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General Hydrogeochemical Characterization of Groundwater in Coastal Aquifers of Kilwa Kisiwani Oceanic Island, South East Tanzania

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ABSTRACT

The main objective of this study was to determine the hydrogeochemical processes controlling the groundwater chemistry on the Island and assess its suitability for human consumption and irrigation. The methodology used in the study include hydrogeological assessment of the study area and laboratory analysis for general physico-chemical parameters of groundwater. Other parameters such as Soluble sodium percentage (SSP) or % Na⁺, Sodium Adsorption Ratio (SAR), Magnesium adsorption ratio (MAR), Residual sodium carbonate (RSC), hydrochemical facies classification, and Water Quality Index (WQI) were calculated using empirical formulae. The effects of salinization of groundwater were classified using the chloride-Bicarbonate (Cl/HCO₃) and the $Na^+/Cl^$ ratios. The major geological units of the study area are sandstone, clays, alluvium, beach sands and laterite soils of Cretaceous to Quaternary age. A total of 21 groundwater samples were collected and analyzed for physical parameters and major ions. Analysis results for pH shows a mean value of 7.47 while the mean value for TDS is 1618.47mg/L. Groundwater classification based on the piper trilinear diagram shows that the dominant hydrochemical facies are Ca-Cl (42%), Ca-Mg-Cl (33%) and Ca-HCO₃ (23%). The cation exchange processes indicates that Ca^{2+} replaced the Na⁺ and this is an indication of freshening geochemical processes in the aquifer matrix. The findings also show that mean value for total hardness (TH) is 92.44 mg/L, soluble sodium percentage (SSP) or Na% is 15.29%, Sodium adsorption ratio (SAR) is 1.08, Electrical conductivity (EC) is 2447.1 µS/cm, Residual sodium carbonate (RSC) is -11.29 meg/L, and Magnesium adsorption ratio (MAR) is 56.89%. Water quality index (WQI) results show that the groundwater is of very poor quality since the WQI value is 298.8 which is in the range of (200 - 300), this range is designated as very poor water quality for human consumption.

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INTRODUCTION

Together with ease of access to surface water sources, groundwater is regarded as

the second most important and significant source of water supply for industrial, agricultural, and domestic use. According to Nickson et al. (2005), 30% of the world's population relies on underground water supplies for domestic water supply. Additionally, it has been noted that the interactions between various hydrochemical processes, such as seawater hydrogeological intrusion, processes (weathering, ion exchange, and rock-water interaction), and anthropogenic activities, which may include agriculture, industrial processes, and urbanization, determine the quality of groundwater in coastal subsurface formations (Melchioly, 2018). Groundwater quality degradation in coastal aquifers is mainly associated with seawater intrusion and this phenomenon has been a very critical challenge in many countries around the world (Walraevens and Alfarrah, 2018; Fatema et al., 2018; Naser et al., 2017). It was also found that the efficient and sustainable use of groundwater in coastal aquifers depends on both quantity and quality, with the main focus being on salinity. Islam et al. (2020) explains that the suitability of groundwater for domestic purposes could potentially be limited by groundwater salinity and generally poor water quality due to the presence of hazardous chemical elements such as arsenic, nitrate, fluoride, mercury and other heavy metals. The presence of hazardous chemical elements and heavy metals in groundwater is harmful to human health (Adimalla, 2020; Wen et al., 2013; Mtoni et al., 2013).

The coastal island of Kilwa Kisiwani, which is located in Tanzania's southeastern coast along the Indian Ocean, is home to 2317 people (Census 2022). According to Melchioly (2018), the island has an estimated area of 20 km² and is located around 2 km offshore of Kilwa Masoko town. Communities on the Island are forced to drink tainted surface water and shallow saline groundwater from largely hand-dug wells due to a lack of freshwater. Seawater intrusion has been the Island's main problem with regard to groundwater quality. In a study by Comte et al. (2016), it was shown that only 14% of the samples' EC fell within the permitted range of concentration (1400 mg/L), while (42%) exhibited higher values of TDS.

Similar studies have been carried out in different areas using the same methodologies to characterise groundwater quality. Nishi et al. (2018) used bivariate diagrams to characterize the hydrogeochemistry and groundwater quality in a section of the Precambrian Terrain in Eastern India, finding that the groundwater chemistry is influenced by both geogenic (carbonate and silicate weathering and exchange. dissolution, ion and evaporation). Patil et al. (2020) used the multivariate statistical and groundwater quality index (WQI) analysis to characterise groundwater quality in northern parts of India.

It is crucial to conduct thorough scientific the research on groundwater hydrogeochemistry and water quality in shallow coastal aquifers (Sefie et al., 2015; Comte et al., 2017). Hence the current study's goal is to establish the hydrogeochemical processes that govern groundwater quality and its suitability for both human consumption and irrigation purposes in the study area.

METHODS AND MATERIALS

Description of the study area

The study area (Figure 1) is located in Kilwa District in Lindi Region, southeastern Tanzania. The study area is estimated to have an area of 20 km² and population of 2317 (Census 2022).

The study area geographically lies between UTM Northing from 9002000 to 9008700 South and UTM Easting from 555000 to The datum 560800 east. for the geographical coordinates is WGS 84 zone 37 South. Study sites were chosen based on ease of accessibility and potential of human settlements. Kilwa Kisiwani Island has a coastal warm and humid climate with the average temperature range between 22°C to 30°C. Humidity is high, nearly 98-100% during the long rain season. It receives annual average rainfall of about 800-1400 mm/year (TMA 2020).



Figure 1: Map showing study area, geology and sampling points' locations. Geological Map of the study area (Digitized from Quarter Degree Sheet, QDS No. 256).

The principal geological features on the Island are represented by the quaternary, Neogene, and Cretaceous formations in Figure 1, which summarizes the geology of the research region. Unconsolidated sediments like as coral limestones, gravel, beach sand, dunes, and alluvium make up the majority of the island's lithologies (Pearson et al., 2004). The research area is in a hydrogeological zone with beds dating from the Neogene to the Quaternary period, and unconsolidated sand and gravels are the predominant water-bearing formations in the majority of Tanzania's coastal regions. According to hydrogeology, coastal aquifers from the Quaternary and Neogene are expected to yield higher amounts of groundwater than those from the Jurassic and Cretaceous eras. Neogene aquifers can hold up to 30 m³/hr, while Quaternary aquifers can hold up to 40 m3/hr (Mtoni *et al.*, 2013; Mjemah, 2007).

Field sampling and Water Analysis

Twenty-one (21) groundwater samples were taken from the shallow wells and boreholes available in the study area for laboratory analysis. The field sampling campaign was carried in April 2023. In addition to physical data that were measured on-site, such as pH, temperature, color, turbidity (NTU), total dissolved solids (TDS), and electrical conductivity (EC), the study also required identifying the concentration of common anions and A small, hand-held HACH cations. conductivity meter kit model HQ1140 Portable, made by the HACH firm, was used measure the physical to characteristics. Multiple parameters are measured simultaneously by the HACH meter. PVC containers were used to collect water samples that were gathered in the field. The geochemistry lab at the University of Dar es Salaam's department of geosciences conducted the analysis of water quality for physico-chemical parameters. In 500 mL polyethylene bottles, samples for the measurement of the principal cations and anions $(Na^+, K^+, Ca^{2+},$ Mg^{2+} , Cl⁻, SO₄²⁻, NO₃⁻, and HCO₃⁻) were gathered. Before adding the water sample, each bottle was washed with distilled water. The bottles had labels and were tightly sealed. Each location provided two sets of samples, which were then run 0.45 cellulose through m nitrate hydrophilic syringe filters. Major cations and anions were examined using inductively coupled plasma mass spectrometry (ICP-MS) model NexION 1000. The relative standard deviation of the main ions detected in the samples was determined to be within \pm 2% after numerous diluting steps.

Also, it is crucial to perform pre-treatment in accordance with the APHA (2012) standard procedures and recommendations in order to preserve the appropriate quality because it takes some time for water samples to travel from the field to the laboratory for examination. Groundwater samples were treated with concentrated nitric acid (HNO3) at a ratio of 0.15 ml for 100 ml of sample in order to reduce the pH of the sample since cations and anions are important parameters to detect. As advised by the APHA (2012), all samples were filtered according to standards.

Methods for Hydrogeochemical and Water Quality Evaluation

In order to assess water quality and geochemical processes the following parameters were established; general physico-chemical parameters of groundwater, Soluble sodium percentage (SSP) or % Na⁺, Sodium Adsorption Ratio (SAR), Magnesium adsorption ratio (MAR, Residual sodium carbonate (RSC), hydrochemical facies classification, and Water Quality Index (WQI). The groundwater samples were analysed for the above parameters and some parameters were calculated using empirical formulae.

RESULTS AND DISCUSSION

General Hydrogeochemistry

Table 2 displays the findings for several physical and hydrochemical parameters of groundwater samples. Water has a pH that ranges from 5.7 to 8.6 with a mean of 7.47, making it somewhat alkaline. The amount of CO_2 , CO_3^{2-} , and HCO_3^{-} concentrations regulates the pH, which measures how well the water reacts with acidic or alkaline chemical compounds found in groundwater

(Hem, 1991; Zhou et al., 2015). The findings shown in Table 2 demonstrate that the ionic concentrations and types of ions present in the water determine the variance in electrical conductivity (EC)of groundwater. According to the literature, groundwater's maximum allowable electrical conductivity (EC) level is 1500 S/cm (WHO, 2011). According to the study's findings, the mean electrical conductivity (EC) of the groundwater in the studied area is 2447.1 S/cm, with a range of 1160 to 4620 S/cm.

Total dissolved solids (TDS) measurements from the study indicate that the levels vary from 754 to 3003 mg/L, with a mean of 1618.47 mg/L. The US EPA (1984, 1986, and 2020), Fetter (2001), TBS (TZS 789:2008) and other sources have all explained that a TDS concentration of 1,000 mg/L can be regarded as the arbitrary upper limit of freshwater for human consumption. However, in many nations around the world, where water with a lower TDS concentration is not readily available, groundwater with TDS values greater than 1,000 mg/L is still used for household supplies. Although it is typically too unpleasant to consume such groundwater, in some regions the top limit for TDS is 3,000 regarded to be mg/L. The aforementioned information enables the classification of groundwater based on TDS values, where groundwater with a TDS concentration of less than 3,000 mg/L being deemed fresh water and groundwater with a TDS concentration of between 3,000 and 10,000 mg/L being termed brackish. groundwater with Finally, TDS concentrations above saltwater (about 35,000 mg/L) will be referred to as brine solution and will be deemed saline if they are larger than 10,000 mg/L. According to Fetter (2001), brackish water is defined as having a TDS value between 1000 and 10,000 mg/L, and the majority of the groundwater samples in the research area fall into this category. High TDS concentration leads to hard water which is not suitable for drinking.

With concentration values ranging from 56.7 to 436.5 mg/L and a mean value of 232.12 mg/L, calcium (Ca²⁺) concentration is the predominant cation in groundwater samples, accounting for 41% of all cations. The second most abundant cation is magnesium (Mg^{2+}) , with values ranging from 63.2 to 422.6 mg/L and a mean value of 187.57 mg/L. It accounts for 33% of the overall cation concentration in percentage terms. In terms of dominance, sodium (Na⁺) concentrations are third, with a mean value of 91.68 mg/L and a fairly wide range between maximum and minimum values that range from 12.6 to 312.2 mg/L and represent 16% of all cations. Potassium (K+), the final major cation, has the lowest amounts in all ground waters that have been studied and makes up 10% of all cation concentrations. According to the study's findings, the mean value is 52.78 mg/L, with the minimum and maximum values ranging from 6.2 to 223.3 mg/L. Thus, the pattern of the principal cation concentrations in the groundwater samples can be shown to be Ca2+>Mg2+>Na+>K+.

Hydrogen bicarbonates (HCO_3) , which make up 31% of all major anions and have a concentration range of 218.6 to 890.0 mg/L and a mean value of 450.32 mg/L, are the most prevalent major anion, according to research data. Chloride (Cl⁻), which can range in concentration from 118.4 to 960.0 mg/L and has a mean value of 418.67 mg/L, is the second dominating major anion. In the groundwater samples taken in the study area, chloride (Cl⁻) concentration makes up 28% of all significant anions. According to WHO guidelines, the maximum permitted level of chloride in groundwater is 250 mg/L (WHO 2004, 2011). However, only one (1) sample out of the twenty-one (21) samples used for this research exceeds the TZS 789:2008 standard for chloride Sulphate (SO_4^{2-}) , with concentrations. concentration values ranging from 54.0 to 865.4 mg/L and a mean value of 331.47 mg/L, is the third most prevalent anion concentration. Sulfate (SO_4^{2-}) makes up 22% of all the anions found in the groundwater samples that were taken. $(CO_3^{2-}),$ Carbonate which has а concentration range of 56.4 to 452.1 mg/L and a mean value of 225.91 mg/L, is the fourth most prevalent anion. Results also show that 15% of the total anions in all the groundwater samples that were obtained are carbonate (CO_3^{2-}) . Nitrate (NO_3^{-}) , with concentration values ranging from 22.4 to 365.0 mg/L and a mean value of 53.95 mg/L, is the last dominant anion concentration. All of the groundwater samples that were taken included 4% of the total anions as nitrate (NO_3^{-}). Groundwater in the research area has an anionic concentration trend of $HCO_3^- > Cl^- > SO_4^{2-}$ $> CO_3^{2-} > NO_3^{-}$.

The results, compare well with similar earlier investigations and studies in water quality research in other Tanzanian coastal regions. Notably also most observations are generally within the accepted allowed limits are shown in Table 3. This indicates that shallow aquifers near the coast are more susceptible to pollution than deep aquifers because practically all water quality metrics are significantly higher than those from prior research in Tanzanian coastal areas and for results from deep aquifers. The research findings, which are shown in Table 3, indicate that most water quality measures, with the exception of electrical conductivity (EC), total dissolved solids (TDS), potassium (K⁺), magnesium (Mg^{2+}) , and nitrate (NO_3) , appear to be over the allowable levels for drinking and irrigation. According to the results of the correlation Pearson matrix of parameters hydrogeochemical in groundwater (Table 4), TDS has a relatively strong association with calcium (Ca^{2+}) , magnesium (Mg^{2+}) , and sodium (Na+), but a weak correlation with chloride (Cl⁻) and sulphate (SO₄²⁻). The Pearson correlation matrix's findings also reveal that pH has a poor correlation with Mg^{2+} , Na⁺, and K⁺ whereas EC has a significant correlation with TDS, SO42-, and Cl- and a moderate correlation with Ca^{2+} , Mg^{2+} , and

Na⁺. The Pearson correlation matrix shown in Table 4 further demonstrates that almost all of the variables, with the exception of NO₃⁻, Residual Sodium Carbonate (RSC), and Magnesium adsorption ratio, have positive relationships between calcium (Ca²⁺), sodium (Na⁺), potassium (K⁺), and chloride (Cl⁻) (MAR). With the exception of SSP, SAR, and RSC, magnesium (Mg²⁺) has positive relationships with practically all of the variables.

Table 2: Physico-chemical and calculated parameters of the groundwater samples from study area. All the units are mg/L except for EC (µS/cm), SS
(%) and MAR (%).

Sample ID	Ca ²⁺	Mg^{2+}	Na ⁺	K^+	Mn^{2+}	Fe ²⁺	HCO ₃ -	SO4 ²⁻	Cl-	CO3 ²⁻	NO ₃ -	PO4 ³⁻	TDS	EC	pН	TH	SSP	SAR	RSC	MAR	KR
W1	236.2	275.4	98.23	13.65	0.7981	0.67	374.6	453.6	370.2	278.3	365	123.6	1831.05	2817	6.45	122.69	11.83	1.03	-19.03	65.78	0.124
W2	163.2	200.3	76.3	26.4	3.26	3.65	456.2	423.5	286.3	69.51	86.32	87.26	1842.75	2835	6.49	88.15	13.96	0.95	-14.83	66.93	0.135
W3	334	112	312	113.6	0.6002	3.48	546	256	630	321	22.4	33.5	1950.00	3000	8.1	79.55	38.89	3.77	-6.24	35.60	0.524
W4	334	112	312.2	112.5	0.6002	3.7	452.9	312.5	630	412	22.4	41.3	1992.25	3065	8.1	79.55	38.87	3.77	-4.73	35.60	0.525
W5	182.3	165.3	23.5	9.32	0.6002	3.66	546	362.1	532.1	321	33.6	2.6	1300.00	2000	8.1	78.68	5.26	0.30	-3.05	59.92	0.045
W6	334	112	113.2	112.5	0.6002	3.7	423.5	256	630	289.6	22.4	35.4	1892.80	2912	8.1	79.55	23.16	1.37	-9.29	35.60	0.190
BH1	100.3	63.2	60.2	24.3	0.5986	0.01	224.3	120.2	253.1	223.1	33.2	23.5	754.00	1160	5.7	33.90	24.10	1.16	0.91	50.96	0.257
W7	143.2	100.6	53.2	29.4	0.1995	0.02	312.5	193.2	348	118.3	24.3	16.54	1059.50	1630	6.42	51.91	16.58	0.83	-6.36	53.67	0.150
W8	72.3	163.7	66.4	26.4	0.2992	0.16	236	154.3	290	236.3	25.6	26.54	1118.00	1720	7.09	64.44	17.26	0.99	-1.36	78.87	0.169
W9	168.5	189.7	33.2	16.4	0.2994	0.06	221.3	186.5	312.5	123.3	56.2	44.5	1352.00	2080	7.99	85.23	7.20	0.42	-10.11	64.99	0.060
W10	188.8	154.8	58	22	0.09975	0.12	253.1	143.6	425.8	89.3	65.2	56.4	1329.25	2045	7.41	75.95	12.22	0.76	-9.94	57.49	0.114
W11	190.5	160.2	12.6	13.5	0.09975	1.9	218.6	178.2	230	68.3	35.2	22.1	1196.00	1840	7.56	77.97	3.79	0.16	-10.38	58.10	0.024
W12	122.2	189.5	56.4	16.8	0.3988	0.05	256.3	322.5	122.9	56.4	45.3	89.7	1300.00	2000	7.41	79.38	11.73	0.74	-9.09	71.88	0.113
W13	56.7	148.6	16.5	22.5	0.2991	3.62	223.6	156.2	118.4	98.2	33.2	15.6	910.00	1400	7.48	57.39	7.91	0.26	-2.54	81.21	0.048
W14	146.4	146.8	42.5	23.5	0.7979	0.53	436.4	268.4	364	89.2	69.2	55.4	1177.80	1812	6.49	67.95	11.22	0.59	-9.26	62.31	0.095
W15	312	264.5	41.6	11.2	0.0898	0.09	654	426.8	413	230	45.2	22.3	1880.45	2893	7.9	128.46	5.31	0.42	-18.95	58.30	0.048
W16	235.5	412.6	86.5	223.3	0.5989	0.65	630	864.7	630	413	30.2	41.2	2567.50	3950	7.6	169.04	17.17	0.79	-21.62	74.29	0.082
W17	436.5	344.5	153	83	0.6002	3.6	766.5	865.4	634.2	452.1	35.2	23.6	2574.00	3960	7.9	171.04	12.11	1.33	-33.07	56.55	0.133
W18	423.5	422.6	186.4	89.5	2.81	5.4	890	636.4	960	411.3	36.8	74.2	3003.00	4620	8.6	195.84	15.68	1.53	-33.64	62.20	0.145
BH2	334	112	89.8	112.5	0.6002	3.7	546	326.8	321.6	321	22.4	56.2	1625.00	2500	8.1	79.55	20.76	1.09	-6.24	35.60	0.151
W19	360.5	88.6	33.6	6.2	0.2992	0.06	789	54	290	123	23.6	23.6	1332.50	2050	7.9	74.92	6.02	0.41	-8.25	28.84	0.058
Max	436.5	422.6	312.2	223.3	3.26	5.4	890	865.4	960	452.1	365	123.6	3003	4620	8.6	195.84	38.89	3.77	0.91	81.21	0.525
Min	56.7	63.2	12.6	6.2	0.0898	0.01	218.6	54	118.4	56.4	22.4	2.6	754	1160	5.7	33.90	3.79	0.16	-33.64	28.84	0.024

Mean 232.12 187.57 91.68 52.78 0.69 1.85 450.32 331.47 418.6 225.91 53.95 43.57 1618.47 2447.1 7.471 92.44 15.29 1.08 -11.29 56.89 0.152

		Comparison wit	h others coastal	area studies				Standard per	missible limi	t
Parameters	This Study	Dar es Salaam (Mjemah, 2007)	Dar es Salaam (Mtoni, 2013)	Kilwa (Melchioly, 2018)	Zanzibar (Mato, 2015)	Kigamboni (Nkotagu, 1989)	Tanga (Prusty,2020)	TZS (2008)	FAO (1985)	WHO (2011)
Aquifer depth	Shallow	Shallow	Shallow	Shallow	Shallow	Shallow	Deep	-	-	-
pН	7.47	6.6	7.55	6.76	7.42	7.65	7.62	6.5 - 9.2	6.0 - 8.5	7.5
EC (µS/cm)	2490	1803	3003.4	2048	4973	2547	1617.8	1400	3000	1400
TDS (mg/L)	1618.47	1215	1564.54	1108	2829	1238.67	860.44	1000	2000	2000
Na ⁺ (mg/L)	91.68	261	773.3	271.3	863	112.6	221.96	200	900	200
K^+ (mg/L)	52.78	19	22.8	49.32	76.16	56.8	16.4	50	20	50
Mg^{2+} (mg/L)	187.57	148	65.2	96.6	255	212.6	18.13	100	60	100
Ca ²⁺ (mg/L)	232.12	167	89.39	206.7	189.6	198.7	64.8	300	400	300
Cl ⁻ (mg/L)	418.67	427	955.2	281.8	968.6	422.8	116.8	800	1100	800
SO4 ²⁻ (mg/L)	331.47	112	123.5	156.8	119.48	264.3	16.78	600	1000	600
NO3 ⁻ (mg/L)	53.95	81	73.7	39.5	24.12	48.2	12.86	75	10	50
HCO_3^- (mg/L)	450.32	207	265.1	245.8	354.2	386.4	224.56	600	600	600
CO ₃ ²⁻ (mg/L)	225.91	112.6	89.75	106.7	138.4	233.8	9.58	-	-	-

Table 3: Comparing the groundwater quality with others study in coastal areas of Tanzania and standard permissible limit

	-				_																
	Са	Mg	Na	K	Fe	Mn	HCO_3	SO_4	Cl-	CO_3	NO_3	PO_4	TDS	EC	pH	TH	SSP	SAR	RSC	MAR	KR
Ca	1																				
Mg	0.3530	1																			
Na	0.5792	0.0904	1																		
Κ	0.3507	0.2734	0.5155	1																	
Fe	0.4853	0.1810	0.5138	0.3193	1																
Mn	0.1973	0.3857	0.2391	0.1301	0.5350	1															
HCO3	0.5447	0.5681	0.0572	0.0457	0.2601	0.1411	1														
SO4	0.4839	0.8762	0.2772	0.4284	0.3383	0.3708	0.4055	1													
Cl-	0.7427	0.5252	0.7096	0.5969	0.4291	0.3566	0.3306	0.5582	1												
CO3	0.3864	0.1489	0.5546	0.7227	0.3029	-0.031	1 -0.1236	0.3337	0.4477	1											
NO3	-0.0673	0.2274	-0.0597	-0.2296	-0.1820	0.1324	-0.2506	0.1291	-0.0764	0.0112	1										
PO4	0.0435	0.3166	0.1358	0.0394	-0.0095	0.4941	-0.0177	0.2290	0.1342	-0.0778	0.7045	1									
TDS	0.7794	0.7789	0.5790	0.5539	0.5160	0.4898	0.5389	0.8387	0.8507	0.4364	0.0634	0.2901	1								
EC	0.7794	0.7789	0.5790	0.5539	0.5160	0.4898	0.5389	0.8387	0.8507	0.4364	0.0634	0.2901	0.9723	1							
pН	0.6533	0.2648	0.3587	0.3425	0.5226	-0.039	0.7295	0.2456	0.4352	0.3344	-0.3832	2 -0.2085	0.5267	0.5267	1						
TH	0.6332	0.9477	0.2723	0.3458	0.3153	0.3864	0.6558	0.8900	0.6878	0.2550	0.1652	0.2768	0.9103	0.9103	0.4419	1					
SSP	0.2603	-0.2490	0.8528	0.5975	0.3175	0.0966	6 -0.3500	0.0011	0.4863	0.5946	-0.1709	0.0358	0.2377	0.2377	0.0615	-0.1171	1				
SAR	0.4371	-0.1134	0.9728	0.4777	0.4188	0.1480	-0.1215	0.0985	0.5762	0.5457	-0.0911	0.0809	0.3923	0.3923	0.2387	0.0553	0.9270	1			
RSC	-0.6130	-0.8890	-0.1891	-0.1482	-0.2600	-0.4379	9 -0.6117	-0.8273	-0.6448	0.0081	-0.2271	-0.3460	-0.8406	-0.8406	-0.2939	-0.9446	0.2111	0.0260	1		
MAR	-0.6224	0.4757	-0.4524	-0.2093	-0.2180	0.1222	0.0393	0.2382	-0.2891	-0.3133	0.2300	0.1949	-0.0973	-0.0973	-0.3067	0.1812	-0.4867	-0.4966	-0.1647	1	
KR	0.2722	-0.2928	0.8948	0.4121	0.3021	0.0675	-0.2974	-0.0696	0.4308	0.5074	-0.1256	5 0.0147	0.1925	0.1925	0.0829	-0.1493	0.9575	0.9725	0.2218	-0.5049	9 1

Table 4: Pearson correlation matrix of the hydrochemical, physical and calculated parameters of groundwater samples

Hydrogeochemical classification of groundwater

Hydrochemical facies and water type

The principal cations and anions in the piper trilinear diagram are typically plotted to provide a clearer picture of the hydrogeochemical development of groundwater (Piper 1944, 1953). Because samples with comparable hydrochemical facies tend to plot together as groups on the piper plot, it highlights similarities and contrasts across groundwater samples (Todd and Mays, 2004). The hydrochemical facies of groundwater are always determined by the chemical parameters that make up their chemical compositions. The Piper Trilinear diagram, shown in Figure 2, illustrates the hydrochemical facies classification of groundwater. In the majority of groundwater investigations, Piper (1944) devised this method of classifying groundwater according to its hydrochemical facies. The piper diagram is excellent for recognizing the mixing of groundwater, and it makes it simple to follow changes in the water mixture's spatial and temporal linkages (Sivasubramanian et al., 2014).

The dominating dissolved chemical ion must make up more than 50% of the overall concentration in order to distinguish the different types of water. For instance, if a water sample is labelled as CaCl-type, it signifies that more than 50% of the total cation milli-equivalents are in the form of Ca^{2+} and more than 50% of the total anion milli-equivalents are in the form of Cl⁻. When neither the dominating cation nor anion (which surpasses 50%) is present, the water is typically categorized as mixed type (Wen et al., 2007). The two most frequent cations or anions will therefore be used in the categorization to characterize the type of water, but the naming scheme must be in decreasing order of abundance. The classification of the water samples shown in Figure 2 shows that nine (9) samples

(42.9%) fall in zone 5, which is described as the Ca-Cl water type, while the remaining five (5) samples (23.8%) fall in zone 1, which is described as the Ca-HCO3 water type. Seven (7) samples (33.3%) fall in zone 4, which is described as a mixed water type zone with a Ca-Mg-Cl water type. According to the findings in Figure 2, the dominating hydrochemical facies for cations is Ca-Mg, whereas the major hydrochemical facies for anions is Cl-HCO₃.

The results are shown in Figure 3(a), which demonstrates the link between Mg²⁺ and Cl⁻ . It can be seen that the coefficient of determination R^2 is 0.27, indicating a poor correlation between the two parameters. The fact that evaporation precipitation and seawater intrusion were both dominant in the ionic exchanges may be responsible for this phenomena. Similar circumstances are shown in Figure 3(b), where a lower R^2 coefficient of 0.38 denotes a non-direct link between K⁺ and Cl⁻. This condition results from Ca²⁺ and Mg²⁺ being the two most prevalent cations in groundwater's hydrochemical facies. When comparing Na⁺ and TDS, the correlation finding in Figure 3(c) has been improved. As can be seen, an R² coefficient of determination of 0.57 was attained, indicating that Na+ has significantly contributed to the dissolved salts in the groundwater. Key criteria that can be utilized to identify the impact of important components and groundwater salinity include sodium and total dissolved solids (TDS). A similar pattern can be seen in Fig. 3(d), which displays a relationship between Ca^{2+} and Cl^{-} , with an R^{2} coefficient of 0.53 and results showing a positive association. Plotting the Cl⁻ concentration in groundwater against TDS in Figure 3(e) reveals that the majority of the Cl⁻ ions in groundwater have a positive correlation ($R^2 = 0.68$) with TDS. The groundwater's Na⁺ concentration is plotted against Cl⁻ using the findings of the bivariate correlation (Figure 3(f)), and the plot reveals that the majority of the groundwater's Na⁺ ions have a positive

correlation with Cl^- ($R^2 = 0.60$). The groundwater likely comes from the same aquifer system as the bivariate correlation results for major cations Na⁺, Ca²⁺, Mg²⁺, and K⁺ showed positive association with Cl^- .

The correlations between cation and anion concentrations in respect to pH and total dissolved solids (TDS) are presented graphically in Fig. 5(d). This analytical method was created by Durov in 1950 and now enables the study of chemical compositions along with total dissolved solids (TDS) and pH. It is crucial to categorize groundwater according to the main hydro-geochemical facies when performing hydro-geochemical a assessment of groundwater. Researchers have created a number of groundwater methods and categorization charting techniques (Schoeller, 1935; Piper, 1944; Durov, 1950). Facies are defined as any distinguishable components of various characters that belong to any genetically connected system.

In light of this, hydro-geochemical facies are defined as separate hydrogeological zones with the same categories of cation and anion concentration (Kumaresan, 2006). Presenting the chemical connections the principal ions in for various groundwater samples using Piper Trilinear and Durov diagrams is still very helpful today (Freeze and Cherry, 1979). Prior to usage, the Piper plot's principal cation and anion concentrations must be translated to milliequivalents per liter (meq/l).

As seen in Figure 5(d), two (2) samples, or 10% of the total water samples, are located in the area with low total dissolved solids (TDS) concentration (1000 mg/L), while the remaining 90% are located in the area with high TDS concentration (> 1000

mg/L). Additionally, the Durov plot demonstrates that samples taken from hand-dug wells near to the grand mosque have significant concentrations of total dissolved solids (TDS). The same graphic, however, shows that the 10% of water samples that seem to have low TDS values actually contain high chloride The Durov plot concentrations (Cl-). classifies cations and anions individually, which makes it a different classification method than the Piper diagram. As a result, the classification of water types based on dominating hydrochemical facies produces similar results. According to the classification of the samples based on pH values, five (5) samples (23.8%) have lower pH values (6.5), which is an indication of acidic conditions since HCO₃⁻ hydrochemical facies are present.

For the case of pH, a total of five (5) samples (23.8%) fit into the second group of samples, which suggests moderately alkaline circumstances. This group includes samples with pH values greater than 6.5 but less than 7.5 (6.5<pH<7.5). The group of groundwater samples with pH values more than 7.5, as shown in Figure 5(d), constitutes the last classification of the samples, and there are eleven (11) samples (52.4%) in this class. According to literature, mineral deposits increase the water's alkalinity, which results in higher pH values, if the soil or bedrock near groundwater sources contains carbonate, bicarbonate, or hydroxide compounds. These materials dissolve and travel with the water (US EPA, 1998). This explains why samples with higher pH values tend to Ca^{2+} and Mg^{2+} carbonates, contain bicarbonates, and hydroxides in large amounts.



Figure 2: Piper Tri-linear diagram showing classification of water samples and zones of various water types.

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Figure 3: Bivariate plots for selected hydrochemical facies. (a) Correlation between Mg^{2+} and Cl^{-} (b) Correlation between K^{+} and Cl^{-} , (c) Correlation between Na^{+} and TDS, (d) Correlation between Ca^{2+} and Cl^{-} , (e) Correlation between Cl^{-} and TDS, (f) Correlation between Na^{+} and Cl^{-} .

Total hardness (TH)

Total hardness (TH) is a crucial factor for determining whether groundwater is suitable for household, agricultural, and industrial use (Vandenbohede et al., 2010; Melchioly, 2018; Mjemah, 2007). The precipitate that formed when soap is dissolved in water can be used to identify the physical properties of hard water. This is due to the fact that Ca^{2+} and Mg^{2+} ions typically precipitate soap. As a result, the overall hardness of water is now referred to as the sum of the Ca^{2+} and Mg^{2+} ion concentrations represented in mg/L of CaCO3. The classification of groundwater from the study area by Sawyer and McCarthy (1967) based on total hardness indicates that six (6) samples (28.6%) have values less than 75 mg/L, which is a sign of soft water. With values ranging from 75 mg/L to 150 mg/L in twelve (12) samples

(57.1%), the water is moderately hard. The final group has three (3) samples (14.3%)with hardness between 150 mg/L and 300 mg/L, indicating hard water. Table 2 lists the maximum, minimum, and mean values as 195.84 mg/L, 33.89 mg/L, and 92.43 mg/L, respectively. Several investigations have found that the average hardness values in Tanzania's coastal aquifers are 196.3 mg/L (Mtoni, 2013), 156.5 mg/L (Nkotagu, 1989), 166.8 mg/L (Melchioly, 2018) and 156.9 mg/L (Mjemah et al., 2007). Total hardness (TH) values are categorized as soft (0-60 mg/l), moderately hard (60-120 mg/L), hard (120–180 mg/L), and very hard (> 180 mg/L) based on US EPA (1986) standards. When compared to the classifications provided above by Sawyer and McCarthy (1967), these values vary somewhat less. In order to prevent corrosion of the water pipelines, it is typically advised to keep the TH value at or below 100 mg/L.

Soluble sodium percentage (SSP) or Na%

Sodium is regarded as a crucial cation that is essential for plant growth. Equation (2) presents the mathematical expression for establishing SSP. But this valuable metal shouldn't be used more than is allowed because doing so could damage the soil's structure and lower agricultural production (Srinivasamoorthy et al., 2005; Singh et al., 2008).

The permeability of soil is significantly influenced by the sodium content of irrigation water, which is extremely important (Ayers and Westcot, 1976; FAO, 2010). SSP levels less than 50%, according to USDA (1954), indicate adequate irrigation groundwater quality for applications, whereas higher values beyond 50% indicate that the water is unfit for such use. Wilcox (1955) divided the SSP values

into four categories: excellent to good (values between 0 and 20%), good to permissible (20 to 40%), permissible to doubtful (40 to 60%), doubtful to inappropriate (values between 60 and 80%), and unsuitable (numbers greater than 80%). The impacts of groundwater's electrical conductivity (EC), however, must be taken into account while evaluating the validity of the SSP categories based on Wilcox's (1955) diagram.

The findings of this study indicate that a total of eleven (11) samples, or 52.4% of all samples, fell in the good to permitted zone, while seven (7), or 33.3% falls in the doubtful to unsuitable region and three (3) samples falls in the unsuitable region of the Wilcox diagram in Figure 4(a). Eaton (1950) classified the SSP values such that less than 60% falls in safe zone while greater than 60% falls in unsafe zone. Based on this classification the results for this study indicates that eighteen (18) samples (85.7%) falls in the safe category hence the groundwater is suitable for irrigation purposes. It can be observed from the results in Figure 4(a) that although the %Na⁺ are low but the EC values in some of the samples are very high and hence to make the groundwater for those respective samples unsuitable for irrigation purposes.

Sodium absorption ratio (SAR)

The Sodium adsorption ratio (SAR) is an index commonly used for evaluating the sodium hazard related with irrigation water supply. The mathematical expression for establishing SAR is presented in equation (3). Richards (1954) and also Bower and Maasland (1963) explains that persistent use of certain irrigation water excessive in sodium concentration results in reduced crop yields due to deterioration of soil physical properties.

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Figure 4: (a) Groundwater classification based on Wilcox (1955) diagram. (b) Groundwater classification for irrigation according to US Salinity Laboratory's (USSL) diagram (Richards 1954).

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Accumulation of sodium (Na⁺) ion on the soil creates instability to the soil aggregates mobility and this effect results in dispersion of clay particles which eventually clogs the pore spaces of the soil and makes it impermeable EPA, 1998). (US The classification of SAR values based on Richard (1954) categorizes the groundwater into four classes; excellent (0 - 10), good (10 - 18), doubtful (18 - 26) and unsuitable (> 26). The results from this study (Fig. 5(b)) shows that based on sodium hazard, all the samples falls in region S₁ which indicates SAR value less than 10, meaning low hazard level and according to Richard (1954), groundwater could be classified as falling the excellent zone (0 - 10).

However, considering both the SAR and EC hazards, the groundwater could be classified as falling in two regions or zones such that; thirteen (13) samples (62%) falls in the S₁-C₃ region which indicates low sodium hazard but high salinity hazard and the remaining eight (8) samples (38%) falls in the S₁-C₄ region of the USSL plot, and this indicates low sodium hazard but very high salinity hazard. These results therefore (Figure 4(b)) shows that the groundwater in the study area is suitable for irrigation purposes since sodium hazard (SAR) is less than 10 and salinity hazard (EC) is less than 5000 μ S/cm.

Salinization, Freshening and Cation Exchange

The bivariate plot in Figure 5(a) presents the effects of salinization on the groundwater samples using the chloride-Bicarbonate ratio (Cl/HCO₃). The effects of salinization of groundwater in the study area based on the above mentioned ratio (Cl/HCO₃) was classified using the Revelle (1941) approach in which; ratio < 0.5 is for unaffected groundwater, 0.5 - 6.6 for slightly and moderately affected, and > 6.6 for strongly affected groundwater by salinization. It can be observed from Figure 5(a) that one (1) groundwater sample (4.7%) falls in the region

that is not affected by salinization and the rest of the groundwater samples fall in the region that is moderately affected by salinization.

Another bivariate plot presents the effects of salinization due to the displacement of Sodium cation (Na⁺). The plot is shown in Figure 5(b) in which Na⁺/Cl⁻ is plotted against Cl⁻ and both constituents must be in meq/l. This plot is usually used to compare with the Na⁺/Cl⁻ Molar ratio of seawater intrusion which has been given as 0.86 (Bear et al., 1999; HydroMetrics, 2008). Usually the discrepancies of the calculated ratio of seawater could be attributed to ion exchange processes that may lead to either surplus or depletion of Na⁺ relative to Cl⁻.

The research results show that all the groundwater samples fall below (< 0.86) the seawater ratio boundary and this is an indication of salinization, these results gives a clear picture that the samples could be affected or moderately affected by the effects of salinization. This fact also has been reflected by the Cl⁻/HCO₃⁻ Versus Cl⁻ (mg/L) plot in Figure 5(a) which shows that only one (1) sample falls below the margin of 0.5 but all other samples appears to be moderately affected by salinization since the ratio falls in the range $0.5 \ge X \le 6.6$.

A different phenomenon has been presented by the Ca^{2+}/Mg^{2+} versus Cl^{-} bivariate plot (Figure 5(c)) whereby it appears the concentration of calcium cations are more than those of magnesium. The cation exchange geochemical process that describes the freshening of groundwater has been explained by Bear et al. (1999) and Panno et al. (2006). It can be observed that seven (7) samples have the Ca^{2+}/Mg^{2+} ratio less than 1 while the remaining fourteen (14) have the Ca^{2+}/Mg^{2+} ratio higher than 1. Still there are no effects of salinization as the Cl⁻ values are lower but the Mg^{2+} ion has been replaced by Ca^{2+} ion through the cation exchange processes. Figure 5(c) shows the salinization processes freshening and that are accompanied by cation exchanges

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Figure 5: (a) Log-Log plot of Cl⁻/HCO₃⁻ Versus Cl- (mg/L); (b) Log-Log plot of Na⁺/Cl⁻ against Cl⁻; (c) Log-Log plot of Ca²⁺/Mg²⁺ against Cl⁻ and (d) Durov Diagram showing the relationship between the Cation/Anions concentrations with the total dissolved solids (TDS).

. These results gives an indication that in some groundwater samples the Ca²⁺ has replaced Mg²⁺ due to cation exchange processes while in some other groundwater samples the Na⁺ has been replaced by Ca²⁺ ion mainly due to dissolution of carbonate minerals (Calcite and Dolomite) in the aquifer matrix. Usually when the Ca^{2+}/Mg^{2+} ratio is very high than those encountered in seawater then this could be an indication of dissolution of carbonate minerals (Calcite and Dolomite) in groundwater in which Ca^{2+} is enriched.

Water Quality Index (WQI) assessment results

The importance of water quality index (WQI) in evaluating the quality of water for any particular use has been described by Brown et al. (1972). The WQI was calculated by considering key water quality parameters both physical and chemical which included pH, electrical conductivity (EC), total dissolved solids (TDS), nitrates (NO₃⁻), $(SO_4^{2-}),$ Calcium $(Ca^{2+}),$ sulphates (Mg²⁺), Magnesium Sodium $(Na^{+}),$ Potassium (K^+) and total hardness (TH). The mathematical expressions for determining WOI values are presented by equations (13). (14) and (15).

 Table 10: Calculation of overall Water Quality Index (WQI) for the groundwater samples taken from the study area

Parameter	Measured value (C _i)	Water quality standard (S _i) (Ramakrishnaiah <i>et al.</i> , 2009)	Unit weights (Wi = 1/S _i)	Quality rating scale (qi = (C _i /S _i) x 100)	Water Quality Index (WQI)
pН	7.47	6.5 - 8.5	0.133	99.6	13.2468
Electrical conductivity (EC)	2447	1000	0.001	244.7	0.2447

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Magnesium (Mg^{2+}) 18Sodium (Na^+) 91Potassium (K^+) 52	1.68 2 2.78	20 10 ΣW	0.02 0.05 0.1 $i_1 = 0.343$	458.4 527.8 Σqiv	22.92 52.78 $vi = 102.5069$
$\begin{array}{c} \text{Magnesium} \\ (\text{Mg}^{2+}) \\ \text{Sodium} (\text{Na}^{+}) \\ \text{Potassium} (\text{K}^{+}) \\ \end{array} \begin{array}{c} 18 \\ 91 \\ 91 \\ 52 \end{array}$	1.57 1.68 2.78	20 10	0.05 0.1	458.4 527.8	22.92 52.78
$\begin{array}{c} Magnesium \\ (Mg^{2+}) \\ Sodium (Na^{+}) \end{array} 18 \end{array}$	1.57 1.68	20	0.05	458.4	22.92
Magnesium (Mg ²⁺) 18'	1.57	30	0.02	575.14	7.3028
		50	0.02	375 14	7 5029
Calcium (Ca ²⁺) 232	2.12 1	.00	0.01	232.12	2.3212
Total hardness 92 (TH)	2.44 3	800	0.003	30.81333	0.09244
Sulphates (SO ₄ ²⁻) 33	1.47 5	500	0.002	66.294	0.132588
Nitrates (NO ₃ - 53	3.57	45	0.022	19.0444	2.618977
Total dissolved 161 solids (TDS)	18.46 5	500	0.002	323.692	0.647384

Overall WQI = $\Sigma qiwi / \Sigma W_i = 102.5/0.343 = 298.83$.

The water quality index (WQI) results presented in Table 9 and Table 10 shows that the overall WQI value is 298.83 of which according to Ramakrishnaiah et al. (2009) and Bhuven et al. (2011) in Table 1, the water quality status from the study area is described as Very poor or very bad since its WQI value lies between 200 and 300. But according to Mishra and Patel (2001) the water quality status from the study area based on WQI value, it is described as Unfit or unsuitable because its WOI value is greater than 100. Therefore based on the standard permissible values for WQI given in the literature and comparing with the calculated WQI using the actual concentration values measured from the study area, it can be clearly stated that the water quality status from the study area is of very poor quality.

CONCLUSION

The findings of this study reveal that the groundwater in shallow coastal aquifer in Kilwa Kisiwani oceanic Island is slightly affected by salinity due to seawater intrusion. However, research results for pH shows slightly neutral conditions and the mean values are within range of acceptable values of 7.47. The results also show that mean value for TDS is 1618.47 mg/L which is slightly higher than the permissible limit of 1000 mg/L, however TDS values ranging between 1000 to 2000 mg/L is regarded as moderately classification acceptable. EC indicate majority of the samples grouped within permissible and doubtful categories according to Wilcox (1955). Groundwater samples classification based on the piper trilinear diagram (Piper 1944, 1953) shows that the dominant hydrochemical facies are Ca-Cl (42%), Ca-Mg-Cl (33%) and Ca-HCO₃ (23%). The cation exchange processes indicates that Ca²⁺ replaced the Na⁺ and this is an indication freshening geochemical processes in the aquifer matrix.

The research results for total hardness (TH) indicates to be within the permissible limits while the soluble sodium percentage (SSP) or classification of groundwater for Na% irrigation purposes shows that majority of the samples falls in the excellent to good group and the remaining in the good to permissible category (Wilcox, 1955), hence groundwater from the study area is suitable for irrigation The plot of SSP against EC purposes. (Wilcox diagram) also shows that only 15% of the samples fall in the unsuitable region for irrigation purposes. For the case of sodium adsorption ratio (SAR) the results indicates that the values are less than 10 hence groundwater is suitable for irrigation purposes. Electrical conductivity (EC) values appear to be slightly higher but less than 5000 µS/cm hence groundwater can be used for irrigation purposes. Residual sodium carbonate (RSC) results shows that the values are within permissible range (<1.25) hence groundwater is good for irrigation use. Magnesium adsorption ratio (MAR) results shows that 23% of all the samples fall in the suitable category and hence the groundwater from the study area is moderately suitable for irrigation purposes.

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The research results for Kelly's ratio (KR) indicates that all the samples have KR value less than 1 hence groundwater is suitable for irrigation purposes., The cation exchange indicated a freshening geochemical process since Na + K were replaced by Ca + Mgresults confirms a formation of Calcite and Dolomite dissolutions. The effects of salinization of groundwater samples was classified using the chloride-Bicarbonate (Cl/HCO₃) and the Na⁺/Cl⁻ ratios, the results shows that groundwater is moderately affected by seawater due to the ratios being slightly below the maximum permissible values. Finally the overall groundwater quality assessment based on the water quality index (WQI) and the research results show that the groundwater is of very poor quality since the WOI value is 298.8 which is in the range of (200 - 300), this range is designated as very poor water quality for human consumption.

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No any potential conflict of interest related to this work as individual self initiative was involved in all activities pertaining to this work.

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