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Qualitative Evaluation of Groundwater from parts of Upper Benue River Basin for Compliance with Regulated Guidelines

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ABSTRACT

The quality of groundwater from Zing and environs in north-eastern Nigeria was evaluated to establish its compliance with the World Health organization (WHO), United State Environmental Protection Agency (EPA) and Nigeria Industrial Standard (NIS) and determine its safety for domestic use. Ten groundwater samples were collected in April, 2010 using EPA's groundwater sampling protocol and analyzed for major and minor elements using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Atomic Absorption Spectrometer (AAS). The results were evaluated using spreadsheet for groundwater analysis (AQQA) and contouring software (SUFER). Two water types (salts) were identified; these are Ca-Cl and Na-Cl. Total Dissolved Solids (TDS) values recorded ranges from 191mg/L to 308mg/L, Sodium Adsorption Ratio (SAR) ranges from 1.02 to 3.11, Exchangeable Sodium Ratio (ESR) ranges from 0.44 to 2.0. It was determined that groundwater from the study area were of medium salinity indicating that the water could be used for irrigation except for crops that are sensitive to salinity, where detrimental effects may be expected. Groundwater from the study area is good for domestic use. Although one sample had iron and other two had nitrate content slightly above the established standards, but almost all other parameters measured fall within the WHO, EPA and NIS drinking water Standard. **Keywords:** Standard, hydrochemistry, quality, Sodium Adsorption Ratio, Salinity

INTRODUCTION

The availability of clean and safe water supply has direct influence on economic well being, health and quality of life of a nation. Groundwater is most favoured as a source of drinking water in sub-Saharan Africa [1]. It is often thought to be cleaner and easier to treat as compared to surface water and as a result, many wells have either been sunk or drilled. However, groundwater can be contaminated by anthropogenic activities while naturally it contains several chemical components, which can lead to different kinds of health problems. According to [2] a groundwater source can potentially contain several naturally occurring chemical elements, many of which are not tested routinely as indices of water quality despite their known toxicity. In this study, ten groundwater samples were collected from boreholes equipped with hand pumps in parts of north-eastern Nigeria (Fig. 1) and analyzed for major and minor elements for the purpose of comparing its compliance with safe drinking water standards set by WHO, EPA and NIS.

The geology of the area studied comprises the crystalline basement made of poorly foliated granite and lenses of banded gneiss [3]. Groundwater in the crystalline basement rocks is localized in pockets and patches of weathered rock and fractures. Wells usually encounter water at shallow depths but yields are often low and subject to seasonal fluctuations. Boreholes are usually sited near river channels and where overburden is often thickest.

The result obtained showed that six of the samples studied were Ca-CI water type, indicating that water from these sources is stagnant [4], while five samples were Na-CI water type (fig....) and the Salinity value determined for all samples was medium type which shows that the water can be used for the irrigation of salinity tolerable crops. Results of major and minor elements showed good compliance to WHO, EPA and NIS standards for safe drinking water indicating that most of the water samples analysed complied well with the set standards.

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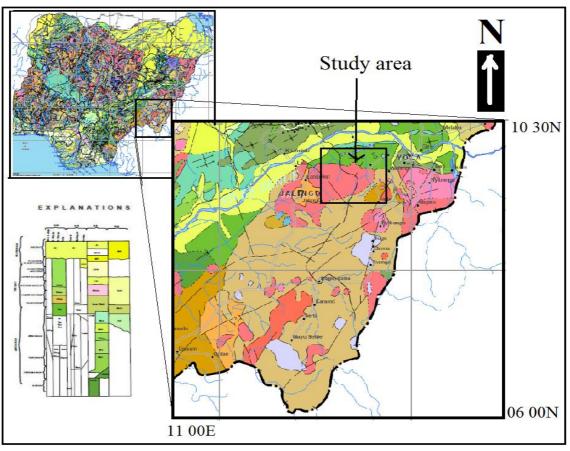


Fig. 1: Geologic map of north-eastern Nigeria (inset: map of Nigeria showing location of the study area, modified from GSNA, 2004)

MATERIALS AND METHODS

The study area is sparsely populated; therefore, samples obtained were the only obtainable around the area. Before sampling, the study area was gridded using Spatial Analysis and Decision Assistance [5] software which requires that at least one sample be collected from each grid. Sample collection was based on in EPA's document on sampling protocol. Before each sample was collected, the well was purged for about thirty minutes using an environmental sampler model 7571-05 "Cole-Parmer" make. In-situ measurements of conductivity, Total Dissolved Solids (TDS), pH and temperature were carried out using a "HACH" make pH and conductivity meter.

Major and minor elements were analyzed with Atomic Absorption Spectrometer (AAS) and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). An uncertainty is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurement [6]. The uncertainty applied to test methods in this study is within the ISO/IEC 17025-1999 Standard General requirements for the Competence of Testing and calibration [7]. It is based on the general rules outlined in the Guide to Expression of Uncertainty in Measurement [8]. Components that contribute to analytical measurement uncertainty include sampling, handling, transport, storage, preparation and testing [7]. To check for uncertainty during sampling, some samples were duplicated (replicate). These samples were taken from the same population and carried through stages of in-situ and laboratory measurements/testing.

In the laboratory, Instrument calibration Standard (ICS) was used to calibrate the various analytical equipments used. ICS is a reference material used to standardize an analytical instrument. Analysis of the ICS were later carried out to verify initial and continuing calibration, this is called Instrument Performance Check (IPC). The IPC is used to quantify the instrumental testing repeatability variance and bias. At some stage of the analysis, a clean matrix reference material with an established analyte concentration derived from a source independent of the instrument calibration standard (laboratory control sample) (LCS)) was carried through the entire samples preparation and testing procedure in

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order to quantify the variance and bias of the chemical preparation and instrument testing stages without matrix interference.

RESULTS

Results obtained from in-situ measurement are presented in Table 1 while results of analysis of major and minor elements are presented in Table 2.

				WELL						
	SAMPLE	COOR	DINATES	ELEV	SWL	H-HEAD		COND.	TEMPT.	TDS
S/N	ID	LATITUDE	LONGITUDE	(masl)	(mbgl)	(m)	PH	(µs/cm)	(°C)	(mg/L)
1	ST101	09°08.264´	11°40.034´	361.8	0.4	361.4	6.23	90.4	31.4	42.8
2	BH091	09°00.687´	11°45.332´	500.48	8.69	491.8	6.48	201	29.9	96.2
3	BHO81	08°59.535´	11°37.529´	446.53	8.14	438.39	6.58	203	30.4	96.9
4	BH071	09°03.000´	11°36.299´	387.71	8.08	379.63	7.06	654	30.4	318
5	BH061	09°05.129´	11°31.910´	270.05	10.79	259.26	6.69	518	31.4	251
6	BH051	08°57.649´	11°30.701´	515.42	11.77	503.65	6.2	138.1	30.4	65.8
7	BH041	08°54.486´	11°34.673´	508.1	10.36	497.74	7.23	599	30.3	291
8	BH031	08°50.989´	11°41.869´	540.11	9.14	530.96	6.95	286	29.8	137.4
9	ST021	08°52.728´	11°41.741´	5,10.00	0.7	5,10.00	7.29	194.8	32.5	93.2
10	BH011	08°55.965´	11°42.586´	2,37.35	10.36	2,37.99	6.85	576	31.2	280

Table 1: Posults of in situ measurement for the studied aroundwater

masl: meters above sea level, mblg: meters below ground level.

Table 2: Results of analysis of major and minor elements in studied groundwater

S/N	SAMPLE ID	Na (mg/L)	K (mg/L)	Fe (mg/L)	NO ₃ (mg/L)	Mg (mg/L)	Ca (mg/L)	SO₄ (mg/L)	HCO ₃ (mg/L)	CI (mg/L)
1	ST101	29.7±0.011	2.5±0.10	2.03±0.01	46.5±0.22	2.46±0.03	32.00±2.3	0.01±0.001	17.80±0.12	107.3 ±1.20
2	BH091	38.6±0.051	2.6±0.03	0.25±0.011	39.31±0.31	3.86±0.02	22.10±0.9	0.08±0.01	12.9. ±0.08	108.3 ±0.28
3	BHO81	27.6±0.031	0.9±0.021	0.42±0.03	36.2±0.22	1.56±0.21	42.0±1.34	0.03±0.001	5.60 ±0.51	121.7 ±0.36
4	BH071	33.4±0.05	2.7±0.057	0.013±0.005	39.3±0.23	3.75±0.54	49.33±2.01	0.33±0.021	56.90 ±0.36	110.8 ±0.51
5	BH061	38.9±0.025	3.4±0.021	0.02±0.001	36.4±0.91	3.6±0.10	27.42±1.21	0.23±0.001	20.80±0.51	118.00 ±0.14
6	BH051	33.5±0.03	3.7±0.001	0.37±0.002	47.3±0.21	4.01±0.12	27.00±0.77	0.04±0.001	36.00±0.03	109.7 ±0.92
7	BH041	3407±0.04	3.8±0.02	0.04 ± 0.001	34.3±0.23	3.9±0.31	43.42±0.91	0.27±0.01	37.00 ±0.21	123.5±0.32
8	BH031	37.2±0.025	3.5±0.06	0.02±0.003	46.32±0.21	3.21±0.21	34.87±2.0	0.04±0.001	31.00 ±0.61	119.0±0.85
9	ST021	56.4±0.02	12.6±0.12	0.02±0.001	52.4±0.61	7.21±0.02	13.20±1.43	1.75±0.021	6.08 ±0.02	143.00±0.32
10	BH011	29.6±0.07	1.2±0.012	0.17±0.18	54.3±0.51	3.49±0.32	46.35±0.37	0.73±0.01	35.00±0.56	123.5± 0.91

DISCUSSIONS

Results of in-situ measurements obtained indicate that static water levels range from 0.4 to 11.77m, pH values recorded range from 6.2 to 7.29, conductivity of water samples ranged from 90.4 to 654us/cm. Total Dissolved Solids ranged from 42.8 to 318mg/L (Table 1). A plot of conductivity against TDS gave a linear plot as expected for these measurements for all water samples (Fig. 2).

Both conductivity and TDS recorded for the water samples falls below the WHO and NIS standard of 1400 and 1000µS/cm for conductivity and WHO, EPA and NIS standard of 1000, 500 and 500mg/L for TDS, respectively. Based on Cheboratev[8] classification of waters, all the water samples falls under fresh category because all the TDS values recorded are all <1500mg/L.

Hydraulic head was calculated from ground surface elevation and static water levels measurements, assuming groundwater within the overburden to be occuring in a single and continues aquifer, the direction of groundwater flow in the study area was contoured using Sufer 9 contouring software. From the contoured map, it was clear that the direction of groundwater flow is from higher hydraulic head to low hydraulic head as discribed in Fig. 3.



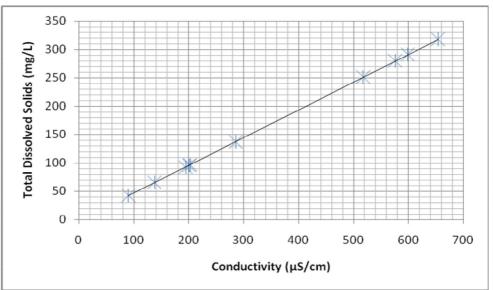


Fig. 2: Plot of conductivity against TDS.

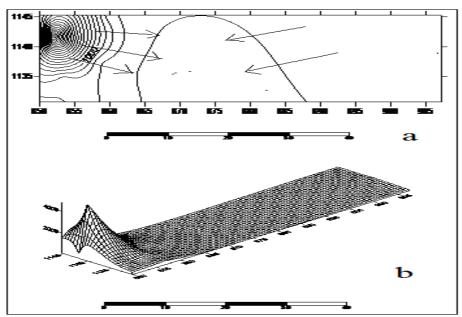


Fig. 3: Groundwater flow in the study area (a: flow contour, b: wireframe plot of flow contour)

Calcium (Ca): Calcium is essential for the human body, it is essential in the formation of bones and teeth. In addition, it plays a role in neuromuscular excitability (decreases it), good function of the conducting myocardial system, heart and muscle contractility, intracellular information transmission and blood coagulability. Osteoporosis and osteomalacia are the most common manifestations of calcium deficiency; a less common but proved disorder attributable to calcium deficiency is hypertension.

The recommended calcium daily intake for adults ranges between 700 and 1000mg/L [9]; [10]. Some population groups may need a higher intake. There is no health guide recommendation for calcium in all the three reference documents [11]; [12]; [13].

The recorded calcium values in the studied groundwater samples ranged from 13.2 to 49.33mg/L all the samples analysed had calcium values less than 1000mg/L, people taking more than 1000mg/L per day may be exposed to certain risks as reported in Scientific Committee for Food, 1993 and Committee on Dietary Reference Intake, 1997.

Chloride (CI): High concentrations of chloride give a salty taste to water and beverages. Taste thresholds for the chloride anion depend on the associated cation and are in the range of 200–300mg/L for sodium, potassium and calcium chloride. Concentrations in excess of 250mg/L are increasingly likely to be detected by taste, but some consumers may become accustomed to low

levels of chloride-induced taste. No health-based guideline value is proposed for chloride in drinking-water.

EPA has identified 250mg/L as a concentration at which chloride can be expected to cause a salty taste in drinking water. Water users typically notice the presence of high chloride exposed to an equal amount of sodium. The secondary level of 250mg/L is based on aesthetic concerns, and is only advisory in the Federal Safe Drinking Water program.

The chloride values recorded for the studied groundwater sample ranges from 107.3 to 143mg/L. This shows that all the studied water samples had chloride value below the 250mg/L above which aesthetic concern is envisaged as advised by the Federal Safe Drinking Water program.

Iron (Fe): Anaerobic groundwater may contain ferrous iron at concentrations of up to several milligrams per litre without discoloration or turbidity in the water when directly pumped from a well. On exposure to the atmosphere, however, the ferrous iron oxidizes to ferric iron, giving an objectionable reddish-brown colour to the water. Iron also promotes the growth of "iron bacteria," which derive their energy from the oxidation of ferrous iron to ferric iron and in the process deposit a slimy coating on the piping. At levels above 0.3 mg/L, iron stains laundry and plumbing fixtures. There is usually no noticeable taste at iron concentrations below 0.3 mg/L, although turbidity and colour may develop. No health-based guideline value is proposed for iron in either WHO (2011), EPA (2000) or NIS (2007). The values recorded for iron in the studied groundwater samples ranges between 0.013 to 2.0mg/L The concentration of calcium, Chloride and sulphate also influence iron corrosion. Only one sample (ST101) had iron content greater than the WHO's 1mg/L, while three samples (ST101, BH081 and BH051) had values greater than NIS's 0.3mg/L.

Potassium (K): Potassium occurs in various minerals, from which it may be dissolved through weathering processes. Examples are feldspars (orthoclase and microcline), which are however not very significant for potassium compounds production, and chlorine minerals such as carnalite and sylvite, which are most favourable for production purposes. Some clay minerals contain potassium. It ends up in seawater through natural processes, where it mainly settles in sediments. Potassium is a dietary requirement for humans, and we take up about 1-6g/day at a requirement of 2-3.5g/day. The total potassium amount in the human body lies somewhere between 110 and 140g and mainly depends upon muscle mass. The muscles contain most potassium after red blood cells and brain tissue. Whereas its opponent sodium is present in intracellular fluids, potassium is mainly present within cells. It preserves osmotic pressure. The relation of potassium in cells to potassium in plasma is 27:1, and is regulated by means of sodium-potassium pumps. Vital functions of potassium include its role in nerve stimulus, muscle contractions, blood pressure regulation and protein dissolution. It protects the heart and arteries, and may even prevent cardiovascular disease. The relation of sodium to potassium used to be 1:16, and is now about 3:1, which mainly prevents high sodium uptake. Potassium shortages are relatively rare, but may lead to depression, muscle weakness, heart rhythm disorder and confusion. Potassium loss may be a consequence of chronic diarrhoea or kidney disease, because the physical potassium balance is regulated by the kidneys. When kidneys operate insufficiently, potassium intake must be limited to prevent greater losses. The values of potassium recorded in the studied water samples ranges from 10.9 to 12.6mg/L. There is no health guide for potassium in the NIS and EPA Guide line but WHO has set a secondary health guide of 55mg/L which shows all the samples studied had potassium content less than the 55mg/L secondary guide set by WHO(2008).

Magnesium (Mg): Magnesium is usually less abundant in water than calcium, which is easy to understand since magnesium is found in the Earth's crust in much lower amount compared to calcium. In common underground and surface waters the weight concentration of Ca is usually several times higher compared to that of Mg, the Ca to Mg ratio reaching up to 10.

Nevertheless, a common Ca to Mg ratio is about 4, which corresponds to a substance ratio of 2.4 [14]. In low- and medium-mineralized underground and surface waters (as drinking waters are), calcium and magnesium are mainly present as simple ions Ca²⁺ and Mg²⁺, the Ca levels varying from tens to hundreds of mg/l and the Mg concentrations varying from units to tens of mg/l.

Magnesium plays an important role as a cofactor and activator of more than 300 enzymatic reactions including glycolysis, ATP metabolism, transport of elements such as Na, K and Ca through membranes, synthesis of proteins and nucleic acids, neuromuscular excitability and muscle contraction etc. It acts as a natural antagonist of calcium.

PARAMETER	UNIT	WHO (2011)	EPA (2004)	NIS (2007)	THIS WORK		- REMARK
					RANGE	MEAN	
Temperature	°C	-			25 - 35	30.21	
Conductivity	µohm/cm	1,400		1000	65.9 - 3840	419.88	Within limit
Hardness(Total)	mg/L	500		150			-
TDS	mg/L	1,000	500	500	34.6 - 2260	291.20	Within limit
рН	рН	6.5 - 8.5	6.5 - 8.5	6.5 - 8.5	5.6 - 7.7	6.80	Within limit
Са	mg/L	75			3.1 - 1524	239.56	Within limit
Mg	mg/L	50		0.2	21 - 1375	228.50	Within WHO and EPA limi
Na	mg/L	200		200	14.8 - 350	99.36	Within limit
Fe	mg/L	<1		0.3	0.7 - 17.5	7.88	All with WHO, 3 >NIS limi
К	mg/L	55			16.9 - 308	116.11	Within limit
HCO3-	mg/L	1,000			157 - 270	194.11	Within limit
SO 4 ²⁻	mg/L	400	250	100	11.7 - 64.6	24.56	Within limit
CI	mg/L	250	250	250	41.34 - 81	48.61	Within 250mg/L limit
NO ₃	mg/L	50	10	50	29 - 65	44.34	2 > WHO & NIS, all > EPA lir

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Magnesium deficiency increases risk to humans of developing various pathological conditions such as vasoconstrictions, hypertension, cardiac arrhythmia, atherosclerotic vascular diseases, and acute myocardial infection, eclampsia in pregnant women, possibly diabetes mellitus of type II and osteoporosis [15]; [16]; [17]. These relationships reported in multiple clinical and epidemiological studies have recently been more and more supported by the results of many experimental studies on animals [18]. The recommended magnesium daily intake for an adult is about 300-400mg/L [9]; [10]. The values of magnesium recorded in the studied groundwater ranges from 1.56 to 7.21mg/L. All samples studied had magnesium values that results to less than 400mgpd intake for adult as suggested by the Scientific Committee for Food, 1993; Committee on Dietary Reference Intake, 1997. *Nitrate (NO₃):* The source of nitrate as contaminant in drinking water is runoff from fertilizer use; leakage from septic tanks, sewage; erosion of natural deposits. Nitrate may be present as a consequence of tillage when there is no growth to take up nitrate released from decomposing plants, from the application of excess inorganic or organic fertilizer and in slurry from animal production. WHO and NIS has set the MCL for nitrate at 50mg/L, while for EPA is 10mg/L. Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome. Nitrate concentration in the studied water samples ranged from 34.3 to 54.3mg/L. Two of the samples (ST021 and BH011) studied had nitrate content exceeding the WHO and NIS's MCL of 50mg/L while all the sample had nitrate exceeding the EPA MCL of 10mg/L. The high nitrate concentration recorded in the sample might be as a result of excess use of chemical fertilizers in the area.

Sodium (Na): The taste threshold concentration of sodium in water depends on the associated anion and the temperature of the solution. At room temperature, the average taste threshold for sodium is about 200mg/L. No health-based guideline value has been derived for WHO and EPA, but the NIS has set a secondary MCL at 200mg/L. Values of sodium recorded for the studied water samples ranges between 22.6 to 56.4mg/L. Values recorded showed that sodium contents of all the samples fall within NIS's MCL of 200mg/L.

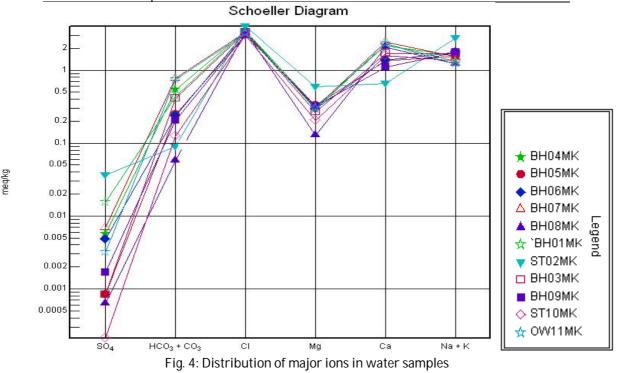
Sulfate (SO₄): The presence of sulfate in drinking-water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers. Taste impairment varies with the nature of the associated cation; taste thresholds have been found to range from 250mg/L for sodium

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sulphate to 1000mg/L for calcium sulfate. It is generally considered that taste impairment is minimal at levels below 250mg/L. Only a secondary health-based guideline value has been derived for sulphate, this is set at 400mg/L, 250mg/L and 100mg/L by WHO, EPA and NIS, respectively. The recorded sulfate value in the studied water samples ranged between 0.01 to 1.75mg/L (Table 2), suggesting that all the groundwater samples studied had sulphate content below the secondary MCL set by all the regulatory bodies (WHO, EPA and NIS).

Two water types (salts) were identified; these are Ca-Cl and Na-Cl. Total Dissolved Solids (TDS) values recorded ranges from 191mg/L to 308mg/L, Sodium Adsorption Ratio (SAR) ranged from 1.02 to 3.11, Exchangeable Sodium Ratio (ESR) ranged from 0.44 to 2.0.

<u> </u>	fication with corresponding	conductivity and TDS
Salinity classification	Conductivity (µohms/cm)	TDS (mg/L)
Low salinity, no detrimental effects expected	< 250	< 200
Medium salinity, detrimental effects to sensitive crops	250 – 750	200 - 500
High salinity, adverse effects on many crops	750 - 2250	500 - 1500
Very high salinity, suitable only for salt tolerant plants	2250 - 5000	1500 - 3000



It was determined that groundwater from the studied area are of medium salinity (Table 3) indicating that the water can be used irrigation except for crops that are sensitive to salinity, detrimental effects could be expected. The distribution of major constituents SO_4 , HCO_3 , CI, Mg, Ca and Na as could observed from Fig. 4 is in the order $CI > Ca > Na+K > HCO_3 > SO_4$.

CONCLUSION

Water is the most essential ingredient of Earth's life support system that flows through every human endeavour. Access to clean drinking water is a basic human right. This study has discovered that

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groundwater from the study area is good for domestic use, though three samples had iron and two had nitrate content slightly above standard. But all the other parameters measured fell within the WHO, EPA and NIS Standard (Table 3). While most water samples studied had nitrate contents within WHO, EPA and NIS standard, Arabi et al., 2010 carried out a study of Suitability of Groundwater for Household and Irrigation Purposes in Parts of Adamawa State, North-eastern, Nigeria and reported that groundwater from the area had nitrate content exceeding the standard which they attributed to the use of nitrate fertilizers. Arabi et al., 2011 also reported nitrate above standard in shallow groundwater from Mika and attributed it to chemical fertilizer used by farmers. In this study, the nitrate concentrations in the sample were mostly below standard though from same area but in this case, the source of water samples were from borehole believed to be deeper than hand dug wells sampled for earlier from workers. Therefore, this clearly indicates that water from deeper wells is not affected by nitrate from fertilizers as a result of leaching as reported for shallow wells.

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