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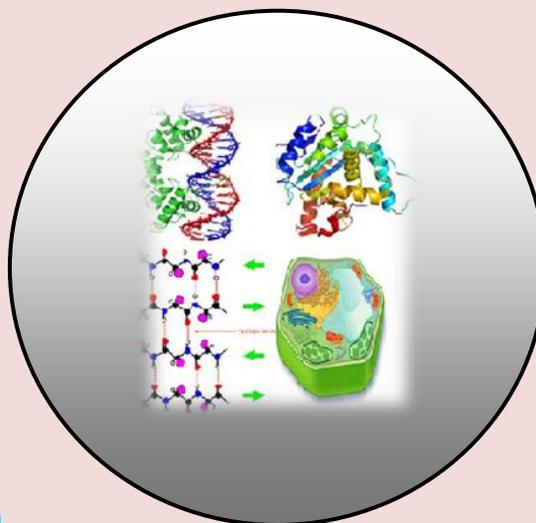
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## **Geochemical Investigation of Groundwater in Some Parts of Birnin Kebbi, Northwestern Nigeria**

**A.O. Ola-Buraimo and \*O. Ologe**

**Department of Geology, Federal University Birnin Kebbi, Birnin Kebbi, Nigeria**

**\*Department of Applied Geophysics, Federal University Birnin Kebbi, Birnin Kebbi, Nigeria**

### **ABSTRACT**

*Geochemical study on groundwater quality was undertaken from Bayankara, Badariya and Old Town areas in Birnin Kebbi, situated in sedimentary basin, northwestern Nigeria. The hydrogeo chemical study was carried out on 30 water samples, 10 from each of the 3 locations with the intent to determining the quality of the water sources such as tap water, borehole, and hand-dug well used for drinking and domestic purposes; to determine the causes, sources of the pollutants and suggest solutions towards solving the problem. The 30 water samples were analyzed for major elements and important anions. Atomic Absorption Spectrometer (AAS) was used to analyze the cations while  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  were determined using Spectrophotometer. Both  $\text{F}^-$  and  $\text{Cl}^-$  were determined by titration method. The results show that all the cations Na, K, Ca, Mg, Fe, Cu, and Zn ions have values far less than maximum limit recommended by WHO except Mn ion that exhibits average concentration values in Bayankara 0.39mg/l, Badariya 0.16mg/l greater than 0.05mg/l tolerable limit by WHO standard. However, Old Town area has Mn ion values within the recommended limit. PI index on manganese ion further show that Bayankara is more polluted than Badariya having PI index > 1 probably due to unhygienic conditions of the areas and possibly due to dissolution of manganese mineral present in the sandstone aquifer. The anions analyzed Cl, F,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  have ion concentrations within the limits of WHO recommended for drinking water with the exception of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ion concentration values that are anomalously high in the 3 locations; showing values greater than 0.5mg/l for  $\text{NH}_4^+$  and 0.3mg/l for  $\text{PO}_4^{3-}$ . In Bayankara, average  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ion concentration values are 3.7mg/l and 0.81mg/l respectively; Badariya, 4.0mg/l and 0.75mg/l respectively, while Old Town is 3.8mg/l and 0.87mg/l respectively. The contaminants resulted from anthropogenic means such as poor hygienic condition from sewage leaching and excessive application of leached fertilizer and manure rich in  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  in farming, aided by tectonic and sedimentary structures that characterize the study areas.*

*Keywords: Geochemical, Groundwater, Anthropogenic, Leaching and Contaminant.*

### **INTRODUCTION**

Geochemical study of water quality in Birnin Kebbi, Kebbi State, Nigeria became very important considering the geometric rise in population due to urbanization, citing of Federal University and relatively peaceful security atmosphere in the state capital. The study area is geologically mainly sedimentary terrain consisting exclusively of Gwandu Formation. Geologically, the study area is characterized by two types of structures, categorized into sedimentary and tectonic structures (Ola-Buraimo *et al.*, 2019). The study area consists of 3 different parts of Birnin Kebbi, covering Bayankara, Badariya and Old Town; situated in the southwestern and southeastern part of Birnin Kebbi (Fig. 1).

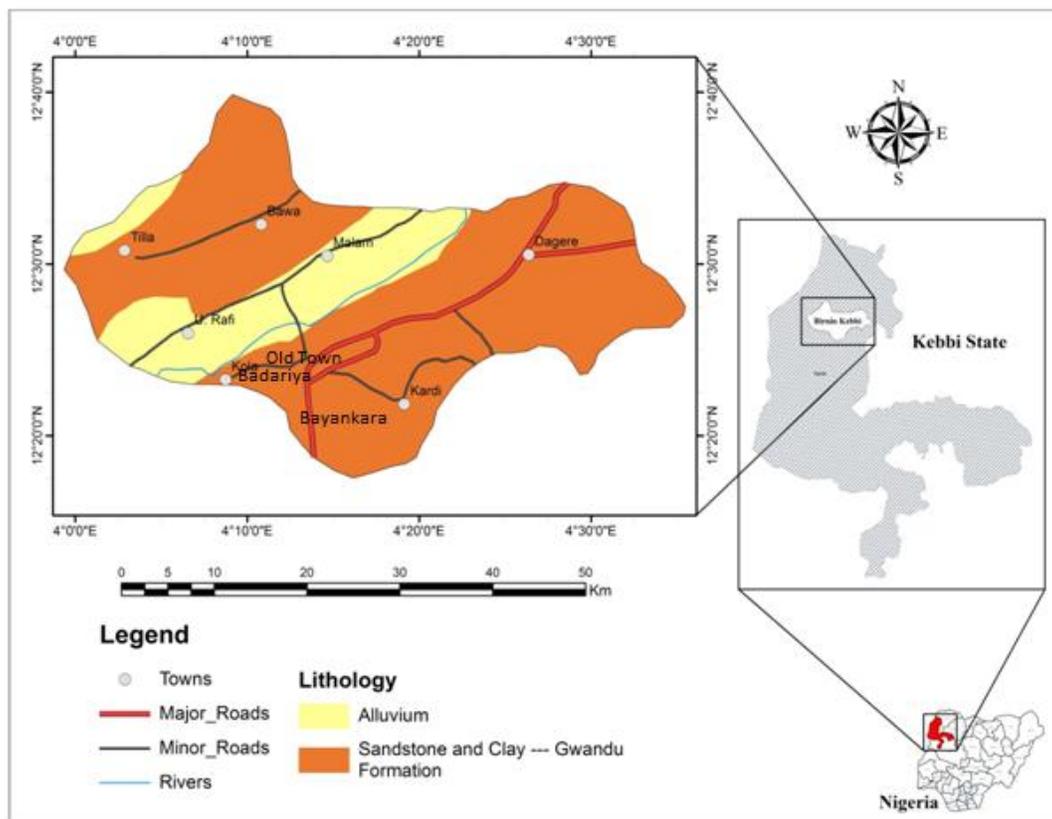


Figure 1. Location map of the study area, Birnin Kebbi, Nigeria (After Ola-Buraimo *et al.*, 2019).

### Geology of the Area

The structural pattern from field investigation shows that the structural intensity vary from place to place but intensively reported in Badariya, Bayankara and comparatively low in Old Town (Ola-Buraimo *et al.*, 2019). Study on the geochemistry of water supply in Birnin Kebbi is not well documented except the recent one on the geology and microbiological investigation of different sources of water supply in Birnin Kebbi area (Ola-Buraimo *et al.*, 2019). However, other recently investigated works on the geochemistry of water in the Cretaceous basement complex of Kebbi State was reported in the works of Wali *et al.* (2018a, b and 2019). On a wider scale quite a number of documented groundwater researches were carried out on Sokoto Basin, these include the works of Anderson and Ogilbee (1973), Adelana *et al.* (2003), Ekpoh and Ekpeyong (2011), Amadi *et al.* (2015), and Ette *et al.* (2016). Other notable researchers are Toyin *et al.* (2016), Wali *et al.* (2016), Wali *et al.* (2018a, 2018b and 2019). Importantly the works of Wali *et al.* (2018a, 2018b and 2019) were hydrochemical studies on basement complex area of Kebbi State unlike the sedimentary basin aspect of Kebbi State (Birnin Kebbi) that this study focused on. The hydrogeochemical study of different sources of water such as borehole, public tap water and hand-dug wells and there suitability for consumption is imperative considering the consequence of unsafe water supply to the inhabitants.

This study is principally investigated to determine the groundwater quality of the populated parts of Birnin Kebbi viz-a-viz the impact of the poor sanitary condition and the effect of the geologic facies (aquifer) interaction with the groundwater system in the area and to compare the presence of chemical elements and compounds present with the World Health Organization Standard in order to know if the groundwater consumed through different sources by the populace is of good quality and safe for drinking and possibly there would be need for remediation of the water system before consumption.

### The Gwandu Formation

The sedimentary deposit of the study area belongs to Gwandu Formation, with type section and type area in the Gwandu Emirate of northwestern Nigeria (Kogbe, 1972). Outcrops of the formation cover a vast area dotted with a number of prominent ridges and groups of flat-topped, steep-sided hills capped by ironstone.

Some of the isolated hills covered with ironstone debris occur in all stages of disintegration due to varying degree of weathering, rising out of the sandy plain over which the products of erosion have been distributed. The hills are flat at the top but steep sided with falloff of ironstone boulders on it and screes at the foot of the hills.

The best outcrops of the Gwandu Formation occur around Birnin-Kebbi and Argungu. The sediments consist of massive white clays interbedded with coarse and medium-grained red sandstones and mudstones with occasional peat bands. The type section proposed for the formation by Kogbe (1976d) shows the typical lithologic characteristic of the formation. By correlation with palynomorphs from tropical Tertiary deposits earlier mentioned, the age of the Gwandu Formation was tentatively put as Eocene- Miocene (Kogbe, 1976d); but this is yet to be corroborated by recent studies. The geology of the study area is not well documented; the few field work on the geology of the area located within the Birnin Kebbi has been a private property of Department of Geology, Federal University Birnin Kebbi, Nigeria. The only recent and documented field geology of the study area is contained in the work of Ola-Buraimo *et al.* (2019). The geology of the area was described to contain different lithofacies varying from one location to another. Generally, the litho-sequence was described to vary from high energy fluvial deposits of poorly sorted sandstone sitting unconformably on conglomeratic bed. The conglomerate is underlain by sandstone, siltstone and carbonaceous shale at the bottom; suggesting downward decrease in grain size and energy of transportation and deposition of the sediments (Ola-Buraimo *et al.*, 2019). The downward sequence was described to indicate varying paleoenvironment of deposition, suggested to vary from fluvial environment at the top, but prograded into deltaic setting at the bottom (Ola-Buraimo *et al.*, 2019). In other parts of the study area especially at Dukku River, close to Kebbi State Water cooperation, the facies vary considerably displaying cyclic deposit of claystone and sandstone. A part of the sequence shows evidence of macrofossils suggesting deposition of the facies in a marine setting. However, not too far from the conspicuous outcrop is a great vast exposure of fine grain, well sorted sandstone characterized by cross lamination, well rounded grains suggesting recycled sediment of fluvial deposit.

Therefore, field evidence from field work conducted in this research suggests that most of the aquifers within the Birnin Kebbi are located in the well sorted fine sandstone; this may be responsible for high yield of groundwater in the study area.

Structural features of the study area are well documented in the work of Ola-Buraimo *et al.* (2019). The structures are described to be of two types; sedimentation and tectonic structures. The tectonic structures are mainly faults, joints and fractures which characterize the sediment deposits in Birnin Kebbi, resulting to gullies and poor road networks in the interiors and house failures. However, the sedimentary structures are bedding, cross lamination, channel fills, clinoform, load cast, bioturbation and ichnofossils (Ola-Buraimo *et al.*, 2019). Ola-Buraimo *et al.* (2019) posited that the geologic structures are one of the contributory factors serving as conduit and responsible for rapid drive of pathogens, contaminating the groundwater system; thereby make the water unclean and unsafe for human consumption.

## MATERIAL AND METHODS

Three locations- Bayankara, Badariya and Old Town are parts of Birnin Kebbi selected for hydrogeochemical study based on population, social economic activities and environmental sanitation standard of the residents. There are different sources of water supply in the areas such as borehole, public tap water and hand-dug wells. They serve as sources of collecting water samples for geochemical analysis. The water samples collected from the borehole were represented by "bg", public tap water represented by "tg" and hand-dug well represented by "wg". The collection of water samples from the 3 locations was randomly carried out, spread across the investigated areas.

At the visited locations, the borehole waters were stored in overhead tanks mostly privately owned but made accessible for public use outside the compounds. The public taps water are sparsely located and in all cases were erected in public places for use, while the hand-dug wells were only encountered at Bayankara area, mostly characterized by unhygienic conditions where the wells were left uncovered, waterlogged surroundings and un-kept fetchers dropped in the dirty waterlogged surrounding of the wells.

### Water Sampling

Thirty water samples, ten each from the locations were collected into 75cl sterile plastic bottles from borehole, public tap water and hand-dug wells. The collected water samples were chlorinated with drops of concentrated hydrochloric acid (HCl) for preservation in the field. The collected samples were later preserved in refrigerator for about a week to complete the sample collection exercise before transportation to the laboratory. Field observations were noted in the field note book by considering sampling points and location names; bottles were well labeled and coded to reflect the location name, type of source water collected- borehole (bh), public tap water (pt), hand dug well (hd) and location number.

Water samples collected undergo laboratory tests to determine the concentration of major cations such as  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Mn^+$ , while major anions considered are  $F^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $PO_4^{3-}$ . The major elements were analyzed using Atomic Absorbance Spectrometer (AAS) Perkin Elmer, while for the anions, the  $NO_3^-$ ,  $PO_4^{3-}$ ,  $NH_3^{2-}$  and  $SO_4^{2-}$  were determined using Spectrophotometer (Model Genesys 20);  $F^-$  and  $Cl^-$  were determined by titration in chemical units. The results obtained were compared with recommended standards to determine the water geochemistry and its quality for drinking and domestic purposes.

## RESULTS AND INTERPRETATION

The summary of the concentrations of dissolved elements in the groundwater collected from Bayankara, Badariya and Old Town in Birnin Kebbi, Kebbi State, Northwestern Nigeria is presented in Tables 1-3. Analytical results of investigated cations and anions were compared with United State Environmental Protection Standards and World Health Organisation standards. The initial standards considered include maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs) erected by USEPA (2012) and WHO (2012). The implications of the MCLs are the enforceable standards which specify allowable level of a contaminant in public water.

### Bayankara

The geochemical analysis of water samples from Bayankara show that  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  contain contamination values that are within standard limits of WHO (2012) standards (Fig. 2). The  $Na^+$  concentration shows a minimum value of 4.1mg/l, highest value of 7.24mg/l and an average value of 7.51mg/l (Fig. 3). These values are far less than the maximum concentration limit specified by WHO put at 200mg/l. Potassium ion ( $K^+$ ) concentration vary between 3.95-9.11mg/l and an average of 5.92mg/l compared to 200mg/l of WHO standard. Thus,  $K^+$  concentration is safe and fall less than the maximum limit of 200mg/l specified by WHO (2012).  $Ca^{2+}$  varies from 9.6 to 31.6mg/l; average value of 14.05mg/l, less than the 75mg/l specified limit by WHO. Magnesium ion ( $Mg^{2+}$ ) concentration varies between 2.14-4.65mg/l, average value of 3.65mg/l compared to 50mg/l standard limit (Fig. 4).  $Fe^{2+}$  concentration varies from 0.20-0.77mg/l with average value of 0.41mg/l compared with 1.0mg/l standard limit. Zinc ion ( $Zn^{2+}$ ) concentration follows same trend with others varying in concentration from 0.00-0.07mg/l, average value of 0.04mg/l compared with 5.0mg/l as standard limit.

**Table 1. Summary of geochemical analysis of water samples from Bayankara area.**

Loc.	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	Cu mg/l	Zn mg/l	Mn mg/l	Cl mg/l	F mg/l	$NO_3^-$ mg/l	$NH_4^+$ mg/l	$PO_4^{3-}$ mg/l	$SO_4^{2-}$ mg/l
K1bg	5.25	6.35	14.80	3.64	0.05	0.28	0.05	0.14	4.22	0	0.047	3	0.8	0.034
K2bg	4.1	8.99	13.60	4.65	0.05	0.20	0.03	0.22	2.13	0	0.027	3	0.6	0.123
K3bg	5.15	5.49	12.20	3.40	0.05	0.79	0.07	0.40	8.24	0	0.019	5	0.6	0.135
K4bg	4.2	6.35	9.60	4.50	0.03	0.18	0.02	0.54	5.83	0	0.027	4	1.2	0.012
K5bg	7.24	5.51	12.90	2.44	0.01	0.40	0.04	0.14	5.53	0	0.009	2	0.8	0.016
K6bg	5.65	9.11	10.20	3.30	0.06	0.22	0.03	0.82	7.75	0	0.030	4	0.8	0.208
K7wg	4.25	5.44	13.80	4.40	0.04	0.40	0.00	0.64	4.36	0	0.056	4	1.0	0.205
K8bg	5.20	3.95	31.60	4.20	0.04	0.38	0.05	0.74	3.16	0	0.043	4	0.8	0.018
K9wg	4.25	3.99	11.40	2.50	0.06	0.60	0.05	0.22	3.36	0	0.042	5	0.7	0.114
K10bg	5.7	3.99	10.40	3.55	0.08	0.65	0.04	0.04	5.12	0	0.034	3	0.8	0.123
High-Est	7.24	9.11	31.6	4.65	0.08	0.79	0.07	0.82	8.24	0	0.056	5	1.2	0.208
Low-Est	4.1	3.95	9.6	2.44	0.01	0.20	0.00	0.04	2.13	0	0.009	2	0.6	0.012
Average	5.10	5.92	14.05	3.65	0.05	0.41	0.04	0.39	4.97	0	0.033	3.7	0.81	0.098
WHO mg/l	200	200	75	50	0.3	1.0	5.0	0.05	250	1.4	45	0.5	0.3	250

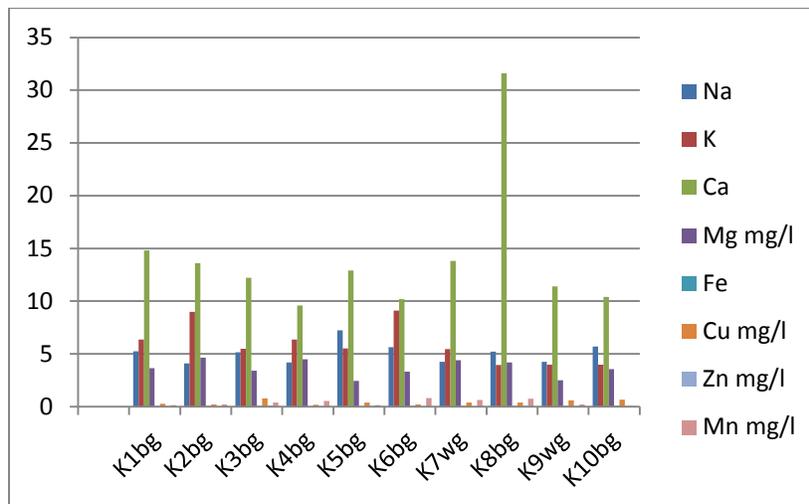


Figure 2. Summary of geochemical analysis of major elements in Bayankara area.

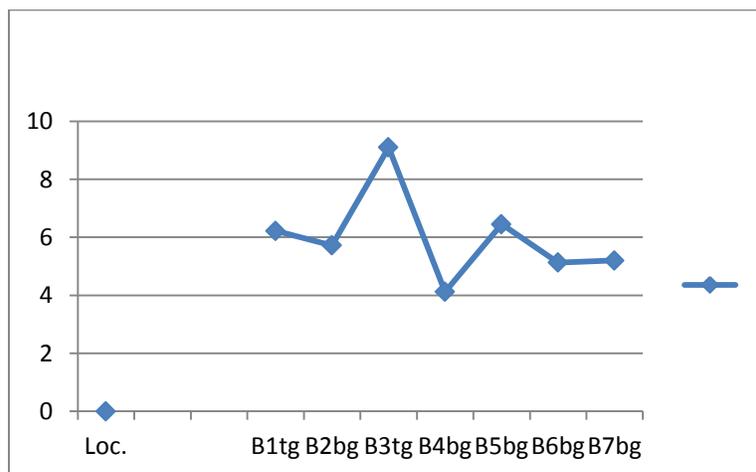


Figure 3. Variation plot of Na ion concentration in Bayankara area.

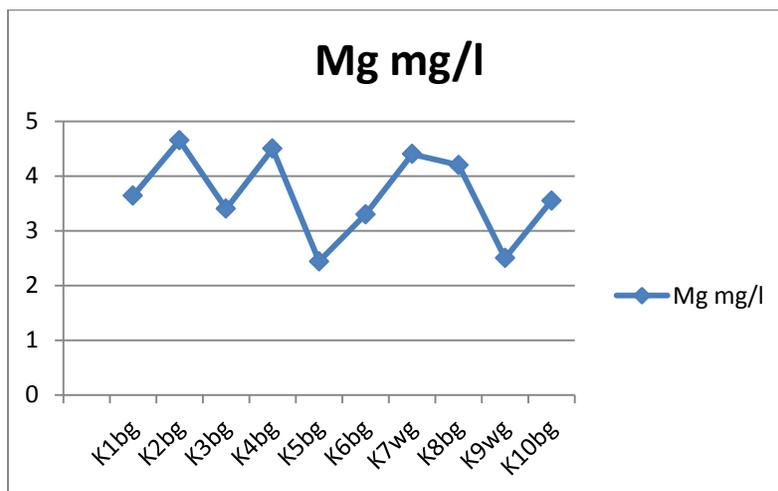


Figure 4. Variation plot of Mg ion concentration in Bayankara area.

However, Manganese ion ( $Mn^{+}$ ) concentration value in the water samples ranges from 0.04-0.82mg/l, average value is 0.39mg/l compared to 0.05mg/l recommended limit value. The recorded  $Mn^{+}$  values from the 10 samples are greater than the recommended value. Therefore, the Mn ion is the only cation found having more concentration values greater than the recommended value for drinking water. This concentration anomaly may be as a result of reactions between the groundwater and the aquifer minerals. However, since most of the stratigraphy sequences are mostly clastic and siliciclastic facies, then some of the Mn ion could be antropogenic in nature. However, the low values of other cations in the analyzed water samples from Bayankara suggest that the aquifer is mainly sandstone and not readily weathered into solution. The overlying claystones and sandstones did not weather by dissolution method. The effect of weathering and mineral dissolution in sedimentary basins cannot be compared with basement complex which contains minerals such olivine, pyroxene, amphibolites, feldspar, mica and quartz in varying composition depending on the rock type in higher concentration than sedimentary rocks.

The anions which include Cl, F,  $NO_3$  and  $SO_4$  ions have their concentration values lower than the WHO maximum limits while  $NH_4^{+}$  and  $PO_4^{2+}$  recorded concentration values greater than the recommended limits (Fig. 5). The  $NH_4$  ion concentration varies between 2.0-5.0mg/l with an average value of 3.7mg/l compared to maximum recommended limit of 0.5mg/l. In the case of  $PO_4$  ion, the concentration value recorded in the 10 sample show a range of 0.6-1.2mg/l with an average value of 0.81mg/l compared to WHO standard limit of 0.3mg/l.

The manganese, though it is an essential element needed by man but its excess concentration intake from water could lead to neurological effects (Canavanet *et al.*, 1934; Cook *et al.*, 1974; Roels *et al.*, 1999; ATSDR, 2000). High manganese intake can as well lead to diseases-like syndrome such as weakness, anorexin, muscle pain, apathy, slow speech, monotonous tone of voice, emotionless facial expression and slow clumsy movements of limbs.

### Badariya

The Badariya area with locations B1-B10 show the same trend of cations concentration with values very low compared to WHO standard limits, thus, meeting the required limits for good water quality (Figs. 6, 7). However, the manganese ion concentration of higher value was noticed at locations B1tg, B2bg, B3tg and B4bg only out of 10 locations (Table2). The Mn ion values vary between 0.14-0.54mg/l compared to 0.05mg/l standard maximum limit recommended by WHO (2012). The anions concentration values in Badariya also follow the same trend with that of Bayankara area where Cl, F,  $NO_3$  and  $SO_4$  have concentration levels within the standard limits of WHO (2012) with the exception of  $NH_4$  and  $PO_4$  (Table 2, Fig. 8). The phosphorous ion concentration values vary from 0.6-1.2mg/l, exceeding the standard concentration limit of 0.3mg/l. The  $NH_4$  ion concentration value at Badariya varies from 2.0-5.0mg/l with an average value of 4.0mg/l; exhibiting values greater than standard WHO limit of 0.5mg/l (Table 2).

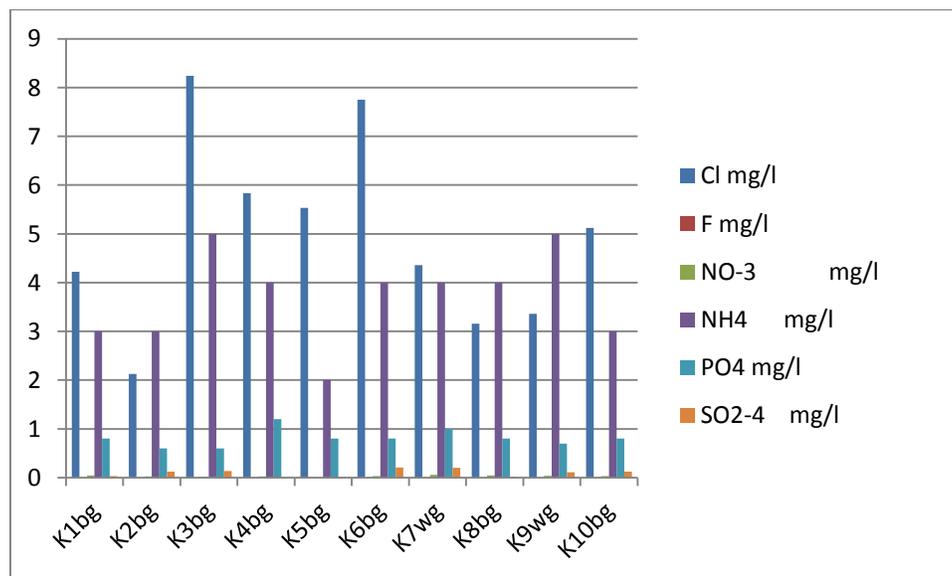
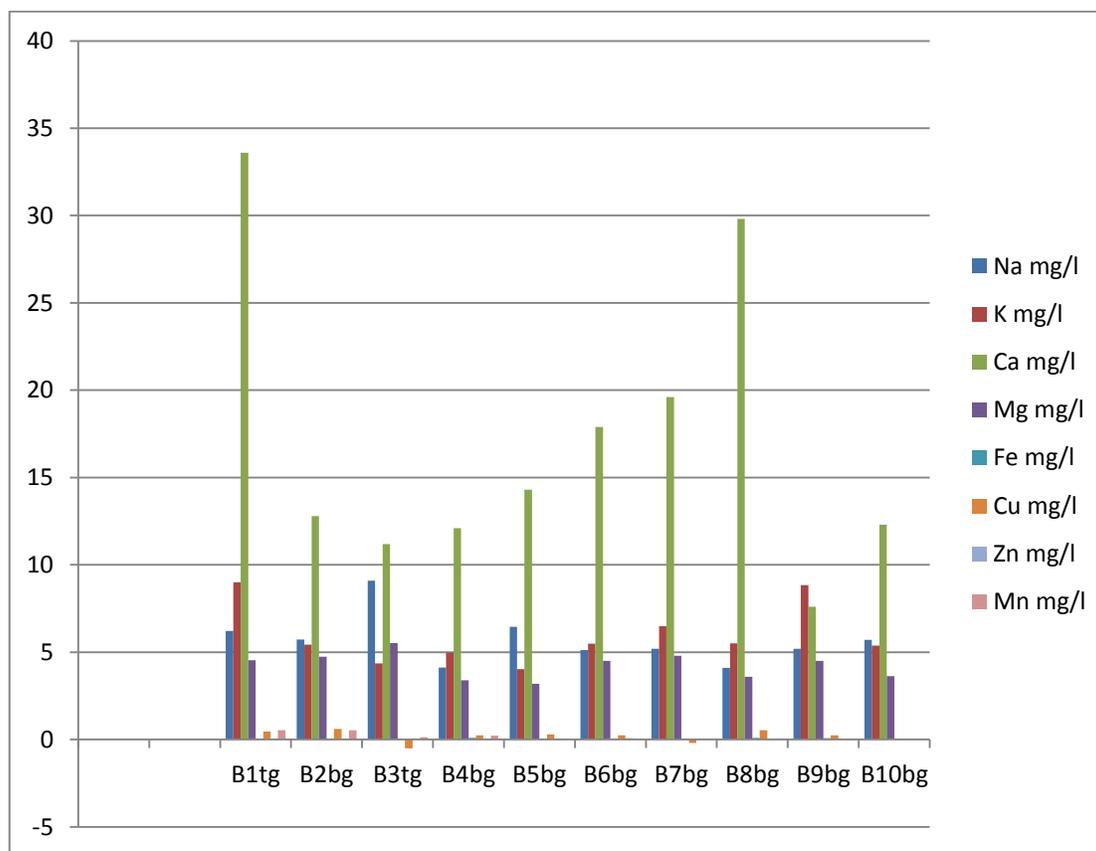


Figure 5. Summary of geochemical analysis of Anion elements in Bayankara area

**Table 2. Summary of geochemical analysis of water samples from Badariya area.**

Loc.	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	Cu mg/l	Zn mg/l	Mn mg/l	Cl mg/l	F mg/l	NO <sub>3</sub> mg/l	NH <sub>4</sub> mg/l	PO <sub>4</sub> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l
B1tg	6.22	9.01	33.60	4.55	0.06	0.47	0.02	0.54	4.15	0	0.074	5	0.6	0.014
B2bg	5.72	5.44	12.80	4.74	0.06	0.60	0.02	0.54	5.20	0	0.049	2	1.0	0.013
B3tg	9.10	4.36	11.20	5.53	0.03	-0.50	0.06	0.14	2.55	0	0.044	4	0.6	0.205
B4bg	4.12	4.98	12.10	3.40	0.09	0.25	0.04	0.22	7.65	0	0.028	5	0.6	0.017
B5bg	6.45	4.04	14.30	3.20	0.06	0.30	0.05	0.04	4.37	0.1	0.016	3	0.8	0.055
B6bg	5.13	5.49	17.90	4.50	0.06	0.25	0.08	0.04	3.12	0	0.038	5	0.7	0.074
B7bg	5.2	6.49	19.60	4.80	0.06	-0.20	0.05	0.04	3.38	0	0.057	2	1.2	0.148
B8bg	4.10	5.51	29.80	3.60	0.09	0.53	0.05	0.02	5.27	0	0.066	4	0.6	0.135
B9bg	5.2	8.84	7.60	4.51	0.08	0.25	0.04	0.02	3.12	0	0.038	5	0.6	0.089
B10bg	5.7	5.39	12.30	3.64	0.01	0.01	0.02	0.04	3.33	0	0.007	4	0.8	0.015
High-Est	9.1	9.01	33.6	4.80	0.09	0.60	0.08	0.54	7.65	0.1	0.074	5	1.2	0.205
Low-Est	4.10	4.04	7.60	3.20	0.03	-0.20	0.02	0.02	2.55	0	0.007	2	0.6	0.013
Average m/l	5.69	5.96	17.12	4.23	0.06	0.20	0.04	0.16	4.21	0.02	0.042	4.0	0.75	0.077
WHO STD	200	200	75	50	0.3	1.0	5.0	0.05	250	1.4	45	0.5	0.3	250



**Figure 6. Summary of geochemical analysis of major elements in Badariya area.**

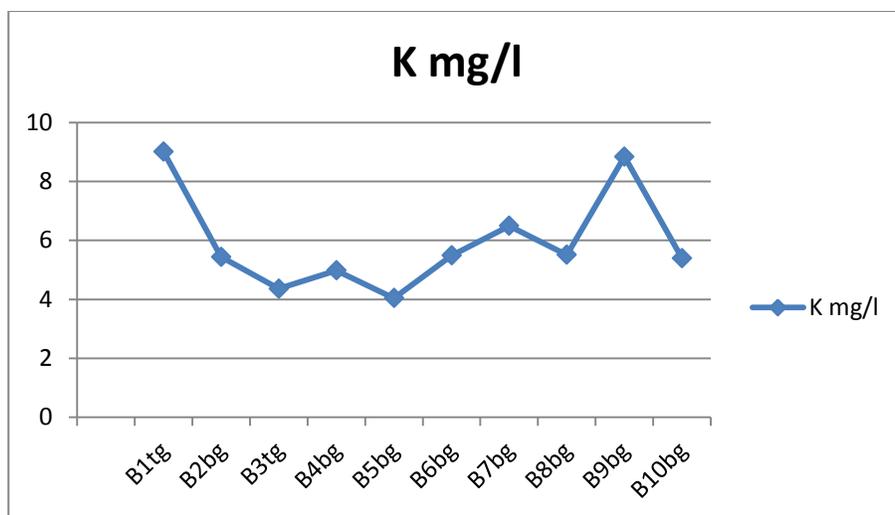


Figure 7. Variation plot of K ion concentration in Badariya area.

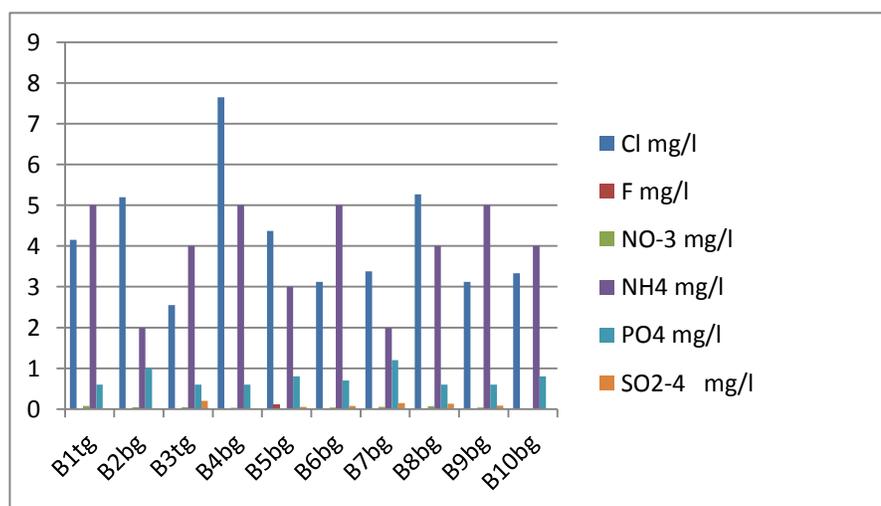


Figure 8. Summary of geochemical analysis of anion elements in Badariya area.

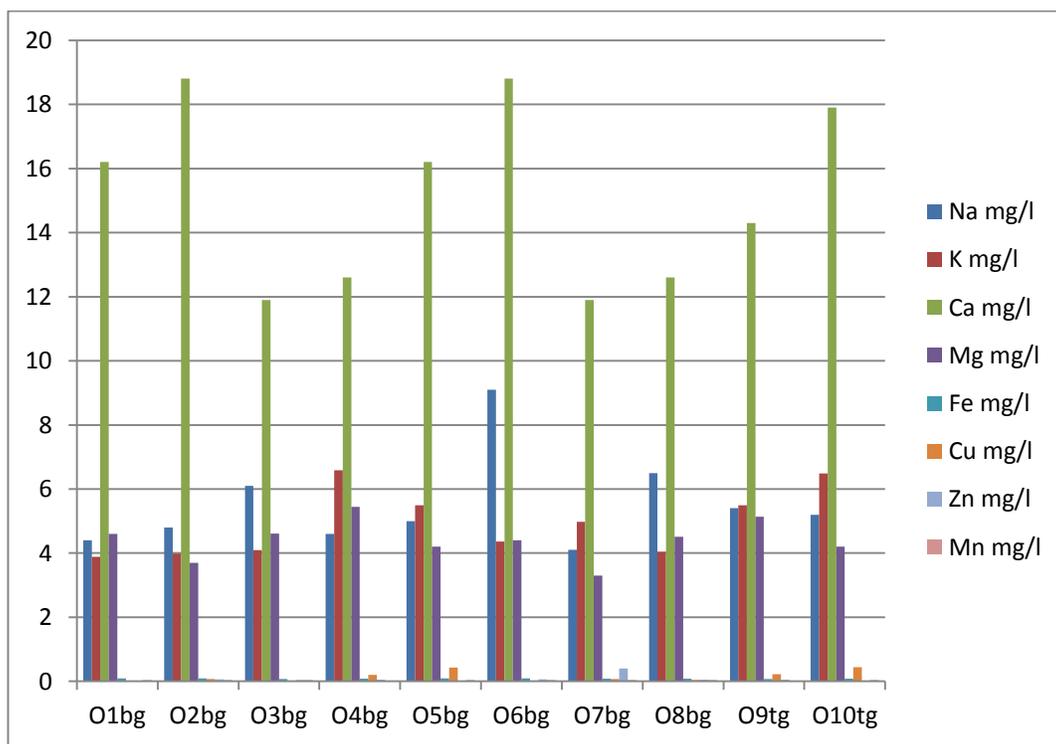
### Old Town

Old Town water sample analysis for both cations and anions concentration values are presented in Table 3. The Na, K, Ca, Mg, Fe, Cu and Zn concentration values are within the prescribed limits by WHO (2012), thereby, tentatively classifying the water to be good and healthy for consumption (Fig. 9, 10). However, the other two location involving Bayankara and Badariya have all their samples tested for high Mn ion concentration, no sample location out of 10 locations in Old Town had Mn concentration values greater than WHO standard limit. The Mn ion concentration values range from 0.02-0.04mg/l with an average value of 0.03mg/l. The trend deviates from those values obtained from Bayankara and Badaraya areas. It is opined that this could be as a result of better hygienic condition of Old Town than Bayankara and Badariya areas in terms of sanitation and protection and preservation of contamination of their groundwater from anthropogenic sources.

Anions such as Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> have concentration values lower than their recommended standards by WHO (2012). The other two anions NH<sub>4</sub> and PO<sub>4</sub> ions have concentration values greater than required limits (Fig. 11). The NH<sub>4</sub> concentration values range from 2.0-6.0mg/l with an average of 3.8mg/l compared to 0.5mg/l standard limit by WHO (2012). The phosphorous (PO<sub>4</sub><sup>3-</sup>) ion concentration value ranges between 0.7-1.2mg/l with an average of 0.87mg/l compared with 0.3mg/l recommended allowable maximum concentration limit for portable water (Table 3).

**Table 3.** Summary of geochemical analysis of water samples from Old Town area.

Loc.	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	Cu mg/l	Zn mg/l	Mn mg/l	Cl mg/l	F mg/l	NO <sub>3</sub> <sup>-</sup> mg/l	NH <sub>4</sub> mg/l	PO <sub>4</sub> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l
O1bg	4.4	3.89	16.20	4.60	0.09	0.02	0.02	0.04	5.14	0.2	0.08	3.0	0.8	0.20
O2bg	4.8	3.99	18.80	3.70	0.09	0.07	0.06	0.04	5.20	0.0	0.06	4.0	0.8	0.14
O3bg	6.1	4.09	11.90	4.61	0.07	0.02	0.04	0.04	3.12	0.0	0.03	4.0	1.2	0.09
O4bg	4.6	6.59	12.60	5.44	0.08	0.20	0.05	0.02	3.33	0.0	0.04	2.0	1.0	0.02
O5bg	5.0	5.49	16.20	4.20	0.09	0.43	0.02	0.04	5.14	0.0	0.01	4.0	0.7	0.20
O6bg	9.1	4.36	18.80	4.40	0.09	0.02	0.06	0.04	4.15	0.1	0.08	6.0	0.8	0.23
O7bg	4.1	4.98	11.90	3.30	0.08	0.07	0.40	0.04	5.66	0.0	0.06	4.0	0.8	0.02
O8bg	6.5	4.04	12.60	4.51	0.08	0.04	0.05	0.04	2.57	0.0	0.03	4.0	0.8	0.11
O9tg	5.4	5.49	14.30	5.14	0.07	0.22	0.05	0.02	5.69	0.0	0.06	3.0	1.0	0.13
O10tg	5.2	6.49	17.90	4.20	0.08	0.44	0.02	0.04	3.12	0.0	0.05	4.0	0.8	0.08
High-Est	9.1	6.59	18.80	5.44	0.09	0.44	0.40	0.04	5.69	0.2	0.08	6.0	1.2	0.23
Low-Est	4.1	3.89	11.90	3.30	0.07	0.22	0.02	0.02	2.57	0.0	0.01	2.0	0.7	0.02
Average	5.52	4.94	15.12	4.41	0.08	0.09	0.08	0.03	4.31	0.05	0.05	3.8	0.87	0.12
WHO STD	200	200	75	50	0.3	1.0	5.0	0.05	250	1.4	45	0.5	0.3	250



**Figure 9.** Summary of geochemical analysis of major elements in Old Town.

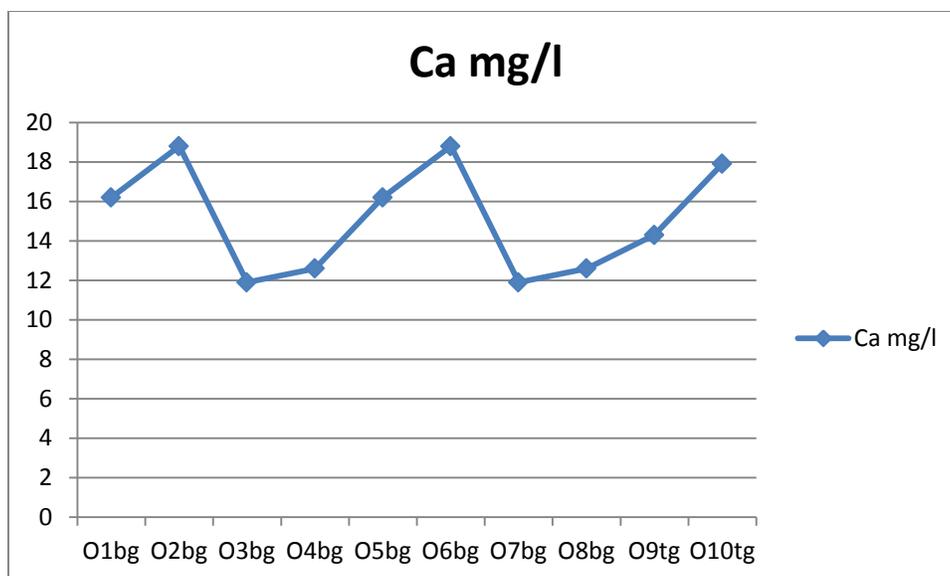


Figure 10. Variation plot of Ca ion concentration in Old Town area.

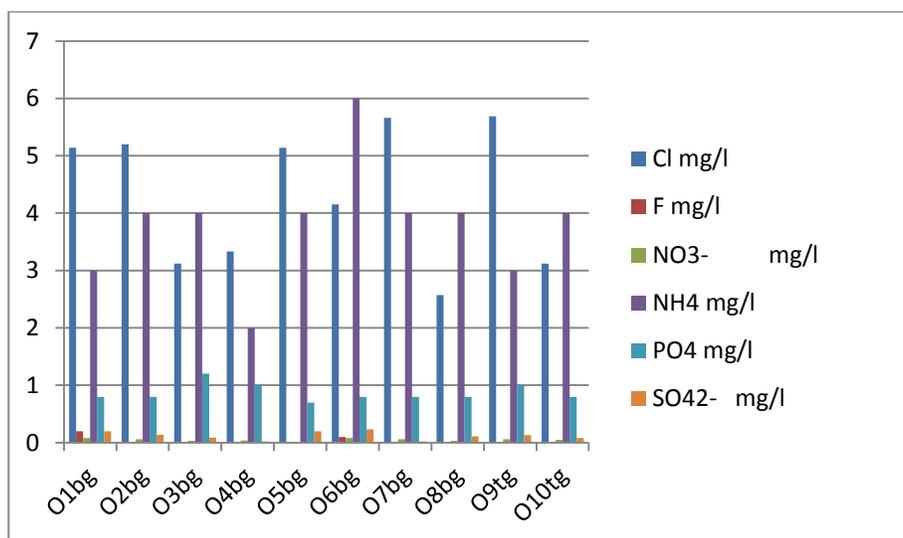
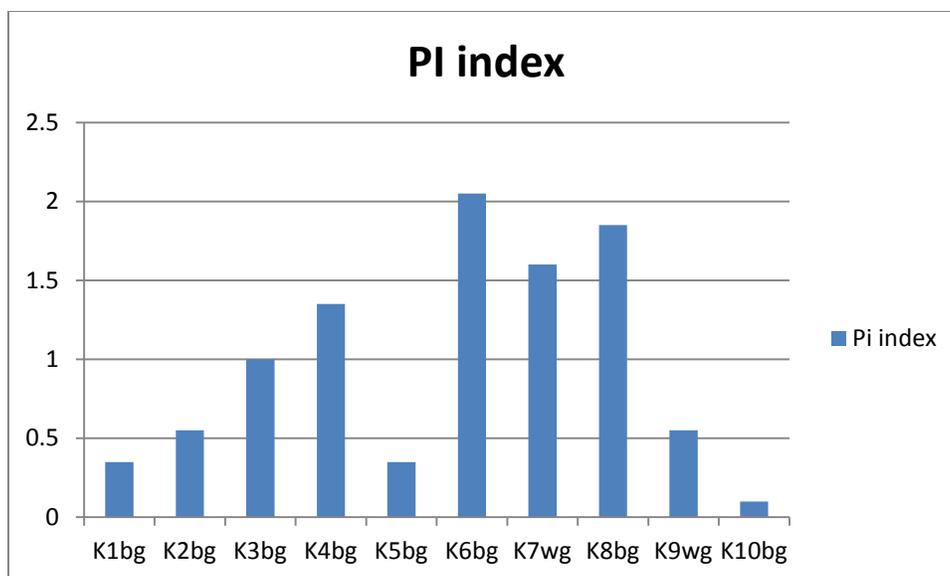


Figure 11. Summary of geochemical analysis of anion elements in Old Town.

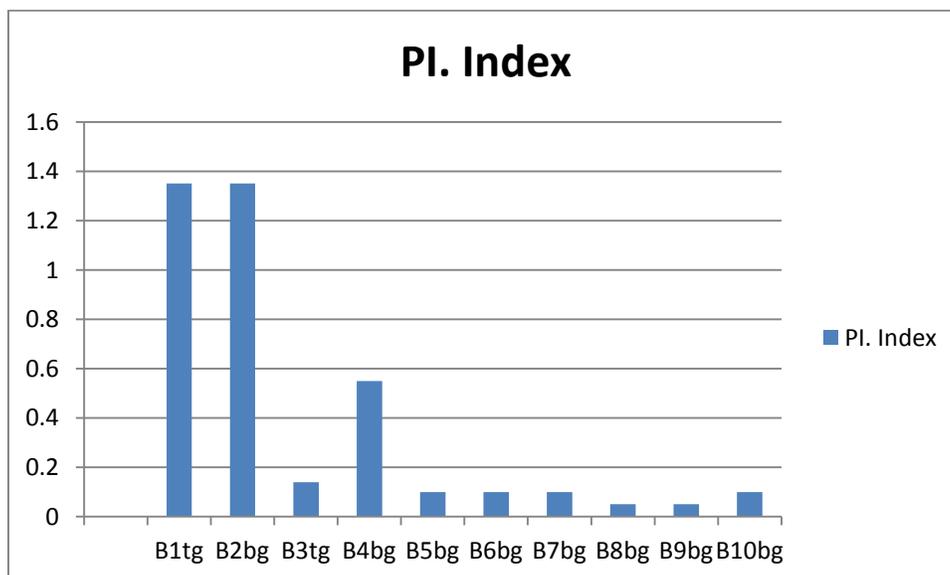
In this study pollution index was used to further evaluate the degree of major metal contamination in the water samples. Adopted is US Environmental Protection Agency (2002, 2008 and 2009). The pollution index (PI index) depicts the allowable levels of elemental concentration limits safe for human consumption. Therefore, United State Environmental Protection Agency (2012) tolerable level was used for water and the pollution index was calculated using the formula:

$$PI = (\text{Heavy metal concentration in water} / \text{Tolerable level}) / \text{Number of heavy metals}$$

Among the major elements analyzed for the water samples in the 3 areas of study only Mn ion show evidence of ion concentration higher than the recommended WHO limit while all other heavy metals such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> CU<sup>2+</sup> and Zn<sup>2+</sup> have ion concentration lower than the WHO standard tolerable limit. Therefore, PI index was calculated only for Mn ion for the Bayankara and Badariya areas that are characterized with higher Mn level greater than WHO (2012) standard limit. Water samples with pollution index > 1 is regarded as being contaminated but the values obtained for Bayankara water samples suggests that five locations K3bg, K4bg, K6bg, K7wg and K8bg have PI index > 1 (Fig. 12). Therefore, those locations are classified to have polluted water unfit for drinking based on manganese level above recommended.



**Figure 12. PI index for Bayankara area** PI index calculated for Badariya shows that only two locations have PI index > 1; this suggested that the locations B1tg and B2bg are polluted of manganese ion, thus, not fit for drinking purpose (Fig. 13).



**Figure 13. PI index for Badariya area.**

The presence of high concentration of Mn ion in the groundwater at Bayankara and Badariya may likely be from weathering of groundwater reaction with the sandstone aquifer rich in manganese minerals. It is also most likely to be due to environmental factors such as drainage or leaching from sewage dumps that litter the environment, couple with geological structures such as fractures, fault and joints that act as conduit pipes for transmission of leached manganese ions from sewages and landfills; thereby contaminated the local groundwater system. The intake of excess Mn ion from water could lead to liver damage and other health hazard.

The phosphorous anomalous values recorded in the 3 locations could result from decomposition of the aquifer system with production phosphorous if the aquifer is rich in it. It may as well be due to decaying sewages resulting from poor environmental sanitation. The source of phosphorous could be anthropogenic in nature due to application of chemical fertilizers to the farms, especially fertilizers that are rich in phosphates. The leached phosphorous percolate easily and readily into the groundwater as a result of peculiar structural features of the study areas which permit rapid percolation into the subsurface (Ola-Buraimo *et al.*, 2019).

Crops harvested from phosphate fertilizers fed on animals could as well increase the amount of phosphorous leached into the groundwater during rainfall as a result of application of manures derived from animal feces in addition to phosphate fertilizer. This situation will rather compound and increase the concentration of phosphorous in the groundwater system. There is also possibility of deriving phosphorous from detergents. Therefore, one of the best ways to curb excess concentration of phosphorous in groundwater is by avoiding over-fertilization of the farms and proper improvement in environmental sanitation.

High concentration of ammonia ions was recorded in all the 3 locations studied. This was attributed to contamination by sewage water or as a result of leaching of manure of chemical fertilizers applied to farms in the areas. The trends in average concentration of phosphate and ammonia ions tend to suggest the effect of environmental sanitation and agricultural activities in the areas. Bayankara is most affected with average contamination values of relatively high concentration of PO<sub>4</sub> ion and lowest concentration of NH<sub>4</sub> ion to be 0.81mg/l and 3.7mg/l respectively; Bayankara exhibits relatively lower concentration of PO<sub>4</sub> ion and highest concentration of NH<sub>4</sub> ion to be 0.75mg/l and 4.0mg/l respectively, while Old Town shows highest concentration of PO<sub>4</sub> ion and moderate concentration of NH<sub>4</sub> ion containing 0.87mg/l and 3.8mg/l respectively. However, WHO (1986), stated that ammonia has a toxic effects on human only if the intake is higher than the capacity to detoxify, at a dose of more than 100mg/kg of body weight per day, it influences metabolism by shifting the acid-base equilibrium, disturbing the glucose tolerance equilibrium, and reducing the tissue sensitivity to insulin.

## CONCLUSION

Thirty water samples from 3 locations in Birnin kebbi, Northwestern Nigeria were analyzed for geochemical study to determine water quality for drinking.

The results show that all the cations Na, K, Ca, Mg, Fe, Cu, and Zn ions from the 3 locations have values far less than maximum limit recommended by WHO except Mn ion that exhibits average concentration values in Bayankara 0.39mg/l, Badariya 0.16mg/l greater than 0.05mg/l tolerable limit by WHO standard. However, Old Town area has Mn ion values within the recommended limit. The PI index on manganese ion show that Bayankara is more polluted than Badariya probably due to unhygienic conditions of the areas and possibly due to dissolution of manganese mineral present in the sandstone aquifer.

The anions analyzed Cl, F, NO<sub>3</sub> and SO<sub>4</sub> have ion concentrations within the limits of WHO recommended for drinking water with the exception of NH<sub>4</sub> and PO<sub>4</sub> ion concentration values that are high in the 3 locations; showing values greater than 0.5mg/l for NH<sub>4</sub> and 0.3mg/l for PO<sub>4</sub>. The contaminants might have resulted from anthropogenic means including sewage leaching and excessive application of leached fertilizer and manure. The pollutants migrated through tectonic and sedimentary structures which serve as conduit pipes for rapid transmission to groundwater system in the study areas.

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**Corresponding author: A.O. Ola-Buraimo, Department of Geology, Federal University Birnin Kebbi, Birnin Kebbi, Nigeria**  
**Email: [rolaburaimo@yahoo.com](mailto:rolaburaimo@yahoo.com), [olatunji.ola-buraimo@fubk.edu.ng](mailto:olatunji.ola-buraimo@fubk.edu.ng) Phone: +2348033714079**