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Hydro-geochemical investigation and Water Quality Mapping in the Upper Beshilo Watershed, Southern Wollo, Ethiopia

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Abstract

The Upper Beshilo watershed within the Upper Blue Nile Basin (UBNB) is a region experiencing escalating groundwater reliance for domestic and agricultural purposes. Yet, it lacks comprehensive hydrogeochemical and isotopic characterization. This study addresses this critical knowledge gap by investigating the hydrogeochemical characteristics and isotopic signatures of groundwater from various sources (springs, boreholes, hand-dug wells, rivers, and marsh areas) across the watershed. The objective is to elucidate groundwater flow patterns, recharge and discharge dynamics, sources of contamination (including waste from Mekdela Amba University and Ginba town), and the overall hydrogeological evolution of the system. Twenty-six water samples were collected and analyzed for major ions and stable isotopes ($\delta^{2}H$ and $\delta^{18}O$). Results indicate that precipitation is the primary recharge source, with the dominant water types identified as Ca-Na-HCO_3 and Ca-HCO_3, suggestive of fresh recharge and early to intermediate stages of groundwater evolution. However, the hydrochemical data also reveals the impact of anthropogenic activities, with elevated levels of nitrate, sulfate, and chloride near discharge zones and downstream areas, particularly around Ginba town and the Mekdela Amba University waste site. Isotopic analysis confirms that the groundwater system is recharged by precipitation, with deeper boreholes showing more depleted isotope signatures indicative of past climate conditions, while shallow groundwater sources show evidence of more recent recharge. Additionally, evaporation processes were observed in surface water. A conceptual hydrogeological model was constructed depicting recharge areas in the south and southwestern highlands and discharge zones towards the lowlands and the Beshilo River, following a general northward flow pattern. This comprehensive study provides crucial insights into the hydrogeological system of the Upper Beshilo watershed, underscoring the need for sustainable groundwater management practices. These include the importance of protecting recharge zones, implementing proper waste management strategies, and emphasizing ongoing monitoring to prevent future degradation of this valuable resource, while also guiding the development of the resource in terms of drinking water provision, bottled water production, and location of boreholes.

Keywords: Anthropogenic impact; Water quality; Upper Beshilo watershed; Upper Blue Nile Basin

Introduction

Surface water is rarely utilized as a primary water supply due to its susceptibility to seasonal variations, contamination risks, and the absence of adequate retention technologies (Kebede et al., 2005). In contrast, groundwater serves as the most significant and valuable freshwater resource globally, supporting human needs and economic growth (Healy, 2010). It is particularly crucial in arid regions where surface water is limited and seasonal, often serving as the primary source of domestic water supply (BGS, 2001). Healy (2010) estimates that over 6 billion people worldwide rely on groundwater for drinking water. In Ethiopia, groundwater quality is influenced by both natural and anthropogenic factors. The chemical composition of groundwater is often linked to surface water quality due to hydraulic interactions (Alemayehu, 2006). Kebede (2013) highlights that groundwater composition in Ethiopia is shaped by lithologic variations, soil zone salt dissolution, and thermodynamic processes, which dictate reactions based on rock type, temperature, and ionic activity. Studies reveal that sodium and calcium are the dominant cations in Ethiopian groundwater (Alemayehu, 2006). The Upper Blue Nile Basin (UBNB) exhibits two primary groundwater systems: low-salinity Ca-Mg-HCO3 type waters from basaltic plateaus and high- Total dissolved Solid (TDS) Na-HCO3 type thermal waters from faulted grabens (Kebede et al., 2005). The UBNB's geology, comprising crystalline basement rocks, volcanic rocks, and sediments, has been extensively studied (Asrat et al., 2001; Kebede et al., 1999; Assefa, 1991; Yemane et al., 1985). The Upper Beshilo watershed, located within the UBNB, is predominantly covered by Cenozoic volcanic rocks (Kebede et al., 2005). Hydrogeochemistry has historically been understudied due to limited instrumentation and lesser emphasis on water quality. However, with growing concerns over water quality and health impacts, coupled with advancements in technology, it has emerged as a critical field of study. Previous research has explored groundwater flow, recharge, and chemical evolution at basin scales (Ayenew et al., 2008; Alemayehu and Kebede, 2011; Kebede et al., 2005). Despite these efforts, the groundwater chemistry and isotopic characteristics of the Upper Beshilo watershed remain poorly understood. While Kebede et al. (2005) investigated the geochemical evolution of the UBNB using geochemical and isotopic data, and Mamo (2015) employed techniques like multivariate analysis and hydrochemical facies to study groundwater sources, no detailed geochemical evolution study has been conducted at the watershed level. This research represents a best of knowledge for comprehensive hydrogeochemical analysis in the Upper Beshilo watershed.

Methodology

Description of the Study Area

The Upper Beshilo watershed, situated in the Amhara National Regional State (ANRS), Northwestern Ethiopia, forms part of the Upper Blue Nile Basin (UBNB). Geographically, it extends between 518,591 to 538,747 m Easting and 1,202,204 to 1,221,058 m Northing (Fig 1). The watershed spans two administrative districts (Woredas): Tenta (119 km²) and Legambo (101 km²), covering a total area of 220 km². It is accessible via asphalt roads from Mekane Selam to Tulu-Awuliya and Tenta, or from Dessie (the capital of South Wollo Zone) to Tulu Awulia and Tenta.

The watershed's river system flows into the Beshilo River, eventually draining into the Blue Nile River (locally known as Abay River). Elevation ranges from 2,344 m in the north to 4,032 m in the southwest. The climate varies from temperate (Woina Dega) to cool temperate (Dega and Kur), with a mean annual temperature of 10–20°C (Alemayehu, 2006). Annual precipitation averages 1,245 mm in Tenta and 933 mm in Legambo, with the majority occurring during the main rainy season ("Kiremt"), which lasts from June to September (National Atlas of Ethiopia, 1981).

The Upper Beshilo watershed is characterized by flat to gently sloping plain or rugged morphology. However, an extensive area of gently rolling to hilly upland (steep-slope) is observed in the Southwest and Southeast part of the area. The highest elevation is about 4032m in the Southwest part of the study, mainly the Tenta highland regions, and the lowest elevation is 2344m in the North part of the watershed

(Fig 2). The Upper Beshilo watershed has an average elevation of 3188m. Generally, the watershed can broadly be divided into five physiographic regions: smooth or flat plain (valley floor), Pediment/pediplain, plateau, low mountain, and high mountainous region, where the majority of the area is characterized by low to high mountainous regions.

The Kulkul River drains from the South to the North and joins the Beshilo River, which is finally drained and reaches the Blue Nile River (Fig 3). Their drainage patterns are generally parallel and rectangular in the lowland areas owing to the orientation of geological structures. However, the highlands part of the watershed shows a dendritic drainage pattern. In general, the direction of flow of these streams is controlled by the topography and structural factors of the area in the highlands and lowlands, respectively.

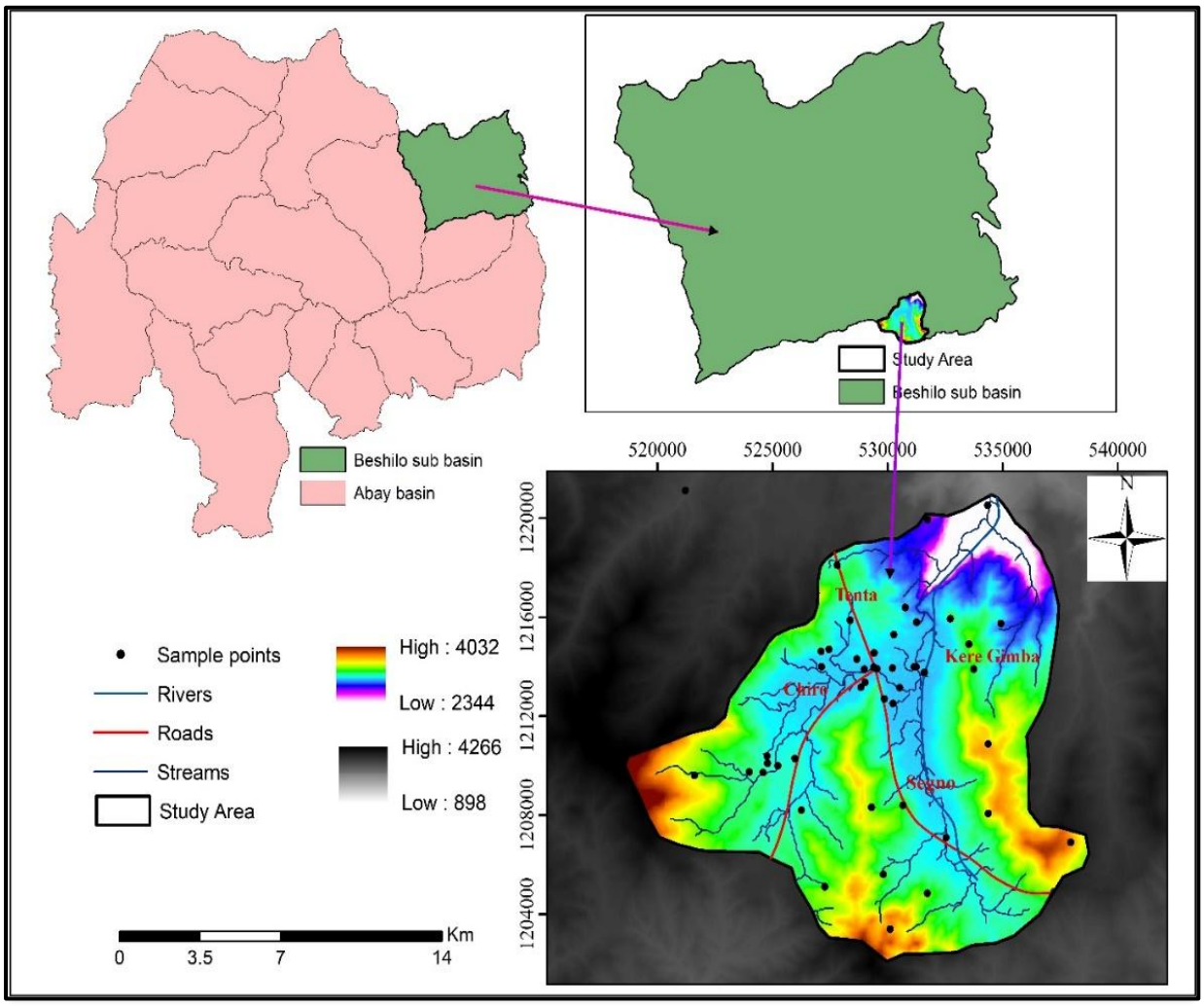

Fig. 1: Location map of the Upper Beshilo watershed

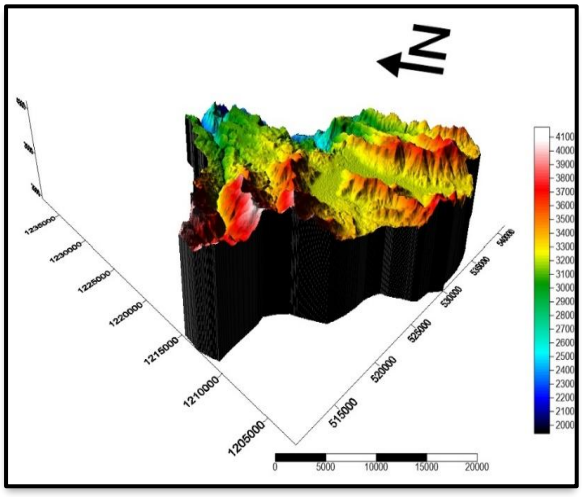

Fig 2: 3D view of the Upper Beshilo watershed

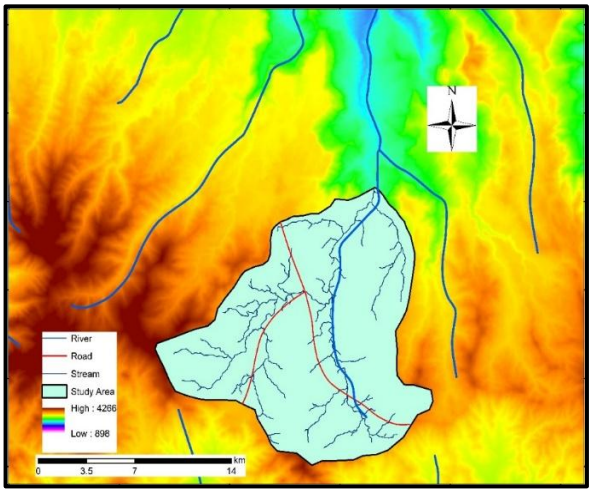

Fig. 3: Drainage map of Upper Beshilo watershed

Sample Collection and Hydrochemical Analysis

Twenty-six groundwater samples were collected from April to May 2023 across various hydrogeologic settings, including springs (11), hand-dug wells (7), rivers (6), a marsh area/seepage spring (1), and a borehole (1). Sampling sites were strategically selected to ensure diverse hydrogeologic representation. Strict quality assurance and control (QA/QC) measures were implemented to maintain data integrity and prevent contamination. Pre-cleaned, deionized water-rinsed, one-liter polyethylene bottles were used for collection, with duplicate samples systematically taken for further laboratory verification. This meticulous approach ensures the accuracy and reliability of the hydrogeochemical data, providing a comprehensive assessment of water composition in the study area.

Laboratory analyses were conducted at the Water, Soil, and Geotechnics Laboratory within the Competence Design and Supervision Corporation (CDSC) and the Ethiopian Engineering Corporation. Various analytical methods were employed: Atomic Absorption Spectrophotometry (AAS) for Ca^{2+}, Mg^{2+}, Fe, and Mn; flame photometry for Na^{+} and K^{+}; titration for HCO_3^{-} and SO_4^{2-}; and colorimetric techniques for F^{-}, NO_3^{2-}, and Cl^{-}. Electrical methods were used to re-evaluate EC, pH, and TDS for quality assurance.

To ensure data credibility, chemical results were rigorously assessed using the cation-anion equilibrium relationship in milliequivalents per liter (meq/L), detecting potential analytical errors. The electroneutrality principle (EN) was applied using the AquaChem 10 software equation (1) to compute charge balance. Reliable geochemical data require a near-equal balance between total cations and anions (Freeze and Cherry, 1979). According to Singhal and Gupta (2010), water samples with charge balance errors within ±5% are deemed acceptable, though some studies extend this threshold to ±10% for interpretation. This evaluation ensures the validity of the data for hydrogeochemical analysis.

$$Electro\ neutrality(\%) = \left(\frac{\sum Xcation - \sum Yanion}{\sum Xcation + \sum Yanion}\right) * 100 \quad (1)$$

The analytical results, including major ions, hydrochemical parameters, and water classifications, were visualized using various graphical techniques such as box-whisker plots, histograms, Piper diagrams, scatter plots, Wilcox plots, and bi-variant plots. These visualizations help identify groundwater flow patterns, water chemistry evolution, salinity sources, and potential interactions between different water sources.

Stable Isotopic Data ($\delta^{18}o$ and δd) Analysis

Combining isotopic data with hydrochemical information provides precise insights into interpreting and

analyzing groundwater dynamics. A total of 26 samples; 7 from surface waters, and 19 from groundwater underwent δD and $\delta^{18}O$ isotopic composition analysis. Collected in pre-rinsed 500 ml polyethylene bottles, the samples were analyzed at Addis Ababa University, School of Earth Sciences, using a liquid water isotope analyzer (LGR). Isotopic composition, expressed in per mill (‰), deviates from the internationally accepted standard of mean ocean water (Craig, 1961), now modified as Vienna Standard Mean Ocean Water (V-SMOW).

The Global Network of Isotopes in Precipitation (GNIP) database for Addis Ababa served as a surrogate for precipitation data. Despite the significant distance between Addis Ababa and the study area, shared topography (1433–2755m for Upper Beshilo and Addis Ababa) and a consistent mono-modal rainfall distribution (between June to September) facilitated the use of GNIP data. Kebede (2013) underscores the difficulty in determining the isotopic concentration of a specific isotope in a given water system due to the minuscule abundance of heavy isotopes. It is therefore easier to express isotopic abundances using the isotopic ratio R (R<1) equation (2).

$$R = \frac{Abundance\ of\ rare\ (heavy)\ isotope}{Abundance\ of\ abundant\ (light) isotope} \quad (2)$$

R is normally a very small number (in nature $^{18}O/^{16}O = (2005.2 \pm 0.45) *10^{-6}$), and $^{2}H/^{1}H = (155.76 \pm 0.05) *10^{-6}$)) and are standards to use them.

Integration of stable isotope data ($\delta^{18}O$ and $\delta^{2}H$) with hydrogeochemical and hydrogeological information and findings has been instrumental in the comprehensive characterization, identification, and analysis of various aspects related to groundwater dynamics. These include understanding groundwater flow systems, examining paleo-groundwater conditions, investigating evaporation processes, assessing the mixing of groundwater and surface waters, scrutinizing groundwater recharge mechanisms, and pinpointing the outflow area within the Upper Beshilo watershed.

Results and Discussion

Hydrogeochemical Analysis

The following parameters were analyzed in the laboratory: Na^{+}, K^{+}, Ca^{2+}, Mg^{+2}, Mn^{+2}, total Fe, Cu^{2+}, Cl^{-}, F^{-}, NO^{3-}, HCO_3^{-}, SO_4^{2-}, TDS, EC, and pH. As shown in Fig 4, from the analyzed samples, 66.67% (n = 20) of the samples exhibited an electro-neutrality (EN) within ±5% of perfect balance, indicating reliable analytical results. An additional 20% (n = 6) of samples portray an EN range of ±5% to ±10%, suggesting a minor degree of analytical error. However, four samples (13.33%) displayed an EN exceeding ±10%, indicating significant analytical discrepancies. This sample has been excluded from further interpretation and data analysis due to the authors' concern about the data quality. The units of concentration used in the text, unless specified differently, are mg/l. The EC values are given in µS/cm, and residual alkalinity values are given in meq/l. The samples with an EN within ±5% and ±5% to ±10% were considered suitable for hydrogeochemical interpretation and data analysis. However, samples with electro neutrality exceeding ± 10% have been rejected and not used for further analysis (Appelo and Postma, 2005).

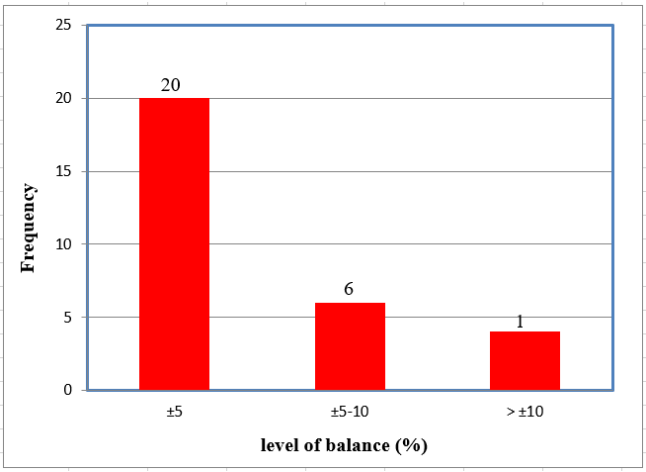

Fig. 4: Graph of electro-neutrality of water samples

Evaluation of Hydrochemical Parameters and Ions

Evaluating the hydrochemical parameters and analyzing their geochemical signature is essential to understand and interpret the groundwater hydrodynamics in the area. Identifying the possible sources, groundwater type distribution, and relations of ion ratio with TDS in the area have also been evaluated.

Table 1: Summary statistics for hydrochemical parameters and ions (mg/l)

PARAMETER	UNIT	MIN	MAX	AVERAGE	ST. DEV.	Q25	Q50	Q75	
CA	mg/l	12.3	48.7	32.54231	9.79944	26.45	32.8	38.6	
MG	mg/l	0.1	21.1	3.71269	4.87697	0.7	2.5	3.75	
NA	mg/l	1.2	63.7	19.6	16.84264	8.05	12.2	34.1	
CL	mg/l	0.3	55.6	14.59615	16.14984	3	5.1	20.25	
HCO_3	mg/l	35.6	355.5	117.4269	66.25253	68.1	110.5	127.65	
SO_4	mg/l	0	46.1	8.00885	11.93429	0	0	13.35	
PH		5.92	9.1	6.8709	6.57492	0	0	0	
COND	uS/cm	80	1320	377.4615	275.8185	180	250	569.5	
TDS	mg/l	45.5	1120.3	288.2423	257.5732	105.15	146.4	483.75	
K	mg/l	0.1	4.2	0.95808	1.10306	0.11	0.3	1.8	
F	mg/l	0.02	1.3	0.32231	0.25463	0.16	0.25	0.425	
NO_3	mg/l	1.28	38.2	12.24423	9.09336	4.15	10.1	16.6	
SAMPLE NUM									N= 26

In-situ (lab-measured) parameters (pH, TDS, and EC)

The pH of groundwater samples in the study area ranged from 5.92 (SP8) to 9.1 (HDW3), indicating slightly acidic to slightly alkaline conditions (Fig 5). Over 80% of the samples exhibited pH values between 6.8 and 8.0, which align with the drinking water quality standards set by the Ethiopian Ministry of Water Resources and the World Health Organization (WHO, 2017). Deep groundwater systems, characterized by limited atmospheric exchange, can serve as long-term CO_2 reservoirs (Hitchcock and Wright, 2003). Notably, the southwest region displayed lower pH levels compared to other areas, likely due to higher CO_2 concentrations and deeper water tables. No systematic variation in pH was observed along the inferred groundwater flow path, suggesting that local geological formations and biological activity may play a more significant role in influencing groundwater pH than flow distance.

Total dissolved solids (TDS) and electrical conductivity (EC) are key indicators of water quality,

primarily reflecting salinity levels. Total dissolved solid represents the mass of dissolved constituents remaining after complete evaporation of a water sample (Hem, 1985), with major contributions from cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, SO_4^{2-}, CO_3^{2-}, HCO_3^{-}), alongside minor constituents such as Fe^{2+}, Mn^{2+}, Cu^{2+}, F^{-}, and NO_3^{-}. In this study, EC and TDS values ranged from 80 µS/cm and 45.5 mg/L (SP12, Southeast/West) to 1320 µS/cm and 1120 mg/L (R6, Northern, "Upper Beshilo River") (Fig 6). Elevated EC and TDS levels at R6, located downstream, indicate a slightly saline nature in the Beshilo River, suggesting potential salinity risks in downstream areas, including the river itself.

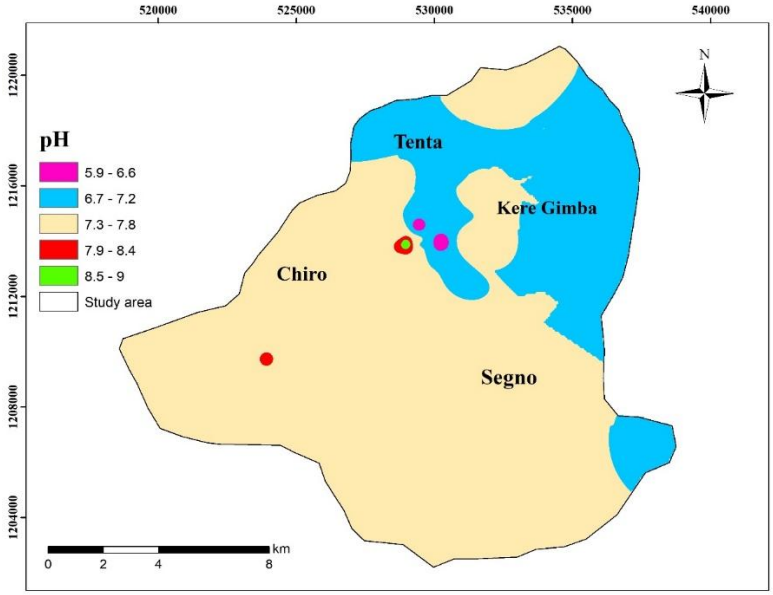

Fig. 5: Spatial distribution map of pH in the Upper Beshilo watershed

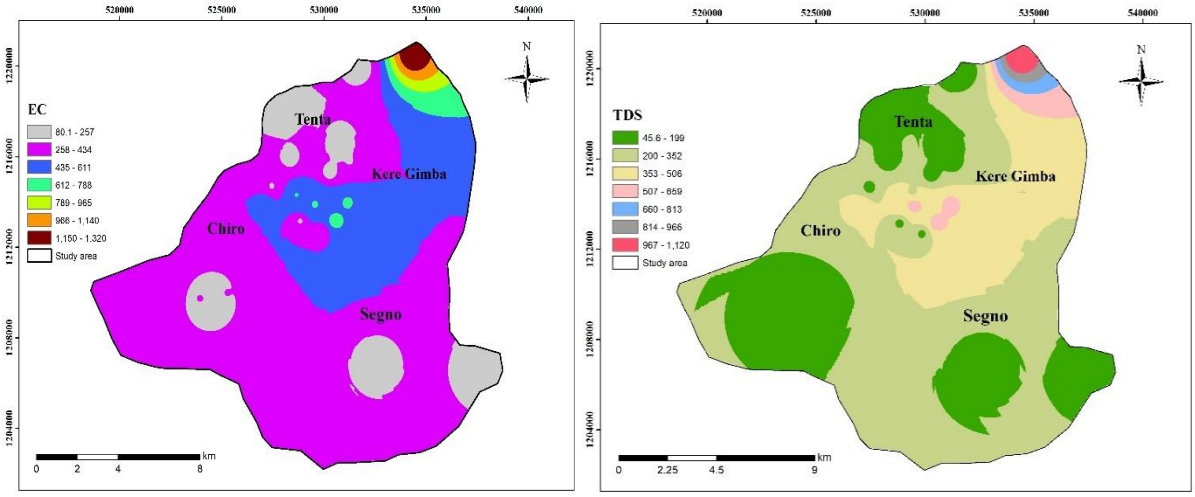

Fig. 6: Spatial distribution map of EC and TDS in the Upper Beshilo watershed

Major Cations (Ca and Na)

Calcium (Ca^{2+}) Groundwater calcium and sodium concentrations exhibit distinct spatial and geochemical trends influenced by geological formations, hydrological processes, and aquifer evolution. Calcium levels range from 12.3 mg/L in downstream areas (e.g., SP12) to 48.7 mg/L in regions like Tenta and Chiro (SP6), where elevated concentrations result from rock-water interactions, dissolution of calcium-bearing minerals (e.g., limestone, gypsum), and prolonged aquifer residence time. The general decline in calcium along the groundwater flow path reflects dilution, mineral precipitation (e.g.,

calcite), and cation exchange, where calcium is replaced by sodium or other ions in clay or soil matrices. Variations in borehole depth and geochemically distinct deeper groundwater sources also contribute to localized calcium anomalies.

Sodium concentrations range from 1.2 mg/L in southern areas to 63.7 mg/L in boreholes such as BH1 in the Ginba Graben, with increasing levels downstream. This pattern aligns with the dissolution of sodium-rich minerals (e.g., feldspar, halite), cation exchange processes that deplete calcium or magnesium, and groundwater mixing at greater depths. The progressive increase in sodium along the flow path suggests prolonged interaction with sodium-bearing formations and extended residence times, leading to enrichment. Anthropogenic factors, such as agricultural runoff containing sodium-based fertilizers, may further contribute to elevated sodium levels in certain areas.

These geochemical patterns, illustrated in Fig 7, are shaped by aquifer characteristics such as lithology, permeability, and recharge rates. Broader influences, including groundwater stratification, tectonic structures affecting flow dynamics, and climatic factors influencing evaporation and recharge, also play significant roles. The observed spatial and chemical variability in calcium and sodium highlights the complex interplay between natural processes and human activities, with implications for groundwater management, drinking water quality, and ecosystem health.

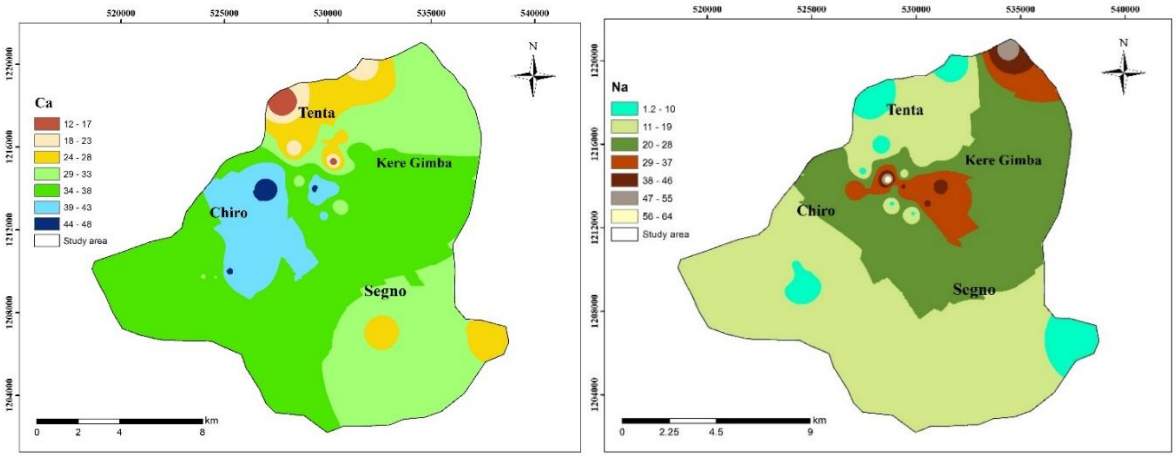

Fig. 7: Spatial distribution map of a) Ca and b) Na in the Upper Beshilo watershed

Anions and Anthropogenic parameters (HCO_3^-, Cl^-, SO_4^{2-}, F^-, NO_3^-)

The groundwater analysis reveals that bicarbonate (HCO_3^-) is the dominant anion across the study area, indicating carbonation processes involving the dissolution of CO_2 in water. HCO_3^- concentrations range from 35.6 mg/L (SP12) to 355.5 mg/L (BH1), all within WHO drinking water standards, and show variability linked to differences in recharge conditions and rock-water interaction. Unlike typical hydrogeological systems, no clear evolutionary trend among anions was observed, although chloride (Cl^-), fluoride (F^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) remain within safe limits. Elevated nitrate levels in downstream areas likely result from agricultural fertilizers and waste from Mekdela Amba University (MAU), while increased sulfate and chloride concentrations near the MAU waste site and downstream to the Beshilo River suggest anthropogenic influences, especially in shallow wells. Calcium (Ca^{2+}) and sodium (Na^+) dominate the cation composition, reflecting recharge from mountainous areas where carbonate and silicate dissolution occurs. While groundwater quality remains permissible, ongoing monitoring of anthropogenic impacts and preservation of recharge zones, including the wastes from Mekdela Amba University, is crucial to prevent future degradation. Figures 8a, b, and **c** show the spatial distribution of HCO_3^-, Cl^-, and SO_4^{2-}. Elevated nitrate, chloride, and sulfate levels in some samples were linked to anthropogenic sources, including waste disposal from Mekdela Amba University (MAU) and Ginba town, agricultural runoff, and evaporation effects, particularly downstream

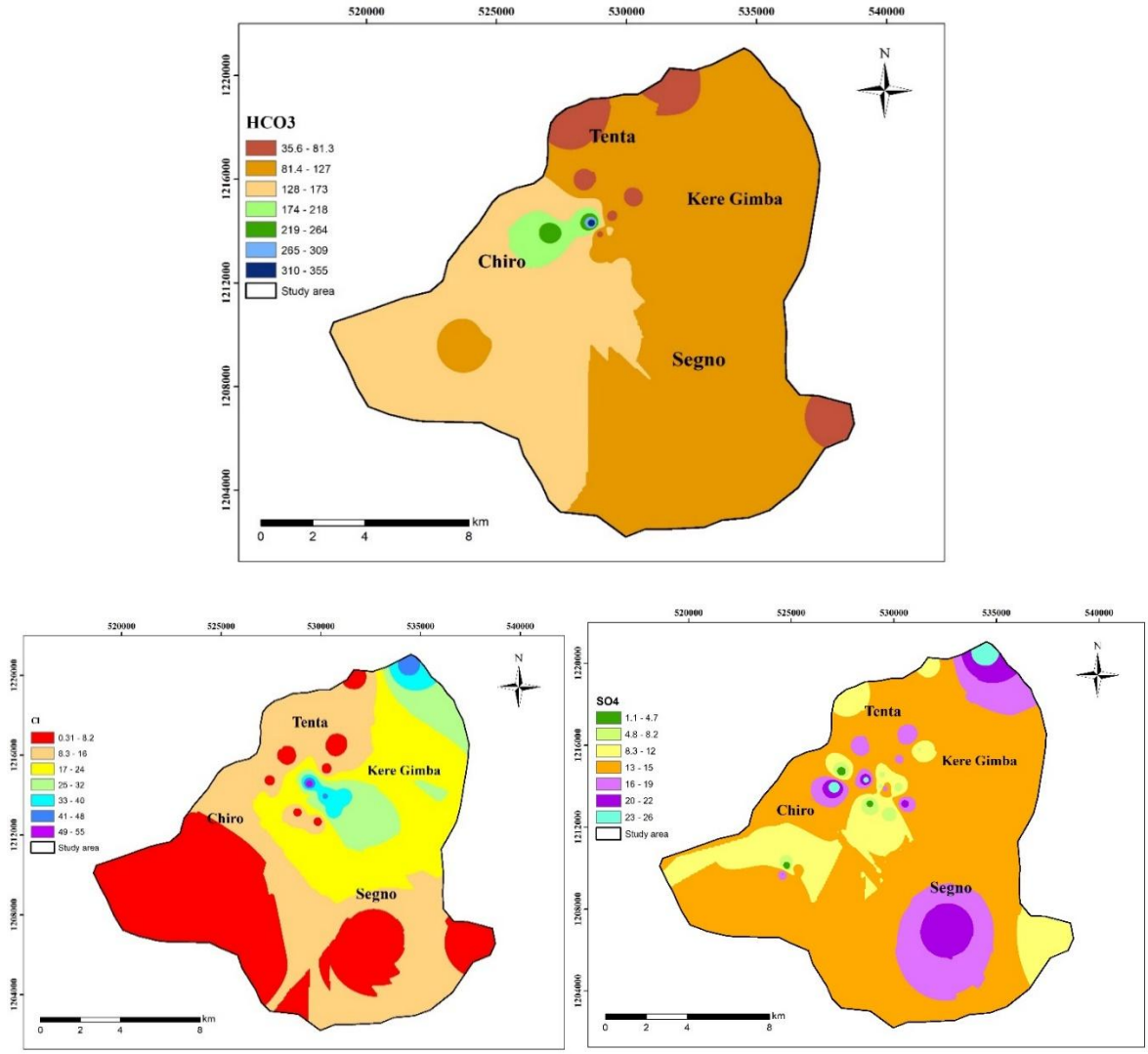

Fig. 8: The spatial distribution map of a) HCO3, b) Cl, and c) SO4 in the Upper Beshilo watershed

Groundwater types

The hydrochemical data, analyzed using AquaChem 10 software, reveal six major water types in the study area: Ca-Na/Na-Ca-HCO_3, Ca-HCO_3, Ca-Cl-HCO_3, Ca-Na/Na-Ca-HCO_3-Cl, Ca-Na-SO_4-HCO_3, and Ca-HCO_3-SO_4-Cl (Fig 9, Table 2).

Table 2: Water types in the study area

Sample ID	X coordinate (m)	Y coordinate (m)	Station ID	Water Type
1	524788	1210093	SP1	Ca-Na-HCO3
10	527814	1218094	SP12	Ca-HCO3-SO4-Cl
11	531739	1219936	SP13	Ca-HCO3
12	523996	1209743	HDW1	Ca-Na-HCO3
13	525232	1209993	HDW2	Ca-HCO3
14	528983	1213895	HDW3	Ca-Na-SO4-HCO3
15	531159	1213989	HDW5	Ca-Na-HCO3-Cl

16	530272	1215292	HDW6	Ca-Na-HCO3
17	528365	1215879	HDW7	Ca-HCO3
18	530771	1216382	HDW8	Ca-Na-HCO3
19	524592	1209718	R1	Ca-HCO3
2	527453	1214700	SP4	Ca-HCO3
20	529541	1213906	R2	Ca-Mg-Na-HCO3-Cl
21	530528	1213149	R3	Na-Ca-HCO3-Cl
22	532545	1207089	R4	Ca-Na-HCO3
23	521218	1221107	R5	Ca-Na-HCO3
24	534349	1220514	R6	Na-Ca-HCO3-Cl
25	528670	1214300	BH1	Na-Ca-HCO3
26	527134	1213994	MR1	Ca-Na-HCO3
3	528846	1213164	SP5	Ca-HCO3
4	529397	1213973	SP6	Ca-Na-HCO3
5	529860	1212696	SP7	Ca-HCO3
6	530210	1213940	SP8	Ca-Na-HCO3-Cl
7	529421	1214551	SP9	Ca-Cl-HCO3
8	531256	1215797	SP10	Ca-HCO3
9	537958	1206898	SP11	Ca-HCO3

Dominant hydrochemical facies (69.23%) include Ca-Na-HCO_3, Ca-HCO_3, and Na-HCO_3, indicative of early to intermediate groundwater evolution. These facies reflect a transition from young, recharge-dominated water to moderately altered groundwater, supported by low to intermediate total dissolved solids (TDS) values, suggesting limited water-rock interaction and characterizing the area as a recharge zone.

The presence of calcium (Ca^{2+}) ions is attributed to the dissolution of calcium-bearing minerals, such as anorthite ($CaAl_2Si_2O_8$), commonly found in the region's volcanic rocks. Bicarbonate (HCO_3^-) dominance further indicates silicate mineral weathering, consistent with early-stage groundwater geochemical evolution in volcanic terrains. However, anthropogenic influences are evident, with elevated chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-) concentrations in some samples, linked to municipal waste disposal and agricultural fertilizer use. Contamination is particularly pronounced in the Ginba Graben and downstream areas toward the Beshilo River, where shallow aquifers are vulnerable due to proximity to pollution sources and hydrological openness.

Nitrate presence, a marker of agricultural runoff and waste seepage, raises environmental and health concerns, including eutrophication and methemoglobinemia risks. These findings underscore the need for sustainable land-use and waste management practices, such as establishing buffer zones around recharge areas, optimizing fertilizer use, improving waste disposal systems, and implementing regular groundwater quality monitoring.

This study highlights the interplay between natural geochemical processes and anthropogenic impacts on groundwater quality, emphasizing the importance of balancing resource use with conservation to ensure regional water sustainability.

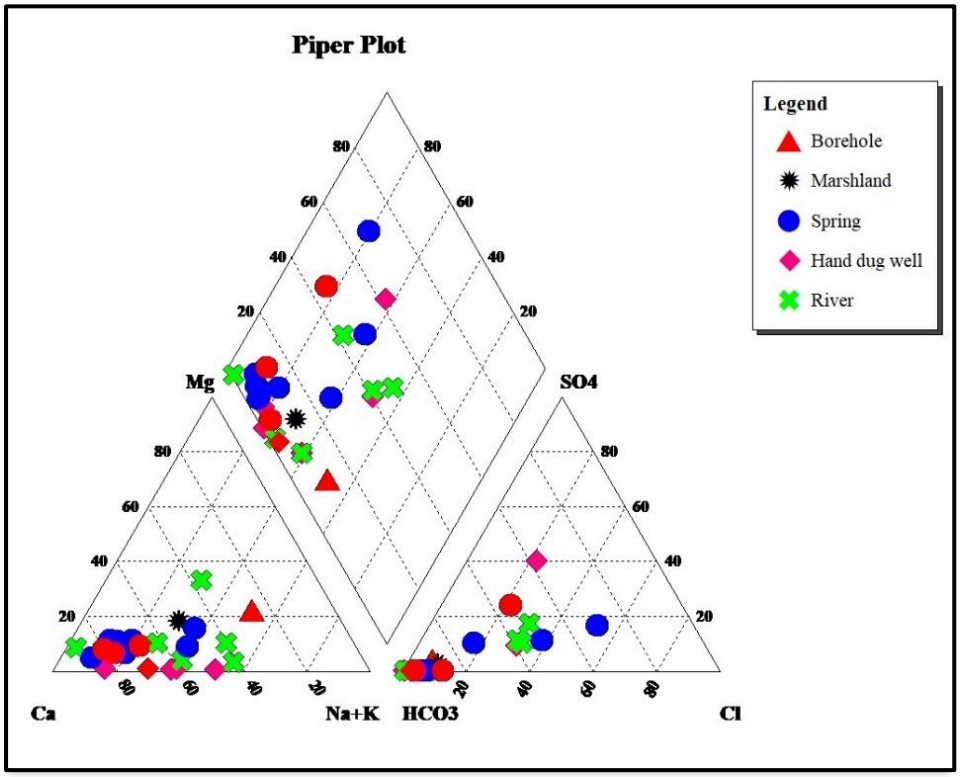

Fig. 9: Piper plot of all water samples of the study area

Evolution of major ions and their possible governing factors

The Gibbs diagram (Fig 10) is a fundamental tool in hydrogeochemistry for classifying water samples and identifying the primary processes controlling water chemistry. It plots Total Dissolved Solids (TDS), representing dissolved inorganic concentrations and water salinity, on a logarithmic scale, against the Na/(Na+Ca) ratio on a linear scale, reflecting the balance between sodium and calcium ions. The diagram is divided into three zones: evaporation dominance, rock dominance, and precipitation dominance. The evaporation dominance zone, characterized by high TDS and variable Na/(Na+Ca) ratios, indicates salt concentration through evaporation. The rock dominance zone, with intermediate TDS values, reflects influences from rock weathering and mineral dissolution. The precipitation dominance zone, marked by low TDS, represents waters primarily shaped by precipitation with minimal geological interaction.

Water samples, depicted as blue data points, predominantly cluster in the low TDS range (20–300 mg/L) with Na/(Na+Ca) ratios between 0.1 and 0.4, suggesting a combination of precipitation and early rock-water interaction. One sample in the rock dominance zone (Na/(Na+Ca) ≈0.7, TDS ~700 mg/L) indicates prolonged subsurface residence and significant geological interaction. A few downstream samples, including those from the Beshilo River, fall within the evaporation dominance zone (TDS ~1000 mg/L), highlighting salt concentration due to evaporation.

Hydrogeologically, the Gibbs diagram reveals that most samples originate from precipitation, with limited salinity concerns and some rock-water interaction. Samples in the rock dominance zone suggest extended groundwater residence times and interactions with calcium-rich rocks, while evaporation-influenced samples indicate localized salinity issues or high evaporation rates. These patterns imply a high-altitude recharge zone, with groundwater chemistry evolving through flow paths, residence times, and mixing processes.

The Cl/(Cl+HCO_3) vs. TDS plot further elucidates these processes. Chloride (Cl^-) increases primarily through evaporation, while bicarbonate (HCO_3^-) is influenced by both evaporation and carbonate weathering. Together, these plots distinguish between evaporative concentration and rock weathering as dominant processes. The increasing Na/(Na+Ca) ratio with TDS suggests progressive chemical evolution driven by silicate weathering, carbonate dissolution, and cation exchange. Evaporation and mixing processes further contribute to higher TDS and varied ionic ratios, offering a comprehensive understanding of water sources, flow systems, and geochemical evolution.

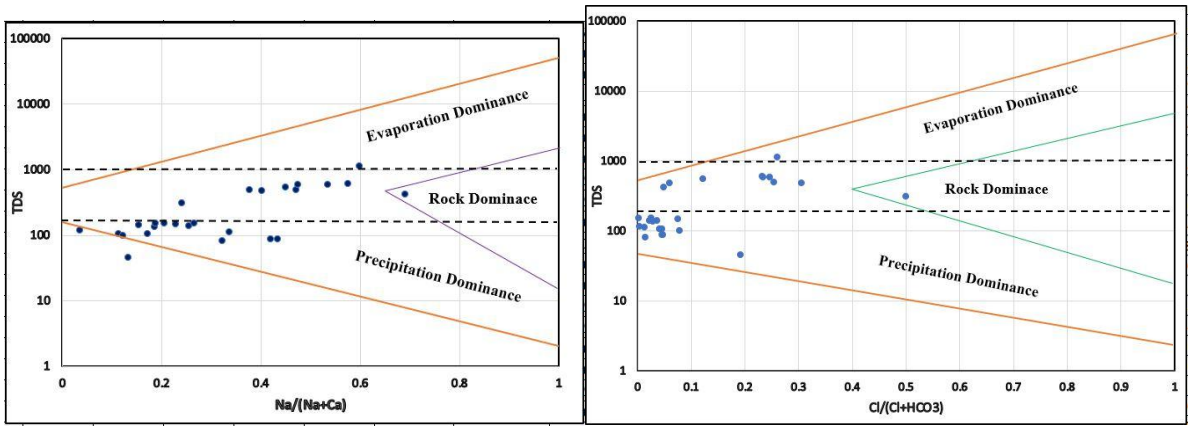

Fig. 10: Gibbs diagrams (1970) to reveal water chemistry controlling mechanisms; cations: a) TDS vs Na/ (Na + Ca) and anions: b) TDS vs Cl/ (Cl + HCO3).

Groundwater recharge-discharge condition and its flow direction

The hydrogeological and hydrogeochemical characteristics of the study area play a pivotal role in governing groundwater recharge, discharge, and flow patterns. Recharge primarily occurs in the elevated highlands of the southern and southwestern mountainous regions (Fig 11), which serve as critical sources for replenishing groundwater systems, including deep and shallow boreholes, springs, and hand-dug wells. The groundwater in these recharge zones is predominantly of Ca-HCO_3 and Ca-Mg-HCO_3 types, indicating fresh water derived directly from precipitation. The presence of bicarbonate ions suggests limited water-rock interaction, consistent with relatively short subsurface residence times. These high-altitude recharge zones are essential for sustaining groundwater resources in the region.

In contrast, discharge zones are concentrated in low-lying areas, such as Gimba town and downstream regions extending to the Beshilo River. These zones are characterized by springs and high-discharge boreholes, reflecting longer groundwater residence times and enhanced water-rock interactions. The groundwater here typically exhibits Na-Ca/Ca-Na-HCO_3-Cl-SO_4 water types, indicative of mixed influences from geological processes and anthropogenic activities. Elevated chloride and sulfate concentrations suggest contributions from evaporative processes or human-induced contamination, such as municipal waste and agricultural runoff, particularly in areas like Ginba town and MAU. These anthropogenic inputs pose risks to water quality, complicating the hydrogeochemical dynamics of the discharge zones.

Groundwater discharge occurs primarily through seepage and spring flow, underscoring the importance of these lowland areas in groundwater outflow and surface water interactions. Springs, in particular, serve as vital water sources for local communities while also reflecting the culmination of subsurface processes, including prolonged water-rock interaction, ion exchange, and potential mixing of water sources.

The groundwater flow direction aligns with the topographic gradient, moving northward from the recharge zones in the southern and southwestern highlands to the discharge zones near the Beshilo

River. This flow pattern is driven by gravitational gradients, with steeper slopes in the highlands facilitating rapid recharge and flatter terrains in the lowlands promoting discharge.

The interplay between recharge, flow, and discharge processes highlights the complexity of the area's hydrogeological system. Recharge zones contribute fresh, low-mineralized water, while discharge zones exhibit geochemical evolution due to extended subsurface residence and interactions with geological formations. Anthropogenic activities further influence this evolution, necessitating careful water resource management to ensure sustainability and prevent contamination. The distinct hydrogeochemical signatures of recharge and discharge zones underscore the importance of integrating local geology, land use, and climatic conditions into effective aquifer management strategies.

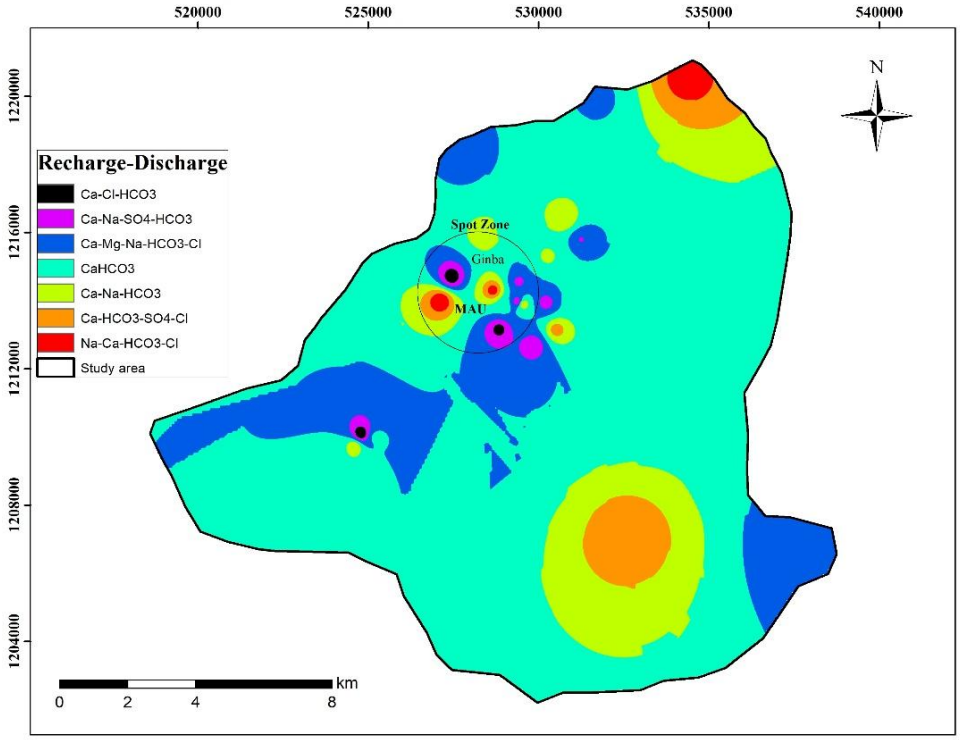

Fig. 11: Recharge – discharge of the Upper Beshilo watershed

Environmental Stable Isotopes Analysis

Over 24 years (1990–2014), monthly rainfall data from the IAEA station in Addis Ababa delineated a local meteoric line (LMWL) with a formulation: $\delta D = 7.2\ \delta^{18}O + 11.9$. The weighted mean summer precipitation had $\delta^{18}O$ and δD compositions of -1.56 and +1.48, respectively, while spring precipitations registered +0.47 and +17.36, respectively (Kebede and Travi, 2012).

Fig 12 presents a delta-deuterium (δ^2H or δD) versus delta-oxygen-18 ($\delta^{18}O$) plot, a fundamental tool for assessing the isotopic composition of water. These stable isotopes provide essential information on water origin, movement, and historical dynamics within the hydrological cycle. The plot effectively illustrates isotopic variations and their correlation with environmental and climatic factors.

The vertical axis represents δ^2D, indicating the relative abundance of deuterium (^2H), while the horizontal axis denotes $\delta^{18}O$, reflecting oxygen-18 (^{18}O) levels. More negative values on both axes suggest isotopically lighter water, typically associated with precipitation formed in colder conditions, higher altitudes, or latitudes. This two-dimensional framework facilitates the interpretation of isotopic trends in groundwater and surface water.

Key reference lines include the Local Meteoric Water Line (LMWL), which reflects the regional

precipitation isotopic signature, and the Global Meteoric Water Line (GMWL), serving as a benchmark for global precipitation. The colored symbols represent water samples from different sources such as springs, rivers, boreholes, hand-dug wells, and marsh areas, each exhibiting a distinct isotopic signature.

The proximity of most samples to the LMWL and GMWL indicates that precipitation is the dominant recharge source for both groundwater and surface water systems. Borehole samples with highly negative δ^2D and $\delta^{18}O$ values suggest recharge in colder climates or higher elevations, pointing to older groundwater formed under past climatic conditions. Conversely, shallow boreholes and hand-dug wells show isotopic signatures resembling recent precipitation, indicating young, actively recharged water.

A cluster of samples within a dotted rectangular box signifies mixing trends, suggesting interactions between groundwater and surface water from different sources. Some points align along a shallower slope labeled "Evaporation," indicating isotopic enrichment due to evaporation, a phenomenon commonly observed in exposed surface waters like rivers.

The spatial distribution of isotopic signatures highlights diverse recharge conditions. Deep boreholes with depleted isotopic values suggest recharge from historical climatic conditions, while shallow sources show recent precipitation influence. Springs and rivers display isotopic shifts linked to evaporation, reflecting exposure to atmospheric conditions.

Overall, the isotope analysis underscores precipitation as the primary recharge source, with groundwater exhibiting distinct isotopic variations shaped by climatic, geographical, and hydrological factors. The presence of mixing and evaporation further illustrates the complexity of groundwater evolution and interaction within the study area.

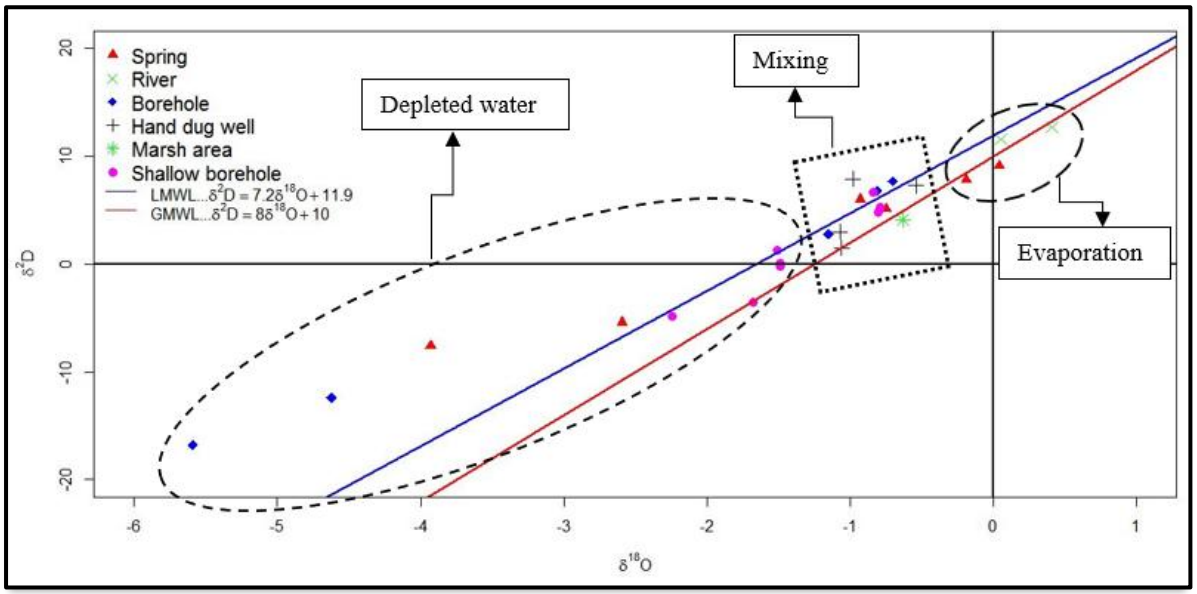

Fig. 12: Distribution of stable isotopes of water in the Upper Beshilo watershed

Conclusion

This study of the Upper Beshilo watershed highlights the intricate relationship between natural geochemical processes and anthropogenic activities affecting groundwater resources. Hydrogeochemical analyses revealed diverse water types, primarily Ca-Na-HCO_3 and Ca-HCO_3, reflecting an early to intermediate evolutionary stage driven by silicate mineral weathering in volcanic terrains. Most groundwater samples met acceptable drinking water standards, with pH levels ranging from 6.8 to 8.0. However, variations in total dissolved solids (TDS) and electrical conductivity (EC) indicated a transition from fresh recharge zones to more saline downstream areas. Spatial differentiation

was evident: recharge zones in the southern and southwestern highlands contained fresh, low-TDS water, while discharge zones in low-lying areas exhibited higher mineralization and potential contamination.

Isotopic analysis provided critical insights into groundwater origins and recharge mechanisms. Precipitation was identified as the primary recharge source, with deep boreholes showing isotopic signatures of older, depleted waters likely recharged under colder climatic conditions, contrasting with shallower sources reflecting recent recharge. The data also indicated mixing of groundwater from different origins and confirmed evaporation impacts on surface water bodies, such as rivers and marshes. Groundwater flow generally followed topographic gradients, moving northward from highland recharge zones to lowland areas near the Beshilo River, with local variations influenced by hydrogeological and geochemical factors.

In conclusion, the Upper Beshilo watershed exhibits a hydrogeological system where fresh, recharge-dominated groundwater in highland areas transitions to more mineralized and potentially contaminated water in lowland and downstream regions. While current groundwater quality is largely acceptable, anthropogenic influences underscore the need for proactive management strategies. These include establishing buffer zones around recharge areas, promoting sustainable agricultural practices, and improving waste disposal systems to ensure long-term groundwater sustainability. This study emphasizes the importance of an integrated water resource management approach that balances natural hydrogeochemical processes with human impacts to secure clean and safe water availability.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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