DISTRIBUTION ANALYSIS OF FLUORIDE IN GROUNDWATER OF HAWASSA ZURIA WOREDA, SIDAMA ZONE

MASTER OF SCIENCE THESIS

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HAWASSA UNIVERSITY, HAWASSA, ETHIOPIA

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Examiners' Approval Sheet 1 (Submission Sheet 2)

We, the undersigned members of the Board of Examiners of the final open defense by **Iyasu Markos Chichola**have read and evaluated his/her thesis entitled **"Distribution Analysis of Fluoride in Groundwater of HawassaZuriaWoreda, Sidama Zone"** and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirement for the Degree of **Master's**of**Science** in **Civil Engineering**with **Specialization** in **Hydraulic Engineering.**

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DECLARATION

I hereby declare that this **Master of Science** thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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DEDICATION

I dedicate this thesis manuscript to all my family for nursing me with affection and love and for their dedicated partnership in the success of my life.

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SYMBOLS AND ACRONYMS

WHO	World Health Organization
SAWQG	South African Water Quality Guidelines
Ks	Solubility Product Constant
Ppm	Parts Per Million
GDWQ	Guidelines for Drinking Water Quality
WRC	Water Research Commission
CaF^2	Calcium Fluoride
$(AlF_6)^{3-}$	Aluminum Fluoride Ion
DWAF	Department of Water Affairs and Forestry
$CaCO_3$	Calcite
SBH	Shallow borehole
DBH	Deep borehole
$MgCO_3$	Magnesite
$NaHCO_3$	Sodium Bicarbonate
HCO_3^-	Hydrogen Carbonate
FeO.OH	Goethite
USA	United States ofAmerica
CGWB	Central Groundwater Board
H_2SiF_6	Fluor silicicAcid
Na_2SiF_6	Sodium Hexafluoro silicate
SF_6	Sulfur Hexafluoride
UF_4	Uranium Tetrafluoride
UF_6	Uranium Hexafluoride
SNNPR	Southern Nations Nationalities and Peoples Region
IPMS	International Program on Meteorology Safety
GPS	Global Positioning System
UTM	Universal Transverse Mercator
EPA	Environmental Protection Agency
CAS	Chemical Abstracts Service

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ABSTRACT

As per the Woreda Water Supply Office's study, the water source from the ground and surface water is polluted in Hawassa Zuria Woreda but their distribution and extent of pollution is not well understood.The main aim of this study is to determine the distribution of the fluoride ion concentration levels in Hawassa Zuria Woreda in the groundwater. The collected primary data were used to assess the distribution of the fluoride concentration levels in all groundwater sources. Fluoride concentration from twenty-three Kebeles was analyzed at laboratory of Fluorides in this research area. The delineation and mapping of Fluorides were carried out using GIS software, based on sampling at random bore holes during 2016/17 year of seasons. Areas of particularly high or low fluoride levels were identified. High fluoride greater than 6mg/l concentrations were found in Kajma Umbulo, Sama Ejersa, Jara Damuwa and Jara Karara provinces. Those provinces need for partial de-fluoridation and this must receive serious consideration since the water from those sources is currently being used for drinking purpose. From temporal distribution high fluoride distribution expected to occur during wet season which shows the best cares during this season than the others.

Key words; Fluoride, groundwater, water quality, de-fluoridation, spatial and temporal variation, dental and skeletal fluorosis, polluted water sources

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the Study

Fluoride is the ionic form of the element fluorine, which is found in abundance in nature, primarily in water and soil. Given its extreme reactivity, fluorine is never found in nature in its elementary form, only in the form compounds known as fluorides (Hem, 1989). Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. It is the most electronegative of all the elements (Hem, 1989). It has a strong tendency to acquire a negative charge in solution forms of F^- ions. Fluorides can be present: in air, as gases or particulates; in water, as fluoride ions or molecular compounds; in soils, typically as molecular compounds with calcium or aluminum; and in living organisms (Bégin, 2003). Volcanic eruptions and weathering of fluoride containing minerals comprise the natural sources, and of anthropogenic sources, application of phosphate fertilizers emission from aluminum smelter and phosphate fertilizer factories and burning of fossil fuels can be mentioned (Arnesen 1998).

The beneficial attributes of fluoride to human health have been known for many years **(**WHO**,** 1970**).** The fluoride is a very important dietary substance. When ingested at specific doses, the fluoride is beneficial to both bone and dental development in human beings**(**WHO**,** 1970**)**.At correct intake levels it plays a very important role in the formation of teeth. Too low fluoride intake levels during childhood may give rise to the occurrence of preventable dental caries in later years. However, high fluoride concentration intake normally gives rise to teeth mottling and related problems. Chronic endemic fluorosis is a condition which is caused by an excess of fluorides in drinking water and which affects the calcification of the teeth, resulting in what is commonly known as dental fluorosis. Fluoride can occur naturally in water in concentrations well above recommended levels, which can have several long term adverse effects, including severe dental fluorosis, skeletal fluorosis and weakened bones (WHO, 1970). According to SAWQD (1996) the effect of fluoride is most rapid on young especially children up to age seven years are the most susceptible. But its effect and accumulation continue up to the age of 55. Due to this, the world health organization (WHO) recommends maximum fluoride level of 1.5mg/l.

High fluoride concentrations may be expected in groundwater from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride concentrations may also increase in groundwater in which cation exchange of sodium and calcium occurs. However, knowingly or unknowingly people may use those groundwater with high fluoride concentration which may cause adverse effects. As Hawassa Zuria Woreda Water Supply Office's study, the polluted water source was from ground and surface water. Thus, this study attempts to assess the spatial and temporal distribution of fluoride in the groundwater of Hawassa Zuria Woreda which is being used for different purposes including drinking water. This helps to know the adverse effect due to fluoride and put the possible solution before sever problem occurred to the community at all.

1.2. Statement of the Problem

The occurrence of high ion fluoride concentration in groundwater in most cases a natural phenomenon and constitutes a serious water quality problem in groundwater worldwide (Nair, et al, 1984; Mccaffrey, 1995, Rao 1997; Agrawal and Vaish, 1998). The same is true for some parts of Ethiopia as problem of groundwater fluoride ion concentration levels causes problems. In most parts of country groundwater is the source of drinking water and its effects on the teeth are visible in individuals including around Hawassa. Specifically, as evidence assessed from local health center and observation in Hawassa Zuria Woreda there are problems like severe dental fluorosis, skeletal fluorosis and weakened bones due to consumption of too high fluoride through drinking groundwater and other use of groundwater (MoWR,2002).Furthermore, as rough assessment of the Woreda Water Supply, Mines and Energy showsthat there is an extreme variation between wet and dry season of groundwater fluoride concentration in Hawassa Zuria Woreda. In fact, there has no detailed and systematic survey on the spatial and temporal distribution of fluoride in Hawassa Zuria Woreda. Knowing the spatial and temporal distribution in the country is necessary for current decision making concerning fluoridation and defluoridation. To this extent this study attempts to study the spatial and temporal fluoride concentration to make decision for the solution current fluoride problem by concerning body(Berhanu G 1996).

1.3. Objectives

1.3.1. General Objectives

The main objective of this study is to assess the distribution of fluoride ion concentration in groundwater of Hawassa Zuria Woreda.

1.3.2. Specific Objectives

- To determine the spatial distribution of fluoride concentrations in Groundwater sources across Hawassa Zuria Woreda.
- To determine the temporal distribution of fluoride concentrations in Groundwater sources across Hawassa Zuria Woreda.
- To map the risk of fluoride concentration in the study area as per different standards

1.4 Significance of the Study

The higher intakes of fluoride taken over a long period of time can result in changes to bone, a condition known as skeletal fluorosis. This can cause joint pain, restriction of mobility, and possibly increase the risk of some bone fractures. Thus, knowing timely the concentration of fluoride both spatially and temporally is necessary to make decision for concerned stakeholders before sever problem occurs to the community. Thus, knowing the distribution of fluoride concentration of Hawassa Zuria Woreda helps to make decision on alternative sources.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Occurrence of Fluorides

2.1.1. Natural Water

In natural water fluorine normally occurs as the fluoride ion, F^-. Fluoride is thought to be one of the main ions that allow the solubilizations of beryllium, scandium, niobium, tantalum, and tin. Most simple compounds of F^- are readily soluble in water (WRC, 2001). The fluoride ion reacts readily with the calcium ion to form CaF_2, which is reasonably insoluble and can be found in sediments (DWAF,1996). Where phosphate is present, an even more insoluble apatite or hydroxyl apatite may form. Fluoride also reacts very readily with aluminum, a process that is made use of in the removal of fluoride from water (WRC, 2001). It forms complexes such as $(ALF_6)^{3-}$or ALF^{2+}. The formation of these complexes takes place rapidly, at low or high PH and temperature of groundwater and their formation can be regarded in the hydrological context as an equilibrium process (Plankey and Patterson, 1986). The formation of these complexes depends on several other factors such as complex stability constant, the concentration of the fluoride ion in solution and complexing spaces (Rao et al, 1993).

2.1.1.1. Mineral- Aqueous Fluoride Interactions

Ionic compounds of fluoride dissolve in water and these are believed to be the cause of fluoride release in to groundwater. The dissolution of other F^- bearing alumino silicate minerals have also been reported (WRC, 2001).

During the mineralization of various fluoride rich minerals, solubility plays an important role. Table 1, below shows the solubility products (Ksp) values of some minerals relevant to the chemistry of groundwater (Gaciri and Davies, 1993).

The concentrations of fluoride in groundwater have been shown to be limited by the mineral's solubility especially fluorite, such that in the presence of 10^{-3}M of Calcium, the fluoride ion concentration is limited to 3.1mg/l of fluoride. It is, therefore, the absence of calcium in solution, which allows higher concentrations to be stable (Edmunds and Smedley, 1996). High fluoride ion concentrations may, therefore, be expected in groundwater in calcium-poor aquifers and in areas where fluoride-bearing minerals are common.

Table 1: Solubility products for some minerals

Mineral	Ksp	Temp.^{o}c/PH
Fluoride(CaF^2)	$3.4x10^{-11}$	18
Calcite ($CaCO_3$)	$1X10^{-8}$	25
Aragonite($CaCO_3$)	$1X10^{-8}$	25
OH- apatite	$2.6x10^{-45}$	18, PH=7.0
OH-apatite	$2.3x10^{-41}$	40,PH=7.4
Selaite(MgF_2)	$6.4x10^{-9}$	27
Halite(NaCl)	38 or $1x10^{1.58}$	25
Siderite($FeCO_3$)	$1x10^{-16.5}$	25
Magnesite($MgCO_3$)	$1x10^{-5}$	25
Dolomite	$1x10^{-16.7}$	25

The concentrations of fluoride in groundwater have been shown to be limited by the mineral's solubility especially fluorite, such that in the presence of 10^{-3}M of Calcium, the fluoride ion concentration is limited to 3.1mg/l of fluoride. It is, therefore, the absence of calcium in solution, which allows higher concentrations to be stable (Edmunds and Smedley, 1996). High fluoride ion concentrations may therefore be expected in groundwater in calcium-poor aquifers and in areas where fluoride-bearing minerals are common.

2.1.2. Occurrence of Fluorides in Soils

Soils absorb F^- from dilute and concentrated solutions and this process is being used industrially (Ginster and Fey, 1995). It has been noted that the fluoride ion mobility depends on soil type, PH of the system and fluoride ion concentrations. Retention of F^- in the soil system is favored in acidic sediments containing clays and poorly ordered hydrous oxides of aluminum (Jinadasa, et al, 1993) investigated the F^- adsorption on the surface of goethite (FeO.OH). They found that fluoride adsorption is mineral above PH 7 and increased with decreasing PH, being greatest at PH 4. Meeusen et.al, (1996), concluded that the behavior of F^- in a soil profile was mainly determined by adsorption on to the metal oxide and hydroxide surfaces, specifically with goethite and gibbsite.

Factors that influence the mobility of inorganic fluorides in soil are pH and the formation of aluminum and calcium complexes (Pickering, 1985; Environment Canada, 1994). In more acidic soils, concentrations of inorganic fluoride were considerably higher in the deeper horizons. The low affinity of fluorides for organic material results in leaching from the more acidic surface horizon and increased retention by clay minerals and silts in the more alkaline, deeper horizons (Davison, 1983; Kabata-Pendias and Pendias, 1984). This distribution profile is not observed in either alkaline or saline soils (Gilpin and Johnson, 1980; Davison, 1983). The fate of inorganic fluorides released to soil also depends on the chemical form, rate of deposition, soil chemistry and climate (Davison, 1983). Fluoride in soil is mainly bound in complexes. The maximum adsorption of fluoride to soil was reported to occur at pH 5.5 (Barrow and Ellis, 1986). In acidic soils with pH below 6, most of the fluoride is in complexes with either aluminum or iron (e.g, AlF^{2+}, AlF^{+}, AlF^{0}, AlF^{-}, $FeF_{2+,}$ $Fe\ F_{+}$, FeF_{o}) (Perrott et al., 1976; Murray, 1984b; Elrashidi and Lindsay, 1986). Fluoride in alkaline soils at pH 6.5 and above is almost completely fixed in soils as calcium fluoride, if sufficient calcium carbonate is available (Brewer, 1966). Fluoride binds to clay by displacing hydroxide from the surface of the clay (Huang and Jackson, 1965; Bower and Hatcher, 1967; Meeussen et al., 1996). The adsorption follows Langmuir adsorption isotherm and is strongly dependent upon pH and fluoride concentration. It is most significant at pH 3–4, and it decreases above pH 6.5. Pickering et al. (1988) determined changes in free fluoride ions and total fluoride levels following equilibration of either poorly soluble fluoride species, such as calcium fluoride and aluminum fluoride, or wastes from aluminum smelters. The experiments were carried out on materials that had different cation-exchange capacities, such as synthetic resins, clay minerals, manganese oxide and a humic acid. Increased amounts of fluoride were released from fluoride salts and fluoride-rich wastes when solids capable of exchanging cations were present. The effect was greatest when there were more exchange sites available and when the fluoride compound cation had greater affinity for the exchange material. In a few cases, soluble complex ions were formed when the released fluoride attacked the substrate, such as illite or alumina wastes. Fluoride is extremely immobile in soil, as determined by lysimeter experiments. MacIntire et al. (1955) reported that 75.8–99.6% of added fluoride was retained by loam soil for 4 years. Fluoride retention was correlated with the soil aluminum content. The leaching of fluoride occurred simultaneously with the leaching of aluminum, iron and organic material from soil (Polomski et al., 1982). Soil phosphate may contribute to the mobility of inorganic fluoride (Kabata-Pendias and Pendias, 1984). In sandy acidic soils, fluoride tends to be present in water-soluble forms (Shacklette et al., 1974). Street and Elwali (1983) determined the activity of the fluoride ion in acid sandy soils that had been limed.

Fluorite was shown to be the solid phase controlling fluoride ion activity in soils between pH 5.5 and 7.0. At pH values below 5.0, the fluoride ion activity indicated super saturation with respect to fluorite. These data indicate that liming of acid soils may precipitate fluorite, with a subsequent reduction in the concentration of fluoride ion in solution.

Murray (1984b) reported that low amounts of fluoride were leached from a highly disturbed sandy podzol soil of no distinct structure. Even at high fluoride application rates (3.2–80 g per soil column of diameter 0.1 m with a depth of 2 m), only 2.6–4.6% of the fluoride applied was leached in the water-soluble form. The pH of the evaluate increased with increasing fluoride application, and this was probably due to adsorption of fluoride, releasing hydroxide ions from the soil metal hydroxides. Over time, the concentration of water-soluble fluoride decreased due to increased adsorption on soil particles.

Mean soil concentrations of Fluoride in Pennsylvania, USA, were 377, 0.38 and 21.7 mg/kg for total fluoride, water-soluble fluoride and resin exchangeable fluoride, respectively. The authors suggested that fluoride is relatively immobile in soil, since most of the fluoride was not readily soluble or exchangeable (Gilpin and Johnson, 1980).

The water-soluble fluoride in sodic surface soil treated with gypsum increased with increasing exchangeable sodium percent (Chhabra et al., 1979). The increase in exchangeable sodium percent also caused an increase in soil pH, which in turn caused an increase in water soluble fluoride. Incubation studies revealed that a major portion of the added fluoride was adsorbed to soil within the first 8 days. Calcium fluoride was formed in soils irrigated with fluoride solutions. Calcium fluoride is formed when the fluoride adsorption capacity is exceeded and the fluoride and calcium ion activities exceed the ion activity product of calcium fluoride (Tracy et al., 1984). Less than 2% of applied fluoride was measured in the leachate, and between 15 and 20% of added fluoride was precipitated as calcium fluoride. Fluoride was precipitated in the upper profile, although the authors expected that once the adsorption mechanisms were exceeded, soluble fluoride was leaching deeper into the soil with continued irrigation. A large fraction of the fluoride in topsoil sampled at a distance of 0.5–1.0 km from an aluminum smelter was reported to be in water soluble form (Polomski et al., 1982). The authors concluded that the fluoride was present as calcium fluoride.

Breimer et al. (1989) determined the vertical distribution of fluoride in the soil profiles sampled near an industrial region. In calcareous soils, fluoride (as extractable with hydrochloric acid) was restricted to the top 40–50 cm, probably due to the precipitation of calcium fluoride in the presence of lime. A slight leaching of fluoride into the B and C horizons was reported in non-calcareous soils. Water-extractable fluoride showed an increase with depth in the A horizons and subsequently decreased to base levels in the lower subsoil. The adsorption of fluoride from the water phase may be an important transport characteristic in calcareous soils at low flow rates, but this exchange may be rate-limited at high flow rates (Flühleret al., 1982). Dissolved fluoride concentrations may be high around the root zone in soils with a high fluoride input such as from atmospheric deposition. The high concentrations exist only for a limited time until the fluoride is withdrawn from the solution. The adsorption isotherm was reported to be non-linear between initial concentrations of 10 and 50 mg/l. Retention of fluoride in uncontaminated calcareous soil was higher than retention in calcareous soil from areas with fluoride contamination. The adsorption and desorption of fluoride in acidic soil were not related to previous fluoride contamination.

Fluoride-containing solutions increased the mobilization and leaching of aluminum from soils. Leaching of aluminum was reported to be greater from soil contaminated from an aluminum smelter than from uncontaminated soil (Haidouti, 1995). In the uncontaminated soil, losses of aluminum from the acid soil were higher than those from the calcareous soil. Arnesen (1998) also found that fluoride can solubilize aluminum, iron and organic material and can increase soil pH through exchange with hydroxide ions.

Unlike other soluble salts, fluoride was not leached from naturally salinized salt-affected soil. It was redistributed within the soil profile (Lavado et al., 1983). The adsorption of fluoride to soils increased with decreasing pH within the pH range 8.5–6. Retention of fluoride in the soil was positively correlated with ammonium acetate extractable iron.

2.2. Guidelines and Standards

2.2.1. Guidelines

The WHO guideline for fluoride is 1.5mg/lit, while the Ethiopian Drinking water quality guideline (EDWQG) recommended 3mg/l (MoWR,2002).

A lot of work has been done to establish drinking groundwater standards for fluoride in the world (Laksham, 1979 Hammer, 1986; Brouwet, et al., 1988; WHO, 1996). The general conclusion emanating from all findings is that it is particularly important to consider climatic conditions, volumes of water intake and other factors in setting national standards for fluoride. This point is extremely important, not only in setting national standards for fluoride but also in taking data from one part of the world and applying it in regions where local conditions are significantly different.

Temperature has been used in most cases to determine the optimum fluoride concentration at which minimal or no health effects will occur. This is because of general understanding that water consumption is dependent up on environmental temperature.

A source of additional fluoride at higher pH could be the exchange of hydroxyl ions for fluoride ions in liable positions on fluorine containing phyllosilicates, mainly clays and weathered micas such as biotite and muscovite that are present in the fine-grained sediments (Shivanna et al., 2003).

In groundwater, fluoride concentrations vary with the type of rock the water flows through but do not usually exceed 10 mg/liter (US EPA, 1985a). In the Rhine in the Netherlands, levels are below 0.2mg/l. In the Meuse, concentrations fluctuate (0.2–1.3 mg/l) as a result of industrial processes (Slooff et al., 1988).

In groundwater low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Concentrations in water are limited by fluorite solubility, so that in the presence of 40 mg /1 calcium it should be limited to 3.1 mg /1 (Hem, 1989).PH values of greater than 8.5 are probably necessary for this process to be a substantial fluoride source relative to dissolution of fluoride bearing minerals because the hydroxyl ion concentration would be too low at lower pH values. (Ramamohana Rao et al, 1993).

Table 2: Recommended quality (health) guidelines for drinking water for elements and ions

Parameter in mg/l except for EC andpH	Maximum limit of no risk, ideal good	Low risk rang, Marginal	Medium- high risk range, poor un-acceptable
EC(mS/m, 25^{o}c)	150	150-370	370
PH low	4.5	4.5-4.0	<4.0

PH high	10	10-10.5	>10.5
Ca	150	150-300	>300
Mg	100	100-200	>200
Na	200	200-400	>400
K	50	50-100	>100
Cl	200	200-400	>600
SO_4	400	400-600	>600
F	1.0	1.0-1.5	>1.5

Source: Republic of South Africa (RSA) water, (DW AF, 1996).

According to WRC (2001) South Africa is among the noted in the world for experience high level of fluoride ion concentrations in groundwater on a regional scale. Several researchers have noted the F^- content of certain groundwater in South Africa. Ockerse in 1946 measured rock, soil and groundwater concentration of F^- in an attempt to understand the cause of endemic dental fluorosis. The study covered the whole of South Africa than the farmer union of south Africa but fortunately gave the western bushveld only superficial attention.

Table 3: Fluoride guideline (WRC, 1998)

Fluoride range(mg/l)	Drinking		Food preparation	Bathing	Laundry
	Health	Aesthetic			
<0.7	No health effect	No effects	No effects	No effects	No effects
0.7-1.0	Insignificant health effects insensitive groups insignificant tooth staining	No effects	Insignificant health effects in sensitive groups	No effects	No effects
1.0-1.5	Increasing effects in	No effects	Increasing effects insensitive groups	No effects	No effects

	sensitive groups and tooth staining				
1.5-3.5	Possible health effects in all individuals and marked tooth staining	No effects	Possible health effects in all individuals	No effects	No efects
>3.5	Increasing risk of health effects and severe tooth staining	No effects	Increasing risk of health effects	No effects	No effects

Anon 1998 the optimum fluoride content of drinking water means a fluoride concentration of not more than 0.7mg/l in public water supply. It is however known that the optimum fluoride dosage is dependent on annual average maximum daily temperature there is a certainty as to the prices concentration of F^- in drinking water that is optimal for human healthy as these will vary country to country (Globler and Dreyer 1998).

Table 4: The maximum fluoride ion concentration limits recommended for drinking water

Organization	Proposed effects mg/l in drinking water		
	Objectable dental fluoride	Skeletal fluoride	Crippling skeletal
WHO	>1.5	3.0-6.0	>1.0
US EPA	>2.0	-	>4.0
Tanzania	_	>8.0	-
Argentina	>1.5	-	-
Ethiopia	>3	-	-

(DWAF 1996) as a warning recommend that the concentration of fluoride in potable water never exceed 4.0mg/l, due to the likelihood of skeletal fluorosis with crippling, as well as the loss of teeth.

Table 5: Effects of fluorine on human health (DWAF 1996)

F(mg/l)	Effects
0-1.0	The concentration in water necessary to meet requirements for health tooth structure is the function of daily water intake and hence varies with annual maximum daily air temperature. A concentration of approximately 0.75mg/l corresponds to a maximum daily temperature of approximately 26^{o}c-28^{o}c. No adverse health effects or tooth damage occurs.
1-1.5	Slight mottling of dental enamel may occur in sensitive individuals. No other health effects are expected.
1.5-3.5	The threshold for marked dental mottling with associated tooth damage due to softening of enamel is 1.5mg/l. Above this mottling and tooth damage will probably be noticeable in most continues users of the water. No other health effects occur.
3.5-4.0	Sever tooth damage especially to infants' temporary and permanent teeth; softening of enamel and dentine will occur on continues use of water. Threshold for chronic effects of fluoride exposure, manifested as skeletal effects. Effects at this concentration are detected mainly by radiological examination, rather than overt
4.0-6.0	Sever tooth damage especially to the temporary and permanent teeth of infants; softening of the enamel and dentine will occur on continues use of water. Skeletal fluorosis occurs on long term exposure
6.0-8.0	Sever tooth damage as above. Pronounced skeletal fluorosis occurs on long term exposure

2.2.2. Chemical Water Quality Standards

Table 6: Chemical water quality standards of South Africa (DWAF 1996).

Type of impurity	Max. permissible limit
Chloride	250mg/l
Nitrate(NO_3)	45mg/l
Iron	0.3mg/l

Manganese	0.05mg/l
Arsenic	0.05mg/l
Selenium	0.05 mg/l
Barium	1.0 mg/l
Cadmium	0.01 mg/l
Chromium	0.05 mg/l
Silver	0.054 mg/l
Lead	0.05-0.1 mg/l
Copper	1.0-3.0 mg/l
Zink	15 mg/l
Magnesium	125 mg/l
Sulphate	250 mg/l
Fluoride	1.5 mg/l
Cyanide	0.2 mg/l

2.2.3. Physical Water Quality Standards

Table 7: Physical water quality standards of South Africa(DWAF 1996).

Type of impurity	Maximum permissible limit
Turbidity	5-10mg/l on JTU scale
Color	10 to 20 color number on platinum-cobalt scale
Taste	Un objectionable
Odour	Threshold odor number limited among 1 to 3
PH value	6.5 to 8.0
Hardness	75-115
Total solids	500-1000

2.3. De-fluoridation Techniques

This section introduces the basic characterization of the removal methods, followed by discussion of the most promising defluoridation methods; bone charcoal, contact precipitation, Nalgonda, activated alumina and clay. All of the de-fluoridation techniques are not discussed in this thesis, but some of them are as follows.

2.3.1. Bone Charcoal

Bone charcoal is a blackish, porous, granular material. The major components of bone charcoal are calcium phosphate 57–80 percent, calcium carbonate 6–10 percent, and activated carbon 7–10 percent. In contact with water the bone charcoal is able to a limited extent, to absorb a wide range of pollutants such as color, taste and odor components. Water treated with poor bone charcoal may taste and smell like rotten meat and be aesthetically unacceptable. Once consumers are exposed to such a smell or taste, they may reject the bone charcoal treatment process and it may be difficult to persuade them to try water from the process again. It is therefore essential to ensure that the bone charcoal quality is always good. Even single failures in the production may be disastrous for a defluoridation project (Dahi and Bregnhøj, 1997). Bone charcoal is prepared by heating ground bone in retorts or in pots stacked in a furnace resembling a potter's kiln, without or with only limited admission of atmospheric oxygen. Ground bone is prepared industrially by degreasing, boiling, washing and drying, prior to grinding and sifting out. The bone grains are normally available from the manufacturing of bone meal used as fodder additive (Mantell, 1968). The potential disadvantage of bone charcoal is related to the problems of supply to local users. Industrially prepared bone charcoal used to be commercially widely available some decades ago. Today the commercial distribution of bone charcoal is much more limited. One option may therefore be to prepare the bone charcoal at village factory or household level (Jacobsen and Dahi, 1998).

2.3.2. Activated Alumina

Activated alumina is aluminum oxide (Al_2O_3) grains prepared to have a sportive surface. When the water passes through a packed column of activated alumina, pollutants and other components in the water are adsorbed onto the surface of the grains.

Eventually the column becomes saturated: first at its upstream zone and later, as more water is passed through, the saturated zone moves downstream with the column eventually becoming totally saturated.

Total saturation means that the concentration of fluoride in the effluent water increases to the same value as the influent water. Total saturation of the column must be avoided. The column should only be operated to a break point, where the effluent concentration is at normal saturation.

The alumina process is designed as a sorption process according to the same principle as bone charcoal. Similar considerations about the flow and the mix are valid. Also in the case of alumina the key design parameter is the operational defluoridation capacity, which may deviate from the theoretical capacity.

During this process about 5–10 percent of the alumina is lost, and the capacity of the remaining medium is reduced by 30–40 percent. After 3–4 regenerations the medium has to be replaced. Alternatively, in order to avoid on-site regeneration, the saturated alumina can be recycled to a dealer, who can adjust the capacity of the activated alumina to the desired value by using an appropriate mixture of fresh and regenerated media.

According to Hao and Huang (1986) the fluoride removal capacity of alumina is between 4 and 15 mg/l. Experience from the field, however, shows that the removal capacity is often about 1 mg/l. Thus, there seems to be a large difference in the degree of "activation" of alumina products. One of the explanations may be due to variation in pH. The capacity of alumina is highly dependent on pH, the optimum being about pH 5. While it may be easy to adjust pH for maximum removal at a waterworks, it is necessary to depend on the actual pH of the raw water in domestic and small community treatments. Activated alumina is a widely available industrial chemical. It is, however, not as widely distributed at the grass roots level as aluminum sulfate. Furthermore, its use has been limited by the difficulties of regeneration, the low capacity of less purified technical grade products and the relatively high price. Activated alumina has become less costly and more popular, especially where it is manufactured.

2.4. Physical and Chemical Properties of Fluoride

There is one stable isotope of fluorine (F), with an atomic mass of 18.9984. There are also several radioactive isotopes (17F, 18F, 20F, 21F and 22F), with 18F having the longest half-life (109.7 min) (Weast, 1986). At room temperature, hydrogen fluoride (HF) (relative molecular Mass 20.01; density 0.991 g/l) is a colorless, pungent, acrid liquid or gas with a melting point of 83 °C and a boiling point of 19.5 °C. Hydrogen fluoride is highly soluble in many organic solvents and in water, in which it forms hydrofluoric acid (Neumüller, 1981; Weast, 1986). Calcium fluoride (CaF_2) (relative molecular mass 78.08) is a colorless solid with a melting point of 1403 °C and a boiling point of 2513 °C. It is relatively insoluble in water — approximately 3000 times less soluble in water than sodium fluoride (McIvor, 1990) — as well as in dilute acids and bases (Neumüller, 1981). Calcium fluoride is also known as fluorite. Fluorspar is a mineral containing 60–97% calcium fluoride, depending on the grade. Sodium fluoride (NaF) (relative molecular mass 41.99) is a colorless to white solid with high melting (988–1012 °C) and boiling (1695 °C) points. It is moderately soluble in water (Neumüller, 1981). Fluor silicic acid (H_2SiF_6) (relative molecular mass 144.08), which is also known as hexafluoro silicic acid, hydrofluorosilic acid, fluosilicic acid or fluorosilicic acid, is a colorless solid that is highly soluble in water. Sodium hexafluorosilicate(Na_2SiF_6) (relative molecular mass 188.05), also known as disodium hexafluoro silicate or sodium silicofluoride, is a colorless solid that is moderately soluble in water. Sulfur hexafluoride (SF6) (relative molecular mass 146.05; density 6.16 g/l) is a colorless, odorless, tasteless, chemically inert and non-flammable gas. It is slightly soluble in water but readily soluble in ethanol and bases (Weast, 1986).

2.5. Anthropogenic Sources

2.5.1. Production and Use

2.5.1.1. Hydrogen Fluoride

Hydrogen fluoride (hydrofluoric acid) is an important industrial compound, with an estimated annual world consumption in excess of 1 million tons (Greenwood and Earnshaw, 1984). Hydrogen fluoride is manufactured from calcium fluoride and is used mainly in the production of synthetic Cryolite, Aluminum fluoride (AlF_3), motor gasoline alkylates and chlorofluorocarbons; however, the demand for chlorofluorocarbons is decreasing as a result of efforts to restrict their use. Hydrogen fluoride is also used in the synthesis of uranium tetrafluoride(UF_4) and uranium hexafluoride (UF_6), both of which are used in the nuclear industry (Neumüller, 1981). It is also used in etching semiconductor devices, cleaning and etching glass, cleaning brick and aluminum and tanning leather, as well as in petrochemical manufacturing processes. Hydrogen fluoride may also be found in commercial rust removers (Upfal and Doyle, 1990).

2.5.1.2. Calcium Fluoride

Industrially, calcium fluoride is the principal fluoride-containing mineral used (WHO, 1984). Identified production data were confined to the USA, where the average annual production of calcium fluoride was estimated to range from 118 000 to 225 000 tones during 1972–1978 (ATSDR, 1993). The consumption of calcium fluoride (as fluorspar) in Canada in 1989 was estimated at 180 000 tones (Government of Canada, 1993); in 1977, the estimated consumption of calcium fluoride in the USA was 1 063 000 tones (ATSDR, 1993). Calcium fluoride is used as a flux in steel, glass and enamel production and as the raw material for the production of hydrofluoric acid and anhydrous hydrogen fluoride (Neumüller, 1981). Calcium fluoride is also used as a molten electrolyte for the separation of oxygen and alumina in aluminum production.

2.5.1.3. Sodium Fluoride

Data concerning the total annual consumption or production of sodium fluoride worldwide were not identified. Sodium fluoride is usually prepared from hydrofluoric acid and sodium carbonate or sodium hydroxide (Neumüller, 1981); it is used in the controlled fluoridation of drinking-water, as a preservative in certain glues, in glass and enamel production, as a flux in steel and aluminum production,as an insecticide and as a wood preservative (Neumüller, 1981).

2.5.1.4. Fluor silicic Acid

Fluor silicic acid is an aqueous solution that is most commonly manufactured as a co-product from the manufacture of phosphate fertilizers. It is used widely for the fluoridation of drinking-water, in which it hydrolyses to release fluoride ions. When used for the fluoridation of drinking-water, Fluor silicic acid should meet appropriate standards, such as those published by the American Water Works Association and the European Committee for Standardization or other approved schemes for drinking-water chemicals (Neumüller, 1981).

2.5.1.5. Sodium Hexafluoro silicate

Sodium hexafluoro silicate, like Fluor silicic acid, is used in the fluoridation of drinking-water. It is normally completely dissolved in water prior to dosing, when it hydrolyses to give fluoride ions. When used for drinking-water fluoridation, it too should meet appropriate standards of purity for drinking-water chemicals (Upfal and Doyle, 1990).

2.5.1.6. Sulfur Hexafluoride

More than 110 tons of sulfur hexafluoride are imported into Canada annually (Government of Canada, 1993). This substance is used extensively as an insulation and current interruption medium in electrical switchgear, such as power circuit breakers, in various components in electrical substations (Government of Canada, 1993) and as a protective inert gas over molten metals, such as magnesium andaluminum (Neumüller, 1987). Over 90% of the total amount of sulfur hexafluoride imported into Canada is used in the production of magnesium; the remainder is used in electrical switchgear (Government of Canada, 1993).

2.5.1.7. Fluorapatite

Fluorapatite, an important calcium and fluoride-containing mineral, is used as a source of phosphates in the fertilizer industry (Neumüller, 1981).

2.5.1.8. Phosphate fertilizers

Phosphate fertilizers are the major source of fluoride contamination of agricultural soils. They are manufactured from rock phosphates, which generally contain around 3.5% fluorine (Hart et al., 1934). However, during the manufacture of phosphate fertilizers, part of the fluoride is lost into the atmosphere during the acidulation process, and the concentration of fluoride in the final fertilizer is lowered further through dilution with sulfur (superphosphates) or ammonium ion (Ammoniated phosphates); the final product commonly contains between 1.3 and 3.0% fluorine (McLaughlin et al., 1996). In Australia, an average annual addition of fluoride to soil through fertilization has been estimated to be 1.1 kg/ha.

2.6. Beneficial Uses of Fluorides

The beneficial attributes of fluorides to human health have been known for some years (WHO, 1970; WHO, 1984). When ingested at specific doses, the fluoride ion is beneficial to both bone and dental development in human beings. The beneficial plateau is generally between 0.5mg/l and 2.0mg/l depending on average ambient temperatures which control fluid intake and thus the total dose/day. The total daily intake of fluoride from food is about 0.2-0.5mg, which is only 10-15% of the desirable dose (Pontius, 1991, Boyle and Chagnon, 1995). It has been noted that the fluoride ion is a normal constituent of all diets and at correct concentrations it has beneficial effects in preventing dental caries (Pontius, 1991).

Dental caries is a disease caused by specific bacteria harbored in dental plaque, fermenting carbohydrate to produce acid that can demineralize tooth enamel (Hammer, 1986). If this demineralization is allowed to continue, the enamel is penetrated permitting bacterial invasion and eventual loss of the tooth by decay in the absence of restorative dental care. It can be reduced by the use of fluoride products. The level of dental caries (measured as the mean number of decayed missing or filled teeth) falls from seven at a fluoride concentration of 0.1mg/l to around 3.5 at a fluoride concentration of 1.0mg/l as the fluoride ion concentration increases further (up to 2.6mg/l) dental decay continues to fall, but only slightly (Dean, 1942; USPHS, 1991). The optimal level of fluoride for a temperate climate has been found to be around

1.0mg/l. This concentration seems to be associated with substantial resistance to tooth decay but with only a small and cosmetically insignificant increase in prevalence of dental fluorosis for individual, other effective methods for the prevention and control of caries is to restrict intake of dietary sugars and plaque control by flossing and brushing.

2.7. Factors that Affect the Distribution of Fluoride in Groundwater

Fluoride ion concentrations in natural water have been found to depend on a number of factors. These include temperature, pH, presence or absence of complexing and precipitating ions, solubility of fluoride-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F), type of geological formations traversed by water and the amount of time that water is in contact with a certain geological formation as discovered by Apambire, et al., 1997. However, the main source of F is most probably the dissolution of the various minerals of which the most important is fluorite, CaF_2. The inverse relationship between F and Ca and the positive relationship between F and HCO^{-3} and F and Na are in agreement with the following equations:

$$CaF_2 + Na_2\,C0_3 \sim CaC0_3 + 2\ Na+ 2F$$

$$CaF_2 + 2NaHCO_3 \sim CaCO_3 + 2Na+ + 2F + H_20 \text{ and } CO_2$$

In a country such as Ethiopia with its extreme climatic variations between very wet and very dry seasons one might anticipate a variation in the fluoride content of the groundwater. If this were true it would be important not only to know the fluoride levels in groundwater used for drinking purposes but also the range of variation. The variation in fluoride content is considered to be the result of the interplay of a number of factors of which the more important it is important to understand these factors in order to be able to properly manage fluoride in water resources. It was observed during this study that the fluoride levels in groundwater sources varied from one season to another and from one month to another. It was observed that in other sources the changes were minimal. This raised the interest of determining some of the factors that could contribute to this behavior. These are the following;

- The effect of climate, e.g. rainfall
- The role of other water quality parameters,

2.7.1. The Role of Climate

During the dry months, the water evaporates from the main rocks and soils that contain fluorides. This contributes to an increase in concentration as the various geological forms withhold the fluoride ion. More important is the fact of low inflow into aquifers. As a result, the fluoride content increases. During and after the rains, the Fluoride content decreases owing to dilution however, that is not always the case in some boreholes. The rains promote chemical weathering and leaching of various rocks rich in fluoride. The fluoride rich water might be carried down the direction of flow increasing the fluoride levels at the final basins in which the water ends. The nature of variations observed raised the need to look into other possible contributors such as the interactions of the fluoride ion with other water quality parameters and the role played by the geology of the area.

2.7.2. Correlation of F with Hardness

Water hardness is commonly defined as the sum of the Bivalent cations dissolved in water. The most common such cations are calcium and magnesium, although iron, strontium and manganese may contribute. Hardness is usually reported as an equivalent quantity of calcium carbonate ($CaCO_3$). It is primarily a function of the geology of the area with which the water is associated. Water underlain by limestone are likely to be hard because rainwater containing CO_2 continually dissolves the rock and carries the dissolved cations to the water system. These metals can precipitate the fluoride ion as their respective fluorides. The level of maximum possible calcium and magnesium in the presence of the fluoride ion in water is governed by the solubility principle.

2.8. Factors that Contribute to the Occurrence of High Fluoride in Groundwater

The incidences of high fluoride ion concentrations in groundwater have been attributed to various causes;

- High fluoride content of aquifers
- Low groundwater flow rates
- Semi-arid climate increasing potential evaporation
- High PH water
- Weathering of alkaline volcanic rocks rich in F
- Fluorspar mineralization and occurrences of rock phosphate deposits

Granites, Gneisses and other crystalline rocks having many fluorides bearing minerals as their essential and accessory mineral composition

- Residual soils including micaceous sand

- Variation in soil texture
- Industrial activities and use of pesticides and insecticides are less common and rare in most cases.

Various volcanic activities (Rao, et al, 1993, Fayazi, 1994, Rao, 1997, Agrawal and vaish, 1998, WRC, 2001).

In the majority of cases, the incidence of high fluoride ion concentrations in groundwater mainly a natural phenomenon, influenced basically by the local and regional lithological setting, mineralization characteristics and hydrological conditions (Fayazi, 1994, Rao, 1997, Agrawal and vish, 1998). The continues and long-term weathering and leaching mainly by moving and percolating water play the important role in the release of fluoride from minerals soils and rocks in to groundwater (Fayazi, 1994, Rao, 1997, Agrawal and vish, 1998). In South Africa it has been confirmed that the general distribution of the fluoride ion in ‘’problem areas’’ is controlled by the geochemistry of the rock in which the groundwater is encountered (MCaffrey, 1993, Fayazi, 1994, WRC, 2001). Lithological controls suggest that the causes of high fluoride concentrations in groundwater is due to the dissolution of fluoride bearing minerals in bedrock and soils (MCaffrey, 1993). The above factors can be classified in to three major classes as described below

1. Climatic conditions comparatively temperatures and precipitation favor effective chemical weathering (Nanyaro, et al., 1984). The composition of water therefore reflects partly the lithology of the drainage basins. During arid episodes and the process of erosion, weathered products derived from granitic rocks containing fluorite in the groundwater at this point (Fayaz, 1994). Groundwater associated with dolerite dykes and silts which have intruded sedimentary rocks often, have relatively high fluoride content.

   It has been found that higher fluoride concentrations are obtained in discharge area than in recharge areas, with a trend of fluoride enriched along the direction of flow. These features have been attributed to the smaller quantities of dissolved solids in the recharge areas (Gaciri and Davies, 1993).
2. Volcanism is an important factor determining fluoride content of the natural water (Gaciri and Davies, 1993). Four major geological systems are evident: metamorphic rocks of Precambrian age, sedimentary rocks of carboniferous to cretaceous age, tertiary and quaternary volcanic and unconsolidated tertiary and quaternary sediments. It is the chemical

leaching, weathering of these rocks and their associates that contribute to the release of fluoride in to the groundwater. Water from these volcanic rocks have shown relatively high fluoride content, up to180ppm or more. The fluoride content of amphiboles from metamorphic rocks worldwide varies from 30 to 21,400mg/kg (Gaciri and Davies, 1993). In this process the solubility of the mineral plays an important role.

3. Besides geological changes, which result in changes in recharge composition and mixing, several chemical processes have been identified as being important in controlling the major ion chemistry. Other existing minerals in the sub surface and other major and minor ionic constituents of groundwater may affect the dissolution characteristics of minerals, for example fluoride, CaF_2, (Rao, 1997).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Description of the Study Area

3.1.1. Location

This research was carried out in HawassaZuriaWoreda which is one of the nineteen Woredas of Sidama Administrative Zone of the Southern Nations Nationalities and Peoples Region (SNNPR). It is located 298 km south of Addis Ababa and 24km from Hawassa. This woreda is bordered on the south by Boricha, on the west and north by the Oromia region, and east by Hawassa Lake and Tula sub city. The geographic location of HawassaZuria site lies in 420000m to 437000m Easting and 766000m to 792000m Northing (Figure 1). The Woreda has 23 kebele administrations. The annual average rainfall at Woreda is 1016 mm in summer and the mean temperature ranges between 12^0C and 27.1^0C (IPMS, 2005). The altitude of the Woreda ranges from 1126 to 2123 m.a.s.l.

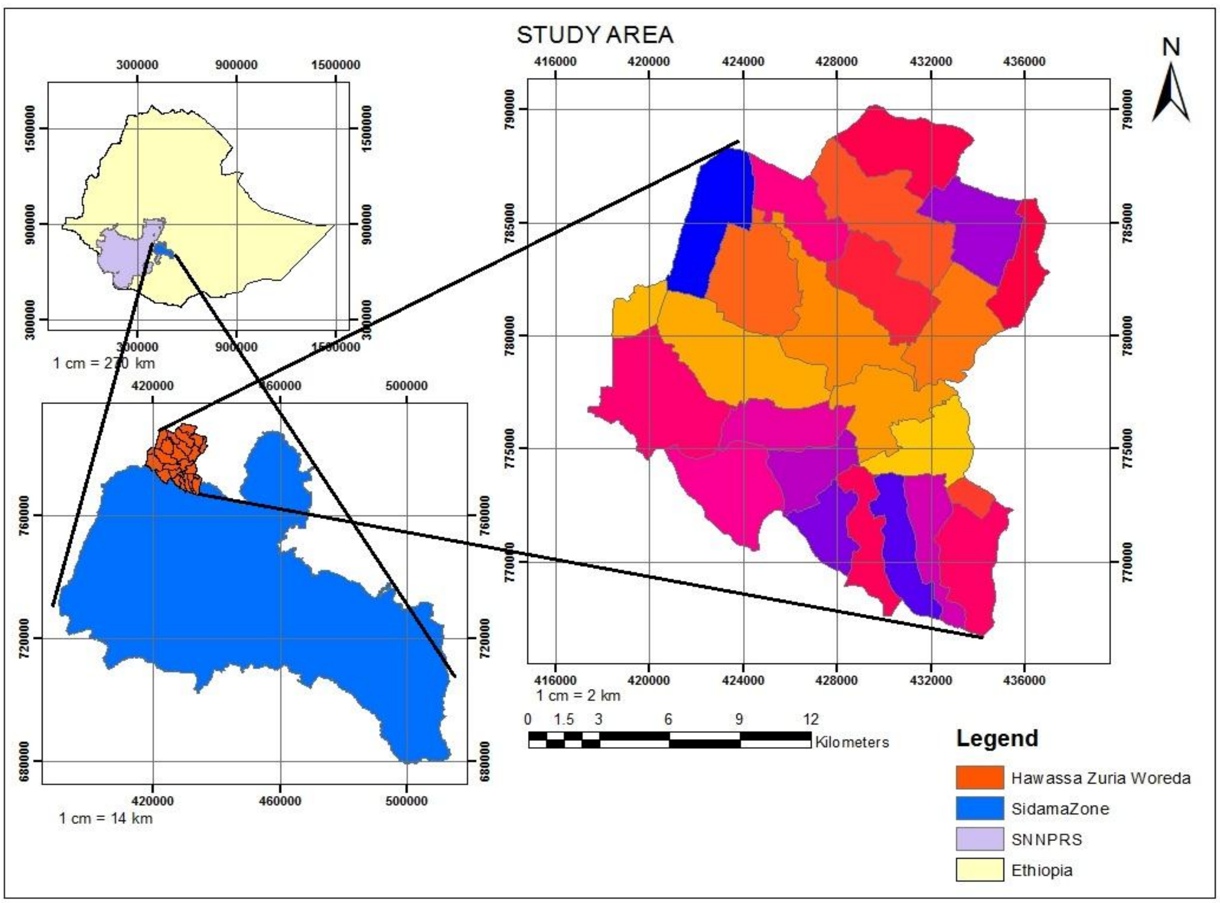

Figure 1: Map of Study Area

3.1.2. Agro-Ecology

According to MoA (2000) classification, agro-ecology of Ethiopia is classified as: Wurch, Dega, Weina-dega, Kolla, and Bereha. Similarly, the landform in HawassaZuriaWoredaalsoshowsvariations in agro-ecology as Dega, Woina–dega (dry and moist Woina–dega), Kola and wetmoistBereha.

Table: 8 Ethiopia's Agro-Climatic Zones (source: CARE Ethiopia, August 2014)

Name of Zone	Description	Altitude(masl)	Average temp(^{o}c)	Annual RF(mm)	Studyarea coverage (%)
Wurch	Cold, moist	>3200	<11.5	900-220	2.4%
Dega	Coo,humid	2400-3200	11.5-17.5	900-1200	15%
Wayna-dega	Cool, sub-humid	1500-2300	16-20	800-1200	37%
Kola	Warm,sumi-arid	500-1500	20-27.5	200-800	39.4%
Bereha	Hot, arid	<500	>27.5	<200	6.2%

This agro- ecological variation in landforms has had a significant influence on climatic condition of the Woreda.

3.1.3. Rainfall

The average monthly rainfall and temperature of HawassaZuriaWoreda recorded at HawassaMereologicalStation from the year 1990-2017 presented graphically as follows.

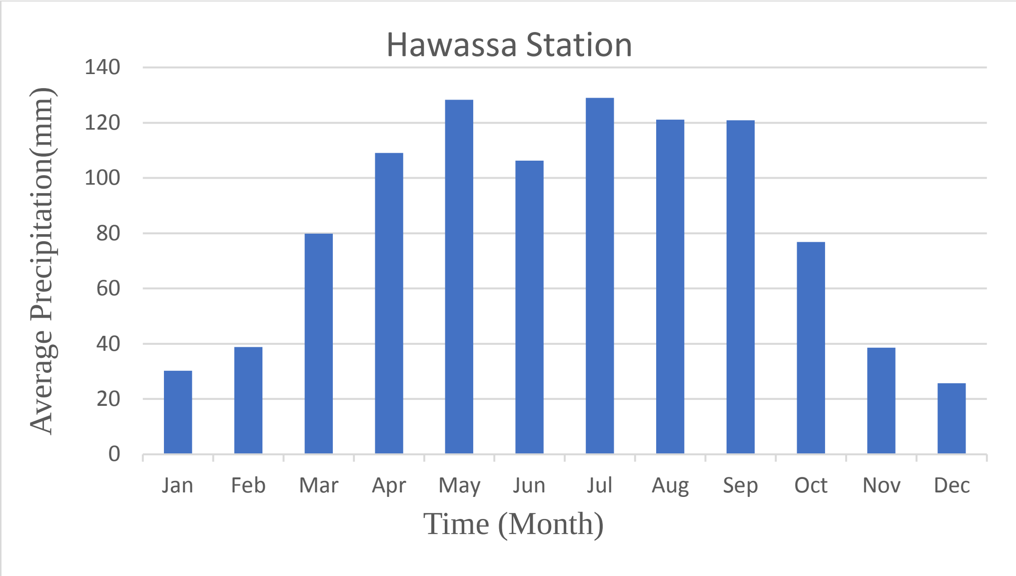

Figure 2: Average Monthly Rainfall distribution in the study area (1990-2017) (Source:NMSA)

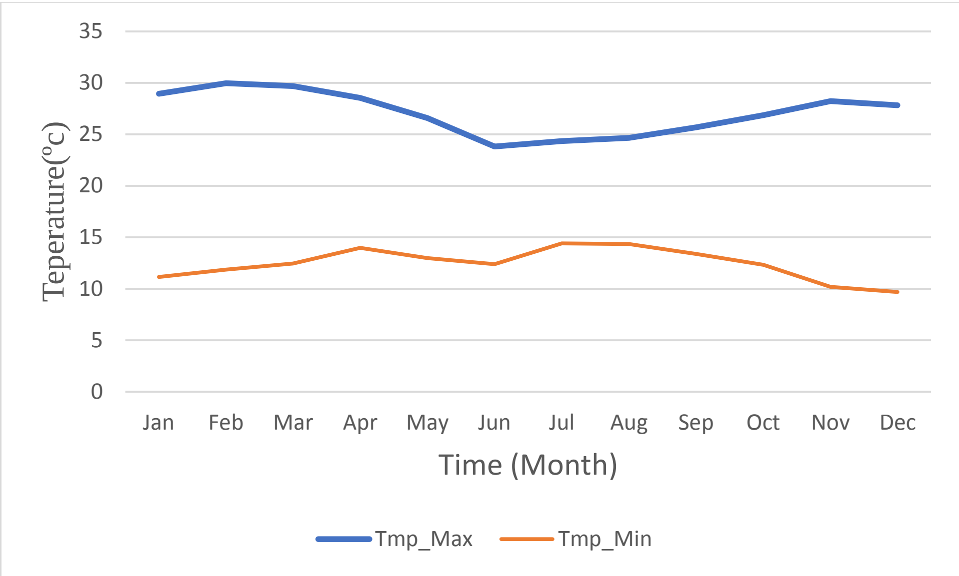

Figure 3: Average Monthly Minimum and Maximum Temperature for the study area (1990-2017)(Source:NMSA)

3.1.4 Geology

The geologic, volcanic and tectonic formation the study area was entirely associated with past and former geological formation of the rift valley (Mohr 1968, GidayWoldeGebriel, et al., 1990).

The present occurring geologic units in the study area or the rift valley and in the floor, are characterized by geological formations of before, during and after formation of the main Ethiopian rift valley. The formation of the study area was characterized by recent volcanic event which was part of rift valley materials and structures including land surface of the HawassaZuriaWoreda around Lake Hawassa. As extracted from Ministry of Water, Irrigation and Electricity map product which shown below (figure 4) theHawassaZuriaWoredawas composed of Lissies formation (Lacustrine volcanic rock deposit), Dino formation (gravel rock deposit) and Abaya rhyolite.

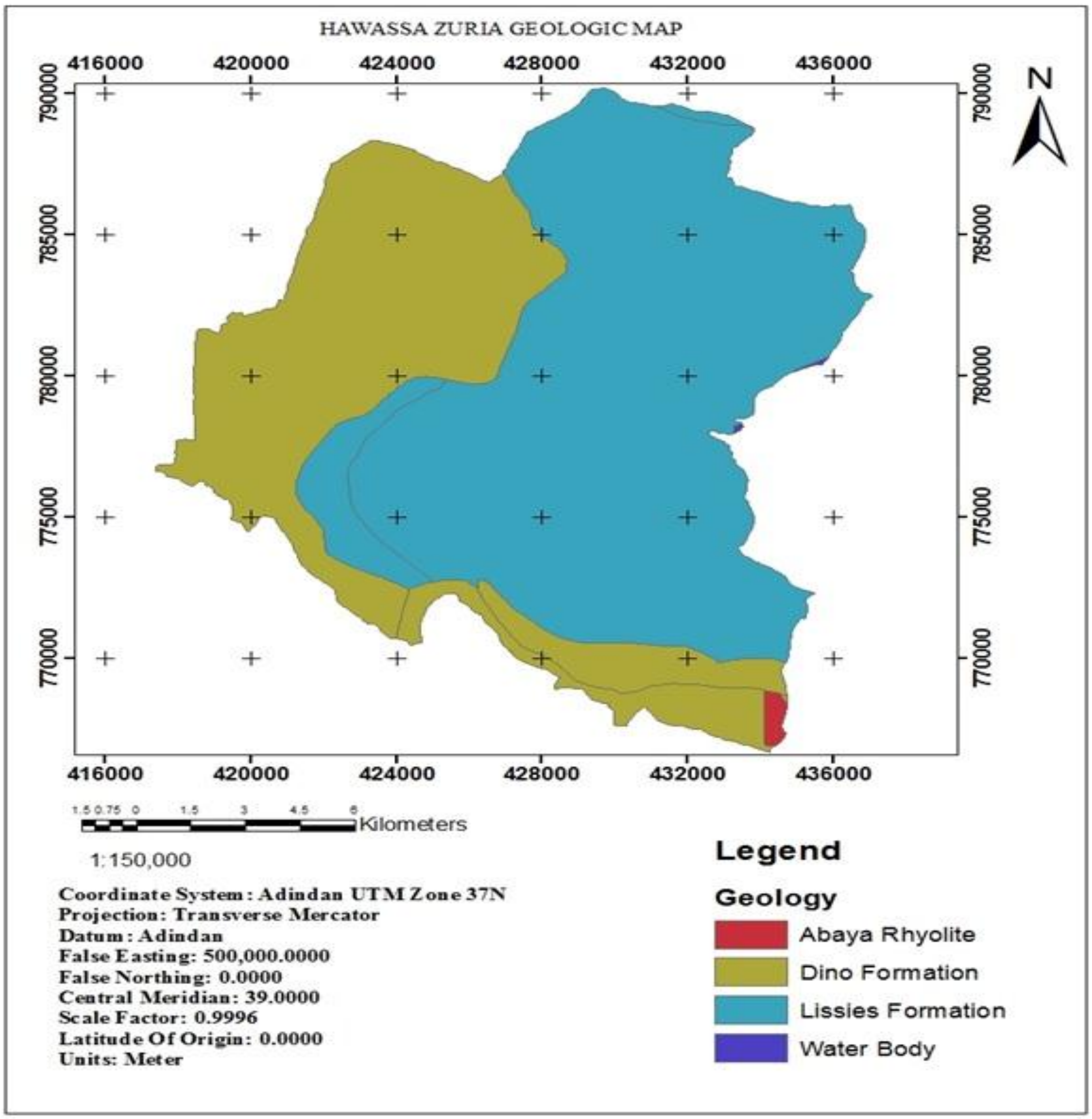

Figure 4: Geological Map of HawassaZuriaWoreda

3.2. Materials Used

3.2.1. Computer Requirements and Data

This study requires some software and hardware specification in order to install the software and analyze the data. Therefore, in addition to stationery materials and Global Positioning System (GPS) Arc-GIS were used to obtain spatialand temporal distribution of fluoride geographically.

The main input data used to know spatial and temporal distribution of fluoride is the location and fluoride concentration of sample well water points. To provide these data raw sample point data is collected from field including its location using GPS and the fluoride concentration is tested in laboratory.

3.3. Methods of Data Collection and Analysis

3.3.1. Sample Data Collection

To know the spatial distribution first of all sample data were subsequently collected from each exposed borehole of each kebele's by following combination of systematic and random sampling techniques while kebeles were identified as systematically technique each sample from the kebeles were taken randomly (Figure 5).

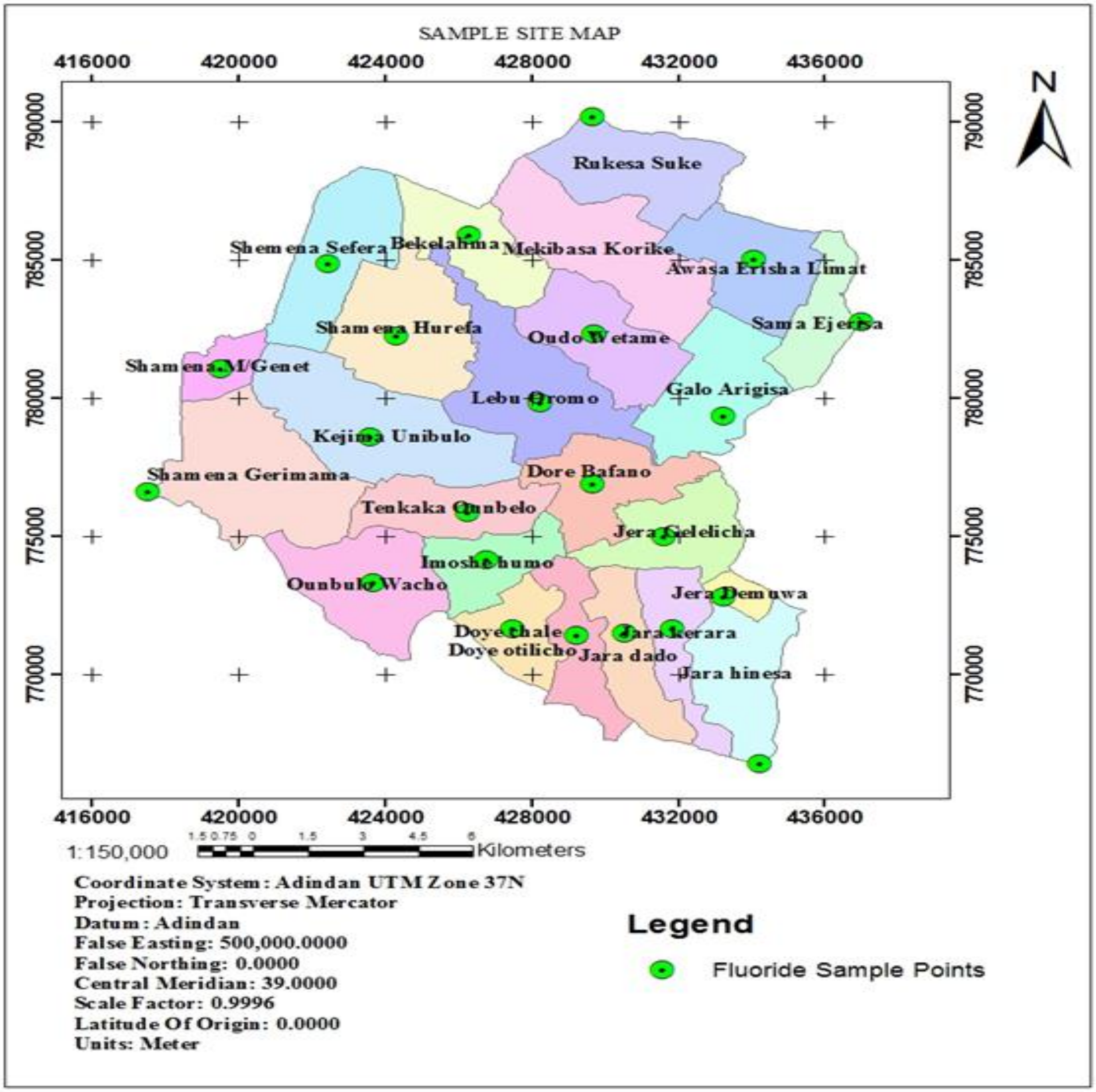

Figure 5: Sample Site Location within Twenty-Three Kebeles

To know the temporal distribution of different season in one year that is autumn, winter, spring and summer is used to collect the data for every sample points across the Kebele. Then, the samples collected underwent several analyses including: PH, Electrical conductivity, total dissolved solids and Fluoride. However, since this study focuses only on the fluoride concentration the procedure followed to determine the fluoride concentration is presented below.

3.3.2. Distribution and Risk of Fluoride Concentration

Once the fluoride concentration of each sample was determined the next steps is to determine the spatial distribution to clearly show variation due to change of location. To do this the location of sample points collected using GPS and the corresponding tested results were organized in Microsoft excel software. Then, this data is imported into ArcGIS and exported as point data to prepared geodatabase as per their location. Then, to represent the surface spatial distribution of the fluoride concentration interpolation were performed using the attribute of fluoride concentration as input again in ArcGIS environment. To analyze the temporal distribution of fluoride concentration the same procedure performed for the spatial distribution generations followed for collected data at different seasons throughout the year i.e. summer, spring, winter and autumn. Furthermore, to show the drop-in fluoride concentration due to change in the seasons throughout the year at sample points graphical analysis is performed.

To state risk of fluoride concentration in different place of study area at different season the fluoride concentration results were compared with different standards and guidelines for fluoride concentration through document review.

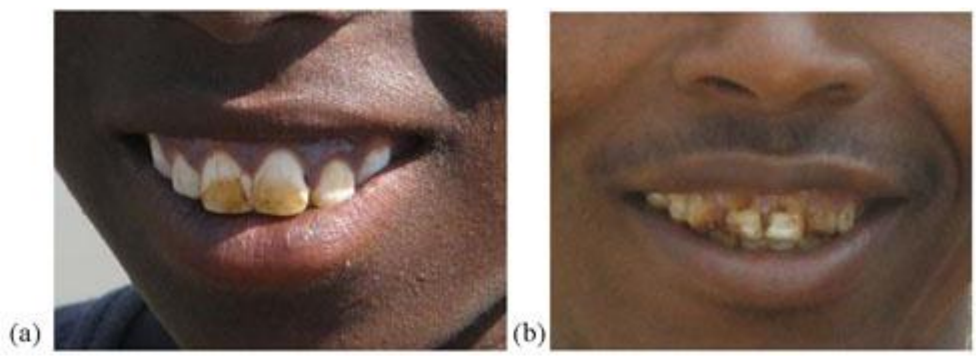

Fig 6: The health impact of high level fluoride in water dental fluorosis.

3.3.3. Statistical Analysis of Fluoride Concentration

Only descriptive statistics were calculated for fluoride concentrations measured. To do this the descriptive Statistics tool in Microsoft Excel was used to calculate mean, standard error, median, mode, standard deviation, sample variance, kurtosis, skewness, range, minimum, maximum, sum and count. Finally, the Pearson product moment correlation coefficient and the r square value were calculated for fluoride verses all other measured values individually with fluoride as the dependent value. The Pearson coefficient, r, is a dimensionless index that ranges from -1.0 to 1.0

inclusive and reflects the extent of a linear relationship between two data sets. The equation to calculate the Pearson coefficient is: while the squared, r^2, is the square of the Pearson coefficient and can be interpreted as the proportion of the variance in y attributable to the variance in x. For this study, fluoride is considered to be the x value. Following is a list of all the independent, or y values used. More information about methods and analysis for each of these values can be found in the main study report by McLemore, et al. (2009a).

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1 Fluoride Concentration Test and Groundwater Sources Inventory

Hand dug wells

There are 68 hand dug wells within the study area those are mainly used for public and livestock consumptions. Among which around 12 hand dug wells have been collected from primary data sources.

Depth and static water level of the majority of dug wells could not be obtained due to lack of the information and problem faced to measure them. However, from the existing data, the range of their depthis from 5 to 15m. The dominant aquifer formation is known to be lacustrine and alluvial deposits in thenorthern and central parts of the study corridor respectively.

Most of the hand dug wells yield is substantially decreasing during dry season. The seasonal fluctuation of the static water levels in most of the wells is highly attributed to the direct recharge condition from precipitation into the well which intern indicates the unconfined nature of the aquifers. Hand dug wells are constructed in both of recharging and discharging zones of the study area.

Boreholes

Both deep and shallow boreholes are drilled in the study area by Governmental, Non-Governmental and Private Drilling Company. There are about 48 deep boreholes where the depth varies between 56 to 224m, and 29 shallow boreholes with the range of 15 to 70m depth. Most of the deeper boreholes are fitted with submersible electrical pumps and the others boreholes are equipped with Indian mark II.

The main aquifer formations of the boreholes are Lacustrine and volcanic sediments, pyroclastic deposits, weathered and fractured basalt, ignimbrite, rhyolites and welded tuff having a variable thickness, weathering and fracturing intensity.

The fluoride concentration test of fluoride concentration HawassaZuriaKebeles at different season is presented below (Table 9).

Table 9: Fluoride Concentration Test of HawassaZuriaKebelefor Different Seasons.

No	Name of sampling site	Autumn	Winter	Spring	Summer	Elevation(m)	Easting	Northing	Well depth(m)	Well type
1	Udo Wotate	1.45	1.4	1.5	1.8	1710	430913	782321	18	SBH
2	Galo Argisa	1.71	1.7	1.72	1.9	2076	426378	778842	8	HDW
3	KajmaUmbulo	4.11	6.5	1.72	7.8	1722	426505	778864	153	DBH
4	MakbasaKorke	2.35	2.5	2.2	3.1	1750	432345	778775	87	DBH
5	ShamenaGarmama	0.5	0.45	0.55	0.4	1692	432590	778720	24	SBH
6	ShamenaMidre Genet	0.46	0.62	0.61	0.6	2071	422234	784331	35	SBH
7	ShamenaSefer	0.6	0.45	0.75	0.9	2078	422113	782797	43	SBH
8	Bake Lalima	1.25	1.3	1.2	1.4	2076	422290	783280	41	SBH
9	Hurufa	0.77	0.62	0.92	0.62	2074	423802	781033	20	SBH
10	LabuKoromo	1.86	1.9	1.82	2.91	1703	428680	778712	145	DBH
11	RukesaSuke	3.45	3.2	3.7	4.5	1705	432290	778711	33	SBH
12	SamaEjersa	7.10	7.01	7.2	8	1726	432189	778840	24	SBH
13	Dore Bafano	2.20	2.01	2.40	4.50	1709	429666	776863	15	HDW
14	JaraGalalcha	7.80	7.80	7.80	8.81	1702	431613	774982	19	SBH
15	JaraDamuwa	5.91	5.80	6.02	6.64	1703	433252	772780	5	HDW
16	JaraHinesa	4.25	3.70	4.80	5.15	1701	434681	771593	21	SBH
17	JaraKarara	6.36	6.02	6.70	7.01	1699	431756	773484	27	SBH
18	Jara Dado	1.82	1.75	1.89	2.90	1711	430930	773825	58	SBH

19	DoyoOtilcho	2.36	2.02	2.70	3.04	1760	427515	772688	70	SBH
20	DoyoChale	1.39	1.86	0.92	1.85	1765	426970	772069	30	SBH
21	ImosheHumo	1.67	1.65	1.70	2.06	1731	426824	773252	97	DBH
22	UmbuloWacho	1.35	1.25	1.45	2.06	1730	426521	774520	64	SBH
23	UmbuloTankaka	1.77	1.65	1.9	1.7	1715	426261	775842	52	SBH

As the Table 9 shows the distribution of fluoride ion concentration in HawassaZuriaKebeles at different season is ranges from 0.4 to 8.81 mg/l. As per the table, higher fluoride concentrations greater than recommended one by WHO, occur in some sample groundwater. The Kebeles with high fluoride ion concentrations include KajmaUmbulo, SamaEjersa, JaraDamuwa, JaraKarara,Dore Bafana andJaraHinasaprovinces. Other provinces experience the problem in a limited number of groundwater sources. As per the WHO recommendation the administrative kebele that are safe include ShamenaGarmama, ShamenaMidre Genet, ShamenaSefera and Hurufa. It should be noted, however, that all levels and ranges of fluoride occur to a certain degree in almost all provinces.

The situation of the fluoride distribution in this study area was such that no clear-cut demarcation can be made of the areas deficient in fluoride since some of those areas have sources in which the fluoride ion concentration was higher than the WHO recommended limits for drinking water. In addition, groundwater sources in the KajmaUmbulo, SamaEjersa, JaraDamuwa and JaraKarara provinces need for partial de-fluoridation. This must receive serious consideration if the water from those sources is currently being used for drinking purpose.

4.1. Frequency of Fluoride Concentration

The distribution of the fluoride ion concentrations calculated for the 23 Kebeles are shown in a bar chart below (Figure 7). From the chart it is evident that the population is highly skewed towards high fluoride concentrations. Although the tail of the graph is irregular, there is an increased frequency of occurrence of groundwater sources with fluoride ion concentrations in the range greater than 0.7 mg/l. This is not concern, as the health impacts on teeth and cannot become a problem at these levels.

As Figure 3 clearly showed the first range account for 4.35% had fluoride ion concentrations less than 0.5mg/l. According to the WHO a concentration of 0.5 mg/l is ideal for dental health (WHO, 1994). Also, Fluoride ion concentrations less than 0.5mg/l fall within the safe and ideal range (DWAF, 1996). Hence the concentrations will not cause dental crises if the water is consumed for a long period of time. The second range account for 8.69% had fluoride ion concentrations between 0.5mg/l and 0.7mg/l. This indicates that according to fluoride guidelines (WRC, 1998) this range has health effects and the DWAF and WHO agree on the safe limit of less than 0.7 mg/l for the fluoride ion concentration as ideal for health teeth. The third range account for 4.35% had fluoride ion concentrations between 0.7mg/l and 1mg/l. According to fluoride guidelines (WRC, 1998) this range has insignificant health effects. The fourth range from 1 mg/l to 1.5 mg/l shows no change in percentage from previous range. This range has an effect on dental fluorosis if consumed for a long period of time. The fifth range shows an increase in the number of sources with fluoride ion concentration which account for 52.17% is higher than 1.5 mg/l but than 4 mg/l. This is within the threshold limit for chronic effects of fluoride exposure.

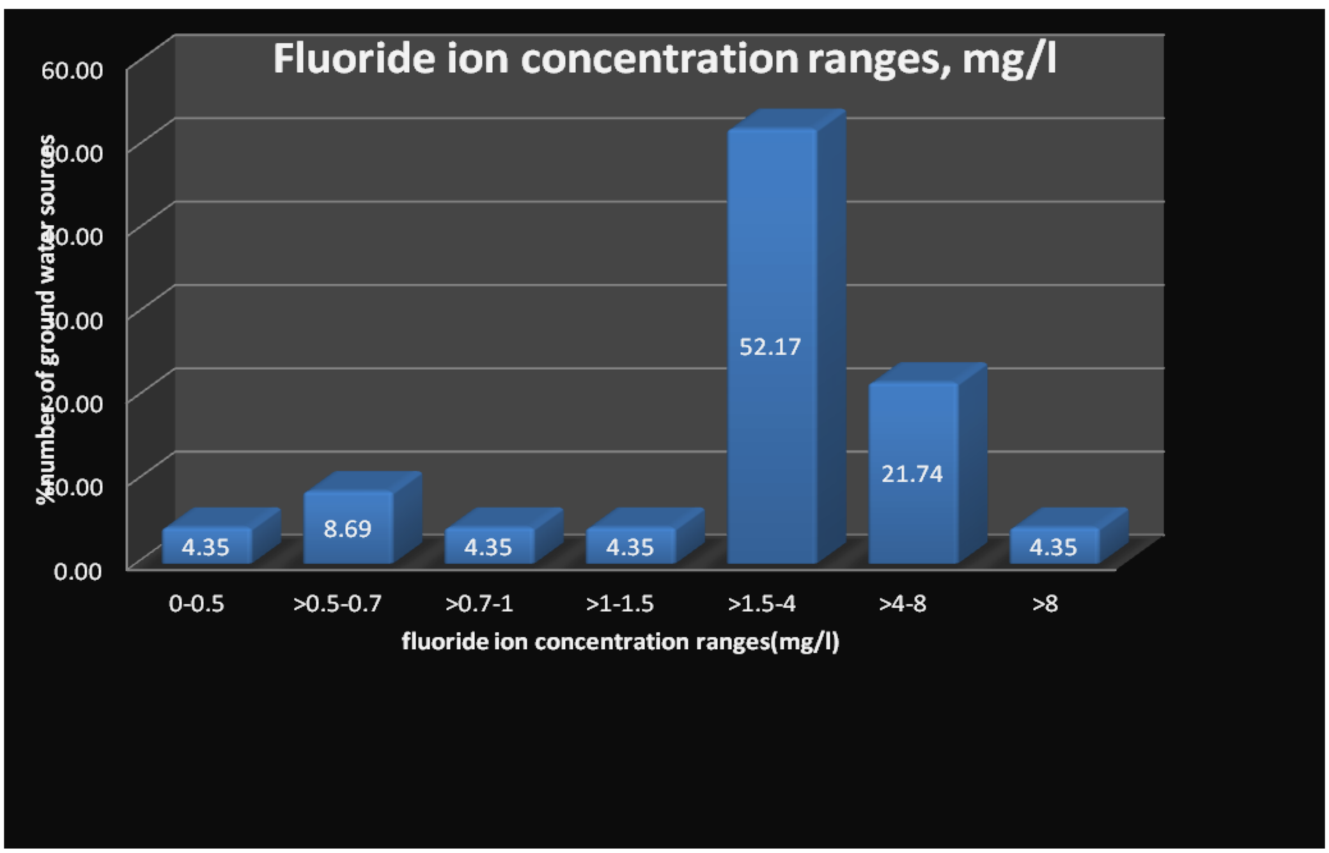

Figure 7: The Frequency Distribution of Fluoride Ion Concentrations of summer season.

Both dental fluorosis and skeletal fluorosis may be detected if the water is consumed for a long period since childhood. This range is not recommended by the DWAF for drinking water (DWAF, 1996). The sixth range which accounts for 21.74% had fluoride ion concentrations higher than 4mg/lbut less than 8mg/l.WHO recommends this range as sever tooth damage especially to the temporary and permanent teeth of infants, softening of the enamel and dentine may occur on continues use of water. Skeletal fluorosis occurs on long term exposure (WHO, 1994). At this level, slight mottling of teeth may occur in sensitive individuals (DWAF, 1996; WRC, 1998). Of the studied groundwater sources, the last range account for 4.35% had fluoride ion concentrations higher than 8.0 mg/l. It should be noted however that it is not the quantity of the groundwater sources that is important but the level of fluoride ion concentrations of the water, the impact on health and the population at risk due to the consumption of such water. It should be noted that there is a contradiction in what is understood as the safe limit for fluoride in drinking water. According to fluoride guideline (WRC, 1998) range increases risk of health effects and severe tooth staining. Generally, more than 82.5% of the water in HawassaZuriaWoreda groundwater sources is not good quality or enough for drinking water.

4.2. Occurrence and Distribution of Fluoride Concentrations

4.2.1. Spatial Distribution

The overall spatial distribution of fluoride ion concentrations in groundwater of HawassaZuriaWoredaKebeles for a sample one season is shown in map (Figure 8) and the other season spatial distribution is presented in appendices (Appendix V to VIII). The maps are separated to facilitate the delineation of those areas deficient in fluoride and those with high potential for dental fluorosis. The maximum allowable limit for fluoride ion concentration in drinking water is 1.5 mg/l. According to the WHO this water can be consumed for a maximum period of one year in order to avoid the occurrence of dental fluorosis. In all the maps a comparison of the fluoride levels and their distribution compared to the WHO standards for drinking water and guidelines as described in Chapter Two. Thus, as the map (Figure 8) below showed on most parts of the area the distribution of fluoride ion concentrations is beyond the safe recommended limits for drinking water.

As distribution shows, there are fluoride ion concentrations between 0.3 and 1.5 mg/l. Such areas are generally considered as deficient in fluoride where these levels persist for a long time. If such a situation persists, then the people using the water for drinking purposes will be susceptible to dental caries problems and they might be a need for fluoride supplementation in the form of fluoridation. However, caution must be exercised as the other sources were exhibit higher concentrations between 1.5mg/l and 7.8 mg/l at any time given the climatic conditions, type of aquifer, and type of geology among other factors. It was noted that prolonged consumption of this water could result in severe dental fluorosis or skeletal fluorosis.

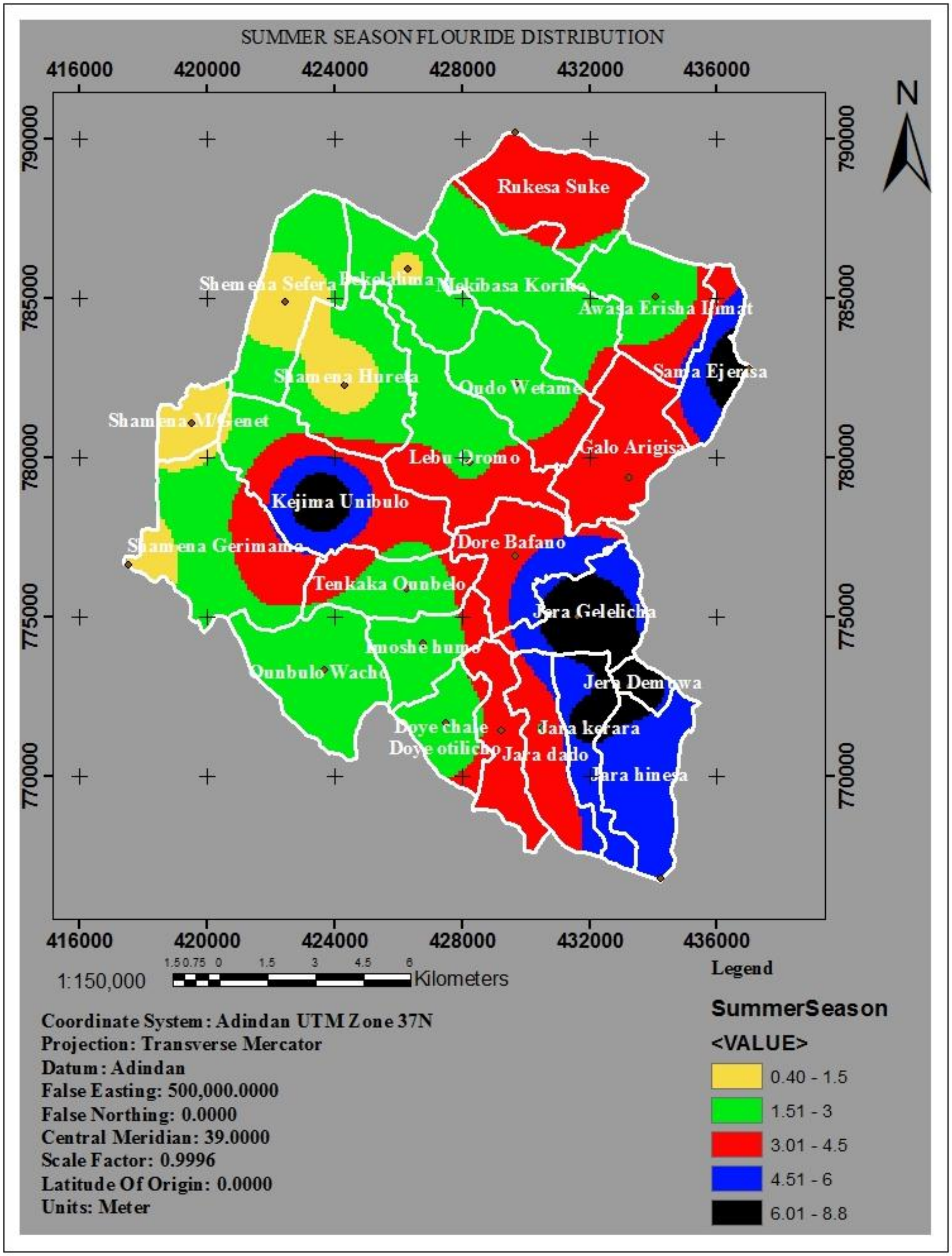

Figure 8: Spatial Distribution of Fluoride Concentration of Summer Season

4.3.2 Distribution of Fluoride Vertically

Many parts of the country have limited supplies of groundwater because of the poor permeability of the crystalline rocks and variable water-table depths.

Success with obtaining groundwater in these areas depends upon locating water-bearing fractures.

UN (1989) estimated that more than 20% of tube wells drilled in Ethiopia had been abandoned as a result of a combination of these reasons. Tube well depths vary considerably across the country.

Many in the Rift and highlands are in the range 50–100 m. Depths in the sediments of eastern Ethiopia (Ogaden) are often in excess of 200 m because of deep water tables.

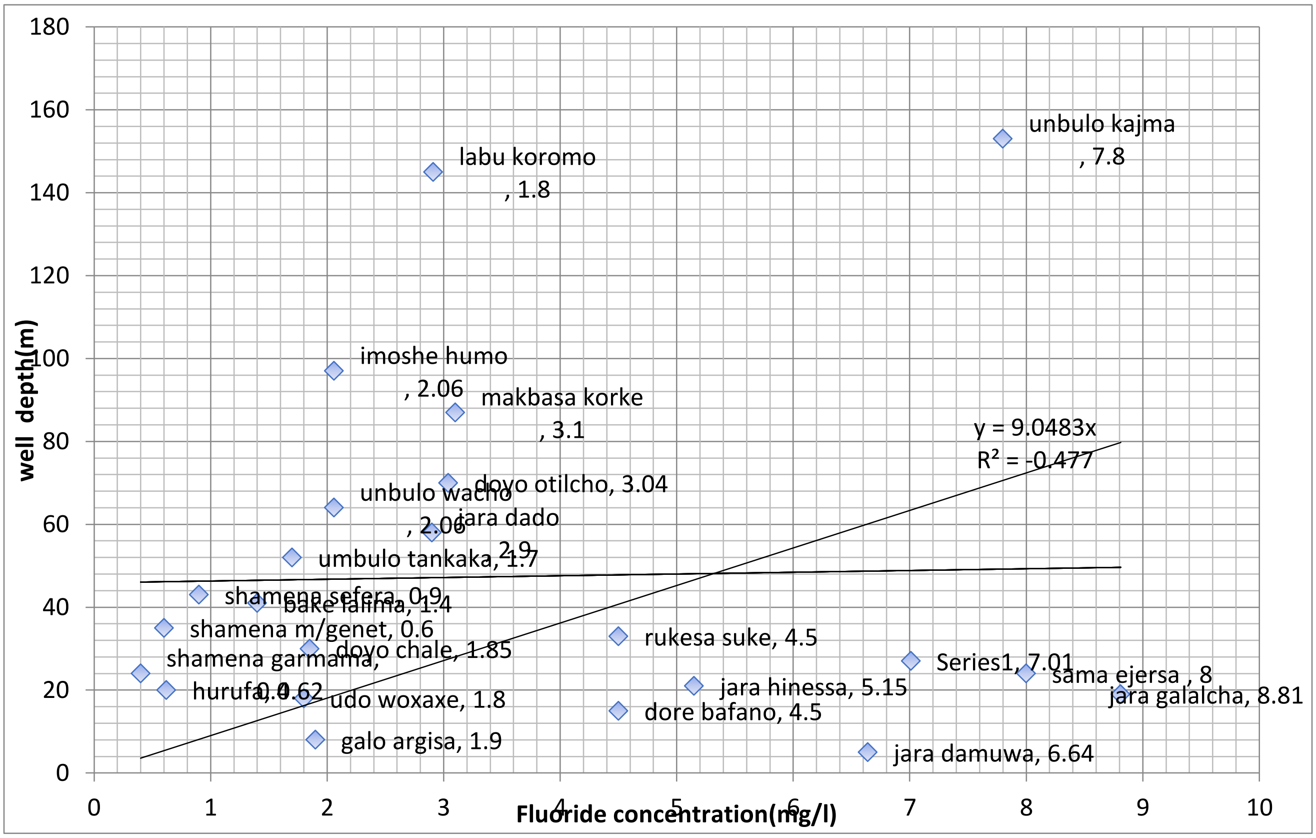

Fig 9: Vertical trends in fluoride concentration of study area.

4.3.3 Temporal Distribution

The surface temporal distribution of fluoride concentration for four seasons throughout the year is presented below (Figure 10).

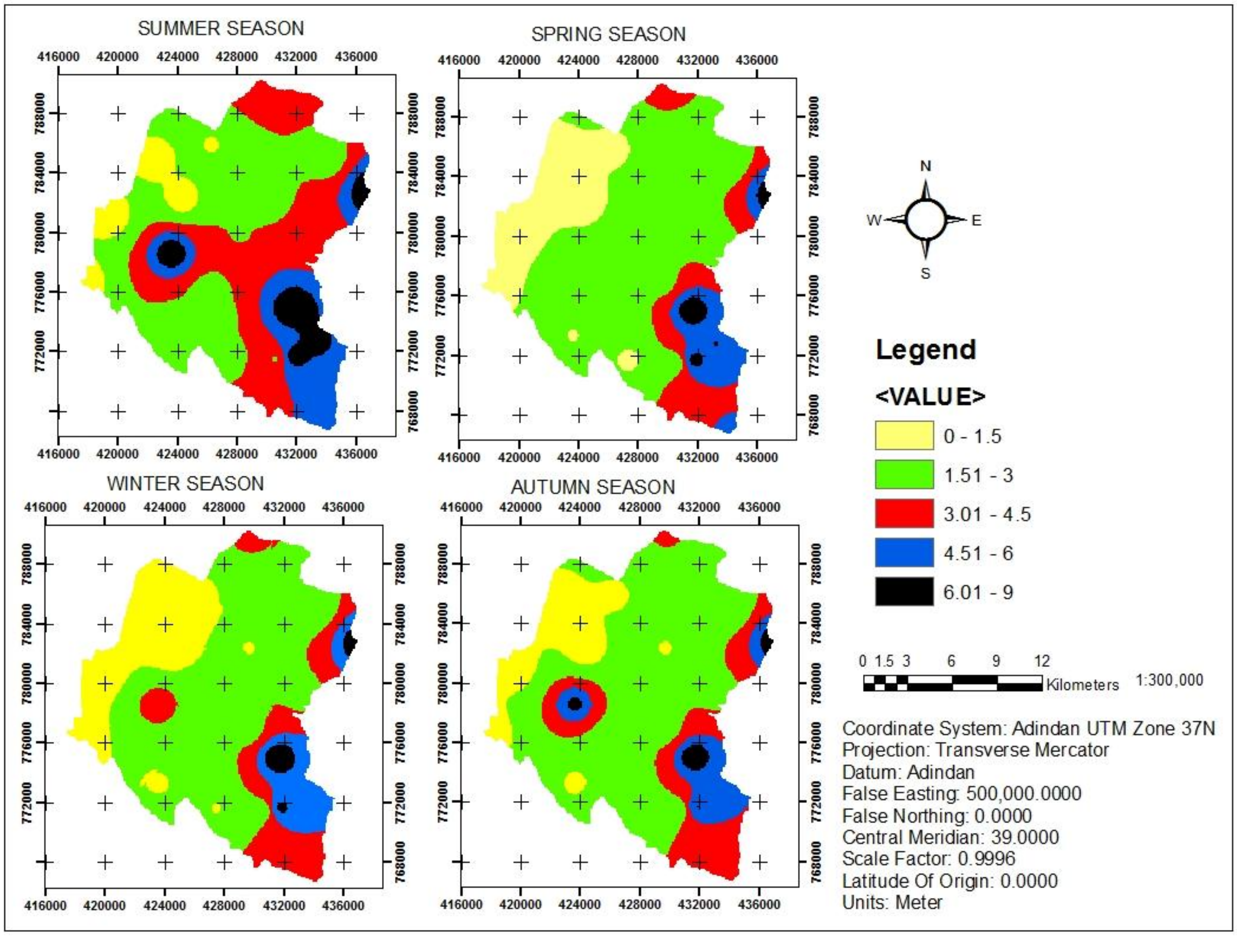

Figure 10: Temporal distribution of Fluoride Concentration

From Figure 10, it is clearly shown that approximately half of the study area is more than 3mg/l fluoride concentration which shows high risk of dental fluorosis or skeletal fluorosis. During spring season, the risk reduced almost by half i.e. 25% in coverage. Decrease in fluoride concentration continues towards and during winter season which shows less risk of dental fluorosis or skeletal fluorosis from the year. During autumn season the fluoride concentration starts toincrease and approach the spring season floured concentration distribution. Generally, the fluoride concentration is severe during wet season than dry season that the risk of fluoride consumption is high during wet season.

The graphical representation that compares and contrasts the drop-in fluoride concentration at sample points due to change in season is presented below (Figure 11). As the graph shows in most parts of the Kebele as the wetness increase the fluoride concentration also increases and vice versa.

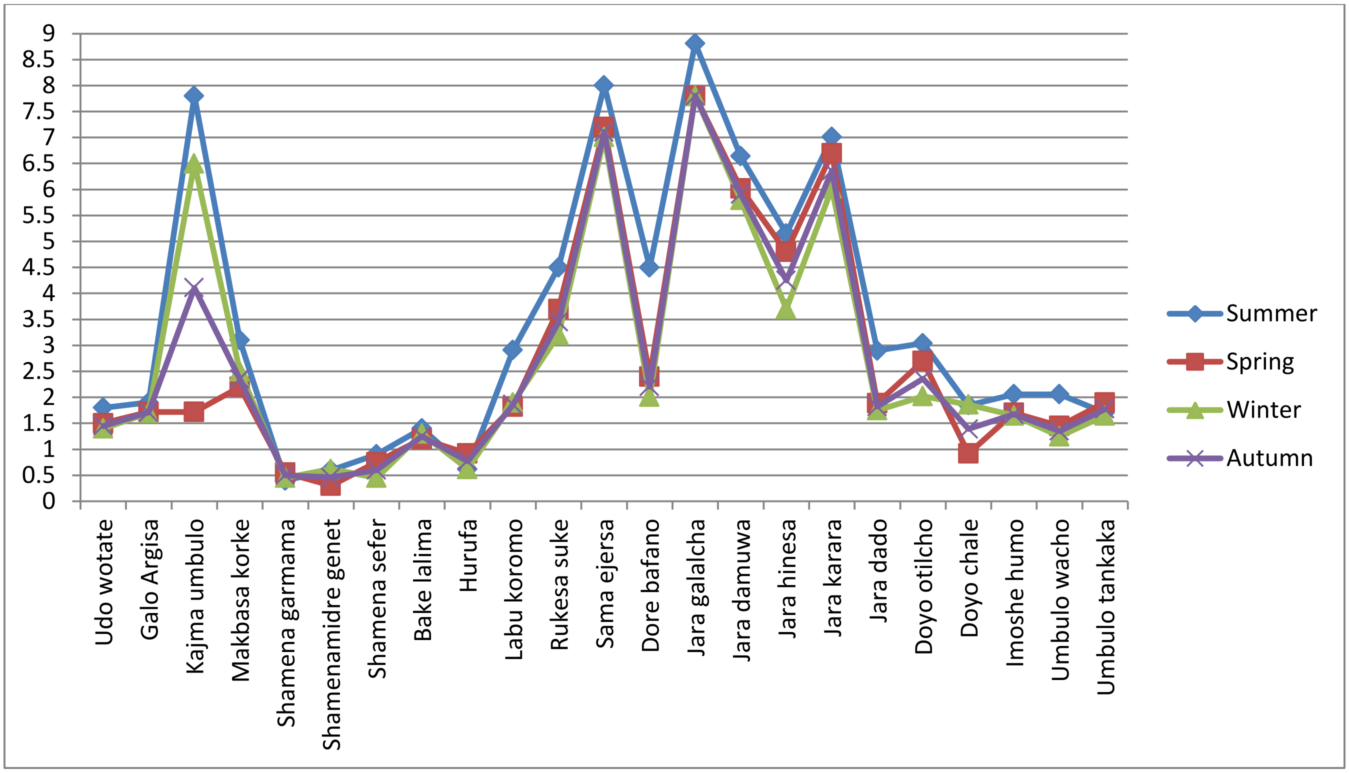

Figure 11: Temporal Variation of Fluoride

The results from the above graphs show the changes in fluoride ion concentration in different boreholes in different seasons. The first 3 boreholes at season 1 show variations of fluoride concentration and also insignificant variations over the remaining seasons. Above graph shows variations of fluoride concentration in twenty-three different sites. Climatic influences affect the fluoride concentrations in water considerably in areas with high levels of fluoride. It is observed from the results that during dry months the fluoride content increases and during and after the rains, the content goes down. However, it is very difficult to generalize from the observations since the pattern of variations changes from season to season in some cases. This is an indication that besides the climate, there are other factors like Geologic condition, Industry wastage,Population increase and Agricultural activity also influence the level of fluoride ion concentrations in groundwater.

4.3.4 Altitude and Temperature Relation

The altitude and air temperature relation over Ethiopia are related by:

Temp(^{O}C)=-0.006*Elev+32

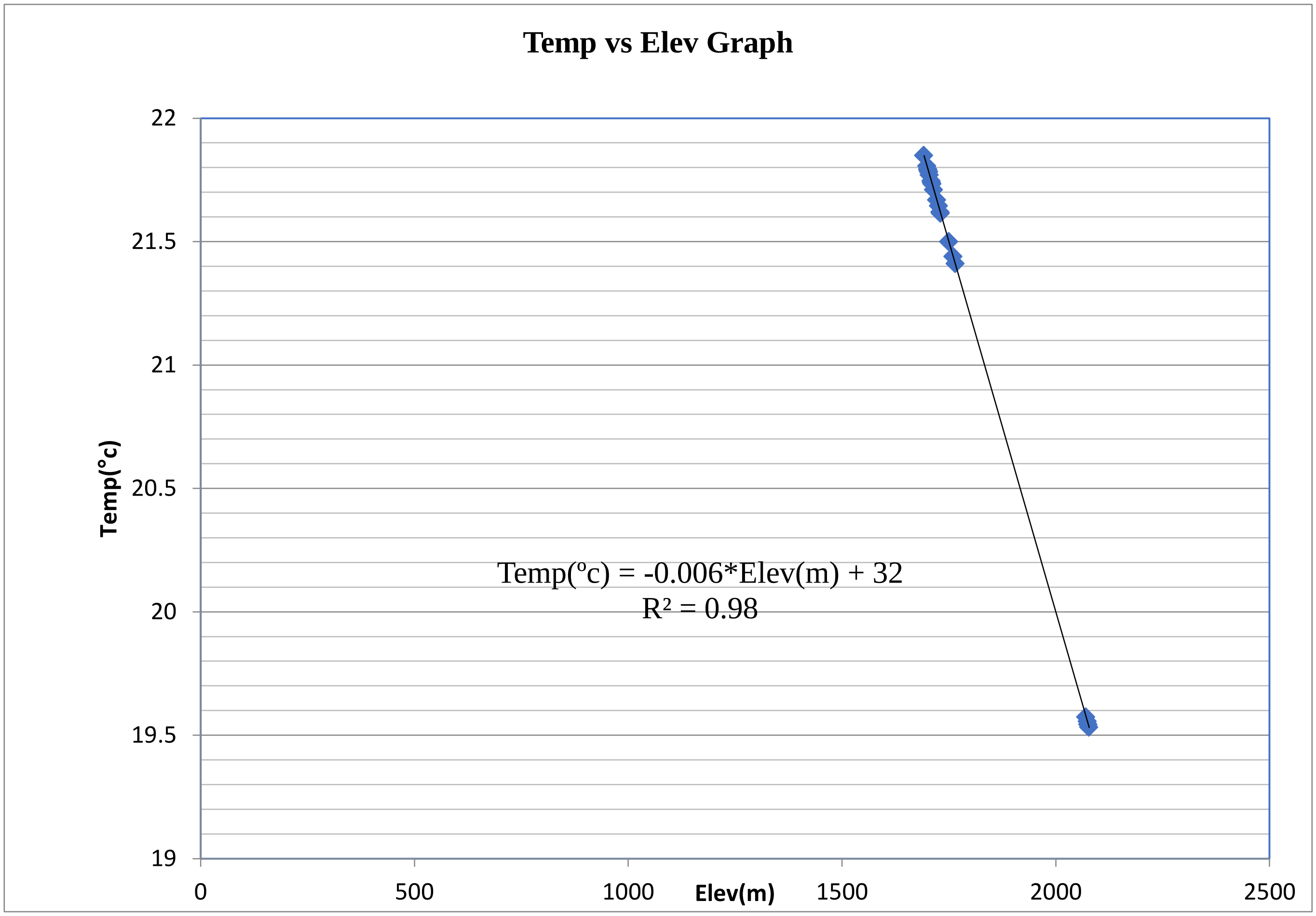

Fig 12: Altitude and temperature relation

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The most appropriate and widely used source of drinking water for the population of Hawassa ZuriaWoreda was groundwater. However, considering the levels of fluoride, in general, groundwater was not acceptable quality except for some provinces in which elevated levels of natural groundwater fluoride occurs. Fluoride concentration is varying due to spatial variation at different sample sites. Very high levels of fluoride greater than1.5 mg/l occur in more than some groundwater sources in some provinces of woreda especially in the Jara Galalcha, Sama Ejersa, Jara Karara and Jara Damuwa provinces. In some areas like Midre Genet, Shamena Safara, and Hurufa the minimum amount of fluoride concentration occurred.

The Fluoride concentrations in bore holes were at sample sites also vary due to variation of time or temporal variation.During dry season the level of fluoride concentration low which decreases risk of fluoride while during wet season the risk is high since the fluoride concentration increases.

5.2. Recommendations

According to this study the following recommendations aresuggested:

- ✓ Proper research need to be initiated into investigating cheap and new technological simple processes for removal of fluoride from fluoride-rich groundwater or developing alternative methods of water supply in areas where there is high fluoride concentration occurs.
- ✓ The installation of future boreholes should be accompanied by simple and suitable de-fluoridation techniques.
- ✓ The other thing which is highly recommended is that the concentration of fluoride should be determined both in ground and surface water in order to improve the cleanness. Hence, it is highly recommended to establish good fluoride treatment plant.

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LIST OF APPENDECES

Appendix I: Laboratory Results of Summer Season

S. no	Sample site name	Elements			
1	Udowotate(uw)	Chemical parameter(mg/l)		Physical parameter	
		1	Calcium(Ca^{+2})= 4.8	1	Conductivity=1611µs/m
		2	Sodium(Na^{+})=0.93	2	TDS=805.5mg/l
		3	Nitrate(No^{-}_{2})=0.52	3	Salinity=0.8ppt
		4	Nitrite(No^{-}_{3})=0.26	4	Resistivity=623kΩ
		5	Magnesium(Mg^{+2})=0.34	5	Turbidity=6.61NTU
		6	Fluoride(F^{-})=1.8	6	Temperature=20.0^{0}c
2	GaloArgisa(ga)	1	Calcium(Ca^{+2})= 6.3	1	Conductivity=1752µs/m
		2	Sodium(Na^{+})=1.2	2	TDS=876mg/l
		3	Nitrate(No^{-}_{2})=0.33	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.15	4	Resistivity=547kΩ
		5	Magnesium(Mg^{+2})=0.54	5	Turbidity=48.4NTU
		6	Fluoride(F^{-})=1.9	6	Temperature=24.0^{0}c
3	Kajmaumbulo(ku)	1	Calcium(Ca^{+2})= 2.5	1	Conductivity=1136µs/m
		2	Sodium(Na^{+})=1.8	2	TDS=568mg/l
		3	Nitrate(No^{-}_{2})=0.28	3	Salinity=0.57ppt
		4	Nitrite(No^{-}_{3})=0.55	4	Resistivity=861kΩ
		5	Magnesium(Mg^{+2})=0.61	5	Turbidity=20.8NTU
		6	Fluoride(F^{-})=7.8	6	Temperature=23.7^{0}c
4	Makbasakorke(mk)	1	Calcium(Ca^{+2})= 7.5	1	Conductivity=1640µs/m
		2	Sodium(Na^{+})=1.9	2	TDS=820mg/l
		3	Nitrate(No^{-}_{2})=0.21	3	Salinity=0.82ppt
		4	Nitrite(No^{-}_{3})=0.34	4	Resistivity=611kΩ
		5	Magnesium(Mg^{+2})=0.34	5	Turbidity=8.01NTU
		6	Fluoride(F^{-})=3.1	6	Temperature=24.1^{0}c

5	Shamenagarmama(sg)	1	Calcium(Ca^{+2})= 2.3	1	Conductivity=1643μs/m
		2	Sodium(Na^{+})=2.5	2	TDS=821.5mg/l
		3	Nitrate(No^{-}_{2})=0.41	3	Salinity=0.09ppt
		4	Nitrite(No^{-}_{3})=0.36	4	Resistivity=6.08kΩ
		5	Magnesium(Mg^{+2})=0.63	5	Turbidity=400NTU
		6	Fluoride(F^{-})=0.4	6	Temperature=18.1^{0}c
6	Shamenamidre genet(mg)	1	Calcium(Ca^{+2})= 2.5	1	Conductivity=1545μs/m
		2	Sodium(Na^{+})=2.8	2	TDS=772.5mg/l
		3	Nitrate(No^{-}_{2})=0.6	3	Salinity=0.07ppt
		4	Nitrite(No^{-}_{3})=0.5	4	Resistivity=6.10kΩ
		5	Magnesium(Mg^{+2})=0.26	5	Turbidity=350NTU
		6	Fluoride(F^{-})=0.6	6	Temperature=19.0^{0}c
7	Shamenasefer(ss)	1	Calcium(Ca^{+2})= 3.20	1	Conductivity=1261μs/m
		2	Sodium(Na^{+})=0.98	2	TDS=540.7mg/l
		3	Nitrate(No^{-}_{2})=0.72	3	Salinity=0.63ppt
		4	Nitrite(No^{-}_{3})=0.6	4	Resistivity=12kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=212NTU
		6	Fluoride(F^{-})=0.9	6	Temperature=18^{0}c
8	Bake lalima(bk)	1	Calcium(Ca^{+2})= 2.1	1	Conductivity=1423μs/m
		2	Sodium(Na^{+})=2.3	2	TDS=800mg/l
		3	Nitrate(No^{-}_{2})=0.45	3	Salinity=0.068ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=81kΩ
		5	Magnesium(Mg^{+2})=0.59	5	Turbidity=280NTU
		6	Fluoride(F^{-})=1.4	6	Temperature=22.0^{0}c
9	Hurufa (hu)	1	Calcium(Ca^{+2})= 1.92	1	Conductivity=1721μs/m
		2	Sodium(Na^{+})=2.82	2	TDS=872mg/l
		3	Nitrate(No^{-}_{2})=0.59	3	Salinity=0.031ppt
		4	Nitrite(No^{-}_{3})=0.40	4	Resistivity=18.02kΩ
		5	Magnesium(Mg^{+2})=0.52	5	Turbidity=291NTU
		6	Fluoride(F^{-})=0.62	6	Temperature=25^{0}c

10	Labukoromo(lk)	1	Calcium(Ca^{+2})= 7.0	1	Conductivity=1200µs/m
		2	Sodium(Na^{+})=1.5	2	TDS=600mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.19ppt
		4	Nitrite(No^{-}_{3})=0.21	4	Resistivity=70kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=321NTU
		6	Fluoride(F^{-})=2.91	6	Temperature=23^{0}c
11	Rukesasuke(rk)	1	Calcium(Ca^{+2})= 8.2	1	Conductivity=1801µs/m
		2	Sodium(Na^{+})=2.1	2	TDS=900mg/l
		3	Nitrate(No^{-}_{2})=0.18	3	Salinity=0.87ppt
		4	Nitrite(No^{-}_{3})=0.31	4	Resistivity=721kΩ
		5	Magnesium(Mg^{+2})=0.51	5	Turbidity=11NTU
		6	Fluoride(F^{-})=4.5	6	Temperature=21.4^{0}c
12	Samaejersa(se)	1	Calcium(Ca^{+2})= 8.7	1	Conductivity=1722µs/m
		2	Sodium(Na^{+})=1.29	2	TDS=922mg/l
		3	Nitrate(No^{-}_{2})=0.15	3	Salinity=0.72ppt
		4	Nitrite(No^{-}_{3})=0.32	4	Resistivity=650kΩ
		5	Magnesium(Mg^{+2})=0.28	5	Turbidity=22NTU
		6	Fluoride(F^{-})=8	6	Temperature=18.3^{0}c
		14	Power of hydrogen(PH)=8.25		
13	HawassaZuria(db)	1	Calcium(Ca^{+2})= 5.8	1	Conductivity=1902µs/m
		2	Sodium(Na^{+})=1.7	2	TDS=915mg/l
		3	Nitrate(No^{-}_{2})=0.25	3	Salinity=0.99ppt
		4	Nitrite(No^{-}_{3})=0.37	4	Resistivity=715kΩ
		5	Magnesium(Mg^{+2})=0.8	5	Turbidity=5NTU
		6	Fluoride(F^{-})=4.5	6	Temperature=25.9^{0}c
14	Jaragalalcha(jg)	1	Calcium(Ca^{+2})= 6.8	1	Conductivity=1010µs/m
		2	Sodium(Na^{+})=1.02	2	TDS=505mg/l
		3	Nitrate(No^{-}_{2})=0.22	3	Salinity=0.16ppt
		4	Nitrite(No^{-}_{3})=0.21	4	Resistivity=519kΩ
		5	Magnesium(Mg^{+2})=0.72	5	Turbidity=54.04NTU

		6	Fluoride(F^-)=8.81	6	Temperature=19.6^{0}c
15	Jaradamuwa(da)	1	Calcium(Ca^{+2})= 2.9	1	Conductivity=1305µs/m
		2	Sodium(Na^+)=1.65	2	TDS=707mg/l
		3	Nitrate(No^-_2)=0.20	3	Salinity=0.65ppt
		4	Nitrite(No^-_3)=0.75	4	Resistivity=852kΩ
		5	Magnesium(Mg^{+2})=0.9	5	Turbidity=42.8NTU
		6	Fluoride(F^-)=6.64	6	Temperature=26^{0}c
16	Jarahinesa(jh)	1	Calcium(Ca^{+2})= 5.3	1	Conductivity=1610µs/m
		2	Sodium(Na^+)=0.85	2	TDS=805mg/l
		3	Nitrate(No^-_2)=0.102	3	Salinity=0.86ppt
		4	Nitrite(No^-_3)=0.18	4	Resistivity=680kΩ
		5	Magnesium(Mg^{+2})=0.35	5	Turbidity=62NTU
		6	Fluoride(F^-)=5.15	6	Temperature=25.8^{0}c
17	Jarakarara(jk)	1	Calcium(Ca^{+2})= 1.9	1	Conductivity=1121µs/m
		2	Sodium(Na^+)=1	2	TDS=740mg/l
		3	Nitrate(No^-_2)=0.18	3	Salinity=0.92ppt
		4	Nitrite(No^-_3)=0.11	4	Resistivity=721kΩ
		5	Magnesium(Mg^{+2})=0.56	5	Turbidity=43NTU
		6	Fluoride(F^-)=7.01	6	Temperature=23.3^{0}c
18	Jara dado(jd)	1	Calcium(Ca^{+2})= 2.18	1	Conductivity=1809µs/m
		2	Sodium(Na^+)=1.1	2	TDS=904mg/l
		3	Nitrate(No^-_2)=0.17	3	Salinity=0.72ppt
		4	Nitrite(No^-_3)=0.95	4	Resistivity=702kΩ
		5	Magnesium(Mg^{+2})=1.2	5	Turbidity=11.03NTU
		6	Fluoride(F^-)=2.9	6	Temperature=19.7^{0}c
19	Doyootilcho(do)	1	Calcium(Ca^{+2})= 1.72	1	Conductivity=1342µs/m
		2	Sodium(Na^+)=0.98	2	TDS=724mg/l
		3	Nitrate(No^-_2)=0.16	3	Salinity=0.95ppt
		4	Nitrite(No^-_3)=0.34	4	Resistivity=832kΩ
		5	Magnesium(Mg^{+2})=0.34	5	Turbidity=70.03NTU

		6	Fluoride(F^-)=3.04	6	Temperature=21.2^{0}c
20	Doyochale(dc)	1	Calcium(Ca^{+2})= 5.2	1	Conductivity=1180.05µs/m
		2	Sodium(Na^+)=1.3	2	TDS=901mg/l
		3	Nitrate($No^-{}_2$)=0.65	3	Salinity=0.84ppt
		4	Nitrite($No^-{}_3$)=0.21	4	Resistivity=778kΩ
		5	Magnesium(Mg^{+2})=1.18	5	Turbidity=21.9NTU
		6	Fluoride(F^-)=1.85	6	Temperature=22.2^{0}c
21	Imoshehumo(ih)	1	Calcium(Ca^{+2})= 1.08	1	Conductivity=988µs/m
		2	Sodium(Na^+)=0.15	2	TDS=508mg/l
		3	Nitrate($No^-{}_2$)=0.17	3	Salinity=0.78ppt
		4	Nitrite($No^-{}_3$)=0.29	4	Resistivity=80.03kΩ
		5	Magnesium(Mg^{+2})=1.07	5	Turbidity=121.07NTU
		6	Fluoride(F^-)=2.06	6	Temperature=20.09^{0}c
22	Umbulowacho(wa)	1	Calcium(Ca^{+2})= 7.18	1	Conductivity=1009.8µs/m
		2	Sodium(Na^+)=1.57	2	TDS=714mg/l
		3	Nitrate($No^-{}_2$)=0.18	3	Salinity=0.79ppt
		4	Nitrite($No^-{}_3$)=0.27	4	Resistivity=679kΩ
		5	Magnesium(Mg^{+2})=0.77	5	Turbidity=189.08NTU
		6	Fluoride(F^-)=1.56	6	Temperature=19.2^{0}c
23	Umbulotankaka(ut)	1	Calcium(Ca^{+2})= 1.9	1	Conductivity=782µs/m
		2	Sodium(Na^+)=2.1	2	TDS=435mg/l
		3	Nitrate($No^-{}_2$)=0.29	3	Salinity=0.58ppt
		4	Nitrite($No^-{}_3$)=0.98	4	Resistivity=18.09kΩ
		5	Magnesium(Mg^{+2})=0.87	5	Turbidity=53.25NTU
		6	Fluoride(F^-)=1.7	6	Temperature=19.9^{0}c

Appendix II:Laboratory Results of Spring Season

. no	Sample site name	Elements			
1	Udowotate(uw)	Chemical parameter(mg/l)		Physical parameter	
		1	Calcium(Ca^{+2})= 4.2	1	Conductivity=1202µs/m
		2	Sodium(Na^{+})=0.81	2	TDS=601mg/l
		3	Nitrate(No^{-}_{2})=0.42	3	Salinity=0.71ppt
		4	Nitrite(No^{-}_{3})=0.19	4	Resistivity=598kΩ
		5	Magnesium(Mg^{+2})=0.3	5	Turbidity=12.07NTU
		6	Fluoride(F^{-})=1.5	6	Temperature=22.0^{0}c
2	GaloArgisa(ga)	1	Calcium(Ca^{+2})= 4.0	1	Conductivity=1802µs/m
		2	Sodium(Na^{+})=0.8	2	TDS=917mg/l
		3	Nitrate(No^{-}_{2})=0.09	3	Salinity=0.67ppt
		4	Nitrite(No^{-}_{3})=0.38	4	Resistivity=831kΩ
		5	Magnesium(Mg^{+2})=0.68	5	Turbidity=30.1NTU
		6	Fluoride(F^{-})=1.72	6	Temperature=22.0^{0}c
3	Kajmaumbulo(ku)	1	Calcium(Ca^{+2})= 1.82	1	Conductivity=1136µs/m
		2	Sodium(Na^{+})=1.92	2	TDS=568mg/l
		3	Nitrate(No^{-}_{2})=0.28	3	Salinity=0.57ppt
		4	Nitrite(No^{-}_{3})=0.98	4	Resistivity=861kΩ
		5	Magnesium(Mg^{+2})=0.18	5	Turbidity=20.8NTU
		6	Fluoride(F^{-})=5.6	6	Temperature=23.7^{0}c
4	Makbasakorke(mk)	1	Calcium(Ca^{+2})= 2.7	1	Conductivity=1307µs/m
		2	Sodium(Na^{+})=0.9	2	TDS=1008mg/l
		3	Nitrate(No^{-}_{2})=0.34	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.31	4	Resistivity=580kΩ
		5	Magnesium(Mg^{+2})=0.25	5	Turbidity=13NTU
		6	Fluoride(F^{-})=2.2	6	Temperature=19^{0}c

5	Shamenagarmama(sg)	1	Calcium(Ca^{+2})= 1.5	1	Conductivity=1604µs/m
		2	Sodium(Na^{+})=3.2	2	TDS=802mg/l
		3	Nitrate(No^{-}_{2})=028	3	Salinity=0.85ppt
		4	Nitrite(No^{-}_{3})=0.22	4	Resistivity=11.05kΩ
		5	Magnesium(Mg^{+2})=0.58	5	Turbidity=190NTU
		6	Fluoride(F^{-})=0.55	6	Temperature=19^{0}c
6	Shamenamidre genet(mg)	1	Calcium(Ca^{+2})= 2.8	1	Conductivity=1002µs/m
		2	Sodium(Na^{+})=2.2	2	TDS=532mg/l
		3	Nitrate(No^{-}_{2})=0.2	3	Salinity=0.09ppt
		4	Nitrite(No^{-}_{3})=0.5	4	Resistivity=17.08kΩ
		5	Magnesium(Mg^{+2})=0.12	5	Turbidity=50NTU
		6	Fluoride(F^{-})=0.3	6	Temperature=23^{0}c
7	Shamenasefer(ss)	1	Calcium(Ca^{+2})= 1.5	1	Conductivity=1371µs/m
		2	Sodium(Na^{+})=0.92	2	TDS=630.5mg/l
		3	Nitrate(No^{-}_{2})=0.65	3	Salinity=0.93ppt
		4	Nitrite(No^{-}_{3})=0.52	4	Resistivity=18kΩ
		5	Magnesium(Mg^{+2})=0.23	5	Turbidity=180NTU
		6	Fluoride(F^{-})=0.75	6	Temperature=20^{0}c
8	Bake lalima(bk)	1	Calcium(Ca^{+2})= 2.7	1	Conductivity=1600µs/m
		2	Sodium(Na^{+})=2.05	2	TDS=705mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.088ppt
		4	Nitrite(No^{-}_{3})=0.42	4	Resistivity=89kΩ
		5	Magnesium(Mg^{+2})=0.78	5	Turbidity=180NTU
		6	Fluoride(F^{-})=1.2	6	Temperature=12.0^{0}c
9	Hurufa (hu)	1	Calcium(Ca^{+2})= 1.52	1	Conductivity=1207µs/m
		2	Sodium(Na^{+})=1.58	2	TDS=603mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.042ppt
		4	Nitrite(No^{-}_{3})=0.78	4	Resistivity=22.7kΩ
		5	Magnesium(Mg^{+2})=0.38	5	Turbidity=320NTU
		6	Fluoride(F^{-})=0.92	6	Temperature=11^{0}c

10	Labukoromo(lk)	1	Calcium(Ca^{+2})= 1.5	1	Conductivity=1617µs/m
		2	Sodium(Na^{+})=0.85	2	TDS=843mg/l
		3	Nitrate(No^{-}_{2})=0.101	3	Salinity=0.08ppt
		4	Nitrite(No^{-}_{3})=0.19	4	Resistivity=52kΩ
		5	Magnesium(Mg^{+2})=0.33	5	Turbidity=430NTU
		6	Fluoride(F^{-})=1.82	6	Temperature=18^{0}c
11	Rukesasuke(rk)	1	Calcium(Ca^{+2})= 2.2	1	Conductivity=1007µs/m
		2	Sodium(Na^{+})=1.8	2	TDS=500mg/l
		3	Nitrate(No^{-}_{2})=0.08	3	Salinity=0.081ppt
		4	Nitrite(No^{-}_{3})=0.18	4	Resistivity=623kΩ
		5	Magnesium(Mg^{+2})=0.25	5	Turbidity=21NTU
		6	Fluoride(F^{-})=3.7	6	Temperature=19^{0}c
12	Samaejersa(se)	1	Calcium(Ca^{+2})= 2.7	1	Conductivity=1637µs/m
		2	Sodium(Na^{+})=0.91	2	TDS=842mg/l
		3	Nitrate(No^{-}_{2})=0.30	3	Salinity=0.67ppt
		4	Nitrite(No^{-}_{3})=0.67	4	Resistivity=517kΩ
		5	Magnesium(Mg^{+2})=0.03	5	Turbidity=19NTU
		6	Fluoride(F^{-})=7.2	6	Temperature=12^{0}c
13	HawassaZuria(db)	1	Calcium(Ca^{+2})= 1.9	1	Conductivity=1760µs/m
		2	Sodium(Na^{+})=1.8	2	TDS=863mg/l
		3	Nitrate(No^{-}_{2})=0.4	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.3	4	Resistivity=780kΩ
		5	Magnesium(Mg^{+2})=0.9	5	Turbidity=35NTU
		6	Fluoride(F^{-})=2.4	6	Temperature=23^{0}c
14	Jaragalalcha(jg)	1	Calcium(Ca^{+2})= 3.2	1	Conductivity=1208µs/m
		2	Sodium(Na^{+})=1.92	2	TDS=604mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.9ppt
		4	Nitrite(No^{-}_{3})=0.17	4	Resistivity=680kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=65NTU
		6	Fluoride(F^{-})=7.8	6	Temperature=12^{0}c

15	Jaradamuwa(da)	1	Calcium(Ca^{+2})= 2.1	1	Conductivity=1208µs/m
		2	Sodium(Na^{+})=1.02	2	TDS=604mg/l
		3	Nitrate(No^{-}_{2})=0.62	3	Salinity=0.77ppt
		4	Nitrite(No^{-}_{3})=0.19	4	Resistivity=617kΩ
		5	Magnesium(Mg^{+2})=0.82	5	Turbidity=53NTU
		6	Fluoride(F^{-})=6.02	6	Temperature=19^{0}c
16	Jarahinesa(jh)	1	Calcium(Ca^{+2})= 5.2	1	Conductivity=1370µs/m
		2	Sodium(Na^{+})=0.72	2	TDS=730mg/l
		3	Nitrate(No^{-}_{2})=0.12	3	Salinity=0.9ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=717kΩ
		5	Magnesium(Mg^{+2})=0.27	5	Turbidity=53NTU
		6	Fluoride(F^{-})=4.8	6	Temperature=22^{0}c
17	Jarakarara(jk)	1	Calcium(Ca^{+2})= 1.25	1	Conductivity=1207µs/m
		2	Sodium(Na^{+})=0.9	2	TDS=630mg/l
		3	Nitrate(No^{-}_{2})=0.01	3	Salinity=0.89ppt
		4	Nitrite(No^{-}_{3})=0.37	4	Resistivity=617kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=58NTU
		6	Fluoride(F^{-})=6.7	6	Temperature=19^{0}c
18	Jara dado(jd)	1	Calcium(Ca^{+2})= 1.89	1	Conductivity=1702µs/m
		2	Sodium(Na^{+})=1.27	2	TDS=814mg/l
		3	Nitrate(No^{-}_{2})=0.65	3	Salinity=0.87ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=615kΩ
		5	Magnesium(Mg^{+2})=1.25	5	Turbidity=13.08NTU
		6	Fluoride(F^{-})=1.89	6	Temperature=17^{0}c
19	Doyootilcho(do)	1	Calcium(Ca^{+2})= 1.21	1	Conductivity=1020µs/m
		2	Sodium(Na^{+})=0.52	2	TDS=562mg/l
		3	Nitrate(No^{-}_{2})=0.31	3	Salinity=0.78ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=482kΩ
		5	Magnesium(Mg^{+2})=0.22	5	Turbidity=43.05NTU
		6	Fluoride(F^{-})=2.7	6	Temperature=19^{0}c

20	Doyochale(dc)	1	Calcium(Ca^{+2})=1.7	1	Conductivity=980μs/m
		2	Sodium(Na^{+})=1.05	2	TDS=540mg/l
		3	Nitrate(No^{-}_{2})=0.20	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.62	4	Resistivity=672kΩ
		5	Magnesium(Mg^{+2})=1.02	5	Turbidity=33.5NTU
		6	Fluoride(F^{-})=0.92	6	Temperature=12^{0}c
21	Imoshehumo(ih)	1	Calcium(Ca^{+2})= 1.8	1	Conductivity=1242μs/m
		2	Sodium(Na^{+})=0.25	2	TDS=608mg/l
		3	Nitrate(No^{-}_{2})=0.29	3	Salinity=0.67ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=120.07kΩ
		5	Magnesium(Mg^{+2})=1.98	5	Turbidity=180.09NTU
		6	Fluoride(F^{-})=1.7	6	Temperature=10.5^{0}c
22	Umbulowacho(wa)	1	Calcium(Ca^{+2})= 6.7	1	Conductivity=1207μs/m
		2	Sodium(Na^{+})=1.08	2	TDS=682mg/l
		3	Nitrate(No^{-}_{2})=0.37	3	Salinity=0.69ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=717kΩ
		5	Magnesium(Mg^{+2})=0.97	5	Turbidity=200NTU
		6	Fluoride(F^{-})=1.45	6	Temperature=20^{0}c
23	Umbulotankaka(ut)	1	Calcium(Ca^{+2})= 1.7	1	Conductivity=1370μs/m
		2	Sodium(Na^{+})=2.07	2	TDS=517mg/l
		3	Nitrate(No^{-}_{2})=0.92	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.97	4	Resistivity=9.08kΩ
		5	Magnesium(Mg^{+2})=0.92	5	Turbidity=58.7NTU
		6	Fluoride(F^{-})=1.9	6	Temperature=22^{0}c

Appendix III:Laboratory Results of Autumn Season

no	Sample site name	Elements			
1	Udowotate(uw)	Chemical parameter(mg/l)		Physical parameter	
		1	Calcium(Ca^{+2})= 4.2	1	Conductivity=1202µs/m
		2	Sodium(Na^{+})=0.81	2	TDS=601mg/l
		3	Nitrate(No^{-}_{2})=0.42	3	Salinity=0.71ppt
		4	Nitrite(No^{-}_{3})=0.19	4	Resistivity=598kΩ
		5	Magnesium(Mg^{+2})=0.3	5	Turbidity=12.07NTU
		6	Fluoride(F^{-})=1.45	6	Temperature=22.0^{0}c
2	GaloArgisa(ga)	1	Calcium(Ca^{+2})= 4.0	1	Conductivity=1802µs/m
		2	Sodium(Na^{+})=0.8	2	TDS=917mg/l
		3	Nitrate(No^{-}_{2})=0.09	3	Salinity=0.67ppt
		4	Nitrite(No^{-}_{3})=0.38	4	Resistivity=831kΩ
		5	Magnesium(Mg^{+2})=0.68	5	Turbidity=30.1NTU
		6	Fluoride(F^{-})=1.71	6	Temperature=22.0^{0}c
3	Kajmaumbulo(ku)	1	Calcium(Ca^{+2})= 1.82	1	Conductivity=1136µs/m
		2	Sodium(Na^{+})=1.92	2	TDS=568mg/l
		3	Nitrate(No^{-}_{2})=0.28	3	Salinity=0.57ppt
		4	Nitrite(No^{-}_{3})=0.98	4	Resistivity=861kΩ
		5	Magnesium(Mg^{+2})=0.18	5	Turbidity=20.8NTU
		6	Fluoride(F^{-})=4.11	6	Temperature=23.7^{0}c
4	Makbasakorke(mk)	1	Calcium(Ca^{+2})= 2.7	1	Conductivity=1307µs/m
		2	Sodium(Na^{+})=0.9	2	TDS=1008mg/l
		3	Nitrate(No^{-}_{2})=0.34	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.31	4	Resistivity=580kΩ
		5	Magnesium(Mg^{+2})=0.25	5	Turbidity=13NTU
		6	Fluoride(F^{-})=2.35	6	Temperature=19^{0}c
5	Shamenagarmama(sg)	1	Calcium(Ca^{+2})= 0.5	1	Conductivity=1604µs/m

		2	Sodium(Na^{+})=3.2	2	TDS=802mg/l
		3	Nitrate(No^{-}_{2})=028	3	Salinity=0.85ppt
		4	Nitrite(No^{-}_{3})=0.22	4	Resistivity=11.05kΩ
		5	Magnesium(Mg^{+2})=0.58	5	Turbidity=190NTU
		6	Fluoride(F^{-})=0.55	6	Temperature=19^{0}c
6	Shamenamidre genet(mg)	1	Calcium(Ca^{+2})= 2.8	1	Conductivity=1002μs/m
		2	Sodium(Na^{+})=2.2	2	TDS=532mg/l
		3	Nitrate(No^{-}_{2})=0.2	3	Salinity=0.09ppt
		4	Nitrite(No^{-}_{3})=0.5	4	Resistivity=17.08kΩ
		5	Magnesium(Mg^{+2})=0.12	5	Turbidity=50NTU
		6	Fluoride(F^{-})=0.46	6	Temperature=23^{0}c
7	Shamenasefer(ss)	1	Calcium(Ca^{+2})= 1.5	1	Conductivity=1371μs/m
		2	Sodium(Na^{+})=0.92	2	TDS=630.5mg/l
		3	Nitrate(No^{-}_{2})=0.65	3	Salinity=0.93ppt
		4	Nitrite(No^{-}_{3})=0.52	4	Resistivity=18kΩ
		5	Magnesium(Mg^{+2})=0.23	5	Turbidity=180NTU
		6	Fluoride(F^{-})=0.75	6	Temperature=20^{0}c
8	Bake lalima(bk)	1	Calcium(Ca^{+2})= 2.7	1	Conductivity=1600μs/m
		2	Sodium(Na^{+})=2.05	2	TDS=705mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.088ppt
		4	Nitrite(No^{-}_{3})=0.42	4	Resistivity=89kΩ
		5	Magnesium(Mg^{+2})=0.78	5	Turbidity=180NTU
		6	Fluoride(F^{-})=1.25	6	Temperature=12.0^{0}c
9	Hurufa (hu)	1	Calcium(Ca^{+2})= 1.52	1	Conductivity=1207μs/m
		2	Sodium(Na^{+})=1.58	2	TDS=603mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.042ppt
		4	Nitrite(No^{-}_{3})=0.78	4	Resistivity=22.7kΩ
		5	Magnesium(Mg^{+2})=0.38	5	Turbidity=320NTU
		6	Fluoride(F^{-})=0.77	6	Temperature=11^{0}c
10	Labukoromo(lk)	1	Calcium(Ca^{+2})= 1.5	1	Conductivity=1617μs/m

		2	Sodium(Na^+)=0.85	2	TDS=843mg/l
		3	Nitrate(No^-_2)=0.101	3	Salinity=0.08ppt
		4	Nitrite(No^-_3)=0.19	4	Resistivity=52kΩ
		5	Magnesium(Mg^{+2})=0.33	5	Turbidity=430NTU
		6	Fluoride(F^-)=1.86	6	Temperature=18^0c
11	Rukesasuke(rk)	1	Calcium(Ca^{+2})= 2.2	1	Conductivity=1007µs/m
		2	Sodium(Na^+)=1.8	2	TDS=500mg/l
		3	Nitrate(No^-_2)=0.08	3	Salinity=0.081ppt
		4	Nitrite(No^-_3)=0.18	4	Resistivity=623kΩ
		5	Magnesium(Mg^{+2})=0.25	5	Turbidity=21NTU
		6	Fluoride(F^-)=3.45	6	Temperature=19^0c
12	Samaejersa(se)	1	Calcium(Ca^{+2})= 2.7	1	Conductivity=1637µs/m
		2	Sodium(Na^+)=0.91	2	TDS=842mg/l
		3	Nitrate(No^-_2)=0.30	3	Salinity=0.67ppt
		4	Nitrite(No^-_3)=0.67	4	Resistivity=517kΩ
		5	Magnesium(Mg^{+2})=0.03	5	Turbidity=19NTU
		6	Fluoride(F^-)=7.1	6	Temperature=12^0c
13	HawassaZuria(db)	1	Calcium(Ca^{+2})= 1.9	1	Conductivity=1760µs/m
		2	Sodium(Na^+)=1.8	2	TDS=863mg/l
		3	Nitrate(No^-_2)=0.4	3	Salinity=0.92ppt
		4	Nitrite(No^-_3)=0.3	4	Resistivity=780kΩ
		5	Magnesium(Mg^{+2})=0.9	5	Turbidity=35NTU
		6	Fluoride(F^-)=2.205	6	Temperature=23^0c
14	Jaragalalcha(jg)	1	Calcium(Ca^{+2})= 3.2	1	Conductivity=1208µs/m
		2	Sodium(Na^+)=1.92	2	TDS=604mg/l
		3	Nitrate(No^-_2)=0.19	3	Salinity=0.9ppt
		4	Nitrite(No^-_3)=0.17	4	Resistivity=680kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=65NTU
		6	Fluoride(F^-)=7.8	6	Temperature=12^0c
15	Jaradamuwa(da)	1	Calcium(Ca^{+2})= 2.1	1	Conductivity=1208µs/m

		2	Sodium(Na^{+})=1.02	2	TDS=604mg/l
		3	Nitrate(No^{-}_{2})=0.62	3	Salinity=0.77ppt
		4	Nitrite(No^{-}_{3})=0.19	4	Resistivity=617kΩ
		5	Magnesium(Mg^{+2})=0.82	5	Turbidity=53NTU
		6	Fluoride(F^{-})=5.91	6	Temperature=19^{0}c
16	Jarahinesa(jh)	1	Calcium(Ca^{+2})= 5.2	1	Conductivity=1370μs/m
		2	Sodium(Na^{+})=0.72	2	TDS=730mg/l
		3	Nitrate(No^{-}_{2})=0.12	3	Salinity=0.9ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=717kΩ
		5	Magnesium(Mg^{+2})=0.27	5	Turbidity=53NTU
		6	Fluoride(F^{-})=4.25	6	Temperature=22^{0}c
17	Jarakarara(jk)	1	Calcium(Ca^{+2})= 1.25	1	Conductivity=1207μs/m
		2	Sodium(Na^{+})=0.9	2	TDS=630mg/l
		3	Nitrate(No^{-}_{2})=0.01	3	Salinity=0.89ppt
		4	Nitrite(No^{-}_{3})=0.37	4	Resistivity=617kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=58NTU
		6	Fluoride(F^{-})=6.36	6	Temperature=19^{0}c
18	Jara dado(jd)	1	Calcium(Ca^{+2})= 1.89	1	Conductivity=1702μs/m
		2	Sodium(Na^{+})=1.27	2	TDS=814mg/l
		3	Nitrate(No^{-}_{2})=0.65	3	Salinity=0.87ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=615kΩ
		5	Magnesium(Mg^{+2})=1.25	5	Turbidity=13.08NTU
		6	Fluoride(F^{-})=1.82	6	Temperature=17^{0}c
19	Doyootilcho(do)	1	Calcium(Ca^{+2})= 1.21	1	Conductivity=1020μs/m
		2	Sodium(Na^{+})=0.52	2	TDS=562mg/l
		3	Nitrate(No^{-}_{2})=0.31	3	Salinity=0.78ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=482kΩ
		5	Magnesium(Mg^{+2})=0.22	5	Turbidity=43.05NTU
		6	Fluoride(F^{-})=2.36	6	Temperature=19^{0}c
20	Doyochale(dc)	1	Calcium(Ca^{+2})=1.7	1	Conductivity=980μs/m

		2	Sodium(Na^{+})=1.05	2	TDS=540mg/l
		3	Nitrate(No^{-}_{2})=0.20	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.62	4	Resistivity=672kΩ
		5	Magnesium(Mg^{+2})=1.02	5	Turbidity=33.5NTU
		6	Fluoride(F^{-})=1.39	6	Temperature=12^{0}c
21	Imoshehumo(ih)	1	Calcium(Ca^{+2})= 1.8	1	Conductivity=1242µs/m
		2	Sodium(Na^{+})=0.25	2	TDS=608mg/l
		3	Nitrate(No^{-}_{2})=0.29	3	Salinity=0.67ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=120.07kΩ
		5	Magnesium(Mg^{+2})=1.98	5	Turbidity=180.09NTU
		6	Fluoride(F^{-})=1.675	6	Temperature=10.5^{0}c
22	Umbulowacho(wa)	1	Calcium(Ca^{+2})= 6.7	1	Conductivity=1207µs/m
		2	Sodium(Na^{+})=1.08	2	TDS=682mg/l
		3	Nitrate(No^{-}_{2})=0.37	3	Salinity=0.69ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=717kΩ
		5	Magnesium(Mg^{+2})=0.97	5	Turbidity=200NTU
		6	Fluoride(F^{-})=1.35	6	Temperature=20^{0}c
23	Umbulotankaka(ut)	1	Calcium(Ca^{+2})= 1.7	1	Conductivity=1370µs/m
		2	Sodium(Na^{+})=2.07	2	TDS=517mg/l
		3	Nitrate(No^{-}_{2})=0.92	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.97	4	Resistivity=9.08kΩ
		5	Magnesium(Mg^{+2})=0.92	5	Turbidity=58.7NTU
		6	Fluoride(F^{-})=1.775	6	Temperature=22^{0}c

Appendix IV: Laboratory result of Winter Season

s. no	Sample site name	Elements			
		Chemical parameter(mg/l)		Physical parameter	
1	Udowotate(uw)	1	Calcium(Ca^{+2})= 1.5	1	Conductivity=1424µs/m
		2	Sodium(Na^{+})=0.12	2	TDS=750.5mg/l
		3	Nitrate(No^{-}_{2})=0.3	3	Salinity=0.85ppt
		4	Nitrite(No^{-}_{3})=0.2	4	Resistivity=650kΩ
		5	Magnesium(Mg^{+2})=0.15	5	Turbidity=7.5NTU
		6	Fluoride(F^{-})=1.4	6	Temperature=15^{0}c
2	GaloArgisa(ga)	1	Calcium(Ca^{+2})= 5	1	Conductivity=1305µs/m
		2	Sodium(Na^{+})=0.9	2	TDS=581mg/l
		3	Nitrate(No^{-}_{2})=0.25	3	Salinity=0.78ppt
		4	Nitrite(No^{-}_{3})=0.15	4	Resistivity=635kΩ
		5	Magnesium(Mg^{+2})=0.57	5	Turbidity=85.19NTU
		6	Fluoride(F^{-})=1.7	6	Temperature=19^{0}c
3	Kajmaumbulo(ku)	1	Calcium(Ca^{+2})= 1.9	1	Conductivity=1313µs/m
		2	Sodium(Na^{+})=1.7	2	TDS=517mg/l
		3	Nitrate(No^{-}_{2})=0.63	3	Salinity=0.89ppt
		4	Nitrite(No^{-}_{3})=0.3	4	Resistivity=786kΩ
		5	Magnesium(Mg^{+2})=0.5	5	Turbidity=50.2NTU
		6	Fluoride(F^{-})=6.5	6	Temperature=24^{0}c
4	Makbasakorke(mk)	1	Calcium(Ca^{+2})= 2.5	1	Conductivity=1270µs/m
		2	Sodium(Na^{+})=0.82	2	TDS=930mg/l
		3	Nitrate(No^{-}_{2})=0.26	3	Salinity=0.78ppt
		4	Nitrite(No^{-}_{3})=0.19	4	Resistivity=516kΩ
		5	Magnesium(Mg^{+2})=0.33	5	Turbidity=12NTU
		6	Fluoride(F^{-})=2.5	6	Temperature=14^{0}c

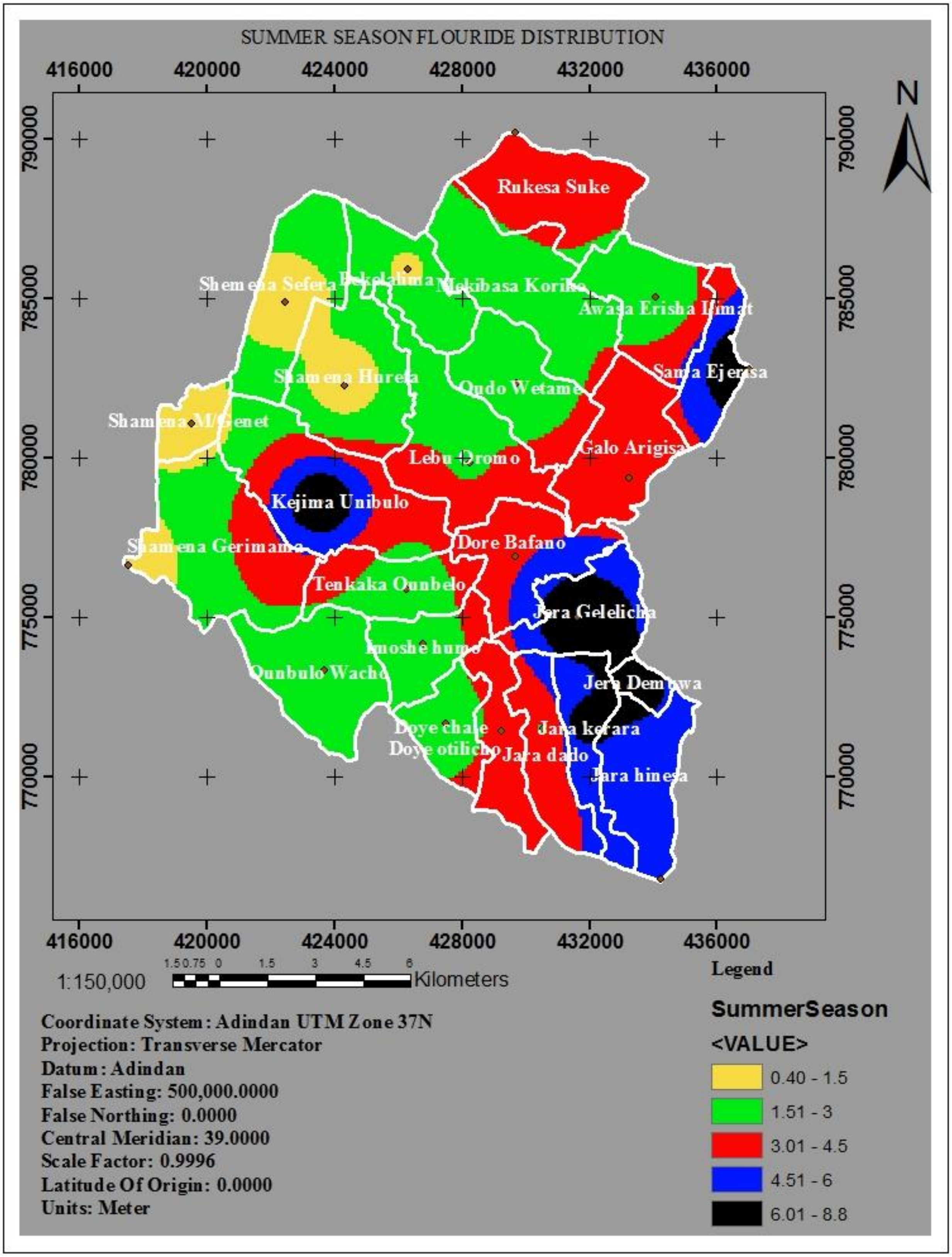
5	Shamenagarmama(sg)	1	Calcium(Ca^{+2})= 1.07	1	Conductivity=1345µs/m
		2	Sodium(Na^{+})=2.8	2	TDS=731mg/l
		3	Nitrate(No^{-}_{2})=0.25	3	Salinity=0.08ppt
		4	Nitrite(No^{-}_{3})=0.38	4	Resistivity=7.8kΩ
		5	Magnesium(Mg^{+2})=0.61	5	Turbidity=501NTU
		6	Fluoride(F^{-})=0.45	6	Temperature=17^{0}c
6	Shamenamidre genet(mg)	1	Calcium(Ca^{+2})= 1.9	1	Conductivity=1362µs/m
		2	Sodium(Na^{+})=1.85	2	TDS=680mg/l
		3	Nitrate(No^{-}_{2})=0.35	3	Salinity=0.085ppt
		4	Nitrite(No^{-}_{3})=0.65	4	Resistivity=7.01kΩ
		5	Magnesium(Mg^{+2})=0.25	5	Turbidity=720NTU
		6	Fluoride(F^{-})=0.62	6	Temperature=17^{0}c
7	Shamenasefer(ss)	1	Calcium(Ca^{+2})= 3.25	1	Conductivity=1532µs/m
		2	Sodium(Na^{+})=0.89	2	TDS=540.7mg/l
		3	Nitrate(No^{-}_{2})=0.70	3	Salinity=0.72ppt
		4	Nitrite(No^{-}_{3})=0.75	4	Resistivity=11.05kΩ
		5	Magnesium(Mg^{+2})=0.35	5	Turbidity=530NTU
		6	Fluoride(F^{-})=0.45	6	Temperature=18^{0}c
8	Bake lalima(bk)	1	Calcium(Ca^{+2})= 2.01	1	Conductivity=1450µs/m
		2	Sodium(Na^{+})=2.7	2	TDS=710.6mg/l
		3	Nitrate(No^{-}_{2})=2.25	3	Salinity=0.079ppt
		4	Nitrite(No^{-}_{3})=0.47	4	Resistivity=100kΩ
		5	Magnesium(Mg^{+2})=0.58	5	Turbidity=604NTU
		6	Fluoride(F^{-})=1.3	6	Temperature=17.0^{0}c
9	Hurufa (hu)	1	Calcium(Ca^{+2})= 1.62	1	Conductivity=1305µs/m
		2	Sodium(Na^{+})=1.72	2	TDS=890mg/l
		3	Nitrate(No^{-}_{2})=0.17	3	Salinity=0.05ppt
		4	Nitrite(No^{-}_{3})=0.58	4	Resistivity=19.07kΩ
		5	Magnesium(Mg^{+2})=0.42	5	Turbidity=530NTU
		6	Fluoride(F^{-})=0.62	6	Temperature=18^{0}c

10	Labukoromo(lk)	1	Calcium(Ca^{+2})= 1.8	1	Conductivity=1407µs/m
		2	Sodium(Na^{+})=0.89	2	TDS=580mg/l
		3	Nitrate(No^{-}_{2})=0.37	3	Salinity=0.98ppt
		4	Nitrite(No^{-}_{3})=0.27	4	Resistivity=82kΩ
		5	Magnesium(Mg^{+2})=0.25	5	Turbidity=480NTU
		6	Fluoride(F^{-})=1.9	6	Temperature=19^{0}c
11	Rukesasuke(rk)	1	Calcium(Ca^{+2})= 0.82	1	Conductivity=989µs/m
		2	Sodium(Na^{+})=1.82	2	TDS=482mg/l
		3	Nitrate(No^{-}_{2})=0.39	3	Salinity=0.93ppt
		4	Nitrite(No^{-}_{3})=0.092	4	Resistivity=650kΩ
		5	Magnesium(Mg^{+2})=0.55	5	Turbidity=12NTU
		6	Fluoride(F^{-})=3.2	6	Temperature=18.8^{0}c
12	Samaejersa(se)	1	Calcium(Ca^{+2})= 1.8	1	Conductivity=1365µs/m
		2	Sodium(Na^{+})=1.37	2	TDS=890mg/l
		3	Nitrate(No^{-}_{2})=0.37	3	Salinity=0.78ppt
		4	Nitrite(No^{-}_{3})=0.68	4	Resistivity=581.8kΩ
		5	Magnesium(Mg^{+2})=0.04	5	Turbidity=32NTU
		6	Fluoride(F^{-})=7.01	6	Temperature=22.8^{0}c
13	HawassaZuria(db)	1	Calcium(Ca^{+2})= 1.	1	Conductivity=1342µs/m
		2	Sodium(Na^{+})=1.75	2	TDS=680mg/l
		3	Nitrate(No^{-}_{2})=0.25	3	Salinity=0.75ppt
		4	Nitrite(No^{-}_{3})=0.35	4	Resistivity=620kΩ
		5	Magnesium(Mg^{+2})=0.98	5	Turbidity=62NTU
		6	Fluoride(F^{-})=2.01	6	Temperature=18.8^{0}c
14	Jaragalalcha(jg)	1	Calcium(Ca^{+2})= 5.02	1	Conductivity=1210µs/m
		2	Sodium(Na^{+})=1.82	2	TDS=676mg/l
		3	Nitrate(No^{-}_{2})=0.21	3	Salinity=0.99ppt
		4	Nitrite(No^{-}_{3})=0.18	4	Resistivity=667kΩ
		5	Magnesium(Mg^{+2})=0.38	5	Turbidity=85NTU
		6	Fluoride(F^{-})=7.8	6	Temperature=12.9^{0}c

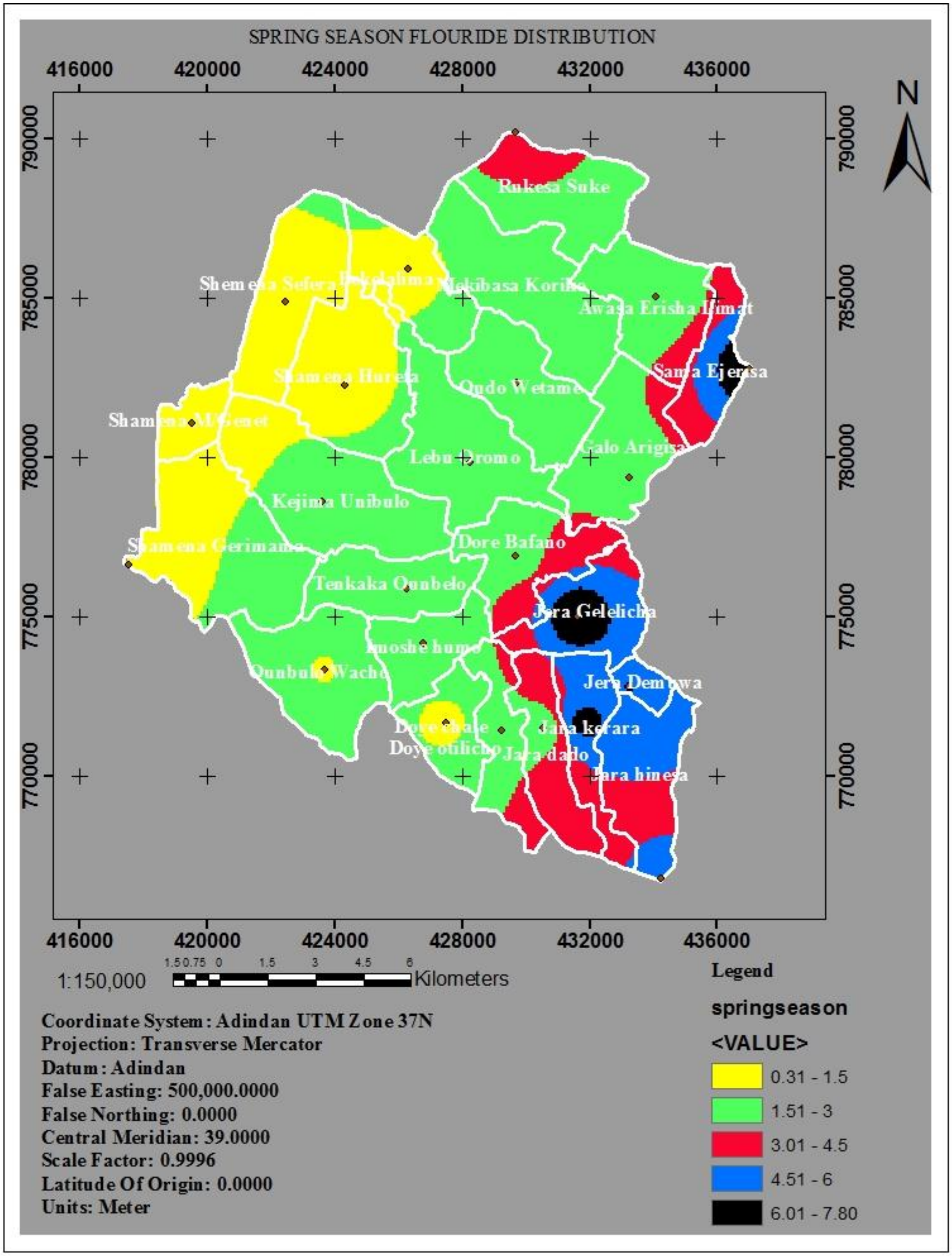
15	Jaradamuwa(da)	1	Calcium(Ca^{+2})= 1.8	1	Conductivity=1215µs/m
		2	Sodium(Na^{+})=1.35	2	TDS=630mg/l
		3	Nitrate(No^{-}_{2})=0.65	3	Salinity=0.91ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=583kΩ
		5	Magnesium(Mg^{+2})=0.85	5	Turbidity=67NTU
		6	Fluoride(F^{-})=5.8	6	Temperature=17.8^{0}c
16	Jarahinesa(jh)	1	Calcium(Ca^{+2})= 1.8	1	Conductivity=1760µs/m
		2	Sodium(Na^{+})=0.75	2	TDS=480mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.82ppt
		4	Nitrite(No^{-}_{3})=0.37	4	Resistivity=830kΩ
		5	Magnesium(Mg^{+2})=0.40	5	Turbidity=73NTU
		6	Fluoride(F^{-})=3.7	6	Temperature=19^{0}c
17	Jarakarara(jk)	1	Calcium(Ca^{+2})= 1.32	1	Conductivity=1630µs/m
		2	Sodium(Na^{+})=0.75	2	TDS=820mg/l
		3	Nitrate(No^{-}_{2})=0.19	3	Salinity=0.75ppt
		4	Nitrite(No^{-}_{3})=0.025	4	Resistivity=830kΩ
		5	Magnesium(Mg^{+2})=0.62	5	Turbidity=62.7NTU
		6	Fluoride(F^{-})=6.02	6	Temperature=25^{0}c
18	Jara dado(jd)	1	Calcium(Ca^{+2})= 1.53	1	Conductivity=1321µs/m
		2	Sodium(Na^{+})=1.07	2	TDS=720mg/l
		3	Nitrate(No^{-}_{2})=0.82	3	Salinity=0.92ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=620kΩ
		5	Magnesium(Mg^{+2})=1.7	5	Turbidity=12.07NTU
		6	Fluoride(F^{-})=1.75	6	Temperature=19.9^{0}c
19	Doyootilcho(do)	1	Calcium(Ca^{+2})= 1.08	1	Conductivity=1230µs/m
		2	Sodium(Na^{+})=0.62	2	TDS=530mg/l
		3	Nitrate(No^{-}_{2})=0.27	3	Salinity=0.62ppt
		4	Nitrite(No^{-}_{3})=0.35	4	Resistivity=780kΩ
		5	Magnesium(Mg^{+2})=0.26	5	Turbidity=56NTU
		6	Fluoride(F^{-})=2.02	6	Temperature=23.8^{0}c

20	Doyochale(dc)	1	Calcium(Ca^{+2})=1.75	1	Conductivity=1260µs/m
		2	Sodium(Na^{+})=1.02	2	TDS=630mg/l
		3	Nitrate(No^{-}_{2})=0.63	3	Salinity=0.97ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=820kΩ
		5	Magnesium(Mg^{+2})=1.9	5	Turbidity=32.8NTU
		6	Fluoride(F^{-})=1.86	6	Temperature=16.7^{0}c
21	Imoshehumo(ih)	1	Calcium(Ca^{+2})= 1.52	1	Conductivity=1250µs/m
		2	Sodium(Na^{+})=0.37	2	TDS=580mg/l
		3	Nitrate(No^{-}_{2})=0.37	3	Salinity=0.98ppt
		4	Nitrite(No^{-}_{3})=0.37	4	Resistivity=120kΩ
		5	Magnesium(Mg^{+2})=1.92	5	Turbidity=18NTU
		6	Fluoride(F^{-})=1.65	6	Temperature=18.3^{0}c
22	Umbulowacho(wa)	1	Calcium(Ca^{+2})= 1.85	1	Conductivity=1065µs/m
		2	Sodium(Na^{+})=1.25	2	TDS=582mg/l
		3	Nitrate(No^{-}_{2})=0.38	3	Salinity=0.85ppt
		4	Nitrite(No^{-}_{3})=0.25	4	Resistivity=582kΩ
		5	Magnesium(Mg^{+2})=0.75	5	Turbidity=240NTU
		6	Fluoride(F^{-})=1.25	6	Temperature=20.7^{0}c
23	Umbulotankaka(ut)	1	Calcium(Ca^{+2})= 0.92	1	Conductivity=1262µs/m
		2	Sodium(Na^{+})=2.8	2	TDS=650mg/l
		3	Nitrate(No^{-}_{2})=0.32	3	Salinity=0.95ppt
		4	Nitrite(No^{-}_{3})=0.97	4	Resistivity=19.07kΩ
		5	Magnesium(Mg^{+2})=0.92	5	Turbidity=65.2NTU
		6	Fluoride(F^{-})=1.65	6	Temperature=19.2^{0}c

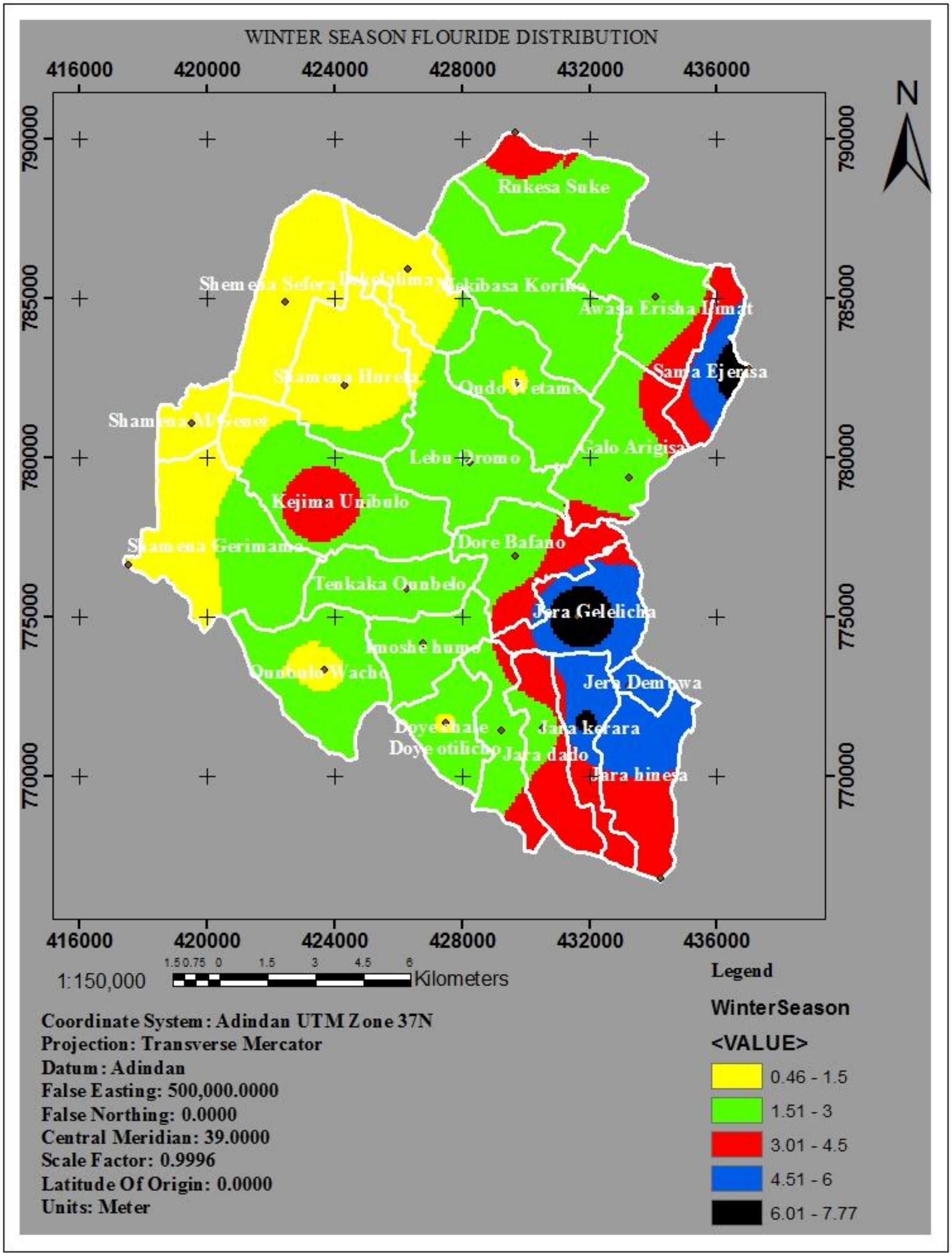
Appendix V: Spatial Distribution of Summer Season



AppendixVI: Spatial Distribution of Spring Season



AppendixVII: Spatial Distribution of Winter Season



AppendixVIII: Spatial Distribution of Autumn Season