

ACADEMIC JOURNAL

Assessment of Physico-chemical properties, Heavy metal concentrations and levels of Radioisotopes in Borehole and Well water underground sources in Kaduna State, Nigeria.

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ABSTRACT

The water quality assessment in the three senatorial areas (Zaria, Kaduna, Kafanchan) of Kaduna State was conducted by determining the physico-chemical parameters and heavy metal concentration of water samples collected from 72 sampled locations via borehole and well water underground source during the wet season. The physico-chemical parameters were determined using Standard methods and the heavy metal concentrations (Pb, Fe, Cd, Co, Cr, Cu, Ni) were determined using Atomic Absorption Spectrophotometer (AAS) while the radioisotopes were determined using X-rays Fluorescence method (XRF). The Physico-chemical parameter result for the water samples obtained from the borehole and well water source showed that pH ranged from (4.03 – 6.66, 2.12-6.56), Temperature (^oC) (23.7 – 27.3, 25.2 – 28.4), Conductivity (mS/cm)(0.05-1.44, 0.14 – 0.78), Total Dissolved Solid (mg/L)(0.02- 0.72, 0.07 – 0.72) and Chemical Oxygen Demand (mg/L) (9.36 – 21.12, 11.52 – 27.52). The values obtained from the physicochemical parameters analysis were compared with the WHO and NIS standards for drinking water and the results showed that the values were within the acceptable range for drinking water except for some water samples which has pH, COD and EC that were higher in some sites. The result showed that there were no significant difference ($P < 0.05$) in all the physico-chemical values obtained from the borehole and underground water samples of the three zones. The heavy metal concentration result showed that Cu (mg/L) ranged from (0.0001 – 0.0088, 0.0000 – 0.0560), Cr (mg/L) (0.0000 – 0.0360, 0.0005 – 0.0056), Cd (mg/L) (0.0001 – 0.0028, 0.0000 – 0.0040), Pb (mg/L) (0.0001 – 0.0040, 0.0005 – 0.0080), Ni (mg/L) (0.0004 – 0.0090, 0.0000 – 0.0048), Fe (mg/L) (0.0001 – 0.0200, 0.0000 – 0.0900) and Co (mg/L) (0.0001 – 0.0022, 0.0001 – 0.0040). The heavy metals (Pb, Fe, Co and Cu) were present in the water samples at values that were within the permissible limit recommended for heavy metals in water while Ni, Cr and Cd in some of the sampling locations have higher values than WHO and NIS permissible recommended limits while the radioisotopes were not present during the wet seasons. The water samples were considered unsafe for consumption. Majority of the water samples obtained from the borehole and well water source were considered safe.

Keywords: Borehole, Well water, AAS, physico-chemical parameters.

INTRODUCTION

Water is a universal solvent essential to man for various activities such as drinking, cooking, industrial and agricultural processes, waste disposal and human recreation (Oluyemiet *al.*, 2010). Ground water is an important source of drinking water for humankind, it contains over 90% of the fresh water resources and it is an important reserve of good quality water. Groundwater, like any other water resource, is not just of public health to the consumers alone but of economic value to the government (Armonet *al.*, 1994). Water does not only quench thirst but provide some of the metals that are essential to sustain life such as calcium, magnesium, potassium and sodium for normal body functions. Also, cobalt, copper, iron, manganese, molybdenum and zinc are needed at low levels as catalyst for effective enzyme activities in the body (Adepoju-Bello *et al.*, 2009).

The two main problems man contends with are the quantity (source and amount) and quality of water (Adeniyi, 2004). Drinking water has always been a major issue in many countries like Nigeria (Rajiniyet *al.*, 2010) and majority of the rural populace in Nigeria do not have access to potable water. Only few people can afford and rely on purified and treated bottled water particularly for consumption therefore, borehole water serve as one of the major source of both drinking and domestic water used in the local population of Nigeria (Abajeet *al.*, 2009). Historically, Well water has long been considered as one of the purest form of water in nature and meets the overall demand of rural and semi-urban people (Gamboet *al.*, 2015). Studies have shown that the surface water (river, lake and streams) systems are susceptible to pollution than groundwater. However, it has been reported that groundwater contains enhanced concentrations of arsenic, iron, fluoride, radioactive elements and nitrates attributed to natural processes as well as human-mediated activities such as seepages from underground storage facilities and faulty septic systems (Anakeet *al.*, 2014).

Unfortunately borehole water like water from other sources is never entirely pure. It varies in purity depending on the geological conditions of the soil through which the ground water flows and some anthropogenic activities (Ukpong and Okon, 2013). In 1997, the World Health Organization (WHO) reported that 40% of deaths in developing nations occur due to infection from water related diseases and estimated 500 million cases of diarrhoea occurs every year in children below 5 years in parts of Asia, Africa and Latin America (WHO, 2011). Improper management of solid waste is one of the main causes of environmental (water and soil) pollution and degradation in many cities, especially in developing countries. Many of these cities lack serious regulations and proper disposal facilities, including for harmful waste. Such waste may be infectious, toxic or radioactive (Tslalom and Kiflom, 2015). In Nigeria, open dumping of municipal solid wastes, is mainly the existing method of waste disposal used even in capital cities except perhaps among few and affluent institutions (Okoye and Okoye, 2008). Other sources of contamination include effluents from industries, abattoir activities and pesticides (Iornumbe and Onah, 2008) and from animal faecal discharges into surface and ground waters due to run-off (Oko, 2008). Some trace constituents that are associated with industrial pollution, such as arsenic and chromium, may also occur in completely pristine ground water at concentrations that are high enough to make that water unsuitable for drinking (Muhammad, 2012). Much worrisome, is the direct consumption of water from underground sources without adequate treatment, as such norm

had led to the death of people in Kaduna South Local Government from Cholera and Typhoid in 2001(Ugyaet *al.*, 2015).

Drinking water produced by public and private water supplies are not constantly monitored by regulatory agencies such as National Environmental Standards and Regulations Enforcement Agency(NESREA) and National Agency for Food and Drugs Administration and Control (NAFDAC) respectively in Nigeria, resulting in proliferation and distribution of unsafe and substandard drinking water to consumers.It is in this light that constant monitoring of underground water qualities be encouraged by the consumers themselves with the help of the government as the borehole and well water source are becoming the alternatives of drinking water which resulted of inconsistent flow of pipe borne water supply as often experienced in some states in Nigeria, including Kaduna State.

MATERIALS AND METHODS

STUDY AREA

The study area, Kaduna usually referred to as Kaduna State is a state in the North West. It is located at the northern plan of high plains, latitudes 10°N and between longitudes 7°E and 8°E and at an altitude of 645m above sea level (Bununuet *al.*, 2015). Kaduna is characterised by two distinct seasons in the year, the dry season and rainy season. The dry season run from October to April and is characterized by cold and dry conditions with harmattan wind that blows from north east toward south-west. The rainy season which runs from May to early October is characterized by warm and humid conditions with wind blowing from the South-West towards north-east. The average monthly temperature for the city is between 26°C and 34°C (Bununuet *al.*, 2015).

SAMPLE COLLECTION, PRE-TREATMENT AND PRESERVATION.

Groundwater samples were collected in April, 2015, according to standard procedures by (APHA, 1998) from the three senatorial district of Kaduna state. Thirty six water samples were collected from hand-dug wells and thirty six water samples from boreholes all within the senatorial districts. This gave a total of seventy two samples. Samples were collected in 1L polyethylene container. The sample containers were washed with 20 % analytical grade nitric acid and rigorously rinsed with distilled deionized water. Prior to sampling, the sample containers were further rinsed with the actual sample. Collected samples were preserved by chemical adjustment of the pH < 2, by acidifying with 5 milliliters of analytical grade nitric acid. This reduces precipitation and sorption losses to the container walls. The samples were stored under ice on transit and then refrigerated after arriving at the laboratory at a temperature of (4°C) prior to analysis (Anakeet *al.*, 2014).

HEAVY METALS ANALYSIS

Water sample(100 cm³)was collected and transferred into a beaker and digested using 5cm³ of concentrated HNO₃. The beaker was placed in a hotplate and heated until the final volume was 5cm³. After heating the water samples was transferred into a 100cm³ volumetric flask and made up to the mark with de-ionised water (Nouriet *al.*, 2006). Furthermore, the water samples were analysed for (Cu, Cr, Cd, Pb, Ni, Fe and Co) using an Atomic Absorption Spectrophotometer.The digestion was done in order to destroy the organic matrix capable of trapping the trace metals, and thus making them unavailable for the instrumental analysis.

Also, prior to metal ion analyses, calibration solutions of the target metal ions were prepared from standard stock by serial dilution.

DETERMINATION OF TDS, pH, TEMPERATURE AND ELECTRICAL CONDUCTIVITY.

These parameters were determined using the HACH complete water laboratory model 44600 and Nahita pH meter model 903 instrument. Water samples (100 cm³) were collected in 250 cm³ pyrex beaker and the probe of the meter dipped into the container. TDS, pH, Temp and electrical conductivity were determined and recorded. This was repeated for all the water samples in all the sampled locations.

DETERMINATION OF COD

Drinking water samples, 50 cm³ was collected and transferred to a 250 cm³ beaker containing 10 cm³ of 0.01M KMnO₄ and 2 cm³ of 25% H₂SO₄ already mixed. The solution was refluxed using a reflux condenser for one hour and allowed to cool at room temperature. Then 1% Ammonium Oxalate (NH₄)₂C₂O₄.H₂O was carefully prepared and added drop wise to the solution until colourless solution was observed. The solution obtained was then titrated with 0.01M KMnO₄ until a pink solution was observed. The COD of the water samples are obtained as shown below.

$$\text{COD (mg/L)} = (B - A) \times M \times 16000 \div \text{Volume of the water sample}$$

Where A is titre value of sample, B is titre value of blank, M = Molarity of KMnO₄ and 16000 (Constant).

DETERMINATION OF RADIOISOTOPES

The determination of radioisotopes in the water samples was carried out by measuring 100 cm³ of the water samples using a measuring cylinder. The measured water samples was pre-concentrated by heating in clean beaker on hot plate to the volume of 5 mL, de-ionized distilled water (5 mL) was used to rinse the concentrated sample into measuring sample cups for analysis of the radioisotopes using EDXRF. Model: minipal 4. NO. DY 1055 machine (Injuk and Grieken, 1993).

RESULTS AND DISCUSSIONS

The water samples obtained from the well and borehole underground sources are meant to comply with the World Health Organization (WHO) and the Nigerian Industrial Standards (NIS) regulatory limits for drinking water. All physico-chemical parameter and heavy metal values obtained from both underground sources were evaluated using the regulatory standard that was shown below. The results of the physicochemical parameters analysis for the underground water samples obtained from the senatorial districts are shown in Tables 1(a) – 2 (d).

Table 1(a): The result of physicochemical parameters determination of the borehole water samples from the three senatorial districts.

ID No	Location of sample	Temperature (°C)	PH	Conductivity (mS/cm)	TDS (g/L)	COD (mg/L)
BH 01	WUSASA- ZA	26.1±0.02	5.01±0.22	0.45±0.10	0.22±0.05	17.23±1.99
BH 02	KOFA DOKA- ZA	26.7±0.62	5.02±0.21	0.58±0.23	0.29±0.12	12.16±3.08
BH 03	KONGO- ZA	27.1±1.02	5.78±0.55	1.00±0.65	0.50±0.33	13.41±1.83
BH 04	SABO GARI- ZA	27.3±1.22	4.03±1.20	0.12±0.23	0.06±0.11	21.12±5.88
BH 05	EMANTO- ZA	26.9±0.82	6.19±0.96	1.44±1.09	0.72±0.55	18.56±3.32
BH 06	SAMARU- ZA	27.2±1.12	6.21±0.98	1.15±0.80	0.53±0.36	15.30±0.06
BH 07	DUTSE- ZA	26.8±0.72	6.24±1.01	0.42±0.07	0.56±0.39	17.20±1.96
BH 08	BASSAWA- ZA	27.1±1.02	4.04±1.19	0.52±0.19	0.20±0.03	12.10±3.14
BH 09	CHIKA- ZA	27.2±1.12	5.68±0.45	0.10±0.25	0.28±0.11	13.40±1.84
BH 10	GRACELAND- ZA	26.1±0.02	5.02±0.21	1.24±0.89	0.51±0.34	18.56±3.32
BH 11	TUDUN WADA- ZA	26.2±0.12	5.41±0.18	0.52±0.17	0.06±0.11	12.11±3.13
BH 12	U/GODO- KD	27.1±1.02	5.44±0.21	1.14±0.79	0.08±0.09	12.12±3.12
BH 13	NARAYI – KD	25.9±0.18	4.82±0.41	0.48±0.13	0.24±0.07	16.64±1.40
BH 14	TELEVISION- KD	25.6±0.48	5.13±0.10	0.09±0.26	0.04±0.13	11.52±3.72
BH 15	GONIGORA- KD	25.4±0.68	5.26±0.03	0.05±0.30	0.02±0.15	16.41±1.17
BH 16	C/ MARKET- KD	25.2±0.88	5.78±0.55	0.46±0.11	0.23±0.06	13.41±1.83
BH 17	MANDO- KD	25.2±0.88	4.05±1.18	0.09±0.26	0.02±0.15	17.40±2.16
BH 18	H/ DAMANI- KD	23.7±2.38	4.44±0.79	0.05±0.30	0.02±0.15	20.40±5.16
BH 19	KAWO- KD	25.4±0.68	4.44±0.79	0.05±0.30	0.02±0.15	16.60±1.36
BH 20	MALALI- KD	25.3±0.78	4.05±1.18	0.09±0.26	0.02±0.15	11.52±3.72
BH 21	TUDUNWADA- KD	25.4±0.68	5.78±0.55	0.42±0.07	0.22±0.05	13.40±1.84
BH 22	KAKURI- KD	25.2±0.88	5.26±0.03	0.41±0.06	0.02±0.15	13.40±1.84
BH 23	HAYAN BAKIN- KD	25.2±0.88	5.26±0.03	0.16±0.19	0.02±0.15	13.22±2.02
BH 24	SABO- KD	25.3±0.78	5.50±0.27	0.34±0.01	0.02±0.15	13.44±1.80
BH 25	ADWANI I- KF	25.0±1.08	5.38±0.15	0.13±0.22	0.08±0.09	21.12±5.88
BH 26	U/RIMI	26.7±0.62	6.66±1.43	0.06±0.29	0.57±0.40	14.72±0.52
BH 27	GARAJI ROAD- KF	26.3±0.22	5.88±0.65	0.18±0.17	0.06±0.11	17.92±2.68
BH 28	KATSIT- KF	26.1±0.02	4.87±0.36	0.06±0.29	0.03±0.14	13.44±1.80
BH 29	MADAKIA- KF	26.1±0.02	5.14±0.09	0.15±0.02	0.08±0.09	15.36±0.12
BH 30	TAKAU – KF	26.3±0.22	5.23±0.00	0.06±0.29	0.03±0.14	9.36±5.88
BH 31	ADWANI II- KF	26.4±0.32	5.14±0.09	0.18±0.17	0.08±0.09	15.36±0.12
BH 32	KANIKON –KF	26.4±0.32	4.87±0.36	0.06±0.29	0.08±0.09	13.44±1.80
BH 33	FASAN – KF	26.1±0.02	5.88±0.65	0.08±0.27	0.03±0.14	14.72±0.52
BH 34	LOKO- KF	26.2±0.12	5.11±0.12	0.07±0.28	0.06±0.11	21.12±5.88
BH 35	U/FARI –KF	26.3±0.22	5.23±0.00	0.06±0.29	0.07±0.10	17.92±2.68
BH 36	U/BAKI –KF	26.4±0.32	5.14±0.09	0.16±0.19	0.05±0.12	13.44±1.80
	MEAN±STD	26.08±0.80	5.23±0.64	0.35±0.39	0.17±0.20	15.24±3.02

Key: ZA - Zaria, KD – Kaduna, KF-Kafanchan. **BH01 – BH36:** Borehole water sample of dry season

Table 1(b): Comparison of observed values of the physicochemical parameters of borehole water in the three senatorial districts with Nigeria and World health Organisation (WHO) standards.

	Units	NIS (2007)	WHO (2011)	MINIMUM	MAXIMUM	MEAN
Temperature	°C	25	30-35	23.7	27.3	26.08
pH		6.8-8.5	6.5-9.2	4.03	6.66	5.23
Conductivity	mS/cm	250	250	0.05	1.44	0.35
TDS	mg/L	500	500	0.02	0.72	0.17
COD	mg/L	10	10	9.36	21.12	15.24

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Table 1 (c): The result of physicochemical parameters determination of the well water samples from three senatorial districts.

ID No	Location of sample	Temperature (0°C)	PH	Conductivity (mS/cm)	TDS (g/L)	COD (mg/L)
WW 01	WUSASA- ZA	28.3±1.60	5.98±1.24	0.76±0.28	0.38±0.12	20.48±3.83
WW 02	KOFA DOKA- ZA	28.1±1.40	5.34±0.60	0.41±0.07	0.20±0.06	20.48±3.83
WW 03	KONGO- ZA	28.2±1.50	5.15±0.41	0.61±0.13	0.30±0.04	15.56±1.09
WW 04	SABO GARI- ZA	28.2±1.50	5.46±0.72	0.31±0.17	0.15±0.11	16.00±0.65
WW 05	EMANTO- ZA	28.4±1.70	5.69±0.95	0.44±0.04	0.22±0.04	27.52±10.87
WW 06	SAMARU- ZA	28.2±1.50	6.01±1.27	0.14±0.34	0.07±0.19	17.28±0.63
WW 07	DUTSE- ZA	28.3±1.60	5.15±0.41	0.76±0.28	0.38±0.12	20.48±3.83
WW 08	BASSAWA- ZA	28.1±1.40	5.46±0.72	0.41±0.07	0.20±0.06	18.56±1.91
WW 09	CHIKA- ZA	28.2±1.50	5.69±0.95	0.61±0.13	0.30±0.04	16.00±0.65
WW 10	GRACELAND- ZA	28.3±1.60	5.34±0.60	0.44±0.04	0.15±0.11	20.48±3.83
WW 11	TUDUN WADA- ZA	28.2±1.50	5.98±1.24	0.31±0.17	0.30±0.04	18.56±1.91
WW 12	U/GODO- KD	28.2±1.50	5.15±0.41	0.61±0.13	0.07±0.19	15.00±1.65
WW 13	NARAYI – KD	25.2±1.50	5.13±0.39	0.67±0.19	0.33±0.07	19.20±2.55
WW 14	TELEVISION- KD	25.3±1.40	5.05±0.31	0.40±0.08	0.20±0.06	16.64±0.01
WW 15	GONIGORA- KD	25.7±1.00	6.56±1.82	0.78±0.30	0.39±0.13	16.0±0.65
WW 16	C/ MARKET-KD	25.4±1.30	5.37±0.63	0.55±0.07	0.27±0.01	14.72±1.93
WW 17	MANDO-KD	25.7±1.00	3.90±0.84	0.27±0.21	0.13±0.13	13.44±3.21
WW 18	H/ DAMANI- KD	25.7±1.00	3.90±0.84	0.27±0.21	0.13±0.13	14.70±1.95
WW 19	KAWO- KD	25.4±1.30	5.37±0.63	0.40±0.08	0.27±0.01	13.44±3.21
WW 20	MALALI- KD	25.7±1.00	6.56±1.82	0.78±0.30	0.78±0.52	14.72±1.93
WW 21	TUDUNWADA- KD	25.4±1.30	5.05±0.31	0.55±0.07	0.55±0.29	16.00±0.65
WW 22	KAKURI- KD	25.2±1.50	5.13±0.39	0.27±0.21	0.27±0.01	16.40±0.25
WW 23	HAYAN BAKIN- KD	25.7±1.00	5.13±0.39	0.67±0.19	0.33±0.07	16.44±0.21
WW 24	SABO- KD	25.7±1.00	5.06±0.32	0.78±0.30	0.39±0.13	14.72±1.93
WW 25	ADWANI I- KF	25.4±1.30	4.99±0.25	0.35±0.13	0.17±0.09	17.28±0.63
WW 26	U/RIMI	26.4±0.30	5.59±0.85	0.77±0.29	0.38±0.12	11.52±5.13
WW 27	GARAJI ROAD- KF	26.6±0.10	2.40±2.34	0.24±0.24	0.12±0.14	13.44±3.21
WW 28	KATSIT- KF	27.2±0.50	4.46±0.28	0.60±0.12	0.30±0.63	17.28±0.63
WW 29	MADAKIA- KF	27.0±0.30	2.12±2.62	0.45±0.03	0.22±0.56	17.21±0.56
WW 30	TAKAU – KF	27.3±0.60	2.29±2.45	0.19±0.29	0.09±2.55	19.20±2.55
WW 31	ADWANI II- KF	25.4±1.30	2.40±2.34	0.19±0.29	0.30±0.63	17.28±0.63
WW 32	KANIKON –KF	26.4±0.30	5.59±0.85	0.45±0.03	0.12±3.21	13.44±3.21
WW 33	FASAN – KF	26.4±0.30	4.99±0.25	0.60±0.12	0.30±5.13	11.52±5.13
WW 34	LOKO- KF	27.3±0.60	2.06±2.68	0.45±0.03	0.30±0.60	17.25±0.60
WW 35	U/FARI –KF	25.4±1.30	2.40±2.34	0.45±0.30	0.22±1.93	14.72±1.93
WW 36	U/BAKI –KF	26.4±0.30	2.88±1.86	0.19±0.29	0.09±0.21	16.44±0.21
	MEAN±STD	26.7±1.23	4.74±1.31	0.48±0.20	0.26±0.14	16.65±3.01

Key: ZA - Zaria, KD – Kaduna, KF-Kafanchan. **WW01 – WW36:** Well water sample of dry season

Table 1 (d): Comparison of observed values of the physicochemical parameters of well water in the three senatorial districts with Nigeria and World health Organisation (WHO) standards.

	Units	NIS	WHO	MINIMUM	MAXIMUM	MEAN
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		(2007)	(2011)			
Temperature	°C	25	30-35	25.2	28.4	26.7
pH		6.8-8.5	6.5-9.2	2.06	6.56	4.74
Conductivity	mS/cm	250	250	0.14	0.78	0.48
TDS	mg/L	500	500	0.07	0.78	0.26
COD	mg/L	10	10	11.52	27.52	16.65

The pH of the water samples obtained from the borehole source ranges from 4.03 – 6.66 with a mean of 5.23. While that of the well water source ranged from 2.06 – 6.56 with a mean value of 4.74 as shown in Table 1a – 1d. Most of the water samples obtained from both underground sources during the dry season were below the WHO/NIS regulatory limits which means the water samples were more acidic than the standards. It was also observed that the water samples from the well were more acidic than the water samples obtained from the borehole source. The affected water samples had a pH values that were either strongly acidic – slightly acidic. These values were however different from values presented by Ilechukwu (2010) and Adetunde *et al.*, (2011) for well water and borehole underground source. The low pH values as recorded in some water samples, were possibly as a result of anthropogenic factors, and as such could attack geological materials and leach toxic metals. Metal corrosion is often the main problem especially when it's aided in high temperature and low pH leading to corrosion of iron plumbing materials in water systems (Onwughara *et al.*, 2013).

The temperature of the water samples from the borehole source ranged from 23.70°C – 27.30°C with a mean value of 26.08°C. While that of the well water samples ranged from 25.20°C – 28.4°C with a mean value of 26.7. These values from both underground sources were within the limits as recommended by WHO /NIS except for some water samples obtained from the borehole water sources which were lower than the room temperature of 25°C. The lower temperature values recorded in this research could be as a result of in-direct heating of the sunrays to the water in the underground source. While the high temperature of 28.4°C observed in the well water source could be associated with the low depth of the well water source and its exposure to the direct heat from the sun. Okoye and Okoye (2008) stated that cool waters are generally more potable for drinking purposes, because high water temperature enhances the growth of micro-organisms and hence, taste, odour, colour, and corrosion problem may increase. Low EC values were recorded in the water samples obtained from both underground sources, as they were all less than the recommended EC value of 250 mS/cm. This result is in agreement with Adetunde *et al.*, (2011) results which stated that water samples obtained in the north had an EC value ranging from 0.14 - .0.95 mS/cm. This low electrical conductivity reported in the well and borehole source could be attributed to the low pH values as recorded in this analysis, since pH and electrical conductivity are dependable as reported by Mahmood *et al.*, (2005) and Ugya and Imam, (2015).

Low TDS results were observed for all the water samples obtained from the different sampled locations in all the two underground sources. The values were below the recommended standard values of 500 mg/L. This shows that the water is less contaminated. TDS in drinking water may originate from natural sources, sewage, urban run-off, industrial waste water and chemicals been used in the sampled areas. High level of total solid in the water bodies might

be as a result of deposit of soluble (such as borax, kornelite, potassium alum and nitratine) or insoluble (such as clay, pyrite) minerals in the underground soil which in turn gets into the underground water (APHA, 1992). Water with extremely low concentrations of TDS may be unacceptable to consumers because of its flat insipid taste; it is also often corrosive to water supply systems (WHO, 2003). High COD was observed in all the water samples obtained from the well water samples with values ranging from 11.52 – 27.52 mg/L with a mean value of 16.65 mg/L, While for the borehole water source, the water samples had a COD value ranging from 9.36 mg/L (which is almost the threshold) - 21.12 mg/L. The COD water samples values from both sources were above the recommended limit of 10 mg/L as stated above by WHO/NIS. The COD values obtained from the both underground sources were within the same range except for Emanto sampling area in Zaria which had the highest value at 27.52 mg/L. The COD correspond to the amount of oxygen required to oxidize the organic fractions of the sample (Ademoroti, 1996). High chemical oxygen demand has an impact on the people and industries reliant on water, it kills natural vegetation, the water becomes unsuitable for livestock and on farm supplies. It reduces crop yields; it makes the land unsuitable for agricultural purposes (Sule, 2009).

The results for (temperature, conductivity and TDS) of both bore hole and well water underground sources showed that there is a statistically significant difference since their p-values are less than 0.05 level of significance at 95% confidence limit. Meanwhile, there was no significant difference in the pH and COD values for the borehole and well water samples from the different sampling locations.

The concentration of copper in the bore hole and well water samples collected from the three senatorial districts presented in Tables 2 (a) – 2 (d) ranged from 0.0001 -0.0088 mg/L with mean concentration of 0.0034 mg/L for the borehole, while the value for the well water ranged from 0.0000-0.0560 mg/L with a mean concentration of 0.0070 mg/L. The concentrations of Cu in the entire locations were below the NIS and WHO standards for drinking water. Although, the water samples gotten from the underground sources were not contaminated with copper but sampling areas which had metal work activities in that vicinity like T/Wada, Kakuri and Mando which had the same concentration at 0.0340 mg /L, showed exceptional copper build-up in the well water underground source amidst other water samples. Contamination of drinking water with high level of copper may lead to chronic anaemia. Studies have shown that ingesting copper may also implicated in coronary heart diseases and high blood pressures although coronary heart diseases have also been linked to copper deficiency (Mohod and Dhote, 2013). Cr concentrations in the water samples ranged from 0.0000-0.0360 mg/L with a mean concentration of 0.0038mg/L for the borehole water source, while the value for the well water ranged from 0.0005-0.0056 mg/L with a mean concentration of 0.0017 mg/L. The values were below the WHO and NIS guidelines for drinking water except for Goni-Gora sampling site in Kaduna senatorial areas which had a concentration of 0.0360 mg/L and U/Rimi in Kafanchan senatorial district which had a concentration of 0.0160 mg/L all in the borehole water source. Ngaret *et al.*, (2012) reported that chromium were absent in the sampled boreholes conducted in Cross River State, Nigeria and attributed such observation to lack of visible industries in the sampled site. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration, while long-term exposure can cause kidney, liver, circulatory and nerve tissue damage. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Lennotech, 2011).

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Table 2(a): Concentrations (mg/L) of heavy metals in the borehole water samples of the three Senatorial Districts.

Location Samples	ID No.	Cu	Cr	Cd	Pb	Ni	Fe	Co
WUSASA- ZA	BH01	0.0050	0.0040	0.0007	0.0030	0.0090	0.0040	0.0001

KOFA DOKA- ZA	BH02	0.0018	0.0080	0.0028	0.0014	0.0050	0.0060	0.0007
KONGO- ZA	BH03	0.0046	0.0018	0.0002	0.0015	0.0008	0.0010	0.0001
SABO GARI- ZA	BH04	0.0031	0.0042	0.0001	0.0006	0.0008	0.0010	0.0013
EMANTO- ZA	BH05	0.0088	0.0022	0.0007	0.0021	0.0030	0.0200	0.0001
SAMARU- ZA	BH06	0.0018	0.0043	0.0002	0.0010	0.0008	0.0200	0.0001
DUTSE- ZA	BH07	0.0066	0.0008	0.0002	0.0015	0.0008	0.0100	0.0001
BASSAWA- ZA	BH08	0.0032	0.0018	0.0028	0.0010	0.0008	0.0001	0.0013
CHIKA- ZA	BH09	0.0050	0.0016	0.0002	0.0021	0.0008	0.0006	0.0001
G/LAND- ZA	BH10	0.0046	0.0042	0.0028	0.0030	0.0008	0.0005	0.0013
T/ WADA- ZA	BH11	0.0044	0.0040	0.0026	0.0025	0.0008	0.0040	0.0011
U/GODO- KD	BH12	0.0040	0.0040	0.0026	0.0022	0.0008	0.0020	0.0010
NARAYI – KD	BH13	0.0003	0.0010	0.0001	0.0020	0.0025	0.0001	0.0007
TELEVISION- KD	BH14	0.0022	0.0010	0.0018	0.0020	0.0013	0.0001	0.0001
GONIGORA- KD	BH15	0.0077	0.0360	0.0003	0.0022	0.0031	0.0001	0.0007
C/ MARKET-KD	BH16	0.0020	0.0024	0.0004	0.0005	0.0015	0.0016	0.0001
MANDO-KD	BH17	0.0060	0.0017	0.0012	0.0016	0.0012	0.0031	0.0001
H/ DAMANI- KD	BH18	0.0018	0.0028	0.0007	0.0031	0.0013	0.0001	0.0001
KAWO- KD	BH 19	0.0006	0.0010	0.0001	0.0020	0.0012	0.0001	0.0022
MALALI- KD	BH20	0.0005	0.0010	0.0016	0.0020	0.0012	0.0020	0.0001
T/WADA- KD	BH21	0.0053	0.0036	0.0012	0.0022	0.0031	0.0020	0.0007
KAKURI- KD	BH22	0.0022	0.0024	0.0010	0.0020	0.0030	0.0010	0.0006
H/ BAKIN- KD	BH23	0.0020	0.0028	0.0012	0.0016	0.0025	0.0020	0.0004
SABO- KD	BH24	0.0007	0.0020	0.0001	0.0031	0.0013	0.0010	0.0001
ADWANI I- KF	BH25	0.0019	0.0038	0.0001	0.0017	0.0019	0.0006	0.0001
U/RIMI	BH26	0.0018	0.0160	0.0001	0.0040	0.0030	0.0090	0.0001
G/ ROAD- KF	BH27	0.0078	0.0020	0.0004	0.0001	0.0005	0.0003	0.0001
KATSIT- KF	BH28	0.0018	0.0020	0.0013	0.0003	0.0004	0.0001	0.0001
MADAKIA- KF	BH29	0.0079	0.0030	0.0004	0.0003	0.0013	0.0002	0.0001
TAKAU – KF	BH30	0.0001	0.0013	0.0006	0.0014	0.0027	0.0003	0.0007
ADWANI II- KF	BH31	0.0019	0.0020	0.0004	0.0010	0.0020	0.0001	0.0001
KANIKON –KF	BH32	0.0070	0.0015	0.0010	0.0017	0.0027	0.0006	0.0001
FASAN – KF	BH33	0.0078	0.0036	0.0013	0.0030	0.0050	0.0006	0.0007
LOKO- KF	BH34	0.0018	0.0020	0.0010	0.0040	0.0030	0.0002	0.0001
U/FARI –KF	BH35	0.0005	0.0020	0.0001	0.0014	0.0020	0.0001	0.0001
U/BAKI –KF	BH36	0.0006	0.0000	0.0006	0.0016	0.0015	0.0002	0.0001
Mean		0.0034	0.0038	0.0009	0.0035	0.0020	0.0026	0.0004

Key: ZA - Zaria, KD – Kaduna, KF-Kafanchan. **BH01 – BH36:** Borehole water sample of dry season

Table 2(b): Concentrations (mg/L) of heavy metals in the well water samples of the three Senatorial Districts.

Location Samples	ID No.	Cu	Cr	Cd	Pb	Ni	Fe	Co
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WUSASA- ZA	WW01	0.0020	0.0005	0.0002	0.0040	0.0008	0.0060	0.0011
KOFA DOKA- ZA	WW02	0.0040	0.0006	0.0000	0.0013	0.0025	0.0010	0.0040
KONGO- ZA	WW03	0.0018	0.0056	0.0007	0.0005	0.0036	0.0010	0.0040
SABO GARI- ZA	WW04	0.0058	0.0012	0.0028	0.0005	0.0020	0.0010	0.0001
EMANTO- ZA	WW05	0.0011	0.0010	0.0020	0.0004	0.0048	0.0010	0.0001
SAMARU- ZA	WW06	0.0012	0.0019	0.0003	0.0023	0.0005	0.0060	0.0001
DUTSE- ZA	WW07	0.0018	0.0006	0.0001	0.0014	0.0008	0.0000	0.0001
BASSAWA- ZA	WW08	0.0012	0.0005	0.0002	0.0040	0.0025	0.0001	0.0001
CHIKA- ZA	WW09	0.0040	0.0018	0.0007	0.0040	0.0020	0.0050	0.0001
G/LAND- ZA	WW10	0.0088	0.0056	0.0025	0.0035	0.0048	0.0060	0.0014
T/ WADA- ZA	WW11	0.0015	0.0014	0.0026	0.0050	0.0036	0.0050	0.0010
U/GODO- KD	WW12	0.0000	0.0010	0.0020	0.0011	0.0018	0.0040	0.0001
NARAYI – KD	WW13	0.0560	0.0009	0.0001	0.0016	0.0011	0.0080	0.0012
TELEVISION- KD	WW14	0.0026	0.0012	0.0025	0.0080	0.0006	0.0040	0.0012
GONIGORA- KD	WW15	0.0086	0.0026	0.0023	0.0018	0.0008	0.0050	0.0013
C/ MARKET-KD	WW16	0.0006	0.0018	0.0018	0.0010	0.0002	0.0900	0.0012
MANDO-KD	WW17	0.0340	0.0017	0.0002	0.0010	0.0006	0.0050	0.0001
H/ DAMANI- KD	WW18	0.0006	0.0018	0.0011	0.0012	0.0006	0.0050	0.0012
KAWO- KD	WW19	0.0026	0.0016	0.0023	0.0016	0.0010	0.0050	0.0011
MALALI- KD	WW20	0.0006	0.0009	0.0006	0.0011	0.0011	0.0500	0.0013
T/WADA- KD	WW21	0.0340	0.0026	0.0024	0.0018	0.0011	0.0900	0.0013
KAKURI- KD	WW22	0.0340	0.0024	0.0025	0.0018	0.0008	0.0600	0.0012
H/ BAKIN- KD	WW23	0.0080	0.0022	0.0018	0.0016	0.0006	0.0400	0.0012
SABO- KD	WW24	0.0066	0.0018	0.0022	0.0018	0.0004	0.0900	0.0001
ADWANI I- KF	WW25	0.0004	0.0038	0.0010	0.0017	0.0002	0.0040	0.0001
U/RIMI	WW26	0.0036	0.0009	0.0028	0.0010	0.0032	0.0120	0.0013
G/ ROAD- KF	WW27	0.0022	0.0012	0.0028	0.0006	0.0011	0.0040	0.0014
KATSIT- KF	WW28	0.0020	0.0022	0.0023	0.0005	0.0020	0.0030	0.0001
MADAKIA- KF	WW29	0.0066	0.0005	0.0010	0.0010	0.0009	0.0001	0.0001
TAKAU – KF	WW30	0.0014	0.0012	0.0010	0.0040	0.0035	0.0001	0.0001
ADWANI II- KF	WW31	0.0012	0.0010	0.0010	0.0040	0.0032	0.0001	0.0001
KANIKON –KF	WW32	0.0022	0.0012	0.0028	0.0016	0.0011	0.0028	0.0001
FASAN – KF	WW33	0.0066	0.0012	0.0040	0.0056	0.0020	0.0040	0.0014
LOKO- KF	WW34	0.0018	0.0022	0.0040	0.0050	0.0008	0.0040	0.0001
U/FARI –KF	WW35	0.0036	0.0009	0.0024	0.0010	0.0018	0.0024	0.0014
U/BAKI –KF	WW36	0.0000	0.0038	0.0001	0.0005	0.0000	0.0001	0.0001
Mean		0.0070	0.0017	0.0016	0.0021	0.0016	0.0145	0.0008

Key: ZA - Zaria, KD – Kaduna, KF-Kafanchan. **WW01 – WW36:** Well water sample of dry season

Table 2 (c): Comparison of observed values of the concentration of selected heavy metals in the borehole of the three senatorial districts with Nigeria and World health Organisation (WHO) standards.

	Units	NIS (2007)	WHO (2011)	MINIMUM	MAXIMUM	MEAN
Cu	mg/L	1.0	1.0	0.0001	0.0088	0.0034
Cr	mg/L	0.01	0.05	0.0000	0.0360	0.0038
Cd	mg/L	0.01	0.003	0.0001	0.0028	0.0009
Pb	mg/L	0.10	0.01	0.0001	0.0040	0.0018
Ni	mg/L	0.01	0.001	0.0004	0.0090	0.0020
Fe	mg/L	1.0	0.3	0.0001	0.0200	0.0026
Co	mg/L	0.01	0.05	0.0001	0.0022	0.0004

Table 2 (d): Comparison of observed values of the concentration of selected heavy metals in the well of the three senatorial districts with Nigeria and World health Organisation (WHO) standards.

	Units	NIS (2007)	WHO (2011)	MINIMUM	MAXIMUM	MEAN
Cu	mg/L	1.0	1.0	0.0000	0.0560	0.0070
Cr	mg/L	0.01	0.05	0.0005	0.0056	0.0017
Cd	mg/L	0.01	0.003	0.0000	0.0040	0.0016
Pb	mg/L	0.10	0.01	0.0004	0.0080	0.0021
Ni	mg/L	0.01	0.001	0.0000	0.0048	0.0016
Fe	mg/L	1.0	0.3	0.0000	0.0900	0.0145
Co	mg/L	0.01	0.05	0.0001	0.0040	0.0008

The concentrations of Cd metal in the water samples obtained in the three senatorial sampling districts were low and below the WHO and NIS permissible limit for cadmium metal in drinking water except for Fasan and Loko sampling location in Kafanchan senatorial district which had a concentrations of 0.0040 mg/L for both locations in the well water source. In low doses, cadmium can produce coughing, headaches, and vomiting. In larger doses, cadmium can accumulate in the liver and kidneys, and can replace calcium in bones, leading to painful bone disorders and to a renal failure. The kidney is considered to be the critical target organ in humans chronically exposed to cadmium by ingestion (EPA, 1999). Pb concentration in the water samples ranged from 0.0001-0.0040 mg/L with a mean value of 0.0018 mg/L for the borehole. While for the well water underground source, the value ranged from 0.0004-0.0080 mg/L with a mean value of 0.0021 mg/L. These values from both underground sources were within the permissible limits of WHO standards of 0.01 mg/L and the NIS guidelines limit of 0.10 mg /L for drinking water quality as shown on Table 2 (a) - 2 (d). It was also observed that the well water source had more Pb concentrations than the borehole, this could be as a result of anthropogenic factors, as the Pb concentrations from the borehole could be attributed to natural weathering of the bedrock in the locations the borehole were located.

Nickel concentration in the water samples ranged from 0.0004 - 0.0090 mg/L with a mean value of 0.0020 mg/L for the borehole water source and the well water ranged from 0.0000-0.0048 mg/L with mean value of 0.0016mg/L. All of the water samples were below the permissible limit recommended by NIS but for the WHO standard limit, some of the water samples had nickel concentrations that were above the recommended limits. Certain amounts of nickel are useful to the human body, but too much nickel can be toxic. About 10% of women and 2% of men are highly sensitive to nickel (Emhemmed *et al.*, 2014). The most serious effects occur when nickel is inhaled. This can lead to increased risk of respiratory infections, asthma and sinus problems (Aremuet *et al.*, 2002). Fe concentration in all the water samples obtained from both the borehole and well water source were below the recommended limits as stated by WHO/NIS. This result disagrees with Ugaret *et al.*, (2015). Iron concentration in water samples ranged from 0.0001 – 0.0200 mg/L with a mean values of

0.026 mg/L for the borehole source and the well water ranged from 0.0001 – 0.0900 mg/L with mean value of 0.0145 mg/L. The low Fe concentrations as observed in this study could be natural. Anthropogenic factors may not have an active role. Usually, Fe occurs in ground water in the form of ferric hydroxide and their concentration less than 500 µg/L (Oyeku and Eludoyin, 2010). The shortage of iron causes disease called anaemia and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as haemosiderosis (Rajappa *et al.*, 2010).

The concentration level of Cobalt metal in the water samples collected from borehole and well water underground source in the three senatorial districts during the dry season values as displayed in Table 2(a) and 2(d) ranged from 0.0001-0.0022 mg/L with mean concentration of 0.0004 mg/L for the borehole. While the value for the well water underground source ranged from 0.0001-0.0040 mg/L with a mean concentration of 0.0008 mg/L. All the water samples were within the permissible limits as recommended.

The Radioisotopes (Uranium -238 and Thorium – 232) were not detected in borehole and water samples tested during the dry season. The absence of the radioisotopes in this work can be attributed to the movement of water bodies and the constant dispersion as compared to the work of (Balakrishna *et al.*, 2001 and Ashraf *et al.*, 2005).

The environmental impact of radioisotopes in water samples is dependent both on the chemical species of the radioisotopes and the response to the biological and physicochemical conditions. These factors are responsible for the mobilization of the radioisotopes from solid into the liquid phase and hence, for the transport within the immediate vicinity influencing the rate of dispersion, dilution, uptake and transfer of into the living system (Naidu *et al.*, 2003).

CONCLUSION

The physico-chemical results show that some of the drinking water had a low pH value and a high COD that were not acceptable when compared with the WHO/NIS regulatory standards. The heavy metals concentration results showed that all the metals were within the permissible limits except for Ni, Pb and Cd whose concentrations in some of the water samples were evident of water contamination. The samples were also free from radioisotopes. It is therefore, observed that the water sources from the studied area have a lot of potentials for wide applications to the people if only they can be subjected to further treatments that will reduce drastically, the concentration of the few identified elements that may pose some danger to health and the society.

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