

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
SCHOOL OF EARTH SCIENCES



Fluoride Genesis in Groundwater of Butajira _Koshe _Ziway Transects
Areas Using Integrated Hydrochemistry and Isotope Techniques, in
Central Ethiopia

By

Temesgen Admas

A thesis submitted to the School of Graduate Studies of Addis Ababa
University in partial fulfillment of the requirements for the degree of
Master of Science in Hydrogeology

June, 2017

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Declaration of originality

I declare and confirm that this thesis is my original work. I have followed all ethical and technical principles of research in the preparation, data collection, data analysis and compilation of this thesis. Any scholarly matter that is included in the thesis has been given acknowledgment through reference.

Temesgen Admas

Signature: -----

Date: June, 2017

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Abbreviations	Meaning
AAU	Addis Ababa University
CMER	Central Main Ethiopian Rift
DEM	Digital Elevation Model
EGS	Ethiopia Geological Survey
EMA	Ethiopian Mapping Agency
GMWL	Global Meteoric Water Line
LMWL	Local Meteoric Water Line
M.A.S.L	Meter above sea level
MoWIE	Ministry of Water, Irrigation and Electricity
RE	Mean absolute error
SDZFZ	Silte Debrezeit Fault Zone
SI	Saturation Index
SNNPR	Southern Nations, Nationalities and People's Region
VSMOW	Vienna Standard Mean Oceanic Water
WFB	Wonji Fault Belt
WWDSE	Water Works Design and Supervision Enterprise

ABSTRACT

This research is conducted to investigate fluoride problems with its genesis in groundwater of Butajira_Koshe_Ziway transect of central main Ethiopian rift by using integrated hydrochemical and isotope analysis techniques. The hydrochemical analysis result reveals that groundwater type of the area evolves from Ca(Mg)-HCO₃ water type of early geochemical evolution in the western highlands and escarpments to Na-HCO₃ water type of highly geochemical evolution in the rift floor (i.e. towards lake Ziway) of the study area. Groundwater supplied from the highlands is typically characterized by low conductivity, low TDS, and a calcium bicarbonate facies. The water geochemistry (i.e. fluoride content) within the study area is widely (extremely) variable due to meteoric water recharge from the surrounding highlands is affected by different degrees of water-rock interaction, evaporation processes, rock type, depth variation, chemical and physical characteristics of the aquifer and acidity of soil and rock, concentration of ion present in the water. The high F geochemical anomaly is associated with high Na ($R^2=0.37$), alkalinity ($R^2=0.25$), TDS, EC ($R^2=0.3$), shallow depth and low calcium content. In general, from correlation matrix of collected and analyzed water sample, there is a negative correlation between calcium, magnesium and fluoride concentrations and positive correlation between bicarbonate, TDS, EC and fluoride concentration in groundwater. Saturation indices (SI) were calculated (using PHREEQC) for the different water groups, highlighting that the studied waters are super saturated with respect to calcite and under saturated with respect to fluorite. Groundwater is supersaturated with respect to calcite, which promotes the removal of Ca and HCO₃ from solution. As a result, groundwater is generally under saturated with respect to fluorite, the mineral that typically controls the upper limit of fluoride concentrations. The stable isotopes result reveals that highly enriched water from hand dug well, few borehole well and lake itself were observed in the downstream part of the study area surrounding the lake Ziway due to evaporation effect and recharged from the lake water rather than precipitation from highlands while the deep ground water located in the highland and escarpment of the study area reveal that slightly to highly depleted due to it recharged at lower temperature/from local meteoric water directly infiltrated rainfall through long subsurface flow from Gurage highland. The general trend for groundwater flow observed from groundwater contour map, hydrochemical evolution and isotopic signature indicates that from western highlands toward the rift floor in the direction of NW to SE of the study area.

Keywords: Fluoride genesis, Ground water flow, Hydrochemistry, Stable isotope ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

CHAPTER ONE

INTRODUCTION

Groundwater proved to be an important source for drinking water supply in the main Ethiopian Rift, where the surface water is scarce (e.g. Kebede et al., 2007; Ayenew et al., 2008; Demlie et al., 2008; Kebede et al., 2010). However, the water quality is a major concern that limits clean water use due to water chemical constituents. The main aquifer formations of the boreholes are lacustrine deposits, weathered and fractured Basalt, ignimbrite, and welded tuff. The volcanic aquifers signify a hydrochemical signature in which the quality is influenced by the reaction between the recharging water, a mineral of surrounding rocks and gas phases. Local hydrogeology and geochemical reactions such as dissolution and precipitation of solids, cation exchange and adsorption also contribute considerably to the variation of chemical constituent in the groundwater. The hydro chemical signature of groundwater in volcanic terrains indicates wide spatial variation owing to differences in rock-water interactions. The Ethiopian Rift Valley waters are the dominantly sodium-bicarbonate type with high salinity and fluoride content (Kebede et al., 2010). The larger portion of the groundwater system of the Rift Valley has high salinity and fluoride content. The high prevalence rate of dental and skeletal fluorosis in several towns in the rift valley reflects the high-fluoride content in drinking water. The concentration of fluoride in groundwater exceeds permissible level more than any other inorganic groundwater contaminants, such as arsenic and hence, special attention has to be given. Fluorides have received huge public and scientific interest because it is likely to be one of the most serious inorganic contaminants with well-recognized health implication in the region. In line with the excessive fluoride contents in drinking water in the Main Rift Valley, the prevalence of dental and skeletal fluorosis is common phenomena (Tekle-himanot et al., 1987). The environmental isotopes are the naturally occurring isotopes of elements found in abundance in our environment: H, C, N, O and S. The environmental stable isotopes of these elements (deuterium (^2H) and oxygen (^{18}O)) serve as tracers of groundwater, recharge process, subsurface process, geochemical reactions and reaction rates. The relationship of a variety of global scale and local scale processes can influence the isotope regime of Ethiopian meteoric waters. The temporal and the spatial variation in the $\delta^{18}\text{O}$ and δD composition of natural water bodies and rainfalls influenced by Temperature, subsurface rock-water interactions, basin topography, seasonal changes associated with moisture sources and moisture from continental evapotranspiration. These variations can provide characteristics that are preserved in the groundwater and useful for tracing. Attempts have been made to organize measured

geochemical data from several Woredas of the Main Ethiopian Rift to determine the distribution and the risk of fluoride contamination in groundwater using GIS (Zewge and Emru, 2011) as cited by DH consultant, 2015. These maps may have contributed a great deal to the understanding of spatial fluoride distribution of the area; nevertheless, they lack comprehensive approach to deal with the fluoride variability as related to other controlling factors that determine the mechanisms for such distribution. Therefore, the data generated from this survey will be an input to the existing data and readily be used to search /located new low fluoride water sources site and provide safe water for rural communities. Locating low fluoride groundwater potential sites requires a thorough knowledge of local geology, hydrogeology, and geochemical reaction that lead to spatial variations in water quality (Teklehailmanotet al, 2006).

1.2 previous studies

The issue of fluoride concentration and genesis in rift valley is critically important; some of the studies have been carried out so far. Among those hydrogeochemical studies that have addressed the fluoride problem in order to elucidate its origin (Gizaw, 1996; Chernet(1982,1998),Chernet et al., 2001; Ayenew, 2005,Rango et al., 2009a, b,Furi et al,2011, Ashley and Burley 1994,Kilham and Hecky 1973,Von Damm and Edmond 1984;Reimann et al. 2003 ,Yirgu et al. 1999,)and others to investigate the associated health problems.

Ashley and Burley (1994)as reported by (Kebede, 2013) found significant difference between Ca content of soils in theWonji Sugar plantation area with that of Metahara Sugar plantation areas. The low Ca in Wonji soils eventually lead to higher enrichment of F in shallow groundwaters. The model is that abundant Ca in soil tends to fix F to form and remove F from waters as CaF₂.

Mineral saturation (Kilham and Hecky 1973; Darling et al. 1996; Gizaw 1996; Chernet et al. 2001):Groundwaters in volcanic terrain rapidly reach saturation with respect to carbonates of Ca and Mg (calcites, aragonites, magnesites) prior to carbonates of Na and K and mineral of F (e.g. Ca₅F(PO₄)₃, CaF₂, MgF₂, NaF). The fixation of Ca to carbonate minerals will lead to significant under-saturation of groundwaters with respect to CaF₂. This will lead to eventual uncontrolled enrichment of F in groundwaters of the rift. An important note here is that as groundwaters move from the recharge areas near the highlands to the discharge zones in the rift the Ca and Mg content in groundwaters diminish. This is mirrored by increase in F concentration along the highland-rift transect (Kebede et al. 2010). **TewodrosRango(2009)** geochemical and isotopic composition of natural waters in the central main Ethiopian rift: emphasis on the study of source and genesis of fluoride. The result showed that high concentrations of fluoride were leached out particularly from the fine ash fraction which in turn suggests pyroclastic materials and interaction of glassy groundmass /weathered and redeposit fluvial/volcano lacustrine sediment with water and carbon dioxide at high PH causes the release of fluoride into the interacting water which leads to the ultimate reservoir of fluoride.

Base cation softening (Rango et al. 2009): The role of base cation softening is similar to that of mineral saturation/solubility control but instead of removal of Ca by carbonate precipitation, base cation softening removes Ca by exchange with Na in the rock matrix. As

groundwater ages or moves along its flow path Ca tends to be fixed to rocks and Na is removed from rocks instead.

Though this process is a common process in mineral reactions, the viability of this model is not widely tested in the rift setting.

Double enrichment model (Chernet 1998): This enrichment mechanism shows that F ion initially leached from rock forming minerals tends to accumulate in groundwaters. Following short or long term changes in hydrology of the rift, water table fluctuates, lake levels changes, and sediment deposition and erosion takes place along with hydrological variations. Fluoride ion in groundwaters is fixed to clay minerals or sediment surfaces when water level is lowered and sediment accumulates (e.g. the shrinkage of the Ziway Shalla lakes from one single mega lake to four isolated lakes over the Holocene left extensive lacustrine sediments). Along with the deposition of extensive alluvio-lacustrine sediments in the rift F which was initially in the waters is now fixed to the sediments. This makes the alluvio-lacustrine sediments secondary reservoir of F ion. Groundwaters now circulating in the alluvio lacustrine sediments remove F from the sediments lead to a significant enhancement of this ion in shallow groundwaters. This model has been shown experimentally by doing extensive leaching experiment by Chernet (1998) and Rango et al. (2009) to isolate the sediment grain size which contributes the highest F in waters.

Porosity and permeability control (Yirgu et al. 1999): In a comparison made between two aquifers of similar rock geochemistry and mineralogy (Pumice vs. Ignimbrite—both being rhyolitic composition but one granular and the other fractured aquifer), the authors found that groundwaters of the Ethiopian rift hosted in pumice (a rock with inter-granular porosity) contain high F than groundwater contained in fractured ignimbrites. The explanation for this is that surface area of rock–water interaction affects the enrichment of F. In pumice because of high water–rock interaction surface area F gets transferred from the rocks to the waters much easily.

Reverse weathering vs. F depletion from the waters of the rift (Von Damm and Edmond 1984; Kebede 1999): This process removes F ion from lake waters in the rift regardless of the fact that none of F containing mineral reached saturation. A process of reverse weathering also called „clay mineral neo-formation“ is a process whereby clay is formed at high pH values and is removed from waters (particularly from the lakes). Along with neo-formation of clay minerals and their eventual removal to lake beds or to the aquifers, F ion is also removed

by being fixed to the clay minerals. The role of reverse weathering in removing F ion from lake water and moving it to lake bed sediments has been shown by conducting mass balance modeling (Von Damm and Edmond 1984) for Ziway Shalla Lakes, Kebede 1999 for BishoftuCrater Lakes). The models, which combines hydrologic model with geochemical model, show annual flux of F to the lakes is far greater than the annual accumulation of F in the lake water. A significant portion of F is lost. Although the recent work by Kebede (1999) shows the same process to take place in the Bishoftu Crater Lakes; comprehensive mass balance modeling should be conducted on the wider lakes of Ethiopia in order to validate this finding.

Evaporative enrichment (Chernet 1982; Gizaw 1996): Lake Waters in the Rift Valley show the highest F content due to the removal of F by neo clay mineral formation and evaporative concentration of F in the lake water.

Accumulation of fluoride along groundwater flow path (Kebede et al. 2010): This work shows how F content in groundwater varies along transects of groundwater flow path from the highlands bordering the rift to the rift center. However, regional flows are not evident in the volcanic aquifers of the region because of faulting, heterogeneity in permeability and dissection of aquifers, and groundwater levels and their development is largely unknown, in the studied region, Central Ethiopian Rift, there is a clear regional trend in groundwater flow and geochemistry. The fact that this region falls at the intersection between an E–W running fault zone and the NNE–SSW running fault zone may be responsible for the flow of groundwater from the highlands to the rift floor. A regular increase in F content is noted with sharp peaks near volcanic centers. This is suggestive of successive accumulation of F along the groundwater flow path.

Geothermal Influx (Darling et al. 1996; Gizaw 1996; Ayenew 2008; Reimann et al. 2003): Direct geothermal input of F is widely mentioned in the literature as pathway of F input to the hydrologic systems in the rift. The challenge though is to address what proportion of F in the groundwaters of the rift is from direct magmatic input. The proportion of F coming from direct input from the geothermal systems to that of rock leaching is unknown though Chernet (1998) subjectively guess that to be 20:80 %. This will remain unsolvable question since F has no isotope. Isotopes are the best indicators of sources of certain ions, or elements in nature and help in deciphering mixing ratios.

Haile, Gashaw.(1999)Hydrogeochemistry of waters in Lake Ziway area.

TenalemAyenew (2008)The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian Rift and adjacent Highlands, the results of the water samples analysed and their localization with respect to the various volcanic stratigraphy shows that high F waters are localized in the acidic volcanic especially ignimbrite, rhyolites, pumice and volcanic glasses in the rift floor and high F groundwater originates in volcanic bedrock with high Na + K and low Ca + Mg geochemical system with dominant HCO₃ anion.

Tenalem Ayenew.et.al (2007). Environmental isotopes and hydro chemical study applied to surface water and groundwater interaction in the Awash River basin. The dominant source of recharge to the Rift aquifers comes from shallow groundwater inflow from the adjacent highlands. However, the presence of variable groundwater chemistry, depth and groundwater occurrence in the region suggests complex groundwater dynamics, often governed by the intensity and attitude of the rift faults and the volcanic stratigraphy and its relation with the various water bodies.

TewodrosRango et al., (2010) Geochemistry and water quality assessment of central Main Ethiopian Rift natural waters with emphasis on source and occurrence of fluoride and arsenic.

WagariFuri et al (2011).Fluoride enrichment mechanism and geospatial distribution in the volcanic aquifers of the Middle Awash basin, Northern Main Ethiopian Rift.

All of the research titled mentions above results of hydrochemistry reveal that high concentration of fluoride are related with high thermal water (temperature) and introduction of high subsurface CO₂ pressure, high concentration of Na⁺, alkalinity, Evaporative concentration, Calcite precipitation, near neutral to alkaline pH and low concentration of Ca²⁺, Mg²⁺ and also Rift associated with acid volcanic rock especially ignimbrite, rhyolites, pumice and reachability of rock/soil, interaction of volcanic glass /weathered and redeposit fluvial/volcano lacustrine sediment with water and carbon dioxide at high P^H in the rift floor.

Moreover, the current study considers vertical and horizontal fluoride distribution related with lithology within high fluoride zones and origin of water recharged those high fluoride water aquifer using hydrochemistry and stable isotopes of δ¹⁸O and δ²H in the area to critically understand the major source of fluoride and the hydraulic interconnection of the lakes with groundwater flow patterns. This study will provide valuable information about the **depth wise and lateral** distribution of fluoride in the transect, which will be useful in

identifying the sites of low fluoride bearing aquifers and future research work as the reference towards effective use of the groundwater resources in the area.

1.2.1. Statement of the problems

In the Butajira-Koshe-Ziway transect, surface water resources are generally scarce due to the arid climate and erratic rainfall in the area, so groundwater is the primary source of water supply, which is largely characterized by geochemical anomalies of high fluoride concentration (Kilham and Hecky, 1973; Chernet, (1982,1998,2001), Von Damm and Edmond 1984; Ashley and Burley 1994, Gizaw, 1996; Darling et al., 1996 Yirgu et al. 1999, Ayenew 2008; Reimann et al. 2003, Rango, 2009) often exceeding the 1.5 mg/L tolerance limit for drinking water (WHO, 2006). Above this standard, the high fluoride concentration causes dental fluorosis (above 1.5mg/L), skeletal fluorosis (above 4 mg/L) and crippling fluorosis (above 10 mg/L; Dissanayaka, 1991). The local population is affected by diseases such as mottled teeth and skeletal fluorosis (Tekle-Haimanot et al., 1987, Kloos and Tekle-Haimanot, 1999). As a result, exposure of people to high fluoride water across the rift is still the main health problem due to the lack of budget and insufficient local management to identify alternative sources of water supply. Therefore, the principal objective of this study is to gain a better knowledge and investigate fluoride problem with respect to its sources, genesis, distribution (vertical) and the origin of waters, mode of enrichment, water/rock interactions and mixings processes (among surface waters and groundwater) in the transect using integrated hydrochemistry and stable isotopes of δD , $\delta^{18}O$ techniques in order to support water quality management issues in the central sector of Main Ethiopian Rift (MER). In this study, the association of fluoride with common hydrochemical variables and hydrogeochemical processes that cause high levels of fluoride in ground waters was examined. Finally, this study will provide valuable information about the depth wise and lateral distribution of fluoride with its sources of recharge along the transect, which will be useful in identifying the sites of low fluoride bearing aquifers towards effective use of the groundwater resources of the area.

1.3. Objective

1.3.1 General objective

The main objective of this research is to investigate fluoride Genesis (source) in groundwater of Butajira_Koshe_Ziway transect of central main Ethiopian rift by using integrated hydrochemistry and stable isotope

1.3.2 Specific objectives

- To characterize major ions hydro chemical and stable isotopes signature in groundwater;
- To characterize fluoride distribution in groundwater along the transect, and
- To determine relationship between fluoride with lithology
- To know source of recharge for waters of different fluoride concentration from major ion chemistry and stable isotope of $\delta^{18}\text{O}$ and $\delta^2\text{H}$
- To characterize the groundwater flow dynamics

1.4. Methodology used

In order to achieve the objective of the research, the following method and materials are listed below.

- Review of existing geological, hydrogeological journal/article, report, related to the title that located in the study area by searching from a different website (i.e Google scholar) with an aim of establishing the relationship between fluoride concentration and geological formations.
- Collect secondary data and review existing geological, topographical map, hydrogeological, lithological log, pumping test, water quality data/borehole inventory and report, DEM, from ministry of water, irrigation and energy (MoWIE), geological survey of Ethiopia (GISE), water work, design and supervision enterprise (WWDSE) and Ethiopian mapping agency (EMA).
- Preparation of base map based on a topographic map at a scale of 1:50,000 and label secondary water quality data collected from MOWIE&WWDSE on the map in order to determine the data gap & sampling site.
- Conducting field work to measure water point inventory of hydrogeological, hydro geochemical and isotope evidences were conducted in all parts of the area where dug wells, river and boreholes and lake are available and measure depth of water level by using deep meter wherever it is accessible (SWL) with water sampling for both chemistry and isotope laboratory analysis after in situ measurements of Total Dissolved Solid (TDS), Electrical Conductivity (EC), p^{H} and Temperature (T) and take appropriate GPS location for sampling point.
- The collected water samples were kept in a 100ml and 20ml polyethylene sample bottles for both chemistry and isotope respectively by completely filled and tightened with double-sealed plastic caps.

- The distribution of Fluoride ,EC,TDS , P^H and ground water contour map in(Shallow &deep) ground water , lake and river are establishing on the basis of interpolation of point data measured from the field by using Arc GIS software10.1.
- Produce Groundwater level (contour) maps and determine groundwater flow directions from water level measurements in the field and relevant water level data obtained from the MoWIE.
- The collected water samples are analysis by the following method from WWDSEfor chemistry and AAU School of Earth Science isotope laboratory for stable isotope of $\delta^2\text{H}$ and $\delta^{18}\text{O}$.

Ca ²⁺ ,Mg ²⁺ ,Alkalinity,Cl ⁻ ,Total hardness	Titration method
Na ⁺ andK ⁺	Flame photometer
TDS,EC,P ^H and Temperature	Direct measurement by EC and P ^H meter
Fluoride, Nitrate and Sulphate.	Spectrophotometer
Stable isotope of $\delta^2\text{H}$ and $\delta^{18}\text{O}$	liquid water stable isotope analyzer

- Interpretation of laboratory results data collected in the field and other literature within the study area by using different software such as Aquachem4,arcgis10.1,surfur10,strater10,microsoftexcel and publisher 2010,Global mapper 12,PHREEQC for SI.

CHAPTER TWO

Description of the study Area

2.1. Location and accessibility

The study was conducted within central Main Ethiopian Rift Valley in the northern sector of the Lakes Region. The study Areas located partly in Oromia (East Shewa zone) and partly in Southern Nations Nationality and Regional State. All the study area is located within Meki River Catchment west of Lake Ziway sub-basin and extends from Gurage highlands in the west to Lake Ziway in the east. The catchment is accessible by Addis Ababa–Ziway and Addis Ababa-Alemgena-Butajira asphalt road. Intra catchment is accessed by much gravel and dry weather roads. Geographically the study area is bounded by UTM 865000 to 935000m latitude and 415000 to 495000m longitudes (Fig2. 1); with an aerial extent of 3498.4Km².

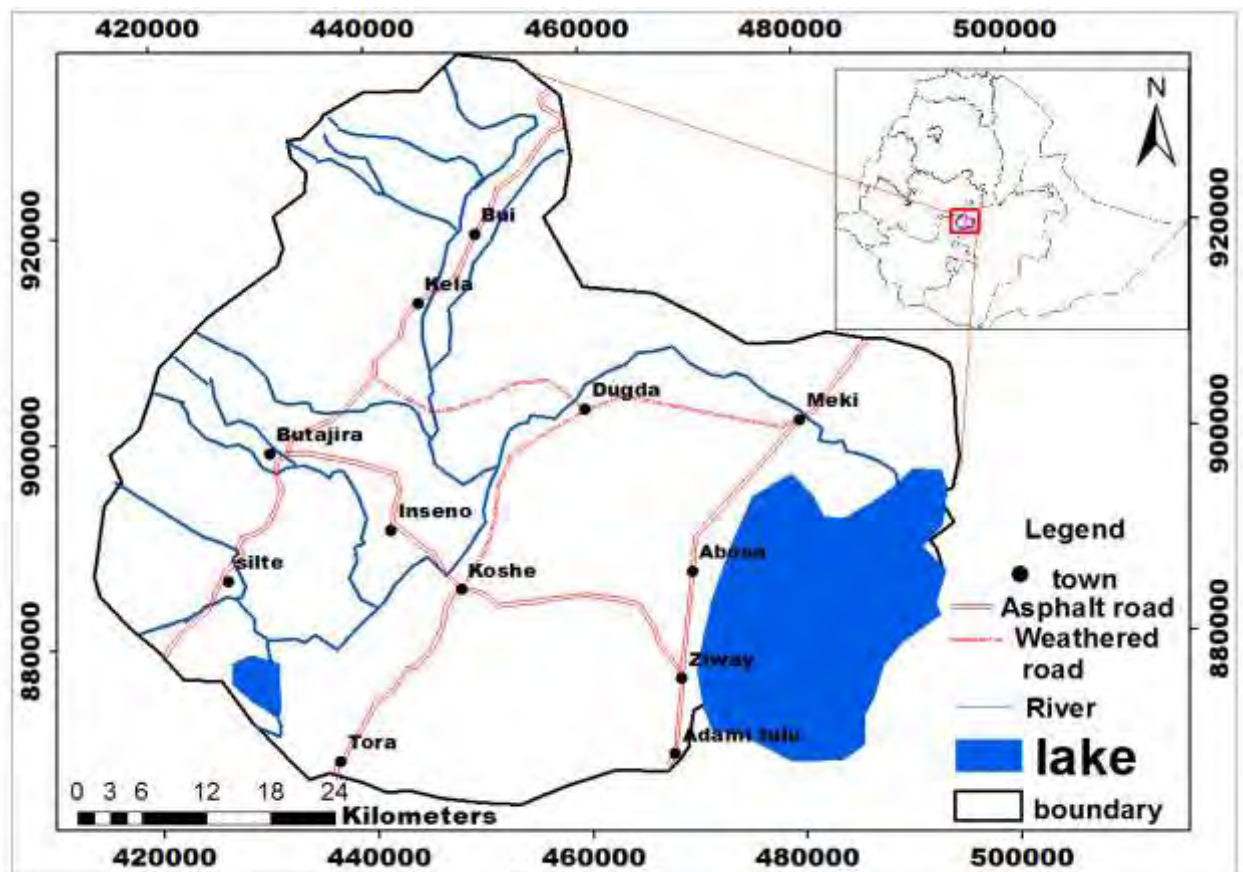


Figure 2.1 location map of the Study Area

2.2. Physiography and Drainage

The physiography of the area is primarily determined by the rift system faulting, volcano-tectonic activities that occurred in the past and deposition of sediments which are largely of lacustrine origin. As a result, the main landscape features in the area include ridges, mountains, calderas, fault escarpments, fault controlled depressions. The drainage patterns of the areas are parallel through the tributaries that fed the main river (Meki) before draining to Lake Ziway and the highlands are characterized by higher drainage density than the escarpment due to differences in rock permeability, fault, climate and slope. Most parts of Plateau area are perennial sources of the river while the tributaries in the Escarpments and rift floor are almost intermittent sources.

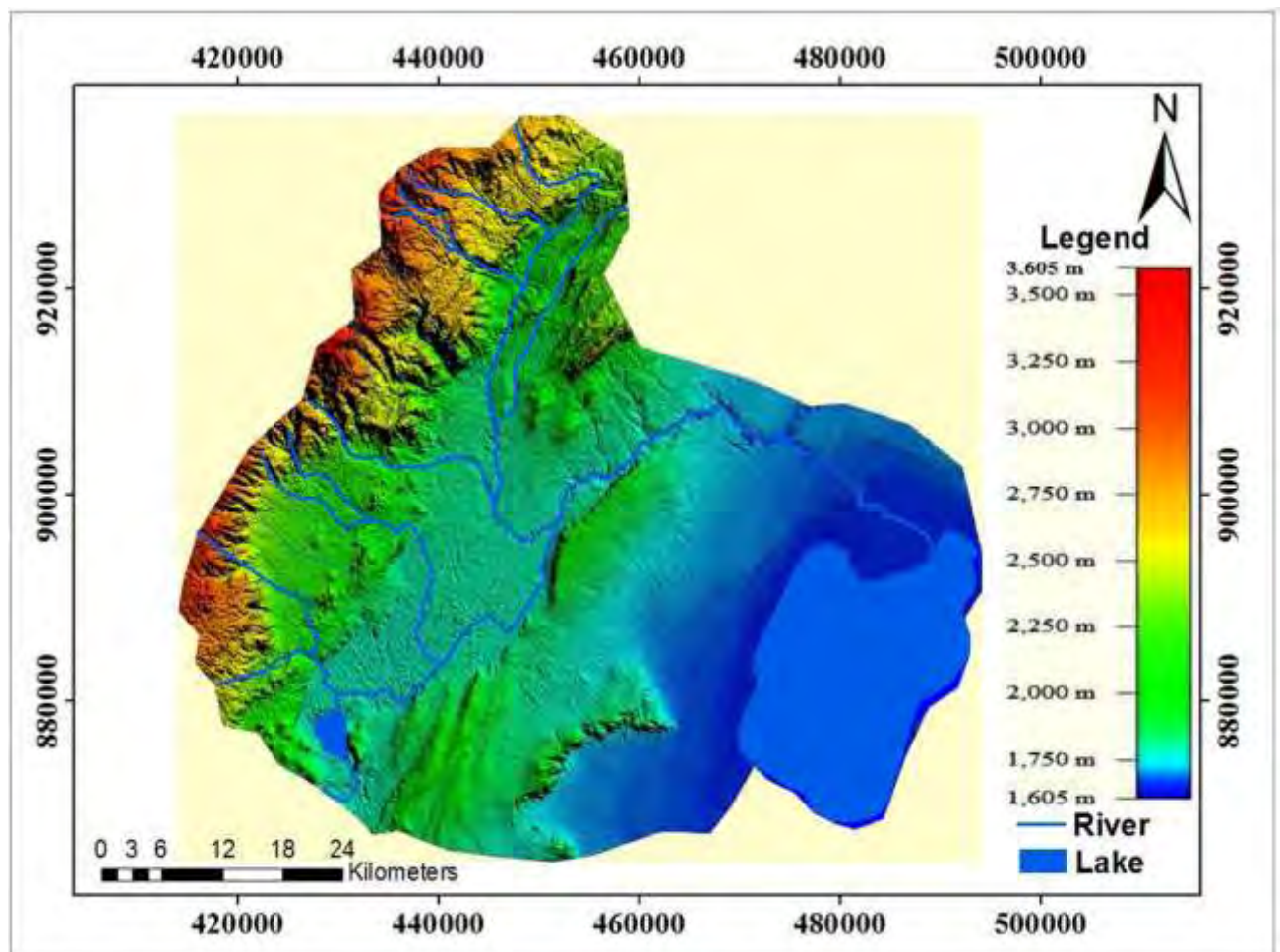


Figure 2.2 physiographic map of the study area from DEM

2.3 Climate and soil

Based on rainfall, the climate of the area can be categorized in to two broad seasons: the dry season (winter) and the wet season (summer) with autumn and spring receiving a slight amount of rain. The average annual rainfall of the study area varies spatially from about 720

mm in lowland to 1022mm at extreme highland areas. The total annual rainfall in the area is 818.57mm on average, and the mean annual temperature is 15.7°C. The climate is characterized by low rainfall and humidity, moderate but persistent winds and by a high rate of evaporation, which averages 5.3 mm/day (Kassa, 2008). According to Makin et al (1975), climate of the study area consists of three ecological zones: humid to dry humid lands, dry sub-humid or semi-arid lands and semiarid or arid lands. Accordingly, the highland areas West of Butajira are categorized under humid to dry sub-humid land while East of Butajira is dry sub-humid lands. The rest of the area which is around the lake is in the semiarid or arid zone.

The major soil types in the Rift Valley clearly show the influence of the parent material and extent of weathering. So that Soils of the study area are closely related to the main parent materials of the Rift Valley soils are basalt, ignimbrites, tuff, lava, gneiss, volcanic ash, alluvium, lacustrine sediment, pumice and degree of weathering (Makin et al 1976).

Generally, the soils of the Ethiopian Rift Valley divided into thirteen major soil mapping units and a further six sub-units based on the FAO/UNESCO soil classification. The major soil units in the study area include Luvisol, Cambisol, vertisol, fluvisol, Andosol Leptisol which characterized by higher drainage density than the escarpment due to differences in rock permeability, fault, climate and slope.

2.4. Geology of the study area

The geologic and geomorphic features observed in the region are the results of Cenozoic volcano-tectonic and sedimentary processes (Tenalem Ayenew, 1998). During this era, there was extensive magmatism and faulting which modified the face of East Africa. Geographic distribution and compositional diversity among the rock units of the Ethiopian volcanic province indicate that there has been a relationship between magma composition and rifting (Woldegabriel and Aronson, 1986; Hart et al., 1989) as cited by Tewodros Rango, 2009. The initial phase of development of the MER is attributed to the influence of a mantle plume beneath the Ethiopian Plateau resulting in widespread flood-basalt volcanism and plateau uplift with two main episodes dated at 45–30 Ma and 18–14 Ma (Davidson and Rex, 1980; Mohr, 1983; Hart et al., 1989; WoldeGabriel et al., 1991; Ebinger et al., 1993; Hofmann et al., 1997) as cited by (Tewodros Rango, 2009). The most important volcano-tectonic event in the central sector of the MER occurred in Early Pliocene, with the eruption of voluminous flows of rhyolitic ignimbrites and the collapse of very large calderas (Di Paola, 1972; Woldegabriel et al., 1990). From early Pleistocene to the present, tectonic and volcanic activity was concentrated along the Wonji Fault Belt (WFB) to the East, and along the

SiltiDebreZeit Fault Zone (SDZFDZ) to the west (Mohr, 1962; Di Paola, 1972). The geologic structure in the study area has been confined to an NNE-SSW trending structures formed by a line of hundreds of young faults and volcanic centers along the rift floor close to the eastern escarpment. This volcano-tectonic axis, named the Wonji Fault Belt (WFB), is considered to be the current axis of crustal extension (Morton et al., 1979 and WoldeGabriel et al., 1990). The western escarpment is primarily characterised by one major fault scarp. It shows a high throw in its north-eastern part, which progressively decreases and dies out to the south-west where it has been covered by volcanic products. However, in the western escarpment of the Guraghe Mountains, more than 1.5km thick flood basalt is displaced by several step faults that strike NNE. The SilteDebrezeit Fault Zone (SDFZ) of the western marginal graben is more than 100km long and 2-5km wide and converges at its southern end with the WFB. The SDFZ contains lacustrine sediments and tuff on which rest several nested scoria cones aligned parallel to the west escarpment (AlemuDrbisa, 2006)

2.4.1. Stratigraphy outline of the Area

The western escarpments are mainly composed of ignimbrite, tuff, recent basalt with some scoria cones and lacustrine sediments. The rift floor is fully occupied by lacustrine sediments and acidic rocks (welded and unwelded tuff, ash flow tuff, and pumice and obsidian-rich lava. Tesfaye Cherenet (1982) indicated that the geology of the large part of the rift valley areas is characterized by Lacustrine Sediments and Volcano-Sedimentary Rocks.

2.4.1. 1. Welded ignimbrite and tuff (Tertiary period)

This formation extends from the Highland boundaries through much of the valley slopes and escarpments, and into the rift floor of the west of Lake Ziway in the rift valley.

These units attain a thickness of around 250m in the rift while on the plateau it reaches only up to 30m that associated with intercalated basalt in the Highland and escarpment and also occasional lacustrine deposit or reworked water laid pyroclastic in the upper part of rift floor. Individual basalt flows vary in thickness from one or two meters up to tens of meters and located in the Escarpment Mountains west of Butajira Area

2.4.1.2. Basalts and associated flows of the rift floor

This unit consists of recent basalts which are located close to the western escarpment, in the Butajira-Silte area. The formations of this group are from Pleistocene to Holocene and include recent basalts of outcropping in the rift floor. The pyroclastic consists of the fine glass material, generally yellowish to brown in color containing small boulders of basaltic

lava. This lava field (Cinder cones and lava flows) are aligned from Silite in the south to Shershera in the north of Butajira. The formation of this group is from Pleistocene to Holocene of the Wonji group and includes recent basalts outcropping in the rift floor. The recent basalts are uninterrupted lava fields elongated parallel to the main tectonic trend of the rift (NNE-SSW) and were produced by fissure eruption. This basaltic group comprises of Wonji and Silte-volcanics. The silte volcanic lava field is located close to the western escarpment just along the main fault which limits the rift in the Butajira-Silte area and in the island of Tulu Gudu within Lake Ziway.

2.4.1.3. The rhyolite and trachyte unit (Quaternary period/Pleistocene to Holocene)

These lithological units are located in the rift valley of Gademota caldera in the southwest of Lake Ziway. The rhyolite and trachytic lava flows found associated with the rift floor ignimbrites and tuffs. The ignimbrites and tuff are the result of gas rich silicic magma and it is limited in terms of area covered relative to others.

3.4.1.4. Volcano lacustrine sediments

These form the second largest outcrop of the rift floor in the study area, mainly surrounding the lakes. They comprise alternating fine and coarse sand beds (a complex mixture of sediments) including sand, gravel, silt, clay, ash, tuff and pumice materials, but are predominantly fine to medium grained in the river cut exposure and the lithological log of a borehole. The lithological unit is predominantly comprised of felsic (volcanic rock)/pyroclastic fall, flow (ashes, tuff,) overlain by lacustrine sediments such as sand, clay shale beds and their weathered and reworked pumice, flavio/volcano lacustrine sediments, and associated alluvial deposits. The sediments must have been deposited during a wide time interval from the end of Pliocene until recent which is suggested by their considerable thickness and by the fact that in many places they underlie young volcanic products and are often rather deeply affected by regional faults. In general, these lithology units are located largely in the Ziway plain of the study area.

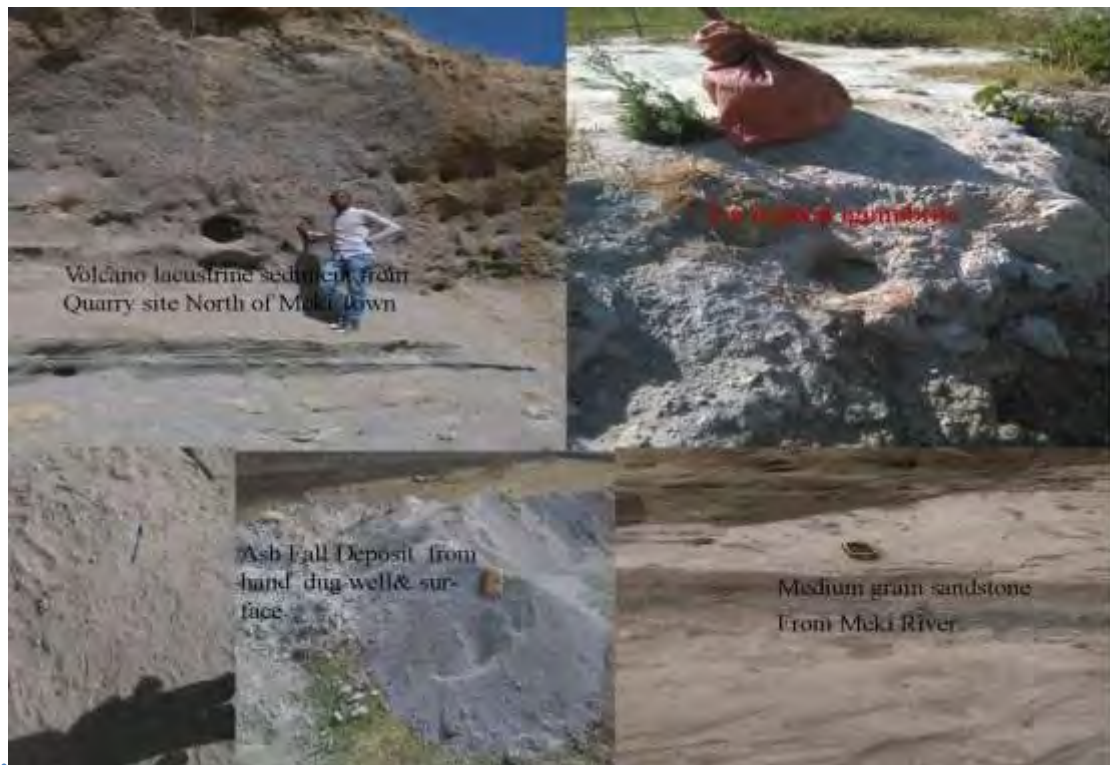


Figure 2.3. Photo from volcano-lacustrine sediment

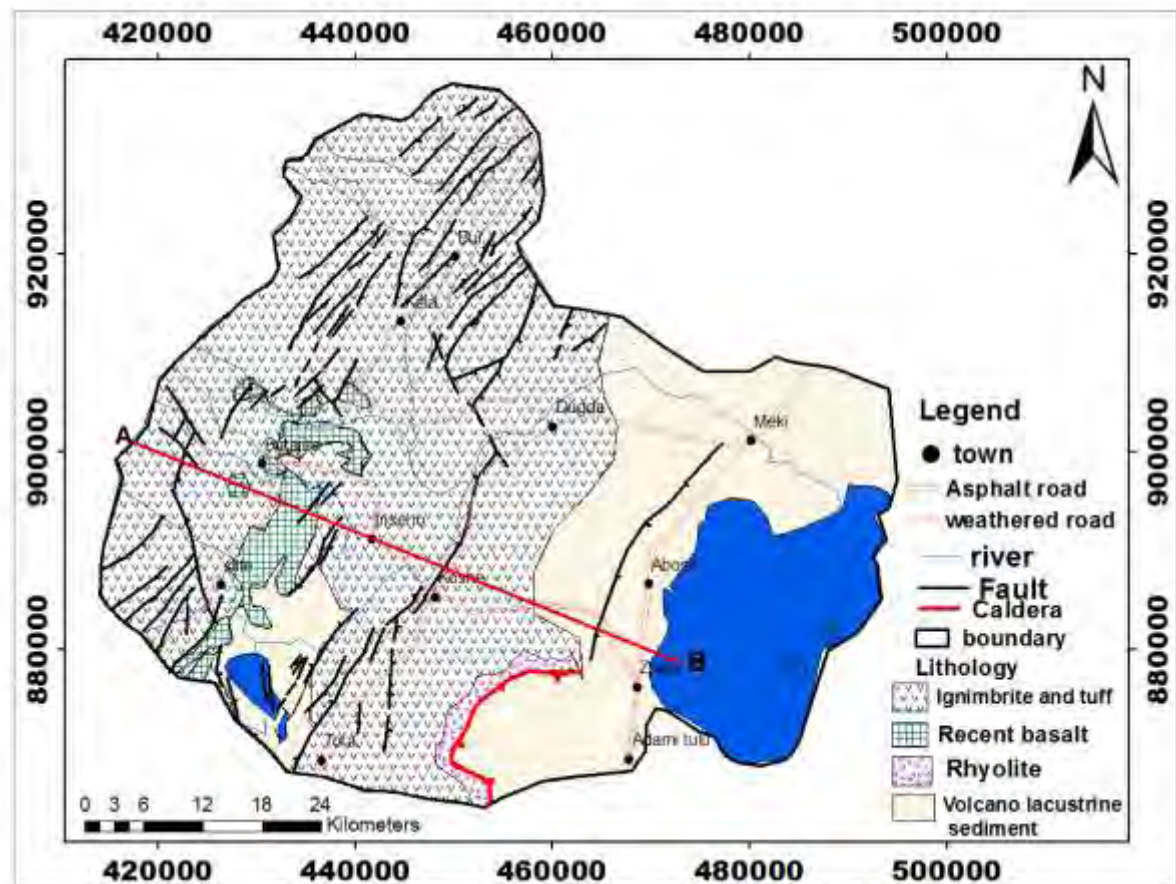


Figure 2.4. Geological map modified from (Tesfaye Chernet, 1982)

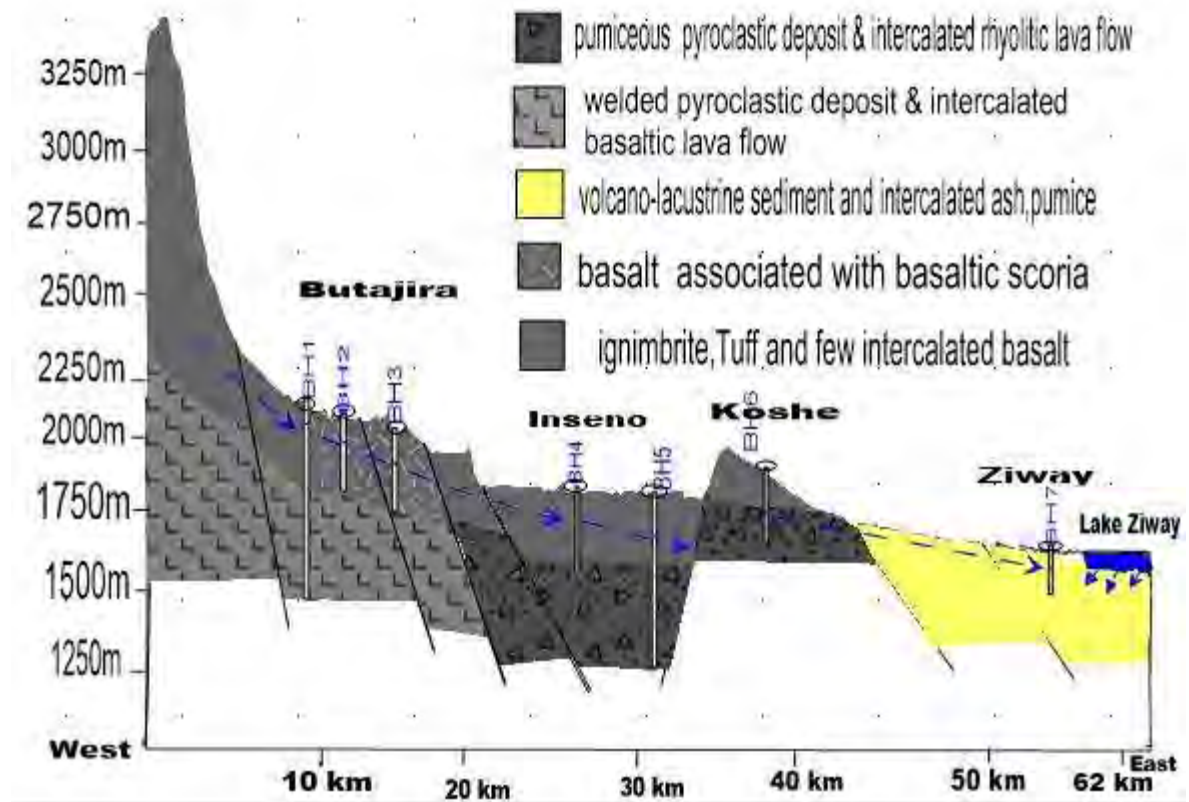


Figure 2.4.1 Geological cross-section from A to B

CHAPTER THREE

HYDROGEOLOGY OF THE AREA

3.1. Hydrogeological Setting

Nazareth Group and Dino Formation undifferentiated include ignimbrite, unwelded tuff, ash flow; rhyolites and trachytes occupy the Mareko and western part of the AdamiTuluJido Kombolcha woredas. These lithological units are well jointed and where dense Wonji Fault Belt cut these rocks their permeability increase.

Fractured ignimbrite and welded tuff which is reported in the western rift escarpment, west of the study areas. They are reported to have a high or moderate permeability (TesfayeCherent, 19982). Silicic pyroclastic materials cover most of the escarpments and the rift floor. They are mainly per alkaline rhyolitic ignimbrites, interlayered with basalt and tuffs layered with pumices. The flow thicknesses in this lithology unit reach up to 250m in the rift.

Pleistocene and Recent to basaltic flows and cones have also been reported in the area, which belongs to Wonji Group. They are up to 100m thick as in the east of Ziway Lake and have moderate to high permeability (TesfayeCherent, 1982).

Rhyolitic and trachytic lava flows and domes (Holocene) and pyroclastic (pumice and unwellded tuff), are also reported around the western part of AdamiTuluJidoKombolcha area. These rocks are reported to have moderate productivity while the pyroclastic have low productivity (Halcrow, 2007).

Lacustrine sediments are reported close to the Lake Ziway that extends up to Langanano and Abijata Lakes. Lacustrine sediments include silts, clays, volcanoclastic sediments and tuffs, and rest on ignimbrite (TesfayeCherent, 1982). The yield of boreholes often ranges 1 to 5 l/s. The permeability of sediments becomes higher where there are a higher proportion of coarser materials like pumice sand beds. The thickness of lacustrine deposit ranges from 40 to more than 200m, with the average of 40 to 50m. They have moderate to high permeability (TesfayeCherent, 1982). According to Kokusai Kogyo (2012), volcanic rocks' aquifer with high productivity occurs around the western rift escarpment and moderate and low productive aquifers in acidic volcano-sedimentary rock at moderate slope and lacustrine sediments in the rift floor, respectively have been reported

3.2. Hydro stratigraphic unit (aquifer and aquifer properties)

The rocks in the study area possess different permeability due to variation in lithology, primary and secondary structure, fragment size of pyroclastic dusts, and grade of weathering.

3.2.1. Fractured Ignimbrite and Welded Tuff Aquifer

This area is mainly composed of pyroclastic fall, pyroclastic deposits such as tuff and Ignimbrite. These are less welded ignimbrites intercalated with pumice fragments, alluvial and colluvial deposits located at the foot of volcanic mountains. Ignimbrites are widespread, occurring in the escarpment slopes and piedmont areas, the plains of eastern and western escarpment and on the rift floor. From indicative hydrogeological parameters, the formation is productive as a result of its secondary fracture porosity and permeability. The formation may have a high or moderate permeability, although yields from both boreholes and springs may vary widely. This permeability zone covers large area. Based on the characteristics of ignimbrite, fracturing and weathering grade, the units possess medium to high permeability. The groundwater in this part of the study area is deep, confined aquifer and typical borehole yields 0 – 6l/s with thickness mostly greater than 200m. The groundwater level in this region suddenly gets deeper probably as a result of the major fault. Existing borehole data indicates the aquifer is composed of ignimbrites and tuffs. Transmissivity varies from 6m²/day to 171 m²/day and hydraulic conductivity 0.25m/day to 4.75 m/day.

3.2.2. Fractured Basalts and Basaltic Scoria Aquifer

These are situated to the east of Butajira and dominantly composed of vesicular basalts and associated scoria cones. Groundwater occurs in these areas at a relatively deeper level with respect to surface topography. Permeability is largely related to joints, faults, vesicles and fragment size of scoria. The existing borehole data indicates the aquifer is composed of scoria, vesicular basalt and at some places sand and gravel deposit underlying thin layer of basaltic flows. The thickness of the basaltic flow is highly variable in areas, such as Shershera EleDirama Shershera Jole areas the underlying sand and gravel deposits contribute to the aquifer. The existing data shows it has transmissivity varying between 16m²/day to 242m²/day and hydraulic conductivity 0.9m/day to 20 m/day. The aquifer varies from unconfined to semi confined. The aquifer within the basaltic formation is unconfined and the one in the underlying sediment is semi-confined. These units have a thickness up to 100m and in general possess moderate to high permeability.

3.2.3. Rhyolite and Trachytic Lava flows Aquifer

These are intermediate to acid lavas, which tend to be more viscous, often thicker than basalts and less widespread (i.e. more closely associated with the source volcano or extrusion) specifically in the Gademotta caldera (Consult, 2015)

3.2.4. Volcano Lacustrine Sediment Aquifer

These form the second largest out crop of the rift floor in the study area, mainly surrounding the lakes. The lacustrine sediments are situated in low lying areas of rift floor and they store large quantities of both fresh and saline groundwater. Generally, hand dug wells or boreholes in volcano lacustrine sediments strike groundwater at depth of less than 50 m having a yield of between 1 and 5 l/s. They comprise alternating fine and coarse sand beds (a complex mixture of sediments) including sand, gravel, silt, clay, ash, and tuff, pumice materials, but are predominantly fine to medium grained. The lithologic groups found in this area are ignimbrites and ash overlain by lacustrine sediments such as: clay and reworked pumice. Thickness of the lake sediments ranges from 40m to more than 260m and important unconfined aquifer in the study area. Groundwater is fairly shallow when it is close to the surface at the lake's shore area and deeper further away from the lake. The depth to water level varies from surface to about 20 m meters below the ground. Because of this there are a number of family owned dug wells and community wells in the area. The Aquifer Characteristics as Poor yields for Massive and/or pumices/pyroclastic, good yields for well jointed or fractured Ignimbrite, Low to medium potential for Lacustrine Sediments. There are local sands and gravels, which often form the primary groundwater bodies within these sediments. The existing data shows it has Transmissivity varying between 1-137(m²/day) and hydraulic conductivity 0.02m/day to 3.8 m/day.

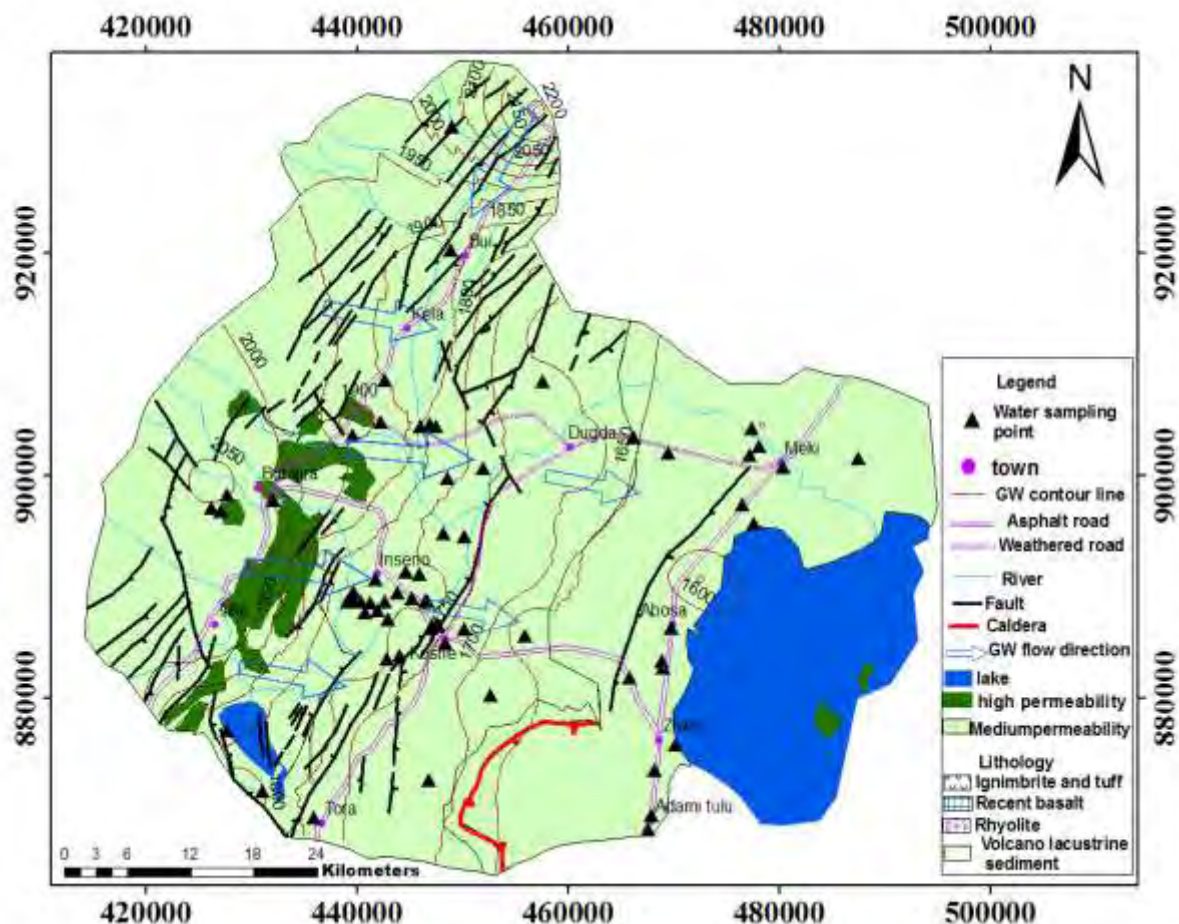


Figure 3. Hydrogeological map of the study Area modified from (Tsfayechnet, 1982 and MoWIE, 2008)

3.3. Groundwater Recharge and discharge areas

Recharge mechanism in the study area has been explained based on lithology, topography and structures through direct infiltration from those highlands of precipitation into the aquifer system, localized recharge through tectonic discontinuities (such as faults, joints, fractures) into the aquifer system. The recharge and discharge area usually determine by high topography and hydraulic gradient which means topographically high area considered as recharge whereas topographically low area considered as discharge area. The Garage Mountain (highland) which is located at high elevation 3600 above mean sea level and the rift floor or ziway plain at elevation 1635 above mean sea level before drain to Lake Ziway is also considered as discharge area. The other possible recharge is direct infiltration of the precipitation on the rift floor (i.e. discharge area). However, due to the relatively higher

annual potential evapotranspiration over the total annual precipitation in the rift floor, direct recharge from precipitation for this lower valley part is unusual.

Based on Geomorphology, the study area can be categorized with different hydrogeological characteristics.

The highland volcanic mountains: The western Garage Mountain ranges (main recharge area of the basin). Mountain front recharge is characteristic feature, defined as recharge occurring along a boundary of the regional aquifer system that parallels a mountain area. Source of recharge is from precipitation of infiltration or in direct recharge from stream flow infiltration. Small portion of the recharge contributes to a deeper groundwater flow system which discharges in the valleys further downstream in the plateau and escarpments.

Escarpment Areas: Are characterized by low rainfall and higher evapotranspiration; Direct and localized recharge from precipitation along high fracture zones; Large depressions of volcano tectonic origin. Some of these depressions are discharge areas of local and intermediate groundwater flow systems. The water in the high altitude depressions is characterized by low EC and TDS indicating possible release of water to the deeper rift groundwater system, Rift Floor: Channel loses from the large rivers in permeable lacustrine sediments. Local flow systems exist in the rift valley. Groundwater flow in the rift is generally characterized by relatively low gradients recharged mainly by indirect sources.

3.4. Groundwater Flow

Major fault systems are aligned NNE-SSW, parallel or sub parallel to the Main Ethiopian Rift, with well-defined escarpments. These are often associated with depressions and plateau that may provide for storage and transmission of groundwater. In some locations, these fault/fracture systems are the major controls over groundwater flow direction. Groundwater contour map has been generated based on the collected (measured static water level) in the field. This map has been constructed to show the groundwater flow direction. Groundwater flow is generally towards the east and southeast from the western and northwestern high lands. The groundwater level is generally flat to gentle slope except at Tora-Koshe-Dugda ridge. In these areas the groundwater contour shows steep slope showing lower permeability, probably due to the nature of the rocks or the fault systems separating these zones. The groundwater level drops from about 2040 m in Butajira to 1640 m amsl in Lake Ziway. From groundwater contour map, hydrochemical evolution and isotope result groundwater flow directions radiate from the Guraghe highland and its escarpment towards eastern

and south-eastern part of the catchment. The flow direction converts to wards west and northwest in the vicinity of Lake Ziway. There is a divergent zone at the western escarpment around mareko; which may probably because of recharging of water from the highlands. Divergent zone is a specific area where the water starts to flow to any other area of different direction and considered as recharging zone. In addition there is also a convergent zone in the rift floor around dugdaworeda in the vicinity of Lake Ziway; which might be considered as discharging zone. Convergent zone is specific area where the water flows toward specific zones that comes from its surrounding of any direction.

CHAPTER FOUR: RESULT AND DISCUSSION

4. HYDROCHEMISTRY AND ISOTOPE HYDROLOGY

4.1. General Hydrochemistry

The chemical composition of natural water is derived from many different sources of solutes, including gases and aerosols from the atmosphere, weathering and erosion of rocks and soil, solution or precipitation reactions occurring below the surface, and cultural effects resulting from human activities (Hem, 1992).

The chemistry of groundwater in the saturated zone is controlled by chemical reaction rate, residence time within the saturated zone, and mineralogy of the rock matrix, where residence time and flow path are determined by factors such as aquifer thickness, permeability and amount of recharge (Griffioen, 2004). These factors combine to different degrees to create diverse water types with compositions that vary with space and time.

Hydrochemical investigations are conducted to understand the functioning of the hydrogeological system by relating the quality of the groundwater to different processes in the aquifer system.

Water chemistry data can be used to infer groundwater flow directions, identify sources and amounts of recharge, estimate groundwater flow rates, and define local, intermediate, and regional flow systems (Anderson and Woessner, 1992). Underlying this hydrochemical approach are a number of assumptions including (1) natural water chemistry is a result of rock-water reaction such as dissolution/precipitation, reactions on aquifer surfaces and biological reactions, (2) distinctive chemical signatures are related to specific sets of reactions, (3) dissolved concentration generally increase along the surface flow path until a maximum value dictated by mineral equilibrium, and (4) hydrochemical facies are directly related to the dominant processes (Thyne et al., 2004). The hydrogeochemistry of water can provide information that can distinguish recharge zone water from transition and discharge ones based on the chemical composition of water type. Moreover, in hydro geochemistry major cations are the most widely and frequently used parameters for characterization of the various water types and deduction of the flow processes and origin of salinity (AddisuDeressa, 2012).

4.2. Physiochemical parameters

Physiochemical parameters analysed for the water samples are characterised into two: those that have been measured both at the field and in the laboratory, and those that have been only analysis in the laboratory. For that reason, the measurement of P^H, Temperature, total dissolved solid (TDS), Electrical conductivity (EC) are measured both at the field and in the laboratory while sodium, potassium, hardness (calcium, magnesium)alkalinity ,sulphate.The selection of the sampling locations was planned to take into consideration the previous hydrogeological/geochemical studies of the area (Fig.3). A total of 60 water samples were collected 57 sample from groundwater wells (both hand dug and borehole well) 2lakes and 1rivers on December 2016 and samples were stored in 100 ml((chemistry)&20mlisotope) polyethylene bottles for chemistry and completely filled and tightened with plastic caps.

Out of the total; 30samples were analysed for major ions(Na⁺, K⁺, Ca²⁺, Mg²⁺ F⁻, Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻), 30 for stable isotopes of δ18O and δD.

TDS, EC, Temperature and pH of waters were measured in situ using the appropriate field kits. Locations of the sampling points are recorded during the fieldworks using Global Positioning System (GPS) and measuring of static water level using deep meter for preparation of groundwater contour map in order to determine flow direction.

Generally,14 water samples for isotopic data points from a previous study (ShimelisFikre, 2006; Winter, 1973,(TenalemAyenew 1994,1996), Crag etal, 77,Rango ,2009) and 40 water samples for major ions /chemistry from (DH Consultant, 2015) Ministry of Water Resource were included in the database.

Samples were analyses of major elements were carried out at the Ethiopian water work design & supervision enterprise by using flame photometry for (Na⁺, K⁺),titration(Ca²⁺, Mg²⁺,alkalinity,total hardness and chloride),spectrophotometry for anions (F⁻, NO₃⁻, SO₄²⁻) and Addis Ababa University School of Earth Science hydrogeology isotope laboratory for stable isotope by using liquid water stable isotope analyzer. The reaction error is the difference between total cations and total anions, expressed as a percentage of the TDI. Analytical accuracy of the analysis for major ions can be estimated from RE (Electrical neutrality) conditions since the sum of anions and cations must balance

RE= $\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} * 100$, Where cations and anions are expressed in meq/l.

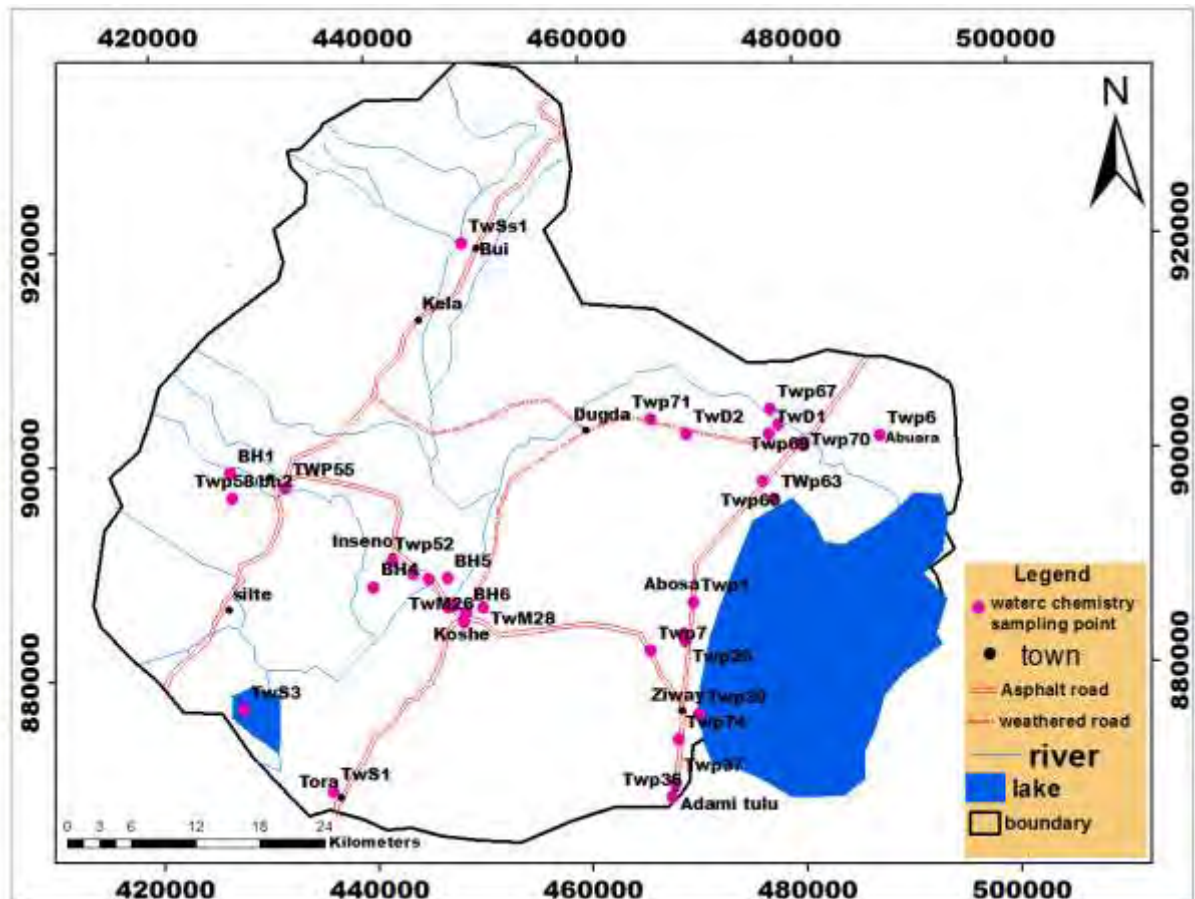


Figure4. Water chemistry sampling point

4.2.1. P^H

The P^H values of the sample collected in the Study area ranges from 6.5 to 8.75. The lowest values measured in the sample from Twp55 at Butajira and the highest value measured in Twp59 at Meki town. The alkalinity of water is due to the presence of carbonates, bicarbonates, alkaline and alkaline-earth hydrates.

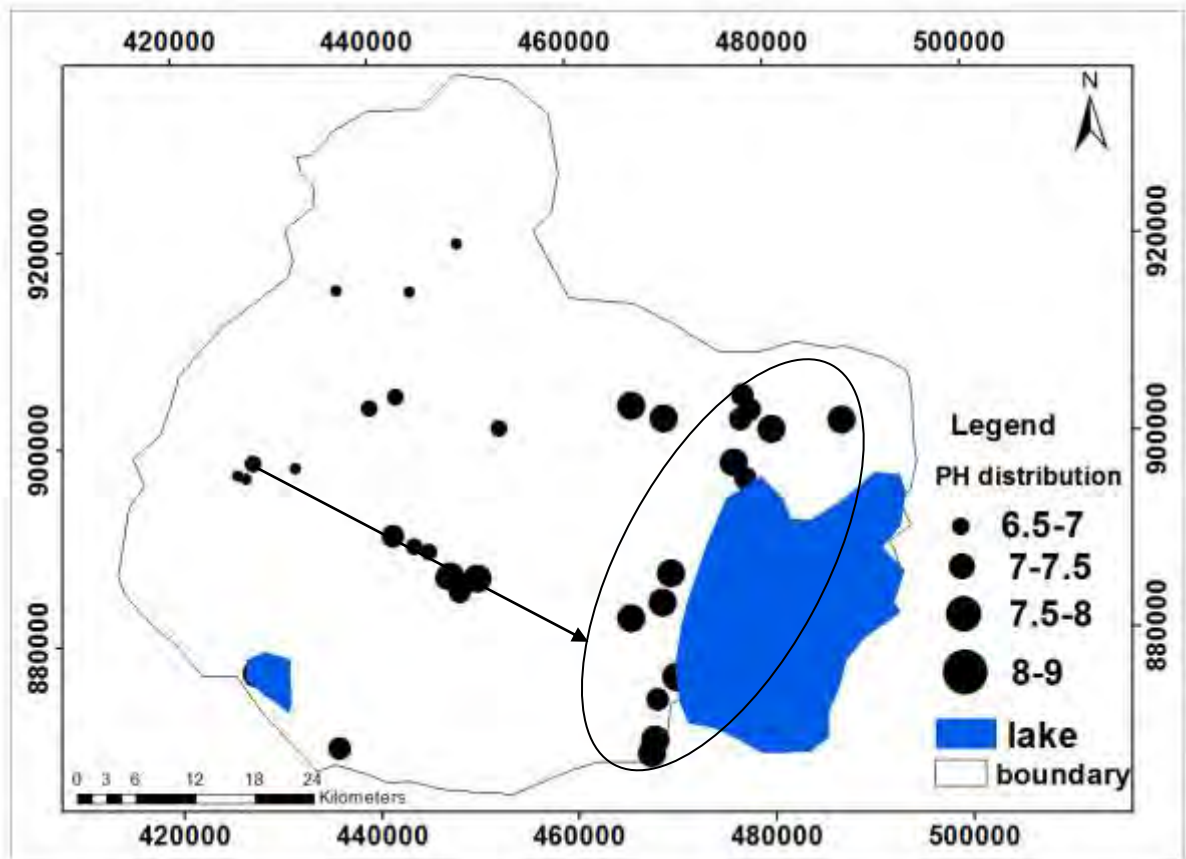


Figure4.1. PH distribution map of the Study Area

4.2.2. Temperature

The temperature of the water is controlled primarily by climate. Temperature also affects P^H , electrical conductivity, the rate of chemical reaction as well as the concentration of the reactants and the products, and solubility of gases in the water. It must be measured in situ or immediately after collecting the water sample. In fact, the temperature of sub-surface waters reflects the environmental condition on which the water flows. In the study area, the water temperature of the sample ranges from 17.9°C to 29.1°C in the field. In general, the temperatures of the water samples show a progressive increase from west to east in the direction of flow paths.

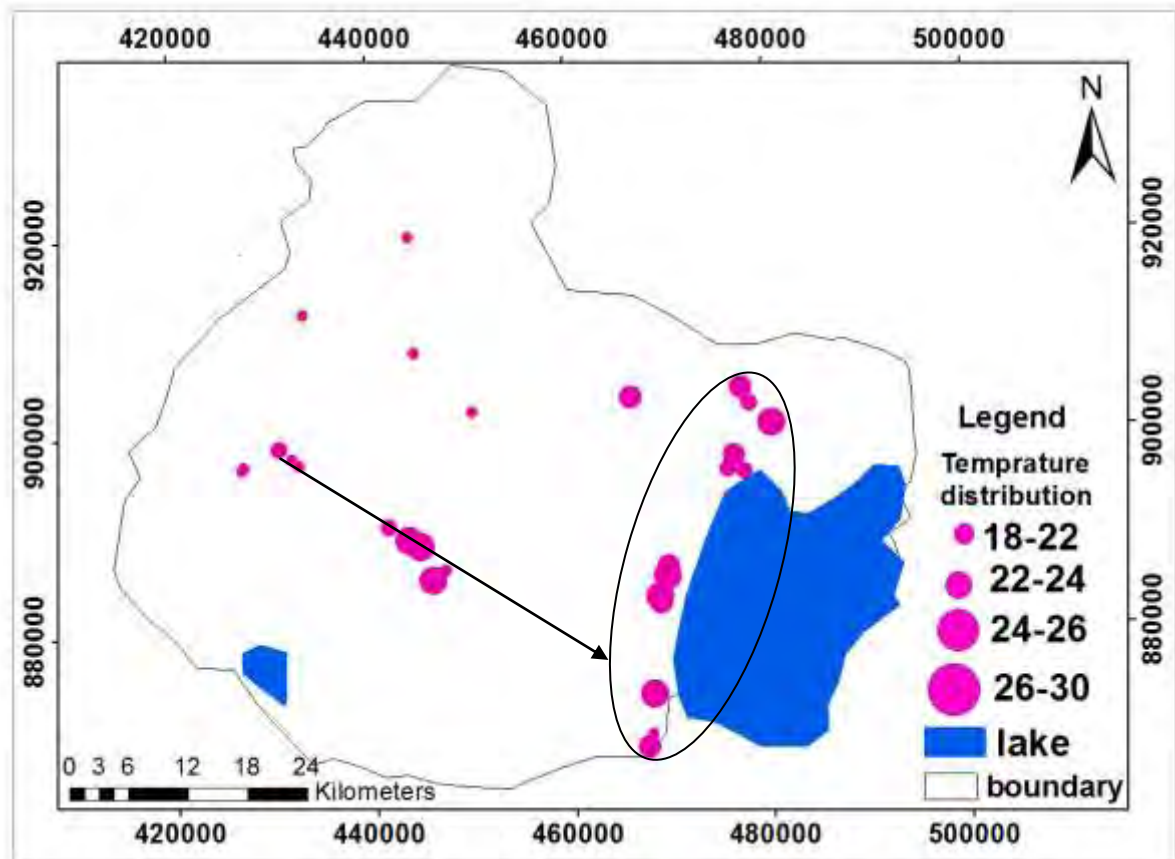


Figure4.2. Temperature distribution map of the Study area

4.2.3. Electrical Conductivity

It is the ability of a substance to conduct an electric current and measured in micro Siemens per centimeter ($\mu\text{S}/\text{cm}$). As ion concentrations increase, a conductance of the solution increases, therefore, the conductance measurement provides an indication of ion concentration (Roaring Fork Conservancy, 2007). The values of EC increase with temperature, between 20°C and 30°C , an increase in 1°C , increases the EC by two percent on the average (Hem, 1992). The EC value indicates that how much is the concentration of dissolved substance in the water which in turn tells us that how far the water travels and how long it stays in the subsurface and the nature of geologic formation. It also helps to identify recharge and discharge areas. The more salts are dissolved in the water; the higher is the value of the electric conductivity. The minimum and maximum EC value for the study areas are 370 ($\mu\text{S}/\text{cm}$) of TWSs at Sodo Renfensho and 3480 ($\mu\text{S}/\text{cm}$) Twp25 at Edokontola near Abosa town respectively. EC does not give specific information about the chemical species present in water, but it gives a determination of TDS, which is an acceptable indicator of water quality.

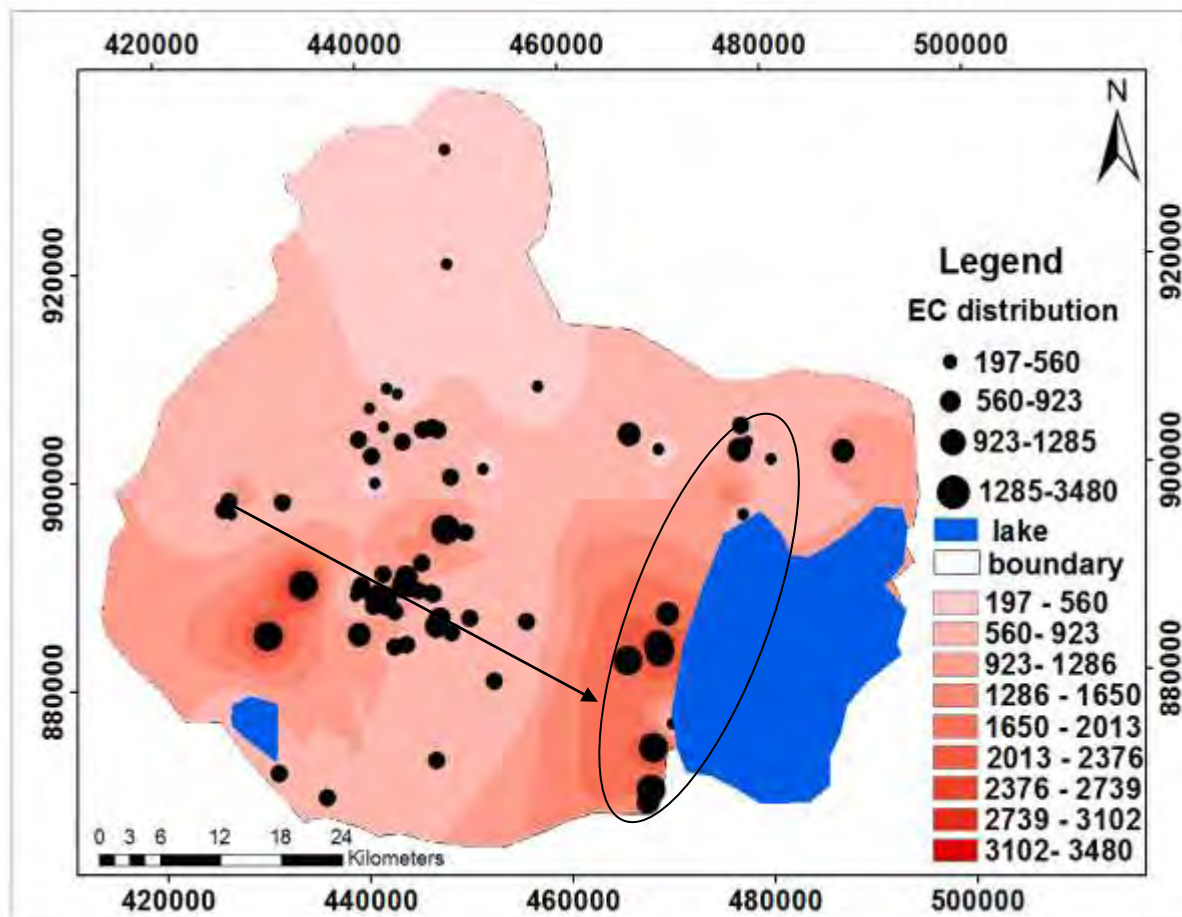


Figure4.3. EC distribution map of the Study Area

4.2.4. Total Dissolved Solid (TDS)

It is a measure of the amount of material (solid) dissolved in the water. This material can include calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulphate. Thenitrate, organic ions, and other ions such as silicates. The wide variations of the value in the study area are mainly due to three major reasons:-

According to (Dennis Nelson, 2002), factors that control the dissolved minerals in groundwater include:-

- Residence time of the groundwater in the aquifer, the value of TDS in the study area increases from Butajira-Koshe to Lake Ziway. This indicates that contact time of groundwater with rocks is longer and the interaction with different earth materials increases.
- The types of minerals that make up the aquifer, in Butajira-Koshe to Lake Ziway most of the area covered with acidic rock, such as ignimbrite, tuff, lacustrine sediments, which causes a reaction with aquifer and contribute high TDS to ground water.

- The chemical state of the groundwater.

The minimum and maximum values of total dissolved solid in the study areas are 240mg/l of sample TWSs1 at SodoRenfense and 2090mg/l of sampleTwp25 at Edokontola near Abosa town respectively. The $TDS=0.6079EC$ relationship for collected and analysis water sample result.

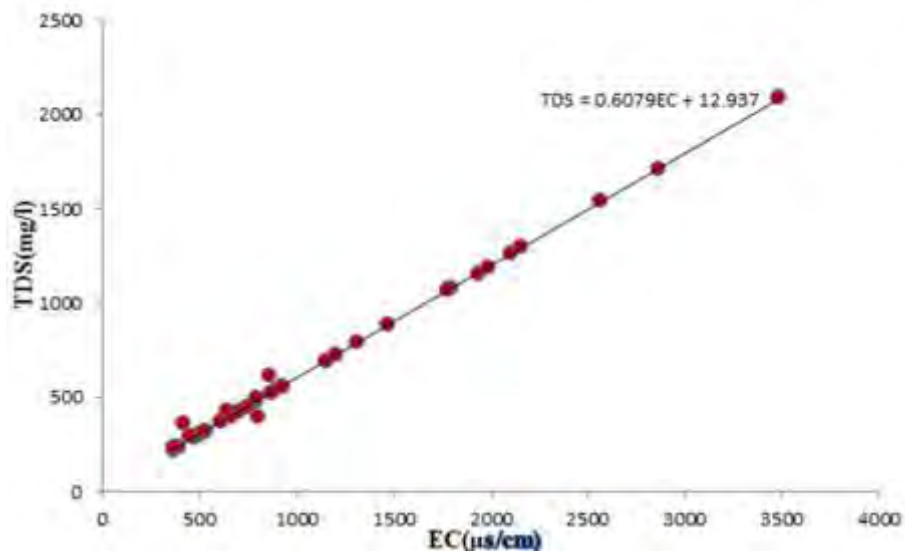


Figure4.4.1 TDS vs. EC

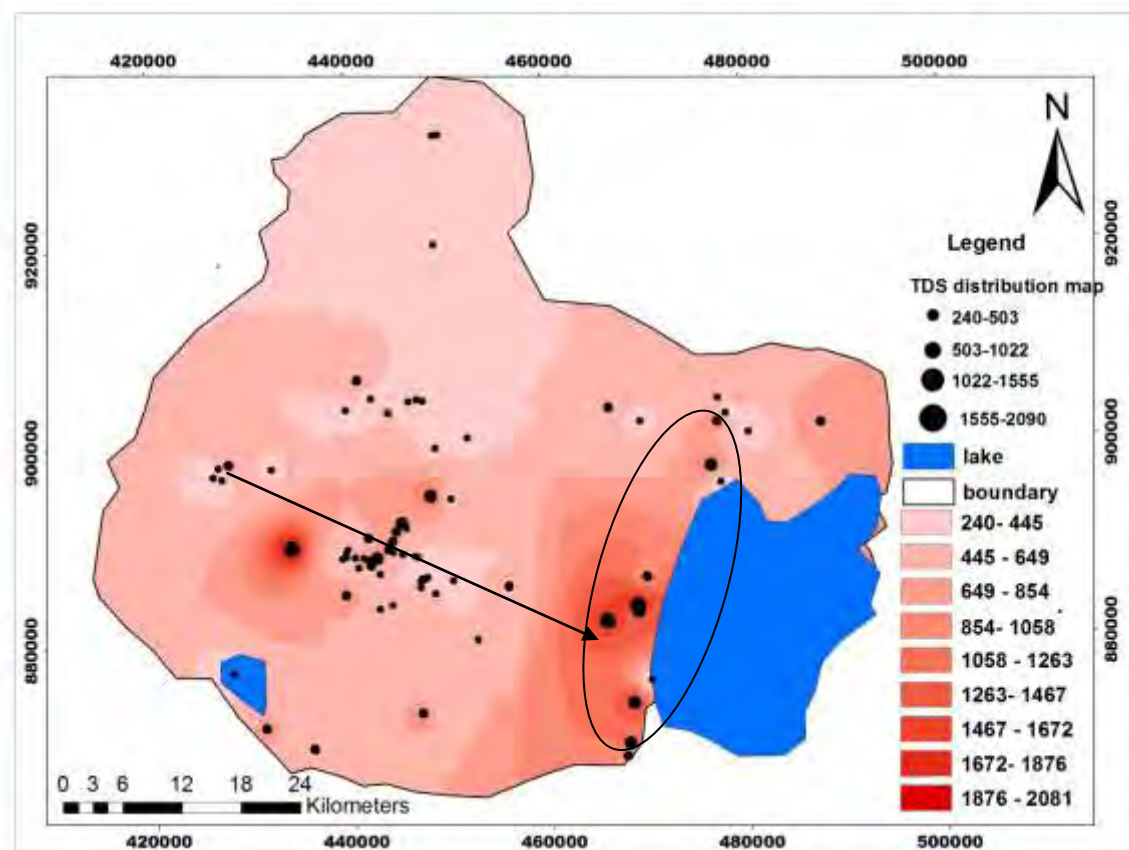


Figure 4.4.TDS distribution map of the Study area

4.4. Geochemical characteristics of major cation and anions

The major cations and anions which have been considered within the study areas are sodium, calcium, magnesium, potassium, bicarbonate, carbonate, chloride and sulphate. The collected and analyzed water samples illustrate that water chemistry changes in different parts of the groundwater flow system. From recharge area to discharge area, the concentrations of various components such as Na^+ , HCO_3^- and F^- in hydro-geochemical system generally increase towards discharge zones (towards Lake Ziway) and the hydro-chemical type generally changes from $\text{Ca}(\text{Mg})\text{-HCO}_3$, Ca-Na-HCO_3 and Na-Ca-HCO_3 to Na-HCO_3 type of water.

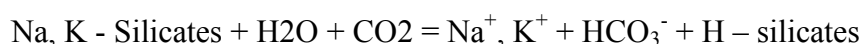
Sodium is the dominant cation followed by calcium and magnesium and Bicarbonate is the dominant anions which also followed by chloride and sulphate within the volcanic aquifers of the study area (fig4.5). Sodium shows significance variation ranges from 32 to 910mg/l. The Na^+ concentration ranges from minimum values in the high land and rift escarpments to maximum values in the rift floor close to Lake Ziway. The dominance of Sodium in the study area is likely to be attributed to the dominance of the acidic volcanic rocks, mainly volcano

lacustrine sediment, ignimbrite, tuff, rhyolite and weathering of Na rich feldspar. In addition this Na dominance could be attributed because of long time of water-rock interactions.

Calcium ranges between 6mg/l to 96mg/l in the ground waters of the study area, the minimum and maximum value is located Edokontola (Twp25) and at Twp27 in the butajira area respectively. This high value is due to the fact that rain water is recharge of the well through infiltration from rain water of surrounding highland and waja river drainage. While low-Ca groundwater conditions arise in volcanic regions dominated by alkaline volcanic rocks (e.g. Ashley and Burley, 1994; Kilham and Hecky, 1973) and also in conditions where cation exchange occurs naturally. Since, removal of Ca^{2+} is achieved by exchange with Na^+ from clay minerals.

Magnesium follows the same trend as calcium but lower than calcium may be due to the fact that magnesium is present in a much lower concentration than calcium in most igneous rocks of the study area. Its range is between 1.9mg/l to 22.1mg/l and this maximum range of magnesium is located at Twp52 of inseno well while lower value was located at Twp25 of Edokotola hand dug well. This maximum value may be the results of surrounding recent basalt which contain high content of ferromagnetic minerals.

Bicarbonate is the dominant anion in the catchment and its proportion to carbonate was being controlled by the P^H values of respective groundwater samples. The carbonate concentration in the study area ranges from 291mg/l to 2170mg/l at Meki River and hand dug well near Lake Ziway. The high concentration of bicarbonate is derived from atmospheric and magmatic CO_2 (Gashaw, 1999), according to the reaction



Chloride is another anion known by its conservative nature in the chemical evolution process and good indicator of the relative age of ground water compare to other major ions. Even though, more important source of Cl is association with sedimentary rocks, volcanic gases from geothermal fields may also introduce in the ground water system and in some rift lakes (Tenalem Ayenew, 2005). The chloride value of the study area ranges from 1.2mg /l to 131mg/l at inseno to near to Lake Ziway respectively. Generally, Cl concentration increase from western highlands and rift escarpment towards the floor of the rift. The main chemical reactions control solubility of fluoride in natural waters are: ion exchange reactions, dissolution reactions and precipitation reactions (Gashaw, 1999).

Sulphate concentrations in the study area are range from 0 to 160.68 mg/l at the Lake and shallow well (Twp74) at Ziway Town. The Schoeller plots are used to show the dominant cation and anions respectively.

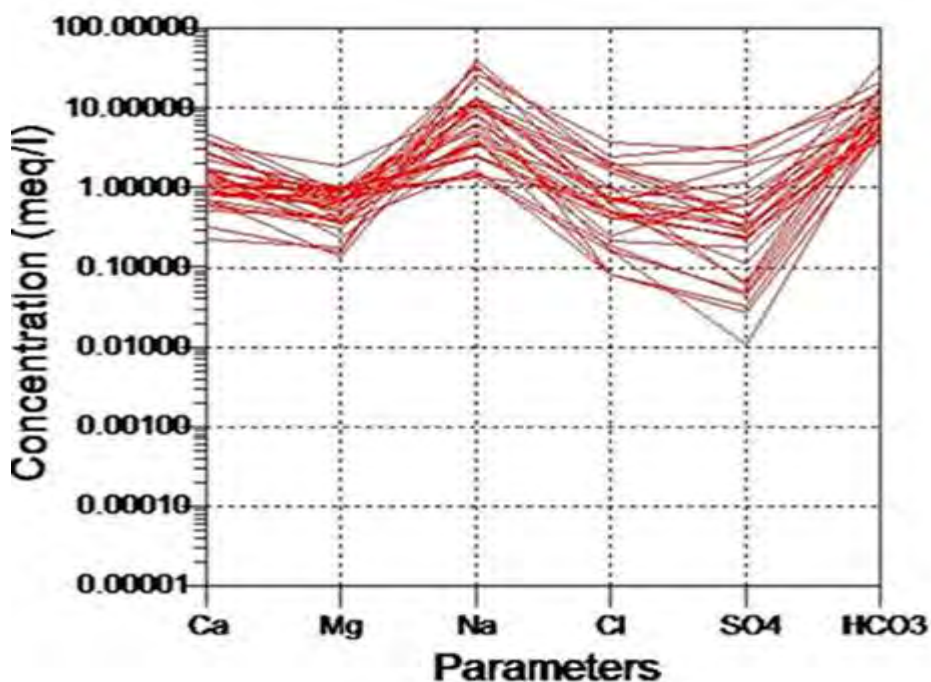


Figure4.5Schoeller plot of major cat ion and anion

4.5. Minor anions

The most essential minor chemical constituents for consideration in the study area are nitrate and fluoride concentrations.

4.5.1. Nitrate

The nitrated concentration in some the hand dug well and boreholes of the study area range from 0.5 to 90.4m/l which is above the maximum permissible contaminant level of WHO (2004) drinking water quality standard is 50 mg/l.The relatively higher nitrate value (90.4 mg/l) observed in some sallow hand dug wells in the study area is attributed to the agricultural practices. Most shallow wells are located at a downstream of extensively cultivated farmland. In this case both the synthetic fertilizers and the manures should have their own contribution as people use both in up grading the soil fertility of their farm land in

the area and lowest value of (0.5mg/l) TWM28 at Semen koshe. Excessive presences of these ions in drinking water are very serious public health problems.

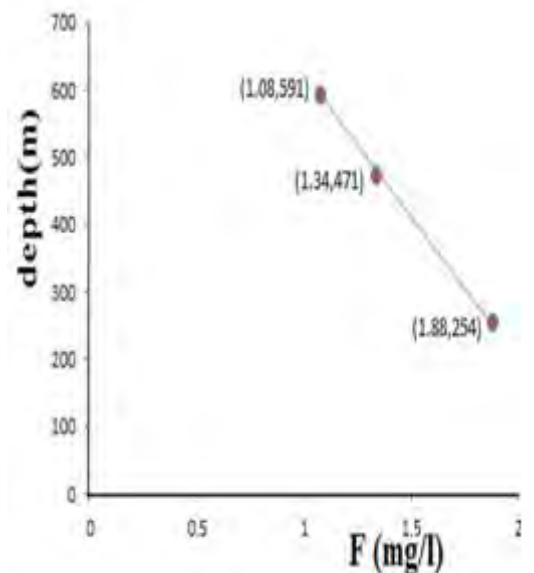
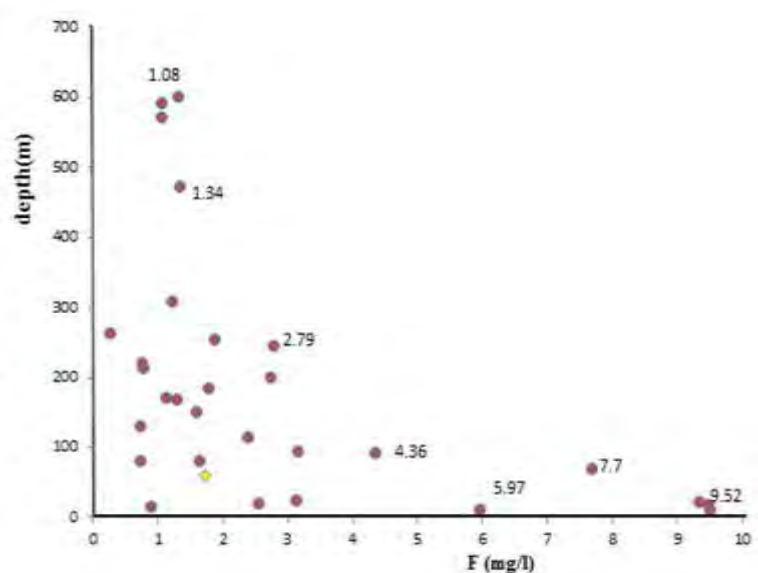
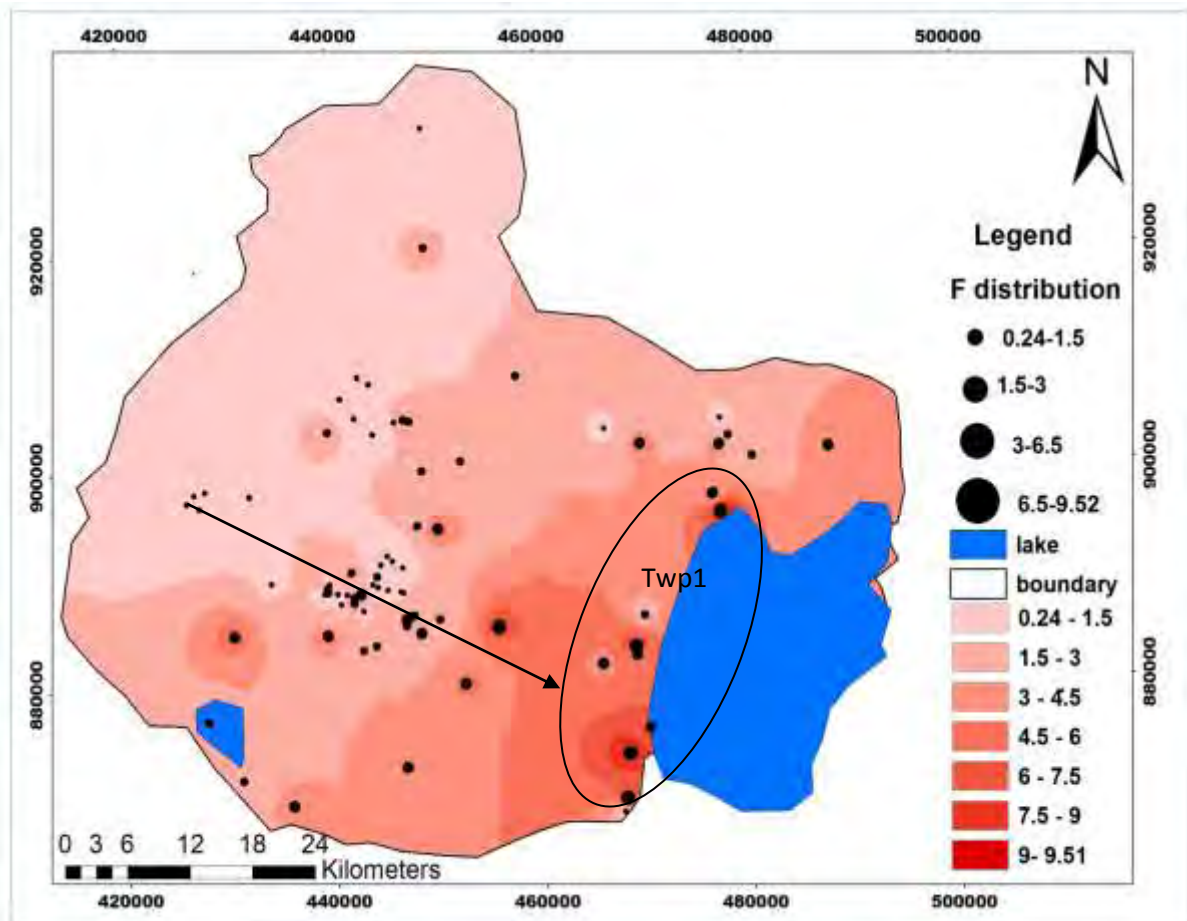
4.5.2. Fluoride of the Study Area

Fluoride is released into the groundwater mostly through water–rock interaction of fluorine-bearing mineral and leaching out the fluoride from easily weathered and redeposit volcanic rock/ sediments is the source of high fluoride levels in water resources of the area. The concentration of fluoride can furthermore be influenced by ion exchange with micaceous minerals and their clay alteration products as the cause of the F- enrichment in groundwater. Moreover, pH rise changes the water into a strong anion exchange medium for the exchange of hydroxyl ions for fluoride, favoring high fluoride concentration. The principal reservoirs for F ion in nature are rock forming silicate minerals containing OH ion in their structures (Seifukebede, 2013). The fluoride solubility and enrichment can be increased by weathering of the volcanic rocks in extended time particularly conspicuous in these tropical environments because high temperature and humidity promote high rates of weathering (Hecky, 1973)

Most of the fluoride in groundwater comes from acidic volcanic rocks such as tuffs, fluvio/volcano lacustrine sediments, pyroclastic deposits, ignimbrite and rhyolite. The leaching process is facilitated by high permeability and rock water interaction with in the fluvio/volcano-lacustrine sediment and pyroclastic fall deposits (Rango, 2009, Gashaw, 1999). The most important sources are acidic volcanic rocks such as tuff, pumice and obsidian and emanations from geothermal systems (TesfayeChernet, 1982; Chernet et al., 2001). High F in saline lakes of the East African Rift reflects the nearly complete removal of Ca by carbonate precipitation usually as calcium carbonate ((Kilham and Hecky 1973, Darling et al. 1996, Gizaw 1996; Chernet et al. 2001) probably from CaF_2) due to groundwater in volcanic terrain rapidly reach saturation with respect to carbonates of Ca and Mg (calcites, aragonites, magnesites) prior to carbonates of Na and K and mineral of F (e.g. $\text{Ca}_5\text{F}(\text{PO}_4)_3$, CaF_2 , MgF_2 , NaF). The fixation of Ca to carbonate minerals will lead to significant under-saturation of groundwaters with respect to CaF_2 .

The fluoride guideline values for World Health Organization and Ethiopian drinking water quality guidelines are 1.5 and 3.0 mg/l respectively (MoWIE, 2003). Fluoride values over 3 mg/l commonly occur in the Ziway Plain and Tora-Koshe-Dugda ridge. The fluoride concentration in the study area ranges from 0.27 to 9.49mg/l for ground water & 9.52mg/l for lakes respectively. The fluoride distribution map of the study area is presented to identify

high and low-fluoride zone both in laterally and vertically (depth wise) and will help to correlate with its source (fig4.6). The map is prepared based on existing and new fluoride data collected from different woredas. The fluoride distribution map is apparent that the variations of fluoride from place to place are closely associated to variation in geology and fault-controlled flow (the type of rock and tectonic structures.) The map is useful in identifying high-risk area which corresponds with the complex spatial distribution of the volcanic rocks and their associated structures. The highly fluoride enriched groundwater zones is confined in central area known for dominant fluvio/volcano lacustrine sediments, rhyolite and welded tuff areas located close to lake and major geothermal centers. Tectonically fault zones in the area are commonly characterized by thermal water that has an important influence in the spatial distribution of fluoride. The hot springs and wells drilled close to thermal centers have very high fluoride and those waters are controlled by fault-related systems. In this context, the thermal springs are developed by geological structures that allow mineralized deep groundwater's to ascend towards to surface and interact with shallow aquifers. The waters which (emanate) originate from highland, surface and marginal faults are related to fast circulating groundwater and surface water of low ionic concentrations and fluoride. The general groundwater flow direction indicates that highland water can infiltrate to the rift system and changes the ionic composition of the waters along the flow path. The high spatial ionic variations follows systematic trend reflects the different groundwater flow systems. When the faults act as conduits of fresh groundwater circulation, the surface water tends to dilute the groundwater system through large step-faults. Lake water and rivers have low ionic composition and fluoride than groundwater, except where they are influenced by the discharge of thermal springs. On the other hand the fault-controlled aquifers with dilution effect of substantial meteoric and highland water can be a source of good quality of groundwater.



Fluoride vs. depth with different location

Fluoride vs. depth with the same location

Figure 4.6. Lateral and Vertical fluoride distribution of the study Area

4.6. WATER type and Ground water flow path

Water type classification of deep bore holes, shallow wells and hand dug well, lake, and river waters are made to observe the major water groups, their relationship and evolution along the flow path by using a piper diagram and Microsoft excel (2010) graphical presentation method. The majority of the shallow well, dug wells and Boreholes from the highlands and escarpments are calcium -magnesium-bicarbonate and Calcium-sodium-bicarbonate water type. These types of waters are often regarded as recharge area waters which are at their early stage of geochemical evolution. In the majority of waters from the rift floor boreholes, shallow wells and hand-dug well sodium dominate their cation species and bicarbonate dominate their anions. The groundwater's fall in the Na₂HPO₃ and NaHCO₃ type, indicating long duration of rock-water interaction.

The major cation and anion ratio indicates that Ca^{2+}/Mg^{2+} , $Ca^{2+}+Mg^{2+}/Na^{+}+K^{+}$ ratio decrease along ground water flow path (upstream towards downstream) maybe due to removal of calcium with bicarbonate. This variation in ionic ratio used to identify recharge area and flow direction following ground water flow path while the Na/HCO_3 , $Na/\sum cat$ ions, $HCO_3/\sum anions$ ratios are increase along ground water flow path indicates the increase of rock water interaction and long residence time of water in the ground.

The concentrations of **in-situ** physical parameter measured in the field and concentration of fluoride from laboratory are also increase following the ground water flow path (from west to east) indicate long residence time/ water- rock interaction as shown from fig 4.9.

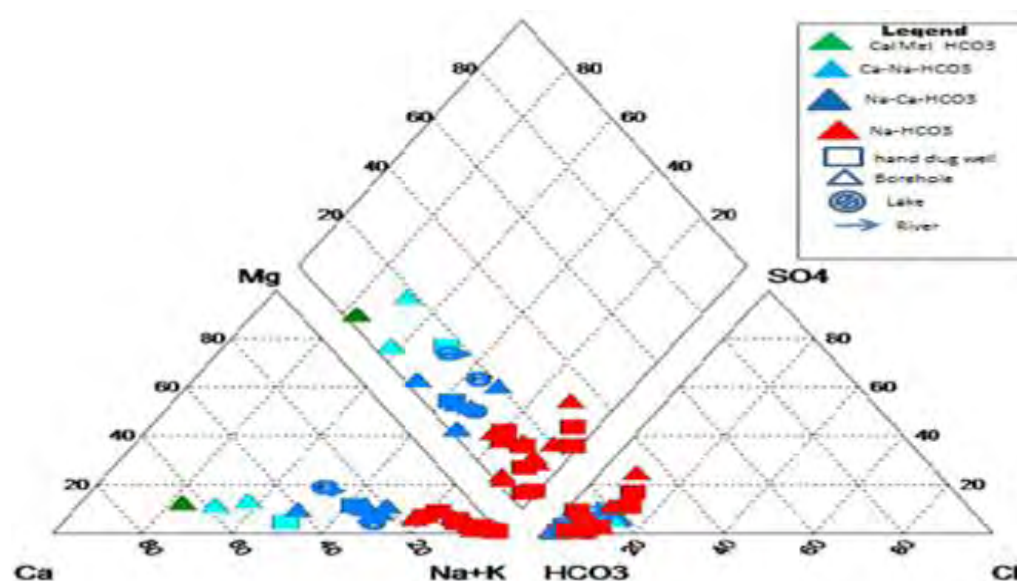


Figure4.7. Piper diagram of different water type in the study area

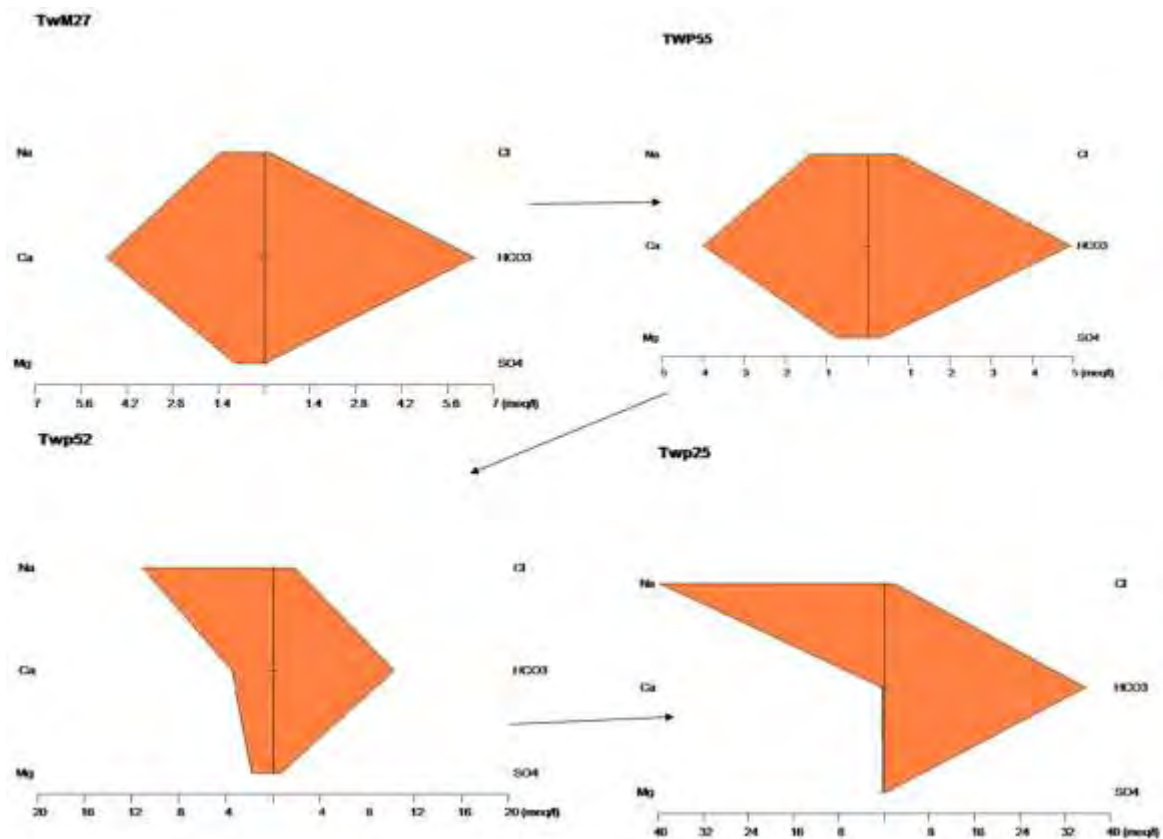


Figure 4.9. Hydrochemical evolution vs elevation/altitude along ground water flow path

Based on hydrodynamic regime the study area may be categorized into three hydrogeochemical zones: - Highland and Escarpment, Transitional and Enrichment zones.

4.6.1. The Highland and Escarpment zone

This region mainly concerned on the Butajira Highland and escarpment and the recent basalt, scoria cones region in the western escarpment situated west of Lake Ziway. When meteoric water containing the considerable amount of CO_2 infiltrates in to the groundwater it introduces HCO_3^- to the groundwater. Generally, groundwater of this region is dominant $\text{Ca}(\text{Mg})\text{-HCO}_3^-$ and Ca-Na-HCO_3 type in which cation enrichment (Na, Ca, Mg) is variable depending on mineral variations within the reservoir and the extent of weathering (Chernet et al., 2001). Most water samples of this zone have TDS less than 600mg/l and the major ions concentration in the groundwater is low suggesting that the groundwater has little interaction with the rock that hosts it. The spatial distribution of Fluoride shows which is relatively well structured in addition to Low contents of fluoride characterizes the waters from the high elevation zones, the escarpments and the plateaus.

4.6.2. The Transitional Zone

This zone located next to the Highland and Escarpment within Inseno area and the groundwater tends to evolve from Calcium-sodium-bicarbonate(Ca-Na-HCO₃) type to Sodium-Calcium Bicarbonate(Na-Ca-HCO₃) type with low concentrations of cations. TDS is a general indicator of the extent of mineralization of groundwater. Most water samples of this zone have TDS values less than 800 mg/l. Thermal springs generate an increase in sodium and bicarbonate alkalinity then the water chemistry remains controlled by Na⁺ and HCO₃⁻, while the Cl⁻ and SO₄²⁻ enrichments are more variable.

4.6.3. The Enrichment Zone

This zone located in the Ziway area and Tora-Koshe-Dugda ridge in which water tends to evolve from sodium- calcium- bicarbonate type with low concentrations of cations in the recharge zone to sodium- bicarbonate water in the acidic rocks and lacustrine sediments of the rift floor. Salinity increases from the recharge area that is characterized by high rainfall and low evaporation to the region of low rainfall and high evaporation of the rift floor. TDS is a general indicator of the extent of mineralization of groundwater and most of the water samples collected in this zone have TDS values greater than 1000mg/l. Alkalinity is, in any case, greater than the equivalents of calcium which characterizes the chemical weathering of the volcanic rocks in the Main Ethiopian Rift. When these waters concentrate, the alkalinity increases despite the precipitation of the calcite and the molality in calcium decreases and stabilizes. The problems of rising are the alkalization and the solidification of the complex exchange which induce degradation of the physical properties of the soils and a lack of mineral supply to the vegetation (Chernet et al., 2001). The groundwater shows fast evolution from Calcium bicarbonate type to sodium bicarbonate type within the short distance in the order of about 40 Km between the escarpment and the rift plain. This is due to the long residence of the groundwater in the rift valley that results in the reaction and dissolution of different minerals.

4.8. Isotope Hydrology

Environmental isotopes now routinely contribute to groundwater investigations, complementing geochemistry and physical hydrogeology. Measurement of the stable isotope composition of salinized water is a useful method for discriminating the cause of salinity because water that is saline due to evaporation will be isotopically more enriched than the source water, whereas water that is saline due to salt addition or transpiration will not change isotopic composition. The stable isotopic composition of water for instance, is modified by

A water molecule is composed of oxygen and hydrogen, which occurs with different isotopic combinations in its molecules. The isotopic composition of precipitation containing these two elements may be reflected directly or modified in the composition of groundwater. The modification of groundwater composition may be due to fractionation or separation of heavier and lighter isotopes because of evaporation processes (phase changes) prior to infiltration or isotopic exchange with aquifer matrixes (Mazor, 2004). The common practice is to plot water sample data on $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ diagrams, along with the meteoric line of local precipitation as a reference line. The meteoric line is a convenient reference line for the understanding and tracing of local groundwater origins and movements using conservative isotopes of water molecules ($\delta^2\text{H}$ and $\delta^{18}\text{O}$). In order to trace the source and mechanism of groundwater recharge isotopic signature of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the groundwater sample are used and 30 representative water samples are gathered from the western and northern part of the lake Ziway sub-basin during field work (Fig 4.11 and appendix2) from different sources (such, dug wells, river water emanating from Highlands, boreholes and analyzed at Addis Ababa University (AAU) isotope laboratory.

4.8.2. Deuterium ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotopes

Deuterium ($\delta^2\text{H}$) and Oxygen ($\delta^{18}\text{O}$) are the most widely used stable environmental isotopes in various hydrological sciences for investigating water resource development and management. The stable isotope content of water molecule $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ is expressed by convention as parts per thousand (‰) deviations relative to the standard VSMOW (Vienna Standard Mean Oceanic Water) VSMOW is standard water prepared from distilled seawater that was modified to have an isotopic composition close to SMOW (Standard Mean Oceanic Water) by IAEA (Clark and Fritz, 1997). This reference is identified as VSMOW and defining the value of δ (delta) = 0 and provide an appropriate reference for meteoric waters, as the oceans are the basis of the meteorological cycle. Delta notation (δ), which is commonly used to report isotopic concentrations of the analyzed water samples, is defined as:

$$\delta = \left(\frac{R_{\text{SAMPLE}}}{R_{\text{STANDARD}}} - 1 \right) \times 1000; [\text{‰}]$$

Where, R_{SAMPLE} and R_{STANDARD} refer to the isotopic ratios of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$. A positive δ value means that the sample contains more of the heavy isotope than the standard; a negative δ value means that the sample contains less of the heavy isotope than the standard. During phase changes, the ratio of heavy to light isotopes in the water molecules will be

changed. For example, as water vapour condenses into rain clouds (a process typically viewed as an equilibrium process), the heavier water isotopes (^{18}O and ^2H) become enriched in the liquid phase while the lighter isotopes (^{16}O and ^1H) remain in the vapour phase (depleted). The paleoclimatic effect in arid regions is manifested by depletion in stable isotopes with respect to modern waters (Seifu kebede, 2013). A plot of $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ for sampled waters readily identifies the influence of evaporation and the effects of mixing from different sources within the hydrologic system. Unevaporated meteoric waters are generally recognised by their proximity to the Global Meteoric Water Line (GMWL; Craig, 1961) whereas waters altered directly by evaporation or mixed with evaporative enriched water plot to the right of the GMWL ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ ‰ SMOW). LMWL of the basin is obtained from (Asela, Ziway, Silte, Butajira, and Awasa towns) rainwater that were collected by (Chernet, 1998) in the period of June-August (1994 -1995) and defined by $\delta^2\text{H} = 7.02 \delta^{18}\text{O} + 9.1$ (Rango, 2009). This equation (LMWL) is used in the basin to determine sources of ground-water recharge, to evaluate surface-water and groundwater interaction, and to analyses other geochemical and hydrologic problems.

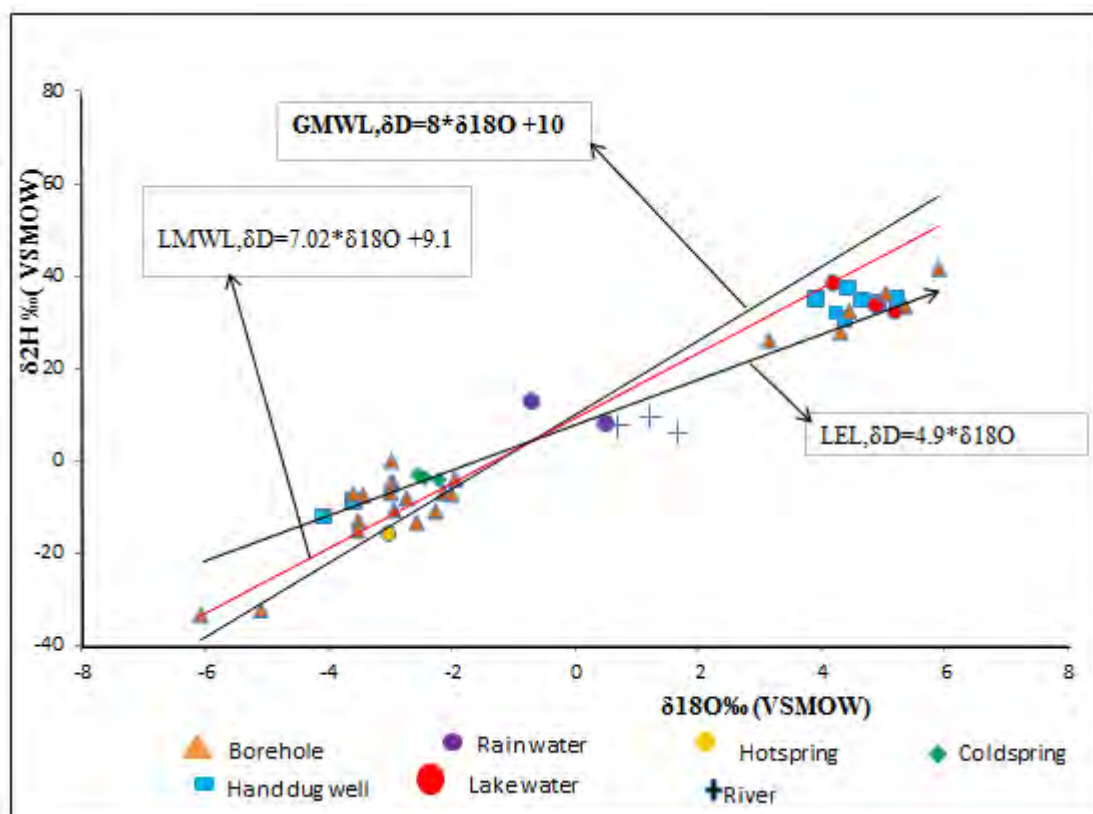


Figure.12. A plot of Deuterium ($\delta^2\text{H}$) vs. $\delta^{18}\text{O}$ isotopes of water samples

This figure has shown that the majority of ground waters, river waters and rain waters are plotted near the LMWL. This indicates the importance of present-day precipitation for groundwater recharge and mainly revealed as secondary fractionation or evaporation after condensation. The river water plotted near to the evaporative line with the slope of 4.9 values corresponding to extensive evaporation of rain droplets in dry atmosphere can take place resulting in enrichment of rainwater's and deviation from the global meteoric water.

The lake Waters are plotted far to the right and shifted right down of the LMWL. This shows that the lakes are more enriched with $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Waters from hot spring from Tulu Gudu island, cold springs, cold wells from Highland) are scattered at different positions on the plot and have differences in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ concentrations. The variations of isotopic concentrations between ground waters reflect the presence of different groundwater flow systems (ShemelisFikre, 2006). The sample collected from the borehole, hand-dug well, and cold springs in the Highland and escarpment started from sample Twp41 to Twp71, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic composition are slightly to highly depleted due to the altitude effect indicate that they are recharged by meteoritic water coming from Highland through infiltration from rainfall. whereas the samples collected from the rift floor near to the lake Ziway, Twp.(1,2,6,21,24,25,36,37,39,59,60,63,64)and Wl13, Lw29 samples are enriched with the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope due to the temperature effect which leads to evaporation. This enrichment of hand-dug and borehole well near to Lake Ziway indicates that there may be the interaction of lake water with groundwater. The collected isotopic data from ground water in the study area is characterized by both highly depleted and enriched isotopic signature. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values range from -6.08 to 5.9 and -33.4 to 41.63 in (‰) respectively. Most of the samples collected from the Highland and escarpment areas are plotted to the left of the GMWL or LMWL and highly depleted compared to Lake Ziway and its surrounding borehole and, hand-dug well. This depleted ground water from the deep wells of Highland and Tora-Koshe-Dugda ridge indicates that deep circulation of groundwater, long residence time and along flow path from adjacent highland. This depletion isotope in the highland is recharged from the summer rainfall related to the difference in source of moisture and to local meteorological processes.

4.8.3. Relation of stable isotope and Hydrochemistry

The integration of stable environmental isotopes such as $\delta^2\text{H}$, $\delta^{18}\text{O}$ and geochemical techniques are used for the investigation of the sources of saline water intrusion into potable fresh groundwater in various parts of the world (IAEA, 1997). During the processes of leaching salt formations or mineral dissolution, the stable isotope content of the water is not affected while the salinity of water increases. The enriched $\delta^{18}\text{O}$ isotope values are directly proportional to the hydrochemistry ($\text{TDS}, \text{Na}^+/\text{Ca}^{2+}$) which indicate high TDS value have also highly enriched in $\delta^{18}\text{O}$ (i.e. Twp25, 2090mg/l and 5.22‰ in $\delta^{18}\text{O}$). This is a unique feature which will enable identification of such processes based on isotopic and chemical data.

The Origin of high fluoride and enriched groundwater surrounding the lake is recharged from local precipitation and lake itself rather than meteoric water recharged directly precipitation (regional) from Guragae highlands.

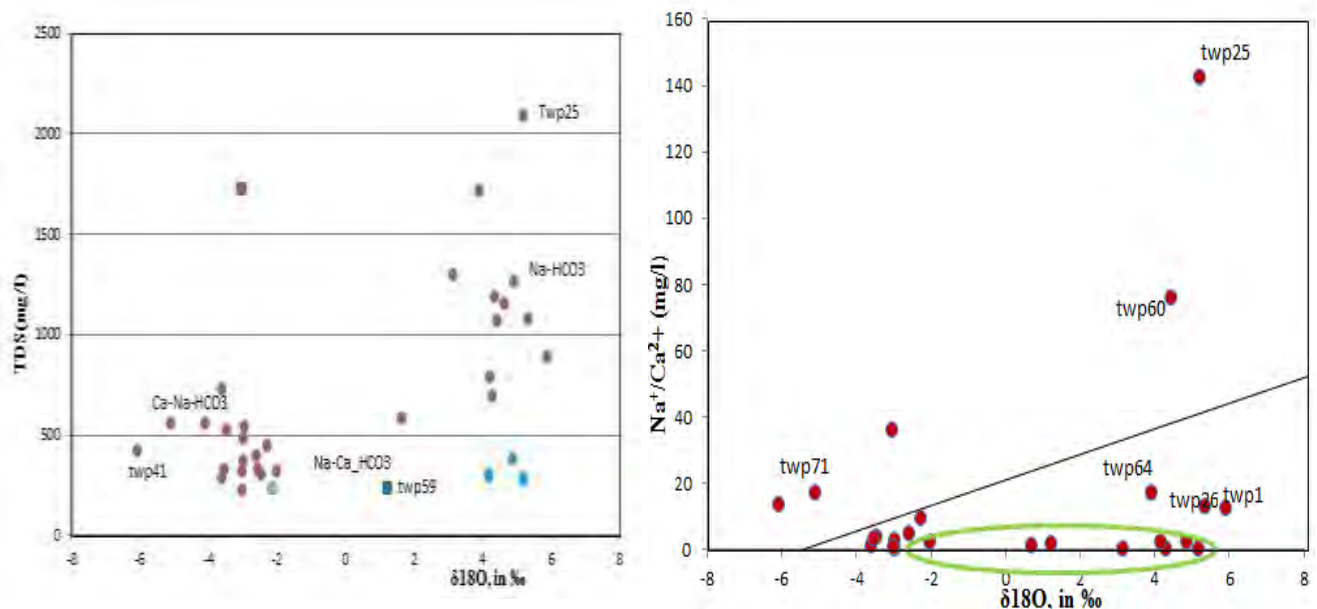


Figure4.13. Chemistry vs. isotope relationship

GENERAL DISCUSSION

The hydro chemical results obtained from the field data (appendix1) show that 76.7% of the samples (n=30) have fluoride concentrations above the permitted WHO standard (>1.5 mg/l) while 23.3% have concentrations below the standard (<1.5 mg/l, n=30). Isotopic and hydro chemical studies across the region revealed that some ground waters (hand dug wells) are affected by lakes. The results shows that there is a strong spatial variation of hydrochemical evolution along ground water flow path i.e. towards Lake Ziway (fig4.9). The highest salinity

and fluoride values are located at lower elevation of the catchment near to Lake Ziway and Adami Tulu Town due to strong rock- water interaction(interaction of fluvio-volcanic lacustrine sediment with water), long residence time and evaporation effect. Shallow ground water (hand-dug well) near to Lake Ziway shows high concentration of fluoride due to the leaching of weathered and redeposit volcanic rock, soil and intimate association(interaction) of lake with surrounding ground water (Chernet,1998,Ayenew, 2003,Rango,2009).The low concentration of TDS,EC and Fluoride in the highland waters indicates that fast circulation of meteoric water at shallow depth with that relatively at low temperature(Ayenew, 2008).Evapotranspiration leads to a precipitation of calcite, a lowering of Ca activity and increase in Na/Ca ratios, and this allows an increase in F levels.(Jacks, 2005)

The general trends of fluoride concentration along the transect increase from highland towards rift floor because of the welded /compacted rock with highly faulted geologic structure allows fast groundwater flow/circulation that didn't have time to dissolve rocks, while towards rift floor the geologic units changed to volcano lacustrine sediments which is the results of weathered and redeposit volcanic rocks are easily interact with water takes long residence time/reduced flow rate i.e. leads to increase fluoride concentration through leaching of rock and soil. Depth wise fluoride concentration indicate high at shallow depth, but decrease with depth (fig4.6).However, there is also low concentration within high fluoride zone (Twp1) due to its depth relative to others.

5. Factors for Fluoride Enrichment/low groundwater quality

5.1. Hydro chemical reaction/thermodynamics control

The role of thermodynamics is to control which kind of reaction is possible under a given rock type, temperature, saturation indices, and ionic activity. The plot of variables on a bivariate diagram further explains the geochemical processes involving the change in hydrochemicalfacies and the fluoride enrichment in solution

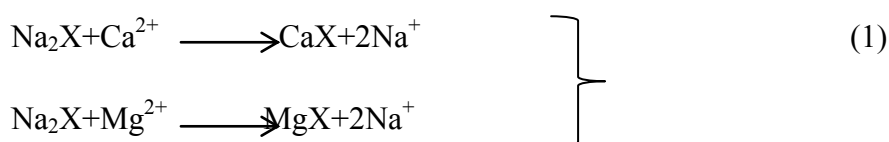
Correlation matrix of variable in mg/l

var.	pH	Cond	TDS	Na	K	Alk	Ca	Mg	HCO3	Cl	SO4	NO3	F
pH	1.0	0.288	0.314	0.405	2.2E-2	0.394	-0.772	-0.29	0.36	0.293	0.26	-0.306	0.324
Cond		1.0	0.972	0.916	0.694	0.912	-0.386	-0.202	0.917	0.719	0.515	0.236	0.576
TDS			1.0	0.909	0.688	0.894	-0.412	-0.258	0.907	0.756	0.569	0.213	0.559
Na				1.0	0.62	0.892	-0.534	-0.224	0.88	0.644	0.525	0.213	0.552
K					1.0	0.453	-7.3E-2	0.169	0.489	0.542	0.565	0.691	0.582
Alk						1.0	-0.441	-0.308	0.992	0.649	0.318	-3.4E-2	0.489
Ca							1.0	0.461	-0.41	-0.241	-0.274	0.268	-0.325
Mg								1.0	-0.288	2.0E-2	-2.7E-2	0.206	-0.161
HCO3									1.0	0.672	0.334	1.1E-2	0.497
Cl										1.0	0.72	0.312	0.384
SO4											1.0	0.508	0.449
NO3												1.0	0.25
F													1.0

Table 5.1. Correlation matrix of collected and analyzed water sample

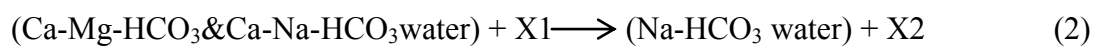
As shown from (table 5.1) of correlation matrix Na^+ , P^H , HCO_3 , salinity, TDS, have been positive relation with fluoride but calcium, magnesium has been negative relationship. In the positive correlation with ratios of Na^+/Ca^{2+} vs altitude increasing in the flow direction due to the decreasing of Na^+/Ca^{2+} with increasing altitude (fig 6a) and increasing of fluoride level with increasing Na/Ca ratio (fig 6c) indicates a systematic hydro chemical reaction involving the removal of the Ca^{2+} cation from a solution and addition of Na^+ cation by the solution from aquifer material in the flow process. The increasing of Fluoride, Na/Ca ratio in this direction is due to the uptake of Ca^{2+} by the aquifer materials in the exchange of Na depends on the nature of surface charge encounter (available) material and the reaction of cation in the solution.

Cations exchange is a reaction in which the calcium and magnesium in the water are exchanged for sodium that is adsorbed to aquifer solids such as clay minerals, resulting in higher sodium concentrations (Hem, 1985). The generalized reactions are as follow (Hem, 1985) and exchange process between cations of $(Ca^{2+} (Mg^{2+}) /Na^+)$ in the flow process can be represented by:



Where X represents aquifer minerals (aquifer solid) commonly found in volcanic rocks (plagioclase, Na-feldspar, clay minerals and to a limited extent calcite from secondary precipitate) in which the major cations can be derived. The increase in the Na^+/Ca^{2+} ratio in the flow direction (fig 6a) explain that when dilute water with dominant Ca^{2+} composition,

such as the Ca(Mg)-HCO₃, Ca-Na-HCO₃-type waters in highland areas, meets Na-materials(Na-feldspar), Ca²⁺ is selectively adsorbed close to the site and Na⁺ is up taken into solution(Furi et al., 2011). The process of enhanced fluoride enrichment in groundwater as a result of Ca²⁺ removal from solution which revealed that compositional changes in the groundwater from Ca-HCO₃/Ca-Na-HCO₃ to Na-Ca-HCO₃ and Na-HCO₃ types from the highland towards the rift floor, respectively. This geochemical reaction causes a systematic removal of Ca²⁺ from solution and enhances fluoride enrichment in the groundwater along flow direction towards the rift. This geochemical process involving a change in the hydro chemical facies in the flow direction can be represented as:



Where X1 represents aquifer minerals met in the flow path that release Na⁺ into solution such as plagioclase feldspar and are involved in the reaction depending on the saturation index of minerals, X2 represents altered rock materials that consume Ca²⁺ from solution such as calcite, Ca-silicate, and clay.

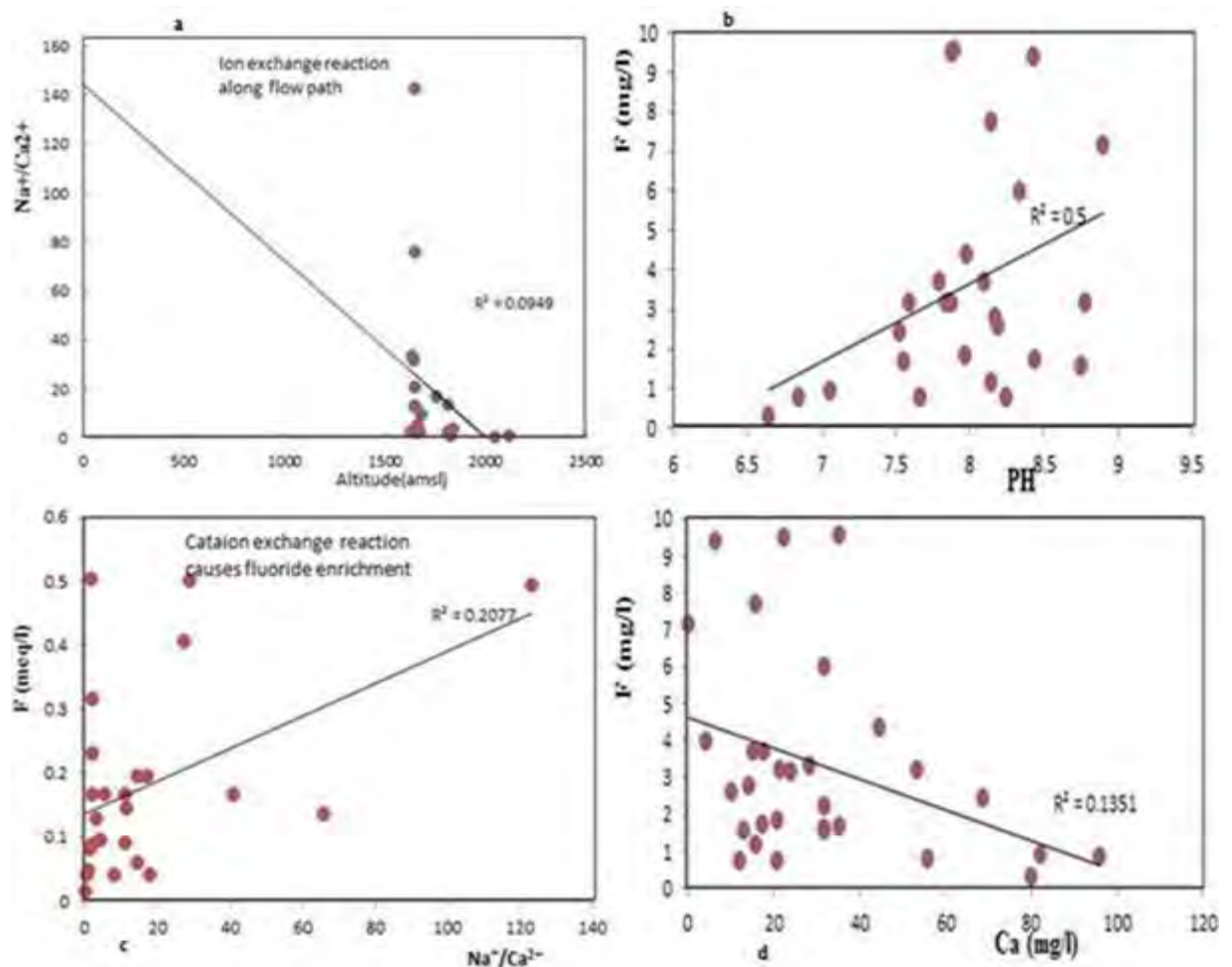


Figure5. (a-d) Bivariate plot of water variable

5.2. Geochemical processes

5.2.1 Geology/lithological variation—Rock type is an ultimate control of water quality as it determines the minerals available to undergo rock water interaction and release the ions to the groundwaters. It has strong influence on the concentration and distribution of fluoride which favorable geological and hydrogeological conditions enhance mobilization of the fluoride in local groundwater. Genesis of high fluoride waters are correlated with low Ca^{2+} concentrations and high sodium content due to weathering of sodium-rich alkaline igneous rocks causes increase a pH resulting in an increase in HCO_3^- and CO_3^{2-} by dissolution of CO_2 . Groundwater becomes oversaturated compared to calcite and calcite precipitation occurs, leading to a decrease in Ca^{2+} . This causes a sub-saturation with respect to fluorite and dissolution of fluorite increases the F- concentration (Coetsiers, Kilonzo, & Walraevens, 2009). A preliminary study of TDS/chemical elements relationships carried out by T. Chernet (1998) showed that: (1) in most diluted waters (escarpment and plateau waters); calcium content is increasing, and then decreases regularly. This change could be attributed to calcite precipitation; (2) the Na enrichment seems to be rather uniform and could correspond to dilution or concentration of a unique salinity source (silicate hydrolysis); (3) chloride and sulphate mainly follows an evaporative pattern, but are locally enhanced. This evolution may reflect a distinct secondary salinity source which involves salt supplies of different origins, like thermal springs of Kontane marsh.

The high fluoride content in the areas is also related to the dominance of volcano-lacustrine sediments in the Adamitulu jido Kombolcha and Dugdaworeda and the welded tuff in the Marekoworeda while good quality or low levels of fluoride in ground waters from these areas may be due to either to the absence of fluoride-bearing magmatic solution or of fluoride containing minerals in the strata through which ground water is circulating and also be due to too rapid fresh-water exchange, with the result that the normal process of concentration through evaporation or evapotranspiration is not very effective in raising the fluoride content of the ground waters to the values prevalent in some areas of fractured ignimbrite and basalt units in the highland . The solubility and enrichment of fluoride can be increased by weathering of the acidic volcanic rocks in extended time but fast circulating groundwater tends to dilute the water. Sample collected (Twp55at Butajira&Twp74at ziway) showed that fluoride content range from 0.27 mg/l to 9.49 mg/l respectively. The evolution of groundwater chemistry in relation to fluoride enrichment is controlled by dissociation, precipitation and cation-exchange reactions (equation 1). Several authors have indicated that the occurrence of elevated fluoride is mainly associated with the presence of Na- HCO_3 water type that are common for almost all ground waters in the Rift Valley (e.g Rango et al., 2009). According to Rango et al. (2009) elevated fluoride concentrations exist in wells that have low Ca^{2+} content, which controls the precipitation of fluoride as fluorite. Groundwater

characterized by Na-HCO₃ water type and low Ca²⁺ has always very high fluoride content. The high concentration of Na in the rift waters is likely to be attributed to the dominance of the acidic volcanic. Fluoride solubility can be increased as result of precipitation at high p^H, which removes Ca²⁺ from solution allowing more fluorite to dissolve (Chernet et al., 2001).

5.2.2 Dilution Effect

Differences in water quality were noted among the samples collected from surface water, boreholes. Concentrations of fluoride appeared to decrease slightly with depth due to dilution effect in the process of surface water and ground waters interaction as highland water recharge. This is mainly the case when the wells are close to major perennial rivers (e.g. Woja River) and the infiltration water that lack enough time for the influence of mineral weathering of the volcanic rocks. Groundwater's including springs tend to contain higher fluoride concentrations than river because groundwater contact with the surrounding rocks for longer time than surface waters.

A vertical water chemistry variation is noted in borehole constructed recently in Koshe town water supply test well and Samples taken at various depth of 254, 471, and 591 meters shows different water chemical composition (from table 5.2). The water analysis below revealed that the sodium and fluoride contents decrease with depth while the calcium concentration increases suggesting dilution effect that might be attributed to the control of geological structure in groundwater circulation. Analysis of fluoride concentrations of the samples indicated that highest fluoride contents were found in Twp25 (9.36mg/l) & Twp74 (9.49mg/l) surrounding the lake Ziway respectively in shallow ground water. The surrounding villages are entirely dependent on water from shallow (hand-dug) wells of vary quality. The area is highly mineralized shallow aquifer with salty build-up due to long resident time, strong rock water interaction, evaporation enrichment effects related with low elevation and high temperature at the top soil layer that appears to cause high TDS and fluoride water. The mineralization is attributed to cyclic evaporation of mineralized water of the wetland on the flat area. Groundwater quality in shallow aquifer in the Ziway area and some parts of Western Mareko locations is generally showed that high salinity which indicating that water quality of these area affected by increasing salinity due to above mention reason & in the soil.

depth of well	254m	471m	591m
TDS	460	430	430
EC($\mu\text{s}/\text{cm}$)	678	626	628
p ^H	8.15	7.97	8.14
Na ⁺ (mg/l)	128	104	91
Cl ⁻ (mg/l)	0.91	5.46	2.73
Ca ²⁺ (mg/l)	22.4	51.20	53.6
Mg ²⁺⁺ (mg/l)	14.4	10.56	7.2
F ⁻ (mg/l)	1.88	1.34	1.08
Alkalinity(mg/l)	348	360	352
Nitrate(mg/l)	2.33	12.34	11.21
Bicarbonate(mg/l)	348	439.20	429.44
sulphate.(mg/l)	37.12	8.09	0.11

Table 5.2 Fluoride concentrations with different depth in the same location of Koshe town test well

5.2.3. Saturation index (mineral equilibrium)

Weathering of Na-feldspars consumes protons and causes a rise in p^H due to this p^H increase, the equilibrium with CO₂ will no longer be attained, and more HCO₃⁻ and CO₃²⁻ will be produced while more CO₂ will dissolve. The increase in HCO₃⁻ and CO₃²⁻ results in calcite precipitation, as the solution becomes supersaturated compared to calcite. The precipitation of calcite causes a drop in Ca²⁺ which makes the solution sub-saturated compared to fluorite. Fluorite will dissolve leading to elevated fluoride concentrations in groundwater. The high fluoride content in groundwater can be positively associated to sodium, alkalinity, TDS, EC and bicarbonate concentration whereas calcium is negatively correlated with fluoride. The saturation indices of fluorite and calcite of the collected and analyzed water samples were calculated using PHREEQC in which the result shows the samples of 93 % is oversaturated with respect to calcite, whereas, all sample except four have been found to be under saturated with respect to fluorite. The fluoride concentrations of groundwater are continuously enriched even after the groundwater reaches an equilibrium state with respect to fluorite (CaF₂) due to removal of Ca²⁺ by precipitation of calcite (CaCO₃). The sample Twp37 and MR7 indicate near equilibrium with respect to fluorite. These observations indicate that the higher concentration of fluoride can be explained by the fact that fluoride ions in groundwater can be increased as a result of precipitation of CaCO₃ from solution allowing

more fluorite to dissolve. In general, the saturation indices are used to express the water tendency towards precipitation or dissolution. The degree of water saturation with respect to a mineral is given by:

$$SI = \log (KIAP/ K_{sp})$$

Where: KIAP is the ionic activity product,

K_{sp} : is the solubility product, and

SI: is the saturation index of the concerned mineral.

When SI is equal to zero then the water is at equilibrium with the mineral phase, whereas SI values less than zero (negative values) indicate under-saturation and that the mineral phase tends to dissolve, while SI values over zero (positive values) indicate super saturation and that the mineral phases tends to precipitate. The most SI of Calcite groups oscillates around zero, suggesting conditions close to equilibrium for this mineral phase and calcite precipitation is unlikely, and cannot be considered the major cause of calcium depletion. This means that the observed hydrochemical evolution of groundwater from the highlands to the rift cannot be related to significant calcite precipitation. This in turn implies that cation exchange is the most probable process which leads to increase of F concentration in the local groundwater.

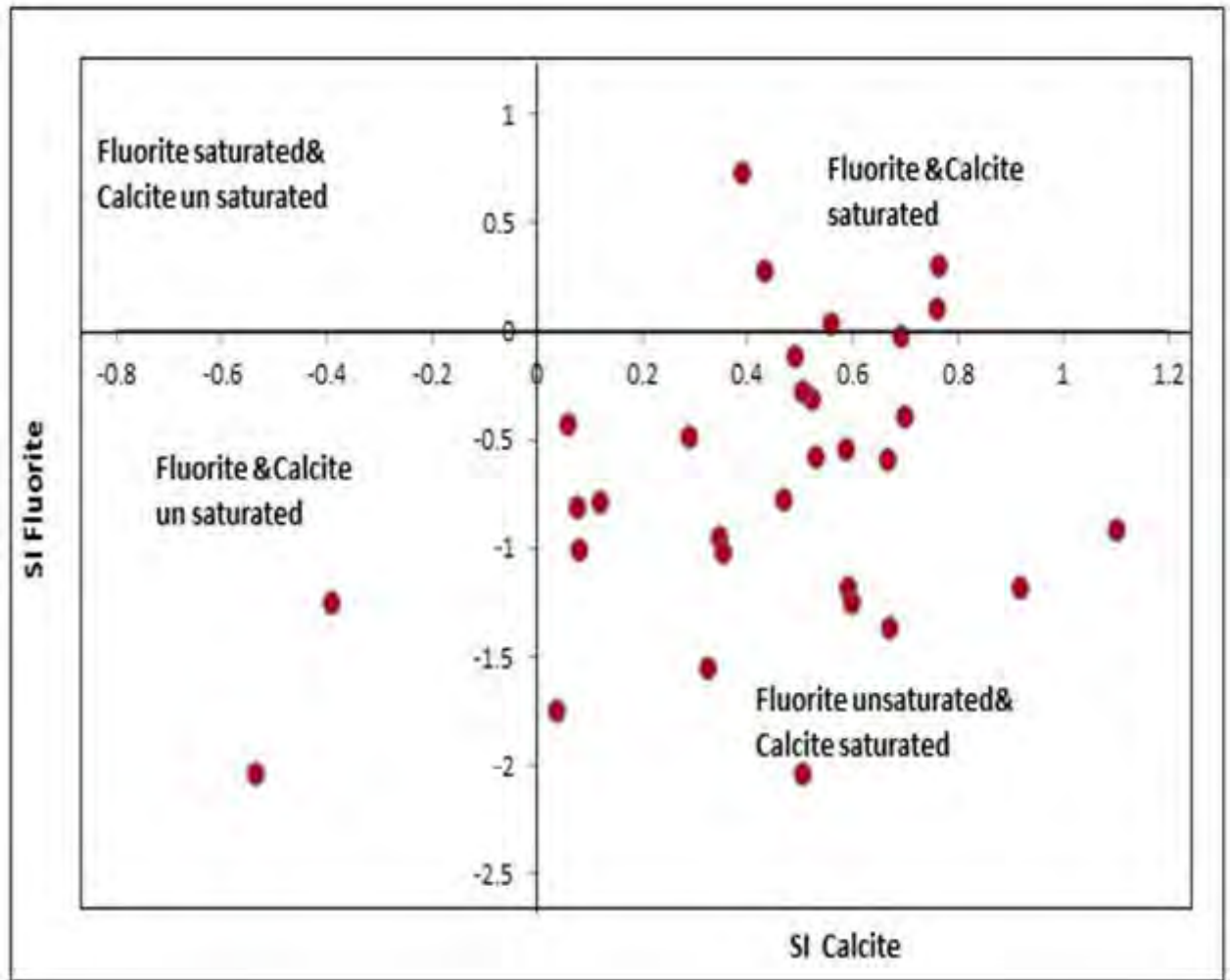


Figure5.2. Fluorite vs. calcite saturation

CHAPTER FIVE

Conclusion

Integrated hydro chemical and isotope techniques were applied to understand the genesis/source of fluoride, vertical and lateral distribution of fluoride, relationship of fluoride with lithological unit, groundwater flow system and interaction of lake with surrounding wells in the Meki River catchment. Interpretations of the graphical analysis coupled with that of chemical analysis results of the hydrochemical data and results from analysis of the isotopes data in the area are critically showed the high salinity and groundwater flow system.

- The majority of the highlands and escarpments waters have low TDS, EC and F of Ca-HCO₃ waters type. This shows that there is shallow groundwater circulation /at their early stage of geochemical evolution from direct recharge of precipitation and these waters have undergone no marked rock-water interactions.
- The increasing of salinity, total dissolved solid and change of geochemical evolution to Na-HCO₃ facies towards the lake Ziway indicate a long duration of rock-water interaction, and high evaporation
- The high spatial variations of major cations and anions follow systematic trend along the transect from W to E. This reflects that when ground water of highland and escarpment progressively migrating downhill reacts with different interacting lithology increase dissolved components and changes the hydro chemical evolution of waters towards rift floor.
- The high fluoride content in relation to the geological unit associated within the volcano lacustrine sediment and weathered welded tuff of rift floor easily interact with ground water and reduce its flow rate while the weathered & fractured basalt and ignimbrite of the highland and escarpment areas are good water quality due to dilution effect
- Genesis of high fluoride waters are related with low Ca²⁺ concentrations, shallow depth and high PH, alkalinity, salinity and high Na⁺ content ,mineral saturation, calcite precipitation and Na-HCO₃ water type.
- Groundwater becomes oversaturated with respect to calcite and calcite precipitation occurs, leading to a decrease in Ca²⁺. This causes a sub-saturation with respect to fluorite and dissolution of fluorite (CaF₂) increases the F⁻ concentration

- The lateral distribution of fluoride in the rift floor and Tora-Koshe-Dugda ridge shows high F concentration along transect following flow path beyond the WHO standard (1.5mg/l) and decrease with depth due to dilution effect and
- Shallow ground water (hand-dug well) near to Lake Ziway shows high concentration of fluoride due to the leaching of weathered and redeposit volcanic rock, soil and intimate association(interaction) of lake with surrounding ground water.
- The majority of groundwater (hand-dug well, borehole) and rain waters are plotted near the LMWL.This indicates the importance of present-day precipitation for groundwater recharge.
- The variation of isotopic concentrations between groundwater of Highland and Rift water reflects the altitude and evaporation effect in the groundwater flow systems.
- The stable isotopes signature of the deep groundwater of Butajira and Koshe areas showed highly depleted than aquifers found near to Lake Ziway. This indicates that the aquifer recharges through long subsurface flow from the adjacent highland recharged by rainfall and provides an evidence for deep penetration of recently recharged groundwater into the wide fault zone, indicating that the hydrologic condition of the fault is also an important factor controlling the occurrence of high F groundwater
- The high fluoride shallow ground water (i.e. hand-dug well) surrounding lake Ziway are enriched with $\delta^2\text{H}$ and $\delta^{18}\text{O}$ stable isotopes due to the extensive evaporative fractionation and recharged from the lake ziway rather than meteoric water directly infiltrate from highlands.
- The reacting of water with volcano lacustrine sediment for a long period could increase the concentrations of F in groundwater even after the groundwater reaches an equilibrium state with respect to fluorite (CaF_2) due to the removal of Ca by precipitation of calcite (CaCO_3). These observations reflect that rock chemistry, well depth, and geologic structure are the important factors controlling the occurrence of high F groundwater. However, high F ground waters are rarely observed in the fault zones of SDZFFZ where the associated fractures are widely developed.
- From the groundwater contour map, hydrochemistry and isotope result, shows that groundwater flows from highland towards Lake Ziway.

Recommendation

- Observation pipes should be installed in the existing and newly constructed boreholes especially for the wells that could be significant for scientific purpose
- Detailed work on rock-water interaction from hydrochemical, isotope and rock mineralogy
- It is strongly recommended to drill deep wells than shallow wells in the studied area especially near to lake Ziway for public water consumption to minimize fluoride concentration

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Fluoride Genesis in Ground water of Butajira_Koshe_ZiwayTransect Areas, in Central Ethiopia

Appendix1: Over all physiochemical analysis result of water sample in Ziway-Koshe-Butajira areas

Sample ID.	Longitude	Latitude	TDS	EC	Temp	PH	Na ⁺	K ⁺	T. H	Ca ²⁺	Mg ²⁺	Alk.	CO ₃ ²⁻	HC O ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻	Data source
Twp25	468906	883340	2090	3480	26	8.43	910	61	24	6.4	1.92	2002	134	2170	62.32	19.9	0.97	9.36	this study
Twp26	468990	882659	1075	1791	29.1	7.88	312	45	104	24	10.6	832	0	1015	74.6	19.1	0.82	3.14	this study
Twp36	467541	868129	690	1149	27.8	8.25	250	27	50	12	4.8	525	74.9	488.5	26.44	21.4	5.6	0.74	this study
Twp37	467853	869448	1298	2150	28.4	8.15	510	29	72	16	7.68	988	112	977	68.93	10.1	4.56	7.7	this study
Twp39	470120	875770	284	474	19.5	8.34	79	29	92	32	2.88	239	0	291.8	17	0	2.91	5.97	MoWIE
Twp41	447457	886437	421	702	18	8.17	195	20	56	14.4	4.8	442	0	539.2	5.67	2.34	4.86	2.76	this study
Twp42	446999	886226	477	792	20.6	7.98	119	29	164	44.8	12.5	429	24.9	472.6	17	5.49	3.15	4.36	this study
Twp51	443757	889463	725	1205	24	7.06	86	31	226	82.4	4.8	403	0	491.7	34.94	27.9	15.69	0.9	this study
Twp52	441756	890635	521	872	23.7	7.53	255	40	264	68.8	22.1	515	0	628.1	63.27	34.5	26.21	2.41	this study
TWP55	431997	897751	371	612	20.1	6.64	32	29	238	80	9.12	247	0	301.3	26.44	15.3	44.73	0.27	this study
Twp58/bh2	427005	896812	315	526	25.8	6.85	36	22	176	56	8.64	283	0	345.8	6.61	2.18	2.69	0.76	this study
Twp59	480377	900723	237	394	17.9	8.75	56	23	128	32	11.5	234	0	285.5	14.16	28.3	2.04	1.54	this study

Fluoride Genesis in Ground water of Butajira_Koshe_ZiwayTransect Areas, in Central Ethiopia

Twp60	476526	897409	1067	1779	26.6	8.19	790	30	48	10.4	5.28	1134	131	1117	21.72	3.16	0.56	2.57	this study
TWp63	477550	895728	300	500	21.7	7.9	80	27	120	35.2	7.68	252	25.2	256.2	17	16.6	2.02	9.52	this study
Twp67	477354	904197	447	740	26.5	7.67	197.5	16	100	20.8	11.5	341	0	415.5	17.94	10.6	1.21	0.74	this study
Twp69	478094	902659	317	527	22.2	7.56	83	18	124	35.2	8.64	291	0	355.3	7.55	8.42	0.5	1.65	this study
Twp70	480380	900736	394	657	24.5	7.97	105	18	70	20.8	4.32	333	0	406	15.11	11.6	1.17	1.8	this study
Twp71	466207	903427	557	930	28.2	8.15	270	33	80	16	9.6	325	37.4	320.4	22.66	92.4	0.63	1.13	this study
Twp74	468204	873525	1539	2560	24	7.88	750	110	100	22.4	10.6	746	0	909.5	85.93	160	90.4	9.49	this study
TwS1	435852	869258	616	860	24.9	7.59	148	26	169	53.4	8.64	483	0	589.3	25.2	13.7	8.5	3.16	this study
TwS3	427645	877058	296	450	22	8.27	58	8.8	129	32.0	11.9	227	14.4	247.4	17.5	11.1	18.25	2.2	this study
TwSs1	448882	920224	240	370	20	7.69	39.5	10	97.8	32	4.32	197	0	240.8	2.9	1.32	10.7	1.6	this study
TwM27	445207	888966	432	642	23	7.34	31	15	284	96.12	10.8	321	0	392	5.8	0.53	13.5	0.8	this study
TwM28	450174	886198	399	799	21	8.36	258.4	14	479	13.1	3.68	680	0	680	36.2	2.87	0.42	1.55	this study
TwM26	448380	884901	494	790	22.1	7.84	139	15	79.9	21.4	6.48	411		502	8.7	40.2	7	3.16	this study
TwD1	477198	901824	972	1120	23.8	7.8	300	16	73.3	17.8	7.02	315	0	384.3	2.9	1.58	7	3.7	this study
TwD2	469448	901986	360	420	25	8.01	94	10	95.5	28.5	5.9	315	0	384.3	2.9	1.58	7	3.3	this study

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TwA6	487538	901528	858	1030	28.7	8.1	300	19	44.4	15.13	1.62	666	4.8	802.4	25	55.4	7.5	3.7	this study
TwA7	465779	881853	1632	1920	29.3	8.67	600	20	20	4.4	2.2	1136	0	1269	131.9	138	7.5	3.96	this study
BH4	440020	888300	261		21.7	7.36	107.5	4.3	52	18.8	1.2	254	52	202	1.2	7	0.28	1.3	MOWIE(DH 2015)
BH6	448646	885794	528		22	7.66	202.2	31	28	8.4	1.68	450	37	413	7.8	7	0.3	5	MOWIE(DH 2015)
BH1	426868	899213	248	381	30.7	7.56	78	8	18.9	8.04	1.51	186	0	226.9	10.41	0.48	1.05	1.33	WWDSE 2015
BH5	446946	888984	400	629	31.5	7.55	92	11	120	42.4	3.36	332	0	405	3.64	8.2	9.56	1.79	WWDSE 2015
Mk3	439583	903579	386	644		7.43	64	4.2	240	64	19.4	400	0	488	9.5	8	3.52	2.5	MoWIE 2008
Mk4	442225	904758	322	534		7.19	54.05	0	190	28	29.2	260	0	305	7.5	0	44.5	0.5	MoWIE 2008
Mk8	427667	898301	810	1350		7.11	108	7.2	610	108	82.6	680	36	756.4	52.5	110	15.4	1.55	MoWIE 2008
Mk10	426169	897100	295	588		6.7	72	7.5	870	32	192	190	0	231.8	25.5	2.7	7.92	0.34	MoWIE 2008
Mk11	441230	899505	225	375		7.98	90	1.8	186	44	18.5	310	0	378.2	11	1.4	70	0.39	MoWIE 2008
MR1	455901	885579	511	850		8.9	305.6	14.2	1.77	0.11	0.36	425	0	385	31.9	25.3	Trace	7.15	MOWIE(DH 2015)
MR2	452621	880199	490	816		8.13	289	18.5	83.2	27.62	3.45	415	0	415	38.3	30.4	Trace	4.78	MOWIE(DH 2015)
MR3	444019	883804	495	824		7.78	251.8	19.1	103.8	26.86	8.91	420	0	420	21.3	20.3	Trace	2.86	MOWIE(DH 2015)
MR4	447088	886429	470	771		7.65	214.8	20.4	153.3	37.4	14.54	410	0	410	31.9	26.4	Trace	2.59	MOWIE(DH 2015)

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MR5	442808	883470	459	774		7.5 9	26 5.1	34 .6	15 8.8	51.5 8	7.2 7	470	0	470	23.4	11. 5	Tra ce	2.8 2	MOWIE(DH 2015)
MR6	442855	887029	402	670		7.7 9	15 9.2	14 .4	99. 6	20.2 1	11. 92	290	0	290	34	82. 9	Tra ce	0.4 1	MOWIE(DH 2015)
MR7	441906	887872	633	1053		7.5 1	16 6.2	16 .2	39 1.1	115. 1	25. 17	430	0	430	93.6	10 6.4	Tra ce	2.7 9	MOWIE(DH 2015)
MR12	450174	886198	399	799		8.3 6	25 8.4	13 .7	18 1.9	13.1	3.6 8	680	0	680	36.2	2.8 7	0.4 2	1.5 5	MOWIE(DH 2015)
MR13	446690	888662	439	876		7.8 8	13 1.6	12 .2	47. 9	30.9	9.5 2	370	0	370	36.2	4.5 5	3.4	1.4 8	MOWIE(DH 2015)
MR35	446444	888773	375	626		7.2 2	10 0	1. 6	11 6	100	21. 9	420	0	512. 4	7.5	0.5	26. 4	0.7 6	MOWIE(DH 2015)
MR39	439588	889537	418	702		7.2 3	84	5. 5	41 0	84	48. 6	440	48	439. 2	12.5	0.8	15	0.5 1	MOWIE(DH 2015)
MR41	440368	888672	230	459		7.3	32	1. 5	19 0	32	26. 7	196	0	239. 1	2.5	1.6	10. 56	1.3 5	MOWIE(DH 2015)
MR42	439432	888813	276	550		7	71. 2	3	26 0	71.2	19. 9	370	0	451. 4	2.5	2.3	5.2 8	1.6 8	MOWIE(DH 2015)
MR44	447688	886575	248	496		6.9	48	4. 1	21 0	48	21. 9	225	0	274. 5	4	1.4	34. 76	1.8 9	MOWIE(DH 2015)
MR46	445831	891099	288	575		7.1	18 4	22	85 6	184	96. 2	940	0	1147	1161	23 65	11	1.8 3	MOWIE(DH 2015)
MR47	441252	888594	909	1512		6.8 8	22 4	3. 6	89 2	224	80. 7	616	0	751. 5	105	40. 7	129 .8	0.5 5	MOWIE(DH 2015)
MR48	444549	891289	711	1184		7.4 6	44	6. 2	25 0	44	34	778	26.4	895. 5	30	3.8	12. 32	0.2 7	MOWIE(DH 2015)
MR50	439080	888655	200	399		7	32	3. 8	18 0	32	24. 3	216	0	263. 5	2.5	1.9	3.9 6	0.2 4	MOWIE(DH 2015)
MR53	440738	887646	386	769		6.8	12 0	5. 1	52 0	120	53. 5	530	0	646. 6	8.5	18	10. 56	1	MOWIE(DH 2015)

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MR54	442592	888612	1160	2320		8.5	3.2	6.8	30	3.2	5.4	830	0	944.3	16	58.1	15.4	4.5	MOWIE(DH 2015)
MR61	439437	889185	468	802		8.46	88.6	1	260	93.6	6.3	400	0	488	0.5	0	54.21	3.375	MOWIE(DH 2015)
MR64	450125	894490	367	612		7.81	72.1	0	180	56	9.72	300		366	4	10.6	11.6	5.35	MOWIE(DH 2015)
MR67	448119	894803	481	800		7.56	47.9	0	220	64	14.6	296	4.2	353	1	0.7	25	2.25	MOWIE(DH 2015)
SBH2	446742	872640	676	900		8.78	210	11		4.45	1.6	374	26.4	402.3	60.1	55.4	12.5	3.16	MOWIE(DH 2015)
Ss2	457559	908463	144	330		8.02	20.5	7.1		20.5	3.2	113	0	138.3	1	1.05	7.5	1.68	MOWIE(DH 2015)
Ss3	446896	904607	366	709		7.29	68	12		48.1	6.5	315	0	384.3	9.7	1.85	7.5	2.58	MOWIE(DH 2015)
SBH4	431044	871595	664	810		7.23	111	44		97.9	8.64	546	0	666	17.5	8.44	10.7	2.48	MOWIE(DH 2015)
Ss4	448587	899749	393	656		7.2	70.63	0.1		48	24.3	340	0	414.8	0.5	1.8	31	2.17	MOWIE(DH 2015)
Ss6	451897	900673	270	448		7.35	60.32	0.1		40	9.72	240	0	292.8	2.5	0.3	27.1	1.975	MOWIE(DH 2015)
Ss7	447478	904432	400	664		7.36	110.2	0		40	9.72	345		420.9	5	1	29	1.82	MOWIE(DH 2015)
Ss8	446006	904388	410	680		7.18	83.23	0		65.6	7.78	340	0	414.8	6.5	1.8	31	1.35	MOWIE(DH 2015)
Ss9	448997	931321	292	487		7.33	67.46	0		44	10.2	250	0	305	2.5	2.2	50.3	0.88	MOWIE(DH 2015)
Note: TDS-total dissolved solid, EC-electrical conductivity, T.H-total hardness, Alk-alkalinity																			

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Appendix 2: isotope chemical analysis result of water for the study area

Sample ID	Longitude	latitude(N)	Elevation	$\delta^{18}\text{O}$, in ‰	$\delta^2\text{H}$, in ‰	TDS	EC($\mu\text{s}/\text{cm}$)	Temp rature	p ^H	D= $\delta^2\text{H}-8*\delta^{18}\text{O}$	sample type	data source
TWP 1	469796	886237	1654	5.9	41.63	888	1469	27.9	8.44	-5.57	BH	this study
TWP 2	469723	886014	1654	4.23	31.92	789	1310	27	8.64	-1.92	HD	this study
TWP 6	469458	883754	1640	4.66	34.8	1153	1933	23.5	7.79	-2.48	HD	this study
TWP 21	469643	885338	1654	4.38	30.79	1186	1985	25.4	7.77	-4.25	HD	this study
TWP 24	469514	884237	1651	4.92	34.15	1265	2100	22.8	7.99	-5.21	HD	this study
TWP 25	468906	883340	1651	5.22	35.12	2090	3480	26	8.43	-6.64	HD	this study
TWP 26	468990	882659	1650	5.35	33.47	1075	1791	29.1	7.88	-9.33	BH	this study
TWP 36	467541	868129	1652	4.31	27.8	690	1149	27.8	8.25	-6.68	BH	this study
TWP 37	467853	869448	1647	3.15	26.04	1298	2150	28.4	8.15	0.84	BH	this study
TWP 39	470120	875770	1634	5.19	32.3	284	474	19.5	8.34	-9.22	Lake	this study
TWP 41	447457	886437	1817	-6.08	-33.4	421	702	18	8.17	15.24	BH	this study
TWP 42	446999	886226	1817	-2.97	-4.42	477	792	20.6	7.98	19.34	BH	this study
TWP 44	445875	885396	1819	-2.94	-10.75	536	893	24.3	7.43	12.77	BH	this study
TWP 48	444632	888897	1833	-4.09	-11.98	553	926	24.8	7.24	20.74	HD	this study
TWP 51	443757	889463	1829	-3.6	-8.76	725	1205	24	7.06	20.04	HD	this study
TWP 52	441756	890635	1843	-3.44	-7.46	521	872	23.7	7.53	20.06	BH	this study
TWP 54	432668	897231	2058	-2.14	-6.86	237	396	20	6.93	10.26	BH	this study
TWP 55	431997	897751	2048	-2.98	0.01	371	612	20.1	6.64	23.85	BH	this study
TWP 56	430742	898825	2070	-3	-5.12	220	366	21.8	6.93	18.88	BH	this study
TWP 57	427153	897065	2121	-3.6	-7.18	283	472	25.8	6.93	21.62	BH	this study
TWP 58	427005	896812	2123	-2.99	-6.94	315	526	25	6.85	16.98	BH	this study
TWP 59	480377	900723	1659	1.22	9.6	237	394	17.9	8.75	-0.16	R	this study
TWP 60	476526	897409	1651	4.43	37.49	1067	1779	26.6	8.19	2.05	BH	this study
TWP 63	477550	895728	1634	4.18	38.44	300	500	21.7	7.9	5	Lake	this study
TWP 64	475911	895965	1647	3.91	35.04	1711	2860	23.4	8.83	3.76	BH	this study

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TWP 65	478196	904468	1649	-3.52	-13.01	322	536	21	7.87	15.15	BH	this study
TWP 67	477354	904197	1683	-2.26	-10.9	447	740	26.5	7.67	7.18	HD	this study
TWP 69	478094	902659	1677	-2.01	-7.23	317	527	22.2	7.56	8.85	BH	this study
TWP 70	480380	900736	1662	-2.57	-13.41	394	657		7.97	7.15	BH	this study
TWP 71	466207	903427	1759	-5.1	-32.31	557	930		8.15	8.49	BH	this study
R30	477528.98	903418	1760	1.67	6.14	583				-7.22	R	Rango 2009
Hs2	484327	8771589	1890	-3.03	-15.65	1728				8.59	HS	Rango 2009
LW 29	430213	907159	1632	4.88	33.82	379				-5.22	Lake	Rango 2009
RV-3	451466	897888		0.7	7.5		480		8	1.9	R	winter 1973
wl-12	479438	899958		-1.95	-3.93					11.67	BH	Tenalem1996
wl-13	467892	869314	1643	4.45	32.38					-3.22	BH	Tenalem1996
wl-2	467797	878153	161	5.04	36.2		900	24	7.6	-4.12	BH	Craig etal 77
wl-3	479815	900819		-2.73	-8.1		1100	45	7.8	13.74	BH	Craig etal 77
wl-4	456844	884690		-3.53	-15		690	35	7.6	13.24	BH	Craig etal 77
CS-1	424762	885865		-2.44	-3.7		208			15.82	CS	Craig etal 77
CS-2	425733	898162		-2.55	-3.1		390			17.3	CS	Craig etal 77
CS-5	839648	913371		-2.21	-4.05					13.63	CS	Tenalem1996
RN-3	431210	898294		0.49	8.05					4.13	RN	Tenalem1996
RN-4	468775	877076		-0.7	12.85					18.45	RN	Tenalem1996
HD =hand dug well,L= lake water,BH= bore hole,R= river,Cs=cold spring,HS=hot spring,RN=rain water												

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Appendix3: groundwater inventory measured in the field &received/collected from MoWIE

Region	Zone	Woreda	Kebele	UTM E	UTM N	Elevation, AMSL	Depth (m)	SWL (m)	Altitude of SWL mamsl	Scheme ID
SNNPR	Guragae	Sodo	Tiya Town	456837	932873	2318	136	114	2204	BH
SNNPR	Guragae	Sodo	Kela	444918	911937	1886	50	1.86	1884.14	BH
SNNPR	Guragae	Sodo	Dugda Goro	460865	901754	1925	301	185	1740	BH
SNNPR	Guragae	Sodo	Refenso	457559	908463	1891	200	170	1721	BH
SNNPR	Guragae	Meskan	Inseno	441974	890758	1832	63	15.2	1816.8	BH
SNNPR	Guragae	Meskan	Inseno Ousme	440025	890823	1833	66	8.7	1824.3	BH
SNNPR	Guragae	Meskan	Shershera Mechmena	439461	904709	1914	75	33.9	1880.1	BH
SNNPR	Guragae	Meskan	Dirama Shershera	436158	901900	2008	128.55	43.9	1964.1	BH
SNNPR	Silte	Silty	Kibet town	426285	887327	2095	118	50	2045	BH
SNNPR	Silte	Silty	Kibet town	426927	887719	2094	174	50	2044	BH
SNNPR	Silte	Silty	Alkeso	415084	877224	2301	183	162	2139	BH
SNNPR	Silte	Silty	Yekertef Gibato	424695	875670	2054	256	180	1874	BH
SNNPR	Silte	Silty	Woger Ourdubo	427800	871600	1920	202	160	1760	BH
SNNPR	Silte	Silty	Dobo Sabola	436818	892494	1845	65	8.25	1836.75	BH
SNNPR	Silte	Silty	Debub Goto	435517	877276	1860	95	35	1825	BH
SNNPR	Silte	Silty	Udasa	442073	875289	2016	370	300	1716	BH
SNNPR	Guragae	Mareko	Argo Wolilati	454319	891741	1928	267	182	1746	BH
SNNPR	Guragae	Mareko	Ilala Gebiba	455912	885586	1786	216	172	1614	BH
SNNPR	Guragae	Mareko	Ilala Jirano	453015	883724	1809	267	167	1642	BH
SNNPR	Guragae	Mareko	Semen Koshe	450074	886127	1884	210	158	1726	BH
SNNPR	Guragae	Mareko	Koshe 01	448478	885096	1884	220	180	1704	BH
SNNPR	Guragae	Mareko	Koshe Zuria	447700	886562	1834	56	18	1816	BH
SNNPR	Guragae	Mareko	Bidara Faka	452613	880214	1811	218	160	1651	BH

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SNNPR	Guragae	Mareko	Shirinto	447720	875620	1894	300	260	1634	BH
SNNPR	Guragae	Mareko	Udasa Washe Faka	447740	875650	1878	267	151.55	1726.45	BH
SNNPR	Guragae	Mareko	Dida Halibo	447247	889418	1830	106	20	1810	BH
Oromiya	East shewa	Adame Tulu	Abosa 01	469886	886446	1654	80.7	31	1623	BH
Oromiya	East shewa	Dugda	Weyo	472425	890622	1556	90	8	1548	BH
Oromiya	East shewa	Dugda	Burka Dalocha	492763	900233	1674	73	33.4	1640.6	BH
Oromiya	East shewa	Ziway Dugda	Meja Natile	496211	897486	1676	64	30	1646	BH
SNNPR	Guragae	Sodo	Suluke	458882	911780	1934	295	270	1664	BH
Oromiya	East shewa	Adame Tulu	Abine Germama	464718	883354	1676		60	1616	BH(Solar)
SNNPR	Guragae	Meskan	Butajira Town	432756	897440	2058	154	54.7	2003.3	BH
Oromiya	East shewa	Adame Tulu	Adame Tulu	467644	868349	1658	80.5	31	1627	BH
Oromiya	East shewa	Dugda Bora	Meki Town	480497	900763	1662	84	49	1613	BH
SNNPR	Guragae	Meskan	Butajira Town	432084	897957	2056	65	13.4	2042.6	BH
Oromiya	East shewa	Adame Tulu	Adame Tulu	467945	869660	1654	66.4	30.47	1623.53	BH
Oromiya	East shewa	Adame Tulu	Ziway Town	468735	875680	1647		22.15	1624.85	BH
Oromiya	East shewa	Dugda	Meki Town	480694	901824	1661	82.5	29	1632	BH
SNNPR	Guragae	Meskan	Butajira Town	430941	896250	2070	86	22	2048	BTW
Oromiya	East shewa	Adame Tulu	Asebo Genet	456338	873026	1710	127	93	1617	BH
Oromiya	East	Adame	Galo Repi	462137	883385	1707	108	81	1626	BH

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	shewa	Tulu								
Oromiya	East shewa	Dugda	Sera Wekele	477313	906916	1721	92	81	1640	BH
Oromiya	East shewa	Dugda	Cheleleke 2 (Germeji)	469824	896035	1705	110	79	1626	BH
Oromiya	East shewa	Dugda	Choroke	471570	898358	1722	93	78	1644	BH
Oromiya	East shewa	Dugda	Laluna Dero	469448	901986	1721	100	85	1636	BH
Oromiya	East shewa	Dugda	Ate Meti	472425	902009	1709	80	65	1644	BH
Oromiya	East shewa	Dugda	Wolda Kocha	481416	909593	1712	105	84	1628	BH
Oromiya	East shewa	Adame Tulu	Haleku Gulenta	465363	869206	1658	82	58	1600	BH
Oromiya	East shewa	Adami tulu	Abosa	469796	886237	1654	60	32	1622	BH
Oromiya	Guragae	meskan	Butajiratown/netsa sefer	432668	897231	2058	150	80	1978	BH
Oromiya	Guragae	meskan	Butajiratown/police station	431997	897751	2048	60	49	1999	BH
Oromiya	Guragae	meskan	Butajiratown/hospital	430742	898825	2070	260	59	2011	BH
Oromiya	Guragae	meskan	Butajiratown/mamuja02	427153	897065	2121	213	72.25	2048.75	BH
Oromiya	Guragae	meskan	Butajiratown/mamuja01	427005	896812	2123	220	77	2046	BH
Oromiya	East shewa	Dugda	graba korkadi	476208	897663	1658	35	30	1628	BH
Oromiya	East shewa	Dugda	graba korkadi	476287	897406	1656	30	28.5	1627.5	BH
Oromiya	East shewa	Dugda	sera wakelo	478196	904468	1649	135	59.3	1589.7	BH

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Oromiya	East shewa	Dugda	sera wakelo	478054	904159	1681	130	57.2	1623.8	BH
Oromiya	East shewa	Dugda	sera wakelo	477354	904197	1683	130	55.37	1627.63	BH
Oromiya	East shewa	Dugda	meki town/01	480380	900736	1662	182.5	29	1633	BH
Oromiya	Guragae	meskan	Butajiratown/netsa sefer	432668	897231	2058	150	80	1978	BH
Oromiya	Guragae	meskan	Butajiratown/police station	431997	897751	2048	60	49	1999	BH
Oromiya	Guragae	meskan	Butajiratown/hospital	430742	898825	2070	262	59	2011	BH3
Oromiya	Guragae	meskan	Butajiratown/mamuja02	427153	897065	2121	213	72.25	2048.75	BH
Oromiya	Guragae	meskan	Butajiratown/mamuja01	427005	896812	2123	220	77	2046	BH2
Oromiya	East shewa	Dugda	graba korkadi	476208	897663	1658	35	30	1628	BH
Oromiya	East shewa	Dugda	graba korkadi	476287	897406	1656	30	28.5	1627.5	BH
Oromiya	East shewa	Dugda	sera wakelo	478196	904468	1649	135	59.3	1589.7	BH
Oromiya	East shewa	Dugda	sera wakelo	478054	904159	1681	130	57.2	1623.8	BH
Oromiya	East shewa	Dugda	sera wakelo	477354	904197	1683	130	55.37	1627.63	BH
Oromiya	East shewa	Dugda	meki town/01	480380	900736	1662	182.5	29	1633	BH
SNNP	Gurage	Mareko	Gebiba Borehole	455901	885579	1780	192	172	1608	BH
SNNP	Gurage	Mareko	Semen Koshe	450174	886198	1881	222	173.8	1707.2	BH
SNNP	Gurage	Mareko	JICA Test well5	446999	886227	1798	64	9.6	1788.4	BH
SNNP	Gurage	Mareko	Gaye Faro	453015	883724	1809	230	131	1678	BH
SNNP	Gurage	Mareko	Inseno	440020	888300	1854	168	11.44	1842.56	BH

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SNNP	Gurage	Mareko	Koshe Test well5	448646	885794	1864	244	132	1732	BH6
SNNP	Gurage	Mareko	Adas Rapa	447720	875620	1894	312	208	1686	BH
SNNP	Gurage	Mareko	Dida Halebo	446946	888984	1855	591	17.46	1837.54	BH5
SNNP	Gurage	Mareko	Koshe 01	440020	888300	1854	163	11.15	1842.85	BH
SNNP	Gurage	Mareko	Koshe Zuria	448646	885794	1864	244	18	1846	BH
SNNP	Gurage	Mareko	Udasa Washe Faka	447700	886562	1834	56	15.55	1818.45	BH
SNNP	Gurage	Mareko	Dida Halibo	440550	883900	1840	230	20	1820	BH
SNNP	Gurage	Meskan	maricho	426868	899213	2147	600	62.5	2084.5	BH1
SNNP	Gurage	Meskan	inseno	440020	888300	1854	168	11.4	1842.6	BH4
Oromiya	East shewa	Adami tulu	ziwy prizon	467227	878173	1655	50	34	1621	BH7

Appendix 3.1 Shallow and handdug well inventory data

Region	Zone	Woreda	Kebele	UTM E	UTM N	Elevation, AMSL	Depth (m)	SWL (m)	Altitude of SWL mamsl	Scheme ID
SNNPR	Guragae	Sodo	Gere	449101	931543	2573	85	53	2520	SW
SNNPR	Guragae	Sodo	Amawte Gufutige	449315	931983	2565	61	25	2540	SW
SNNPR	Guragae	Sodo	Semero Michaele	459571	927132	2156	85	58	2098	SW
SNNPR	Guragae	Sodo	Negesa	448077	914575	1950	70	50	1900	SW
SNNPR	Guragae	Sodo	Delelesa	443290	912291	1917	46	16	1901	SW
SNNPR	Guragae	Sodo	Gose Salen	447042	906854	1873	54	18	1855	SW
SNNPR	Guragae	Meskan	Mekicho	429210	898363	2093	32	3	2090	SW
SNNPR	Guragae	Meskan	Mekicho	428066	898717	2107	50	3.65	2103.35	SW
SNNPR	Guragae	Meskan	Inseno	441913	891311	1837	17	14.5	1822.5	SW
SNNPR	Guragae	Meskan	Inseno	441811	891169	1832	17	14.5	1817.5	SW
SNNPR	Guragae	Meskan	Jole	440195	905619	1901	60	15	1886	SW
SNNPR	Silte	Silty	Ashute Burako	431626	885597	1825	17	3	1822	SW

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SNNPR	Silte	Silty	Ashute Burako	432220	885690	1823	18	3	1820	SW
SNNPR	Silte	Silty	Shele Washo	437435	888235	1825		4.2	1820.8	SW
SNNPR	Silte	Silty	Shele Washo	437645	890366	1837	30	4	1833	SW
SNNPR	Guragae	Meskan	Ile	439118	899060	1890	30	22.93	1867.07	HDW
SNNPR	Guragae	Meskan	Inseno	442017	891450	1840	17	15	1825	HDW
SNNPR	Guragae	Meskan	Bati Lejano	441186	894429	1846	10	8.6	1837.4	HDW
SNNPR	Guragae	Meskan	Mirab Meskan	426836	895151	2128	12	9.7	2118.3	HDW
SNNPR	Silte	Silty	Danecho Mukere	420549	880486	2345	12	6.2	2338.8	HDW
SNNPR	Guragae	Silty	Dobo Sabola	436810	889806	1831	6	1.35	1829.65	HDW
SNNPR	Guragae	Mareko	Mekak Jare Dembeka	443812	884830	1844	31	27.6	1816.4	HDW
SNNPR	Guragae	Mareko	Gola Jare Dembeka	442910	883379	1855	45	42	1813	HDW
SNNPR	Guragae	Mareko	Gola Jare Dembeka	441641	884059	1848	40	38.3	1809.7	HDW
SNNPR	Guragae	Mareko	Dida Midore	445207	888966	1837	25	19.1	1817.9	HDW
Oromiya	East shewa	Adame Tulu	Adame Tulu pesticide	467495	870454	1644	30	28	1616	HDW
Oromiya	East shewa	Adame Tulu	Gerbi Widena Boremo	465326	871755	1653	45	44.7	1608.3	HDW
Oromiya	East shewa	Adame Tulu	Gerbi Widena Boremo	467869	872202	1647	26	24.2	1622.8	HDW
Oromiya	East shewa	Adame Tulu	Abine Germama	465355	881409	1669	45	39.58	1629.42	HDW
Oromiya	East shewa	Adame Tulu	Abine Germama	465779	881853	1667	42	38.6	1628.4	HDW
Oromiya	East shewa	Adame Tulu	Welinbula	469350	888450	1677	40	36.78	1640.22	HDW
Oromiya	East shewa	Adame Tulu	Elka Chelemo	468819	885619	1661	36	33.9	1627.1	HDW
Oromiya	East shewa	Adame Tulu	Elka Chelemo	469687	885034	1655	20.5	19.6	1635.4	HDW
Oromiya	East shewa	Adame Tulu	Elka Chelemo	469520	883590	1653	15	14.36	1638.64	HDW
Oromiya	East shewa	Adame Tulu	Abine Germama	468896	878903	1648	14	12.55	1635.45	HDW
Oromiya	East shewa	Dugda	Giraba Korke Adi	477158	900110	1665	35	33.35	1631.65	HDW
Oromiya	East shewa	Dugda	Bekele & Girisa	479270	898325	1647	17	14.5	1632.5	HDW
Oromiya	East shewa	Dugda	Oda Bokata	483933	904334	1670	35	33	1637	HDW

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Oromiya	East shewa	Dugda	Burka Dalocha	492403	900545	1674	35	33.4	1640.6	HDW
SNNPR	Guragae	Sodo	Amawte Morege	449205	935753	2784	15	0	2784	HDWP
SNNPR	Guragae	Sodo	Atene Endebuyo	439531	918800	2743	10	0	2743	HDWP
SNNPR	Guragae	Meskan	Misrak Embor	429313	897129	2117	40	25	2092	HDWP
SNNPR	Guragae	Meskan	Bidara	422929	895181	2244	16	13.2	2230.8	HDWP
SNNPR	Guragae	Meskan	Mirab Meskan	424292	894735	2186	27.2	15	2171	HDWP
SNNPR	Guragae	Meskan	Odo	424247	893157	2169	22	8.5	2160.5	HDWP
SNNPR	Guragae	Meskan	Odo	424926	892693	2150	22	10	2140	HDWP
SNNPR	Silte	Silty	Agode	427712	888971	2091	16	10	2081	HDWP
SNNPR	Guragae	Mareko	Hobe Jare Dembeka	440456	888867	1840	30	15	1825	HDWP
SNNPR	Guragae	Mareko	Kuno Kertefa	438218	887357	1824	6.5	4.6	1819.4	HDWP
SNNPR	Silte	Lamfuro	Washa Shanka	431708	870363	1823	24	10	1813	HDWP
SNNPR	Silte	Lamfuro	Lamfuro Gebaba	434772	874449	1857	40	32.9	1824.1	HDWP
SNNPR	Silte	Lamfuro	Lamfuro Gebaba	433909	874956	1842	16	13	1829	HDWP
SNNPR	Silte	Lamfuro	Lamfuro Gebaba	433720	875735	1844	30	27	1817	HDWP
Oromiya	East shewa	Adame Tulu	Welinbula	468848	889123	1684	40	35	1649	Windmill
Oromiya	East shewa	Adame Tulu	Negalegn	468604	886521	1669	40	30	1639	Windmill
Oromiya	East shewa	Adame Tulu	Abosa 01	469440	886823	1671	51	31.5	1639.5	Windmill
Oromiya	East shewa	Adame Tulu	Elka Chelemo	468446	885274	1663	45	35	1628	Windmill
Oromiya	East shewa	Adame Tulu	Edo Kontola	469069	882869	1654	37	18	1636	Windmill
Oromiya	East shewa	Adame Tulu	Abine Germama	468333	879382	1655	25	22	1633	Windmill
Oromiya	East shewa	Adame Tulu	Gush Gula	465797	875905	1661	60	45	1616	Windmill
Oromiya	East shewa	Adame Tulu	Gush Gula	466857	876078	1660	56	42	1618	Windmill
Oromiya	East shewa	Adame Tulu	Ziway Town	467525	877495	1658	50	34	1624	Windmill
Oromiya	East shewa	Adame Tulu	Ziway Town	468215	876905	1658	60	33	1625	Windmill
Oromiya	East shewa	Dugda	Giraba Jarso	477198	901824	1688	75	60	1628	Windmill
Oromiya	East shewa	Dugda	Korke Adi	476306	897835	1664	51	30	1634	Windmill
Oromiya	East shewa	Dugda	Abono 01	471764	892451	1675	50	35	1640	Windmill

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Oromiya	East shewa	Dugda	Weyo	471669	891730	1675	60.5	33.2	1641.8	Windmill
Oromiya	East shewa	Dugda	Toch Gabriel	469500	889800	1687	75	53	1634	Windmill
Oromiya	East shewa	Dugda	Alem Tena	472200	902400	1660	90	57	1603	Windmill
Oromiya	East shewa	Dugda	Birbirs Guda Sabole	470565	914133	1747	62	54	1693	Windmill
Oromiya	East shewa	Dugda	Tuchi Sumeyan	487438	902563	1677	50	26	1651	Windmill
Oromiya	East shewa	Dugda	Oda Bokata	480034	902598	1685	41	34	1651	Windmill
Oromiya	East shewa	Adami tulu	Abosa town	469721	886014	1654	21	20.6	1633.4	HDW
Oromiya	East shewa	Adami tulu	Abosa town	469704	885981	1657	21	20.4	1636.6	HDW
Oromiya	East shewa	Adami tulu	Abosa town	469714	885865	1653	20	20.59	1632.41	HDW
Oromiya	East shewa	Adami tulu	Abosa	469458	885782	1652	21.5	19.3	1632.7	HDW
Oromiya	East shewa	Adami tulu	Elka chalemo	469474	883754	1640	16	13.4	1626.6	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	Elka chalemo	469450	883811	1643	16	13.75	1629.25	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469361	8837	1646	16	13.5	1632.5	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469444	883689	1648	16	14.5	1633.5	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469424	883644	1647	16	13.9	1633.1	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469325	883498	1641	16	13.65	1627.35	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469369	883155	1653	17	13.75	1639.25	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469390	883038	1640	16	13.5	1626.5	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469300	882864	1644	15	13.5	1630.5	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	elka/kontola	469566	882868	1654	15	13.7	1640.3	HDW

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Oromiya	East shewa	Adami tulu gido kombolcha	Abosa	469660	886021	1654	35	26.8	1627.2	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	Abosa	469715	885910	1655	25	22.01	1632.99	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	Abosa	469673	885781	1654	22	19.45	1634.55	HDW
Oromiya	East shewa	Adami tulu gido kombolcha	Gari babiftu	469643	885584	1655	22	19.5	1635.5	HDW
Oromiya	East shewa	Adami tulu	Elka	469562	885338	1654	22	19.01	1634.99	HDW
Oromiya	East shewa	Adami tulu	elka/chefeoda	469529	885020	1652	21	19.1	1632.9	HDW
Oromiya	East shewa	Adami tulu	elka/chefeoda	469514	884723	1656	22	19	1637	HDW
Oromiya	East shewa	Adami tulu	elka/chefeoda	468906	884237	1651	16	14.1	1636.9	HDW
Oromiya	East shewa	Adami tulu	1th level Gari/edokolkola	469122	883340	1651	22	20.3	1630.7	HDW
Oromiya	East shewa	Adami tulu	eado kontola	469306	882683	1645	22	19	1626	HDW
Oromiya	East shewa	Adami tulu	eado kontola	469185	882291	1643	15	13.3	1629.7	HDW
Oromiya	East shewa	Adami tulu	eado kontola	469091	881879	1644	12	10.3	1633.7	HDW
Oromiya	East shewa	Adami tulu	eado kontola	468959	881315	1642	13	10.4	1631.6	HDW
Oromiya	East shewa	Adami tulu	eado kontola	468952	879956	1640	12	9.8	1630.2	HDW
Oromiya	East shewa	Adami tulu	Hizbay nuro	468874	879412	1638	12	9.7	1628.3	HDW
Oromiya	East shewa	Adami tulu	Hizbay nuro	467851	878816	1646	12	9.5	1636.5	HDW
Oromiya	East shewa	Adami tulu	tulutown /01	445275	869661	1648	29	25	1623	HDW
Oromiya	Guragae	Mareko	didam edore/ketea01	445155	888626	1829	20	18	1811	HDW
Oromiya	Guragae	Mareko	didam edore/ketea01	444966	888658	1834	25	17.7	1816.3	HDW
Oromiya	Guragae	Mareko	didam edore	444215	888787	1831	22.5	17.55	1813.45	HDW
Oromiya	Guragae	mareko	Didam edore	443757	889042	1831	23	19	1812	HDW
Oromiya	Guragae	mareko	Didam edore	476526	889463	1829	14	13	1816	HDW
Oromiya	East shewa	dugda	graba korkadi/meki town	475911	897409	1651	18	15.5	1635.5	HDW

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Appenix3.2: fluoride distribution with depth

Sample ID.	longitude	Latitude	depth(m)	TDS	EC	PH	Na+	K+	Ca2+	Mg2+	Alk.	HCO3-	Cl-	SO4 2-	NO3-	F-
Twp1	469796	886237	60	888	1469	8.44	222.5	30	17.6	8.64	666	735.7	57.6	14.1	2.02	1.73
Twp25	468906	883340	22	2090	3480	8.43	910	61	6.4	1.92	2002	2170	62.32	19.9	0.97	9.36
Twp26	468990	882659	24	1075	1791	7.88	312	45	24	10.6	832	1015	74.6	19.1	0.82	3.14
Twp36	467541	868129	80	690	1149	8.25	250	27	12	4.8	525	488.5	26.44	21.4	5.6	0.74
Twp37	467853	869448	69	1298	2150	8.15	510	29	16	7.68	988	977	68.93	101	4.56	7.7
Twp41	447457	886437	200	421	702	8.17	195	20	14.4	4.8	442	539.2	5.67	2.34	4.86	2.76
Twp42	446999	886226	90	477	792	7.98	119	29	44.8	12.5	429	472.6	17	5.49	3.15	4.36
Twp51	443757	889463	14	725	1205	7.06	86	31	82.4	4.8	403	491.7	34.94	27.9	15.69	0.9
Twp52	441756	890635	113	521	872	7.53	255	40	68.8	22.1	515	628.1	63.27	34.5	26.21	2.41
TWP55	431997	897751	262	371	612	6.64	32	29	80	9.12	247	301.3	26.44	15.3	44.73	0.27
Twp58/bh2	427005	896812	220	315	526	6.85	36	22	56	8.64	283	345.8	6.61	2.18	2.69	0.76
Twp60	476526	897409	18	1067	1779	8.19	790	30	10.4	5.28	1134	1117	21.72	3.16	0.56	2.57
TWP63	477550	895728	10	300	500	7.9	80	27	35.2	7.68	252	256.2	17	16.6	2.02	9.52
Twp67	477354	904197	130	447	740	7.67	197.5	16	20.8	11.5	341	415.5	17.94	10.6	1.21	0.74
Twp69	478094	902659	80	317	527	7.56	83	18	35.2	8.64	291	355.3	7.55	8.42	0.5	1.65
Twp70	480380	900736	182.5	394	657	7.97	105	18	20.8	4.32	333	406	15.11	11.6	1.17	1.8
Twp71	466207	903427	170	557	930	8.15	270	33	16	9.6	325	320.4	22.66	92.4	0.63	1.13
Twp74	468204	873525	17	1539	2560	7.88	750	110	22.4	10.6	746	909.5	85.93	160	90.4	9.49
TwS1	435852	869258	93	616	860	7.59	148	26	53.4	8.64	483	589.3	25.2	13.7	8.5	3.16
TwSs1	448882	920224	150	240	370	7.69	39.5	10	32	4.32	197	240.8	2.9	1.32	10.7	1.6
Twp27	445207	888966	213	432	642	7.34	31	15	96.12	10.8	321	392	5.8	0.53	13.5	0.8
BH4	440020	888300	168	261		7.36	107.5	4.3	18.8	1.2	254	202	1.2	7	0.28	1.3
BH6	448646	885794	244	528		7.66	202.2	31	8.4	1.68	450	413	7.8	7	0.3	2.79
BH1	426868	899213	600	248	381	7.56	78	8	8.04	1.51	186	226.9	10.41	0.48	1.05	1.33
BH5	446946	888984	591	400	629	7.55	92	11	42.4	3.36	332	405	3.64	8.2	9.56	1.08

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Mr25	446946	888984	254	460	678	8.15	128	11	22.4	14.4	348	424.6	0.9137.12		2.33	1.88
Mr25	446946	888984	471	430	626	7.97	104	12	51.2	10.6	360	439.2	5.46	8.09	12.34	1.34
Mr25	446946	888984	571	430	628	8.14	91	12	53.6	7.2	352	429.4	2.73	0.11	11.21	1.08
Aj12	467623	868353	306	590	1155	8.92	336.4	25	2.3	8.92	450	450	119.1	145	0.28	1.23

Appendix 4: Table for lithological log description

Borehole locality-Ziway prison(BH7) Drilled by WWDE,1993 E.C		Depth-143.7m,Swl-32.95m
		Transmissivity-354.5m ² /day
from	To	Lithology
0	8	Volcanic Ash? (probably Lacustrine Deposit)
8	12	Volcanic ash
12	42	Fine Indurated white ash? (probably Lacustrine Deposit)
42	48	Grey Indurated Sticky Clay
48	58	Coarse Grained Pyroclastic fall deposit
58	66	Indurated grey ash
66	74	Coarse Grained Pyroclastic fall deposit
74	106	Indurated grey ash
106	114	Ash
114	116	Ash
116	124	Ash
124	126	Ash
126	135	Ash
135	143.7	black cotton clay
Borehole locality-Adami Tulu,Depth-71m		Transmissivity-95.28m ² /day, hydraulic conductivity-3.97m/day
		Pump position-47-71m

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from	To	Lithology
0	15	Fine to coarse sand, lake sediment
15	20	lacustrine clay
20	23	Fine to coarse sand, lake sediment
23	30	lacustrine clay
30	34	Coarse grained Pyroclastic material
34	66	Fine to coarse sand, lake sediment
66	71	lacustrine clay
Borehole locality-meki townWSS(08)		
from	To	Lithology
0	4	top soil
4	36	medium grained pumice
36	44	Sand
44	60	fractured ignimbrite
60	66	medium grained sand
66	74	coarse grained pumice
74	85	alluvial deposit
85	94	medium grain pumice
94	126	sand/alluvial deposite
126	130	Pumice
Borehole localilty –Meki town06		
from	To	Lithology
0	6	top soil
6	16	coarse grain pumice
16	20	alluvial deposit

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20	52	fine grain pumice
52	56	sand deposited
56	68	massive ignimbrite
68	74	fractured ignimbrite
74	122	sand/alluvial deposit
122	130	weathered ignimbrite
Borehole locality-Butajira town(BH3)		
from	To	lithology description
0	10	brownish clay
10	22	tuff, pumice
22	24	Boulder
24	46	decomposed tuff
46	72	weathered ignimbrite
72	90	fractured &slightly weathered ignimbrite
90	94	slightly fractured ignimbrite
94	102	highly weathered ignimbrite
102	104	contact layer
104	124	fractured and slightly weathered ignimbrite
124	126	reddish contact time
126	128	slightly fractured ignimbrite
128	158	weathered and fractured ignimbrite
158	164	fresh basalt
164	170	fractured and weathered ignimbrite
170	172	contact layer
172	190	fresh to slightly weathered amygdaloidal basalt
190	200	Pumice

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200	214	fractured and decomposed basalt
214	216	Pumice
216	258	highly weathered basalt
258	262	fresh basalt
Borehole locality- mamuja(BH2)		Depth -262m Swl-77m
from	To	Lithology
0	4	brown clay
4	10	peble,cobble,bouder
10	30	decomposed tuff
30	70	weathered and fractured tuff
70	106	highly weathered tuff
106	122	fresh to slightly weathered ignimbrite
122	144	fresh ignimbrite
144	148	weathered ignimbrite
148	158	highly weathered and fractured basalt
158	164	weathered and fractured tuff
164	192	highly weathered and fractured basalt
192	220	slightly fractured ignimbrite
Borehole location- Mekicho kebele(BH1)		Depth-600m,Swl-62.5m Transmissivity-38.75m ² /day
From	To	Lithology
0	34	silt and sandy clay with some basaltic pebbles, Fine sand with silt with more clay at the bottom 2 meters
34	48	highly weathered and fractured scoriaceous& massive basalt with slight weathering at the bottom

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48	68	highly fractured to slightly weathered Massive basalt
68	74	Basaltic tuff & Highly weathered ignimbrite tuff
74	96	highly weathered and fractured ignimbrite mixed with basalt
96	178	highly fractured and slightly weathered ignimbrite with slight and moderate fracturing and tuff
178	196	slightly to highly fractured massive basalt
196	220	Highly fractured and weathered ignimbrite with some basalt
220	240	Highly fractured and slightly weathered light grayish ignimbrite
240	280	slightly to highly weathered and fractured ignimbrite from top to the bottom
280	288	Fractured and moderately weathered basalt with ignimbrite , occasional fracturing
288	300	slightly fractured basalt
300	310	unwedded tuff and highly weathered and fractured ignimbrite
310	320	highly weathered and fractured basalt with thin tuff bed at the bottom
320	322	Welded tuff
322	336	slightly fractured and weathered Rhyolite
336	354	light grey to whitish welded tuff
354	356	slightly fractured Rhyolite
356	400	Ash/tuff with Fractured ignimbrite and welded tuff at the top and fresh ignimbrite at the bottom
400	406	Highly weathered and fractured ignimbrite
406	436	Slightly fractured ignimbrite with high fracture at the bottom

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436	464	highly weathered and fractured ignimbrite with some heat effect and slight fracturing
464	466	Welded tuff
466	542	Moderately weathered and slightly fractured ignimbrite
542	600	slightly fractured and weathered ignimbrite and fresh ignimbrite with fresh rock in the middle
Borehole locality-Inseno deep test well(BH4)		Depth-168m
from	To	lithology description
0	4	Brown weathredpumaceouspayroclastic fall
4	20	weathredpumaceouspayroclastic fall deposit
20	40	pyroclastic deposit with pumice, ash,
40	56	Grey pyroclastic deposit with pumice and lithic
56	72	Grey pyroclastic deposit with pumice
72	74	Pumaceous, lithic pyroclastic deposit (tuff).
74	78	Pumaceous lithic pyroclastic deposit (tuff).
78	110	Relatively hard tuff
110	116	Pumaceous lithic pyroclastic deposit.
116	168	Pumaceous, lithic pyroclastic deposit.
Bore hole locality-Didahalibo(BH5) in Marekoworeda		Depth-591m,swl-17.46m Transmissivity-2100m ² /day Pumposition-67.67m
From	To	Lithological Description
0	4	silly clay with some sandy materials
4	22	fine grained sand with some pyroclastic material
22	32	moderately welded weathered tuff
32	38	less welded tuff

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38	60	welded tuff
60	74	loose tuff
74	84	moderately to highly fractured welded tuff
84	104	loose tuff
104	116	moderately fractured ignimbrite
116	132	light brown loose tuff
132	246	light greenish loose tuff
246	258	slightly weathered and fractured ignimbrite
258	306	highly fractured and weathered welded tuff with reddish stain
306	356	slightly weathered and fractured rhyolite
356	358	loose tuff
358	376	slightly fractured rhyolite(rhyolite tuff)
376	386	highly fractured and moderately weathered rhyolite
386	408	highly weathered & fractured welded tuff
408	426	loose tuff
426	432	highly fractured rhyolite
432	462	loose tuff
462	472	moderately fractured rhyolite
472	486	loose tuff
486	496	welded tuff with rhyolite material
496	522	loose tuff
522	524	fractured rhyolite
524	562	loose tuff
562	583	ignimbrite with rhyolite with thin intercalation
583	591	welded tuff with rhyolite material

