Pollution potential and causative hydrogeochemical processes in unconfined aquifer systems in a typical urban setting: emphasis on recharge and discharge areas

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Abstract

The inhabitants of Akure Metropolis, south-western Nigeria, depend solely on groundwater for their domestic, industrial and irrigation purposes. There is a need to delineate recharge and discharge areas for assessment and management of groundwater in these areas. One hundred and ninety (190) dug wells were selected for this assessment. Elevation and water table data aided accurate delineation of recharge, discharge and groundwater divide areas. Thirty-six wells representative of recharge and discharge areas were subjected to pollution assessment [DRASTIC, water quality index (WQI) and runoff potential]. The results revealed that the recharge areas have higher pollution potential and runoff amount than the discharge areas. This implied that groundwater sourced from recharge areas was more pollution prone than that sourced from discharge areas. WQI results revealed that the waters from recharge and discharge areas fall within excellent, good, poor, and unsuitable quality categories. Hydrogeochemical results revealed that concentrations of cations and anions are in order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ with a predominant Ca-HCO_3 facies typifying water from a basement complex environment. Gibbs plot and chloro-alkaline index affirmed the rock dominance and existence of imprints of ion-exchange processes influencing the groundwater quality. Intense weathering activities aided with long resident time spent by the water in the voids of the aquifer media are characteristic in this terrain. Recharge of precipitating water through infiltration into the weathered basement aquifers is a pointer to the greater yield of water in the wells. The possibility that precipitation-weathering process has led to the increase in concentrations of all ionic species and possible pollution of the groundwaters from the recharge and discharge areas cannot be ruled out at all.

Keywords Groundwater · Recharge · Discharge · Hydrogeochemical facies · Pollution assessment

Introduction

It has been projected that by the year 2030, the world population will have geometrically risen to 8.5 billion, of which 60% of this population will reside in urban areas (UNDE-SAPD 2015). As a matter of fact, urban cities are evidently the engines of the world's economic development. Urban land mass comprises a wide diversity of land use practices (e.g. commercial hubs, educational institutions and

residential areas, etc.) with its consequential effects. One of the many consequential effects occurs in the form of modification of recharge rate, pattern and groundwater quality with high prevalence in urban areas as compared to rural areas (Foster et al. 1998; Oke 2015).

However, there is evidently high demand for water from these increasing urban populace. This is due to their economic activities and commercial enterprises (MacDonald et al. 2005), and total reliance on groundwater for varied purposes. This high demand has been sourced from several hand-dug wells and borehole systems which were mostly or sometimes ill-designed, ill-constructed and non-maintained water systems leading to groundwater pollution and groundwater scarcity in recharge and discharge areas (Ocheri 2006; Ocheri and Mile 2010). Several works have attributed the increased records of groundwater contamination and pollution in the urban cities to several urban human activities

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(anthropogenic sources). These have been categorized into the following: high population of individuals, increasing industrial and agricultural activities such as leakages from underground storage tanks, chemicals and waste dump-sites, industrial effluents, sewage pits, land spreading of sludge, brine disposal from the petroleum industry, mine waste, animal feeds, radioactive waste, highway run-offs and acidic rain; which has also been found to be associated with various deadly diseases (Kehinde 1998; Punmia and Jain 1998; Sridhar 2000; Adelana et al. 2003, 2004, 2005, 2008; Ikem et al. 2002; Akujieze et al. 2003; Ajala 2005; Ocheri 2006; Gbadebo et al. 2010; Eni et al. 2011; Naidu et al. 2011; Ocheri et al. 2014; Laniyan et al. 2015). Furthermore, the impact of natural activities (leaching and rock weathering) on urban groundwater quality cannot also be underrated in urban areas.

Groundwater recharge and discharge areas serve as important areas for drinking, industrial and agricultural purposes. These areas are also vulnerable to pollution (Owoseni et al. 2013). The delineation of these areas can be attributed solely to the direction of groundwater locally and regionally (Freeze and Cherry 1979; Fetter 1994). Co-occurrence of recharge and discharge areas depends on the type of geological and hydrogeological setting influencing groundwater flow and direction. Ignorantly, urban populace in the fight for survival site their houses, companies and institutions in these areas endangering the natural resource (groundwater) in Akure Metropolis.

Many researchers (Olorunfemi et al. 1999; Akintorinwa and Olowolafe 2012; Anifowose and Kolawole 2012; Asiwaju-Bello et al. 2013; Owoseni et al. 2013; Owoseni and Komolafe 2014; Aladejana et al. 2016; Yenne et al. 2018) have worked on the several aspects of groundwater resources of Akure area for different purposes. However, they did not consider the identification and assessment of the groundwater recharge and discharge areas in Akure area. Lawrence and Upchurch (1982) employed geochemical factor analysis for the identification of recharge areas of Floridan Aquifer, the USA. Other studies (e.g. Mahmoud 2014; Senanayake et al. 2016) used remote sensing and GIS tools in the delineation of groundwater recharge and discharge areas. DRASTIC approach has practically been employed for the quantification of groundwater susceptibility all over the world (Hernandez-Espriu et al. 2014). Cautiously, Villumssen et al. (1983) emphasized that the chemical composition of groundwater can be used as an indicator of vulnerability, which can also serve for preliminary verification/validation of the vulnerability maps produced by different vulnerability approaches such as AVI, DRASTIC, GOD, IRISH and SINTACS.

Groundwater pollution assessment studies have aided accurate assessment of the vulnerability of groundwater to

pollution coupled with in-depth understanding and knowledge of hydrogeochemical processes which have been found important in groundwater quality assessment. Hydrogeochemical processes greatly influence the pollution or contamination of groundwater all over the world (Krishna Kumar et al. 2014; Batabyal and Chakraborty 2015; Adewumi et al. 2018; Batabyal 2017; Lapworth et al. 2017; Olofinlade et al. 2018; Oyedele et al. 2019). This study is, however, aimed at the delineation of groundwater recharge and discharge areas in an urban metropolis, like Akure, the capital city of Ondo State, south-western Nigeria, for their pollution potential as well as the hydrogeochemical processes prevailing in the area. This will be achieved with pollution assessments such as DRASTIC, water quality index (WQI), runoff potential (RP) and multivariate statistical analyses (descriptive, principal component analyses, hierarchical cluster analyses and correlation analyses). Piper diagram, Gibbs plot and Chloro-Alkaline Index were employed to understand the hydrogeochemical processes in the waters. This study will support the protection of these unconfined aquifers from several urban activities that can endanger the populace that consume these waters.

Drainage, climate, vegetation and topography of the study area

Akure, a Metropolitan city of Ondo State in south-western part of Nigeria, lies within latitudes $07^{\circ} 12'$ and $07^{\circ} 19' N$ and longitudes $005^{\circ} 8'$ and $005^{\circ} 17' E$ with total area coverage of 217.41 km^2 (Fig. 1). Akure area is, however, drained by River Ala with its dense tributaries of streams forming dendritic drainage system of flow in two directions namely south-eastern and north-western (Asiwaju-Bello et al. 2013) (Fig. 1). Akure area experiences two seasons in a year: the wet and dry seasons. The wet season spans between April and September, but March to November receives most of the fall which is evident by an excess of 40 mm on a single day, while the dry season period is from October to March. The main rain-bearing system affecting the area is embedded in the easterly wind current. The average annual rainfall is 1309.6 mm (OSMEPB 2012). Annual temperature for Akure area ranges from 18 to $31^{\circ} C$, respectively. Evaporation is usually low from June through September, ranging from 3.3 to 4.5 mm/day. Sunshine duration is short (2.7–2.9 h/day) during the month of July to September, while the relative humidity ranges from 5.0 to 90%, depending on the season (OSMLHE 2000). Akure's vegetation is characterized with regrowth rainforest type evident as grasses and trees. There is a varied topography with high elevation at the southern part and pockets of hills found in the north-eastern part of the study area ranging from 315 to 402 m above mean of sea level (Faniran 1970; Asiwaju-Bello et al. 2013) (Fig. 1).

Fig. 1 Topographical map of the study area

Geologic and hydrogeologic settings of the study area

Akure area is underlain by basement rocks of south-western Nigeria such as quartzite, granite gneiss, porphyritic granite and charnockite (Rahaman 1976; Anifowose 2000) (Fig. 2). Overburden of thick weathered regoliths which varies from place to place overlay these rocks in some places. These rocks generally lack primary porosity but possess secondary porosity due to weathering and fracturing activities (Acworth 1987; Olorunfemi et al. 1999; Owoseni et al. 2013; Aladejana et al. 2016). Groundwater recharge is primarily through infiltration by direct precipitation with mean annual value of about 1350 mm. Secondary recharge occurs by influent flow condition from Ala River and its tributaries. Groundwater discharge in Akure area occurs through seepages, springs, well water abstraction, and flow into surface water bodies (rivers and streams) (Owoseni et al. 2013). Groundwater is usually sourced through hand-dug wells and bore hole with variable yield. The aquifers of Akure area are weathered and fractured aquifers typical of any crystalline basement terrain (Olabode 2019).

Materials and methods

One hundred and ninety (190) shallow hand-dug wells scattered all around Akure area were initially selected for the study during well campaign. The approach employed for this study follows a sequential stages from well campaign, water table mapping, water level measurement, pollution assessment [DRASTIC and runoff potential (RP)], physiochemical, cationic and anionic species determination, water quality index, Gibbs plot and multivariate statistical analysis. The procedures are explained in different sections.

Water level measurement

Water level indicator was used to measure the level of water in all the selected one hundred and ninety (190) hand-dug wells of the study area. The data obtained were then related to mean sea level and used in the generation of water table distribution map for the area. The groundwater levels and flow direction were plotted in the form of a map using Surfer software version 10. The local groundwater flow directions and its flow vectors were deduced from the map, which was later used in the identification of groundwater recharge, discharge and divide areas.

Fig. 2 Geological map of Akure area (NGSA 2006)

DRASTIC

DRASTIC, a score-based, empirical (numerical ranking) and parametric system which assigns weights and ratings to all the seven knowledge-based hydrogeological parameters, was used for the pollution potential assessment of the unconfined aquifer systems due to its large extent (regional scale) in an urban setting like Akure area (Aller et al. 1987; Oke 2015). The seven knowledge-based worldwide accepted hydrogeological factors considered in the study are depth to groundwater (*D*), net recharge rate (*R*), aquifer media (*A*), soil media (*S*), topography/slope (*T*), impact of the vadose zone (*I*) and hydraulic conductivity of the aquifer (*C*). The values of the ratings and weights for each hydrogeological parameter were plugged into Eq. 1 to determine the pollution potential for all the recharge and discharge areas otherwise known as the DRASTIC Index (Aller et al. 1987).

$$P = DrDw + RrRw + ArAw + SrSw + TrTw + IrIw + CrCw \quad (1)$$

where *P* is the pollution potential and the small letters *r* and *w* are the corresponding ratings and weights, respectively. The calculated DRASTIC Index used in the study was referred to as pollution potential which enabled the possibility of identifying areas that are vulnerable to groundwater pollution. However, areas characterized with higher DRASTIC Index values are posed to be highly vulnerable with greater propensity of aquifer contamination. Unarguably, the DRASTIC Index/pollution potential had been further categorized into three vulnerability groups, namely low, moderate and high (Owoseni and Komolafe 2014).

Runoff classification using SCS-CN

Curve number (CN), a coefficient, was employed in the determination of runoff potential of Akure area and its effect on the recharge and discharge areas. This was found on the equation for water balance in Eqs. 2 and 3 (Deshmukh et al. 2013; Soulis and Valiantzas 2012)

$$P = I_a + F + Q \quad (2)$$

$$\frac{Q}{P - I_a} = \frac{F}{S} \quad (3)$$

The expression of SCS-CN was obtained from the following equations

$$Q = \frac{(P - I_a)^2}{(P - I_a)} + S \quad \text{if } P > I_a \quad (4)$$

$Q=0$, otherwise $I_a = \lambda S$ where direct runoff (mm) is Q , total precipitation (mm) is P , initial abstraction (mm) is I_a , potential maximum retention (mm) is S , actual retention after runoff commences is F , and lastly, the abstraction coefficient (dimensionless) is λ .

$$S = \left(\frac{25400}{\text{CN}} \right) - 254 \quad (5)$$

Curve number (CN) is influenced by the soil type and subsoil condition, land cover, and condition of the hydrological regime of the area under study.

The land use/cover image and hydrological soil group (HSG) were used in the runoff analysis. The runoff potential of Akure area was generated by the intersection of the land cover and soil maps. CN value usually ranges from 0 to 100, and the increasing value of CN signifies the reduction in infiltration amount and high amount of runoff (Aladejana et al. 2016). However, this assertion is due to the combined influence of the prevailing slope, soil type and subsoil conditions, density of vegetation, rate of human activities and intensity of rainfall and hydrological regime of the area under investigation. Curve number estimation for Akure area followed the method of Aladejana et al. (2016).

Physiochemical, cationic and anionic species determination

Parameters such as temperature, electrical conductivity, total dissolved solids (TDS) and hydrogen ion concentration (pH) were measured in situ using EC/pH/TDS-temperature meter in the groundwater samples. Flame photometer was used to determine the dissolved concentrations of calcium, magnesium, sodium and potassium ions in the groundwater samples. Turbidimetric technique using spectrophotometer that was used in the determination of dissolved concentrations of bicarbonate, chloride and sulphate ions was carried out in the Geochemistry laboratory of the Applied Geology Department of the Federal University of Technology, Akure, Ondo State, Nigeria, following APHA standard (1995).

Water Quality Index (WQI) approach

Hydrochemical data were subjected to water quality index (WQI) evaluation, a rating technique that provides the composite influence of individual water quality parameters such as anions (HCO_3^- , Cl^- and SO_4^{2-}) and cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) on the overall quality of water. For the calculation of WQI, World Health Organization (2011) drinking water standard was considered. Assumption was made for the assigned water quality parameters weightage to be indirectly of standard recommendations for these parameters. Vasanthavigar et al. (2010) approach was employed in the assignment of weights to the chemical variables in the following manner. Maximum weight of 4 has been assigned for sulphate and electrical conductivity, 3 for bicarbonate and chloride, 2 for calcium, sodium and potassium and 1 for magnesium.

The quality rating scale for each parameter, Q_i , was calculated by using this expression (Eq. 6):

$$\text{Quality rating } Q_i = 100 \left(\frac{V_n - V_i}{V_s - V_i} \right) \quad (6)$$

where Q_i = quality rating, V_n = measured values of the chemical variables (e.g. dissolved cations and anions), V_i = initial values for all the chemical parameters, it is zero for all the chemical parameters but 0 and 14.6 for pH and dissolved oxygen, respectively, and V_s = standard value for all the chemical variables according to WHO 2011 standard. Relative weight (W_i) was calculated by a value inversely proportional to the recommended standard (S_i) of the corresponding parameter.

$$W_i = \frac{K}{S_i} \quad \text{where } K = \frac{1}{\sum \left(\frac{1}{S_i} \right)} \quad (7)$$

where W_i = weight, S_i = standard value for all the chemical variables such as TDS, EC, Ca, Mg, Na, K, HCO_3 , Cl, SO_4 according to WHO 2011 standard, K = constant. The overall WQI was calculated using Eq. 4

$$\text{Water Quality Index } WQI = \frac{\sum Q_i}{\sum W_i} \quad (8)$$

The WQI range and type of water were classified according to Adewumi et al. (2018) (Table 4).

Hydrogeochemical processes and evolution approach

The hydrogeochemical processes and evolution of groundwater in Akure area were achieved through Chloro-Alkaline Index (CAI), Gibbs and Pipers plot.

Ion-exchange approach

Chloro-Alkaline Index was employed to determine the types of ion-exchange processes at play in the waters of Akure area according to Schoeller (1967).

$$CAI = \frac{Cl - Na + K}{Cl} \quad (9)$$

where the concentrations of Cl, Na and K are in meq/l

Gibbs plot approach

Gibbs diagram was employed in order to establish relations prevailing between water composition and aquifer lithological characteristics, identify the dominant geochemical processes and mechanisms prevailing in waters sourced from recharge and discharge areas with strong replication of a particular environment. These relations, geochemical processes and mechanisms have a strong effect on the overall quality of water usage and can also guide towards its remediation if water quality is found unsuitable for many varied purposes (Gibbs 1970; Olofinlade et al. 2018). The Gibbs diagram consists of three different zones, namely evaporation, atmospheric (precipitation) and rock–water interaction dominance (Gibbs 1970). Accurate Gibbs plots for recharge and discharge of Akure area were obtained by the plots of TDS against ionic ratios (Na/(Na + Ca) and Cl/(Cl + HCO₃)).

Water type approach

The chemical results obtained from the chemical analysis were computed and plotted on the Piper diagram (Piper 1944) using the USGS GW Chart software. The Piper diagram was used in the determination of the predominant water facie type of recharge and discharge areas of Akure area.

Multivariate statistical analysis

The obtained concentrations of dissolved ions for recharge and discharge areas were subjected to multivariate statistical analyses. These analyses are known for their ability to illuminate the relations between the individual chemical variables, thereby providing insight into the compositional dissimilarity between the water chemistry and establishment of various controlling factors influencing the chemistry of the aquifers. This is achieved in Excel and IBM SPSS Statistics 18 environments.

Descriptive analysis

This describes the hydrochemical data set with respect to minimum, maximum, mean and standard deviation values for all the nine (9) chemical variables such as EC, TDS, Ca, Mg, Na, K, HCO₃, SO₄²⁻ and Cl and other variables such as Chloro Alkaline Index for the present study.

Correlation analysis

This analysis was performed using Excel software, where all the chemical variables were inputted in order to establish relationship between them. This relationship will provide information about the quality and evolution of the waters in the recharge and discharge areas. A pair of chemical variables having correlation coefficient lower than 0.5 suggests no weighty connection, while greater than 0.5 and equal to 0.8 depicts strong connection and greater than or equal to 0.8 depicts a very strong connection. The correlation analysis employed in the interpretation of the results presented on the correlation table was carried out after Jeyaraj et al. (2006).

Principal component analysis and hierarchical cluster analysis

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were employed for this study using the statistical software package (IBM Statistics 18). Principal component analysis is usually aimed at reduction in the hydrochemical data to a smaller number without loss of necessary facts. It also converts the data matrix into a new set of fused variables [principal components (PCs)] based on variance–covariance matrix. The variance and covariance of chemical parameters are determined based on standardized data. The PCs are by definition uncorrelated with each other. The chemical variables used for PCA were electrical conductivity (EC), total dissolved solids (TDS), Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, SO₄²⁻ and Cl⁻. PCs with eigenvalues greater than 1 were only extracted, while those lower than 1 were eliminated following the assumption of Chatfield and Collin (1980). Calculated components loadings, eigenvalues, % total variance and cumulative variance and scree plots of the eigenvalues of observed components were extracted and represented, which were then subjected for interpretation. Marghade (2015) classification of positive PC loadings was employed in the classification and interpretation of the delineated principal components (PCs) loadings for the recharge and discharge areas. The PC loadings are classified as thus very low positive PC loadings with value lower than 0.45, low-positive PC loadings with values ranging between 0.45 and 0.6, medium-positive

PC loadings with values ranging between 0.6 and 0.75, high-positive PC loadings with values ranging between 0.75 and 0.90 and very high positive PC loadings with values greater than 0.9.

For Q-mode hierarchical cluster analysis (HCA), ward linkage (rescaled distance cluster combine) method was employed which aided the clustering and delineating of similarities between the wells. This method recognized relatively homogeneous groups of locations based on the chemical variables. This was achieved through the aid of two dendrograms representative of recharge and discharge areas of Akure.

Results and discussion

The water table head and flow vector distribution map generated for the area are presented in Fig. 3. Deductions from Fig. 3 enabled the identification of six recharge and

discharge areas as well as several divide areas. The recharge areas are designated as R1–R6, while the discharge areas are designated as D1–D6 (Fig. 3). The groundwater flow is localized in the form of discrete bodies (replicate of pockets or mini-basins), which are structurally and topographically controlled due to weathering and fracturing activities of the underlying rocks typified of a basement complex environment. This view is believed to be the prevailing scenario in Nigerian basement complex terrain (Offodile 2014; Olabode 2019). Comparison of the water table elevation data with the topographical map indicates that the areas of lowest water table are representative of the main topographical highs. The topographical high areas were regarded as the recharge areas, while the relatively plains/lowland areas with shallowest water table were regarded as the discharge areas. The shallow nature of the water table was believed to be influenced by pumping pattern and outcropping nature of the rocks. This also followed the results obtained by the work of Nwankwor et al. (1988). Groundwater divides in the

Fig. 3 Groundwater table heads distribution map showing flow vectors, recharge (R) discharge (D) areas and groundwater divides

Table 1 Calculated pollution potential (*P*) and its qualitative risk category (QRC) for the recharge areas (RA)

Location	<i>D</i>	<i>R</i>	<i>A</i>	<i>S</i>	<i>T</i>	<i>I</i>	<i>C</i>	<i>P</i>	QRC	RA #
1	45	24	12	18	9	15	3	126	Moderate	R1
2	35	24	12	18	9	15	3	116	Low	R1
3	35	24	12	18	9	15	3	116	Low	R1
4	45	24	12	18	5	15	3	122	Moderate	R2
5	45	24	12	18	3	15	3	120	Moderate	R2
6	45	24	12	18	9	15	3	126	Moderate	R2
7	45	24	12	4	3	15	3	106	Low	R3
8	35	24	12	4	9	15	3	102	Low	R3
9	45	24	12	4	9	15	3	112	Low	R3
10	45	24	12	18	5	15	3	122	Moderate	R4
11	45	24	12	18	5	15	3	122	Moderate	R4
12	35	24	12	18	5	15	3	112	Low	R4
13	45	24	12	18	5	15	3	122	Moderate	R5
14	45	24	12	18	9	15	6	129	Moderate	R5
15	45	24	12	18	3	15	3	120	Moderate	R5
16	45	24	12	18	5	15	3	122	Moderate	R6
17	45	24	12	18	9	15	3	126	Moderate	R6
18	45	24	12	18	9	15	6	129	Moderate	R6

Table 2 Calculated pollution potential (*P*) and its qualitative risk category (QRC) for the discharge areas (DA)

Location	<i>D</i>	<i>R</i>	<i>A</i>	<i>S</i>	<i>T</i>	<i>I</i>	<i>C</i>	<i>P</i>	QRC	DA #
1	45	24	12	4	3	15	3	106	Low	D1
2	35	24	12	4	9	15	3	102	Low	D1
3	25	24	12	4	3	15	3	86	Low	D1
4	45	24	12	18	10	15	3	127	Moderate	D2
5	45	24	12	18	10	15	3	127	Moderate	D2
6	35	24	12	18	9	15	3	116	Low	D2
7	45	24	12	18	5	15	3	122	Moderate	D3
8	35	24	12	18	5	15	3	112	Low	D3
9	45	24	12	18	9	15	3	126	Moderate	D3
10	50	24	12	18	5	15	3	127	Moderate	D4
11	45	24	12	18	9	15	3	126	Moderate	D4
12	35	24	12	18	9	15	3	116	Low	D4
13	35	24	12	18	9	15	3	116	Low	D5
14	45	24	12	18	9	15	3	126	Moderate	D5
15	45	24	12	18	9	15	3	126	Moderate	D5
16	50	24	12	18	5	15	3	127	Moderate	D6
17	25	24	12	18	5	15	3	102	Low	D6
18	45	24	12	18	5	15	3	122	Moderate	D6

study area were observed to occur along the boundaries of groundwater recharge and discharge areas. It actually separates areas where the water flows in opposite direction. Some divides were found to flow towards nearby surface water bodies (streams) following the prevailing elevation, pumping pattern, water usage and nearness to the delineated groundwater recharge and discharge areas of Akure area (Fig. 3).

DRASTIC approach

Summary of calculated values of DRASTIC Index/pollution potential for the recharge and discharge areas are presented in Tables 1 and 2. The result shows that weightage values assigned for the first hydrogeological parameter (depth to water table) ranges from 35 to 45 for the recharge areas and 25 to 50 in the discharge areas. This reveals the distinct variation in the depth to water table for Akure metropolis.

It also submits that the water table depth ranges from shallow to moderately deep. The shallow aquifers are found at the plain areas and moderately deep aquifers found at the elevated areas. Fixed net recharge weightage value of 24 was assigned for all the wells representative of both recharge and discharge areas. The weightage value for Aquifer Media was fixed at 12 for both the recharge and discharge areas because the unconfined aquifers taps its water from the weathered layers above the basement rocks underlying Akure area. Variable weightage value of 4–18 was assigned for soil media representative of the recharge and discharge areas due to the variabilities and different soil classes observed in the area reflecting clay and sand content of the soils according to Smyth and Montgomery (1962) soil classification (a classification found relevant to Akure area). There is, however, variation in the weightage values obtained for the topography which is another hydrogeological parameter due to the ruggedness of Akure area. The weightage values range from 3 to 9 and 3 to 10 for the recharge and discharge areas, respectively. The impact of vadose zone weightage value for all the recharge and discharge areas was fixed at 15 since the materials within this zone comprises sand, silt and clay. The weightage value for hydraulic conductivity ranges from 3 to 6 in recharge areas and fixed at 3 for the discharge areas. The degree of weathering activities is responsible for the hydraulic conductivity influenced by permeable nature of material making up the unconfined aquifers in Akure area (Table 3).

The pollution potential (DRASTIC Index) was obtained for each of the wells in each recharge area. The Pollution Potentials were summed up for each of the six recharge areas (R1, R2, R3, R4, R5 and R6). The approach was also applied to all the six discharge areas (D1, D2, D3, D4, D5 and D6) and is presented in Tables 1 and 2 and Fig. 4. The results showed that the recharge areas have higher pollution potential values than the discharge areas with pollution potential values for recharge areas ranging from 102 to 129 with average value of 120 while the discharge areas ranges from 86 to 127 with average value of 117. This indicates that groundwater sourced from recharge areas are possibly more pollution prone than that from discharge areas.

Runoff approach

The intense and growing development in every urban setting especially in Akure area has led to the construction of several civil engineering structures with consequent extensive and vast surface coverage such as buildings, roads, pavements, motor parks, etc. Activities prevailing in this area usually lead to the compaction and hardening of the land surfaces, thereby yielding low infiltration rate but supportive of high runoff rate. Soil type and sub soil conditions, land use type, type and intensity of vegetation and prevailing rainfall are among many factors that influence the runoff rate

Table 3 The aquifer media rating and weighting of DRASTIC model (Aller et al. 1987)

Depth to water table	Net recharge			Aquifer media			Soil media			Topography (slope)			Impact of vadose zone			Hydraulic conductivity		
	Range (ft)	T	Rating	Range (inches)	Rating	Type	Rating	Type	Rating	Range (% slope)	Rating	Type	Rating	Type	Rating	Range (gpd/ft ²)	Rating	Rating
0–5	10			0–2	1	Massive shale		Clay	1	0–2	10	Fresh rock	1			1–100	1	
05–15	9			2–4	3	Metamorphic/igneous		Clay	2	2–6	9	Sand, silt and clay	3			100–300	2	
15–30	7			4–7	6	Weathered metamorphic/igneous		Clay loam	3	6–12	5	Metamorphic rock	4			300–700	4	
30–50	5			7–10	8	Bedded sandstone/limestone/shale	5	Silty loam	4	12–18	3	Sand and gravel	6			700–1000	6	
50–75	3			> 10	9	Massive sandstone	6	Sandy loam	5	> 18	1	Limestone	6			1000–2000	8	
75–100	2					Massive limestone	6	Peat	8			Boulders/rubbles	9			> 2000	10	
> 100	1					Sand and gravel	8	Sand	9									
						Basalt	9	Gravel	10									
						Karst Limestone	10	Thin/absent	10									
	5**				4**		3**		2**		2**				5**			3**

** Depicts the weightage values allotted for all the seven hydrogeological factors (DRASTIC) employed for the present study

Fig. 4 Groundwater pollution potential map for the study area

(Offodile 2014; Fagbohun et al. 2017). Areas with runoff amount reaching 100 have been adjudged to be underlain by unfractured and totally impermeable lithological units and aided with high rainfall amount falling and reaching ultimately the surface water bodies. Areas with lower runoff amount or zero amount are underlain by highly permeable lithological units with not so much rain fall amount (Offodile 2014; Aladejana et al. 2016; Olabode 2019). High runoff observed in parts of Akure area is suggestive of the leading sources of water quality impairments on both groundwater and surface water. This impairment to the water quality in Akure area is due to the possible carriage of harmful substances during rain as runoff move from one area to another. The generated terrain-based map for Akure area shows that runoff ranges from 58 to 83 with the discharge areas possessing moderate runoff (Fig. 5). The recharge areas experience high runoff amount. Generally, areas delineated with moderate to high runoff in the study area were observed to be underlain with basement rocks such as charnockite and granite gneiss. These rocks are usually characterized by their low degree of weathering and fracturing. They are found to be impermeable thereby supportive of high runoff

events. Areas with the fair to moderate runoff amount were underlain by granitic rocks. These rocks are usually weathered, thereby supporting appreciable amount of infiltrating water from the runoff water. It was also observed that wells in recharge areas were found in elevated areas with attendant high runoff amount indicating probable high pollution potential or threat. The less pollution potential or threat will be experienced in the discharge areas found in depressed areas due to their low runoff amount.

Water quality

Water quality index results range from 13.32 to 109.94 with mean value of 38.970 for discharge areas, while water quality index results range from 19.18 to 55.35 with mean value of 32.187 for recharge areas (Tables 4, 5; Fig. 6). WQI results were compared with the delineated recharge and discharge areas, and it was discovered that seventeen wells fall into good to very good water type except for a well which falls into poor water type. In discharge areas, thirteen wells fall within good to very good water type category with four and one wells falling into poor and unsuitable water type

Fig. 5 Terrain-based runoff map of the study area

Table 4 Water quality index range and types of water

Range	Types of water	Recharge area	Discharge area
< 25	Excellent/very good water	5	5
26–50	Good water	12	8
51–75	Poor water	1	4
76–100	Very poor water	Nil	Nil
> 100	Water unsuitable for drinking purposes	Nil	1

categories, respectively. The chemical quality of the water samples from each of the identified recharge and discharge areas was all found to be within the acceptable limits of the World Health Organization (WHO 2011) standards for drinking and domestic purposes. The water quality index, however, disagrees with the results of the pollution potential and runoff amount.

Table 5 Various physico-chemical parameters for WQI

Parameters	Relative weight (W_i)	Standard concentration (S_i)
Calcium	0.19802	75
Magnesium	0.29703	50
Sodium	0.07426	200
Potassium	0.14857	100
Bicarbonate	0.14851	100
Sulphate	0.07426	200
Chloride	0.05941	250

Hydrogeochemistry and evolution of Akure groundwater

The trilinear plots (Piper diagram) (Fig. 7) show that the Ca-HCO_3 hydrochemical facies type dominated Akure area, a typical basement complex area. This water type is rich in alkaline earth cation (calcium) and weak acids (bicarbonates), thereby exceeding the alkalies and strong acids usually termed as alkaline waters. The water of this type

Fig. 6 Water quality index spatial distribution map for Akure area

is usually wholesome, natural and harmless for drinking purpose (Oyedele et al. 2019). The dominant anion (HCO_3^-) in the groundwater from recharge and discharge areas indicates carbonic acid silicate weathering of basement complex rocks as the probable source of bicarbonate in these water (Rogers 1989). All the sample representatives of recharge and discharge areas have Na/Cl ratio less than 1 reflecting the prevalence of ion-exchange process acting in the Akure area (Elango et al. 2003). All the groundwater samples from recharge areas have positive Chloro Alkaline Indices values which suggest the presence of direct ion exchange of Na and K from water with magnesium and calcium in the aquifer material/rocks underlying Akure area (Bozdog 2016).

Three groundwater samples in the discharge areas have negative CAI values suggesting the presence of ion (cation–anion) exchange, and this exchange is indirect (Schoeller 1967; Marghade 2015). The remaining fifteen groundwater samples with positive indices value greater than zero suggest the presence of strong direct ion exchange of Na and K from water with magnesium and calcium in the aquifer material/rock underlying Akure area and also introducing addition of Cl in the groundwater of the study area (Schoeller 1967; Marghade 2015; Bozdog 2016).

Accurate Gibbs plots for recharge and discharge of Akure area were obtained by the plots of TDS against ionic ratios ($\text{Na}/(\text{Na} + \text{Ca})$ and $\text{Cl}/(\text{Cl} + \text{HCO}_3^-)$). All the samples from the recharge and discharge areas fall both in the rock–water interaction dominance zones of the Gibbs diagram (Figs. 8a, b, 9a, b). The water–rock interaction dominance indicates that there is a strong interaction between the chemistry of the underlying rock lithologies and the chemistry of the groundwater. This was induced by intense weathering activities aided with long resident time spent by the water in the voids of the aquifer media. The contribution of precipitation in the waters of the study area, a typical rainforest environment, can not also be jettisoned. The conjunctive source of water from precipitation and chemical weathering activities in the subsurface media will aid high infiltration into the aquifer which will bring about projected increase in amount of recharge water to the unconfined aquifers in Akure. The plots also align in agreement with previous works carried out in similar geological environment and climate as the study area, a typical basement complex, which usually experience dominant activities of rock weathering, leading to the creation of the storage point for groundwater. The possibility that precipitation-weathering process has led to the increase

Fig. 7 Trilinear Piper diagram plots of dissolved ions

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 ● 339

in concentrations of all ionic species in the groundwaters from the recharge and discharge areas cannot be ruled out at all. No sample falls within the evaporation and precipitation dominance which presumed that the aquifer materials were made of highly permeable materials.

Descriptive analysis

The standard deviation values of EC (93 and 171) are the highest from the recharge and discharge areas (Tables 6, 7). The standard deviation of EC is lower in the recharge areas than the discharge areas, with their means values of 182 $\mu\text{S}/\text{cm}$, 260 $\mu\text{S}/\text{cm}$, 93 $\mu\text{S}/\text{cm}$ and 171 $\mu\text{S}/\text{cm}$. These values are in accordance with the water quality index result. Due to this observed high standard deviations in its concentrations, the result submits that its major contribution in the classification of the water type is related to its ionic strength. This is found to be responsible for the dissolution of all the other dissolved ions present in the waters.

Correlation matrix

Statistical analysis was performed on the data of physico-chemical parameters and major ion concentration to detect the relationship and differences between the groundwater samples. The average value of all the variables (Ca, Mg, Na, K, HCO₃, SO₄, Cl, TDS, EC) was determined and is tabulated as matrix (9 × 16) in Tables 8 and 9.

For the recharge areas, electrical conductivity shows strong to very strong correlation with Na (0.7), Cl (0.7) and TDS (0.9) which means that conductivity increases with dissolution of ions through ion-exchange reaction in the unconfined aquifer groundwater system of Akure area (Subba Rao 2002). The correlation evident between Na with Cl (0.7), Mg (0.6), TDS (0.7), and EC (0.7) suggests high mobility of ions aided with strong ionic strength. There is also strong positive correlation between Na and Mg (0.6), Ca and Cl (0.66) associated with anthropogenic activities, a characteristic of any urban setting. Na and Cl (0.7), Na and TDS (0.7), Na and EC (0.7), Cl-TDS (0.7) support the effectiveness in the mineralization and salinization of the groundwater in Akure, Cl-EC (0.7) and TDS-EC (0.9). The good positive correlations of Na-Cl (0.7) infer progressive reaction with feldspars from the minerals and groundwater in the unconfined aquifer system. The contribution of anthropogenic activities is also a major factor in an urban metropolis like Akure area thereby supportive of pollution.

For the discharge areas, electrical conductivity shows strong and very strong correlation with Na (0.8), Cl (0.7) and TDS (0.9); moderate correlation with Mg (0.5), which means that conductivity increases with dissolution of ions via ion-exchange or oxidation-reduction reaction in the unconfined aquifer groundwater system (Subba Rao 2002; Jeyaraj et al. 2006). The strong to very strong correlation evident between Na with Cl (0.7), TDS (0.8) and EC (0.8) and moderate correlation with Mg (0.5) and Ca (0.5) suggest

Fig. 8 a, b Gibbs plot for recharge areas

high mobility of ions aided with strong ionic strength. There is also significant positive strong correlation between Na and Mg (0.5), Ca and Mg (0.6) raising possible ion-exchange process but however masked by anthropogenic inputs from domestic and industrial wastes. Mg and Na (0.5), Mg and HCO_3^- (0.7), Mg and TDS (0.5), Mg and EC (0.5), Na and Cl (0.7), and Na and TDS (0.85) support the effectiveness in the mineralization and salinization of the groundwater in Akure. Strong to very strong correlation between the following variables: Na and EC (0.8), Cl and TDS (0.7) were

Fig. 9 a, b Gibbs plot for discharge areas

observed which support the effectiveness in the mineralization and salinization of groundwater in Akure. The correlation between Cl and EC (0.7), and TDS and EC (0.9) indicates the presence of anthropogenic input through leaching of pollutants into the groundwater. The good positive correlations of Na–Cl (0.7) also imply progressive reaction with feldspars in the aquifer system in the form of pollution.

Principal component analysis

The results of the principal component analysis are presented as Tables 10 and 11. Scree plots are presented in

Table 6 Descriptive statistics table for discharge areas

Descriptive statistics	Cappm	Caepm	Mgppm	Mgepm	Nappm	Naepm	Kppm	Kepm	HCO ₃ ppm	HCOepm	SO ₄ ppm	SO ₄ epm	Clppm	Clepm	Na/Clppm	Na/Clepm	TDS	EC	WQI
Mean	31.2785	1.563925	4.852241	0.404353	2.955556	0.128502	6.977778	0.178917	172.1556	2.822222	9.111111	0.189815	32.44944	0.914069	0.117032	0.180636	130	260.6111	38.97056
SE	3.124229	0.156211	0.827482	0.068957	0.372083	0.016178	0.692894	0.017767	28.82138	0.472482	1.157566	0.024116	5.079881	0.143095	0.019173	0.029593	20.23134	40.42755	5.141155
Median	27.7568	1.38784	4.732424	0.394369	2.85	0.123913	6.05	0.155128	146.4	2.4	9.5	0.197917	28.4	0.8	0.096948	0.149638	125.5	252	33.925
Mode	15.14	0.757		3.7		0.16087	5.8	0.148718	97.6	1.6	9.5	0.197917	12.43	0.350141	0.107042	0.165217	182		
SD	13.25498	0.662749	3.510709	0.292559	1.578615	0.068635	2.939699	0.075377	122.2788	2.00457	4.911138	0.102315	21.55211	0.607102	0.081343	0.125551	85.83431	171.5196	21.81207
Sample variance	175.6945	0.439236	12.32508	0.085591	2.492026	0.004711	8.64183	0.005682	14.952.1	4.018301	24.11928	0.010468	464.4934	0.368572	0.006617	0.015763	7367.529	29.418.96	475.7665
Kurtosis	-1.27739	1.56396	1.56396	-0.05762	-0.05762	-0.05762	-1.22026	-1.22026	7.598845	7.598845	-1.11803	-1.11803	0.806523	0.806523	2.893338	2.893338	0.821481	0.818552	6.136511
Skewness	0.418535	0.418535	0.856666	0.856666	0.680616	0.680616	0.121984	0.121984	2.411231	2.411231	-0.00565	-0.00565	1.146823	1.146823	1.663903	1.663903	1.047597	1.05034	2.101279
Range	38.69	1.9345	14.17755	1.181463	5.7	0.247826	9.6	0.246154	536.8	8.8	15.25	0.317708	72.77	2.049859	0.324451	0.500783	303	603	96.62
Minimum	15.14	0.757	0.008784	0.000732	0.7	0.030435	2.4	0.061538	48.8	0.8	1.75	0.036458	8.88	0.250141	0.024648	0.038043	36	75	13.32
Maximum	53.83	2.6915	14.18634	1.182195	6.4	0.278261	12	0.307692	585.6	9.6	17	0.354167	81.65	2.3	0.349099	0.538827	339	678	109.94
Sum	563.013	28.15065	87.34034	7.278361	53.2	2.313043	125.6	3.220513	3098.8	50.8	164	3.416667	584.09	16.45324	2.106568	3.251441	2340	4691	701.47
Count	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Confidence level (95.0%)	6.591547	0.329577	1.745835	0.145486	0.785027	0.034132	1.461878	0.037484	60.8078	0.996849	2.442252	0.05088	10.71761	0.301905	0.040451	0.062435	42.6844	85.29467	10.84689
WHO 2011	75	50	200	200	200	200	200	200	500	250	250	250	250	250	500	500	1500		

Table 7 Descriptive statistics table for recharge areas

Descriptive statistics	Cappm	Caepm	Mgppm	Mgepm	Nappm	Naepm	Kppm	Keppm	HCO3ppm	SO4epm	SO4ppm	Clppm	TDS	EC	Na/Clppm	WQI				
	Mean	23.54953	1.177476	3.267229	0.272269	2.244444	0.097585	5.922222	0.151852	149.1111	2.444444	6.611111	0.137731	28.40389	0.80011	91.05556	182.3333	0.090172	0.139179	32.18778
	SE	2.347479	0.117374	0.569413	0.047451	0.295635	0.012854	0.733447	0.018806	15.8902	0.260495	0.981075	0.020439	4.476274	0.126092	10.96771	21.92098	0.011306	0.017451	2.392694
	Median	21.86865	1.093433	2.624688	0.218724	1.9	0.082609	5.15	0.132051	134.2	2.2	5.625	0.117188	23.08	0.650141	72.5	146	0.072968	0.112625	30.085
	Mode	25.23	1.2615			1.4	0.06087	3.4	0.087179	97.6	1.6	4.25	0.088542	23.08	0.650141	53	106	0.06338	0.097826	#N/A
	SD	9.959512	0.497976	2.415816	0.201318	1.254274	0.054534	3.111753	0.079789	67.4164	1.105187	4.162351	0.086716	18.99122	0.534964	46.53205	93.00285	0.047967	0.074036	10.15134
	Sample variance	99.19188	0.24798	5.836166	0.040529	1.573203	0.002974	9.683007	0.006366	4544.97	1.221438	17.32516	0.00752	360.6664	0.286186	2165.232	8649.529	0.002301	0.005481	103.0497
	Kurtosis	1.625282	1.625282	-0.70001	-0.70001	-1.0634	-1.0634	-1.01954	-1.01954	0.986464	0.986464	-0.95513	-0.95513	0.840481	0.840481	-0.44691	-0.45382	2.521691	2.521691	-0.02615
	Skewness	1.216625	1.216625	0.559431	0.559431	0.485903	0.485903	0.351312	0.351312	1.150552	1.150552	0.498886	0.498886	1.382797	1.382797	1.017254	1.013398	1.471226	1.471226	0.77748
	Range	38.6888	1.93444	7.70635	0.642196	3.8	0.165217	10.6	0.271795	244	4	13.5	0.28125	60.35	1.7	134	268	0.190599	0.294186	36.17
Minimum	8.41	0.4205	0.137616	0.011468	0.7	0.030435	0.9	0.023077	73.2	1.2	0.5	0.010417	10.65	0.3	45	90	0.034662	0.0535	19.18	
Maximum	47.0988	2.35494	7.843966	0.653664	4.5	0.195652	11.5	0.294872	317.2	5.2	14	0.291667	71	2	179	358	0.225261	0.347686	55.35	
Sum	423.8915	21.19458	58.81012	4.900844	40.4	1.756522	106.6	2.733333	2684	44	119	2.479167	511.27	14.40197	1639	3282	1.623101	2.505221	579.38	
Count	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Confidence level (95.0%)	4.952749	0.247637	1.201357	0.100113	0.623736	0.027119	1.547438	0.039678	33.52539	0.549596	2.069888	0.043123	9.444112	0.266031	23.13985	46.24923	0.023854	0.036817	5.048143	
WHO 2011	75		50		200		200		500		250		250		500		1500			

Table 8 Correlation table for recharge areas

	Cappm	Mgppm	Nappm	Kppm	HCO ₃ ppm	SO ₄ ppm	Clppm	TDS	EC
Cappm	1								
Mgppm	0.340432	1							
Nappm	0.470463	0.64037*	1						
Kppm	−0.21899	0.063317	−0.15565	1					
HCO ₃ ppm	−0.19063	0.060695	−0.03715	−0.03246	1				
SO ₄ ppm	−0.05974	0.066774	0.167726	−0.43937	−0.05868	1			
Clppm	0.660213*	0.405971	0.728494*	−0.47386	−0.22483	0.130133	1		
TDS	0.471585	0.411509	0.7352**	−0.34162	0.268979	0.206262	0.717752*	1	
EC	0.469653	0.411559	0.734939*	−0.33819	0.268597	0.203747	0.715681*	0.999962**	1

*Depicts strong connection, **depicts very strong connection

Table 9 Correlation table for discharge areas

	Cappm	Mgppm	Nappm	Kppm	HCO ₃ ppm	SO ₄ ppm	Clppm	TDS	EC
Cappm	1								
Mgppm	0.654648*	1							
Nappm	0.594448*	0.551947*	1						
Kppm	0.236889	0.011256	0.304752	1					
HCO ₃ ppm	0.452545	0.78324*	0.179527	−0.09614	1				
SO ₄ ppm	−0.26963	0.057213	−0.05528	−0.26853	−0.00744	1			
Clppm	0.470332	0.339628	0.735713*	0.16907	0.024993	−0.08168	1		
TDS	0.456492	0.520376*	0.845934**	0.196197	0.141537	0.156079	0.724049*	1	
EC	0.455868	0.521194*	0.84645**	0.194716	0.141139	0.155047	0.724252*	0.999986**	1

*Depicts strong connection, **depicts very strong connection

Figs. 10 and 11. They include the loading for the rotated component matrix, eigenvalues for each component, and the percent and cumulative percent of variance explained by each component and communality, indicating the proportion of variance of each variable controlled by the set of components. From Tables 10 and 11, three principal components were extracted with eigenvalue more than 1 which together account for recharge and discharge areas are 77.151% and 82.173% of the total variance in the dataset, in which the first principal component, second principal component and third principal component for recharge and discharge areas are 46.881% and 15.560%, 14.710% and 48.722%, 18.000% and 15.451%, respectively. The communalities of all the chemical variables range from 0.541 to 0.920, and 0.563 to 0.947 for recharge and discharge areas indicating different contributions in the changing quality of groundwater in Akure (Marghade 2015). However, all the variables have their communalities greater than 0.50.

Principal component analysis for recharge areas

Na, Cl, TDS and EC have high loading factor (0.863, 0.881, 0.915 and 0.913) and moderate positive loading

of Ca (0.657), Mg (0.584) on the principal component 1 according to Marghade 2015 classification of principal component (Table 10). The positive PC loadings are usually used to understand the relative contribution of the chemical variables on the groundwater quality (Marghade 2015). The combinations of high loading factor for the following dissolved Ca, Mg, Na, Cl ions and EC, observed on the first principal component (Table 10), suggest association of various hydrogeochemical processes responsible to enrichment of more mineralized water (TDS) but masked by anthropogenic urban activities. The moderate loading of Ca (0.657) suggests the release of this cation from the chemical weathering of rocks containing the following minerals; feldspar, pyroxene, mica and clay minerals in these rocks (granitic gneisses, charnockites and granites). The high loading factor of Na (0.863) and Cl (0.881) suggest non-lithological origin (absence of sedimentary rocks in basement complex area), but connected to culturally influenced shallow water overflow or unwanted causes typical of an urban area (Lawrence and Upchurch 1982). This, however, gives a picture of the rate at which the wells are being recharged and the degree of weathering of the aquifer medium. Na and Cl have the highest loading in

Table 10 Principal component analysis result for recharge areas (3 components extracted)

Chemical parameters	I	II	III	Communality	Initial
Ca	0.657**	0	−0.375	0.64	1
Mg	0.584*	0.435	0	0.541	1
Na	0.863***	0	0	0.791	1
K	−0.433	0.74**	0	0.766	1
HCO ₃	0	0	0.933****	0.886	1
SO ₄	0	−0.728	0	0.602	1
Cl	0.881**	0	−0.321	0.879	1
TDS	0.915****	0	0	0.92	1
EC	0.913****	0	0	0.918	1
%Total variance	46.881	15.56	14.71		
%Cumulative	46.881	62.44	77.151		
Eigenvalues	4.219	1.4	1.324		

*Depicts low positive, **depicts medium positive, ***depicts high positive, ****very high positive

Table 11 Principal component analysis result for discharge areas (3 components extracted)

Chemical parameters	I	II	III	Communality	Initial
Ca	0.728**	0.309	−0.37	0.763	1
Mg	0.738**	0.609**	0	0.919	1
Na	0.916****	0	0	0.878	1
K	0	−0.356	−0.603	0.563	1
HCO ₃	0.39	0.86***	0	0.893	1
SO ₄	0	0	0.876***	0.768	1
Cl	0.779***	−0.336	0	0.719	1
TDS	0.906****	0	0	0.947	1
EC	0.906****	0	0	0.947	1
%Total variance	48.722	18	15.451		
%Cumulative	48.722	66.722	82.173		
Eigenvalues	4.385	1.62	1.391		

*Depicts low positive, **depicts medium positive, ***depicts high positive, ****very high positive

terms of ions, which indicate their contribution among the water quality parameters, raising the pollution concern in waters of Akure area.

On the second principal component (PC2), the component is cation dominated of K which have high-positive loading of (0.740). The high loading of K could be traced to the dissolved minerals such as feldspars (orthoclase and microcline), micas and clay minerals released from the weathering of the host rocks (granitic gneisses, charnockites, and granites).

On the third principal component (PC3), only HCO₃ have high-positive loading of (0.933). The strong loading of HCO₃ is attributed to the reaction of feldspar minerals with carbonic acid in the presence of water (Elango et al. 2003). Meanwhile, the deficiency of sulphate ions in all the three principal components suggests that the waters have more cations of Mg and Ca in the groundwater (Khan 2015).

Principal component analysis for discharge areas

Ca, Mg, Na, Cl, TDS and EC have high loading factor (0.728, 0.738, 0.916, 0.779, 0.906 and 0.906) on the principal component 1. The combinations of Ca, Mg, Na, Cl ions and EC, influencing the high-positive loadings observed on the first principal component (Table 11), suggest that the first principal component is associated with similar hydrogeochemical processes as explained for the recharge areas responsible for the enrichment of more mineralized water (TDS) through ionic strength processes though masked by anthropogenic activities. The high loading factor of Na (0.916) and Cl (0.779) also suggests non-lithological origin (absence of sedimentary in the basement complex), but associated with culturally influenced surface runoff or waste sources typical of an urban area (Lawrence and Upchurch 1982). The very high positive loading could have resulted from the formation of clay products from the weathering of the underlying rocks.

Fig. 10 Scree plot for recharge area **Fig. 11** Scree plot for discharge area

This was aided by their slow nature of drainage conditions (Hem 1991). This, however, gives a picture about the rate at which the wells are being recharged and degree of weathering of the aquifer medium. Na and Cl have the highest loading in terms of ions, which indicate their contribution among the quality parameters, which control the pollution in Akure area.

On the second principal component, only HCO_3 have high-positive loading of (0.860) and moderate positive loading of Mg (0.609). The strong loading of HCO_3 is attributed to the reaction of feldspar minerals with carbonic acid in the presence of water (Elango et al. 2003). It also indicates the strong interaction of infiltrating recharging water (precipitating water), with the soil and/lithology. During recharge,

water absorbs large amount of CO_2 , released from the soil due to the decay of organic matter, root respiration, etc., and converts into HCO_3 during weathering reactions (Jacks 1973; Berner and Berner 1987). The magnesium ions are attributed to the weathering of the minerals such as amphiboles, olivine, pyroxene and clay minerals which are the major constituents of the host rocks.

On the third principal component, only sulphates have high-positive loading of (0.876) which signifies the depletion of cations in the groundwater.

For *Q-mode hierarchical analysis, ward linkage method revealed the results of parameters and are presented in two groups each for the recharge and discharge areas in Figs. 12 and 13.*

For the *recharge areas*, fifteen samples from recharge areas classified in Group 1 show good correlation with the concentration of K, HCO_3 , Cl, TDS, EC and SO_4 , while Group II comprises three samples displaying good correlation of concentration of Ca, Cl, TDS and EC.

For the *discharge areas*, ten samples from discharge areas classified in Group 1 show good correlation with the concentration of Mg, Cl, HCO_3 and SO_4 , while Group II comprises eight samples displaying good correlation of high concentration of Ca, Na Mg, HCO_3 , TDS and EC.

Conclusion

Recharge and discharge areas of a growing urban area like Akure area have been delineated with the aid of elevation and well data. The quality of groundwater in these areas falls within the acceptable limits of the World Health Organization (WHO) standards for domestic purpose. The Ca-HCO_3 hydrochemical facies type dominates the association of ions present in the samples which was believed to be consequent of the conjunctive activities of the intense weathering (rock–water and silicate weathering) and precipitation prevailing in Akure area. These activities contributed to the increasing concentrations of dissolved ions in the recharge and discharge areas as observed from the correlation and multivariate statistical studies. The results also showed that recharge areas have higher pollution potential values and runoff amount than the discharge areas, which indicates that groundwater in recharge areas is more susceptible to pollution than that in discharge areas. Among many factors or sources that are responsible for the high pollution potential in the recharge areas, critical ones include appreciable dissolved ions in the waters, high degree of weathering and anthropogenic activities which were not the case in the discharge areas making it less prone to pollution. This study has revealed

Fig. 12 Dendrogram for recharge area

Fig. 13 Dendrogram for discharge area

the present state of the quality of water representative of recharge and discharge areas and provided insights into the probable causes of pollution in this area. Areas prone to pollution should be checked by quick reduction and decentralizing of urban activities, and also formulation and enforcement of the best urban planning policies should be adopted by the local government authorities.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest in this manuscript.

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