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A multi-criteria approach to drinking and irrigation water assessment of spring water in Igbo-Etiti, Nigeria

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Abstract
The study aimed at assessing the spring water within Igbo-Etiti, Nigeria, for drinking and irrigation applications using physicochemical parameters, water quality index, mineral and trace elements, pollution indices, and risk assessment. Standard methods were used to determine the physicochemical properties of the spring water in rainy and dry seasons. Trace metals such as Pb, Cd, Zn and Cu were determined with atomic absorption spectrophotometer. The results showed that most of the physicochemical properties studied were within the guideline values set by Nigeria Standard for Drinking Water Quality (NSDWQ), WHO and US EPA for drinking water purposes. However, pH of all the spring water (4.27–4.73; and 4.95–5.73) for dry and rainy seasons, respectively, were slightly acidic. Lead (Pb) (0.01–1.08 mg/L) and cadmium (Cd) (0.01–0.15 mg/L) concentrations were above the guideline values in both seasons. This could be attributed to the lithology of the study area which is Nsukka FORMATION. Leaching of lead and sulphides from the embedded coal deposits could be responsible for the increased lead levels and made the water acidic. The mineral and trace elements examined were within WHO and NSDWQ limits for drinking water except Cd and Pb. The permeability index and other irrigation indices showed that all the spring water was suitable for irrigation purposes. The pollution index suggested that the pollution level of all the samples in the dry season was insignificant (PIS < 1). Two-way ANOVA showed significant differences in most of the parameters studied in the dry and rainy seasons. Pearson correlation analysis and cluster analysis showed strong significant positive and negative correlations in some of the parameters studied in both seasons. The water quality index showed that none of the spring water had excellent water status. However, one spring (Iyi Ase) had poor water status in dry season and is considered unsafe for drinking. Iyi Ase was also considered not suitable for irrigation application as predicted by most of the pollution indices, while others were generally considered suitable for irrigation application. Probable cancer and non-cancer risk assessment revealed a probable risk associated with the consumption of the spring in Igbo-Ettiti area, Nigeria.

Keywords Risk assessment · Igbo-Ettiti · Water quality · Pollution index · Physicochemical parameters

Introduction

Water resources are significant due to the cultural, social, and economic benefits which they provide for the society and being a crucial support for the biodiversity of the ecosystems (Rosca et al. 2020; Dippong et al. 2019). The water quality has a great impact on health and, certainly, on life (Rosca et al. 2020). The overuse of water, climate change, and pollution are threatening factors for the natural and limited water resources such as springs (Rosca et al. 2020).

Goldscheider et al. (2020) report that 15.2% of the global land surface is covered by karstic terrains, and freshwater springs are known to supply partially or entirely 25–50% of drinking water to the world's population (Hartmann et al. 2014). United Nations Sustainable Development Goal (SDG) 6 is to ensure access to safe drinking water and sanitation for all by 2030 (United Nations 2018), and proper water and sanitation are critical to achieving SDGs of good health and gender equality.

Springs are widely distributed across landscapes and sustain and support millions of people across the globe including in Nigeria (Bhat et al. 2020, 2022). Spring is a

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point at which water flows from an aquifer to the earth's surface. It is also a point in the hydrological cycle when underground water enters the land surface and afterward flows into a stream (Water science school, 2018; Chukwu, 1999). A spring may be the result of karst topography where surface water has infiltrated the earth's surface (recharge area), becoming part of the area groundwater. The quality of the water at the surfacing point is usually good as the water has penetrated through thick strata of soil. The water picks dissolved minerals (such as magnesium, calcium and iron, etc.), during the percolation process and is purified of biological organisms, (disease-producing pathogens) example bilharzias FAO (2002).

The quality of spring water can be altered by geochemical reactions, agricultural activities (Ehiemere et al. 2022), saline water intrusion, improper waste disposal (Alum et al. 2021), urbanization, and others that are classed as natural or anthropogenic (Akhtar et al. 2014). Spring water quality monitoring on regular basis, most importantly in areas with a high risk of pollution, is paramount for the protection of the rural dweller's health especially in developing countries like Nigeria. Jones et al. (2014) noted that the strategies for the assessment of spring water or groundwater quality generally are purported at establishing the present status and appraisal of environmental parameter trends. These enhance the determination of the level of danger the polluted spring water could pose to the rural dwellers in particular and the environment in general. The chemical composition of groundwater is influenced and altered by the fast development of society (urbanism, industrialization, mining activities, radioactive activities, domestic and agricultural sources) and also by natural processes (volcanism, weathering of rocks, evaporation processes) implicitly affecting the human health and the natural environment (Dippong et al. 2020; Rosca et al. 2020; Dippong et al. 2018).

Besides, the danger associated with water is heterogeneous and differs from one locality or region to another, and so, assessment and investigation need to be local or regional as well (Biswas & Tortajada, 2010). In recent time, countries in sub-Saharan Africa have made a substantive improvement in the provision of potable water to their populace to which about 43% has access to. However, this is through private boreholes that are usually not monitored or assessed regularly (WHO/UNICEF, 2015). Nigeria has a population of over 205 million people (Worldometer, 2020) and is still among the countries in sub-Saharan Africa battling with the provision of potable water to its teaming citizens. This has led its citizens to seek for alternatives (spring and other groundwaters) given the near-zero pipe-born water scheme in the country (Owamah et al. 2013; Dahunsi et al. 2014).

Igbo-Etiti is one of the local government areas (LGA) in Enugu state and as is the case in Enugu state generally, the major source of drinking water is the springs and sometimes boreholes for those that can afford to sink one or connect from the state government-owned water system. In recent times, the cultivation of vegetables and other crops around the springs in the area has been on the increase and the quality of the agricultural output has been questionable as a result of the activities that go on in and around the springs in Igbo-Etiti which are assumed to be polluted. Besides, the pollution of these main sources of water for the rural populace poses a serious threat to the health of the rural dwellers in Igbo-Etiti as they are used without any kind of treatment. This research aims to assess the quality of spring water resources in Igbo-Etiti, Nigeria for drinking and irrigation application. Due to the increasing applications of spring water as an alternative to pipe-borne water schemes, for drinking, irrigation, and domestic uses in Igbo-Etiti, Enugu state, Nigeria, there is a need for frequent appraisal of the spring water in the area, hence, the need for this study.

Materials and methods

Study area

Enugu state is one of the 36 states of Nigeria of which Igbo Etitiis a local government among the 17 local government areas in Enugu state (Fig. 1). It is located in the southern part of Enugu North, southeast of Nigeria, and it is bounded between latitude 6º36′N to 6º47′N and longitude 7º15′E and 7º32′E (Ofomata 1978). Its notable towns are Ekwegbe, Ukehe, Ogbede and Aku. The sampling points are quite accessible due to good networks of minor and major roads. The road network links Ninth-mile corner and subsequently Onitsha which are popular towns in the state and neighbouring state, respectively. The area is known by its undulating hills and enormous low-lying plains with height fluctuating from about 50 to more than 400 m above sea level (Ifediegwu et al. 2019). There are many rivers (Adada, Ajali, Obinna and Karawa) traversing the study area. The Adada River is a significant tributary of River Niger, while Obinna is a significant tributary of Anambra River. The inhabitants of these LGAs depend on streams, lakes, springs, rivers and shallow hand-dug wells, although there are few private boreholes (Alum and Okoye 2020). The study area has two distinct climatic seasons; dry and rainy seasons. The dry season begins around October, while the rainy season starts around April. These seasons are caused by the north–south fluctuations of discontinuity between the dry continental (Sahara) air and the humid Atlantic air (Ifediegwu et al. 2019). The Harmattan period is characterized by cold, dry and windy weather, while the rainy season is characterized by heavy, intense rainfall (Iloeje1995). The major agricultural products in the area are rice, yam, banana, maize, cassava, okra and pineapple.
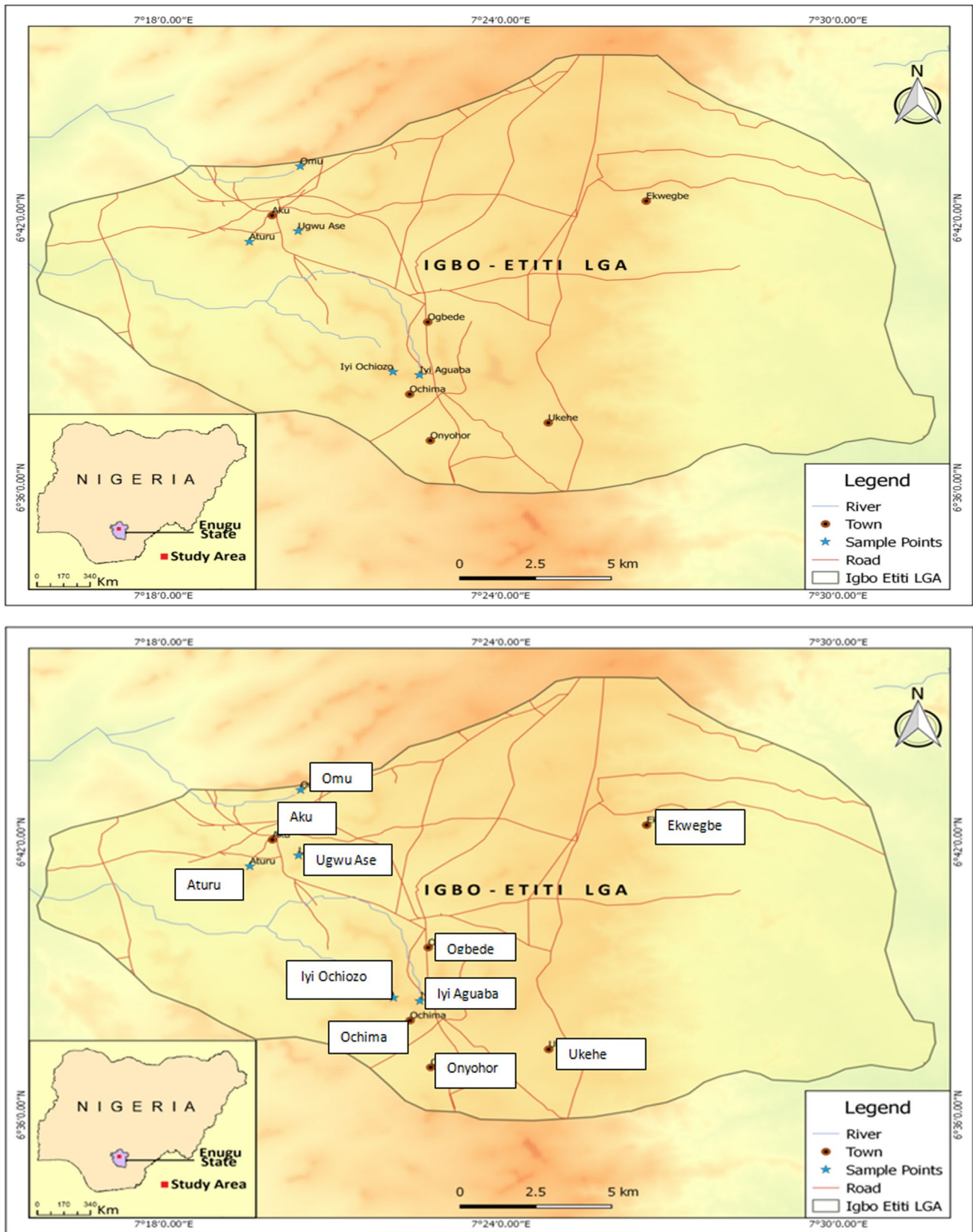
Fig. 1 Map of Igbo-Etiti LGA showing the Sampling Points

Possible sources of contamination to these spring water

The topographic condition, as well as the anthropogenic activities, 30 m around the springs was taken into consideration at the time of sampling since they have a high tendency of contributing to the levels and types of contaminants of the springs. Indiscriminate dumping of refuse, defecation around the water sources especially on the uphill side of the springs and the agricultural activities can be linked to spring water contamination. The members of these communities around these spring water sources engage in these activities such as the use of animal waste as fertilizer for agricultural activities than inorganic fertilizers and this may also cause spring water contamination. During raining season, all these pollutants will likely be washed down along with free-ranging cattle droppings from the upstream by runoff to contaminate the springs. All these pose the threat of contamination of these spring waters.

Geo-hydrology of the study area

The underlying geologic formations are mainly three (Ajali, Nsukka and Imo FORMATIONS) which are part of the Anambra and Niger Delta sedimentary basins (Ifediegwu et al. 2019). The main underlying geology is predominantly sandstone (Ajali and Nsukka). This is a result of the lithography of the area which is chiefly Nsukka FORMATION. The lithology of Nsukka FORMATION has mainly interbedded shales, siltstone shale, sandy shale and thin coal seams which have become lateralized in many places where they characteristically form resistant capping on mesas and buttes (Akande et al. 2007). The Ajali Sandstone FORMATION is considered a good aquifer and there is existing groundwater exploitation (although not necessarily in the study town). The sandstone is thick and has high values of hydraulic conductivity, and specific yields have been reported (Obasi et al. 2013). The aquifer properties imply that it could be possible to abstract good yields without excessive drawdown of water levels. There are relatively few surface water features because of the permeable surface geology: spring-fed streams are often ephemeral (Lesley and Phil 2009).

Quality assurance procedure

The polyethylene sampling containers and standard flasks were soaked in water and detergent for at least 6 h and rinsed with deionized water and with a mixture consisting of 520 mL de-ionized water, 200 mL concentrated HCl and 80 mL H_2O_2 Yousif AM (2019). They were then rinsed with de-ionized water and then turned upside down on a clean surface to dry without contamination.

Sample collection and preservation

Five spring water locations were identified in the study area (Aku and Ochima), and water samples were collected seasonally (dry and rainy seasons). A total of thirty (30) water samples comprising of three samples from each spring for each season were collected from the five different springs in January to early February and July to August 2019, representing the dry and rainy seasons, respectively. Each sample was collected with a clean two liter screw-capped polyethylene container which was thoroughly washed with detergent, rinsed with analytical grade 1:1 HCl/deionized water and finally rinsed with deionized water. At the point of water collection, the polyethylene containers were rinsed three times with the water samples. The polyethylene containers were positioned at the point source of the spring water to minimize the contamination of water samples by surface films. The polyethylene was filled leaving no air space and immediately covered. Temperature and pH of the samples were determined on the spot and the samples were transported to the laboratory in a cool box at a temperature of 4 °C to maintain the concentrations of the analytes. The stored samples were analysed within 4 days of collection.

Water quality index (WQI)

The water quality index is used to assess the combined effect of individual parameters on the prevailing quality of water. In all, twelve (12) essential parameters were selected for the water quality index evaluation. Evaluation of the WQI of the spring water samples was done using the weighted arithmetic index method by Chatterji and Raziuddin (2002), which is basically on the studied values of the physical parameters. WHO guidelines were used to assess the quality of the different water samples. The WQI was calculated once for each season (dry and raining, respectively). The water quality status, according to Chatterji and Raziuddin, (2002), was classified as WQI of 0–25 (excellent), 26–50 (Drinking, Irrigation and Industrial), 51–75 (Irrigation and Industrial), 76–100 (irrigation), and more than 100 (Proper treatment required before use).

Determination of physicohemical parameters

Turbidity, sulphate, total dissolved solids (TDS), total suspended solids (TSS), nitrates, total alkalinity, phosphate, total hardness, pH (Jenway pH meter, model 3510), conductivity (WTW Conductivity Meter, Model LF.90) and odour were analysed according to APHA, (2005) standard methods.

Sodium and potassium concentration

Flame photometer (Sherwood 410 model) was used to determine sodium (Na) and potassium (K). Blanks were aspirated and blanks control were adjusted to show 0.0. The highest standard was aspirated, and the coarse and fine control were adjusted to show 200 for 20.0 mg/L, followed by the quality control standard (10.0 mg/L) to check recovery. Thereafter, other standards in ascending order were aspirated and then followed by samples. However, their concentrations were determined against their intensities extrapolated from the graph. 10 mL of water sample was measured into a 10 mL sample cell. The sample was nebulized into the off flame, and the emission intensity was recorded (Table 1).

Pollution index of the spring water

According to Rao (2012), the pollution index of spring water (PIS) is a scale of numbers used to express the extent to which drinking water is polluted. It shows, in a non-ambiguous way, the extent to which individual water chemical variables affect the overall quality of water. Although the PISmodel was initially applied for groundwater quality assessment (Rao 2012; Egbueri and Unigwe 2019; Egbueri et al. 2020), it was applied in the current study for spring water. This decision was based on the fact that the same parameters were analyzed for all the samples. Moreover, all the samples were analyzed under the same set of conditions. Five steps were involved in determining the PIS of a water sample. In the first step, a relative weight (R_w) ranging from 1 to 5 was allotted to each water quality variable (Table 2). The weight assignment was based on the extent to which such a variable impacts human health. In the second step, the weight parameter (W_p) for each water quality measure is calculated using Eq. 4 (through Eqs. 1, 2 and 3) to get the relative share of each water quality measure on the overall water quality. It is the ratio of Rw of every water quality measured to the sum of all relative weights (Eq. 4).

$$W_p = R_w / \sum R_w \tag{1}$$

The third step involved working out the status of concentration (S_c) of water quality measure of each water

Table 2 PIS components required for evaluation

Parameter	Relative weight Rw	Weight parameter Wp	Standard limit (WHO 2017a, b)
pH	5	0.1162791	7.5
TDS	5	0.1162791	500
TH	2	0.0465116	150
Na^+	4	0.0930233	200
K^+	1	0.0232558	12
Ca^{2+}	2	0.0465116	75
Mg^{2+}	2	0.0465116	50
SO_4^{2-}	5	0.1162791	250
Cl^-	4	0.0930233	250
HCO_3^-	3	0.0697674	250
NO_3^-	5	0.1162791	50
Pb	5	0.1162791	0.01
	$\Sigma Rw = 43$	$\Sigma Wp = 1$	

sample to its drinking water quality standard. The S_c was computed by dividing the concentration (C) of each water quality measure of every water sample by its respective drinking water quality standard (D_s) (Eq. 2.

$$S_c = C/D_s \tag{2}$$

The fourth step involved deriving the overall water quality by multiplying W_p of each water quality measure with its corresponding Sc (Eq. 3.

$$O_w = W_p * S_c \tag{3}$$

The final step was the computation of PIS by adding all values of Ow contributed by all water quality measures of every water sample as described in Eq. 4.

$$PIS = \sum O_w \tag{4}$$

Based on the PIS scores, water samples can be classified as having insignificant pollution (PIS < 1), low pollution (PIS of 1.0 and 1.5), moderate pollution (PIS of

Table 1 GPS Location of the Sampling Sites

Sample Location/Village	Short name	GPS Location	Elevation (m/msl)
Iyi Ochiozo Ochima (EziamaOchima)	Och	6.64294 ºN7.36806 ºE	480
Iyi Aguaba Ochima (Amaudora Ochima)	Agu	6.64174 ºN7.37589 ºE	488
Iyi Attturu Aku (Ugwunani Aku)	Atu	6.69113 ºN7.32547 ºE	387
Iyi Ugwu Ase Aku (Amogwu Aku)	Ase	6.69507 ºN7.33990 ºE	419
Iyi Omu Aku Omu (Ohemuga Aku)	Omu	6.72066 ºN7.34054 ºE	451

1.5–2.0), high pollution (PIS of 2.0–2.5) and very high pollution (PIS > 2.5) (Rao, 2012).

Trace metals analysis

Atomic Adsorption Spectrometer (Model AA-7000 Shimadzu) equipped with air-acetylene flame was used to determine the concentrations of the trace metals. All the glasswares used were soaked in 3 M HNO_3 overnight and washed with de-ionized water to reduce the chances of interferences. All the reagents used were of analytical grade and 30 cm^3 of aqua regia (HNO_3 and HCl in 1:3 ratio) was used for the sample digestion.

Water quality assessment for irrigation purposes

In the evaluation for the usability of the spring water for irrigation, the following water quality indices were used:

1. Permeability index (PI) according to Doneen (1964) was applied to classify the spring water for irrigation application. The PI equation is

$$PI = ((Na^+ + \sqrt{HCO_3^-})/Na^+ + Mg^{2+} + Ca^{2+}) \times 100 \tag{5}$$

2. Doneen (1964) classification pattern using soluble sodium percent (SSP) was also used to evaluate the spring water and the equation is written as

$$SSP = \frac{Na^+ + K^+}{Na^+ + Ca^{2+} + Mg^{2+} + K^+} \times 100 \tag{6}$$

An SSP of about 60% could result in sodium accumulations that will lead to a breakdown in the soil's physical properties.

3. The classification according to Kelly's ratio was used (Kelly 1940) as in Eq. 7.

$$KR = Na^+/(Ca^{2+} + Mg^{2+}) \tag{7}$$

4. The irrigation water classification using magnesium adsorption ratio (MAR) as proposed by Raghunath (1987) was also used as in Eq. 8:

$$MAR = (Mg^{2+}/(Ca^{2+} + Mg^{2+})) \times 100 \tag{8}$$

5. Residual sodium carbonate (RSC) or Residual alkalinity (RA) as suggested by Richards (1954) and Eaton (1950):

$$RSC = (HCO_3^- + CO_3) - (Ca^{2+} + Mg^{2+}) \tag{9}$$

6. Chloro-alkaline indices (CAI) are defined as

$$CAI = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{10}$$

7. Richards (1954) also proposed sodium adsorption ratio (SAR) to classify water irrigation as noted in Eq. 11:

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}} \tag{11}$$

An indication of the level to which irrigation water undergoes cation exchange reaction in the soil is given by SAR.

Percent sodium

The permeability of soil is reduced when Na reacts with it (Todd, 1980). Sodium content is usually expressed in terms of percent sodium (sodium percentage), defined by

$$mathrm\%Na = ((Na + K)/(Ca + Mg + Na + K)) \times 100 \tag{12}$$

%Na values classify water as excellent (< 20), good (21–40), permissible (41–60), doubtful (61–80) and unsuitable (> 81) (Wilcox 1955).

Noncarcinogenic and carcinogenic health risk assessment

The non-carcinogenic health risks associated with the consumption of water contaminated by trace elements have been reported by many authors (Egwuonwu et al. 2021; Zhang et al. 2018; Ukah et al. 2019; Ezugwu et al. 2019; Egbueri, 2020a).

Chronic daily intake (CDI)

The chronic daily intake (CDI in mg/kg/day) risks associated with ingesting a trace metal were calculated for both adult and children population using Eq. 13 (US-EPA 1999).

$$CDI = (Cw * IRW * EF * ED)/(BW * AT) \tag{13}$$

where Cw = concentration of trace element in water (mg/L); IRW = ingestion rate of water (2 L for adults and 1 L for children); EF = the exposure frequency (365 days per year); ED = exposure duration (children = 6 years and adult = 70 years); BW is the body weight (15 kg and 70 kg for children and adult, respectively); AT = average exposure time (70 years * 365 days and 6 years × 365 days for adult and children, respectively) (Barzegar et al. 2018; Ihedioha et al. 2019, 2016; Duggal et al. 2017; Mgbenu and Egbueri, 2019; Egbueri, 2020a).

Hazard quotients (HQ)

The non-carcinogenic risk for each trace element was calculated as hazard quotient using Eq. 14:

$$HQ = CDI/Rfd \tag{14}$$

where RfD = oral reference dose of a particular trace element (mg/kg/day), CDI = chronic daily intake. The RfD for Cu = 0.04, Cd = 0.001 and Pb = 0.004, mg/kg/day (U.S. EPA 2011, 1999; Egwuonwu et al. 2021; Oluwasola et al. 2021; Nwoke et al. 2021; Odum et al. 2021).

Hazard index (HI)

The summation of the HQ gives the HI of each trace element's non-carcinogenic risk

$$HI = \Sigma HQ \tag{15}$$

If HI is greater than 1, it indicates that ingestion of trace elements could have a non-carcinogenic detrimental effect. Therefore, on the basis that HI values, the non-carcinogenic risk is classed into negligible (risk level 1; HI < 0.1), low risk (risk level 2; HI ≥ 0.1 < 1), medium risk (risk level 3; HI ≥ 1 < 4), and high risk (risk level 4; HI ≥ 4) (Bortey-Sam et al. 2015; Mgbenu and Egbueri, 2019; Egbueri 2020a).

Carcinogenic health risk assessment

The cancer risks relating to the ingestion of the water resources were evaluated as the incremental threat of a person developing cancer over a lifetime, emanating from the exposure to a potential carcinogen (Rahman et al. 2017). The probability of cancer risk (PCR) was estimated by multiplying the CDI (mg/kg/day) with the slope factor (SF) (mg/kg/day).

$$PCR = CDI * SF \tag{16}$$

The acceptable value is $\leq 1 \times 10^{-6}$, which means that approximately 1 per 1,000,000 will probably develop cancer as a result of the exposure to a carcinogen (Adamu et al. 2014; Ihedioha JN et al. 2021). However, risk in the range of $1 \times 10^{-6} - 1 \times 10^{-4}$ typically has been reported to be acceptable (US-EPA1999; Rahman et al. 2015). SF values for Cd are 0.38 (Egbueri et al. 2020) and Pb is 0.0085 (Patrick-Iwuanyanwu and Chioma, 2017; Naveedullah et al. 2014).

Statistical analysis

Statistical analysis was performed using Origin Pro 9. Multivariate analysis of water quality data was explored using Pearson correlation (PC) and cluster analysis (CA).

Hierarchical clustering was performed to measure the similarities between the clusters. ANOVA and Tukey's post hoc multiple comparisons were done to compare water quality parameters.

Results and discussion

The results of the physicochemical parameters analyzed for the dry and rainy season samples are presented in Table 3. The water temperature ranged from 21.73 to 30.33 °C in the dry season and 20.93–22.47 °C in the rainy season. The spring water sample temperatures were relatively low. Cold waters are generally more suitable for drinking because high water temperature enhances the growth of micro-organism and causes taste, odour, colour, and corrosion problem (Okoye et al. 2006). Temperature values obtained during the dry season in Iyi Ase, Iyi Atturu and Iyi Omu were all above ambient level (25 °C) of the Nigerian Standard for Drinking Water Quality (NSDWQ 2007) (Fig. 2). This could be as a result of the period of collection. The dry season is usually characterized by high temperatures that could be above 40 °C. However, the temperature of Iyi Ochiozo and Iyi Aguaba spring water were very low, while in the rainy season, the whole sampled locations recorded temperature below ambient level.

The pH values of the spring water were slightly acidic (4.95–5.73 in dry season and 4.23 to 4.73 in rainy season). These values were below 6.5–8.5 recommended by WHO (2017a, b), NSDWQ (2007) and EPA (2009) (Fig. 2). Water with a pH of less than 6.5 can leach metal ions like Fe, Mn, Cu, Pb and Zn from pipes and plumbing materials. Also, water with pH value above the range of 6.5–8.5 is termed secondary contaminant according to US EPA (2022). Consumption of acidic water may expose humans to some negative health effects (Egbueri et al. 2021). For example, there is an increased dissolution and absorption of heavy metals in human body under acidic conditions, thereby leading to bioavailability and bioaccumulation of heavy metals in the human system. Continuous ingestion of acidic water can lead to the erosion of enamel (which is the hard part of the tooth) and exposure of dental soft tissues. The acidic nature of the spring water could be attributed to the lithography of the study area. Nsukka FORMATION (Upper coal measures) is stratified mainly as interbedded shales, siltstone shale, sandy shale, and coal shale. Leaching of minerals from the embedded coal deposit releases acidic oxides which increase the acidity of the spring water. The relative abundance of major dissolved chemical constituents in water is dependent upon weathering process and inputs from anthropogenic activities and the type of geological rock (Singh and Hasnain 1999). The pH values obtained in this study were slightly lower than the mean value (6.8) reported by Dippong et al. (2018)

Table 3 Physicochemical Parameters (mean ± SE) of the spring water samples

Parameters	Ase	Atu	Omu	Och	Agu	WHO (2017a, b)	EPA (2009)	NSDWQ (2007)
Dry season								
pH	5.52 ± 0.32	5.12 ± 0.06	4.95 ± 0.23	5.73 ± 0.51	5.31 ± 0.39	6.5–8.5	6.5–8.5	6.5–8.5
Temp. (°C)	30.33 ± 0.58	29.67 ± 0.58	29.33 ± 0.58	22.53 ± 0.55	21.73 ± 0.55	40	–	–
Total H.(mg/L)	2.67 ± 4.62	8.00 ± 2.00	3.33 ± 3.06	ND	ND	500	–	–
T.D.S(mg/L)	73.33 ± 11.55	66.67 ± 11.55	53.33 ± 11.55	20.00 ± 34.64	46.67 ± 11.55	500	500	500
T.S.S(mg/L)	13.33 ± 11.55	6.00 ± 0.00	6.67 ± 11.55	ND	ND	25	–	–
T.S(mg/L)	86.67 ± 11.55	66.67 ± 11.55	60.00 ± 20.00	20.00 ± 34.64	46.67 ± 1.55	–	–	–
E.C(µS/cm)	6.26 ± 1.80	5.46 ± 0.66	5.47 ± 0.22	6.09 ± 2.77	7.97 ± 0.99	1000	–	–
Chloride(mg/L)	18.17 ± 1.46	19.19 ± 2.07	21.17 ± 7.52	11.92 ± 0.50	16.55 ± 5.31	250	250	–
Total Alk.(mg/L	200 ± 50	300 ± 50	250 ± 100	83.33 ± 28.87	100 ± 0.00	200	–	200
HCO_3(mg/L)	200 ± 50	300 ± 50	250 ± 50	83.32 ± 28.87	100 ± 0.00	250	–	–
Nitrate(mg/L)	1.06 ± 0.04	1.15 ± 0.19	1.16 ± 0.03	1.20 ± 0.06	1.41 ± 0.44	50	44	50
Sulphate(mg/L)	40.07 ± 13.57	32.29 ± 5.43	34.05 ± 5.55	45.54 ± 1.88	40.23 ± 3.48	250	250	250
CO_3^{2-}	1.32 ± 0.21	3.62 ± 0.84	1.88 ± 0.11	2.32 ± 0.91	1.65 ± 0.74			
Rainy season								
pH	4.43 ± 0.15	4.73 ± 0.06	4.73 ± 0.21	4.63 ± 0.38	4.27 ± 0.12	6.5–8.5	6.5–8.5	6.5–8.5
Temp. (°C)	22.47 ± 0.35	20.83 ± 0.29	21.30 ± 0.44	22.37 ± 0.23	20.93 ± 1.62	40	–	–
Total H.(mg/L)	12.67 ± 6.11	21.33 ± 9.02	50.67 ± 3.06	64.67 ± 2.31	30.67 ± 4.16	500	–	–
T.D.S(mg/L)	87.50 ± 2.73	88.22 ± 4.22	89.44 ± 3.57	86.62 ± 4.63	92.24 ± 1.76	500	500	500
T.S.S(mg/L)	8.06 ± 0.82	8.58 ± 1.27	7.54 ± 0.69	8.84 ± 0.44	7.93 ± 0.69	25	–	–
T.S(mg/L)	96.36 ± 3.59	97.36 ± 3.59	97.19 ± 2.85	95.74 ± 4.18	100.63 ± 2.01	–	–	–
E.C(µS/cm)	4.53 ± 0.49	5.16 ± 1.14	4.70 ± 3.12	4.63 ± 0.38	5.70 ± 0.89	1000	–	–
Chloride(mg/L)	31.24 ± 16.00	16.09 ± 10.75	20.83 ± 15.18	12.78 ± 0.00	18.46 ± 17.74	250	250	250
Total Alk. (mg/L)	ND	ND	ND	ND	ND	200	–	200
HCO_3(mg/L)	22.67 ± 3.06	29.33 ± 2.31	27.33 ± 3.06	44.67 ± 4.16	56.00 ± 4.00	250	–	–
Nitrate(mg/L)	5.13 ± 0.39	3.27 ± 0.81	3.97 ± 0.40	5.13 ± 0.80	2.57 ± 0.40	50	44	50
Sulphate(mg/L)	4.48 ± 0.55	5.44 ± 1.11	5.12 ± 0.55	7.04 ± 0.55	6.40 ± 1.11	250	250	250
CO_3^{2-}	1.44 ± 0.26	2.67 ± 0.70	1.98 ± 0.51	3.32 ± 0.71	2.95 ± 0.94	–	–	–

ND = Not Detected, WHO = World Health Organization Guideline Value, NSDWQ = Nigeria Standard for Drinking Water Quality Guideline Value, US EPA = United State Environment Protection Agency

in the assessment of water in the Strᵔımtori-Firiza reservoir in Northwest Romania. Also, Oladipo et al. (2005) reported higher mean pH values (6.60) of spring water of Ikogosi Warm Spring in Southwestern Nigeria.

The total dissolved solids (20–92.24 mg/L) for all the five sampled locations were within the guideline values of 500 mg/L of (NSDWQ 2007, WHO 2017a, b, US EPA 2009). TDS in water indicates the presence of both organic and inorganic material in the water (Rahmanian 2015). The lower values of the TDS show that the level of saltwater incursion, human input through bunkering activities and the redox potential of the water system, which are a major contributor to higher TDS values of water, are still within the bearable limit (Epkete 2002).

The total suspended solids (TSS) were within the guideline values of 25 mg/L of (WHO 2017a, b; NSDWQ 2007) for all the sampled locations. TSS has a direct relationship

with turbidity, and it ranged from 7.54 to 8.84 mg/L in the rainy season, while in the dry season, it was 6.00 – 13.33 mg/L. Seasonal variation showed that virtually, all sites have appreciable higher values of TSS during the dry season compared with that of the rainy season ($p < 0.05$).

The hardness of water is mainly due to dissolved alkaline earth metals, such as Ca and Mg, with other divalent cations also enhancing the hardness (Barakat et al. 2018). The rocks surrounding the water body are largely the source of total hardness (TH), although some anthropogenic activity could contribute to different concentrations (Bouslah et al. 2017). The total hardness for all the sampled locations was within the guideline values of 500 mg/L (WHO 2017a, b). There was a significant ($p < 0.05$), seasonal variation in the TH values. This could be traced to the solvent action of rainwater (runoff from nearby farmland) coming into contact with soil

Fig. 2 Seasonal variations of the mineral elements
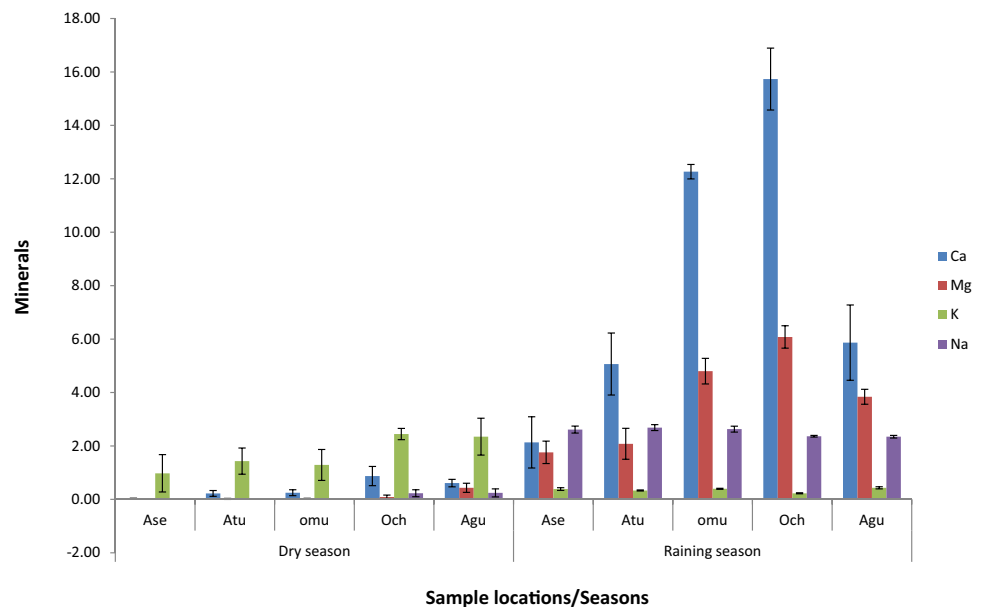
and rocks capable of dissolving Ca and Mg. This is in line with the observation of Vilane and Dlamini, (2016).

Total alkalinity (TA) values for the spring water samples ranged from 83.33 to 300 mg/L in the dry season and were undetected during the rainy season. The TA in all the sampled locations were significantly different ($p < 0.05$). The total alkalinity obtained from Iyi Ase, Iyi Ochiozo and Iyi Aguaba was within the limits of WHO (2017a, b) and NSDWQ (2007), while Iyi Atturu and Iyi Omu were above the guideline values of 200 mg/L. The total alkalinity in water is primarily attributed to the presence of weak acid salts, although strong bases may also contribute (OH^-) in some extreme environmental conditions (Abdulwahi 2013).

The chloride values ranged from 11.92 to 21.17 mg/L in the dry season and 12.78 to 31.24 mg/L in the rainy season. These differences could be attributed to the variations in rainfall, geology, dissolution of fluid inclusions, or the existence of potentially polluted sources, fertilizers, Cl^- bearing minerals at these sites, such as domestic effluent, and open grazing of cattle. The Cl^- values during rainy and dry seasons were all within the guideline values (250 mg/L) for drinking water which is in line with the EPA and NSDWQ standards (EPA 2009 and NSDWQ 2007). Chloride values in all the spring water were found to be significantly higher ($p < 0.05$) in rainy season than in dry season. This could be attributed to runoffs into groundwater and lithography of the study area. Chloride ions from water bedded coal bed, and shale coned could have been leached into the water (Taylor, 1987). The presence of higher levels of SO_4^{2-} could lead to a detectable taste and may cause a laxative effect in unfamiliar consumers (WHO 2017a, b). Sulphates in the aquifer system are derived mainly from pyrite and gypsum weathering, in addition to the inputs from anthropogenic activities (Ziani

et al. 2017). The SO_4^{2-} values of the sampled spring water in the dry and rainy seasons ranged from 32.29 to 45.54 mg/L and 4.48 to 7.04 mg/L, respectively. The lowest value of SO_4^{2-} was observed in dry season in Iyi Ase (4.48 mg/L) (Table 4). Sulphate values were within the guideline values (250 mg/L) recommended by the EPA for drinking water (EPA, 2009). The low concentration of SO_4^{2-} in the rainy season reflects the dilution of groundwater by runoffs from different sources.

The electrical conductivity (EC) is a valuable measure of the amount of dissolved metal ions in water. The values of EC in all sampling points ranged from 5.46 to 7.97 µS/cm in the dry season and 4.53 to 5.70 µS/cm in the rainy season. The values obtained were within the standard values (1000 µS/cm) of NSDWQ (2007) and WHO (2017a, b) for drinking water quality. There were no significant differences ($p > 0.05$) in the conductivity values of all the different sampled locations in the dry and rainy season.

The NO_3^- concentrations in all the samples ranged from 2.57 to 5.13 mg/L in the dry season and 1.06 to 1.16 mg/L in the rainy season. The NO^{3-} values of all the spring water samples were within the guideline value of 50 mg/L (WHO 2017a, b; NSDWQ 2007). The NO_3^- concentration during the rainy season was significantly lower ($p < 0.05$) than the concentration in the dry season.

One of the most important groups of mineral water is the alkaline waters, which are characterized by the presence, in predominating quantities, of one or more of the alkaline or alkaline earth carbonates or bicarbonates. These are the carbonates and bicarbonates of Na, Mg, Li, K and Ca. HCO_3^- and CO_3^{2-}, which produce an alkaline environment, were observed to be within the acceptable limit (250 mg/L and 0–3 mg/L, respectively) by WHO (2017a, b)

Table 4 Mean Concentration of Mineral Elements and Trace Metals in the Spring Water (mg/L)

SampleName	Ca	Mg	K	Na	Pb	Cd	Zn	Cu
Dry season								
Ase	0.03 ± 0.03	0.01 ± 0.01	0.98 ± 1.22	0.17 ± 0.29	ND	0.15 ± 0.03	0.03 ± 0.05	0.35 ± 0.14
Atu	0.22 ± 0.19	0.02 ± 0.03	1.43 ± 0.85	ND	0.02 ± 0.01	0.05 ± 0.01	0.28 ± 0.41	0.22 ± 0.28
Omu	0.25 ± 0.19	0.02 ± 0.03	1.29 ± 1.00	ND	0.01 ± 0.01	0.12 ± 0.08	0.29 ± 0.41	0.07 ± 0.05
Och	0.87 ± 0.63	0.09 ± 0.12	2.45 ± 0.36	0.23 ± 0.23	0.05 ± 0.08	0.02 ± 0.02	6.13 ± 0.16	0.06 ± 0.05
Agu	0.61 ± 0.24	0.43 ± 0.30	2.35 ± 1.20	0.24 ± 0.26	ND	0.01 ± 0.02	0.17 ± 0.02	0.01 ± 0.01
Rainy season								
Ase	2.13 ± 1.67	1.76 ± 0.73	0.39 ± 0.08	2.61 ± 0.23	0.25 ± 0.25	ND	0.06 ± 0.02	0.11 ± 0.07
Atu	5.07 ± 2.01	2.08 ± 0.99	0.33 ± 0.04	2.69 ± 0.19	1.08 ± 0.38	0.01 ± 0.02	0.03 ± 0.01	0.14 ± 0.16
Omu	12.27 ± 0.46	4.80 ± 0.83	0.40 ± 0.04	2.63 ± 0.18	0.08 ± 0.14	0.01 ± 0.02	0.25 ± 0.05	0.73 ± 0.53
Och	5.87 ± 2.44	3.84 ± 0.48	0.43 ± 0.06	2.35 ± 0.08	0.67 ± 0.63	0.02 ± 0.01	0.05 ± 0.03	0.16 ± 0.05
Agu	13.07 ± 4.82	6.08 ± 0.73	0.23 ± 0.03	2.36 ± 0.05	0.08 ± 0.14	0.10 ± 0.07	0.05 ± 0.02	0.04 ± 0.02
WHO	75	50	12	200	0.01	0.003	–	2
EPA	–	50	–	200	0.015	0.005	5	1.3
NSDWQ	75	20	12	200	0.01	0.003	3	1

ND = Not Detected, WHO = World Health Organization Guideline Value (2017), NSDWQ = Nigeria Standard for Drinking Water Quality Guideline Value (2007), US EPA = United State Environment Protection Agency (2009)

and FAO (1004) in both seasons, except for Atu spring water (300 mg/L and 3.65 mg/L, respectively). Similar results were observed in Ajali River, Nigeria (Abugu et al. 2021). Carbonates and bicarbonates are generated by the action of CO_2 in water on carbonate rocks such as limestone and dolomite. Bicarbonate is of little significance in public water supplies except in large amounts, where taste is affected or where the alkalinity affects the corrosiveness of the water.

Mineral elements

A mineral is a chemical element required as an essential nutrient by organisms to perform functions necessary for life (Zoroddu et al. 2019). However, the four major structural elements in the human body by weight (oxygen, hydrogen, carbon, and nitrogen), are usually not included in the list of major nutrient minerals (nitrogen is considered a "mineral" for plants, as it is often included in fertilizers). These four elements compose about 96% of the weight of the human body, and major minerals (macro-minerals) and minor minerals (also called trace elements) compose the remainder (Berdanier et al. 2013).

Table 4 presents the mean concentration of mineral elements in the spring water in both seasons. Ca and Mg are essential parameters for evaluating water quality because of their direct relationship with a hardness of water development. The concentrations of these two metals in natural water depend upon the type of rocks (Sharma and Bhattacharya 2017). They are both essential to human health in limited amounts. Magnesium is part of the chlorophyll, stimulating the nitrogen fixing algae (Roșca et al. 2020; Dippong

et al. 2020). The Mg/Ca ratio exchange can cause density reduction in somezooplankton and freshwater fish species (Roșca et al. 2020; Vigh, 2008). The mean concentration of calcium ranged from 0.03 to 0.87 mg/L in dry season and 2.13 to 13.07 mg/L in rainy season (Fig. 3). The values obtained were within the standard guideline values of 75 mg/L (NSDWQ 2007; WHO 2017a, b) for drinking water quality. On the other hand, the magnesium values ranged from 0.01 to 0.43 mg/L in dry season and 1.76 to 6.08 mg/L in rainy season (Table 5). The results revealed that the values of Mg^{2+} at all sampled locations did not exceed the guideline values of 50 mg/L (NSDWQ 2007; WHO 2017a, b; US EPA, 2009). Okechukwu et al. (2013) obtained higher concentrations of calcium in Asho and Ajie springs (26.65 and 24.04 mg/l, respectively) in the water quality evaluation of spring waters in Nsukka, Nigeria. The variation in Ca^{2+} and Mg^{2+} levels might be related to the weathering of rocks and mineral content of each ion, such as the acidic nature of the spring water which could be attributed to the lithography of the study area. Nsukka FORMATION (Upper coal measures) is stratified mainly as interbedded shales, siltstones shale, sandy shale and coal shale. Magnesium and calcium concentrations were significantly ($p < 0.05$) higher during the rainy season than in the dry season in all the spring water samples. Higher concentration of calcium was observed in Iyi Ochiozo in dry season and Iyi Aguaba in rainy season, while that of magnesium was observed in Iyi Aguaba in both seasons. Generally, the concentrations of calcium were more than that of magnesium and could be attributed to the chemical properties of the soil and geological origin of spring water source in the sampled area (Toma et al. 2013).

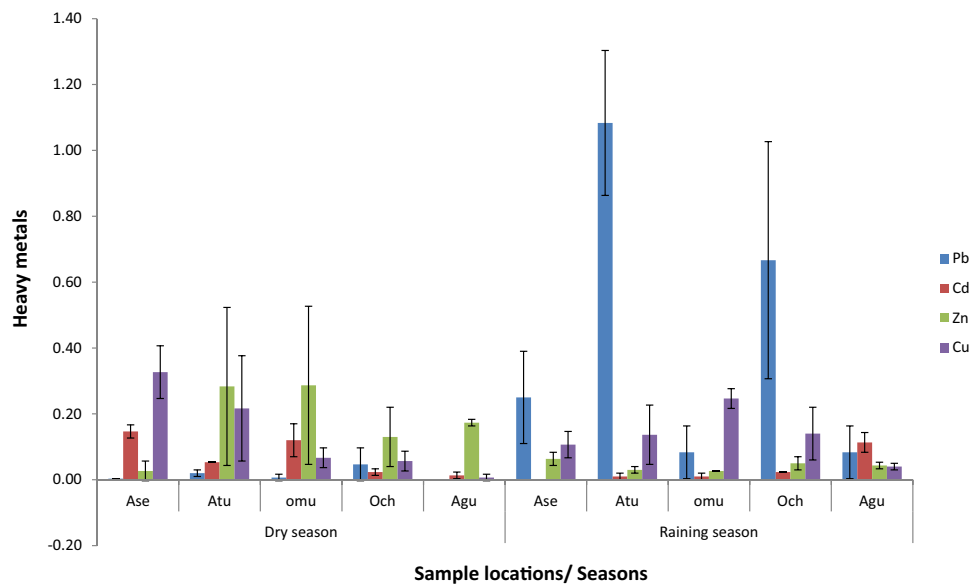**Fig. 3** Seasonal variations of the trace metal content

Table 5 The Water Quality Index and Water quality status of all the samples

Sample sites	Water quality index values	Water quality status
Dry season		
Iyi Ase	55.54	Poor
Iyi Atu	48.67	Good
Iyi Omu	47.45	Good
Iyi Ochiozo	43.66	Good
Iyi Aguaba	41.08	Good
Rainy season		
Iyi Ase	41.09	Good
Iyi Atu	42.49	Good
Iyi Omu	42.05	Good
Iyi Ochiozo	42.86	Good
Iyi Aguaba	39.09	Good

Sodium and potassium are also widely used as essential indicators for assessing water quality. Sodium in the aquifer system is primarily derived from the dissolution of salt minerals and silicate weathering (Ziani et al. 2017). In the present study, the values of Na^+ ranged from 0.17 to 0.24 mg/L in dry season and 2.35 to 2.69 mg/L in rainy season (Fig. 3). The differences in Na^+ values could be related to the geological variation or rock mineral composition of the sampled locations. On the other hand, K^+ values ranged from 0.98 to 2.45 mg/L in dry season and 0.23 to 0.43 mg/L in rainy season (Fig. 3). The Na^+ and K^+ concentrations from the sampled locations were lower than the guideline values during dry and rainy seasons. In almost all the spring water sampled, the concentrations of K^+ were slightly lower than Na^+. Potassium ion is fixed by clay minerals and participates in

the formation of secondary minerals, and this could explain the low K^+ levels (Scheytt 1997). The seasonal variation showed that Na^+ concentrations in all the sampled locations were significantly higher ($p < 0.05$) in rainy season than dry season, while that of K^+ values at all the sampled locations were significantly higher ($p < 0.05$) in dry season than rainy season.

Trace metals

The mean concentration of trace metals (Table 4) was compared with the local and international standards for water quality. The concentration of copper ranged from 0.01 to 0.35 mg/L in dry season and 0.04 to 0.73 mg/L in rainy season (Fig. 4). Cu concentrations in all the samples were within the guideline values of 1 mg/L (NSDWQ 2007), 2 mg/L (WHO 2017a, b) and 1.3 mg/L (US EPA 2009). Cu concentration in all the sampled location was significantly higher ($p < 0.05$) in rainy season than in dry season. Chemical weathering and soil leaching are the two important natural sources contributing to the increase in trace metal concentration in water (Drever 1988).

Zinc concentrations in all the spring water samples were within the guideline values of 3 mg/L (NSDWQ 2007) and 5 mg/L (US EPA 2009). However, the mean concentration of Zn in one of the springs (Iyi Ochiozo) (Table 5) was above the guideline value. In this study, the concentrations of zinc ranged from 0.03 to 6.13 mg/L in dry season and 0.03 to 0.25 mg/L in rainy season (Fig. 4). It was observed that Zn concentration in all the samples was significantly higher ($p < 0.05$) in dry season than in rainy season.

Cd concentrations ranged from 0.01 to 0.15 mg/L in dry season and 0.01 to 0.02 mg/L in rainy season (Fig. 4). Cadmium concentrations in all the spring water samples were

Fig. 4 Hierarchical cluster dendogram of the physicochemical parameters in the spring water
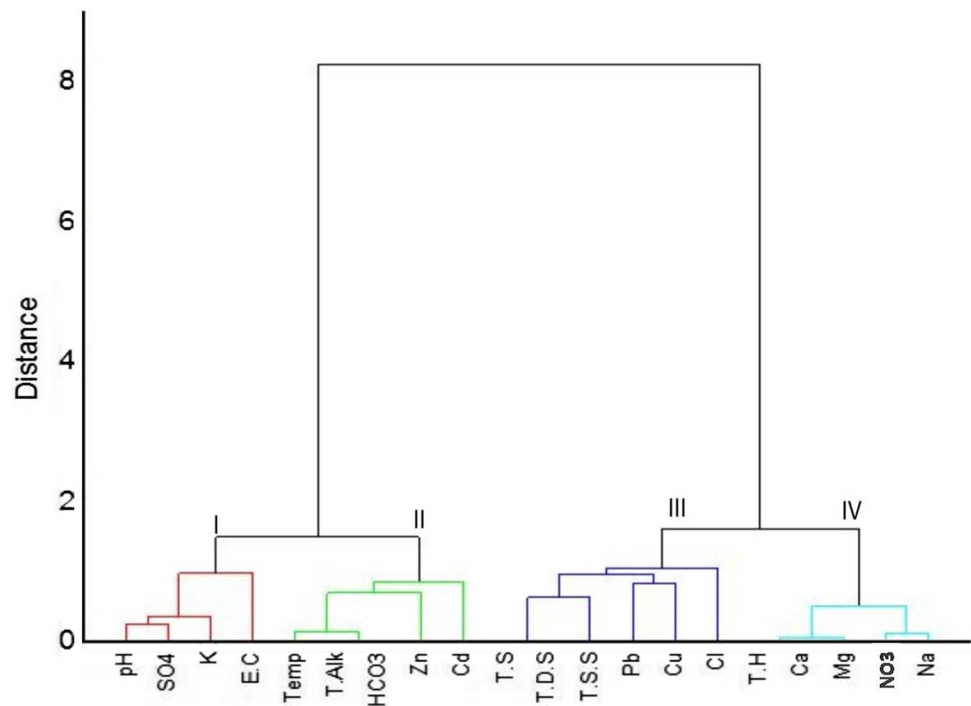
above the guideline values of 0.003 mg/L (WHO 2017a, b; NSDWQ 2007) and 0.005 mg/L (US EPA 2009). The Cd concentrations were significantly different ($p < 0.05$) in all the samples. The high concentrations of the Cd in all the samples could be as a result of leaching of Cd from the embedded coal deposit.

Pb concentrations ranged from 0.01 to 0.05 mg/L in dry season and 0.08 to 1.08 mg/L in rainy season (Fig. 4). Lead concentrations in all the spring water samples were above the guideline values of 0.01 mg/L (NSDWQ 2007; WHO 2017a, b) and 0.015 mg/L (US EPA 2009). The high concentrations of Pb in all the samples could be as a result of leaching of minerals like lead sulphides from the embedded coal deposit.

Correlation analysis

Pearson correlation determines whether there is a linear component of association between two continuous variables and is denoted by r. Table 6 presents the correlation analysis performed on the data obtained. A strong positive and significant ($p < 0.01$) correlation was observed between pH and SO_4^{2-} ($r = 0.746$), indicating that SO_4^{2-} could be one of the major causes of the acidity in the spring. The relationship between pH and SO_4^{2-} is in agreement with the report of Bhandari and Nayal, (2008) in Kosi River Water, Uttarakhand. The pH alternatively, strongly correlated negatively with TS, TDS, TH, NO_3^-, Mg and Na. Also, SO_4^{2-} had strong and negative correlation with Na ($r = -0.932$), NO_3^- ($r = -0.827$), TS ($r = -0.781$), TDS

($r = -0.767$), and TH ($r = -0.723$). There were strong positive and significant correlations at 0.01 levels for total dissolved solids and total solids ($r = 0.981$) indicating that TDS was the major contributing factor to TS since spring water is usually clear and has little or no suspended solids. TDS showed strong positive and significant ($p < 0.01$) correlations with TH, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+. TH similarly had a strong positive and significant ($p < 0.01$) correlation with Ca ($r = 0.979$) and Mg ($r = 0.960$), indicating the two ions as the source of hardness in water. This shows the influence of organic and inorganic salts in the quality of spring water (Basamba et al. 2013).

A strong positive and significant ($p < 0.01$) correlation was also observed between HCO_3^- and alkalinity ($r = 0.991$) and temperature ($r = 0.877$), showing that bicarbonate is major source of the alkalinity in water and was influenced by temperature. There were strong positive and significant correlations at 0.01 levels for Na and NO_3^- ($r = 0.869$), Zn and HO_3^- ($r = 0.595$) and Zn with total alkalinity ($r = 0.582$). However, weak positive and significant correlations at 0.05 level were observed for total suspended solids (TSS) and copper ($r = 0.358$), Pb and TSS ($r = 0.380$), Pb and TDS ($r = 0.380$), cadmium and total alkalinity ($r = 0.433$). EC is the measure of liquid capacity to conduct an electric charge (Marandi et al. 2013; Kumar et al. 2015). This gives an indication of the amount of total dissolved substitution in water (Yilmaz and Koc, 2014). Therefore, its ability to conduct electricity depends on dissolved ion concentrations (TDS), ionic strength, and temperature of measurements (Hem, 1985). However, the EC showed weak and insignificant

Table 6 Correlation Coefficient of the Physicochemical Parameters of Spring water samples

	pH	Temp	EC	TS	TSS	TDS	Cl	TALK	TH	HCO$_3$	NO$_3^-$	SO$_4^{2-}$	Ca	Mg	K	Na	Pb	Cd	Zn	Cu
pH	1																			
Temp	0.389*	1																		
EC	0.048	0.005	1																	
TS	−0.751**	−0.181	−0.106	1																
TSS	−0.227	0.048	−0.024	0.603**	1															
TDS	−0.789**	−0.211	−0.111	0.981**	0.439*	1														
Cl	−0.264	0.036	−0.269	0.230	0.177	0.215	1													
TALK	0.464**	0.883*	0.080	−0.434*	−0.337	−0.404*	−0.042	1												
TH	−0.537**	−0.455*	−0.205	0.573**	0.261	0.582**	−0.032	−0.567**	1											
HCO$_3$	0.380*	0.877**	0.056	−0.361*	−0.320	−0.326	−0.047	0.991**	−0.488**	1										
NO$_3^-$	−0.604**	−0.570**	−0.353	0.600**	0.283	0.603**	0.193	−0.715**	0.723**	−0.676**	1									
SO$_4^{2-}$	0.746**	0.550*	0.304	−0.781**	−0.455**	−0.767**	−0.176	0.722**	−0.723**	0.653**	−0.827**	1								
Ca	−0.472**	−0.512**	−0.152	0.502**	0.237	0.508**	−0.057	−0.603**	0.979**	−0.539**	0.711**	−0.668**	1							
Mg	−0.609**	−0.565**	−0.180	0.595**	0.264	0.605**	−0.018	−0.682**	0.960**	−0.604**	0.752**	−0.758**	0.926**	1						
K	0.642**	0.186	0.365*	−0.733**	−0.378*	−0.734**	−0.208	0.418*	−0.573**	0.352	−0.576**	0.672**	−0.502**	−0.568**	1					
Na	−0.706**	−0.722**	−0.345	0.674**	0.313	0.680**	0.164	−0.835**	0.727**	−0.779**	0.869**	−0.932**	0.702**	0.792**	−0.649**	1				
Pb	−0.292	−0.380*	−0.074	0.380*	0.192	0.380*	−0.034	−0.420*	0.368*	−0.396*	0.440*	−0.489**	0.422*	0.294	−0.369**	0.523**	1			
Cd	0.128	0.559**	0.033	0.055	0.206	0.016	0.080	0.433*	−0.224	0.472**	−0.460*	0.259	−0.275	−0.256	−0.024	−0.403*	−0.285	1		
Zn	0.226	0.340	−0.030	−0.455**	−0.416*	−0.412*	−0.042	0.582**	−0.268	0.595**	−0.314	0.403*	−0.271	−0.304	0.531**	−0.373**	−0.206	−0.029	1	
Cu	0.122	0.298	−0.012	0.215	0.358	0.158	0.012	0.084	0.215	0.087	0.052	−0.106	0.180	0.082	−0.222	0.020	0.159	0.104	−0.162	1

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed)

relationships with the physicochemical parameters evaluated except K (r − 0.365) which was significant at $p < 0.05$. These results were however in contrast with the reports of Bhandari and Nayal, (2008), Basamba et al. (2013) and Oyem et al. (2014) who reported a strong correlation of EC with other parameters mostly TDS in river water, borehole and groundwater, respectively. These discrepancies could possibly be a pointer that the spring water evaluated was devoid of contamination or contains less amount of dissolved substitutions.

Cluster analysis

Cluster analysis (CA) is a data analysis tool used to group data having similar characteristics (Prakash and Dagaonkar 2011). The results as presented in Fig. 4 show the dendogram on hierarchical cluster analysis of the physicochemical parameters evaluated. The physicochemical parameters were grouped into four clusters. This was similar to the report of Prakash and Dagaonkar (2011) who reported that the physicochemical properties of water samples were divided into four clusters. However, there were variations in the type of parameter grouped into one cluster. This could be attributed to the differences in sample source and the concentration of the parameters in the water sample.

Cluster I comprised of pH, SO_4, K and EC. This group showed that the pH of the water evaluated was strongly influenced by the concentration of SO_4^{2-}, while K controls the relation between pH and SO_4^{2-}. This observation was in agreement with the correlation result. In cluster II, HCO_3^- strongly determines the total alkalinity of the water regulated by the water temperature. More so, the concentration of Zn and Cd was slight contributors to the alkalinity of the evaluated spring water. Cluster III comprises of TS, TDS, TSS, Pb, Cu and Cl−and it showed a close relationship between TS and TDS. The total solids in the water evaluated were slightly as a result of the concentration of Pb and Cu. However, the total hardness of the water samples was as a result of the presence of Ca and Mg. This agrees with the report of Radha-Krishnan et al. (2007), Praveen et al. (2008), Oparaocha et al. (2010) and Basamba et al. (2013) that Ca as a result of anthropogenic activities, terrigenous influx in runoff, and/or natural processes within the aquifers is a major source of hardness in water. These are in agreement with the predictions by the correlation results.

Water quality index (WQI)

The water quality index estimation showed values ranging from 41.08 to 55.54 and 39.09 to 42.86 for dry and rainy seasons, respectively (Table 6). None of the spring water had excellent water status, but four of the spring's water had good water status in both seasons. However, one

spring water (Iyi Ase) had poor water status in dry season and thus is unfit for consumption. The unsuitability of the spring water samples could be due to dissolution of ions into the surface aquifer or other various anthropogenic activities within the study area such as fertilizer application, open grazing of cattle and washing of cloths. Egbueri et al. (2020) and Alum and Okoye (2020) observed similar trend in the assessment of drinking water in Ojoto area, SE, Nigeria and monitoring of pollution status of major rivers in an agricultural belt in eastern Nigeria, respectively. Nnorom et al. (2019) worked on multivariate statistical approach and water quality assessment of natural springs and other drinking water sources in Southeastern Nigeria and recorded WQI range of 3.75–70.58, 7.51–71.04, 5.81–45.92 and 1.52–132.34 for samples from springs, streams, hand-dug wells and boreholes, respectively. Paiu et al. (2014) assessed the water quality index on surface water quality in the Eastern part of Romania and got values ranging from 73.25 to 79.5, 64.25 to 60.

The spring water suitability for irrigation application

In agricultural production, water is required and is an essential resource in plants growth (Tiwari et al. 2013). Thus, spring water quality appraisal is required to determine their suitability for irrigation in Igbo-etiti farmlands. All the criteria usually used are based on the total concentrations of soluble salts, relative proportion of sodium to other cations and chemical concentration of other ions (Michael, 1992).

The PI of the spring water was calculated taking into consideration the Mg^{2+}, Ca^{2+}, Na^+ and HCO_3^- concentration in the water. The prolonged use of water rich in these ions affects the permeability of the soil (Singh et al. 1999). Doneen (1964) classified irrigation based on the PI into class I, II and III. Class I and II represent 75% maximum permeability which indicates that the water sample is suitable for irrigation, while PI of 25% maximum permeability or below is seen as unsuitable for irrigation application (Doneen 1964; Raju 2007). The PI of all the analysed spring waters (Table 7) showed that they were suitable (> 75% permeability) for irrigation application.

The SSP values (Table 7) predicted that during the dry season, the spring water were not suitable (> 60%) for irrigation purposes, but showed otherwise during the rainy season (< 60%). This could be attributed to the dilution effect of rainfall on the spring water during the rainy season. SSP above 60% is not desirable in water for irrigation since it could lead to sodium accumulations which can cause a breakdown in the physical properties of the soil (Doneen 1964).

Another criterion to evaluate the suitability of water for irrigation application is the Kelly's ratio (KR). According

Table 7 Water quality indices and percent sodium

Sample Sites	PI	SSP	KR	MAR	RSC	CAI	SAR	%Na
Dry season								
Ase	6815.303	96.63866	4.25000	25	201.28	0.936709	1.202082	96.63866
Atu	7216.878	85.62874	0.00000	8.333333	303.38	0.925482	0.00000	85.62874
Omu	5856.070	82.69231	0.00000	7.407407	251.61	0.939065	0.00000	82.69231
Och	786.3848	73.62637	0.239583	9.375000	84.680	0.775168	0.331976	73.62637
Agu	800.0000	71.34986	0.230769	41.34615	100.61	0.843505	0.33282	71.34986
Rainy season								
Ase	113.4047	43.54136	0.670951	45.24422	20.220	0.903969	1.871461	43.54136
Atu	82.37518	29.69518	0.376224	29.09091	24.850	0.812306	1.422703	29.69518
Omu	40.02960	15.12731	0.154706	28.23529	12.310	0.854537	0.902083	15.12731
Och	74.90516	22.25781	0.242019	39.54686	38.280	0.782473	1.06653	22.25781
Agu	45.91098	11.95201	0.123690	31.86583	39.870	0.859697	0.764078	11.95201

to KR, values less than unity (KR < 1) are suitable for irrigation, and unsuitable if KR > 1. From Table 7, both the rainy season and dry season spring water were suitable for irrigation application except Iyi Ase (KR = 4.25) during the dry season.

The magnesium adsorption ration (MAR) was also used to assess the suitability of the spring water for irrigation application. It predicted all the spring water to be within the acceptable suitability limit (MAR < 50%). MAR is based on the Mg and Ca concentration in water. According to Raghunath (1987), magnesium hazard value > 50% is detrimental to crop yield as it will make the soil more alkaline.

Chloro-alkaline indices (CAI) criterion predicted that there is no ion exchange (between K + Na with Mg and Ca), having recorded positive CAI values in all the samples. CAI gives an account of the ion exchange between the water and rock indicated.

Sodium absorption ratio (SAR) predicts sodium hazards which reduces soil permeability and inhibits water absorption by the crops (Tahmasebi et al. 2018). SAR classifies water as excellent (SAR < 10), good (SAR 10–18), doubtful

(18–26) and unsuitable (SAR > 26) (Ravikumar et al. 2011). The SAR values showed excellent water for irrigation application in both seasons. Ibeneme et al. (2013) reported a similar result from the assessment of the chemical characteristics of a spring water source at Ife-Owutu, Ezinihite-Mbaise, Southeastern Nigeria.

Percent Na of the spring water samples predicted Iyi Ase, IyiAturu and Iyi Omu as unsuitable (%Na > 80) for irrigation application, Iyi Ochiozo and Iyi Aguaba as doubtful (%Na, 61 – 80) in the dry season. In rainy season, it predicted Iyi-Omu and Iyi Aguaba as excellent (%Na < 20), Iyi Ase as permissible and Iyi Aturu and Iyi Ochiozo as good.

Pollution index of the spring water

The pollution index (Table 8) suggested that the pollution level of all samples in dry season was insignificant (PIS < 1), while for rainy season samples, it predicted Omu and Agu to have a low pollution index (PIS > 1). Iyi Atu, Iyi Ochiozo and Iyi Ase were predicted to be heavily polluted (PIS > 2.5) which represent about 60% of the rainy season samples (Rao,

Table 8 Pollution index of the spring water (PIS) (ΣOw) and the overall water quality (Ow)

Sample	Ow pH	TH	TDS	Na$^+$	K$^+$	Ca$^+$	Mg$^+$	SO$_4^{2-}$	Cl$^-$	HCO$^-$	Pb	NO$_3^{-1}$	ΣOw
Ase	0.08558	0.00083	0.01705	0.00008	0.00190	0.00002	0.00001	0.01864	0.00676	0.05582	0.00000	0.00247	0.18915
Atu	0.07938	0.00248	0.01550	0.00000	0.00277	0.00014	0.00002	0.01502	0.00714	0.08372	0.23256	0.00267	0.44141
Omu	0.07674	0.00103	0.01240	0.00000	0.00250	0.00016	0.00002	0.01584	0.00788	0.06977	0.11628	0.00270	0.30532
Ochi	0.08884	0.00000	0.00465	0.00011	0.00475	0.00054	0.00008	0.02118	0.00444	0.02325	0.58140	0.00279	0.73203
Agu	0.08233	0.00000	0.01085	0.00011	0.00456	0.00038	0.00040	0.01871	0.00616	0.02791	0.00000	0.00328	0.15468
Rainy season													
Ase	0.06868	0.00393	0.02035	0.00121	0.00076	0.00132	0.00000	0.00208	0.01162	0.00633	2.90700	0.01193	3.03522
Atu	0.07333	0.00661	0.02052	0.00125	0.00064	0.00314	0.00000	0.00253	0.00599	0.00819	12.55824	0.00760	12.68804
Omu	0.07333	0.01571	0.02080	0.00122	0.00078	0.00761	0.00001	0.00238	0.00775	0.00763	0.93024	0.00923	1.07669
Och	0.07178	0.02005	0.02014	0.00109	0.00083	0.00364	0.00000	0.00327	0.00476	0.01247	7.79076	0.01193	7.94074
Agu	0.06620	0.00951	0.02145	0.00110	0.00045	0.00811	0.00001	0.00298	0.00687	0.01563	0.93024	0.00598	1.06852

2012). This is similar to the result obtained by Egbueri et al. (2021) in underground water in Umunya area, Southeastern Nigeria. The high pollution index during the rainy season was attributed to Pb. Pb is very poisonous, even at a very low concentration (WHO 2017a, b). According to WHO (2017a, b), there is no safe Pb threshold for blood production in the body. In infants, lead can cause serious neurodevelopment problems and IQ loss. In adults, it leads to anxiety, nervous systems disorder, hypertension, kidney problems, failure of the reproductive organs, and cancer (Ukah et al. 2019; Brown & Margolis, 2012).

Health risk assessment

Spring water is one of the best sources of natural water for drinking purposes but it has been threatened by anthropogenic activities which have made some spring water unsafe for drinking. Trace metals being one of the pollutants, in this regard, were assessed for its toxicity in the spring waters. CDI, HQ, HI and PCR indices were considered, and the chronic daily intake for Pb, Cd and Cu was 0.0033, 0.0100 and 0.0233, respectively. The CDI for Cd was above the recommended daily intake of 0.003 mg/L (WHO 2017a, b), while Pb and Cu were within the limit. The HQ for Cd was greater than one across the age brackets indicating a probable non-cancer risk in the ingestion of the spring water, most especially Ase, Atu and Och spring waters in dry season and Och and Agu in rainy season (Table 9). In the rainy season samples, Pb was observed to record HQ > 1 in both adult and children. The order of non-cancer risk contribution by each metal is Cd > Pb > Cu for dry season, while Pb > Cd > Cu

was the order for rainy season. These contributions led to the HI being greater than unity showing a non-cancer risk involved in the ingestion of most of the spring water in Igbo-Ettiti area of Enugu state, Nigeria. The probable cancer risk analysis of the spring waters showed a probable cancer risk, PCR value > 1×10^{-4}, (Cao et al. 2014) in almost all the spring water in Igbo-Ettiti. This is inline with observation of Egbueri (2020a,b) in groundwater samples in Onitsha, Nigeria.

Conclusion

This study was conducted to assess the quality of spring water in Igbo-Etiti, Nigeria, for drinking and irrigation purposes based on several physicochemical parameters, mineral elements and trace metal analysis. The spring water was generally acidic and this was attributed to the leaching of minerals from the embedded coal deposit that releases acidic oxides. Virtually, all the physicochemical parameters were within their respective standard limits, just as the mineral elements were within the required standard in both sampled seasons. Lead and cadmium concentrations were above the guideline values of NSDWQ, WHO and US EPA and this was attributed to the leaching of minerals like lead sulphides from the embedded coal deposit. Strong correlation was observed between the parameters indicating similarity in their sources. The CA confirms that the correlation analysis was very strong within the similar group (homogeneous) which confirmed the observation made by correlation analysis. All the

Table 9 Chronic daily intake (CDI), hazard quotient (HQ), hazard index (HI) and probable cancer risk (PCR) for children and adult

Samples	CDI (mg/per/day)						HQ						PCR			
	Children			Adult			Children			Adult			Children		Adult	
	Pb	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Pb	Cd
Dry season																
Ase	0.0000	0.0100	0.0233	0.0000	0.0043	0.0100	0.00	10.00	0.58	0.00	4.29	0.25	0.0000	0.0263	0.0000	0.0113
Atu	0.0013	0.0033	0.0147	0.0006	0.0014	0.0063	0.33	3.33	0.37	0.14	1.43	0.16	0.1568	0.0088	0.0672	0.0038
Omu	0.0007	0.0080	0.0047	0.0003	0.0034	0.0020	0.17	8.00	0.12	0.07	3.43	0.05	0.0785	0.0211	0.0336	0.0090
Och	0.0033	0.0013	0.0040	0.0014	0.0006	0.0017	0.83	1.33	0.10	0.36	0.57	0.04	0.3921	0.0035	0.1681	0.0015
Agu	0.0000	0.0007	0.0007	0.0000	0.0003	0.0003	0.00	0.67	0.02	0.00	0.29	0.01	0.0000	0.0018	0.0000	0.0008
	HI						1.33	23.33	1.18	0.57	10.00	0.51				
Rainy season																
Ase	0.0167	0.0000	0.0073	0.0071	0.0000	0.0031	4.17	0.00	0.18	1.79	0.00	0.08	1.9608	0.0000	0.8404	0.0000
Atu	0.0720	0.0007	0.0093	0.0309	0.0003	0.0040	18.00	0.67	0.23	7.71	0.29	0.10	8.4706	0.0018	3.6302	0.0008
Omu	0.0053	0.0007	0.0487	0.0023	0.0003	0.0209	1.33	0.67	1.22	0.57	0.29	0.52	0.6274	0.0018	0.2689	0.0008
Och	0.0447	0.0013	0.0107	0.0191	0.0006	0.0046	11.17	1.33	0.27	4.79	0.57	0.11	5.2549	0.0035	2.2521	0.0015
Agu	0.0053	0.0067	0.0027	0.0023	0.0029	0.0011	1.33	6.67	0.07	0.57	2.86	0.03	0.6274	0.0175	0.2689	0.0075
	HI						36.00	9.33	1.97	15.43	4.00	0.84				

spring water samples had good water status except one (Iyi Ase) is considered unsafe for drinking. For irrigation application, the water quality indices and percent sodium of the spring water were generally predicted to be suitable except Iyi Ase. The pollution indices suggested that the pollution level was insignificant in both season and the probable cancer risk analysis of the spring water showed a probable cancer risk (PCR value $> 1 \times 10^{-4}$). These observations are in contrast to reports by Rao (2012). Therefore, it is strongly recommended that the spring water must be treated before use.

Declarations

Conflict of interest There are no conflict of interest.

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