
7	Circular Road	، ا ا ⁰ 48.53	13 ⁰ 08.81 [°]	7	208	30.8	0.59	56.0
8	202 estate	11 ⁰ 48.12 [']	13 ⁰ 11.27 [']	7.42	255	27.7	0.30	47.0
9	Mainok	11 ⁰ 49.69 [']	12 ⁰ 37.53 [°]	7	161	30.8	0.58	58.0
10	Ngamadu	11 ⁰ 45.50 [°]	12 ⁰ 15.38	6.66	918	30.2	0.31	62.0
11	Mainok	11 ⁰ 4961 [']	12 ⁰ 37.98 [°]	6.76	267	31.0	0.53	53.0
12	Damboa Rd	11 ⁰ 48.61"	13 ⁰ 08.00 [°]	7.03	185	33.3	0.01	92.0
13	Kuluri	11 ⁰ 48.39 [']	13 ⁰ 07.63 [°]	7.34	186	32.4	0.49	89.0
14	Kuluri	11 ⁰ 48.34 [°]	13 ⁰ 07.27 [']	6.64	110	31.9	0.57	40.0
15	Masludemami	11 ⁰ 48.04 [']	13 ⁰ 07.03 [°]	6.91	145	32.3	0.45	42.0
16	Tudun Wada	11 ⁰ 50.23 [°]	13 ⁰ 06.68 [°]	6.82	155	31.6	0.36	65.0
17	Dala	11 ⁰ 49.42 [']	13 ⁰ 06.05 [°]	6.88	169	33.1	0.45	96.0
18	Umaranri	11 ⁰ 52.52 [°]	13 ⁰ 08.55 [°]	7.4	550	31.8	0.00	85.0
19	Ngarannam	11 ⁰ 52.67 [']	13 ⁰ 08.60 [°]	7.38	513	32.0	0.45	73.0
20	Bulabulin.	11 ⁰ 53.18 [°]	13 ⁰ 08.45 [°]	7.23	611	31.9	0.00	78.0
21	Bulabulin 2	11 ⁰ 53.31 [°]	13 ⁰ 09.05 [°]	7.27	410	32.1	0.20	93.0
22	Rail Quarters	11 ⁰ 52.46 [°]	13 ⁰ 09.29 [']	7.26	511	31.6	0.00	47.0
23	Bolori Layout	11 ⁰ 51.27 [']	13 ⁰ 07.70 [°]	7.28	357	2.7	0.20	56.0
24	Bolori Bunu	11 ⁰ 51.68 [°]	13 ⁰ 07.88 [°]	7.06	875	32.0	0.28	59.0
25	Bolori Cross	11 ⁰ 51.56 [°]	13 ⁰ 07.69 [°]	7.03	668	31.8	0.10	61.0
26	Low Cost II	11 ⁰ 51.58 [°]	13 ⁰ 07.32 [°]	7.1	317	33.0	0.13	68.0
27	Kwana Yobe	11 ⁰ 50.44 [']	13 ⁰ 11.47 [°]	7.31	670	32.7	0.47	72.0
28	Jajeri.	11 ⁰ 52.25 [°]	13 ⁰ 07.50 [°]	7.03	405	31.5	0.34	95.0
29	Alamderi	11 ⁰ 49.09 [']	13 ⁰ 04.01 [°]	6.89	215	31.6	0.25	94.0
30	GRA	11 ⁰ 48.10 [']	13 ⁰ 08.50 [°]	7.63	201	30.0	0.32	96.0
31	Gambori	12 ⁰ 51.97 [']	12 ⁰ 33.24	8.02	382	32.6	0.91	42.0
32	Goni bukarli	12 ⁰ 49.21 [']	12 ⁰ 37.22 [°]	7.93	431	31.6	0.82	48.0
33	Mallumti	12 ⁰ 42.64	12 ⁰ 40.34 [°]	8.03	851	32.0	0.00	56.0

Table continuded...

S/ no	Location	Latitude	Longitude	рΗ	EC (µS/ cm)	т (°С)	F (mg/l)	Depth (m)
34	Zaimolo	12 ⁰ 38.70 [°]	12 ⁰ 42.69 [']	7.71	1071	32.2	0.32	47
35	Kareem	12 ⁰ 09.57 [°]	12 ⁰ 48.39 [']	7.94	217	32.0	0.38	NA
36	Magumeri F	12 ⁰ 06.92 [']	12 ⁰ 48.86 [°]	7.64	411	NA	1.81	96
37	Fashar	12 ⁰ 06.06	12 ⁰ 56.94 [°]	8.18	347	31.6	0.36	83
38	Gajiganna	12 ⁰ 51.44 [°]	13 ⁰ 06.31 [°]	7.04	568	32.0	0.43	105
39	Ala	12 ⁰ 12.41 [°]	13 ⁰ 52.66 [°]	7.07	756	31.1	0.11	46
40	Old marte	12 ⁰ 21.68 [°]	13 ⁰ 49.84 [°]	8.07	953	31.7	0.35	56
41	Bama	11 ⁰ 31.51 [°]	13 ⁰ 41.16 [°]	6.78	470	30.5	1.25	95
42	Kawuri	11 ⁰ 35.41 [°]	13 ⁰ 32.12 [°]	6.81	841	29.3	1.32	76
43	Kinjiram	12 ⁰ 21.72 [°]	13 ⁰ 08.37 [°]	7.6	607	31.0	0.28	54
44	Burimari	12 ⁰ 34.19 [']	13 ⁰ 18.29 [']	8.14	2977	31.0	0.60	49
45	Gasarwa	12 ⁰ 37.01 [°]	13 ⁰ 19.82	7.94	3163	30.6	0.81	65
46	Aljari	12 ⁰ 40.48 [°]	13 ⁰ 23.74	7.88	2529	31.5	0.39	48
47	Alimatari I	12 ⁰ 41.03 [°]	13 ⁰ 33.08 [°]	8.52	676	29.7	0.60	38
48	Kijimatari II	12 ⁰ 41.02 [']	13 ⁰ 33.07 [°]	8.39	752	29.2	0.33	36
49	Mile 90	12 ⁰ 46.72 [°]	13 ⁰ 39.86 [°]	7.97	1147	33.1	1.45	85
50	Dogoshi	12 ⁰ 51.67 [°]	13 ⁰ 40.64 [°]	8.13	3238	29.5	1.01	73
51	Cross Kauwa	12 ⁰ 56.56	13 ⁰ 40.37 [']	8.41	3511	31.8	0.40	46
52	Cross kauwa	12 ⁰ 56.53 [°]	13 ⁰ 40.32 [']	8.47	3754	29.2	1.14	51
53	Garin Giwa	13 ⁰ 00.13 [°]	13 ⁰ 43.59 [°]	7.84	1599	33.3	0.60	40.0
54	Baga Military	13 ⁰ 03.64	13 ⁰ 45.73 [°]	8.17	1269	29	0.77	43.0
55	Baga Hausa	13 ⁰ 05.81 [°]	13 ⁰ 49.29 [']	8.32	1511	28.8	1.01	39.0
56	Baga Kasuwa	13 ⁰ 06.02 [']	13 ⁰ 49.16 [°]	7.92	1726	30.2	0.66	42.0
57	Gajagaja I	13 ⁰ 05.48 [°]	13 ⁰ 49.35 [°]	7.53	1690		0.48	37.0
58	Gajagaja II	13 ⁰ 05.46 [°]	13 ⁰ 49.34 [°]	7.5	1692	30.5	0.75	38.0
59	Gajagaja III	13 ⁰ 05.44 [°]	13 ⁰ 49.35 [°]	7.07	1351	31.0	0.77	39.0
60	Gudunbali	12 ⁰ 56.57 [']	13 ⁰ 10.80 [°]	7.61	1704	32.0	0.75	45.0
61	Damasak	13 ⁰ 05.93 [°]	12 ⁰ 30.72 [°]	7.77	236	32.0	0.33	45.0
62	Damasak Za	13 ⁰ 06.00 [°]	12 ⁰ 30.57 [°]	7.46	876	29.2	0.00	39.0
63	Damasak I	13 ⁰ 06.03 [°]	12 ⁰ 30.55 [°]	7.31	468	29.7	0.17	33.0
64	Damasak 2	13 ⁰ 05.95 [°]	12 ⁰ 30.58 [°]	7.5	233	29.7	0.25	31.0
65	Damasak Za	13 ⁰ 05.90 [°]	12 ⁰ 30.59 [°]	7.5	197	29.9	0.30	39.0
66	Damasak W	13 ⁰ 06.33 [°]	12 ⁰ 30.52 [°]	7.31	190	29.4	0.77	47.0
67	Damasak N	13 ⁰ 05.61 [°]	12 ⁰ 31.08 [°]	7.09	164	28.7	0.63	53.0
68	Kinnari	13 ⁰ 00.71	12 ⁰ 33.91 [°]	8.01	291	30.8	0.33	42.0
69	Layi I	12 ⁰ 55.05	12 ⁰ 37.02 [°]	8.21	676	31.0	0.69	35.0
70	Layi II	12 ⁰ 55.04	12 ⁰ 37.10 [°]	8.29	677	30.4	0.94	33.0
71	Gremari	12 ⁰ 52.57 [°]	12 ⁰ 31.82	8	292	30.1	0.03	46.0
72	Bama 2	11 ⁰ 32.30 [°]	13 ⁰ 42.18 [°]	6.89	512	30.3	0.85	115
73	Kawuri	11 ⁰ 34.51 [°]	13 ⁰ 32.28 [°]	6.79	831	30.1	0.65	98
74	Kawuri I	11 ⁰ 34.59 [°]	13 ⁰ 32.39 [°]	6.12	210	30.0	0.51	89

S/no	Location	Latitude (N)	Long. (E)	pН	EC (μS/cm)	T (°C)	F (mg/l)	Depth (m)
I	Maiwa	11 ⁰ 52.93 [']	13 ⁰ 27.11	6.78	1080	36.4	0.97	303
2	Ngarannam	11 ⁰ 52.93 [°]	13 ⁰ 34.55 [°]	6.66	1040	36.4	0.01	318
3	Mafa west	۱۱ ⁰ 52.93 [°]	13 ⁰ 35.75 [°]	6.76	790	36.4	0.25	336
4	Ajiri yoberi	11 ⁰ 52.93 [°]	13 ⁰ 42.50 [°]	6.55	840	36.4	1.08	296
5	Ajiri	11 ⁰ 52.93 [°]	13 ⁰ 45.23 [°]	6.63	869	36.4	0	325
6	Farjalari	۱۱ ⁰ 58.82 [°]	13 ⁰ 59.11	6.59	829	39.4	0	318
7	Gajibo	12 ⁰ 06.59 [']	13 ⁰ 51.57 [°]	6.75	939	38.3	0	322
8	N/Marte ISQ	12 ⁰ 15.09 [°]	13 ⁰ 08.09 [']	7.61	581	37.3	1.4	380
9	Umarari	11 ⁰ 52.46 [°]	13 ⁰ 09.05 [°]	6.8	408	38.3	1.7	273
10	Hausari	۱۱ ⁰ 50.39 [']	13 ⁰ 09.08 [°]	7.36	190	36	0.67	264
П	Hausari Goro	۱۱ ⁰ 50.48 [°]	13 ⁰ 00.99 [']	6.8	390	36.4	0.29	258
12	Njimtilo	11 ⁰ 54.91 [°]	12 ⁰ 29.27 [°]	6.87	630	37	0.95	279
13	Benisheikh	11 ⁰ 48.44 [']	12 ⁰ 29.68 [°]	6.87	233	35.3	0.08	262
14	Benisheikh K	11 ⁰ 48.63 [']	12 ⁰ 15.76 [°]	7.1	253	35.5	0.56	253
15	Ngamdu Alh	11 ⁰ 45.67 [']	12 ⁰ 15.45 [°]	7.35	225	36.6	0.19	252
16	Ngamdu	11 ⁰ 45.26 [']	12 ⁰ 16.45 [°]	7.91	467	35.8	0.52	264
17	TC Ngamdu	11 ⁰ 46.42 [']	12 ⁰ 37.96 [°]	7.25	323	36	0.61	257
18	Mainok East	11 ⁰ 49.78 [°]	12 ⁰ 45.51	7.3	202	35.4	0.41	253
19	Jakana West	11 ⁰ 50.26 [']	13 ⁰ 07.74 [°]	6.32	555	36.2	0	215
20	Shuwari	11 ⁰ 48.35 [']	13 ⁰ 04.91	7.1	158	36.3	0.68	282
21	Ngomari	11 ⁰ 49.87 [']	13 ⁰ 04.82 [']	7.59	218	35.2	0	278
22	Ngomari Bus Stop	11 ⁰ 49.50 [°]	13 ⁰ 08.87 [°]	7.16	186	35.I	0.08	269
23	Bulabulin	11 ⁰ 53.52 [°]	13 ⁰ 08.92 [']	7.18	440	38.2	0.94	253
24	Umararil	11 ⁰ 51.17 [']	13 ⁰ 52.76 [°]	6.85	415	37.9	0.3	263
25	Ala	12 ⁰ 12.87 [°]	1 ⁰ 303.69 [°]	7.11	588	36.7	1.1	344
26	Tungusher	12 ⁰ 01.78 [°]	14 ⁰ 10.77 [']	7.21	650	36.1	0.06	285
27	Ngala CBDA	12 ⁰ 20.84 [°]	13 ⁰ 41.76 [°]	8.06	693	40.2	3.2	314
28	Bundur	12 ⁰ 53.47 [']	13 ⁰ 54.66 [°]	7.3	477	41.1	0.86	390
29	Ala	12 ⁰ 08.93 [°]	13 ⁰ 04.44 [°]	6.66	950	38	0.35	344
30	Suwurmari	12 ⁰ 07.65 [°]	13 ⁰ 04.45 [°]	7.03	586	40. I	1.74	360
31	Karnowa	12 ⁰ 08.35 [°]	13 ⁰ 04.67 [']	7.11	581	39.5	0.57	345
32	Wulomari	12 ⁰ 10.64	13 ⁰ 06.57 [°]	7.1	601	38.9	0.22	328
33	Gajiganna	12 ⁰ 15.66 [°]	13 ⁰ 07.81	7.2	615	40.I	0.3	341
34	Zindur	12 ⁰ 18.76 [']	13 ⁰ 07.81 [°]	7.17	576	40.2	0.73	354
35	Kulu Kawiya	12 ⁰ 24.33 [']	13 ⁰ 09.95 [°]	7.66	616	39.2	0.47	315
36	Kote	12 ⁰ 26.96 [°]	13 ⁰ 11.12 [']	7.37	575	38.7	0.38	296
37	Kalaa	12 ⁰ 27.69 [']	13 ⁰ 11.67 [']	7.08	545	40.2	0.27	325
38	Gajiram	12 ⁰ 29.69 [']	13 ⁰ 12.71 [°]	7.67	541	39.6	0.32	342
39	Ali Gambori	12 ⁰ 39.59 [']	13 ⁰ 22.13 [']	7.31	406	39.8	0.5	336
40	Garu kime l	12 ⁰ 41.14	13 ⁰ 34.97 [']	7.37	440	39.9	0.43	358

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

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

S/no	Location	Latitude (N)	Long. (E)	рΗ	EC (µS/cm)	T (°C)	F (mg/l)	Depth (m
41	Mongun Est	12 ⁰ 41.03 [°]	13 ⁰ 36.50 [°]	7.31	427	39.4	0.61	362
42	Monguno	12 ⁰ 40.07 [']	13 ⁰ 37.16 [°]	7.28	386	38.2	0.39	358
43	Monguno S	12 ⁰ 39.89 [']	13 ⁰ 37.17 [']	7.26	433	38.8	1.17	360
44	Monguno C	12 ⁰ 40.47 [']	13 ⁰ 36.35 [°]	7.33	415	39.9	0.54	373
45	Mile 90	12 ⁰ 46.66 [°]	13 ⁰ 39.74 [°]	7.31	372	41.6	1.39	348
46	Yoyo	12 ⁰ 42.80 [°]	13 ⁰ 38.24	731	378	39.6	1.19	311
47	Baga tasha	12 ⁰ 05.60 [°]	13 ⁰ 49.13 [']	7.1	1337	39.2	0.68	451
48	Kukawa I	12v55.75	13 ⁰ 34.54 [']	7.27	734	39.1	0	325
49	Kukawa 2	12 ⁰ 55.16	13 ⁰ 34.63 [']	7.12	611	39.3	0.13	318
50	Kukawa 3	12 ⁰ 55.55 [°]	13 ⁰ 33.77 [']	7.35	382	40.3	1.58	299
51	Kukawa 4	12 ⁰ 55.43 [°]	13 ⁰ 33.61 [°]	7.25	567	35.8	0.42	321
52	Damasak I	13 ⁰ 05.94	12 ⁰ 30.92 [']	7.73	184	36.1	0.35	325
53	Damasak 2	13 ⁰ 06.37 [°]	12 ⁰ 30.46 [°]	7.6	160	39.6	0	333
54	Wakilti	12 ⁰ 53.69 [°]	12 ⁰ 32.53 [°]	6.87	1166	37.3	0.78	321
55	Kareto	12 ⁰ 53.30 [°]	12 ⁰ 30.48 [°]	7.21	1177	37.5	0.86	311
56	Gubio park	12 ⁰ 29.72	12 ⁰ 46.54 [°]	7.67	256	38.2	1.75	339
57	Gubio kumbu	12 ⁰ 30.12	12 ⁰ 46.81 [°]	7.45	257	38.1	1.7	341
58	Gubio Central	12 ⁰ 29.89 [']	12 ⁰ 46.99 [']	7.43	256	39.1	1.5	344
59	Gubio Cross	12 ⁰ 29.58	12 ⁰ 47.17 [']	7.56	255	37.2	4.6	325
60	Golaram	12 ⁰ 21.80 [°]	12 ⁰ 47.78 [°]	7.36	394	38.4	0.64	346
61	Madamari	12 ⁰ 17.33 [°]	12 ⁰ 47.08 [°]	7.73	294	38.9	1.35	327
62	Magumeri I	12 ⁰ 06.87 [°]	12 ⁰ 49.43 [°]	7.55	402	39.2	1.9	339
63	Magumeri 2	12 ⁰ 06.85 [°]	12 ⁰ 49.57 [°]	7.51	339	37.8	4.5	354
64	Goniri	12 ⁰ 59.49 [°]	12 ⁰ 57.63 [°]	7.93	430	38	0.94	298
65	Ноуо	12 ⁰ 58.41 [°]	12 ⁰ 58.47 [°]	8.31	435	37.5	0.34	313
66	Wulgo	12 ⁰ 29.32 [°]	12 ⁰ 10.67 [°]	6.85	658	38.6	0.48	341
67	Kaje	12 ⁰ 08.94	13 ⁰ 54.66 [']	6.86	812	39.2	0.48	334
68	Wulgo2	12 ⁰ 29.65	14 ⁰ 10.85 [°]	6.93	739	38.8	0.56	325
69	Limanti	13 ⁰ 22.35 [°]	11 ⁰ 52.84 [']	6.85	825	37.9	0.25	308
70	Kirenowa	12 ⁰ 25.70 [°]	13 ⁰ 55.57	6.83	612	38.7	0.62	296
71	Tungushe	12 ⁰ 01.65 [°]	13 ⁰ 03.72 [']	6.8	637	36.1	0.33	285
72	Ngala East	12 ⁰ 21.05 [°]	14 ⁰ 10.93 [']	8.01	701	39.5	1.95	321
73	Tungushe I	12 ⁰ 02.33	13 ⁰ 04.32	6.78	801	36.7	0.05	264
74	Baale	12 ⁰ 03.00 [°]	13 ⁰ 46.00 [°]	7.23	573	37.1	0.15	307

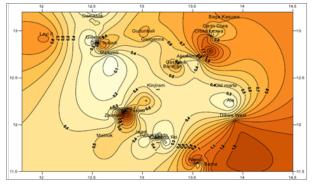


Figure 3 Distribution of fluoride in the upper aquifer groundwater of the chad formation.

Citation: Bura B, Goni IB, Sheriff BM, et al. Occurrence and distribution of fluoride in groundwater of chad formation aquifers in Borno state, Nigeria. Int J Hydro. 2018;2(4):528–537. DOI: 10.15406/ijh.2018.02.00121

S/no	Location	Latitude (N)	Longitude (E)	рΗ	EC (µS/cm)	T (°C)	F (mg/l)	Depth (m)
I	Mafa Hausari	11 ⁰ 55.15 [']	13 ⁰ 36.15 [°]	7.04	573	44.4	1.42	575
2	Dikwa Ajari	12 ⁰ 01.92 [°]	13 ⁰ 55.38 [°]	6.75	791	43.3	1.05	563
3	Logomani	12 ⁰ 12.11 [°]	14 ⁰ 01.08 [°]	6.83	817	44.5	0.32	590
4	Albanya	12 ⁰ 07.18	13 ⁰ 54.85 [']	6.84	870	41.4	0.54	597
5	N/Marte ISQ	12 ⁰ 14.72 [°]	13 ⁰ 51.97 [']	8.00	623	43.2	9.00	589
6	N/MarteSSQ	12 ⁰ 15.04	13 ⁰ 51.90 [°]	7.99	522	44.5	6.00	593
7	Pompomari	11 ⁰ 51.44"	13 ⁰ 06.59 [']	7.52	304	41.6	2.26	612
8	Bolori	11 ⁰ 51.63 [°]	13 ⁰ 06.63 [°]	7.48	320	50.6	3.30	618
9	Bulumkutu	۱۱ ⁰ 50.05 [°]	13 ⁰ 06.51 [°]	7.45	282	43.6	0.77	598
10	Ngarannam PTF	11 ⁰ 52.67 [°]	13 ⁰ 09.05 [°]	7.48	334	49.8	3.15	618
11	Old Maidugu	11 ⁰ 51.69 [°]	13 ⁰ 10.43 [']	7.34	276	42.6	0.63	594
12	777 Estate	11 ⁰ 49.83 [°]	13 ⁰ 03.58 [°]	7.53	325	42.1	1.11	468
13	Kekeno	12 ⁰ 47.46	13 ⁰ 40.30 [°]	7.36	380	41.2	0.89	563
14	Suleimanti F	۱۱ ⁰ 47.84 [°]	13 ⁰ 07.80 [°]	7.49	273	40.8	0.60	588
15	Cross kauwa	12 ⁰ 56.75 [°]	13 ⁰ 40.38 [°]	7.13	700	42.9	1.13	577
16	Gajiganna NNPC	12 ⁰ 15.19 [']	13 ⁰ 07.11	6.91	894	41.5	0.40	610
17	Gajiganna	12 ⁰ 14.85 [°]	13 ⁰ 06.32	7.76	393	45.7	2.10	596
18	Jigalta	12 ⁰ 36.31 [°]	13 ⁰ 19.17	7.16	412	40.6	0.43	578
19	Baga CBDA	13 ⁰ 04.00 [°]	13 ⁰ 46.25 [']	7.18	1050	42.9	0.30	524
20	Baga Fishery	13 ⁰ 04.79 [']	13 ⁰ 46.92 [']	6.98	1418	41.1	0.19	563
21	Baga Bud	13 ⁰ 05.95 [°]	13 ⁰ 49.80 [°]	6.95	1040	42.5	0.69	571
22	Kukawa Gwange	12 ⁰ 55.88 [°]	13 ⁰ 36.77 [']	7.18	576	42.I	0.08	523
23	Mile I Kukaw	12 ⁰ 55.59 [']	13 ⁰ 35.17 [']	7.30	360	43.7	2.90	585
24	Lawsa Filling Station	11 ⁰ 54.29 [']	13 ⁰ 04.25 [']	8.22	312	43	3.80	611
25	Monguno Irrigation	12 ⁰ 41.22 [']	13 ⁰ 37.23 [']	7.28	363	40.9	0.88	566
26	Madari	12 ⁰ 50.75 [°]	13 ⁰ 39.94	7.3	436	40.9	0.19	590
27	Mairari	12 ⁰ 41.02 [°]	13 ⁰ 26.33 [°]	7.36	422	40.1	4.60	588
28	Lingir	12 ⁰ 41.29 [']	13 ⁰ 30.59 [']	7.23	392	40.3	0.83	596
29	Mongunu Forestry	12 ⁰ 41.23 [°]	13 ⁰ 35.87 [']	7.32	408	41.3	0.97	578
30	Monguno BH5	12 ⁰ 39.81 [°]	13 ⁰ 36.62 [']	7.35	401	40.5	0.97	568
31	Baga Mission	13 ⁰ 05.71 [°]	13 ⁰ 48.86 [°]	6.95	1295	41.4	0.04	563
32	Sijjin	12 ⁰ 55.67 [']	13 ⁰ 32.42 [']	7.24	398	43	0.85	578
33	Kukawa Garage	12 ⁰ 55.59 [°]	13 ⁰ 33.58 [°]	7.32	381	42	0.26	593
34	Gudumbali kagunri	12 ⁰ 56.34	13 ⁰ 10.98 [°]	6.97	959	43.1	1.11	603
35	Kukawa View Center	12 ⁰ 55.47	13 ⁰ 34.01	7.08	723	40.5	0.67	611
36	Garu Kimel	12 ⁰ 40.98	13 ⁰ 34.95	7.63	374	40.3	0.87	589
37	Wulgo	12 ⁰ 29.15	14 ⁰ 10.65	6.61	522	41.8	0.67	593
38	Granda	12 ⁰ 59.21	13 ⁰ 00.05	6.51	725	40.7	1.25	573

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

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 WHO¹⁶ permissible limit of 1.5mg/l. About 75% of the samples have fluoride concentration below the permissible limit. Four samples collected within Gubio Town recoded 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 41.3°C at Mile 90. Over 80% of the samples from this aquifer have groundwater temperature greater than 36°C. 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.

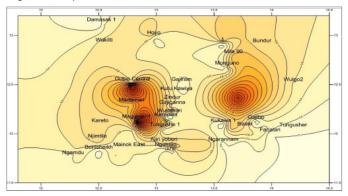


Figure 4 Distribution of fluoride in the middle aquifer groundwater of the chad formation.

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 44.5°C 43.2°C 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, Pompommari, recorded about 3.30, 2.26, 3.15, 3.80mg/l respectively. The maximum temperature of 50.6°C was recorded at Bolori in Maiduguri, the southern part of the study area (Figure 5). The lowest temperature (40.1°C) in the zone was obtained at Mairari 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.

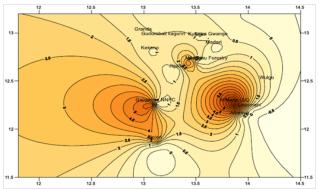
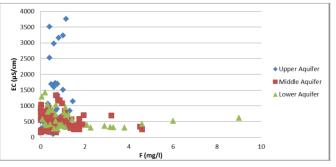
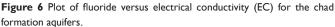


Figure 5 Distribution of fluoride in the lower aquifer groundwater of the chad formation.





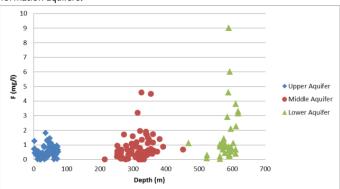


Figure 7 Plot of flouride concentrations to groundwater sample depth for the chad formation aquifers.

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 WHO¹⁶ 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,¹⁸ recharged between 24,000 and 18,400 years before present.¹⁵ Similar conclusions were reached by Ramakrishnan¹⁹ 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 foregone, 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. Chandrasekharam & 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.¹⁷ 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 Pompommari 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.²⁸

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.

Acknowledgement

None.

Conflict of interest

The authors declare there is no conflict of interest.

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