ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

COLLEGE OF SCIENCE

DEPARTMENT OF EARTH SCIENCE

EVALUATING THE SOURCE AND FATE OF NITRATE IN SURFACE AND GROUND WATERS IN ADDIS ABABA AREA: ISOTOPIC AND GEOCHEMICAL APPROCHS.

BY RUHAMA KIFLE

Advisor: Seifu Kebede (PhD)

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Abstract

This study was conducted to evaluate the source and fate of nitrate in surface and ground water. The characterization of nitrate (NO3) in major rivers and aquifers of the Addis Ababa area were investigated by Isotopic and geochemical conditions. And an overall understanding on the sources and fate of NO3 in the surface water and the groundwater was obtained. The NO3 concentrations in both surface and ground water were very low and no samples exceed the WHO standards while concentration of other nutrients such as PO4-, Cl- and NH4+ were higher on surface waters.

The Redox condition estimated based on measurements of redox parameters of Eh, The analysis revealed that most of the surface water had anaerobic condition and presence of strong reducing conditions in the surface water and the recharge ground water. The anoxic condition is provided by high organic matter content in the surface water and result depletion of oxygen's.

Here the δ2H_H2O and 8δ18O_H2O result shows that the source of ground water in the city is heavy rain fall of different regime and shallow ground water recharge hypostasis is from rain fall. The recharge of surface water is from dam reservoirs and mixing between tap waters and ground waters. This study brings some clear evidences that unwanted anthropogenic nutrients can be released in both surface waters and shallow groundwater from rapidly growing cities. In addition, these polluted waters can create a serious treat for the downstream populations, with the need to implement expensive tertiary treatment plants to remove nitrate.

The chemical data shows that the concentrations of nutrients other than nitrate were higher and shows the pollution of surface waters but low nitrate. From the correlation of nitrate specious with other geochemical parameters reveals that the source for nitrate and other nutrients were the same such as wastes from manure, septic systems, fertilizer and industries.

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I could not have accomplished this without the help of many, all of whom cannot be listed here.

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Additionally my deep thank to Addis Ababa Water and Sewerage Authority (AAWSA) project office, ministry of water, irrigation and electricity, and water work design and supervision enterprise, National Meteorological Agency and Dr. Tillahun Azagegn for providing me valuable data used for my research.

I would like to thank to Addis Ababa University, Department of Earth science laboratory for allowing and supporting this work to be done.

And my wonderful family who has always been there for me, I extend my special thank you for your love, words of encouragement and for always believing in me no matter what.

Above all, I wish to thank God for the grace, love, and patience He has shown me in my life. I could never have scaled this wall without Him and the people He put in my life.

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List of Acronyms

AAEPA- Addis Ababa Environmental Protection Authority

AAU- Addis Ababa University

APHA – American Public Health Association

AWSA- Addis Ababa Water and Sewerage Authority

conc. - concentration

DMAL- Desirable Maximum Allowable Limit

Eh- redox condition

EC- Electrical Conductivity

ECA- Economic Commission for Africa

EEC- European Economic Commission

ES- Ethiopian Standards

ESA- Ecological Society of America

FEPA- Federal Environmental Protection Agency

FEDB - Finance and Economic Development Bureau of Addis Ababa City GL-Guideline Value

GPS- Global Positioning System

GW- Ground waters

LULC - Land use land cover

m- Meter

M.a.s.l- meter above sea level

MAC- Maximum Allowable Concentration

MAL- Maximum Allowable Limit

MCNCs- Most Common Natural Concentrations Mg/l or mgL-1 - milligram per liter

MoWR- Ministry of Water Resources

µs- micro siemens

MV- Maximum Value

NMSA- National Meteorological Service Agency

RADWQ-Rapid Assessment of Drinking Water Quality

SBPDA- Sanitation, Beautification &Parks Development Agency

SW- surface waters

TDS- Total Dissolved Solids

UK- United Kingdom

UNESCO- United Nations Educational, Scientific and Cultural Organization

USEPA- United States Environmental Protection Agency

USFEPA- United States Federal Environmental Protection Agency

USNAS- United States National Academy of Science

USPHS- United States Public Health Service

WHO- World Health Organization ACCRONUMES

1 INTRODUCTION

1.1Background of the Study

Water is the most abundant substance on earth. Comprising over 70% of the earth's surface it is the principal component of all living things and a major force constantly shaping the surface of the earth. Water obtained from rivers, lakes, springs and wells has been used for different purposes like domestic, agriculture, industrial and manufacturing purpose. The need of water is more complex due to population growth, urbanization and industrialization. Any developmental activity is related, either directly or indirectly, with water utilization.

Water pollution is the direct or indirect alteration of the physical, chemical and/or biological properties of a water system in such a way as to create a hazard or potential hazard to health, safety and welfare of any living species. This day's water pollution resulted from industrialization, urbanization and population explosion has become a global problem. Ethiopia is also facing the problem of water quality degradation, however, the extent and degree of severity of water pollution is more pronounced in major cities, like Addis Ababa where the problem is at its peak currently (Tamiru Alemayehu et.al (2005).

In many developed country proper urbanization takes in to consideration equivalent growth in wastes removal facilities. In case of Addis Ababa the waste collection system both solid and liquid is not progress in proportion to its expansion and consequently the impact of these waste on the water environment is increasing. In order to reduce and eventually overcome water pollution, one must understand the problems to design mitigation measures.

The level of nutrients such as nitrate and phosphate in fresh water ecosystems is a worldwide problem. Natural waters have very low concentration of nitrate (a soluble form of nitrogen) and phosphate, because they exist in forms not readily available to the biota.

However excessive inputs of nitrogen (N) into surface waters from various human activities made water bodies unsuitable for designated uses such as drinking, irrigation, industry, recreation, or fishing. These pollutants may enter into water bodies as raw sewage, effluents from sewage Treatment plants, urban and rural run off, septic tanks, landfills, open damps and agricultural practices (WHO, 2004).

Nitrogen and phosphorous act as fertilizers, stimulating algal blooms and may bring Eutrophication of many inland waters. Eutrophication leads to changes in the structure of ecological community indirectly through oxygen depletion and directly by increasing nutrient concentrations.

However, a shortage in phosphorous limit the productivity of most fresh water systems due to its immobilization in the biota and insolubility of its compounds (Beeby, 1993 and ESA, 2000).

Now there exists a considerable public concern over the possible hazards linked with elevated levels of nitrate in drinking water such as its carcinogenic potential and Methemoglobinemia (blue-baby syndrome).

Ammonia in water is an indicator of possible bacterial, sewage and animal waste pollution (WHO, 2004). In water it originates from the breakdown of nitrogenous organic and inorganic matter from excretion by organisms, reduction of nitrogen gas (N2) by micro organisms, urban and rural run off and releases from industrial processes (Chapman, 1996 and Manahan, 2000). The Environmental Protection Agency (EPA) has since adopted the 10 mg/L standard as the maximum contaminant level (MCL) for nitrate-nitrogen and 1 mg/L for nitrite-nitrogen for regulated public water systems.

Natural levels in surface and groundwater are below 0.2 mg/l (Chapman, 1996). It mostly exists in water in the form of ammonium ion (Manahan, 2000). The presence of higher level of ammonia in drinking water comprises lower disinfection efficiency, result in nitrite formation in distribution systems, causes the failure of filters for the removal of manganese and also results in taste and odor problems in water (WHO, 2004).

Surface water is the main receiver and transmitter of pollutant into the groundwater body. Hence, protection of surface water pollution is directly related to the protection of groundwater system, because the two systems form a link through the geologic medium. Very high nitrogen concentrations may occur due to anthropogenic activities such as waste disposal and agricultural activities (Bouwer, 1978).

The fate of nitrate is complex and includes several physical and biological processes of which de nitrification plays a major role. Isotopic approach with Geochemistry is useful method for understanding De nitrification reaction in aquifer and surface water system. In this study the geo chemical tools and nitrogen specious (NH_4^+, NO_2^-, NO_3^-) analysis ware used to give an overall understanding on the source and conversion process of nitrate in the surface water and ground water in Addis Ababa. Therefore this study will attempt to present the conversion behavior of nitrate once it gets in to the water.

1.2 Statement of problems

The nitrate enrichment of many localities in Addis Ababa could arise from different sources such as liquid and solid domestic wastes and industrial effluents and to some extent agricultural activities. In Addis Ababa, it was reported in some studies that urban and industrial centers play a role in polluting surface and groundwater (Tamiru Alemayehu (2001). Chemical analysis of surface and shallow groundwater samples taken at various points along streams and different springs show that the level of unwanted chemical constituents such as nitrate and chromium, for example, are higher than the background level due to the in adequacy of controlled waste management strategies (Mohammed Ali, 2002; Tamiru Alemayehu et. al., 2005; AAEPA, 2005 and Macha Chan argachew, 2009).

The industries, residential areas and commercial institutions in and around the city are seriously polluting the river water by discharging solid and liquid wastes (Tamiru Alemayehu et,al 2002). Although groundwater pollution from heavy metals and bacteriological contamination has been reported by some authors like Yesahak Worku et.al. (1999), Samuel Melaku et.al. (2004) and Molla Demlie et.al, (2006) nitrate has been given little importance, particularly.

For instance Girma Hailu (2011) studies assessment of the status of nitrate pollution in selected ground water sources in Addis Ababa, Shilima Abebe (2011) conduct on Ground water quality problems in summit-Bole and Kotebe area. However, the scopes of these studies have been limited, because, Girma Hailu studied only the nitrate spatial distribution of Addis Ababa city. Shilma also studied ground water quality problems, but his boundary is focused only the summit bole and Yeka kotebe part of Addis Ababa. Physicochemical pollution pattern in akaki river basin of Addis Ababa by (Frizer Eshetu et al, 2012) And Kassa Aynalem et.al, (2015) also evaluate ground water nitrate transport model in Akaki catchment assuming no nitrate conversion is happing.

Therefore Nitrate contamination of ground water is most studied phenomenon worldwide (Ahmed, 2004) and less so in the study area (e.g. Ferezer Eshetu, 2012). Particularly the fate of nitrate once it gets in to the water and specific source of nitrate in the water of Addis Ababa is not known.

Nitrogen cannot be considered conservative because it is biologically modified through e.g. nitrification and De nitrification reactions causing isotopic fractionation that modifies the isotopic signatures of the dissolved nitrogen species. It is the most stable and end product of nitrogen transformation, before the cycle has restarted by the means of denitrification. When nitrate joins the groundwater, it does not form insoluble minerals that precipitate nor does it go other complexities (Ahmed, 2004). But, there is a probability of nitrate to be degraded under some complex requirements; the presence of absolute anoxic condition, presence of electron donors (organic carbon, pyrite) nitrate conversion will happen.

Therefore successful investigation of nitrate behavior once it get in the water and distribution must take into account the many environmental and historical factors that affect nitrate fate and source. These include local hydrogeology, changing land use practices, variable conditions that

support an array of natural nitrogen cycling reactions, and geochemical approaches (Kendall and Aravena, 2000).

1.3 General Objective

- The general objective of the study is to evaluate the fate and source of nitrate in surface and ground water in waters in Addis Ababa.

1.3.1 The specific objectives of the study include

- To investigate conversion factor affecting No3 concentration of ground water and surface water.
- To identify the mixing process of different NO3- source in the region.
- To estimate the recharge of surface and ground waters.
- To investigate the Implication of nitrogen source and fate in water management practice.

1.4. Significance of the study

Scientifically the result will provide baseline information on groundwater hydro chemical Behavior, the source and mechanisms of nitrate pollution caused by human activities compared to the natural background. Knowing the relative contributions of anthropogenic sources will help to devise appropriate mitigation measures for future interventions.

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CHAPTER TWO
2. LITERATURE REVIEW.

2.1 Previous Studies

Some works have been conducted in the study area by different researchers in the last few years including studies on the Effect of water hyacinth on the level of dissolved Oxygen in Aba Samuel Reservoir (Zeleke Teferi, 1992) and preliminary survey of pollutant load on great Akaki, Little Akaki, and Kebena rivers (EPA, 1997) and the degradation of Abo-Kebena River in Addis Ababa (Tesfaye Berhe, 1988). Yesahak Worku et.al.1999 also studied the physical, chemical and microbiological characteristic of various sources of water in and around Addis Ababa City and produced an explicit data on few samples from little Akaki River and has indicated the pollution of the river.

Then Tamiru Alemayehu (2001) studied the impact of uncontrolled waste disposal on the surface water quality in Addis Ababa and found out higher than background values for pollutants such as Cr and Nitrates and associated it with poor economy and lack of proper waste disposal systems. Berhanu Gizaw (2002) had environmentally investigated the hydrogeology of the Addis Ababa city and produced an explicit data on few samples from little Akaki River and indicated the pollution of the river. Besides, EPA (2002) assessed the pollution status of the great and little Akaki Rivers with the objective to investigate the pollution load of Akaki River and its effect on the surrounding environment and found that the BOD and Total Coliforms load is high and the DO level is low. Moreover, confirmed on the pollution of both rivers and their potential to cause health effects on human and animals in addition to their impact on the aquatic life. In addition, it linked some industries and residential wastes with TDS values above the recommended limit and also found high chloride concentrations in little Akaki river.

However, few researches pertaining specifically to little Akaki River basin have been carried out with the objectives of learning about the status, causes and effects of its pollution. In addition few studies relate the pollution in the little Akaki River basin with the contamination of groundwater reserves of the vicinity. Thus only the major ones are listed below:

Mohammed Ali (2002) studied industrial pollution and its impact on the little Akaki River and show that industrial effluents surpass the Ethiopian provisional industrial effluents discharge permit limits. Besides he identified Tanneries as the major polluter industrial sector. And using ANOVA (analysis of variance) he also indicated that the river is grossly polluted in all seasons and throughout its course. Above all he concluded that river water cannot be used for irrigation, drinking, livestock watering and washing. Tamiru Alemayehu, et.al. (2003) conducted a study on surface and ground water pollution status in Addis Ababa. Besides, Samuel Melaku et.al (2004) had simultaneously determined the trace elements of litle Akaki River Water samples and found out that out of the eight elements analyzed except two (Cr and Mn) all fulfill the surface water quality standard of class 2 and 4.

Thus he concluded that the water can be used for irrigation. Tenalem Ayenew, 2005.Major ions composition of the groundwater and surface water systems and their geological and geochemical controls in the Ethiopian volcanic terrain. Samuel Melaku et.al (2005) had carried out multi element analysis of little Akaki River sediments and found out that the heavy metals pollution

load in the sediments of TAR and its tributaries is alarming. Then he associated this pollution load with untreated domestic, municipal and industrial sources. Then Molla Demlie et.al (2006) analyzed soils and ground water samples for trace metal pollution and witnessed Instances of ground water contamination with Cr and Cd in the industrial and highly urbanized centers of the city. And he associated the case with fractures, joints and related preferential flow paths.

Samuel Melaku et.al (2007) evaluated the pollution status of the little Akaki River and Its tributaries using some physicochemical parameters, major ions and nutrients, and provided data on the physicochemical parameters: pH, temperature, EC, TDS, BOD, COD, DO, major ions and nutrients. They assessed the pollution status of the river by comparing values of the parameters with accepted standards and most common natural concentrations (MCNC) and found out that certain parameters violate standards. Besides he also shows the increases in BOD, Nitrate, Ammonia, Phosphates and the decrease in DO downstream of TAR. And he also observed that the average concentrations of the major ions and nutrients surpassing the MCNCs and associated the situation with increasing domestic, industrial and agricultural activities Macha Chanargachew (2009) and AAEPA (2005) assessed and reported the status of the Akaki River water quality. Although the above indicated works addressed major issues on pollution states, water quality parameters, water quality degradation and surface and groundwater vulnerability to pollution, but the conversation factor of nitrate once it get in to the water and its source discrimination has not been addressed.

2.2 The nitrogen cycle

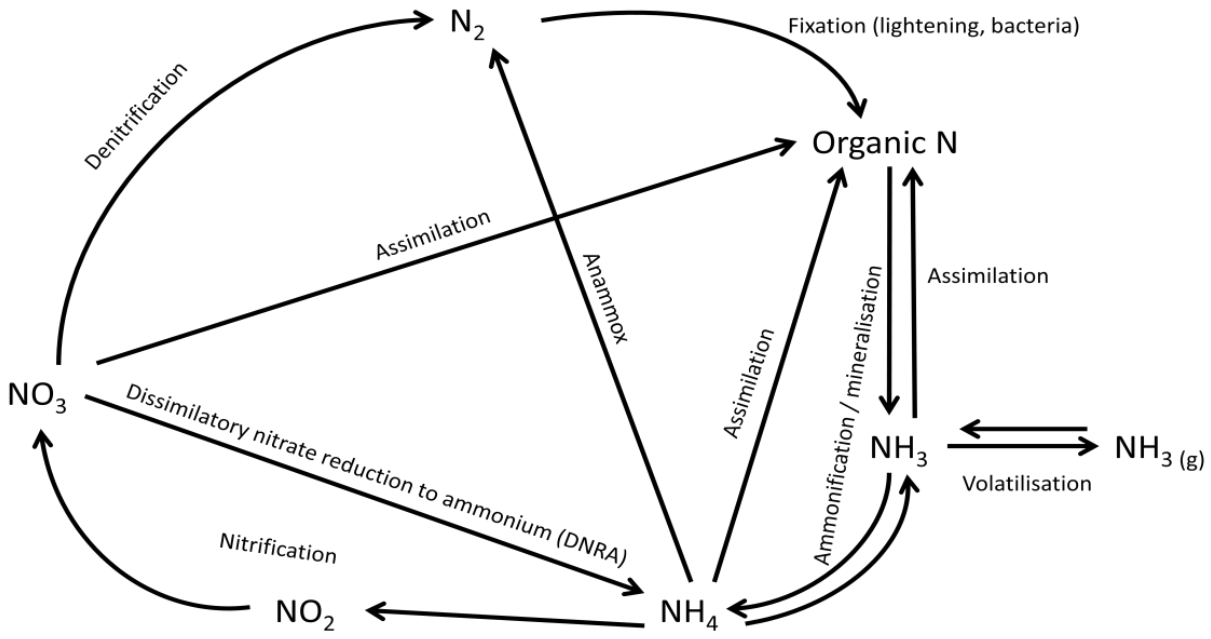
Nitrogen (N) cycling is a fundamental ecological process, gaining in prominence because of concerns about the impact of excess Nitrogen on ecosystems and the contribution of gases, such as N2O, to global warming.

Nitrate (NO3-), nitrite (NO2-) and ammonium (NH4+) are reactive inorganic forms of nitrogen which pose most concern to water quality status (Hatch et al. 2002). NO3 is the most prevalent form of nitrogen in the hydrological cycle and is highly mobile in water (Pärn et al. 2012). It is therefore the focus of much N related research, including this study. NO3 is not subject to precipitation or adsorption processes (Appelo and Postma 2005), as its negative charge prevents interaction with negatively charged soil or organic particles enhancing its leaching capacity. Therefore, reduction of NO3 concentrations in hydrogeological pathways must be achieved through plant uptake, leaching and biogeochemical processing (Hatch et al. 2002).

Ammonification, which produces NH4 from organic N will proceed more rapidly under aerobic conditions, but can also occur within anaerobic conditions (Reddy and Patrick 1984). NH4 is relatively immobile due to its positive charge which causes it to bind tightly to negatively charged clay minerals and organic matter, which determines the cation exchange capacity.

Although NO2- is highly toxic to aquatic life, it is highly reactive and has a short half life minimizing the potential risk A summary of nitrogen biogeochemical cycling is displayed in

Figure1 Summary of biogeochemical processes involved in the nitrogen cycle



In order for isotopes to be useful as tracers of various N sources to aquatic systems, an understanding of how biogeochemical cycling affects the isotopic composition of various inorganic forms of N is critical. Here we briefly present the state of our understanding regarding major factors that can affect isotopic composition of N species in environmental systems.

The main biologically mediated reactions that control nitrogen dynamics in ecosystems are: Nitrogen Fixation, Assimilation, Mineralization, Nitrification, and Denitrification. These reactions commonly result in increases in the δ15N of the substrate and decreases in the δ15N of the product, unless the reactions go to completion. Physical processes, specifically ammonia volatilization, also significantly influence the δ15N of the released ammonia, residual NH4+, and any subsequently formed NO3−. Processes that consume NO3− (primarily denitrification and assimilation by phytoplankton and/or prokaryotes) generally cause the δ15N and δ18O in the remaining pool of NO3− to increase in a relatively predictable pattern. These processes and their impact on isotopic compositions of selected N-bearing compounds are discussed below.

2.2.1. Nitrification

Nitrification is a microbial oxidation process by which NH4+ is converted NO2- and subsequently NO3- (Fetter 1999). Nitrification occurs under aerobic conditions and is mediated by autotrophic organisms (Kendall 1998). The nitrification process has two separate parts outlined in Equation 2.1 and Equation 2.2 (Willey et al. 2011). The first part of the reaction is the rate determining step as NO2- is unstable and does not tend to accumulate in the natural environment (Kowalchuk and Stephen 2001). As shown in Equations 2.1 and 2.2, nitrification can produce acidity.

$NH4+ + 1\ ½\ O2 \rightarrow NO2- + H2O + 2H+$ Equation 2.1

$NO2^- + ½\ O2 \rightarrow NO3$ Equation 2.2

2.2.2. Nitrogen Fixation

Nitrogen gas (N_2) makes up nearly 80% of the Earth's atmosphere, yet nitrogen is often the nutrient that limits primary production in many ecosystems. For nitrogen to be available to make proteins, DNA, and other biologically important compounds, it must first be converted into a different chemical form. The process of converting N_2 into biologically available nitrogen is called nitrogen fixation. N_2 gas is a very stable compound due to the strength of the triple bond between the nitrogen atoms, and it requires a large amount of energy to break this bond. As a result, only a select group of prokaryotes are able to carry out this energetically demanding process. Although most nitrogen fixation is carried out by prokaryotes, some nitrogen can be fixed abiotically by lightning or certain industrial processes, including the combustion of fossil fuels.

2.2.3. Denitrification

Denitrification is the process that converts nitrate to nitrogen gas, thus removing bio available nitrogen and returning it to the atmosphere. Dinitrogen gas (N_2) is the ultimate end product of denitrification, but other intermediate gaseous forms of nitrogen exist some of these gases, such as nitrous oxide (N_2O), are considered greenhouse gasses, reacting with ozone and contributing to air pollution.

Another process that can result in an enriched d15N value is denitrification. In this process, bacteria degrade nitrate to nitrogen gases that are released to the atmosphere. The 14N of the nitrate is preferentially utilized resulting in an enriched d15N in the remaining nitrate. Indicators of possible denitrification are low nitrate values (commonly < 1 mg/L) (Korom, 1992) and enriched d15N values.

Unlike nitrification, denitrification is an anaerobic process, occurring mostly in soils and sediments and anoxic zones in lakes and oceans. Similar to nitrogen fixation, denitrification is carried out by a diverse group of prokaryotes, and there is recent evidence that some eukaryotes are also capable of denitrification (Risgaard-Petersen *et al*. 2006).

Some denitrifying bacteria include species in the genera *Bacillus*, *Paracoccus*, and *Pseudomonas)*. Denitrifiers are chemoorganotrophs and thus must also be supplied with some form of organic carbon. Denitrification is important in that it removes fixed nitrogen (i.e., nitrate) from the ecosystem and returns it to the atmosphere in a biologically inert form (N_2). This is particularly important in agriculture where the loss of nitrates in fertilizer is detrimental and costly. However, denitrification in wastewater treatment plays a very beneficial role by removing unwanted nitrates from the wastewater effluent, thereby reducing the chances that the water discharged from the treatment plants will cause undesirable consequences (e.g., algal blooms)

$NO3—N \rightarrow NO2—N \rightarrow NH3 \text{ or } N2$ Denitrification (Reduction)

Denitrification results in an enrichment of the oxygen-18 and nitrogen-15 in the remaining nitrate of about 2 to 1 (Amberger and Schmidt 1987; Bottcher et al. 1990).

2.2.4 Ammonification

When an organism excretes waste or dies, the nitrogen in its tissues is in the form of organic nitrogen (e.g. amino acids, DNA). Various fungi and prokaryotes then decompose the tissue and release inorganic nitrogen back into the ecosystem as ammonia in the process known as ammonification. The ammonia then becomes available for uptake by plants and other microorganisms for growth.

2.2.5 Assimilation

Assimilation refers to the transformation of inorganic N-bearing compounds into an organic form during biosynthesis by living organisms. Generally, oxidized forms of N are initially reduced to NH_4^+ and then assimilated into organic matter.

Assimilation, like other biological reactions, discriminates between isotopes and generally favors the incorporation of the isotope with the lower mass. A large range of N fractionations (−30 to 0‰) has been measured in filed studies (Cifuentes et al. 1989; Montoya et al. 1991), and in laboratory experiments for nitrate and ammonium assimilation by algae (Pennock et al. 1996; Waser et al. 1998; Altabet et al.1999; Granger et al. 2004), and bacteria (Hoch et al. 1992) in aquatic environments.

CHAPTER THREE
MATTERIAL AND METHODOLOGY
3.1. Description of the study area

3.1.1. Location,

Addis Ababa is located in the central highlands of Ethiopia, with the altitude that ranges from 2100 m.a.s.l to 2700 m.a.s.l which covers an area of about 540 km2 with a population of more than 3 million inhabitants. Its geographic location is between 38.638o and 38.906o east and 8.832o and 9.09o north. The administration of the city is divided in to ten sub-cities: Bole, Arada, Cherkos, Kolfe Keraniyo,Addis ketema, Lidata, Akaki-Kaliti, Gullele, Nefas-Silk Lafto and Yeka.

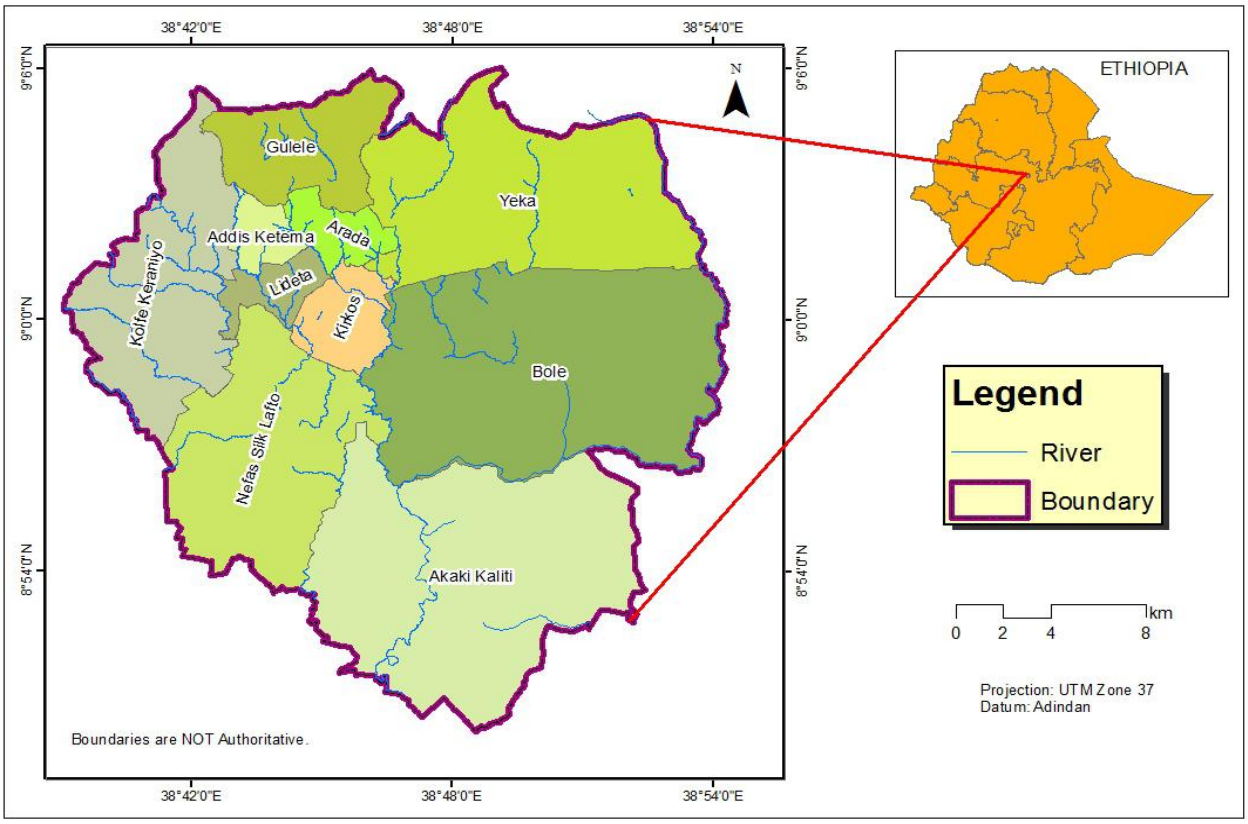


Fig 2 Location map of Study Area

3.1.2 Population

According to UN-Habitat (2012) report Addis Ababa is one of the fastest growing cities on the continent. Its population has nearly doubled every decade the population of Addis Ababa has grown from 2 million to about 4 millions in the last fifteen years with the administrative area expansion from 220 to 540 square kilometers.

This has been resulted in a heavy pressure on the Addis Ababa City Administration and the Addis Ababa Water and Sewerage Authority to extend safe drinking water supply and sanitation services (GWIACCES, 2012).

In 1984 the population was 1, 412, 575, in 1994 it was 2,112, 737, and this number will continue to rise, According to city government of Addis Ababa 2011/2012 report, the total population of Addis Ababa was estimated to 3,048,631 reaching 12 million in 2024. Lack of water scheme maintenance and lack of new facilities combined with rapid population growth has brought water shortage in Addis Ababa. High volume of water wastage due to faulty piping (as high as 35 percent), and needs priority given to industries, also contribute to the shortage. In terms of urban population it currently accounts for at least 22.9% of the country‟s total urban population (CSA, 2012). Addis Ababa is divided into 10 sub-cities with the population of each sub city as shown in the Table 3.1 below kolfe keraniye , yeka and nifas silk lafto sub city are highly populated.

Addis Ababa sub-cities population 2008 (CSA, 2012)

Sub-cities	Population
Akaki-Kaliti sub-city	281.201
Nefas Silk Lafto sub-city	396.107
Kolfe Keranyo sub-city	532.653
Gulele sub-city	327.381
Lideta sub-city	201.613
Kirkos sub-city	260.991
Arada sub-city	282.009
Addis Ketema sub-city	321.192
Yeka sub-city	445.484
Bole sub-city	388.711
Total	3,048,631

Table 1 population of sub cities of study area

3.1.3 Rainfall

Addis Ababa has three distinct seasonal periods with seven main rainy months from March to September. The dry season (Bega) is between the months of October to February, the short rain season is between March to May and the big rainy season is between the months of June to September (Feven Solomon, 2007).

stations	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Des	Ann. Mean
bole station	12.4	27.9	55	81.7	73.2	115.2	237.4	252.7	128.4	31.7	5.3	8.3	1029.2
Akaki station	13.7	43.1	60.1	95.1	66.5	128.8	271.1	303.8	140.9	23.9	4.3	3.4	1145.4
AA Observt.	17.2	43.2	65.0	93.7	86.5	128.9	257.8	279.7	176.5	38.9	6.4	5.4	1205.2

Table-2: Mean monthly rainfall (mm) in the three stations of Addis Ababa (1983-2015).

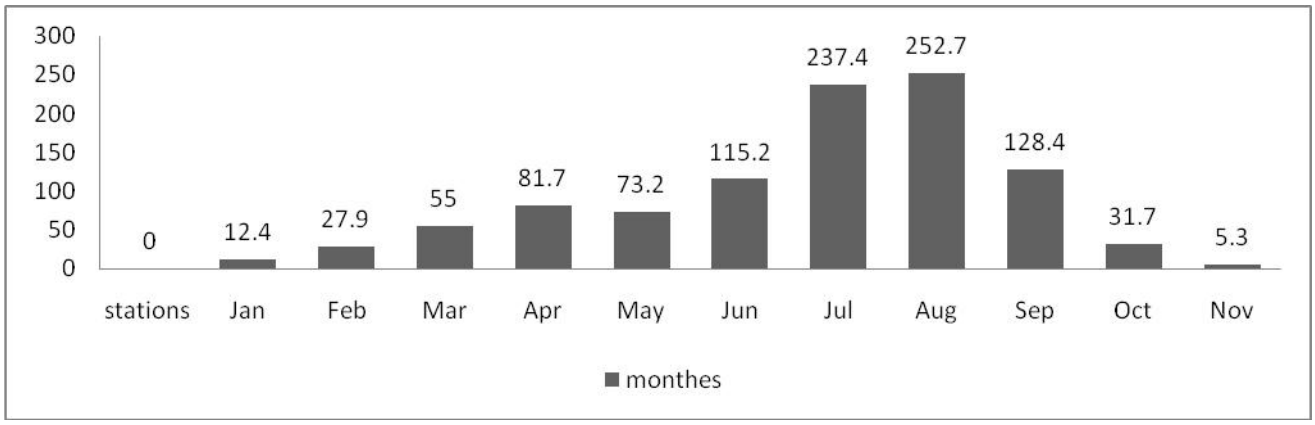


Figure 3: Mean monthly rainfall (mm) at Addis Ababa Observatory (1981-2015)

3.1.4 Land use

Most of the upper part of the study area is occupied by settlement, mixed land use practices and planted trees (Eucalyptus) in the up hills of the Entoto ridge whereas the southern part is dominated by non-irrigated agriculture. Most industries are concentrated along little and Big Akaki Rivers, which offer prospect for their effluents to get easily in to the rivers and end up in to the

Abasamuel reservoir (the confluence of Big and Little Akaki Rivers). Land use activities have direct impacts on water quality, while water quality greatly influences the sitting of land use activities. Presently industries areas are located in the southern sectors along the river channel.Inappropriate land use, particularly poor land management, causes chronic groundwater quality problems. Acute groundwater quality problems are common and arise from unsuitable land use (Omran, 2012).

For effective urbanization and organized urban development, a well thought urban planning exercise is a prerequisite. Even though land is the largest economic resource of Addis Ababa, the land use pattern is characterized by haphazard development which mainly geared towards horizontal expansion (Finance and economic development office report, 2010). Particularly, most of the riverside areas in the city are not well kept and utilized as per the acceptable standard.

For this research the city of Addis Ababa is classified in to five generalized land use land cover categories. The land use class is; residential, rainfed agriculture, Market area, Vegetation area, and slum area.

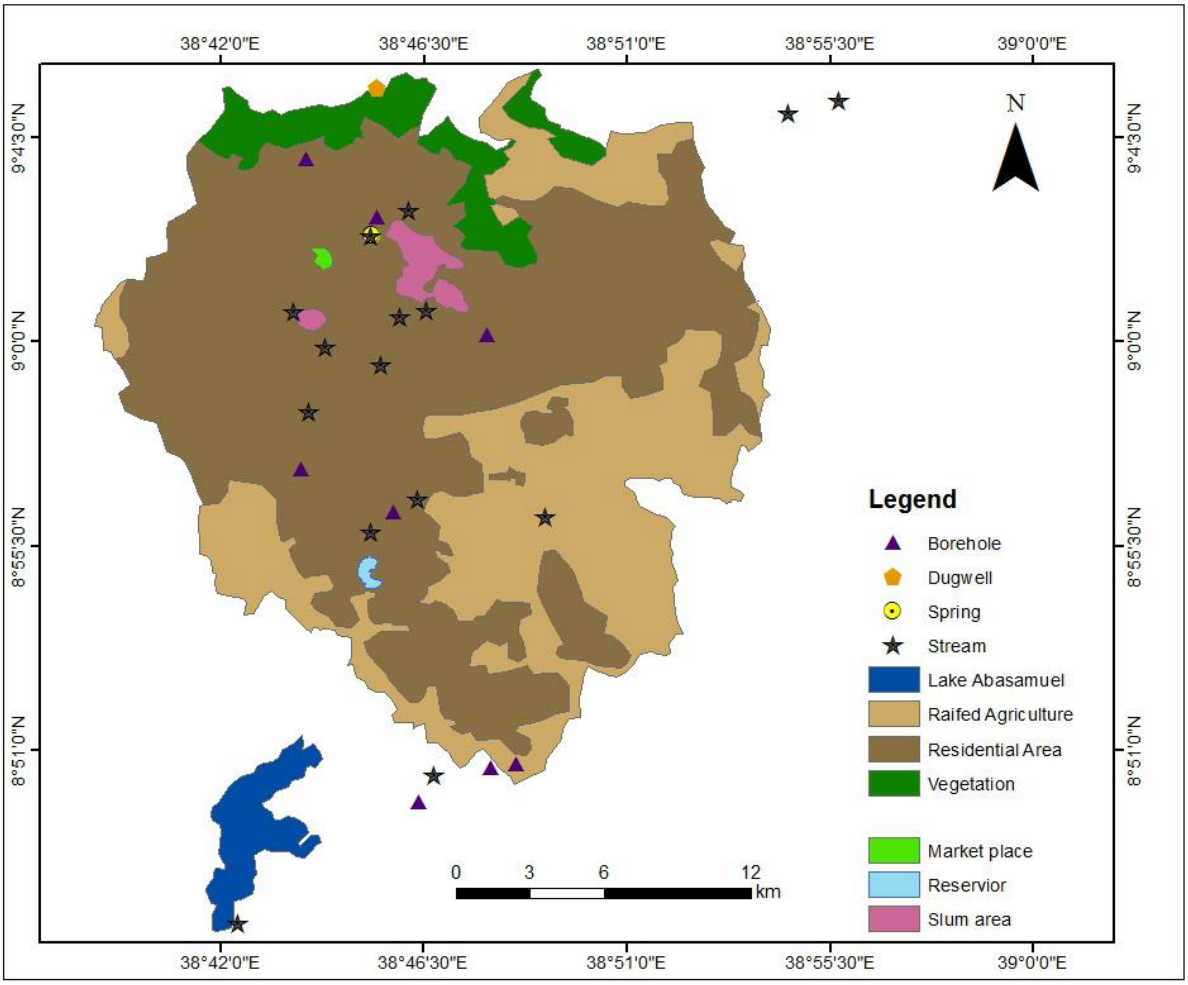


Figure 4 land use land cover map of Addis Ababa area with the sampling point.

3.1.5. Drainage

The Addis Ababa area located in Akaki catchment's which consists of Akaki River catchments and numerous small rivers. The dominant ones are the Big Akaki, which drains the Eastern part of the catchment's area, has many a tributaries among which genfile, kebena, kechene, kurtume and yeka all are founded in the easter part of the city boundaries. And the Little Akaki that drains the Western part of the catchments and their respective tributaries.

The two rivers form one of the biggest tributaries of the Awash River called Akaki River that enters Abba Samuel Lake, leaves the lake and passes through a gorge up to 100 m deep which extends for about 8 km before it joins the Awash River. Both Big Akaki River basin with catchments area of 900Km2 and Little Akaki River with catchments area of 540 Km2 with their tributaries drain the city of Addis Ababa from North to South (Feven Solomon, 2007).

3.1.6 GEOLOGY AND HYDROGEOLOGY OF THE AREA

3.1.6.1 Geology

The geological formation of Akaki catchment is categorized as Miocene–Pleistocene volcanic successions in which basaltic lava flows, acidic and intermediate lava flows, and pyroclastic flows interlayer and frequently intersected by Quaternary normal faults (Alemayehu et.al., 2009).

The study area being part of the Main Ethiopian Rift (MER) its geological setup arises from the evolution and development history of the Ethiopian Plateau and the Rift system. Thus, the catchment is covered by range of volcanic rocks overlain by fluvial and residual soils varying in thickness from a few cm to about 19 m in which black cotton soil being the predominant type. The volcanic formation includes mainly basalts, rhyolites, trachytes, scoria, trachybasalts, ignimbrites and tuff belonging to wide range ages most of which are highly weathered and fractured (Demlie et.al. 2007a).

Stating different sources, the summary made by Ayenew et.al. (2008) about the lithostratigraphy of the study area was as follows:

Generally the litho stratigraphy was classified in to four groups saying Alaji Formation, Addis Ababa basalts, younger volcanic and rent deposits. The Alaji Formation group includes the rhyolites, trachytes, tuff, agglomerate, and aphianitic basalt dominating the northern and central part. This was also further into Alaji rhyolites and Intoto Silicics in which the Intoto Silicics represents massive Oligocene fissure-basalt, rhyolites, and trachytes with minor welded tuff and obsidian. The second groups, the Addis Ababa basalts, overlay the Intoto Silicics and cover the central and southern part of Addis Ababa.

Paleosol and scoraceous horizons are common and Olivine porphyritic basalt outcrop in central Addis Ababa with a thickness varying from 1 m in the foothills of Intoto to more than 130 meters in central Addis Ababa. Third ones, the Younger Volcanics, include the Nazareth Group and Bishoftu Formations. The Nazareth Group contains aphianitic basalts, welded tuffs, ignimbrites, trachytes, and rhyolites being the aphianitic at the top and porphyritic at the bottom.

These rocks found dominantly south of the Filwuha Fault. On the other, the Bishoftu Formations consists of olivine porphyritic basalt, scoria, vesicular and scoriaceous basalt, and locally trachy-basalt lava flows overlaid by scoria, tuff, sand, and gravel. These are dominant in the southern part in which Akaki well field is found forming the major aquifers. Their thickness varies from 20-40 m in the well field. The last group, Recent Deposits, includes alluvial, residual, and lacustrine deposits.

Overlaid by dark younger black cotton clayey soils in some parts, their thicknesses of these deposits varies from 5 m to 50 m and are dominant in the southern part. Further, Alluvial deposits are found along the Little- and Big-Akaki rivers and in most flat plains.

Moreover, Akaki catchment being near the MER, rocks were subjected to rift tectonics that is manifested by a number of fault systems having a general trend of the rift system NE and some are also oriented in EW, NW and NS (Ebasa Oljira, 2006).

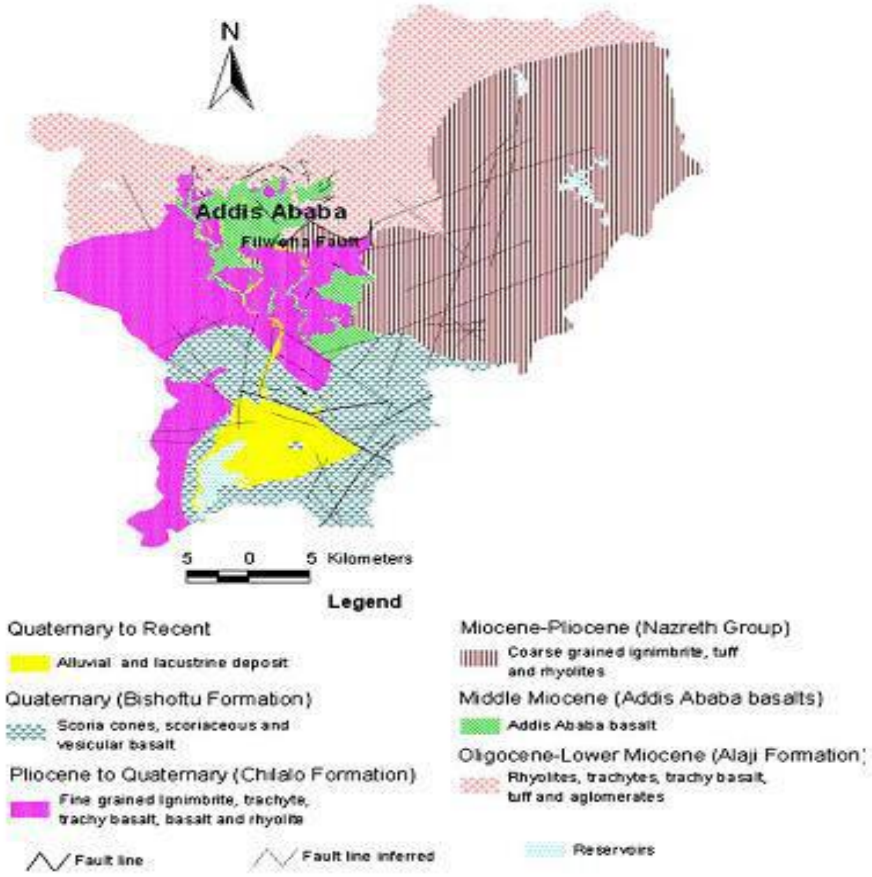


Fig 5 Geological map of Addis Ababa (Source Demlieet.al., 2007a)

3.1.6.2. Hydrogeology

With this intricate lithostratigraphy, varying spatio-temporal distribution, different reciprocal stratigraphic relationships, contacts with ancient and recent rocks, their great compositional, structural and complex textural variability, and their different level of tectonization and weathering (Davis and De Wiest 1966; Vernier 1993-as cited in Demlie et.al. 2007a), the hydraulic characteristics of the study were found to be complex.

Generally, Scoria, scoriaceous, vesicular and fractured basalt of the Bishoftu Group located in the southern part of the catchment including the Akaki well- field are judged to be highly productive, Fractured and weathered Addis Ababa basalt aquifer with some inter-volcanic coarse sediment, located in central, western and northern Addis Ababa are considered to be moderately productive; the Young fractured ignimbrite of the Yerer volcano covering the eastern part of the catchment and young fractured trachyte of the Wechecha volcano covering the western part as low productive aquifers and the Weathered and fractured rhyolites and trachyte of the Intoto silicics covering the Intoto Mountain Range could be considered as non-aquifer.

3.2 METHODOLOGY

3.2.1. Identification of sampling sites

Sampling sites were selected from three spatial domains of the study sites (Fig.6) River, spring and ground water borehole. After setting the relevant objectives and identifying sampling sites

proper field planning has been conducted for taking water samples from each site (Up-stream,-Mid- stream, and down-stream.). In the Study sites we selected 14 streams 10 BH and 1spring.

I. Upstream (Entoto Mariam hand dug well, French embassy river, legedade river inlet and legedade river out late
II. Midstream (central part) of the study area which is highly populated, slummy area and the most suspected areas with the risk of different nutrient pollutants (Ras mekonen brg spring, kechene river at piassa, kebena R at urael, kechene R at bambies, akaki R at bole, mercato drinag at TH, borehole at tsion hotel, borehole at imperial and borhole at germen squire…).
III. Downstream of the study area like (Akaki river at bole bulbula, akaki river at new road brige, jica well at kality, akaki wellfilds, abasamuel in late and Aba Samuel Lake..).

NO	**Locality of sampling site**	**Sample ID**
1	River at berchiko fac	SW1
2	River at rench Embassy	SW3
3	Kechene River. at Pissa	SW4
4	River. at Merkato	SW5
5	Lededadi inlet	SW6
6	Lededadi outlet	SW7
7	Kebena River.at Ourael	SW8
8	Merkato driange atTH	SW9
9	Kechene River. at Bambis	SW10
10	Small Akaki Riverat Mekanisa	SW11
11	Akaki River. at Bulbula	SW12
12	NFS Lafto River.	SW13
13	Abasamuel lake outlet	SW14
14	AK new brg River.	SW15
1	Rasmekonen spring.	Sp1
16	Akaki well field	GW1
17	Jica well, Kality HD	GW2
18	Imperial Hotel Well	GW3
19	Entoto HD	GW4
20	Tsion Hotel BH	GW5
21	AAU BH	GW6

22	German Square well BH	GW7
23	Han Mariam BH	GW8
24	Akaki well filed	GW9
25	Akaki well field	GW10

Table-3: representations of location of primary water data points

3.2.2 Field procedure

Sampling ware collected at different point along the length of each stream found in the city. Appropriate plastic bottles and glove were used for sample collection and ground water from deep and shallow aquifer has also been collected. The fate and source identification of nitrate in study area was investigated based on 25 water sample which ware collected starting from January 20, 2016 to January 26, 2016.

The sample included 14 surface water samples from river, 10 ground water from deep and shallow Aquifer and one from spring. The temperature (T 0C), pH values, Eh (mv) and electrical conductivity (EC) were measured on site. Alkalinity was determined by titration within 24 h after sampling. Samples were filtered through 0.45 μm membrane of filtering paper.

Well information such as well depth location and operating interval ware recorded by GPS. Samples were collected in acidified for analysis of concentrations and values for anion, deuterium, and oxygen isotopes. Samples for nitrate isotopes were collected in 50 ml plastic bottles that were filtered through a Millipore Filtration apparatus and refrigerated before shipping to the Isotopic Ecology laboratory research institute for human and nature (Japan). For stable isotope analysis the samples were collected in 20ml plastic bottles. Cool box were used on field work during sampling and then all samples were transferred and stored in refrigerant of 4 °C prior to measurement of Nitrogen , Oxygen and Hydrogen isotopic analyses.

3.2.3. Analytical procedure

3.2.3.1. Isotope Analyses

Environmental isotopes data for the water sample in the study area collected are given in Table 5. Deuterium (2H or D) and Oxygen 18 (δ18O) were used as tracers in the context of this study. Analyses of the stable isotopes 18O and 2H determine the isotope partitioning behavior (fractionation), or the separation into heavy and light fractions that occurs from natural processes such as groundwater and surface water mixing, evaporation, precipitation events, and groundwater recharge that occurs at different elevations and temperatures. Fractionation is measured by comparing a known standard ratio with the sample ratio. For this study, samples were collected to measure the oxygen-deuterium isotopic signatures (18O/16O and 2H/H).

Isotopic analysis included δ18O and δ2H of water to identify the source of water and also to estimate the fraction of water derived from imported water having a wastewater history, and δ18O and δ2H of water ware analyzed in Addis Ababa science faculty laboratory to identify the source of waters. Results are reported in delta notation (δ) as per mil (‰) differences relative to Vienna Standard Mean Ocean Water (VSMOW).

3.2.3.2 Chemical analysis

Chemical analysis is included nitrogen Specious (ammonium, nitrate, and nitrite) and phosphorus concentrations. Nitrogen specious (NH4, NO3, NO2), and SO4 , PO4, Cl, Fluoride(F) analyses have been conducted in Addis Ababa science faculty laboratory with full facilitation of equipment and chemicals. PH, Temperature (T), electrical conductivity (EC) of the sample, Redox potential Eh (mv) was measured and HCO3 was determined by acid neutralizing titration on site. Eh (redox potential) measurement ware carried out and modified PH instrument used to measure redaction-oxidation (redox) potential of the water sample.

All the samples ware brought back to the laboratory and stored at 4 °C Temperature before laboratory analysis. Analyses of water samples for major anions and cations, nitrogen and oxygen isotopes of nitrate, dissolved excess nitrogen, and trace organic compounds, and has been used to show source of nitrate in ground water, and that weather the Denitrfication is significant process in the fate of nitrate in the surface and ground water or not.

The major element, and stable isotope analyses, the geochemical parameters and major ion composition of surface water (SW), and groundwater (GW) samples have been summarized. The correlation between dominant anion and cation has been used to determine effective processes in ground water.

Hydro-chemical tracers (δ2H, δ18O) have been used to understand water quality types, origin and variation of hydro-chemical parameters and to identify the likely sources of water and its contribution with the source of the nutrients and the pollution patterns in the region. Nutrient Analyses Filtered (0.2 mm) samples were analyzed for nitrate (NO3-), nitrite (NO2-), and ammonium (NH4 +).

Therefore chemically, nitrogen specious, other major ions and cations, Eh and (δ2H H2O and δ18O H2O) techniques were characterized to identify the source of nitrate and to address the conversation factor of nitrate once it gets in to the water.

CHAPTER FOUR
RESULT AND DESCUTION
4.1 RESOULTS

4.1.1 Chemical data

The SW samples were alkaline with a pH of 8.1 to 9.2. Water temperatures ranged from 16 to 23°C. Electrical conductivities (EC) varied from 143 to 1437µS/cm. The pH values of GW samples ranged from 7.0 to 7.6, and temperatures ranged from 16 to 24 °C. Concentrations of NO3 of local surface water and groundwater show no significant variation. Concentrations of NO3 in SW samples varied in a small range from 0.34 to 3.34 mg/L. The contents of NO3 in the GW samples were determined in the range of 0.3 to 0.47 mg/L (average 0.38mg/L). For the SW the highest concentration of NO3- was 3.34 mg/l in Abasamuel out late river. the Cl- concentration of abasamuel river was also high with the value of 680 mg/l. central part at piassa river has the second highest NO3- concentration of 2.5 mg/l and Cl- concentration of piassa river was 650 mg/l which was the second highest among the streams.

Redox conditions in the study area were estimated based on measurements of redox parameters of Eh, The Eh values of surface water ranged from -58 to -130mV. And for ground water it ranges from -50 to -80 this low values indicate that the both surface and ground water is anaerobic conditions.

Sample ID	Sampling Site	Elv. m.s.l	x	Y	EC	TDS	PH	Temp
SW1	River at Bercheko Fact.	2516	466616	1001194	403	258	7.64	21
SP1	Rasmekonen spring	2399	493524	1004846	710	454	7.58	21
SW2	River at French Embassy	2443	474665	1000080	655	419	7.66	17
SW3	River at Pissa	2443	473110	999073	713	456	7.83	20
SW4	River at Merkato	2442	471224	998656	1437	920	7.82	22
SW5	Lededadi inlet	2393	492162	1004528	239	153	8.35	18
SW6	Lededadi outlet	2385	490074	1004015	226	145	8.19	18
SW7	Kebena river .at Ourael	2342	475387	996018	212	136	6.54	22
SW8	Merkato driange atTH	2341	470006	995967	645	413	7.83	22
SW9	Kechene	2333	474303	995777	1300	832	7.47	21

	river at Bambis							
SW10	S.Akaki river at Mekanisa	2233	470634	991923	646	413	7.76	21
SW11	Akaki river at Bulbula	2183	475024	988350	620	397	8.09	23
SW12	NFS Lafto river	2125	472552	990529	882	564	7.63	20
SW13	Abasamuel lake outlet	2043	467739	971123	683	437	7.63	23
SW14	AK new brg river.	2193	480217	987665	513	437	19	20
GW1	Jica well, Kality	2195	474028	987831	393	252	7.64	16
GW2	Imperial Hotel Well	2344	477838	995028	212	136	6.54	22
GW3	Entoto HD	2828	473382	1005077	150	96	6.5	18
GW4	Tsion Hotel	2610	470507	1002173	143	92	7.69	16
GW5	AAU BH	2510	473404	999808	274	175	7.8	17
GW6	Gsqr well	2146	470282	989572	433	277	7.38	24
GW7	HanaMariam	2139	472409	986046	409	262	8.48	21
GW8	Akaki wellfield BH	2094	479028	977603	500	365	7.51	23
GW9	Akaki wellfield	2080	478031	977477	570	365	8.48	20
GW10	Akaki well fild	2075	477920	977270	433	277	7.25	21

Table 4 in-situ measured water quality parameters of samples

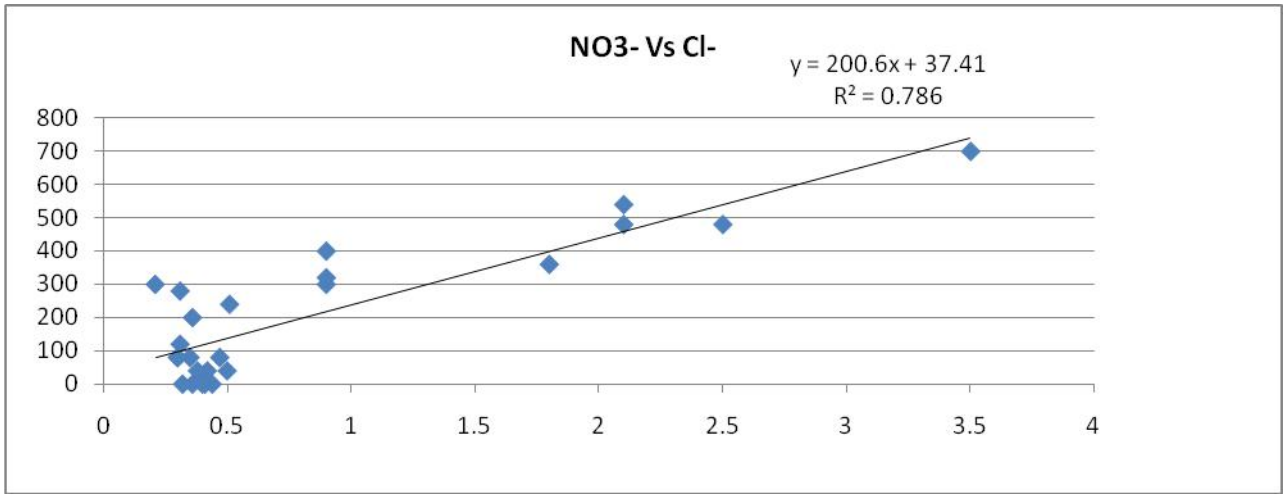
4.1.2. Relationships b/n nitrate and other variables

The relationship between major chemical parameters of surface and groundwater is presented in fig 7. Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of the other parameter.

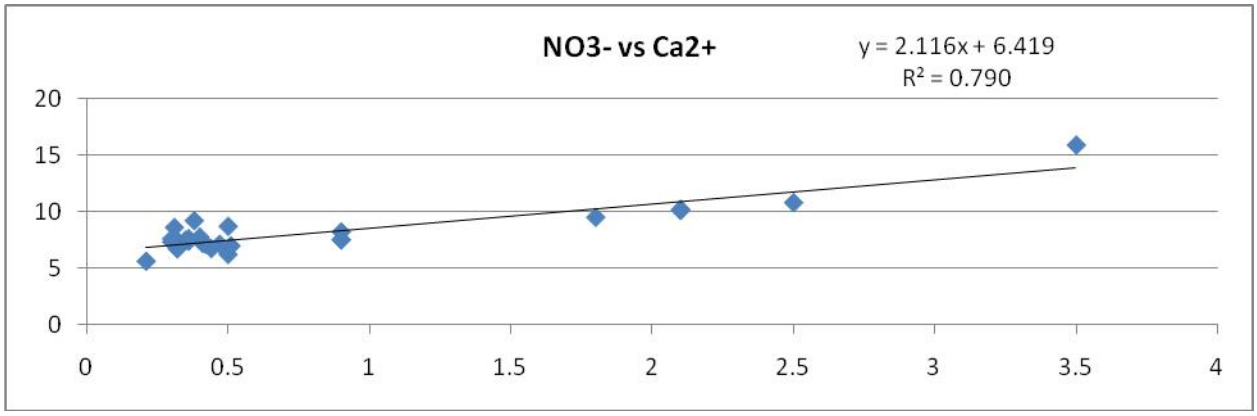
The strong to perfect correlation between the chemical parameters is an indication of common source. A significant positive correlation between Nitrates and chlorides concentration in Surface and ground water samples was found NO3 showed close affinities with Cl- contents as the r–value is Positively correlated (R2 = 0.786,) suggesting a common source for these contaminants, could be from the same sources like seepage of pit latrines, septic tanks, public and communal toilets and infiltration from industrial effluents.

In Figure 7, NO3 and cation concentrations (Ca2+) showed positive correlation (R2 = 0.790) indicating that they originated from the same sources. Species such as Ca2+ and NO3− may be derived from chemical fertilizers and manure.Aqufer contaminated with west water contain hard water which is characterized by high concentration of Ca2+and Mg2+.

The plots of anions (Cl− and SO42−) and NO3-N also show strong correlations. The strong positive correlation between NO3 and SO4 suggests a common source. Both ions would be introduced with the urea and during fertilization of the croplands. Another contributing source can be by water filtration rate and possibly contributing in nitrate leaching to underground shallow waters these two ions are not adsorbed to the negatively charged sites on soil clay minerals and would rapidly migrate downward to the groundwater.



b



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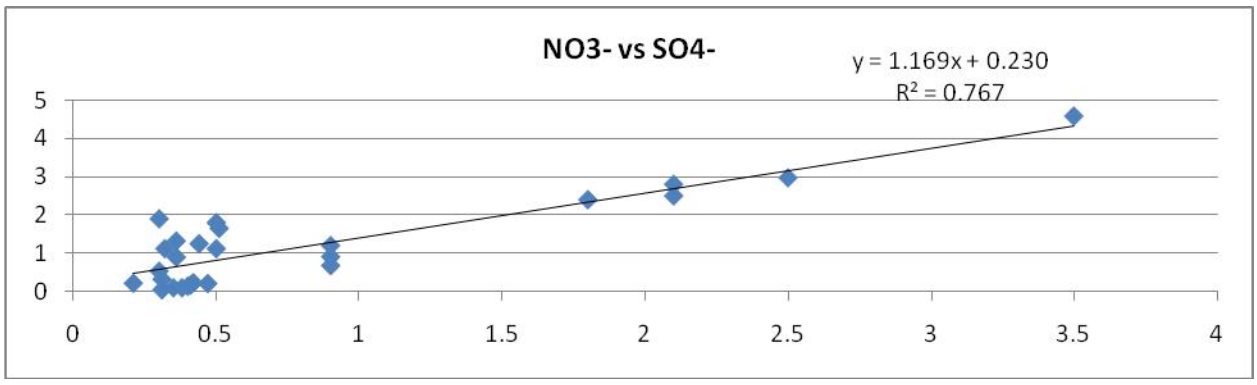


Figure 6. Correlation for nitrate against calcium (Ca2+), chloride (Cl-) and sulphate (SO4-)

4.1.3 Isotopic data

The isotope ratios of the surface water showed a range of -1.7‰ to 5.9‰ for δ2H_H2O and -3.56‰ to 0.11‰ for δ18O_H2O, with negative d-excess values (d-excess = δ2H_H2O-8δ18O_H2O) of −17.68‰ to 6.72‰. The δ2H_H2O and δ18O_H2O values of the shallow groundwater ranged from -20.4‰ to -1.7‰ and −3.79‰ to 1.6‰, respectively, with d-excess values varying range of −11.68‰ to -8.08‰.

The isotope ratios of the deep groundwater were generally lower than that of surface water and shallow groundwater ranging from −19.6‰ to −2.1‰ for δ2HH2O and from −4.09‰ to −1.63‰ for δ18OH2O. The d-excess values displayed considerable variability ranging from−20.48‰ to -2.24‰.

the result Plotted in the conventional δ18O versus δ2H diagram together with the Local Meteoric Water Line (LMWL) of Craig (1961) with the equation is δD = 8 δ18O + 10.8, the surface water values deviate significantly from and lie below the LMWL with a best-fit curve of δD =8 δ18O + 10.8. This is consistence with the general observed local evaporation line for East Africa (Craig 1961, Tenalem Ayenaew 1998, Seifu Kebede et, al 2009).

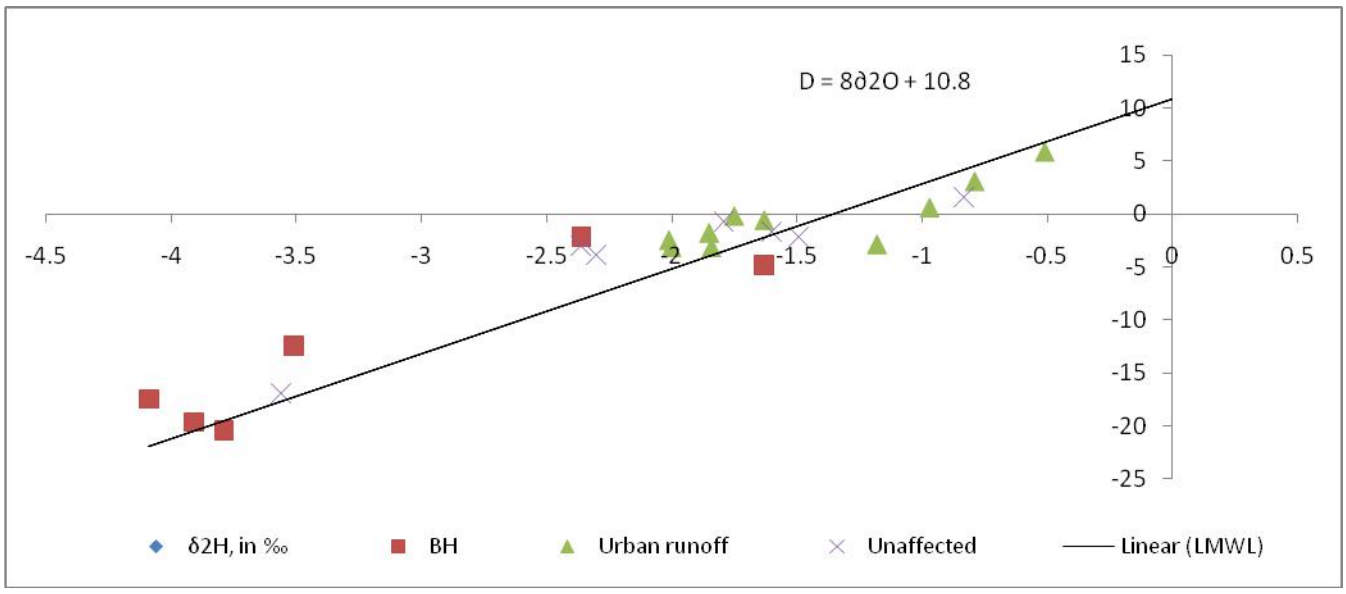
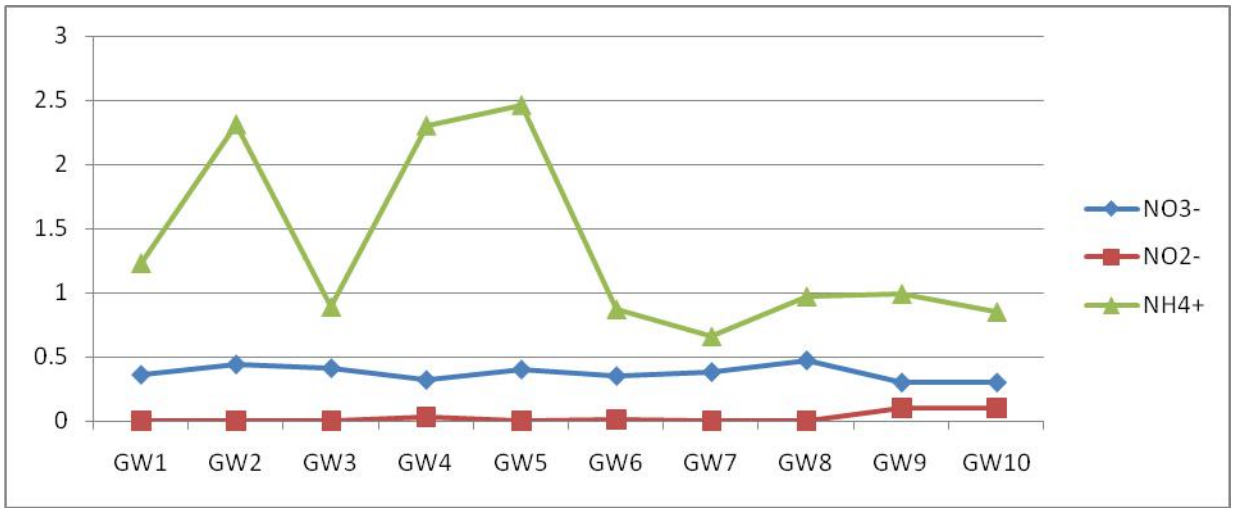


Figure 7 Plot of δ2H against δ18OH2O for surface and ground water samples from the Addis Ababa area. Local meteoric water line (LMWL, solid line).

4.1.4 Pattern of NO3 from upland to Low land

In general the overall nitrate levels observed in the investigated sites were fairly seen as low concentrated. Ammonium level is relatively higher in both surface and grown waters Therefore, Nitrogen occurs in the water as a form of ammonium ion.

A,



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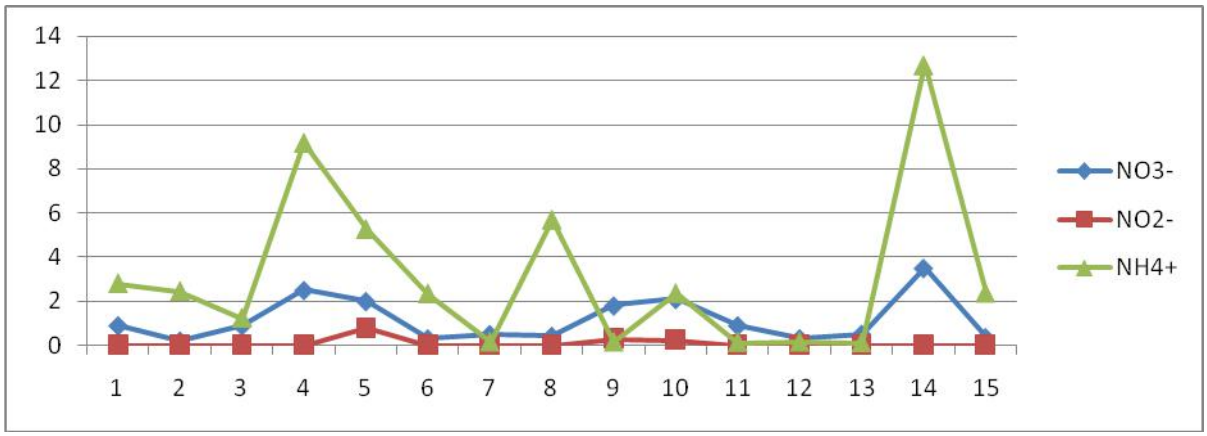

Fig 8 Nitrate spacious pattern on surface (b) and ground water (a) downstream.

4.2. Surface and Ground water sources

The use of stable water isotopes helped to clarify the sources of groundwater (recharge from rainfall or deep groundwater) and the interaction with the polluted surface waters. The water samples all plots on and close to the local meteoric water line (LMWL) Fig (7) suggesting that surface and ground water originate from local precipitation.

The most depleted samples plotted in the lower corner of the δ18O_H2O vs. δ2H_H2O (fig 7) are Deeper ground waters which is isotopicaly lighter that has experienced rain out with loss of heavier isotopes during precipitation so this deep ground water were originate from rains of different regime therefore the hypothesis of the recharge of deep ground water is from local heavy rain falls or from high altitude recharges. While the two shallow ground water samples plotted at the center of the graph shows little enrichment which is recharged from rain falls.

The urban runoff plotted at the Upper corner go large isotopic fractionation (enriched) since most of the urban tap waters are sourced directly from a dam reservoir that undergoes large isotope

fractionation (enrichment) due to evaporation. The hypothesis of the recharge is directly from Dam reservoir. urban runoff at the center of the graph (fig7) are plotted on a mixing line between the composition of shallow ground water and tap water reservoir. therefore to estimate the recharge effect can make mixing proportion it could be from 40% from tap water and 60 % from shallow ground water.

4.2.1. Nitrate on Surface and ground water

The evaluating fate of nitrate on surface and ground water are taken during dry seasons. Surface water and ground water had neutral to slightly alkaline pH. All samples had lower NO3 content than the WHO limits (50 mg/L for NO3-N) for drinking water .NO3− was generally absent in surface water whereas NH4+ and PO4 3− concentrations were generally high. Hence, the only possible source of N as ammonium and P as orthophosphate in surface water was through wastewater discharged directly to surface water. Because of poor on-site sanitation systems, it is common practice to discharge wastewater directly to surface water, which eventually may discharge into shallow ground water.

From the geochemical analysis result alkalinity of surface water is ranged from 122-760 mg/l. Eh value of SW ranges from -50 to -100 and for the GW. Pollution from households is also reflected by the elevated concentrations of major cations and anions.

There was a positive correlation between Cl− (a pollution indicator) and most of the cations and anions, (Fig. 6). Nitrogen measured as NH4+ in surface water was ranged from 3 – 5.1 mgL-1which is much higher than the standared limit of 1.5mgL-1, whereas phosphorus measured as PO43− was ranged from 0.3 to 3.6mgL-1.

This study brings some clear evidences that unwanted anthropogenic nutrients can be released in both surface waters and shallow groundwater from rapidly growing cities. In addition, these polluted waters can create a serious treat for the downstream populations, with the need to implement expensive tertiary treatment plants to remove nitrate.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

The main objective of this study was to evaluate the fate of nitrate once it get in to the water and it is carried out by using the geochemical approaches and the following conclusions can be drawn from this study:

Environmental isotopic data (18O and 2H) for groundwater and surface water samples in the study area shows distinct isotopic signatures for local groundwater and surface water. Deep ground water flow system exhibiting depleted isotopic signature indicating groundwater recharge from heavy rain falls. Shallow ground water shows recharged from rain fall. Urban runoff waters shows enriched isotopic signature which are recharged from dam reservoir water and from mixing of shallow ground waters and tap waters.

Based on in-situ measured and laboratory determined physico-chemical parameters NO3 showed significant positive correlations with chlorides, calcium, and sulphate suggesting a common source for these contaminants, such as animal wastes, fertilizer, or domestic wastes. The analysis result showed that the degree of correlation between NO3- and Cl- concentrations (R2 = 0.723) is positive. The positive correlation coefficient R2 = 0.723 (72%) is an indirect indication of similar pollution sources for both NO3- and Cl- which could be seepage from pit latrines, septic tanks , public and communal toilets and open field sanitation and also chlorination process in some wells.

The possible sources and mechanisms of NH4+ and Cl- pollution are downward infiltration and seepage of industrial effluents and municipal solid wastes (residential, commercial, industrial and institutional), municipal liquid wastes through overflowing and seepage of pit latrines, septic tanks, public and communal toilets and to some extent upstream agricultural chemicals and slaughter houses wastes and pharmaceutical wastes. Pit latrines present nearby rivers and wells of high density population may significantly increase concentration of NH4, and Cl- .

From the many findings in the study area both the surface and ground water of the Akaki River basin are severely polluted. The nitrate level in all the water wells were far below 50mg/l of the WHO level. This is likely because most of the nitrates are intercepted or retained on the upper part of soil strata or taken up by plant roots for growth while percolating with water vertically through open spaces and the porous media of different soil horizons.

There are areas surrounding the river that are very urbanized and so have many industries and other type of pollution which can be easily transferred in to the river. When the river is polluted there will be more bacteria with it. As bacteria are organism they need oxygen to survive Ammonium nitrite and nitrate serve as a nitrogen nutrient for the growth of aquatic plants eg Algae when the plant die dissolved oxygen is removed from the receiving water by microbial activities to decompose the plants . This will therefore mean that the more pollution there is, the more bacteria there will also be and so the less oxygen there will be available as it will be used by the bacteria.

Therefore Oxygenation is not favored Nitrification and Dinitrification process are occurs inside living cell and bacteria Hence, Redox condition analysis reflecting the similar redox environments

where surface water was anaerobic and ground water is also anoxic which means oxygenation is not favored and no conversion processes take place.

Therefore Low level of nitrate and increasing level of NH4 indicate that there is no conversion process down streams. Ammonium (NH4+) accumulates only under anoxic conditions in which nitrification does not occur which indicates there is release of nitrogen to the water bodies. at Abasamuel lake out late show regeneration of oxygen state therefore there will be relatively higher nitrate downstream to koka and eventually this caused NO3 level picked as one goes down to the koka reservoir.

6 RECOMENDATIONS

The result of the study shows that the level of nitrate in the study area is very low but other nitrate specious such as Ammonium (NH4+) is high which indicate that low level of nitrate in the water doesn't mean that there is no pollution source. Therefore regarding with Effective management of water resources for the provision of reliable and safe water supply further investigations is recommended. Also the following recommendation is forwarded

- The seasonal variation is not pronounced in this study Sampling from different season will give spatial and temporal variation of nitrate behaviors and its evolution.

- It requires further investigation of other highly polluted chemicals with high precision instruments must be carried out in order to study the degree of pollution and anthropogenic effect on surface and groundwater of the study area.
- at Abasamuel lake out late shows a little elevation of nitrate and positive Eh value therefore there will be relatively higher nitrate downstream to koka and eventually this caused NO3 level picked as one goes down to the koka reservoir. It also requires further investigation downstream from Abasamuel out late to Koka River.

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Apendex 1: Result of analyzed chemical parameters of water samples

Sample ID	Sampling Site	Elv. m.s.l	X	Y	NO3- mgL-1	NO2- mgL-1	NH4+ mgL-1	Eh (mv)	SO4-	PO4-	Cl-
SW1	R.at Bercheko Fact.	2516	466616	1001194	0.39	0.01	2.31	-98	0.07	0.4	640
SP1	Rasmekonen spring	2399	1004836	493112	0.39	0.01	1.23	-88	0.6	5.5	760
SW3	R. at F'rench Embassy	2443	474665	1000080	0.34	0.01	1.51	-50	0.05	0.3	480
SW4	Kechene R. at Pissa	2443	473110	999073	0.39	0.02	9.18	-58	4.5	1.4	680
SW5	R. at Merkato	2442	471224	998656	0.56	0.79	3.38	60	0.233	3.2	560
SW6	Lededadi inlet	2393	492162	1004528	1.9	0.02	0.14	-48	0.355	1.7	120
SW7	Lededadi outlet	2385	490074	1004015	2.0	0	0.15	-52	0.61	0.8	40
SW8	Kebena R.at Ourael	2342	475387	996018	0.5	0	16.2	-120	0.08	1.2	40
SW9	Merkato driange atTH	2341	470006	995967	0.34	0.03	0.14	-80	0.322	2.2	360
SW1	Kechene R.	2333	474303	995777	0.36	0.23	1.5	-93	2.95	2.2	640

0	at Bambis										
SW1 1	S.Akaki R.at Mekanisa	2233	470634	991923	0.41	0.02	0.13	-50	4.71	0	600
SW1 2	Akaki R. at Bulbula	2183	475024	988350	0.34	0.02	0.14	-102	0.14	0.4	400
SW1 3	NFS Lafto R.	2125	472552	990529	0.44	0.02	0.11	-96	0.21	0.6	240
SW1 4	Abasamuel lake outlet	2043	467739	971123	3.34	0.02	12.7	-100	4.58	2. 05	400
SW1 5	AK new brg R.	2193	480217	987665	0.37	0.01	0.6	-130	1.17	0. 08	200
GW1	Jicawell,	2195	474028	987831	0.36	0	0.13	0.3	2.05	1.9	40
GW2	Imperial Hotel	2344	477838	995028	0.44	0	0.13	0.4	0.08	1.2	40
GW3	Entoto HD	2828	473382	1005077	0.41	0	0.18	0.3	0.5	0.1	60
GW4	Tsion Hotel	2610	470507	1002173	0.32	0.03	0.2	0.3	0.09	3.4	0
GW5	AAU BH	2510	473404	999808	0.4	0	0.15	0.4	1.17	0	80
GW6	Gsqr well	2146	470282	989572	0.35	0.01	0.12	0.3	0.1	0.4	40
GW7	Han Mariam	2139	472409	986046	0.38	0	0.14	0.3	0.1	0.3	80
GW8	Akaki wellfield	2094	479028	977603	0.47	0	0.12	0.3	1.17	0.1	80
GW9	Akaki wellfield	2080	478031	977477	0.3	0.1	0.12	0.3	0.53	0.1	80
GW1 0	Akaki well fild	2068	478024	977170	0.3	0.1	0.15	-74	0.62	0.12	75

Appendix 2: values of in-situ measured water quality parameters of samples.

Sample ID	Sampling Site	Elv. m.s.l	X	y	EC	TDS	PH	Temp
SW1	River.at Bercheko Fact.	2516	466616	1001194	403	258	7.64	21
SP1	Ras mekonn spring .	2399	1004836	493112	710	454	7.58	21
SW2	river at F'rench Embassy	2443	474665	1000080	655	419	7.66	17
SW3	Kechene River. at Pissa	2443	473110	999073	713	456	7.83	19.3
SW4	River. at Merkato	2442	471224	998656	1437	920	7.82	21.9
SW5	Lededadi inlet	2393	492162	1004528	239	153	8.35	18
SW6	Lededadi outlet	2385	490074	1004015	226	145	8.19	18
SW7	Kebena River.at Ourael	2342	475387	996018	212	136	6.54	21.8
SW8	Merkato driange at TH	2341	470006	995967	645	413	7.83	22.3
SW9	Kechene River. at Bambis	2333	474303	995777	1300	832	7.47	21
SW10	S.AkakiRiver.at Mekanisa	2233	470634	991923	646	413	7.76	21
SW11	Akaki River. at Bulbula	2183	475024	988350	620	397	8.09	22.6
SW12	NFS Lafto River.	2125	472552	990529	882	564	7.63	20
SW13	Abasamuel lake	2043	467739	971123	683	437	7.63	23
SW14	AK new brg R.	2193	480217	987665	513	437	19	20
GW1	Jica well, Kality	2195	474028	987831	393	252	7.64	15.3
GW2	Imperial Hotel	2344	477838	995028	212	136	6.54	21.8

GW3	Entoto HD	2828	473382	1005077	150	96	6.5	18
GW4	Tsion Hotel BH	2610	470507	1002173	143	92	7.69	16
GW5	AAU BH	2510	473404	999808	274	175	7.8	17
GW6	Gsqr well BH	2146	470282	989572	433	277	7.38	23.9
GW7	Han Mariam	2139	472409	986046	409	262	8.48	21
GW8	Akaki wellfield	2094	479028	977603	500	365	7.51	23
GW9	Akaki wellfield	2080	478031	977477	570	365	8.48	20
GW10	Akaki well fild	2075	477920	977270	433	277	7.25	21

Apendex 3 Environmental isotope data of waters

ID	Sample ID	Elv. (m.s.l)	North	East	δ18O, in ‰	δ2H (‰)	D excess
SW1	R.Bercheko Fact.	2516	1001194	466616	-2.36	-3	-8.08
SW2	R. at French Embassy	2443	1000080	474665	-1.18	-2.9	1.36
SW3	KecheneR. at Pissa	2443	999073	473110	-1.75	-0.2	-3.2
SW4	Merkato River	2442	998656	471224	-3.56	-17	-17.68
SW5	Lededadi inlet	2393	1004528	492162	-0.83	0.24	-3.52
SW6	Lededadi outlet	2385	1004015	490074	-1.79	-0.7	-3.52
SW7	KebenaR.at Ourael	2342	996018	475387	0.11	-0.6	-3.2
SW8	Kechene R. Bambis	2333	995777	474303	-2.01	-2.5	-3.4
SW9	S.Akaki R. at Mekanisa	2233	991923	470634	-2	-3.2	-5.2
SW10	Jemo River	2228	989524	468614	-2.3	-3.9	-5.2
SW11	Akaki R. at Bulbula	2183	988350	475024	-0.97	0.6	-7.6
SW12	Nefasleke Lafto River	2125	990529	472552	-1.63	-0.6	3.04

SW13	Abasamuel lake outlet	2043	971123	467739	-0.51	5.9	-2.24
SW14	AKaki new brg River	2193	987665	480217	-0.79	1.41	6.72
GW1	Jica well	2195	987831	474028	-2.36	-2.1	-8.08
GW2	Yerer BH	2263	992237	480906	-1.6	-1.7	-8.08
GW3	Imperial Hotel Well	2344	995028	477838	0.11	-0.6	
GW4	Entoto HD	2828	1005077	473382	-3.79	-20.4	-11.68
GW5	Tsion Hotel BH	2610	1002173	470507	-4.09	-17.4	-19.2
GW6	AAU Borhole	2510	999808	473404	-3.51	-12.4	- 21.9
GW7	German Square well BH	2146	989572	470282	-3.91	-19.6	-17.28
GW8	Han Mariam BH	2139	986046	472409	-1.63	-4.8	-20.48
GW9	Akaki well field BH	2094	977603	479028	-1.60	-4.3	-2.24
GW10	Akaki wellfield BH	2080	977477	478031	-2.36	-2.1	-2.3

Appendix 4 Specification limits and standard guideline values for nitrate in drinking water

Organization	Year	Limits of specification	Con.(mg/l) as NO3-	Con.(mg/l) as N
WHO(European standard)	1970	Recommended Acceptable	50 11.3 -22.6	
WHO (International) WHO	1971 1984	Guideline	45 (44.3)	10.2 10
USEPA	1977		(44.3)	10
European communities	1980 1980	Maximum admissible Guide level	50 25	(11.3) 5.6
SABS	1984	Recommended3 Maximum allowable3	(26.6) 44.3	6 10
NFEPA	1991	Recommended	45	10
FEPA	2003	Guideline	50	11.3

Appendex-5: Drinking Water Quality Guidelines/Standard

S.N	Water Quality parameters	Guideline standards			
	Inorganic parameters(mg/l)	WHO	EU	MoWR	AAWSA
1	PH	6.5-8.5	-	-	-
2	TDS	1000	500	2175.99	1000
3	Total alkalinity as CaCO3	500	-	-	-
4	total hardnes as CaCO3	300		392	500
5	sodium(Na)	200	150	350.53	200
6	potasium(K)	11			
7	calcium(Ca)	100	-	-	-
8	magnisum(Mg)	30			
9	chloride(Cl)	250	25	532.67	250
10	sulphate(SO4)	250	250	482.69	250
11	fluoride (F-)	1.6	1.5	3.02	1.6
12	nitrate(NO3)	50	50	130.57	50
13	ammonium (NH4)	1.5	-	2.08	1.5
14	sulphide (H2S)	0.05		0.07	
15	aluminum(Al)	0.05	0.2	0.43	0.2
16	nitrite (NO2-)	3	0.1	7.52	
17	Phosphate (PO4-)	0.54	-	-	-

ID	Sample	Elvation	North	East	Eh(mv)	NO3-mgL-1	NO2-mgL-1	NH4+mgL-1	So4	CL	ca	F mg/l	PO4	HCO3
SW1	R. at Bercheko Fact.	2516	1001194	466616	-98	0.9	0.006	2.8	0.07	300	7.23	0.51	0.38	597.9
SP1	Ras mekonen spring	2399	1004836	493112	-88	0.21	0.012	2.45	0.6	300	6.2	5.35	5.5	488.1
SW3	R. at French Embassy	2443	1000080	474665	-50	0.9	0.009	1.23	0.05	320	7.65	1.21	0.29	341.7
SW4	Kechene R. at Pissa	2443	999073	473110	-58	2.5	0.013	9.18	4.5	480	6.95	8.86	1.4	500.8
SW5	Merkato River	2442	998656	471224	60	2.1	0.79	5.26	0.23	480	7.11	12.38	3.22	450
SW6	Legedadi inlet	2393	1004528	492162	-48	1.9	0.015	2.34	0.36	120	43.02	0.31	1.65	300
SW7	Legedadi outlet	2385	1004015	490074	-52	2.0	0	0.15	0.61	40	8.41	0.21	0.81	310
SW8	Kebena R. at Ourael	2342	996018	475387	-120	0.42	0	5.69	0.08	40	8.232	0.64	1.18	122
SW9	Merkato driange and TH	2341	995967	470006	-80	1.8	0.308	0.14	0.32	360	39.5	0.5	2.15	400
SW10	Kechene R. at Bambis	2333	995777	474303	-93	2.1	0.238	2.35	2.95	540	6.97	1.41	2.2	549.1
SW11	S. Akaki R. at Mekanisa	2233	991923	470634	-50	0.9	0.022	0.13	4.71	400	6.72	1.04	0.016	500
SW12	Akaki R at Bulbula	2183	988350	475024	-102	0.31	0.027	0.14	0.14	280	7.74	4.34	0.41	300

SW13	Nefasleke Lafto River	2125	990529	472552	-96	0.51	0.021	0.11	0.21	240	7.11	3.34	0.55	290
SW14	Abasamuel lake outlet	2043	971123	467739	-100	3.5	0.024	12.7	4.58	700	44.88	0.327	2. 05	300
SW15	AK new brg R.	2193	987665	480217	-130	0.36	0.005	2.36	1.17	200	42.7	0.365	0. 08	378
GW1	Jica well	2195	987831	474028	0.3	0.36	0.004	1.23	1.34	0	0	1.04	7.64	200
GW2	Yerer BH	2263	992237	480906	0.4	0.44	0.003	2.31	2.05	0	0	4.93	6.78	150
GW3	Imperial Hotel	2344	995028	477838	0.3	0.41	0	0.89	0.08	0	0	4.51	6.54	200
GW4	Entoto HD	2828	1005077	473382	0.3	0.32	0.028	2.3	0.5	0	0	5.2	7.2	180
GW5	Tsion Hotel	2610	1002173	470507	0.4	0.4	0	2.46	0.09	0	10.25	0.41	3.4	378.3
GW6	AAU BH	2510	999808	473404	0.3	0.35	0.007	0.87	1.17	80	9.97	0.21	0.016	160
GW7	Gsqr. well BH	2146	989572	470282	0.3	0.38	0.004	0.66	0.1	40	7.48	0.44	0.4	475.9
GW8	Han Mariam BH	2139	986046	472409	0.3	0.47	0.002	0.97	0.1	80	9.81	6.35	0.34	210
GW9	Akaki wellfield	2094	977603	479028	0.3	0.3	0.1	0.99	1.17	80	9.97	0.61	0.07	292.8
GW10	Akaki wellfield	2080	977477	478031	-74	0.3	0.1	0.85	0.15	80	0	12.7	0.52	290