

Groundwater quality for socio-economic purposes in central-southern parts of Ghana: Implication from multi-technique approach

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Abstract

Natural and anthropogenic activities are known to have continuously affected the domestic and other socio-economic suitability of groundwater, notwithstanding being a reliable source for domestic and other socio-economic usage. This justifies the need for its routine quality assessment. In this study, the safety of groundwater in the area for socio-economic usage was assessed. The study characterized groundwater evolution, safety for drinking, and agricultural usage, using hydrochemical indexical proxies, water quality indices, and regression modeling. The results of physico-chemical concentration revealed $TDS > HCO_3^- > Ca^{2+} > Cl^- > Na^+ > NO_3^- > Mg^{2+} > SO_4^{2-} > K^+ > F^- > CO_3^{2-}$ with $Na-HCO_3$ and $Ca-SO_4$ as the main water types. Except for F^- and NO_3^- having high values above WHO standards in some communities, the physicochemical parameters are within allowable recommended levels. The dominant groundwater mineralization control is mineral dissolution resulting in a reverse ion exchange process within the catchment although the input of anthropogenic activities cannot be precluded from SO_4^{2-}/Cl^- and NO_3^-/Cl^- values. The WQI, PPI, and WPI suggest that the area has 63.65%, 37%, and 100% excellent to good waters, poor waters, and moderate to highly polluted waters, respectively. The WPI model has better performance with higher R, R², and low standard error estimate (SSE) values than that for WQI, and should be used in the quality forecasting of groundwater from the study instead of WQI. Except for RSC and PI values, the groundwater is safe for irrigation purposes.

Keywords

Hydrochemistry; regression model; indexical proxies; socio-economic purposes; central-southern Ghana

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DOI: 10.26796/jenrm.v10i1.251

Received: January 12, 2024; Received in revised form: March 11, 2024; Accepted: April 18, 2024; Published: April 30, 2024

Contents

1	Introduction	1
2	Materials and Methods	2
2.1	Study area	2
2.2	Sample collection and analytic procedure	3
2.3	Mineralization assessment	3
2.4	Water quality assessment	3
2.5	Regression modeling	3
2.6	Irrigation assessment	3
3	Results and discussion	4
3.1	The physicochemical concentration	4
3.2	Water facies	5
3.3	Controls of groundwater mineralization	5
3.4	Water quality assessment for domestic usage	6
3.5	Quality Forecasting using MRM	8
3.6	Suitability for Agricultural Purposes	9
4	Conclusion and Recommendation	11
	References	11

1. Introduction

1 Globally, groundwater is the safest water source for human daily needs including domestic, irrigation, industrial, agriculture, and other socioeconomic purposes (Li et al., 2019; Wu et al., 2019; Chidichimo et al., 2020). To one-third of the world's population, groundwater is a known source of water supply (Falkenmark, 2005) and the known reliable and safe source of water available in semi-arid and arid climatic zones globally (Li et al., 2017; Wu et al., 2019; Ahmed et al., 2019). Groundwater is reported to have fulfilled only 20% of human needs globally (Stone et al., 2020). It is estimated that about 70% of groundwater is used for farming while 21% of the resources is used for drinking and other domestic activities according to Stone et al. (2020). Also, the fast depletion of surface water resources has increased the demand for the resource for commercial agricultural activities (Egbueri and Agbasi, 2022). Arid to semi-arid regions often have limited annual rainfall, which exacerbates their demand for good-quality groundwater (Gao et al., 2019; Ahmed et al., 2019). Groundwater generally, is considered to be

fresh and does not need any rigorous treatment before usage according to Yidana et al. (2012) and Sunkari et al. (2019), reports on groundwater resources being contaminated and unsuitable for socio-economic activities of man have been well documented (Zango et al., 2019; Ahmad et al., 2020; Sunkari et al., 2020). The reported factors responsible for groundwater contamination include: water-rock interaction, increased human activities e.g. industrialization, commercial farming, waste disposal, and mining activities are the main factors and activities leading to groundwater contamination (Sunkari and Abu, 2019; Chidichimo et al., 2020; Zango et al., 2021). Groundwater contamination has become a universal problem that needs continuous chemical (quality) evaluation to unravel the causes of its chemical modification and contamination. This has over the years been carried out using hydrochemical parameters concentration levels relative to WHO standards, selected ratio proxies e.g. Na^+/Cl^- , $Na^+/(Ca^{2+} + Mg^{2+})$, NO_3^-/Cl^- , their bivariate discriminant plots among others (Yidana et al., 2012; Kumar et al., 2018; Sunkari et al., 2021). Also, multivariate statistical approaches have proven to be reliable in groundwater mineralization assessment (Yidana et al., 2018; Zango et al., 2021). However, in this 21st century with its scarce groundwater resources coupled with extensive groundwater contamination-prone activities, groundwater quality forecasting has become the recent and fast-evolving approach to groundwater quality assessment (Egbueri et al., 2020; Egbueri, 2023). To this end, adopting multivariate linear regression (MRL) modeling as a groundwater quality forecasting via prediction modeling has proven effective and has been extensively applied in this regard (Kouadri et al., 2021; Kontos et al., 2022). This will enhance groundwater monitoring and management to ensure its quality sustainability even when in scarce quantity.

The central-southern parts of Ghana are within the semi-arid zone of the country. This part of Ghana depends largely on agriculture and the biennial rainfall in these parts makes the catchment a suitable location for agricultural produce to thrive. However, the challenges of surface water availability have worsened, and the need to augment the rainfall water with groundwater via irrigation to sustain the agriculture sector in this area is imperative. The levels of sodium, magnesium, the adsorption rate of sodium, and the level of residual sodium and carbonate in groundwater targeted for irrigation need to be evaluated due to the harmful effects of high levels of these aforementioned groundwater ions pose to the cultivated soils and, on the crops (Wagh et al., 2016; Gautam et al., 2023). For this reason, sodium percentage (% Na), index of permeability (PI), residual sodium carbonate (RSC), and Kelly's ratio (KR) by Wilcox (1948), Eaton (1950), Richard (1954), Paliwal (1972) and Kelly (1963) respectively were applied in the assessment of the

groundwater acceptability for agricultural purposes.

The study examines the causes of groundwater mineralization, and the acceptability for domestic, and other socio-economic purposes with a focus on agricultural activities within the catchment, from a multi-technique approach involving hydrochemistry, discriminant diagrams, water quality indices, multiple linear regression modeling (MRM), and irrigation indices. The findings of the study will enhance groundwater monitoring and management, forecasting, and planning of irrigation farming in the area. This will culminate in an effective decision-making process regarding groundwater usage in the catchment.

2. Materials and Methods

2.1 Study area

Geologically, the area is within the Paleoproterozoic Birimian geological province consisting of granitoids, volcanic and sedimentary rocks (Figure 1), and metasedimentary rocks (Kesse, 1985; Key, 1992).

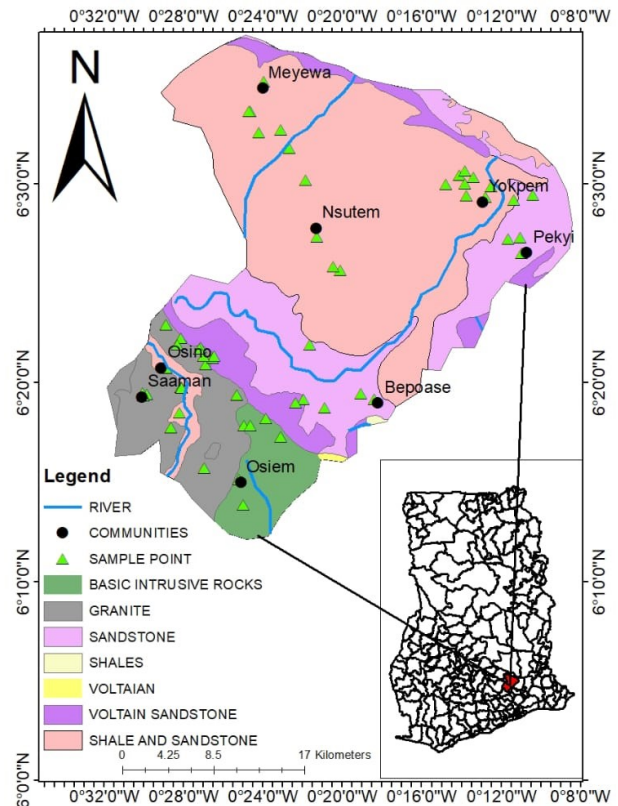


Figure 1. The geological setting of the area within the sample locations in perspective.

This geological domain defined as the Birimian Super-group in Ghana has alternating belts and basins characterized by volcanic rocks and sedimentary rocks, respectively. The Birimian terrain is a typical crystalline geological terrain where there is poor primary porosity and permeability (Key, 1992), hence groundwater within this domain

is within discontinuities following deformation as well as within the regolith where the aquifers are termed weathered aquifers (Tay et al., 2019). The mode of recharge of the groundwater aquifers within these terrains globally is by and large via precipitation, and has been critical to the water budget of the country according to Tay et al. (2019). The area is within the forest zones of Ghana and has 2 rainfall sessions within a year allowing for all-year-round recharging of the aquifers within the area generally. As a typical humid climatic zone, evapotranspiration is low due to the thick forest in this part of the country and hence groundwater is almost always available for human usage unlike in the semi-arid and arid parts in northern Ghana.

2.2 Sample collection and analytic procedure

The study was conducted using 55 groundwater samples collected from boreholes within the catchment following standard sample collection procedures outlined in APHA (1998) between February and March 2021. Sterilized unused bottles were used in the collection of the samples and later submitted to the laboratory for analysis. The physicochemical parameters analytical procedure was per the analytical procedures of APHA (1998, 1995) in analyzing the physicochemical parameters for groundwater studies. The reliability of the results obtained from the laboratory was checked through the ion balance error (IBE) method using Domenico and Schwartz's (1990) equation. The results are certified to be suitable and reliable to make this assessment with an IBE value that is within ± 10 (Adimalla and Wu, 2019).

2.3 Mineralization assessment

The mineralization evaluation of the groundwater in the area was done using indexical proxies, saturation index (SI), and some selected discriminant plots e.g. Gibbs plot, using Grapher.

2.4 Water quality assessment

There are several indices for groundwater assessment, however, those that were used to assess the groundwater acceptance level in the area were the water quality index (WQI) of Horton (1965) equation 1- 4, percentage pollution index (PPI) by Pacheco and Van Der Weijden (1996) equation 5 and water pollution index (WPI) of Hossain and Patra (2020) equation 6.

$$W_i = W_j / \sum_{i=1}^n W_j \quad (1)$$

$$q_i = (C_m / C_s) \times 100 \quad (2)$$

$$SI = W_i \times q_i \quad (3)$$

$$WQI = \sum SI \quad (4)$$

With W_j as the provisional weight for the i^{th} water quality parameter, W_i as relative weight of the i^{th} parameter, q_i is the rating scale of the quality, C_m is the measured i^{th} parameter concentration level and C_s representing WHO standard.

$$PPI = [(Cl^- + SO_4^{2-} + NO_3^-) / (Cl^- + SO_4^{2-} + NO_3^- + CO_3^{2-} + HCO_3^-)] \times 100\% \quad (5)$$

$$WPI = 1 / n \sum_{i=1}^n PLI \quad (6)$$

$$PLI = 1 + (Mc \sim Sc / Sc) \quad (7)$$

with Mc and Sc as the measured concentration of the WHO acceptable limit of the i^{th} parameter, respectively.

2.5 Regression modeling

A multilinear regression model (MRM) was generated taking into consideration parameters with a ρ -value of < 0.05 at a confidence level of 95%. The performance of the model depends on how close the R and R^2 are to 1, with an MRM with R and R^2 of 1 being an indication of a model with good performance. The model generated in the process is a mathematical function

$$y = b^0 + b_{x_2} + b_{x_2} + \dots + b_{ix_i} + \varepsilon \quad (8)$$

where b_0 represents the regression constant, x_i is the i^{th} predictor's value, b_i is the correlation coefficient of the i^{th} predictor, and ε is the error for the individual i^{th} parameter which also indicates the variations in the observed values.

2.6 Irrigation assessment

The assessment of groundwater suitability for irrigation purposes was from several equations. High sodium concentration in groundwaters meant for agricultural purposes could be of threat to cultivated crops, hence, sodium concentration which is often assessed by calculating the sodium percentage in groundwater, is a relevant indicator in groundwater evaluation for agricultural purposes (Chung et al., 2014). The % Na (Wilcox, 1948), magnesium hazard ratio (MHR) (Paliwal, 1972), permeability index (PI) (Doneen, 1964), sodium adsorption ratio (SAR) (Richard, 1954), residual sodium carbonate (RSC) (Eaton, 1950), and Kelly's ratio (KR) (Kelly, 1963), have been applied in the evaluation of how suitable groundwater is for irrigation purposes.

$$\%Na = ([Na + K]/[Ca + Mg + Na + K]) \times 100 \quad (9)$$

$$SAR = Na^+ / \sqrt{([Ca^{2+} + Mg^{2+}]/2)} \quad (10)$$

$$RSC = (HCO_3^- + CO_3^{2-}) \sqrt{Ca^{2+} + Mg^{2+}} \quad (11)$$

$$MHR = [Mg^{2+} / (Ca^{2+} + Mg^{2+})] \times 100 \quad (12)$$

$$KR = Na^+ / (Ca^{2+} + Mg^{2+}) \quad (13)$$

$$(Na + (HCO_3)^{\frac{1}{2}}) / (Ca + Mg + Na) \times 100 \quad (14)$$

$$PS = [Cl / (SO_4^{2-})] / 2 \quad (15)$$

3. Results and discussion

3.1 The physicochemical concentration

The general measured parameters of the samples collected have been presented in Table 1. pH based on a defined scale (0-14), is a measure of how acidic or alkaline water is. The pH levels in the groundwater from the study area range from 5.63 to 8.35 with an average of 7.40 (Table 1) suggesting that the groundwater in the area is moderately acidic to moderately alkaline based on Hounslow's (1995) classification. The source of the low pH values in the groundwater could be attributed to the reaction of oxygen with iron sulfide (FeS₂) minerals (Candella and Morell, 2009) within the catchment. Another source of low pH in groundwater is the dissolution of carbon dioxide in rainwater to form weak carbonic acid (H^2CO_3) and hydrogen ions (H^+).

The release of hydrogen ions into the water decreases the pH of the water (Kemker-Christine, 2013). The electrical conductivity (EC) of groundwater is considered acceptable within the range of 500 – 700 $\mu S/cm$ according to WHO (2017). The groundwater samples collected have an EC range of 0.01 $\mu S/cm$ to 920 $\mu S/cm$ with an average of 183.83 $\mu S/cm$ (Table 1). All the samples are within acceptable levels except in 1 sample location, thus Osiem. This could be controlled by the content of the TDS in the groundwater as the Osiem community recorded the highest level of TDS in the area. The acceptable level of total hardness (TH) of groundwater for domestic usage is 200 mg/l (WHO, 2017). The samples studied have TH levels within the range of 1.85 mg/l

Table 1. Statistical summaries of the physical and chemical parameters of the studied samples relative to WHO (2017) standards, MAL = Maximum allowable levels

Parameters	Min	Max	Average	STDEV	MAL of WHO (2017)
pH	5.63	8.35	7.4	0.72	6.5 – 8.5
EC ($\mu S/cm$)	0.01	920	183.83	191.69	500 - 700
TH (mg/l)	1.85	221.46	66.7	58.01	200
Alk (mg/l)	3.5	229	71.04	61.67	-
F ⁻ (mg/l)	0	1.7	0.2	0.26	1.5
NO ₃ ⁻ (mg/l)	0	102.3	9.1	15.78	50
Cl ⁻ (mg/l)	1.7	164.2	15	24.36	250
SO ₄ ²⁻ (mg/l)	0.2	44.6	5.7	7.98	200
CO ₃ ²⁻ (mg/l)	0	2.1	0.1	0.28	NA
HCO ₃ ⁻ (mg/l)	4.3	275.1	86.5	75.04	NA
Na ⁺ (mg/l)	1	85.7	13.2	15.11	200
K ⁺ (mg/l)	0.2	22.4	2.6	3.21	12
Ca ²⁺ (mg/l)	0.4	60	16.7	15.59	200
Mg ²⁺ (mg/l)	0.2	25	6.2	5.44	150
TDS (mg/l)	8.9	494.7	109	89.11	1000

to 221.46 mg/l with a value of 66.70 mg/l (Table 1). The TH is generally within acceptable levels for usage in the area. Alkalinity is the measure of the ability of groundwater to neutralize its acidity (Lal et al., 2022). This, in groundwater, is mainly controlled by carbonate, bicarbonate, borate, and silicate minerals according to Lal et al. (2022). Groundwater with alkalinity levels ≥ 9 is considered to be alkaline according to Lal et al. (2022). The samples alkalinity ranges from 3.50 to 229 with a mean value of 71.04 in the study area. The general ionic concentration is in the order; $TDS > HCO_3^- > Ca^{2+} > Cl^- > Na^+ > NO_3^- > Mg^{2+} > SO_4^{2-} > K^+ > F^-$, and CO_3^{2-} with the following average concentration levels: 109.0, 86.5, 16.7, 15.0, 13.2, 9.1, 6.2, 5.7, 2.6, 0.2, and 0.1, respectively (Table 1). The dominant anions; HCO_3^- , Cl^- , NO_3^- , and SO_4^{2-} in groundwater, could be attributed to carbonates and gypsum dissolution as well as anthropogenic activities of agriculture sources involving the application sulfate-bearing chemical fertilizers within catchments of the aquifers of the groundwater (Hassani et al., 2016). Cations in groundwater are the dissolution effects of phyllosilicate minerals like albite, anorthite, biotite, and microcline (Sunkari et al., 2022). Carbonate dissolution could also account for the calcium and magnesium ions. Calcium ion abundance over sodium as well as the Mg^{2+} dominance over K^+ could be as a result of the ion exchange process where Ca^{2+} and Mg^{2+} replace Na^+ and K^+ after their release during a reverse ion exchange process within the aquifer (Adimalla and Wu, 2019; Liu et al., 2020). Except for high levels of F^- and NO_3^- above WHO (2017) standards in Owusukrom and Osiem communities, respectively, all the other parameters are within acceptable levels compared to WHO (2017) acceptable limits. The style of groundwater mineralization can be said to be due to mineral dissolution, hence geogenically controlled (Sunkari et al.,

2022; Zango et al., 2022), although the effect of human activities of agricultural origin, cannot be ruled out in the alteration of the groundwater chemistry processes in the area.

3.2 Water facies

The water type classification in the area was carried out using the Piper (1953) diagram (Figure 2). Two main water types of $Na^{\sim}HCO_3$ and $Ca^{\sim}SO_4$ transformed into $HCO_3^{\sim}Na$ and $Cl(SO_4)^{\sim}Na(Mg)$ (Figure 2). The dominant water type ($Na^{\sim}HCO_3$) and the subordinate type ($Ca^{\sim}SO_4$) can both be attributed to geogenic sources resulting from rock-water interactions within the aquifers in the catchment. Silicate mineral dissolution (e.g. albite and anorthite), carbonate minerals (calcite and dolomite), and gypsum might have significant effects on the alteration of the groundwater chemistry within the catchment.

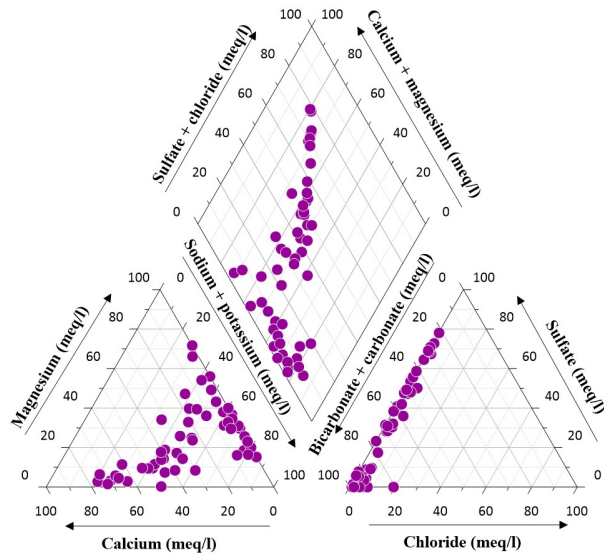


Figure 2. Classification of the groundwater types after Piper (1953)

3.3 Controls of groundwater mineralization

3.3.1 Anthropogenic effects

Anthropogenic activities have contributed significantly to the alteration of the quality of groundwater (Lee and Song, 2007; Ahmad et al., 2019). SO_4^{2-} source in groundwater has been linked to sources including run-offs/ leaching of sulfate-containing chemical fertilizers from farmlands (Lee and Song, 2007). Nitrate contents in groundwater have also been attributed to organic manure and chemical fertilizers (Liu et al., 2006), whereas the Cl^- concentrations in groundwater could be due to intrusion of saline or seawater (where there is a sea within proximity to the catchment) or from other sources including silicate mineral dissolution, domestic effluent, and animal waste (Liu et al., 2020). SO_4^{2-}/Cl^- and NO_3^-/Cl^- have been used to assess the level of impact human activities have

on groundwater mineralization, with SO_4^{2-}/Cl^- values of 0.1 – 0.15 suggesting saline water intrusion (where the catchment is close to a sea) else could be due to other sources including silicate mineral dissolution and ratio values > 0.15 suggestive of anthropogenic activities effect (Lee and Song, 2007). Also, NO_3^-/Cl^- values > 1 mean anthropogenic activities whereas < 1 could be attributed to the effect of seawater intrusion and others including animal waste, silicate mineral dissolution, or chemical fertilizer sources. The studied samples had 7 samples with SO_4^{2-}/Cl^- values between 0.1 – 0.15 while 48 samples had ratio values > 0.15 (Table 3). This implies that the groundwater has experienced anthropogenic activities within the area with possible influence from sulfate fertilizer influence and other factors like silicate mineral dissolution or domestic waste since there is no known seawater or saline water source within to have accounted for the 12.72% (7 samples with ratio values 0.1 – 0.15) (Table 3). From the NO_3^-/Cl^- values, 13 samples have ratio values > 1 while 42 samples have ratio values < 1 (Table 3). It could be said that anthropogenic activities have contributed significantly to the groundwater from NO_3^-/Cl^- values since there is no sea within the catchment to explain the 13 samples with > 1 values according to Liu et al. (2006).

3.3.2 Ion exchange effects

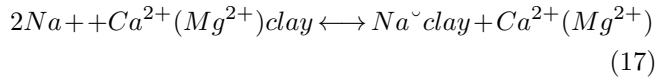
Ion exchange within groundwater aquifer system is known to have had an impact on the groundwater chemical evolution over the years has been elucidated using Schoeller's (1965) chloro-alkaline indices (CAI) 1 and 2 through equations 16 and 17.

$$CAI - 2 = \frac{Cl^- ((Na^+ + K^+))}{((SO_4^{2-}) + HCO_3^- + CO_3^{2-}) + NO_3^-} \quad (16)$$

From equations 16 and 17, when CAI-1 and CAI-2 values are positive, then reverse ion exchange has taken place with Ca^{2+} and Mg^{2+} replacing Na^+ and K^+ within the aquifer, whereas negative CAI-1 and CAI-2 values implies forward ion exchange.

In the samples studied, CAI – 1 value ranges from -3.1 – 163.6 and an average value of 13.3 while CAI – 2 values are in the range of 1.6 – 163.6 with an average of 14.8 (Table 2). The reverse ion-exchange process (RIEP) is the major ion exchange process in the catchment from chloro-alkaline indices with only two samples having negative CAI – 1 value, recorded in the Yokpem and Korhweh Kuminyam communities in the area. With the dominant RIEP, the excess of $Ca^{2+} + Mg^{2+}$ over $HCO_3^- + SO_4^{2-}$ will shift the chemical reaction to the left side of the stoichiometric equation (equation 18) according to McLean and Jankowski (2000). The ion exchange processes within the area are predominantly within the aquifer-facilitated process and by implication, a water-rock interaction pro-

cess controlled the ion exchange process within the catchment. Also, the Na/Cl values > 1 suggest a replacement of sodium ions by calcium ions in a reverse ion exchange process. 27 samples had Na/Cl values > 1, representing 49.1% of the samples, indicating a reverse ion exchange effect within the area.



3.3.3 Rock-water interaction

Several ionic proxies e.g. Na^{+}/Cl^{-} , $Na^{+}/[Na^{+} + Ca^{2+}]$, $Mg^{2+}/[Ca^{2+} + Mg^{2+}]$, and Ca^{2+}/Mg^{2+} aside from the water-rock interaction bivariate discriminant diagram of Gibbs (1970) for the assessment of groundwater mineralization (Maya and Loucks, 1995; Yidana et al., 2018, Sunkari et al., 2022). The values of these ratios are > 1 [$Na^{+}/(Na^{+} + Ca^{2+})$], < 1 [Na^{+}/Cl^{-}], < 1 [$Mg^{2+}/(Ca^{2+} + Mg^{2+})$], and ≥ 2 (Ca^{2+}/Mg^{2+}) are indicative of silicate minerals dissolution with < 2 ratio value of Ca^{2+}/Mg^{2+} suggestive of carbonate mineral dissolution according to Kumar et al. (2018). In the samples studied from the Osino catchment, $Na^{+}/[Na^{+} + Ca^{2+}]$, $Mg^{2+}/[Ca^{2+} + Mg^{2+}]$, Na^{+}/Cl^{-} , and Ca^{2+}/Mg^{2+} have 45, 55, 27, and 50 samples with ratio values < 1, < 1, > 1, and ≥ 2 , respectively in the area. These represent 81.1%, 100%, 49.1%, and 90.9% of silicate mineral dissolution from these selected ratios. Carbonate rocks are not known in the area, however, carbonate-bearing minerals e.g. ankerite [$Ca(Fe, Mn, Mg)(CO_3)_2$] and siderite ($FeCO_3$), are calcite-bearing minerals that are common in high-temperature minerals and are part of the ore mineralogy in the Birimian (Amponsah et al., 2016), could be the source of the carbonate mineral dissolution from the Ca^{2+}/Mg^{2+} . Mineral dissolution has been an active process altering the hydrochemistry in the catchment with silicate minerals being the dominant mineral dissolution process.

Gibbs plot has been used over the years in assessing the effect of evaporation, weathering, and atmospheric precipitation on groundwater chemistry using bivariate plots of TDS against $Na^{+}/(Na^{+} + Ca^{2+})$ and $Cl^{-}/(Cl^{-} + HCO_3^{-})$. Plotting the samples on this diagram (Figure 3), have the samples plot within the weathering dominance and evaporation effect zones (Figure 3). This bivariate plot means that although water-rock interaction is dominant, the evaporation effect has had a significant influence on the hydrochemistry of the area.

From the ratios used together with the discriminant diagrams of Gibbs (1953), the hydrochemistry within the catchment is modified by the dissolution of rock-forming minerals via rock-water interaction and evaporation. The dominant mineral dissolution is that of silicate mineral dissolution relative to carbonate mineral dissolution. With no known carbonate rocks within the catchment and as

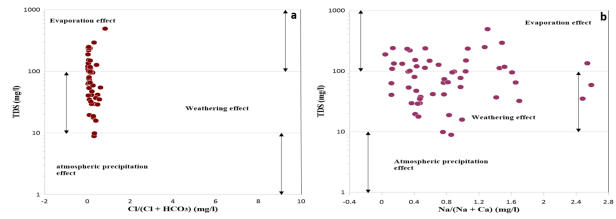


Figure 3. Water-rock effect on the groundwater quality in the area according to Gibbs (1970)

Table 2. Statistical summaries of selected proxies for groundwater characterization

Proxies/Indices	CAI - 1	CAI - 2	Na/(Na+Ca)	Mg/(Ca+Mg)	Na/Cl	NO3/Cl	SO4/Cl
Min	-4145.2	-47.92	-7.16	0.08	2.4	0	0.01
Max	0.16	2.25	15.3	6.27	4066.99	3.6	2.53
Mean	-374.68	-6.95	2.7	0.65	363.42	0.8	0.54

a Birimian terrain, the carbonate mineral dissolution indication could be explained by ankerite or siderite or both, which are known ore-controlling minerals in the Birimian and are often associated with mafic minerals in Precambrian terrains.

3.3.4 Saturation Index (SI)

Mineral dissolution influence on the changes in the hydrochemistry within the catchment was examined by computing the SI of a suite of minerals to assess their level of contribution to groundwater chemistry (Sunkari et al., 2019). This evaluation was done using PREEQC (Parkhurst and Appelo, 1999) and has been extensively applied. To assess the possible minerals that dissolved within the aquifers to modify the groundwater within the study area, the SI indices of a suite of minerals were evaluated (Table 3). Several iron oxides, silicate minerals, and calcite have SI values > 0 suggesting the dissolution of these minerals and an indication that these minerals played an integral part in the hydrochemical modification in the catchment (Table 3 and Figure 4). The silicate minerals talc, K-mica, anorthite, and albite are most likely due to mafic rocks weathering (chemical weathering) and shallow aquifers within the catchment. Only calcite is the carbonate mineral with SI > 0 (0.14) (Table 3), which contributed to the hydrochemical alteration of groundwater minerals within the catchment.

3.4 Water quality assessment for domestic usage

3.4.1 Water Quality Index (WQI)

The groundwater suitability for domestic usage within the catchment has been assessed using WQI (Horton, 1965). Groundwater has been grouped into five classes; < 50 (Excellent water), 50 – 100 (Good waters), 100 – 200 (poor waters), 200 – 300 (very poor waters), and > 300 (unfit for usage). The WQI studied samples (Table 4) are within the range between 6.05 and 2262.20 with an average value of 216.85. Nineteen and 16 samples have

Table 3. Saturation indices of some selected mineral phases in the study area

Phase	SI	log IAP	LogKT
Albite	0	4.66	4.66
Anhydrite	0	-4.36	-4.36
Anorthite	-1.91	23.7	25.62
Calcite	0.14	-8.34	-8.34
Aragonite	0	-8.34	-8.34
Dolomite	-2.51	-19.6	-17.09
Fluorite	0	-10.6	-10.6
Goethite	5.60	17.62	12.02
Gypsum	0	-4.58	-4.58
Halite	0	1.58	1.58
K-mica	5.83	18.53	12.70
K-feldspar	0	2.09	2.09
Hematite	13.31	35.34	22.03
Talc	0.07	21.47	21.40

WQI values < 50 and within 50 – 100 indicating excellent and good waters respectively (supplementary data).

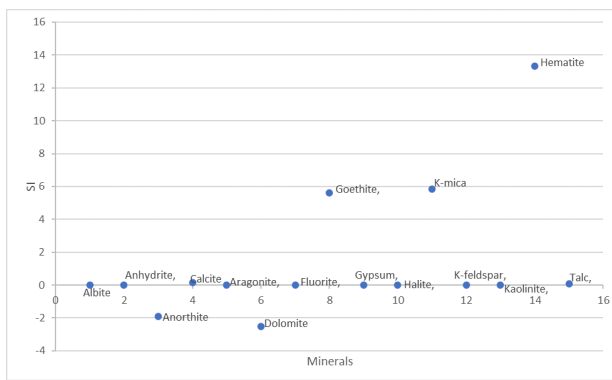


Figure 4. A plot of the SI indicating the minerals that dissolved during water-rock contact within the aquifers

This is a representation of 34.55% and 29.18% respectively, of the total collected samples in the area. Also, 9, 4, and 7 samples indicate poor, very poor, and unfit waters, respectively, and represent 36.35% cumulatively of the total samples studied (supplementary data). Hence, based on the WQI, the excellent and good waters in the area dominate the poor to unfit waters in the area with 63.65% as against 36.35%. These very poor and unfit waters are found in Krobo Meyewa and Osiem and their environs (Figure 5).

3.4.2 Percentage of pollution index (PPI)

The level of pollution groundwater in the area has been exposed to has been evaluated using the PPI of Pacheco and Van Der Weijden (1996) and Soumya et al. (2013) (equation 5), with Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , and HCO_3^- as the pollutants. These pollution loads; Cl^- , CO_3^{2-} , and HCO_3^- are attributed to geological processes, whereas

SO_4^{2-} , and NO_3^- are considered to be due to anthropogenic activities (Soumya et al. 2013), largely agricultural activities. PPI values < 40% and > 40% are unpolluted and human-activities-induced pollution, respectively according to Soumya et al. (2013).

Statistically, the summarized results of the PPI values (Table 4), range from 3.13 to 89.47% with an average of 30.60%. The samples studied have 18 samples with PPI values > 40% representing 32.73% of the total samples collected with 37 samples having PPI values < 40%, thus 67.27%, which is indicative of chemical weathering (Rahman et al., 2020) (supplementary data and Figure 5). This is a representation of about 33% of human activities' effect on the groundwater suitability within the catchment. These high spots are observable (Figure 5) in the Osino, Akoradarko, Osiem, Dominase, Seseaman, and Kuradaso catchments within the study area (Figure 5).

3.4.3 Water Pollution Index (WPI)

The assessment of the groundwater drinking safety using WPI has been classified into < 0.5 (excellent water), 0.5 – 0.75 (good water), 0.75 – 1 (moderately poor water), and > 1 (highly polluted water) according to Hossain and Patra (2020). The WPI values for the studied samples vary between 0.77 to 5.28 with a mean value of 1.56 (Table 4). With this range of WPI values, 5 and 50 samples are within the category of moderately polluted and highly polluted waters and represent 9.1% and 90.9%, respectively. Moderately polluted groundwaters are observable in Dominasi, Seseaman, Bepoase, Kuradaso, and Akoradarko areas (Figure 6), while highly polluted groundwaters are in Osino, Osiem, and Krobo Meyewa areas (Figure 6). The WPI values suggest that the groundwater within the catchment is not safe for potable water (thus for drinking and other latent domestic usages).

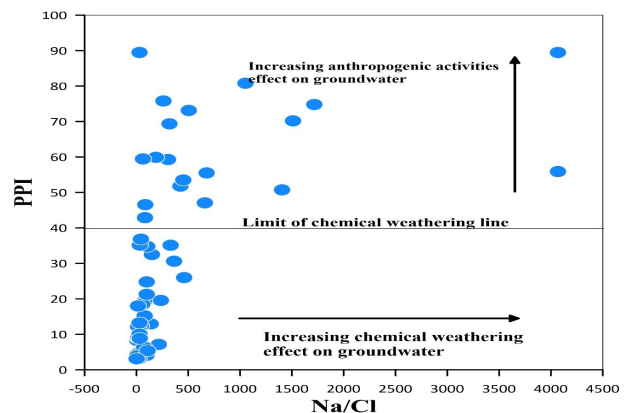


Figure 5. Bivariate plot of pollution indices versus chemical weathering effect in the Osino catchment

Corrosion ratio (CR) measures the relative proportion of alkaline metals to the salinity coupled with sulfates

Table 4. Statistics of the water quality indexal proxies used in the study

Statistics	WQI	PPI	WPI
Min	6.05	3.13	0.77
Max	2262.2	89.47	5.28
Mean	216.85	30.6	1.56

in groundwater (Hwang et al., 2017). Corrosion is an important aspect to consider in groundwater for its domestic purposes as it affects the hydraulic capacity of pipes which are conveyors of groundwater in the domestic setting. A high concentration of chloride and sulfates coupled with a low concentration of carbonates catalyzes the corrosion of pipes (Hwang et al., 2017). The CR assessment of the groundwater with values > 1 and < 1 are indicative of corrosive and non-corrosive, respectively. Groundwater with $CR < 1$ is safe for passage through any type of water piping system in the domestic setting. Of the samples studied, 8 and 47 have $CR > 1$ and < 1 values, respectively. This is indicative of 85% suitability for the total studied samples and can be considered safe for passage through metal pipes within domestic and industrial settings.

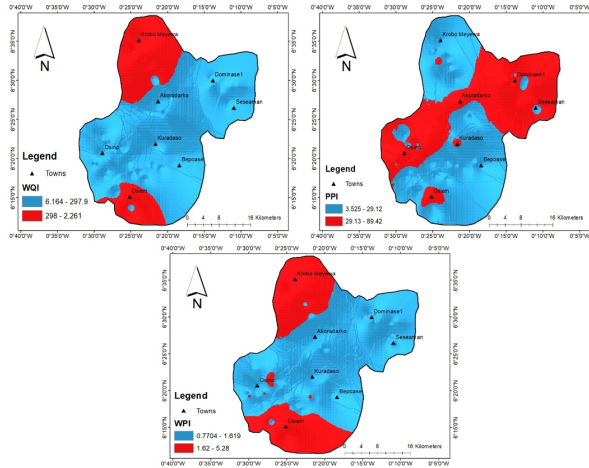


Figure 6. The distribution of PPI, WQI, and WPI within the study catchment

The quality indices applied suggest the groundwater has been exposed to varying degrees within the catchment (Table 4). However, the groundwater quality spatial distribution indicates that Osiem, Osino, Dominase, Seseaman, Krobo Meyewa, Kuradaso, and Akoradarko communities are areas within the catchment with pollution concerns that need urgent attention.

3.5 Quality Forecasting using MRM

The performance of the MRM and the independent variables used in the prediction of the WQI and WPI are pre-

sented in Table 5. From the prediction models of WQI and WPI (equations 18 and 19), the WPI model gave good performance in predicting the water quality in the catchment with high R , R^2 , and low standard error of estimate (SEE) (Table 5). From the predicted models, the water quality parameters that are sensitive and will influence the quality of the groundwater alteration in the central-southern parts of Ghana using WQI are Cl^- , HCO_3^- , and TH. These parameters have ρ values that are less than 0.05; Cl^- ($\rho = 0.000$), HCO_3^- ($\rho = 0.005$), and TH ($\rho = 0.001$), thus suggesting their significance, statistically. Hence, a change in the content of these parameters in the groundwater will affect its quality in the area from the predicted WQI model (equation 19) in the area.

SEE = standard error estimate

$$\begin{aligned}
 WQI = & 31.895 + (0.890Ec) + (-0.399pH) + (-1.118F^-) \\
 & + (-1.594NO_3^-) + (17.120Cl^-) + (0.234SO_4^{2-}) \\
 & + (2.977HCO_3^-) + (-0.678Na^+) + (-1.679K^+) \\
 & + (1.462Mg^{2+}) + (-3.456TH) + 116.04319
 \end{aligned} \tag{18}$$

From the predicted WPI model (equation 20), all the groundwater parameters (independent parameters) in the models have ρ values < 0.05 except Ec ($\rho = 0.361$), and hence are statistically significant in the prediction and for that matter, are sensitive to groundwater quality variation within the catchment, using the WPI as a criterion in predicting the groundwater quality.

$$\begin{aligned}
 WPI = & -0.001 + (0.923Ec) + (121.365pH) \\
 & + (221.973F^-) + (73.288Cl^-) + (51.050SO_4^{2-}) \\
 & + (11.040HCO_3^-) + (38.097Na^+) + (12.507K^+) \\
 & + (-43.738Mg^{2+}) + (42.237TH) + 0.007
 \end{aligned} \tag{19}$$

The prediction models generated for the groundwater quality forecasting, aside from the good performance of the WPI over the WQI, will also likely undermine the effect of the other parameters while focusing on the effect of Cl^- , HCO_3^- , and TH. Hence, using the WPI approach in modeling the quality of groundwater as revealed, is preferred due to the good performance of its model and also the relevance of all the predictors in the model.

Table 5. Summary of the performance of the MRMs of WQI and WPI and the independent variables of the model

Independent variables	Dependent variable	R	R2	Adjusted R2	SEE
Ec, pH, TH, TDS, Cations, and anions	WQI	0.993	0.986	0.982	52.36620
Ec, pH, TH, TDS, Cations, and anions	WPI	1.000	1.000	1.000	0.00305

3.6 Suitability for Agricultural Purposes

The basic statistical summaries (Table 6) of the proxies used in the assessment of the groundwater suitability for farming purposes within the catchment indicate the following ranges; %Na values are between 6.40 and 79.02 with an average value of 43.39, SAR values are in the range of 0.31 to 12.05 with a mean value of 2.98. Also, RSC has a -12.15 to 199.85 range of values with an average value of 63.42, while MHR values are from 7.58 to 61.43 with an average of 29.52 (Table 6), KR has a 0.03 to 2.55 range of values with 0.79 as the average value. Potential salinity and PI have 0.00 to 90.00 and 1.00 to 86.00 range of values with respective average values of 4.82 and 13.26 (Table 6).

3.6.1 EC

In drainage-restricted areas, saline groundwaters are not suitable for irrigational farming (Adimalla and Wu 2019). The electrical conductivity (EC) has been used to characterize the salinity of groundwater, with low saline groundwater represented by EC values > 250 ($\mu\text{S}/\text{cm}$), $250 - 750$ ($\mu\text{S}/\text{cm}$) implying medium salinity and high salinity values are within the range of $750 - 2250$ ($\mu\text{S}/\text{cm}$), and > 2250 ($\mu\text{S}/\text{cm}$) indicative of very saline groundwater. The EC values of the samples vary between 0.01 and 920.00 ($\mu\text{S}/\text{cm}$) (Table 6), with 54 samples having EC values within $0.01 - 750$ ($\mu\text{S}/\text{cm}$), thus representing 98.2% and indicative of low to medium saline water while a sample has an EC value of 920 representing 1.8% and suggestive of high saline waters (Table 7).

3.6.2 Sodium percentage

The percentage of Sodium (Na%) has been used by Wilcox (1948) to characterize the safety of groundwater for irrigation purposes from Equation 9. The following ranges of Na%; ≤ 20 , $21 - 40$, $41 - 60$, $61 - 80$, and > 80 have been grouped to mean excellent, good, permissible, doubtful, and unsafe respectively, for agricultural usage. The samples studied, 8, 17, 15, and 15 samples have sodium percentage values within the ranges of ≤ 20 , $21 - 40$, $41 - 60$, and $61 - 80$ respectively (Table 6).

This represents 14.55%, 30.91%, 27.27%, and 27.27% of excellent, good, acceptable, and doubtful waters respectively, for agricultural usage in the Osino areas (Table 7). The samples collected for the study are 72.73% acceptable for irrigation farming usage with 27.27% probable waters in the catchment from the studied samples.

Table 6. The statistical summaries of the irrigation indices used

	%Na	SAR	RSC	MHR	KR	PS	PI
Min	6.40	0.31	-21.15	7.58	0.03	0.00	1.00
Max	79.02	12.05	199.85	61.43	2.55	90.00	86.00
Mean	43.39	2.98	63.42	29.52	0.79	4.82	13.26

Table 7. Groundwater irrigation acceptance assessment after Wilcox (1948); Richard (1954); Eaton (1950); Paliwal (1972); Kelly (1963); Panneerselvam et al. (2020)

Proxies	Ranges	Implication	The average range of samples	No. of Samples	Percentages (%)
EC	<250	Low Salinity	0.01 – 920 (183.83)	38	69.09
	250 - 750	Medium Salinity		16	29.09
	750 - 2250	High Salinity		1	1.82
%Na	>2250	Very High Salinity	6.40 - 62.38 (11.42)	0	0
	≤ 20	Excellent		8	14.55
	>20 <40	Good/ Suitable		17	30.91
	>40 <60	Permissible		15	27.27
SAR	>60 <80	Doubtful	0.31 - 12.05 (2.98)	15	27.27
	>80	Not Safe		0	0
	≤ 10	Excellent		54	98.2
	>10 <18	Good/Suitable		1	1.8
	>18 <26	Doubtful		0	0
RSC	>26	Not Safe	-21.15 - 199.85 (63.42)	0	0
	<1.25	Good/ Suitable		1	1.8
	1.5 - 2.5	Doubtful		0	0
MHR	>2.5	Not Suitable	7.58 - 61.43 (29.52)	54	98.2
	<50	Suitable		53	96.36
	>50	Not Suitable		2	3.64
KR	<1	Suitable	0.03 -2.55 (0.79)	39	70.91
	>1	Not Suitable		16	29.09
PI	>75% - I	Suitable	1.1 – 85.7 % (13.2)	1	1.8
	75 – 25% -II	Suitable		6	10.9
	<25% - III	Not Suitable		48	87.3
PS	<5	Suitable	0 – 90 (5)	52	94.6
	5 – 10	Marginal		2	3.6
	>10	Not Suitable		1	1.8

3.6.3 Sodium adsorption ratio

The SAR is indicative of the alkalinity and the hazardous effect of sodium that crops are exposed to when the SAR exceeds 26 according to Richard (1954); Jalali (2007); Li et al. (2016). Sodium adsorption ratios ≤ 10 , $> 10 - 18$, $> 10 - 26$, and > 26 of groundwater are considered excellent, good, doubtful, and unsafe quality for agricultural purposes respectively. The ratio is calculated from Richard's (1954) equation (equation 10). The samples collected from the area have 54 samples representing 98.2%, with SAR ≤ 10 , hence indicating excellent for agriculture purposes (Table 7). A sample has a SAR value within $> 10 - 18$ suggesting good quality groundwater for irrigation activities in the area.

3.6.4 Residual sodium carbonate

The physical properties of cultivated soils are affected by high sodium bicarbonate contents in irrigated soils. Sodium bicarbonate-induced soil organic matter content dissolution could result in a surficial stain on the soil, making RSC a relevant parameter to be considered in the evaluation of groundwater for irrigation farming. This was evaluated using Eaton's (1950) residual sodium carbonate (RSC) equation (equation 11).

The following ranges of RSC in groundwater; < 1.25 , $1.5 - 2.5$, and > 2.5 are considered to be good, doubtful, and unsuitable for agricultural activities. The samples of the Osino areas have 54 samples representing 98.2% of the area with RSC values within > 2.5 ranges with a sample having an RSC value of < 1.25 (Table 6). This range of RSC values is indicative of an unsuitable groundwater for agricultural activities within the catchment.

3.6.5 Magnesium hazard ratio

Saline and elevated levels of sodium in groundwater could have a negative effect on the structure of the cultivated soil and also, the high levels of magnesium in groundwater

targeted for irrigation purposes can be harmful to crops where potassium content in the soils is low hence the significance of MHR assessment in groundwater earmarked for irrigation (Paliwal, 1972; Thapa et al., 2017). The equation of Paliwal (1972) (equation 12) has been used over the years in the assessment of magnesium hazards in groundwater.

Magnesium hazard ratio < 50 and > 50 in groundwater is considered suitable and unsuitable, respectively, for irrigation purposes. The study area has 53 samples representing 96.36% with MHR < 50 (Table 7) whereas 2 samples (3.64%) have MHR values > 50 . This implies safe groundwater usage for irrigation purposes within the catchment with no possibility of causing harm to the irrigated crops.

3.6.6 Kelly's ratio

The introduction of the KR by Kelly (1963), is an additional proxy for sodium concentration in groundwater compared to calcium and magnesium concentrations (equation 13). In this ratio, values of KR > 1 in groundwater are considered unacceptable while < 1 values are considered acceptable for irrigation farming. The groundwater samples within the catchment have 39 and 16 samples with KR values < 1 and > 1 respectively (Table 4). This represents 70.91% suitable and 29.09% unsuitable waters respectively, for irrigational purposes within the catchment.

The applied proxies in the evaluation of the acceptability of groundwater for farming purposes in the catchment, all suggested that the groundwater is safe for farming except for the RSC, with 98.20% suitability and 1.80%. KR has also indicated significantly, 29% of unsuitable groundwater for irrigation in the area (Table 7). Generally, the groundwater can be said to be of good quality for irrigational farming activities within the catchment.

3.6.7 Permeability index

The concentration of Ca^{2+} , Na^+ , Mg^{2+} , and HCO_3^- in groundwater, affects the soil permeability of such waters, and hence these parameters in groundwater serve as proxies in the evaluation of groundwater safety for irrigated farming (Panneerselvam et al., 2020). From equation 14; the permeability index (PI) which characterizes the level of acceptability of groundwater for irrigated farming has been adopted to classify groundwater into three classes; class I with a PI value $> 75\%$, class II with a PI value within the range of $> 75 - 25\%$, and class III with PI value $< 25\%$.

The samples studied have PI within the range of $1.1 - 85.7\%$ with a mean of 13.2% (Table 7). 48 of the samples have PI $< 25\%$ (class III) representing 87.3% of the study while 7 samples are within the range of $> 25\%$ (class I and II) representing 12.7%. The studied samples suggest that the groundwater is largely not acceptable/safe for irrigation with a dominant class III type of groundwater.

This could affect crop yield in the area if the groundwater is earmarked for irrigation farming due to poor soil water carry ability (Panneerselvam et al., 2020).

3.6.8 Potential salinity

Alkaline minerals dissolution within aquifer systems affects the salinity of soil when such waters are used for agricultural activities. The potential salinity (PS) of groundwater has been used to assess the suitability of groundwater for irrigation farming (equation 15) and grouped into 3 classes with < 5 , $5 - 10$, and > 10 being acceptable, moderate, and unacceptable groundwaters for irrigated farming, respectively.

The following number of samples; 52, 2, and 1 have PS values < 5 , $5 - 10$, and > 10 , respectively (Table 7) (Panneerselvam et al., 2020). Largely, the groundwater under consideration is not saline, with only a sample within the area showing a possible salinity effect on the soil if used for irrigation for some time within the catchment.

The groundwater is largely within allowable levels for irrigation purposes in the catchment. Much safe irrigation waters are found in the southeastern parts of the area (Figure 7), with some isolated hot spots in the north and middle parts of the area, especially in Krobo Meyewa, Osino, Akuradarko, Dominasi, and Seseama areas (Figure 7).

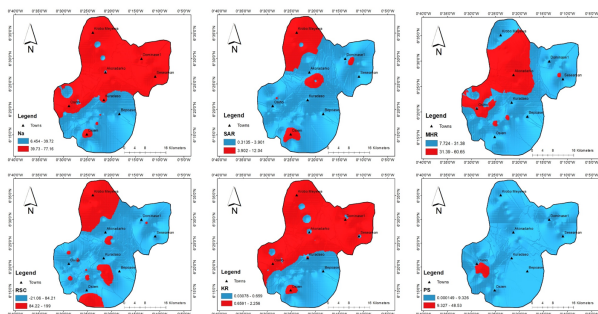


Figure 7. Spatial characterization of the groundwater suitability for irrigation purposes in the area

4. Conclusion and Recommendation

The hydrochemical implication on the groundwater quality, quality prediction modeling, and the suitability for irrigation farming was evaluated in the study, and the following findings were made: The physicochemical concentration levels of the parameters were found to be: $TDS > HCO_3^- > Ca^{2+} > Cl^- > Na^+ > NO_3^- > Mg^{2+} > SO_4^{2-} > K^+ > F^- > CO_3^{2-}$. The main water types; $Na - HCO_3$ and $Ca - SO_4$ evolved into $HCO_3 - Na$ and $Cl(SO_4) - Na(Mg)$ waters in the area. All the ions are within their WHO-acceptable limits for drinking water except NO_3^- and F^- in a few communities.

The indexical and selected ratios proxies on ion-exchange process evaluation support the influence of a dominant

ion-exchange process contribution to the groundwater modification facilitated by the dissolution of minerals of both silicate, iron oxides origin, and calcite within the aquifers in the catchment. However, the effect of human activities on the alteration of groundwater chemistry in the catchment cannot be precluded considering SO_4^{2-}/Cl^- and NO_3^-/Cl^- proxies

Based on the indices used in the groundwater evaluation, 63.65% of the studied area has good to excellent waters with 36.35% poor to unfit waters considering the WQI, and about 37% of polluted waters has also been indicated by the PPI. The WPI, on the contrary, suggests that the groundwater within the central-southern parts of Ghana is entirely polluted with 9.1% and 90.9% of moderately and highly polluted waters, respectively. The CR also indicates that the groundwater is largely safe to pass through any type of piping system with 85% of the samples having CR values < 1 .

The prediction model for WPI has a better performance than that of WQI. The model for WPI also indicates that all parameters used in the model except for Ec, affect the groundwater quality while only Cl^- , HCO_3^- , and TH affect the suitability of the groundwater in the area considering the model for the WQI. Osiem, Osino, Dominase, Seseaman, Krobo Meyewa, Kuradaso, and Akoradarko indicate observable polluted/poor to unfit groundwaters by all the quality assessment indices used.

On the suitability for agricultural activities, EC, %Na, SAR, RSC, MHR, and KR were used. Based on EC, SAR, MHR, %Na, KR, and PI, the groundwater is largely acceptable for agricultural activities with a suitability percentage > 70 for all these parameters. RSC and PS however suggest unsuitable groundwater for irrigational farming with 98.20% and 83.7% respectively, of unsuitable groundwater from the samples studied. Generally, Krobo Meyewa, Osino, Akuradarko, Dominasi, and Seseama communities do not have good irrigation waters from the interpolation maps.

Although agriculture is the main source of income for the people within the catchment, its indirect effect on the groundwater quality needs to be monitored. Future groundwater quality modeling should make use of the WPI in the area due to its effectiveness in the quality assessment of groundwater, prediction, and forecasting than the WQI model. Osiem, Osino, Dominase, Seseaman, Krobo Meyewa, Kuradaso, and Akoradarko are areas within the catchment that require other groundwater-related health risk evaluation due to the observable polluted waters in these communities and their environs.

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