



Appraising drinking water quality in Ikem rural area (Nigeria) based on chemometrics and multiple indexical methods

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Abstract The continuous deterioration of drinking water quality supplies by several anthropogenic activities is a serious global challenge in recent times. In this current study, the drinking water quality of Ikem rural agricultural area (southeastern Nigeria) was assessed using chemometrics and multiple indexical methods. Twenty-five groundwater samples were collected from hand-dug wells and analyzed for physicochemical parameters such as pH, major ions, and heavy metals. The pH of the samples (which ranged between 5.2 and 6.7) indicated that waters were slightly acidic. Cations and

anions (except for phosphate) were within their respective standard limits. Except for Mn, heavy metals were also found to be below their maximum allowable limits. Factor analysis identified both geogenic processes and anthropogenic inputs as possible origins of the analyzed physicochemical parameters. Modified heavy metal index, geoaccumulation index, and overall index of pollution revealed that all the hand-dug wells were in excellent condition, and hence safe for drinking purposes. However, pollution load index, water quality index (WQI), and entropy-weighted water quality index

Highlights

- Rural water supply in the study area currently does not face serious pollution threats.
- Factor analysis successfully identified the possible sources of the physicochemical parameters.
- Heavy metal index was modified and successfully used in the water quality assessment.
- The indexical methods used in this study proved to be efficient in water quality assessment.
- Hierarchical cluster analysis identified the wells that have slight pollution imprints.

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(EWQI) revealed that some wells (about 8–12%) were slightly contaminated, and hence are placed in good water category. A hierarchical cluster analysis (HCA) was performed based on the integration of the WQI and EWQI results. The HCA revealed two major quality categories of the samples. While the first cluster comprises of samples classified as excellent drinking water by both WQI and EWQI models, the second cluster comprises of about 12% samples which were identified as good water by either the WQI or EWQI.

Keywords Chemometric analysis · Entropy water quality index (EWQI) · Environmental pollution indices · Rural water supply · Water quality index (WQI)

Introduction

Almost all sectors of the human economy such as industry, agriculture, forestry, fishery, sports, recreation, tourism, and hydropower extensively rely on water resources for their well-being and sustainability. High-quality and safe water supply is very essential to these sectors for such reasons as increased productivity, economic breakthroughs, public and environmental health sustainability (Mgbenu and Egbueri 2019; Wang et al. 2019; Egbueri et al. 2019; Tian and Wu 2019; Rahman et al. 2019; Li and Wu 2019). Of all the numerous uses of water, water for drinking and domestic usages is the most greatly desired. However, for drinking water to be considered safe and desirable for human consumption, it must be free from every kind of contamination or pollution (Nigerian Industrial Standard (NIS) 2007; World Health Organization (WHO) 2017). In recent times, the attention of many researchers round the globe has been caught by the increasing rates at which water supplies for drinking and domestic purposes are being contaminated by several human activities (including agriculture, industry, urbanization, commerce, poor waste disposal, and negligence) (Egbueri 2018, 2019a, b; Li and Wu 2019; Rahman et al. 2019). Nevertheless, several types of researches conducted in different parts of the world also show that geogenic processes play contributory roles in the continuous deterioration of the drinking water quality (Egbueri 2018, 2019a, b; Wang et al. 2019; Egbueri et al. 2019; Rahman et al. 2019; Li and Wu 2019).

Although all lives on the earth depend on water for sustainability, water is also reported to be an effective

pollutant carrier which facilitates several disease transmissions (Wang et al. 2019; Egbueri 2019a; Rahman et al. 2019; Mgbenu and Egbueri 2019). Exposure of drinking water supplies to processes that pollute them is the genesis of the scarcity of high-quality water supply. In many rural areas in the developing countries, one of the major challenges faced by their citizens is the difficulty in sustaining high-quality water supplies. Excessive use of agrochemicals and poor sanitation conditions in rural agricultural areas predispose water sources to both chemical and biological contaminations, which in turn pose high risks of disease outbreaks to the local residents (Wang et al. 2019; Egbueri 2019a, b). The rate of spread of waterborne diseases has continued to increase over the past few decades, resulting in widespread health risks (Rahman et al. 2019; Li and Wu 2019; Wang et al. 2019). Research has shown that about 80% of all deaths and illnesses suffered every year by over five million people in developing countries are connected to various waterborne diseases (United Nations Educational Scientific and Cultural Organization, UNESCO 2007; Rahman et al. 2019). Therefore, it is an important research focus to regularly examine the pollution statuses and quality of different water supplies. Such research focal point is usually targeted at ensuring the protection and sustainability of good water supply.

An important prerequisite for ensuring the safety of water supply is the provision of constant good quality source of water. Although it is currently facing rapid pollution threats, groundwater remains the most desirable source of high-quality water for human consumption, ecosystem maintenance, and other purposes (Tian and Wu 2019; Egbueri 2019b; Rawat et al. 2019; Egbueri et al. 2019). Considering its major role in different sectors of human existence, groundwater quality research is now widely conducted in all parts of the world in an attempt to increase the awareness of water supply protection (Li and Wu 2019). Developing relevant methods for assessing water quality is an important issue (Simonyan et al. 2018) in a world where the rate of water pollution is highly disturbing. Over the years, many researchers have developed several water quality assessment methods (Simonyan et al. 2018; Wang et al. 2019). Of special interest is the fact that the extent of water pollution and the quality can now be examined and represented using numerical (indexical or stochastic) models such as pollution indices (PIs) and water quality indices (WQIs). A water source that has been

described to be of excellent quality based on a parameter may turn out to be of very poor quality considering another parameter. Given the myriad of factors that affect the quality of water, it is only fair to describe the quality of water by cumulative numerical expressions that consider the influence of every such factors (Amiri et al. 2014; Singh et al. 2019; Feng et al. 2019). Literature is rich with numerous splinter assessment of water quality with such numerical expressions (Wu et al. 2011; Ur Rehman et al. 2018; Ghaderpoori 2018; Rakotondrabe et al. 2018; Ayandiran et al. 2018; Mgbenu and Egbueri 2019; Radfard et al. 2019; Hamuna et al. 2019; Wang et al. 2019; Egbueri et al. 2019; Li and Wu 2019). Additionally, statistical methods such as linear regression, factor, and cluster analyses have been widely used in water quality researches. All of these research methods have proven to be efficient in water quality analysis, favoring the assessment and management of groundwater quality.

In Ikem rural area (southeast Nigeria), boreholes are very scarce such that the residents exclusively rely on both surface water and hand-dug well water for their drinking, domestic, and agricultural usages. The scarcity of borehole water supplies (which are usually sourced from aquifers farther away from the surface processes) in this area is believed to be due to such factors as geology, poverty, lack of skilled manpower, and negligence, etc. However, scientific researches investigating the quality and suitability of the available water sources for various purposes are scarce, hence the need for this study.

The major focus of this current study is to assess the extent of chemical contamination (due to anthropogenic activities) and the suitability of the groundwater (sourced from hand-dug wells) for drinking purposes in this rural district, using integrated chemometric and multiple indexical approaches. The analytical tools used in this study include (1) environmental pollution indices such as geoaccumulation index (I_{geo}), pollution load index (PLI), modified heavy metal index (MHMI) and overall index of pollution (OIP); (2) the conventional water quality index (WQI); (3) entropy water quality index (EWQI); and (4) chemometric analyses, including factor analysis (FA) and hierarchical cluster analysis (HCA). In this work, results from the indexical methods were compared to establish their efficacy relationships. To the best of our knowledge, this current study is the first water quality assessment using the I_{geo} , PLI, MHMI, OIP, and EWQI in the southeast region of Nigeria. The integrative and comparative

approaches utilized in this study were targeted at eliminating the obvious subjectivity associated with the use of a single indexical method. Therefore, it is hoped that this work will be useful for (1) understanding the current level of chemical pollution in the available hand-dug wells in Ikem area, (2) understanding the suitability of the groundwater for human consumption, (3) understanding the limitations and strength of the different measurement indices, and (4) promoting the awareness of rational development, utilization, management, and protection of the available groundwater resources in Ikem and its environs.

Materials and methods

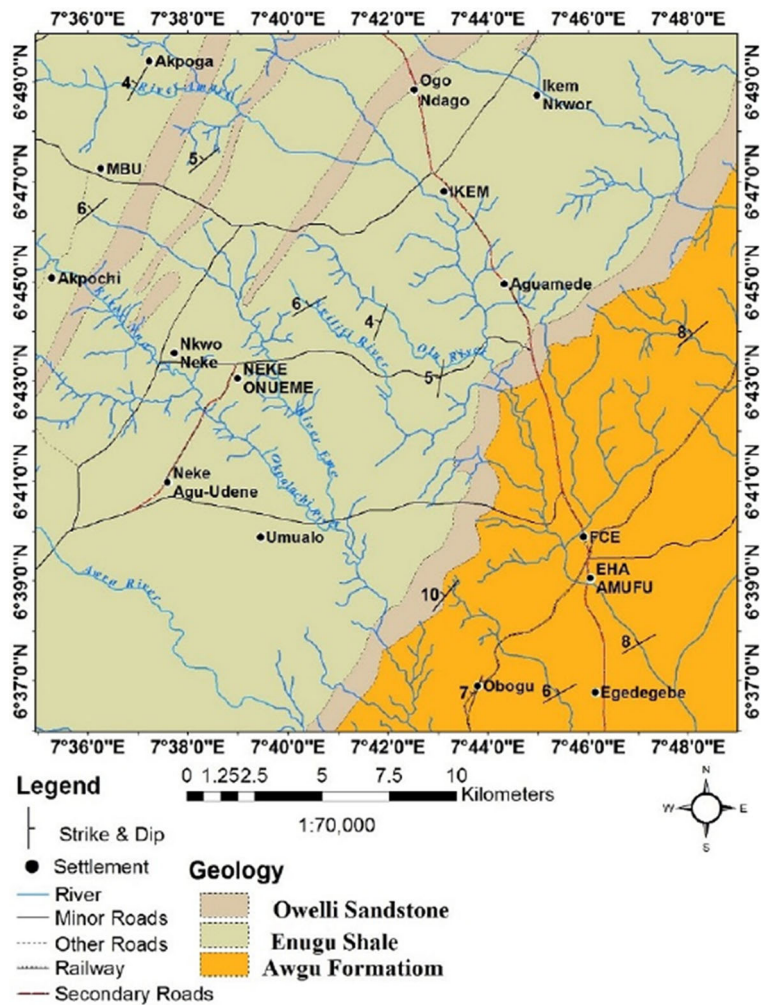
Study site

Ikem rural agricultural province (southeast Nigeria) is within latitudes $6^{\circ} 36'$ to $6^{\circ} 50'$ N and longitudes $7^{\circ} 35'$ to $7^{\circ} 49'$ E (Fig. 1). The major villages considered in this study are Ikem, Umualor, Mbu, Eha-Amufu, and Neke. Based on the reports of the National Population Commission (NPC 2006), this study region has over 165,000 inhabitants (Onwuka and Ezugwu 2019). The majority of the inhabitants rely on agriculture for livelihood. In this rural setting, unregulated use of agrochemicals and poor management of agricultural wastes were suspected to be a major possible source of water pollution in the area. In terms of geology, the Ikem area is seated on the Nkporo Group (comprising of Enugu and Oweli formations, and is Late Campanian in age) and the Awgu Formation (Coniacian in age) (Fig. 1); both of which are dominantly composed of mudrocks such as shales and claystones, with little occurrences of limestones and sandstones (Nwajide 2013). The groundwater depths in the hand-dug wells are in the range of 7 to 15 m, indicating the presence of a shallow (possibly a perched) aquiferous system. Groundwater flow direction in this is believed to be controlled by such factors as topography and lithologic fractures (Fig. 2). In the southeast region of Nigeria, annual rainfall intensity is usually in the range of 1500 to 2000 mm (Nwajide 2013; Egbueri et al. 2019).

Sample collection and analysis

The target of the fieldwork was to identify and sample all existent hand-dug wells in Ikem localities with high population distribution and intense agricultural

Fig. 1 Geologic map of the study area



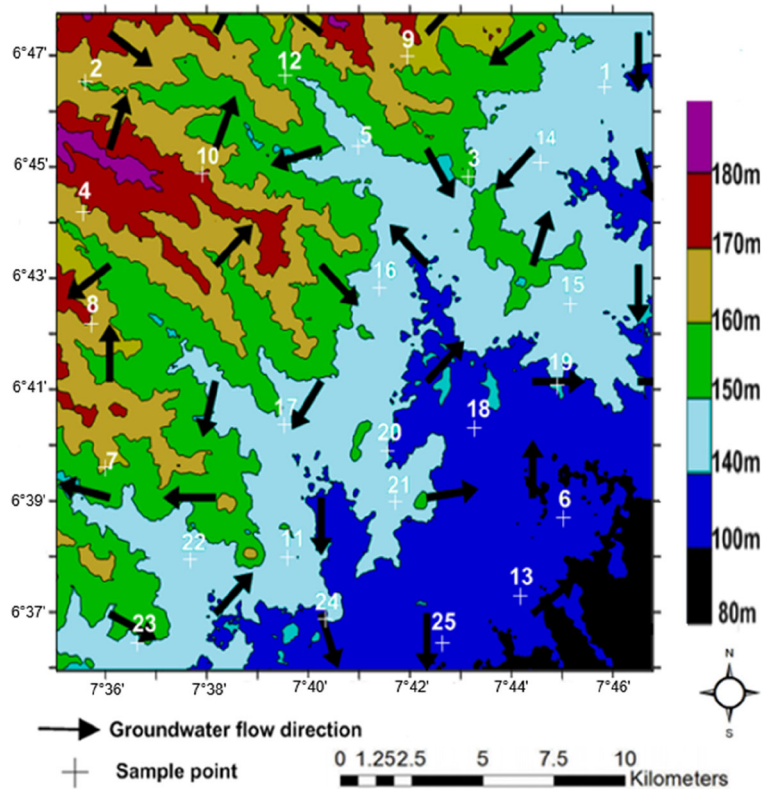
activities. However, hand-dug wells distribution was observed to be relatively scarce. Only twenty-five hand-dug wells were identified and sampled from the target areas. Figure 2 highlights the sample locations. All the samples were collected using prewashed and sterilized 1-L plastic bottles. The sampling was conducted at the peak of the rainy season (August 2017). pH was measured in situ using a Hach portable pH meter while other parameters such as chloride (Cl^-), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), phosphate (PO_4^{3-}), magnesium (Mg^{2+}), nitrate (NO_3^-), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), manganese (Mn), iron (Fe), zinc (Zn), and lead (Pb) were analyzed in the laboratory using standardized methods for anions, cations, and heavy metals as recommended by American Public Health Association (APHA 2005). The SO_4^{2-} and NO_3^- concentrations were determined by Hach

DR/2000 spectrophotometer with turbidimetric formula. The Na^+ and K^+ were measured using a Gallenkamp Flame instrument (flame analyzer model FGA 330c) whereas Cl^- and HCO_3^- concentrations were determined using titrimetric method. However, the heavy metals were determined with atomic absorption spectrophotometer (AAS, Scientific 210 VGP).

Water chemistry and quality assessment by chemometric methods

Chemometric analysis is a very important method used in the evaluation and characterization of the quality of water resources. In this study, factor analysis (FA) and hierarchical cluster analysis (HCA) are the two chemometric tools used for the water quality assessment. Both analyses were performed with the aid of SPSS (version

Fig. 2 Groundwater flow map showing the sample points



22). In order to obtain the optimal distribution of the variances for parameters, Varimax rotation (with Kaiser normalization) was used in extracting the component factors in the FA whereas the Ward’s linkage method (with squared Euclidean distance and z-score standardization) was used for the HCA.

Water quality assessment by indexical methods

Modified heavy metal index

Heavy metal index (HMI) is an indexical method used for the analysis of heavy metals’ impacts in the ecosystem. In this study, the HMI proposed by Dash et al. (2019) was modified. The major focus of the modification was regarding the weightage assignment to the water quality parameters. Dash et al. (2019) assigned weights to parameters based on the integration of information obtained from cluster groupings and eigenvalues of principal component analysis. However, in the current study, the weights were assigned to the analyzed heavy metals on a scale of 1 to 5, based on the significance of the heavy metals in water quality assessment

of the agricultural area and human health impact. Afterwards, the relative weights of the parameters (Table 1) were obtained using the function described in Eq. 1. The final modified heavy metal index (MHMI) values for each of the samples were then calculated using Eq. 2.

$$R_w = \frac{w_i}{\sum_{i=1}^n w_i} \tag{1}$$

$$MHMI = \sum_{i=1}^n \left[R_w * \frac{M_i}{S_i} \right] \tag{2}$$

Table 1 Relative weights of heavy metals used for MHMI

Parameter	Weight (w _i)	Relative weight (R _w)
Fe	3	0.23
Zn	3	0.23
Pb	4	0.31
Mn	3	0.23
	∑w _i = 13	∑R _w = 1.00

where R_w is the relative weight; w_i is the weight assigned to parameter; n is the total number of parameters; M_i is metal concentration in the water sample; and S_i is the WHO (2017) standard limit for the heavy metal.

Geoaccumulation index (I_{geo})

Geoaccumulation index has been employed for the assessment of pollution in various geoenvironmental systems (soil and water) by different authors (Müller 1969; Bhutiani et al. 2017; Adimalla and Wang 2018). In this study, four heavy metals which include Fe, Mn, Pb, Zn and two trace elements PO_4^{3-} and NO_3^- analyzed using the I_{geo} model. These trace elements were added to this analysis following the use of NPK fertilizers (their major source) in the Ikem agricultural area.

$$I_{geo} = \text{Log}_2 \frac{C_{HMS}}{1.5 \times GBV} \quad (3)$$

where C_{HMS} = concentration of heavy metals in the water sample; GBV = geochemical background value. The constant 1.5 allows analyzing natural fluctuations in the content of a given substance in the environment (Müller 1969; Bhutiani et al. 2017; Adimalla and Wang 2018; Egbueri and Unigwe 2020; Ukah et al. 2020). The following classification scheme was used for the I_{geo} assessment: uncontaminated ($I_{geo} \leq 0$); uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderately to heavily contaminated ($2 < I_{geo} \leq 3$); heavily contaminated ($3 < I_{geo} \leq 4$); heavily to extremely contaminated ($4 < I_{geo} \leq 5$); and extremely contaminated ($I_{geo} \geq 5$) (Müller 1969; Bhutiani et al. 2017; Adimalla and Wang 2018; Egbueri and Unigwe 2020).

Pollution load index

To further investigate the impact of the analyzed heavy metals on the groundwater quality of the area under study, pollution load index (PLI) was evaluated. In assessing the degree of pollution in a system, the PLI is used to represent the number of times by which a heavy metal's concentrations in the groundwater exceeds its background concentration. The PLI also gives a summative indication of

the overall level of heavy metal pollution. Details of the PLI for the groundwater samples were obtained using Eq. 4 and Eq. 5.

$$PLI = \sum (PI_1 * PI_2 * PI_3 * PI_4 * \dots * PI_n)^{1/n} \quad (4)$$

$$PI = C_s / C_b \quad (5)$$

where PI = the pollution index; n = the number of heavy metals; C_s = the concentration of heavy metals in the sample; C_b = the corresponding background values of NIS (2007) (Bhutiani et al. 2017; Adimalla et al. 2019). The samples were classified based on PI as: Unpolluted ($PI < 1$); unpolluted to moderately polluted ($PI = 1$ to 2); moderately polluted ($PI = 2$ to 3); moderately to highly polluted ($PI = 3$ to 4); highly polluted ($PI = 4$ to 5); very highly polluted ($PI > 5$) (Bhutiani et al. 2017; Adimalla et al. 2019).

Overall index of pollution

The overall index of pollution (OIP) is another water quality evaluation parameter proposed by Sargaonkar and Deshpande (2003) for the assessment of the level of pollution in drinking water sources (Egbueri and Unigwe 2019). In this study, the OIP was computed for nine physicochemical parameters (pH , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , HCO_3^- and NO_3^-) using the functions described in Eq. 6 and Eq. 7.

$$OIP = \frac{1}{n} \sum_{i=1}^n PI \quad (6)$$

$$PI = \frac{V_n (\text{observed value of parameter})}{V_s (\text{standard value of parameter})} \quad (7)$$

where PI = pollution index for the i th parameters; n = number of parameters. According to Sargaonkar and Deshpande (2003), the OIP classifies water quality into five categories: OIP value < 1.9 is said to have an excellent water quality and classified under class C_1 . If the OIP score is < 3.9 , then the water quality is said to be acceptable and categorized under class C_2 . However, OIP scores < 7.9 , < 15.9 , and > 16 indicate slightly polluted (class C_3), polluted (class C_4), and heavily polluted (class C_5) water, respectively.

Water quality index

The water quality index (WQI) is believed to provide a comprehensive summary of quality status of the water samples (Mgbenu and Egbueri 2019). Four steps and equations were used for obtaining the WQI. The first step was to assign weights (w_i) (on a scale of 1 to 5) to the analyzed water quality parameters and consequently obtaining their relative weight (W_i). The weights were assigned to the parameters based on their relative importance and concentrations in the drinking water (Egbueri et al. 2019; Egbueri 2020). The relative weights (W_i) shown in Table 2 were obtained using Eq. 8.

$$W_i = w_i / \sum_{i=1}^n (w_i) \tag{8}$$

where n is the total number of parameters.

The second step taken in the WQI evaluation was estimating the quality rating scale for each parameter (q_i) using Eq. 9.

$$q_i = (C_i / S_i) \times 100 \tag{9}$$

where C_i is the parameter concentration in water; S_i is the WHO (2017) standard limit of parameter.

The third step in the WQI evaluation is the estimation of the sub-index of i th parameter (SI), expressed in Eq. 10.

$$SI = W_i \times q_i \tag{10}$$

Finally, the WQI value for each sample was obtained using Eq. 11.

$$WQI = \sum_{i=1}^n (SI) \tag{11}$$

Entropy water quality index

Although the WQI is the most widely used indexical method in water quality assessment, the assessment it provides is usually dependent on the accuracy of expert judgment, as the weighted factor is determined by discretion (Amiri et al. 2014; Ukah et al. 2020). Similarly, other assessment methods have the limitation of exclusivity to some selected parameters. However, at present, the entropy water quality index (EWQI) is a measure that is believed to provide the most unbiased and justifiable assessment of groundwater quality (Li et al. 2010; Amiri et al. 2014; Singh et al. 2019; Feng et al. 2019; Ukah et al. 2020). Therefore, in this current study, the EWQI was employed to further investigate the groundwater quality and to possibly validate the results of other indexical methods.

In the computation of the EWQI, the first step is to determine the information entropy (e_j). Information entropy was first introduced by Shannon in 1948 to address the uncertainty related to stochastic information (Li et al. 2010). Imagine there are y samples of water ($i = 1, 2, 3 \dots z$) on which x number of parameters ($j = 1, 2, 3 \dots n$) are to be tested to measure the quality of the water, the matrix of such distribution will be given as:

$$X = \begin{vmatrix} x_{11} & x_{12} \dots & x_{1n} \\ x_{21} & x_{22} \dots & x_{2n} \\ \vdots & \vdots & \vdots \\ x_{z1} & x_{z2} \dots & x_{zn} \end{vmatrix} \tag{12}$$

Upon transformation, the Y matrix becomes:

$$Y = \begin{vmatrix} y_{11} & y_{12} \dots & y_{1n} \\ y_{21} & y_{22} \dots & y_{2n} \\ \vdots & \vdots & \vdots \\ y_{z1} & y_{z2} \dots & y_{zn} \end{vmatrix} \tag{13}$$

Thus, the ratio of index values of j and i in the sample is given by:

$$P_{ij} = \frac{y_{ij}}{\sum_{i=1}^z y_{ij}} \tag{14}$$

Table 2 Relative weights of parameters used in WQI

Parameter	Weight (w_i)	Relative weight (W_i)
Calcium	2	0.050
Chloride	4	0.100
Magnesium	3	0.075
Iron	4	0.100
Manganese	3	0.075
Nitrate	4	0.100
Potassium	3	0.075
Sulfate	3	0.075
Zinc	3	0.075
Bicarbonate	1	0.025
Sodium	1	0.025
pH	5	0.125
Lead	4	0.100
	$\sum w_i = 40$	$\sum W_i = 1.000$

The information entropy for each parameter is given as:

$$e_j = -\frac{1}{\ln} n \sum_{i=1}^z P_{ij} \ln P_{ij} \quad (15)$$

where n is the total number of samples and P_{ij} denotes the probability of occurrence of the normalized value of the parameter j expressed as:

$$P_{ij} = \frac{P_{ij}}{\sum P_{ij}} \quad (16)$$

The second step is to calculate the entropy weight of each parameter (w_j):

$$w_j = \frac{1-e_j}{\sum_{j=1}^n (1-e_j)} \quad (17)$$

The third step is to calculate the quality rating scale (q_j) for each parameter in every sample using the formula:

$$q_j = \frac{C_j}{S_j} \times 100 \quad (18)$$

where C_j is the concentration of parameters in each water sample in mg/L and S_j is the measured standard of each parameter in water samples in mg/L as given by NIS (2007). For the parameters with no NIS (2007) limits, the WHO (2017) limits were used. Where the standard is in range, the upper limit was used.

Finally, the entropy water quality index (EWQI) is calculated as:

$$EWQI = \sum_{j=1}^n w_j \cdot q_j \quad (19)$$

The obtained EWQI values were then used for the quality classification of the groundwater samples as follow: EWQI < 50 (Rank 1, excellent water quality); 50–100 (Rank 2, Good water quality); 100–150 (Rank 3, Average water quality); 150–200 (Rank 4, Poor water quality); and > 200 (Rank 5, Extremely poor water quality) (Li et al. 2010; Wu et al. 2011; Amiri et al. 2014; Singh et al. 2019; Feng et al. 2019; Ukah et al. 2020).

Results and discussion

General characteristics of groundwater

Table 3 lists the statistical summary of the chemical indicators of the analyzed hand-dug wells in the study area. Temperature of the samples ranged from 10 to 31 °C. The pH examinations revealed that the groundwater in this rural agricultural area is generally slightly acidic, with the pH values ranging from 5.2 to 6.7 and a mean value of 5.92. Except for Mn, other heavy metals in the groundwater samples were found to be low (Table 3; NIS 2007). The cations and anions results indicate that the groundwater samples are fresh waters, with all their concentrations below their respective maximum allowable limits set by NIS (2007) and WHO (2017), except for PO_4^{3-} (Table 3). However, for cations, it was noticed that the concentrations of Na^+ and Ca^{2+} were predominant than Mg^{2+} and K^+ in the area (Table 3). This could be signifying that ion exchange processes between sodium and calcium take place in the aquifer (Mgbenu and Egbueri 2019; Egbueri et al. 2019). For the anions, Cl^- and PO_4^{3-} were predominant more than HCO_3^- , SO_4^{2-} , and NO_3^- , indicating the possible impact of agriculture on the groundwater chemistry (Egbueri 2019a, b). Overall, the trend of dominance for the ions is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (for the cations) and $\text{Cl}^- > \text{PO}_4^{3-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ (for the anions). Additionally, a Piper diagram (Fig. 3) was drawn and used to reveal the predominant hydrogeochemical facies of the groundwater samples. The obtained results show that the chemical facies of the groundwater samples are dominantly $\text{Cl}\text{-SO}_4\text{-Ca}\text{-Mg}$ and $\text{Cl}\text{-SO}_4\text{-Na}\text{-K}$ types.

Groundwater chemistry assessment and source apportionment by factor analysis

Factor analysis has been successfully used by different authors for water chemistry and quality assessment (Onwuka et al. 2018; Egbueri 2018, 2019a, b; Ukah et al. 2019), as it helps in the distribution analysis and possible source(s) apportionment of the chemical components in water (Mgbenu and Egbueri 2018). In this study, six factors were extracted using the Varimax rotation technique. In addition, only factor loadings $\geq \pm 5.0$ were considered significant in this study. Table 4 shows the factor loadings and their percentages of variance. The first factor is an assemblage of parameters

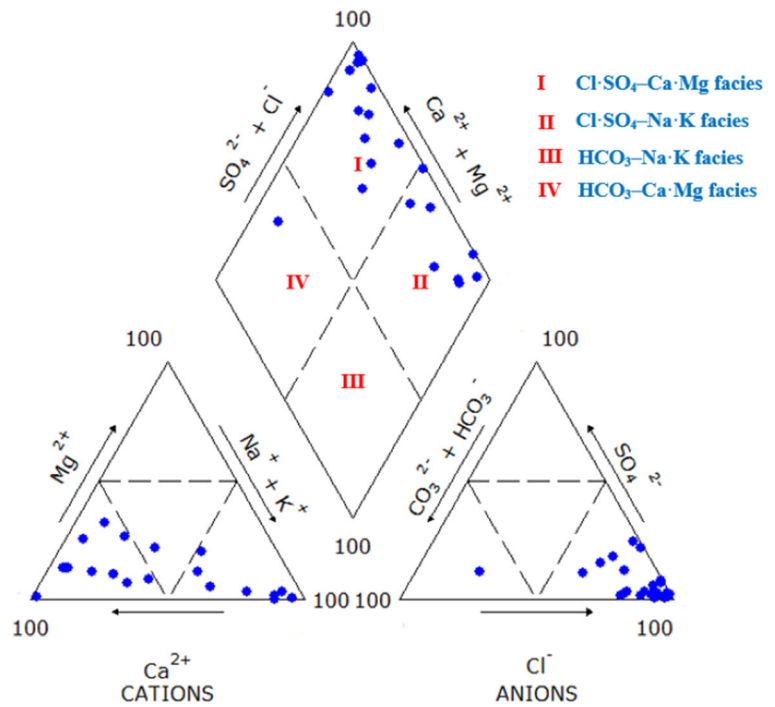
Table 3 Univariate statistics of analytical data and their comparison with standard limits

Sample number	Temperature (°C)	pH	Fe	Mn	Pb	Zn	Na ⁺	K ⁺
No. of wells	25	25	25	25	25	25	25	25
Range	10–31	5.2–6.7	0.114–0.214	0.162–1.82	0.048–0.141	0.1–0.2	0.188–254	0.59–39.86
Mean	26.64	5.916	0.1628	0.3293	0.09148	0.136	50.7708	7.3324
SD	4.75	0.4643	0.0226	0.3486	0.0251	0.049	85.7007	8.7195
NIS (2007)	–	6.5–8.5	0.3	0.2	0.01	3	200	–
WHO (2017)	–	6.5–8.5	0.3	0.4	0.01	4	200	12

Sample number	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	PO ₄ ³⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
No. of wells	25	25	25	25	25	25	25
Range	10–205	0–33.8	0.16–11	7.749–29.981	8–248.5	0.02–0.16	0.64–11.92
Mean	44.16	9.5856	3.8339	10.5203	79.288	0.0908	3.6748
SD	58.0389	10.7933	3.515	4.2607	65.2444	0.02397	3.1166
NIS (2007)	–	0.20	–	–	250	50	100
WHO (2017)	75	50	250	10	250	50	250

SD standard deviation

Fig. 3 A Piper diagram showing the dominant hydrogeochemical facies in the area



(Pb, Zn, Na, and K) that can be attributed to origins due to both anthropogenic and geogenic processes. The Pb and Zn are linked to anthropogenic origins (Egbueri

et al. 2019; Mgbenu and Egbueri 2019; Egbueri 2019b). However, the significant negative loading on Pb suggests that it has a peculiar anthropogenic origin

Table 4 Varimax rotated factor analysis results

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
pH	0.086	0.183	<i>0.562</i>	- 0.133	- 0.436	- 0.399	0.724
Fe	0.118	0.223	0.076	<i>0.891</i>	- 0.107	- 0.060	0.878
Mn	0.033	- 0.044	- 0.035	- 0.007	<i>0.920</i>	- 0.022	0.851
Pb	- <i>0.716</i>	- 0.289	0.253	- 0.083	- 0.220	- 0.272	0.790
Zn	<i>0.815</i>	0.255	0.051	0.069	- 0.050	0.086	0.747
Na ⁺	<i>0.794</i>	- 0.063	- 0.197	- 0.215	0.017	- 0.117	0.734
K ⁺	<i>0.691</i>	- 0.134	0.496	0.038	- 0.155	- 0.092	0.775
Ca ²⁺	- 0.065	0.157	<i>0.782</i>	0.005	<i>0.541</i>	- 0.040	0.934
Mg ²⁺	- 0.120	0.022	<i>0.928</i>	- 0.067	- 0.122	0.092	0.903
HCO ₃ ⁻	0.033	0.171	0.016	- 0.028	- 0.024	<i>0.944</i>	0.923
PO ₄ ³⁻	0.179	<i>0.804</i>	0.026	0.073	- 0.140	0.240	0.761
Cl ⁻	0.162	<i>0.749</i>	0.034	- 0.034	0.074	0.240	0.653
NO ₃ ⁻	- 0.108	<i>0.797</i>	0.113	- 0.018	- 0.006	- 0.370	0.797
SO ₄ ²⁻	- 0.212	- 0.272	- 0.233	<i>0.799</i>	0.160	0.063	0.841
Total	2.443	2.225	2.216	1.521	1.482	1.425	-
% variance	17.453	15.894	15.826	10.866	10.588	10.176	-
Cumulative (%)	17.453	33.347	49.173	60.039	70.627	80.803	-

Considered significant factor loadings are in italics

different from that of Zn. The Na and K (the alkali metals) are believed to be leached into the water by geogenic processes (Mgbenu and Egbueri 2019; Egbueri 2019a) such as the weathering of silicate minerals rich in orthoclase and plagioclase. However, the Factor 2 comprises of parameters (PO₄, Cl, and NO₃) that are characteristic of anthropogenic (agricultural) inputs (Onwuka et al. 2018; Egbueri 2019a, b).

The Factor 3 has high loadings on pH, Ca, and Mg. Although much is not known about this association, it could be indicating that the occurrence of the alkaline earth metals (Ca and Mg) in the groundwater is controlled by the pH. Naturally, Ca and Mg are released in water by both silicate and carbonate mineral dissolutions. In Factor 4, Fe and SO₄ are the significant parameters. Studies have shown that these two parameters could be released in water by such geogenic processes as redox reactions (Egbueri et al. 2019; Mgbenu and Egbueri 2019). Factor 5 has significant loadings on Mn and Ca, suggesting geogenic origins such as mineral-rock weathering. Although Mn in water is linkable to geogenic origin (e.g., weathering of siderites and pyrites) (Egbueri 2019b), it could also be leached into groundwater by such anthropogenic sources as agriculture (agrochemicals). In the Factor 6, only HCO₃ is loaded. The occurrence of HCO₃ in the groundwater can be attributed to geogenic sources such as dissolution of carbon(iv)oxide (CO₂) and oxidation processes.

Groundwater quality assessment by indexical methods

Modified heavy metal index

The modified heavy metal index (MHMI) results classify water samples into five groups: MHMI < 50 indicates excellent water; 50 ≤ MHMI < 100 represents good drinking water; 100 ≤ MHMI < 200 indicates poor water; 200 ≤ MHMI < 300 signifies very poor drinking water; and MHMI ≥ 300 indicates unsuitable water for drinking purposes. Based on the results presented in Table 5, the final MHMI values for this study range from 1.7429 to 4.6460 with an average value of 3.1578. The results indicate that all the samples are in excellent conditions.

Geoaccumulation index (I_{geo})

The I_{geo} assessment revealed that the order of impact of the analyzed trace elements is Mn < PO₄³⁻ < Zn < NO₃⁻ < Fe < Pb. Table 5 also shows a summary of the I_{geo} for

Table 5 Results of the various indices for the individual water samples

Sample ID	MHMI	I _{geo}	PLI	OIP	WQI
W1	2.3729	- 272.272	0.682	0.2927	10.242
W2	1.7429	- 305.823	0.358	0.3957	50.015
W3	1.7615	- 304.172	0.329	0.3425	6.912
W4	3.1715	- 241.232	0.896	0.3293	0.943
W5	3.0055	- 256.584	2.680	0.3111	12.800
W6	2.4236	- 270.036	0.646	0.7606	57.020
W7	3.2484	- 238.678	0.819	0.2405	19.331
W8	2.9522	- 248.586	0.809	0.6394	23.881
W9	3.0699	- 244.553	0.339	0.2705	1.062
W10	2.9789	- 247.584	0.753	0.1433	4.889
W11	2.3918	- 270.893	0.265	0.2321	17.166
W12	3.6503	- 246.602	2.491	0.379	22.344
W13	2.4284	- 269.848	0.271	0.1878	3.666
W14	2.4059	- 270.91	0.360	0.1766	15.733
W15	2.8509	- 252.824	0.292	0.2078	13.652
W16	3.2068	- 239.953	0.306	0.1933	1.025
W17	3.6750	- 226.065	0.271	0.2071	13.342
W18	4.2032	- 211.707	0.530	0.5767	2.157
W19	4.1176	- 213.685	0.659	0.2753	19.22
W20	4.6460	- 201.455	0.642	0.3285	11.754
W21	3.1582	- 241.416	0.416	0.3234	8.993
W22	4.0513	- 216.289	0.502	0.1165	7.626
W23	3.9914	- 217.047	0.528	0.1259	18.556
W24	4.2277	- 211.169	0.505	0.127	7.894
W25	3.2138	- 239.674	0.489	0.1404	2.553

the twenty-five (25) groundwater samples in Ikem area. Based on the classification reported in Müller (1969), Bhutiani et al. (2017), and Adimalla and Wang (2018), it was observed that 100% of the analyzed samples are uncontaminated, signifying that the groundwater is safe for drinking purposes.

Pollution load index

In Table 5, the summary of the pollution load index (PLI) results for all the twenty-five groundwater samples is presented. In this study, 92% of the groundwater samples are unpolluted. However, 8% of the samples (W5 and W12) are moderately polluted. Overall, the PLI results indicate that the groundwater samples from the shallow aquifer in the Ikem rural community stand to pose no significant health threat to the consumers.

Overall index of pollution

The overall index of pollution (OIP) values of all the sampling sites are presented in Table 5. Based on the OIP index scores obtained, the groundwater samples from the hand-dug wells are adjudged to be in excellent condition ($OIP < 1$), with values in the range of 0.1165 to 0.7606 and average value of 0.2929.

Water quality index

The water quality index (WQI) classifies drinking water into five different groups: $WQI < 50$ represents excellent drinking water; 50–100 represents good water; 100–200 indicates poor water; 200–300 indicates very poor water; and > 300 signifies water unsuitable for drinking (Mgbenu and Egbueri 2019; Egbueri et al. 2019; Egbueri 2020). From the WQI results obtained in this study, 92% of the total samples are excellent water while 8% are within the good water range (Table 5). Based on this classification presented, the groundwater from the hand-dug wells is adjudged as chemically uncontaminated and thus suitable for human consumption.

Entropy water quality index

Table 6 presents the information entropy (e_j) and entropy weight (w_j) of each parameter for the samples. The computed entropy water quality index (EQWI) shows that water from the sources is of

Table 6 The information entropy (e_j) and entropy. Weight (w_j) of each parameter

Parameter	e_j	w_j
pH	0.9989	0.0009
Fe	0.9969	0.0025
Mn	0.9057	0.0754
Pb	0.9885	0.0092
Zn	0.9814	0.0149
Na ⁺	0.6670	0.2661
K ⁺	0.8459	0.1232
Ca ²⁺	0.8272	0.1381
Mg ²⁺	0.8382	0.1293
HCO ₃ ⁻	0.9096	0.0723
PO ₄ ³⁻	0.9824	0.0141
Cl ⁻	0.9061	0.0750
NO ₃ ⁻	0.9885	0.0092
SO ₄ ²⁻	0.9125	0.0699

excellent quality for human consumption, with 92% (23 wells) and 8% (2 wells) ranking as excellent and good quality water respectively (Table 7). In this study, it was observed that parameters with the highest entropy weight and the lowest information entropy value have the highest effect on the quality of water (Gorgij et al. 2017). Also, the lower the EWQI, the better the quality. Mean analysis revealed that about 86% of all the analyzed parameters fall within the standard for drinking quality. Only the pH and PO₄³⁻ were seen to be outside the standard range. While the water is slightly more acidic than desirable, the waters from the area contain about 5% more PO₄³⁻ than the normal acceptable standard. However, this is not a problem because PO₄³⁻ is not known to pose any obvious health challenge to humans (Cotruvo 2017).

In Tables 8 and 9, we present the summaries of the percentages of parameters that were found to be outside the range of their standard limits and the wells in which the parameters are outside the standard respectively. These two tables would be useful quality control data as they show the percentage quality-defect in each hand-dug well as well as the identity of the defecting wells for all the parameters. While Table 8 gives information on the kind of treatment that may be needed for water from each well, Table 9 tells the number of wells that are affected by a particular defect and hence the quantum of effort or resources that would be needed if the entire area is to be treated. Information about the likely water-related health challenge or water quality complaint that may arise from individuals using each well may also be predicted from those tables. It can be seen from Tables 7 and 8 that W24 has the highest quality water followed by W23 and W25. Furthermore, this study exposed that 4%, 44%, 36%, 8%, and 8% of the total wells defected in 0, 1, 2, 3, and 4 parameters respectively. However, these defects are benign as they were only found in parameters that are considered not to pose any health hazard to humans. Ca²⁺ is also not known to pose any health danger except that it causes water to be hard (Egbueri 2019a) and to have undesirable taste (Cotruvo 2017). Depending on the sensitivity of taste-buds, consumers may complain of undesirable taste in water collected from W12 and W18, even though they are within limit. No water-related health challenge is expected from people consuming these waters as all such hazardous parameters (e.g., nitrate and heavy metals) are nearly absent or very low.

Table 7 The computed EQWI and ranks for each sample

Sample	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13
EWQI	27.27	46.19	46.22	43.15	42.2	69.73	22.68	89.37	28.38	10.73	19.87	15.44	13.08
Rank	1	1	1	1	1	2	1	2	1	1	1	1	1
EWQI	12.58	15.86	13.71	17.16	47.54	29.5	31.81	41.79	5.46	6.17	5.02	6.84	–
Rank	1	1	1	1	1	1	1	1	1	1	1	1	–

Water quality comparison and classification by hierarchical cluster analysis

So far, the results of the indexical methods used in this study have shown that the majority of the hand-dug wells in the Ikem area are safe for human consumption. Fifty percent (i.e., MHMI, I_{geo} , and OIP) of the indexical methods used in this study showed that 100% of the hand-dug wells are chemically unpolluted and thus in excellent conditions suitable for drinking purposes. However, the remaining 50% (PLI, WQI, and EWQI) of the indexical methods revealed that all the samples were not in excellent condition. These indices showed that 92% the total samples are excellent drinking water while 8% have mild pollution, thus they were classified as good water.

The hierarchical cluster analysis (HCA) has been widely used in water quality assessments to classify water resources based on their genetics and quality (Egbueri 2018, 2019b, c; Egbueri and Unigwe 2019; Egbueri et al. 2019). In this study, a dendrogram was produced from a hierarchical cluster analysis based on the integration of the WQI and EWQI results (Fig. 4). Based on the result presented in Fig. 4, it was observed that two major quality categories (branches/clusters) were formed. The first cluster comprises of the groundwater samples which were classified as excellent drinking water by both WQI and EWQI models. On the other hand, the second cluster comprises 12% of the total samples (i.e., samples W2, W6, and W8) which were identified as good water by either the WQI or EWQI. The HCA result presented in this study proves to be

useful in the identification of those wells that have received slight pollution imprints.

More discussion on water quality of Ikem rural

Generally, the quality of groundwater in the area is excellent. This observation is surprising but comforting. Groundwater, which is a major source of drinking water, is largely affected by such factors as the geology (Mohammadi et al. 2019; Mistry et al. 2019; Jebreen et al. 2018; Lintern et al. 2018), land use, and lifestyle of the area (You et al. 2019; Florea 2019; Motew et al. 2019). The area is largely rural and agrarian. The samples were collected at the peak of rainy season (August 2017) and the depth of water at that time ranged from 7 to 15 m. From this information, one would expect agrochemicals (especially aided by the high rainfall) to readily contaminate the groundwater system as reported by some authors (Ashraf et al. 2019; Anim-Gyampo et al. 2019c; Anim-Gyampo et al. 2019b). More so, shallow aquifers such as those in the study area have been reported to be highly vulnerable to contamination (da Silva et al. 2019; Kozak et al. 2019; Song et al. 2019; Egbueri 2019b). As have been implied by Anim-Gyampo et al. (2019a), our findings suggest that farming activities in this area do not involve excessive use of chemical additives. Hence, the groundwater is not currently predisposed to any danger of pollution outbreak. A study of the water sampled during the dry season would be attempted in future to alienate the effect of rainfall and percolation on the water chemistry.

Table 8 The percentage of parameters that are over the standard limit for each sample source

Sample	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13
% parameter overage	7.1	21.4	21.4	28.6	14.3	14.3	7.1	28.6	7.1	7.1	14.3	14.3	14.3
Sample	W14	W15	W16	W17	W18	W19	W20	W21	W22	W23	W24	W25	–
% parameter overage	7.1	7.1	7.1	7.1	14.3	14.3	7.1	14.3	14.3	7.1	0	7.1	–

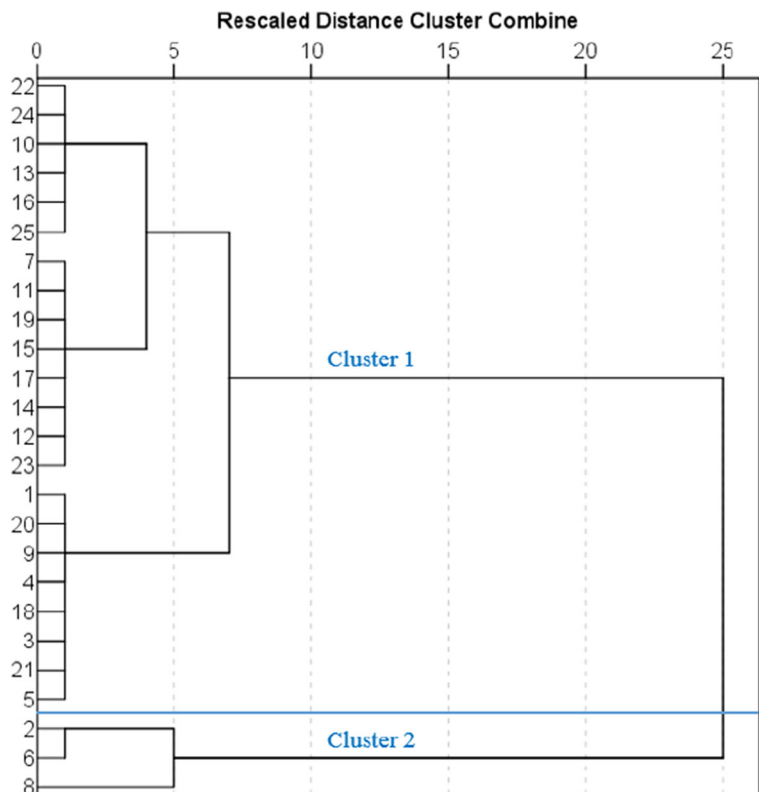
Table 9 The well overage for each parameter

Parameter	pH	Fe	Mn	Pb	Zn	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	PO ₄ ³⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Wells	2-5, 7-19, 21-23, 25	0	0	0	0	3, 5, 8, 21	2, 4, 8, 11, 18	0	4, 6, 19, 20	0	1, 2, 3, 6, 8, 12, 13	0	0	0

Furthermore, given the rural nature of the area with poor sanitary conditions and high incidence of open defecation, one would expect their imprints in the groundwater chemistry as reported by Mukate et al. (2018) and Bhallamudi et al. (2019). Results (e.g., the nitrate concentrations) from this study point that the poor sanitary condition of the study area may not have had much effect on the groundwater chemistry. This observation is consistent with the findings of Malan and Sharma (2018) of some open-defecation-free villages in India. Such defect may be better seen in microbiological (coliform) analysis which was not considered in this current research. Ezenwaji and Ezenweani (2019) demonstrated this in their spatial analysis of groundwater quality in Warri Urban, Nigeria, using physicochemical and microbiological parameters. However, our

thought now is that the study area may have huge microbial fauna making biodegradation very efficient (Luo et al. 2019; Conant et al. 2019; Barba et al. 2019; Spurr et al. 2019) or that the area has active aqui-filters (Gao et al. 2019). These may be the reasons why effects of agrochemicals (if they were used in significant quantity in farm practices) were completely buffered. Similarly, given the temperature range, the ionic concentrations indicate that no excessive effect of rock leaching/dissolution is imprinted in the chemistry and quality of the groundwater samples, as all the cations and anions attributable to geogenic origins are well below their respective standard limits of the NIS (2007) and WHO (2017). This further indicates that the stratigraphy of the area may be comprised of rocks essentially made of inert or non-dissolving minerals such that they only serve to

Fig. 4 Dendrogram classification produced by integration of the WQI and EWQI results



provide an efficient filter for the groundwater (Subba Rao 2018; Gao et al. 2019). This filtering mechanism is thought to be controlled by mineral-suction or redox processes.

Conclusions

The present study investigated the drinking water quality (with special emphasis on the chemical pollution) of Ikem rural agricultural area using integrated chemometric analyses and indexical methods. The results of the research suggest that the hand-dug wells are safe sources of rural water supply. Additionally, this study exposes a reserve of high-quality groundwater that could be of use to other areas with lower quality water supply. Moreover, this study has shown that the use of integrated chemometric and indexical methods is very useful for a better understanding of water quality issues. In order words, this study shows that the application of chemometrics and multiple indexical methods paves way for better and comprehensive water quality assessment. Based on the gross research findings, the following conclusions are drawn:

- Temperature of the natural waters was in the range of 10–31 °C.
- The pH of the samples indicated that they were slightly acidic, with the pH values ranging from 5.2 to 6.7 and an average value of 5.916.
- All the cations and anions (except for PO_4^{3-}) were within their respective standard limits. However, the order of dominance for the ions is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (for the cations) and $\text{Cl}^- > \text{PO}_4^{3-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ (for the anions).
- $\text{Cl}\text{-SO}_4\text{-Ca-Mg}$ and $\text{Cl}\text{-SO}_4\text{-Na-K}$ water types are the predominant hydrogeochemical facies of the groundwater samples.
- Except for Mn, the concentrations of the heavy metals were found below their maximum allowable limits.
- The factor analysis (FA) revealed that both geogenic processes and anthropogenic inputs determine the concentrations of the chemical ions and the heavy metals.
- The modified heavy metal index (MHMI), geoaccumulation index (I_{geo}), and overall index of pollution (OIP) revealed that all the hand-dug wells were in excellent condition, and hence safe for drinking purposes. However, the pollution load

index (PLI), water quality index (WQI), and entropy water quality index (EWQI) revealed that some wells (about 8–12%) were slightly contaminated, and hence are placed in good water category.

- The hierarchical cluster analysis (HCA) revealed two major quality categories of the samples. While the first cluster comprises of samples classified as excellent drinking water by both the WQI and EWQI models, the second cluster comprises of about 12% samples which were identified as good water by either the WQI or EWQI.

On a general note, this study provided a newer approach (i.e., the MHMI) for heavy metal pollution analysis and fostered the understanding of the efficacy relationships between the utilized models. The MHMI utilized in the current study can be applied globally for heavy metal assessment in water. Moreover, the analysis of the models used in this study provided more insights into their suitability for water quality assessment. Furthermore, the paper provided a basis for better use of water quality indices in future groundwater modeling, hinting on the application of integrated study approach that provides an unbiased water quality assessment in regions with plethora of contaminants/pollutants.

Limitation and recommendation

This paper did not consider the microbiological aspect of water quality assessment. Although the results of the study have provided evidences of slight and negligible levels of chemical pollution in the shallow hand-dug wells of Ikem area, an in-depth microbiological examination of these drinking water sources is necessary to help establish a more comprehensive understanding of the suitability of the hand-dug wells for drinking and domestic purposes. Regular monitoring and assessment of the water resources is recommended and well encouraged. Land use, lifestyle, and farming practices that would help preserve the quality of the groundwater should be adopted and encouraged. For the purposes of drinking desirability and storability (where necessary), efforts should be made to adjust the pH of the water.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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