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Geochemical Characterization of Sediment and Ground Water Contamination From Petroleum Stations in Addis Ababa City

A Thesis Submitted to the School of Earth sciences of Addis Ababa University in Partial Fulfillment of the Requirement for the Degree of Master of Science in Geochemistry

GEBRU HADUSH

JUNE 2015

ADDIS ABABA UNIVERSITY

SCHOOL OF EARTH SCIENCES

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A Thesis Submitted to the School of Earth sciences,

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ADDIS ABABA UNIVERSITY
School of Earth sciences
June 2015

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

Geochemical Characterization of Sediment and ground Water Contamination in Addis Ababa City from Petroleum Stations

(Case study of Addis Ababa City)

A thesis submitted to the School of Earth sciences, Addis Ababa University in the Partial Fulfillment of the requirement for the award Degree of Masters of Science in Geochemistry

Gebru Hadush

June 2015

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DECLARATION

I hereby declare that the thesis entitled "Geochemical characterization of sediment and ground water contamination in Addis Ababa city from petroleum stations" has been carried out by me under the supervision of Dr. Asfawossen Asrat, School of Earth Sciences, and Addis Ababa University during the year 2015 as part of Master of Science Program in geochemistry. I further declare that this work has not been submitted to any other University or institution for the award of any degree or diploma and all sources of materials used for the thesis have duly acknowledged.

Gebru Hadush

Signature_____________________________

ABSTRACT

Addis Ababa is located on the shoulder of the Western Main Ethiopian Rift Escarpment in which the city is surrounded by mountain ridges from north and northwest and gentle slope to south and southeast part. The general surface and groundwater movement direction is dominated by north-south and east-west flow. Hydrogeologically the area characterized by fracture porosity and interstitial porosity and lithostratigraphic units from bottom to top includes Alaji basalts, Entoto silicics, Addis Ababa basalts, Nazareth group, and Bofa basalts associated. The main focus of the study is geochemical characterization of groundwater contamination in Addis Ababa mainly related to organic contaminants from petroleum station. Physico-chemical parameters: such as EC, TDS and PH, measured in-situ and from secondary sources; redox sensitive compounds and major ions analysis from secondary data; laboratory analysis of COD and Organic Carbon from ground water samples taken in the field were used to characterize the chemistry and possible contamination of groundwater. These secondary groundwater quality parameters were obtained from two different sources: from Addis Ababa Water and Sewerage Authority (AAWSA) and Addis Ababa water work design and supervision. Each parameter has been determined in order to assess the contaminant distribution in the study area. The values of the parameters have been evaluated with respect to the maximum acceptable standard level of WHO (World Health Organization) for drinking and groundwater. The result of physio-chemical analysis (TDS, EC H, redos-sensitive compounds) from groundwater wells reveals that the source of the organic contaminants in the study area is difficult to identify while physical evidence from gas stations and garages suggests that organic compounds are entering surface and subsurface environment. Finally for effective remediation program this work proposes in-situ capping for sediment and air sparging for groundwater.

Key words

Addis Ababa, Physio-chemical, organic contaminant, Redox condition, Groundwater, COD

ACKNOWLEDGEMENT

I wish to express my gratitude to my advisor, Dr. Asfawossen Asrat , for his excellent efforts, useful suggestions, and encouragements, which provided valuable guidance throughout my study period and specially during the research work.

I am thankful to my family for their great support at all the time and for giving me a confidence every once in a while, without their support the research work would be impossible.

I also forward special thanks to ato Zeleke Teferi (Addis Ababa Water and Sewerage Authority) and Ato Engda Zemedagegnehu (Addis Ababa Water Works Design and Supervision) for providing all the necessary suggestions and required data.

Specific gratitude is given to all laboratory technicians at Addis Ababa Water and Sewerage Authority, for his valuable assistance in measuring laboratory and field data.

I would like to thank to Total Ethiopia, Yetebaberut National Petroleum, National Oil Ethiopia, Libya Oil Ethiopia and Kobil Ethiopia all provided & helped me with the necessary information and data.

Finally, I wish to thank all those who have helped me by one way or another during this research work.

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No.	Particuars
AAWSA	Addis Ababa Water and Sewerage Authority
a.m.s.l	above mean see level
COD	Chemical Oxygen Demand
DNAPLs	Dens Non-aqueous Phase Liquids
EC	Electrical Conductivity
Eh	Redox potential
LNAPLs	Light Non-aqueous Phase Liquids
NAPLs	Non-aqueous Phase Liquids
OC	Organic Carbon
PH	The negative logarithm of hydrogen ion
TDS	Total Dissolved Solids
TPH	Total Petroleum Hydrocarbons
UTM	Universal Transverse Mercator
VOC	Volatile Organic Compounds
WWDSE	Water Works Design and supervision Enterprise

List of Appendix

1. Introduction

1.1. Background

Groundwater has long been regarded as the best water resource for all types of use. Owing to the natural interaction among the earth's subsystems, pure water does not exist by default and its quality can be affected by some dissolved and or suspended substances of natural or anthropogenic origin, and consequently gets polluted. Its quality involves a long list of physical, chemical and microbial characteristics of both surface and subsurface water sources.

Water naturally contains a variety of dissolved substances like those resulting from the dissolution of minerals and some potentially quite harmful substances and manufactured contaminants that have reached the water system in varies ways posing a significant treat to water quality and community health Behailu (2007). Moreover, the chemistry of water changes as agriculture becomes more intensive, the increase over time in population or extent of cities and town is more prominent and industry grow. Pollutants enter the water system when we dispose of wastes improperly allowing them to seep directly to the water table or into an aquifer.

Naturally occurring contaminants are present in the rocks and sediments. As ground water flows through sediments, organic and inorganic compounds are dissolved and may later be found in high concentrations in the water. The physical properties of an aquifer, such as thickness, rock or sediment type and location, play a large part in determining whether contaminants from the land surface will reach the ground water.

In addition contaminants from different human activities also can change the overall chemistry of groundwater. The chemical and physical properties, source type of contaminant and resident time determines their concentration in groundwater. Contaminants from organic substance have complex nature, in which they undergoes series chemical reactions and can exist in different phases, when they are released to the environment.

The risk of contamination is greater for unconfined aquifers than for confined aquifers because they usually are nearer to the land surface and lack an overlying layer to impede the movement of contaminants. Because ground water moves slowly in the subsurface and many contaminants are sorbed to the sediments, restoration of a contaminated aquifer is difficult and may require years, decades, centuries or even millennia and it is unlikely to clean polluted aquifers (Tamiru Alemayehu 2005).

1.2. Problem identification and justification of the research

As it has been explained in most of the reviewed previous works a lot of studies have been undergone in the area by different bodies. The studies were carried out with respect to groundwater characteristics, flow modeling, quality assessment, vulnerability mapping, occurrence, recharge, hydrochemical and isotopic characteristics, contaminant transport modeling (inorganic), characterization of solid wastes, hydrochemical evolution of the area on general and regional basis. Nevertheless, there are some data gaps with respect to detail hydrogeologic description of the area especially data related to aquifer characteristics, groundwater, rock and contaminant interaction, litho-stratographic, etc. Beside that there are different thoughts about the groundwater recharge and aquifer type. But groundwater contamination characterization related to organic contaminants was not yet done beside they indicate it is one of the contaminant source of the study area. Therefore in this study, hydrochemistry and physio-chemical approach will be integrated and used to characterize organic contaminant on groundwater.

Groundwater pollution with organic contaminant is a global problem and commonly associated with diffuse and point sources .The possible sources for the organic contaminant could likely be petrol station, garages and chemical industries in Addis Ababa. The organic contaminants released to the environment will contaminate surface and groundwater which affect the water quality as well as human health.

In Addis Ababa, it was reported in some studies that urban and industrial centers play a role in polluting surface and groundwater. Significant amount of organic and inorganic pollutants from the west-central part of the city including the big market center "Merkato" and a number of factories including a winery, a brewery, a soft drink factory, a liquor factory, several tanneries, a slaughter house, from petrol station and others are introduced and polluted surface and ground water. So the need to study organic contaminant from petroleum stations as the major pollutant in the study area is due to the following reasons:

The petrol stations in Addis Ababa are characterized by various activities such as distribution of fuels, car washing and greasing services. These activities, coupled with the random and inappropriate distribution of the petrol station nearer to streams, possible recharge zones, and water wells have a great chance to pollute sediment and groundwater. Sediment and groundwater degradation system are believed to have to great health risks to the local communities and also the environment as a whole.

The water supply distribution of Addis Ababa has enormous leakage problem. This may lead to mixing of contaminants from surrounding areas such as from polluted reservoirs and wells, leaking underground storage tanks and liquid waste transport system. The study of organic contaminant will provide important information on this and other urban source of pollution of surface and subsurface water.

1.3. Research Objectives

1.3.1. General Objectives

The general objective of the this study is to identify possible sediment and ground water contamination from petrol stations and their geochemical characterization as they interact with water and soil.

1.3.2. Specific Objectives:

Produce a map of physio-chemical parameters and possible contamination zones to groundwater in Addis Ababa.

- Characterize the chemical composition and evolution of ground water and sediment from existing sources and available geochemical data including pH, EC, TDS and all other available geochemical data
- Understand the physical and chemical processes that affect the transport of contaminants and the transport mechanisms and ground-water flow system at a site.
- To propose remediation mechanism or method depending on the site condition

1.4. Research Question

To address the above mentioned objectives, the research questions for this study are:

- Is there a leakage of organic contaminants to subsurface environment from petrol stations?
- How can we determine organic contaminants in groundwater?
- Does geology and hydrogeology of the area control the occurrence and transport of organic contaminants?
- How organic contaminant changes the overall quality of groundwater?

1.5. General Methodology

1.5.1 Compilation of Existing Data

To fulfill the above objectives of the research work the following approaches will be implemented:

Literatures (both published and unpublished) were reviewed and compiled to understand some of Hydrogeological (groundwater flow system, hydraulic conductivity, and aquifer type) and lithological (soil and rock type, and structures) condition of the study area. In addition how organic contaminants behaves and migrate on surface and subsurface condition, and how the physical and chemical aspect of groundwater and sediment changes as contaminant introduces to the system and the geological environment that controls fate and transportation of contaminants and their magnitude on affecting the environment.

The secondary data used in this research work includes physio-chemical data of existing groundwater wells collected from Addis Ababa Water and Sewerage Authority (AAWSA) and Addis Ababa Water Works Design and Supervision (AAWWDS), and information regarding petrol stations found in Addis Ababa is collected from Total Ethiopia, Yetebaberut National Petroleum Share Company (YTP), Libya oil Ethiopia, National Oil Ethiopia (NOC) and Kobil Ethiopia companies.

The compiled physio-chemical data were reviewed and filtered for data quality and data gaps. This filtering was necessary because compilation results in a large and mixed physio-chemical data set, with many locations having incomplete element analyses or, in some cases, having multiple sample events. Data were compiled from original reports and laboratory sheets as well as previous compilations by other researchers. Data originating directly from technical reports and records of the analyzing laboratory met the highest data quality standards. Where either the spatial or chemical accuracy of the data could not be verified, the data were either omitted from the compilation or marked as being inadequate for use in final interpretations.

1.5.2 Data collection

1.5.2.1. Petroleum stations

First of all location of (72) petrol stations were collected using GPS (Geographic Positioning System).In addition to this elevation and information regarding actual site condition such us type of fuel (regular, diesel, and kerosene), name of station (NOC, Total, Yetebaberut, oilibya and kobill, etc), activities carried out in each station (car wash, maintenance, cafe, shopping (librucants, gas cylinders, abyssinia cards), tire service, garages etc.) and description of the area such as distance from stream and liquid waste management all supported by photos were collected on site. Then additional information including size, number and depth of tanks, coating, thickness and materials tanker made of, and date of establishment were collected from their representative supervision offices. Also their spatial distributions were displayed on a map having distribution of groundwater wells and groundwater flow information.

1.5.2.2. In-situ measurements of EC, TDS and PH

In-situ measurement of this parameter was taken from the area for 25 wells and one spring. Selection of wells is based on: 1) distance and it position from petrol station 2) their distribution regarding to different characteristic of the area such as groundwater, geology and elevation. Based on this most of the wells are near to petrol stations on the downstream position. And few wells in the up steam position to petrol station.

Then feild measurement of EC, TDS, PH and temperature was taken from each well. Measurement was done using EC/TDS and PH meter. Instruments were calibrated first using known solution: pH meters require two pH calibration solutions of 7.0 and 4.0 and EC with --- solution. All parameters were measured at a time after some water was removed (water on the submersed tube to avoid contamination) and electrodes were cleand before each measurements.

1.5.2.3 Laboratory analysis

Samples from 8 wells were collected for laboratory analysis of organic carbon and COD (chemical oxygen demand). A minimum of one litter of water was taken from each sample station and immediately they were taken to laboratory. Analysis of these water samples was done in WWDSE.

1.5.3. Data Interpretation

The nature and distribution of chemical constituents are illustrated and interpreted through the use of Piper plots, concentration contour maps and correlation statistics by using different software's such as GIS, AquaChem 3.70, Microsoft excel and others. The distribution of most of the physio-chemical parameters is interpreted in the context of the geologic formations, geologic structures and hydrologic features that form the framework of the surface and groundwater systems as well as the distribution of gas stations of the study area.

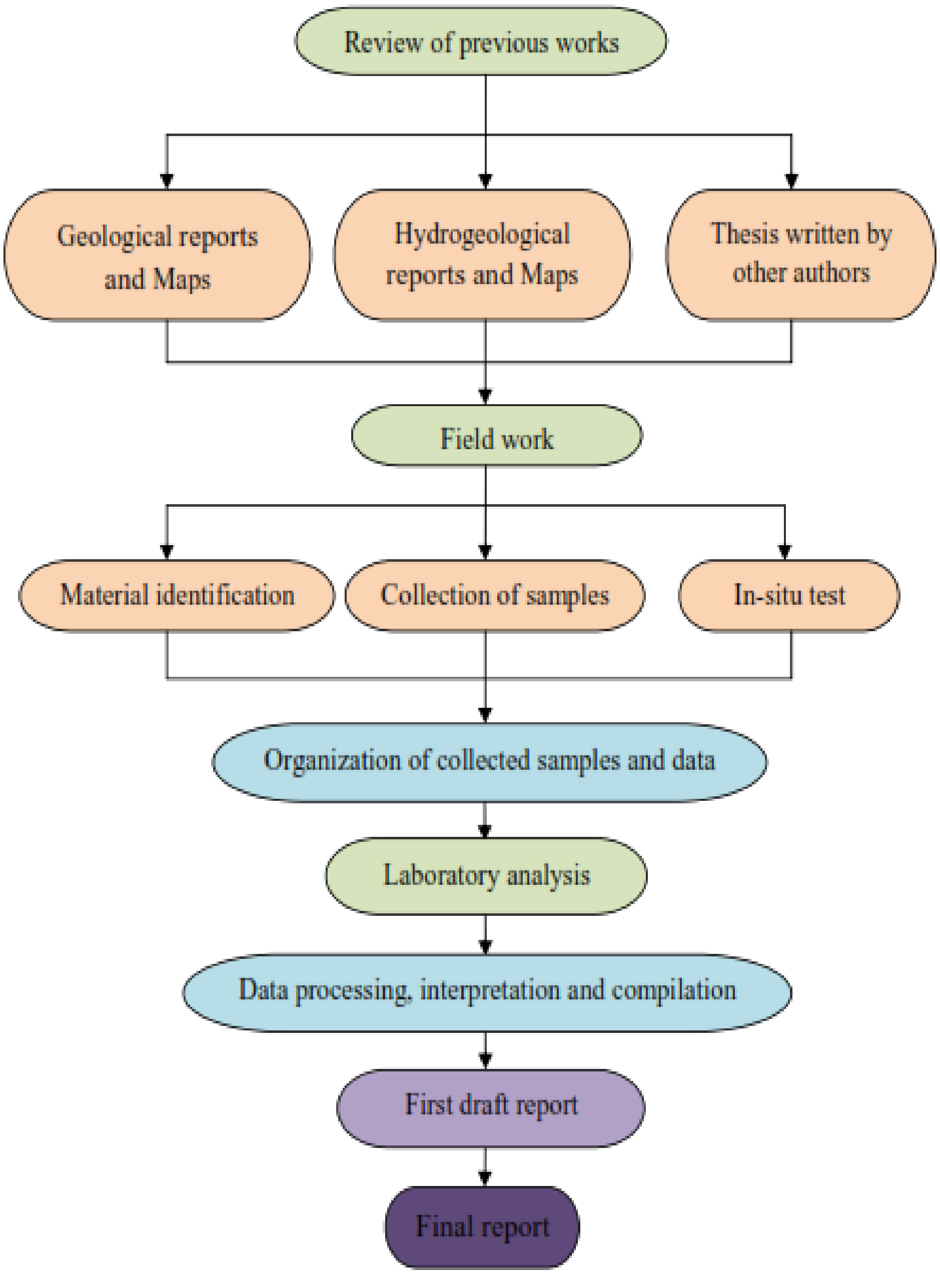

Fig:1.1 methodology flow chart

1.6. APPLICATION OF THE RESULT

Groundwater contamination in the city of Addis Ababa tends to rise with increasing human population and low level of economic development. Consequently contamination of surface and groundwater is one of the most serious problems affecting the health of the population.

After compiling and examining all the available data what we expect from the final result is:

- The presence or absence of leakage of organic contaminants from underground storage tanks, the geological environment controlling the transportation and chemistry of the contaminants and their impact on geological environment.
- The results of this study will help the relevant authorities to improve laws, regulations and norms on groundwater quality monitoring and assessment, and also on establishing law to restrict areas for petrol stations and regular inspection of the storage tanks.
- In addition, results might identify priority areas for further detailed studies in order to provide remediation mechanisms and to ensure groundwater quality.

1.7. LIMITATIONS

All efforts were made to carry out the present study in a very systematic and organized way, well supported by the actual field data, laboratory tests and the secondary data obtained from various sources. However, these efforts were made under time, resources and financial constraints and further studies might be necessary on some aspects of the research findings before implementing the results of the present study.

These are some of the limitations encounter during the accomplishment of the research work in which they might add basic information's and make the research easy and more reliable. Some of these are:

- Determination of redox conditions in contaminant plumes is still no simple task and no universally accepted procedures exist which is an important in actual contaminant plumes mapping, risk evaluation and remediation. Thus there is no solid background information regarding the different thermodynamic reactions on the surface and subsurface environment of Addis Ababa. For example what are the redox environments, how and what factors control the interaction of minerals with groundwater with contaminants (mineral dissolution and precipitation), and attenuation processes, based on the actual geology and hydrogeology of the study area.
- This research work focuses on characterizing of organic contaminants in groundwater indirectly from physio-chemical parameters because the Total Organic Carbon of the area in not determined, which is very important evidence to deal with contaminant distribution, source, plume identification etc.
- The information gap regarding some of the gas station in the area thus establishment date, tanks burial depth, monitoring activities and other previous history is unknown.

1.8 SCHEME OF PRESENTATION

The present research work is compiled and presented in following order;

Chapter-1 presents the research work stating the problem, objectives to attain, questions to deal with, methodology followed, application of result, limitation and scheme of presentation.

Chapter-2 explains about general background of the study area and described with regard to its location, physiography, general geological setup, soil, structure and hydrogeology of the present study area etc...

Chapter-3 is devoted to literature review, an explanation on Previous Studies, Organic Contaminant of Groundwater, Source and occurrence, and Fate and transport of organic of organic contaminants, Redox environment in contaminant plume and Types of groundwater organic contamination.

Chapter-4 presents the results discussion and interpretations as outlined in 7-main sections: surface water and sediment contamination, Physicochemical Analysis, Graphical Presentation and Interpretation of Laboratory Measured Parameters, Major Ions, Relationships b/n different parameters , Distribution and Extent of organic contaminants , Possible sources of contaminants & descriptions of sampling sites

Chapter-5 presents the general conclusion and the recommendation.

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2. LITERATURE REVIEW

2.1. Previous Studies

In the past several geological, hydrogeological, pollution studies and other related works have been performed for different objectives in the Addis Ababa. The main objective of contamination studies were to ensure and protect water quality for the city of Addis Ababa and surrounding towns in the catchment.

Some works have been conducted in Addis Ababa by different researchers in the last few years including studies on groundwater vulnerability mapping (UNESCO, 2003). The main sources of pollutants that depreciate the quality of water in the project area are wastes generated from industries, domestic activities, garages, health centers and petrol stations. The pollutants identified in surface and ground water bodies include organic wastes, nutrients, inorganic constituents and microorganisms. The preliminary intrinsic vulnerability mapping for the water supply aquifers revealed that major part of the city lies on medium risk area while the southern aquifer is highly vulnerable to pollution. Low vulnerable areas are aerially quite small. Thick clay deposits around Lake Aba Samuel fall in medium vulnerability category. The southern industrial area is situated in high vulnerability zone.

According to Biruk, (2010) Addis Ababa, the capital and by far the biggest urban center in Ethiopia, the open space dumping is major problem to the environment. The groundwater circulation and the dispersion of pollutants depends on the hydrogeological characteristics of the material more specifically hydraulic properties such as porosity, permeability, transmissivity etc. The origin, flow and chemical constituent of groundwater is controlled by the type of lithology, distribution, thickness and structure of hydrogeological units through which it moves.

This is also stated by Tenalem et al. (2008) that existence of different water types with indications of groundwater pollution in few places. Conventional hydrochemical analysis indicated a very dilute Ca- HCO3, Ca-Na-HCO3 type water in the north (Intoto range) draining the Intoto silicics; Ca-Mg-HCO3, Mg- Ca-HCO3 type water draining the Addis Ababa basalt in the central sector and the Bischoftu basalt aquifers in the south and Na-HCO3 type water of the 'Filwuha' thermal system, which have rock dominated hydrochemistry. While a Ca-NO3 and Ca-Cl type water circulating in the central sector of the catchment is a result of anthropogenic influences, demonstrating pollution. The comprehensive hydrochemical survey signify that most of shallow wells, springs and rivers are polluted by heavy metals and nitrate.

In addition to this Molla et al. (2007) states despite the complexity in the lithology of the volcanic rocks, the systematic increment in EC and all major ions from Intoto in the north to the Akaki well-field in the south demonstrates the existence of a hydraulic continuity between the different aquifers and hydrochemical evolution from north to south following the flow direction. In spite of the fact that recharge takes place through the entire surface area, major recharge takes place within the Intoto sector of the catchment, serving as a so-called mountain block recharge. Moreover, hydrochemical and environmental isotope data indicated additional recharge sources from wastewater, leakage from mains and reservoirs.

The stable and radioactive isotope measurements by Molla et al. (2005) further revealed that groundwater in the Akaki catchment is compartmentalized into zones and it appears that a complete mixing following the flow paths is lacking and corresponding with lithologic complexity. The unconfined aquifer in the central sector of the catchment contains a relatively high ^{3}H value. These young waters with active recharge are highly vulnerable to anthropogenic pollution and, thus, require protection. An uncommon highly depleted stable isotope and pre-bomb groundwater observed in a nearly east–west stretch in the central sector of the catchment is coincident with the Filwoha Fault zone. Here, deep circulating meteoric water has either lost its isotopic content through exchange reactions with CO2 originating from deeper sources or has recharged with precipitation from a different rainfall regime with a depleted isotopic content.

Groundwater Movement in Addis Ababa is generally from north to south Tenalem et al. (2008). The water level contour is the subdued replica of the topographic contours. Flow converges from all sides towards the Akaki well field and its surrounding plains. The large hydraulic gradient and the presence of highly permeable rocks resulted in the emergence of springs and seepage zones at different elevations, mainly in the foothills of Intoto ridge and along the major regional faults. The high elevation difference between the northern mountainous and the flat southern plain favor occurrence of local and intermediate flow systems. Large flow from the rivers into aquifers is dominant along the course of the Big and Small Akaki rivers. The major recharge from the surrounding mountains contributes to the aquifers in the southern and central part of at an altitude below 2500 m.a.s.l. The north-south cross-sectional model simulation indicates that the southern springs have direct connections with the high recharge in the northern wellhead protection areas. Despite previous assertions from hydrochemical and isotopic evidences indicating the presence of local subsurface groundwater barrier between the Akaki well field and northern Intoto ridge, all the aerial and cross-sectional model simulation revealed the continuity of flow in the north-south direction. The location of the major well field downstream of the polluted urban centre may lead to future contamination if excessive pumping continues.

Previous water quality studies in Addis Ababa indicate that petrol stations are among the sources of sediment and groundwater contaminants. According Tamiru et al (2003), observation made during site visit and analytical results, industrial establishment, agricultural activities, municipal wastes, petrol stations, garages and health centers have been considered as major category of sources of pollutants in the Addis Ababa city. The random distribution of petrol stations in the city is the main cause of ground water contamination by organic contaminant. Petroleum stations nearer to streams, possible recharge zones, and water wells have a great chance to pollute sediment and groundwater in addition to the absence of regular inspection of the storage tank.

As stated by Tamiru et al (2003), the weathering process creates favorable conditions for infiltration of surface water. Consequently there could be direct contact between the shallow subsurface water and the storage tank. This usually results in the formation of reddish brown stain (rust) on the outer surface of the container and pipeline. The effect become deep, widespread and causes leakage of oil from the container with time. The problem becomes severe in the rainy season when there is high amount of water infiltration and the water table rises high. The oil that leaks from the underground storage moves down ward through the permeable material until it reaches the nearby subsurface water. On the other hand, if the leakage is not continuous it produces local wetting zone. Leakage also occurs when storage tanks are subjected to structural failures and accident occurs upon fuel tanker trucks. The other way of oil loss is through drip during re-filling service. For most people, this seems too small in amount and not to have an impact on the environment.

Freeze and Cherry (1979) mentioned also the leakage and spill of oil from different sources are increasing threats to ground water quality. Moreover, contamination of groundwater by petroleum products differs from other major sources of contaminants. In the study area, although there is no written document that justifies the leakage of oil from the underground storage tanker, it is reasonable to infer from other sources. The other way that may indicate seepage from underground reservoir can be inferred from the losses, which the owners face as the storage, tankers become old. Most services provided in petrol station is washing and greasing services for different size vehicles. They clean the car using high-jet pressure water that may contain washing solvents. In washing, they remove not only the dirt due to natural phenomena but also the chemicals (lubricants), which were used in previous greasing services. The liquid wastes from the station and surface runoff from contaminated ground are directly discharged to the nearby drainage system. The drainage systems in the city are designed to use the advantage of gravity and connected to nearby streams crossing the c---ity. Therefore, the petrol stations without any doubt are one of the significant polluting centers in the city.

Addis Ababa Bureau of Trade, Industry and Tourism (1999) identifies that most of the petrol stations in the city are engaged in retail distribution of fuels, car washing and greasing services. The owners built underground steel storage tanker beneath the station at a shallow depth. Usually, the depths vary from 10-15m below the surface of the ground. At this depth, fresh bedrocks are rarely found. Instead, the subsurface in most parts of the city is dominantly constituted by different types of soil and /or weathering products of the underlying rock units (UNESCO, 1972).

Water, Irrigation and Energy Minister (WIEM consultative meeting of 2013) of Ethiopia reported that out of the 630 petrol stations in the country and inspected by the Ministry, only 25 per cent conform to sector standard. Adulteration is the common problem globally and so is in the country which does not occur in petrol stations alone rather, starting from the routes until it is delivered to stations. Petrol adulteration causes many problems. For example Kerosene mostly mixed illegally with petrol and supplied to the market. As a result, it damages fuel-system and engines affecting vehicles durability.

2.2. Organic Contaminant in Groundwater

2.2.1. Source and occurrence

The interaction between basic components of the environment (soil, rock and groundwater) is the main process that controls material redistribution and interaction of both reacting units and the system as a whole (František et al, 2003). Such complex system of interacting factors is very often complicated by anthropogenic activities (contaminants). As a consequence of various spills, organic and inorganic compounds contaminate soils and groundwater or surface water and become involved in fluid migration. Factors determining migration rate and the subsequent fate of both organic and inorganic contaminants in natural environment are mainly interactions between water and the soil with other geological environments. A complete understanding of the processes of interaction between water environment and sediments requires not only the combination of theoretical studies, computational modeling and laboratory experiments, but also necessary to compare with contaminant behavior in natural systems. Depending on its physical and chemical properties, a contaminant that has been released into the environment may move within an aquifer in the same manner that ground water moves.

According to Domenico and Schwartz (1990) three important attributes distinguish source of groundwater contamination: (1) Their degree of localization which describes by point and nonpoint sources: point source is characterized by the presence of an identifiable, small scale source, such as leaking storage tanks and: nonpoint source refers to large-scale, relatively diffuse contamination originating from many smaller sources, whose locations are poorly defined , (2) Their loading history :describes how the concentration of the contaminant or its rate production varies as a function of time at the source which can be continuous source loading when there is long term leakage from storage tanks at constant concentration, pulse loading refers to short-term loading at fixed concentration or variable source loading refers to variation in concentration with time and (3) The kind of contaminant emanating from them and Domenico and Schwartz (1990) grouped contaminants into six based on reaction type and mode of occurrence:(1) radioactive contaminants (2) trace metals (3) nutrients (4) other inorganic species(5) organic contaminnts (6) biological contaminants.

Battelle (2007) explains that Crude petroleum is an extremely complex compounds which contains thousands of organic, and a smaller number of inorganic, compounds. A particular crude oil may contain organic compounds ranging in molecular weight from methane (molecular weight 16), a gas at room temperature and pressure, to complex polymeric structures, such as asphaltenes with molecular weights up to at least 100,000. H ydrocarbons, organic chemicals composed solely of carbon and hydrogen, are by far the most abundant chemicals in crude and refined oils.

The hydrocarbons in petroleum are aliphatic (saturated), aromatic (unsaturated), or a combination of both. Some refined oils, particularly light fuels, such as gasoline and kerosene, may contain olefins generated during the refining process. Aromatic hydrocarbons in petroleum are composed of one or more benzene rings, a six-carbon ring containing nine equally shared carbon-carbon covalent bonds. Benzene and alkyl benzenes with one or two methyl or ethyl groups are the most abundant aromatic hydrocarbons in most crude and refined oils.

Refined oil products include gasoline and middle distillate fuels, such as diesel fuel, jet fuel, kerosene, and home heating oil. The petroleum fraction remaining after removal of light and middle distillate fractions is called residual oil, which is used to fuel ships and power plants or to produce road paving asphalt. Lubricating oils and petroleum tars also are made from residual oil.

Following release to the environment, refined and residual petroleum products may accumulate in soils and sediments where they undergo several dispersal and weathering processes include dispersion, evaporation, dissolution, and biodegradation that affect the composition and toxicity of the hydrocarbon mixtures (U.S.EPA. (1995**)**). According the U.S. Environmental Protection Agency (1995) one gallon of gasoline is enough to render one million gallons of groundwater unusable drinking water standards. When released in large volumes to aquatic environments and sediment, refined and residual petroleum products tend to retain their identity as a separate oil phase (*i.e.*, nonaqueous-phase liquid) in which their rate and extent of migration into and through soil, sediment, and groundwater depends on the viscosity, density, and interfacial tension of the oil, and the permeability and porosity of the medium (Thomas et al., 1992).

Domenico, and Schwartz,(1990) also states that contamination of ground water by organic compounds is a logical consequence of the large quantities of unrefined petroleum products percolating downward through the unsaturated zone towards the water table by gravity-driven flow. Type of source, capillary force and hydraulic conductivity controls the flow of non-aqueous phase liquids. In the case of non-continous source the volume of free product decreases because some of the liquids is trapped in each pore at residual saturation. Non-aqueous phase liquids (NAPLs) also tend to spread horizontally as it moves downward because of the capillary force. In addition, even a relatively thin, low permeability unit will inhabit downward percolation and the free product to move laterally. Domenico, and Schwartz, (1990) explains the conceptual models for the occurrence of light non-aqueous liquid phases (LNAPLs) and dense non-aqueous phase liquid (DNAPLs):

Occurrence of LNAPLs**:** as LNAPL flowed downward toward the water table, it would encounter the capillary fringe and because of increasing water saturation the relative permeability to the LNAPLs declines, and buoyancy forces become important. Thus less dense fluids will float at the water table. The free product would accumulate along the top of the capillary fringe until some critical thickness achieves and then NAPLs would flow down-gradient just above the water table. Most recent studies have shown this conceptual model to be erroneous instead of occurring as discrete layer at the top of the capillary fringe, NAPL will be distributed throughout and even above the capillary fringe. Water saturation within the capillary fringe usually remain high, and NAPL saturations re relatively low. This pattern of saturation means that the actual volume of NAPL in the capillary fringe is relatively small.

Occurrence of DNAPLs**:** for simple geological setting, DNAPLs have the potential to move downward to the base of the aquifer. Downward- moving DNAPLs displace water because they have specific gravity much greater than that of water. DNSPLs accumulate on low-permeable unit will move down-hill following the topography of the boundary. This flow in many cases will be in a direction that is different from that of groundwater. Spreading continues until the spill is at residual saturation. Within both the saturated and the unsaturated flow systems, these zones of residual saturation are source of dissolved contaminants as long as DNAPL remains.

Total Petroleum Hydrocarbons (TPH) and chlorinated hydrocarbons (VOC-Cl) may occur in four different forms: dissolved in water, sorbed on solid particles, comprising the soil gas and, forming an individual liquid phase, known as NAPL (non-aqueous phase liquid)(František et al *(*2003)).The recent large scale introduction of an oxygenated methyl tertiary butyl ether (MTBE) in to gasoline fuel which is miscible in water and extremely mobile made groundwater contamination from petroleum products become urgent phenomena in the environmental and hygrogeological society (Saracino and Phipps, 2002).

Howard, (1991) as stated by EPA's Office of Underground Storage Tanks (2012) the foremost difference between petroleum hydrocarbon (PHC) and chlorinated solvent vapors in the subsurface is that PHCs biodegrade readily under aerobic (oxygenated) environmental conditions, whereas chlorinated solvents typically biodegrade much more slowly and under anaerobic conditions. Because PHC biodegradation is relatively rapid when oxygen is present, aerobic biodegradation can typically limit the concentration and subsurface migration of petroleum vapors in unsaturated soils. In addition, biodegradation of chlorinated solvents can produce toxic degradation products, such as dichloroethylene and vinyl chloride, while petroleum degradation usually produces carbon dioxide, water, and sometimes methane or other simple hydrocarbons. A second primary difference is density: PHC liquids (e.g., gasoline, diesel fuel) are less dense than water and when released from a leaking underground storage tanks(UST), can float on the groundwater surface (water table), whereas chlorinated solvents (e.g., Trichloroethylene (TCE) are heavier than water and sink through the groundwater column to the bottom of the aquifer. The differences in biodegradability and density lead to very different subsurface behavior that often reduces the potential for human exposure.

Groundwater contamination may be localized or spread over a large area, depending on the nature and source of the contaminant and on the nature of the groundwater system. The cumulative impact of contamination of a regional aquifer from non-point sources such as those created by intensive use of fertilizers, herbicides, pesticides, and point sources such as petroleum storage tanks, numerous domestic septic tanks or small accidental spills from both agricultural and industrial source threaten the quality of regional aquifers.

2.2.2. Fate and transport of organic contaminants

Contaminant transport & fate refers to the physical, chemical, and biological processes that impact the movement of the contaminants from one point to another and how these contaminants may be altered while they are transported. According to U.S.EPA, (2012) the fate-and-transport of liquid petroleum products in the subsurface is determined primarily by the properties of the liquid and the characteristics of the geologic media into which the product has been released. Important liquid properties include density, viscosity and interfacial tension. Soil properties that influence the movement of petroleum hydrocarbons include porosity and permeability. Other additional properties, which are functions of both the liquid and the media, include capillary pressure, relative permeability, wettability, saturation, and residual saturation. Site-specific physical conditions (e.g., depth to groundwater, volume of the release, direction of groundwater flow) also contribute to the migration and dispersion of released petroleum products.

Volatile hydrocarbons, such as those in the lowest carbon fractions of aliphatic and aromatic hydrocarbons evaporate rapidly from the surface of sediments and the overlying water column and slower from deep sediment layers, particularly if the sediments are fine-grained (silts and clays) with low permeability. Hydrocarbons are lost from buried sediment layers mainly by dissolution or dispersion in water percolating through the oiled sediment layer, or by microbial degradation **(**Battelle. 2007).

Generally speaking, the aqueous solubility of petroleum hydrocarbons is inversely proportional to molecular weight, and aliphatic hydrocarbons are less soluble than aromatic hydrocarbons of similar molecular weight. Thus, low molecular weight aromatic hydrocarbons and, to a lesser extent, lower molecular weight aliphatic hydrocarbons tend to dissolve slowly from the petroleum-contaminated sediment or NAPL into the pore-water and are carried away from the oil deposit with pore-water or surface water flow. Low molecular weight normal alkanes are degraded most rapidly, followed by branched alkanes and higher molecular weight normal alkanes.

The effects of the combined weathering processes generally reduce the concentration of low molecular weight slightly soluble aliphatic and aromatic hydrocarbons in petroleum-contaminated sediment. Thus, the composition of a TPH fraction that has weathered for some time is quite different from that of the TPH fraction of the refined or residual petroleum product that was originally released. Because the compositions of TPH fractions of different refined and residual petroleum products vary widely and change during natural weathering, it is difficult to predict the concentration of TPH in sediment that does not pose potential risk to the aquatic environment.

2.2.2.1. Hydrogeochemical Processes on Contaminant Transportation

Once contaminants are released to an aquifer system, a series of physical, chemical and biological processes occur which act to transport and attenuate the contaminant concentration in groundwater along a flow path. Their transport property on groundwater depends on their physical properties; velocity, viscosity, miscibility, density, etc. (Chapelle, F. 1992, and Robert, A. and Randy, A. 2006).

Dilution: Dilution is a general term for the reduction of contaminant concentration through the distribution of contaminants throughout larger volumes of water. The process of dilution ultimately decreases the concentration of contaminants in groundwater. The simplest dilution mechanism is mixing of contaminant flow from source with groundwater flow in contaminant and groundwater includes fluctuations in local groundwater gradients in and around landfills due to groundwater mounding.

Advection: A contaminant moves with the flow of groundwater i.e. transport of solute by the bulk movement of the solvent. Therefore, when only advection is considered, a contaminant moves with the groundwater flow at the same rate as water, and no diminution of concentration is observed. In reality, however, the movement of the contaminant is also influenced by dispersion and retardation. Advection refers to the movement of soil gas in response to pressure gradients. Advection can be an important mechanism for drawing soil gas and contaminant vapors into or out of a building. Heating and cooling systems can create differential pressures inside the building. When the pressure inside the building is lower than the pressure in the subsurface, vapors are drawn into the building. When the pressure inside the building is greater than the pressure in the subsurface, air within the building may be forced into the subsurface causing some degree of reoxygenation.

Hydrodynamic Dispersion: is an attenuation process that occurs as a result of a solution moving through a porous medium, and is comprised of both mechanical dispersion and diffusion. Factors that contribute to dispersion include: faster flow at the center of the pores than at the edges, some pathways are longer than others, the flow velocity is larger in smaller pores than in larger ones. This is known as mechanical dispersion.

Diffusion refers to the process whereby molecules move from an area of higher concentration to an area of lower concentration. Diffusion will lead to chemical migration within unsaturated soils away from the highest concentration source area (i.e., NAPL or a dissolved plume). Diffusion is faster in the gaseous phase than in the aqueous phase, so that a layer of clean recharge water above a contaminant plume can decrease the rate of volatilization of contaminants from the plume.

Sorption: Sorption processes refer to a number of surface-related physical and chemical reactions responsible for binding dissolved species to solid phase minerals and organic matter, including: adsorption, absorption, surface complexation, and ion exchange. Adsorption is affected by sediments and soil properties, such as organic percentage, the type and quantity of clay minerals, cation exchange, pH and the physical and chemical properties of the contaminants. During the adsorption, the organic contaminants in the water adsorbed on the surface of the soil particles by the simultaneous distribution role of both water and solid, the driving force is mainly based on principle of "like dissolves like" and electrostatic adsorption of the polar group. Ion exchange operates on the premise that the weak electrical charge on the surfaces of clay minerals attracts and binds ions of the opposite charge. Because clay surfaces typically exhibit a negative electrical charge in the near neutral pH range of most natural waters, ion exchange pertains almost exclusively to cations, although anion exchange is also possible in acidic conditions (US EPA, 1992).

Degradation: Degradation refers to the microbially mediated oxidation of dissolved or particulate organic matter into benign end members. Microorganisms may play an important role in contamination transformations within groundwater and on the soil. They can act as catalysts for many types of reactions. When microbial reactions are significant, there is a possibility of clogging of pores due to precipitation reactions or to biomass accumulation. Biodegradation mainly depends on two factors, the intrinsic characteristics of the pollutants (the structure of organics, physical and chemical properties) and microorganism (the activity of microbial populations), and the environmental factors controlling the reaction rate (temperature, pH, humidity, dissolved oxygen). As the U.S. Environmental Protection Agency researched, soil microbial degradation of organic pollutants can be expressed as a one-order response equation.

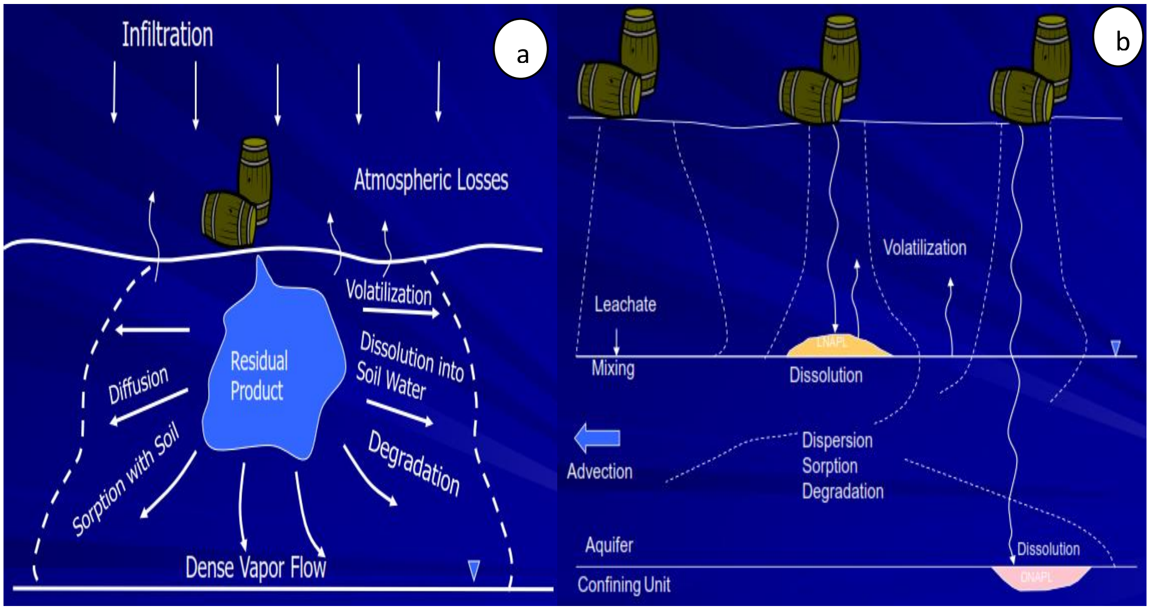

Fig: 2.1 process controlling organic contaminant migration from source above (a) below (b) ground water (source: Wireman 2012. US.EPA).

Mineral dissolution/precipitation: The dissolution of aquifer minerals and precipitation of aqueous species are intimately related to the redox processes occurring in a contaminant plume. Dissolution and precipitation reactions are important mechanisms for both the mobilization and attenuation of major cations and anions from solution.

Volatilization: Volatilization occurs in the vadose zone or saturated zone when the dissolved contaminants and non-aqueous phase contaminants exposed to gas. The factors affecting volatilization include solubility of the compound, molecular weight and water-saturated state of the geological media. The evaporation rate must be measured fundamentally in order to determine pollutions transporting into the atmosphere, changes of the pollution load in the vadose zone and groundwater. The process that the contaminants of deep soil volatilize to the atmosphere can be assumed as one-dimensional diffusion.

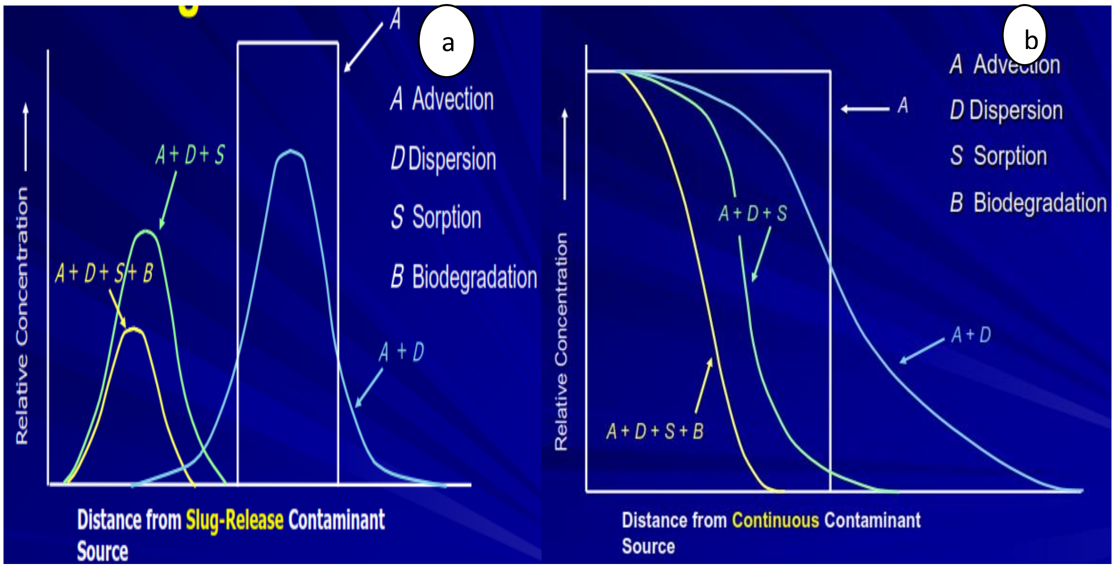

Fig 2.2: Shows the change in concentration of contaminants as result of different processes as distance increases from source (a) slug contaminant source (b) continuous contaminant source (source: Wireman 2012. US.EPA).

Complexation: Complexation can act as either a mobilization or an attenuation process, depending on the type of complex formed. Complexation is the formation of complexes through the combination of cations, anions and dissolved organic molecules (US EPA, 1992). The main impact of complex formation in the context of a contaminant plume is the increased mobility of metals, as metal complexes can remain soluble in conditions that normally would result in their precipitation.

Redox transformation: Redox reactions associated with the degradation of dissolved organic compounds result in the transformation of electron acceptors involved in the reactions. The major elements that are typically involved in these reactions are: NO_3^-/NH_4^+, Mn (IV)$^-$oxide/Mn_2^+, Fe (III)$^-$oxide/Fe_2^+, SO_4^{2-}/S^{2-}, and CO_2/CH_4. Redox transformations can result in both the mobilization and attenuation of contaminants, depending on the behavior of the contaminants in different redox environments. Redox condition of contaminants is discussed below.

Generally the processes mention above are responsible for the distribution of contaminants either by mobilization or attenuation. Even though the distribution of different species is controlled by many factors the movement of contaminants can be block or traveled long distance (depth) to form a contaminant plume by these processes. for example a contaminant may not reach groundwater if its initial concentration small not enough to pass volatilization, dissolution it soil, diffusion, sorption with soil and degradation in the vadose zone which totally consumed before it reaches the groundwater table.

2.3. Redox environment in contaminant plume

Aqueous systems contain no free electrons, but the relative electron activity, as an intensity parameter, can still be defined (Stumm and Morgan, 1996). Electron activity, measures the tendency of a system to accept or transfer electrons. In a highly reducing system, the tendency to donate electrons, which is the hypothetical electron activity, is relatively large and $p\varepsilon$ is low. In contrast, high $p\varepsilon$ values indicate a relatively low electron activity and a relatively oxidized system (Thomas et al. 2000).

Redox conditions of a groundwater contaminant plume from a point source usually differ from the redox condition of the pristine aquifer Naudet et al. (2004). When sufficient organic matter and other reduced components leak from a point source into an aquifer, strongly reduced redox conditions will develop close to the source and the plume will develop a redox gradient along as well as transversal to the main groundwater flow direction. In the outskirts of the plume, the redox conditions will approach the redox conditions of the pristine aquifer**.** I.e. as the concentration of organic contaminant decreases from the source to outskirt of the plum the redox condition will goes from reduced to oxidizing environment.

The redox conditions of a contaminant plume constitute an important part of the chemical framework controlling the behavior of the contaminants in the plume. Knowledge of the actual redox conditions, therefore, is important for interpretation of field observations, evaluation of plume development and risks to down gradient groundwater resources, assessment of natural attenuation as a remediation option, and in engineering of remedial measures.

Naudet et al. (2004) also stated that accurate mapping of the electrical conductivity and redox potential of groundwater is important in delineating the shape of contaminant plum. A map of redox potential in an aquifer is indicative of biodegradation of organic matter and of concentration of redox-active components; a map of electrical conductivity provides information on the mineralization of the groundwater.

The entry of strong reducing leachate such as organic compounds into the pristine aquifer modifies the redox environment. The reduced leachate is rich in organic matter, with grate capacity to donate electrons during redox reaction catalyzed by bacteria. The figure (#) below shows schematically how the concentrations of various redox species vary with increasing degrees of reduction by organic matter. Initially, oxygen is reduced and so its concentration falls very early in the process. In the meantime, the nitrate concentration may initially increase as molecular oxygen oxidizes any reduced nitrogen contained in the organic matter. After oxygen is completely consumed, nitrate is reduced by the organic matter and so the concentration of NO_3^- begins to fall. Soon, most of the nitrate is reduced. Manganese oxides and iron oxides are then reduced by the organic matter, producing dissolved, divalent Mn and Fe. Once all the Mn and Fe are consumed, sulfate is then reduced. As the concentration of SO_4^{2-} decreases and the concentration of its reduction product, H_2S increases, Fe^{2+} is removed by precipitation as iron sulfides. Eventually, if sufficient organic matter is available, the entire sulfate is consumed and, the only remaining electron acceptor is CO_2, which is reduced to form methane. Late in the process, if the entire sulfide is tied up in sulfide minerals, then the concentration of Fe^{2+} may rise again. A series of redox gradient becomes established in the contaminant plume, with an increase in the redox potential value with distance from the source.

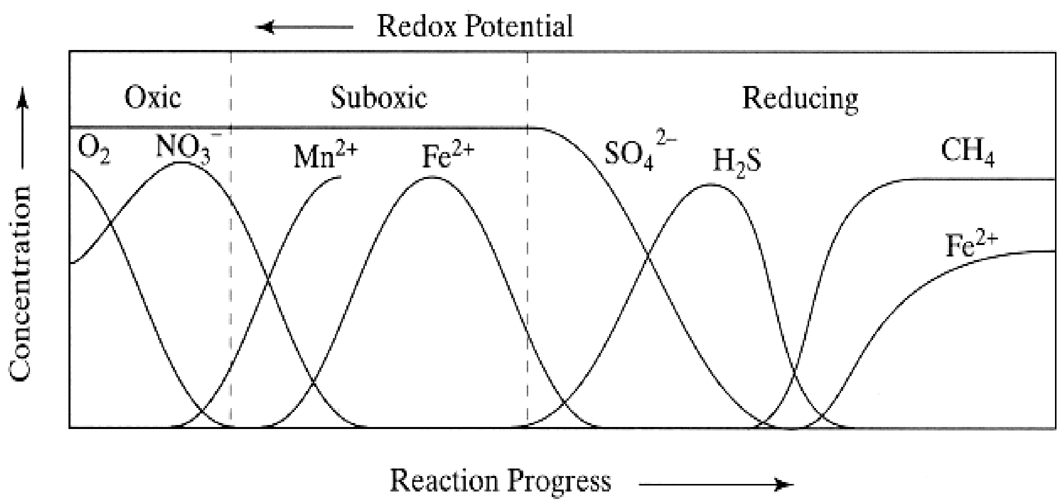

Fig 2.3: Changes in concentrations of redox species with time assumed organic carbon as electron donor

According Baas-Becking et al. (1960) the measured Eh (pe)-pH value could tell us the common geological environments. The measured Eh values waters in contact with the atmosphere, such as acid mine waters, rain water, streams, lakes and oceans, do not plot along the upper stability limit for water as we might expect. Bog waters and ground waters usually tend to be moderately reduced, because they are not in contact with atmospheric oxygen. Even more reduced are waterlogged, organic-rich soils, euxenic marine basins and organic-rich brines. Eh is a measurement of electrical potential and thus commonly expressed in volts. Values of Eh in nature range from -0.6 to +0.9V, with 0.0 characterizing a solution with no drive to either oxidize or reduce.

2.3.1. Approaches to determine redox conditions in contaminant plumes

Determination of redox conditions in contaminant plumes is still no simple task and no universally accepted procedures exist (Thomas et al. (2000)). However, the need to understand contaminant behavior in plumes has fostered several approaches and attempts to characterize redox conditions of contaminant plumes. The various approaches according Thomas et al. (200) are: (1) electrochemical redox potentials, (2) groundwater sample composition with respect to redox-sensitive parameters, (3) hydrogen concentrations in groundwater, (4) volatile fatty acid concentrations in groundwater, (5) sediment characteristics (6) microbial characteristics in terms of biomass composition, (7) biomarkers, and (8) redox bioassays.

Electrochemical redox potentials: The electrochemical measurement involves two electrodes, a nonpolarisable reference electrode and a polarisable working electrode. The working electrode will respond to kinetically fast redox couples and the potential between the working electrode and the reference electrode, measured when no current flows, corresponds to electrochemical equilibrium for the redox couple. The main problem in applying these principles to measuring redox potentials in polluted groundwater is the very slow chemical kinetics of redox reactions involving C, S and N species.

Redox measurements are not valid in aerobic groundwater due to the presence of O2. A standard configuration is a gas-tight cylinder through which groundwater can pass, and into which electrodes are inserted while maintaining a gas-tight seal around openings for flow connections and electrodes. Measurement must take place in a gas impermeable cell since diffusion of oxygen and slow oxidation of ferrous iron species can result in mixed potentials that drift slowly.

Electrochemical measurements of redox potentials have only been reported in very few cases for contaminant plumes, supposedly due to lack of confidence in their usefulness. Redox potential measurements, however, have often been made in the field as a means to identify strongly anaerobic samples when mapping plumes. It seems clear that redox potential measurements can be routinely carried out at field sites, within a standard sampling protocol, and may help to at least rapidly distinguish between strongly reducing zones and zones representing higher redox conditions.

Groundwater composition: The primary redox-sensitive species in groundwater are the dissolved ions SO^{2-}_4 ,HS^- ,Fe^{2+} Mn^{2+} ,NH^+_4 ,NO_2^-,NO_3^- and the dissolved gasses CH_4 , N_2 and O_2. These could be quantified analytically with good accuracy and that the solute species were in equilibrium with the solid species, a redox potential could be calculated for each redox couple. But due to: Analytical methods may have detection limits too high to quantify both species of a redox couple due to a very low concentration of one of them: Analytical methods may not exist for both redox species: and Several redox-sensitive species are also precipitates and the dissolution/precipitation reactions are not necessarily at equilibrium or the actual precipitate is not known.

Using redox-sensitive compounds for redox characterization requires proper sampling of redox-sensitive species from representative screens. When sampling at the ground surface, electrode measurements e.g., oxygen should be performed in-line tubing connected directly to a flow cell to avoid contact with the atmosphere. Similarly, samples used for analysis of compounds where solid species may interfere should be properly filtered.

Redox-sensitive compounds have been used in at least three different ways: identification of reduced and oxidized conditions: Assignment of redox zones: and Determination of predominant redox reactions.

Quantifying redox-sensitive species in groundwater samples is a simple and useful tool for identifying the redox conditions of a groundwater contaminant plume. The basic principles are thermodynamically sound; but the actual criteria for assigning the redox status depend, to some extent, on local conditions, such as the natural groundwater geochemistry, compounds leaching from the source and quality of sampling and analytical equipment. The major limitation in using the concept is related to migration of redox-sensitive species away from active zones, geochemical processes involving precipitation of compounds and the actual overlap between different redox zones.

Hydrogen*:* An alternative method for identifying the predominant redox processes in anaerobic ground water is through direct measurement and interpretation of dissolved H_2 concentrations in ground water (Lovely and others, 1994; Chapelle and others, 1995). Hydrogen is continuously produced and consumed by different microorganisms during anaerobic decomposition of organic matter. For natural ground waters, different microorganisms that facilitate nitrate-, manganese , iron-, sulfate-, and carbon dioxide-reduction reactions exhibit different efficiencies using H_2 (Lovely and Goodwin, 1988). Nitrate-reducers are efficient at using H_2 and keeping dissolved H_2 concentrations in ground water at levels of less than 0.1nM. Manganese- and iron-reducers use H_2 less efficiently and keep H_2 concentrations between 0.1–0.2 and 0.2–0.8nM, respectively. Sulfate-reducers are less efficient still and keep H_2 concentrations at between 1 and 4nM, and carbon-dioxide reducers are relatively inefficient, resulting in H_2 concentrations greater than 5nM. The result of competition for H_2 is that each anaerobic redox condition is characterized by a distinct H_2concentration in ground water (Lovely and others, 1994; Chapelle and others, 1995).

Anaerobic oxidation of organic matter from complex organic compounds generally goes through a three step process. hydrolyzation of the organic substances, fermentation of this into smaller organic molecules, and then used as electron donors by the bacteria mediating processes. One of the dominant products is H_2. The nanomolar concentrations of H_2 found in groundwater are quantified by gas chromatography with a reduced gas detector calibrated with standards of H diluted in N. H_2 measurements are a potentially powerful tool for studying microbial processes, in general, and more specifically TEA degradation processes involving H_2. But Depending on aquifer conditions, sampling method, as well as electron donor and acceptor distributions, bulk and stagnant water may be represented differently and the H concentrations in the two might well be different.

In practice, identifying redox conditions from specific steady-state H_2 concentrations is not applicable to all contaminant plumes (Hoehler and others, 1998; Jakobsen and others, 1998; Christensen and others, 2000). Uncertainty in identifying a predominant redox condition from H_2 concentrations alone is due to factors such as variation in the iron-oxide minerals that serve as electron acceptors, ground water temperature effects on equilibrium H_2 concentrations, and overlapping and non-exclusive redox conditions. Despite those limitations, H_2 concentrations do indicate redox conditions in a relative sense, in that higher H_2 concentrations are always detected in more strongly reduced ground waters. In terms of contaminant biodegradation, identifying the presence of strongly reducing conditions or knowing where H_2 concentrations exceed 1 nM may be more critical than knowing the specific inorganic compound that is the predominant electron acceptor. Quantifying oxidized and reduced inorganic compounds as well as steady-state

H_2 concentrations throughout a contaminant plume can be used with reasonable confidence to identify favorable and less favorable conditions for contaminant biodegradation.

Aquifer sediment characterization: Sediment redox characterisation may involve: Identification of the nature of individual sediment minerals; Species capacity quantification of the bulk content of individual species, such as a total iron content; Reactive fraction measurements: and Redox capacity measurements. Reliable sediment analysis heavily depends on obtaining a representative solid sample and keeping the reactive species intact during sampling, handling and storage. Rapid sample handling in the field, flushing with an inert gas, sealing and cold storage in an inert atmosphere, such as nitrogen or argon for only a limited time is recommended.

The actual length and time scales related to the plume as well as to the different redox zones a volume of the plume with somewhat homogeneous redox conditions depend strongly on the size and strength of the point source, the groundwater flow velocity and the geochemistry of the aquifer. These factors, thus, may also change the importance of the various redox zones. While the progressive development in redox zones of a contaminant plume is partly supported by experiences from real plumes, the regressive development is still fairly speculative. However, it is likely that after the source term is fully depleted, the aquifer will have permanently changed.

Understanding of the dynamics of the contaminant plume and the purpose of the redox characterization will be useful in selecting the appropriate methods for the redox characterization.

In this paper Hydrogen and Groundwater composition approach are used to Determination redox conditions in groundwater from contaminant plumes. By determine the relative concentration of H and redox sensitive compounds it is possible to identify at least a general sense of reducing or oxidizing environment of an area.

2.4. Properties of Geologic Media and Fluids

2.4.1. Properties of geological media

The extent and rate of petroleum hydrocarbon migration depends in part on the properties of the subsurface medium in which it is released. The subsurface medium may be naturally occurring geologic materials (e.g., sedimentary, metamorphic, or igneous rock or sediments) or artificial fill that has been imported to the site by human activity. In order to design effective and efficient free product recovery systems, you need to characterize both the type and the distribution of geologic media (or fill material) so that you can determine the likely migration routes and travel times.

In the context of fluid flow in the subsurface, geologic media can be classified on the basis of the dominant characteristics of pore space, fractures, or channels through which fluids move. In porous media, fluids move through the interconnected voids between solid grains of soil. Fractured media are those in which fluids migrate readily through fractures rather than the adjacent soil or rock matrix. Fracturing is usually associated with consolidated materials, but it can also occur in unconsolidated clays due to desiccation. Karst media are those in which fluids flow through solution features and channels.

Porosity and permeability are the two most important media-specific properties of a natural geologic material. Porosity characterizes the ability of media to store fluids, and permeability characterizes the ability of the media to transport fluids.

Porosity: All geological formations contain pore spaces. The percentage of the total volume of an unconsolidated material or rock that consists of pores is called porosity. Characterization of the flow of groundwater and free product through intergranular and intragranular pore-spaces, solution channels, fractures, and joints can be especially problematic. The flow of groundwater and free product through the larger openings can sometimes even be under conditions of open channel flow. Once free product enters these larger openings, it can migrate undetected over relatively great distances in a matter of weeks or months.

Permeability: is related to hydraulic conductivity, which is a measure of the ability of the geologic medium to transmit non-viscous fluids. Geologic media with high hydraulic conductivities are highly permeable and can easily transmit non-viscous fluids, especially water and many types of petroleum products.

A geologic medium can be isotropic if the measured permeability is the same in all directions: i.e. flow is parallel to the hydraulic gradient, or anisotropy if the permeability of a geologic medium is often observed to vary depending upon the direction in which it is measured: i.e. flow of groundwater and free product is in a direction that is not necessarily the same as the principle direction of the hydraulic gradient. On the other hand geologic medium can be homogeneous which have uniform properties over a large area or heterogeneous that varies in grain size from place to place. These changes strongly influence the direction and rate of the flow of groundwater, free product, and vapor through the subsurface. For example, free product may migrate farther and faster in heterogeneous than it would in homogeneous media because hydrocarbons tend to move through the most permeable pathways and bypass extremely low permeability zones.

2.4.2 Properties of fluids

Density and Viscosity are the most significant physical properties of fluid migration in the subsurface condition.

Density: refers to the mass per unit volume of a substance. The densities of petroleum hydrocarbons typically found in USTs are less than 1.0 which is less than density of water (1.0 g/ml). Densities of some common petroleum hydrocarbons are presented in appendix4. Petroleum hydrocarbons that are less dense than water will float; these are also referred to as light non-aqueous phase liquids, or LNAPLs.

Viscosity: describes a fluid's resistance to flow, and is caused by the internal friction developed between molecules within the fluid. Fluids with a low viscosity are often referred to as thin, while higher viscosity fluids are described as thick. Thinner fluids move more rapidly through the subsurface than thicker fluids. This means that a thinner petroleum product (i.e., gasoline) is generally more easily flow on the subsurface and leaves a lower residual saturation than a thicker petroleum product (e.g., fuel oil). Viscosity is inversely proportional to temperature: As the temperature of the fluid increases, the viscosity decreases. The viscosity of free product in the subsurface environment typically changes over time, becoming thicker as the more volatile components evaporate and dissolve from the liquid hydrocarbon mass.

Capillary pressure, relative permeability, wettability, saturation, and residual saturation are factors which can affect the movement of free product in which are functions of properties of both the fluid and the geologic media. These factors are.

Capillary pressure: is the difference in pressure observed between two phases (e.g., hydrocarbon liquid and water) that occupy the same pore space. In the vadose zone capillary pressure is negative and is referred to as suction or tension. Capillary pressures are larger in fine-grained media than in coarse-grained media. The capillary fringe above the water table is a familiar consequence of capillary pressure. Because capillary pressure resistance is inversely proportional to pore size, the height of the capillary fringe is greater in finer grained media.

The distribution and accumulation of free product in the subsurface is influenced by capillary pressure. Penetration of free product into the subsurface is enhanced by dry soil conditions and facilitated by inclined, relatively permeable pathways such as those provided by secondary permeability features. Upon reaching the capillary fringe, resistance to downward movement will be increased and hydrocarbons will spread laterally and accumulate above the saturated media. This accumulation is sometimes referred to as a lens or pancake. As long as there is a sufficient supply of hydrocarbons from above, the lens thickness and downward pressure will continue to increase. Eventually, the petroleum product will begin to displace water and enter the largest pores.

2.5. Remediation Mechanisms for Organic Contaminant

Remediation is required when concentrations of contaminants exceed or are expected to exceed predetermined levels for the type of resource that is impacted. The method for remediation depends on the several factors: Hydrogeologic setting, Contaminant characteristics, Physical properties (sink or float), Chemical properties (solubility, sorption), subsurface access, land use, toxicity-risk, cost and remediation goals, including (containment, stabilization, sequestration, assimilation, reduction, detoxification, degradation, mobilization, and / or mineralization).

In situ treatment techniques

Many new technologies are under development in the area of physical and/or chemical treatment of contaminated matrices. Using these technologies can expand in situ cleanup opportunities to medium and low permeability soils, semi-volatile organic compounds, and volatile organic compounds.

In-situ capping: refers to placement of a subaqueous covering or cap of clean material (sand, gravel, geotextiles, liners or organic carbon) over contaminated sediment to attenuate the flux of contaminants. This remediation of contaminated media is due to the nature of the interaction of the capping material with the subaqueous sediments which either destroy the contamination or sequester contaminants through a combination of adsorption, absorption, ion exchange, and precipitation.

In-situ chemical oxidation: is designed to destroy organic contaminants either dissolved in groundwater, sorbed to the aquifer material, or present in their free phase. The method involves thoroughly permeating the contaminated zone with sufficient quantities of chemical oxidants so that the chemical can contact and fully react with contaminants. Oxidants used in the systems include potassium and sodium permanganate, hydrogen peroxide, and ozone. Common contaminants treated by chemical oxidation are amines, phenols, chlorophenols, cyanides, halogenated aliphatic compounds, mercaptans, and certain pesticides in liquid waste streams. Chemical Oxidation technology is applicable to sites with contaminants in the vadose zone or in aquifers

Permeable reactive barriers: is an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant into environmentally acceptable forms to attain remediation concentration goals down gradient of the barrier. Methanes, Ethanes, benzene, toluene, ethylbenzene, and trichloropropane are some of organic contaminants treated by this method. The contaminants are either mobilized or chemically transformed to less toxic compounds. The Permeable reactive barrier serves as a barrier to the contaminants, but not to the groundwater flow.

Air sparging: refers to the process of injecting clean air directly into an aquifer for remediation of contaminated groundwater. The objective of air sparging is to force air through contaminated aquifer materials to provide oxygen for bioremediation and/or to strip contaminants out of the aquifer. Potentially, air sparging is applicable to sites contaminated with petroleum hydrocarbons such as jet fuels, diesel fuel, and gasoline, as well as volatile compounds. Air sparging may clean a petroleum-contaminated aquifer easily, by promoting biodegradation; it has the potential to completely destroy contaminants, instead of transferring them to another media. It leaves the site intact, yet removes the contaminant. And it costs less and is more effective than an on-site pump and treatment system.

Bioremediation: involves chemical transformations mediated by microorganisms that degrade organic contaminants in either excavated or in-situ soil, sludge, and solids. The microorganisms break down contaminants by using them as a food source or cometabolizing them with a food source. In some instances, bioremediation is used with other technologies to accomplish a greater total removal efficiency of organic contaminants.

Phytoremediation: Is a set of technologies using plants (roots, shoots, tissues, and leaves) to remove, transfer, stabilize, or destroy contaminants in soil sediments and groundwater. Phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants that aid the cleanup of contaminated substances.

Plants naturally remove man-made contaminants through several mechanisms. Some plants degrade organic pollutants directly or indirectly by supporting microbial communities. Other plants take up organic contaminants from soil or water and concentrate them in the plant tissue where the contaminant can be removed and disposed of separately, leaving the soil clean

***Electroheating*:** refers heating of the soil using an electric current, evaporating the volatile organics and separate the vapors, which in turn are trapped in the appropriate absorbent such as active carbon to be finally eliminated by incineration(burning at high temperatures). This shows several advantages form other technologies designed for the removal of volatile organics from soils.

Electrokinetic remediation: is an environmental technique especially developed for the removal of contaminants in soil, sediments and sludge, although it can be applied to any solid porous material. It is based in the application of a direct electric current of low intensity to the porous matrix to be decontaminated. The effect of the electric field induces the mobilization and transportation of contaminants through the porous matrix towards the electrodes, where they are collected, pumped out and treated. Contaminants are transported out of the soil due several transportation mechanisms induced by the electric field.

"Any ground-water cleanup effort will be undermined unless inorganic and organic contaminant sources are identified, located, and eliminated, or at least controlled, to prevent further contamination of the aquifer."

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3. Geology and Hydrogeology of the area

3.1 Description of the study area

3.1.1 Location

Addis Ababa is located on the shoulder of the Western Main Ethiopian Rift Escarpment. Geographically the area is bounded by UTM coordinates of about 978000N, 1005500N and 456000E, 495000E.

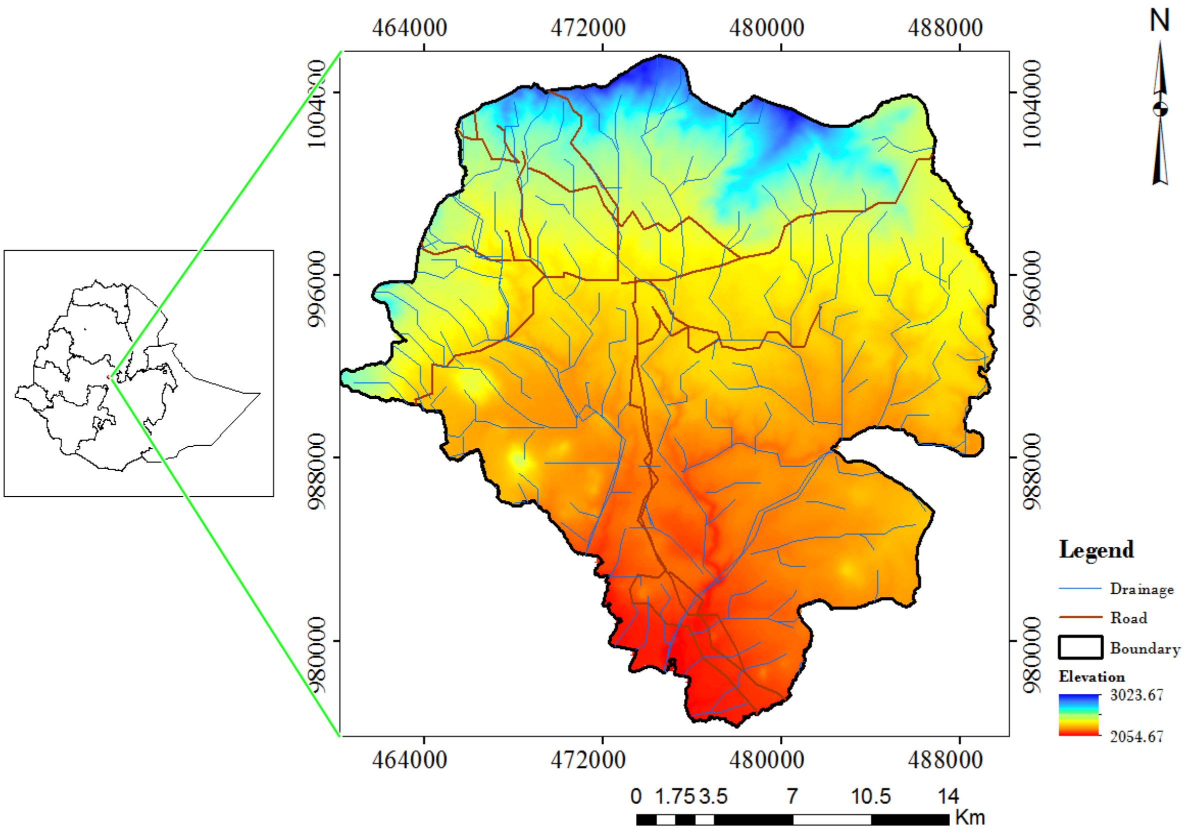

Fig3.1: Location map of Addis Ababa

3.1.2 Physiography

The morphology of Addis Ababa is a direct reflection of the different volcanic stratigraphic successions, tectonic activities and the action of erosion between successive lava flows.

The city was founded at the southern flank of Entoto ridge (3199m a.s.l.) and expanded in all directions. This ridge marks the northern boundary of the city following the east-west trending major fault (Ambo-Kassam). Other prominent volcanic features surrounding the city are Mt. Wochacha in the west (3385m a.s.l.), Mt. Furi (2839m a.s.l.) in the southwest and Mt. Yerer (3100 a.s.l.) in the southeast.

These typical volcanic features are mainly built up of acidic and intermediate lava flows characterized by rugged landscapes and steeper slopes. The topography is undulating and form plateau in the northern, western and southwestern parts of the city, while gentle morphology and flat land areas characterize the central, southern and southeastern parts of the city. On the top of the hills and ridges streams are dense and form radial drainage pattern, whereas on the slope and most parts of the study area they form denderitic features.

Residual soils are commonly seen in most parts of the city with varying thickness. On the other hand, due to intensive erosional activities there is a poor soil development occurrence on most parts of the slope. The dominant type of soil in the southern parts of the city is black cotton soil. Moreover, waterlogged areas are found in the central parts of the city around Filowha, in the eastern parts of the city around Lamberet and in other different parts with small aerial extent.

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, and the Little Akaki that drains the Western part of the catchments and their respective tributaries like Kebena River. Almost all the streams in the catchments originate from the Northern part of the catchment and flows to the south part of Addis Ababa. This entire river carry tremendous amount of contaminant when they cross the city and pollutes surface and groundwater.

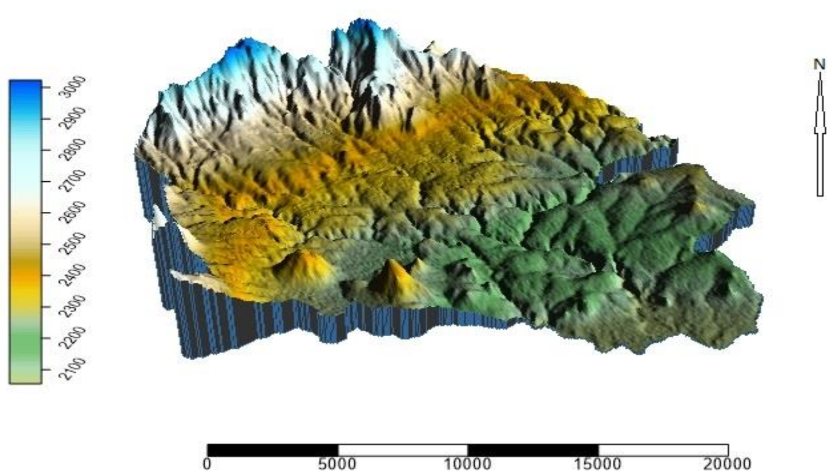

Fig3.2: Physiogrophy of the study area

3.2. Geological Setting

Many researchers systematically proposed the geology and volcanic stratigraphic sequences of Addis Ababa area. HaileselassieGirmay and GetanehAssefa (1989) proposed the stratigraphy of the area starting from Sululta to Nazareth, based on Morton's geological map, K/Ar absolute age determination taken from different literature and fieldwork to clarify some geological uncertainties. They redefine the lithostratigraphic units and modified the existing stratigraphic sequence. The suggested Miocene-Pleistocene volcanic succession in the Addis Ababa area from bottom to top are: Alaji basalts, Entotosilicics, Addis Ababa basalts, Nazareth group, and Bofa basalts.

3.2.1. Alaji Basalt

The Alaji group volcanic rocks (Alaji rhyolite and Basalt) in this part of the escarpment were outpoured from the end of Oligocene until middle Miocene (Zanettin et al., 1974). This unit is composed of basalts, which show variation in texture from highly pophyric to aphyric. Within this unit there is an intercalation of gray and glassy welded tuff. The outcrop of Alaji basalt extends from the crest of Entoto (ridge bordering the northern parts of Addis Ababa) towards the north (HaileselassieGirmay and GetanehAssefa, 1989). This unit is underlain by tuffs and ignimbrites; on the other hand its stratigraphic relationship with the Entotosilicics is difficult to determine as they occur in a fault contact.

3.2.2. EntotoSilicics

These early Miocene age silicic volcanics could represent localized terminal episodes to massive Oligocene fissure- basalt activity in the Addis Ababa region (Morton et.al. 1979). The unit is unconformably overlain by Addis Ababa basalt on the foothill of Entoto and underlain by Alaji basalt. The Entotosilicics composed of rhyolite and trachyte with minor amount of welded tuff and obsidian (HaileselassieGirmay and GetanehAssefa 1989). The rhyolitic lava flow outcrops on the top and the foothills of the Entoto ridge, predominantly in the western side. It also outcrops in the eastern part of the town from the KokebeTsebah School to the Benin Embassy. The rhyolites are overlain by feldspar porphyritic trachyte and underlain by a sequence of tuffs and ignimbrites. The trachytic lava flow outcrops on the top of Entoto ridge and its foothills. It shows a quite uniform texture, and is constituted by phenocrysts of oligoclase, sandine and rebeckite within a groundmass of plagioclase, iron oxide and minor quartz and mafic minerals. Two varieties of trachytic lava flows have been identified in the eastern side of the town, near

Kotebe: a pale gray and a pink trachyte. The latter one is characterized by veins of hematized opal and by feldspar phenocrysts, which are often completely or partially altered with fine fractures filling of hematite (Varnier et al., 1985). Thus from the general stratigraphy established by Zaneitin et al. (1974) both rhyolite and trachyte of the Entotosilicics belong to the "Miocene Alaji Rhyolite and Basalt" sequences.

3.2.3. Addis Abeba Basalt

In the area the oldest visible rock post-dating the Entoto silicic is the Addis Ababa basalt. These units, which are mainly present in the central part of the town, are underlain by the Entotosilicics and overlain by Lower welded Tuff of the Nazareth group. The ground mass is made of andesine, labradorite, olivine, magnetite and pyroxene (HaileselassieGirmay and GetanehAssefa 1989). Olivine porphyritic basalts outcrop in the central part of the town that includes Mercato, Teklehaymanote and Sidist Kilo. It outcrops in an area, which includes Sidist Kilo, General Winget School and French Embassy. The Lower Welded Tuff overlies both types of basalt nearby the Building College, the Kolfe Police School, the KokobeTseba School and YecaMariam Church. On the other hand, only in the gorge of the Ketchane stream the olivine pophyric basalt is overlain by the plagioclase porphyritic basalt, while elsewhere the relationship between them is very difficult to determine (Varnier et al., 1985).

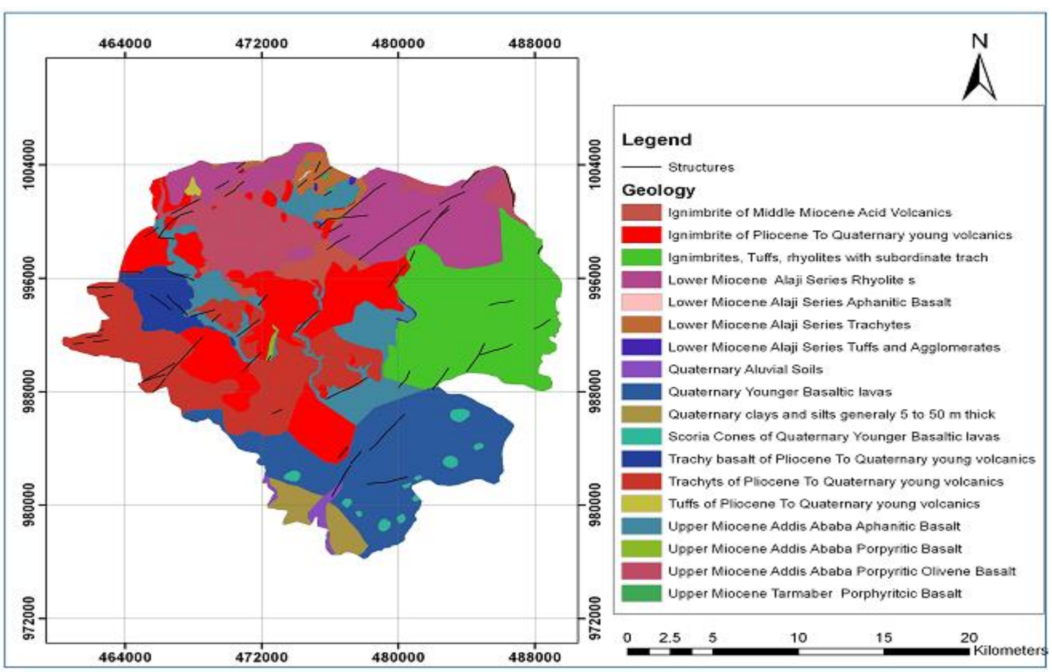

Fig3.3: Geology of the study area (after ShilimaAbebe, 2011)3.2.4. Nazaret Group

The units identified in this group denoted as Lower Welded Tuff, Aphanitic basalt and Upper Welded Tuff. The group is underlain by Addis Ababa basal and overlain by Bofa basalts. The rocks outcrop mainly south of Filowha fault and extend towards Nazareth.

3.2.5. Lower Welded Tuff

This rock outcrops as small discontinuous body in Filwoha, western parts of Addis Ababa and Sululta. It is glassy with abundant fiamme and has columnar joints. Generally it is overlain by the aphanitic basalt and underlain by the olivine and plagioclase prophyritic basalt localities (Morton et al., 1979).

3.2.6. Aphanitic Basalt

This basalt covers the southern part of the town, especially the areas of Bole International Airport and Lideta Airfield. The rock body shows vertical curved columnar jointing together with sub-horizontal sheet jointing. Kaolin, lenses are present at the contact of this basalt with the younger ignimbrite. This is a sure evidence for the hydrothermal alterations along a NE-SW fracture system, which may affects both the basalt and the Entoto trachyte. Moreover the basalt is overlain by pumeacoues pyroclastic falls and the pyroclastic falls. It is underlain by a soil horizon that covers the plagioclase porphyritic basalt and overlain by soil horizon and tufflayers that lie below the young ignimbrite. It consists of: Labradorite, augite, rarely olivine and magnetite. The crystals of plagioclase show marked flow alignments. Trachy-basalt outcrops around Repi and nearby General Wingate School. It is underlain by the plagioclase and olivine porphyritic basalt and overlain by the younger ignimbrite from which it is separated by tuffs and agglomerates. Moreover, phenocrysts that occur mainly in the rock are: sandine, labradorite, magnetite and augite.

3.2.7. Upper Welded Tuff

This rock outcrops all over the southern part of the town including Bole, Nefas Silk and Railway station; nevertheless it is also present in the central and northern parts of the town. It is gray colored, vertically and horizontally jointed and composed of sandine, anorthoclase, rebecite, quartz, pumice and unidentified volcanic fragments (GetanehAssefa et al., 1989). The welded tuff is underlain by aphanitic basalts and overlain by young olivine basalts.

3.2.8. Young Trachyitic Flow

This rock is predominating in the southwest part of the town, from Dama hotel towards Furi and Repi along the hills and foothills of Hana Mariama and Tulu Iyou. It is porphyritic with phenocrysts of plagioclase (albite-oligoclase) sandine, biotite within a groundmass of microlities of feldspar. Moreover, it is underlain by the tuff that cover the young ignimbrite and overlaying by alternating flows of plagioclase porphyritic basalt and rhyolite especially in the Repi hill. Its relation with the young olivine prophyrytic basalt is not clear as they outcrop in different parts of the areas, however, in a small outcrop nearby Aba Samuel Lake south of the project area, the trachyte underlies the olivine porphyritic basalt.

3.2.9. Young Olivine porphyritic basalt

They outcrop southward from Akaki River where they appear in the form of boulders reaching a thickness of 10 meter. They are restricted and dominant in the southeast part of the town i.e. DebreZeit Road. They contain phencorysts of plagioclase, olivine that is partially and completely altered to iddingisite and augite within a groundmass composed of plagioclase magnetite pyroxene and olivine. This basalt is underlain by the tuffs, which cover the welded tuff.

3.3. Geologic structures

In the project area the occurrence of faults, joints and other structures within the different volcanic rocks were reported by different authors. Long fault line running east west via Kassam river, Addis Ababa and Ambo, cut across the western rift escarpment and uplifted its northern block (Zanettin et al., 1978). However, Haileselassie (1985) carried out detail mapping of the Filowha Fault using resistivity method and found that the fault has down thrown to the south, shallow depth and covered by very thin soil layer (1-4m). Haileselassie Girmay (1989) found that the fault is not vertical and its throw can be estimated to be about 40m, which is approximately the thickness of the welded glassy ignimbrite. Kundo (1958) proposed that the hot springs in Filowha are controlled by this fault. The presence of hot springs, south of the fault gives resistivity contrast on the either side of the fault.

The other major structural feature in the study area is joints, which have different spacing, opening and orientation. The dominant preferred orientation of joints occurring in different rock unit is NNE-SSW (Kebede et al., 1990), which is sub parallel with the general trend of rifting.

These rocks are the major groundwater supply for large parts of Addis Ababa The chemical dissolution of different rock types exposed in different part of the area controls the chemistry of the groundwater. Tenalemet al. (1998) indicates the existence of different water types with indications of groundwater pollution in few places in Addis Ababa. On the other hand, variation in lithology also affects the occurrence and transport of contaminant.

3.4. Pedolog

The soil development in the study area is mostly due to the physical disintegration and chemical decomposition of volcanic rocks. The weathering products are either remain in places and form residual soils or transported and deposited in the areas of Addis Ababa. Meanwhile, the difference observed in the type and development of soils in the city is mostly depends on the topography, parent materials and the degree of weathering. In the localities where the topography is plain to gentle (central and southern part) of the area is covered by thick soil profile. The type of parent material and the length of time to which the parent material is subjected to weathering, control the variation in the thickness of soil.

In areas where there is great contrast in the topography colluvial soils are found. These are loose and incoherent deposits, consisting of fine to coarse grain. The shape of the particles varies from angular to sub-round. Therefore the thickness, permeability, porosity and shrink/swell characteristics of soils are crucial and control largely the infiltration of pollutants into subsurface. The variation in the characteristics (resulting porosity and permeability) of soils makes them different in water infiltration and holding capacity which, on the other hand, control the vertical as well as horizontal movements of contaminants.

The soil of Addis Ababa is classified in to seven major types namely Calcic Xerosols, Chromic Luvisols, Chromic Vertisols, EutricNitisols, Leptosols, OrticSolonchaks and PellicVertisols (Ministry of Water and Energy, 2004)

The permeability and infiltration of each soil depends on its textural composition. Accordingly, Vertisol (Pellic and Chromic Vertisols) is characterized by fine textured soil with >60% clay in composition. As a result, the porosity of such soil is very fine making the movement of material difficult within the soil. Hence, the permeability of Vertisol is very low except within the cracks that are formed during dry seasons. The permeability of EutricNitisol is moderate as its texture is generally characterized as moderately fine sized textured and with relatively less clay content than Vertisol. The permeability of Chromic Luvisol, which is found in the north-west part of the center, is also moderate like the case of EutricNitisol. Leptosol is characterized by shallow depth underlined by hard rock and with less developed soil. This type of soil is found in the Northern part of the center. The textural class is moderately coarse textured soil with high permeability. Topography (slope) is the major soil forming factors that determine the type and properties of soil mainly depth and texture via determining the degree of weathering and erosion. Generally the steeper the slope the less soil development and higher erosion rate and the shallower thedepth and the courser the texture and vice versa.

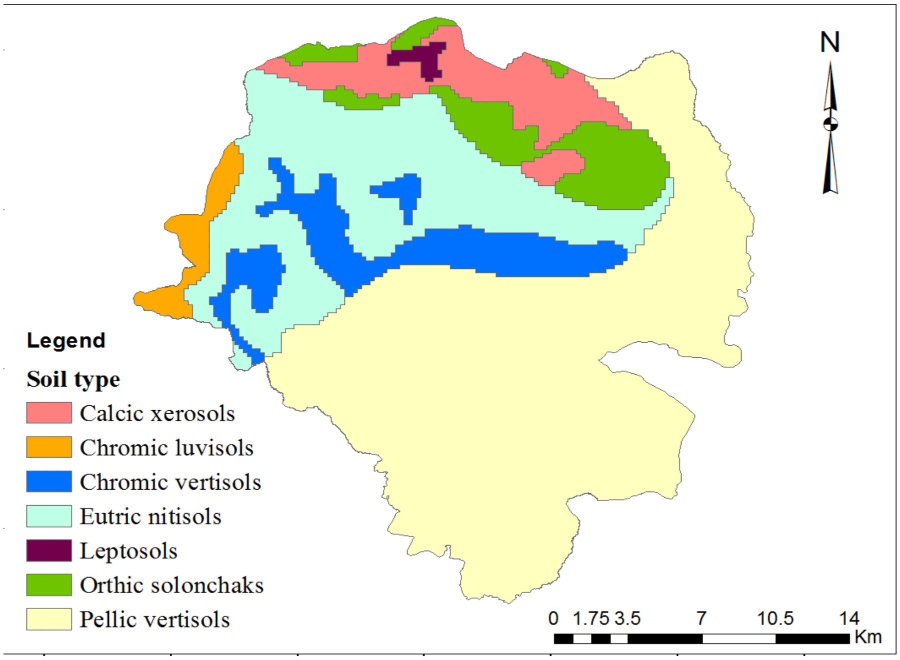

Fig3.4: soil map of the area

3.5. Hydrogeology

According Tamiru, (2004) groundwater circulation and the dispersion of pollutants depend on the hydrogeological characteristics of the material more specifically hydraulic properties such as porosity, permeability, transmissivity etc. The origin, flow and chemical constituent of groundwater are controlled by the type of lithology, distribution, thickness and structure of hydrogeological units through which it moves. Moreover, the stresses due to tectonism and weathering govern the hydrogeochemical characteristics of earth materials. Therefore, the project area is characterized by alternate eruption of basic and acidic lava flows from different centers. In between successive lava flows physical disintegration and chemical decomposition of rocks exposed at the surface; subsequent erosion and deposition; and tectonic activity taken place that has modified significantly the geomorphologic set up of the area.

3.5.1. Porosity

Tamiru, (2004), and UNESCO (2003).Identified the main porosity groups as fracture and interstitial porosity.

3.5.1.1. Fracture porosity

Basaltic lava flows: Basically, high water storage and transmitting capacity of basaltic lava flows is due to joints caused by cooling, lava tubes, vesicles that are interconnected, tree moulds, fractures caused by buckling of partly congealed lava (aa lava surface) and voids left between successive flows. Its water circulation and storage capacity is dependent on the degree of weathering and secondary fractures (weathering types). The presence of faults and fractures modify the hydraulic properties of the rock

Depending on the degree of weathering and the resulting weathering zones the porphyritic basalts show difference in water infiltration properties. Around KidaneMehrat Church (east of ShiroMeda), and near ALERT large concentration of deeply weathered fractures that have different orientation and opening increases the overall water transmitting properties of the rock body. On the other hand, the degree of weathering and associated fractures is less developed in the lava flows that outcrop in the central and western part of the study area. The young porphyritic basalt in the southern parts of Addis Ababa varies from massive to fractured type. Aphanitic basalts dominantly cover the southern and southwestern parts of Addis Ababa vary from massive to vesicular (interconnected) type except near Bole Air Port which is interconnected due to weathering fractures and/or tectonic discontinuity.

Welded tuff: According to Davis (1966) welded tuffs have medium to low primary porosity and very low permeability. Thus the water circulation and storage capacity of welded tuff depends on the secondary porosity and permeability developed through fracturing and weathering processes. Unlike in the flat-laying areas of southern and southeastern and along most river valleys parts of Addis Ababa in which the welded tuff are deeply weathered In most places the welded tuffs are fresh to slightly weathered. Therefore, in most localities welded tuff developed good secondary permeability largely from open fractures and to some extent from weathering zone. When there is high degree of fracturing and weathering, welded tuffs have the capacity to hold water and become a productive aquifer.

Sililic lava flows and domes: The rhyolitic and trachytic lava flows are mostly considered as impervious rocks. The water storage and transmitting capacity is thus largely dependent upon secondary porosity and permeability.

In the western parts of Addis Ababa weathering deeply obliterated the rhyolite that occurred in gentle slopes of Entoto. The weathering fractures and weathering zone significantly modify the limited primary porosity and permeability of rhyolitic lava flows. On the other hand, the rhyolitic lava flows outcrop in eastern parts of Entoto ridges is slightly weathered and less fractured. Therefore, in some place where the rhyolitic lava flows are intensively weathered and highly fractured, infiltrated water through fractures feeds the aquifers that lie on flat-laying areas. In slightly weathered massive part most of the precipitated water is readily lost as runoff.

The trachytic lava flows cover the foothills and moderately dipping topography of the southern and southwestern parts of Addis Ababa is slightly to moderately weathered and intersected by fractures. The fractures separate the flows into different columns, which may extend to the bottom of the flow.The occurrence of major tectonic displacement and deep weathering zone in trachytic lava flows strongly changes the hydraulic characteristics of the rock and minor fractures have local permeability effect. The trachy-basalts outcrop in the western parts of Addis Ababa, around Repi and General Wingate School are slightly weathered and intersected by fractures result in minimum water infiltration capacity.

3.5.1.2. Intergranular porosity

Intergranular porosity in the study area is mainly associated to the volcanic activity and /or weathering and erosion processes. Alluvial sediments are deposited in the southern and southwestern parts of Addis Ababa along the channel and terrace of the major valley. It is a loose material consisting of clay, silt, sand and gravel in different proportions. The thickness of alluvium deposits varies from place to place depending on the topographic variation in the area. The primary porosity and permeability in alluvial sediments result from voids between the grains and the magnitude in turn depends on the size, shape, sorting and packing of grains. The alluvial sediments in Addis Ababa are poorly sorted, highly porous and permeable which may store appreciable amount of water and characterized by high water infiltration capacity

The black cotton soils in the south have a swelling and shrinkage properties. In the dry season cracks that have different aperture and lateral extent commonly observed. The infiltration capacity of black cotton soil thus become high in the beginning of the rainy season and reduces when the amount of precipitation increase. As a consequence the black cotton soils become saturated and act as impervious materials. On the other hand when clay is not a dominant constituent of the soil, relatively there is a constant infiltration of water in the rainy season depending on other different factors.

The two major faults i.e. east west running fault at Entoto and NE-SW oriented Filowha fault changes the topography of Addis Ababa and its surrounding significantly. The occurrence of many springs at the foot of the former and thermal water along the latter is indicating conducive nature of these faults. Moreover, during faulting associated fractures and fissures developed on different lithologies modify the hydrogeological characteristics of the rock units affected by the fault. Paleosols are interbeded with successive lava flows and/or unconsolidated materials. They are made of clayey fragments and are less permeable and act as a confining bed. The main aquifers in the project area can be categorized into three groups Tamiru (2004).

- Shallow aquifer: made of weathered volcanic rocks and alluvial sediments.
- Deep aquifers: made of fractured volcanic rocks that tap fresh ground water.
- Thermal aquifer: that is located at depth greater than 300m.

Generally the Occurrence of groundwater in study area is associated mainly to the volcanic rocks and minor alluvial aquifers do exist along the banks of both Big and Little Akaki rivers. These Volcanic aquifers have primary porosities like vesicles and joints and secondary porosities like faults, fractures & fissures produced as a result of tectonic activities and weathered zones. In the volcanic rocks groundwater circulation and occurrence is associated with these porosities while in the alluvial aquifers, it is in the interstitial spaces in between the sediments. The geometry of the aquifer systems in the area is highly variable, discontinuous and not well defined. In most area, the volcanic aquifers show semi- confined to unconfined nature which in few area (kerchelie and kality), confined aquifers are penetrated. Correlation of the litho-hydrostratigrahic units is very difficult and yet not established. The Potentiometric surface indicates that the groundwater is in connection with the surface water. Thus the base flow of the rivers is contributed from the groundwater in some part and contributing to in other part of the area. As a result of the variability and complex nature of the volcanic aquifers in the catchment area, the hydraulic properties of the aquifers are also highly variable. From the hydraulic characteristics of the aquifers, it is clear that aquifer parameters are lower in the upper & western part of the catchment area, relatively higher in the central, southern and south-eastern part and extremely high at Akaki well field.

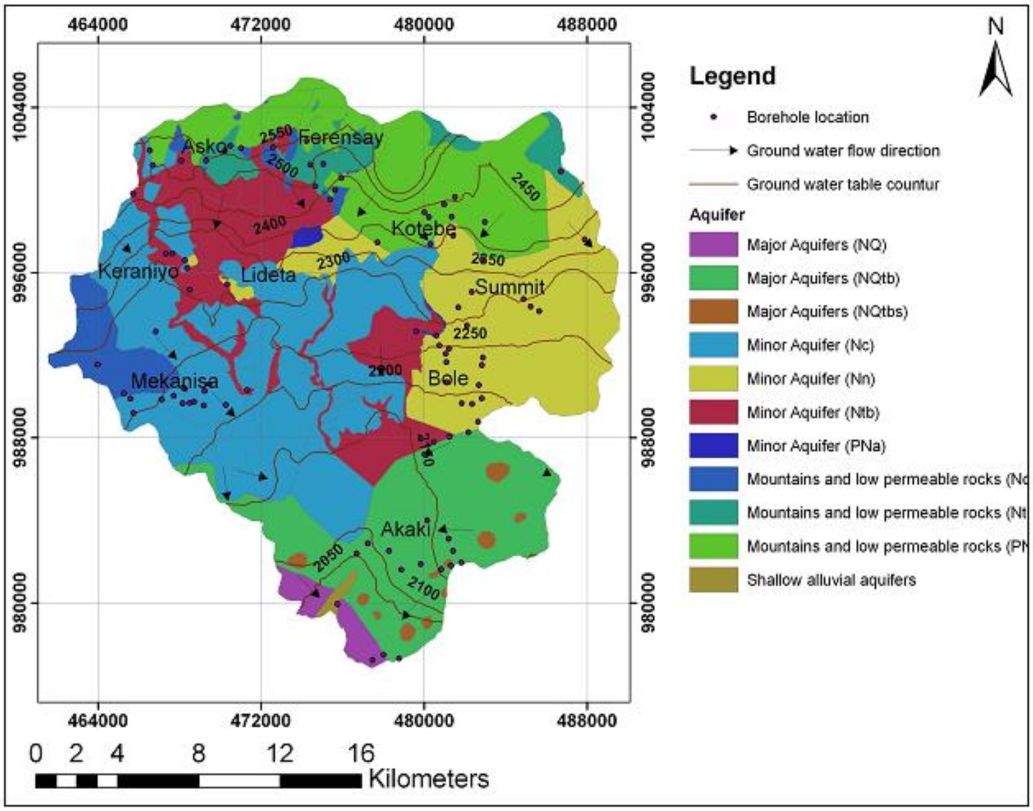

Fig3.5: Simplified hydrogeological map of study area (after ShilimaAbebe, 2011)

3.5.2. Groundwater flow

Tamiru (2004). The movement of water between surface and groundwater provides a major pathway for chemical transfer between terrestrial and aquatic systems. This transfer of chemicals affects the supply of carbon, oxygen, nutrients such as nitrogen and phosphorus and other chemical constituents that enhance biogeochemical processes on both side of the interface. Nearly all-surface water features (streams, lakes, reservoirs, wetlands, and estuaries) interact with groundwater. This interaction takes different forms. In many situations, surface water bodies gain water and solute from groundwater systems while in others surface water is a source of groundwater recharge and causes change in groundwater quality. Pollution of surface water can cause degradation of groundwater quality and conversely pollution of groundwater can degrade surface water.

According the Tenalem et al, (2008), UNESCO, (2003) in the akaki catchment the groundwater movement direction is dominated by north-south and east-west flow. The flow lines converge towards the southern parts of the investigated area. Besides, SEURECA (1990) stated groundwater flow from Southwest to southeast in western parts of the city and from east to west in the eastern parts of the city. In some localities, however, the groundwater flow direction changes, mostly towards the nearby streams. The study area as part of the akaki catchment also follows the same groundwater flow direction. In general the groundwater movement is sub parallel to the surface water flow direction and more or less controlled by the topography of the area.

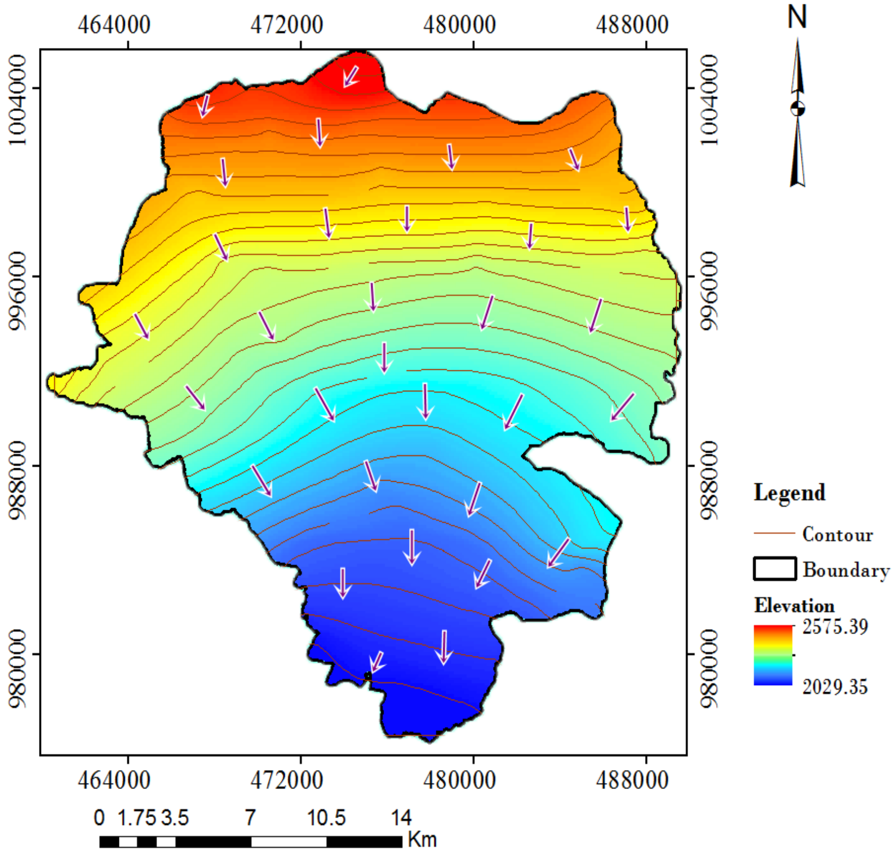

Fig3.6: conceptual groundwater flow

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4. RESULT AND DISCUSION

Apart from the anthropogenic activities, natural geological and geochemical environment may also give rise to undesirable or toxic properties through a deficiency or an excess of various elements to groundwater which also provides beneficial mineral content and bio-essentials.

4.1 Surface water and sediment contamination

The growing threat to the natural environment caused by oil products due to leakage from tanks and pipes, truck tanks, during distribution process as well as by car and railway transport and petrol station is growing. These oil products, including petrol will modify the physico-chemical and biological properties of the water and soil which in turn affects the quality of surface and ground water and that these products are potentially dangerous for human health.

Sediment pollution due to petroleum products: gasoline, diesel and heavy oils as well as their possibility of groundwater contamination is one of the major currently environmental issues for great concern due to the toxicity of some volatile organic compounds and semi-volatile organic compounds present in these fuels. A sediment contamination could be produced by petroleum products spill and leaks related to activities of refinement and fuel supply at petrol stations. Although pipelines and tanks are designed to avoid this kind of accidents, the large amount of fuel dispensed at petrol stations during the years which are operating may cause a very important damage in the surrounding area.

In Addis Ababa improper management and handling of fuel in petrol stations related to activities such as car wash, lubricant utilization, fuel distribution, machine maintenance (garage) are the main source of Surface water and sediment organic contaminants. Different cleaners are used in order to clean car bodies and engines. In most gas stations these organic cleaners, liquid waste after washing and maintenance, are dumped in open pits or flow in open channel to the surrounding areas. Letter on these liquid wastes will be mixed with surface water or incorporated with sediments and change the chemistry of the surface environment.

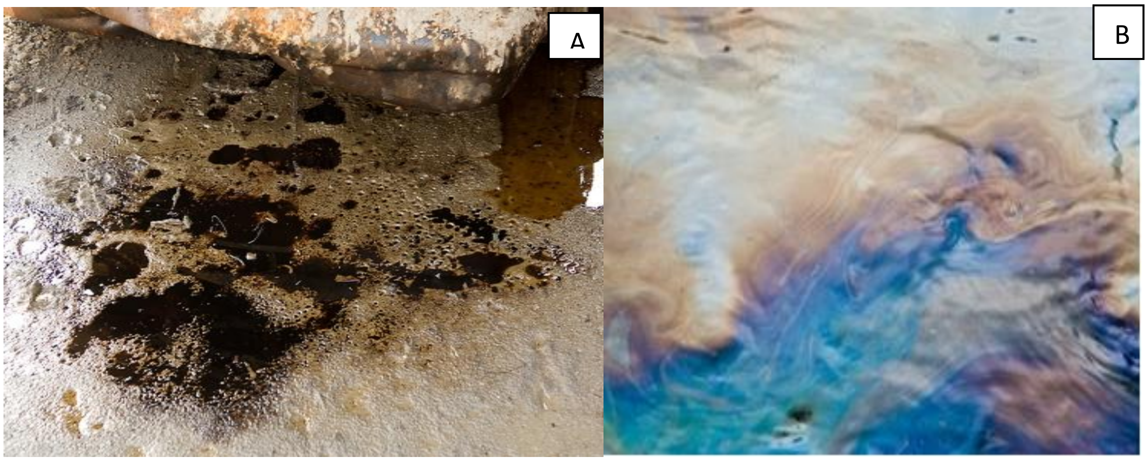


Figure 4.1: organic contaminants: (a) on surface sediment after engine cleaning (b) mixed with flowing stream showing different colors.

Hence a small drop of fuel pollutes large, each drop from nozzle during serving many customers will contribute significant amount of organic matter to the geological environment. In the study area in most of gas station these organic matter reach the surface will latter washed by rain water or cleaned out of the station and enter to the surface water or sediment as contaminant. In addition to this, many organic contaminants are introducing from leaking temporary surface thanks and lubricant containers which again pollutes the environment.

Figure 4.2 organic contaminants from temporary surface tanks

4.2 PHYSICO-CHEMICAL ANALYSIS

Analysis was carried out for various water quality parameters such as Eh, pH, electrical conductivity (EC), total dissolved solids (TDS), calcium (Ca^{2+}) magnesium (Mg^{2+}), sodium

(Na^+), potassium (K^+), chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{-2}), iron (Fe), floride (F^-) using standard method.

4.2.1 Data Availability and Quality

After review and collection of existing chemical data of boreholes from different organizations, field work was carried out to fill the data gap. During the field work in-situ measurement of EC, PH, TDS, and temperature were made to account the physico-chemical change that could take place together with observation of some major structures of geological and hydrogeological importance. Water samples collection for chemical oxygen demand (COD) and organic carbon (OC) analysis were carried out from different localities to represent the study area.

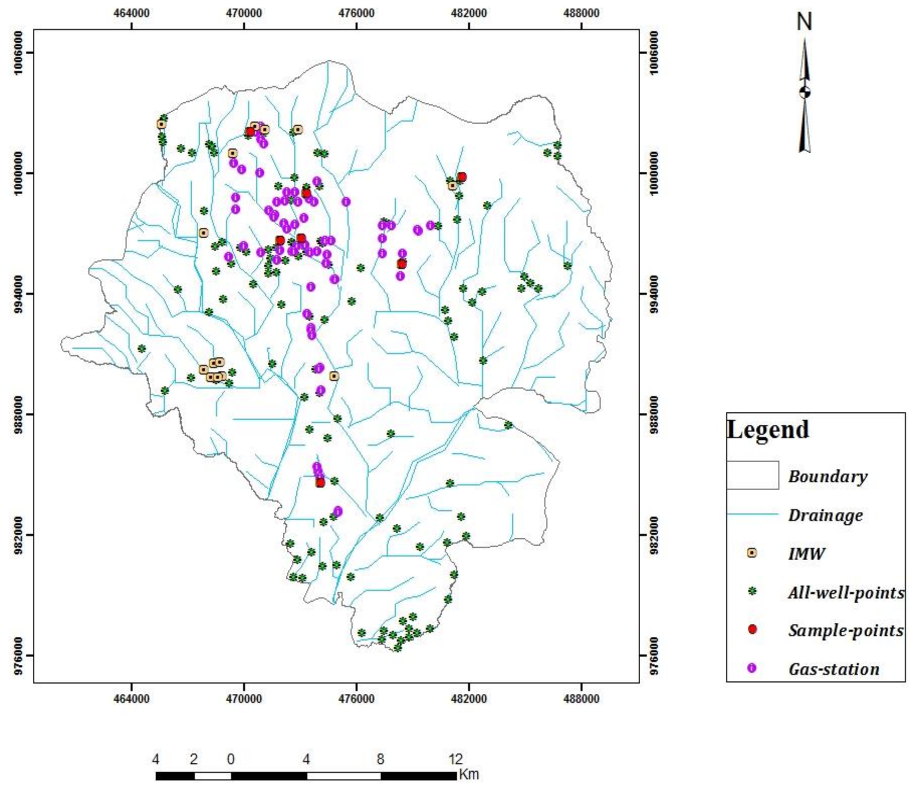


fig4.3: Data distribution map of the area

The collected Hydrochemical data has to be checked before using for interpretations of hydrochemical studies. All solutions must be electrically neutral i.e. in a given volume of water sample that has been analyzed for inorganic constituents, the sum of all the cations (meq/ l) nearly equal to the sum of all the anions (meq/ l). If the analysis reveals the presence of cations and anions in solution, an equation for the electroneutrality condition may be written as:

$$\text{Electroneutrality} = \frac{\Sigma\text{Cations} - \Sigma\text{anions}}{\Sigma\text{Cations} + \Sigma\text{anions}} * 100$$

When the results of a water analysis are closed into the above equation, it should prove to be close to equality. If the two sides of this equation differ by more than a few percent, either the analysis is mistaken or one or more significant ions were omitted from the analysis. Thus, after charge balance calculation, those hydrochemical analysis results with charge balance error less than 5% is regarded as acceptable however, in very dilute or saline water, up to 10% error may be considered as acceptable due to the errors introduced in measuring major ions in dilute groundwater or in the multiple dilution require for analysis of Concentrated groundwater (Fetter, 2001). Thus, the chemical data with charge balance error greater than 10% and those missing any one of the four major cations and anions were discarded. In this study therefore, 98.5% of the data falls in the acceptable 5% criterion and the remaining 1.5% falls in the range of 5-6% criterion.

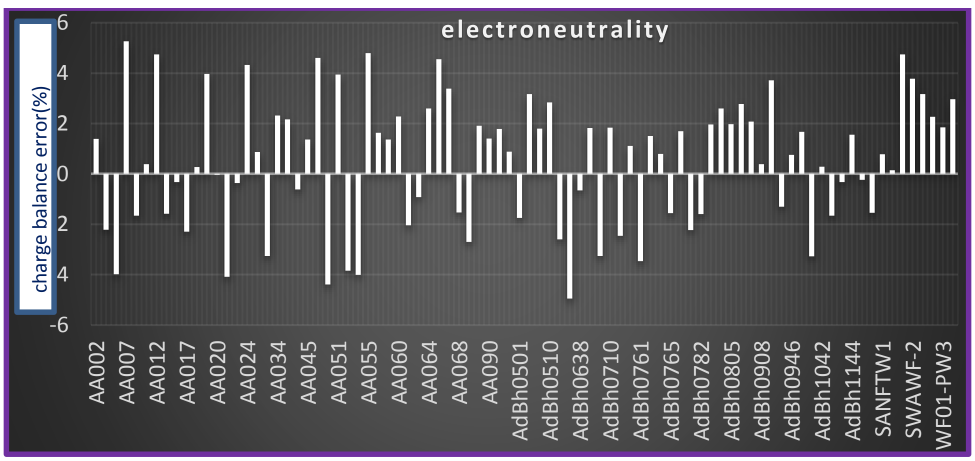


Figure 4.4: Charge balance error graph of hydrochemical data

4.2.2 PH, EC and TDS

PH: The pH is an important variable in water quality assessment as it influences many biological and chemical processes within a water body and all processes associated with water supply and treatment. It is a measure of the acidity of groundwater: the lower the pH, the more acidic is the water. A guideline value pH range of 6.5–8.5 was established for drinking water (WHO International Standards for Drinking-water, 1984).

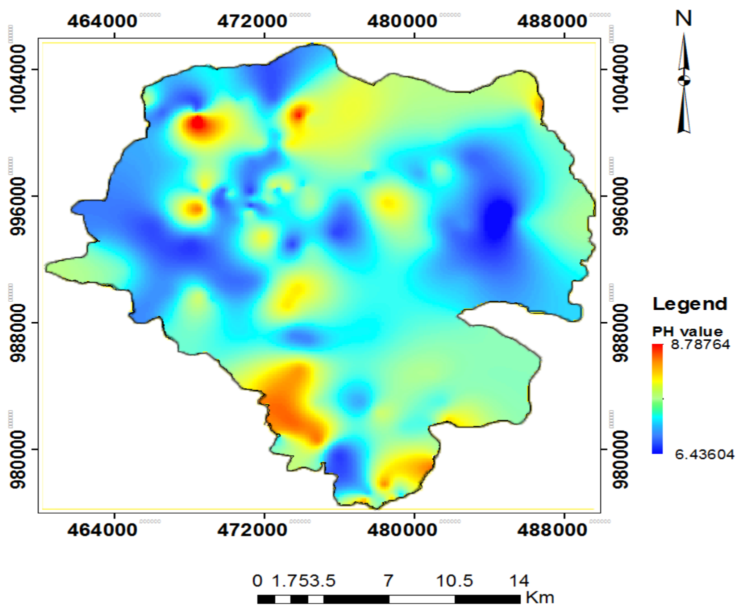


Figure 4.5: PH map of the area

Most ground waters found in the study area have pH values ranging from about 6 .46 to 8.78 i.e., between the range of WHO recommended unit.

Electrical conductivity (EC): Conductivity, or Specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids mostly mineral salts. The degrees to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution all have an influence on conductivity. Conductivity is expressed as micro siemens per centimeter (µS/ cm) and, for a given water body, is related to the concentrations of total dissolved solids and major ions. The conductivity of most freshwaters ranges from 10 to 1,000 µS /cm but may exceed 1,000 µS /cm especially in polluted waters, or those receiving large quantities of land run-off.

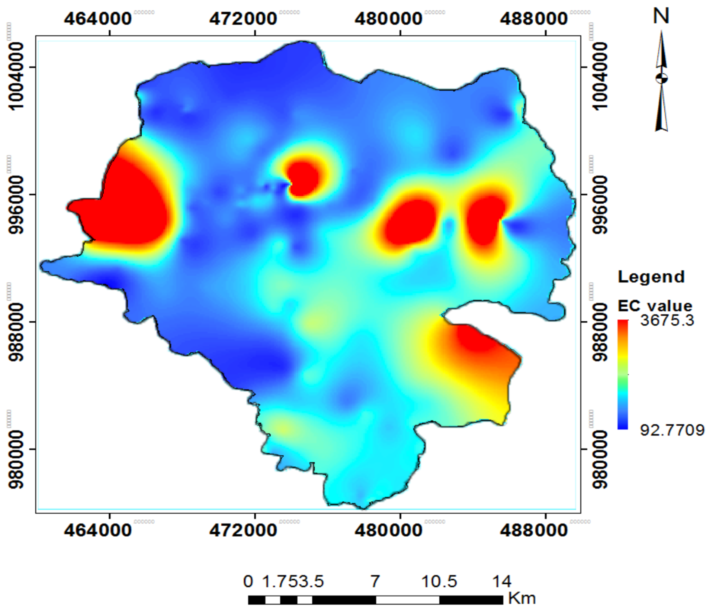


Figure 4.6: EC map of the area

In the research area, most of the water samples have low conductivity ranging from 92 to 800 µS/cm which is in the range of the WHO allowable limit and the EC value increases to water samples near high discharge (filwoha fault) zones and waste disposal site (Addis Ababa waste site) that may attain values greater than 2500 µS/cm.

Total Dissolved Solids (TDS): TDS is a measure of the amount of material dissolved in water. This material can include carbonate, bicarbonate, chloride, sulphate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. Factors that control the dissolved minerals in groundwater include: (a) The types of minerals that make up the aquifer (b) Residence time of the groundwater in the aquifer, and (c) The chemical state of the groundwater.

The result of laboratory analysis indicate that TDS was lower for Boreholes in the highland part of the area concentrations indicating the rock-water interaction (residence time) is short and the resistance of volcanic rocks to weathering and the value increases towards boreholes in the lowland part indicating residence time is long. The maximum value is2085 mg/l, and few samples exceed the guideline value for WHO (1000mg/l) from water sample of filwoha fault zone and waste disposal site.

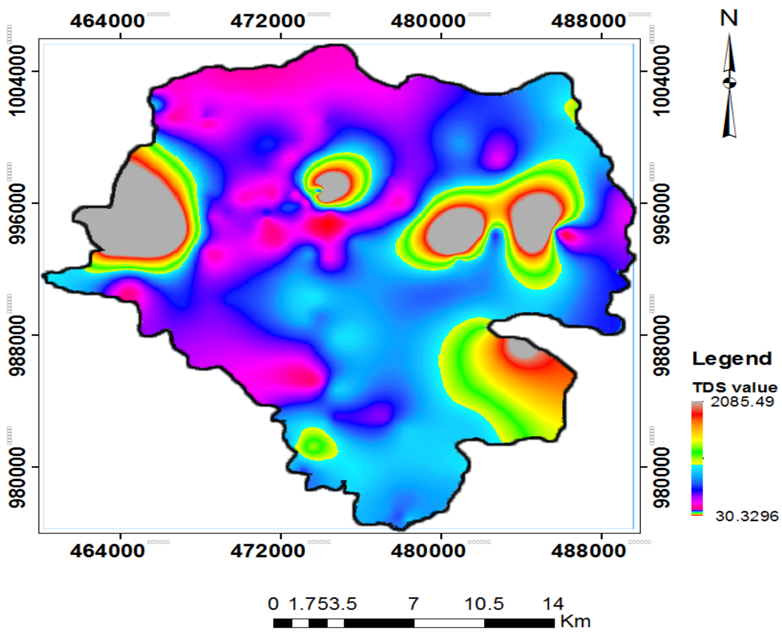


Figure 4.7: TDS map of the area

Depending on international water quality guide line (WHO) and Ethopian Water quality standard the water of the study area categorized as fresh (TDS < 1,000 mg L-1) in most part of the study area except in few well having TDS value 2070 mg-l.

Major ions

Groundwater becomes mineralized due to rock-water interactions resulting in the dissolution of certain minerals and chemical elements which remain in solution in the groundwater. The degree of dissolution depends on the length of time that the rock / water is in contact, the length of the flow-path through the rock, the solubility of the rock materials and the amount of dilution by fresh recharge water. Major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, and $HCO3^{-}$) are naturally very variable in surface and groundwater due to local geological, climatic and geographical conditions.

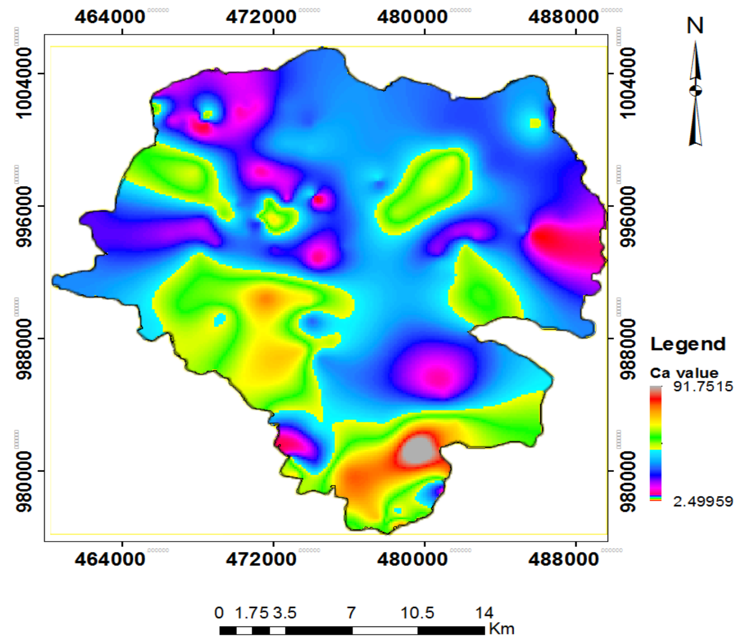
Sodium: All natural waters contain some sodium since sodium salts are highly water soluble and it is one of the most abundant elements on earth. Increased concentrations in surface and ground water may arise from sewage and industrial effluents and from the use of salts on roads to control snow and ice. The latter source can also contribute to increased sodium in groundwater. Concentrations of sodium in natural surface waters vary considerably depending on local geological conditions, wastewater discharges and seasonal use of road salt. Values can range from 1 mgl^{-1}or less to 105mgl^{-1}or more in natural brines. The WHO guideline limit for sodium in drinking water is 200 mgl^{-1}. Many surface waters, including those receiving wastewaters, have concentrations well below 50 mgl^{-1}. However, ground-water concentrations frequently exceed 50 mgl^{-1}.

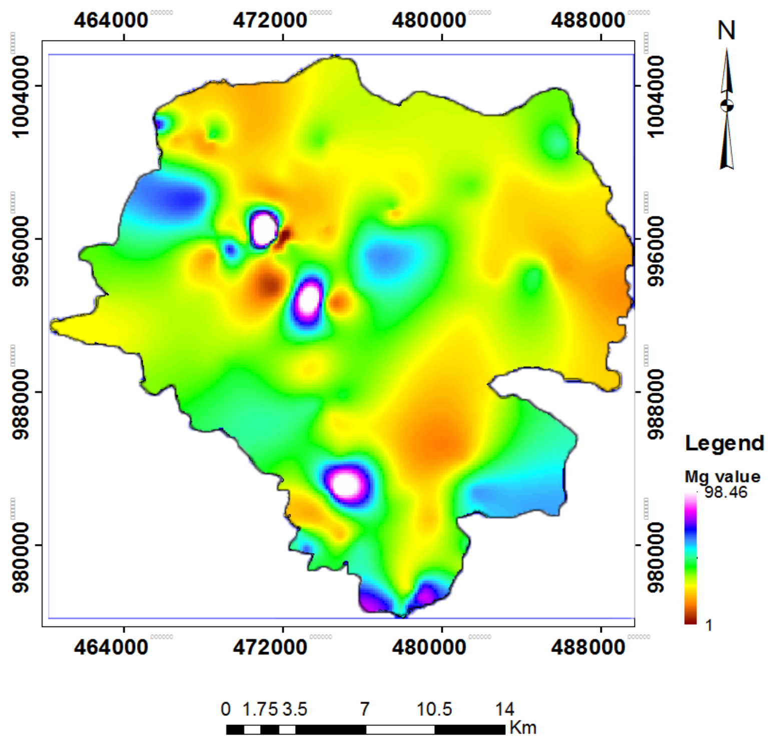
***Potassium*: **Potassium (K^+) is found in low concentrations in natural waters since rocks which contain potassium are relatively resistant to weathering. However, potassium salts are widely used in industry and in fertilisers for agriculture and enter freshwaters with industrial discharges and run-off from agricultural land. Potassium is usually found in the ionic form and the salts are highly soluble. It is readily incorporated into mineral structures and accumulated by aquatic biota as it is an essential nutritional element. Concentrations in natural waters are usually less than 10mg l^{-1}, whereas concentrations as high as 100 and 25,000 mg l^{-1}can occur in hot springs and brines, respectively.

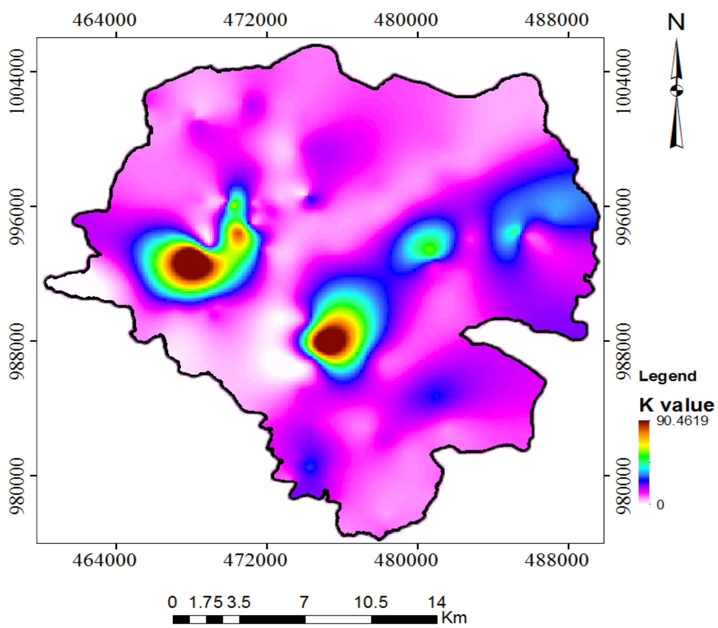
Calcium: Calcium is present in all waters as Ca^{2+} and is readily dissolved from rocks rich in calcium minerals, particularly as carbonates and sulphates, especially limestone and gypsum. The salts of calcium, together with those of magnesium, are responsible for the hardness of water. Industrial, as well as water and wastewater treatment, processes also contribute calcium to surface waters. Acidic rainwater can increase the leaching of calcium from soils. Calcium compounds are stable in water when carbon dioxide is present, but calcium concentrations can fall when calcium carbonate precipitates due to increased water temperature, photosynthetic activity or loss of carbon dioxide due to increases in pressure. Concentration of calcium in normal potable groundwater generally ranges between 10 mg/L and 100 mg/L (Hem 1985) typically For waters associated with carbonate-rich rocks, concentrations may reach 30-100 mg l^{-1}.The concentrations of Ca2+ in the area is within the normal range according to WHO (5-91.5 mg/L).

Magnesium: Magnesium is common in natural waters as Mg^{2+}, and along with calcium, is a main contributor to water hardness. Magnesium arises principally from the weathering of rocks containing ferromagnesium minerals and from some carbonate rocks. Magnesium occurs in many organometallic compounds and in organic matter. Natural concentrations of magnesium in fresh-waters may range from 1 to > 100 mgl^{-1}, depending on the rock types within the catchment.

Although magnesium is used in many industrial processes, these contribute relatively little to the total magnesium in groundwater.







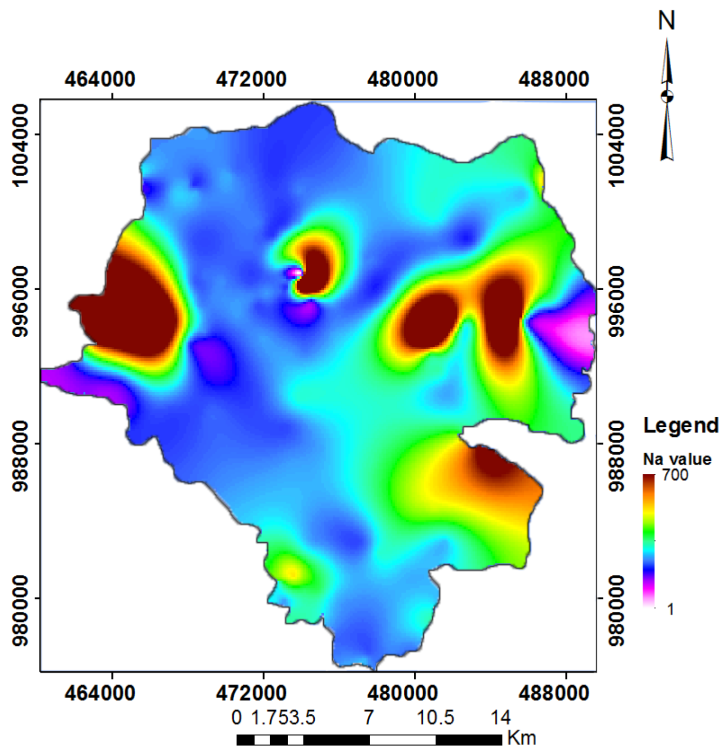


Figure 4.8: concentration map of some cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} respectively)

Bicarbonates: Bicarbonates (HCO3) are the product of weathering product of basaltic lithology. The presence of bicarbonates (HCO_3^-) influences the hardness and alkalinity of water. In areas of non-carbonate rocks, the HCO_3^- originate entirely from the atmosphere and soil CO_2, whereas in areas of carbonate rocks, the rock itself contributes approximately 50 per cent of the carbonate and bicarbonate present. The relative amounts of carbonates, bicarbonates and carbonic acid in pure water are related to the pH. Bicarbonate concentrations in surface and ground waters are usually < 500 mg l-1, and commonly < 25 mgl^1.

Chloride: Most chlorine occurs as chloride (Cl^-) in solution. It enters surface and ground waters with the weathering of some sedimentary rocks (mostly rock salt deposits) and from industrial and sewage effluents, and agricultural and road run-off. High concentrations of chloride can make waters unpalatable and, therefore, unfit for drinking or livestock watering.

In pristine freshwaters chloride concentrations are usually lower than 10 mg l^{-1} and sometimes less than 2 mg l^{-1}. But in the study area concentration of chloride ranges between 0.8-95 mgl^{-1} and most of the wells have values grate than 10 mgl^{-1}. This higher concentrations occurs because the study area urban area which can introduce high amount of chloride from different sewage and other waste outlets. Apart from this, irrigation drains can be source of chloride in groundwater. As chloride is frequently associated with sewage, it is often incorporated into assessments as an indication of possible contamination or as a measure of the extent of the dispersion of sewage discharges in water bodies. According to WHO chlorine permissible limit is 250 mg/L.

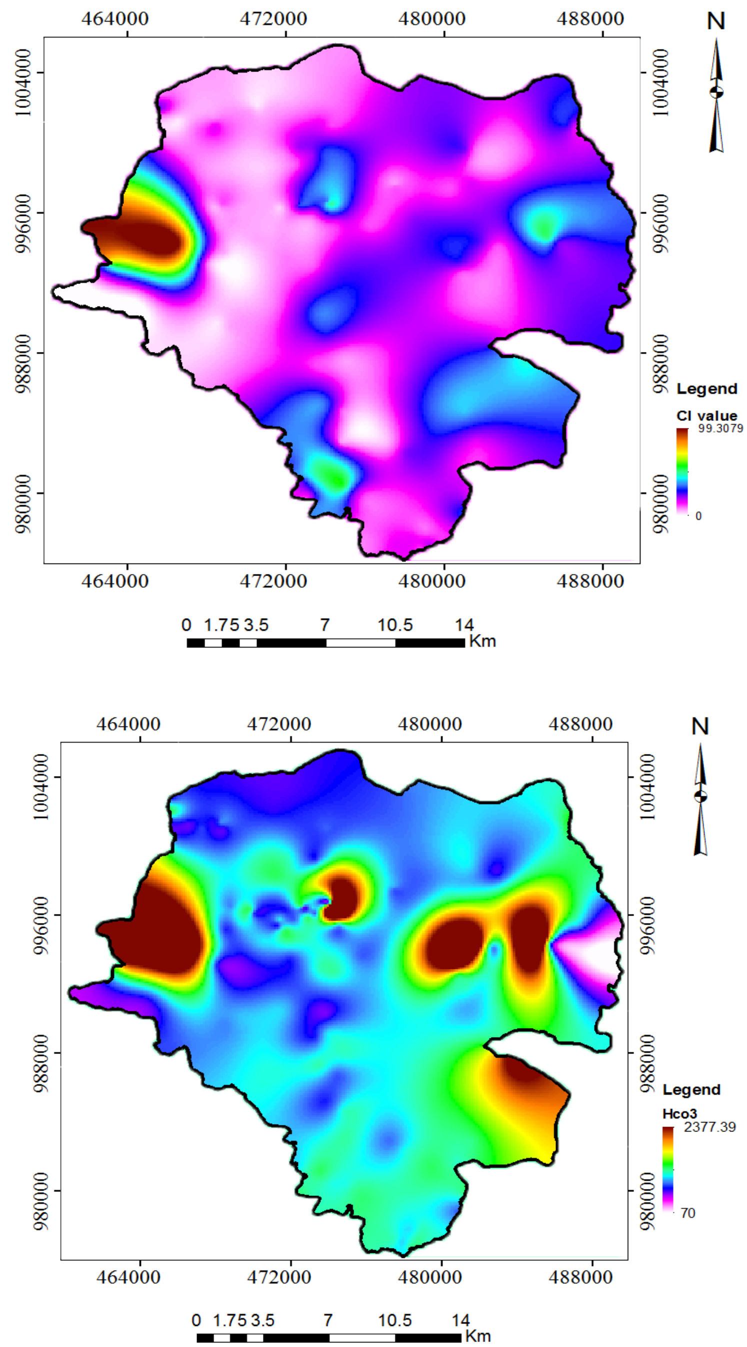


Figure 4.9 concentration map of some anion (Cl^- and HCO_3^-)

4.2.3. Graphical Presentation and Interpretation of Analytical Results of Laboratory Measured Parameters

As described in the geology of the area, the whole terrain on which the study area falls were volcanic rocks mainly basalts, rhyolites, trachytes, scoria, trachy-basalts, and ignimbrites, welded and unwelded tuffs. The composition of the majority of the highland volcanic plateau was silicate minerals of mostly plagioclase feldspars of the albite and anorthite group and pyroxene composition. These minerals were rich in Ca, Mg and Na. Hydrolysis, decomposition and/or leaching of these silicate minerals enriches the water in the highlands by Ca, Mg, and Na cations. These rocks are dominantly affected by fracturing and weathering.

Piper Trillinear Diagram

A Piper diagram is a form of the trilinear diagram that provides a visual representation of the concentrations of major ions in water (Hem, 1992). This diagram can be useful for looking at similarities and differences among water samples.. The total cations and the total anions are set equal to 100% and the data points in the two triangles are projected onto an adjacent grid. This plot reveals useful properties and relationships for large sample groups. The main purpose of the Piper diagram is to show clustering of data points to indicate samples that have similar compositions. From different part of the area groundwater samples are analyzed based on their major cations and anions percentage and the following water types were identified: *"**Ca-HCO3** type, **Ca-Na-HCO3** type, **Na-Ca-HCO3** type, and **Na-HCO3** type of water".*

Generally, the piper plot shows that most of water samples were of Calcium and Sodium Bicarbonate type with small amount of Mg and Cl ions in few water samples.

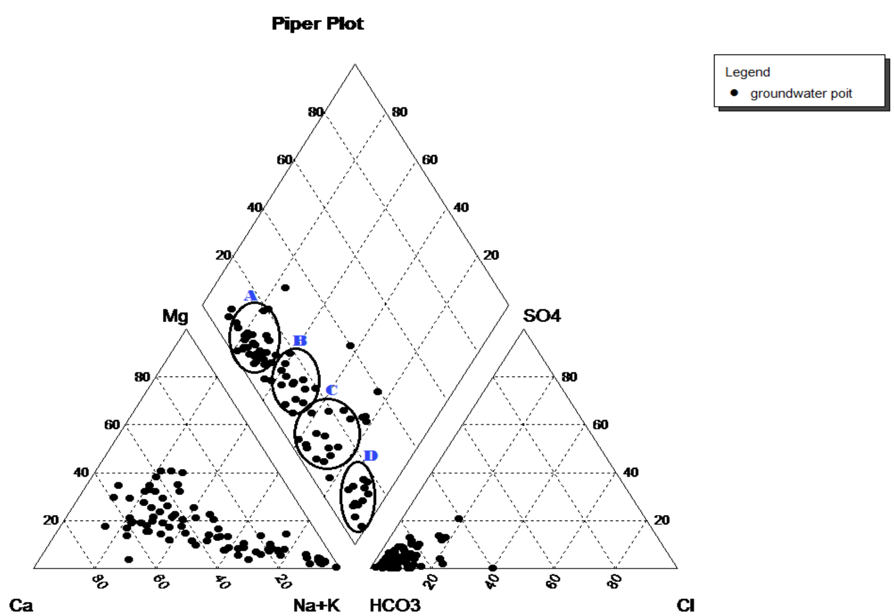


Figure 4.10: piper plots of chemically analyzed water samples of the area

In the study area most water types obtained from laboratory analysis at/or near recharge area have low TDS and most of them were Ca- HCO3 type (in the foot of mountains) evolving down the flow path to Ca-Na and Na-Ca-HCO3 type and finally to dominantly Na- HCO3 water type (in akaki area). The water type differences are the result of the rocks contacted during ground water circulation.

4.2.4 Redox potential (Eh)

The redox potential (Eh) characterizes the oxidation-reduction state of natural waters. Ions of the same element but different oxidation states form the redox-system which is characterized by a certain value. Organic compounds can also form redox-systems. Oxygen, nitrate, iron and sulphate, as well as some organic systems are the most influential in determining Eh. For example, Eh values increase and may reach + 700 mV when dissolved oxygen concentrations increase. The presence of hydrogen sulphide is usually associated with a sharp decrease in Eh (down to - 100 mV or more) and is evidence of reducing conditions. The Eh may vary in natural waters from - 500 mV to + 700 mV. Surface waters and groundwaters containing dissolved oxygen are usually characterised by a range of Eh values between + 100 mV and + 500 mV. The Eh of mineral waters connected with oil deposits is significantly lower than zero and may even reach the limit value of - 500 mV.

Redox potential is determined potentiometrically and may be measured in situ in the field. Considerable difficulty has been experienced by many workers in obtaining reliable Eh measurements. Therefore, the results and interpretation of any Eh measurements should be treated with caution. One approach to determine redox conditions in contaminant plumes is using Redox-sensitive compounds which can be used in at least three different ways: identification of reduced and oxidized conditions: Assignment of redox zones: and Determination of predominant redox reactions.

Initially, oxygen is reduced and so its concentration falls very early in the process. then the nitrate concentration may initially increase as molecular oxygen reduced nitrogen contained in the organic matter. After oxygen is completely consumed, nitrate is reduced by the organic matter and so the concentration of NO_3^- begins to fall. Soon, most of the nitrate is reduced. Iron oxide is then reduced by the organic matter, producing dissolved, divalent Fe. Once all Fe is consumed, sulfate is then reduced. As the concentration of SO_4^{2-} decreases and the concentration of its reduction product, H_2S increases, Fe^{2+} is removed by precipitation as iron sulfides. Eventually, if sufficient organic matter is available, the entire sulfate is consumed and, the only remaining electron acceptor is CO_2, which is reduced to form methane. Late in the process, if the entire sulfide is tied up in sulfide minerals, then the concentration of Fe^{2+} may rise again. A series of redox gradient becomes established in the contaminant plume, with an increase in the redox potential value with distance from the source.

Nitrate and nitrite: The nitrate ion (NO_3^-) is the common form of combined nitrogen found in natural waters. It may be biochemically reduced to nitrite (NO_2^-) by denitrification processes, usually under anaerobic conditions. The nitrite ion is rapidly oxidised to nitrate. Natural sources of nitrate to surface waters include igneous rocks, land drainage and plant and animal debris. Natural concentrations, which seldom exceed 0.1 mg l^{-1} NO_3^-N, may be enhanced by municipal and industrial waste-waters, including leachates from waste disposal sites and sanitary landfills. In rural and suburban areas, the use of inorganic nitrate fertilisers can be a significant source. When influenced by human activities, surface and ground waters can have nitrate concentrations up to 5 mg l^{-1} NO_3^-N, but often less than 1 mg l^{-1} NO_3^-N. Concentrations in excess of 5 mg l^{-1} NO_3^-N usually indicate pollution by human or animal waste, or fertiliser run-off. In cases of extreme pollution, concentrations may reach 200 mg l^{-1} NO_3^-N. The World Health Organization (WHO) recommended maximum limit for NO_3^- in drinking water is 50 mg l^{-1} and waters with higher concentrations can represent a significant health risk. Nitrate occurs naturally in groundwaters as a result of soil leaching but in areas of high nitrogen fertiliser application it may reach very high concentrations (~500 mg l-1 NO3-N). Nitrite concentrations in freshwaters are usually very low, 0.001 mg l^{-1} NO_2^-N, and rarely higher than 1 mg l^{-1} NO_2^-N. High nitrite concentrations are generally indicative of industrial effluents and are often associated with unsatisfactory microbiological quality of water. Determination of nitrate plus nitrite in surface waters gives a general indication of the nutrient status and level of organic pollution. Consequently, these species are included in most basic water quality surveys and multipurpose or background monitoring programs, and are specifically included in programs monitoring the impact of organic or relevant industrial inputs. In the study area the concentration of NO^3 ranges 0.1-42 mg/l which is in the WHO allowable limit. The greater values (>5mg/l) in most part of the area indicates the presence of pollution by anthropogenic activities such.

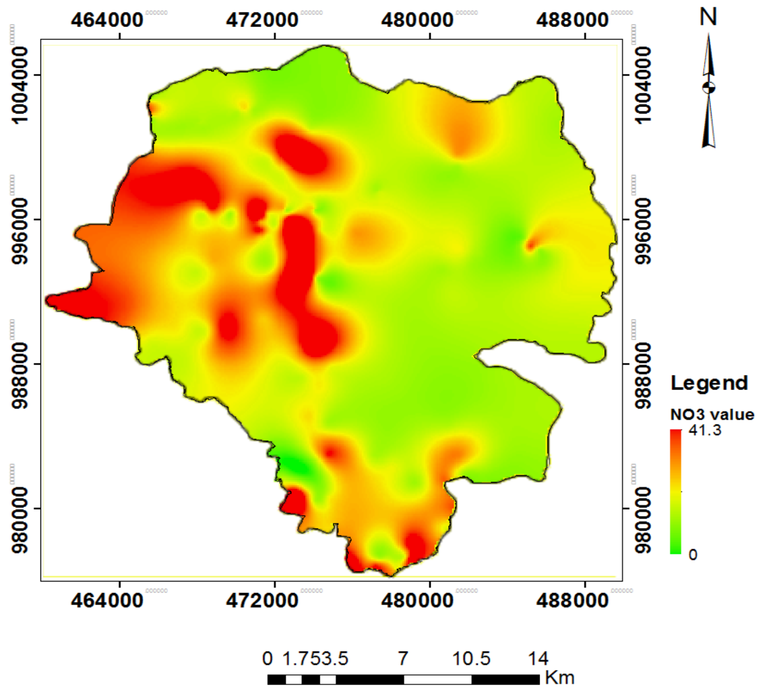


Figure 4.11: nitrate concentration map of the area

Iron: The primary sources of iron in the hydrosphere are the iron minerals in igneous and metamorphic rocks. Among the silicates and aluminosilicates these include olivine, the pyroxene and amphibole mineral groups, and the mica biotite (Deer et al., 1992). Large part of the study area is also covered by olivine-pyroxene rich basaltic rocks which can be the main source iron concentration in groundwater. Iron is largely mobilized and redistributed during the chemical weathering of igneous and metamorphic rocks. Mobilization is chiefly as dissolved Fe (lI) under reducing conditions and as particulate Fe (lIl) hydroxides in oxygenated environments.

The occurrence of iron in aqueous solution is dependent on environmental conditions, especially oxidation and reduction. The extent to which Fe dissolve in groundwater depends on the amount of oxygen in the water and, to a lesser extent, upon its degree of acidity, i.e., its pH. When levels of dissolved oxygen in groundwater are greater than 1-2 mg/L, iron occurs as Fe^{3+}, while at lower dissolved oxygen levels, the iron occurs as Fe^{2+}. If the groundwater is oxygen poor, iron (and manganese) will dissolve more readily, particularly if the pH of the water is on the low side (less than 5). Dissolved oxygen content is typically low in deep aquifers, particularly if the aquifer contains organic matter. At concentrations greater than 0.3 mg/L Fe, could make the water importable.

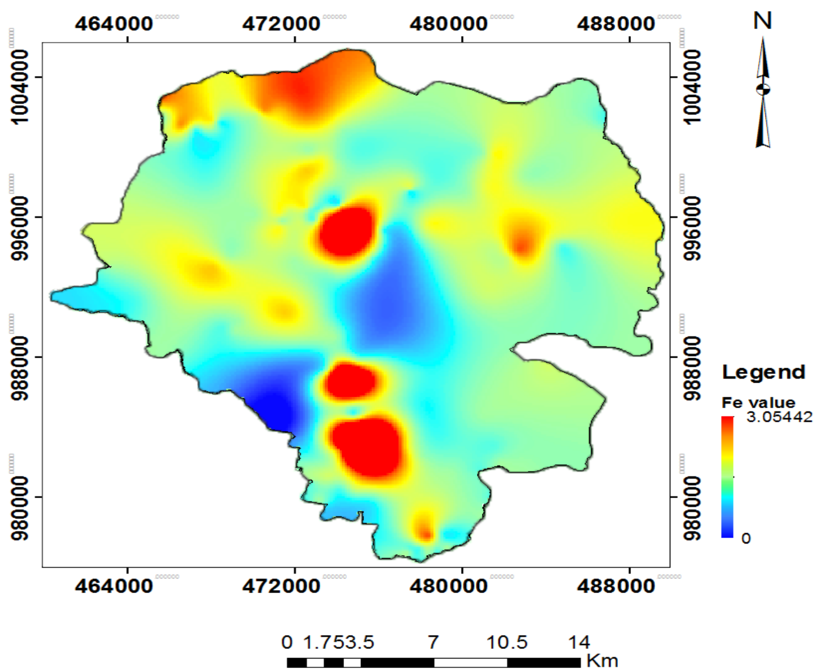


Figure 4.12: iron concentration map of the area

Sulphate: Sulphate is naturally present in water as SO_4^{2-}. It arises from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as pyrite, from sedimentary rocks. It is the stable, oxidised form of sulphur and is readily soluble in water (with the exception of lead, barium and strontium sulphates which precipitate). Industrial discharges and atmospheric precipitation can also add significant amounts of sulphate to water. Sulphate can be used as an oxygen source by bacteria which convert it to hydrogen sulphide (H_2S, HS^-) under anaerobic conditions. Sulphate concentrations in natural waters are usually between 2 and 80 mg/l, although they may exceed 1,000 mg l^{-1} near industrial discharges or in arid regions where sulphate minerals, such as gypsum, are present. Since those minerals are not present in the study area, it not expected to gate high concentration of sulphate in groundwater. The sulphate concentration measured in most wells of the area ranges from1-60mg/l which is within the range of natural water. Few wells have high values ranging up to 100 mg/l.. High concentrations (> 400 mg/l) may make water unpleasant to drink.

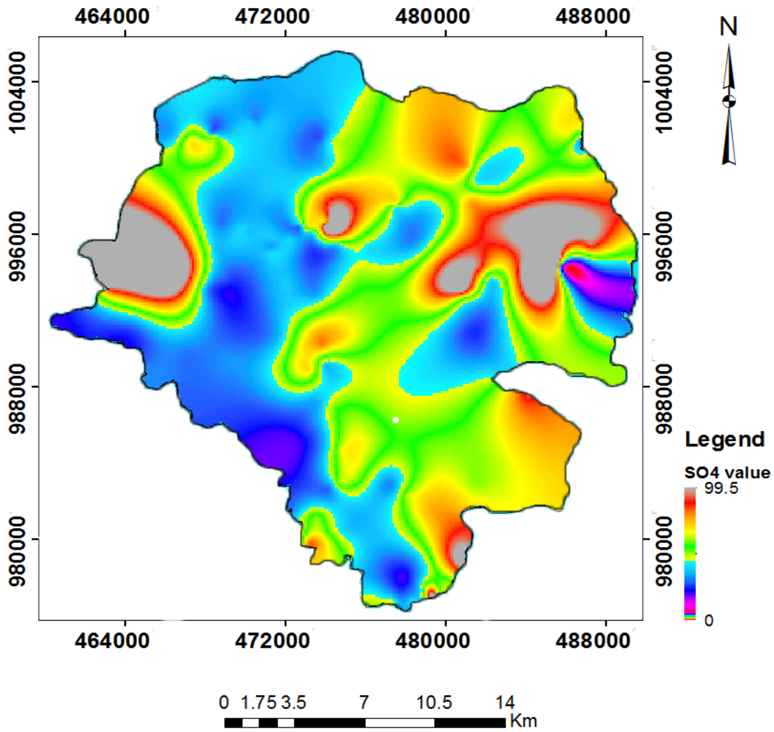


Figure 4.13: sulphate concentration map of the area

An alternative method for identifying the predominant redox processes is measuring dissolved H_2 concentrations in ground water. Hydrogen is continuously produced and consumed by different microorganisms during anaerobic decomposition of organic matter. Anaerobic oxidation of organic matter from complex organic compounds generally goes through a three step process. hydrolyzation of the organic substances, fermentation of this into smaller organic molecules, and then used as electron donors by the bacteria mediating processes. One of the dominant products is H_2. in the area H_2 concentrations ranges from 21 to 294 mg/lwhich indicate redox conditions in a relative sense, in that higher H_2 concentrations are always detected in more strongly reduced ground waters.

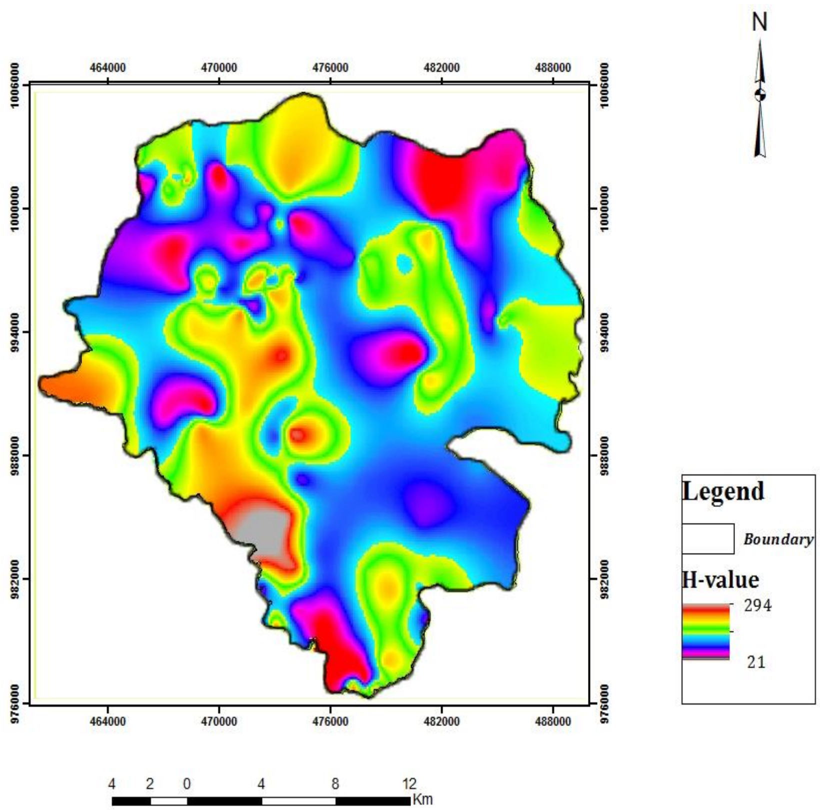


fig4.14: Hydrogen concentration map of the area

4.2.5. *Chemical oxygen demand (COD),* and Organic Carbon (OC)

Chemical oxygen demand (COD): COD analysis is a measurement of the oxygen-depletion capacity of a water sample contaminated with organic waste matter i.e. the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. Specifically, it measures the equivalent amount of oxygen required to chemically oxidize organic compounds in water. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes..

Organic Carbon (OC): Organic matter in groundwater plays important roles in controlling geochemical processes by acting as proton donors/acceptors and as pH buffers, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution/precipitation reactions. Many contaminants which are immobile in aqueous systems can interact with dissolved organic carbon or colloidal organic matter, resulting in migration of hydrophobic chemicals far beyond distances predicted. Although organic matter is often present in low concentrations in subsurface systems, this organic matter can exhibit significant reactivity with contaminants.

ID	X	Y	ELEVATION(m)	EC (mg/l)	TDS (mg/l)	PH	$T^0(^oC)$	Organic Carbon (%)	COD (mg/l)
GW4	470295	1002089	2475	270	180	7.8	23	trace	trace
GW7	471916	996679	2399	200	125	8	23	0.0014	44
GW9	474060	984627	2128	359	234	8	26	trace	trace
GW10	468828	989930	2140	320	192	7.5	25	trace	trace
GW16	478401	995532	2302	181	106	8.3	29.3	trace	trace
GW18	481627	999842	2386	400	240	8	23	0.0007	26.4
GW20	473063	996786	2349	1982	260	8.1	65	trace	trace
GW21	473301	999073	2460	302	213	7.2	25	0.0007	trace

Table 4.1: laboratory result of Chemical oxygen demand (COD), and Organic Carbon (OC)

In general groundwater sample were taken from 8 (GW4, GW7, GW9, GW10, GW16, GW18, GW20, and 21) boreholes and except in borehole GW7 and GW18 the chemical oxygen demand of the other boreholes is insignificant i.e. trace in amount. That means there is no oxygen consumed to chemically oxidize organic compounds in the groundwater. That implies significant amount of organic matter were not introduced to the subsurface environment. Instead there is a clue of groundwater pollution on the other two wells. In groundwater wells GW7 and GW18 the COD measured is 44 mg/l and OC 0.0014 % and 26.4mg/l and OC 0.007 % respectively which relativelly higher than the permissible limit.

4.3. Relationships b/n different parameters

Although many sources and reactions influence the concentrations of the groundwater solutes, the predominant sources of these solutes to ground water in the study area was derived from the hydrolysis, dissolution of silicate minerals, such as plagioclase feldspars and pyroxene group, and ion exchange reactions where by sodium is released to the water in exchange for calcium or magnesium. In areas of non-carbonate rocks, HCO3- , originate entirely from the atmosphere and soil CO2 and hydrolysis of silicate minerals. The whole study area was covered by volcanic rocks and due to absence of non-carbonate rocks, bicarbonate ion was the product of atmospheric and soil CO2 and hydrolysis of silicate minerals. Therefore, bicarbonate water type was the predominant in the study area.

Plots below and (figure 4.14) illustrates the different source for the K^+ from Mg^{2+} and Ca^{2+} (figure4.13) and the dominance of Na^+ and HCO_3^- in the groundwater as a result of in exchange for calcium or magnesium and hydrolysis of silicate minerals respectively.

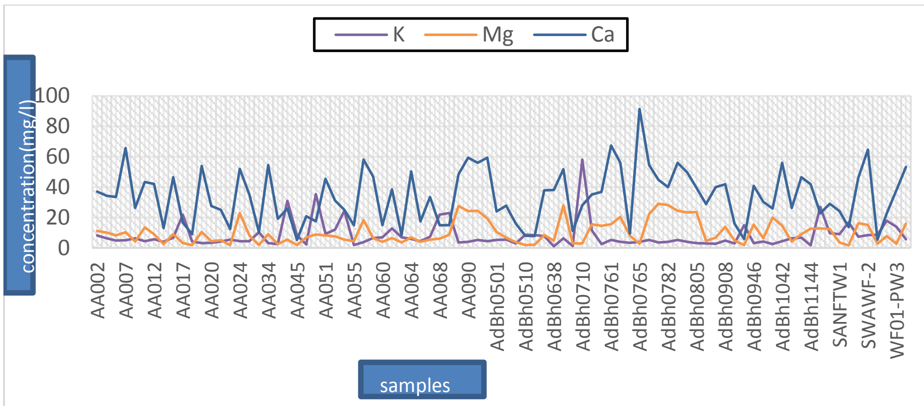


Figure 4.15: Plots of K^+ vs. Mg^{2+} vs. Ca^{2+} against samples ID.

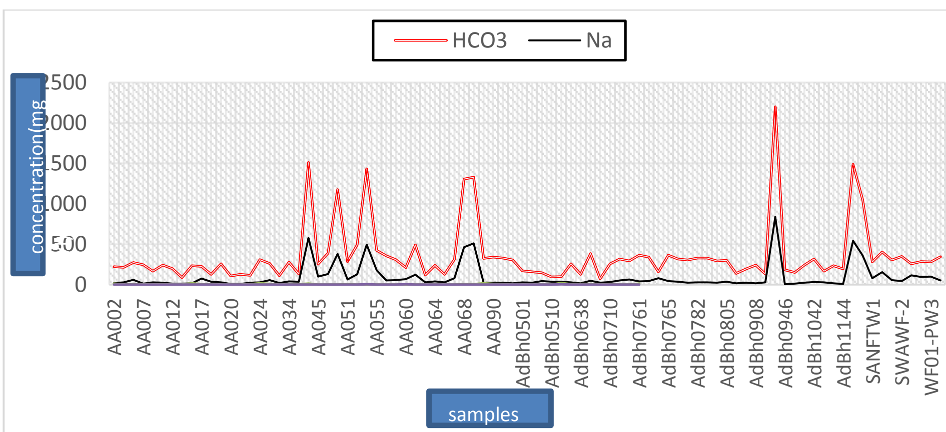


Figure 4.16: Plots of HCO_3^- vs. Na^+ against samples ID.

In the graph below (H_2 vs. SO_4 plot) the lower value SO_4 and higher value of H_2 corresponds to the reducing environment hence sulfate-reducers are less efficient in using H_2 and keep its concentrations higher. So the more reducing environment we have then we can detect high H_2 concentration.

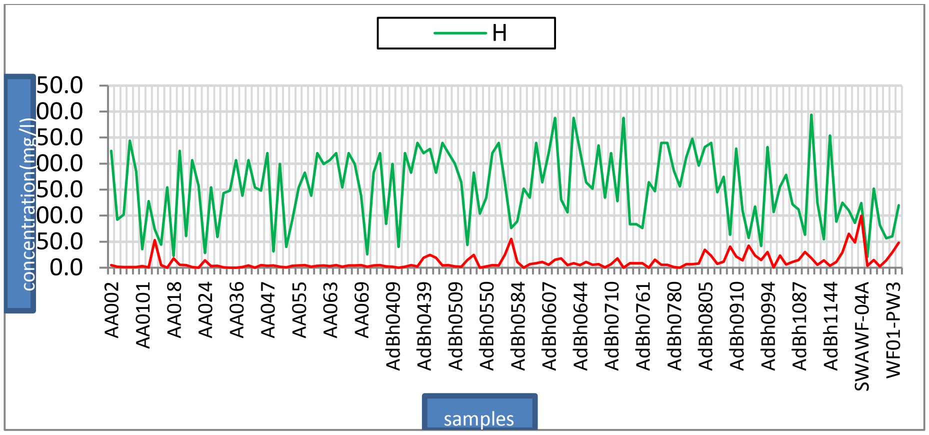


Figure 4.17: Plots of H_2 vs. SO_4^{-2} against samples ID.

TDS vs. elevation plot below indicated an inverse relationship. Samples from Northern part of the area were located at higher altitude and have lower TDS, and those at lower elevations have higher TDS values. As groundwater table is a subdued replica of surface topography, samples to the North were expected to have shallow water table compared to the South ones. As groundwater flows from an area of shallow water table to an area of deeper water table, this was used to infer that groundwater flows from North to South in the area following the surface morphology. In addition to this the local change in TDS value from the slope of the graph along the groundwater flow indicates supply of dissolved constitutes by anthropogenic activities. Fig: 4.17 illustrates also the direct relationship of TDS and EC i.e. the more TDS in groundwater the large conductivity.

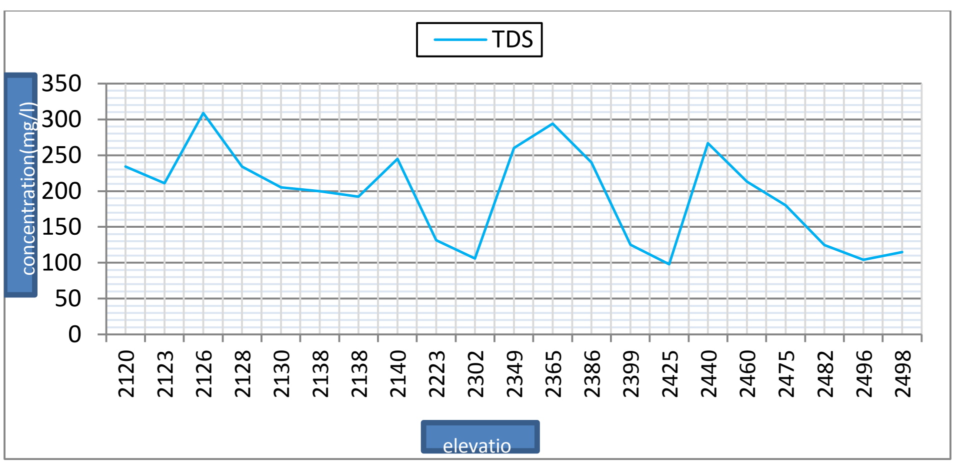


Figure 4.18: Plots of TDS vs. elevation of samples

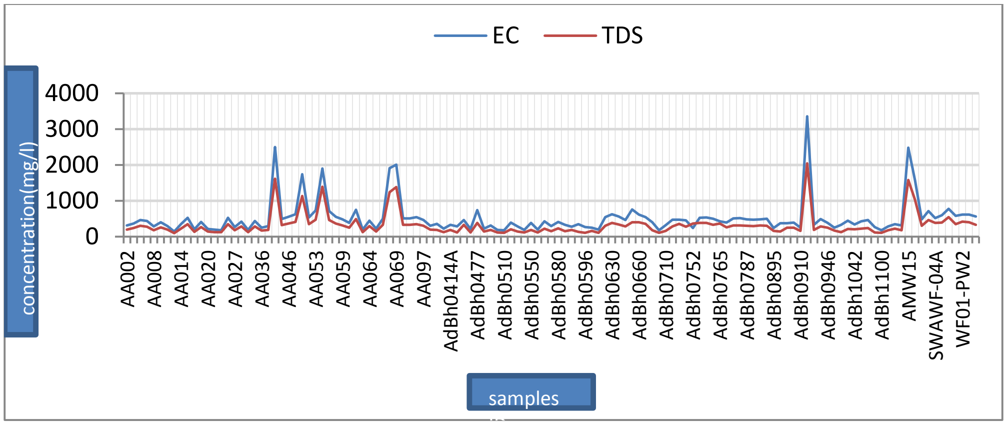


Figure4.19: Plots of TDS vs. EC against samples ID.

Redox sensitive compounds are supposed to be reduced one after another (first NO_3^- then Fe finally SO_4^{-2}) when organic contaminant introduced to groundwater resulted in reduced environment after they are consumed totally. The figure below illustrates the relationship between some of the redox sensitive compounds. So even though lower SO4 concentration is an indication of reducing environment presence of small amount of NO3 concentration makes it is initially absence in the groundwater rather than reduced by organic contaminant.

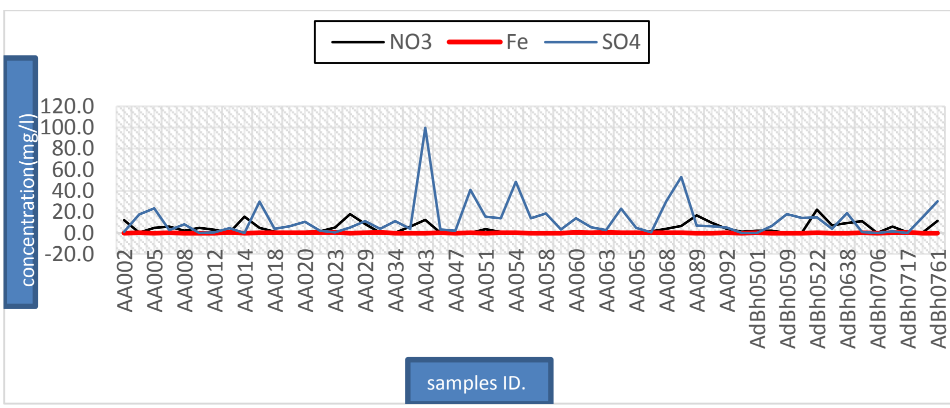


Figure 4.20: Plots of NO_3^- vs. Fe vs. SO_4^{-2} against samples ID

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5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The result of physio-chemical analysis (TDS, EC H, redos-sensitive compounds) from groundwater wells reveals that the source of the organic contaminants in the study area is difficult to identify while physical evidence from gas stations and garages suggests that organic compounds are entering surface and subsurface environment.

In the area petrol station of NOC, Total, Oilibya, Yetebaberut and Kobill were identified with age ranging from 1-25years (young) to above 25 years (old). Most of the gas stations are found at the central part of the city and are characterized by: most of them have three type of fuel (regular, diesel and kerosene); with 30-50m^3 tank volume; 4-5m burial depth; activities such as car wash, lubricant shopping, tire service, garage and cafe; most of them are near stream and no liquid waste treatment mechanism.

Apart from the slightly weathered to highly weathered lithological variations different set of joints, minor and major fault, and poorly sorted, highly porous and permeable alluvial sediments have a role in determining the hydraulic characteristics of the area. I.e. the area is a high recharge zone allowing surface water and contaminant to percolate easily to the ground. On the other hand the fine texture soils (>60% clay) covered most part of the area which have very low to moderate permeability and most underground storage tanks laid on decreases the infiltration rate (may take 10-100years to reach groundwater) of fluid media (organic compounds) to subsurface environment.

Different physical and chemical processes control the movement of contaminants in different zones either by transporting along the flow path or attenuating them. The absence of clear indication of organic contaminant from physio-chemical results in the area can be discussed as: (a) a contaminant entering to the ground will percolate and pass a low permeability soil zone volatilization on the surface, then sorption and dissolution into soil particles. Diffusion, and degradation in the vadose zone and finally advection and diluted to groundwater. All this decreases and distributes significantly and contaminant from a particular station will be consumed totally and may not reach or detected in groundwater. (b) Or there in no leaking underground storage tank and the only contamination is from surface activities carried out in gas station and garages which cannot form a contaminant plume and detected from a particular source.

Potentiometric surface indicates that the groundwater is in connection with the surface water and the groundwater movement is sub parallel to the surface water flow direction and more or less controlled by the topography of the area. Thus the base flow of the rivers is contributed from the groundwater in some part and contributing to in other part of the area. In study area the following water types were identified: *"**Ca-HCO3** type, **Ca-Na-HCO3** type, **Na-Ca-HCO3** type, and **Na-HCO3** type of water*" and the piper plot shows that most of water samples were of Calcium and Sodium Bicarbonate type with small amount of Mg and Cl ions in few water samples.

The variation in TDS and EC value measured in the area are resulted from the high discharge area along filwoha fault zone, high recharge and waste disposal site rather than to the petrol stations found in the area.

Interpretation of redox sensitive compounds and hydrogen concentration indicates there is a range of redox condition from oxic to suboxic but the high value of hydrogen (detected in high reduced environment) is not related either to SO_4 reduction or petrol stations. SO_4 reduction is the beginning of reducing condition and Sulfate-reducers are inefficient in using hydrogen leaving in high concentration.

Based on the nature and volume of aquifer and contaminant, zone of contamination (vados or below water table) and groundwater flow different physical and chemical remediation mechanisms of organic contaminants applied nowadays. Considering these conditions this paper proposes in-situ capping for sediment and air sparging for groundwater. Both of these techniques are coast effective, easily operated, applied to almost all environment and contaminant, and finally are capable of clean or destroy organic contaminant totally without disturbing surface and subsurface environment.

5.2. Recommendation

The research on Geochemical characterization of groundwater and sediment contamination will help to understand the relationship between the pollutants and groundwater conditions, identify the high-risk regions of groundwater pollution, provide basic information on groundwater quality and groundwater resource management, and help the policy maker and managers to develop effective management strategies and protection measures on groundwater. So we can offer some suggestions as following:

Continue to strengthen the research on the fate and transport in hydrogeological conditions. Hydrogeological conditions of the contaminated sites have a vital role in organic pollution of groundwater. We should pay attention to the impact that the thickness and lithology of the unsaturated zone, the groundwater and runoff conditions on the organic pollution investigation and contaminated aquifer restoration. In the protection of groundwater quality, we should take impact of the physical, chemical, and biological characteristics of the unsaturated zone on the transport and degradation of organic pollutants into consideration.

In the future research, the natural attenuation of typical organic contamination in groundwater should be reinforcing research, especially the organic degradation mechanism. Sufficient groundwater level monitoring wells should be placed in the whole area in order to understand the fluctuations and level of contaminants in ground water. This helps to identify contaminant plumes of particular source.

Governmental must take an action adequately and improving the laws, regulations and norms on groundwater quality monitor and assessment and establishing law to restrict areas for sources of organic contaminants and regular inspection of their activities. Strengthening the cross-disciplinary exchanges and studies and establishing the groundwater pollution monitor network.

Finally this work is a clue for the future studies that possible contaminant plumes may exist and properly identify if special monitoring wells for organic contaminants are installed nearby petrol station, garages and other large industries and special techniques and instruments such as chromatography are used to measure organic substances directly.

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Appendixes

Appendix 1:physio-chemical characteristics of some selected borehole (AAWSA and AAWWD 2013)

IDSource	UTME	UTMN	EC	TDS	pH	NH4	Na	K	Ca	Mg	Fe	Mn	Cl	NO2	NO3	F	HCO3	CO3	SO4	PO4	H
AA045	485733	994302	490	318.0	7.2	0.0	102.0	8.2	5.4	2.0	0.1	0.0	23.8	0.0	0.4	3.0	256.2	0.0	3.5	0.6	21.0
WF01-PW17	472460	981553	581	346.0	8.3	0.0	118.0	8.8	5.6	2.9	0.1	0.0	29.9	0.0	2.7	3.0	258.6	12.0	1.6	0.1	26.0
AdBh0919	474175	996550	3359	2049.0	7.5	0.0	840.0	15.0	6.0	2.0	0.4	0.0	43.0	0.1	0.0	21.1	2198.0	0.0	55.0	0.1	76.0
AdBh0510	468400	1001016	176	107.0	8.6	0.0	38.0	8.7	8.0	2.0	0.0	0.0	14.2	0.1	0.3	0.6	98.0	0.0	14.3	0.1	28.0
AdBh0458	474300	992700	213	119.0	7.4	0.0	28.0	7.3	8.0	2.0	0.1	0.1	20.1	0.0	0.7	1.3	327.0	12.0	8.6	0.0	240.0
AA063	465729	1002755	192	128.0	7.4	0.0	30.5	7.1	8.4	3.6	0.6	0.2	8.2	0.0	0.2	0.8	120.4	0.0	2.9	0.2	35.7
AdBh0410A	471300	998200	360	188.0	7.0	0.3	25.0	9.8	8.7	2.0	0.3	0.1	5.0	0.1	4.6	0.7	366.2	9.1	4.1	0.1	154.0
AA018	470218	1001886	209	138.0	7.6	0.2	38.0	4.3	9.2	2.0	0.2	0.0	6.0	0.0	1.2	1.2	129.3	0.0	4.1	0.1	31.5
AdBh0764	480900	978800	500	330.0	8.4	0.0	78.9	3.4	9.6	8.0	0.1	0.0	28.4	0.0	2.7	0.6	158.6	9.0	42.4	0.3	57.0
AA033	471026	1002023	189	126.0	7.4	0.3	22.5	10.5	10.4	2.0	0.4	0.1	5.0	0.0	0.4	0.9	112.2	0.0	3.9	0.1	92.0
AdBh0706	472700	996500	174	106.0	7.2	0.1	23.8	1.3	11.2	3.0	0.1	0.0	28.4	0.0	0.2	0.3	73.2	0.0	0.0	0.1	40.0
WF01 PW1	473595	981135	778	542.0	8.3	0.1	176.0	11.6	11.4	3.6	0.2	0.0	44.6	0.0	4.1	0.6	366.2	9.1	14.5	0.2	43.7
AA023	470504	1002135	181	128.0	7.3	0.0	24.0	5.5	12.6	2.0	0.5	0.1	2.0	0.0	5.4	0.8	117.1	0.0	0.8	0.6	39.9
AA013	466601	1001250	147	98.0	6.9	0.2	12.7	4.1	13.2	2.7	0.5	0.1	1.8	0.0	0.5	1.4	87.8	0.0	4.7	0.1	44.0
SANFTW3	481012	984597	711	460.0	7.6	0.1	154.0	17.0	13.7	1.8	0.1	0.1	35.5	0.0	0.6	1.6	405.0	0.0	14.6	0.3	41.8
AdBh0689	472500	996600	398	178.0	77.0	0.0	23.0	1.8	15.0	2.0	0.3	0.0	20.1	0.0	7.4	4.7	366.2	9.1	4.1	0.2	182.7
AA069	466430	994219	2010	1388.0	6.9	0.5	510.0	23.0	15.1	8.7	0.3	1.2	95.3	0.0	6.8	2.4	1329.8	0.0	53.1	0.5	73.5
AA068	481681	994296	1908	1246.0	7.0	0.6	465.0	22.0	15.1	6.1	0.2	0.0	23.8	0.0	4.1	1.9	1307.8	0.0	30.1	1.1	63.0
AA060	482682	994124	381	250.0	7.0	0.2	68.0	7.0	15.1	4.1	0.6	0.1	10.9	0.0	0.2	5.8	209.8	0.0	14.1	0.1	54.6
AA055	486738	1001391	715	468.0	8.3	0.0	180.0	1.9	15.1	4.6	0.0	0.1	21.8	0.0	0.1	1.6	424.6	9.6	14.1	0.1	56.7
AdBh0509	467200	1001017	188	115.0	7.4	0.0	43.4	3.0	16.0	3.9	0.0	0.0	7.1	0.2	0.1	2.0	146.4	0.0	18.0	0.0	22.5
AdBh0910	468875	993750	251	163.0	7.2	0.0	29.0	3.0	16.0	5.0	0.1	0.0	6.0	0.1	7.4	0.4	134.0	0.0	0.0	0.1	206.8
AA017	487268	995400	524	344.0	7.4	0.4	77.0	22.0	16.6	3.2	0.3	0.1	32.8	0.0	5.0	1.7	225.5	0.0	29.7	0.0	60.0
AdBh0610	473500	992900	547	304.0	6.8	0.0	32.0	2.5	17.4	51.0	0.1	0.1	11.0	0.1	30.0	2.3	307.4	0.0	1.6	0.5	164.0

AA065	468094	1001478	220	140.0	7.3	0.0	30.0	4.6	17.6	4.1	0.3	0.1	7.2	0.1	0.5	0.6	128.1	0.0	5.1	0.0	60.9
AA049	480717	993193	1742	1132.0	7.4	0.2	380.0	35.5	17.6	8.9	0.2	0.1	23.8	0.0	0.2	2.5	1176.1	0.0	40.8	0.2	63.0
AdBh0607	472000	993500	192	103.0	7.9	0.0	36.0	5.7	19.0	3,8	0.1	0.0	8.5	0.1	2.2	0.6	134.0	0.0	4.3	0.2	199.5
AA036	468505	995156	253	166.0	8.3	0.0	37.0	2.6	19.3	2.6	0.1	0.1	8.9	0.0	6.1	3.0	131.8	7.2	3.9	0.1	58.8
AA047	486723	1000881	625	410.0	7.9	0.0	132.0	2.4	21.0	7.1	0.1	0.0	12.4	0.0	0.2	0.9	389.4	0.0	2.3	0.0	81.9
AdBh1095	472500	998700	269	114.0	7.0	0.5	13.0	1.5	22.0	3.1	0.4	0.0	11.0	0.1	4.7	0.2	258.6	0.0	5.0	0.2	220.0
WF01-PW2	474204	980459	618	416.0	8.0	0.1	98.0	18.0	22.8	7.8	0.0	0.0	46.4	0.0	0.7	1.3	285.1	0.0	11.2	0.2	89.3
AMW15	484821	994284	2480	1580.0	6.5	0.2	545.0	27.0	22.9	13.0	0.0	0.1	35.5	0.0	0.2	2.5	1487.2	0.0	65.4	0.6	110.0
AdBh0903	474500	995450	379	142.0	7.6	0.3	42.0	3.8	22.9	6.6	2.0	0.0	14.2	0.1	3.8	0.6	329.4	0.0	5.4	0.2	220.0
AdBh0938	475750	993650	491	289.0	6.8	0.0	39.0	4.0	24.0	15.0	0.0	0.0	20.1	0.0	4.7	1.3	169.1	0.0	11.2	0.1	164.0
AdBh0501	473900	1001050	227	139.0	8.6	0.3	28.9	5.3	24.1	10.7	0.2	0.0	14.2	0.3	2.1	0.2	170.8	12.0	0.0	0.1	104.0
SANFTW1	477819	987018	484	308.0	7.3	0.1	82.0	9.1	24.3	3.7	0.0	0.0	15.5	0.0	0.4	1.0	281.8	0.0	8.6	0.6	76.0
AdBh0433A	471300	995050	290	114.0	7.5	0.5	27.0	3.6	25.0	4.0	0.3	0.0	5.2	0.1	7.4	3.0	258.6	0.0	5.0	0.2	182.7
AdBh0640	474000	989100	467	286.0	7.8	0.4	32.0	6.8	25.0	6.0	0.1	0.1	26.3	0.1	22.3	3.0	258.6	12.0	4.1	0.1	240.0
AA021	472608	1002066	194	128.0	6.9	0.1	9.0	4.3	25.2	5.1	0.6	0.1	7.0	0.0	1.5	0.6	129.3	0.0	2.3	0.2	84.0
AA054	484971	994879	1904	1394.0	6.5	0.0	495.0	24.5	25.2	5.6	0.2	0.0	47.7	0.0	0.3	6.4	1434.7	0.0	48.6	0.4	86.1
AdBh1063	471799	999371	425	220.0	7.6	0.2	26.0	3.5	26.0	5.4	0.2	0.0	7.9	0.0	3.8	0.9	307.4	0.0	4.1	0.1	220.0
AdBh0998	476235	995275	332	129.0	7.0	0.0	26.0	2.6	26.0	20.0	0.0	0.0	11.0	0.1	8.3	0.6	244.0	0.0	5.4	0.0	152.0
AA043	485290	994522	2500	1620.0	6.8	0.0	580.0	31.0	26.0	5.6	0.1	0.1	44.7	0.0	12.6	3.1	1512.8	0.0	99.5	0.8	1240.0
AdBh1105	477515	997474	284	182.0	7.3	0.4	29.5	6.4	26.4	4.3	0.0	0.1	9.9	0.0	2.3	1.1	169.1	0.0	8.3	0.1	83.6
AA008	477715	997474	284	182.0	7.3	0.0	29.5	6.4	26.4	4.3	0.0	0.1	9.9	0.0	2.3	1.1	169.1	0.0	8.3	0.1	83.6
AdBh0540	470100	996100	189	112.0	7.4	0.6	28.0	39.0	27.0	5.0	0.1	0.1	6.1	0.1	4.6	3.0	134.0	0.0	3.9	0.6	220.0
AdBh0550	473100	996400	387	187.0	7.8	0.3	26.0	2.1	27.0	3.8	0.0	0.0	28.4	0.1	5.3	3.0	258.6	12.0	18.9	0.1	220.0
AA020	482994	998429	213	142.0	6.9	0.0	9.8	3.4	27.7	4.6	0.1	0.1	8.9	0.1	1.0	1.7	109.8	0.0	10.8	0.1	88.2
AdBh0507	474300	1001005	310	189.0	7.9	0.1	26.6	5.5	27.8	6.9	0.1	0.0	11.4	0.1	2.1	0.1	158.0	0.0	6.8	0.0	134.4
AdBh0710	470500	994500	320	165.0	7.1	0.1	34.0	58.0	28.0	3.0	0.2	0.0	6.0	0.1	6.1	0.6	258.6	0.0	1.6	0.2	199.5
AdBh0895	460850	985850	244	159.0	6.7	0.0	16.0	3.1	28.8	4.8	0.8	0.0	3.9	0.1	14.0	0.6	141.5	0.0	1.8	0.3	92.0
AdBh0718	474429	986829	457	281.0	7.0	0.0	38.0	9.6	29.0	5.7	2.0	0.1	11.0	0.1	4.7	1.1	169.1	0.0	11.2	0.2	164.0
SANFTW 2	484094	987465	1571	1026.0	7.5	0.8	360.0	9.8	29.0	12.5	0.2	0.0	40.7	0.0	0.3	0.8	1049.2	0.0	29.6	0.2	124.7

AdBh0522	473300	999300	290	145.0	7.9	0.2	18.0	1.3	29.3	3.6	0.3	0.1	18.0	0.0	22.3	4.7	129.3	0.0	4.1	0.1	240.0
AdBh0553	473300	996100	198	114.0	7.4	0.0	11.0	2.5	30.0	4.8	0.3	0.0	16.0	0.1	15.6	1.2	170.8	9.1	5.0	0.1	220.0
AdBh0994	464538	991302	248	168.0	7.4	0.0	14.0	4.3	30.4	6.3	0.0	0.2	4.4	0.0	12.0	0.5	153.7	0.0	1.0	0.2	102.0
AdBh0920	472700	999800	329	183.0	7.2	0.0	11.0	0.9	31.0	4.0	0.1	0.1	19.1	0.1	22.3	4.7	170.8	0.0	1.6	0.2	220.0
AA053	480863	992647	735	477.0	7.3	0.2	128.0	12.1	31.1	7.7	0.2	0.1	11.9	0.0	1.0	1.1	492.9	0.0	14.1	0.2	109.5
AdBh0409	441901	981393	300	200.0	7.1	0.3	27.0	9.4	32.0	5.6	0.6	0.1	4.6	0.1	12.0	0.6	384.3	0.0	4.7	0.5	224.7
AdBh0593	471300	996200	345	131.0	6.8	6.0	17.0	4.5	32.0	98.0	0.3	0.1	5.2	0.1	22.3	0.6	134.0	0.0	3.9	0.1	220.0
AdBh0518	474000	999400	392	204.0	7.9	0.3	45.0	8.8	32.0	4.7	0.1	0.1	28.4	0.1	18.9	0.7	258.6	0.0	5.0	0.5	220.0
AdBh0644	474050	996650	762	398.0	7.3	0.0	21.0	1.2	32.0	3.7	0.0	0.1	32.1	0.0	5.3	1.2	366.2	9.1	24.7	0.2	164.0
AdBh0662	474800	984700	545	354.0	7.8	2.7	36.1	9.4	33.3	11.7	0.0	0.0	10.5	0.0	0.5	0.6	298.9	0.0	17.6	0.0	131.0
AA005	480999	999648	464	308.0	7.4	0.1	62.0	5.0	33.6	8.2	0.1	0.0	21.9	0.0	5.0	1.7	274.5	0.0	23.5	0.2	117.6
AA067	481213	991853	498	332.0	7.1	0.0	80.0	7.4	33.6	5.6	0.2	0.1	8.9	0.1	1.7	0.9	314.8	0.0	0.8	0.3	107.1
AA003	477446	997611	367	240.0	7.5	0.3	27.5	6.3	34.4	10.2	0.2	0.1	7.0	0.0	0.5	1.3	215.2	0.0	17.6	0.1	128.0
AdBh0411A	469800	996300	222	123.0	6.9	0.3	32.0	6.8	35.0	5.7	0.1	0.0	6.1	0.1	0.3	0.7	366.2	9.1	5.0	0.0	148.0
AA029	481519	999648	422	282.0	7.4	4.0	55.0	4.6	35.3	8.2	0.3	0.1	10.9	0.0	8.5	1.6	263.5	0.0	11.3	0.2	121.8
AdBh0717	474225	982650	470	356.0	8.0	0.1	54.4	11.6	35.3	15.6	0.7	0.0	28.4	0.1	0.7	1.1	317.0	0.0	0.0	0.0	152.0
AA027	465741	989188	265	174.0	7.0	0.0	10.4	4.5	36.1	9.2	0.1	0.1	2.9	0.0	2.7	1.0	161.0	0.0	0.9	0.3	127.6
AdBh0752	486200	1001042	240	369.0	7.5	0.0	65.5	2.7	36.9	14.6	0.1	0.1	25.5	0.0	0.5	0.7	292.8	0.0	15.0	0.7	152.0
AA002	469191	989547	309	200.0	7.3	0.0	22.0	8.3	37.0	11.2	0.1	0.0	6.0	0.0	12.3	0.9	221.8	0.0	1.2	0.1	138.6
AdBh1040	474788	982924	443	216.0	7.6	0.2	33.0	8.3	37.0	46.0	3.0	0.1	7.0	0.1	13.7	1.3	327.0	0.0	15.6	0.2	288.0
AdBh0715	478462	977721	470	287.0	8.3	0.0	30.0	2.5	37.0	9.0	0.6	0.0	13.0	0.1	4.3	0.5	259.0	0.0	0.0	0.0	156.0
AA038	477248	982879	295	186.0	7.1	0.0	18.0	4.0	37.8	9.7	0.4	0.1	6.0	0.0	0.7	0.9	183.0	0.0	0.7	0.2	134.4
AdBh0568	471400	995800	299	154.0	7.3	0.0	29.0	7.8	38.0	8.4	0.1	0.1	5.2	0.0	7.4	0.7	258.6	0.0	4.1	0.1	199.5
WF01-PW3	474918	980496	612	398.0	8.3	0.5	99.0	14.0	38.0	2.8	0.2	0.0	49.7	0.0	4.7	1.4	283.0	12.0	5.0	0.3	106.5
AdBh0638	473230	988879	560	342.0	8.0	0.0	16.0	1.2	38.1	5.0	0.1	0.1	20.1	0.1	9.4	2.3	129.3	0.0	18.9	0.5	182.7
AA061	482163	993603	750	492.0	6.9	0.0	123.0	12.9	38.6	6.6	0.2	0.1	11.9	0.0	0.4	0.7	490.4	0.0	5.6	0.3	123.9
AdBh0603	468100	993100	250	160.0	6.8	0.5	19.0	87.0	39.0	6.9	0.4	0.1	8.0	0.1	2.0	0.9	134.0	12.0	1.2	0.1	206.8
AdBh0558	472900	995900	427	219.0	7.3	0.0	23.0	4.4	39.0	4.7	0.0	0.0	11.0	0.0	30.0	0.2	366.2	0.0	2.3	0.1	240.0
AdBh0805	478998	977937	496	303.0	7.8	0.0	36.6	3.3	39.7	23.6	0.0	0.0	9.2	0.0	16.4	0.5	302.6	0.0	7.9	0.0	196.0

AdBh0782	478780	977307	516	315.0	7.7	0.1	30.6	4.0	40.0	28.2	0.1	0.1	14.2	0.2	3.9	0.4	329.4	0.0	6.6	0.0	212.0
AdBh0904	468800	996600	375	253.0	7.9	0.3	23.8	2.8	40.1	6.8	0.1	0.0	11.3	0.3	15.1	0.2	195.2	0.0	0.0	0.0	148.0
AdBh0477	475000	987800	743	381.0	7.3	0.0	37.0	82.0	40.3	12.2	0.2	0.1	7.0	0.1	3.8	1.1	292.8	0.0	8.6	0.3	288.0
AdBh0946	465651	1001575	380	250.0	7.4	0.0	7.4	3.2	40.8	15.5	0.0	0.0	10.0	0.1	0.0	0.4	185.4	9.6	0.9	0.5	185.0
AdBh1144	468295	1001339	311	174.0	7.0	0.1	8.4	1.8	42.0	12.8	0.0	0.0	7.9	0.0	1.0	1.3	197.0	0.0	0.0	0.2	157.5
AdBh0908	468425	996350	395	246.0	7.3	0.0	19.0	5.0	42.0	14.0	0.1	0.0	5.0	0.1	2.8	0.2	242.0	0.0	3.0	0.6	154.0
AA012	468515	989719	295	194.0	7.7	0.0	14.5	5.7	42.2	9.2	0.0	0.1	2.0	0.5	3.1	1.1	197.6	0.0	0.7	0.1	143.0
AdBh0588	469300	995500	280	190.0	7.0	0.6	30.0	8.5	43.0	25.0	0.1	0.0	7.0	0.1	5.4	0.6	258.6	12.0	4.1	0.1	206.8
AdBh1087	472200	995700	466	242.0	7.5	0.0	35.0	8.7	43.0	7.5	0.2	0.0	8.5	0.0	3.0	0.7	170.8	0.0	5.0	0.2	138.6
AdBh1100	473900	985100	179	103.0	8.2	0.2	43.0	7.8	43.0	12.0	0.2	0.0	32.1	0.0	5.3	3.0	129.3	0.0	2.3	0.2	134.4
AA0101	477945	976985	398	258.7	7.5	0.0	23.8	4.6	43.3	13.6	0.0	0.0	14.2	0.0	4.9	0.6	244.0	0.0	0.0	0.0	164.0
AdBh0780	479246	977104	512	312.0	7.3	0.5	27.2	3.6	44.9	29.2	0.1	0.0	17.0	0.0	25.7	0.2	305.0	0.0	34.1	0.1	232.0
AdBh0596	471700	996300	270	109.0	7.2	0.3	19.0	6.7	45.0	7.5	0.2	0.0	3.5	0.0	6.1	4.7	117.1	9.1	1.6	0.1	154.0
AA051	478130	982300	532	344.0	7.7	0.2	66.0	9.3	45.4	8.2	0.1	0.1	20.8	0.0	3.8	0.9	285.5	0.0	15.6	0.1	147.0
AdBh0580	471300	995400	412	231.0	6.8	0.0	31.0	5.6	46.0	7.9	0.3	0.0	5.2	0.0	15.6	0.9	117.1	12.0	1.6	0.0	138.6
SWAWF-04A	472826	980785	518	382.0	7.3	0.2	58.0	7.4	46.2	16.3	0.0	0.0	22.7	0.0	41.3	1.2	307.4	0.0	5.0	0.1	182.7
AdBh1113	467135	989840	344	226.0	7.1	0.4	17.0	6.8	46.6	9.2	0.1	0.0	6.0	0.1	4.6	0.6	235.0	0.0	0.1	0.2	154.0
AA014	469360	990078	344	226.0	7.1	0.0	17.0	6.8	46.6	9.2	0.1	0.1	6.0	0.1	15.6	0.6	235.0	0.0	0.1	0.2	154.0
AA059	482757	990710	478	314.0	7.1	0.2	58.0	6.6	47.0	6.6	0.1	0.0	9.9	0.0	1.0	0.8	309.9	0.0	3.4	0.3	254.0
AA089	476246	977104	512	332.8	7.3	0.0	27.2	3.6	48.5	27.7	0.0	0.0	8.7	0.0	16.7	0.4	327.0	0.0	7.0	0.0	235.0
AdBh0794	477330	976793	477	291.0	8.1	0.1	40.8	4.3	49.7	23.4	0.1	0.1	14.2	0.7	13.7	0.4	292.8	0.0	7.0	0.4	220.0
AdBh0801	479942	977322	480	310.0	7.8	0.1	24.5	4.0	49.7	23.4	0.0	0.0	12.0	0.0	12.3	0.6	292.8	0.0	7.4	0.2	145.0
AA064	481368	997713	445	292.0	7.5	0.2	42.0	5.9	50.4	7.1	0.3	0.0	14.9	0.0	0.3	2.2	239.1	0.0	23.1	0.1	155.4
AdBh0660	465600	1001855	615	400.0	7.7	0.1	49.0	6.3	51.7	28.0	0.1	0.0	21.3	0.1	11.3	0.6	384.3	0.0	1.0	0.1	244.0
AA024	467830	998168	528	344.0	7.3	0.0	30.0	4.6	52.1	23.0	0.0	0.0	8.2	0.0	17.9	0.2	310.0	0.0	5.4	0.0	224.7
AdBh0584	471700	995100	333	154.0	7.0	0.0	14.0	5.3	53.0	8.7	0.2	0.1	6.4	0.1	4.5	0.6	366.2	0.0	5.0	0.2	220.0
WF01-PW6	472630	979912	562	330.0	7.5	0.3	54.0	5.8	53.2	16.0	0.0	0.0	13.7	0.0	15.6	1.2	345.9	0.0	2.0	0.5	199.5
AA019	481462	998906	414	272.0	7.2	0.0	30.5	3.2	53.8	10.7	0.3	0.1	7.9	0.0	0.2	2.5	258.6	0.0	6.4	0.1	178.5
AdBh0770	473108	979851	397	258.1	7.6	0.0	37.4	5.3	54.5	22.4	0.1	0.1	14.2	0.0	18.9	0.7	317.2	0.0	24.7	0.2	228.0

AA034	480321	997370	440	286.0	7.1	0.2	41.0	3.2	54.6	9.2	0.1	0.1	10.9	0.0	0.4	3.2	278.2	0.0	11.4	0.1	174.3
AdBh0630	473800	990250	621	385.0	8.0	0.0	65.0	10.3	55.2	7.9	0.0	0.1	32.1	0.1	15.6	5.0	73.2	0.0	24.7	0.1	182.7
AdBh1042	473466	987247	337	206.0	7.0	0.0	34.0	4.6	56.1	14.6	0.1	0.1	11.4	0.0	1.8	0.5	317.0	0.0	2.3	0.1	200.0
AdBh0787	478199	976361	486	300.0	8.0	0.0	27.7	5.3	56.1	24.4	0.1	0.1	14.2	0.2	3.9	0.4	329.4	0.0	5.4	0.1	240.0
AA092	478347	976752	542	352.6	7.5	0.0	27.2	5.3	56.1	24.4	0.1	0.0	14.2	0.2	3.9	0.4	329.4	0.0	5.4	0.0	240.0
AdBh0762	481600	982900	540	380.0	7.4	0.0	44.2	4.0	56.1	20.4	0.0	0.1	14.2	0.0	9.6	0.7	341.6	0.0	15.0	0.5	112.0
AA058	481828	981943	558	364.0	8.0	0.0	53.0	3.9	58.1	18.4	0.1	0.0	11.9	0.0	0.4	0.7	358.7	0.0	18.5	0.2	294.0
AA097	477477	977216	463	300.8	7.2	0.0	18.7	4.6	59.3	19.5	0.0	0.0	14.2	0.1	1.3	0.5	305.0	0.0	0.0	0.0	288.0
AA090	478808	976897	508	330.3	8.0	0.0	27.2	4.0	59.3	24.3	0.0	0.0	12.0	0.0	9.8	0.5	341.6	0.0	6.5	0.0	248.0
SWAWF-2	475697	979915	595	390.0	6.9	0.3	46.0	8.6	64.7	15.3	0.0	0.0	14.4	0.1	7.2	1.4	348.4	0.0	5.0	0.1	224.7
AA007	471500	990500	438	280.0	7.0	0.1	13.8	5.2	65.6	10.3	0.4	0.1	9.9	0.0	6.2	0.8	246.0	0.0	2.8	0.2	206.8
AA046	480847	981623	552	362.0	7.4	0.0	43.0	4.9	66.9	15.1		0.0	12.9	0.0	11.1	1.1	300.1	0.0	21.2	1.5	228.8
AdBh0761	481200	980000	530	385.0	7.6	0.0	40.8	5.3	67.3	15.6	0.0	0.1	14.2	0.1	11.7	1.0	366.0	0.0	30.0	0.2	232.0
AdBh0765	479400	981400	430	362.0	7.4	0.0	44.2	4.0	91.4	2.9	0.1	0.1	20.0	0.0	0.1	0.7	366.0	0.0	23.0	0.1	240.0
AdBh0439	562015	1071000	468	327.0	7.8	0.1	89.0	16.0	293	30.0	4.0	0.1	21.8	0.2	9.0	4.2	298.0	0.0	48.1	0.6	120.0
AdBh0414A	478450	995600	328	183.0	8.0	0.2	32.0	3.6	506	19.0	0.3	0.0	20.1	0.1	4.9	0.4	333.0	0.0	1.0	0.0	187.0

Appendix 2: Description of petroleum station in Addis Ababa city

			UTM Location		Station history					
Name of station	Geographic Name of Locality	Elevation	x	y	Type of fuel	size	Depth of tanks	Number of tanks	tanker is made of and thickness	Type of activities
NOC Bole	millennium hall	2229	476487	993575	regular, diesel,and kerosen	2*30m^3, 1*50m^3 and 1*30m^3	4.30m-5.00 m	4	stee of 6mm	car wash, librucants, gas cylinders
NOC sunshine	bambis	2236	474435	996023	regular, diesel,and kerosen	1*50m^3, 1*50m^3 and 1*50m^3	4.30m-5.00 m	3	stee of 6mm	car wash, shoping,
NOC legehar	legehar	2254	472582	996156	regular, diesel,and kerosen	1*50m^3, 1*50m^3 and 1*50m^3	4.30m-5.00 m	3	stee of 6mm	car wash,librucants, gas cylinders, abyssinia cards
NOC gerji	ring road	2238	478385	994922	regular, diesel,and kerosen	1*50m^3, 1*50m^3 and 1*50m^3	4.30m-5.00 m	3	stee of 6mm	car wash, librucants, gas cylinders
NOC beklo bet	beklobet	2227	473580	994404	regular, diesel,and kerosen	1*30m^3, 1*30m^3 and 1*30m^3	4.30m-5.00 m	3	stee of 6mm	shop and café
NOC lem		2272	477392	996795	regular, diesel,and kerosen	2*30m^3, 2*30m^3 and 1*30m^3	4.30m-5.00 m	5	stee of 6mm	car wash, shoping,café
Total bole brass hospital	bole brigde	2228	477375	996048	regular, diesel,and kerosen	1*30m^3, 1*30m^3 and 1*30m^3	4.75m-5m	3	stell of 6-6.5mm	car wash, maintenance , librucants, gas cylinders, abyssinia cards
Total harambe fil wuha	harambe hotel	2250	473053	996798	regular, diesel,and kerosen	1*30m^3, 1*30m^3 and 1*30m^3	?	3	stell of 6-6.5mm	car wash, maintenance , librucants, gas cylinders, abyssinia cards, tire service
Total kality crown		2067	473955	985229	regular, and diesel	2*30m^3 and 2*30m^3	4.75m-5m	4	stell of 6-6.5mm	librucants, gas cylinders, abyssinia cards, tire service
Total kolfe road	mesalemia	2368	469541	998835	regular, diesel,and kerosen	2*30m^3, 2*30m^3 and 1*30m^3	4.75m-5m	5	stell of 6-6.5mm	car wash, librucants, gas cylinders
Total meganegna	shola road	2303	477868	997424	regular, and diesel	1*30m^3 and 1*30m^3	4.75m-5m	2	stell of 6-6.5mm	car wash,librucants, gas cylinders, abyssinia cards
Total meskel square	meskel square	2246	473528	996090	regular, and diesel	1*30$m^3$and 1*30m^3	?	2	stell of 6-6.5mm	car wash, maintenance , café, shop, librucants, gas cylinders, abyssinia cards
Total nifas silk		2160	474075	990375	regular, diesel,and kerosen	2*30m^3, 2*30m^3 and 1*30m^3	4.75m-5m	5	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, abyssinia cards , tire service
Total partiors sebera babur	baharzaf alchohol factory	2343	472306	999097	regular, diesel,and kerosen	2*30m^3, 2*30m^3 and 1*30m^3	4.75m-5m	5	stell of 6-6.5mm	car wash, librucants, gas cylinders, abyssinia cards , tire service
Total bole road	yeshi building	2235	474843	994752	regular, diesel,and kerosen	2*30m^3, 2*30m^3 and 1*30m^3	4.75m-5m	5	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, abyssinia cards , tire service
Total Arat killo	Ethiopia press	2327	473772	998599	regular, and diesel	1*50m^3 and	?	2	stell of 6-6.5mm	maintenance , café, librucants, gas

	agency					1*50m³				cylinders, abyssinia cards
Total Casanchis	post office	2270	479200	996043	regular, and diesel	1*50m³ and 1*50m³	4.75m-5m	2	stell of 6-6.5mm	car wash , shoping, librucants, gas cylinders, abyssinia cards
Total Sidist killolion	lions park	2366	473917	999641	regular, diesel,and kerosen	1*30m³, 1*30m³ and 1*30m³	4.75m-5m	3	stell of 6-6.5mm	car wash,librucants, gas cylinders, abyssinia cards
Total meganegna	lem hotel	2276	477392	997424	regular, diesel,and kerosen	1*30m³, 1*30m³ and 1*30m³	?	3	stell of 6-6.5mm	librucants, gas cylinders, abyssinia cards, tire service
Total akaki	bridgestone PLC	2052	475044	983235	regular, diesel,and kerosen	1*50m³, 1*50m³ and 1*50m³	4.75m-5m	3	stell of 6-6.5mm	car wash, librucants, gas cylinders, abyssinia cards , tire service
kobil rass mekonen bridge	st. george church	2334	473352	998950	regular, diesel,and kerosen	1*50m³, 1*50m³ and 1*50m³	4.75m-5m	3	stell of 6-6.5mm	car wash, shoping, librucants, tire service
kobil	chercher street	2278	472724	997500	regular, and diesel	???	4.75m-5m	?	??	car wash, shoping,cafe, tire service
kobil gotera	gotera ring road	2225	473366	993049	regular, diesel,and kerosen	???	?	?	??	car wash, shoping,café
kobil teklehymanot church		2282	472113	997544	regular, diesel,and kerosen	???	?	?	??	car wash, shoping,
YBP akaki	akaki	2066	473935	985420	regular, diesel,and kerosen	1*50m³, 2*50m³ and 1*50m³	4.20m	4		car wash, librucants, gas cylinders, abyssinia cards , tire service
YBP kolfe	kolfe	2275	470001	996401	regular, diesel,and kerosen	1*30m³, 1*50m³ and 1*50m⁸	4.20m	3		car wash,librucants, gas cylinders, abyssinia cards
oilibya kebea	kebena square	2319	475445	998599	regular, diesel,and kerosen	1*30m³, 1*50m³ and 1*50m⁸	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, abyssinia cards , tire service
oilibya rasmekonen bridge	rasmekonen bridge	2334	473300	999070	regular, diesel,and kerosen	1*30m³, 1*50m³ and 1*50m⁸	4.50m-5m	3	stell of 6-6.5mm	car wash, café, librucants shop
oilibya ras hotel	beherawi tiatir	2250	472823	996428	regular, diesel,and kerosen	1*30m³, 1*50m³ and 1*50m⁸	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, abyssinia cards , tire service
oilibya stadium	stadium	2247	473268	996467	regular, and diesel	1*50m³ and 1*50m³	4.50m-5m	2	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, abyssinia cards , tire service
oilibya gotera	oilibya head office	2205	473593	992334	regular, diesel, and kerosen	2*30m³, 2*30m³ and 1*30m³	4.50m-5m	5	stell of 6-6.5mm	car wash, café, librucants shop, tire service
oilibya gotera	oilibya head office	2204	473601	992241	regular, and diesel	1*50m³ and 1*50m³	4.50m-5m	2	stell of 6-6.5mm	car wash, shop
oilibya gotera	oilibya head office	2206	473663	991956	regular, and diesel	1*50m³ and 1*50m³	4.50m-5m	2	stell of 6-6.5mm	tyre service
oilibya mexico	mexico ssquare	2244	471784	995711	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, cleaning, café, librucants shop , tire service
oilibya piasa	piasa	2340	472903	998607	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, abyssinia cards , tire service
oilibya habtgeorgis bridge	kelifa bissnes center	2325	472185	998671	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, tire service
oilibya habtgeorgis	kurtu building	2310	471787	998640	regular, diesel, and kerosen	1*50m³, 2*50m³ and 1*50m³	4.50m-5m	4	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, tire service

bridge											
oilibya lideta	tukur ambesa referal hosptal	2276	472274	997271	regular, diesel, and kerosen	1*50m³, 2*50m³ and 1*50m³	4.50m-5m	4	stell of 6-6.5mm	liburicant shop	
oilibya mexico	mexico square	2251	471945	996197	regular, and diesel	1*30m³ and 1*30m³	4.50m-5m	2	stell of 6-6.5mm	liburicant shop	
oilibya legehar	ethiopia insurance company	2252	472658	996136	regular, diesel, and kerosen	1*50m³, 2*50m³ and 1*50m³	4.50m-5m	4	stell of 6-6.5mm	gas distribution only	
oilibya meskel square	estiphanos church	2242	473907	996154	regular, and diesel	1*30m³ and 1*30m³	4.50m-5m	2	stell of 6-6.5mm	car wash, shop	
oilibya dembel	dembel city center	2248	474418	995549	regular, diesel, and kerosen	2*30m³, 2*30m³ and 1*30m³	4.50m-5m	5	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, tire service	
oilibya bole road	yeshi building	2235	474855	994747	regular, diesel, and kerosen	2*30m³, 2*30m³ and 1*30m³	4.50m-5m	5	stell of 6-6.5mm	car wash, shop	
oilibya mexico	atlas college	2263	470889	996112	regular, diesel, and kerosen	2*30m³, 2*30m³ and 1*30m³	4.50m-5m	5	stell of 6-6.5mm	car wash, café, librucants shop	
oilibya markato	markato	2354	479639	996237	regular, diesel, and kerosen	2*30m³, 2*30m³ and 1*30m³	4.50m-5m	5	stell of 6-6.5mm	car wash, café, librucants shop	
oilibya meslemia	mesalemia market	2359	469567	998276	regular, and kerosen	1*50m³ and 1*50m³	4.50m-5m	2	stell of 6-6.5mm	car wash, café, librucants shop	
oilibya tor hayloch	tor hayloch bridge	2280	469214	995863	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, tire service	
oilibya kasanchise	jupiter hotel	2275	474341	996705	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, café, librucants shop, tire service	
oilibya kality	bus station	2052	475050	983189	regular, and kerosen	1*50m³ and 1*50m³	4.50m-5m	2	stell of 6-6.5mm	car wash, café, librucants shop	
oilibya kality		2063	474069	984919	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, tire service	
oilibya saris		2156	474035	990322	regular, diesel, and kerosen	1*50m³, 1*50m³ and 1*50m³	4.50m-5m	3	stell of 6-6.5mm	car wash, maintenance , café, librucants, gas cylinders, tire service	
oilibya saris	horizone addis tyre PLC.	2146	474114	989256	regular, and kerosen	1*30m³ and 1*30m³	4.50m-5m	2	stell of 6-6.5mm	car wash, maintenance , café, librucants, tire service	

Appendix3: In-situ measured parameters of some selected boreholes

ID	LOCATION		ELEVATION	MEASURED PARAMETERS			
	X	Y		EC	TDS	PH	T^0
GW1	472896	1002213	2482	207	124.6	7.13	24.5
GW2	471125	1002242	2498	194	115	8	25.3
GW3	470596	1002378	2496	1714	104	7.5	28
GW4	470295	1002089	2475	270	180	7.8	23
GW5	469414	1001038	2440	416	267	8	20
GW6	465611	1002487	2425	188	98	8	29
GW7	466801	1001417	2399	200	125	8	23
GW8	467824	997091	2223	220	131.5	9	28
GW9	470322	991067	2128	359	234	8	26
GW10	468364	990571	3138	320	192	7.5	25
GW11	467853	990266	2120	388	234	7.7	26
GW12	468236	989865	2123	345	211	8	24
GW13	468613	989896	2130	344	205	8	25.5
GW14	468828	989930	2140	402	245	7.8	26
GW15	474825	989939	2126	513	309	8.2	25.5
GW16	480425	997955	2302	181	106	8.3	29.3
GW17	468695	990638	2138	337	200	7.7	27.1
GW18	481627	999842	2386	400	240	8	23
GW19	481127	999427	2365	496	294	8	24.5
GW20	473377	999810	2349	1982	260	8.1	65
GW21	433262	999319	2460	302	213	7.2	25