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ORIGINAL ARTICLE

An integrated geochemical and spatiotemporal assessment of groundwater resources within an industrial suburb, Southeastern Nigeria

J. R. Okamkpa[1] · M. E. Omeka[2] · O. Igwe[3] · M. U. Iyioku[1]

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Abstract

The indiscriminate discharge of industrial effluents from beverage industries into nearby streams and lands within the Udi area of Enugu State has resulted in a decline in the drinking water quality. In this study, geochemical, indexical, statistical and spatiotemporal models were generated to assess the drinking water quality of the area. Seventeen borehole samples were randomly collected across the area and examined for 18 chemical parameters using standard methods. Results revealed that the groundwater is slightly acidic. Hydrochemical modeling identified Ca^{2+}–Mg^{2+}–Cl^{-}–SO_4^{2-} as the major hydrogeochemical facies and Ca^{2+}–Mg^{2+} and Cl^{-}–SO_4^{2-} as the dominant water type, implying that the water is permanently hard and unfit for laundry. The hydrochemical model, PHREEQC, was used in trace element species assessment. Results from the model revealed that trace elements were immobile under the prevailing pH conditions owing to the presence of limiting mineral phases (e.g. sulphates and carbonates). The pollution index of groundwater revealed that 29.5% of the water samples recorded high pollution, hence are unsuitable for drinking, while 17% recorded insignificant pollution and were adjudged fit for drinking. Similarly, water quality index and GIS-based spatiotemporal analysis revealed that 64.7% of boreholes around the northeastern, west-central and southern parts of the area are unsuitable for drinking, however, boreholes within the central parts are drinkable. The groundwater flow map showed that groundwater flow in the area is predominantly from the northeastern to the southwestern direction. Hence, untreated wastewater and industrial effluents disposal sites should be restricted to the southern parts of the study area.

Keywords Groundwater pollution · Chemical speciation · Water quality index · Hydrogeochemistry

Introduction

Recently, research has shown that there is a growing global scarcity of good quality water for human consumption, agriculture and industry. This problem is further compounded in developing countries due to underdevelopment, poor and/or inadequacy of effective water management and conservation measures, pollution and over-exploitation of the water systems. Nigeria boasts of the highest human population among the black African nations, with an estimated population of one-hundred and ninety-nine million (Ighalo et al., 2020). However, among this population, a staggering number of people accounting for about 66.3 million do not have access to quality and safe drinking water sources (Ighalo et al., 2020). Recently, there is an increasing demand for the exploitation of groundwater resources. This is due to its high relative abundance in the hydrological cycle and reduced risks of exposure to contamination compared to the surface

✉ J. R. Okamkpa
jokamkpa@gouni.edu.ng

M. E. Omeka
omeka.ekuru@unical.edu.ng

O. Igwe
ogbonnaya.igwe@unn.edu.ng

M. U. Iyioku
miyioku@gouni.edu.ng

1 Department of Geology, Faculty of Physical Sciences, Godfrey Okoye University, Ugwuomu, Enugu State, Nigeria

2 Department of Geology, University of Calabar, P.M.B. 1115, Calabar, Cross River State, Nigeria

3 Department of Geology, Faculty of Physical Sciences, University of Nigeria, Nsukka, Nigeria

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water bodies (Egbueri et al., 2021). Contrary to this belief, findings have shown that, like surface water, groundwater is not safe from contamination (Egbueri et al., 2021; Igwe & Omeka, 2021; Nganje et al., 2019; Wagh et al., 2018). This has been majorly attributed to anthropogenic controls such as increasing population, poor waste management, agriculture, mining and industrialization (Abbasnia et al., 2018; Egbueri et al., 2021; Igwe & Omeka, 2021; Nganje et al., 2019; Wagh et al., 2018).

In reality, the quality of groundwater is dependent on its chemical, biological and physical characteristics. These processes may be influenced by both anthropogenic and geogenic (natural) factors. Natural factors may be attributed to the hydrogeochemical characteristics of the groundwater system, the rock-water interaction within the aquifer, the topography, regional rainfall intensity and the hydrodynamic characteristics of the groundwater system (Barzegar et al., 2018; Egbueri et al., 2021; Igwe & Omeka, 2021). Anthropogenic factors include influx from human-induced activities such as poor waste disposal practices, urbanization, mining, industrialization, etc. that tend to have a direct bearing on the modification of the natural hydrogeochemical mechanism through pollutant influx (Gao et al., 2020; Xiao et al., 2021). Therefore, the quality of drinking water may be marred by these factors and may exact a negative effect on public health directly through the ingestion and dermal contact from contaminated water resources (Egbueri et al., 2021; US-EPA, 2017). Hence, understanding the various geochemical processes and mechanisms within the aquifer as well as the pollution status of groundwater will serve as a tool towards adequate groundwater resource management, protection and sustainability (Egbueri et al., 2020a, 2021; Xiao et al., 2021). To this end, regular monitoring and assessment of groundwater resources in pollution-prone areas become very important. Keeping this in perspective, several legislative groundwater quality guidelines have been set up globally to serve as the benchmark for the assessment of groundwater quality (SON, 2015; WHO, 2017). Additionally, several researchers have employed conventional scientific techniques in an attempt to monitor and assess the quality of water resources (Adamu et al., 2014, 2015; Aghazadeh et al., 2017). These techniques include a range of single methodological approaches such as pollution load index (PLI), groundwater water quality index (WQI), geo-accumulation index (I-geo), heavy metal evaluation indices (HEI), pollution index of groundwater (PIG), the overall index of pollution (OIP), degree of contamination (Cdeg) and contamination factor (CF) in water quality assessment/monitoring (Edet & Offiong, 2002; Mohebbi et al., 2013; Rahman et al., 2017). Each of these models has its advantages and disadvantages; a particular model may identify a water source as fit for drinking; however, the other one may not agree. The major drawback to the use of the single indexical models is in their failure to provide comprehensive and holistic information required for decision making (Egbueri et al., 2020a, 2020b, 2021; Nnorom et al., 2019; Omeka & Igwe, 2021; Singh et al., 2019), as the overall impact of the water quality on the human health and other uses cannot be adequately ascertained. Information on the geochemical behviour of contaminanted water in the groundwater system in terms of fate, bioavailability and mobility cannot be evaluated with the use of a single conventional approach. Therefore, it is thought that the integrated multiple indexical approaches will provide an equitable and unbiased evaluation of the overall water quality in a particular studied system. Hence, in the present study, an integrated based assessment of the impact of potentially toxic elements on the groundwater quality within the area was carried out using several numerical water quality indices such as the water quality index (WQI), pollution index of groundwater (PIG), modified heavy metal index (MHMI) and heavy metal pollution index (HPI). Further, the hydrogeochemical dynamics of the aquifer system have also been analysed using stoichiometric models such as piper plots. The Ajali river may act as a potential source of recharge to the groundwater aquifer system, therefore knowing the pollution status will provide precautionary measures for water consumers in the area before government intervention. Moreover, due to the highly complex geochemical processes that occur within the aquifer system, this study needed to carry out a chemical speciation assessment of the analysed trace elements within the groundwater system using the computer simulation geochemical model, PHREEQC. Knowing the level and type of species of these elements will provide information on the geochemical behaviour of elements in the water in terms of their fate, bioavailability and mobility within the aquifer system and will serve as an indirect measure of their potential human and environmental toxicity (Edet et al., 2004; Ekwere & Edet, 2012). The presence of limiting mineral phases such as sulphates and carbonates in water can influence the bioavailability and mobility of trace elements in water (Edet et al., 2004). Hence, trace element speciation analysis was considered integral in this study. Additionally, GIS-based spatiotemporal models have also been employed to ascertain the possible flow paths of pollutants in the area. Further, multivariate statistical tools such as hierarchical cluster analysis (HCA) and correlation analysis (CA) have also been employed to identify the likely sources of contaminants and attempt a genetic classification of the different contaminants. Multivariate statistical models are considered very efficient as they are capable of detecting the relationships between various water parameters, hence providing adequate information on the water quality and the likely contamination sources (Nnorom et al., 2019; Singh et al., 2019). It is thought that knowledge of the pollution source will serve as a basis for pollution control and mitigation.

The present study is focused on Udi industrial area and its environs. The inhabitants of the area are majorly reliant on boreholes and hand-dug wells for drinking, domestic, agricultural and industrial activities. The area can be described as a semi-urban area characterized by commercial, agricultural and industrial activities. Additionally, the area is undergoing rapid human and socio-economic development. This has further generated a lot of stress on the available groundwater sources within the area. It is, therefore, thought that the poor management of waste effluents will have a devastating impact on the groundwater quality. The major industrial activities in the area include beverage and brewing industries. The beverage industries are located around 9th Mile Corner Ngwo. The unregulated discharge of industrial wastewater by these industries onto lands and surrounding surface water bodies such as the Ajali river within the area has marred the quality and quantity of water resources within the area; some of these effluents are transported into nearby streams as a run-off and eventually make their way into the groundwater aquifer by way of recharge. Some studies have been carried out in the study area on the physicochemical and microbial characteristics of surface water bodies from brewery effluents (Egwuonwu et al., 2012; Ogbu et al., 2016). Reports by Egwuonwu et al. (2012) concluded that the analysed physicochemical parameters of water from the Ajali river were within the required standard. However, reports by Ogbu et al. (2016) suggest that the surface water resources are slightly polluted and unsuitable for consumption. Recently, Abugu et al. (2021) carried out a hydrochemical evaluation of the Ajali river for its suitability for irrigation purposes using several numerical irrigation indices such as Permeability index, Soluble sodium percent, Kelly ratio, Sodium adsorption ratio, Magnesium adsorption ratio and Chloro-alkaline index. Results from their study showed that albeit some samples recorded higher values of carbonates above the FAO/UN (2017) required standards, the water samples are generally suitable for irrigation purposes. Although the impact of industrial activities on the quality of surface water bodies has been considered by these researchers, there seems to be no literature available regarding the impact of industrial effluents on groundwater quality.

Hence, this study aims to access the impact of industrially derived effluents on the quality of groundwater resources within Udi and its environs. The specific objectives include the following: (1) evaluating the pollution status of groundwater from toxic elements using the integrated HPI-MHMI indexical study approaches; (2) assessing the suitability of groundwater, for drinking and domestic purposes using the integrated WQI-PIG study approaches; (3) assessing the hydraulic characteristics of the aquifer system and flow paths of contaminants using GIS-based spatiotemporal models; (4) and to attempt a genetic identification and classification of possible contaminants' sources using multivariate statistical models. It is expected that the finding from this pilot study will serve as a baseline database of the quality of groundwater within the area for future planning, monitoring and management of water resources in the area, for public health sustainability and protection.

Study area description

The present study was carried out within Udi and Ezeagu Enugu State. The area can be described as a suburban district, located about 10 km southeast of the Enugu mega-city, southeastern Nigeria. The area lies between longitude 7°0.9' and 7°0.28' E and latitudes 6° 0.12' and 6°0.41' N. It is bounded to the north by Igbo-Etiti, L.G.A, to the south by Oji river L.G.A, to the east by Enugu L.G.A and to the West by Ezeagu L.G.A. (Fig. 1). Demographically, it spans over an area of about 897km^2, with a population of about 234,002 (Abugu et al., 2021). The area occurs within the tropical rainforest with vegetation and climate that is characteristic of the equatorial region. The area is predominated by two distinct kinds of weather: the rainy season spans from March to October with a mean annual rainfall ranging from 1750 to 2000 mm (Abugu et al., 2021) and the dry season spans from November to February characterized by dry dusty winds. Three beverage companies (Coca-Cola bottling company, Nigeria breweries, and Seven-Up bottling company) are located within the Udi axis. The effluents from these industries are being indiscriminately channeled into nearby streams such as the Ajali river, Ekulu and Nvene river. These rivers are structurally controlled occurring in a dendritic drainage pattern (Fig. 1). The Ajali River is underlain by Ajali and Nsukka Formations at upland and Mamu Formations in the lowlands (Nwajide, 2013; Reyment, 1965). The Ajali sandstone is predominantly characterized by thick friable, highly permeable, highly porous, poorly sorted arkosic sandstones. The major lithostratigraphic units of the Nsukka formation include sandy shale and siltstones with shale intercalations and thin coal seams (Nwajide, 2013). Due to the porous and highly permeable nature of the underlying Ajali sands, they can easily be washed off during intensive rainfall activities (Abugu et al., 2021). It is thought that the highly porous and permeable sandstone units may act as a conduit for the movement of contaminants into the surrounding groundwater aquifer system. Further, soils around the area are predominantly sandy, with occasional occurrence of silt/clay fractions along with the matrixes (Nweke, 2015). The poorly disposed of effluents on the soil can sorb onto the soil surfaces and act as a temporary repository of toxic elements, which during rainfall activities can leach and infiltrate into the groundwater

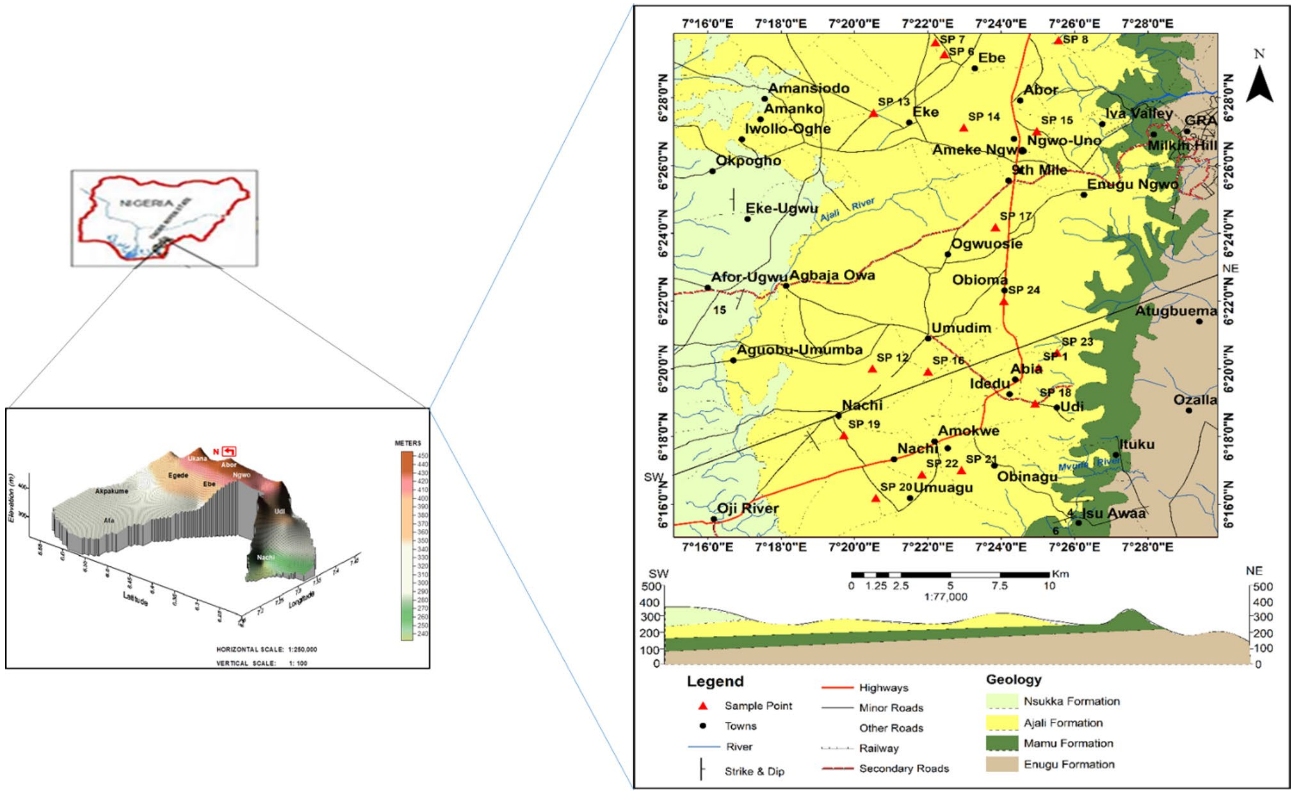


Fig. 1 Location, digital elevation model, and Geologic map of the study area

system thereby exposing the groundwater to the risk of contamination. Moreover, both surface and groundwater from this area are being used by the inhabitants for domestic, drinking and irrigation purposes. Therefore, it is pertinent to carry out a comprehensive assessment of the groundwater resources in the area for health and environmental safety and sustainability.

The major hydrogeologic units within the area include confined, semi-confined, unconfined and perched aquifers. Confined conditions exist over Ajalli sandstones in areas overlain by the Nsukka Formation and Mamu Formation, where overlying Ajali sandstone are considerably reduced in thickness or eroded. Semi-confined conditions occur in a few places and are made up of an interbedded thick sequence of sand and sandy clay or clayey sand aquicludes. Various aquifers in this group occur in the upper to middle horizons of Ajali Sandstone and in the Upper section of Mamu Formation which constitutes the partial recharging zones, for the deeper-seated confined aquifer. (Nwajide, 2013; Nweke, 2015). Unconfined aquifer units occur mostly in the Ajali sandstone and where semi-permeable or impermeable cap beds have either been eroded and/or are absent. Perched Aquifer conditions occur mostly in the Lateritic or red earth cover over the Nsukka Formation and the Upper sandy units of the Formations. It is thought that the unconfined aquifer units may be exposed to contamination from the effluent-derived River Ajali.

An observation of Fig. 1 reveals that the area is characterized by two major topographic landforms as follows: valleys and lowlands areas and high relief zones characterized by undulating residual hills. The residual hills are thought to be the remnants of Udi hills around the southern part of the study area. The lowlands are concentrated around the central parts of the area around 9th Mile Ngwo. The central part of the area is considered the most prolific aquifer in the southeastern zone and serves as a major source of drinking water for the inhabitants. A lot of boreholes are being concentrated within the central part of the area and these boreholes may be exposed to an influx of contaminants from industrial sludge and human waste materials. Moreover, geophysical studies of static water level within areas underlain by Ajali/Nsukka Formations revealed that the depth to water table ranged from 30.8 m (around Eke areas) to 189 m (within Egede) (Ezeh et al., 2013). At this depth, the groundwater aquifer system may be vulnerable to the influx of contaminants washed off from nearby contaminated industrial and agricultural lands.

Materials and methods

Groundwater sample collection and analysis

A total of 17 groundwater samples, comprising two samples from each point, were collected towards the end of the rainy season (September–October 2019). Samples were collected using a 2-L polythene container. The container was sterilized by thoroughly washing and rinsing with dilute 1:1 HCL and thereafter rinsed using distilled water). At each sampling station, the polythene bottles were thoroughly rinsed with the source water. A drop (0.5ML) of concentrated nitric acid was added to one portion of the sample to preserve it to prevent microbial degradation, adsorption to the container wall and cation precipitation. Physicochemical parameters such as temperature, TDS, pH and EC were determined in the field using the calibrated temperature/TDS meter (model TDS-3), pH meter (Hanna model HI-8733) and conductivity meter, respectively. Ice crested coolers (at a temperature of < 4 °C) were used in preserving the water samples in the field before laboratory analysis. In the laboratory, both the physicochemical and heavy metal analyses were carried out. Physicochemical analysis was integral in the measurement of major cations and anions. Anions (e.g. Cl and HCO_3) were measured using the complexometric titration method, using EDTA solution as a chelating agent following the standard procedure described by Tucker and Kurtz (1961); the Hach DR/2000 spectrophotometry was used in SO_4 analysis. The Gallenkamp flame analyser (at 33 °C) was used to measure major cations such as Ca^{2+}, and Mg^{2+}. The PerkinElmer Analyst 200 atomic absorption spectrophotometer (AAS) was used in the analysis of selected heavy metals (As, Cu, Fe, Mn, Zn and Cr) following the procedure as described by Moran et al. (1994). All analytical procedures were in line with the American Public Health Association's (APHA, 2005, 2017) recommended standards.

Chemical speciation analysis

The geochemical behaviour of elements in water (in terms of solubility, mobility, precipitation, bioavailability and adsorption/desorption behaviour) can be influenced by the different species in which they exist. The species in which a particularly toxic element exists in water has a direct bearing on the water chemistry and consequently on human health (Nganje et al., 2019). According to the Toxic Substances Disease and Registry (ASTDR, 2018), mineral phases and species of elements such as Pb, Cd, As and Cr are ranked among the most toxic elements on the toxicological profile. Hence, this study needed to carry out a comprehensive speciation analysis of analysed elements to determine their overall influence on the groundwater chemistry and potential impact on human health (Edet & Offiong, 2004; Ekwere & Edet, 2012). The analysis was carried out using a computer simulating program PHREEQC interactive (ver. 3.7) using the Specific Ion Interaction Theory (SIT) aqueous model.

Environmental pollution assessment

Heavy metal pollution index

The combined impacts of each heavy metal on the drinking water quality can be quantitatively assessed using the HPI. The HPI has been widely used by many researchers (e.g. Brown et al., 1970; Edet & Offiong, 2002; Egbueri, 2018, 2020; Herojeet et al., 2015; Odukoya & Abimbola, 2010; Wagh et al., 2018) to evaluate the general drinking water quality from the concentration of heavy metals. In this study, the SON (2015) standard for drinking water quality was utilized as a background standard for the assessment of heavy metal indices in the analysed water samples. Six selected trace elements (As, Cu, Fe, Mn, Zn, Cr) were considered for the assessment following the relation given in Eq. (1):

$$HPI = \frac{\mathrm{HMC}}{\mathrm{AL}}/n, \tag{1}$$

where HMC is the concentration of heavy metal in each water sample; n refers to the total number of analysed trace metal elements; AL is the SON (2015) allowable limit.

Modified heavy metal index

The heavy metal index (HMI) was proposed by Dash et al. (2019) for the assessment of the impact of heavy metals on the ecosystem by assigning weights to heavy metal parameters from the results of cluster groupings and eigenvalues from the principal component analysis. However, the model was modified by Egbueri et al. (2020b) by assigning different weights on a scale of 1–5 to various heavy metal parameters based on the impact of each water quality parameter on the overall water quality evaluation, including agriculture and human health. In the present study, different weights (ranging from 1 to 5) were assigned for each metal based on their impact on drinking water quality. The relative weights of each parameter were then obtained based on the relationship described in Eq. (2). Finally, the heavy metal index (modified heavy metal index) values for each analysed sample were determined using the following relation described in Eq. (3):

$$RW = \frac{wi}{\sum_{i=1}^{n} wi} \quad (2)$$

$$MHMI = \sum_{i=1}^{n} [Rw * Mi/Si], \quad (3)$$

where R_w refers to the relative weight; w_i represents the assigned weight of each parameter; n represents the number of analysed heavy metal parameters; M_i refers to the value of the analyzed heavy metal concentration in each groundwater sample; S_i represents the SON (2015) allowable limit for the given heavy metal.

Drinking water quality assessment

Pollution index of groundwater

The PIG was also integrated into this study to assess the drinking water quality based on input from different pollution sources. PIG is an important water quality index that has been used in several studies to show the variation in the quality of groundwater as a result of anthropogenic and geogenic inputs (Egbueri, 2020; Subba Rao, 2012; Subba Rao et al., 2019). As proposed by Subba Rao (2012), the model evaluates the relative level of the impacts a particular chemical parameter exerts on the drinking water quality of groundwater. The model uses a combination of both physicochemical and trace element parameters in its computation. To achieve this, the relative weight (*Rw*) ranging from 1 to 5 is being assigned for each quality parameter according to their relative impact on the human health system (Table 1). The weight parameter (*Wp*) was then derived for each analysd parameter to determine their relative impact on the general drinking water quality as shown in Eq. (4). Thereafter, the concentration status (*Sc*) of each sample was computed; this was done by dividing each parameter in the water sample by the given drinking water quality standard allowable limit (Eq. 5). In the present study, the WHO standard limit was considered. Then, the overall drinking water quality (O_w) was computed following the relation expressed in Eq. (6). Last, the PIG values (pollution status) for each water sample were derived by taking a sum of all O_w values (Eq. 7)

$$W_p = \frac{Rw}{\sum Rw} \quad (4)$$

$$S_c = \frac{C}{Ds} \quad (5)$$

$$O_w = W_p \times S_c \quad (6)$$

$$PIG = \sum O_W \quad (7)$$

Following the PIG classification criteria (Subba Rao, 2012), PIG < 1.0 indicates negligible pollution level, PIG between 1.0 to 1.5 indicates low pollution, PIG between 1.5 and 2.0 depicts moderate or mild pollution level, PIG between 2.0 to 2.5 implies high pollution, while PIG > 2.5 is an indication of very high pollution level.

Table 1 Weights used in WQI and PIG assessment

Parameter	Parameter weight (wi)	Unit	Relative weight (Wi)	SON (2015)
pH	3	–	0.078947368	6.5
Mg	3	mg/L	0.078947368	200
Ca	2	mg/L	0.052631579	200
SO_4	3	mg/L	0.078947368	100
Cl	4	mg/L	0.105263158	250
HCO_3	1	mg/L	0.026315789	250
As	5	mg/L	0.131578947	0.003
Cu	4	mg/L	0.105263158	0.01
Fe	4	mg/L	0.105263158	0.3
Mn	3	mg/L	0.078947368	0.2
Zn	3	mg/L	0.078947368	3
Cr	3	mg/L	0.078947368	0.02
	∑wi = 38		∑Wi = 1.0	

Water quality index

A comprehensive summary assessment of the drinking water quality level of groundwater samples can be obtained using the WQI (Igwe & Omeka, 2021; Mgbenu & Egbueri, 2019). To achieve this, different weights (*wi*) ranging from 1 to 5 are being assigned to the different water quality variables based on their relative concentration and importance on the drinking water quality; the relative weights (*Wi*) of each parameter is then obtained (Eq. 8, Table 1) (Egbueri, 2020; Egbueri et al., 2019).

$$Wi = \frac{wi}{\sum_{i=1}^{n} (wi)}, \quad (8)$$

where n = total number of parameters.

The quality rating scale for each parameter (qi) was then computed using the relation in Eq. (9):

$$qi = (Ci/Si) \times 100, \quad (9)$$

where Ci = the concentration of each parameter in water; Si = WHO (2017) allowable limit.

The sub-index of the ith parameter, (*SI*), was thereafter computed using Eq. (10). The final WQI was then estimated using the relation expressed in Eq. (11) as follows:

$$SI = Wi \times qi \tag{10}$$

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

GIS-based spatiotemporal analysis

The GIS-based geospatial analysis was carried out to determine the groundwater flow direction and delineate zones with unsuitable drinking water quality in the area. knowing the direction of groundwater flow would provide adequate knowledge on the flow of contaminants as well as avail water resource managers with the necessary information on the best locations to cite or drill boreholes. The input parameter used for drinking water quality zonation was obtained from the calculated WQI values, while those for groundwater flow direction analysis were derived from hydraulic head values. The hydraulic head values were obtained following the relation expressed in Eq. (12):

$$H = GSE - SWL, \tag{12}$$

where H is the hydraulic head layer; GSE is the ground surface elevation values expressed in meters, SWL is the static water level expressed in meters (S1).

The inverse distance weighting (IDW) interpolation method was used in both analyses using ArcGIS (ver. 10.4.1). IDW is a deterministic linear statistical method that determines cell values from a combination of a linearly weighted sets of sample points (Philips & Watson, 1982). The groundwater quality zonation assessment was carried out from the surface interpolation of WQI values for each sample point. The derived WQI map was then delineated into different zones such as suitable, moderate and unsuitable (Igwe & Omeka, 2021).

Multivariate statistical analysis

In the present investigation, Pearson's correlation coefficient was employed to determine the major factors that modify the groundwater chemistry as a function of their origin. The Pearson's correlation coefficient was able to determine the strength between the different groundwater quality parameters by predicting the linearity as well as the associations between them. With this information, the source of the different chemical elements can easily be apportioned based on their associations (Igwe & Omeka, 2021). A significant level between the analytes was established at 0.05 using a 2-tailed correlation coefficient (Mustapha, 2012). Correlation coefficients of $p > 0.5$ were considered significant, while those at $p < 0.5$ were considered insignificant. To validate the results from the various assessment models and show the relationship between them, the hierarchical cluster analysis (HCA) and Spearman's correlation coefficient were integrated. All analysis was carried out using the IBM SPSS statistical package (v. 25.0).

Results and discussion

Overview of the general groundwater quality

The univariate descriptive statistical results of analysed groundwater quality parameters are presented in Table 2. The obtained results were compared with the World Health Organization (WHO, 2017) and Standard Organization of Nigeria (SON, 2015) required standards for drinking water. The groundwater pH ranged from 4.1 to 7.2 with a recorded mean of 6.2 describing the water as acidic to slightly acidic, with a few samples recording neutral to alkaline pH. Generally, the physical and major ion concentration of analysed groundwater samples was observed to be within required standards. The low pH observed among the water samples can be attributed to rock–water interaction and inputs from anthropogenic influx such as effluents from human and industrial wastes. Moreover, the geology of the area is dominated by thick friable, poorly sorted arkosic sandstones with intercalations of sandy shale and siltstones units. The low pH of the water is thought to be from the breakdown and mineral dissolution of sandstone and shales giving rise to the release of orthosilicic acid (H_4SiO_4) (Nganje et al., 2019). Also, sampling was carried out during the rainy season, accompanied by high vegetation cover. The acidity of the water may have also been influenced by the rotting of vegetation cover (Nganje et al., 2019). Ingestion of acidic water has been reported to result in gastrointestinal disorder and mucous membrane deterioration in humans (Gaikwad et al., 2019).

A total of six selected trace elements (Fe, As, Cu, Cr, Zn, Mn) were analysed to determine their pollution levels in groundwater. According to their mean concentration, the order of dominance was Zn > Mn > Cu > Cr > As > Fe. Generally, all analysed trace elements except for Fe and Zn recorded values above the WHO (2017) and SON (2015) maximum required limits. The concentration Cu varied between 0.01 mg/L and 0.76 mg/L with a mean concentration of 0.18 mg/L. Naturally, the concentration of Cu in water occurs from the dissolution of sulphide minerals such as chalcopyrite ($CuFeS_2$) (Obasi & Akudinobi, 2020) from the underlying rock or soil. Cu is known to have low mobility potential; hence its concentration is expected to be very low (Egbueri et al., 2021). However, the recorded high concentration above the required standard can be attributed to anthropogenic sources such as leaching of municipal waste materials, industrial chemical effluents and car batteries

Table 2 Univariate descriptive statistical results of analysed groundwater quality parameters

Sample ID	Location	pH	Na (Mg/L)	K (Mg/L)	Ca (Mg/L)	Mg (Mg/L)	HCO_3 (Mg/L)	Fe (Mg/L)	Mn (Mg/L)	Cl (Mg/L)	SO_4 (Mg/L)	NO_3^- (Mg/L)	TDS (Mg/L)	TSS (Mg/L)	TS (Mg/L)	EC (µs/cm)	Turbidity (NT)	As (Mg/L)	Cu (Mg/L)	Cr (Mg/L)	Zn (Mg/L)
GWs 1	Abia	5.4	0.4	0.2	3.2	0.3	9	0.08	0.76	33.5	14.38	0.65	6.72	0.1	27.8	12	152	0.03	0.06	0.02	0.01
GWs 2	Abor	6.9	0.02	0.03	6.9	0.01	13.6	0.04	0.65	8.7	25.3	1.2	69.2	2.3	245	41.3	3.7	0.54	0.76	0.09	0.008
GWs 3	Awhum	6.9	0.04	0.02	12.3	0.04	10.6	0.03	0.005	11.6	32	0.7	120	3.01	23.5	54.1	3.5	0.002	0.07	0.003	0.43
GWs 4	Afah	7.2	0.02	0.01	7.6	0.03	12.6	0.04	0.65	9.6	16.7	0.4	76.8	2.01	29	44.1	3.6	0.003	0.02	0.007	1.76
GWs 5	Akpa-kwume	6.2	0.4	0.03	17.2	0.6	45	0.08	0.78	57.5	22.04	0.98	22.4	0.06	–	40	2	0.04	0.01	0.12	2.87
GWs 6	Ameke	7.1	0.02	0.02	7.4	0.03	9.4	0.06	0.067	7.3	26.2	0.7	53.7	3.02	27.4	39.4	2.4	0.07	0.01	0.07	3.09
GWs 7	Amofi-aAfa	5.1	0.03	0.02	5.9	0.01	11	0.02	0.43	7.4	12.4	0.2	45.9	1.54	7.28	42	2.3	0.001	0.41	0.21	0.34
GWs 8	Amokwe	4.1	0.2	0.01	16.2	0.3	5.16	0.1	0.002	0.76	8.31	0.32	32.9	3.31	18.3	92.4	2.6	0.006	0.03	0.67	7.02
GWs 9	Ebe	5.6	7.2	4.3	53.8	12.7	0.3	0.24	0.24	96.8	75.04	1.2	379	47.2	245	92.4	2.6	0.12	0.02	0.174	6.02
GWs 10	Egede	6.2	0.3	0.2	3.6	0.3	10	0.08	0.32	42.5	4.941	5.43	3.92	0.02	3.94	7	0	0.21	0.65	0.65	0.87
GWs 11	Eke	6.9	3.2	2.1	15.1	4	6.32	0.2	0.54	0.97	7.22	0.87	30.8	4.73	27.8	89.6	2.3	0.08	0.08	0.008	2.4
GWs 12	Nachi	6.7	1.7	1.2	0.07	1.9	12.3	0.2	0.2	12.87	4.03	1.2	9.43	47.2	245	198	1.2	0.11	0.05	0.02	3.12
GWs 13	9th Mile	7.2	0.5	0.3	12.3	0.7	12	0.02	0.01	0.89	12.34	0.45	24.2	2.3	23.5	98.5	2.01	0.1	0.09	0.03	0.07
GWs 14	Ngwo	5.6	0.01	0.03	8	0.02	12	0.03	0.05	10.2	29	0.9	60	2.31	29	50.3	3.3	0.001	0.03	0.001	1.21
GWs 15	Nsude	6.9	0.02	0.01	5.9	0.02	10.6	0.03	0.12	6.9	23.8	1	59	4	0	40.5	3.2	0.03	0.21	0.12	0.02
GWs 16	Obinagu	6	3.2	5.2	37.6	12	98	0.15	0.007	23.9	66.82	0.15	27.4	0.08	27.52	49	8	0.002	0.4	0.21	0.02
GWs 17	Obioma	6.1	0.4	0.3	10	0.6	27	0.08	0.21	49.9	32.1	0.15	7.28	0.08	7.36	13	8	0.02	0.1	0.09	0.04
MIN		4.1	0.01	0.01	0.07	0.01	0.3	0.02	0.002	0.76	4.03	0.15	3.92	0.02	0	7	0	0.001	0.01	0.001	0.008
MAX		7.2	7.2	5.2	53.8	12.7	98	0.24	0.78	96.8	75.04	5.43	379	47.2	245	198	152	0.54	0.76	0.67	7.02
SD		0.89	1.90	1.59	13.59	4.16	22.86	0.069	0.29	26.05	19.88	1.23	87.53	15.14	91.49	45.57	36.18	0.16	0.29	0.29	2.16
MEAN		6.26	1.04	0.83	13.22	1.98	17.94	0.088	0.29	22.46	24.28	0.98	60.52	7.26	61.72	59.04	11.93	0.09	0.18	0.15	1.73
WHO (2017)		6.5–8.5	200	12	75	50	600	0.3	0.2	250	250	50	600–1000	1000	–	1000	–	0.01	0.05	0.02	3
SON (2015)		7.0	200	–	–	–	250	0.3	0.2	250	100	50	1000	1000	–	1000	–	0.01	0.05	0.02	3

WHO (2017) = World Health Organization; SON (2015) = Standards Organization of Nigeria

(Onyemesili et al., 2020; US-EPA, 2017; Wagh et al., 2018). The indiscriminate disposal of these waste materials is a common practice in the study area. The ingestion of Cu in excess by humans has been known to be responsible for chronic illnesses such as liver damage (Wagh et al., 2018). Nausea, vomiting and diarrhea have also been reported from the excessive ingestion of Cu in drinking water (US-EPA, 2017; WHO, 2017). The concentration of As and Cr ranged from 0.001 mg/L to 0.54 mg/L and 0.001 mg/L to 0.67 mg/L with an average concentration of 0.09 mg/L and 0.15 mg/L respectively. According to the Toxic Substances Disease and Registry (ASTDR 2018), As and Cr are ranked among the most toxic elements on the toxicological profile. Cr in the analysed water samples (Table 3) was observed to be in the form of chromium (III) (Cr^{3+}), although other forms such as Chromium (VI) are known to exist under different environmental conditions. Kimbrough et al. (1999) noted that the reduction of chromium (VI) to chromium (III) is highly favorable under acidic conditions. The low pH values observed among the water samples in the present study validate this assertion. Chromium (VI) is considered to be the most toxic species of Chromium, compared to Chromium (III). Corrosion of metallic storage facilities and allergic reactions (irritation of the nose lining resulting in nose ulcer) are some of the recorded devastating effects associated with Chromium (VI) (Kimbrough et al., 1999; Obasi & Akudinobi, 2020). Chronic cardiovascular, respiratory, gastrointestinal and neurological conditions have also been reported (Engwa et al., 2018). The geology of the area is composed of sandy shales and siltstones units, this can serve as a natural source of chromium in the area (Obasi & Akudinobi, 2020). Moreover, in the study area, metallic storage facilities are used for the storage and distribution of municipal water, this could constitute an anthropogenic source of Cr contamination in the water. According to WHO (2011), groundwater underlain by sedimentary rocks (e.g. shales) can be significantly enriched in Arsenic (As) in concentration up to 12 mg/L. This is because As is a chalcophile element (i.e. it has the propensity or affinity to bond with sulfur to form highly insoluble sulphides). The geology of the study area is composed of sandy shales and siltstones units. The shales are highly enriched with sulphide minerals which may occur in association with potentially toxic elements such as As as a result of similarity in their geochemical behaviour (Nganje et al., 2019). Anthropogenic sources of As in the area are attributed to indiscriminate disposal of industrial effluents and agricultural activities such as the use of phosphatic fertilizer which consequently drains their residues or percolates into the groundwater system. The major source of phosphatic fertilizers is from phosphorus-rich rocks enriched in apatite naturally enriched in transition metals (e.g. Cu, Ni, Zn) in trace amounts; Fe and Mn (as major elements) and metalloids (e.g. As) in trace quantity (Boumaza et al., 2021). Among the analysed elements, Zn records the highest concentration among the groundwater samples with concentrations varying between 0.008 mg/L and 7.02 mg/L and a mean concentration of 1.73 mg/L. Zn is highly chalcophile (i.e. it exhibits a high affinity to sulphide minerals) (Mason & Moore, 1982; Nganje et al., 2020). Shales makes up the major lithostratigraphic unit of the area and sulphide-rich ores mineral such as sphalerite (ZnS) is known to be the major mineralogical constituent of shales (Igwe & Omeka, 2021; Nganje et al., 2020). Additionally, the high concentration of Zn among the water samples can be attributed to its low mobility potential in water; Zn solubility increases with a decrease in water pH (Gundersen & Steinnes, 2003). Zn concentration from the analysed water samples recorded values within the recommended standards. Human toxicity from ingestion of Zn in water occurs at a concentration of 3 mg/L. Consumption of Zn in excess has been attributed to muscular pains and stiffness, nausea and loss of appetite (WHO, 2011, 2017). Fe appears to have the least concentration among the groundwater samples with a concentration ranging from 0.02 mg/L to 0.78 mg/L with an average concentration of 0.008 mg/L. All samples recorded values below the WHO (2017) and SON (2015) maximum admissible limits for drinking water quality. Fe concentration in groundwater occurs from the weathering of iron-rich rocks. The low concentration of Fe among the water samples can be attributed to the low occurrence of Fe-bearing formations from the geology of the area. Nevertheless, anthropogenic sources of Fe could be from discharge from industrial effluents and solid wastes in the area, and the unregulated mining of the ferruginous lateritic soil, as well as dissolution

Table 3 Major species distribution of toxic elements in water

PTE	Major Component	Percentage concentration (%)	Other identified chemical species
Mn	Mn^{2+}	67.29	$MnSO_4$, $Mn[HCO_3]^+$, $Mn[NO_3]^+$
Fe	Fe^{2+}	63.42	$FeSO_4$, $Fe[HCO_3]^+$, $Fe[Cl]^+$, $Fe[Cl_2]$
Cr	Cr^{3+}	85.87	$Cr[Cl]^{2+}$, $[CrCl_2]^+$
Zn	Zn^{2+}	87.96	$ZnSO_4$, $Zn[Cl]^+$, $ZnCl_2$, $Zn[Cl_3]^-$, $Zn[Cl_4]^{2-}$
As	AsO_4^-	73.52	$As(OH)^{4-}$
Cu	Cu^+	77.96	$Cu[Cl_2]^-$, $Cu[Cl_3]^{2-}$, $CuFeO_2$

of metallic water storage facilities. Fe when found elevated concentration has been known to cause "red-hot diseases" in humans (Egbueri et al., 2021; Onyemesili et al., 2020).

Chemical speciation analysis

Metals exist in different species in water and this has a direct bearing on the geochemical behaviour of elements in the water regarding their solubility, mobility, precipitation, bioavailability and adsorption/desorption. Results of the predicted major chemical (aqueous) species identified from the PHREEQC model are presented in Table 3. Among the identified mineral phases, the major species identified include Zn^{2+} (87.96%), Mn^{2+} (67.29%), Cu^{+} (77.96%), Cr^{3+} (85.87%), $H_2AsO_4^{-}$ (73.52%) and Fe^{2+} (63.42%). The implication of this is that the groundwater conditions are majorly influenced by the solubility of these components in water. Zn occurred in several aqueous species such as Zn^{2+}(aq), $ZnSO_4$(aq), $ZnCl^{+}$(aq), $ZnCl_2$(aq), $ZnCl_3^{-}$(aq), $ZnCl_4^{2-}$(aq). However, Zn^{2+}(aq) (67.96%) made up the major chemical species, occurring as free ion. As reported by WHO (2011; 2017) human toxicity from Zn ingestion in water occurs at a concentration of 3 mg/L. Under the prevailing pH conditions, Zn^{2+} is said to be immobile: however, its immobility is further enhanced by precipitation as Zn sulphate ($ZnSO_4$) (Gundersen & Steinnes, 2003). Mn existed in different species such as Mn^{2+}, $MnSO_4$, $Mn(HCO_3)^{+}$ and $Mn(NO_3)_{2(aq)}$, with the dominant species being the ionic Mn^{2+} (67.29%). Based on the prevailing pH condition, Mn^{2+} is said to be immobile. Moreover, the occurrence of sulphate and bicarbonate species (($MnSO_4$, $Mn(HCO_3)^{+}$) also hindered its mobility. No toxicity potential from the ingestion of Mn in water has been reported (Ekwere & Edet, 2012). The various species of Fe were Fe^{2+}, $FeSO_4$, $Fe(HCO_3)^{+}$, $Fe(Cl)^{+}$ and $Fe(Cl_2)$, among the species, the dominant species was Fe^{2+} making up about 64%. The human toxicity level of Fe in drinking water is reported to be at a concentration of > 200 mg/L (Reimann & Caritat, 1998). Fe^{2+} is immobile under the present pH condition. Moreover, the precipitation of Fe oxides such as Fe_2O_3 (hematite), and Fe_2O_4 (Magnetite), and other associated metal phases (e.g. $FeSO_4$, $Fe(HCO_3)$) further hindered its mobility (Edet et al., 2004; Ekwere & Edet, 2012). Cu^{+} appears to be the major identified ionic species making up about 77% of the total copper species in the groundwater of the study area. In the present environmental condition, Cu^{+} is immobile. The presence of Cuprous ferrite ($CuFeO_2$) among the species will inhibit its mobility in the groundwater (Edet et al., 2004). Nevertheless, the marked anomalous concentration of Cu^{+} reported in this study is attributed to elevated anthropogenic activities in the area. Although the mean concentration of As (mean 0.09 mg/L) slightly exceeded the permissible limit for drinking water, its concentration was generally very low among individual water samples. As reported by Smedley and Kinniburgh (2002), environmental conditions such as Eh and pH are the major controls on the speciation of As. H_2AsO^{4-} constitutes the major species at pH < 6.9, while at increasing pH (pH > 6.9), $HASO_4^{2-}$ is the dominant species (Yan et al., 2000). Under the present groundwater pH condition of the study area, $H_2AsO_4^{2-}$, was identified as the dominant species accounting for about 73% of the total As. This species is relatively immobile in water (Edet et al., 2004) and its mobility will further be hindered by adsorption onto sediments and clay mineral surfaces (Reimann & Caritat, 1998). Three species of Cr were identified (Cr^{3+}, $CrCl^{2+}$ and $CrCl_2^{+}$), with Cr^{3+} being the dominant species. Cr is known to exist in a wide range of valences (+ 2 to + 6) and the form in which they exist in water is dependent on the prevailing environmental conditions. According to Kimbrough et al. (1999), at pH < 6.9, Cr^{6+} can be reduced to Cr^{3+} which is less toxic.

The application of the hydrochemical prediction model in species assessment has successfully provided a better understanding of the geochemical behaviour of elements in the water. Metals existing as free ions are known to be highly toxic and bioavailable (Apte et al., 1995) and mobile under prevailing environmental conditions (Eh–Ph) (Edet et al., 2004). However, the use of the prediction model in this study has shown that their low concentration among the groundwater sample is owed to the low pH and the presence of "limiting mineral phases" or precipitates such as sulphates and carbonates (Edet et al., 2004).

Hydrochemical and facies evaluation of groundwater

Stoichiometric evaluation of the groundwater samples was carried out to understand the prevalent geochemical controls on the groundwater system. This was done by conducting a geochemical analysis of the major ionic composition of the water samples. Additionally, the identification of different facies and water types based on their origin was represented visually using hydrogeochemical models such as Piper trilinear diagram (Fig. 2). Based on their mean values, the concentration of major ions among the water samples decreased in the order of $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and $SO_4^{2-} > Cl^{-} > HCO_3^{-} > NO_3^{-}$ for cations and anions, respectively (Table 2). The dissolution of feldspar and calcium-rich minerals as well as ferromagnesian minerals from shales and sandstone units that underlie the area was responsible for the prevalence of alkaline earth metals (Ca^{2+}, Mg^{2+}) (Barzegar et al., 2018; Mgbenu & Egbueri, 2019). Ionic exchange reactions occurring between the alkaline-earth metals and alkali metals may also have been responsible for their enrichment in water (Barzegar et al., 2018; Igwe & Omeka, 2021). The prevalence of

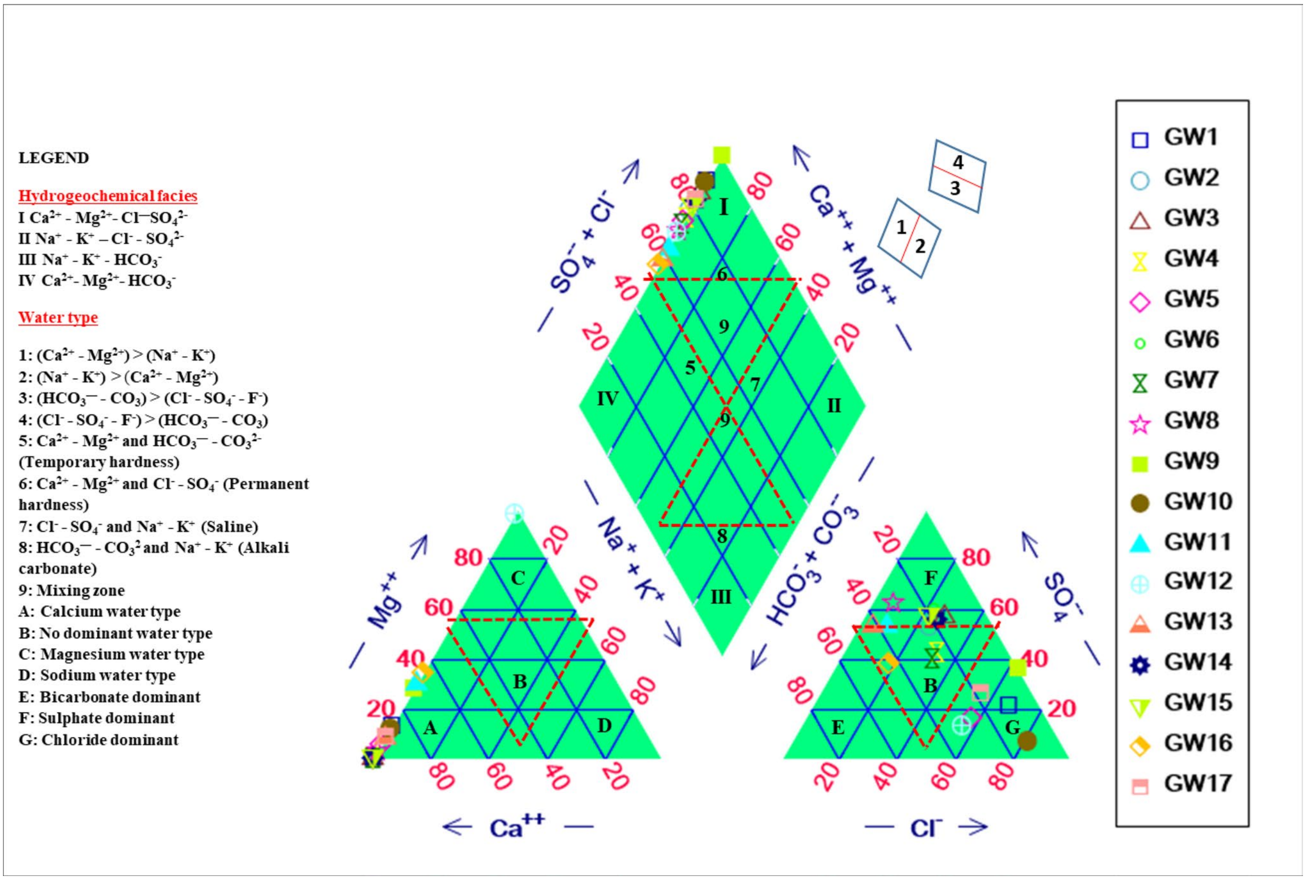


Fig. 2 Piper trilinear diagram showing the dominant water facies and type

SO_4^{2-} and Cl^{-} among the anions can be attributed to anthropogenic and geogenic inputs. SO_4 can be sourced from the dissolution of sulphide minerals (H_2S) from agricultural soils and organic matter decomposition (Egbueri, 2019). Cl concentration was from anthropogenic activities such as run-offs from agricultural lands and industrial waste discharge from the beverage companies. A visual representation of the water facies and type is shown in the ternary piper diagram in Fig. 2. From the diagram, Ca^{2+}–Mg^{2+}–Cl^{-}–SO_4^{2-} is identified as the major hydrogeochemical facies while Ca^{2+}–Mg^{2+} and Cl^{-}–SO_4^{2-} was identified as the dominant water type, an implication that the water is permanently hard and would be unsuitable for domestic purposes such as laundry. Hard water is known to cause scales on metallic storage facilities and does not readily form lather with soap (WHO, 2017). Furthermore, the prevalence of SO_4^{2-} and Cl^{-} among the water type implies that strong acids ($Cl^{-} + SO_4$), have a greater influence on the modification of the groundwater chemistry than weak acids ($CO_3 + HCO_3$) in the study area. The strong acids may have taken their source from the oxidation of sulphide minerals in the groundwater system (Igwe & Omeka, 2021; Mgbenu & Egbueri, 2019).

Environmental pollution assessment using numerical models

Heavy metal pollution index and modified heavy metal index

The HPI and MHMI were integrated into this study to numerically ascertain the pollution level of groundwater from toxic elements. Calculated results for both indices are presented in Table 4. As observed from Table 4, HPI values ranged from 0.22 to 10.34. According to the HPI classification criteria (Brown et al., 1970; Edet & Offiong, 2002), HPI < 20 indicates safe water quality, while HPI > 20 depicts critical water quality. Based on the results in Table 4, all the HPI values are < 20 implying that the waters are adjudged safe although some water samples in some areas (Abor, and Egede) recorded higher HPI values, implying that these sites may portend high pollution potential if no remedial measures are put in place. MHMI values ranged from 0.04 to

0.91. According to the MHMI classification scheme as per Dash et al. 2019 and Egbueri et al. 2020b), MHMI < 50 indicates excellent water quality, MHMI 50–100 indicates good water quality, MHMI 100–200 depicts good water quality, MHMI 200–300 indicates very poor water quality, and MHMI > 300 indicates unsuitable water quality. Based on these criteria, all the analysed water samples appear to be in excellent condition and are, therefore, adjudged safe for drinking. These results are consistent with findings by Igwe and Omeka (2021).

Integrated drinking water quality assessment indicators

Pollution index of groundwater

In this study, the PIG was used to assess the drinking water quality of groundwater by determining the relative impact of each analysed chemical parameter in each water sample. According to Subba Rao (2012) "if the overall chemical quality of water (*Ow*), is greater than 0.1, there will be a 10% value of 1.0 of the PIG". Hence at a PIG > 1, distinct information regarding the impact of contamination from chemical parameters contained in the groundwater can be given. Table 5 shows the results of the overall PIG (*OW*) for each chemical element and the final PIG ($\sum$OW). From the results, the OW for all the analysed chemical elements except for Cr and As was below 1.0, implying that these two elements have a greater impact on the pollution level of groundwater in the area. 76.47% of the groundwater samples recorded negligible pollution levels from Arsenic pollution, 5.88% (GWS-6) recorded low pollution, 5.88% (GWS-9) recorded moderate pollution. However, 11.77% of the groundwater samples (GWS-2, GWS-10) recorded a very high level of As pollution. Conversely, 52.95% of the total water samples (GWS-10, GWS-11, GWS-12, GWS-13, GWS-14, GWS-15, GWS-16 and GWS-17) recorded very high pollution levels from Cr. The final PIG ($\sum$OW) values obtained varied from 0.1902 to 9.8982 (Table 5). Based on the PIG classification criteria, 29% of the water samples (GWS-2, GWS-8, GWS-10, GWS-12) have very high pollution levels and are hence unsuitable for drinking; 35% (GWS-5, GWS-6, GWS-7, GWS-13, GWS-15, GWS-16) have moderate pollution level; 11% (GWS-1, GWS-17) have low pollution level, while the remaining 17% (GWS-3, GWS-4, GWS-14) recorded insignificant pollution and are hence adjudged to be fit for human consumption. These results are consistent with the observation of Egbueri et al. (2021).

Table 4 Results of indicators used for environmental pollution assessment (HPI, MHMI)

Sample ID	GWs 1	GWs 2	GWs 3	GWs 4	GWs 5	GWs 6	GWs 7	GWs 8	GWs 9	GWs 10	GWs 11	GWs 12	GWs 13	GWs 14	GWs 15	GWs 16	GWs 17
Location	Abia	Abor	Awhum	Afah	Akpakwume	AmekeNgwo	AmofiaAfa	Amokwe	Ebe	Egede	Eke	Nachi	9thMile	Ngwo	Nsude	Obinagu	Obioma
HPI	1.44	11.58	0.22	0.83	2.52	2.028	2.83	6.56	4.11	10.34	2.28	2.54	2.09	0.26	1.98	2.58	1.47
MHMI	0.04	0.09	0.045	0.17	0.13	0.15	0.06	0.18	0.37	0.14	0.37	0.12	0.05	0.91	0.21	0.04	0.05

Table 5 Groundwater quality assessment based on pollution index of groundwater (PIG)

Sample ID	OW (PH)	OW (Fe)	OW (Mn)	OW (CL)	OW (As)	OW (Cu)	OW (Cr)	OW (Zn)	OW (NO_3)	OW (TDS)	$\sum$ (OW)	Pollution status
GWs 1	0.05034965	0.032323232	0.3454545	0.01624	0.454545	0.072727	0.090909	0.000303	0.00131313	0.000407	1.064575	Low pollution
GWs 2	0.06433566	0.016161616	0.2954545	0.00422	8.181818	0.921212	0.409091	0.000242	0.00242424	0.004194	9.899152	Very high
GWs 3	0.06433566	0.012121212	0.0022727	0.00562	0.030303	0.084848	0.013636	0.01303	0.00141414	0.007273	0.234859	Insignificant
GWs 4	0.06713287	0.016161616	0.2954545	0.00465	0.045455	0.024242	0.031818	0.053333	0.00080808	0.004655	0.543715	Insignificant
GWs 5	0.05780886	0.032323232	0.3545455	0.02788	0.606061	0.012121	0.545455	0.08697	0.0019798	0.001358	1.7265	Moderate
GWs 6	0.06620047	0.024242424	0.0304545	0.00354	1.060606	0.012121	0.318182	0.093636	0.00141414	0.003255	1.613651	Moderate
GWs 7	0.04755245	0.008080808	0.1954545	0.00359	0.015152	0.49697	0.954545	0.010303	0.00040404	0.002782	1.734831	Moderate
GWs 8	0.03822844	0.04040404	0.0009091	0.00037	0.090909	0.036364	3.045455	0.212727	0.00064646	0.001994	3.468005	Very high
GWs 9	0.05221445	0.096969697	0.1090909	0.04693	1.818182	0.024242	0.790909	0.182424	0.00242424	0.02297	3.14636	Very high
GWs 10	0.05780886	0.032323232	0.1454545	0.02061	3.181818	0.787879	2.954545	0.026364	0.0109697	0.000238	7.218006	Very high
GWs 11	0.00274895	0.000261198	0.0284298	7.4E-05	0.048209	0.391552	2.820248	0.000272	4.4322E-06	6.61E-07	1.812875	Moderate
GWs 12	0.00010509	1.05534E-05	2.585E-05	2.7E-08	0.004383	0.014238	8.588937	5.78E-05	2.8653E-09	1.32E-09	2.156151	High
GWs 13	5.4871E-06	1.02336E-06	2.819E-06	1.3E-09	0.007968	0.000345	6.793068	1.05E-05	6.9461E-12	3.03E-11	1.845294	Moderate
GWs 14	3.172E-07	3.30785E-08	4.101E-07	2.6E-11	0.025354	0.000272	20.07043	2.78E-07	7.6196E-14	7.19E-15	0.19019	Insignificant
GWs 15	8.7198E-10	8.64002E-12	1.166E-08	1.9E-15	0.001222	0.000106	56.60359	7.55E-11	3.3772E-19	4.75E-21	1.395095	Moderate
GWs 16	9.1635E-14	9.1182E-17	3.013E-13	5.3E-23	5.36E-06	1.52E-06	486.1646	4.36E-15	9.6765E-28	6.26E-30	1.603586	Moderate
GWs 17	5.0281E-19	9.33124E-23	8.496E-19	6.8E-32	4.27E-08	5.23E-10	3302.549	4.6E-20	6.7214E-39	1.9E-40	1.044138	Low pollution

Ow overall chemical quality of water

Water quality index zonation

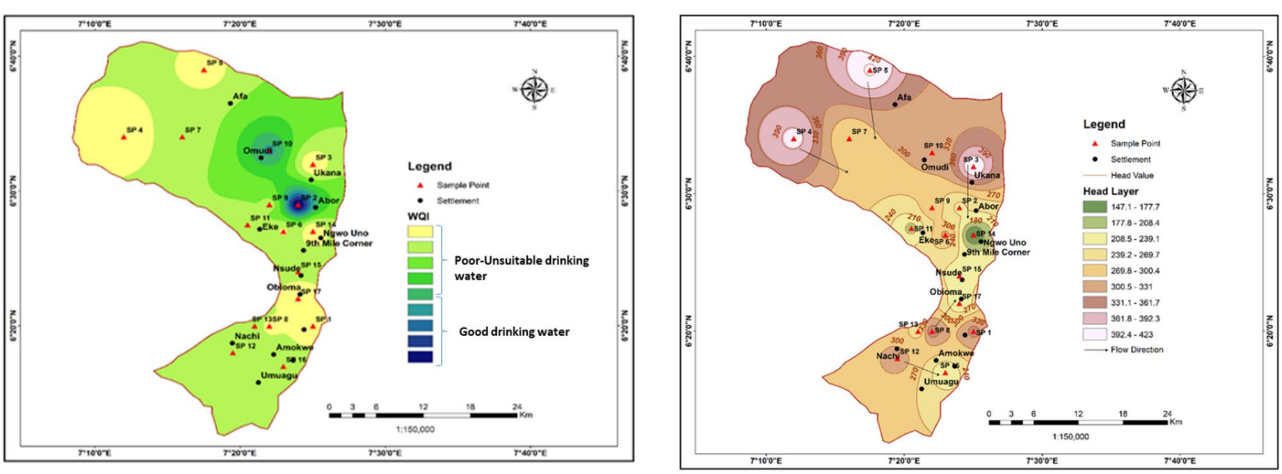
The results of WQI are presented in Table 6. To have an overall and visual assessment of the drinking water quality status of the entire area, it was necessary to delineate the drinking water quality status of the entire area into different zones by generating a zonation map from GIS spatiotemporal analysis (Fig. 3a). The final WQI results were used as input values for generating the drinking water quality zonation map of the area. It is thought that knowing the pollution status of the different zones in the area will aid the inhabitants, researchers, and environmental policy and decision-makers in proper groundwater resource management and sustainability. From the WQI results presented in Table 4, it is observed that 64.7% of the water samples (found around Abor, Ameke-Ngwo, Amofia-Afa, Amokwe, Ebe, Egede, Eke, Nachi, 9th Mile, Nsude and Obinagu) all fall within the "unsuitable" class and hence are unsuitable for drinking purposes, while very poor water quality was recorded in three samples (GWS-1, GWS-5, GWS-17) within Abia, Akpakwume and Obioma, respectively. However, good drinking water quality was recorded in only three samples (GWS-3, GWS-4, GWS-14) found around Awhum, Afah and Ngwo areas of the study area (Table 6) and are hence adjudged suitable for human consumption. The drinking water quality zonation map reveals that poor and unsuitable drinking waters are found in patches around the northeastern, west-central and southern parts of the study area, while good drinking water quality is noticeable within the central parts of the study area (Fig. 3a).

Table 6 Water quality index (WQI) and class category results

Sample ID	Location	Long	Lat	WQI	Class
GWs 1	Abia	7.417	6.333	244.75388	Very poor
GWs 2	Abor	7.4	6.483	3242.09921	Unsuitable
GWs 3	Awhum	7.417	6.533	97.8540756	Good
GWs 4	Afah	7.2	6.567	79.4680533	Good
GWs 5	Akpakwume	7.292	6.65	286.334399	Very poor
GWs 6	AmekeNgwo	7.383	6.45	369.351157	Unsuitable
GWs 7	AmofiaAfa	7.267	6.567	545.18613	Unsuitable
GWs 8	Amokwe	7.367	6.333	350.590108	Unsuitable
GWs 9	Ebe	7.367	6.483	668.432409	Unsuitable
GWs 10	Egede	7.367	6.55	1889.49193	Unsuitable
GWs 11	Eke	7.342	6.458	482.507935	Unsuitable
GWs 12	Nachi	7.325	6.3	575.309283	Unsuitable
GWs 13	9th Mile	7.35	6.333	556.689553	Unsuitable
GWs 14	Ngwo	7.417	6.45	52.4283738	Good
GWs 15	Nsude	7.4	6.4	416.659777	Unsuitable
GWs 16	Obinagu	7.383	6.283	534.375169	Unsuitable
GWs 17	Obioma	7.4	6.367	252.325749	Very poor

Groundwater flow system

The results of the groundwater static water level and hydraulic head are presented in S1. The groundwater flow direction map is shown in Fig. 3b. An observation of the map reveals that groundwater flow direction is predominantly from the northeastern to the southwestern parts of the study area. The implication of this concerning groundwater pollution vulnerability is that the pollutants will be majorly transported from the northern to the southern parts of the area. It is, therefore, recommended to site municipal boreholes within the northern parts of the study



(a) (b)

Fig. 3 **a** Water quality index zonation map of the study area **b** groundwater flow direction map of the study area

area. Untreated wastewater and industrial effluent disposal sites, as well as intensive agricultural activities, should be restricted to the southern parts of the study area.

Multivariate statistical analysis of groundwater samples

Pearson's correlation analysis

Table 7 shows the linearity as well as the strength between the analysed groundwater parameters. It is generally observed that most of the physicochemical parameters have strong linearity between them. The implication of this is that these parameters have a strong influence on the concentration of each other. KrishnaKumar et al. (2014) have pointed out that the greater the correlation between geochemical parameters, the greater the variation in geochemical components responsible for their concentration. Hence, the strong correlation observed among these parameters implies that different environmental factors (both geogenic and anthropogenic) were responsible for their concentration in the groundwater. A strong positive correlation is observed between Mg and Ca (0.909), K and Mg (0.985), Na and K (0.875) and SO_4 and Ca (0.85). This association implies that each of these element pairs influences the concentration of each other. The significant positive correlation between TDS and Mg, Ca and Na implies that the weathering and dissolution of these ions in the water had a major influence on the groundwater's total dissolved solids. The poor correlation observed between Na and Cl reflects that there is no occurrence of mixture or intrusion of saltwater into the groundwater system. It also suggests that the aquifer system is not underlain by salt-forming rocks such as evaporate. This assertion is further affirmed by the poor correlation observed between EC and all the major ions. A strong correlation is observed between SO_4 and Mg, Ca, indicating that weathering and oxidation of carbonate rocks (mostly from shale) that make up the major lithostratigraphic units are the major controls on the modification of the groundwater chemistry. The negative correlation observed between TDS and NO_3, and K implies that agricultural activities such as the use of fertilizers (N–P–K-based fertilizer) had little or no influence on the groundwater chemistry. The poor linearity observed between pH and all the analyzed chemical parameters is an indication that pH had little to no influence on mineral dissolution in the groundwater system, and as such played a very little role in the modification of the groundwater chemistry.

Except for Zn, Cu and Fe, a poor correlation was observed among the heavy metals, suggesting that their concentration in the groundwater was under varying environmental conditions; the positive correlation observed between Cu and Fe (0.694) can be attributed to a similar environmental condition such as leaching of sulphide-rich minerals, e.g. chalcopyrite ($CuFeS_2$).

Establishing the relationship between the assessment models using multivariate statistical simulation models

To show the relationship between the various environmental pollution and drinking water quality models and to test the validity of the models in environmental pollution and water quality assessment, two multivariate statistical models—Hierarchical cluster analysis (HCA) and the Spearman's correlation coefficient—were integrated into this study. For Spearman's correlation, significant correlations were taken at $p=0.05$, using the 2-tailed correlation matrix coefficient (Mustapha, 2012). The HCA was performed using Ward's linkage method, squared Euclidean distance and z-score data standardization algorithm. The *z* score data standardization is considered as a better algorithm due to its efficiency in minimizing bias due to disparity in various measurement units (Yidana, 2010), as it can transform data set into a uniform scale (Amiri et al., 2020; Subba Rao & Chaudhary, 2019). From Spearman's correlation matrix scores (Table S2), a strong significant correlation was observed between WQI, PIG and HPI. This shows that the results of the various models used in this study agree and validate each other and that the different pollution and water quality models accurately validated the results of their counterparts. However, a poor correlation was observed between MHMI and all other models. This may have been a result of the peculiarities involved in its computation.

Additionally, the dendrogram generated for all the assessment models showed a similar trend (Fig. S3), further affirming that findings from the various models is in tandem. Two cluster classes were extracted with cluster 1 accounting for WQI, PIG and HPI, while Cluster 2 recorded only MHMI. The results from the dendrogram are in strong agreement with those obtained for the Spearman's correlation coefficients which further affirms and validates the results from these models.

Comparison of WQI and PIG with other related studies

These two models were integrated into this study to assess the drinking water quality of groundwater samples from Udi and its environs. To the best of the authors' knowledge, these models have not been utilized in this area by any study to assess groundwater quality. However, Nganje

Table 7 Results of Pearson's correlation analysis of groundwater parameters

Parameters	pH	Ca	Mg	k	Na	HCO	Fe	Mn	Cl	SO4	NO3	TDS	TSS	EC	Turbidity	As	Cu	Cr	Zn
pH	1																		
Ca	− 0.231	1																	
Mg	− 0.139	**0.909**	1																
k	− 0.091	**0.837**	**0.985**	1															
Na	− 0.107	**0.853**	**0.915**	**0.878**	1														
HCO	− 0.014	0.356	0.466	**0.53**	0.122	1													
Fe	− 0.138	**0.582**	**0.737**	**0.753**	**0.856**	0.111	1												
Mn	0.064	− 0.196	− 0.182	− 0.19	− 0.067	− 0.082	0.012	1											
Cl	− 0.23	**0.605**	0.525	0.421	0.321	0.114	0.461	0.211	1										
SO4	− 0.08	**0.85**	–	**0.74**	**0.656**	0.464	0.334	− 0.264	0.573	1									
NO3	0.079	− 0.166	− 0.087	− 0.092	− 0.012	− 0.196	0.07	0.088	0.255	− 0.231	1								
TDS	− 0.072	**0.731**	**0.587**	0.462	**0.717**	− 0.251	0.388	− 0.103	**0.576**	**0.682**	− 0.044	1							
TSS	− 0.015	0.377	0.481	0.443	**0.675**	− 0.24	0.718	− 0.128	0.412	0.269	0.049	**0.589**	1						
EC	0.074	0.109	0.223	0.258	0.365	− 0.158	**0.546**	− 0.276	**− 0.166**	-0.119	− 0.174	0.141	**0.745**	1					
Turbidity	− 0.253	− 0.173	− 0.088	− 0.08	− 0.082	− 0.065	− 0.027	0.412	0.114	-0.096	− 0.098	− 0.161	− 0.136	− 0.283	1				
As	0.278	− 0.092	− 0.051	− 0.058	0.015	− 0.167	0.012	0.298	0.025	-0.056	0.394	0.079	0.1	0.003	− 0.109	1			
Cu	0.038	− 0.129	− 0.005	0.027	− 0.14	0.192	**0.694**	0.156	− 0.075	-0.026	0.495	− 0.173	− 0.249	− 0.329	− 0.127	**0.692**	1		
Cr	− 0.578	0.101	0.033	0.004	− 0.025	0.002	0.069	− 0.191	0.119	-0.13	**0.524**	− 0.077	− 0.107	− 0.132	− 0.171	0.074	0.371	1	
Zn	− 0.419	0.428	0.279	0.205	0.443	− 0.277	**0.553**	− 0.124	0.266	0.094	− 0.029	0.45	**0.522**	0.47	− 0.224	− 0.114	− 0.446	0.391	1

Bold = Correlation is significant at the 0.05 level (2 tailed) et al. (2019) used the WQI to assess the surface and groundwater quality in Kumba, Cameroon. The use of the model showed excellent results for the evaluation of water from different sources such as catchment water (CW), pipe-born water (PW), stream/surface water (SW) and hand-dug wells (HDW). According to their findings, a greater portion of water samples from CW (75%) was unfit for drinking purposes while 25% were drinkable. However, about 57.1% of water samples from PW were of good quality while 42.8% fell within the poor class. Conversely, 40% of SW fell within the good and very poor quality class respectively; however, 20% were in the poor class. Similarly, 2.1% of the water samples from HDW were in the excellent class, 62.5% fell in the good water class, 14.5% were in the poor class, 6.3% fell under the very poor class while 8.3 of the HDW were under the unfit class. Results from this study revealed that the water from hand-dug wells in the area was more suitable for consumption than those from other sources. The poor water quality observed in the catchment area was attributed to the presence of coliform and microbial load from poor sanitary conditions in the area.

On the other hand, the PIG has been used by a few researchers for groundwater quality assessment, but there has not been any reports using this model in the present study area. Egbueri et al. (2021) reported the use of PIG to assess the drinking water quality of the Nnewi and Awka metropolises, southeastern Nigeria. According to the findings results of the PIG from the Nnewi and Awka metropolises varied between 0.1607–3.9015 and 0.2431–44.7418, respectively, with insignificant pollution levels reported in about that 40% of the groundwater samples in the Nnewi area and 20% having high level of pollution level. The Awka area, however, recorded greater pollution levels with a staggering 80% of the groundwater samples recording very high pollution levels while 20% recorded insignificant pollution levels. The elevated pollution level observed in these water samples was attributed to high anthropogenic activities in the area.

An observation of the results from WQI and PIG in the present study reveals that both models validated each other as a similar trend was observed with results from other studies.

Conclusion

In this study, the impact of industrially derived effluents on the quality of groundwater resources within Udi and its environs, southeastern Nigeria have been investigated using an integrated geochemical, indexical, statistical and spatiotemporal modeling approach. All the measured physicochemical parameters were within the required standards of the World Health Organization (WHO, 2017) and Standard Organization of Nigeria (SON, 2015) for drinking purposes except for pH (mean 6.2), describing the water as acidic to slightly acidic. Hydrochemical and facies modeling identified Ca^{2+}–Mg^{2+}–Cl^{-}–SO_4^{2-} as the major hydrogeochemical facies and Ca^{2+}–Mg^{2+} and Cl^{-}–SO_4^{2-} as the dominant water type, an implication that the water is permanently hard and would be unsuitable for domestic purposes such as laundry. According to their mean concentration, the order of dominance of trace elements was Zn > Mn > Cu > Cr > As > Fe. Generally, all analysed trace elements except for Fe and Zn recorded values above the WHO and SON maximum required limits. The application of the hydrochemical prediction model, PHREEQC, in trace element species assessment was successful in providing a better understanding of the geochemical behaviour of elements in the water. Results from the model showed that most of the trace elements were immobile under the prevailing pH condition (4.1 to 7.2), hence their recorded low concentration among the water samples. However, the mobile ones are very low in concentration owing to the presence of limiting mineral phases such as sulphates and carbonates. Environmental pollution assessment numerical indices such as heavy metal pollution index and modified heavy metal index revealed that groundwater of the area is in excellent condition. Conversely, the pollution index of groundwater (PIG) revealed that 29.5% of the water samples have very high pollution levels and are hence unsuitable for drinking, while 35% and 11% of the samples recorded moderate and low pollution levels, respectively, while the remaining 17% recorded insignificant pollution and are adjudged to be fit for drinking. Similarly, water quality index and GIS-based spatiotemporal analysis revealed that 64.7% of the water samples (found around Abor, Ameke-Ngwo, Amofia-Afa, Amokwe, Ebe, Egede, Eke, Nachi, 9th Mile, Nsude and Obinagu) occurring within the northeastern, west-central and southern parts of the study area are unsuitable for drinking purposes; however, good drinking water quality is noticeable within the central parts of the study area. Additionally, the groundwater flow map showed that groundwater flow direction in the area is predominantly from the northeastern to the southwestern direction of the study area. The implication of this concerning groundwater pollution vulnerability is that the pollutants will be majorly transported from the northern to the southern parts of the area. Correlation analysis showed a significant relationship between all analysed physicochemical parameters, at $p > 0.05$, implying that these parameters have a strong influence on the concentration of each other and they occurred from a similar source. Additionally, hierarchical cluster analysis and Spearman's correlation coefficients successfully validated the results from the various assessment models with a strong correlation observed between most of the models.

Therefore it can be concluded that the use of the integrated geochemical, spatiotemporal and indexical approach is highly effective in groundwater pollution assessment as compared to the conventional assessment method. Additionally, the integration of speciation analysis in this study has successfully given a clear-cut knowledge on the geochemical behaviour (in terms of mobility) of trace elements in water under the prevailing environmental conditions. Their mobility potential has been attributed to the presence of limiting mineral phases in water such as sulphates and carbonates.

Recommendation and limitation of the study

From the information obtained from the groundwater flow system, it is highly recommended to site municipal boreholes within the northern parts of the study area. Additionally, untreated wastewater and industrial effluent disposal sites, as well as intensive agricultural activities, should be restricted to the southern parts of the study area. Furthermore, since most of the inhabitants of the area are not well educated, it is recommended that more environmental awareness programs be established by the government and policymakers. Regular monitoring and assessment of the groundwater sources in the area are highly recommended. Land use, industrial ad municipal waste disposal practices, that would help preserve the quality of the groundwater should be adopted.

The limitation of the present study is that sampling and analysis of human health risk from the consumption of contaminated water sources in the area were not carried out. Hence, a detailed evaluation of human health risks to further determine the long-term exposure of heavy metals among the inhabitants is highly recommended for further studies in the area.

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Declarations

Conflict of interest The authors declare that there are no conflicts of interest regarding this paper.

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