

**IDENTIFICATION OF GROUNDWATER TYPE AND
RECHARGE ESTIMATION THROUGH
HYDROCHEMICAL ANALYSIS: A CASE STUDY IN
AYANALEM WELL FIELD, NORTHERN ETHIOPIA**

GOVINDU VANUM*

GEBRERUFAEL HAILU**

ABSTRACT:

The study focused on groundwater type identification and groundwater recharge estimation through hydro chemical analysis in Aynalem well field Northern Ethiopia. Aynalem wellfield is the main source of water for domestic water supply of Mekele town, capital of Tigray regional state. From the hydro chemical data analysis, there exist at least two classes of water types in Aynalem catchment. Ca-HCO₃ dominated water type at the upper catchment and Ca-SO₄ dominated water type at the lower western extreme of the catchment are present with a clear evolutionary trend between the two types. The groundwater in the area is pumped with little consideration to groundwater recharge and effects of climatic forcing on the recharge. The main recharge mechanism considered was direct recharge from rainfall. Annual recharge of 30-40 mm (4.5-6% of the average annual rainfall) is estimated by applying the Chloride mass balance method.

* Assistant Professor, Geo-Information and Earth Observation Sciences, Mekelle University, Mekelle, Tegrai, Ethiopia.

** Lecturer, Geo-Information and Earth Observation Sciences, Mekelle University, Mekelle, Tegrai, Ethiopia.

INTRODUCTION:

Groundwater recharge is a process of water movement downward through the saturated zone under the force of gravity or in a direction determined by the hydraulic condition (Simmers, 1988). Natural recharge of groundwater could be occurring from precipitation, from rivers and canals and from lakes. As discussed by Simmers et al. (1997), quantifying the current rate of groundwater recharge is a basic prerequisite for efficient groundwater resource management and is practically vital in arid regions where such resources are often the key to economic development.

Groundwater recharge quantification is fraught with problems of varying magnitude and hence substantial uncertainties. It is therefore desirable to always apply and compare a number of independent approaches. Various techniques are available to quantify recharge; however, choosing appropriate techniques is often difficult. According to Scanlon et al. (2002), important considerations in choosing a technique include space or time scales, range, and reliability of recharge estimates based on different techniques. Each of the methods has its own limitations in terms of applicability and reliability. Techniques of recharge estimation vary based on source and process of recharge mechanisms. Simmers et al. (1997) indicate that the procedures to quantify recharge from various sources are direct measurements, water balance methods, tracer techniques and empirical methods. As it was applied for the estimation of groundwater recharge in semi-arid climate India by Sharda et al. (2006), a number of methods were used to estimate the recharge. As part of the study, water table fluctuation and chloride mass balance methods were applied. The water table fluctuation is based on the principle that the rise in groundwater level in any aquifer is proportional to the water reaching the water table. The recharge component contributed to groundwater is expressed as:

$$R_{gw} = S \Delta W T A_w \quad \text{Equation- (1)}$$

Where, S is storativity, $\Delta W T$ is change in water table depth, and A_w is area of the watershed. The chloride mass balance method is based on the assumption of conservation of mass between the input of atmospheric chloride and the chloride flux in the subsurface (Yongxin & Beekman, 2003).

As described by Bear & Verruijt (1987), the basic equation applicable for the estimation of recharge using chloride mass balance method is:

$$R_{gw} = P_{year} \frac{Cl_p}{Cl_{gw}} \quad \text{Equation-(2)}$$

Where, R_{gw} is the annual recharge rate (mm), P_{year} is the average annual rainfall (mm) and Cl_p and Cl_{gw} are the chloride concentrations of the rainfall and groundwater (mg l^{-1}), respectively. The technique regards chloride as an inert element, and compared with other inorganic ions, it is not added or removed by water rock interaction. The element is considered as an inert in the hydrological cycle having its source from the atmosphere. It has the advantage over tracers involving water molecules in a sense that atmospheric inputs are conserved during recharge processes allowing a mass balance approach to be used. Commonly water balance method is applied for recharge estimation in many climatic zones of the world. Estimation of recharge using this method is largely dependent on the precision with which the water balance components were determined. The application of the water balance method in arid and semi-arid regions is more difficult than in humid regions because precipitation is frequently only slightly different from actual evapotranspiration, small errors in these two components cause large errors in recharge estimation. Simmers et al. (1997) identified two different precipitation mechanisms, diffuse and localized recharge. Direct or diffuse recharge results from wide spread infiltration of rain water at the point of impact whereas localized recharge resulted from horizontal flows that occurs into local depression that are not connected to any draining water courses. The same authors discussed the methods available for estimation of groundwater recharge directly from precipitation include inflow, aquifer response and outflow methods. Lysimeter measurements, tracers and soil moisture budget models are considered as inflow methods of recharge estimation. In the aquifer response method of recharge estimation, groundwater level changes are transformed to the amount of water by using the specific yield concept. In the outflow method of recharge estimation groundwater recharge and groundwater discharge are considered equal.

STUDY AREA:

Aynalem sub-basin is located in Tigray regional state (northern part of Ethiopia) at about 5kms south of Mekele town, capital of the regional state. The geographic location of the area is between 39°21' to 39°43' East and 13°24'to13°30'North. Aynalem area is part of the Ethiopian central plateau just to the west of Afar rift valley, located at about 770 km north of Addis Ababa (The capital city of Ethiopia).

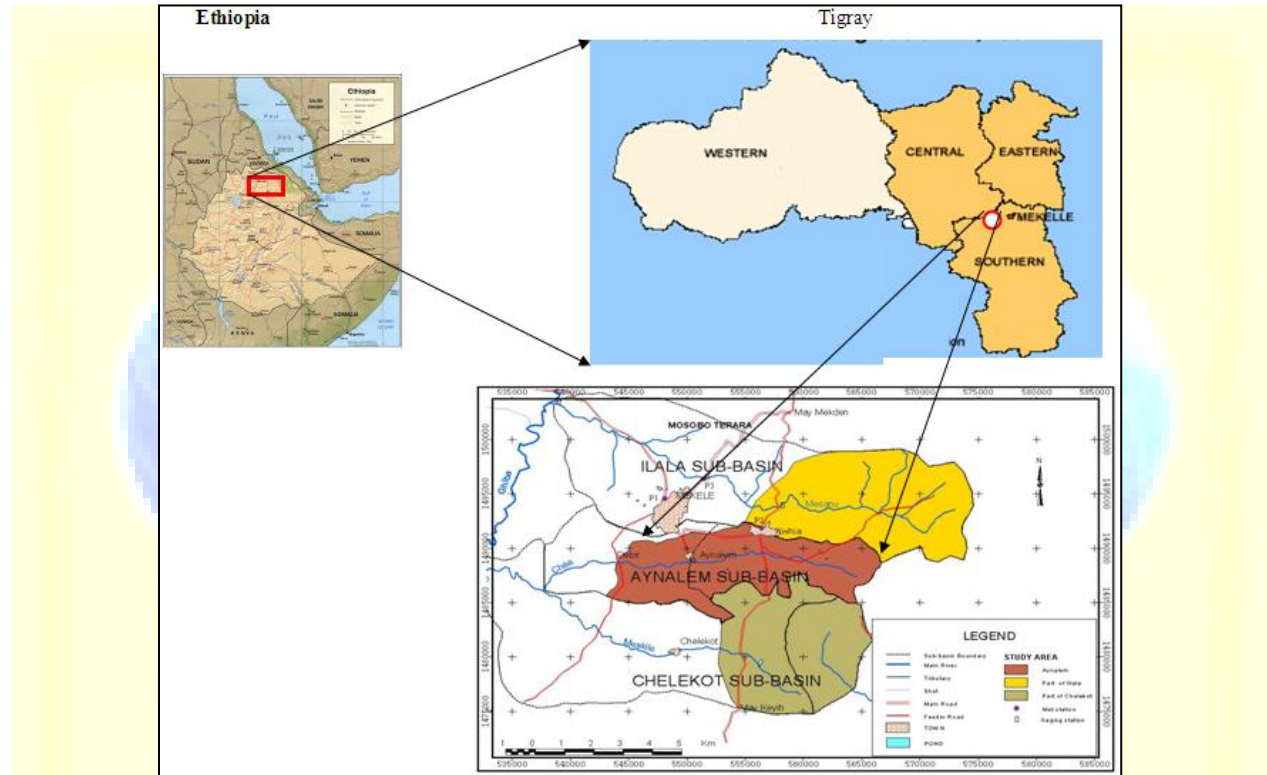


Fig.1: Location map of the study area

Geomorphology and Drainage:

The study area covers about 104 km² with a mean altitude of 2200 m above sea level. The altitude of the catchment varies from 2100 meters above mean sea level at the mouth of the basin to 2540 meters above mean sea level at the extreme east of the catchment boundary (Fig.3). The northern and southern ends of the catchment are bounded by a chain of dolerite ridges mainly oriented N–W and the central part is characterized by relatively flat topography of Mesozoic sedimentary terrain. The Eastern limit of the catchment is physically separated by the dolerite ridge from Afar lowlands.

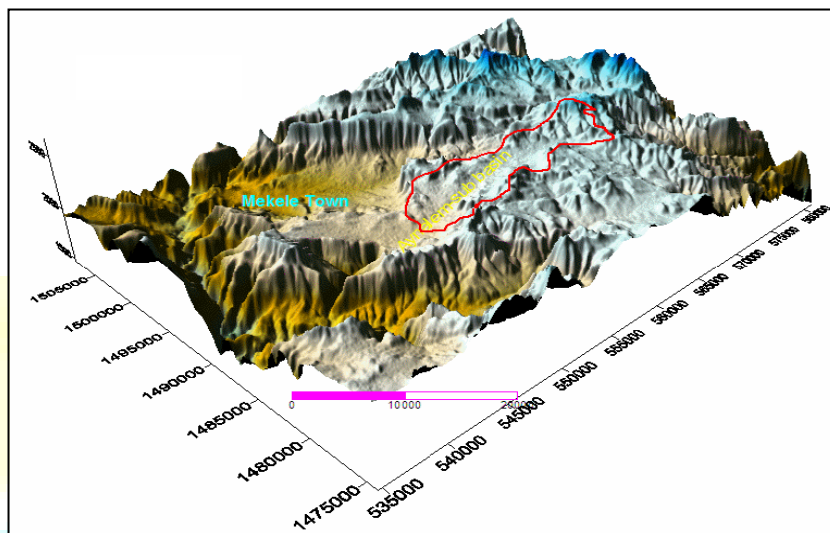


Fig.2: Elevation Model of the Study Area

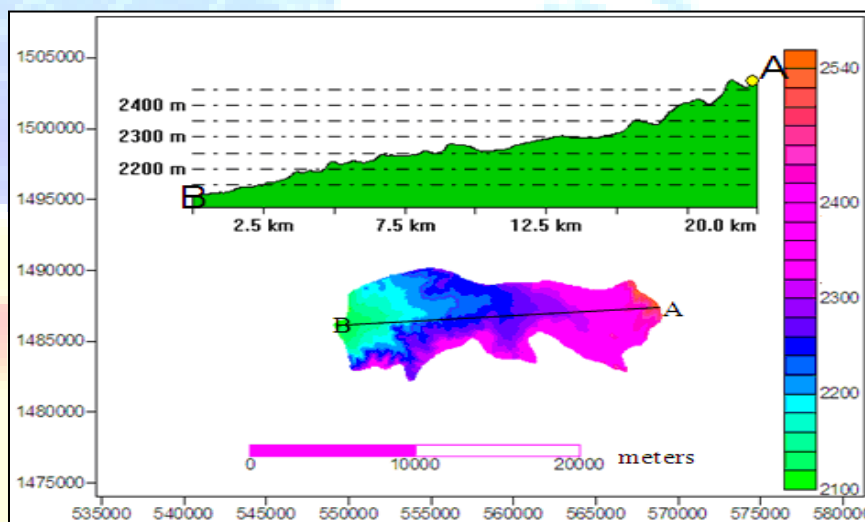


Fig.3: Geomorphologic Features and Elevation Cross-Sections

METHODS AND MATERIALS:

Hydrochemistry:

Hydrochemistry of groundwater aquifer in a region is largely determined by both the natural processes, such as precipitation, wet and dry depositions of atmospheric salts, evapotranspiration, soil/rock–water interactions, and the anthropogenic activities, which can alter these systems by contaminating them or by modifying the hydrological cycle (Singh et al., 2007). Both the natural

processes and the anthropogenic activities vary in time and space. These variations are reflected in groundwater hydrochemistry variations showing spatial and temporal fluctuations in a region. The chemical composition of groundwater is the combined result of the composition of water that enters the groundwater reservoir and the reactions with minerals present in the rock that may modify the water composition (Appelo & Postma, 1992). Dissolved constituents in the water provide clues on its geologic history, its influence on the soil rock masses through which it has a pass, the presence of hidden ore deposits, and its mode of origin within the hydrologic cycle (Freeze & Cherry, 1979). As mentioned by Anderson & Woessner (1992), water chemistry data can be used to infer flow directions, identify sources and amount of recharge and to define local and regional flow systems.

Water Sampling and Analysis:

Representative water samples of boreholes, springs and ponds were collected from Aynalem, Ilala and Chelekot sub-basins for the analysis of major anions and cations.. The location of the water samples are indicated in Fig.4 as Upper Ilala, Lower Ilala, Lower Aynalem, upper Aynalem and Chelekot. Furthermore rain water samples were collected from the area to determine chloride concentration in rainfall for the application of chloride mass balance method of recharge estimation. The groundwater samples were analysed in the Central Laboratory of the Ethiopian Geological Survey. For comparison purpose, control water samples from boreholes that are representative of the lower catchment and the upper catchment were brought to ITC laboratory and the analysis results from both laboratories were compared. The analysis results for most of the groundwater constituents were comparable in both laboratories. But there are also differences in the analysis results mainly for the chloride and nitrate content.

Reliability Check

To evaluate the data quality, the accuracy of the water analysis was checked with the anion-cation balance. The principle of the anion–cation balance is that the sum of cations and sum of anions are equal because the solution must be electrically neutral. In a electrically neutral solution, the sum of the cations should be equal to the sum of anions in meq l⁻¹ (Hounslow, 1995).

$$\text{Electroneutrality} \left(\% \right) = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} * 100 \quad \text{Equation-(3)}$$

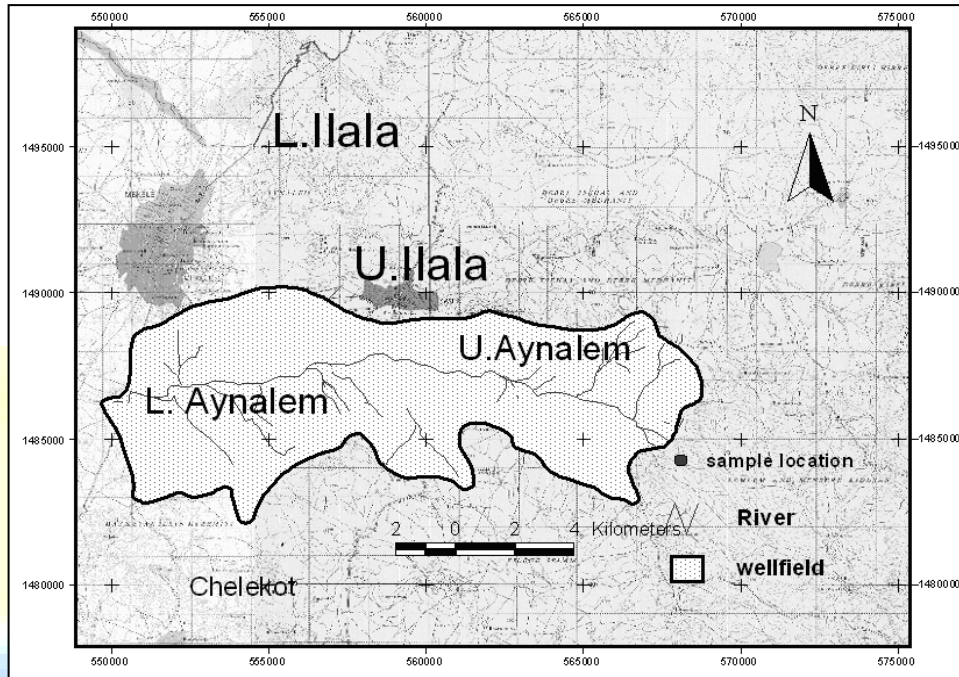


Fig.4. Location Map of Water Sample Points

Based on the electro-neutrality, analysis of water samples with a percent balance error <5% is regarded as acceptable (Fetter, 2001). But in very dilute or saline water, up to 10 % error may be considered as acceptable due to the errors introduced in measuring major ions in dilute groundwater or in the multiple dilution require for analysis of concentrated groundwater. The analysis result of all the samples is within the acceptable range of the reliability check of electro-neutrality. The cations- anions balance results are found to be reliable as the balance does not deviate from the 5% criterion. The analysis results of the water samples indicate that the dominant dissolved cations in the groundwater of the area are Ca^{2+} , Na^{+} , and Mg^{2+} with lower levels of K^{+} . And the major dissolved anions in the groundwater include: SO_4^{2-} , HCO_3^{-} and Cl^{-} . The range and mean of the major inorganic constituents of groundwater samples from Aynalem and nearby catchments are summarised below.

Table.1: Summary Statistics of the Major Groundwater Constituents

Constituent	Minimum	Maximum	Mean
EC (μ S cm-1)	688.0	2540.0	1267.2
TDS (mg l-1)	447.0	2068.0	962.1
Total Hardness	308.7	1486.8	667.2
pH	7.3	7.9	7.5
Ca ²⁺ (mg l-1)	109.2	502.2	244.6

Mg ²⁺ (mg l ⁻¹)	1.9	44.9	12.6
Na ⁺ (mg l ⁻¹)	18.0	81.0	37.0
K ⁺ (mg l ⁻¹)	1.0	4.3	2.3
HCO ₃ ⁻ (mg l ⁻¹)	14.6	351.4	248.0
Cl ⁻ (mg l ⁻¹)	12.5	73.3	24.9
SO ₄ ²⁻ (mg l ⁻¹)	47.5	1100.0	427.7

RESULTS AND DISCUSSION:

The water analysis result of the major anions and cations are plotted in Piper diagrams and Stiff diagrams for quick and tentative conclusion of the water type. According to Hounslow (1995), the position of an analysis that is plotted on a piper diagram can be used to make tentative conclusion as to the origin of the water represented by the analysis. However, the bicarbonate to silica ratio must also be considered when making this deduction. The analysis results are also plotted using Stiff diagrams in which, cations are plotted in meq l⁻¹ on the left of the zero axis and anions are plotted on the right. As discussed in Fetter (2001), Stiff diagrams are useful in making a rapid visual comparison between water from different sources. Selected representative water samples from the three catchments are presented in the plots of Piper and Stiff diagrams (Fig.5 to 8).

Water Type:

The major inorganic constituents of water originate when water in precipitation dissolves atmospheric gasses such as carbon dioxide and reacts with minerals on the surface of the earth (Hounslow, 1995). The major water types identified from the hydrochemistry analysis of the groundwater samples are Ca-SO₄, Ca-HCO₃-SO₄, Ca-SO₄-HCO₃ and Ca-HCO₃. The water type in the basin and its surroundings is not uniform in composition. Lower Aynalem, Chelekot and lower Ilala are dominated by a Ca- SO₄ type of water whereas the upper Aynalem and upper Ilala are dominated by a Ca-HCO₃ and Ca -SO₄- HCO₃ type of water. The chemical ions of the water samples plotted on a piper diagram show that the major cations composition has a limited range of variation, mainly calcium rich. On the other hand, the anions composition has a range of variation from sulphate to bicarbonate. As it can be clearly observed from the stiff pattern, there is variation in groundwater chemistry in the water samples from upper and lower Aynalem, Ilala and Chelekot. It is possible to relate the variation in groundwater chemistry with a change in lithology and groundwater flow direction. From the drilling well logs at the lower Aynalem, there is

evidence for the existence of a gypsum layer which attributes to the Ca-SO₄ dominating water chemistry.

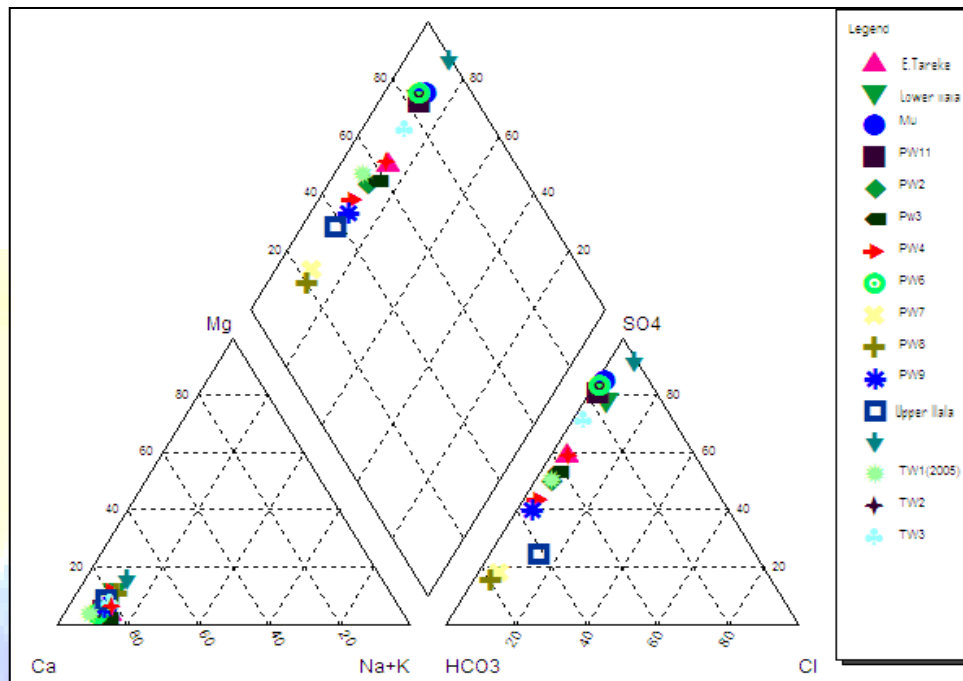


Fig.5: Piper Diagram of Water Samples from Boreholes

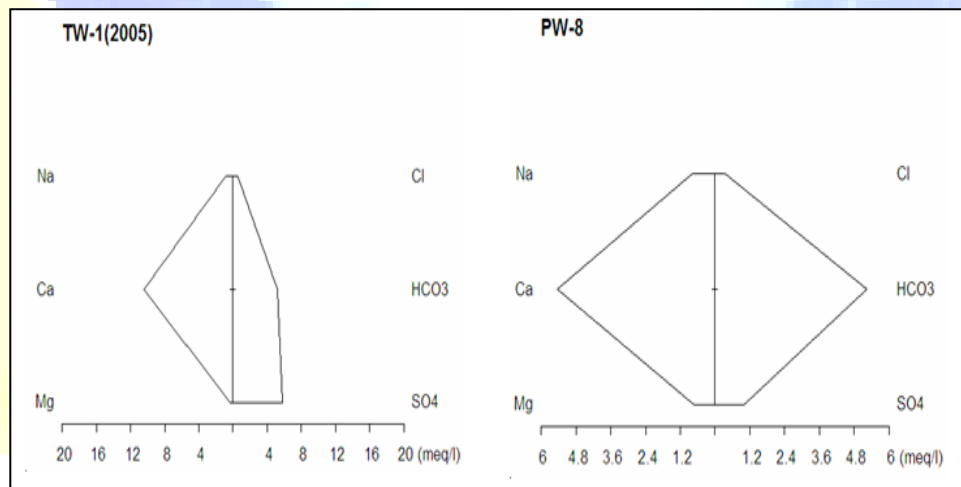


Fig.6: Stiff Diagrams of Water Samples from Upper Aynalem

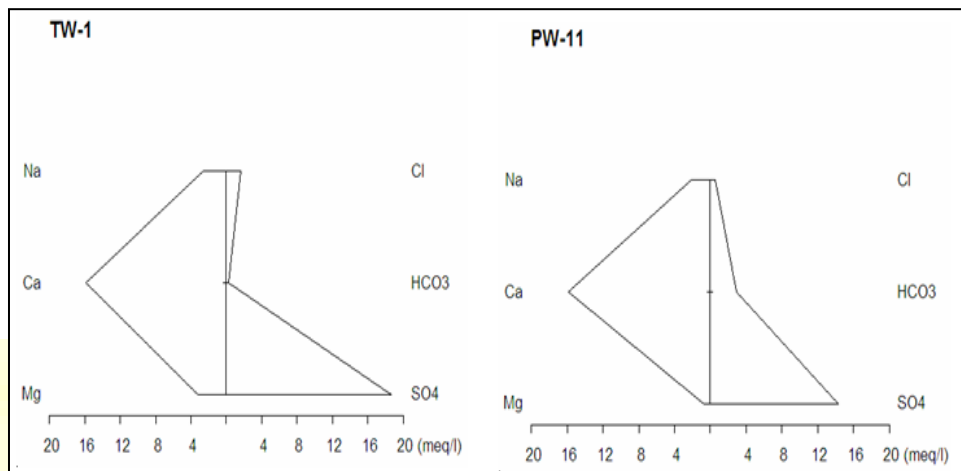


Fig.7: Stiff Diagrams of Water Samples from Lower Aynalem

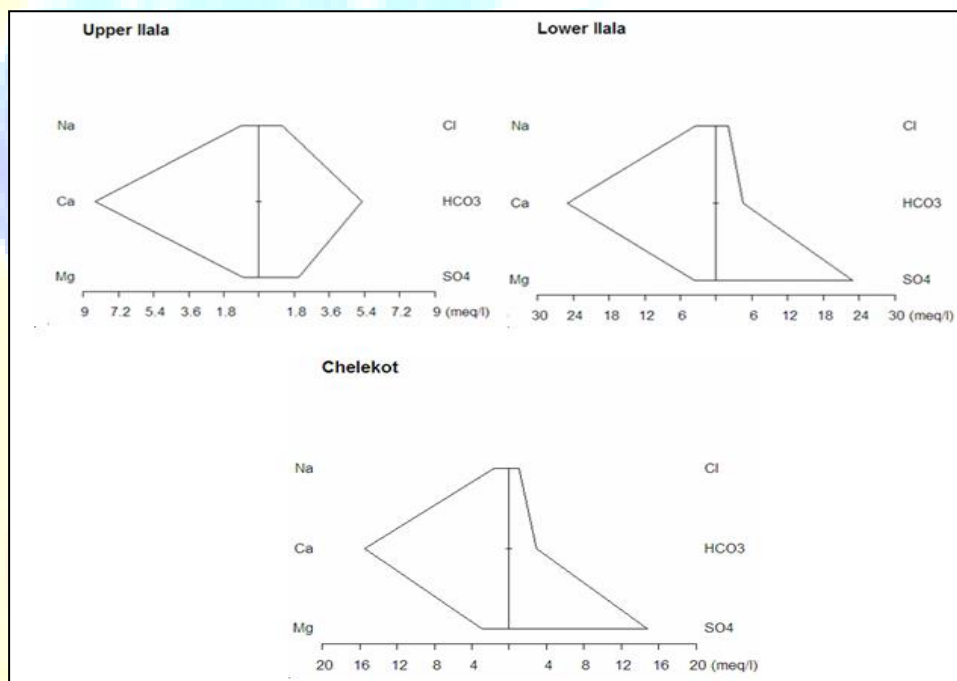


Fig.8: Stiff patterns of Water Samples from Ilala and Chelekot

Source Rock Deduction:

The purpose of source rock deduction is to gain insight into the possible origin of water analysis. The initial composition of groundwater originates from rainfall which may be considered to be diluted sea water (Hounslow, 1995). During its return path to the ocean, the water composition is altered by rock weathering. During rock weathering the major cations and anions are added to the

water. The source rock deduction for the study area is carried out with the help of AQUACHEM software. Water samples are selected from different areas within the catchment and out of the catchment for the source rock deduction analysis. The objective of the selection of samples from different areas is to compare the source rock within the different sub-basins and to see whether there is a connection of Aynalem groundwater sub-basin with adjacent river basins. As there is no silica analysis result in any of the samples, simple ionic comparisons are used for the analysis of source rock deduction. The ionic comparisons applied in the source rock deduction analysis are:

- Na/ (Na+ Cl)
- Ca/ (Ca+SO₄)
- TDS
- Cl/Sum of anions
- HCO₃/Sum of anions

This simplistic mass balance approach to deduce the source rock is not perfect, but it can be very helpful in understanding the origin of the groundwater. Based on the Na / (Na+ Cl) ionic ratio, the water samples show sodium source other than halite (albite, ion exchange) except for the water sample from upper Ilala (which shows reverse softening). Applying Ca/(Ca+SO₄) ionic ratio indicate that lower Ilala and Chelekot resulted from gypsum dissolution whereas the water samples from upper Ilala and Aynalem sub-catchment show calcium source other than gypsum (carbonate or silicate). The source rock deduced based on the TDS is carbonate weathering or brine except for the upper Aynalem (from silica weathering). And Cl/ (Sum Anion) ionic ratio shows that all of the samples are result from rock weathering. On the basis of HCO₃/ (Sum of anions), the water samples result from silicate or carbonate weathering and gypsum dissolution. The ionic ratio analysis show that the source rock of Aynalem is relatively different from the adjacent sub basins. That is the water from Ilala and Chelekot is rich in gypsum as compared to the Aynalem sub basin. This is supported by the fact that the water from boreholes of Ilala has a high hardness while the hardness of the water from Aynalem especially from the upper part is much lower.

Table.2: Parameters Used for Source Rock Deduction

Sample Location	Na/(Na+Cl) (meq l-1)	Ca/(Ca+SO ₄) (meq l-1)	TDS (mg l-1)	Cl/ (SumAnion) (meq l-1)	HCO ₃ / (SumAnion) (meq l-1)
Lower Ilala	0.747	0.552	2068	0.114	0.821

Upper Ilala	0.439	0.805	708	0.140	0.618
Upper Aynalem	0.690	0.846	447	0.055	0.819
Lower Aynalem	0.709	0.614	812	0.077	0.505
Chelekot	0.616	0.551	1380	0.090	0.256

Chloride Mass Balance Method (CMB):

Groundwater resource studies require the estimation of the quantity of water moving downwards from the soil zones as a potential recharge (Rushton et al., 2006). The methodology selected for the estimation of recharge should be applicable in a wide variety of climatic and hydrologic situations. In this study, the Chloride Mass Balance method is applied to estimate the groundwater recharge. According to Simmers et al. (1997), chloride is the most important environmental tracer and has been used to estimate rates of groundwater recharge under a wide range of climatic, geologic and soil conditions. Yongxin & Beekman (2003) added that the chloride mass balance method was applied for recharge estimation worldwide in recent time. The basic equation used to calculate the annual groundwater recharge with the assumption negligible chloride dry deposition in an area is based on equation (4). Despite the fact that the method is simple and inexpensive, there are a number of uncertainties associated with the method in estimating recharge.

In most cases, the long-term average chloride in rainfall is not available. Measured atmospheric input of chloride, often only short term records of chloride is assumed to be representative for a long period. But an area of concern as rainfall and chloride deposition during the past may be different from today. As discussed by Yongxin & Beekman (2003), other areas of concern include the uncertainty in the measured chloride content of rainfall and rainfall amount. The largest uncertainty associated with recharge estimation that utilises the chloride mass balance approach is the determination of chloride concentration in the rainfall. Furthermore rainfall amount is generally difficult to measure, and is highly variable. The absence of long-term rainfall quality data in the present study is one of the main limiting factors affecting the accuracy of the method. Another uncertainty source for the chloride mass balance approach is the sampling density and analysis accuracy of the chloride concentration of the groundwater. As part of the fieldwork,

samples from rainwater and groundwater were collected and analysed for their chloride content that are utilised in the chloride mass balance method of recharge estimation.

Chloride in Rainwater:

The chloride concentration in the rainwater of the study area has a low detection limit. As a result, rain water samples that are collected from Mekele and Bahrdar in August 2007 are sent to a special geochemical laboratory in Utrecht, the Netherlands for the determination of chloride concentration. Since the rainfall in Bahrdar and Mekele has the same origin (ITCZ), the data set from Bahrdar in combination to the rainfall water sample from Mekele is used to analyse the standard deviation from the mean value of the chloride concentration in rain water.

Table.3: Chloride Concentration in Rain

Time of Sampling	Chloride Concentration (mg l-1)	Station
June1-17,2002	0.43	Bahrdar
June17-30,2002	0.30	Bahrdar
July 1-15,2002	0.65	Bahrdar
July 1-15,2002	0.61	Bahrdar
August 9,2007	0.52	Bahrdar
August 10+11,2007	1.42	Bahrdar
August 12,2007	0.62	Mekele
August 12,2007	0.66	Bahrdar
Standard deviation	0.2	
Average Cl-1 rain for the samples taken in August 2007		0.8 ± 0.2 mg l-1

Chloride Content in Groundwater:

Thirty three groundwater samples were collected and analysed for their chloride content. The chloride content of the collected ground water samples ranges from 10 to 81 mg l⁻¹.

Table.4: Statistics of the chloride concentration in groundwater

Chloride concentration in the collected groundwater samples (mg l-1)			
Minimum	Maximum	Arithmetic mean	Standard deviation
10	81	24	11

As it is shown by the standard deviation of the chloride concentration, the variability of the chloride concentration in the groundwater of the area is considerable and this affects the value of the estimated recharge. Groundwater chloride concentrations may originate from various flow components in the unsaturated zone, thus the recharge calculation by chloride mass balance gives an average long-term estimate of recharge. The method has several shortcomings, one of which is that the method can not be used in environments affected by other sources of chloride other than total atmospheric fallout. Thus the following assumptions are made in applying the method.

- Precipitation is the only chloride source in groundwater
- Chloride is conservative and will not undergo any chemical reaction with the geologic material

According to Eriksson (1985), the average groundwater chloride content should be calculated as harmonic mean and is given by equation 4.

$$Cl_{\text{gwave}} = \frac{N}{\sum_{i=1}^N \frac{1}{Cl_{\text{gw}}}} \quad \text{Equation-(4)}$$

Where

Cl_{gw} is the individual chloride concentration of samples (mg l^{-1})

N is the total number of observations

Based on the collected groundwater samples, the harmonic mean of the chloride content in the ground water of Aynalem sub-basin is 18 mg l^{-1} .

Summarizing the above results as:

- Average chloride concentration in rain water (0.8 mg l^{-1})
- Harmonic mean of chloride content in groundwater (18 mg l^{-1})
- Average annual rainfall (670mm)

The estimated recharge is 30 mm year^{-1} which is 4.5% of the average annual rainfall in the area.

Given that input chloride concentrations can vary significantly from site to site within a region of investigation, it is not surprising that CMB estimations are site specific (Yongxin & Beekman, 2003). To see the spatial distribution of the recharge in the sub-basin, the average recharge is estimated at each sample point as indicated in table.5.

The estimated recharge value using the chloride mass balance method is sensitive to concentration variability of the chloride content in the groundwater and rain water. Taking the maximum and minimum values of chloride content both in rain and groundwater into consideration, an average recharge of 37mm year^{-1} which is 5.5% of the average annual rainfall, is estimated while the average recharge estimated by applying the harmonic mean of the chloride content in the groundwater samples and the average chloride content in rain water is 30mm year^{-1} (4.5% of the annual rainfall). Thus the estimated recharge may range between 30 to 40mm year^{-1} depending on the range of chloride concentrations in both rain and groundwater.

Table.5: Groundwater Chloride Content and Estimated Recharge

UTM East	UTM North	Clgw (mg l-1)	Cl rain (mg l-1)	Annual Rainfall (mm)	Recharge (mm year-1)
558941	1489255	22.20	0.81	670	24.45
558284	1489689	42.40	0.81	670	12.80
557809	1488359	12.50	0.81	670	43.42
556722	1487915	18.30	0.81	670	29.66
558268	1488286	12.50	0.81	670	43.42
557115	1487967	17.40	0.81	670	31.19
553941	1488821	20.30	0.81	670	26.73
552945	1488663	17.40	0.81	670	31.19
552219	1488072	22.20	0.81	670	24.45
552590	1488475	17.40	0.81	670	31.19
552313	1488491	19.30	0.81	670	28.12
552490	1489376	18.30	0.81	670	29.66
552506	1489646	19.30	0.81	670	28.12
559953	1484601	64.60	0.81	670	8.40
564070	1486356	9.70	0.81	670	55.95
554920	1480973	34.70	0.81	670	15.64
552650	1485112	81.10	0.81	670	6.69
557115	1487960	12.48	0.81	670	43.49
553706	1488251	13.44	0.81	670	40.38
551965	1487745	56.64	0.81	670	9.58
553320	1488680	15.40	0.81	670	35.24
560968	1487142	20.00	0.81	670	27.14
558901	1489740	19.30	0.81	670	28.12
555901	1486423	36.70	0.81	670	14.79
556519	1487277	11.60	0.81	670	46.78
553549	1488948	17.28	0.81	670	31.41
555526	1487648	15.36	0.81	670	35.33

559405	1487676	22.10	0.81	670	24.56
556050	1487809	17.28	0.81	670	31.41
557487	1488269	15.40	0.81	670	35.24
561072	1484157	15.40	0.81	670	35.24
559545	1480345	21.20	0.81	670	25.60
552160	1485603	36.48	0.81	670	14.88

Hydrochemistry

Water chemistry differs depending on the source of water, the degree to which it has been evaporated, the types of rock and mineral it has encountered, and the time it has been in contact with reactive minerals. The chemical constituents of groundwater give important clues with regard to the geological history of the enclosing rocks, the velocity and direction of water movement (Freeze & Cherry, 1979).

As discussed in previous section, water samples from the existing wells and springs were collected and their physical and chemical characteristics were analysed. Chemical analysis results of water samples collected from wells drilled in Agula shale show high concentrations of Ca^{2+} , SO_4^{2-} and Na^+ . This high concentration is caused by dissolved gypsum and limestone minerals which are found interbedded in the Agula shale. On the other hand, chemical analysis of water samples collected from the wells drilled in Mekele dolerite generally show low concentrations of Ca^{2+} , SO_4^{2-} and Na^+ . The plots of chemical analysis results on Piper diagram, (Fig.5) and Stiff diagrams (Fig.6 to Fig.8) show that the groundwater samples are calcium rich. Among the anion facies a majority of the water samples does not fall in any dominant class and varies from sulphate to bicarbonate. The analysis shows that groundwater in the sub-basin is Ca-HCO₃ type in the upper catchment, changing to Ca-HCO₃-SO₄ type along the groundwater flow direction and finally becoming Ca-SO₄ type near to the outlet of the catchment. Groundwater in the upper zone of the catchment has a low concentration of total dissolved solids (TDS) that ranges from 400 to 700 mg l⁻¹, whereas, the groundwater in the lower part of the catchment has high total dissolved solids (TDS) that ranges from 800 to 1500 mg l⁻¹. The groundwater in the lower part or outlet of the catchment is a combination of water that infiltrates every where in the catchment and has a more chance to interact with the rock materials along its flow path which contributes for the high concentration of total dissolved solids toward the outlet of the catchment. In other words, the increase in TDS toward the western outlet is resulted from water with longer residence time.

Water type and source rock deduction analysis of groundwater samples from Aynalem and adjacent catchments was attempted to see whether there is groundwater connectivity between the catchments. As there is no silica analysis result in any of the samples, simple ionic comparisons were used for the analysis of source rock deduction. In the water type identification the bicarbonate to silica ratio is not considered. Thus, with this simple analysis and with the data at hand, it is not possible to give a clear conclusion whether the similarity in water type is attributed to lithology or groundwater connectivity

Recharge:

Recharge is very difficult to estimate reliably and in many cases more than one recharge estimation method is required. There are as many methods available for quantifying groundwater recharge as there are different sources and processes of recharge. Each of the methods has its own limitations in terms of applicability and reliability (Yongxin & Beekman, 2003). As described in section above, the recharge is estimated using chloride mass balance method as part of the present study. The estimated recharge value may vary depending on errors associated to the method and the standard deviation of the chloride content measurements both in the groundwater and the rain water. Yongxin & Beekman (2003) discuss the uncertainties associated with the chloride mass balance method as: Uncertainties in the measured chloride content, both in rainfall and groundwater Uncertainty in the measured rainfall amount, depending on the type of rain gauge used and analytical errors introduced

CONCLUSION:

From the hydro chemical data analysis, a conclusion can be made that there exist at least two classes of water types in Aynalem catchment. Ca-CHO₃ dominated water type at the upper catchment and Ca-SO₄ dominated water type at the lower western extreme of the catchment are present with a clear evolutionary trend between the two types.

The principal mechanism of groundwater recharge in the area is direct recharge from rainfall. The use of chloride mass balance method to estimate recharge shows that the annual recharge in the catchment is in the order of 30-40 mm year⁻¹ from mean annual rainfall of 670 mm

REFERENCES:

- 1) Appelo, C. A. J., & Postma, D. (1992). *Geochemistry, Groundwater and Pollution*. Lyngby, Amsterdam
- 2) Fetter, C. W. (2001). *Applied hydrogeology + Visual Modflow, Flownet and Aqtesolv student version software on CD - ROM (Fourth edition ed.)*. Upper Saddle River: Prentice Hal
- 3) Hounslow, A. W. (1995). *Water quality data: analysis and interpretation*. Boca Raton etc.: CRC Lewis.
- 4) Rushton, K. R., Eilers, V. H. M., & Carter, R. C. (2006). Improved soil moisture balance methodology for recharge estimation. *Journal of Hydrology*, 318(1-4): 379-399.
- 5) Scanlon, B., Healy, R., & Cook, P. (2002). Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeology Journal*, 10(1): 18-39
- 6) Sharda, V. N., Kurothe, R. S., Sena, D. R., Pande, V. C., & Tiwari, S. P. (2006). Estimation of groundwater recharge from water storage structures in a semi-arid climate of India. *Journal of Hydrology*, 329(1-2): 224-243.
- 7) Simmers, Hendrickx, J. M. H., Kruseman, G. P., & Rushton, K. R. (1997). *Recharge of phreatic aquifers in semi-arid areas*. Rotterdam. Balkema.
- 8) Simmers. (1988). *Estimation of natural groundwater recharge*. Dordrecht. D. Reidel.
- 9) Singh, Kunwar P, Malik, Amrita, Sinha, Sarita, et al. (2007). Exploring groundwater hydrochemistry of alluvial aquifers using multi-way modelling. *Analytica Chimica Acta*, 596(1): 171-182.
- 10) Yongxin, X., & Beekman, H. E. (2003). *Groundwater recharges estimation in southern Africa*. Paris: United Nations Educational Scientific and Cultural Organization (UNESCO).