

Article

Hydrogeochemical Processes and Water Quality Assessment in Volcanic Aquifers of the Gilgel Gibe and Upper Dhidhessa Catchments, Southwestern Ethiopia

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Abstract

Groundwater is a critical resource for domestic, agricultural, and industrial use in the Gilgel Gibe and Dhidhessa catchments of southwestern Ethiopia, where volcanic aquifer systems are the main sources. However, groundwater quality in these catchments has been under pressure from anthropogenic activities such as population growth, land-use changes, and pollution driven by rapid development and poor resource management. This study investigates hydrogeochemical processes and evaluates groundwater quality in volcanic aquifers using hydrochemical analyses and a stable isotope approach applied to 115 water samples. The spatial distribution of various physicochemical and hydrogeochemical parameters shows a distinct contrast between the highland and lowland regions, indicating topography-driven variations in water quality and geochemical processes. In hand-dug wells, springs, and surface waters, the ionic order is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, whereas deep wells show $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. The predominant groundwater type is Ca-HCO₃, followed by Na-HCO₃ and Ca-NO₃, with other types including Ca-Mg-HCO₃, Ca-Na-HCO₃, and Na-Ca-HCO₃. Water types of Ca-HCO₃ and Ca-Mg-HCO₃ dominate the upland areas, indicating relatively young groundwater with moderate total dissolved solids (TDSs) and enrichment in $\delta^{18}\text{O}$ and $\delta^2\text{H}$, where highly mineralized Na-HCO₃ water types prevail in the deep aquifers of the lowland regions, where $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are relatively depleted. Principal component analysis, cross-plots of major cations versus HCO₃⁻, and mineral stability diagrams indicate that aluminosilicate weathering and dissolution are the dominant processes controlling groundwater chemistry in the study area. The higher saturation index values observed in the deep wells indicate water closer to mineral equilibrium, suggesting more extended water–rock interaction relative to the shallow wells. The CO₂ partial pressures calculated using PHREEQC exceed atmospheric levels (~10^{-3.5} atm), indicating sources from atmospheric influx, soil, or biogenic activity for most samples, and deeper sources such as mantle degassing may be found in a few deep wells. Scatter plots of Cl⁻ vs. SO₄²⁻ and Cl⁻ vs. NO₃⁻, associated with Ca(NO₃)₂, NaNO₃, and CaCl₂ water types, suggest that anthropogenic inputs are the second major factor influencing the area's water chemistry.

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Stable isotope analyses and hydrochemical data indicate that groundwater in the area primarily originates from local precipitation, with isotopic signatures reflecting strong groundwater–surface water interaction. These findings improve understanding of regional hydrogeochemistry and groundwater quality and help identify promising zones for sustainable groundwater development. This study provides valuable insights into groundwater resource management both in the study area and in regions sharing comparable geological contexts.

Keywords: hydrogeochemical processes; aluminosilicate dissolution; anthropogenic pollution; stable isotope; Gilgel Gibe; Dhidhessa; Ethiopia

1. Introduction

Water is a vital and limited resource that supports the hydrological cycle and is essential to sustaining life and ecological balance [1,2]. The availability of sufficient quantities of good-quality water is a key criterion for selecting an appropriate water source [3]. In many regions where surface water is inadequate, groundwater constitutes the principal supply for drinking, irrigation, and industrial uses [3,4]. Groundwater abstraction has increased markedly in recent decades, driven by rapid population growth, recurrent droughts, and accelerated economic development [5,6]. It is a critical source of drinking water for billions of people and remains the most reliable supply for rural communities in sub-Saharan Africa [7]. However, its quality often deteriorates in arid and semi-arid regions, where limited rainfall, high evaporation, and overextraction contribute to increased salinity, contamination, and aquifer depletion [5].

Many developing countries, including Ethiopia, struggle to sustainably manage their water resources to meet current and future demands due to a lack of comprehensive assessments of water quality and availability [8]. Understanding the temporal and spatial evolution of groundwater quality and quantity is essential for sustainable management and informed decision-making. Groundwater science employs a variety of tools and methods to assess and quantify groundwater development and changes over time [9]. A widely used approach for evaluating hydrogeochemical dynamics involves standard hydrochemical analysis to identify dominant processes and water types, using ionic ratio plots, cross plots, correlation analysis, principal component analysis, and diagrams (e.g., Piper diagrams, Gibbs and Wilcox diagrams), as well as geochemical modeling [3,10,11]. This is often complemented by spatial interpolation maps and principal component analyses.

Environmental isotopes are widely applied alongside conventional hydrochemical methods to strengthen groundwater quality assessment and the evaluation of groundwater–surface water interactions [3,12,13]. When integrated with ion chemistry, stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) provide essential insight into groundwater origin, mixing patterns, and the processes controlling groundwater composition in the study area [12]. Groundwater quality can be influenced by both natural and human-induced pollution sources [14,15]. Naturally occurring contaminants originate from the rocks and sediments through which the water flows [16]. Geological and tectonic settings significantly influence groundwater recharge and discharge processes within watersheds. Most Ethiopian river basins are characterized by heterogeneous volcanic rock aquifers, which are important sources of groundwater [17–20]. The chemical, mineralogical, and structural heterogeneity of volcanic aquifers leads to pronounced variability in groundwater composition [21]. The influence of these rocks on groundwater chemistry has been discussed in previous

studies [22,23]. However, these studies are largely limited to specific regions of the country [6,24,25].

Groundwater aquifer systems in the southwestern region of Ethiopia are situated within volcanic terrain. The Gilgel Gibe and Upper Dhidhessa catchments are the largest in the region, where a densely populated community relies heavily on groundwater resources. This region is experiencing rapid population growth and economic expansion, with urbanization emerging throughout the catchment [26]. Groundwater through shallow wells, hand-dug wells, and springs is the most extensively used resource, contributing to domestic water supply and irrigation for both rural and urban populations in the study area. Groundwater abstraction rates in the study area have been increasing over time [27], raising concerns about future pressure on local water resources as demand for drinking water and household farming continues to grow [26,28]. Numerous studies have been conducted in these catchments; however, limited attention has been given to groundwater-related aspects. Most previous research has primarily focused on hydrological processes [29], land-use and land-cover dynamics [30], climate change impacts [31], water demand, and reservoir water quality assessments [24,28,32,33]. Although several sub-catchment and local-scale studies have examined groundwater potential, recharge, geological characteristics, and water quality [27,34–36], they remain limited in providing a comprehensive understanding of groundwater dynamics. Therefore, a detailed investigation of hydrogeochemical characteristics and the processes controlling groundwater quality in the volcanic aquifers of the study area is still required.

The hydrogeochemical composition of groundwater provides valuable insights into its origin and its interaction with subsurface materials in both shallow and deep-seated environments. The aquifer systems in the region remain largely undefined due to a general lack of hydrological and hydrogeological data, particularly related to groundwater quality, which poses significant challenges for effective groundwater abstraction planning and management. According to Kitessa et al. [37], groundwater chemistry in the Jimma area is primarily influenced by silicate weathering. However, this study was conducted on a local scale with limited groundwater data and geographic area. There is still a lack of detailed studies on the processes governing hydrogeochemical reactions, groundwater evolution and flow, and water–rock interactions within the complex volcanic sequences of the southwestern plateau, particularly using integrated approaches at a large scale. The current study adopts a broader, regional-scale approach and highlights that significant uncertainties remain in understanding the key processes governing groundwater quality and evolution in a comprehensive way. To address these gaps, an integrated approach that combines hydrogeochemical and environmental stable isotope ($\delta^2\text{H}$, and $\delta^{18}\text{O}$) analyses was used to investigate the hydrogeochemistry of groundwater and the processes influencing its evolution within Gilgel Gibe and Upper Dhidhessa volcanic aquifers. Although widely applied in hydrogeological studies [23,24,27,38,39], this integrated method has not been previously used in these specific catchments. The use of multiple tracers reduces the limitations of individual methods and enhances the understanding of hydrogeological systems. It is particularly effective for characterizing complex aquifers in data-scarce regions such as the Gilgel Gibe and Dhidhessa watersheds. This study also explores additional factors, including anthropogenic pollution, influencing the hydrogeochemical evolution of groundwater. The aim of this study is to evaluate the hydrochemical and isotopic characteristics of surface and groundwater and identify the key processes controlling groundwater chemistry.

2. Materials and Methods

2.1. Study Area

Ethiopia has twelve major river basins (Figure 1a). The study area is situated in the southwestern parts of Ethiopia within the Gilgel Gibe and Upper Dhidhessa catchments, which are parts of the Omo Gibe River Basin and Abay River Basin, respectively. The area is highly dissected by various drainage systems characterized by dendritic, parallel, and sub-parallel systems. Geographically, the study area is found to be between 36°30'00" and 37°27'20.4" E longitude, 7°20'5.8" and 8°6'49" N latitude, having an aerial coverage of about 5128 km² (Figure 1c). The area receives unimodal rainfall from March to October, with annual rainfall ranging from 1200 mm to 2000 mm. Rainfall reaches its peak in July and August [40]. Globally, the area is part of a sub-tropical climate region, which is characterized by moderately warm temperatures and medium to high rainfall (Figure 2). The mean annual temperature varies from 20 to 25 °C. The current geomorphology of the Gilgel Gibe and Dhidhessa catchments results from past volcano-tectonic activity and later exogenic processes. The region features rugged terrain, including deeply incised landscapes, undulating topography, and flat plains, with elevations ranging from about 1336 to over 3300 m above mean sea level. As a result, several streams emerge from the plateaus feeding the major river. The elevated plateaus in the study area serve as potential groundwater recharge zones due to high annual rainfall (1600–2000 mm) and extensively fractured geological formations, especially along northeast-trending faults that enhance infiltration. In contrast, the lower-lying areas act as discharge zones, characterized by small groundwater depth and reliance on shallow wells.

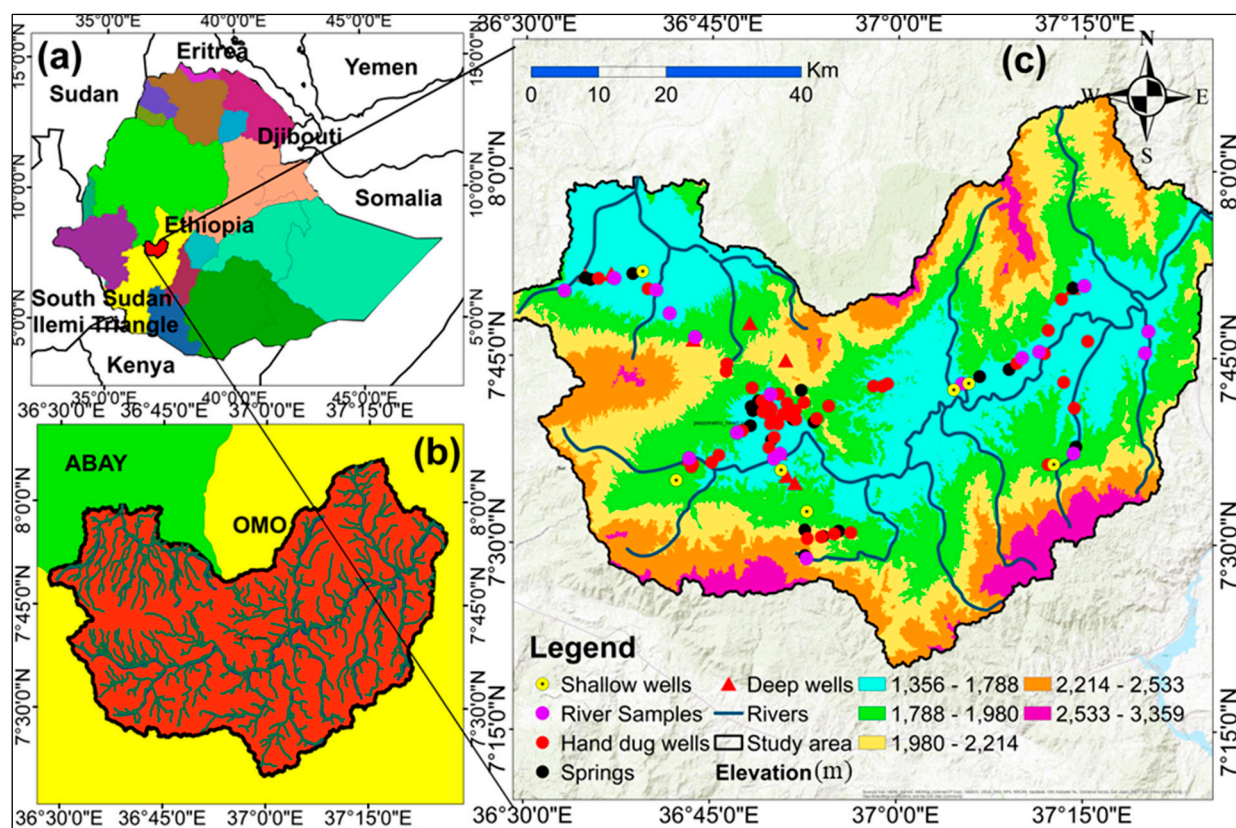


Figure 1. Location of study area: (a) neighbor East African countries and Ethiopian river basins, (b) Omo-Gibe basin (yellow) and Abbay basin (green), and (c) Gilgel Gibe and Dhidhessa catchments.

The land-use/land-cover (LULC) of the Gilgel Gibe and Upper Dhidhessa catchments shows that agriculture is the dominant land use, with cropland covering about 67% of the

area. This is followed by tree cover (14%), built-up areas (10%), grassland (8%), and the remaining 1% consisting of water bodies, bare land, and seasonally flooded vegetation, based on 2018 ESA Sentinel-2 imagery [41]. LULC significantly affects hydrological processes by modifying surface runoff, evapotranspiration, and groundwater recharge depending on land cover characteristics [30,34]. According to the Ministry of Water and Energy (MoWE) soil map, nine distinct soil types are identified within the study catchment. Soil distribution is heterogeneous, with clay-textured soils covering much of the catchment and significantly influencing infiltration and groundwater storage. Sandy clay and sandy clay loam are the next most widespread, while clay loam and loam soils occur mainly in lowland valleys and ridges.

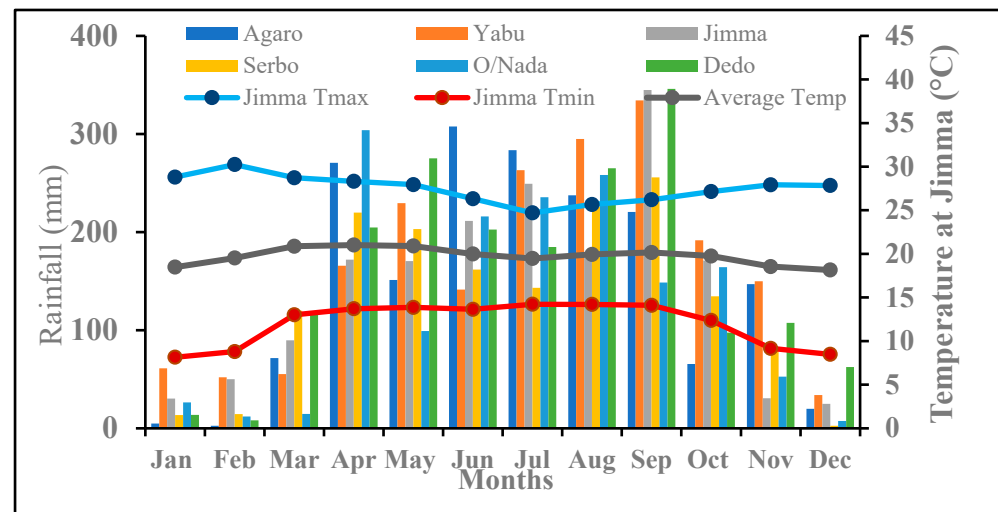


Figure 2. Observed rainfall and temperature for selected stations (2022 to 2024).

2.2. Geological Setting

The Gilgel Gibe and Dhidhessa basins lie within the Ethiopian volcanic highlands and reflect a complex tectono-volcanic history. Early geological descriptions were initiated by Mohr [42], followed by Kazmin [43], and later refined by several researchers. The Jimma Volcanic Succession forms the dominant unit, consisting of lower mafic flows overlain by felsic volcanic rocks, as described by Merla et al. [44]. The catchments are underlain by Precambrian crystalline basement rocks, overlain by Tertiary volcanic formations, with localized Quaternary volcanic flows, lacustrine deposits, and alluvium [45–47]. The region includes Oligocene–Miocene flood basalts (Ashangi, Aiba, Alaji), younger trachytes, pyroclastics, and Quaternary volcanic products [45,48]. Recent studies by Tufa et al. [34], Tadesse [48], Regasa et al. [35], Habtamu et al. [49], and Kitessa et al. [37] provide important refinements to the geological framework of the area. In the area, various volcanic rocks are exposed to the surface [50]. Recent work by Haro et al. [47] provides the most detailed stratigraphic framework, classifying volcanic units into distinct age groups (Figure 3). Pre-Oligocene sequences include lower trachyte flows, basaltic flows, and pyroclastics. Basalts are fine-grained to vesicular, while trachytes contain paleosol horizons, secondary zeolites, and primary sanidine. Pyroclastic deposits, ignimbrites, tuffs, lithic tuffs, and trachytic obsidian are well exposed around the Gilgel Gibe Dam. Oligocene units consist of widespread basaltic and trachytic flows containing boulders, cobbles, and fault breccias. Miocene–Pliocene upper basalts, trachytes, pyroclastics, rhyolites, and Sentema basalts form the higher elevations and are overlain by saprolite and pumice-rich weathered profiles. Quaternary deposits occur mainly in swampy, flat valleys and consist of unconsolidated clayey-silty materials with grass-covered surfaces.

Mineralogically, the basaltic rocks in the area consist mainly of plagioclase and microlites, with subordinate pyroxene (augite), olivine, and magnetite [47]. Rhyolite and trachyte are dominated by quartz, orthoclase, and sanidine, with minor plagioclase and accessory minerals. Moderate to high-intensity weathering has led to significant leaching of alkali elements [35], and the chemical composition, mineralogy, and structure of the parent rocks strongly influence the extent of elemental loss during alteration [35,51]. Intense weathering releases a range of minerals and chemical constituents [52,53]. In mafic basaltic rocks, weathering of plagioclase, pyroxene, and olivine liberates Ca, Na, Si, Mg, and Fe [54], whereas felsic rocks composed of quartz, feldspar, and muscovite release K and promote kaolinite formation [55]. Weathering of pyroclastic and trachytic rocks contributes to Al and alkali metals, enhancing the development of kaolinite and zeolites. These processes strongly influence groundwater chemistry and control the region's hydrogeochemical evolution.

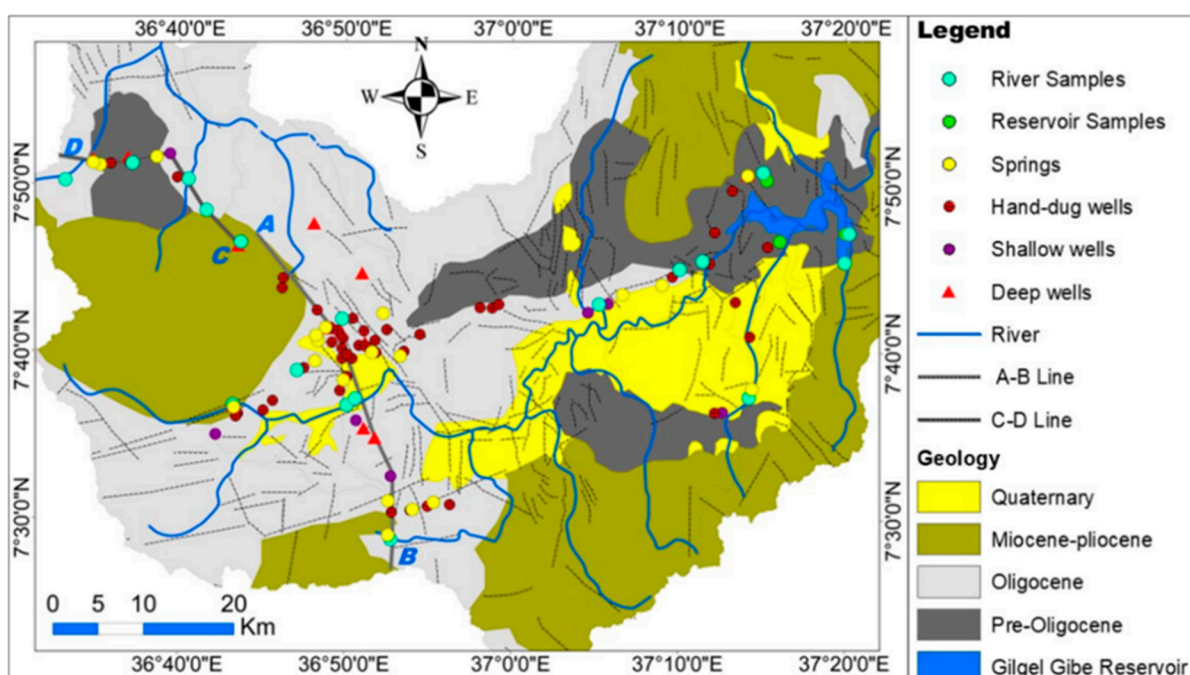


Figure 3. Geological map (modified from GSE, 2012) and location of water samples.

2.3. Hydrogeology

The hydrogeology of the Gilgel Gibe and Upper Dhidhessa catchments is controlled by the geological formations, physiography, and climate, which together influence groundwater occurrence, movement, and storage. The volcanic aquifer system is highly heterogeneous due to lithologic variability, differential weathering, and fracturing, all of which affect groundwater flow and spatial distribution. Studies by Lamessa [56], Agezew et al. [57], Tadesse [48], Kitessa et al. [37], Tufa et al. [34], and Dejen et al. [58] show that groundwater resources are mainly hosted in fractured and weathered volcanic rocks and alluvial deposits, consistent with findings from other volcanic terrains [6,24,54,59–61]. In the highlands and plateaus, aquifers are dominated by weathered and fractured basalts and ignimbrites, whereas downstream lowland aquifers consist of pyroclastic deposits—pumice, tuff, volcanic ash, and alluvial sediments (Figure 4). Based on previous studies, well logs, and pumping test data, two main aquifer systems are identified: These are: (1) Fractured and weathered volcanic rock aquifer. (2) Quaternary alluvial aquifer composed of clay to gravel-sized deposits in the lowland regions. Also, mixed aquifers occur where sediments between lava flows and pyroclastic layers create interbedded permeable zones. The fractured volcanic aquifer supports deep groundwater systems with high potential in

upland areas due to enhanced permeability from weathering and fracturing [57]. The Quaternary alluvial aquifer forms productive shallow groundwater sources, commonly tapped by hand-dug wells, with permeability controlled by grain size, sorting, and thickness. Mixed aquifers further enhance storage by transmitting water from adjacent fractured units. Over the past three years, groundwater levels have shown strong seasonal fluctuations, ranging from 0.7 to 8.2 m across monitoring wells [62], indicating high recharge rates. Rainfall is the primary source of recharge [34,62], and groundwater flow generally follows the regional topographic gradient.

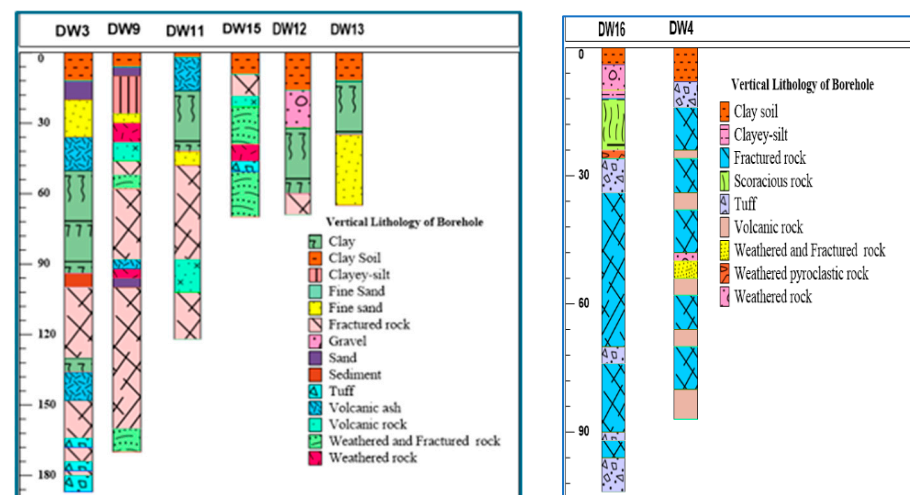


Figure 4. Selected lithologic logs from the highland (DW4, DW11, DW12, DW15) and lowland (DW3, DW9, DW16), showing the multi-layer aquifer nature of the study basin (Jimma Zone Water Office drilling reports).

2.4. Sample Collection

A field survey and reconnaissance study were conducted in the study area before the sampling campaign. Sampling points were strategically chosen to reflect the hydrogeological variations. Four field campaigns were conducted from April 2023 to February 2024 to include seasonal variations: 28 samples in April 2023, 4 rainfall samples from August to September 2023, 72 samples in December 2023, and 13 samples in February 2024. For each sampling water point, two samples were collected using polyethylene bottles of 500 mL, tightly capped to prevent any leakage. Samples designated for cation analysis were filtered using micro filtering papers of 0.45 μm mesh size to avoid suspended particles and subsequently acidified with concentrated nitric acid (HNO_3) intended to lower the pH value and prevent precipitation. The samples designated for anion analysis remained untreated. In addition, for stable isotope analysis of deuterium and oxygen-18, water samples were collected in 50 mL polyethylene (PE) bottles. Physicochemical parameters (pH, Total Dissolved Solid (mg/L), Dissolved Oxygen (mg/L), Electrical Conductivity ($\mu\text{S}/\text{cm}$ at 25 $^\circ\text{C}$), and Temperature ($^\circ\text{C}$)) were measured onsite using a multiparameter probe. The samples collected followed a rigorous sampling protocol and were then stored in a laboratory refrigerator at 4 $^\circ\text{C}$ until the date of analysis. Deep wells connected to the community water supply were sampled at the point of pumping after the pump was started. Previously inactive wells and hand-dug samples were collected after pumping for 10–15 min using a submersible pump through a flow cell. All spring water samples were collected at natural discharge (emergence) points. Samples from rivers and reservoirs were considered at a distance from shore to avoid contamination effects from the surroundings. Rainwater was sampled using a hanging plastic bucket at a height of 2 m on a support and equipped with evaporation-protected collectors to avoid post-collection isotopic

fractionation. In total, 115 water samples were collected: 13 samples from deep wells (>80 m in depth), 7 from shallow wells (30–80 m), 45 hand-dug wells (<30 m), 20 from springs, 19 from rivers, 3 reservoirs, 1 from a wetland (Marsh area), and 8 from rainfall.

Groundwater samples were collected from various lithological units and physiographic regions, including highlands, lowlands, and transitional zones, to assess spatial variability in groundwater flow (Figure 5). The sampling sites encompassed wells in Alluvial Deposits, Stratified Tuff, Sentema Basalt, Upper Basalt, Pyroclastics, Trachyte, Middle Basalt, and Lower Basalt, with their distribution shown in Figure 5.

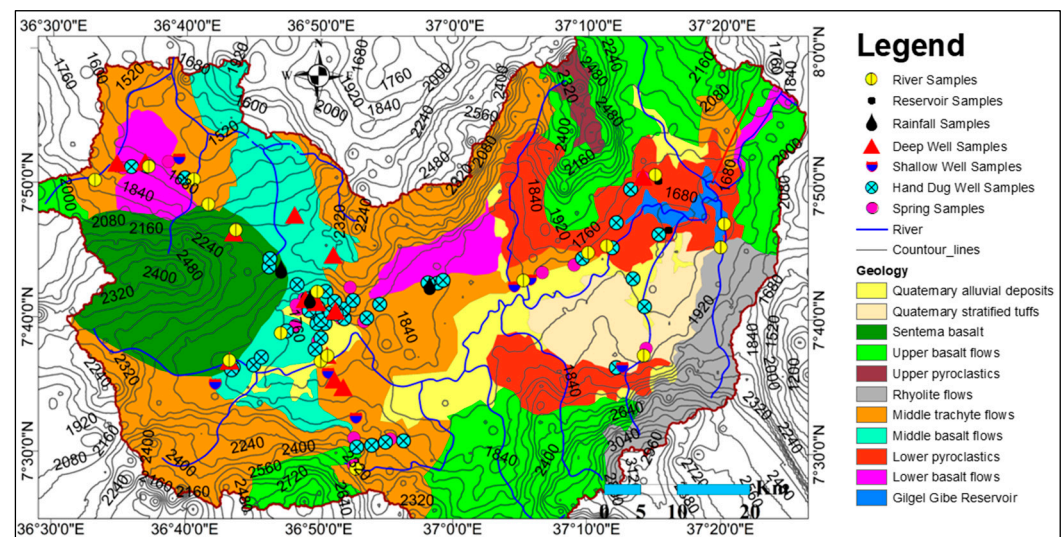


Figure 5. Sample distribution with geology and different physiography.

2.5. Laboratory Analysis of Hydrochemical and Isotopic Parameters

2.5.1. Chemical and Isotope Analysis

All water samples were analyzed for their chemical composition at the Laboratory for Applied Geology and Hydrogeology, Ghent University, Belgium. Stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) were measured at the Isotope Bioscience Laboratory (SOFYS) of the Green Chemistry and Technology Department. Cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Mn^{2+} , Si , Al^{3+}) were analyzed using a flame atomic absorption spectrophotometer (Varian Spectrophotometer AA-400) manufactured by Varian Inc., in Palo Alto, CA, USA, while anions (Cl^- , SO_4^{2-} , NO_2^- , NO_3^- , PO_4^{3-}) and NH_4^+ were measured with a UV-VIS spectrophotometer (Shimadzu UV mini-1240) manufactured by Shimadzu Corporation, Kyoto, Japan. HCO_3^- and CO_3^{2-} were determined by acid titration. pH and electrical conductivity (EC) were measured using standard laboratory meters, and fluoride (F^-) was measured using an ion-selective electrode. Isotopic analysis was conducted using a Triple Isotope Water Analyzer (TIWA, ABB Los Gatos Research), manufactured by ABB Los Gatos Research, San Jose, CA, USA, with analytical precision of $\pm 0.30\%$ for $\delta^2\text{H}$ and $\pm 0.10\%$ for $\delta^{18}\text{O}$. The isotopic abundance ratios, expressed in delta (δ) notation in permille (‰), represent the deviation of the sample from the Vienna Standard Mean Ocean Water (VSMOW). To ensure data reliability, isotopic measurements were normalized to the VSMOW-SLAP scale using three working standards. Stable isotope ratios were quantified as the ratio of rare to abundant isotope, with differences from the reference standard calculated using Equations (1) and (2):

$$\delta^{18}\text{O sample} = \frac{\left(\frac{18\text{O}}{16\text{O}}\right)_{\text{sample}} - \left(\frac{18\text{O}}{16\text{O}}\right)_{\text{reference}}}{\left(\frac{18\text{O}}{16\text{O}}\right)_{\text{reference}}} \times 1000 \text{ permilVSMOW} \quad (1)$$

$$\delta^2 \text{H sample} = \frac{\left(\frac{2\text{H}}{1\text{H}}\right)_{\text{sample}} - \left(\frac{2\text{H}}{1\text{H}}\right)_{\text{reference}}}{\left(\frac{2\text{H}}{1\text{H}}\right)_{\text{reference}}} \times 1000 \text{ permilVSMOW} \quad (2)$$

where delta (δ) indicates the difference in ratio from the standard.

2.5.2. Data Quality Control

The accuracy of the data analysis was verified using the charge balance error (CBE), calculated for each sample using concentrations expressed in meq/L using Equation (3). This method, commonly applied in groundwater chemistry studies [37,59,63], ensures the reliability of analytical data by comparing cation and anion concentrations.

$$\text{CBE (\%)} = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} \times 100 \quad (3)$$

In this study, charge balance errors (CBE) ranged from 0.21% to 5%, with only one sample showing a slightly higher error of 6.16%, originating from a low mineralized water point. All CBE values below 5%, were deemed acceptable for further analysis [9].

2.6. Data Analysis

2.6.1. Statistical and Correlation Analysis

Pearson's correlation coefficient (r), ranging from -1 to 1 , was used to assess the strength and direction of relationships among water quality parameters [64] where $r > 0$ indicates a positive correlation, $r < 0$ a negative one, and $r = 0$ no correlation. The statistical significance of correlations can be evaluated using p -values, where $p < 0.05$ typically indicates a significant association between variables. This analysis helped identify strongly correlated physicochemical parameters within the catchments, enabling the grouping of interrelated variables.

Principal Component Analysis (PCA) was used to identify key water quality parameters and reveal hydrogeochemical processes influencing groundwater composition. By transforming correlated variables into uncorrelated principal components (PCs), PCA reduces data dimensionality and highlights key variability. Components with eigenvalues > 1 were retained based on the scree plot, and parameters with high absolute loadings were classified as strong (>0.75), moderate (0.50 – 0.75), or weak (0.30 – 0.50) contributors [65]. A varimax rotation was applied to improve interpretability, and the analysis, including both numerical and graphical outputs, was performed using R statistical software (RStudio 4.3.1).

2.6.2. Bivariate Plots Analysis

Bivariate diagrams were used to explore the main hydrogeochemical processes influencing groundwater chemistry in the study area. This approach enabled the identification of key reactions, such as mineral dissolution, and highlighted possible anthropogenic contributions.

2.6.3. Groundwater Facies Analysis

Groundwater samples were analyzed and classified using a Piper diagram generated in Grapher 17.3.454 (Golden software), with ion concentrations expressed in meq/L. The triangular cation and anion fields, along with the central diamond, were used to distinguish hydrochemical facies and assess the geochemical evolution and types of groundwater.

2.6.4. Saturation Indices

The saturation index (SI), ion activity, and partial pressure of carbon dioxide were calculated using PHREEQC [66], to evaluate mineral dissolution or precipitation and

assess groundwater mineral stability, providing key insights into the basin's hydrogeochemical conditions [67]. The SI is defined as the logarithm of the ratio between the ion activity product (IAP) and the solubility product (K_s) (Equation (4)). An SI value less than zero indicates undersaturation (mineral dissolution), a value greater than zero indicates supersaturation (mineral precipitation), and an SI of zero signifies equilibrium.

$$SI = \log \frac{IAP}{K_{\text{mineral}}} \quad (4)$$

where both IAP and K_{mineral} are dimensionless quantities.

2.6.5. Isotope Analysis

Hydrogen and oxygen isotope data, characteristics of meteoric water, are widely used to trace groundwater origins [13,22]. The water samples were plotted against the Global Meteoric Water Line (GMWL) and Local Meteoric Water Line for Addis Ababa (LMWL-AA,) [68]. Deviations from the GMWL offer insights into precipitation source characteristics [69].

3. Results and Discussion

3.1. Physico-Chemical Parameters

Descriptive statistics of major ions and physico-chemical parameters are summarized in Table 1. Groundwater components show considerable variation in minimum, maximum, mean, and standard deviation (SD) values. The pH ranges from 4.8 to 8.2, with a low SD of 0.67. Shallow sources (hand-dug wells, springs, and surface water) exhibit acidic to non-alkaline pH (4.8–6.9), while deep groundwater shows neutral to mildly alkaline pH (6.9–8.2), reflecting distinct hydrochemical characteristics between shallow and deep aquifers.

Table 1. Descriptive statistics of major analyzed chemical parameters for groundwater and surface water samples.

Parameters	Hand Dug Wells (N = 45)				Deep and Shallow Wells (N = 20)				Springs (N = 20)				Rivers, Streams, Reservoirs, and Marshes (N = 23)			
	Min	Max	Mean	Std	Min	Max	Mean	Std	Min	Max	Mean	Std	Min	Max	Mean	Std
PH	4.8	7.15	5.9	0.6	5.1	8.1	6.8	0.7	4.9	6.8	5.9	0.5	5.6	6.9	6.4	0.4
EC ($\mu\text{S}/\text{cm}$ at 25 °C)	40.1	1122	361.8	294.8	88.8	4890	703.2	1035.5	45.3	622.0	178.3	149.6	59.9	216.0	104.9	38.1
TDSs (mg/L)	36.2	775.7	249.5	187.7	59.7	4111.7	596.1	870.5	51.2	376.2	153.4	86.3	70.4	178.4	116.6	31.4
Na ⁺ (mg/L)	3.9	57.7	18.4	14.1	6.3	1130	120.7	248.5	2	25.0	9.5	5.8	2.7	10.2	6.1	1.9
K ⁺ (mg/L)	0.7	40.7	6.1	7.4	1.8	18.6	6.4	4.5	0.9	7.5	2.9	1.8	1.1	8.9	2.4	1.6
Ca ²⁺ (mg/L)	1.8	143.5	33.5	31.2	2.6	44	24.1	11.9	2.2	53.7	17.9	14.8	6.2	23.6	11.2	4.4
Mg ²⁺ (mg/L)	0.8	21.9	7.3	6.2	1.4	19.9	7.1	5.1	1.2	13.6	4.6	3.8	1.8	6.2	3.0	1.2
Fe ²⁺ /Fe ³⁺ (mg/L)	0.0	3.0	0.5	0.7	0.0	2.1	0.3	0.5	0.0	1.3	0.3	0.4	0.02	10.2	1.2	2.0
Mn ²⁺ (mg/L)	0.0	4.92	0.4	0.9	0.0	0.6	0.1	0.1	0.0	0.23	0.1	0.1	0.0	4.9	0.2	1.0
Cl [−] (mg/L)	2.2	144.3	34.1	38.5	1.0	151.2	14.1	33.1	1	60.3	11.9	15.1	1.24	16.6	5.9	3.6
SO ₄ ^{2−} (mg/L)	0.0	86.1	13.2	22.7	0.0	21	2.6	5.4	0.0	3.5	0.9	1.1	0.5	7.3	2.2	1.6
NO ₃ [−] (mg/L)	0.0	193.6	41.9	56.5	0.0	9.1	2.1	2.8	0.0	176.6	25.4	46.7	0.1	8.5	3.9	2.2
HCO ₃ [−] (mg/L)	7.3	469.1	87.1	96.8	23.8	2763.3	417.1	587.7	18.3	171.4	57.6	45.7	32.3	109.8	56.5	21.6
SiO ₂ (mg/L)	0.02	44.2	13.8	12.8	0.02	22.4	2.6	6.3	0.02	22.9	5.7	7.4	0.04	23.5	7.6	8.1
F [−] (mg/L)	0.01	0.2	0.03	0.04	0.04	1.4	0.5	0.6	0.01	0.11	0.03	0.03	0.02	0.1	0.03	0.01
TH (mg/L CaCO ₃)	12.6	437.3	113.8	100	15.6	173.4	89.3	44.2	16.9	190.1	63.5	52	24.3	84.3	40.5	15.5

Notes: Min—Minimum; Max—Maximum; Std—Standard Deviation; pH—Potential of Hydrogen; EC—Electrical Conductivity; TDSs—Total Dissolved Solids; TH—Total Hardness.

The electrical conductivity (EC) of water samples ranges from 40 to 4890 $\mu\text{S}/\text{cm}$ at 25 °C, recorded in a hand-dug well (HD16) and a deep well (DW5), respectively, indicating significant variation (Table 1). Hand-dug wells, springs, and surface water exhibit lower mean EC values ($<500 \mu\text{S}/\text{cm}$), whereas deep and shallow wells show higher values ($>500 \mu\text{S}/\text{cm}$). A gradual increase in temperature, EC, and pH was observed along the groundwater flow path from highland to lowland areas. The total dissolved solids (TDS) in groundwater vary widely across sources, ranging from 36 mg/L in a hand-dug well (HD16) in the residual red soil, to 4112 mg/L in a deep artesian well (DW5) in the north-west. Mean TDS values are $105 \pm 38 \text{ mg/L}$ (surface water), $153 \pm 86 \text{ mg/L}$ (springs), $250 \pm 188 \text{ mg/L}$ (hand-dug wells), and $596 \pm 870 \text{ mg/L}$ (deep wells). Elevated EC and TDS in deep aquifers indicate ongoing mineral dissolution. TDS in surface water, springs, and shallow sources remains below 1000 mg/L (freshwater); about 15% of deep wells exceed this limit and are classified as brackish water [70].

3.2. Major Ions

Bicarbonate (HCO_3^-) concentrations show significant variability across water sources, ranging from 7.3 to 470 mg/L (SD: 96.8 mg/L) in hand-dug wells, 24–2763 mg/L (SD: 587.7 mg/L) in deep wells, 18–171.4 mg/L (SD: 45.7 mg/L) in springs, and 32–110 mg/L (SD: 21.6 mg/L) in surface waters (Table 1). High HCO_3^- levels likely reflect the dissolution of CO_2 from both atmospheric and soil sources [13]. Feldspar weathering consumes protons, raising pH and promoting CO_2 dissolution and HCO_3^- formation in deep groundwater [71].

Chloride (Cl^-) concentrations ranged from 0.95 to 151.2 mg/L, with mean values of $34.1 \pm 38.5 \text{ mg/L}$ in hand-dug wells, $14.1 \pm 33.1 \text{ mg/L}$ in deep wells, $11.9 \pm 15.1 \text{ mg/L}$ in springs, and $5.9 \pm 3.6 \text{ mg/L}$ in surface waters. Chloride is mainly an aesthetic, taste, and corrosion concern at typical drinking-water concentrations, and its direct health effects are generally not noticeable at low exposure levels [6]. Nitrate (NO_3^-) levels varied from 0 to 194 mg/L (mean: $23.6 \pm 45.1 \text{ mg/L}$), peaking in the hand-dug well (HD6) and spring (SP12). Nitrate is a highly mobile and soluble anion that naturally occurs at low concentrations in rainfall but is often elevated due to anthropogenic activities [63]. In the shallow aquifer, NO_3^- easily mixes into the groundwater, consistent with [23], who link NO_3^- presence to recent recharge and GW–SW interaction. Sulfate (SO_4^{2-}) ranged from 0 to 86 mg/L (mean: $6.7 \pm 15.8 \text{ mg/L}$), with the highest concentrations of Cl^- , NO_3^- , and SO_4^{2-} found in hand-dug wells and springs near urban areas and agricultural fields. In the study area, HCO_3^- is the dominant anion, comprising about 84% of total anions, followed by NO_3^- (12%) and Cl^- (4%), reflecting the order $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. Elevated HCO_3^- levels are attributed to silicate weathering and the dissolution of atmospheric and soil CO_2 , while high NO_3^- and Cl^- concentrations likely result from sewage and domestic waste, organic matter decomposition, and intensive fertilizer use in agricultural fields [13,37]. Fluoride (F^-) concentrations in groundwater samples range from 0.01 to 1.44 mg/L, with higher levels observed in deeper aquifers compared to shallow ones. This finding is consistent with Eyayu et al. [72], who reported elevated fluoride concentrations in deep wells relative to spring waters. All samples analyzed fall below the WHO guideline of 1.5 mg/L for drinking water [73]. While previous studies reported higher fluoride levels in deep aquifers, the lower concentrations in the current study may be attributed to variations in the composition of the parent rocks from which the groundwater is derived [36,72].

The analysis of cations revealed significant variations in groundwater hydrochemistry. Calcium (Ca^{2+}) concentrations range from 1.85 to 143.5 mg/L, with a mean of 24.15 mg/L; the lowest was found in an alluvial aquifer (HD36), and the highest in a highly mineralized fractured volcanic rock aquifer (HD6), primarily due to the weathering of calcium-rich feldspars. Magnesium (Mg^{2+}) ranges from 0.76 to 22 mg/L (mean 5.85 mg/L), influenced by ferromagnesian minerals like olivine, pyroxene, and biotite in the basement

rock. Sodium (Na^+) shows a wide range from 1.98 to 1130 mg/L (mean 33.26 mg/L), with the lowest concentration in spring water in the recharge area (SP17) and the highest in a deep well in the discharge zone (DW5), reflecting sodium feldspar weathering. Potassium (K^+) ranges from 0.7 to 40 mg/L (mean 4.74 mg/L), sourced from minerals such as orthoclase, microcline, clays, and ion exchange processes, with clay minerals being abundant in the region [74].

The study revealed significant variations in cations and anions across the region, with ion abundance generally following the order: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in hand-dug wells, springs, and surface waters, while deep wells show $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. Low ion concentrations suggest limited weathering and silicate dissolution, whereas relatively high levels of calcium, sodium, and bicarbonate likely result from mineral sources and may also be influenced by non-geogenic activities. Total hardness (TH), expressed as (mg/L CaCO_3), ranges from 12.58 to 438 mg/L in shallow groundwater (mean: 114 mg/L) and from 15.6 to 173 mg/L in deep groundwater (mean: 89.3 mg/L) (Table 1). The higher TH in shallow sources associated with the weathering of Ca- and Mg-bearing silicate minerals such as plagioclase feldspars and mafic minerals, influenced by climate, precipitation, evaporation, topography, and human activities [75].

3.3. Correlation Analysis of Physicochemical Parameters

The relationships between physicochemical and major ion parameters were assessed in Table 2. A strong positive correlation was found between EC and TDS ($r = 0.99$), with both showing strong to moderate correlations with major ions such as Na^+ ($r = 0.96$), HCO_3^- ($r = 0.97$), Cl^- ($r = 0.56$), K^+ ($r = 0.41$), Ca^{2+} ($r = 0.31$), and Mg^{2+} ($r = 0.36$), indicating their contribution to the aquifer's salinity. Weak correlations between Na^+ and Ca^{2+} ($r = 0.06$) and Mg^{2+} ($r = 0.03$) suggest differing ion sources and complex geochemical processes. In contrast, a strong correlation between Ca^{2+} and Mg^{2+} ($r = 0.83$) implies a common origin, likely from the dissolution of the same source rock during water-rock interaction [22].

Table 2. Correlation matrix of physicochemical parameters.

	pH	EC	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	NO_3^-	Cl^-	SO_4^{2-}
pH	1.00										
EC	0.27	1.00									
TDS	0.31	0.99	1.00								
Na^+	0.23	0.93	0.96	1.00							
K^+	0.19	0.46	0.41	0.29	1.00						
Ca^{2+}	0.25	0.40	0.31	0.06	0.43	1.00					
Mg^{2+}	0.17	0.36	0.26	0.03	0.41	0.83	1.00				
HCO_3^-	0.37	0.93	0.97	0.97	0.34	0.16	0.11	1.00			
NO_3^-	−0.28	0.18	0.08	−0.03	0.17	0.46	0.47	−0.14	1.00		
Cl^-	−0.01	0.67	0.56	0.43	0.46	0.67	0.66	0.37	0.56	1.00	
SO_4^{2-}	0.19	0.32	0.26	0.11	0.49	0.57	0.48	0.15	0.07	0.56	1.00

Moderate correlations between Ca^{2+} and K^+ ($r = 0.43$), and between Mg^{2+} and K^+ ($r = 0.41$), suggest that these ions may originate from the dissolution of common source minerals during rock-water interactions within the aquifer system. Chloride (Cl^-) shows moderate correlations with NO_3^- and SO_4^{2-} (both $r = 0.56$), suggesting a common anthropogenic source, such as agricultural runoff, sewage, and domestic waste. The strong correlation between Na^+ and HCO_3^- , along with moderate to weak correlations of K^+ , Ca^{2+} , and Mg^{2+} with each other and with Na^+ and HCO_3^- , points to silicate weathering and mineral hydrolysis as their primary geogenic sources. A moderate correlation between SO_4^{2-} and Ca^{2+}

($r = 0.57$) indicates additional anthropogenic inputs, likely from fertilizers, detergents, wastewater, or atmospheric sulfur deposition [16] and may also reflect geochemical processes such as pyrite oxidation, carbonate–sulfate interactions, or groundwater mixing.

3.4. Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was used to identify key factors influencing groundwater chemistry, and a varimax rotation was applied to improve interpretability. Before PCA, hydrochemical data were log-transformed to evaluate their distribution. The histograms show improved symmetry, indicating suitability for PCA. Major ions (pH, Ca^{2+} , Mg^{2+} , Na^+ , and HCO_3^-) exhibit near-normal to slightly skewed distributions. In contrast, K^+ , Cl^- , NO_3^- , and SO_4^{2-} show positive skewness, indicating localized variability after log-transformation of the major-ion values. Overall, the results confirm that the dataset is appropriate for PCA. The PCA scree plot (Figure 6a) illustrates ten principal components (PC1–PC10) and supports component selection based on explained variance. However, only a few components account for most of the variability, indicating that groundwater chemistry is mainly controlled by a number of processes. These include geochemical reactions such as rock weathering, CO_2 interactions, and anthropogenic influences, as further discussed in subsequent sections and cross-plots. The scree plot of the dataset shows that the first two principal components explain 70.6% of the total variance (PC1 = 44.5% and PC2 = 26.1%), which is considered acceptable for hydrogeochemical analysis. The plot exhibits a sharp decrease from PC1 to PC2 and PC3, followed by a relatively stable slope (Figure 6a). Figure 6b (PCA biplot) shows the distribution of samples and variables based on the first two principal components. Dim1 (44.5%) explains the largest variation, while Dim2 (26.1%) explains the second. Together, they represent the main patterns controlling groundwater chemistry. The arrows indicate the contribution and direction of variables such as Ca^{2+} , Mg^{2+} , Na^+ , and NO_3^- , while the sample points show how individual water samples relate to these variables. Variables pointing in the same direction are positively correlated, whereas those pointing in opposite directions are negatively correlated.

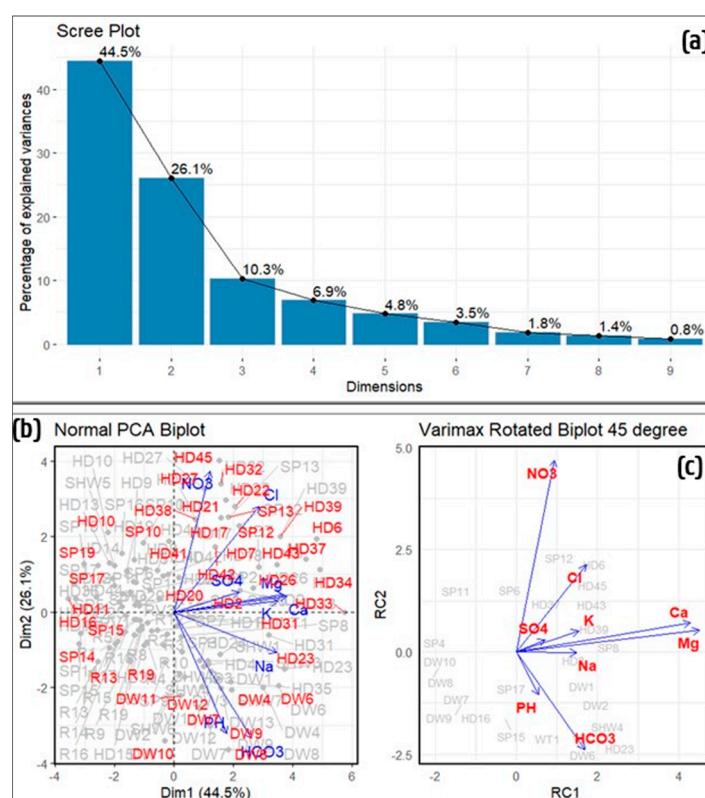


Figure 6. (a) Scree plot showing the percentage of variance explained by each principal component. (b) Normal PCA biplot showing the distribution of groundwater samples and variables. (c) Varimax-rotated PCA biplot, highlighting the relationships among variables. Blue arrows indicate the directions of the variables. The red labels represent the sample IDs, while the blue and red labels represent the variables.

Figure 6c (Varimax-rotated PCA biplot) shows the distribution of variables based on the rotated principal components (RC1 and RC2), which improve the interpretation of underlying processes and explain 44.5% of the variance. RC1 represents the dominant hydrogeochemical process, mainly associated with Ca^{2+} , Mg^{2+} , Na^+ , and HCO_3^- , indicating water-rock interaction, particularly silicate weathering and mineral dissolution. Ca^{2+} and Mg^{2+} are primarily derived from basalt weathering. Anorthite weathering is the main source of Ca^{2+} , while pyroxene and amphibole contribute both Ca^{2+} and Mg^{2+} [22]. Olivine (forsterite) dissolution also supplies Mg^{2+} . In contrast, Na^+ originates from albite weathering, and HCO_3^- is produced through CO_2 water-rock interactions [23]. Albite typically occurs in felsic volcanic rocks such as rhyolites, ignimbrites, and tuffs, as well as in trachytes [76]. RC1 shows high loadings of Ca^{2+} , Mg^{2+} , and HCO_3^- , indicating that Ca- and Mg-bearing rocks undergo greater dissolution in the presence of CO_2 , contributing to bicarbonate levels in the aquifers. The loading of Na^+ still supports the role of weathering processes through Na-bearing rocks, with a significant contribution. Therefore, PC1 represents the hydrogeochemical process of groundwater driven by mineral dissolution. RC2 reflects secondary influences, with strong contributions from NO_3^- , Cl^- , and K^+ , suggesting anthropogenic inputs, and explains about 26.1% of the variance. The high loading of NO_3^- on RC2 indicates anthropogenic sources of pollution in the shallow aquifers [77]. The direction and length of the arrows indicate the strength and relationship of variables within each component. In areas with intensive agriculture, and pit latrines or septic tanks, which collect domestic wastewater, water infiltrates into the soil carrying nitrates, sulfates, and chlorides [77]. The Varimax rotation confirms this separation, where RC1 is driven by natural geochemical processes and RC2 by pollution-related variables (Figure 6c). Sulfate (SO_4^{2-}) shows weak loading and is located near the center of the biplot, suggesting a secondary or mixed origin, possibly related to localized contamination, oxidation processes, or minor lithological effects. pH is aligned with HCO_3^- , suggesting that it is primarily controlled by geochemical equilibrium.

The distribution of samples further supports these interpretations. Deep groundwater samples cluster in the direction of Na^+ and HCO_3^- , indicating more evolved water influenced by prolonged water-rock interaction. In contrast, shallow groundwater sources including hand-dug wells, springs, and rivers are more widely distributed and influenced by both natural processes ($\text{Ca}^{2+}/\text{Mg}^{2+}$) and anthropogenic inputs (NO_3^- and Cl^-). The PCA results demonstrate that groundwater chemistry is controlled by water-rock interaction as the dominant factor and anthropogenic influence as a secondary contributor.

3.5. Graphical Presentation of Hydrochemical Data and Water Types

Figure 7 presents the Piper diagram illustrating groundwater composition and water types, while Figure 8 summarizes the water types and their frequency based on major ions. Eight distinct water types were identified, with CaHCO_3 (62.3%), NaHCO_3 (20.2%), CaNO_3 (10.5%), KHCO_3 (2.6%), and CaCl (2%) being the most dominant, alongside mixed types such as Ca-Mg- HCO_3 , Ca-Na-Mg- HCO_3 , and Na-Ca- HCO_3 . Most samples from hand-dug wells, springs, and surface water plot in the lower left corners of the cation and anion triangles, indicating Ca^{2+} and HCO_3^- dominance. In contrast, deep well samples primarily plot in the lower right (cations) and lower left (anions) triangles, reflecting Na^+ and HCO_3^- dominance.

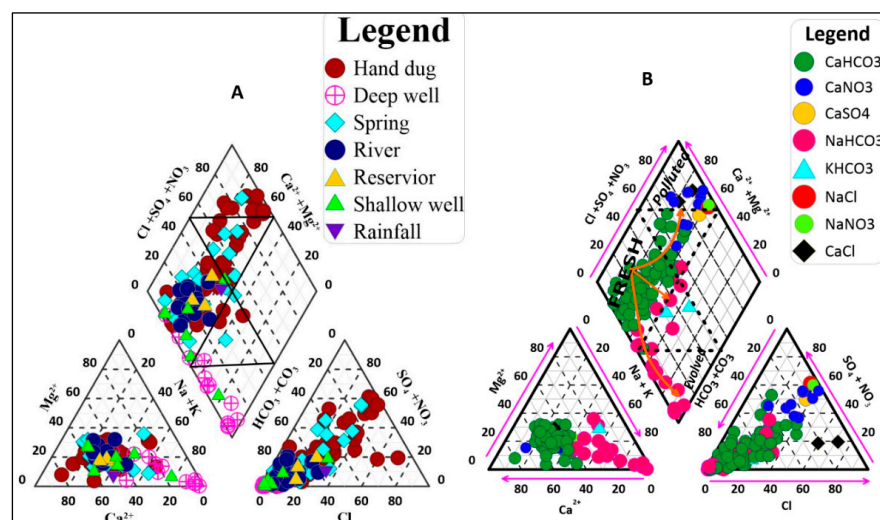


Figure 7. Piper diagram illustrating the distribution of water samples (A) and the classification of groundwater types (B). Pink arrows indicate increasing ionic proportions (0–100%), dashed lines mark the 50% compositional boundaries, and the purple line illustrates the general groundwater evolution trend from fresh to more mature waters.

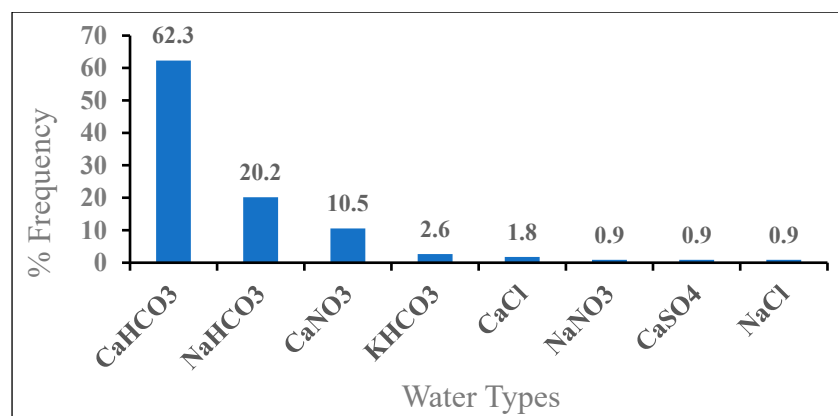


Figure 8. Water types and their frequency classified according to the dominant cations and anions.

In the central diamond of the Piper diagram (Figure 7), deep well samples are mostly positioned toward the bottom edge in the NaHCO_3 field, while most hand-dug wells, springs, and surface waters cluster toward the central and left in the CaHCO_3 field. A few spring and hand-dug well samples plot near the upper or top, corresponding to CaCl , CaNO_3 , and CaSO_4 field (Figure 7B). These water types represent anthropogenically influenced water types with low mineralization, derived from precipitation and distributed across both highland and lowland areas.

The Ca-NO_3 water type is found in springs and hand-dug wells throughout the study area, particularly in the eastern, northwest, central, western, and southern regions. Spring samples show TDS values between 69 and 378 mg/L and elevated NO_3^- concentrations (21–176.6 mg/L), exceeding other ions like Ca^{2+} (8.3–54 mg/L), Na^+ (4.5–25 mg/L), and HCO_3^- (20.1–40.89 mg/L). Hand-dug wells exhibit higher mineralization, with TDS ranging from 68 to 688 mg/L and NO_3^- concentrations between 24 and 194 mg/L, alongside increased levels of other ions. These elevated NO_3^- and Cl^- levels suggest contamination from anthropogenic sources such as fertilizers, human and animal waste, and wastewater. The pollutants persist due to limited degradation in the oxic zone, where shallow and short flow paths dominate [23].

The Ca-HCO₃ water type is the most dominant, comprising about 62.3% of all samples, including all surface waters. This category features both low and highly mineralized sources. Highly mineralized samples include Seka Well (HD23), Bishishe Well (HD33), Ginjo Guduru Well (HD34), Wirtu Yadi Well (HD4), Burka Well (HD3), and Katta Kadida Spring (SP6), with TDS values ranging from 240 to 775.7 mg/L and elevated Ca²⁺ (36–115 mg/L), and HCO₃[−] (160–469 mg/L) concentrations. In contrast, low-mineralized Ca-HCO₃ water sources, such as Kofe Well (HD16), Chalte Bullo Well (HD11), Buyokachama Well (HD14), Dedo Buyo Well (HD12), Gembe Well (HD19), Seto Semero Well (HD44), Jiren Spring (SP17), and Kolobo Well (SHW5) exhibit TDS values between 36.2 and 93.1 mg/L, with low concentrations of Ca²⁺ (4.7–9.1 mg/L), Na⁺ (2–8.9 mg/L), and HCO₃[−] (20.7–29.3 mg/L). This variability in mineralization reflects differences in geological and hydrogeochemical settings, where highly mineralized waters result from longer residence times and greater interaction with geological formations, while low-mineralized waters are typically younger and less chemically evolved. The Na-HCO₃ water type is mainly associated with deep wells, showing high mineralization, while hand-dug wells, springs, and shallow wells in this category exhibit low to intermediate mineralization.

Highly mineralized deep wells include samples from Jimma University Agaro Campus (DW5, TDS = 4112 mg/L), Agaro Tije (DW6, TDS = 668 mg/L), Jimma Agricultural Campus (DW9, TDS = 1184 mg/L), Jimma Main Campus (DW8, TDS = 992 mg/L), Jimma Bore (DW7, TDS = 508 mg/L), and Seka Gibe Boso (DW4, TDS = 553 mg/L), with Na⁺ and HCO₃[−] concentrations ranging from 93 to 1130 mg/L and 349–2763 mg/L, respectively.

In contrast, lower mineralization is observed in sources like Bore hand-dug well (HD25, TDS = 69.3 mg/L), Amanu Spring (SP19, 51 mg/L), Guduru Bore Spring (SP14, 114 mg/L), Bada Buna Spring (SP5, 66.7 mg/L), Nada Chala Spring (SP4, 94.4 mg/L), and Kichimbille Spring (SP1, 87 mg/L), with relatively low Na⁺, Ca²⁺, Mg²⁺, and HCO₃[−] concentrations.

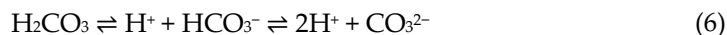
These low-TDS waters are immature, formed from rainwater infiltration and gradually evolving into Na-HCO₃ type through CO₂ dissolution, organic matter oxidation, and weathering of aluminosilicates. The highly mineralized Na-HCO₃ and Ca-HCO₃ waters are predominantly found in depression zones, suggesting enhanced feldspar dissolution, evapotranspiration, and anthropogenic inputs along the flow path. Most groundwater and surface water samples cluster closely and predominantly exhibit Ca-HCO₃ to Ca-Na-Mg-HCO₃ water types.

The geochemical evolution of groundwater in the study area reflects rainwater transformation into Ca-HCO₃ and Na-HCO₃ types, primarily through rock-water interactions. This process involves the dissolution of aluminosilicates, like Na-feldspars and Ca-plagioclase. Water types such as NaCl, CaCl, Na-NO₃, and Ca-NO₃ suggest additional influences from anthropogenic pollution.

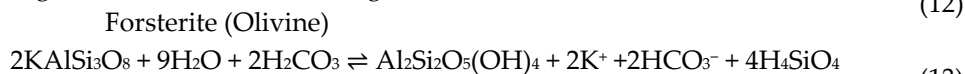
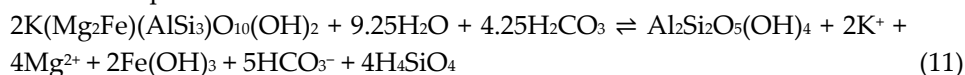
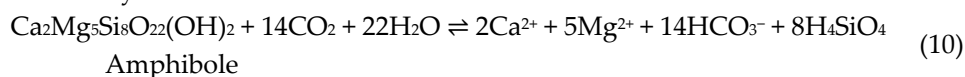
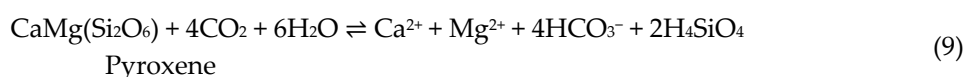
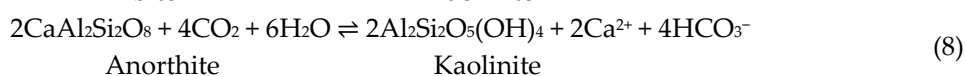
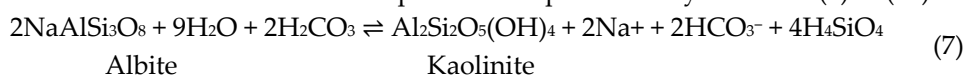
3.6. Geochemical Processes and Hydrogeochemical Interpretation

Hydrogeochemical processes in the aquifer, reveal that groundwater chemistry is shaped by prolonged geochemical evolution and the mineral composition of the host rocks. A clear increase in TDS with decreasing elevation, indicating hydrochemical evolution along the groundwater flow path from slightly mineralized Ca-Mg-HCO₃ in the highlands to highly mineralized Na-HCO₃ in the lowlands. These trends suggest that mineral dissolution is the source of major ions, and elevating pH in the lowland due to acid neutralization. Cross plots (Figures 9–13) were used to further evaluate the hydrogeochemical characteristics of the study area, emphasizing the influence of silicate weathering on groundwater composition. The study area is characterized by the weathering of several silicate minerals [36,47]. Silicate weathering significantly influences groundwater chemistry [78]. Na⁺ is released from albite weathering, Ca²⁺ originates from anorthite and mafic

minerals, Mg^{2+} from amphiboles and biotite, and K^+ from the weathering of K-feldspars, especially in basaltic terrains of Ethiopian volcanic regions [9]. The weathering process is accelerated by carbonic acid (H_2CO_3), formed when atmospheric and soil CO_2 dissolve in water [79]. The resulting acidity enhances mineral dissolution by increasing H^+ concentration and the release of bicarbonate (HCO_3^-), promoting further chemical breakdown of silicate minerals, Equations (5)–(13).



The dissolution reactions of feldspar minerals (Albite, anorthite, and Sanidine), pyroxene (augite), amphibole, biotite, and olivine (forsterite) commonly found in the Gilgel Gibe and Dhidhessa basins of volcanic aquifers are represented by reactions (7) to (13).



3.7. Bivariate Plots

Figure 9 illustrates bivariate plots used to analyze the relationships between major ions (Na^+ , HCO_3^- , Ca^{2+} , Mg^{2+} , K^+), SiO_2 , and electrical conductivity (EC). Elevated EC values indicate chemically mature groundwater with prolonged residence times, reflecting extensive dissolution of rock-forming minerals [23].

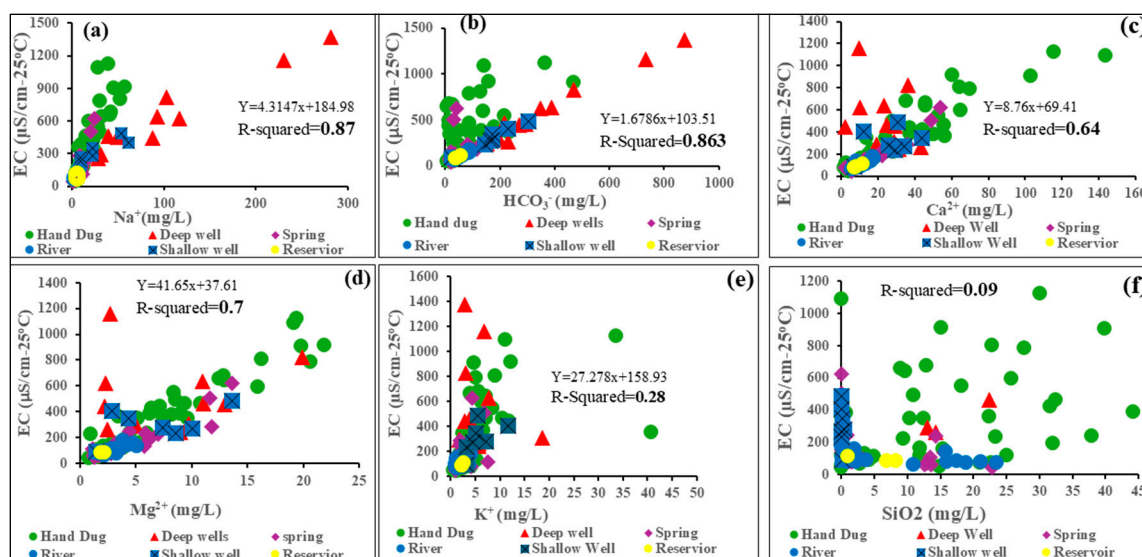


Figure 9. Bivariate plots illustrating the relationship between (EC) and major ions (mg/L) (a–f).

EC reflects the extent of aluminosilicate weathering and anthropogenic pollution in the studied aquifers. The plots in Figure 9a–f show a significant correlation between EC and Na^+ ($R^2 = 0.87$), HCO_3^- ($R^2 = 0.86$), Ca^{2+} ($R^2 = 0.64$), Mg^{2+} ($R^2 = 0.7$), ($\text{K}^+ = 0.28$), and ($\text{SiO}_2 = 0.1$). The degree of groundwater mineralization varies with ion concentration and provides insights into recharge zones and water residence time. Strong coefficients of determination indicate that the concentrations of most analyzed ions increase with rising EC, suggesting enhanced mineral dissolution facilitated by carbonic acid (Figure 9a–d). However, the weak correlation between K^+ and EC ($R^2 = 0.28$) implies that K^+ -bearing minerals contribute minimally to groundwater mineralization, possibly due to low concentrations (Figure 9e). Similarly, the poor correlation between SiO_2 and EC ($R^2 = 0.10$), accompanied by a wide scatter of data, may be attributed to local lithological variability. This suggests that certain aluminosilicate-bearing rocks are less susceptible to weathering compared to others (Figure 9f). The wide scatter of SiO_2 concentrations at low mineralization levels reflects processes like amorphous silica dissolution [23]. Silica concentrations reach up to 44 mg/L in hand-dug wells, which have shorter residence times compared to deep aquifers. According to Davis [80], silica is added more rapidly to groundwater near the surface, a pattern also observed in this study, due to greater CO_2 availability from atmospheric and biogenic sources in the shallow subsurface.

Bivariate plots of HCO_3^- versus major cations (Na^+ , Mg^{2+} , K^+ , and Ca^{2+}) were used to investigate the origins and mechanisms of hydrogeochemical processes (Figures 10–13). The correlation between Na^+ and HCO_3^- (Figure 10a) indicates albite weathering (Reaction (7)), which releases these ions in a 1:1 equivalent ratio. Samples from deep wells, hand-dug wells, and springs align closely with this trend, supporting albite dissolution as a key geochemical process influencing groundwater composition in the study area. Some deviations toward the HCO_3^- axis reflect excess bicarbonate, which may indicate contributions from other aluminosilicate minerals or uptake of Na^+ . Elevated concentrations of Na^+ (ranging up to 1130 mg/L, average 172 mg/L) and HCO_3^- (up to 2763 mg/L, average 548 mg/L) in deep aquifers (Table 1) further support the role of albite dissolution, particularly in deeper groundwater zones. Despite a strong correlation (Table 2), the observed deviations from the 1:1 molar line imply that additional geochemical processes may be enriching or depleting of Na^+ and/or HCO_3^- . In contrast, surface water samples exhibit minimal albite weathering, as most data points deviate toward the HCO_3^- axis only.

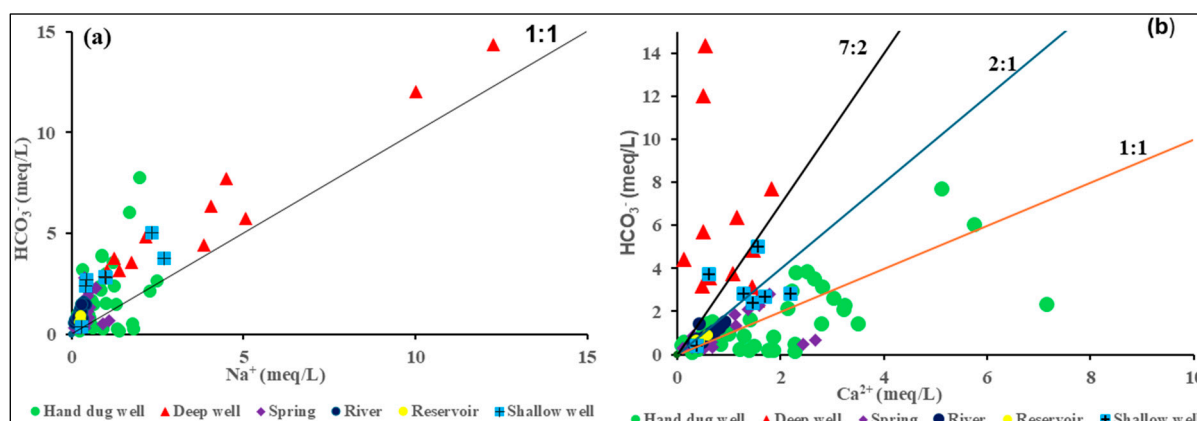


Figure 10. Bivariate plots of (a) Na^+ vs. HCO_3^- and (b) Ca^{2+} vs. HCO_3^- .

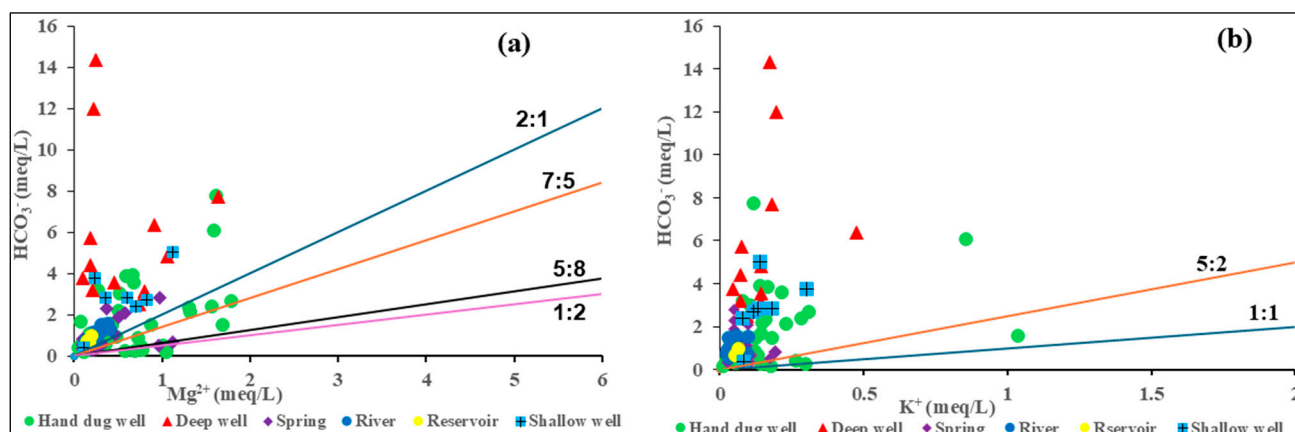


Figure 11. Bivariate plots of (a) Mg^{2+} vs. HCO_3^- and (b) K^+ vs. HCO_3^- .

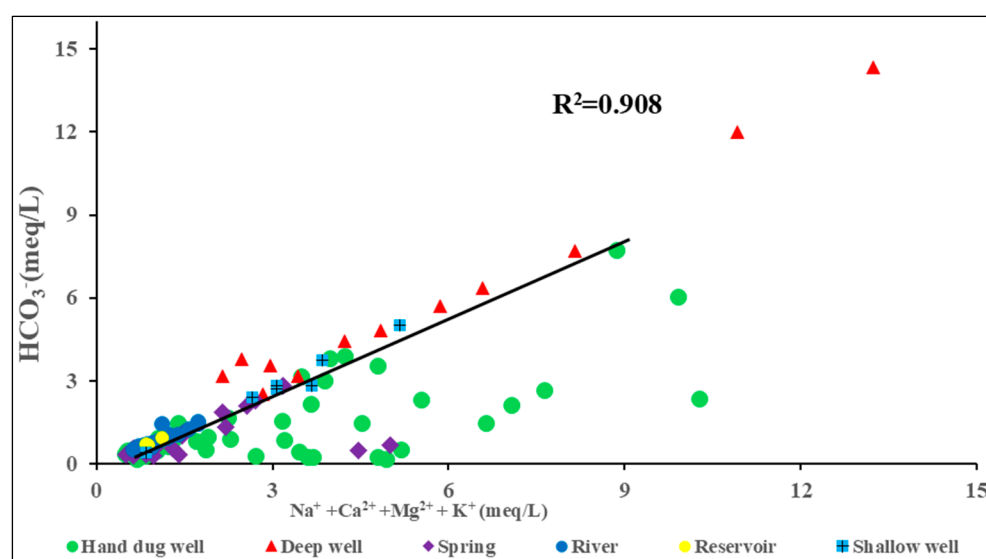


Figure 12. Bivariate plots of HCO_3^- vs. major cations.

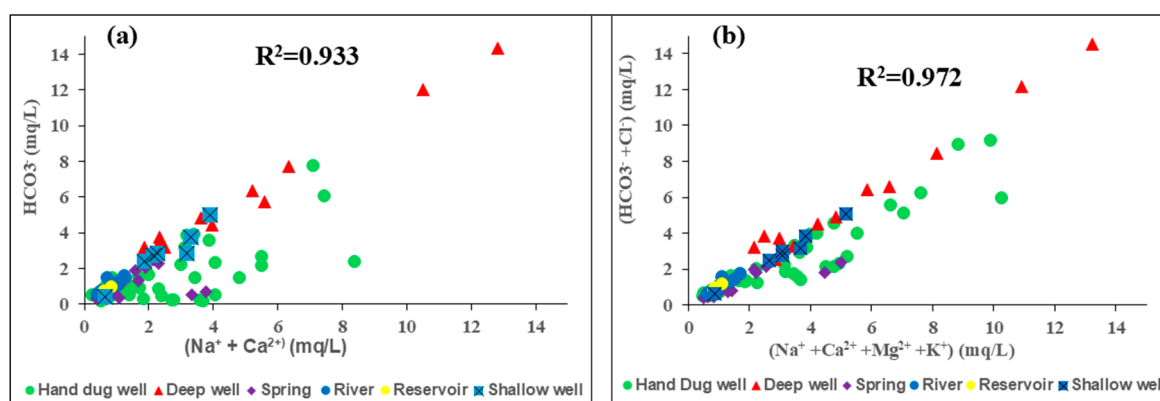


Figure 13. Cross plots of HCO_3^- vs. $(\text{Na}^+ + \text{Ca}^{2+})$ cations (a) and $(\text{HCO}_3^- + \text{Cl}^-)$ vs. all cations (b).

Figure 10b explores the weathering behavior of anorthite, pyroxene, and amphibole (Reactions (8)–(10)), which release Ca^{2+} and HCO_3^- in equivalent ratios of 1:1, 2:1, and 7:2, respectively. These relationships offer further insights into the geochemical evolution of groundwater in the study area. Most samples from hand-dug wells and springs plot along the 1:1 line, suggesting anorthite weathering as a source of Ca^{2+} in shallow aquifers. Also, several other samples, including those from rivers and the reservoir, align with the 2:1 and 7:2 equivalent ratios, indicative of pyroxene and amphibole weathering releasing

these ions to the water. In intermediate-depth wells, a few samples plot along the 2:1 and 7:2 lines, indicating contributions of Ca^{2+} and HCO_3^- from pyroxene and amphibole weathering. However, the majority of deep well samples exhibit a marked excess of HCO_3^- , suggesting the influence of additional bicarbonate sources beyond these silicate weathering or the removal of Ca^{2+} through secondary calcite precipitation. This process was described by Appelo [9] for volcanic rocks and was further modeled using PHREEQC, indicating that calcite precipitation is an important process removing ions from groundwater in volcanic systems [71]. This is confirmed in the next subsection, where the saturation index of carbonate minerals, calculated using PHREEQC, shows supersaturation.

Samples plotting above the 1:1 and 2:1 line suggest surplus HCO_3^- relative to Ca^{2+} from these minerals, while others deviating toward the Ca^{2+} axis reflect extra Ca^{2+} sources. This indicates that weathering of anorthite, pyroxene, and amphibole contributes Ca^{2+} to groundwater, alongside additional processes introducing excess HCO_3^- into the aquifers.

Figure 11a illustrate HCO_3^- versus Mg^{2+} plots, reflecting weathering processes of pyroxene (2:1), amphibole (7:5), biotite (5:8), and olivine (1:2), reaction ((8)–(11)). Few samples from hand-dug wells and springs align with these stoichiometric lines, indicating contributions from these minerals. However, most samples, all shallow and deep groundwater samples plot above these lines, pointing to additional processes enriching HCO_3^- beyond the weathering of these minerals alone. A bivariate plot of HCO_3^- versus K^+ examines the weathering of biotite and sanidine (K-feldspar) as described by Equations (11) and (13) (Figure 11b). The plot reveals that only a few samples from hand-dug wells and springs align or fall near the stoichiometric lines for biotite (5:2) and sanidine (1:1). Most water samples along with all deep groundwater samples plot above these lines (Figure 11b). This suggests a significant increase in HCO_3^- ions in the aquifer system, driven by processes beyond the weathering of pyroxene, amphibole, biotite, olivine, and sanidine. This observation suggests that the release of Mg^{2+} and K^+ from pyroxene, amphibole, biotite, olivine, and sanidine into groundwater, as well as the weathering of these minerals, does not fully explain the elevated HCO_3^- concentrations. Therefore, such processes cannot be conclusively interpreted using cross plots alone, as multiple processes may contribute to the release of these ions. The HCO_3^- is mainly derived from mixed sources, including other aluminosilicate minerals, particularly Na and Ca-feldspars (Figure 10a,b).

Figure 12 illustrates the relationship between HCO_3^- and the sum of alkaline and alkaline earth cations ($\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$) released by the weathering of aluminosilicate minerals (Reactions (7)–(13)). Silicate hydrolysis is the dominant hydrochemical process, contributing to the release of cations such as Ca^{2+} , Mg^{2+} , K^+ , and Na^+ , along with bicarbonate (HCO_3^-) into the groundwater. In the study area, this process is primarily driven by the uptake of atmospheric and biogenic CO_2 , resulting in a close relationship between HCO_3^- concentrations and dissolved cation levels. This can easily be recognized by a strong correlation ($R^2 = 0.908$) between cationic species and HCO_3^- , confirming that cations are balanced mainly by the bicarbonate anion in the Gilgel Gibe and Upper Dhidhessa catchments (Figure 12). However, some samples deviate progressively from the regression line as HCO_3^- and total cation concentrations increase, particularly in hand-dug wells and spring water. The deviation suggests anthropogenic processes are contributing to elevated ion concentrations in the shallow groundwater.

In the highland aquifers, Ca^{2+} and Mg^{2+} primarily originate from the weathering of olivine, pyroxene, and plagioclase-dominant minerals in basaltic rocks [47]. As groundwater flows toward the lowland floor through acidic volcanic formations such as ignimbrite, pumice, tuff, ash, rhyolite, and trachyte, further silicate hydrolysis increases Na^+ and HCO_3^- concentrations, while Ca^{2+} and Mg^{2+} concentrations decrease due to ions precipitation. The relationships between HCO_3^- and Mg^{2+} , as well as K^+ , show weak and

scattered distributions, indicating a limited contribution of these cations to bicarbonate generation from (Figure 11). High HCO_3^- concentrations are observed even at low Mg^{2+} and K^+ levels, suggesting that these ions do not significantly control bicarbonate enrichment. In contrast, the cross plot of $(\text{Na}^+ + \text{Ca}^{2+})$ versus HCO_3^- shows a stronger relationship with improved correlation ($R^2 = 0.933$) compared to cross plots involving all cations, indicating that bicarbonate is primarily derived from Na- and Ca-bearing feldspars associated with silicate weathering processes (Figure 13a). Therefore, Mg^{2+} plays a next role, while K^+ contribution is minimal. In addition to silicate hydrolysis, groundwater chemistry may be modified by mixing different processes. In this case, K^+ may partly originate from pollution sources, a pattern also supported by the PCA results (Figure 6). This is evaluated by adding Cl^- to HCO_3^- in the ordinate and plotting it against the sum of all four cations. The resulting relationship shows a stronger correlation ($R^2 = 0.972$) compared to other cross plots, indicating that pollution represents a secondary process contributing K^+ (Figure 13b).

3.8. Geochemical Modeling

3.8.1. Saturation Index

PHREEQC was used to calculate the saturation indices (SIs) of water samples, which are essential for assessing mineral equilibrium and predicting precipitation or dissolution processes in the system [37,66]. The different mineral saturation indices for various water samples are illustrated (Figure 14). On average, groundwater samples in the study area are generally oversaturated with respect to gibbsite, calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), illite ($\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$), and siderite (FeCO_3). These minerals tend to precipitate from groundwater and, therefore, significantly influence the water chemistry of the area by removing dissolved ions. Thus, calcite precipitation in samples with saturation indices ($\text{SI} > 0$) suggests that calcite forms as a secondary mineral phase [81]. Conversely, anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are undersaturated with respect to the average water samples from different sources. These minerals are not present in the aquifer matrix or the parent rocks of the area and thus do not contribute dissolved ions to the groundwater. Minerals such as chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) and sepiolite ($\text{Mg}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \cdot 3\text{H}_2\text{O}$) are undersaturated in most water samples except for a few hand-dug wells HD22 ($\text{SI} = 2.3$), HD23 ($\text{SI} = 1.6$), HD30 ($\text{SI} = 0.88$), and HD34 ($\text{SI} = 1.80$) and some deep wells DW11 ($\text{SI} = 0.68$), DW12 ($\text{SI} = 4.0$), and DW13 ($\text{SI} = 1.3$) where sepiolite shows positive saturation index (SI) values.

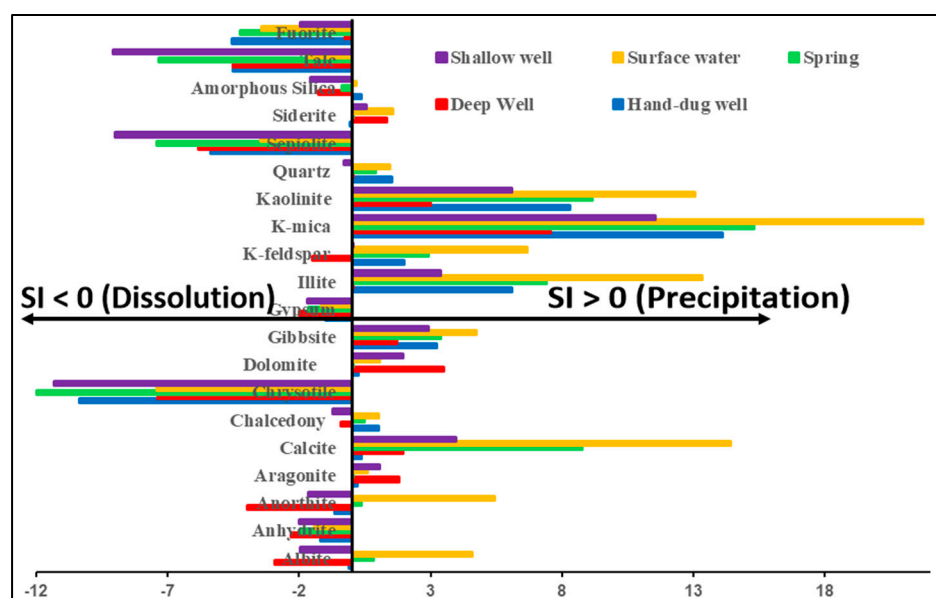


Figure 14. Saturation indices of the major mineral phases.

Amorphous silica, quartz, and chalcedony minerals are undersaturated in some shallow and spring samples. Approximately 73% of hand-dug wells, 77% of deep well samples, and all spring and shallow well samples are undersaturated with respect to talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$). Furthermore, all shallow well samples and 46% of deep well samples are undersaturated with respect to fluorite (CaF_2). Fluorite undersaturation indicates that groundwater has the thermodynamic capacity to dissolve CaF_2 and contribute Ca^{2+} and F^- to solution. Elevated concentrations of SiO_2 , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ in the groundwater are attributed to the weathering of silicate minerals in the aquifer matrix, as supported by silicate stability diagrams.

3.8.2. Mineral Stability Diagrams

The hydrogeochemical evolution of groundwater was further assessed using mineral stability diagrams constructed for three feldspar mineral groups (Figure 15A–C). Activities of major ions (H^+ , Ca^{2+} , K^+ , Na^+ , Mg^{2+} , and H_4SiO_4) were calculated using PHREEQC [66]. These diagrams plot silica concentrations on the x -axis against $\log (\text{Na}^+/\text{H}^+)$, $\log (\text{Ca}^{2+}/(\text{H}^+)^2)$, and $\log (\text{K}^+/\text{H}^+)$ on the y -axis. In Figure 15A, most samples fall within the stability fields of kaolinite and Ca-montmorillonite. Few shallow wells, springs, and hand-dug wells are aligning with the gibbsite equilibrium line. This indicates that groundwater is generally in equilibrium with kaolinite and Ca-montmorillonite. Anorthite is unstable, undergoing weathering to kaolinite. Figure 15B shows equilibrium among more samples with kaolinite and others with Na-montmorillonite, while a few samples align along the equilibrium line between gibbsite and kaolinite. Albite is unstable in all cases, weathering to Na-montmorillonite and, at later stages, to kaolinite. The transition from the kaolinite stability field to Na-montmorillonite reflects the shift from the shallow flow system toward the deeper groundwater system. In Figure 15C, most groundwater samples show equilibrium with kaolinite and some with gibbsite, whereas muscovite and microcline are unstable under the prevailing geochemical conditions, except for a few deep wells that lie near the microcline stability boundary and weather into kaolinite or further into gibbsite. These findings confirm that muscovite, microcline, anorthite, and albite are not stable in the aquifer and are undergoing weathering, consistent with regional studies in the Lake Tana region, which shares the Abay Basin with the Upper Dhidhessa area [22]. Most samples plot to the right of the quartz stability line, indicating oversaturation. Samples fall on both sides of the amorphous silica line, suggesting mixed saturation states. All deep well samples plot to the right of the amorphous silica stability line, which suggests apparent oversaturation on the activity diagram. The stability diagrams show that less mineralized water samples, such as those from hand-dug wells and springs, plot in the lower parts of the kaolinite and gibbsite stability fields, while samples from deep and shallow wells plot slightly higher. This pattern indicates an increase in the y -axis parameters of $\log (a\text{Ca}^{2+}/a^2\text{H}^+)$, $\log (a\text{Na}^+/a\text{H}^+)$, and $\log (a\text{K}^+/a\text{H}^+)$ along the groundwater flow path. The rising values reflect longer residence times and greater dissolution of aluminosilicate minerals, which in turn elevate pH and TDS levels. The geochemical evolution follows a right-to-left trend, opposite to the hydraulic flow direction. Deep wells plot in the Ca- and Na-montmorillonite fields, whereas hand-dug wells, shallow wells, and springs plot in the more weathered Kaolinite and gibbsite field.

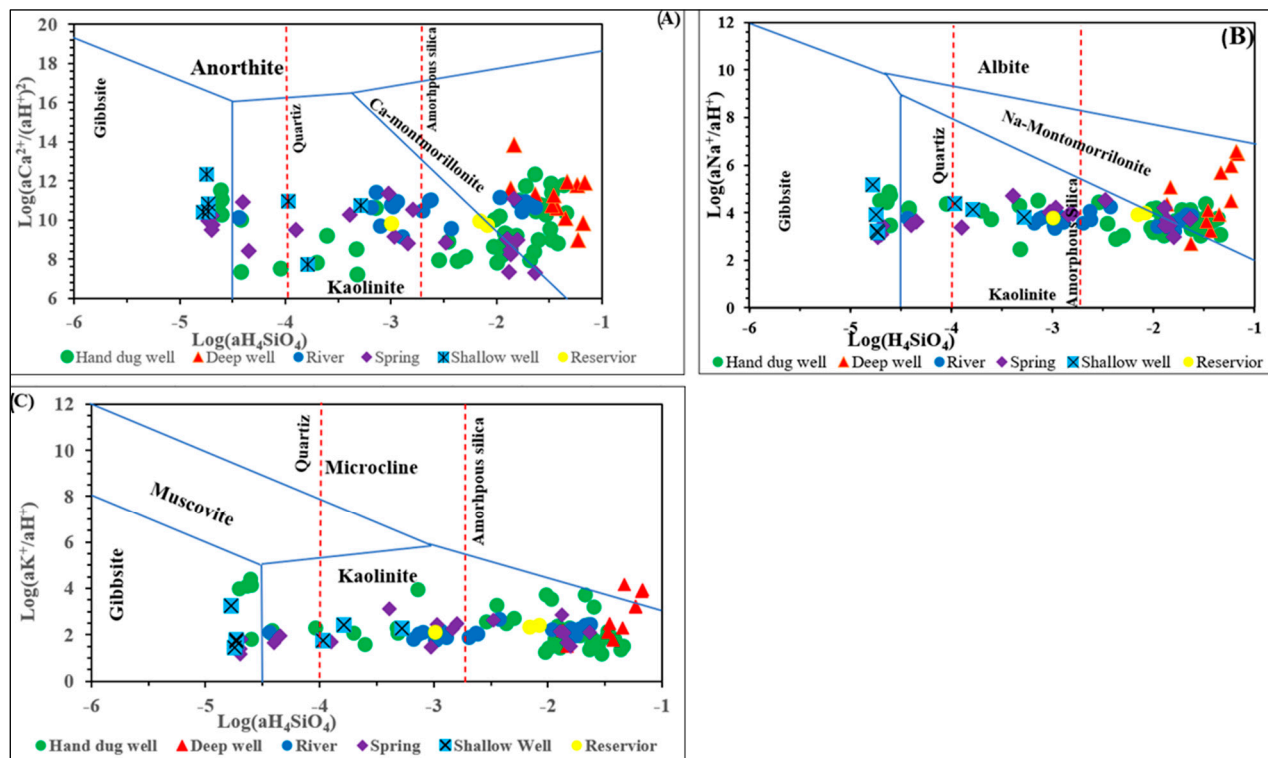


Figure 15. Stability diagram of feldspar minerals and their weathering products. (A) Stability diagram for the calcium–aluminum–silica–water system, illustrating the stability fields of anorthite, Ca-montmorillonite, kaolinite, gibbsite, quartz, and amorphous silica. (B) Stability diagram for the sodium–aluminum–silica–water system, showing the stability fields of albite, Na-montmorillonite, kaolinite, gibbsite, quartz, and amorphous silica. (C) Stability diagram for the potassium–aluminum–silica–water system, showing the stability fields of microcline, muscovite, kaolinite, gibbsite, quartz, and amorphous silica.

3.9. Dissolution and Sources of Carbon Dioxide

Figure 16a indicates that an increase in pH is accompanied by a slight rise in HCO_3^- concentration, particularly before the pH reaches 7.5 in groundwater. A parabolic relationship between pH and HCO_3^- shows that both parameters tend to increase with depth and groundwater residence time. Most samples have pH values between 4.8 and 6.9, with low to moderate HCO_3^- concentrations. Both pH and HCO_3^- concentrations tend to increase with longer subsurface residence time, progressing from rainwater through shallow groundwater to deeper aquifer (Figure 16a). The Jimma University Agaro Campus deep well (DW5) (not shown in Figure 16a due to its high HCO_3^- concentration of 2764 mg/L) and a few other deep wells in Jimma town exhibit elevated bicarbonate levels. This can be attributed to an influx of CO_2 into the system, which increases HCO_3^- concentrations while the pH remains within the range of 6.5 to 7.5. Surface water samples and a few groundwater samples exhibit low HCO_3^- concentrations, suggesting CO_2 consumption through photosynthesis (in lake and river water), which reduces CO_2 without generating HCO_3^- , or CO_2 degassing from the system, leading to increased pH (>7.5). These patterns suggest that groundwater bicarbonate enrichment is driven by CO_2 input and silicate weathering within localized fracture-controlled systems that facilitate deep circulation, whereas surface and shallow waters are influenced by biological processes. HCO_3^- is produced by the hydrolysis of silicate minerals, driven by carbonic acid formed from CO_2 that is transported with groundwater to depth and continues to react with minerals [82]. This process is enhanced by the elevated partial pressure (PCO_2) in groundwater, higher than atmospheric levels (typically $\sim 10^{-3.5}$ atm), due to the decay and decomposition of

organic matter during infiltration through the soil profile [79]. Figure 16b presents a scatter plot of HCO_3^- versus CO_2 saturation, illustrating the sources and behavior of CO_2 in groundwater. The calculated $\log(\text{pCO}_2)$ values range from -1.1 to 1.2 , considerably exceeding the atmospheric $\log(\text{pCO}_2)$ value of about -3.5 and suggesting substantial CO_2 enrichment in the groundwater system. The elevated CO_2 levels are primarily attributed to soil zone respiration and biogenic processes.

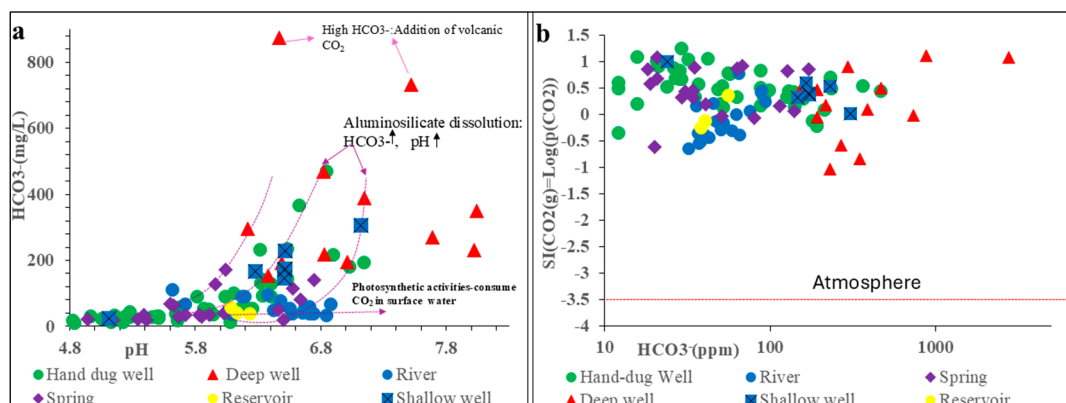


Figure 16. Scatter plot of (a) HCO_3^- versus pH and (b) cross plot HCO_3^- versus $\log\text{PCO}_2$. The black arrow indicates the simultaneous increase in pH and HCO_3^- . The horizontal arrow represents CO_2 consumption by plants, while the dotted parabolic line illustrates the nonlinear increase of HCO_3^- with increasing pH.

All samples show PCO_2 values above atmospheric levels, which enhances mineral dissolution. These elevated PCO_2 values point mainly to atmospheric and biogenic CO_2 sources. Additionally, even more extreme values (up to 1.3 atm) may suggest deep contributions from volcanic emissions. For instance, deep wells DW5 and DW9 may show high PCO_2 due to geothermal influence, where high-temperature conditions increase CO_2 accumulation and mineral solubility. Geothermal springs in the Blue Nile Basin, including the Dhidhessa catchment, indicate deep CO_2 influx to groundwater [22,83]. According to Hilberg et al. [79], such elevated PCO_2 , especially when paired with slight calcite supersaturation, suggests zones with low infiltration and carbonate precipitation. The substantial HCO_3^- concentrations result from silicate weathering driven by abundant CO_2 , releasing Ca^{2+} , Mg^{2+} , Na^+ , and HCO_3^- into groundwater.

3.10. Impact of Anthropogenic Pollution

In the study area, widespread agricultural practices, particularly the use of inorganic fertilizers and pesticides, are a likely source of nitrate (NO_3^-) contamination in groundwater. According to Adela et al. [29], approximately 46 kg/ha of nitrogen is applied during agricultural activities, contributing to NO_3^- infiltration. The catchments are loaded with high levels of agricultural chemicals [84]. Most groundwater samples were collected from borewells near agricultural fields and urban areas, where such anthropogenic inputs are prevalent. Figure 17a,b display scatter plots of Cl^- versus NO_3^- and Cl^- versus SO_4^{2-} , respectively, highlighting the influence of human activities on groundwater chemistry. Samples vary in distribution, some clustering along the Cl^- axis and others toward NO_3^- and SO_4^{2-} , indicating different contributing sources. Elevated concentrations of NO_3^- , Cl^- , and SO_4^{2-} are mostly found in hand-dug wells and springs, with significantly lower levels in deep wells and surface water samples. Groundwater from shallow aquifers, such as springs and hand-dug wells, shows high nitrate levels (>50 mg/L), exceeding safe drinking water standards [73]. In the Gilgel Gibe and Dhidhessa catchments, NO_3^- ranges from 0.1 to 194 mg/L, while Cl^- spans from 0.95 to 151 mg/L. Nitrate, chloride, and sulfate

concentrations are highest in hand-dug wells and springs, moderate in shallow wells, and lowest in deep wells, which may be attributed to pollution in hand-dug wells and springs.

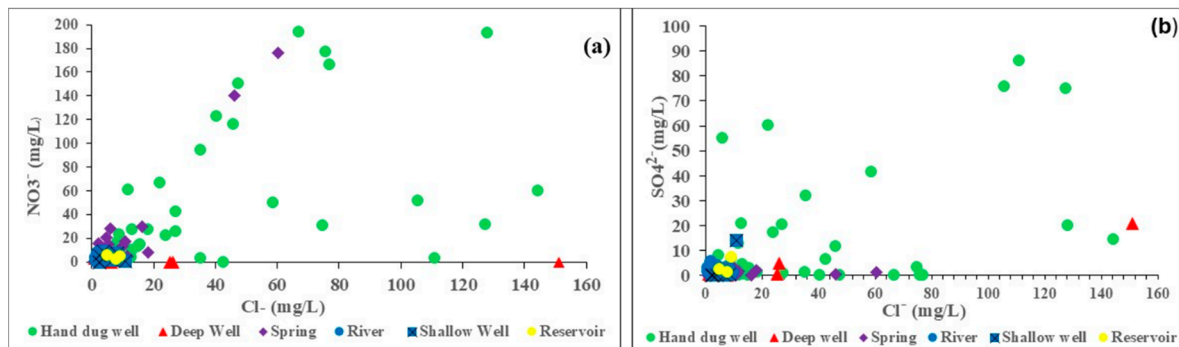


Figure 17. Scatter plot of (a) NO_3^- vs. Cl^- , and (b) SO_4^{2-} vs. Cl^- ion concentrations.

The Cl^- versus NO_3^- relationship displays a broad positive trend, indicating strong anthropogenic influence, likely related to agricultural activities, sewage, and domestic wastewater inputs. Particularly high values are observed in samples such as HD6 (NO_3^- : 194 mg L^{-1} ; Cl^- : 128 mg L^{-1}), HD21 (NO_3^- : 166 mg L^{-1} ; Cl^- : 77 mg L^{-1}), HD32 (NO_3^- : 194 mg L^{-1} ; Cl^- : 67 mg L^{-1}), and SP12 (NO_3^- : 177 mg L^{-1} ; Cl^- : 60 mg L^{-1}), which clearly plot in the high concentration region of the diagram (Figure 17a). In contrast, most rivers, reservoirs, and deep groundwater samples cluster at low concentrations, reflecting limited exposure to surface-derived contamination. This is due to dilution, short residence time, and the biological uptake process for surface water. The Cl^- versus NO_3^- and SO_4^{2-} relationship (Figure 17) shows a more scattered pattern, with elevated sulfate values mainly observed in hand-dug wells, such as HD33 (86 mg L^{-1}), HD34 (75 mg L^{-1}), and HD37 (76 mg L^{-1}). The wide dispersion of NO_3^- and SO_4^{2-} relative to Cl^- suggests mixed sources, including both anthropogenic inputs (agrochemical fertilizers, sewage, pit latrine tank, and domestic wastewater) and localized geochemical processes for sulfate [1]. For example, a hand-dug well at 2255 m a.m.s.l. in the southern highlands, classified as Ca- SO_4 type, has a TDS of 75.63 mg/L and is associated with fresh basaltic aquifers. The water shows little silicate-weathering influence due to its short residence time. The elevated SO_4^{2-} likely results from domestic washing activities near the well. As an open well used for cleansing, it is prone to frequent human contamination [13]. The simultaneous elevation of NO_3^- , Cl^- , and SO_4^{2-} in certain wells underscores the impact of anthropogenic activities, particularly agriculture and urbanization, on groundwater quality. Nitrate pollution in shallow aquifers is linked to agricultural practices [85], while animal waste, domestic refuse, poor sanitation, and pit latrines are major additional sources [77]. Organic waste decomposition can also generate nitrate through nitrification, contributing to NO_3^- pollution in groundwater [13]. A moderate positive correlation between NO_3^- and Cl^- ($r = 0.56$), as well as between SO_4^{2-} and Cl^- ($r = 0.56$), supports the notion that these ions with high concentration are from human-related sources (Table 2). Overall, these patterns indicate that shallow aquifers are highly vulnerable to contamination, with groundwater chemistry controlled by a combination of natural processes and anthropogenic inputs. In contrast, deeper groundwater remains relatively protected. The decrease in NO_3^- , Cl^- , and SO_4^{2-} concentrations with depth confirms that anthropogenic activities predominantly influence the shallow groundwater system (Table 1).

3.11. Stable Isotope Geochemistry

Oxygen and Hydrogen Isotopes

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of 44 water samples are summarized in Table 3. The isotopic composition of groundwater exhibits significant variability. Hand-dug wells show $\delta^{18}\text{O}$ values ranging from -2.18% to -0.89% and $\delta^2\text{H}$ values from -2.84% to 7.67% . Spring waters have $\delta^{18}\text{O}$ values ranging from -1.96% to -1.20% and $\delta^2\text{H}$ values from 1.56% to 5.70% , indicating a relatively narrow range. The most depleted $\delta^{18}\text{O}$ value (-1.96%) was recorded near Dedo Mountain (2052 m a.s.l.), likely explained by high-altitude origins. Boreholes exhibit $\delta^{18}\text{O}$ values from -6.71% to -1.10% and $\delta^2\text{H}$ values from -27.5% to 5.3% . The isotopic composition of groundwater from borewells varies across different locations, even when the wells are situated at similar elevations. This variation suggests that the sources of recharge to the aquifer system differ from place to place [22]. Shallow wells display narrower $\delta^{18}\text{O}$ ranges, whereas deep wells show broader isotopic variation. River water samples exhibit average $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of 4.5% and -1.3% , respectively, which are more enriched and less variable than groundwater, indicating greater isotopic stability. The Gilgel Gibe reservoir shows $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of 2.5% and -1.6% , while wetland (marshland) water is highly enriched, with values of 18.9% for $\delta^2\text{H}$ and 0.78% for $\delta^{18}\text{O}$. This enriched $\delta^{18}\text{O}$ signature in wetland waters reflects evaporative fractionation.

Table 3. Statistical summary of groundwater isotopic composition $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from deep wells, shallow wells, hand-dug wells, springs, and surface water samples.

Water Samples by Sources	$\delta^2\text{H}$				$\delta^{18}\text{O}$			
	Min.	Max.	Mean	Median	Min.	Max.	Mean	Median
Hand-dug well (N = 13)	-2.84	7.67	3.86	4.76	-2.18	-0.89	-1.54	-1.57
Springs (N = 8)	1.56	5.71	3.61	3.46	-1.96	-1.19	-1.56	-1.47
Deep and Shallow wells (N = 10)	-27.52	5.31	-6.12	-7.17	-6.71	-1.05	-2.89	-2.83
Rivers, Streams, Reservoirs, and Marshes (N = 11)	1.07	18.90	5.62	5.39	-1.92	0.78	-1.20	-1.41
Rainfall (N= 2)	24.67	31.47	28.07	28.07	0.56	2.04	1.30	1.30

The mean values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in water samples from all sources are 3.08% and -1.7% , respectively, with $\delta^2\text{H}$ ranging from -27.5% to 31.4% and $\delta^{18}\text{O}$ from -6.7% to 2.0% . The overall average ($\delta^{18}\text{O} = -1.7\%$) value is very close to groundwater from the adjacent Sor and Gebba watersheds in similar agro-climatic zones [13], and also comparable to groundwater from the Lake Tana basin [22]. However, it is slightly higher than the isotopic composition observed in Addis Ababa, indicating mild evaporative effects before recharge, likely related to differences in elevation and climate variation [86].

Figure 18 illustrates the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation, surface water, and groundwater, plotted with reference to the Global Meteoric Water Line (GMWL), typically expressed as ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$) [68], Local Meteoric Water Line for Addis Ababa (LMWL-AA) expressed as $\delta^2\text{H} = 7.2\delta^{18}\text{O} + 11.9$ adapted for local climatic conditions [86], Local Meteoric Water Line for Sor and Gebba Watershed (LMWL-SG), in the adjacent basin in the west, expressed as $\delta^2\text{H} = 7.6 \times \delta^{18}\text{O} + 15.2$ [13]. Analyzed water samples lie within the boundaries of meteoric water lines, indicating a predominantly meteoric origin. Rainfall samples (red triangles) exhibit slightly above the meteoric water line. This position likely reflects differences in moisture source, atmospheric circulation, or rainout processes that influence the isotopic composition of precipitation in the region. A notable characteristic of the watershed is the relatively enriched $\delta^2\text{H}$ and $\delta^{18}\text{O}$ content in some water samples. This enrichment is particularly evident in marshland (wetland) samples, which display clear signs of evaporative effects. As shown in Figure 18, the $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ values place rainwater and marshland samples at the top of the plot, while deep wells and some

shallow wells appear at the bottom, indicating characteristics of infiltrated groundwater. The use of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values to identify recharge sources and isotopic variability among sampled groundwater aligns with global observations summarized in the Global Soil Water Stable Isotope Dataset [87]. Hand-dug wells, springs, rivers, and other shallow wells fall in the middle range, reflecting mixed sources (Figure 18). The isotopic composition of different groundwater sources indicates a progressive enrichment from deep groundwater to hand-dug wells, and further to wetland (marshland) water. Most groundwater samples from deep wells exhibit the most depleted $\delta^{18}\text{O}$ values compared to other sources (Figure 18). Such isotopic depletion generally indicates recharge under cooler conditions or at higher elevations within the regional flow system. This pattern may also reflect differences in recharge source or flow-path characteristics. Isotopic exchange with CO_2 can influence $\delta^{18}\text{O}$ under specific conditions [88]. Water–rock or CO_2 exchange at depth typically affects $\delta^{18}\text{O}$ only and often enriches it under geothermal conditions [89]. In this region, the depletion of $\delta^{18}\text{O}$ in deep groundwater is accompanied by increasing trends in EC and HCO_3^- and attributed to water–rock interactions occurring as groundwater percolates to deeper layers. Such geochemical processes contribute to the observed shift away from the meteoric water lines and the associated $\delta^{18}\text{O}$ depletion, and hydrochemical trends are compatible with deep flow paths shaped by heterogeneous permeability in volcanic aquifers [90]. However, few deep wells plot together with springs, shallow wells, and hand-dug wells, suggesting that these particular deep wells may be hydraulically connected to the shallow aquifer system and influenced by a local shallow flow regime. The similarity between isotopic signatures of shallow and these few deep wells suggests a common recharge source, supported by moderate TDS levels and water types dominated by Ca-HCO_3 to Ca-Mg-HCO_3 , indicating relatively young groundwater. The observed overlap and correlation among hand-dug wells, springs, shallow wells, rivers, and the reservoir indicate strong groundwater surface water (GW–SW) interaction and the influence of local recharge. Supporting evidence from hydrochemical data reveals that groundwater evolution in the watershed is influenced by aluminosilicate hydrolysis. This study’s interpretation of groundwater surface water interaction aligns with recent evidence on interface processes [91]. From a hydrogeological perspective, the shallow aquifer system is dominant and consists of fractured and weathered rock units in the uplands and alluvial sediments in the lowlands. Deep aquifers primarily occur within fractured and weathered volcanic formations.

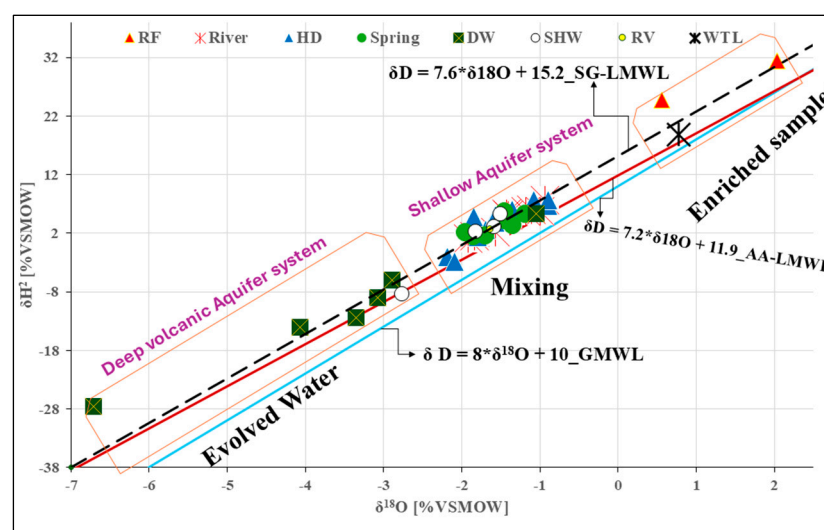


Figure 18. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ relation with LMWL and GMWL for samples from different water sources. Orange boxes highlight clusters of samples, and the purple labels indicate the corresponding aquifer

depths of the sample clusters. (RF—Rainfall, HD—Hand-dug well, DW—Deep well, SHW—Shallow well, RV—Reservoir, WTL—Wetland).

The water samples collected from the Gilgel Gibe and Dhidhessa watersheds in the present study show linear correlations comparable to those observed for Addis Ababa [9], the Lake Tana basin [22], and even the Global Meteoric Water Line [68], as well as a deuterium excess (d-excess) value. Elevated d-excess (>10‰) suggests moisture-source conditions, such as evaporation at the vapor source under low humidity [9,86]. Post-precipitation evaporation of surface water generally lowers d-excess. Furthermore, the results are consistent with those reported for the Sor and Gebba watersheds in western Ethiopia [13], which demonstrated an average slope of 7.6 and a d-excess of 15.2. The findings of this study also agree with previous investigations linking precipitation and groundwater isotopes in Ethiopia, particularly in the Jimma area [92]. In addition, the results show close agreement with those reported from other Ethiopian catchments, including the Bilate River watershed in the Rift Valley [93], and the Shinile and Fafen Jerer catchments in eastern Ethiopia [94].

Figure 19 shows the relationship between $\delta^{18}\text{O}$ and elevation for hand-dug wells, springs, shallow wells, and surface waters. The regression equation ($\delta^{18}\text{O} = -0.0008 \times \text{elevation} + 0.0084$) indicates an isotopic gradient of -0.08‰ per 100 m, which closely aligns with the -0.1‰ per 100 m reported by [83] and Nigate et al. [24] in the Blue Nile source region.

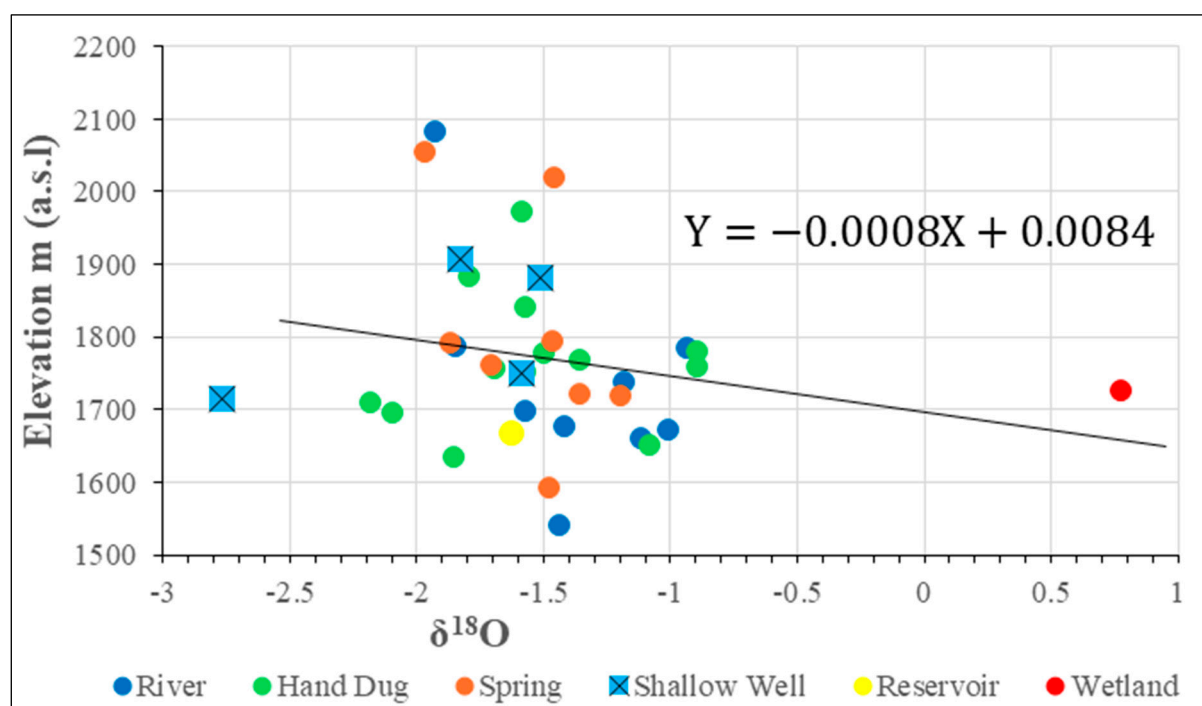


Figure 19. Relationship between shallow groundwater $\delta^{18}\text{O}$ and elevation. The black line indicates the trend line.

4. Conclusions

Hydrogeochemical and isotopic investigations of groundwater and surface water in the Gilgel Gibe and Upper Dhidhessa catchments reveal clear spatial variations in water chemistry associated with groundwater flow evolution from upland recharge zones to lowland discharge areas. Groundwater in upland areas is characterized by low mineralization and slightly acidic conditions, representing recently recharged meteoric water, whereas groundwater in lowland deep aquifers shows higher mineralization and alkaline

conditions, reflecting longer residence times, extended flow paths, and intensified water–rock interaction. The spatial distribution of various physicochemical and hydrogeochemical parameters demonstrates a distinct contrast between different water sources. Measured pH values range from 4.8 to 8.2, while EC varies between 40 and 4890 $\mu\text{S}/\text{cm}$. These results indicate that the water samples span from slightly acidic to mildly alkaline conditions (pH) and from low to high mineralization levels (EC).

The relative abundance of ions in the analyzed water samples follows the order: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in hand-dug wells, springs, and surface waters (rivers, streams, and marshes); and $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ in deep wells. The Piper diagram identifies Ca– HCO_3 , Na– HCO_3 , Ca– NO_3 , and Ca–Cl as the most prevalent water types, along with mixed facies such as Ca–Mg– HCO_3 , Ca–Na–Mg– HCO_3 , and Na–Ca– HCO_3 . The dominant hydrochemical facies show a transition from Ca–Mg– HCO_3 water types in recharge zones to Na– HCO_3 types in deeper lowland aquifers, indicating progressive geochemical evolution primarily controlled by aluminosilicate weathering processes in the presence of CO_2 . Mineral saturation states and stability relationships further support the role of feldspar dissolution and secondary clay mineral formation in shaping groundwater chemistry along flow paths. Most groundwater samples are in equilibrium with kaolinite, Ca-montmorillonite, and Na-montmorillonite within the aquifer. These results show that muscovite, microcline, anorthite, and albite are unstable and undergoing weathering, and the geochemical evolution follows a trend opposite to the hydraulic flow direction. Elevated partial pressures of CO_2 exceeding atmospheric levels suggest contributions from atmospheric, biogenic, and possible deep geological sources for very few deep wells.

Localized increases in NO_3^- , Cl^- , and SO_4^{2-} concentrations in hand-dug wells and springs indicate the influence of anthropogenic activities, particularly in urban and agricultural areas, emphasizing the vulnerability of shallow groundwater to contamination. Despite this, fluoride concentrations in most groundwater samples remain within permissible drinking water limits.

Stable isotope compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) confirm the meteoric origin of groundwater and demonstrate strong hydraulic connectivity between surface water and shallow groundwater systems. The similarity and correlation of isotopic ratios among different water samples suggest strong active recharge processes and groundwater–surface water (GW–SW) interaction within the watershed.

Groundwater chemistry is mainly controlled by aluminosilicate weathering and CO_2 -driven mineral dissolution, with anthropogenic inputs as the secondary influence. Minor effects from calcite precipitation, limited mixing, and evapoconcentration also contribute but are comparatively small. The results provide essential evidence for planning and sustaining groundwater resources, particularly in areas where water quality is influenced by natural processes and anthropogenic pressures. The findings offer policymakers a scientific basis for improving groundwater protection, guiding development in reclamation zones, and supporting long-term sustainable water-resource management. Effective land-use management, controlled application of agrochemicals, as well as sanitary pollution and depth-specific groundwater sampling, are recommended in future work and support long-term water resource sustainability.

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