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Research Article

Groundwater quality assessment and hydrochemical characteristics in Wera Didjo, Southern Ethiopia

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Abstract

Groundwater quality assessment study was conducted in Wera Dijo, Southern Ethiopia. The study's objective is to understand water chemistry suitability for domestic and irrigation activities. In the study area, only regional hydrochemistry work has been done; hence this study focused on the detailed water chemistry of the study area. Twenty-eight shallow and deep water samples were collected, and major physical and chemical parameters were studied. The important hydrochemical facies of water present throughout this region are Ca-Mg-HCO3, Ca-Mg-SO4 and Na-HCO3-Cl. Except for fluoride, sodium, and potassium ion, the levels of major cation and anion were found to be below the World Health Organization's allowable limits for drinking purposes in the majority of the study area. The fluoride ion in groundwater exceeded the highest allowable amount of 1.5 mg/L for drinking water in fifteen of the samples. The sodium percentage, permeability index, sodium absorption ratio and The United States Salinity Laboratory (USSL) categorization were used to evaluate the water in this study location for irrigation purposes. Based on several water quality parameters overall, the research area water chemistry was suitable for drinking, agricultural activity and industrial use.

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Introduction

Around the world, groundwater is used to meet the ever-increasing demand for domestic, agricultural, and industrial demands (Elumalai and Lakshmanan, 2014). A number of physical and chemical constituents influence groundwater quality, the majority of which are produced from soluble products of weathering, dissolution, and decomposition of the region's geology (Muhammad et al., 2015). A variety of contaminants produced from many sources, such as industrial waste, agricultural waste, and municipal waste, contaminate the surface and groundwater. Groundwater scarcity could result from poor water resource management. When concentrations of major and minor ions are above the maximum allowable level, they become unsuitable for agriculture and drinking, which can result from both natural and anthropogenic activity.

Groundwater quality for domestic and agricultural use has received a lot of attention and research around the world. (Benvenuti et al., 2002; Laluraj et al., 2005; Jalali, 2007; Alexakis, 2011; Brindha and Elango, 2011; Gunalan and Lakshmanan, 2015). Due to fast population growth, industrialization, and urbanization, many regions in Ethiopia have experienced significant degradation in groundwater quantity and quality in recent years (Alemayehu, 2000; Ayenew et al., 2008; Demlie et al., 2008; Rango et al., 2010; Jagadeshan et al., 2018).

Several people in Ethiopia rely on groundwater resources for essential purposes due to poor surface water management. The objective of this research was to understand more about the chemistry of water as well as its applicability for drinking and irrigation in Wera Didjo, Ethiopia. Bore well water, both shallow and deep, is a vital source of drinking water, irrigation, and industrial activity in this region. The demand for water has been steadily increasing due to the fast increase of the community's housing and irrigation activity. In this area, groundwater is commonly used directly for drinking purposes without sufficient water treatment. The use of agrochemical chemicals for irrigation purposes may also harm groundwater. Previously, no groundwater chemistry research had been conducted in the Wera Didjo area. As a result, the current investigation is being carried out in order to assess the quality of water for irrigation and drinking applications.

Materials and Methods

Study area

The research area is nearly 1,874 km² in size and is situated in southern Ethiopia on the middle border of the major Ethiopian rift valley. The average annual precipitation is 1,200 mm, with the majority falling between February and June and the rest falling between July and September. Summer temperatures in the study area range from 22 to 35 °C, and winter temperatures range from 13 to 20 °C (February to June. The southern part of the research area is covered by Shala Lake, which is used for drinking, agricultural and industrial uses. This area is highly planted, with groundwater obtained from multiple open wells as well as lake water. The Wera Didjo is characterized topographically by several small residual hills that constitute an undulating region. The regional slope runs north-east, with a maximum elevation of 3187 meters above sea level (masl) in the Northern Mugo Mountain, gradually decreasing to roughly 1551 m asl in the eastern part. The surface region has a dendritic drainage pattern, with Didjo and its tributaries constituting the area's major rivers (Figure 1). The Didjo River is a perennial river that drains into Lake Shala in the research region's southern part.

Geology and hydrogeology

The Wera Didjo region is made up of Cenozoic volcanic rocks such ignimbrite, basalt, rhyolite, and tuff, as well as tertiary and quaternary lacustrine sediment deposits (Benvenuti et al., 2002). Cenozoic volcanic rocks can be found throughout nearly the entire study region. The eastern parts of the research area comprise tertiary and quaternary deposits (Figure 2). Groundwater in this area is mostly found in an unconfined to semi-confined aquifer of weathered and fractured volcanic rock.

Irrigation activities are the region's primary source of revenue. This area has been intensively farmed, owing mostly to the use of water from multiple shallow drilled and bore wells. Maize is the main crop, but the area also grows bananas, cotton, potatoes, sugar cane, corn, beans, mango, and a variety of other fruits and vegetables.



Figure 1. Location and water sampling point of the study region.

Data collection and analysis

Groundwater sample was taken from 28 representative wells across the study area. During the month of May 2019, groundwater sample was taken from bore wells and springs. Figure 1 depicts the locations of water sampling points. Portable digital meters were used at the water sampling location to measure field characteristics such as electrical conductivity (EC), pH, and total dissolved solids (TDS). Volumetric titration with standard Ethylenediamine tetraacetic acid (EDTA) was used to measure calcium and magnesium concentrations in groundwater samples, while an Absorption Spectrophotometer was used to determine sodium and potassium content. The chloride concentration was determined using the silver nitrate measurement by American Public Health Association technique (APHA, 1995).

The concentration of fluoride in water was measured using an ion-selective electrode technique. The carbonate and bicarbonate concentration was measured using an acid titration technique. The amounts of sulphate were determined using a UV visible Spectrophotometer. To assess the general geochemical composition of groundwater in the Wera Didjo River basin, major cations and anions were depicted in a Piper trilinear plot (Piper, 1944). The sodium ion, indicated as Na %, is an important parameter for irrigation water quality. The quantity of sodium ion concentration in irrigation water is usually determined using the formula given in Equation (1) (Wilcox, 1955), where the ion concentrations are measured in meq/L. The Permeability Index (PI), which is given by Equation 3 with concentrations in meq/L, was created by WHO (2004) and Doneen (1964) as a measure for evaluating the quality of groundwater for irrigation applications.



Figure 2. Geological map of the study area.

$$Na\% = \frac{(Na^{+} + K^{+})}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})} \times 100.....(1)$$

SAR is determined by the following Equation 3 (where the concentration of all ions is in meq/L),

$$SAR = \frac{Na^{+}}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}....(2)$$

$$PI = Na^{+} + \sqrt{HCO3} / Ca^{2+} + Mg^{2+} + Na^{+}) \times 100......(3)$$

Results and Discussion

Drinking water quality

The pH value of groundwater system defines the acidic, basic, and neutral states of the solution by showing the effective hydrogen ionic strength. pH levels in water samples from the Didjo river watershed

range from 6.1 to 8.4. From the highland groundwater to the rift plain, the pH value indicates an increasing pattern. The pH of the aquifer water in this location is lower than the WHO's maximum allowable level (6.5– 8.5). The EC value in groundwater in the research region, Didjo river Catchment, ranges from 70 to 1654 (μ S/cm), with a mean value of 448 (μ S/cm). In

comparison to those on the western escarpment, wells in the southern parts of the rift valley have higher conductivities. The groundwater flow and hydrogeology might all be factors in the rise in conductivity toward the valley's floor. TDS concentrations have to be classified in order to determine its acceptability for domestic and agricultural application (Davis and Wiest, 1966). Table 1 depicts the nature of water classification based on Freeze and Cherry's proposed range of TDS levels (1979). In the field of study, groundwater TDS concentrations ranged from 44 to 882 mg/L. The study area has 92.8% fresh water samples and 7.2% brackish water samples. According to the WHO suggested guideline, most of the water locations are under the maximum permissible level for domestic application. TDS levels in the majority of the study region are less than 500 mg/L, indicating a very low amount of soluble salt ions in the water, according to the TDS map. The hardness of groundwater is an essential factor for measuring its appropriateness for home, drinking, and many industrial uses. The principal cations that cause hardness in water are carbonate, calcium, and

magnesium. Bicarbonate, sulphate, nitrate, and chloride are the primary anions that contribute to overall hardness (Elumalai and Lakshmanan, 2014). The collected water sample hardness ranges from 19 to 563 mg/L, with an average of 117 mg/L. Sawyer et al., (2003) introduced a categorization method for water based on the occurrence of total hardness (TH), as indicated in Table 2. Around 47% of the groundwater sample chemistry values were moderately hard, including hardness ranging from 75 to 150 mg/L. The chemical values of 21% of the water samples were hard, with TH varying from 150 to 300 mg/L. The results of a few water samples (32%) were soft, with TH levels of less than 75 mg/L. The maximum allowed hardness level for drinking water, according to the WHO (2004), is 500 mg/L, while the recommended harness level is 100 mg/L. "Hardness reduces lather formed by soap and causes formation of scales in pipes and on plumbing fixtures (Elumalai and Lakshmanan, 2014)". The level of hardness might be either temporary or permanent. The presence of calcium carbonate causes temporary hardness, which may be reduced by heating the water (Kumar et al., 2013).

Table 1. TDS levels in water are classified depending on the Freeze and Cherry (1979).

TDS (mg/L)	Nature of water	Amount of samples	Percentage of samples
<1000	Fresh water	26	92.8
1000 -10000	Brackish water	2	7.2
10000-100000	Saline water	-	Nil
>100000	Brine water	-	Nil

TDS = Total Dissolve Solid

Table 2. Total hardness based water classification.

Total amount of hardness as CaCO3 (mg/L)	Water type	Amount of samples exceeding WHO limits	Percentage of the samples exceeding WHO limits
<75	Soft	9	32
75 - 150	Moderately hard	13	47
150 - 300	Hard	6	21
>300	Very hard	-	Nil

TH = total hardness; WHO = World Health Organization.

Cations

The solubility of calcium and magnesium-rich minerals in the water affects the chemistry of groundwater. The northwestern area of the study region had the highest calcium values, whereas the rift valley floor water samples had the lowest calcium levels. The high amount of calcium in the research region's groundwater is due to weathering of silicate mineral-rich volcanic rock such as feldspar and plagioclase, which is the dominant mineral in the highland and escarpment aquifers, showing higher Ca²⁺ levels. Calcium ions in drinking water can reach a maximum of 200 mg/L (WHO, 2004). The calcium ion concentration in the groundwater in the research region varies from 5 and 57 mg/L (Figure 3). The amount of calcium ions in groundwater of the study region is below the highest permissible level of drinking water recommendations. Magnesium in groundwater might be supplied from the region's calcareous soil. An adequate quantity of magnesium is required for cell activity and enzyme performance. Magnesium at high amounts in water can be laxative, but magnesium shortage can cause structural and functional problems in humans (Sarala and Ravi, 2012). Magnesium ions are found in groundwater in concentrations ranging from 1 to 31 mg/L (Figure 3). The highest acceptable level of magnesium ions in groundwater is 150 mg/L. (WHO, 2004) and most of the water in the area of research was within this range. Figure 3 shows the amount of calcium and magnesium spatial variation in the studied region.



Figure 3 Spatial distributions of calcium and magnesium (mg/L).

Sodium is the primary cation in the majority of the Watershed, particularly in groundwater samples taken from the rift valley floor. The sodium ion concentration in collected water varies from 7 to 304 mg/L (Figure 4). The highest sodium concentrations were measured at the rift floor and escarpment water in the research area. Sodium levels are progressively increasing from highland water to the rift valley bottom. This high amount suggests that sodium was transmitted into groundwater as a result of intense rock-water interaction, silicate weathering, and cation exchange

mechanisms (Ayenew et al., 2008). The increased ingestion of water with a high concentration of sodium may cause health problems such as hypertension, heart disease and kidney problem (Gunalan and Lakshmanan, 2015). The maximum acceptable value of sodium in domestic water is 200 mg/L, according to the World Health Organization (WHO). The amount of potassium values in groundwater ranges from 0.5 to 17 mg/L, with mean value of 6 mg/L, whereas the WHO's maximum acceptable amount for domestic groundwater is 12 mg/L (Figure 4).



Figure 4. Spatial variation of sodium and potassium (mg/L).

The highest potassium concentrations are seen in shallow well water on the rift plain. The area's groundwater contains a high amount of potassium due to the dissolution of potassium source rocks incorporating acidic volcanic rocks, which is greater near the rift floor than in highland water samples. WHO (2004) recommendations were applied to compare the amounts of major cations in the research area's water. The maximum allowable potassium values for drinking water have been exceeded in a few groundwater samples (Table 3).

Anions

Bicarbonate is the most abundant anion in among groundwater samples collected in the research region. The bicarbonate concentrations varied between 49 and 633 mg/L with an average of 362 mg/L (Figure 5). The WHO (2004) standard levels are exceeded in 3.5% of water samples collected from the study region. The amount of bicarbonate in the studied region shows an increasing pattern from the highlands to the rift floor, which correlates to increases in sodium and potassium.



Figure 5. Spatial variation of bicarbonate and chloride (mg/L).

The principal source of carbonate and bicarbonate in groundwater is dissolved carbon dioxide from precipitation, organic matter degradation, and carbonate minerals (Kumar et al., 2015). Prolonged bicarbonate consumption might result in headaches, dizziness, and irritability (Gunalan and Lakshmanan, 2015). The amount of chloride in the measured water sample ranges from 15 to 185 mg/L, with an average value of 64 mg/L (Figure 5). The concentration of chloride rises throughout the groundwater flow channel from the highland groundwater to the rift base groundwater. In humans, too much chloride causes pressure, migraine, cardiac high blood pressure, fractures, kidney stones, and allergy (Gunalan and Lakshmanan, 2015).

Chloride is the predominant ion in both groundwater and surface water because it is found in all types of soils and rocks. The chloride amounts detected in all water samples obtained taken from the research area were lower than the WHO (2004) higher recommended limit of 600 mg/L. The concentration of sulphate in groundwater in the research region ranges from 5 to 73 mg/L, with an average value of 6 mg/L (Figure 6). The concentration of sulphate raises

relatively nearer the rift plain than closer the highland waters. The highest concentration was found on the rift floor. This might suggest that the concentration of sulphide mineral containing rocks rises nearer the rift plain. The sulphate ion concentration in the study region's groundwater is lower than the WHO acceptable standard of 400 mg/L. Human organs are primarily affected by the use of sulphate ion-rich drinking waters (Gunalan and Lakshmanan, 2015). The fluoride ion is a major minor element found in all types of natural water and is usually present as a naturally occurring constituent. Fluorosis, such as dental and skeletal fluorosis, can be caused by high fluoride ion concentrations in drinking water. Fluoride levels in the water of the studied region range from 0.4 to 13.1 mg/L (Figure 6). Fluoride ion concentrations were greater than the WHO (2004) standard in 15 of the 28 groundwater sampling areas. Fluoride levels in groundwater in the research area were high due to the dissolution of fluoride-bearing volcanic rock minerals such as lacustrine sediments, tuffs and pyroclastic deposits. The measured cation's dominance order is Na⁺>Ca²⁺>Mg²⁺>K⁺ and anions are HCO₃²⁻ >Cl⁻ $>SO_4^2 > CO_3^2 > F^-$.



Figure 6. Spatial variation of sulphate and fluoride (mg/L).

The hydrochemical facies can be used to examine the hydrochemical process and the change of groundwater in aquifers because to residence time and flow (Piper 1944). The majority of groundwater samples have Ca–Mg–HCO₃ and Ca–Mg–SO₄ chemistry, with a few water samples having Na–HCO₃–Cl chemistry (Figure 7).

The results of the geochemical analysis of major water chemistry parameters in collected groundwater samples were compared to the World Health Organization's standard recommended limits for domestic and drinking uses (WHO, 2004). Table 3 depicts the study area's maximum permissible and most desirable limits for various parameters. In a few water samples, cation concentrations such as sodium and potassium exceed the maximum allowed levels for drinking. Similarly, the concentration of fluoride anion exceeds 15 water samples. These results indicate that the groundwater in this area is heavily contaminated by fluoride ions.



Figure 7. Classification based on Piper diagram

Parameters	Unit	Minimum	Maximum	Average	WHO (2004)		Number of
					Most	Maximum	samples
					desirable	allowable	exceeding
					Limits	limits	allowable limits
pН	-	6.1	8.4	7.3	6.5	8.5	Nil
EC	μS/cm	70	1654	448	-	1500	1
TDS	mg/L	44	1243	268	500	1500	Nil
TH	mg/L	19	563	117	500	1000	Nil
Ca^{2+}	mg/L	5	174	30	75	200	Nil
Mg^{2+}	mg/L	1	31	9	30	150	Nil
Na^+	mg/L	7	304	65	50	200	2
\mathbf{K}^+	mg/L	0.5	17	6	10	12	4
HCO ₃ -	mg/L	49	633	362	300	600	1
Cl-	mg/L	15	185	64	200	600	Nil
F-	mg/L	0.44	6.1	3.85	0.6	1.5	15
SO4 ²⁻	mg/L	5	73	6	200	400	Nil

Table 3. Summary of the analysed water quality parameter and the number of water samples that exceed WHO recommendations.

EC = Electrical Conductivity; TDS = Total Dissolved Solid; TH = Total Hardness.

Irrigation water quality

The study region's groundwater is heavily utilized for intense agriculture. The amount of major mineral composition occurrence in groundwater influences its suitability for irrigation purposes. The presence of more dissolved major ions in irrigation groundwater, such as carbonate, bicarbonate, potassium, and sodium, might affect crop growth and irrigation soil quality, reducing yield. The osmotic pressure in the plant's internal structure will be reduced when these large cations and anion accumulate; preventing water from reaching the stems, leaves, and branches.

Electrical conductivity and sodium percentage

The sodium content of water samples taken in the research region ranges from 13 to 92%. Excellent (3.5%), good (39%), permissible (21.5%), doubtful (21.5%), and unsuitable (14.5%) are the categories for groundwater samples (Table 4).

Table 4. The nature of groundwater classifications depending on sodium percentage.

Sodium percentage	Types of water	Number of water samples	Percentage of samples
< 20%	Excellent	1	3.5
20-40%	Good	11	39
40-60%	Permissible	6	21.5
60-80%	Doubtful	6	21.5
> 80%	Unsuitable	4	14.5



Figure 8. Classification of water based on electrical conductivity vs sodium percentage.

Wilcox (1955) suggested classifying groundwater based on total sodium percentage and electrical conductivity, which was done and presented in Figure 8. Nearly 78.5% of assessed groundwater quality shows excellent to good results, 3.5% are doubtful to unsuitable for irrigation, and 3.5% are acceptable to permissible. In areas where irrigated groundwater is subjected to doubtful and unsuitable field conditions, agricultural yield is typically lower.

Alkalinity and salinity hazard

Excessive salinity in water can harm plants' osmotic processes, interfering with groundwater and nutrient absorption from soils and rocks (Gunalan and Lakshmanan, 2015). The Sodium Adsorption Ratio (SAR) is a strong indicator for determining if groundwater is suitable for cultivation because it assesses the impact of alkali/sodium danger on plants (Wasim et al., 2014). Irrigation groundwater with a high sodium ion concentration increases sodium exchange in the soil and weathered rock, creates soil permeability problems, and causes clayey soils to expand, making them unsuitable for irrigation. In this study region, the determined SAR value ranges from 0.36 to 11.98, therefore it has been categorized as good for agriculture (Table 5). Irrigation waters with SAR concentrations above 6 may cause permeability issues in the soil zone, resulting in shrinking and expansion (Saleh et al., 1999). The more the risk of sodium in groundwater, the more alkaline soil zones will expand (Todd, 2001), whereas a larger salt content in groundwater will cause a saline soil layer to form (Todd, 2001).

Table 5. Water type description dependent on alkalinity hazard.

SAR	Alkalinity hard	Water class	Number of samples
< 10	S1	Low	24
10-18	S2	Medium	4
18-26	S3	High	Nil
> 26	S4	Very high	Nil



Figure 9. Irrigation water salinity and alkalinity issues.

Table 5 shows the alkalinity hazard classification. Based on the results of the alkalinity hazard categorization, the groundwater in this region is typically acceptable for irrigation. Richards (1954) proposed the United State Salinity Laboratory (USSL) graph for evaluating the acceptance of groundwater in Didjo river basin region for irrigation. Nearly 28.5% of groundwater samples belong into the C1-S1 group, whereas 57% go into the C2-S1 group suggesting groundwater having low salinity and low sodium and medium salinity and low sodium that may be utilized for cultivation with all types of surface soil with little hazard of exchangeable sodium. 11% of measured water quality samples are characterized as C3-S2, denoting high salinity and medium sodium water. 3.5% of groundwater samples are characterized as C3-S1,

showing a high salinity danger and low sodium water (Figure 9).

Permeability index

Continuous irrigation water use impacts soil permeability, which is controlled by soil major cation and anion concentrations. For irrigation applications, groundwater geochemistry was categorized into three parts. With percentage or more of maximum permeability in soil, class I and class II water are acceptable and good for irrigation. With a maximum permeability of 25% in soil, Class III type is unsuitable for irrigation. Around 25% of groundwater samples come from the class III field (Figure 10).



Figure 10. Irrigation water classification based on permeability index.

Conclusion

The Wera Dijo River catchment region high land to rift floor collected 28 shallow and deep bore water samples; the quality is alkaline and the nature of the water varies from fresh to brackish. The measured cation's dominance order is Na⁺>Ca²⁺>Mg²⁺>K⁺ and anions are $HCO_3^2 > CI^2 > SO_4^2 > CO_3^2 > F^2$. The majority of groundwater samples have Ca-Mg-HCO3 and Ca-Mg-SO₄ chemistry, with a few water samples having Na-HCO₃-Cl chemistry. Based on the hardness measurement, the study region findings indicate that the water quality ranges from soft to moderately hard, suggesting that the water is safe to consume. In comparison to highland groundwater, the concentrations of sodium, potassium, fluoride, and bicarbonate in rift valley floor water are greater above the WHO recommended limit. Most groundwater quality steadily increases along the groundwater flow direction into the rift valley due to increased mineral dissolution. In 15 of the 28 groundwater samples, the fluoride ion concentration exceeds the maximum recommended level of 1.5 mg/L. According to Wilcox (1955), US salinity class, and Sodium Adsorption Ratio (SAR) characterization, the majority of the highland to rift floor Didjo river water samples is safe for irrigation activities.

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