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Assessment of Groundwater Hydrochemistry Using Multivariate Statistical Analysis Techniques and Aquachem (Piper Trilinear) the Case Study of Wabishable Basin, Ethiopia

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Abstract

To evaluate the spatial the characterization of the groundwater distribution of the Wabishable basin in Ethiopia using Multivariate statistical Analysis (cluster analysis and R-mode factor analysis) and Aquchem modeling. In this study use 13 physico-chemical parameters were selected Data sets from tested 107 wells samples which include: PH, calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate (SO_4), bicarbonate (HCO_3), nitrate (NO_3), iron (Fe) TDS (total dissolved solid), electrical conductivity (EC). Based on Cluster analysis 107 sampling wells divided into two clusters grouped, such as fresh water (group1), and brackish water (group 2) based on the similarity of water quality characteristics. Factor analysis helped in identifying the factors or sources responsible for water quality variations. The varifactors obtained from factor analysis indicate that the parameters responsible for water quality variations are mainly related to water-rock interaction, agricultural activities and discharge recharge area. Further, SAR (0.28>SAR< 26.47), percent sodium (2.67 > %Na < 55.62). The overall water quality of the basin is good WQI (35 >WQI < 100) values recommended suitability for drinking water is (Good, 85%), for irrigation is (, Excellent, 95%), for Livestock (Good, 92%)

Keywords: Cluster Analysis, Q And R-Factor Analysis, Groundwater Quality, Wabishable Basin, Aquchem Software, Hydrochemistry Map, Ground Water Discharge and Recharge Area, Gis Map, Ethiopia.

1. Introduction

Groundwater is influenced by the geology, topography, tectonics and climate of the country. The variability of these factors in Ethiopia affects the quantity and quality of groundwater in different parts of the river basin. Therefore, the knowledge of hydrochemistry is essential to determine the origin of chemical composition of groundwater [1]. The hydrology and geochemistry of waters have been further discussed in the classic works of Domenico and Schwartz [2]. It is possible to understand the change in quality due to rock-water interaction groundwater recharge, movement and storage [3].

Water quality is defined by the characteristics of the area where water is supplied to the ground as precipitation, the geology of the place where water has passed, the underground structure, and so on. Water quality modified in the movement of water through hydrological cycle depend on bedrock, topography, geology, soils, climate, repeated leaching ground react with soil, rock and organic debris (repeated), dissolving still more chemicals naturally aside from any pollution generated by human activities [4]. Poor quality of water adversely affects the plant growth and human health [5, 6]. The multivariate statistical techniques are the appropriate tool for a meaningful data reduction and interpretation of multi-constituent chemical and physical measurements [7]. The multivariate statistical techniques such as cluster analysis (CA) and factor analysis (FA) have widely been used as unbiased methods in analysis of water quality data for produced meaningful conclusions [8, 9]. The multivariate analysis is widely used to characterized and evaluate groundwater quality and it is useful for evidencing spatial variation caused by natural and anthropogenic processes [8, 10]. The Wabishable Basin is situated in the east of Ethiopia in Somali region (and partly in Oromia Region, add it) and extends from 36° 45' of latitude north to 3° 40'-5° 45' of longitude east (Figure 1).

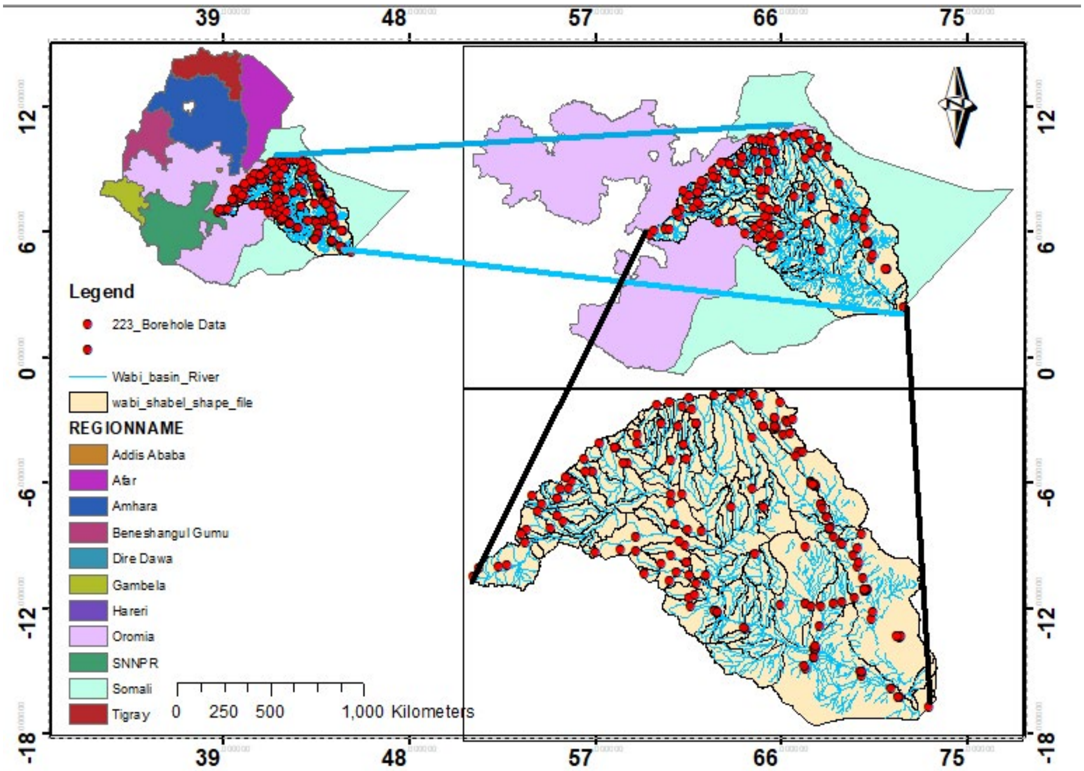

Figure 1: Map Showing the Water Sampling Locations of the Study Area.

The location of Basin is found mainly in Somali & Oromia regional states of Ethiopia extending its out let to Somalia country. The climate of the Wabishable basin contain humid climate and semi-arid in Ethiopia. The mean minimum and maximum temperatures are 11.8 and 30 °C, respectively.

1.1 Objective

The objective of the present study is to analyze the 13 physico-chemical parameters in groundwater samples from the Wabishable Basin with a view to evaluate the spatial variation. The large dataset obtained was subjected to the CA and FA multivariate techniques to evaluate information about the similarities and dissimilarities present among the different sampling sites, to identify water quality variables for spatial dissimilarity, and to ascertain the influence of the pollution sources on the water quality parameters.

2. Materials and Methods

2.1 Geology Of The Study Area

The geological map of Ethiopia (scale 1:2,000,000), first compiled by Kazmin and then revised by Tefera et al, according to Kazmin and Tefera et.al the geological units in Ethiopia fall into one of the following three major categories; the Precambrian Basement, Late Paleozoic to Early Tertiary sediments, and Cenozoic volcanic and associated sedimentary rocks [11]. South-eastern part of Ethiopia is mainly underlain by Mesozoic and Tertiary sedimentary rock successions with sporadic occurrences of Tertiary volcanic rocks. Based on the geological map of Ethiopia.

The mean annual rainfall of the Basin is about 700 mm [12]. Figure-2 show Geological Rocks and unconsolidated deposits in the area represent twelve geologic formations type: among these, 4-geologic formation types are dominant & cover more than 83 .53 % (1) Jurassic (51.61%; (2) Lower Cretaceous (16.37%); (3) Cretaceous (10%) ;) (4) Tertiary extrusiv and itrusiv (5.6%) (Ethiopia Map survey data 2015). Other 8 geology type formation is cover around 16.47%

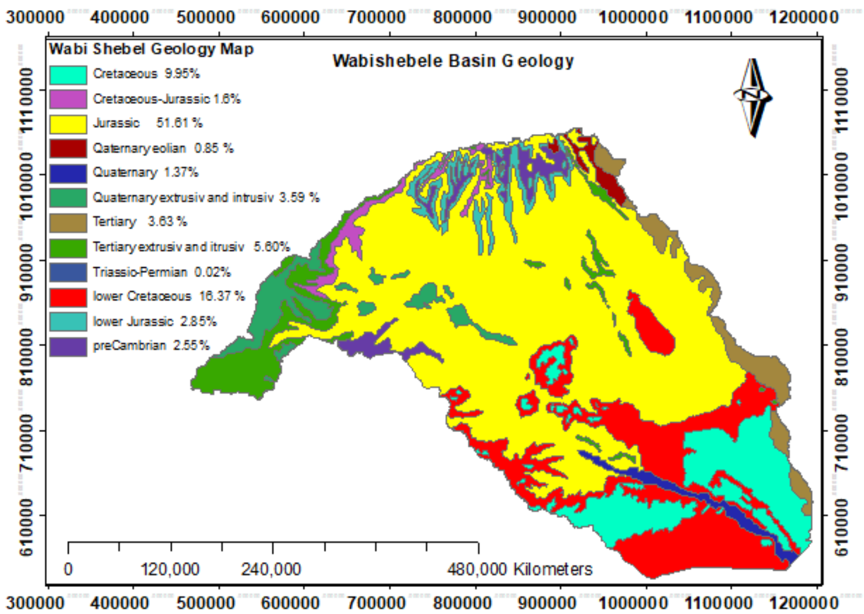

Figure-2: show Ethiopia geology Map (source: Ethiopia map server 2012)

2.2 Land Cover

Land cover deals with the biological and physical cover of the Earth's surface such as vegetation or manmade features. The major types of land cover in the study area include bushed shrub grassland, dense shrubland, exposed sandy soil surfaces, exposed sandy soil surfaces with scattered scrub and grass, open grassland, open shrubland and salt flats (see Fig. 3).

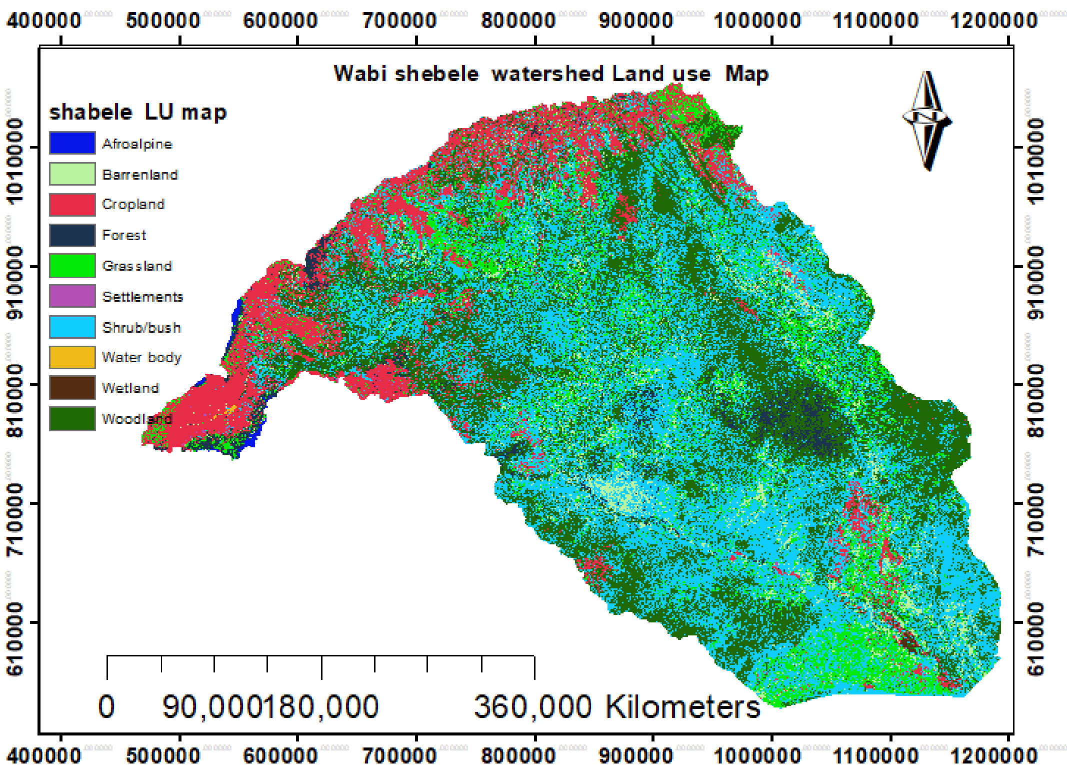

Figure 3: Land cover map of Wabishable basin (source: Ethiopia map server 2015)

2.3 Soil

Soil type distribution, extent, and characteristics in the study area depend on variations in geology, topographic setting and slope gradient, climatic conditions, population density, land use and land cover and agricultural practices. According to soil map of Ethiopia soil survey data prepared there are 13 types of soil in the study area. The soil classification is based on the main soil classification scheme (see Fig 4)

As to the formation soils of the study area is developed mainly from Calcareous materials (it is the Mesozoic rock, mainly from limestone) partially weathered from per alkaline volcanic parent (most part of the area is covered by Mesozoic rock, how can this rock will be the main source) rocks and colluvial and fluvial materials derived from these rocks. Most rocks and land surfaces are therefore relatively young quaternary in age and well developed. According to the Ethiopia map surver data of soil survey report 13 soil groupings were identified in the sub basin. Among this major soil is Calcisol (35.5%), GypSisol (22.7%), Vertisol (12.6%), Leptosol (8.3%), Cambisol (6.7%), Luvisol (5.7%), cover about 90 % of the entire sub- basin and the remaining 10 % Constitute miscellaneous Lands.

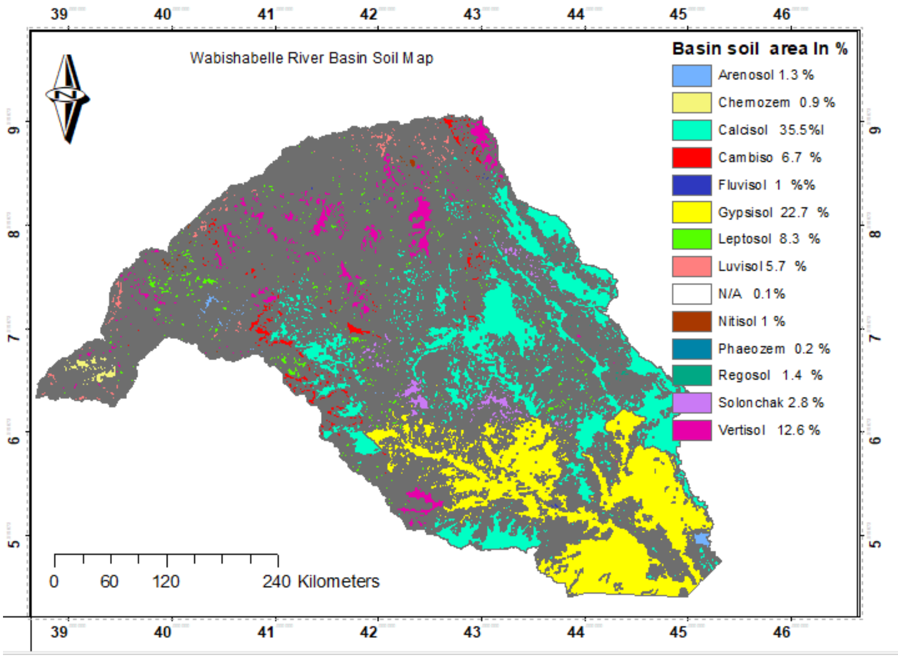

Figure 4: Soil map of the Wabishable Basin (source: Ethiopia map server 2015)

2.4 Groundwater Recharge and Discharge Areas

Groundwater Recharge Area :- The main source of groundwater is precipitation. Groundwater recharge is influenced by topographic, precipitation, land cover (chiefly vegetation cover), prevailing temperature and rock types are the main factors for groundwater recharge. The groundwater recharge in the Shebelle River result in the basin is from 3.5 mm to 3.9 mm/year using the tank model method, which is about 50 % compared to the result of the Base Flow Index (BFI) using the data from the same year [13]. The annual depth of runoff at the Goode Gauge River station is 26 mm/year, which indicates that this area has comparatively abundant water resources with fairly constant runoff, as Wabi Shebelle is a perennial river. A recharge assessment was performed by WWDST based on rainfall infiltration (recharge from rainfall) according to the rainfall infiltration factor (RIF) [14]. The criteria used are shown in Table 1. The recharge area of outcrops of lithological units was considered only if the slope of terrain is less than 20 %.

Lithostratigraphical unit	Rainfall infiltration factor (%)
Alluvium	6
Basement Rocks	5
Basaltic rocks	6
Sandstone and siltstone	5
Limestone	6
Gypsum beds	3
Shale/siltstone	2

Table. 1 Rainfall infiltration factor for the Wabishable Basin by WWDST (2003)

Based on the above data, the surface runoff was estimated to be 1 mm (0.5 % of rainfall) and recharge to aquifers is 10 mm (5.0 % of rainfall).

Ground Water Discharge Area: - Natural groundwater discharge occurs in topographic lowlands. The drilled boreholes and dug wells occur in the lowlands, as do other discharge points. When water moves out of the saturated ground to the surface through springs or seepages, it is referred to as groundwater discharge. Groundwater often discharges into wetlands (local depressions), streams and rivers banks. Discharge of groundwater as springs, seepage zones and baseflow of rivers does not occur in the study area. However, the main groundwater discharge in the study area was found in the Wabi Shabel lowlands

2.5 Groundwater Recharge and Discharge Zone Identification

Groundwater is discharged from springs in highland areas mainly around Aris and Bale highlands, western and eastern Harare plateaus are the margin that forms the north and northwestern water-shed divide of the basin. It is bounded to north by the Awash River basin and the Rift valley lake basin, to the east by Geale River basin (Ethio-Somali political boundary), to the west by Ogden dry basin and in the southern to Ethio-Somali political boundary; and is originated in low land areas. Discharge in nature from groundwater system is appear in the form of water flow into: - Rivers, wetlands and springs and evaporation from upper parts of capillary fringes where groundwater is close to the surface. This situation is likely suited in the low lands of the catchment area where groundwater level is close to the surface. Figure 5 shows groundwater recharge and discharge areas of the catchment.

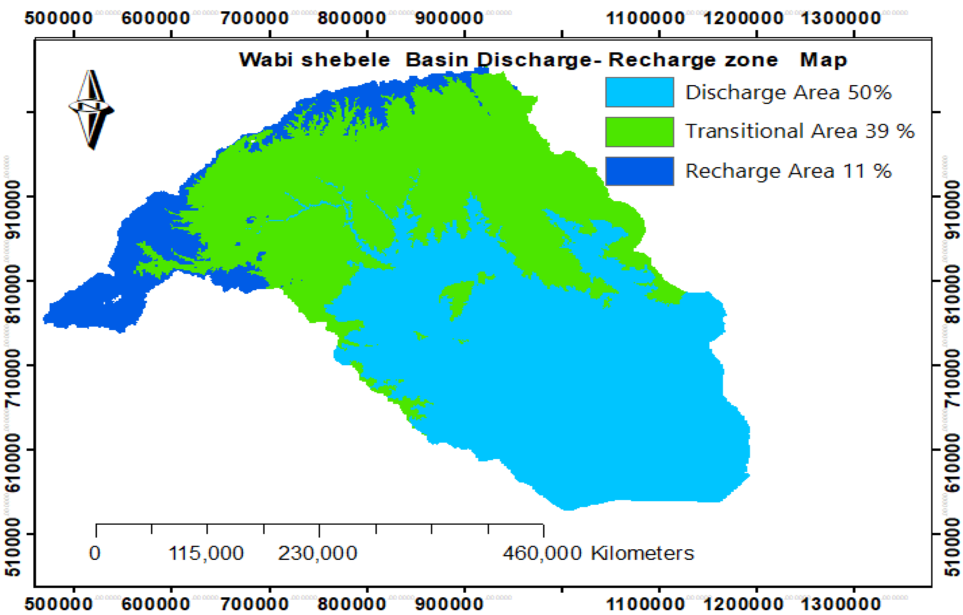

Figure 5: Show the Discharge, Recharge and Transzonal zone

The wabi Shabel basin elevation ranges from 184 to 4250 meters above mean sea level amsl. The discharge zone contributes about 50% of the basin area between (184 to 924 m elevations), transzonal zone about 39% of the basin area has elevation of 924 to 1843 m, recharge zone on top of maintain contributed 11 % of the basin area is between (1843 to 4250 m elevations).

Therefore, with regard to the slopes of the catchment are reversed it. The upper part is the recharge area, so have low ground water. The eastern & south eastern part is low land area, discharge area, surface run off is low (relatively flat), and so has good groundwater).

2.6 Chemical Data in Wabishabele River Basin

The wabishebel Groundwater samples (N = 107) from the Wabishabele basin were collected in April 2014 Figure 6 shows the distribution of sampled wells. The samples were analyzed using the following methods outlined in the world health organization guidelines for Drinking Water quality [15]. Secondary Water samples data were collected from Somali water bureau, design and supervision enterprise and water technology institute strengthening project office. The analyzed water samples were identified by anions and cations. Analyzed anions include sulfate, chloride, bicarbonate and nitrate; cations include calcium, magnesium, sodium and potassium. The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors were generally within 10%. After water quality analysis using Aquachem software the water type in the river basin is mapped as below, figure 7. However, the result shows the upper catchment is characterized by high Ca, Mg, HCO3 and Lower Part of the catchment is high TDS, EC, Na, Cl, SO4 see in below figure 6

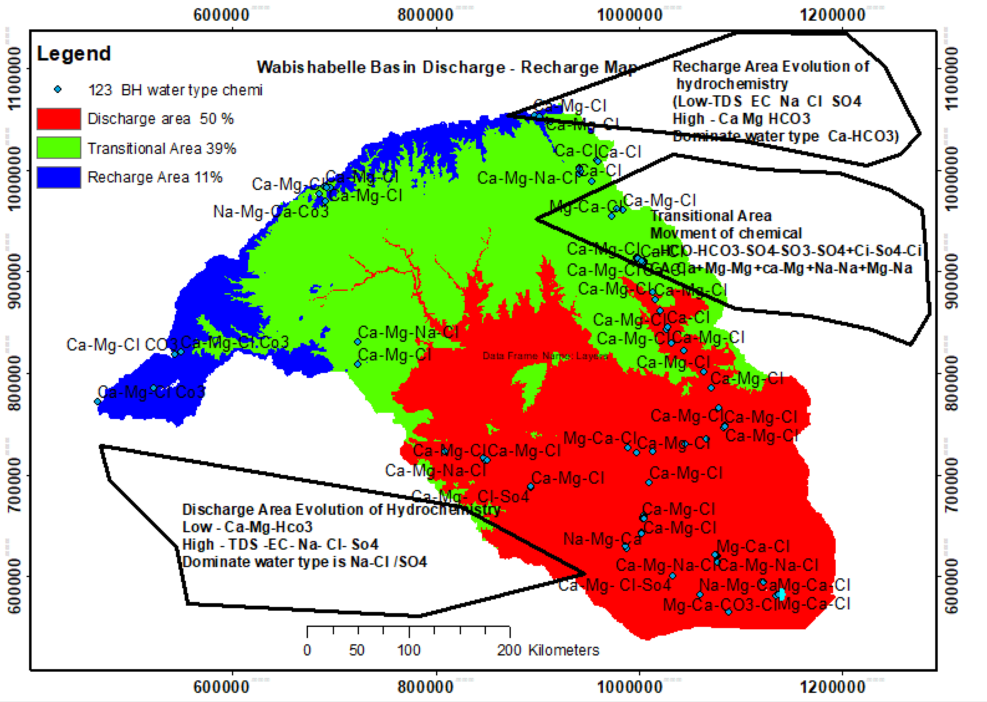

Figure 6: Show the Discharge Recharge Chemical Compostion Through the Cacthement

2.7 Multivariate Statistical Methods

Groundwater quality datasets were subjected to four multivariate techniques: cluster analysis (CA) and factor analysis (FA). CA and FA were applied to experimental data, standardized through z-scale transformation to avoid misclassifications arising from the different orders of magnitude of both numerical values and variance of the parameters analyzed [16, 17]. All mathematical and statistical computations were made using Microsoft Office Excel 2003-97 and cluster analysis version 3 with java tree 1.4

Cluster Analysis:- Cluster analysis is the name given to an assortment of techniques designed to perform classification by assigning observations to groups so each is more-or-less homogeneous and distinct from other groups [18]. As an exploratory technique with graphic output, cluster analysis does not require many of the assumptions that other statistical methods do, except that the data is heterogeneous. It provides an easily understood graphic display (dendrogram), and is a method used frequently in the geological sciences to help classify or group samples/variables of a data set. It helps to identify natural groupings for samples (Q-mode), and in turn, reduces the size of the samples/variables into smaller numbers of groups.

Factor Analysis:- Factor analysis is a multivariate statistical technique, which derives a subset of uncorrelated variables called factors that explain the variance observed in the original dataset [19, 20]. Factor analysis is used to uncover the latent structure of a set of variables. In technical terms, common factor analysis represents the common variance of variables, excluding unique variance, and is thus a correlation focused approach seeking to reproduce the intercorrelation among the variables. On the other hand, components (from PCA) reflect both common and unique variance of the variables and may be seen as a variance focused approach that reproduces both the total variable variance with all components as well as the correlations. PCA is far more commonly used than principal factor analysis (PFA). However, it is common to use ‘‘factors’’ interchangeably with ‘‘components’’ in multivariate analysis. Factor analysis can be performed on any kind of scientific data to establish a pattern of variation among variables or reduce large data sets into factors for easy handling and interpretation. The total number of factors generated from a typical factor analysis indicates the total number of possible sources of variation in the data. Factors are ranked in order of merit. The first factor or component has the highest eigenvector sum and represents the most important source of variation in the data. The last factor is the least important process contributing to the chemical variation. Factor loadings on the factor loadings tables are interpreted as correlation coefficients between the variables and the factors.

3. Results and Discussion

3.1 General Water Chemistry

The pH value of groundwater in the study area ranges from 6.6 to 8.2, (with) an average of 7.5 indicating a slightly alkaline type of groundwater. The electrical conductivity (EC) of groundwater samples ranges from 480 to 7583 µS/cm with a mean value of 1,620 µS/cm (Table 1). The large variation in EC is mainly attributed to geochemical processes prevailing in this region Check it again, 2,000. Most of the groundwater samples exceed the permissible limit.

The mean value of calcium (Ca) and magnesium (Mg) in the ground waters were 561.6 and 140.9 mg/L, respectively. Over all the statistical analysis Wabishabele river basin of calcium and magnesium the concentrations varied from 115 to 1422 mg/L and 22.7 to 353.5

Parameter	pH	Ca	Mg	Na	K	Cl	HCO3	CO3	SO4	NO3	TDS	Fe	EC
Min	6.6	115	22.7	6.0	0.0	10	30	30	80.3	0.0	267.0	0.0	480
Max	8.2	1422	253	590	74	1095	1098	732	242.0	8.0	7859	2	7583
Mean	7.5	562	141	123	12	562	182	139	163.3	1.1	1833	0	1620
SD	0.3	373	56	95	11	373	147	110	31.5	1.6	1360	0	1110
CV	0.04	1	0	1	1	1	1	1	0.19	1.50	1	1	1
Skew	-0.3	1	0	2	3	1	3	2	-0.25	2.90	1	3	2
Kurtoses	-0.1	0	-1	4	10	0	15	8	0.27	8.67	3	12	9

Parameter	pH	Ca	Mg	Na	K	Cl	HCO3	CO3	SO4	NO3	TDS	Fe	EC
Min	6.6	115.2	22.7	6.0	0.0	10.0	30.0	30.0	80.3	0.0	267.0	0.0	0.5
Max	8.2	1422.4	253.5	589.8	73.6	1095.0	1098.2	732.2	242.0	8.0	7859.0	1.6	7.6
Mean	7.5	561.6	140.9	122.8	11.8	561.6	181.6	138.9	163.3	1.1	1832.9	0.2	1.6
SD	0.3	373.1	56.0	95.0	10.8	373.1	146.6	109.5	31.5	1.6	1360.0	0.2	1.1
CV	0.04	0.66	0.40	0.77	0.92	0.66	0.81	0.79	0.19	1.50	0.74	1.15	0.69
Skew	-0.30	0.83	-0.07	1.57	2.55	0.83	3.09	2.37	-0.25	2.90	1.43	2.94	2.37
Kurtoses	-0.13	-0.42	-0.66	4.22	10.21	-0.42	14.93	8.08	0.27	8.67	3.28	12.03	8.92

N.B:- *Min: Minimum; Max: Maximum; SD: Standard Deviation. CV: Covariance. All values are in mg/L except pH and EC (µSiemens/cm).mg/L, respectively.*

Table.2 statistical summary of hydro-chemical parameters

The upper limit of calcium concentration was specified as 1422 mg/L and for magnesium 253 mg/L. It is observed that most samples exceed the desirable limit of calcium and check it again, 150. Na is related with the function of nervous system, membrane system and excretory system. According to WHO guideline the maximum admissible limit is 200 mg/l. Excess sodium causes high pressure, nervous disorder, etc [21]. In the study area, the Na concentration in groundwater ranges from 6 to 590 mg/L with a mean of 141 mg/L. High concentration of Na and Mg in the groundwater are attributed to cation exchange among minerals. The concentration of K in the study area varies from 0.0 to 74 mg/L with a mean of 12 mg/L. Bicarbonate is the dominant anions followed by Cl, SO4 and NO3. The bicarbonate ion ranges from 300 to 1098 mg/L with a mean value of 182 mg/L. Groundwater samples with low values of bicarbonate ion characterize the discharge zones of the study area. Sulfate concentration varied from 80.3 to 242 mg/L with a mean value of 163.3 mg/L. Most of the groundwater samples in study area are within the desirable limit (250 mg/L) prescribed by WHO. The chloride concentration varies between 10 to 1095 mg/L with a mean value of 562. The nitrate concentration of groundwater samples ranges from 0 to 0.8 mg/L with an average value of 1.1 mg/L. The desirable limit of nitrate for drinking water is specified as 50 mg/L; nearly 100% of the samples from the study area below standard (50mg/l). The concentration of Fe in all of the groundwater samples is 93 % below than the standard of 0.3 mg/L (Table 1).

3.2 Q-Mode Cluster Analysis

Q-mode cluster analysis was performed on the water chemistry data to group the samples in terms of water quality [22]. The Ward's method was applied and Euclidean distance was chosen as a measure of similarity. The output of the Q-mode cluster analysis is given as a dendrogram in 7. There are two major groups as shown in 7 and (3). Group 1 includes: 98, 90, 92, 13, 17, 18, 19, where the EC ranged from 267 to 984 µS/cm which is the characteristic of Fresh water. This water is basically bicarbonate and chloride dominated, however; Mg and Na are also present. The samples of this water type are found in the south-western part of the study area. The electrical conductivity is correlated with the Na, Cl and NO3 (Table 3). Group 2 includes the samples: 1, 2, 3, 4, 5, 6, 8, 9, 10, 13, 14, 15, and 20 where the EC ranged from 1,032 to 7858 µS/cm, which is the characteristics of brackish water. This water is bicarbonate and sodium dominated.

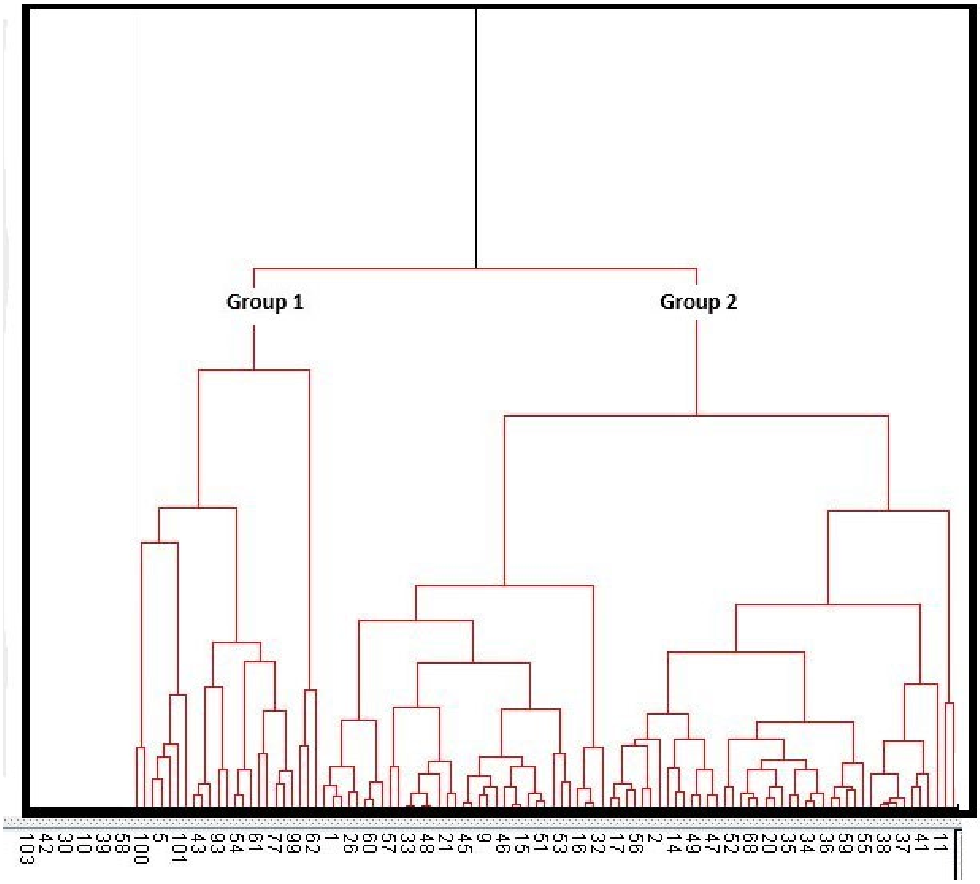

Figure 7: Dendrogram of Q-mode cluster analysis.

But also contains low concentrations of nitrate and potassium. This water type is found in the part of the study area (Figure 1). The electrical conductivity is strong correlation with the sodium and nitrate (Table 3)

Parameter	Group 1					Group 2				
	Min	Max	Mean	SD	CV	Min	Max	Mean	SD	CV
Temp	27.00	33.00	29.50	1.75	0.06	11.00	33.00	29.07	3.22	0.11
pH	6.62	8.00	7.52	0.33	0.04	6.87	8.23	7.52	0.30	0.04
Ca	116.80	1363.20	406.34	285.61	0.70	115.20	1422.40	647.15	389.50	0.60
Mg	22.70	245.87	117.93	61.91	0.52	41.75	253.49	153.59	48.43	0.32
Na	6.00	589.76	114.57	113.47	0.99	7.56	330.14	127.36	83.69	0.66
K	2.39	73.55	9.61	14.16	1.47	0.01	36.58	12.95	8.26	0.64
CO3	30.00	488.10	137.37	120.61	0.88	30.00	732.15	139.78	103.83	0.74
HCO3	30.00	305.06	134.69	72.74	0.54	30.00	1098.23	207.47	169.49	0.82
Cl	115.20	892.80	380.61	240.27	0.63	115.20	1422.40	647.15	389.50	0.60
SO4	80.30	220.80	158.87	31.21	0.20	97.50	242.00	165.69	31.56	0.19
TDS	267.00	984.00	583.34	169.10	0.29	1032.00	7858.96	2521.71	1184.83	0.47
EC	609.00	7583.00	1996.58	1445.98	724.23	480.00	4049.00	1412.25	812.62	575.41
NO3	0.02	1.81	0.53	0.52	1.00	0.04	7.99	1.34	1.96	1.46

Table 3. Parameter values of the two principal water groups.

3.3 R-Mode Factor Analysis

The kind of factor analysis used for this study was the Principal Components Analysis with the application of varimax factor rotation [18, 23& 24]. The first three factors were chosen since they account for 68.15 % (Table 4) of the total variance, and based on the "scree test" where values for all these factors are greater than one [18].

The first factor explains 27.9 % of the total variance, and shows that most of the covariance in the system's properties may be accounted for by the variances of Mg, Cl, and SO4. This factor proves that hydro chemical reactions relating precipitation/dissolution processes with dolomite, halite and gypsum minerals are important in water quality evolution in this area.

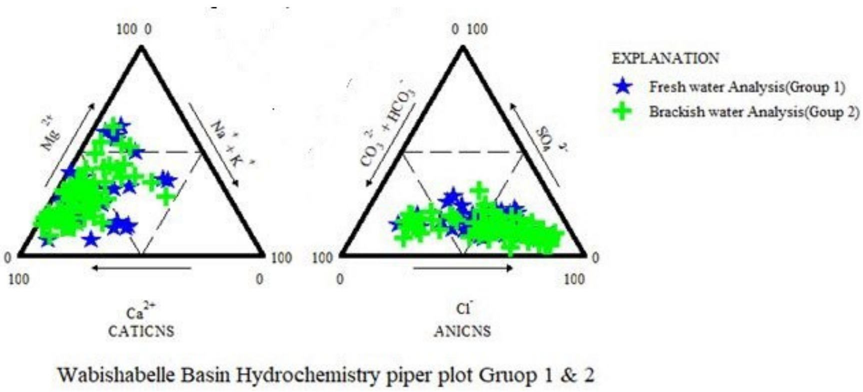

Figure 8: Ca-Mg-(Knack) and HCO3-SO4-Cl-NO3 trilinear diagrams for groundwater samples.

Group 1												
	Temp	**pH**	**Fe**	**NO3**	**EC**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**HCO3**	**CO3**	**SO4**
Temp	1												
pH	0.7186	1											
Fe	0.7048	0.96	1										
NO3	0.8129	0.92	0.966	1									
EC	0.4353	0.86	0.834	0.8	1								
Ca	0.6641	0.94	0.975	0.91	0.763	1							
Mg	0.6369	0.98	0.959	0.9	0.875	0.957	1						
Na	0.6884	0.93	0.956	0.89	0.709	0.987	0.937	1					
K	0.3736	0.81	0.762	0.74	0.948	0.673	0.811	0.6293	1				
Cl	0.7729	0.94	0.967	0.96	0.763	0.961	0.936	0.9343	0.694	1			
HCO3	0.8716	0.74	0.755	0.84	0.563	0.701	0.703	0.7052	0.499	0.788	1		
CO3	0.9137	0.87	0.85	0.92	0.659	0.814	0.817	0.7989	0.6	0.927	0.845	1	
SO4	0.632	0.98	0.918	0.87	0.907	0.896	0.973	0.8805	0.847	0.892	0.673	0.8117	1
Group 2													
	T	**pH**	**Fe**	**NO3**	**EC**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**HCO3**	**CO3**	**SO4**
T	1												
pH	0.9956	1											
Fe	0.9943	1	1										
NO3	0.9909	0.99	0.987	1									
EC	0.9916	0.99	0.985	1	1								
Ca	0.9901	0.99	0.994	0.99	0.987	1							
Mg	0.9693	0.97	0.982	0.96	0.959	0.99	1						
Na	0.9843	0.99	0.986	0.99	0.984	0.996	0.984	1					
K	0.9843	0.99	0.986	0.98	0.982	0.996	0.983	0.9958	1				
Cl	0.987	0.98	0.985	0.99	0.985	0.986	0.969	0.9798	0.979	1			
HCO3	0.98	0.97	0.978	0.99	0.991	0.984	0.961	0.9848	0.981	0.992	1		
CO3	0.9899	0.99	0.987	0.99	0.988	0.994	0.977	0.9892	0.993	0.991	0.99	1	
SO4	0.9802	0.98	0.984	0.99	0.982	0.99	0.979	0.9882	0.986	0.987	0.991	0.993	1

Table 4: Correlation matrix for groundwater samples in the study area

The second factor, which accounts for 14.09% of the total variance, is characterized by high-negative loadings of the K and positive loadings of Na and NO3 and represents the contribution of agricultural activities and ion exchange.

The third factor (12.28%) has the highest positive score on Ca, HCO3 and Fe, derived from the weathering of carbonate minerals from the underlying geology.

Parameter	F1	F2	F3
Ca	-0.72	0.69	0.58
Mg	0.04	-0.64	0.57
Na	-0.12	-0.25	0.62
K	0.43	0.09	0.27
Cl	-0.15	0.35	0.27
HCO3	0.14	0.19	0.02
CO3	0.00	-0.07	0.01
SO4	0.00	0.02	0.00
NO3 (ppm)	0	0	0
Fe(ppm)	0	0	0
EWEIGHT	2.279159	1.150594	1.065001
T variance	27.9	11.5	10.6
Comulative	27.9	39.4	50

Table 5: The Results Show Eigen Value Cumulative Percent of Sample Data

6.2 Ground water Classification

The groundwater chemistry classification based on the hydrochemical map and hydro chemical types with Meq% representation of the main cations and anions by implementing the following scheme:

- **Basic hydrochemical type,** where the content of the main cations and anions is higher than 50 Meq%. This chemical type is expressed on the hydrochemical map by a full colour.
- **Transitional hydrochemical type,** where the content of the main cations and anions ranges between 35 and 50 Meq%, or exceeds 50 % for one ion only. A dominant ion combination is expressed on the hydrogeological map by the relevant coloured stripes (screen) in a horizontal position. The second ion within the type is expressed by an index (e.g.).
- **Mixed hydro chemical type,** where the content of cations and anions is not above 50 Meq% and only one ion has a concentration over 35 Meq%. This type is expressed on the hydrogeological map by the relevant coloured stripes (screen) in a vertical position. The hydrochemistry of the study area is variable; however, the dominant hydrochemical type of groundwater in aquifers developed in **sedimentary rocks (mainly sandstone and limestone)** of the study area is chloride in the western part and sulphate in the eastern part of the study area. In the western part of the study area, a transitional Ca-Cl type is developed in Jurassic. In the eastern part of the area, a transitional Mg-SO4 type is found in Lower Cretaceous and Cretaceous.
- **The transitional Ca-SO4 and transitional (Ca-Mg-Na)-HCO3 types** occur within the eastern part of study area. Relatively high TDS, Sulphate and Chloride groundwater types indicate that the hydrogeological regime is influenced by the lithological composition of the rocks of the aquifers and the aridity of the area, which receives only a relatively low amount of rainfall. To facilitate visualization of the classification of water types, the percentage of major cations and anions of the analyzed samples is plotted on the Piper diagram as shown in Fig. 9. In the Piper graph, samples from the all-river watershed area the data are presented together because the groundwater recharge mechanisms are similar and the aquifers consist of the same types of rocks (sandstone and limestone).

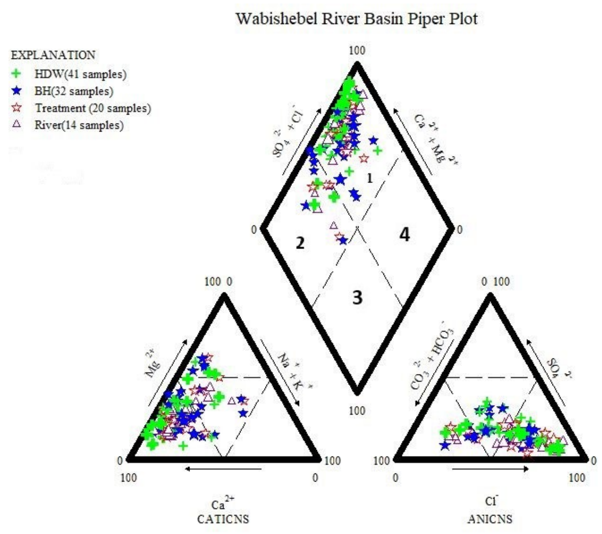

Figure 9: Piper plot of Ground water hydrochemistry in Wabishable River Basin

• **Sulphate (SO4) type:** The sulphate type of groundwater results from dissolution of gypsum material in sedimentary rocks and cation exchange reactions. The source of calcium in the sulphate type is the dissolution of limestone and gypsum, whereas the source of magnesium is dolomite.

• **Chloride (Cl) type:** The source of chloride in groundwater may be livestock waste, particularly in shallow dug wells, and direct evaporation that tends to concentrate the chloride into the soil zone. Some chloride may also be derived from salt layers in evaporite sediments, including limestone, sandstone and shale. The precipitated chloride in the soil can be reached by erosion during the rainy season, when the rain percolates and mixes with the groundwater.

N/S	Hydrochemistry	Type	N0 of cases
1	Ca-CL	Trans	8
2	Ca-Mg-CI	mixed	47
3	Ca-Mg-CI-Co3		3
4	Ca-Mg-CI-HCO3	mixed	4
5	Ca-Mg-CI-SO4		2
6	Ca-Mg-Co3-CI		3
7	Ca-Mg-CO3-HCO3-SO4-Cl	mixed	1
8	Ca-Mg-HCO3-Cl	mixed	1
9	Ca-Mg-Na-Cl		10
10	Ca-Mg-Na-CO3-Cl		1
11	Ca-Mg-Na-CO3-HCO3-Cl	mixed	1
12	Ca-Na-Cl	Trans	5
13	Ca-Na-Cl-HCO3	mixed	1
14	Ca-Na-Mg-Cl		2
15	Ca-Na-Mg-Cl-HCO3	mixed	1
16	Mg-Ca-Cl	Trans	2
17	Mg-Ca-Cl-HCO3	mixed	2
18	Mg-Ca-CO3		1
19	Mg-Ca-CO3-Cl		4
20	Mg-Ca-Na-Cl		1
21	Mg-Ca-Na-CO3		1
22	Mg-Ca-Na-CO3-Cl		1
23	Mg-Ca-Na-HCO3-CO3	mixed	1
24	Na-Mg-Ca-CO3	mixed	4

Table 6: Show the Result of Hydrochemistry Type and Classification

The high variability of groundwater chemistry and low number of samples made compilation of the hydrochemical map difficult and it was necessary to consider the groundwater chemistry of adjacent map sheets.

3.5 Electrical Conductivity and Total Dissolved Solids

The relationship between total dissolved solids (TDS) and electrical conductivity (EC) closely fits a straight-line regression (R = 0.5). The conversion factor between TDS and EC revealed a value for A of 0.96 in the formula: KA = S (where K is the specific conductivity in µS/cm and S is TDS in mg/l (see Fig. 6.2).

Both values are important in assessing groundwater quality. EC is a parameter easily measured in the field and can provide initial information about the character of the groundwater, including pollution in industrial and agricultural areas.

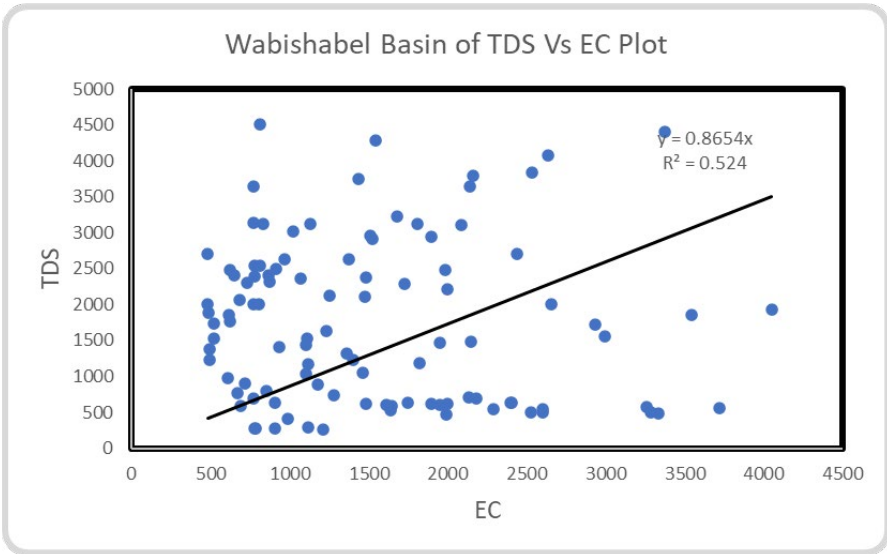

Figure 10: show the EC Scatter Plot

3.6 Majors and Minor Components of Ground Water

The **main cations** in the study area are calcium, magnesium and sodium. The concentration of **calcium** varies significantly from 83 to 353 mg/l with the most frequent concentrations being about 150 mg/l for all of the analyzed water samples. Similar variability is found for **magnesium**, with concentrations varying between 21 and 280 mg/l and the most frequent concentration being less than 100 mg. /l.

High concentrations of magnesium (170 and 280 mg/l) were found in the eastern part of the study area where magnesium is the dominant ion in the groundwater type. The concentration of **sodium** varies from 154 to 265 mg/l with the most frequent concentration being about 200 mg/l. The **main anions** in the study area are **bicarbonate**, chloride and sulfate. The concentrations of bicarbonate are high in almost all of the samples, ranging from 241 to 393 mg/l with the most frequent concentration being about 340 mg/l. The concentration of **chloride** is variable, starting from 189 and reaching up to 498 mg/l relatively lower concentrations of about 200 mg/l are found in dug wells in the western part of the area and high concentrations of about 400 mg are found in deep wells elsewhere in the study area. This fact shows the greater influence of rock - groundwater interaction on the final groundwater composition than the impact of aridity of the area upon groundwater composition. The chloride ion is highly mobile and can contribute to mixing processes. The concentration of **sulphate** varies significantly from 108 to 1,658 mg/l with the most frequent concentrations being about 150 mg/l in the western part and more than55 mg/l in the eastern part of the study area. The sulphate concentration is related to the content of gypsum material, which can easily dissolute in limestone and some parts of the sandstone sequence. Concentrations of the major ions reflect the interaction of the groundwater with the rock during its circulation in aquifers composed mainly of limestone and sandstone.

The **minor constituents** in the study area are represented by nitrate and fluoride. The maximum prescribed limit of nitrate in municipal water supplies is 50 mg/l. In many countries, water supplies having high levels of **nitrate** have been responsible for blue baby disease in infants (infantile methemoglobinemia) and death. Therefore, particular interest is paid to the content of nitrates in groundwater, because the content of nitrates is not related to the rock composition (type) but reflects pollution of groundwater by human and/or animal waste. The background content of nitrates in groundwater is about 5 to 10 mg/l depending on the relevant land cover. In highly vegetated areas, it can be even higher because of the decomposition of various plants and other organic material. The nitrate content in the study area varies from 0.12 mg/l to 16 mg/l. The low concentrations are found in the groundwater of deep wells showing nitrate pollution particularly by animal waste cannot infiltrate to aquifers with deep groundwater level. The concentration of **fluoride** is relatively low, varying from 0.68 to 5.65 mg/l; however, its concentration exceeds drinking water standards in 40 % of the samples.

3.7 Water Quality

The quality of groundwater in the wabi shebel is generally poor. Groundwater is usually saline even though the salinity varies depending on the type of formation and the amount of recharge. Groundwater of an acceptable quality may be locally developed by deep wells from limestone, sandstone and by shallow dug wells from alluvial sediments and eluvial deposits. The water quality in the basin was assessed from the point of view of drinking, agriculture and industrial use.

3.8 Domestic Use

To assess the suitability of water for drinking purposes, the results of the chemical analyses were compared with the Ethiopian standards for drinking water (see Tab. 6.2) published in the Negarit Gazeta No. 12/1990 and the Guidelines of the Ministry of Water Resources [25].

Property	Range(min-max)	Ethiopia standard			
		Highest desirable level	Maximum Permissible level	Highest desirable level	Maximum Permissible level
pH	6.6 -8.23		6.5 - 8.5		0
Na	6 - 589.76		200		25
Mg	22.7 - 253 .49		50		95
Ca	115.2 - 1422.4		75		0
Free ammonia		0.1	1.5		3
Fe	0.019 - 1.585	0.1	0.3		10
Mn	0.006 - 2.529	0.05	0.5	6	7
CI	10 - 1095	200	250	5	84
S04	80.3 - 242	200	250	12	0
TDS	267 -7858.96	500	1000	24	60
K	0.009 - 73.55		1.5		
Nitrate as NO3	0.019 - 7.988		50		
Total Hardness	120-4800		300		

Table 7: Ground Water Chemistry Compared to Ethiopia Drinking Water Standard

The results show that the quality of water in the study area is relatively good for drinking purposes; however, the concentration of fluoride is higher in 2 out of 6 samples. The concentrations in these samples exceeded the maximum desirable (one sample exceeded the highest permissible level) value of the Ethiopian standards, but since the area has high temperatures, concentrations lower than the standards may cause problems as water consumption is very high in arid areas. In areas of higher fluoride concentrations, defluorination can be adopted to supply safe drinking water. This technique involves the addition of lime and aluminum sulphate or aluminum chloride, which helps in the removal of fluoride by flocculation. This method is quite simple and can be used in villages at a domestic level, as well as for small communities. The Ethiopian standards are exceeded in some of the water points in the case of Ca, Mg, and SO4. These high ion concentrations are a common problem in the Ogaden basin. This is shown by the high contents of total dissolved solids (TDS) in the groundwater on the hydrochemical map. The study area generally has TDS levels lower than 2,000 mg/l, but all of the samples exceed the highest desirable level (500 mg/l) and 4 out of 6 samples exceeded the maximum permissible level (1,500 mg/l) for drinking water.

3.9 Irrigations

Water quality criteria for irrigation water generally take into account characteristics such as crop tolerance to salinity, sodium concentration and phototoxic trace elements. Criteria have been published by a number of countries as well as by the Food and Agriculture Organization of the United Nations (FAO). Quality criteria may also differ considerably from one country to another, due to different annual application rates of irrigation water. Agriculture standards of groundwater quality used for irrigation purposes are determined based on the US salinity criteria (USSC) using EC values, as well as the sodium adsorption ratio (SAR) and total dissolved solids (TDS).

The US salinity criteria are based on electrical conductivity (EC) values. The EC values in the study area range from 1,474 µS/cm to 3,950 µS/cm. The laboratory EC measurements show that groundwater is suitable for irrigation purposes only for plants having moderate salt tolerance (33 %) and is satisfactory for salty tolerant crops on soils of good permeability with special leaching (77 %).

EC(µs/cm)	Class	N0 of sample in the range	Remark
<250	Low salinity(C1)	0	
250-750	Moderate(C2)	17	Good Soil permeability is better for vegetations
750-2250	Medium	67	Salt tolerance plant species is good
2250-4000	high	19	high salt tolerance vegetations on good soil permeability with leaching remedy
> 4000	unsuitable	4	very bad

Table 8: Show the Irrigation Suitability Based on EC

Sodium adsorption ratio (SAR): The sodium adsorption ratio (SAR) is used to study the suitability of groundwater for irrigation purposes. SAR is one of the most commonly used water quality criteria for irrigation purposes as the sodium concentration is important in classifying irrigation water because sodium reacts with soil to reduce its permeability. When sodium rich water is applied to soil, some of the sodium is taken up by the clay. Thus, the clay gives up the calcium and magnesium in exchange. The clay that takes up the sodium becomes sticky and slick when wet and has a low permeability. This reaction alters the physical characteristics of the soil and can even lead to growth retardation. In 1954, the United States Salinity Laboratory proposed that the sodium effect can be calculated by the sodium adsorption ratio (SAR method) from the following formula:

SAR=Na/{√[(Ca+Mg)/2]}

Where the concentration of Na,Ca and Mg ions are expressed in milli equivalent per litre

Water Class	EC	SAR Value	Number of samples In SAR Value range
Excellent	<250	< up to 10	83
Good	250-750	10 ---18	18
Medium	750-2250	18--26	5
Bad	2250-4000	> 26	1
Very Bad	>4000		

Table 9: Sodium Adsorption Ratio

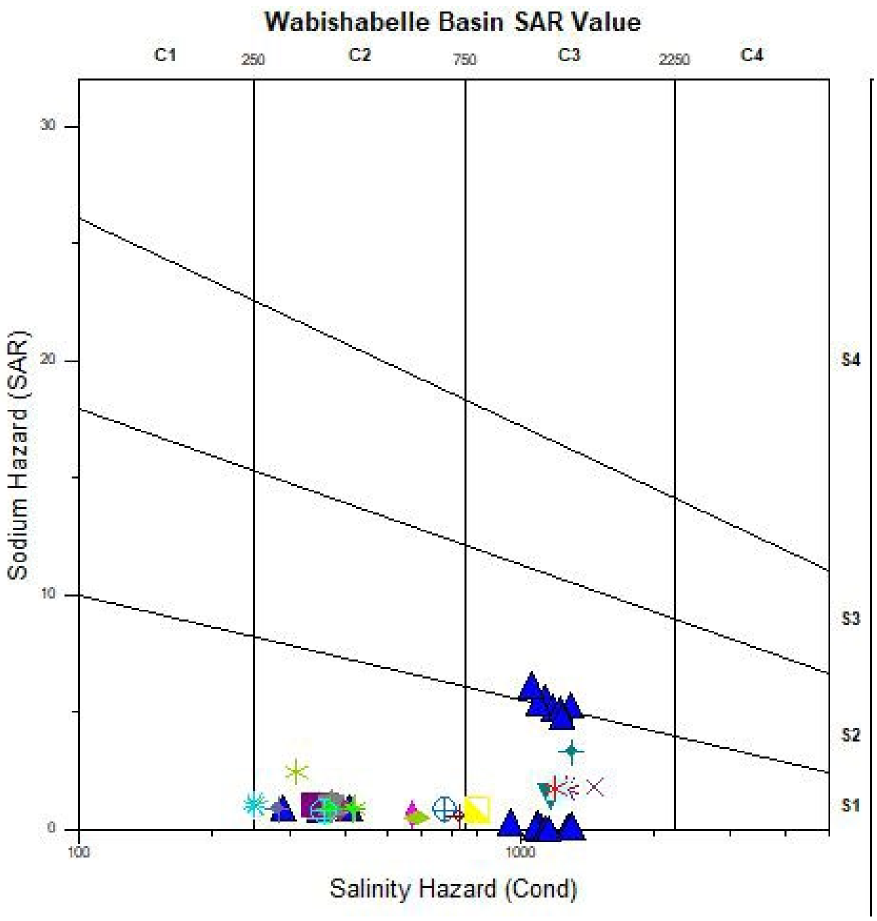

Figure 11: Show the SAR Value Graph

The analysis shows that most of the water samples have SAR values suitable for irrigation. The study area has no restriction for irrigation in the west but has a fair to poor groundwater quality for irrigation in the east.

Total dissolved solids (TDS): For irrigation purposes, the Raghuath criteria is used to evaluate the water samples from the study area [26]. It was found that 50 % of the water samples fall into the suitable category for irrigation.

Water Class	TDS (Mg/l)	N0 of Sample in the range
Excellent	< 1000	39
Suitable	1000 - 1700 If Ca > 25 %(Na+Ca)	16
Unsuitable	1000 - 17000 If Ca< 25 %(Na+Ca)	0
Poor	> 1700	52

Table 11: Show the Result of Industry Use Based on Sample Data

The results of the chemical analysis show that water from the study area is not suitable for use in industry because of the high concentrations of ions. Despite the aridity of the area and the variable sedimentary rocks, including evaporates, there are many water points with moderate quality groundwater that can be used for drinking after treatment as well as for animal husbandry [28-48]. The use of groundwater for agricultural as well as industrial purposes is very limited Wabishable basin Hydrochemistry Map Water type Chemical distribution in the wabishable basin

Industries	Total Solid(mg/L)	Turbidity (mg/L)	Chloride	Hardness as(CaCO3) mg/l	Iron as Fe (mg/l)	Manganese as Mn (mg/l)	Sulfates as S04	PH	Number of samples in Range
Brewing	500- 1500	10	60-100		0.2	0.2		6.5 - 7.0	73
Confectionery	100	0	0	0	0.2	0.2		>70	84
Food general	1500	10		0	0.2	0.2			73
Ice	170-1300	5		0	0.2	0.2			84
Laundering	0	0		50	0.2	0.2		6.0 - 6.5	84
Plastic, clear, uncolored	200	2		0	0.02	0.02			84
Paper and pulp ground wood	300	50	<75	180	1	0.5			73
Kraft pulp	300	25	<75	100	0.2	0.1			84
Soda and sulfite	200	15	<75	100	0.1	0.05			84
High-grade light papers	200	5	<200	50	0.1	0.05			84
Rayon (Viscose) pulp production	100	5	<200	8	0.05	0.03		7.8 - 8.3	73
Carbonate Beverages	<850		<250				<250		73
Dairy	<500	10	<30				<60		73

Figure 12: Piper Plot

Water type Chemical distribution in the wabishable basin

4. Conclusion

In this case study, different multivariate statistical techniques were used to evaluate spatial variations in groundwater quality of the Wabishabele Basin. Three major water types are suggested by the Q-mode cluster analysis: group 1 (35%) belongs to Mg-Na-HCO3-Cl facies and group 2 (65%) belongs to Na-Mg-HCO3-SO4 facies. The three principal factors identified by R-mode. Factor analysis corresponds to three principal processes taking place in the study area: precipitation/dissolution processes of dolomite, halite and gypsum minerals, cation exchange processes occurring in clay layers, and agricultural activities. The results of this study clearly demonstrate the usefulness of multivariate statistical analysis in hadrochemical analysis. Over all the wabi Shebel River upper parts of recharge area more dominate Ca / mg HCO3 Water type with low TDS and EC. The Other Side of Downstream of the catchment more dominating hydrochemistry type is Low Ca, Mg HCO3 / CaCl Water type with High TDS and EC. Over the water quality index, the basin is good.

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