EFFECTS OF GEOLOGICAL VARIABILITY AND SELECTED PHYSICAL PARAMETERS OF WATER QUALITY ON FLUORIDE LEVELS IN RIVER NJORO CATCHMENT, KENYA

BY

GEORGE MORARA ONTUMBI

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DECLARATION

Declaration by the candidate

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GEORGE MORARA ONTUMBI

SENV/EES/P/001/16	**DATE**

Declaration by the supervisors

This thesis has been submitted with our approval as University Supervisors.

PROF. ELIAS K. UCAKUWUN, **DATE**
Department of Environmental Earth Sciences,
School of Environmental Studies,
University of Eldoret, Eldoret, Kenya

DR. THOMAS M. MUNYAO, **DATE**
Department of Environmental Earth Sciences,
School of Environmental Studies,
University of Eldoret, Eldoret, Kenya

DEDICATION

I dedicate this work to my late Father, Mum, beloved Wife, Children and environmentalists whose concerns formed the basis of this research work.

ABSTRACT

Fluoride levels higher than the World Health Organization (WHO) recommended levels of 1.5 mg/l have to raise serious health issues. Therefore fluoride contamination is a pertinent matter that calls for concern by all people and government especially in countries where the phenomenon of volcanicity has been experienced. The study sought to analyse the effects of geological variability and selected physical parameters of water quality on fluoride levels in River Njoro catchment. The study was guided by the following objectives: to determine the relationship between fluoride levels and surface geology in River Njoro catchment, to determine the relationship between borehole stratigraphy formation matrices and fluoride levels in borehole water in River Njoro catchment, determine the relationship between pH, temperature and Electrical conductivity and fluoride levels in groundwater in River Njoro catchment and finally model spatial variation and distribution of fluoride levels in ground water in the River Njoro catchment. The study sought to highlight the levels of fluoride and give recommendations on identification and delineation of potential sites for safe groundwater for the local population and advice on the water treatment and de fluoridation strategies. Past researches on River Njoro catchment gave much emphasis on land use/cover changes and strong condemnation on elevated fluoride levels in the Njoro catchment and therefore the gap in this research was based on the integration of geological variations and geological stratigraphy of River Njoro catchment and ultimately produce a predictive trend. This study adopted purposive longitudinal survey and quasi experimental research designs. In this research borehole and river water, soil and rock samples from designated points along the River Njoro and its tributaries were collected for laboratory analysis of fluoride levels. The research adopted descriptive and correlation statistical analysis. The sources of data included: field surveys which were used to collect data about the fluoride levels, the remotely sensed, GIS and Geostatistical interpolation, content analysis of the literature on the geology of the Njoro catchment and the hydro-meteorological and geological characteristics data. From the results of the study it was observed that: the fluoride levels in River Njoro catchment varied with the geology of the catchment and fluoride levels in groundwater depended on the borehole stratigraphy matrix, the selected physical parameters of water quality (pH, Electrical Conductivity and temperature) had a significant statistical relationship with fluoride levels in River Njoro catchment and land use/cover changes and variations in the borehole depths. The results through Geostatistical interpolation also observed that there is varied distribution and variation of fluoride levels in River Njoro catchment. Therefore geological variations, borehole depths and lithological formations were manifested in the fluoride level variations in the water and rock sampling points that were located either upstream, midstream and downstream of the River Njoro catchment. Finally the study recommends isotopic analysis of water samples from the sources of water in River Njoro catchment to assist in tracing their origin, contamination of fluoride and fluoride enrichment pathways and water quality alteration within the catchment.

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DEFINITION OF OPERATIONAL TERMS

Anthropogenic - Effects, processes or materials derived from human activities, as those occurring in the biophysical environment.

Borehole Stratigraphy – Vertical layers of geological formations in a borehole

Contamination - Addition of impurities or pollutants.

Fluoridation - The addition of fluorides to the public water supply to reduce the incidence of tooth decay.

Groundtruthing - Actual visiting the places to ascertain the facts as recorded by the land sat images.

Hydro Meteorological Factors- The factors or elements associated with water and weather elements.

Land Cover - is the physical material at the surface of the earth.

Land Use - The use by which land cover is put by humans.

Remote Sensing - The science and art of obtaining information about an object, area or phenomena through the analysis of data acquired by a sensor that is not indirect contact with the target of investigation.

Skeletal Fluorosis - Disease associated with infection of the bones of animals or human beings caused by excessive fluorides in the water.

Water Quality- State of water that is suitable for organisms' use.

WHO Standards - Standards acceptable by the World Health Organization as a bench mark or minimum levels.

LIST OF ACRONYMS

DEM- Digital Elevation Model

EC – Electrical Conductivity

GIS - Geographical Information Systems

GPS – Global Positioning System

IDW – Inverse Distance Weighting

GLCF - Global Land Cover Facility

GPS – Global Positioning System

IQ- Intelligent Quotient

ISE – Ion Selective Electrode

IWRM – Integrated Water Resource Management

LULC – Land Use/Land Cover

LULCC - Land Use/Land Cover changes

KBS – Kenya Bureau of Standards

RGS – River Gauging Station

RS - Remote Sensing

RVIST- Rift Valley Institute of Science and Technology

WRI - water-rock interaction

SDG- Sustainable Development Goals

SPSS - Statistical Package for Social Sciences

SRTM – Shuttle Radar Topography Mission

TISAB – Total Ionic Strength Adjustment Buffer

TM – Thematic Mapper

UNEP – United Nations Environmental Programme

UNESCO - United Nations Educational, Scientific and Cultural Organization

UNICEF - United Nations Children's Fund

UNDP – United Nations Development programme

USA – United States of America

VES – Vertical Electrical Sounding

WHO – World Health Organization

WRA- Water Resource Authority

WRMA – Water Resource Management Authority

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CHAPTER ONE

INTRODUCTION

This chapter gives the background information on the fluoride levels in the water, the statement of the problem, the research objectives, research questions, and significance of the study. Finally, this chapter covers: justification of the study, study area, theoretical framework, and the conceptual framework on the premise of the general objective of the study.

1.1 Background to the Study

Water, according to United Nations Environmental Programme (UNEP, 2009) is the basic requirement which determines the quality of life on earth. Consequently, therefore water is essential to man, animals and plants, without which, life on earth would not exist. Good and quality water maintains healthy ecosystems thereby resulting in improved human welfare. Therefore, water that is safe and free from injurious chemicals and pathogens causing diseases is a requisite for a healthy nation. As stipulated in the Sustainable Development Goals (SDG) and similarly according to UNEP (2010) access to safe drinking water at national, regional and local levels is an important health and development related concerns.

Water occupies 70% of the surface of the earth with 96.5% available in oceans and 1.74% in frozen state. But a large portion of the worldwide water wants are supplied by rivers and boreholes. However, borehole water use is comparatively fresh and widely distributed as opposed to the river and spring water. Moreover, the increasing population and their needs pose serious threats to the water sources. Parris & Kates (2003) observed that globally sufficient fresh water supplies are the foundations upon which all Sustainable Development Goals are based. Therefore, there is need to ensure safe water for the citizens of a country. Majority of people living in the developing countries have no access to quality drinking water (WHO, 2004) as per the permissible fluoride levels.

The health concerns of chemical composition of water meant for human drinking differ from those associated with bacterial contamination and this is attributed to negative health effects resulting from prolonged periods of exposure. Surface and groundwater quality would be linked and affected by the type of aquifer where the source of the river is located as observed by Alberta Environment (2009). Naturally the chemicals present in groundwater originate from the rocks and soil facilitated by the processes of percolation and infiltration. The hydrological processes of percolation and infiltration therefore have the potential of causing contamination and thereby affecting both the surface and ground water quality. Water for drinking should be free from pathogenic organisms and compounds that have adverse effects, immediate and long impacts on term on human health as observed by Bartram *et al.* (2003).

Quality water meant for portable human use should have low turbidity, colourless and be non-saline (Sarvade, 2017). Moreover, in the recent past, concerns have been raised on the accessibility and suitability of this water in the developing countries. The woes regarding diminishing surface and ground water resources and fluoride contamination are intertwined and associated to geological formations, volcanicity, uncontrolled growth of urban areas and associated growth of industries (Hassan & Nazem, 2016). Structural deformation of the surface geology is associated with increasing population, contributed by increasing demand for agricultural land, thereby triggering depletion and degradation of water resources.

Fluoride occurrence in groundwater would be attributed to geologically related contamination (Saxena and Ahmad, 2002) however: the source cannot be precisely identified. Generally, contamination of groundwater associated with geogenic processes is dependent on the geological formations of specific areas. The contamination is justified when rainwater penetrates through the soil and gets in contact with the water table, thereby dissolving some minerals of the bedrock. Consequently, the fluoride content of groundwater is a result of the dissolution of the bedrock that is rich in fluorine bearing minerals. According to Chae *et al.* (2007) the minerals forming the bedrock generally is a principal factor responsible for fluoride variations in fluoride levels in boreholes. The elevated fluoride levels in groundwater would be attributed to natural and anthropogenic processes. Moreover, the natural causes are more responsible to degradation of ground water through geological conditions.

Groundwater is considered unsuitable for human use when its chemical composition is not within the prescribed WHO standards for drinking water. The contaminants of great concern include: Arsenic, fluoride, nitrate, iron, manganese, boron and most heavy metals whose presence should be within permissible limits. In many water bodies worldwide, the major contaminate substances are fluorides and organic waste. World Health Organization guidelines observe and recommend that the ideal fluoride concentration in drinking water should remain below 1mg/L in warm climates. Further, WHO recommends 1.2 mg/L in cooler climates (Jiménez-Becerril *et al.*, 2012). The existence of elevated fluorides quantities concentration tends to trigger hazardous health threats as observed by Chelangat (2015). The health complications associated with the teeth and bone fluorosis are irreversible and no existence of treatment. Therefore, the viable solution to the adverse effects associated with elevated fluoride levels in portable water is avoidance by drinking water whose fluoride intake is within the safe limits. High fluoride levels become a case of concern because it is a persistent and non-degradable substance that stores in soil, flora, fauna and human beings.

Fluoride contamination associated with surface and groundwater is related to availability and dissolubility of minerals bearing fluorine, temperature, acidity or alkalinity, concentration levels of calcium and bicarbonate ions dissolved in water. Over 95% of world's available fresh water has their aquifers in groundwater. According to Brindha and Elango (2011) groundwater water is the main source of drinking water for a large percentage of the world's population. Groundwater is found in most environments: however, its quantity, quality, accessibility and recharge are determined by geology, geomorphology, land use and climatic variations. The significant role on storage, transportation and nature of borehole water is played by rock types and geomorphology. MacDonald *et al.* (2009) observe that the geomorphological and geological attributes of a place contribute to a recharge of 10–50 mm of fluoride levels in areas whose annual precipitation is less than 500 mm.

The harmful biological effect of the fluoride ion gives fluoride an important place in the quality of drinking water. The presence of fluoride in small quantities prevents tooth decay: however, when it is in excess quantity it provokes dental and bone fluorosis. Water is central to human life, yet a larger population of the world has no access to safe drinking water sometimes attributed to high fluoride levels (Maheshwari, 2006). Lately, there has been increasing global attention focused on resolving water quality problems especially in relation to high fluoride levels, as the lack of access to clean water denies the most essential of all rights, the right to life.

Regions traversed by the Rift Valley, among them Nakuru County are the worst affected (Näslund & Snell, 2005).

The quality of fresh water sources are of increasing concern in many areas of the world today. Consequently target 6.3 of SDG 6 aims to improve water quality and target some of the root causes of poor water quality by reducing pollution, eliminating dumping and minimizing of hazardous chemicals in water by ensuring availability and sustainable management of water and sanitation for all (UNESCO, 2017). In low-income countries the natural contamination, attributed to geological environments has resulted in limited quantity and quality of water resources. In Kenya especially in Rift Valley, water availability has been threatened by fluoride which is a natural contaminant. In this framework therefore hydrogeological, hydro chemical and biological investigations have to be carried out to define the hydrogeological characteristics in order to provide safe and adequate water supply.

Rivers, shallow wells and boreholes are major sources of water for both domestic and industrial use in many parts around the world (Gleick, 2000). Furthermore, in developing countries, where infrastructure for water supply has not been fully developed, the rivers and wells ultimately provide a direct source of water for domestic use with minimal or no treatment at all. Levels of fluoride in water are among the important criteria that determine its usefulness for a specific need and as such not all the water is good for drinking. The larger population of people in developing countries lack access to safe drinking water (UNICEF, 2008). Major substances that are found to contaminate water are fluorides, heavy metals and organic waste. Kloos and Haimanot (1999) assert that the presence of fluorides in high concentration tends to pose health risks.

Edmunds & Smedley (2013) observes that in parts of India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa there are high groundwater fluoride concentrations associated rocks with volcanic and metamorphic rocks. Further Edmunds & Smedley (2013) observe that in the 28 provinces of China, rampant cases of elevated fluoride levels have been reported in ground water sources. However comparatively shallow borehole sources had less concentrations as compared to deeper ground waters which recorded higher fluoride concentrations. Hallett *et al.* (2015) observed fluoride levels of up to 10 mg/l in borehole water in the dry zone of Sri Lanka where cases of teeth and bone complications are serious. Severe and heavy rainfall resulting in prolonged dissolving of fluoride and other minerals in the wet Zone of Sri Lanka possibly associated with crystalline bedrock contribute to the much lower concentrations of fluoride as observed by Dissanayake (1991).

Boreholes are main sources of water supply in communities living in the non-urban areas in Africa. The borehole water sometimes has quality microbiological and biological properties generally thereby requiring less treatment. However groundwater is contaminated by fluoride which is one of the naturally occurring toxicant. Thole (2013) observes that in some parts of Africa ground water has elevated fluoride levels beyond which are way above the permissible WHO limits. Similarly high fluoride levels have also been reported in Malawi and the Republic of South Africa (Malago *et al*., 2017). An assessment of fluoride in Tanzania's ground water sources observed that approximately a third of the waters used for drinking were beyond the WHO permissible levels. Additionally, fluoride levels exceeding the WHO limits have been reported in Malawi and the Republic of South Africa fluoride.

The nature of rocks in Kenya makes it one of the countries in the world with extraordinary high concentrations of fluoride levels in rocks and soil, surface and ground water. Maximum fluoride concentrations in water sources in Kenya have been observed in some river sources, groundwater and lakes in the Rift Valley (Gikunju *et al.*, 2002). The documented places that experienced magmatic activities are located in the East African Rift valley system. These countries within the Rift Valley system include: Sudan, Ethiopia, Uganda, Kenya and Tanzania. A number of lakes in the Rift Valley region have extremely high fluoride concentrations. The fluoride levels range from 1,640 mg/l to 2,800 mg/l in the Kenyan Lakes of Elementaita and Nakuru respectively according to Nair *et al*. (1984). Further Nair *et al*. (1984) asserted that in a survey involving over 1,000 groundwater sources 61 per cent exceeded 1 mg/l, where 20 per cent exceeded 5 mg/l and 12 per cent exceeded 8 mg/l.

Majority of rocks in places where the phenomena of volcanicity was experienced have fluoride, but with the concentration’s levels are different, relative to the locations of the rock. Conversely, the quantity of fluoride in the water depends on the saturation of the chemical compound in the rock or layer. Fluoride is regarded as an essential element for the formation of healthy bones and teeth: however, levels above 1.5 mg/l in drinking water have been associated with high incidences of dental fluorosis (Maheshwari, 2006). In a study by Moturi (2004) in Njoro Division, in the then Nakuru District, it was established that the groundwater used for cooking and drinking, obtained from boreholes and wells, and had fluoride levels much higher than the World Health Organisation recommended level of 1.5 mg/l.

The government of Kenya in its vision 2030 blue print as observed by Ndungu & Otieno (2011) purposes to supply clean water for its residents with by laying specific attention to a healthy and productive population. The residents living in Njoro catchment mainly get their supplies from rivers, streams, springs, and boreholes. However these communities use the supplied water from these sources without treatment, and therefore quality water monitoring is not possible because many of the regions have no access to piped water. Water contaminated by fluoride result in increased demand among competing multiple water uses and increased medical expenses. Therefore there is need to solve the puzzle of the dynamics of geological variations, borehole stratigraphy matrices and water quality dynamics on the fluoride levels in the River Njoro catchment.

1.2 Statement of the problem

Occurrence of elevated and concentration of fluoride levels of in subsurface and surface water has attracted attention world over because of the repercussions associated with human health. The levels of fluoride in drinking water will determine the impacts which are bound to be either positive or negative on human being's health. The geology of the Rift Valley with the associated phenomena of volcanicity makes it one of the world-wide regions vulnerable to the outcomes of elevated fluoride levels in mineral rocks, soil, surface and ground water. Fluoride fluctuates in different sources of water with increased concentration levels observed within ground water sources. According to WHO (2004) 1.1 billion people in the third world countries have limited access to quality water for drinking and domestic uses and this is no exception in the Njoro catchment. In Kenya, the larger population gets water without any form of treatment from rivers, wells, streams and water pans. However these water sources particularly in Rift valley are contaminated with varying levels of fluoride concentration.

The geology of Njoro catchment makes it a great potential to its surface and groundwater quality attributed to elemental composition as evidenced by the nearby phenomena of volcanicity thereby altering the water's physicochemical parameters. Therefore, the levels of fluoride and physical parameters need to be quantified and thereafter the quality of water determined to ascertain if it exceeds the required limits. Fluoride is a major natural water pollutant in Kenya particularly in the Counties crisscrossed by the East African's Great Rift Valley's geology. Despite the phenomena of the rift valley and fluoride contamination, rivers and boreholes are major sources of water in these Counties. Therefore, the geology of River Njoro catchment would be a great potential risk to the fluoride levels in the region as demonstrated in the river and sub-surface water.

There are many cases of fluorosis that have been recorded in the River Njoro catchment as observed by Gevera (2018) and Mavura *et al.* (2003) with endemic fluorosis in the area being contributed by drinking of ground water with highly fluoridated concentrations. Further fluoride mapping by Kenya Bureau of Standards (KEBS, 2010) report showed Nakuru County as one of the places with at least 50% of its ground water sources having fluorides levels greater than recommended WHO standards, greater than 1.5mg/L. The River Njoro catchment is important to the naturally occurring ecosystems within the catchment and users living in the sub-catchment. However, the ground water that is depended on to provide water for human use in the Njoro catchment to the contrary has high fluoridation levels of fluoride that is demonstrated by the cases of rampant fluorosis.

High fluoride problems occurrence in Njoro catchment is not new as witnessed in the past researches which placed emphasis on the justification of the elevated levels

(Gevera (2018), Kirianki *et al.*, (2018), Mosonik (2015) and Mavura *et al.*, (2003). The subject of geological variation, borehole stratigraphy matrices and fluoride levels in sub surface and ground water has not received overwhelming attention in Kenya despite the findings of a number of researches and studies on existence and dispersal of fluoride levels in the borehole sources of water. Therefore, this study would assist in generating information and data required for evaluating the geology stratigraphy and fluoride levels in the River Njoro catchment.

Consequently, interrogating factors underlying the spatial distribution of fluoride levels becomes a pertinent research issue. Subsequently understanding the possible effects of the geological dynamics and the physical perimeters of water quality on elevated fluoride levels formed a knowledge base and a requisite basis for better and quality water supply in the catchment forming the study area. Ultimately, based on underlying facts on the fluoride phenomena, there was need for systematic and scientific investigation of fluoride level variations in the River Njoro catchment in this study.

1.3 Research Objectives

This study was guided by general and specific objectives as stated below.

1.3.1 General Objective

This research sought to analyse effects of geological variability and selected physical parameters of water quality on fluoride levels in the River Njoro catchment.

1.3.2 Specific Objectives

The study was guided by the following specific objectives:

1. To establish the relationship between surface geology and fluoride levels in River Njoro catchment.
2. To determine the relationship between borehole stratigraphy formation matrices and fluoride levels in borehole water in River Njoro catchment.
3. To determine the relationship between temperature, pH and electrical conductivity and fluoride levels in in River Njoro catchment.
4. To model spatial variation and distribution of fluoride levels in ground water in the River Njoro catchment.

1.3.3 Research Questions

1. What were the levels of Fluoride in the different types of rocks identified in River Njoro catchment?
2. Was there any significant relationship between surface geology and fluoride levels in River Njoro catchment?
3. What was the significant relationship between fluoride levels in the sampled rocks and fluoride in water in River Njoro?
4. How did the variation in borehole stratigraphy formation matrices affect fluoride levels in borehole water in River Njoro catchment?

5. Was there any significant relationship between pH, Temperature and Electrical conductivity of groundwater and fluoride levels in groundwater in River Njoro catchment?

6. How was the variation of fluoride levels in the sampled boreholes in River Njoro catchment?

7. Was there spatial variation of fluoride levels in the surface and ground water in River Njoro catchment?

1.4 Significance of the study

The study assisted to identify and delineate the distribution of fluoride levels in the River Njoro catchment and therefore proposed and recommended preferred zones of alternative safe water sources. Results from the study would be useful to the Ministry of Water and Irrigation, consumer households, Water Resource Authority (WRA) and other agencies that are involved in the formulation of water policies, planning and implementing water development programs and provide social and health services on how to deal with fluorosis to the affected communities living in the study area.

Secondly the findings of this study would highlight the need for more systematic monitoring of water quality in the River Njoro catchment and therefore expand on the existing baseline database of fluoride levels by monitoring the fluoride concentrations in relation to varying land use types, identify longitudinal and seasonal trends in the fluoride levels and relate to the spatial distribution of the fluoride levels as indicator of the water quality status. Consequently, therefore the research forms a data and knowledge bank for future researches in the River Njoro catchment and studies on fluoride pollution in other water catchments of Kenya with geology similar to the one of Njoro catchment.

An understanding of the fluoride dynamics in surface and groundwater fluoride contamination trends would be important to form the background knowledge on the adverse health effects fluorides to the exposed human population in the study area. Finally the environmental authorities would use the results of the study's findings in educating the residents living and working in River Njoro catchment area on dangers of exposing themselves to higher fluoride levels. Subsequently, therefore the study will advise on mitigation measures to save the residents of Njoro from the impacts of naturally occurring fluoride.

1.5 Justification of the study

There is need to understand the water quality issues pertaining water for drinking in addition to other domestic chores so as to check on exposure to high levels of fluoride. People living in the country side use water from their natural sources without considering treating it making water quality monitoring a non-issue. Therefore majority of the rural population have less accessibility to quality water. Therefore considering recent research undertakings, there is need to place emphasis on fluoride campaigns with the aim of establish the risks resulting from increasing fluoride uptake by communities living in fluoride venerable areas (Gikunju *et al.*, 2002).

The use of fluoride rich poses health problem to a big population that is likely to extend to millions worldwide. Drinking water is the main source of fluoride intake by human beings especially in areas where fluoride concentrations of sub surface and surface water are high. In the early years of growth and development fluoride ingested is distributed throughout the body and retained in bones and teeth. Consequently people develop diseases of the teeth and bones which are evidenced by brown teeth and weak bones which fracture with ease (Mkawale, 2011).

According to Jacoben (1993) who conducted studies in the United Kingdom and Unites States of America respectively, excess fluoride in water has been associated with hip fracture. Further, at detrimental stages, skeletal fluorosis affects limb bones making them brittle and weak resulting in development of rickets. Therefore is necessary to be conversant with attributes of water meant for drinking and other domestic chores so as to avoid exposure to high fluoride quantities. Communities living in River Njoro catchment get water for domestic chores from rivers and boreholes without treatment, and therefore there is need to initiate water quality monitoring. Therefore, there is need for more fluoride surveys to be carried out so as to ascertain the threats associated with cumulative fluoride exposure levels in people living in high fluoride occurring areas.

World Health Organization recommends fluoride content not exceeding 1.5 mg/l in portable water. Conversely, people living in Njoro catchment and its environs are victims of dental fluorosis which is associated with consumption of groundwater whose fluoride levels are beyond the WHO limit. Much of the studies and literature available on Njoro watershed and largely extending to the Rift Valley region have been limited to presence, amounts and contamination of groundwater with less emphasis on the geological formations on the sources and aquifers of the water. This study therefore sought to generate information useful in policy formulation so as to check quantities of fluoride in water meant for drinking. By initiating the regulations on permissible levels it would be possible to initiate guidelines to safeguard the public from experiencing harmful levels of fluoride. This study also gave support to past researches by emphasizing the levels of fluoride and allowed for the delineation and prediction of potential sites with permissible fluoride levels for groundwater for use by the local population.

1.6 Study area

The particulars of the study area are as discussed below.

1.6.1 Location and Extend of the study area

The study area is the area covered by the catchment of River Njoro in the Lake Nakuru catchment as shown in Figure 1.1. According to Gichuki *et al.* (1997) River Njoro is averagely 10 m wide and provides approximately two thirds of the total freshwater entering into Lake Nakuru. The River Njoro is located in Nakuru County in the former Rift Valley Province in Kenya whose geology is volcanic and has high incidences of fluoride related diseases. Further according to Enanga *et al.* (2011) River Njoro is estimated to be 50 km long covering a catchment area estimated to be 270 km^2. This catchment area constitutes the River Njoro watershed. The river originates in the escarpment to the East of Mau whose altitude approximately rises to 3,000 m. As the river flows downstream it snakes passing by forest and crop covered lands before being utilised by a number of urban dwellers.

River Njoro drains through many farms and settlements before pouring its water into Lake Nakuru which lies at an elevation of 1755 m. River Njoro’s bed is preoccupied by rocky bottom formations, which have formed many cataracts. The forest covered slopes of Eastern Mau escarpment have witnessed far-reaching encroachment, which in turn has led to increased soil degradation, low restore and remarkable fluctuation in stream flows. The River Njoro watershed is situated to the South-Western Rift Valley at 0°30' South, 35°20' East. The Njoro Watershed is a vital water source for Lake Nakuru: a large shallow saline lake designated as Ramsar Wetland site which has attracted international importance.

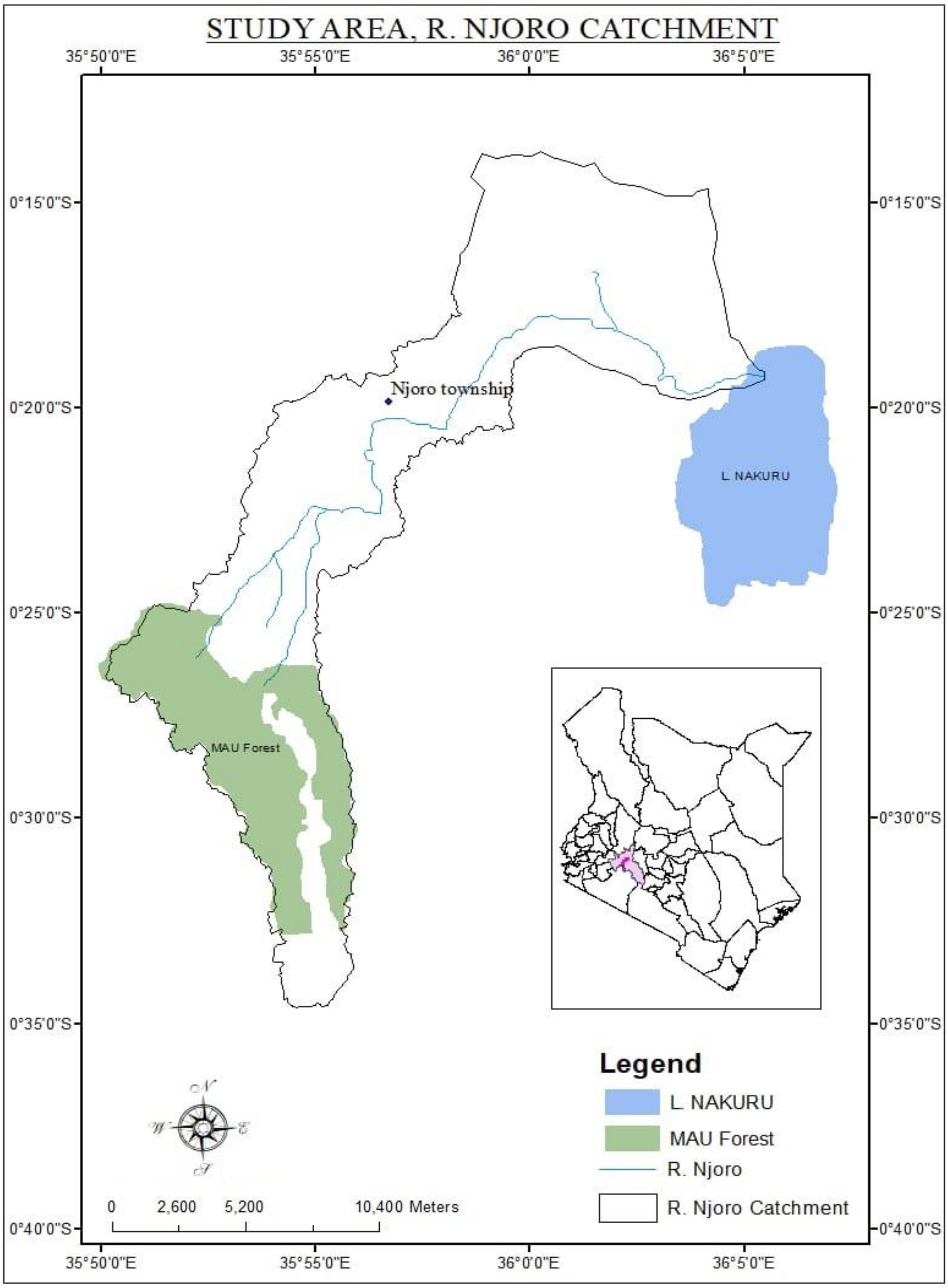

Figure 1.1: Map of the study area

1.6.2 Topography

The source of River Njoro is characterized by mountains and hills which have undulating scenery while the mouth consist of gently sloping plains. River Njoro originates at an elevation of about 3,000 m above sea level in the Eastern Mau Escarpment and descend in a northeast direction finally pouring its water into Lake Nakuru on the floor of the Rift Valley at about 1,800 metres above sea level. The River Njoro catchment is part of the larger Lake Nakuru catchment, and one of the rivers originating from the Eastern Mau Forest of the Mau Complex and draining into the Lake Nakuru.

1.6.3 Geology and Soils

The geology of River Njoro catchment varies significantly from one geomorphologic setting to another, a phenomenon associated with regional tectonic setting of the area. The geology of Njoro area comprises mainly of volcanic soils and rocks (lava and pyroclastics) of Tertiary - Quaternary Age, which has been affected by a series of faulting, and covered by recent sediments. Geology is characterized by porous pumiceous formations. Soils include Humic Acrisols (Ultisols), Phaeozems (Mollisols), Andosols, Planosols (Aqualfs), Plinthosols, and Fluvisols (Mainuri, 2006). The soil textures range from clay loams in the lower watershed to sandy clay in the plantations and indigenous forest areas at higher altitude, the focus of this study.

The study area has soils that are loamy in nature upstream at the forested region and deep grained soils to moderately deep fertile sandy clays while downstream the catchment is comprised of erosive lacustrine soils as observed by Maina and Laude (2016). The geology of River Njoro catchment has close association and similarity to the Great Rift Valley system. There are a few seasonal rivers in the Njoro catchment with their beds covered by huge stones. River Njoro catchment's geology is largely tertiary volcanic rocks of tuff and lava origin which make part of huge gneiss of the Mozambique belt. Stratigraphic formations of River Njoro include: tertiary deposits and volcanic: quaternary deposits, basalts, phonolites and trachytes represent tertiary volcanics. Underlying geology include different types of Gneisses, schist, quartzite and marbles. The tectonic events that occurred when the Rift Valley was being formed resulted in fractures of different magnitudes and degrees.

1.6.4 Climate

Rainfall patterns within the River Njoro Catchment are extremely variable both spatially and temporal and in terms of rainfall intensities. This makes the natural flows of water in the River Njoro and its tributaries highly variable in space and time. The climate is characterized by a trimodal precipitation pattern: High and heavy rains from April to May: little, intense rains in August: and shorter, less intense rains from November to December. Total annual precipitation is 956 mm, and the mean annual temperature is 16.5 °C, ranging from a minimum of 9 °C in July to a maximum of 24 °C January. The rainfall and temperature patterns of Nakuru County and Egerton University Metrological Stations located in the River Njoro catchment are given in presented in Figure 3.6.

1.6.5 Vegetation

Vegetation cover in the Njoro watershed ranges from 0% in areas affected by anthropogenic practices to 90% in upland indigenous forests that are difficult to settle due to rugged topographic relief. The catchment's uplands are characterized by vegetation zones as observed by Mathooko and Kariuki (2000). Heavily grazed moorlands are found in the uppermost section and bordering a dense closed canopy indigenous montane forest mixed with bamboo. According to Mathooko and Kariuki (2000) tracts of intact and deforested plantations are present downstream consisting of various *Cupressus* and *Pinus* species.

The diverse vegetation found in the River Njoro watershed serves a wide range of purposes including timber harvesting, medicine, human food, livestock fodder, building material, and fuel wood. And finally the vegetation cover ranges from 90% in upland indigenous forests that are difficult to reach due to extreme topographic relief on the eastern rift escarpment to 0% in areas affected by anthropogenic practices as observed by Baldyga *et al*. (2004).

1.6.6 Economic Activities

Majority of the later immigrants into River Njoro catchment were initially keeping large herds of livestock however they have turned to be agro-pastoralists. The settlers within the catchment are using cleared forest areas for the rearing of cattle, sheep and donkeys in addition to crop farming. This encroachment into the water catchment has resulted in a third zone, of permanent settlements that range from small to large-scale farms. A long side the small-scale farming, the settlers in the Njoro catchment additionally rear dairy animals and cultivate wheat which is a main crop. Peasant farmers are spread with a few remaining large-scale farms belonging to the former colonialists, which partially covers Egerton University's commercial farm (Lelo *et al.*, 2005).

1.6.7 Population

Lelo *et al*. (2005) observes that the River Njoro catchment has a population of over 300,000 people (Ministry of Finance and Planning, 2002) which also includes 30,000 people the residents of urban centre Njoro Township and a population of 270,000 people occupying much of the Nakuru Municipality. Moreover Lelo *et al.* (2005) observed that approximately 50% of population in River Njoro catchment lived below the poverty line hence increased demands on water one of the natural resources. Livestock was estimated to be 25,700 reared mostly by the Maasai pastoralists and formed part of the poor-farmers' households' livelihoods. River Njoro catchment has been converted from a less densely populated and a large area covered by forests into a region that is occupied by a large settled population, expansively cultivated, and expansive urbanized area during the last 30 years. A main driver in the conversion of this catchment has been the substantial increase in the human population, resulting from both past and continuing extensive resettlement.

1.6.8 Land use/Land cover

The dynamics of land cover in the study area has undergone alteration from the start of the 19th century attributed to large scale settlement in the upstream and midstream by colonialist and thereafter Kenyan settlers in the 1970's and 1980's. River Njoro is approximately 60 km in length and surrounded by degraded indigenous forests in the upper stream. Local vegetation resources are used by the residents for medicinal purposes, firewood, and food for livestock, sub surface and surface water. The semi-arid areas are common for gathering fruits and small-scale hunting for wild meat for the riparian and inhabitants of forest livestock keeping grounds for the Maasai pastoralists.

Land use in the River Njoro catchment varies greatly and depends on the rainfall reliability. In the upper part of the catchment, where forest has been cleared, crop production and livestock keeping are the main activities. The lower part of the catchment receives low rainfall but not reliable as compared to the upper part. In this area, livestock keeping and crop farming is practiced together with irrigation along the river banks. The practice of farming in sloppy areas and near the streams draining within the catchment has contributed to the sediment transported out of the catchment. According to Yillia *et al.* (2008) the degradation of the River Njoro catchment has led to poor soil fertility which has eventually reduced the crop yields.

During the last 20 years River Njoro Catchment has experienced rapid land use change and population growth resulting in negative impacts on the water resources. Land use pattern has been changing since the early 70's with increasing population resulting into increased conversion of forest land into agricultural and settlement areas especially in the upstream Mau Escarpment (Were *et al.*, 2013). At least four land uses are significant, which have resulted in the alteration of the hydrological characteristics of the catchment. Starting at the source of the river, the upper zone is predominantly forested with indigenous plant species. This opens to new settlements on the deforested area which is characterized by settlement and small-scale subsistence farms (Kibichi *et al*., 2007)

Within the River Njoro catchment there are urban centres as another type of land use, mainly in the middle and lower zone, covering Egerton University, Njoro Township and parts of Nakuru Municipality. These zones consist of more densely populated settlements, industries and commercial activity. At the end of the watershed is Lake Nakuru National Park which encloses Lake Nakuru. The main land use/covers in the River Njoro catchment as shown in Figure 1.2 are: agriculture, commercial and residential settlement, forest, grassland and water body. Water resource conflicts are widespread problems in the River Njoro catchment between different communities with fluctuating intensities of water utilization and views about water resource management. This has resulted in disparity in water allocations and therefore community involvement is vital to achieve restoration and conservation of the water resources in the Njoro watershed. Based on GIS and LANDSAT images for spatial analysis of land use activities the main land use activities that were identified in the River Njoro catchment in 2017 were: agriculture, commercial settlement, forest, residential settlement and scrubland. Apparently, the land use/cover activities differed in the three longitudinal zones of the river catchment: Upper, Middle and Lower zones.

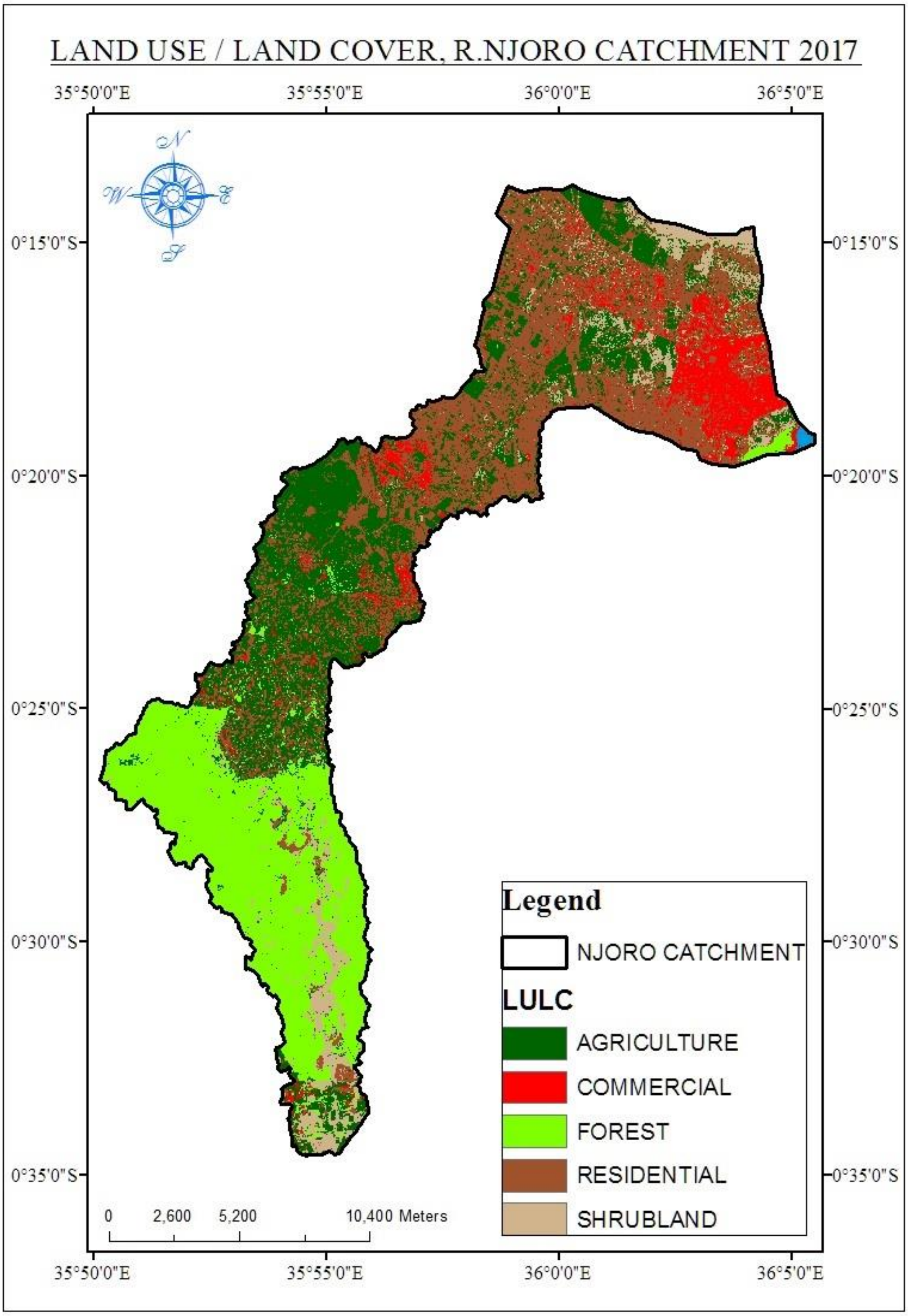

Figure 1.2: River Njoro's Land use/Cover map derived from classified LANDSAT Image bands of 2007 and 2017

1.7 Theoretical Framework

This study adopted the water fluoridation controversy theory. The water fluoridation controversy places emphasis on health considerations as appertains to the removal of excess fluoride from water meant for general public use. The controversy over excess fluoride removal of water meant for drinking is traced to the time after America's Public Health publically started the country's Fluoridation initiative during nineteen sixties. However, over time, the controversy has gained momentum over the years after research supported the anti-fluoride momentum. In this research it is apparent that fluoride levels in Njoro catchment are above the permissible levels and therefore the emphasis is not to plunge into the debate but help to promote defluoridation.

However, little emphasis was placed on the welfare and efficiency of excess fluoride removal in water amongst the disadvantaged groups in developed and developing countries, global and regional organizations and associations treating teeth worldwide (Pizzo *et al.,* 2007). Proponents of excess fluoride removal saw it as a question of public health policy and equated the issue to claiming significant benefits to dental health and minimal risks. To the contrary, persons opposing water fluoridation see the removal of excess fluorides as infringing on person's privileges. The opponents further argue that fluoridation is out rightly violating of health principles because individuals can only drink more expensive bottled water making the individuals to have no choice on the type of water that would be available for their use. Emphasis on defluoridation is based on the irreversible, devastating repercussions associated with fluoride toxins, the imminent impacts, and therefore the cumulative effects of fluoride ingestion to maintain acceptable WHO levels.

Elevated negative consequences associated with fluoride concentrations beyond the WHO recommended levels cannot be ignored. The water fluoridation controversy theory was therefore relevant in this study because toxins associated with excess fluoride are manifested through the teeth and bone diseases in the River Njoro catchment. Permanent, devastating impacts related to fluoride toxins and continuous exposures to fluoride are a debate than can only be brought to an end if the influence of geological dynamics on fluoride levels is understood. Anti-fluoride activists' observations range from proclaiming fluoride as a gradual, increasing toxic substance to fluoridation of water meant for public use as a defilement of human privileges and this can only be supported by the outcome of this research. On the basis of the fluoridation controversy theory the study forms a foundation on the need to adopt defluoridation or use of low fluoride tooth paste in areas vulnerable to high fluorides.

1.8 Conceptual Framework

The bearing and technique of a research is based on the conceptual framework which gives a basis of the developed theoretical concepts. Purposefully the conceptual framework makes research findings more meaningful and satisfactory to the theoretical constructs in the research field by giving bearing on generalization. Finally the conceptual framework helps in inspiring investigation by warranting the addition of awareness in giving both direction and motivation to the research inquiry. The schematic presentation of related concepts of this research is presented in Figure 1.3. The areal dispersal of fluoride levels in borehole and surface waters in Njoro catchment is pegged on the WHO recommended levels of 1.5 mg/l.

Therefore in this study the dependent variable is the fluoride levels. However, these levels are determined by independent variables. The independent variables in this study include: the surface geology, particular water quality attributes borehole depths in addition to the borehole stratigraphy. The physical quality parameters in this study included: pH, temperature and electrical conductivity of the borehole water. The surface geology placed emphasis on the fluoride levels under different rock types in River Njoro. On the other hand, selected physical parameters, borehole depths and borehole stratigraphy were in reference to the groundwater. The association of the input and output parameters would be affected through overriding variables.

Intervening variables in this research included: the slope of the land, soil types, rainfall intensities and water defluoridation or treatment. Subsequently the impacts of fluoride levels that are higher than the recommended WHO levels would be manifested through cases of Poor heath evidenced by dental and skeletal fluorosis. Therefore the sources of fluorides in the water of the River Njoro catchment would be attributed the geological variations, and borehole depth and stratigraphy. Finally considering the independent and intervening variables the fluoride levels in River Njoro catchment are likely to be above or below the WHO levels of levels of 1.5 mg/l.

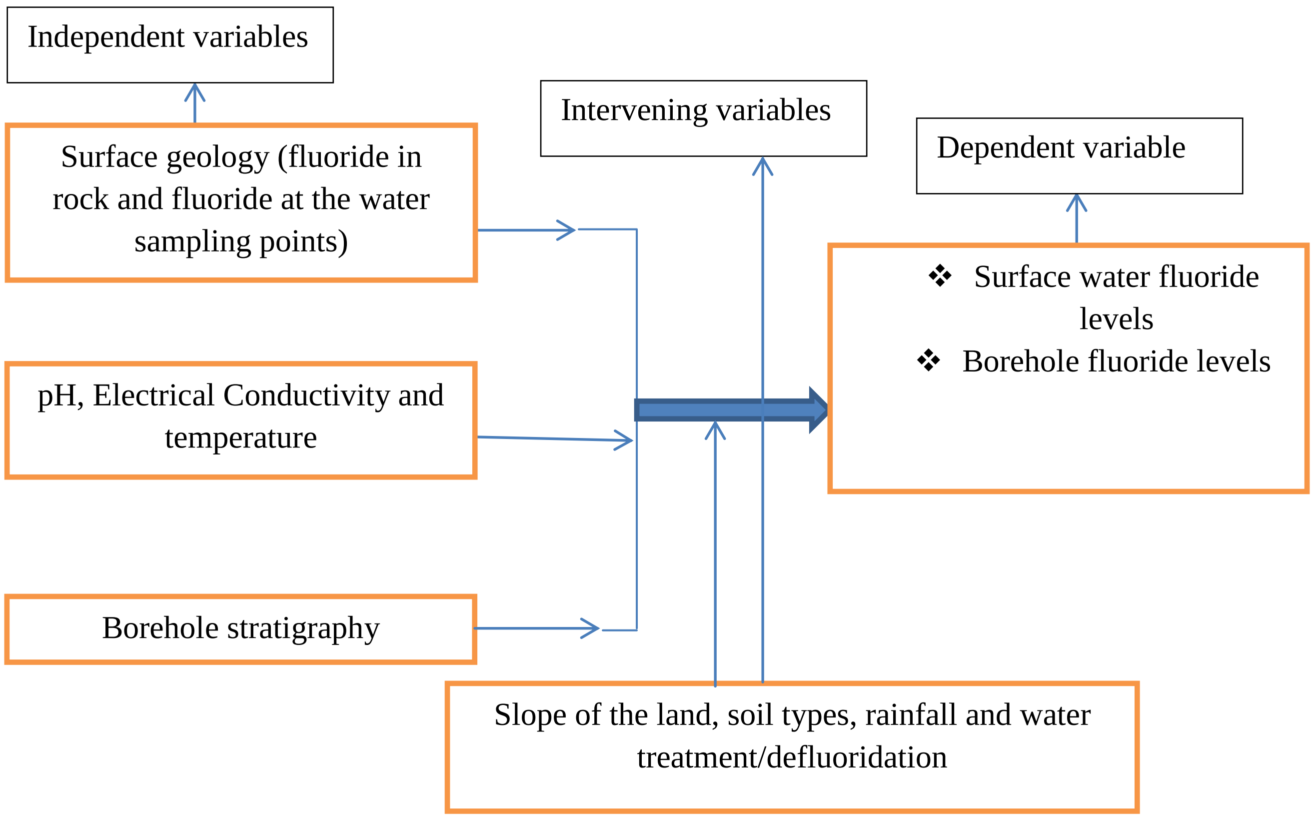

Figure 1.3: Conceptual Framework

CHAPTER TWO

LITERATURE REVIEW

Introduction

This chapter presents review of literature based on the objectives of the study. It presents literature review on: water quality, fluoride levels and distribution and hydrological factors and the fluoride levels. Finally, also the chapter discusses water quality and fluoride levels, geology and fluoride concentration and geological formations in the Rift Valley and ultimately knowledge gap.

2.1 Fluoride

As an ion fluoride an organic element belonging to the halogen group. Naturally in its occurrence in water fluoride can either be above WHO recommended levels. However Fawell *et al.* (2006) observes that surface water usually contain fluoride levels less than 0.5 mg/l, but borehole water, especially in areas that experience volcanicity and rugged areas are known to have more than 50 mg/l which is far beyond the WHO limits. Elevated concentrations of fluoride are available in rocks having high pH. Magmatic rocks, hydrothermal and sedimentary in nature all are volcanic in nature. Elevated fluoride results from the dissolution of fluorine with water in the rocks. Mostly in water meant for drinking, over 95% of total fluoride is the fluoride ion having the compound of magnesium–fluoride. Usually, fluoride levels in aqueous nature are controlled by the solubility of fluorite (CaF_2), resulting in increased fluoride levels that are associated with calcium deficient, alkaline, and soft waters as observed by Ozsvath (2009).

Due to its maximum electronegativity and reactivity among all chemical elements, the elemental fluorine state occurs rarely in nature. Ayoob and Gupta (2007) observe that fluoride mineral complexes and compounds form a significant part of the earth's crust. Traces of fluoride can be found in air, most foodstuffs and beverages, particularly in tea but the principal daily intake source for humans constituting 75% is drinking water (Maleki *et al.*, 2014). It is known now that the 97% of global freshwater is stored in subsurface and groundwater resources. Moreover it has been estimated that more than 50% of the world's population depends on groundwater for survival. However in many parts of the world, especially in arid and semi-arid climates, there is no alternative for communities to supply drinking water. Increasing population expansion accompanied with unrestricted groundwater tapping would probably cause more fluoride contamination associated with geology. However the geogenic contamination would be supplemented by some other anthropogenic sources, such as aluminium and fertilizer industries as asserted by Mahvi and Amini (2011).

The final fluoride concentration in groundwater is largely determined by response and contact period with aquifer fluoride bearing minerals. Elevated quantities of fluoride increase in groundwater which has stayed for long time in the aquifers. Brunt *et al.* (2004) observes that ground water with long residence times has association with deep water sources and a slow groundwater movement. Conversely water sources that are shallow containing recently penetrated rainwater usually have low fluoride. However, there are exceptions when shallow water sources are situated in active volcanic areas affected by hydrothermal modifications. In these conditions, the solubility of fluoride increases as temperature increases and fluoride may be added by dissolution when Hydrogen Fluoride is gaseous (Frencken *et al.*, 1992).

Fluoride has a significant mitigating effect against dental caries if the concentration is approximately 1.0 mg/l as observed by Mbithi (2017). However, continuing consumption of higher concentrations can cause dental fluorosis. Muller (2005) asserts that high fluoride concentrations are especially critical in developing countries, largely because of lack of suitable infrastructure for treatment. Fluoride is a common constitute of ground water where the natural sources are connected to various geological structures and volcanic activities. However, where industrial activities like clay and ceramic industrial activities are established, there would be a possibility of high fluoride concentrations in groundwater.

Fluoride mineral compounds, account for 0.3 g/kg of the earth's crust as observed by Kantharaja *et al*. (2012). Traces of fluoride can be found in air, most foodstuffs and beverages, mainly in tea however the principal daily intake source for humans comprising of 75% is drinking water (Mahvi *et al.,* 2006). It is known now that the 97% of global freshwater is stored in subsurface and groundwater resources. It has also been estimated that more than 50% of the world's population depends on groundwater for survival. Furthermore, in many parts of the world, especially in arid and semi-arid climates, there is no alternative for communities to supply drinking water and therefore the only source of water turns out to be boreholes.

Fluoride concentration in water is an aspect of the hydrochemistry of the water. It is observed that fluoride into water source is mainly released when fluorine-containing minerals undergo weathering and leaching. Commonly the fluorine-bearing minerals in rocks are: fluorine apatite, micas and amphiboles (Naseem *et al*., 2010). The evolution of fluoride rich natural water results from leaching of rocks hence the concept of percolation. The leaching ability of elements in rocks depends on the strength of bonding forces. The more the element is held up to the silicate lattice, the less it is vulnerable to weathering. However, the solubility product of a mineral is also an important aspect that determines the concentration of fluoride in any natural water under a given environment.

Volcanic activities have close relationship with high fluorine contents. Therefore concentrations of high fluoride would usually be found in geothermal waters as observed by Desbarats (2009). Marieta (2007) observes that fluoride is often associated with volcanic activity and fumarolic gases and therefore found in all natural waters at some concentration. Typically, sea water contains about 1mg/l while rivers and lakes generally exhibit concentrations of less than 0.5mg/l. In groundwater, low or high concentration of fluoride can occur depending on the nature of the rock and occurrence of fluoride-bearing minerals (Edmunds and Smedley, 2013). Fluorides are found in significant proportions in fluorspar, rock phosphate, cryolite, apatite, mica and hornblende.

The contents of fluoride in the drinking water vary a lot, even within the same area, depending on several factors. People have different sources of drinking water: rainwater, surface water of lakes and rivers or streams and groundwater. In respect of fluoride content however, rainwater and surface water may absorb dust or pollutants containing fluoride from coal burning or industry as in oil and ceramic manufacture and nuclear industry as observed by Jha *et al*. (2011). The variation of fluoride levels depends on the source or pollution and on the prevailing weather conditions. For example a spring from a groundwater source with high fluoride concentration will contain a lot, and even contaminate rivers or lakes. And after period of high rainfall according to Nanyaro *et al.* (1984) there will be a dilution of fluoride.

The release of fluoride from minerals to the groundwater are determined by the chemical composition of the water, the presence and accessibility of fluoride minerals to water and the contact time between the source mineral and water (Jha *et al*., 2011). The concentration of fluoride increases the deeper into the ground you come, but it also shows great variability within one area. This increase can be explained by accumulation, on the water's way down from the soil: fluoride is leached and accumulated. Another contribution to fluorine in ground water is from gas and steam ascending from the magma chamber towards the surface whereby during its ejection it may get dissolved in the groundwater. This may be one reason for high variability of the fluoride concentrations in different ground water pockets. High concentration of fluoride ions in wells and springs are found in many places notably in Asia and Africa as asserted by Appelo & Postma (2005).

The East African Rift Valley especially in Tanzania and in Ethiopia is a known high fluoride region, (Chernet *et al.*, 2001). Clarke *et al.* (1990) found groundwater to contain up to 180 mg/l. Fluoride levels at Lake Naivasha in Kenya are attributed to the high concentrations due to the leaching of the volcanic rocks in the East African Rift Valley. Volcanic rocks therefore actually have high natural fluoride contents. Gupta *et al.* (2005) found high fluoride concentrations in India to be associated with evaporative enrichment, preferential dissolution of high sulphide-bearing minerals and thermal springs. Similarly, Subba Rao (2003) found a difference in fluoride concentrations in pre- and post-monsoon water in India.

There are health problems associated with high fluoride ingested by humans in the East African Rift Valley in some regions of Tanzania and Ethiopia (Nanyaro *et al.*, 1984 and Chernet *et al.*, 2001). Further Appelo & Postma (2005) observes that fluoride in drinking water constitutes a health hazard at concentrations. Fluoride is basically brought into the groundwater by leaching from minerals in the rocks (Saxena & Ahmed, 2003). Clarke *et al.* (1990) found groundwater to contain up to 180 mg/L of fluoride at Lake Naivasha and attributed these high concentrations to the leaching of the volcanic rocks in the East African Rift Valley. Gupta *et al.* (2005) found high fluoride concentrations in India to be associated with evaporative enrichment, preferential dissolution of high sulphide-bearing minerals and thermal springs.

Geologically Kenya is one of the countries in the world where fluoride occurs in highest concentrations, not only in rocks and soil, but also in surface and ground water. The exceptionally high fluoride concentrations in water occur in some springs, boreholes, and lakes in the Rift Valley. As sources of fresh water, rivers are generally low in fluoride concentration, but many factors affect the concentration of fluoride in them, such as temperature, pH, and the nature and porosity of the rocks and soils over which the water pass. Fluoride basically results from water coming into contact with fluoride bearing minerals such as fluorite (CaF_2), fluor-apatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6) which are found in granite, pegmatite and granite gneisses (Subba Rao, 2009).

Fluoride is essential to living organisms at concentrations between 1-3 mg/day as asserted by Katsonou *et al.* (2013), however when this limit is exceeded it poses a threat to human health due to its high affinity for Calcium ions contained in bones and teeth. The most common disease associated with fluoride is fluorosis. The initial most common symptoms are seen as brown specs on teeth, while later stages result in severe skeletal damage. According to Redda *et al*. (2006), significant variations in fluoride levels in wells within the rift valley have been noted such that shifting the water supply from unsafe surface water to safe groundwater has introduced a fluoride poisoning.

Fluoride is a chemical element that results in major effects on human health through drinking water. Different forms of fluoride exposure are of importance and have shown to affect the body’s fluoride content and thus increasing the risks of fluoride-prone diseases. Medley *et al.* (2002) observes that fluoride is of benefit to the teeth: conversely low concentrations of fluoride increase the risk of tooth decay. Fluoride can also be quite detrimental at higher concentrations at skeletal fluorosis. The most common consequence of exposure to excess fluoride is dental fluorosis also referred to as ‘mottled enamel’ which cause staining or blackening, weakening and possible loss of teeth. Although not life threatening, dental fluorosis adversely affects the quality of life as poor dental health compromises integration into society and can eventually result in bone deformation.

Fluoride has interesting properties related to human health, particularly in preventing dental caries. However, when it is concentrated in drinking water at levels higher than 1 mg/l, a clinical condition called dental fluorosis may appear. This consists of a dental enamel hypomineralization that manifests through greater surface and subsurface porosity than in normal enamel, a condition that develops as a result of excessive fluoride intake. Typical symptoms of dental fluorosis are fine white stripes to dark stains in the teeth surface. Endemic fluorosis is known to affect many millions of people around the world due to chronic exposure to high levels of fluoride in drinking water. The incidence of this illness is also closely correlated with climatic conditions, eating habits, and the social status of the population.

The negative outcomes of fluoride levels are well anticipated by the quantities taken and the time of exposure. Fluoride requirements set for water meant for drinking in moderately warm areas are not directly applicable to hot moist regions, where high amounts of water are taken. To the contrary epidemiological studies as observed by Fawell and Bailey (2006) assert that the effects of fluoride on teeth and bone have been associated with the outcome of fluoride absorption in drinking water. The World Health Organization has established a maximum concentration of 1.5 mg/l as a guideline value for drinking water (Fawell and Bailey, 2006) and most countries have adopted this value in their corresponding national regulations. Long-term intake of high doses of fluoride can also produce alterations in the musculoskeletal, reproductive, developmental, renal, endocrine, neurological, and genotoxic systems. Bones and teeth are the target organs of fluoride, as they tend to accumulate it with age (Ayoob and Gupta, 2006).

Plate 2.1: Case of dental decay (with permission)

2.1.1 Occurrence of fluoride

In the periodic table fluorine is the ninth element. Moreover, its uses and biotic implications were known only in the decades of 1920s. It is the lightest element of the halogen group and among the electronegative elements. Fluorine has both prominent chemical attributes and physiological properties, which are of enormous interest and importance to human health. Fluorine is rarely found free in nature in its elemental form. Fluorine has strong attraction to chemically combine with other elements thereby forming rich fluorides compounds.

Free fluorine has no part to play in addition of toxins because it reacts instantly resulting to the formation of fluoride compounds. The availability of fluoride dissolved fluorides in naturally occurring water is likely only when the surroundings favour long time of residence of the F-species in aqueous state (Fawel *et al.*, 2006). The underlying control on fluoride concentration is geological. Fluorine occurs in almost all types of rocks. Contrary more quantities of fluoride occur within areas associated with hot spots and along rift valley zones. Additionally in geologically unstable places fluids rich in fluoride rise from the Earth's crust or mantle up towards the surface sediments.

In rivers and boreholes the natural occurrence of fluoride is attributed to surface run off whose origin is disintegration of fluoride containing rocks and soils leaching from soil. In the atmosphere deposition of fluoride containing emissions from coal fired power plants and other industrial also contributes to high mounts found in the water as either by direct deposition or by deposition to soil and subsequent runoff into water. Topaz and fluorite are some of the rocks resulting in minerals that have fluorine as important components in their formulae. The other minerals in which fluorine is an essential component are accessory minerals-fluorapatite, fluomical, cryolite, and villiaumite. These fluoride minerals are sparingly soluble in water. The cases of bone and teeth diseases related to high quantities of fluoride related diseases are due large quantities of drinking directly from water sources.

2.1.2 Fluoride in the Environment

The summarized circulation of fluoride in the biogeosphere is presented in figure 2.1. The biosphere cycle discusses to the way in which fluoride compounds circulate in nature. It mainly involves a continuous exchange of fluoride ions between living and non-living things. Fluorine usually arises in joint nature of minerals as fluoride. It is highly reactive and represents about 0.06 to 0.09 % of the earth crust. The presence of fluorine in the groundwater is mainly a natural phenomenon, and mainly influenced by local and regional geological conditions, as the fluoride minerals are nearly insoluble in water.

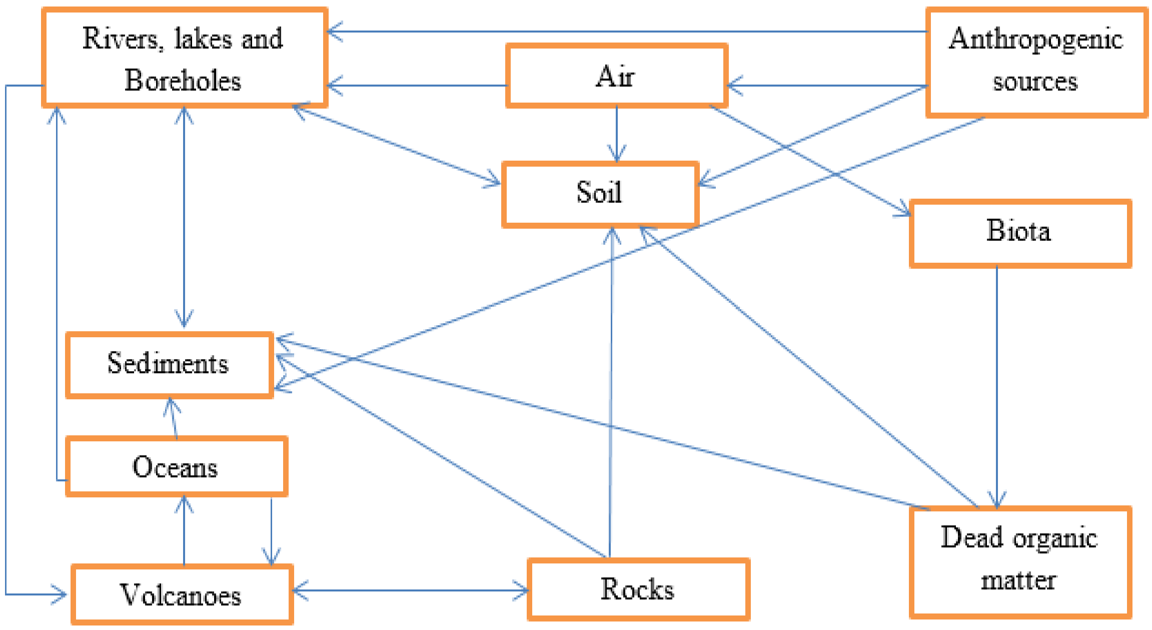

Figure 2.1: Fluoride Biogeocycle (Adopted from Connett (2002).

Occurrence of varied concentration of fluoride in subsurface water is a result of natural or human induced causes or a mixture of both. Natural points of entry have a relationship with the geological conditions of an area. Different geological formations have fluoride bearing minerals like apatite, fluorite, biotite and hornblende. The processes of weathering and infiltration increases fluoride concentration in groundwater. Fluoride which is available in high levels in volcanic ash is soluble with ease in water and this forms another likely source. Human induced additions of fluoride include farming activities and burning of coal. Phosphorous related fertilizers increase fluoride concentration in fields where crops are supplied with water. Coal which is a likely origin of fluoride is used for burning in several industries and in industries making bricks. Release of fluoride into the atmosphere in the form of gases during these activities will reach the surface during rainfall as particulate fluorides.

Naturally occurrence of fluoride in volcanic rocks is associated with its high levels in Precambrian rocks. With Fluorite (fluorspar, CaF_2) being the abundant mineral rich bearing chemical. Soils with clay store high quantities of fluorite in groundwater and lakes in volcanic areas. Moreover sub surface water is the principle source of fluoride. In soils the decomposition and weathering of original geologic material is believed to be responsible for the high concentration of fluoride. Fluoride that is soluble in water is of greatest interest because it may affect lives of plants and animals. In salty soils the dominance of sodium and the resultant greater solubility usually leads to water soluble fluoride concentrations of high levels. Volcanic eruptions contribute large amounts of fluoride to surface soils when volcanic ash is deposited on the terrain. Equally the annual addition of fluoride containing superphosphate fertilizers by farmers also increases the levels of fluoride in the soil. Subsurface water according to Marieta (2007) has the likelihood of having higher fluoride concentration than surface water. Nonetheless a borehole that has deep groundwater with long time of rock contact tends to have higher fluoride concentration as compared to shallow wells.

2.2 Factors influencing fluoride levels

In ground-water, the natural concentration is determined by rock types, aquifer characteristics (chemical and physical), and the porosity and acidity of the soil and rocks. Additionally, as observed by Tahaikt *et al.* (2008) quantities of temperature and chemical reaction of elements contribute to more fluoride. Conversely fluoride concentration within surface water has relationship with hotness or coldness of the water, acidity or alkalinity, availability of precipitating ions and colloids and the nature of solubility minerals bearing fluorine. Additionally, fluoride levels are associated with anion exchange ability of the materials making the water sources, the nature and size of rock formations crisscrossed by water, in addition to residence time during which water takes within particular formation of rocks (Narsimha & Sudarshan, 2017).

2.2.1 Geology

Percolation and dissolution of fluorine into boreholes and hot gases during weathering and flow of water in rocks and soils contribute to fluoride occurrence in particular areas. Consequently, groundwater fluoride quantities fluctuate with variation on the geological formations with fluorite, apatite and micas being the common fluorine-bearing minerals. Subsequently the problems associated with high fluoride levels will be experienced where minerals of volcanic origin are in abundance in the rocks. Generally accumulation of fluorine is enhanced by crystallization of magma and differentiation making the remaining magma to be improved in fluorine. Borehole water from rocks that are crystalized would be principally sensitive to comparatively large quantities of fluoride. Rocks with concentrated fluoride levels predominantly occupy places covered by Precambrian basement rocks. When magma is being crystallized and differentiated, fluorine which cannot be integrated in crystalline stage is stored in hot water solutions. The solutions are ultimately are changed to form accumulations of hot aqueous fluorite and veins. According to Allmann *et al.* (1974) the movement of fluorine in the liquid nature is controlled mainly depending how CaF_2 would be soluble.

In sedimentary rock fluorine levels vary in the range from 200 ppm as observed in limestone and 1000 ppm in shale (Frencken *et al.,* 1992). The occurrence of fluorine is in form of fluorite in carbonate sedimentary rocks. Additionally clastic deposits in micas and illites in the clay segments witness higher fluorine quantities. Frencken *et al.* (1992) asserts that high concentrations could also be found in strata having sedimentary phosphate or volcanic ash. Ultimately fluorine concentration range from 100 ppm to more than 5000 in areas that have undergone regional and contact metamorphism respectively. Therefore the metasomatic processes enrich the original metamorphic rocks with fluorine.

According to Brunt *et al.* (2004) levels of fluoride quantities in extrusive and intrusive igneous rocks has been reported to be as high as 100 ppm and greater than 1000 ppm in ultramafic and alkali rocks, respectively. The process of fractionation during crystallization and differentiation of the magma results in elevated concentration of fluoride in ultramafic and mafic rocks. Moreover: fluoride that is not combined during crystallization and differentiation phases of magma is concentrated in hot water solutions. Though, fluorine is reported to be the most abundant halogen in rocks laid in layers, it is normally in low quantities apart from places which experience mineralization of specific nature. Moreover high fluoride has been observed in groundwater especially in desert related sedimentary water sources with levels in the maximum of 200 ppm of fluorine being observed in the formations of limestone.

Additionally, fluoride is said in plenty in deposits whose origin is in oceans and seas as compared to those originating from land. Equally high fluoride in metamorphic rocks has been reported with relatively high quantities (Fawell *et al.,* 2006). The parent minerals are developed with fluorine by met somatic activities. In areas that have experienced regional metamorphism fluorine levels in the metamorphic rocks are about 100 ppm while in areas that have experienced contact metamorphism the levels are about 5000 ppm. Ozsvath (2006) and Saxena & Ahmed (2003) assert that the fluorite is the main mineral occurring naturally with common attachment with granitic rocks. Fluorine is also obtainable in great quantities in other minerals taking the form of apatite, micas, amphiboles, and clay minerals as observed by Karro and Uppin (2013): Narsimha & Sudarshan (2013) and Rafique *et al*. (2009).

2.2.2 Contact time

Fluoride levels in groundwater are largely dependent on reaction times with sources of minerals. However, occasionally high levels of fluoride can accumulate in boreholes which have taken long time in sources of water. Borehole waters having long residence time are usually associated with deep water sources systems and sluggish sub surface water movement as observed by Brunt *et al.* (2004). Surface aquifers having recently percolated water from rain usually have low fluoride quantities. Nevertheless exceptional cases are experienced in water sources that are shallow and situated in areas experiencing active volcanic activities affected by hydrothermal modification. Beneath conditions related to shallow aquifers, the rate fluorite being soluble increases as temperature increases and consequently the addition of fluoride is facilitated by dissolution of hydrogen fluoride gas.

2.2.3 Climate

Arid and semi-arid places experience a high possibility of high fluoride concentrations. In arid places, sub surface water flow is sluggish and resulting in the rock reaction time to take long. The contents of fluoride in water may increase if solution remains in equilibrium with calcite and alkalinity during evaporation. In arid places dissolution of deposited salt evaporates would be an important source of fluoride. Additionally, fluoride increase is less noticeable in regions within moist tropics associated with plenty rainfall quantities and their dilution outcome on the groundwater chemical structure.

2.2.4 Chemical composition of groundwater

Highly fluoridated borehole water is mainly associated with a sodium-bicarbonate water type with comparatively low quantities of calcium and magnesium. Water that is highly fluoridated normally has high pH values (Brunt *et al.,* 2004). Okoo (2007) on study carried out in Kendu Bay, Kenya observed that alkalinity and acidity of water had major control of fluoride. Evidence on chemical configuration of sub surface water can be referred to as indication of likelihood of adverse effects of problems associated with fluoride. Discrepancy in scattering of fluoride additionally would be related to variations in calcium levels which are as a result of dissolution of calcium minerals when it mixes with the water originating from variable hydrological environment across the rift valley which has different chemical composition (Ayenew, 2008).

Further the availability of high fluoride levels is the result of water rock contact facilitated by weathering of fluoride-embedded rocks and activity of movement of water in soils and rocks. AbuZeid & Elhatow (2007) observes that volcanic, gneissic and granitic rocks are the important rocks bearing fluoride minerals. Moreover high fluoride levels are associated with fluoride bearing minerals which are mainly volcanic in nature.

2.3 Effects of fluoride

The negative effects associated with fluoride contamination are manifested in human, plants and animals.

2.3.1 Effects of fluoride and human health

Proponents against fluoridation argue that toxins associated with fluoride result in diseases related to kidney damage to children. The argument against fluoridation is supported by Researchers who did a study of 210 children living in of China who were drinking water where fluoride levels in water varied from 0.61 to 5.69 mg/l. Conclusively the study observed that the children who were water drinking with more than 2 mg/l and were infected with dental fluorosis had levels of NAG and y-GT in their urine indicating clearly a situation of kidney damage. Additionally, there was possible damage to the liver which was proven by high levels of lactic dehydrogenase in the infant’s urine waste (Luke, 1997). An inflammation of the kidney will result in inefficiency in excretion of fluoride, leaving individuals with likelihood of having complications associated with fluorosis even in situations of normally ingesting ranging from 7–1.2 mg/l.

Mihashi & Tsutsui (1996) observes that fluoride has the possibility of causing chromosome damage and mutations in several cell-tissue researches carried with animals thereby interfering with the enzymes involved with DNA repair. Joseph & Gadhia (2000) and National Toxicology Program (1990) have equally observed in that in recent studies there is a connection between exposure chromosome damage ingestion of fluoride by humans. A research study at University of Harvard University exposed s significant link between addition of fluoride with a type of bone cancer called osteosarcoma affecting young men whose results were in agreement with the animal study results carried out in the 1990s (Bassin *et al.,* 2006).

The findings on the brain functioning were confirmed by a study where groups associated with young people exposed to 8 mg/l fluoride in water were found to have averagely low intelligent quotients (IQs) while fewer children reaching high IQ, and more young people affected by low IQ as confirmed by National Research Council (2006). While 8 mg/l is higher than 0.7 to 1.2 mg/l which was the fluoride level added to water in programs associated with fluoridation, the results concurred with previous studies (Wang *et al*., 2007) that indicated that in China fluoride levels resulted in lower levels of IQ (Xiang *et al*., 2003).

The ingestion of limited quantities of fluoride is beneficial to human health as long as long as ingested quantities in portable water are limited to 1.0 mg/l. drinking of water with limited levels of fluoride assists in improving bones and teeth. However, drinking of water whose fluoride levels are beyond the WHO permissible levels has adverse health effects. Quantities above WHO permissible levels of fluoride in potable water will cause damage to the teeth which is identified by brown and mottling of teeth. The teeth are made very hard and brittle as a result of dental fluorosis. On the other hand concentrations of in the range of 4 mg/l and 8 mg/l contribute to skeleton complications while levels greater of more than 10 mg/l fluoride when ingested for a lengthy period cause crippling fluorosis.

Complications of bone malformation manifested in movement difficulties are obvious incidences of skeletal fluorosis. When bones and bone junctions are weakened by growing together it results in immobility caused by crippling fluorosis. Fibre deterioration, low levels of haemoglobin, red blood cell abnormalities, extreme thirst, headache, skin rashes, in addition to depression, and gastrointestinal problems, are linked to excessive fluoride ingestion. The effects associated with ingestion of high fluorides have received less attention however emphasis has been placed teeth and bone complications that are typical and common in high fluoride areas.

Patients who have kidney dysfunction may be especially vulnerable to fluoride harmfulness. Incidences of severe fluoride toxicity are usually attributed to accidental or suicidal consumption of fluoride. The high intake of fluoride would later result gastrointestinal infections, extreme hypocalcaemia, nephrotoxicity, and eventually trauma. Inhaling high quantities of fluorine, hydrogen fluoride, and other forms of fluorides in the air would to serious irritating breathing and late pulmonary oedema. Equally when the skin is exposed to gaseous fluorine thermal burns will be experienced, while burns and deep necrosis will be attributed to hydrogen fluoride. The reversible water-losing nephritis triggered by metabolic release of fluoride ions from fluoride-containing anaesthetic gases is one of the special cases of acute fluoride toxicity.

Ingestion of fluoride through water is fairly high as compared to food and air. Because of the detrimental effects associated with high fluoride levels, there is need to control concentrations of fluoride concentrations in drinking water meant for drinking. The World Health Organization recommends that in alleviating aftermaths associated with severe cases of fluorosis in prevalent places best method should be hierarchical starting with identifying alternative source of water meant for human use which has low fluoride content, which will dilute high fluoride water with low fluoride water so as to gain a mass balance of within 1.5 mg/l, and finally remove DE fluoridate to meet the WHO permissible levels of 1.5 mg/l.

2.3.2 Effects of fluoride on plants

Activities related to magma expose fauna to fluoride through the soil and in the air. Mainly fluoride enters into animal system through ingestion by making plants important element carriers of fluoride in all ecosystems. Diffusion is the process through which soil fluoride is absorbed by plants and then exits through the shoot and leaves. In weather conditions that are temperate the fluorides are accumulated in small quantities and therefore the average content of leaves in a non-polluted air is less than 10 mg F/kg dry weight. But in places with saline soils or soils enriched in fluoride minerals the concentrations are likely to be higher. In areas such as these the plant intake of F may be significant enough to contribute to the human or animal diet.

However, a number of plant types accrue high levels of fluoride even when planted in soils with low fluoride, a factor attributed to complex formations with aluminium. Gaseous and fluoride particles in the air are deposited on exposed plant surfaces, whilst stomata pores act as entrances for the gaseous fluoride. Over half of the total leaf's fluoride content is attributed to superficial deposits. Despite the superficial deposits having negligible toxicity to the plant, they may be hazardous to grazing animals. When fluoride penetrates the internal tissue of leaves or gets deposited on active surfaces such as stomata thereby affecting variety of metabolic processes are affected resulting in pronounced effects on appearance, growth and reproduction. The visible effects of toxic concentrations of fluoride on plants include chlorosis, leaf distortion, and malformation, peripheral necrosis and abnormal fruit development (Hong *et al.,* 2016).

When fluoride contaminated water is used for irrigation, it results in toxicity symptoms on sensitive plants. Generally, therefore, plants do not readily use soil fluoride but the plant's roots take up soil fluoride in small amounts through the process of diffusion, resulting in a low background concentration in the foliage of the plant. Moreover, according to Ruan *et al*. (2003) tea plants are natural accumulators of fluoride thereby making them to be exceptions. However, because of its high solubility, gaseous uptake of fluoride by leaves is rapid. Gradually, over time, fluoride is an accumulative poison in plant foliage, which strongly hinders plants when they make their food through the process of photosynthesis.

According to Neelam Yadav *et al.* (2018) fluoride accumulates in leaf margins after moving in the transpiration stream from roots and through the stomata. Characteristic fluorine injury indicators on broad leaf plants are manifested through marginal and tip necrosis that spread inward. Conifer needles reveal tip necrosis which spreads to the base of the affected plants however similar symptoms are exhibited by drought stressor salt toxicity. Moreover, a wide range of plants are sensitive to fluoride toxicity with indoor foliage plant like *Dracaena, Tahitian* and the spider plant being the typical examples. Additionally, fruits like apricot, blueberry, grape, peach, and plums belong to the category of sensitive conifers.

Higher fluoride concentrations of have usually been reported in the upper parts of plants grown in uncontaminated areas recording the average fluoride contents not exceeding 5 mg/kg. However, Baunthiyal and Sharma (2012) observe that in some vegetables like spinach leaves the fluoride levels may reach up to 24 mg/kg. Generally, however, fluoride levels in plants seem to be positively associated with the quantities of fluoride in rain water. When grown in polluted areas, several plants, especially forage plants, are reported to contain large amounts of fluoride with most of the fluoride pollution being deposited on the leaf surface as was demonstrated by Fuge and Andrews (1988).

2.3.3 Effects of fluoride on animals

On animals, initial studies indicated fluoride intake and addition within pineal gland resulted in decreased melatonin making and activated instances of maturing earlier. In a number of animal studies, fluoride has been proved to be a neurotoxin. A study on 2006 National Research Council reported that either directly or indirectly fluorides had the ability to interfere with the functions of the brain and the body (Shao *et al.,* 2002: Shashi, 2002). Plants are considered sources of fluoride dietary in animals and human beings. Therefore, the increase of plant fluoride results in a great increase in animal exposure. Cases of adverse fluoride toxicity have been studied in livestock, which have ultimately resulted in development of skeletal and dental fluorosis. Chronic toxicity induced experimentally to rodents is also associated with nephrotoxicity. Symptoms of severe and poisonousness of fluoride concentrations are generally non-specific. Fluoride however has not been known to induce direct mutagenic impacts, however in high concentrations it can change the response attributed to mutagens.

2.4 Fluoridation

Fluorosis is a result of continued consumption of fluoridated water with fluoride levels exceeding fluoride uptake levels. Therefore, the control of fluoride intake is necessary to check on the accumulative levels. It is important to remove excess fluoride from water and therefore need to determine and monitor the causal factors that result in the enrichment of fluoride concentration as observed by Saxena and Ahmed (2003). Subsequently, the removal of fluoride from portable water has seen many attempts using a wide range of materials giving various levels of success over years.

Addition of fluoride in drinking water is among the established top 10 public health achievements of the 20th century (Centre for Disease Control and Prevention, 2018). Fluoridation is defined as the upward or downward adjustment of fluoride levels in drinking water to achieve optimal level enough to prevent caries and not to cause fluorosis (Chandra, 2002). Optimum levels of fluoride vary with climate variation. In warm climates fluoride levels of 0.5 ppm are recommended in due to consumption of more water to the contrary in cold climates, levels as high as 1.5 mg/l are regarded as optimum due to consumption of less water. However, worldwide, an average of 1 mg/l is standardized optimum fluoride level present in water meant for drinking (Chandra, 2002). Known fluoride zones in the world are the areas stretching from Syria, Jordan, passing through Egypt and Libya. The fluoride zone further passes through Algeria, Sudan and Kenya, ending in Turkey through Middle East countries and finally India.

Adding of fluoride in community drinking water is a harmless, cheap and efficient method of reducing dental decay among residents of America across of all age-based social classes according to the US Centre of Disease Control and Prevention. Addition of fluoride in essence forms the foundation to embark on laborious community prevention strategies. One of the USA health objectives places emphases on Healthy People 2010 requiring that three quarters of the residents getting water from community systems have to receive optimal levels of fluoride. However, the current level of fluoride contamination stands at sixty-seven per cent.

The issues concerning the fluoridation of public water supplies originates from water fluoridation controversy in the political, moral, ethical, economic, and safety aspects. Public health authorities worldwide find medically by consensus agree that water fluoridation at appropriate levels is a safe and effective means to prevent dental fluorosis as observed by Pizzo *et al.* (2007). Authorities' opinions on the best and effective fluoride therapy for community prevention of tooth decay are varied. According to Pizzo *et al.* (2007) and Yeung (2008) water fluoridation is most effective, whereas others see no special benefit and give preference to topical application strategies. Those of the contrary opinion argue that water fluoridation has no or little benefits that can cause serious health problems and therefore there is no sufficient reason to justify the enormous costs.

The processes of precipitation or adsorption accomplish defluoridation of drinking waters as observed by Bulusu (1979). Adsorption is the most popular technique for treatment of fluoride contaminated water. However, commercial adsorbents which require frequent regeneration are expensive thereby limiting the application of their technology in many of the developing countries. Therefore, there is need to advocate for more affordable and easier-to-use defluoridation media. A test at a research station in Arusha, Tanzania advocated for the use of Nalgonda technique, where alum is mixed with lime and this helped in reducing fluoride concentration from 21 to 5 mg/l at pH 6.9. According to Mavura *et al.* (2004) the use of cartridge filter which is packed with bone char has been found to have efficiency of about 99.5%.

Vivek *et al.* (2011) observe that the use of bone char has not been accepted by some communities thereby prompting the use of natural plant materials like *Moringa Oleifera* seeds and rice husks. In India, studies conducted have further demonstrated that *Moringa oleifera* seeds have remarkable defluoridation efficiency that was better than activated alumina (Subramanian *et al.*, 1992: Ranjan *et al.*, 2009). The anticipated features of defluoridation processes include affordable cost, easy to use by local population, not to be affected by fluoride concentration, pH (acidity/alkalinity) and temperature. Additionally the defluoridation technique should not have effect on taste of water, and no addition or inclusion of other substances that are not desirable for treatment of water as observed by Hugo and Ruth (2013).

2.5 Fluoride levels in Kenyan water

Fluoride enters the water cycle by leaching from soils and minerals into boreholes and rivers. However, fluoride concentration in water is affected by availability and solubility of fluoride containing minerals, porosity of the rocks or soil through which the water passes. However, in river water much of fluoride exists as free fluoride ions but salinity increases its occurrence. There is wide variation in fluoride levels in rivers and boreholes in Kenya. While in some water bodies the concentrations above are above the WHO levels in others the levels are below the WHO requirements.

Fluoride in surface water generally has fluoride contents within WHO limits whereas ground waters show much higher levels. Lake waters especially in the Rift Valley have the highest fluoride concentrations recorded for Kenyan waters. Regarding ground waters, several fluoride patterns have been observed. High fluoride concentrations are obtained at points of discharge as compared to recharge areas, with a tendency of fluoride addition in river's direction of flow. Kenya's rock types make it one of the countries in the world where there is occurrence of high fluoride levels in rocks, soil, surface and sub-surface water. Nationally highest fluoride levels in water occur in springs, boreholes, and some lakes in the Rift Valley.

According to UNICEF Kenya country program (2009-2013) half of residents in Kenya have no accessibility to water that is suitable for drinking. Within Rift Valley's Lake Nakuru highest fluoride concentration have been recorded. High fluoride concentrations in boreholes in the world are associated with volcanic rocks where fluoride occurs in combined form in minerals such as fluorspar, cryolite and fluorapatite. Water passing through fluoride rich minerals have likelihood of recording high concentration of fluoride suggesting that leaching of rift valley volcanic soil are alkaline with high levels of Potassium, Sodium and bicarbonate.

2.6 Aquifers of River Njoro catchment

In the River Njoro catchment the geological formations are limited to the Kainozoic, Volcanic rocks and sedimentary deposits which are mainly of lacustrine origin which extended in time of deposition from the Tertiary period to the present day. The volcanic rocks include: basalt, phonolite, phonolitic trachyte and trachyte flow, together with intercalated tuffs and reworked tufts which have plenty of water rounded fragments. Further, there is a form of volcanic rock which is widespread throughout the area, best described as welded tuff. The volcanic rocks show a grey or green glassy matrix choked with pyroclastic fragments which are trachytic in composition. These rocks differ from loosely consolidated tuffs in being impervious and their effect on groundwater conditions which is similar to that of trachyte lava flows.

The sediments, which can invariably be detected in borehole samples, from the presence of fragments, grade from the reworked tuff is lacustrine deposits, which show more complete rounding. Dykes which are considered among the old land surfaces between the lava flows provide the main aquifers within the volcanic formations. Whilst this type of aquifer undoubtedly occurs, it is now known that the principal aquifers are sediments extending to several hundred feet in thickness. Sedimentary formations deposited in the lake basins since the cessation of the major faulting in the Rift Valley similarly provided ideal aquifers. These aquifers are mainly composed of well-rounded volcanic grits and diatomites, together with red clays. The types of aquifers in the River Njoro catchment are: sedimentary intercalations in the faulted lava flows, old land surfaces separating lava flows, fissures within the body of the lava flows and welded tuff formations and lacustrine sediments deposited subsequent to the major faulting.

2.7 Fluoride occurrence in the world

In Africa ground water contains fluoride higher than WHO upper limits as compared to surface water. Past researches as observed by Malago *et al.* (2017) in East Africa concluded that East African Rift Valley is considered a region with high fluoride levels. The East African Rift Valley region traverses countries from Jordan valley to Tanzania. Incidences of elevated fluoride countries are witnessed in Malawi and The Republic of South Africa. In Tanzania a survey of fluoride in ground water showed that 30% of the waters used for drinking had fluoride levels exceeding 1.5 mg/l.

According to Thole (2013) a survey of fluoride in borehole water in Further Thole (2013) asserts the occurrence of dental fluorosis in Malawi and the Republic of South Africa has been associated with fluoride levels beyond 1.5 mg/l. High sodium and bicarbonate concentrations and high pH in the water are proxy indicators of high fluoride levels in ground water. In addition to countries traversed by the Great East African Rift Valley high fluoride levels in Africa there are elevated fluoride levels in Ghana, Malawi, Nigeria, Algeria and South Africa (Atia & Hoggui, 2013).

2.7.1 Fluoride in Uganda

In Uganda the serious inorganic contaminants of health issues is Fluoride (British Geological Survey, 2001). Uganda has adopted WHO guideline value of 1.5 mg/l as its fluoride standard in water for drinking water. Nevertheless, water from some sources exceeds the WHO guideline. British Geological Survey (2001) observes that in some incidence's cases of high fluoride levels above the standard value exist in both surface and groundwater. Based on literature review it was found that mean fluoride concentration in Uganda ranged between 0.44 mg/l to 3.31 mg/l. The value of is 3.31 mg/l was comparatively high in relation to Ugandan standard value for drinking water.

The areas that have severely been affected adverse effects of fluoride in Uganda are the places that experienced volcanic activities in slopes of Elgon, Mbale, Moroto and parts of Uganda's western Rift Valley. Studies on fluoride with emphasis on water sources in Uganda witnessed borehole water having high concentration in comparison to other sources of water. Highly fluoridated water levels in borehole in Uganda may be associated with long residence time. Studies and statistics on the fluoride levels in Uganda concluded that surface water showed low fluoride concentration as compared to high levels varying up to 4.0 mg/l which was reported around Kikorongo lake area located in Western Uganda (Mungoma, 1998).

2.7.2 Fluoride in South Africa

According to Louw & Chickte (1997): problems related to excess fluoride in South Africa has been given consideration from 1935s. In South Africa, water quality guidelines adopted 4 mg/l as the maximum acceptable standards of fluoride in portable. However, to the contrary the Committee for Scientific Industrial Research (CSIR) and Industrial Research (CSIR) and Bureau of Standards gave recommendation of the WHO permissible standards. Further, 4.82% of South Africa's sources of water exceed 4mg/l which is the country's Water Quality Guidelines standard (Ncube, 2006).

High fluoride quantities have possibility of being associated to dominant igneous and sedimentary rocks. Prevalence of fluorosis incidences have been described in the Republic of South Africa in high fluoride areas. According to Fawell *et al.* (2006) and Grobler *et al.* (2001) some parts of South Africa experience severe cases of fluorosis.

These locations experiencing endemic fluorosis include: Western and Karoo Regions of Cape Province, the North Western, Northern, Eastern and Western areas of Transvaal, Western and Central Free State. Similarly, boreholes in South Africa have the highest number of water sources with fluoride level above 1.5 mg/l which is beyond the country's fluoride acceptable levels. In research works undertaken in it was found that almost a third of ground water sources in South Africa had fluoride above levels exceeding by far WHO allowed fluoride standards.

Northern Cape and Limpompo provinces dominantly experience of high fluoride levels related problems in comparison to other provinces because a large population is still use ground water for drinking purposes in these rural areas. The prevailing arid conditions in Limpopo Province, the population is dependent on groundwater as a source of water supply as observed by Botha and Van Rooyen (2001). The dependence on groundwater in most parts of South Africa which has high concentrations of fluoride has resulted in the occurrence of dental fluorosis (Feenstra *et al.*, 2007). The provinces of North West, Limpopo, and Northern Cape have cases of high levels of fluorides in groundwater as observed by WHO (2000). According to McCaffrey and Willis (2001) high incidences of fluoride levels in groundwater would be attributed to high fluorine content of aquifers, high pH in water, low groundwater flow rates, arid and semi-arid climatic conditions which increase potential evaporation.

Therefore, the populations that rely on groundwater from boreholes especially from the boreholes that have fluoride level above 1.5 mg/l are likely to be vulnerable to high fluoride complications. Eventually after the passage of time there are high chances of negative health impacts. Therefore, like in many places in the world, surface water comprising of rivers and streams in South Africa have the lowest fluoride concentrations. Therefore, the use of surface water which has low fluoride levels will hence reduce human exposure to fluoride and the associated negative health impacts. South Africa is notably one of the countries in the world that is experiencing high fluoride ion concentrations in borehole water on a regional scale. A number of research works have further noted that there are high fluoride quantities in groundwater in South Africa.

2.7.3 Fluoride in Ethiopia

Ethiopia like other African countries experiencing the phenomenon of the Rift Valley has levels of fluoride that are beyond the WHO recommended in nearly the entire country (Kloos & Tekle-Haimanot, 1999). In past research studies the mean and median concentrations of fluoride levels in Ethiopia country were 10.20 ± 26.17 mg/l and 2.6 mg/l accordingly. These results were clear evidences of high fluoride in a number of sources of water thereby displaying a severe picture of fluoride pandemic in Ethiopia. The problem of fluoride in Ethiopia is made worse by insufficient techniques of defluoridation techniques and therefore the people of Ethiopia get exposed to high fluoridation. Salvaging the Ethiopian population from effects related to fluoride exposure will require urgent intervention.

The Rift Valley in Africa intersects Ethiopia from South West. This area experiences earth quakes and has active volcanoes distributed in north in the depression of near surface, while in middle and southern parts of the Rift Valley there are young volcanic rocks. Much of the Rift Valley is located within the hot, arid lowland zone one of the three major climatic zones of Ethiopia, located below 1500 meters above sea level. Cases of endemic fluorosis have progressively become a serious public health threat in Ethiopia where many cases of teeth and Skelton diseases have been revealed through ancient commercial farms like the sugar belt region (Kloos and Tekle-Haimanot, 1999). Similarly, the problem of elevated fluoride levels extends beyond the Rift Valley region into the highland regions of Ethiopia higher fluoride levels being detected as observed by Tekle-Haimanot *et al*. (2006).

Malago *et al*. (2017) observes that fluoride levels in water bodies in Ethiopia, especially in lakes showed the highest average fluoride concentrations of 113.86 mg/l. Lake Chitu recorded the highest fluoride levels extending up to 250 mg/l. Equally: hot wells and springs had a larger number of its samples exceeding 1.5 mg/l (Malago *et al.*, 2017). Conversely, springs in Ethiopia formed sources of water lowest concentration of fluoride levels. Generally, when comparing fluoride concentrations in sections of Ethiopian Rift Valley to the larger Ethiopia, it was found that the elevated fluoride quantities in water was saturated in the Rift Valley and in the volcanic active lowland (Ayenew, 2008).

Fluoride distribution analysis at the community level in Ethiopia further revealed varying concentrations of fluoride in individual water sources while in some cases low fluoride levels were recorded in some surface and groundwater sources in the Rift Valley areas. Seasonally, seasonal variations of fluoride is witnessed Ethiopia as supported by some longitudinal data gathered on fluoride distribution by an engineering consulting firm which was evaluating whether the surface waters for large-scale irrigation in the Awash and Mille rivers and in lakes Hertale and Gedebasa in the northern part of the Rift Valley was suitable (Gibb *et al*., 1973). The crisis of high fluoride in Ethiopia generally cannot be ignored and therefore there is need for systematic risk analysis and observing of fluoride levels in different times within the year to facilitate provision of safe water supplies.

2.7.4 Fluoride in Nigeria

Nigeria is geologically made up of Proterozoic-Lower Palaeozoic metamorphic basement Complex, Jurassic Younger Granites, volcanic provinces and the Cretaceous sedimentary terrains as the major geologic terrains. The crystalline Basement complex terrain is granitic, which comprises of gneiss, schist and granites which are associated with amphibolites, and diorites (Lar *et al.*, 2014). The Younger Granite terrain is found in north central Nigeria. The eastern half of Nigeria tertiary is covered by Quaternary volcanic which includes the Jos Plateau, Biu Plateau, Longuda Plateau and Benue valley. High fluoride in groundwater is associated with crystal line rocks and their derivatives where it occurs as component fluoride bearing minerals fluorite and fluorapatite. Natural fluoride concentration of borehole water in Nigeria generally varies depending on the types of aquifers. Lar *et al.* (2007) observe that in the crystalline Basement aquifers, fluoride values vary from 1 mg/l to 8 mg/l but Dibal *et al.* (2005) at the same time observes that fluoride in sedimentary aquifers it varies between 1 – 4 mg/l.

The basement aquifer in Nigeria has higher values of fluoride which is related to the long resident time. Based on fluoride data collected from different studies in Nigeria the country's average concentration of fluoride was estimated at 1.78 mg/l. Equally maximum fluoride levels ranged between 4.4 mg/l and 0.03 mg/l. Therefore, there are slightly elevated concentrations of fluoride in water in Nigeria as compared to the WHO standards and presence of almost fifty percent of water sources with fluoride concentration above 1.5 mg/l. The high levels of fluoride in Nigeria increase the chances of exposure to fluoride which in turn increases fluoride negative impact of the people's health. Bano (1987) and Lar (2007) assert that apart from Nigeria's high average fluoride concentration, Central and Northern Nigeria are among much affected areas. Similarly Dibal (2012) report that incidences teeth mottling were reported in areas where concentration of fluoride ranged from 2.5 to 3.9 mg/l. Furthermore, Dibal (2012) observed that dental fluorosis among ages of various groups were found in people habiting places with high fluoride in boreholes.

2.7.5 Fluoride in Algeria

Algeria though not known as a high fluoride country, Sekkoum *et al.* (2012) observes that concentrated fluoride levels in drinking water has been recorded in Algeria. Despite of limited studies on fluoride in Algeria about 48 fluoride data from different researches were collected in Algeria. The results of the data reported that Algeria's average quantities of fluoride were 1.47 mg/l with median of 1.58 mg/l. Moreover, from the study, WHO standards were slightly higher than the country's mean fluoride levels. According to (Amar & Chawki, 2007) fluoride-bone related ailment is a "silent" scattering disease within residents of South Algeria. Similarly, the findings of Amar & Chawki (2007) revealed that 35% of borehole water had excessive fluoride levels greater than the WHO recommended levels while on the other hand the eastern areas with widespread pathology present the highest cases of dental decay.

Furthermore, about half of the water sources out of the sampled 48 sources in the research on Algeria's fluoride levels were above WHO permissible levels for portable water (Messaïtfa, 2008). These levels of recorded fluoride were sufficient to be associated with negatively serious medical effects in many residents. Moreover, the higher levels would be reduced by defluoridation before water supply. Atia and Hoggui (2013) observe that in some areas high severe and excessive total mineralization in water was accompanied by fluoride. Moreover, in some situations the water was the sole source of portable water. It similarly observed that consumption of high quantities of water attributed to the arid and semi-arid conditions that forced people to consume more water thereby raising their daily fluoride uptake rate thereby causing endemic fluorosis (Sekkoum *et al.*, 2012).

2.7.6 Fluoride in India

The two world's largest countries of India and China face severe fluoride-bone related diseases. High fluoride concentration usually beyond WHO recommendations are available in many parts of India constituting severe cases. According to Subarayan *et al.* (2012) almost 50 per cent of India's groundwater sources have been fluoride contaminated with over 90 % of the village's residents get their drinking water from boreholes. Further Karthikeyan *et al.* (2005) asserts that the occurrence of fluoride-teeth related diseases has affected excess of 40 million people. The excessive occurrence of fluorides in India's groundwater is affecting more than 65 million and noticed in nearly 177 districts which covere 20% of India (Gupta *et al.,* 2006). The state of Andhra Pradesh was among the earliest state in India where problems of excessive fluoride in groundwater was first reported in 1937 (Short *et al.,* 1937). Moreover Telangana is one of the states considered harshly affected by endemic fluorosis.

Fluoride health problems as observed by Reddy *et al.* (2010) are common in hot and dry regions of the world. Umarani & Ramu (2014) and Saxena & Saxena (2014) considered fluoride concentration in borehole is a result of local and regional rock types, rock stratification and the water flow directions of the water supported with the desert like conditions of the region. According to Thivya *et al.* (2015) about 20 developing countries and 17 states in India are affected by fluorosis (Yadav and Khan 2010). In the world of 20 countries, it is estimated that 200 million peoples are affected by fluorosis and with the Indian sub-continent having almost 62 million peoples affected (Thivya *et al.,* 2015). The high levels of fluoride in the Indian sub-continent are attributed to fluoride rich water.

Natural contamination is responsible for fluoride contents in ground water as observed by Saxena and Ahmed (2001). Research works by Chidambaram *et al.* (2013): Manivannan *et al*. (2012): Singaraja *et al*. (2012) placed emphasis on the higher fluoride levels in the groundwater of hard rock regions. The studies observed that fluoride sinks in groundwater is activated by weathering of minerals whose composition is mainly Calcium and Magnesium carbonates. Industrial pollution from the manufacture of steel, aluminum and fertilizers and in Bakreswar and Birbhum regions of west Bengal are sources of fluoride pollution (Datta *et al*. 2014). Additionally, the usage of fertilisers having as observed by Loganathan *et al*. (2006) in agricultural related activities further results in potentially elevated fluoride levels in sub surface water.

In the recent years, fluoride emissions from industries have also been found to cause fluorosis in India. Fluoride in both gaseous and particulate/dust form from several industries release fluoride into surrounding habitats causing industrial fluoride pollution as observed by Choubisa & Choubisa (2016). Industry emitted fluoride contaminates both the surrounding varied terrestrial and aquatic ecosystems and their food chains in addition to plants, grasses, crops and many other biotic communities on which humans and domestic wild animals are dependent on (Choubisa, 2015). Cases of severe health hazards in the form of industrial and neighbourhood fluorosis are contributed by prolonged periods of inhalation and ingestion of industrial fluoride (Choubisa & Choubisa, 2015). Ground water is mainly a source of prolonged intoxication associated with fluoride in Rajasthan in people and domesticated animals.

Different studies on elevated concentration of fluoride levels in groundwater of districts of Madurai like Dindugal reported higher levels of fluoride (Manivannan (2010). According to area (Manivannan *et al*. (2012) and Chidambaram *et al.* (2013) rise in temperature and consuming high quantities of water also form the key factors responsible for fluorosis in the other parts of India. In India therefore the higher levels of fluoride have been attributed to the dissolution of fluorite, apatite, micas, amphiboles with OH, F group (Manikandan *et al*., 2012), which are contained in volcanic and Metamorphic rocks.

Anthropogenic activities are not responsible for the presence of abnormally high fluoride concentration in borehole waters in India. Higher levels of fluoride are due to natural cause of higher levels of fluoride bearing minerals in parent rocks and deposits of sediments as observed by Choubisa (2017). The important rocks are granites: gneisses, mica, schists, limestone, sandstone, phosphorite, shales, clays, acid igneous rocks, basalts and alluvium, and these contain fluorotic minerals accounting for fluoride in the average range of 180 gm/l to 3100 gm/l. Gupta (2013) observes that the chemical processes like decomposition, dissociation, dissolution and interaction with water are considered to be the main causes responsible for fluoride in groundwater. Conclusively distribution of F is in India is related to regional hydrogeological and climatic condition and the lithological control. Equally pH has an important role in the dissolution and fluoride percolation into the boreholes (Thivya *et al.*, 2015).

2.7.7 Fluoride in Turkey

In Turkey Oruc (2008) states that cases of endemic fluorosis are related to consumption of high fluoride ranging water whose fluoride concentrations from 1.5 to 4 mg/l. The source of portable water in Isparta, Turkey originates from lakes and springs. The springs' water originates from volcanic rocks, Golcuk pyroclastic and Miocene clastic rocks whose fluoride levels range from 3.71 to 1.02 mg/l. These high fluoride concentrations have resulted in high fluoride levels in borehole water thereby causing dental related diseases in south west Turkey as observed by Davraz *et al.* (2008). Similarly, cases of parti-coloured enamel attributed to elevated fluoride levels beyond WHO standards in drinking waters enamel were reported in Isparta Province. The origin of fluoride in Isparta Province was associated with volcanic rocks whose mineral contents consist of pyroxene, hornblende, biotite, fluorapatite and glassy groundmass minerals.

Elevated fluorides in groundwater in Turkey have association to the rock formations types. Fluorite reserves and volcanic soil structures are most common occurrences in these areas resulting in the disease of natural fluorosis. The high fluoride in water for drinking and dental related fluorosis in Isparta Province South West of Turkey was first observed about 55 years ago (Oruç, 2008). Additionally, Oruç (2001) observes that high fluorine waters in Turkey were realized in various places. In parts of Anatolia, fluoride levels in water varied from 1.5 and 13.7 mg/l attributed to volcanic rocks and geothermal resources. In Sanliurfa the geological structure widely shows volcanically and sedimentary formed rocks to be the main formations. Moreover, the elevated fluoride sources in water are thought to be associated with the deposits of phosphate in Mazı Mountain in Mardin close. Past researches in Sanliurfa observed that fluoride concentrations in waters ranged from 0.06 to 0.13 mg/L (Ayse & Mehmet, 2017).

2.7.8 Fluoride in Saudi Arabia

In Saudi Arabia, high fluoride levels are issues of great health concern among state health officials. The fluoride impacts are felt among the young children attending primary schools aged between 3 and 7 years and adolescents aged 12–19 years. According to Farooqi *et al.* (2015) the overall prevalence of dental caries among children in the Eastern Province was 73% among children aged 6–9 years while it was 68% in the age bracket of 10–12 years. Consequently, water fluoridation is among the cost-effective methods considered for the prevention of cases of high fluoride complications in Saudi Arabia. Further Bakhurji & Alqahtani (2018) observe that in the major cities of Saudi Arabia regulations have been set to fluoridate water. Moreover, despite the benefits and occasionally problems associated with fluorides water fluoride levels are not monitored in Saudi Arabia.

A study by Aldosari *et al.* (2003) found that 75% of public water supplied the cities of Riyadh and Qassim in the Central Province had fluoride levels with maximum levels of 6 mg/l. Additionally another study by Al-Khateeb (1990) conducted in the Western Province of Saudi Arabia revealed that depending on the source of water supply the fluoride levels varied from from 0.3 to 2.5 gm/l. These levels were far higher as compared to the optimal levels of 0.7 mg/l recommended by the US Health and human services Department. Prevalence associated with elevated fluoride levels in Saudi Arabia are responsible with cases of tooth decay among the Saudi population and therefore the control of these fluoride levels to optimal levels could significantly lead to a decrease in the tooth decay.

Ground water provides 40% of the water needs in the Kingdom of Saudi Arabia while and surface water like rain, unconventional sources and desalinated water provide 50% with the remaining 10% coming from the treated wastewater as observed by Griffin (2007). Because of its location in the desert areas and therefore experiencing insufficient natural resources, Al-Zahrani & Baig (2011) observe that Saudi Arabia mainly depends on desalinated water. According to the projection by the Joint Monitoring Program for Water Supply and Sanitation by World Health Organization and United Nations International Children's Emergency Fund, WHO/UNICEF (2018) asserted that by 2015 the entire population of Saudi Arabia was going to have access to improved source of drinking water. The main source of domestic water in the Eastern Province is desalinated from water treatment works at Al Jubail (Griffin *et al.*, 2002). Conclusively the problem of fluoride levels in Saudi Arabia cannot ignored as observed by Alabdulaaly *et al.* (2013) who asserts that fluoride levels in ground waters of Saudi Arabia exceeded the USEPA permissible levels limits for drinking water. However, the water agency in Dammam regulates water additives and distribution of water in the area.

2.7.9 Fluoride in Sri Lanka

Geographically Sri Lanka is within the tropics where the climate is desert and semi desert with the exclusion of the highlands located in Southwest quadrant. The temperatures experience are in the range of 25-30 °C with an annual rainfall of less than 1500 mm/annum during the dry season and in the excess of 2500 mm/annum during the wet season (Ekanayake & van der Hoek, 2002). The arid and semi-arid climate makes Sri Lanka a water country with majority of its population depending on groundwater. However, unlike most other trace elements, fluoride levels in the water are high. In the dry zones cases of endemic fluorosis, evidenced by teeth mottling and colour occurrence among the population has been prevalent for a long time. The sources of fluoride are varied, however much evidences point to drinking water.

The rock formations of Sri Lanka is dominated by Precambrian high-grade metamorphic rocks and which is further categorized into: lithotectonic units namely, the Highland complex, the Vijayan Complex and the Wanni Complex as observed by Chandrajith *et al*. (2004). The Highland Complex among the lithotectonicis units is the largest unit and forming the backbone of the Precambrian bedrock of Sri Lanka. The Highland Complex has a variety of igneous intrusions which are dominated by granitoid banded gneisses rocks. The rocks making up the Highland Complex underwent metamorphosis and the commonly found include: Quartz, feldspar, sillimanite, graphite and marbles.

The Precambrian Sri Lanka is occupied by fluoride-bearing minerals such as micas, hornblende, sphene and apatite which have contributed to elevated fluoride levels in Sri Lanka. Similarly other minerals originating from fluoride rocks like fluorite, tourmaline and topaz are also found in many regions in Si Lanka and these also contributed to high fluoride occurrence through the general geochemical cycle of fluorine in the physical environment as observed by Ekanayake & van der Hoek (2003). The influence of climatic variations in Sri Lanka on the levels of fluorides is justified because under tropical humid climatic conditions, rock weathering is intense and this contributes to fluorides by readily dissolving the fluoride rich minerals. Further in Sri Lanka, research shows that fluoride-rich and fluoride-poor areas would be compared based on the climatic, geomorphological, and geological factors prevailing in the country (Jayawardana *et al.*, 2012). Low fluoride levels in groundwater are common in the wet zone where the average annual rainfall occasionally exceeds 5000 mm equally also high fluoride levels are attributed to high evapotranspiration and slow rate of ground water movement in the dry zone areas. Irrespective of the geology of Sri Lanka, there are low fluoride levels in groundwater in the Wet Zone while fluoride reaches as high as 10.0 mg/1 in the Dry Zone (Young *et al.*, 2011). Finally, the slow rate of groundwater movement in the low plains in Sri Lanka also tends to result in elevated fluoride concentration attributed to prolonged time of contact with groundwater having particular rock formations.

2.8 Geology

Geology is studying of the earth's external and internal surfaces, and other materials constituting the environment and resultant earth formation processes. Broadly the earth's study would refer to geology with emphasis on its interior and exterior composition. Geology would also include movement of surface and ground water and the changes that have occurred over the massive geological time elapse, and the changes are anticipated to take place in the foreseeable future.

2.8.1 Geology of the Rift Valley

Originally Gregory (1894) defined a rift valley as "a linear valley with parallel and almost vertical sides, which has fallen owing to a series of parallel faults". The typical morphology is characterized by a valley floor, between 30 and 100 km wide, separated from the surrounding plateaus by huge scarps that may vary in height from a few hundreds to a few thousands of meters. The rift valleys are enormous fractures affecting the continental plates that widen progressively with time: they represent the first stages in the complex process of extension and rupture of continents and anticipate the development of new oceanic basins between them.

The geology of the study area is closely related to the formation of the East African rift valley system. The study area is covered by over tertiary volcanic rocks (tuffs and lavas), which form a thick blanket over the massive gneiss of the Mozambique belt. Stratigraphically the formations underlying the study area are: Tertiary sediments and volcanic: Quaternary sediments, basalts, phonolites and trachytes represent tertiary volcanics. The East African rift system is widely recognized as the classical example of a continental rift system which is part of the Afro Arabian rift system that extends from the Red Sea to Mozambique in the south. As the rift extends from the Ethiopian segment southwards it bifurcates at about 5^0 N into the Eastern and Western branches.

The two branches of the rift skirts around the Tanzania craton and formed within the Late Proterozoic belts adjacent to the margins of the craton (Smith and Mosley, 1993). However, the Eastern Branch that comprises the Ethiopian and Kenya rifts is older and relatively more volcanically active than the western branch that comprises Albert–Tanganyika-Rukwa-Malawi rifts. The rift valleys are a system of normal faults bordering a 40-60 km wide trough, funneling out toward north in the Afar region. The Kenya Rift diverges into splays towards north (Turkana) and south Tanzania. Domal uplift and extension caused the brittle crust to fracture into a series of normal faults giving the classic horst and graben structure of rift valleys.

Ground waters with high fluoride are associated with crystalline rocks that are comprised of fluorine-rich minerals. The fluorine rich minerals are found mainly granites and volcanic rocks, shallow water sources in desert areas experiencing strong evaporation, sedimentary aquifers experiencing exchange of ions and inputs of geothermal water. East Africa's Rift Valley makes up one of the world's most important fluoridated province. Groundwater having concentrated fluoride is derived from reaction combinations young volcanic rocks, geothermal inputs and evaporation, which occur alongside alkaline lakes and, in some cases, dissolved fluoride concentrations would rise in excess of 300 mg/l. The relationship between high fluoride in sub surface water with granites and acidic volcanic rocks is contributed by relative richness of high fluoride bearing minerals associated with biotite, amphibole, apatite and fluorite. Typically, also groundwater has waters with low concentrations of calcium, conditions which favour solubility of fluorite resulting in increase of dissolved fluoride concentrations.

2.8.2 Geology and the fluoride levels

The sub surface and river water quality is influenced severally or collectively by natural factors and human activities. In the absence of human impacts, changing quality of water would be only be triggered naturally by weathering of minerals making up the bedrock. Additionally, processes in the hydrological cycle of evapotranspiration and deposition of dust and salt by wind influence levels of fluoride in water. Natural leaching of organic matter and nutrients from soil, hydrological factors leading to run-off, and biological processes in the water environment can carry about changes in the physical-chemical properties of water. Thus, water in the natural environment may contain dissolved substance as well as non-dissolved particulate matter (Khatri & Tyagi, 2015). The dissolution and precipitation of carbonate rocks and special hydrogeological conditions determine the fluoride concentration in surface water. Equally climate is also an influencing factor that cannot be ignored to affect the fluoride concentrations of surface and groundwater as observed by Battaleb-Looie *et al*. (2012).

Table 2.1: Rocks and corresponding fluoride levels

Rocks	Fluoride range (mg/kg)	Average (mg/kg)
Basalt	20 – 1060	360
Granites and gneisses	20 – 2700	870
Shales and clay	10 – 7600	800
Limestones	0-1200	220
Sandstone	10-880	180
Coals(ash)	24000-41500	3100
Phosphorite	40-480	80

Source: Menzies (1995)

Groundwater in the rift valley lies in volcanic rock aquifers essentially located on the plateau, and lacustrine sediment aquifers in the bottom of the rift. The volcanic rocks are largely ignimbrites but also alkaline basalts and trachybasalts, recent basalts and acidic complexes (rhyolites, tuffs, pumice and obsidian). Lacustrine sediments, the second extensive unit consist of alternating fine and coarse beds and they are predominantly fine to medium grain. In Ethiopia high concentrations of fluoride in groundwater used for community water supply have resulted in extensive dental and skeletal fluorosis.

Table 2.2: Chemical composition of various fluoride containing minerals

Minerals	**Chemical Composition**	**Rocks of these minerals**
Fluorite (Fluorspar)	CaF_2	Pegmatite Pneumatolitic Deposits as vein deposits
Fluorapatite (Apatite)	$Ca_5(F,Cl)PO_4$	Pegmatite and metamorphosed limestone
Micas Biotite Muscovite	$K(MgFe^{+2})_3(AlSi_3)O_{10}(OH,F)_2K$ $Al_2(AlSi_3O_{10})(OH,F)_2$	Basalts, Permatites, Amphiboites,
Amphiboles Hornblende Tremolite Actinolite	$NaCa_2(MgFe^{+2})_4(AlFe^{+3})(SiAl)_8$ $O_22(OH,F)_2$ $Ca_2(MgFe^{+2})_5(Si_8O_{22})(OH,F)_2$	Gneisses, schists, shales, Clay, Alkaline rocks
Topaz	$Al_2SiO_4(OH,F)_2$	Acid Igneous rocks, Schists, gneisses
Rock Phosphate	$NaCa_2(Mg,Fe^{+2})_4(Al,Fe^{+3})(Si,Al)$ $_8O_22(OH,F)_2$	Limestone, Fossils

Source: Neelam *et al*. (2018)

The distribution of fluoride in groundwater has been investigated, and compared with bedrock geology and pertinent hydro chemical variables (www.researchgate.net). The results indicated extreme spatial variations. Ayenew (2008) observes that high fluoride concentration is often associated with active and sub-active regional thermal fields and acidic volcanic within high temperature rift floor. Variations in fluoride can also be related to changes in calcium concentration resulting from dissolution of calcium minerals and mixing with waters of different chemical composition originated from variable hydrogeological environment across the rift valley. The groundwater can be accessed from natural springs or wells. Fluoride contents in the water from the wells depend on depth and local variation. High fluoride containing water came from lahars and lacustrine deposits and comparatively low-fluoride containing water from basaltic or phonolitic unaltered lava at high altitudes (Ghiglieri *et al.*, 2010).

2.8.3 Hydrogeological dynamics

Hydrogeology as a branch of geology places emphasis on distribution and movement of sub surface water sources of water within earth's crust. Interchangeably hydrogeology is used with groundwater hydrology, geohydrology, and hydrogeology. Relative quantities of fluorides are available in a number water sources: however higher concentrations are frequently related to ground aquifers as observed by Ayenew (2008). Presence of fluoride rich-minerals in the parent rocks and their interaction with water is considered as the cause for fluoride contamination in groundwater. The decomposition, dissociation and dissolution are the main chemical processes for the occurrence of fluoride in groundwater. In the event of rock–water interaction, fluoride levels in rock, solution ionic species and time of rock-water residence form important parameters (Ahmed, 2003).

2.8.4 Hydrogeology and fluoride levels

Water intake being the main route of fluorine into the human body, fluorosis in volcanic areas is generally associated to elevated fluoride content in surface and ground waters. High fluorine content in waters derives either from water-rock interaction (WRI) processes in volcanic aquifers (groundwater) or to contamination due to wet or dry deposition of magmatic fluorine (surface waters reservoirs).

The geology of Kenya makes it one of the countries in the world where fluoride occurs in highest concentrations, not only in rocks and soil, but also in surface and ground water (Fleischer and Robinson, 1963). The highest water fluoride concentrations of more than 1.5 mg/l occur in some springs, boreholes, and lakes in the Rift Valley (Manji and Kapila, 1984). The chemical composition of groundwater is a function of various factors and the interaction of these factors results in different types of water that can affect water consumption purposes. Among the various characteristics of water quality, fluoride has unique properties. The concentration of fluoride in groundwater is variable and depends on several factors such as the pH, temperature, and solubility of fluorine-bearing minerals. Therefore, the amount of fluoride in water in different regions varies according to the chemical composition of water and aquifer conditions.

The principal sources of fluoride are the volcanic deposits of the East African Rift System (Gaciri & Davies, 1993). These alkaline volcanic rocks of the Rift are rich in Na^+ and F^-. Marleen *et al*. (2008) stated that the rocks of the East African Rift System are richer in F^- than other analogous rocks in the world. The volcanic rocks in the Rift are mainly composed of alkali basalts, basanites, thephrites, phonolites and trachytes. Further Marleen *et al*. (2008) observed that fluoride enrichment in groundwater along the flow direction and explained the variation in fluoride ions by the difference in availability of fluoride ions, which were linked to the volcanic activity and the composition of the volcanic rocks, and by the difference in residence times.

The geochemical evolution of groundwater is strongly influenced by the natural and human factors. Studies have shown that specific hydro geochemical processes are associated with distinct hydrogeological settings (Cloutier *et al.,* 2008). The hydrogeological factors however are determined by topography, geology, regional and local meteorological conditions. The influence of natural and anthropogenic factors on groundwater geochemical processes can be assessed by quantitatively evaluating spatial and temporal variations in fluoride ions dissolved along the surface and groundwater flow path.

The presence of highly concentrated fluoride levels in water would be associated with magma activities, thermal waters' availability particularly places experiencing high pH, emissions of gases from the crust, granitic and gneissic rocks. Further Thole (2013) concurs that volcanic activities are associated with the occurrence of elevated fluoride levels in African waters. The occurrence of fluoride in water is considered to be associated with water rock interaction facilitated by weathering of fluoride enriched rocks and water movement within soils and rock strata as observed by Brindha and Elango (2011). However highly fluoridated contents in water have associations with crustal magmatic activities and therefore raised fluoride ion amounts often found in areas experiencing geothermal activities as observed by Desbarats (2009).

AbuZeid and Elhatow (2007) assert that some of the important rocks bearing fluoride minerals include volcanic, gneissic and granitic rocks. Fluoride tends to occur in areas where fluoride bearing minerals such as fluorspar (CaF_2), cryolite (Na_3AlF_6), apatite (Ca_5 $(PO4)_3F$) and hornblende [(ca, Na)$_2$(Mg, F, Al)$_5$(Si, Al)$_8$O$_{22}$(OH)$_2$] are most abundant. The fluoride concentration in both extrusive and intrusive igneous rocks has been reported to be as high as 100 ppm in ultramafic, and greater than 1000 ppm in alkali rocks (Kaseva. 2006). High fluoride concentration in ultramafic and mafic rocks is a result of fractionation process during crystallization and differentiation processes of the magma. Similarly fluoride concentrations have been observed in groundwater especially in arid and semi-arid sedimentary aquifers (Edmunds, 1995). Fawell *et al.* (2006) observe that fluoride has been reported in metamorphic rocks in relative high concentration. The original minerals are enriched with fluorine by metamorphic processes. The highest fluoride levels between 30 and 21000 mg/l have been reported in amphiboles found in metamorphic rocks (Gaciri, & Davies, 1993).

2.8.5 Fluoride in ground water

Groundwater recharge is a result of the complex interplay associated with geology, land cover, geomorphology, climate and ongoing volcano-tectonic processes over spatial and temporal scales. The interconnection between these factors creates complex patterns that affect water availability, reliability and quality. However the hydro chemical evolution of the waters is further complicated by the different climatic regimes and geothermal processes going in the earth's surface. Weathering of fluorine bearing minerals in rocks, volcanic and fumarolic activities are the natural sources of fluoride in waters.

Ground water is one of main source of water supply in Africa for its rural communities. The water has good microbiological and biological characteristics such that it requires minimal treatment. Regrettably contamination of groundwater with naturally occurring chemicals is creating great concern. One such naturally occurring toxicant is fluoride with high fluoride in ground water being a characteristic feature of numerous aquifers across the world. Boreholes are important sources of drinking water with an estimated population of more than 200 million people worldwide drinking groundwater with fluoride concentrations higher than the WHO guideline value. The majority of the people drinking the fluoride contaminated water are found in the developing world. The greater impacts of water-rock reactions in aquifers make ground water more vulnerable to fluoride enrichment than river waters. Boreholes are major sources of drinking water in many places of the world. Groundwater is used for drinking and cooking in homesteads without any physical or chemical treatment. However, a number of health disorders have risen because of non-treatment of the water. Groundwater with fluoride concentration above the WHO permissible limits of 1.5 mg/l has been recorded in several parts of the world. Cases of high fluoride levels in groundwater have been reported by researchers in India, China, Japan, Sri Lanka, Iran, Pakistan, Turkey, Southern Algeria, Mexico, Korea, Italy, Brazil, Malawi, North Jordan, Ethiopia, Canada, Norway, Ghana, Kenya, South Carolina, Wisconsin and Ohio as observed by Brindha and Elango (2011).

Most cases of people affected by high fluoride concentration in groundwater are residents of tropical countries where the per capita consumption of water is more because of the prevailing climate. In many parts of the world fluoride in groundwater is attributed to naturally occurring rocks which are rich in fluoride. The concentration of fluoride levels is attributed to rock water interaction, long residence time and evapotranspiration. Moreover, many studies indicate that the increase in fluoride composition in groundwater is due to increase in depth from ground surface (Edmunds & Smedley, 2005). The geochemistry of high fluoride groundwater is often associated with neutral to alkaline pH, low calcium concentration and high sodium and bicarbonate concentrations in Groundwater. Generally, the natural concentration of fluoride in groundwater depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the surrounding temperature, the action of other chemical elements, depth of the aquifer and intensity of weathering (Feenstra *et al.,* 2007).

The presence of fluoride as a contaminant of ground water worldwide has become a problem, because ground water is the common source. Fluoride is frequently known to be found in higher levels in borehole water, depending on the nature of rocks and natural fluoride-carrying minerals occurring at certain depths. Therefore high fluoride levels generally can be in abundant in calcium-poor aquifers and where there is occurrence of cation exchange of sodium for calcium occurs. However in hotter climates where there is frequent and higher water consumption, the dosage of fluoride within the water meant for drinking needs to be modified based on average daily intake. The problem of high fluoride content in ground water resources is important, because of both toxicological and geo environmental concerns. The level of natural fluoride that occur in ground water ranges from 0.5 to 48 ppm, or more (Susheela, 2003). Most of the fluoride in ground water is naturally present due to weathering of rocks rich in fluoride.

Water with high concentration of fluoride is mostly found in sediments of marine origin and at the foot of mountainous areas (Fawell *et al*., 2006). The extent of fluoride contamination in ground water is influenced by the nature of local and regional geology and the existence of certain hydro-geo chemical conditions. The chief source of fluoride in ground water is fluoride-bearing minerals that exist in rocks and soils. The weathering and aqueous leaching processes that occur in soils play an important role in determining the amounts of fluoride that reaches groundwater.

2.8.6 Soils and fluoride levels

Wet and dry depositions of atmospheric salts, evapotranspiration, and soil-water interactions and anthropogenic processes have a significant influence on groundwater composition (Leung *et al*., 2005). Shekhar *et al*. (2017) observes that the type and extent of chemical contamination of the groundwater is largely dependent on the geochemistry of soil through which water flows before recharging the aquifers. Concentration of fluoride in the environment is highly variable and is often dependent on the presence of particular types of rocks, minerals, and water as observed by Zhu *et al*. (2007). Elevated levels of fluoride in water is common in fractured hard rock zone with pegmatite veins where the fluoride ions from these minerals leach into the groundwater and contribute to high fluoride concentrations.

Fluoride contamination of soil is attributed to the utilization of phosphorous fertilizers which contain less than 1 to more than 1.5% fluorine. The conduct of the fertilizer in the soil relies on soil pH and content of clay minerals in the soil as observed by Bombik *et al.* (2011). The normal total fluoride content of soil ranges from 150-400 mg/kg. However, in heavy clay soils, values surpassing 1000 mg/kg have been enlisted. Polluted soil influences human wellbeing through direct contact with soil, by means of inhalation of soil contaminants which have vaporized, through ingestion of polluted sustenance items and by penetration of soil defilement into groundwater utilized for human utilization (Begum, 2012).

Jezierska-Madziarand Pinskwar (2003) observe that fluoride at high concentration in soils has likelihood of causing different forms of toxicity to plants and grazing animals who feed in such soils Further Jezierska-Madziar and Pinskwar (2003) observed that many leaves of the plant that show symptoms of chlorosis and necrosis are usually the most common signs of fluoride toxicity in plants. Surface soil range from 0 to 75 mm fluoride with contents within the range of 326 to 1085 and 372 to 1461 mg kg-1 may cause severe fluorosis in both cattle and sheep respectively. High fluoride concentrations in surface soils can lead to high fluoride intake by grazing animals if soil ingestion rates by animals are relatively high, and this intake may induce chronic fluorosis in animals. The transport and transformation of fluoride in soil are influenced by pH and the formation of predominantly aluminium and calcium complexes. Adsorption to the soil solid phase is stronger at slightly acidic pH values 5.5–6.5. However, fluoride is not readily leached from soils.

The distribution pattern of fluoride in the soil is related to the process of soil formation which is depended on concentration of fluoride which is derived from the parent soil forming material. Worldwide, 329 μg/mg is the estimated average content of fluoride in the soil. The sandy soil has the lowest fluoride content in relatively humid environments, whereas soil from weathered mafic rocks and heavy clay soils have higher fluoride concentrations. The pH of the soil, clay, and organic carbon content as observed by Kumar *et al.* (2016) are the prime determinants fluoride contents in of soil. Fluoride enters the soil through dry deposition, precipitation, and when contaminated litter is readily absorbed. When fluoride is it increases total soluble fluoride concentration in the soil which subsequently influences the pH of soil and combine with aluminum and heavy metals. Finally in soil fluoride can exist as the free fluoride ion (F–) or combine with elements to form complexes of either iron (Fe), boron (B), calcium (Ca), or aluminum (Al), with Al and F complexes being most prevalent.

2.9 Borehole depths and geological formations

When constructing a good and quality well, knowing the characteristics of various soil types, and their effects on the borehole yield, water quality and its performance would be important. Ideally understanding the soil characteristics are more significant than identifying differentiated soils types with precision. Boreholes provide structural information of the ground surface. Borehole driller logs give the lithological formations and geological formations at site of borehole drilling. The structure of the ground surface is given by borehole logging which give the site information in addition to the available rock types. Borehole's geophysical logging helps in interpreting physical properties, chemical composition, and structural characteristics of drilled rock types.

Borehole logging helps in taking data records concerning geophysical and geology recovered from a borehole. Geophysical borehole logs are complimented with drill cuttings, sidewall samples, and cores which assist in establishing the geological variation in the borehole depth. Thereafter the information generated can be geologically interpreted. The logs can be used in estimating formation porosity, jointing, and characteristics of the fluid, hydrocarbon saturation, and pressures of the formation. When logging water wells devices to detect water flows, levels of inflow, and parameters like temperature and electrical conductivity are used to give quantities of these parameters as encountered.

2.10 Quality of water

Recharge of ground water in the Rift Valley of East African, is contributed by complex interplay between geology, geomorphology, and physical chemical attributes of water quality, climate and ongoing volcano-tectonic over space and time as observed by Oiro *et al.* (2018). The interconnections and association of these elements build complex patterns relating to water availability, its reliability and subsequently its quality. Universally water quality denotes the status of water that meets the upheld valid worldwide standards for use of quality water at all levels of human existence. The usage of the word water quality is attributed to the expansion of requirements of water and capacity to judge and infer characteristics of water. When harmful substances are introduced into the river, the water becomes polluted making its quality to deteriorate in standards. The deterioration of water quality is attributed to industrialization, urbanization and contemporary agricultural practices.

The status of River and borehole water quality would be contributed by physical, chemical and biological parameters attributable to natural forces and influences of human. Criteria of water quality attributes, standards and laws they are associated with are used as managerial ways to accomplish status of water standard so as to achieve specific requirements for use. Moreover, standards related to water quality in river water vary considerably as a result of conditions associated with the environment, ecologies and human intended uses. However, water's different uses water, trigger concerns that are different making it have like hood of being considered for different water use categories. WHO standards are the basic international subscribed levels in a number of countries for water meant for drinking.

Poor water quality has resulted in decreased water quantity which has in turn resulted in increasing demand and completion among multiple water users and lack of infrastructure. Poor water quality can adversely influence human wellbeing particularly infant mortality, production in the economy, and ecological sustainability that dependent upon water resources. The interactions between anthropogenic influences, uptake of water, and health of the ecosystem result in worsening of human portable water resources. Moreover, the inter-connection among institutional controls, anthropogenic activities, status of water, human health, and environmental functioning are multifaceted and would not be well understood. Therefore, an understanding of the nexus and responses between these systems can form a basis for information to the scientists and policymakers on issues associated with status and amount of water.

Highly fluoridated water is associated with widespread cases of fluorosis in some parts of Kenya for many years thereby making it a public health concern. Moreover, currently concerns have been created by wide spread public health campaigns on fate of fluoride embedded in soil and ground water springs, especially within the Great Rift Valley regions as observed by Sudhir and Bashir (2006). Additionally high population growth and Kenya’s climate variability intensified the water scarcity problem hence compelling poor communities living in the country to turn resort to sources of poor quality for their needs. The main water sources in majority of homesteads of Kenya’s rural population are rivers and their tributaries, springs and boreholes.

According to integrated water resources management (IWRM), there is an increasing need for stakeholders to better manage sources of pollution in river basins. This is especially the case in catchments with changing land use practices, and with changing climatic conditions. Excessive loading of nutrients results in eutrophication resulting in loss of function in terms of water supply, fisheries, recreation and an increase of the water treatment costs (Shrestha *et al*., 2008). Moreover, groundwater generally contains high concentrations of contaminants as a result of natural processes of filtration.

Consequently, therefore groundwater is a preferable source of drinking water and often constitutes a relatively reliable source during times of scarcity. However, groundwater suffers from significant water-quality problems, foremost of which in Africa is the problem of naturally high fluoride concentrations resulting primarily from interaction with fluorine in minerals and rocks. Fluoride is an essential element for human health. Although both deficiency and excess of fluoride in the human diet can have detrimental effects, it is the excesses that are now of most concern. Drinking water is an important component of the dietary fluoride intake with concentrations of approximately 1 mg/litre of water. The chronic ingestion of water with concentrations above 1.5 mg/l is beyond the WHO limit and thereby resulting in detrimental health.

Earlier studies on water catchments and water quality in African rivers have identified the potential threats on water resources being more geogenic than anthropogenic activities (Dlamini *et al.,* 2010: Masese and McClain, 2012: Odume and Muller, 2011). Nair and Manji (1984) and Davies (1996) observed that in Kenya, many of the water quality challenges are as a result of mineralization of the geologic materials, making water unfit for human consumption, especially in areas experiencing high levels of fluoride and manganese. The presence of nitrate and related compounds in drinking water has been associated with *methaemoglobinaemia,* as asserted by

Fewtrell (2004). Nitrate would be associated to the leaching of waste water and organic wastes and excessive application of fertilizers into rivers and wells. When analysing trends of water quality, the determination of spatial and temporal trends in the water quality may contribute to identifying and distinguishing between the impacts of natural and anthropogenic factors that cause water quality changes.

Groundwater is a significant water source used in country side and urbanized setups for home use where it is considered as among the purest forms of water naturally available (Kumar *et al.,* 2015). Good water for drinking is vital for existence of human however higher levels of physico-chemical parameters beyond acceptable levels make the water not suitable for drinking purposes. Chemical constituents dissolved in drinking water have influence on the health of human beings as observed by (Kumar *et al.*, 2015). Moreover, water requirements in boreholes are main sources that the rural population depends on worldwide, particularly in Africa.

Groundwater is sustained by the hydrological cycle facilitated by infiltration of rain water into the aquifers through different soils and rock layers. The physic-chemical parameters associated with sub surface water are subjected to the seasonal variations manifested in the hydro meteorological characteristics (Likambo, 2014). When the levels associated with parameters of water quality are within permissible standards the water is considered contaminated thereby making it unfit for human consumption (WHO, 2008). Naturally the ground water is uncontaminated and therefore considered as odorless, colorless and without tastes.

2.11 Physicochemical water parameters

Water whose origins are rivers and boreholes mainly provide water for domestic use in urbanized areas and country side for home use. Quality water meant for drinking is vital for survival but the levels of physico-chemical attributes that are beyond the acceptable standards make it unsuitable for drinking intentions as observed by Onwughara *et al.* (2013). The presence of various dissolved chemical constituents in drinking water affects the health of human beings (Kumar *et al.,* 2015). The rural community worldwide is depended on water from boreholes for their needs. Rain water percolates into water sources through differentiated soils and rock strata to recharge the ground water. According to Likambo (2014) seasonal changes affect the physical and chemical characteristics of groundwater. The contamination of water is a result of higher of physical chemical parameters that are above the permissible standards making the water unsuitable for human portable use (WHO, 2008).

According to Harvey (2011) water and sewage water in third world states, account for 80% of illness. Therefore, health problems associated with ground water are a result of high quantities of physico-chemical parameters water that exceed the KEBS (2010) acceptable standards. The reported cases are more rampant among users of water living within the country side of the states in the third world. Usage of surface and sub-surface water has risks associated with their usage especially where it is vulnerable to pollution from sources such as percolating of fertilizers and naturally occurring chemical compounds whose origins would be traced to rocks as asserted by Gichuki & Gichumbi (2012). For a long time because of rainfall that is little and unpredictable in the desert regions sub surface water has also been used as the key water source for domestic uses Olumuyiwa *et al*. (2012). Therefore, water in Kenya being scarce it makes the country to be referred as a water scarcer country making it to over rely on ground water. Consequently, the affected residents have become victims of dental discolorations and skeletal fluorosis attributed to drinking water that is highly fluoridated.

2.11.1 pH

pH measures water's levels of hydrogen potential. Universally pH in solution is used to express the solution's acidity or alkalinity concentration it is considered an indicator of water that is chemically varying. Low pH characterises acidic water which cause problems related to hyperacidity and ulcers to human as observed by Buridi & Gedala (2014). In water aquifers pH's contact with natural rocks results in their corrosion contributing to the existence of additional chemical substances in water thereby raising levels of contaminants contained therein. Similarly elevated levels of pH make the taste of water to be bitter taste (Ayesh, 2012). The World Health Organization, the European Community and the U.S. Environmental Protection Agency consider 6.5-8.5 as it as the highest levels of contaminant for pH in water meant for drinking water. In Kenya according to KEBS (2010) the permissible levels of pH is 6.5-8.5.

2.11.2 Electrical conductivity

Electrical Conductivity is measures capacity that assists a fluid in transmitting current. Ionic species contained in water determine the water's conductivity ability. The anion and cations at a particular temperature in water determine mobility of the ions (Nirmala *et al*., 2012). The salinity of water is affected by pH thereby affecting the taste of the water a clear indicator of dissolved ions. Jain &Agarwal (2012) asserts that electrical conductivity that is high is attributable to highly ionized salts contained in water. As a parameter of water quality Electrical conductivity has close association with total solids that are dissolved in water (TDS). Additionally EC and TDS levels are manifested through their corrosive effects on soluble compounds in a water sample as manifested by the behaviour of calcium carbonate. Therefore TDS and EC increase the corrosive ability in water.

2.11.3 Total Dissolved Substances (TDS)

Total Dissolved Substances (TDS) is a parameter in water measuring the total transportable amount of charged ions that are dissolving in a specified amount of water. Kenya's KEBS standards consider the acceptable levels of TDS not be greater than 1200 mg/l. Water that contains TDS greater than the recommended limits influences its taste, hardness and corrosiveness and is likely to cause gastrointestinal irritation. Higher values of TDS values in water are indicators of highly mineralized water that is contributed by presence constituent materials present in in the area which are resistant to dissolution as observed by Nirmala *et al.* (2012). TDS in water is contributed by heavy rainfall sweeping areas covered with rocks whose main mineral composition is carbonates, chloride, nitrate, sodium, potassium, calcium and magnesium.

2.11.4 Turbidity

Turbidity measures how a liquid is relatively clear by expressing the light scattering and absorption attributes of the water. The silt availability and matter that is suspended in water causes turbidity which eventually has effects on the water's color thereby promoting microbial proliferation. On the passage of time this results in the decline of water's value (Olumuyiwa *et al.*, 2012). Research works have revealed associations of wet seasons with higher turbidity while dry periods are associated with low turbidity as a result the silt deposition into water sources as observed by Oluyemi *et al.* (2014).

2.11.5 Total alkalinity

Water's alkalinity is its ability to make acids neutralize. In naturally occuring waters alkalinity would be attributable to carbonates and hydroxides. Alkalinity is an important water quality parameter. The availability of compounds of carbonate and hydroxide, calcium, sodium and potassium combing with water contribute to the water being alkaline (Murhekar, 2011). Over time, alkalinity of water results in the consequential effects of eutrophication thereby resulting in its over-enrichment. In the natural environment, alkalinity increases when water comes into contact with rocks containing compounds of carbonate, bicarbonate, hydroxide and phosphates. The pH levels are associated with salts of carbonates, bicarbonates, phosphates, nitrates, borates and silicates together with hydroxyl ions in existing freely. Higher pH levels have effects on water quality by altering water's taste to water and in sometimes it can causeing irritation of the eye and skin in people as observed by Buridi & Gedala (2014). Similarly Ayesha observes that alkalinity of water can affect its colour thereby making the water to be unfit for drinking. KEBS has set permissible levels of alkalinity to be 500mg/l. additionally: alkalinity is a vital water quality parameter that has an influencing implication on water quality by acting on pH neutralization. Therefore alkalinity measurements are used as the means for evaluating the buffering ability of water.

2.11.6 Chloride

Existence of chloride ions in sub surface water is contributed by saline intrusion, discharge of waste water from the sewage system, drainage of water used for irrigation and contamination attributed to garbage leachate (Olumuyiwa *et al.*, 2012). Additionally excess chloride in water would result in bad taste and it would be indicator of contamination from urine and sewerage. High chloride levels impact negatively vegetation growth and also increase metal's corrosive abilities.

In situations when chloride levels are higher than the acceptable standard the water develops a salty taste and over time results in physiological damages as observed by Nirmala *et al.* (2012). Salinity in ground water is an important parameter which is influenced by rainfall, evapotranspiration, rock composition, type of aquifers and sea water intrusion as observed by Mwamati (2017). According to Kenyan standards the permissible chloride levels to be contained in water for drinking is 250 mg/l and if the level is beyond 250mg/l in water, the water becomes toxic to human health resulting in outcomes that are laxative (Murhekar, 2011).

2.11.7 Phosphate

Leaking contributed by domestic solid wastes and soups would result in accumulation of phosphate in sub surface water. Similarly the existence of phosphate in water would be a result of runoff and infiltration from agricultural effluents having dissolved agro chemicals and waste water originating from industries. Concentration of high phosphate is an indicator of ground water pollution as observed by Ombaka *et al.* (2013).

2.11.8 Potassium ions

Natural weathering of rocks is the source of potassium ions in ground water moreover: the higher amounts available in water that is polluted would point to the release of dirty water originating around the groundwater sources. In human beings' potassium ions are essential elements and therefore making intoxication by ingestion to have lesser harmful effects. However, Marian & Ephraim (2009) have observed that consuming higher quantities of potassium ions will overload homeostatic functioning of the kidney and subsequently result in death associated with kidney failure.

2.11.9 Calcium

In all natural sources of water chloride exists however the concentrations vary greatly with the maximum levels in sea water reaching a maximum of up to 35,000 mg/l. Sources where fresh waters originate have naturally occurring calcium in soil and rock formations, sea spray and disposed wastes. Bulky quantities are also contained in Sewage and in some effluents originating from industries. In all natural sources of water chloride is present in appreciable amounts however the concentration varies from a few milligrams to several thousand milligrams per litre. High concentration of Chloride is evidence of pollution originating from organic matter and eventually requires chlorination before it is suitable for drinking. Elevated levels of chloride results in corrosivity and altered taste of water. The permissible level of chloride is 250 mg/l according to WHO.

2.12 GIS and Remote Sensing

Geographic information system (GIS) utilises computer-based tools to mapp and analyse features and occurrences on earth. GIS incorporates common technology in manipulating databases to draw maps. Conversely, as a science remote sensing collects data of an object or a phenomenon while avoiding physically contact with the object. Geographical Information Systems (GIS) provide a platform used in acquiring, storing, and processing spatial datasets for maps (Ngeno, 2016). Tools for GIS are available today for specialized uses to manage data. Remote sensing data and geographic information system are gradually turning to be important tools in water science and analysing anthropogenic activities on land.

RM and GIS over time have become important because much of the data required for hydrological and land-use/cover analysis are obtained with ease from remotely sensed images. Remote sensing has the capability to acquire spectral signatures instantaneously over large areas. Gumidonga (2010) asserts that the spectral signatures acquired from GIS and RM assists in obtaining information concerning land-use and land cover, emissivity, surface temperature and energy. Gumidonga (2010) further observes that land-use and land cover changes can be analysed over a period of time using Landsat Multi Scanner data and Landsat Thematic Mapper (TM) data by image classification techniques.

GIS and RM are effective tools for groundwater quality mapping and the monitoring of environmental change detection. In the map classification of groundwater quality GIS has been used to correlate fluoride ion (F^-) values with land use dynamics and aquifer characteristics (Asadi *et al*., 2007). In other researches GIS has been used as a database system to prepare maps of outlining the water characteristics based on concentration values of different composition of the chemicals. According to Yammani (2007) in such cases GIS is used to locate groundwater quality zones that will provide water for different uses which would be either irrigation or portable uses. In the study by Babiker *et al*. (2007) a GIS based groundwater quality index method is proposed by synthesizing available data on water quality and thereafter indexing them statistically by comparing to the WHO standards. Therefore, the use of GIS expertise has assisted in simplifying the evaluation of God given resources and issues of environment, including ground and surface waters.

GIS in ground water research work is regularly used when analyzing site suitability, management of site inventory data, appraising contamination of groundwater, modeling of groundwater movement and modeling solute transport and leaching. Barber *et al*. (1996) carried out a study using GIS to determine the impact of urbanization on groundwater quality in relation to land-use changes. In the province of Konya, Turkey Nas and Berktay (2010) used GIS in mapping urban groundwater. In urban centers, groundwater quality map helps to evaluate the water safe for drinking and irrigation purposes so as to avoid negative environmental impacts. Additionally, to estimate groundwater quality of locations where samples were not collected, spatial interpolation with a satisfactory level of accuracy is used. Spatial interpolation measures the degree of relationship between near and distance points by placing emphasis on the principle of spatial auto-correlation or spatial interdependence, which measures the degree of correlation in comparing near and distance points.

2.13 Geostatistical modelling

The Geostatistical Analysis uses parameters of sampled points in a landscape under different locations in a landscape to create interpolations in a continuous surface. The sampling points in Geostatistical Analysis would be measurements of some natural phenomenon like an oil spill, or fluoride contamination. In practise analyst of Geostatistics derive a surface using the values from determined locations to forecast values for each site in place under consideration. Analysis by Geostatistics is depended upon the resemblance of neighbouring points of sampling to create the surface. Geostatistics relies on both stochastic in addition to mathematical methods, which assist in creating surfaces so as to assess uncertainty projections. Additionally, the Geostatistical Analyst provides numerous techniques of interpolation in addition to providing many supporting tools (Viswanathan *et al.*, 2009). Geostatistical tools allow one to understand better exploration of the data so that can be created based on information available. When a model provides accurate predictions, then it is required that the standardized error mean be possibly close to 0, while the errors of root-mean-square and average standard be possibly minimized. Finally, the standardized error of root-mean Square is expected to be nearing 1 as observed by Gringarten & Deutsch (2001).

Interpolation and estimation are the major concerns of Geoscientists when investigating sparse data derived from field observations. Originally Geostatistics started from the mining and petroleum industries in the 1950s with the work by Danie Krige (Hassan *et al.*, 2013). Its use was later adopted in the 1960s by Georges Matheron. Overtime since 1960s Geostatistics has been used in earth sciences field related to water, rocks, weather elements and oceanic science. Additionally, Geostatistics has been applied in geochemistry, geography, science of the soils, forestry, and countryside ecosystem. According to Diodato and Ceccarelli (2005) the merits in using Geostatistics is in the use of measurable parameters that are spatially correlated which is expressed in form of a variogram. Geostatistics is the expression of stochastic techniques such as traditional and areal statistics in the science of earth studies.

Statistical modelling refers to the mathematical expression of data that is observed and collected data. Thereafter the statistical fitness is applied in predicting the nature in the range of the conditions being projected or observed. Statistical models will therefore specify the mathematical relationship between random and other non-random variables. According to Lawless (2011) a statistical model is "a formal representation of a theory" which mathematically formalizes a way to approximate reality and optionally make predictions from the approximation.

A model has both input and output parameters. The input variable is the one that describes, explains or predicts the anticipated output. Conversely independent or explanatory variables are the variables that are used use to explain or predict the dependent variable. Geostatistics as technique helps in approximating local values of properties that are varying spatially. Isaake and Srivastava (1989) assert that the theory of Geostatistics concept has foundation on the concept of an arbitrary variable, which expresses a variable that is continuous depending on its location. In Geostatistics it is expected that spatially observations close together would display similarity than those further apart. Further, Burrough and McDonnell (1998) observe that Geostatistical techniques in locations with sparse locations provide important estimates of sample characteristics through the definition of spatial structure of the occurrence through autocorrelation. Autocorrelation uses techniques like semi-variograms where the values are estimated after measuring points considering the degree of areal autocorrelation and covariance of the data.

Kriging is one of the important methods in Geostatistics which is applied widely in the practice natural science fields. Originally Kriging was developed in spatial statistics by the South African mining engineer called Krige. Matheron would further support the works of Kirging. Consequently, over time easier options to Kriging, like the Inverse Distance Weighting (IDW) would be used the purposes of interpolating. The technique of Inverse Distance Weighting is easier to implement because value approximation does not entail any of the measures related to spatially auto correlated or spatially auto-covariance values as observed by (Isaake and Srivastava, 1989). The Kriging techniques are referred to as the linearly the estimator that is unbiased because their mean residual error is equivalent to zero. Kriging techniques aim in reducing the variation of errors and therefore making them have merit over other methods of estimation such as inverse distance weighting or moving average.

Interpolation by Kriging considers the weights from measured surrounding values to forecast values of surrounding locations. To the contrary, with IDW interpolation, measured values in the neighborhood usually have the greatest effect whereas in the Kriging weights for the surrounding measured points are more complicated in relation to IDW. In its application therefore IDW simply applies algorithm which is depended on distance. Conversely weights for Kriging weights are derived from a semi variogram that was advanced from viewing data that is spatially structured as observed by Nazeri-Tahrudi *et al.* (2013). According to the general principle of Kriging: one is supposed to compute the experimental discrete variogram in different points and thereafter fit the discrete experiment points with a mathematical model which is designed as the model variogram. However, the Kriging cannot be applied to all conditions like in the case of when the data is sparsely distributed while at the same time each point is independent of the other points.

2.14 Knowledge Gap

Conclusively there is limited study on methodical, categorical and empirical studies on fluorides conducted in River Njoro catchment. However, Naslund & Snell (2005) developed a digitized map using GIS and ground water information from the Nakuru Catholic Diocese data base. The digitized map had specific fluoride levels in the borehole locations other water characteristics in the sampled boreholes. The focus of Naslund & Snell (2005) was to get a summary of the sources of boreholes water for both the water stakeholders without placing emphasis on the origin of fluoride and its distribution.

In their study, Naslund & Snell (2005) found that fluoride had big variations between boreholes. The highest fluoride content was found to be 40 mg/l while the lowest was 0.l mg/l. conclusively: Naslund & Snell (2005) observed that about half of the sampled boreholes had values that could lead to dental or skeletal fluorosis in human beings. Further Naslund and Snell (2005) established that there were high fluoride levels in the boreholes in Nakuru and Baringo Counties. However, the study was confined to groundwater from deep boreholes, rivers lakes and natural springs. It was established that the Dundori springs and L. Elementaita water had high levels of fluoride.

Later research work by Wambu and Muthakia (2011) in their study identified high mean Fluoride levels of about 7.69 mg/l in borehole water around Elementaita area and further concluded that the level of water Fluoride increased with proximity of the source to the lakes in the Rift Valley. The aftermath of fluoride levels on human health observes that exposure to high levels of fluoride has effects on human health. The Eastern Rift Valley obvious clinical effects are seen on the population, dental fluorosis is a widespread problem in the area and the high concentrations of fluoride in the drinking water come from the alkaline volcanic activity associated with the geologic processes of the rift valley. Tenge *et al.* (2015) asserted that fluoride concentrations in natural waters were established to vary between 0.05 and 100 mg/l, with fresh waters quantities not exceeding 0.1 mg per litter. High concentrations of fluoride, exceeding 1.5 mg/l have been recorded in volcanic aquifers and lakes in the East African Rift system.

Past research studies within the Rift Valley by Moturi *et al.* (2002), and Chelangat (2015) showed that several areas are affected with excess fluoride in groundwater. Chelangat (2015) observed that the Kenya's geology makes it among the countries endowed with concentrated fluoride levels worldwide. Chelangat further observed that fluoride was found commonly in different sources of water, moreover the presence of fluoride bearing mineral rocks with higher fluoride quantities are found in borehole water. Chelangat further asserts that in Kenya a larger portion of the population continues to get water from different sources without any form of treatment. Moreover, the Rift Valley's water sources have high related fluoride toxins where the variations in fluoride levels are clearly visible. Despite Chelangat's study on fluoride occurrence there was little attention and emphasis on the relationship between fluoride levels and geological dynamics.

Further, past studies on River Njoro catchment by Shivoga *et al.* (2014) gave emphasis on the destruction of the Njoro catchment with less emphasis on the high levels of fluoride in the water of River Njoro. According to Shivoga *et al.* (2014) the River Njoro catchment is characterized by six land use/cover categories: indigenous forest: plantation forest, mixed small-scale agriculture, grassland, large-scale agriculture, and bare land. In River Njoro catchment the area under mixed small-scale agriculture and bare land downstream from the uppermost sampled sites increased significantly. Conclusively, in the study the area under mixed small-scale agriculture and grassland in the upper and mid-reaches of the River Njoro witnessed an overall increase between 1986 and 2003. Contrary the area under large scale agriculture, plantation and indigenous forest during the same period witnessed a decrease. Therefore, River Njoro catchment has witnessed degradation due to rapid changes in land uses/covers but at the same time gives a blackout to the serious phenomena of elevated fluoride levels.

Additionally at the African continental level Malago *et al.* (2017) observed that the typically elevated fluoride levels. However as compared to the other African countries the typically highly concentrated fluoride quantities in water was more prevalent in countries located in Rift Valley: Kenya, Tanzania and Ethiopia. Nevertheless, incidences of highest levels of fluoride were available in rivers within Rift Valley countries. As expected the findings were not true because groundwater had high fluoride concentrations comparative to water in rivers with the conditions being associated with interaction of the rocks and water as compared to interaction in surface water.

Knowledge of the means of fluoride dispersion, sources of fluoride and fluoride dispersal in both surface and sub-surface water within River Njoro catchment compared to stratigraphy variations has been given little attention. The Kenya's rift valley is marked by tectonics that are active, magma eruption and fumarolic activity with volcanic rocks the major rocks. The main volcanic rocks include rhyolites, tuffs, basalts and phonolites, in addition to ashes and agglomerates some of which are greatly cracked. This study therefore combined borehole structural information, the surface geology and selected physical parameters of water quality as determinants and predictors of fluoride distribution within River Njoro catchment.

Therefore rivers as fresh water sources would be having WHO permissible fluoride levels. However, variability in climate, pH, and the type coupled with porosity of the rocks and soils which they are in contact have a bearing on fluoride concentration levels. Kanda (2010) on stratigraphy of aquifers and hydro geochemistry of lake Nakuru basin, located within rift valley in Kenya observed that are three aquifer systems with three major aquifer lithologies: fissured trachyte, volcano sediments and pyroclastics revealing dominant trends in the Nakuru area. This study will therefore seek to integrate the combined effects of surface geology, borehole formations and borehole depths on the variation in fluoride distribution levels in Kenya's River Njoro catchment.

CHAPTER THREE

MATERIALS AND METHODS

Introduction

This chapter give a narrative of the methods and materials that were employed in conducting this study. The chapter discusses the different approaches that were used in this study to collect and analyse fluoride levels data from sampled surface rocks, rivers and boreholes in the River Njoro catchment. The methods that were pursued in this study were decided on the basis on the objectives of the study with emphasis on: geology, hydrogeology, fluoride distribution in the River Njoro catchment and Geostatistical analysis.

3.1 Research Design

Purposive longitudinal survey research design was adopted for this study. In this research, the study area was purposefully categorised into upstream, midstream and downstream so as to capture to varied land uses/covers in the sampling points. A purposive longitudinal survey technique does not use possibility method whose characteristics are based on attributes of a population guided by the objective of the study (Holland *et al.,* 2006). Additionally purposive longitudinal survey is judgmental or selective sampling which involves repeated similar happenings of the same variables over some time. Mainly, purposive longitudinal survey sampling seeks to produce a sample that can be rationally taken to represent the population. The water sampling from the river and borehole points were done during the rainy period and sunny seasons with intentions of capturing the seasonal variations during the study period.

This research study involved collecting borehole and river water samples, soil and rock samples from designated points along the River Njoro and its tributaries and selected boreholes for laboratory analysis. Sampling of water and rocks were done at designated points located at upper, middle and lower sections along the catchment representing different elevations. The rocks, water and soil samples collected were carried to the Chemistry Laboratory at University of Eldoret for analysis of the levels of fluorides. The summary of methodological procedure and the materials used during the course of this research are presented in figure 3.1.

DESKTOP STUDIES

Desktop study of the Njoro catchment, Literature review of Njoro catchment, acquisition of available secondary borehole and river Njoro data, studying of the borehole stratigraphy information and assembling of the field work equipment

↓

FIELD WORK

Sampling of water and rocks from the identified river Njoro sampling sites and boreholes, identifying the sampling point locations using GPS, determination of pH, temperature and electric conductivity and analysis of available borehole stratigraphy and geological surveys

↓

LABARATORY ANALYSIS AND CONTENT ANALYSIS

Geostatistical interpolation and analysis interpretation, fluoride levels analysis, inferences and interpretation of driller's logs in relation to borehole depths

Before embarking on field data collection, desktop studies and review of related literature were undertaken. The desktop studies helped in mapping the Njoro catchment and initiating the action plan of the research. The desktop studies involved delineating the River Njoro catchment, collecting Meteorological datasets of rainfall and temperature from the Egerton University and Nakuru County Meteorological stations which are located in the catchment area. Similarly the desktop studies involved obtaining GPS locations of water sampling borehole and river points. Further, desktop studies involved acquiring relevant available secondary borehole and River Njoro data from the Water Resource Authority (WRA) Nakuru office, studying of the borehole stratigraphy information and assembling of the required field work equipment. The original data collected during the period of the research project was complimented by the information collected during the desktop study and review.

3.1.2 Field Work

Activity of field work data comprised of river and borehole water samples collection which was done between July 2018 and May 2019. Fieldwork also involved sampling and collecting rocks and soils at the river water sampling points and places under different land uses/covers respectively. The sampling process involved collecting water samples during the dry and wet seasons. During the fieldwork campaigns, insitu measurements were taken for temperature: electrical conductivity (EC) and pH using a Hanna HI 9828 multi-parameter water quality instrument.

3.1.3 Laboratory Analysis and Content Analysis

Ground and river waters flows from boreholes of varying depths and River Njoro points formed the hydrogeological system. As the water flow along the catchment paths, it interacts with the rocks and thereby changing their chemical composition. Analysis of fluoride in the sampled borehole and river water and soils was done at the University of Eldoret's Chemistry Laboratory. Similarly, analysis of Geostatistical data and geological interpretation of the study area was done at the GIS laboratory of the University of Eldoret. Finally content analysis and interpretation of the available drillers and geological logs surveys in relation to borehole depths.

3.2 Data Collection and Sampling Procedure

The rocks were sampled by breaking pieces of rock from rock outcrops extending from the river bed at the identified water sampling points along River Njoro to help determine the contribution of surface geology to fluoride concentration in River Njoro catchment. The upstream, midstream and downstream zones were distinguished by topographical and geological considerations. The selected river and borehole sampling sites are shown in Figures 3.2 and 3.3 respectively.

Water samples were picked in the identified 10 sampling points along River Njoro while 12 water samples were collected from boreholes within River Njoro Catchment during every fieldwork visit. Similarly, during sample collection, rock samples were collected from the river sampling points during the first fieldwork visit. The researcher also collected secondary data on the borehole stratigraphy and geology of Njoro catchment.

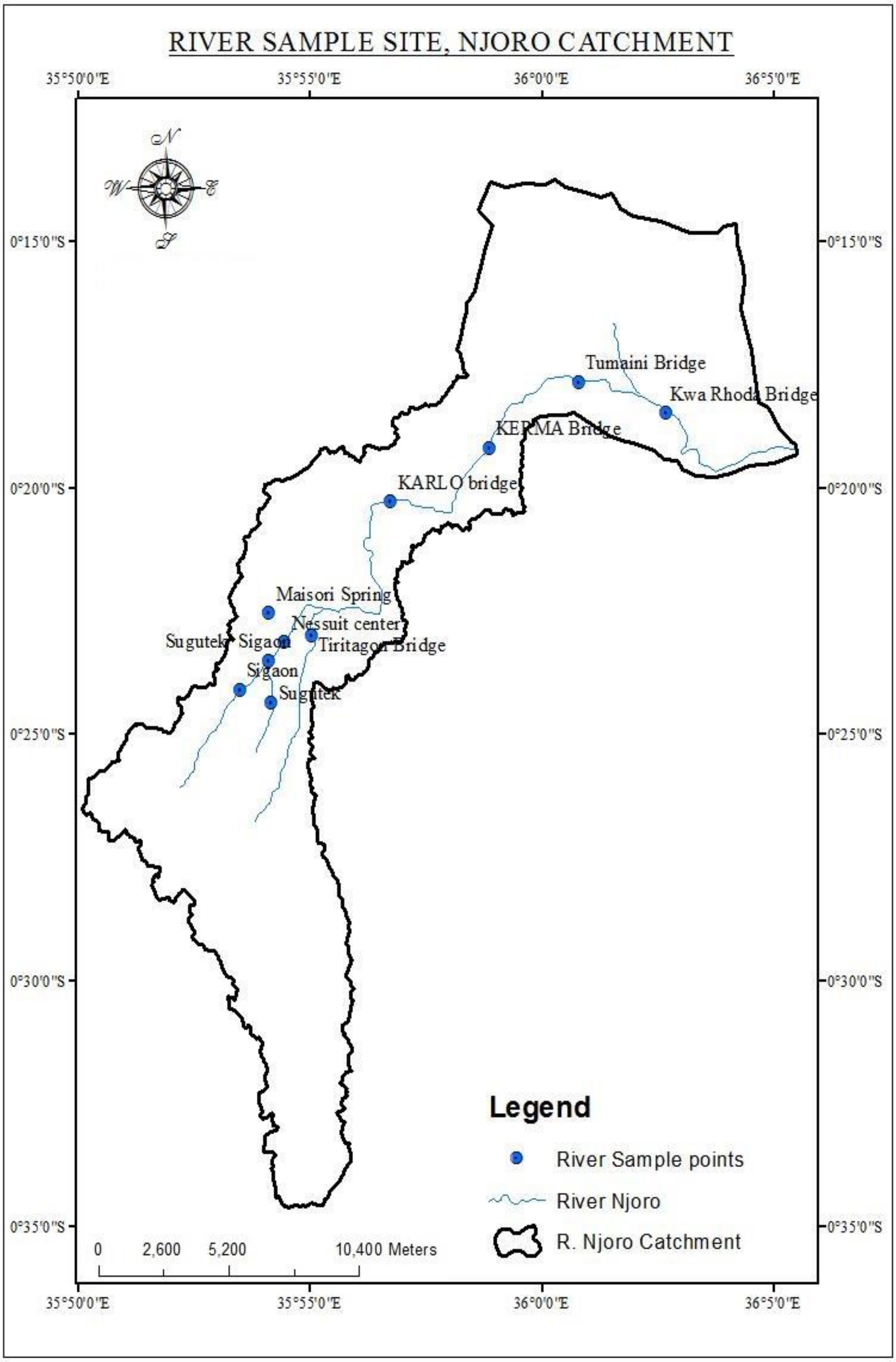

Figure 3.2: River Sampling Sites

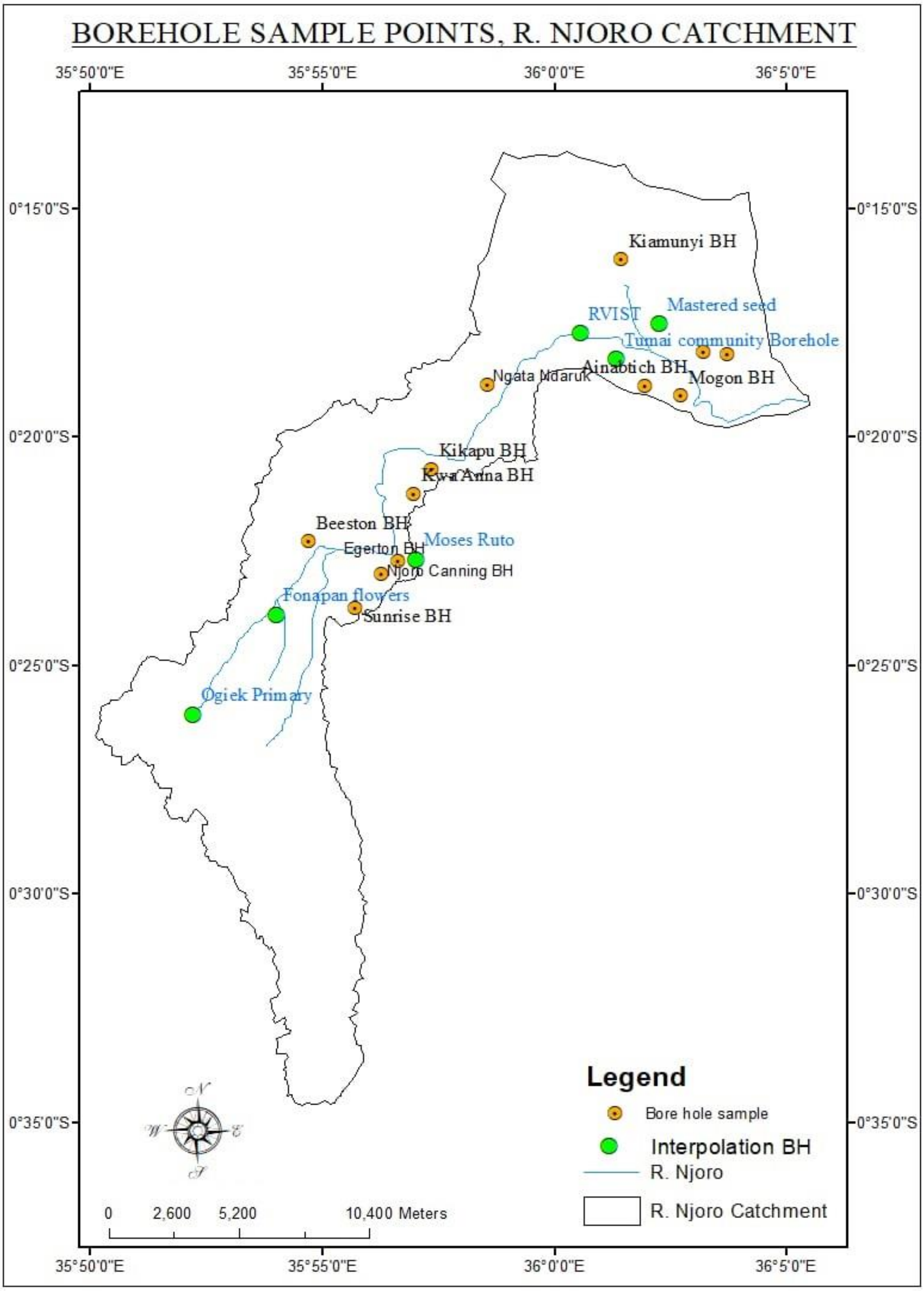

Figure 3.3: Borehole sampling sites

N/B: Borehole sample were the water sampling boreholes while interpolation BH were the boreholes used for the Kirging interpolation.

3.2.1 Rock and Soil Sampling

To establish fluoride contamination in River Njoro through the contact of river water with the underlying bedrocks, samples from the rocks that were in contact with the river water were collected. The rock samples were collected from the 10 River Njoro water sampling points. The breaking and sampling of rocks from the rock outcrops along River Njoro are shown in plates 3.1 and 3.2. Rock samples from rock outcrops and the rocks underlying the River Njoro were broken, with the help of the geological hammer at the identified river water sampling points. The rock samples were packed into carrying bags which were labelled indicating the GPS and location details of the sampling sites as shown in plate 3.2.

During the study also, soils were sampled from the study area at designated points to analyse for presence of fluoride quantities. The hydrological process of infiltration of fluoride originating from anthropogenic or natural sources into the soil would be justified by fluoride levels in the soil. The fluoride contaminated soils through infiltration and surface runoff would result to elevated fluoride levels in water sources. The soil samples were systematically and purposefully collected from the three sections of upstream, middle stream and downstream of the River Njoro catchment. Purposefully the soil samples were a representative of identified land uses/land cover within the River Njoro catchment. Before taking the soil samples from each soil sampled hole, the surface was examined carefully to ensure that neither stocks nor plant remains were present. Three soil samples were collected in every identified category occupied by distinct land cover and depths and thoroughly mixed.

Thereafter sampled soils were collected from the upper layer of top soil at the depth of between 0 and 20 cm and five from the deep layer at the depth of between 20 and 40 cm for sub soil in the different categories of land uses. The top and sub soil samples were analysed separately for fluoride levels. The soil sampling was done by digging vertically and thereafter collecting the soil samples from distinct depths using a soil auger as shown in Plate 3.3. Later the samples of soil were packed into polythene packets and kept into the cool box to maintain its moisture. The plastic bags were labelled appropriately indicating the GPS location, land use/ cover type and whether the soil sampled was top soil or sub soil. Finally the soil samples were transported in the cool box to the University of Eldoret, department of Chemistry laboratory for fluoride content analysis.

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Plate 3.1:Breaking Rock samples from rock outcrops

Plate 3.2: Sampling the broken rock particles from the rock outcrops

Plate 3.3: Soil sampling using a Soil Auger

3.2.2 River Water Sampling

The study involved sampling of water samples from sites that had been determined along River Njoro and its tributaries. The geographical coordinates and altitudes of the sampling sites were picked using a Global Positioning System (GPS). The designated Ten sampling sites along the River Njoro reflected zone variation determined by: land use, surface geological and topographic considerations in the vicinity and upstream of the sampling points. Where the tributaries joined the main river the water samples were collected before the point of confluence of the rivers so as to examine the contribution of fluorides from sub watersheds upstream. Water samples from Kwa Maisori spring was collected at the emergence point to avoid collecting water samples already contaminated by either human or animal.

Pilot sampling in the Ten River Sampling points was carried out on June 20th 2018. During the pilot sampling, triplicate water samples were taken from three points across the river channel from each sampling point. The three sampling points were at the two shallow ends and at the deepest points of the river channel. Sampling of water was carried out during the wet and dry seasons in the months of July 15th to December 18th 2018 and January 10th to May 10th 2019 respectively. During sampling, water was sampled from the two river bank points and at the deepest point in the river channel at each sampling point. In total thirty samples were collected from the ten river sampling points shown in Figure 3.2 during pilot sampling. Thereafter laboratory analysing of fluoride levels of the triplicate samples from each sampling point were statistically analysed.

The statistical analysis of the pilot sampling showed no significant statistical difference among the triplicate samples at each point of the river channel. After the statistical similarity of the pilot data, the researcher subsequently chose to the collection of 1 sample from each of the 10 sampling points along River Njoro during the research field sampling period. During the field sampling period a total of 80 samples of water were collected from the 10 sampling points along River Njoro during the wet and dry season. Fifty water samples were collected from the ten sampling points during the wet season in five field work visits. Conversely 30 water samples were collected from the Ten River sampling sites during the dry seasons during the 3 fieldwork visits. Insitu measurements were done for temperature, pH and electrical conductivity during the water sampling visits in the wet and dry seasons.

Once the sampling of the water was done from the surface water points and springs, GPS coordinates and altitudes of sampling sites were taken during the first sampling sessions and the readings confirmed in the subsequent visits. Before sampling, temperature, electrical conductivity and pH were given time to stabilize before taking their readings in situ as demonstrated in plate 3.4. Upon stabilization of the three parameters water samples were taken from the identified points in the River Njoro and springs in 50 ml clean washed plastic bottles. Collection and storage of water samples was done in plastic bottles because when using metallic containers there is a possibility of contamination by the metals dissolved from the container walls. The clean washed 50 ml plastic sampling bottles were rinsed thoroughly at least thrice with water from the sampling points.

After rinsing the sampling bottles, the water samples for fluoride analysis were filtered using Whatman Glass Fibre Filters (0.45µm, GF/C) as demonstrated in Plate 3.1 and poured into the sampling bottle and the bottle closed tightly. The water samples were immediately labelled by indicating the physical locations and date of the sampling date and refrigerated into the portable field cool box immediately after collection.

Plate 3.4: Measuring of water quality parameters insitu at River Sigaon

Source: Author (2019)

Plate 3.5: Filtering the water samples

After each of the sampling visits, the water samples were transported in a cool box to the Chemistry Laboratory at University of Eldoret for analysis of fluoride levels. The water sampling points on River Njoro, GPS location and altitudes are shown in Table 3.1

Plate 3.6: Measuring Physical Parameters of water samples Insitu

Source: Author (2019)

Table 3.1 River Water Sampling Points

S/NO.	GPS location	Altitude	Sampling name
1	-0.3788,35.879	2464m	Kwa Maisori (spring)
2	-0.417,38.881	2532m	River Sigaon
3	-0.416,35.881	2515m	River Sugutek
4	-0.417,35.880	2506m	Confluence Sugutek/Sigaon
5	-0.396,35.898	2421m	Nesuit centre bridge
6	-0.379,35.899	2387m	River Ndarogo bridge
7	-0.338,35.944	2160m	Njoro town bridge
8	-0.333,35.943	2090m	Kerma bridge
9	-0.297,36.009	1930m	Tumaini bridge
10	-0.367,35.992	1775m	Kwa Rhoda bridge

3.2.3 Borehole water sampling

Boreholes were situated in both private and public lands were identified for sampling in the River Njoro Catchment. The boreholes were located Upstream, Downstream and Midstream in the river catchment. The identified boreholes within the River Njoro catchment were selected on the criteria of: depth, geographical location, and water use. The depth of the boreholes ranged between 110 and 230 metres deep. The categorization of the catchment into Upstream, Downstream and Midstream was based on topography and elevation of the River Njoro catchment. A total of 84 water samples from the boreholes were collected from the identified 12 boreholes during the 7 field sampling visits. The 84 samples comprised of 4 samples from each of the 12 boreholes collected during the wet season between 10th July and 18th December 2019. Similarly 36 samples were collected from the 12 boreholes in 3 fieldwork visits during the dry seasons between 10th January and 10th May 2019.

Before collecting the water sample: temperature, pH and electrical conductivity were allowed to stabilize. The borehole water was pumped and made to pass through a flow through cell as shown in plate 3.6 before entering into the storage tanks to allow temperature, pH and Electrical conductivity parameters to stabilize. Upon the stabilization of electrical conductivity, temperature and pH the water samples were collected into clean washed 50 ml plastic sampling bottles. The sampling bottle and its lid were rinsed three times using water pumped from borehole, and thereafter the samples collected were filtered using Whatman Glass Fibre Filters (0.45µm, GF/C) as shown in plate 3.5. The sample ID indicating the physical location and date of the sampling was written on a label stuck on the bottle, with a waterproof pen. Thereafter the bottle was tightly closed and the water samples were refrigerated and transported in a cool box to the Chemistry Laboratory at the University of Eldoret for fluoride analysis. The sampled boreholes with their coordinates are presented in Table 3.2.

Table 3.2: Borehole Water Sampling Points

S/NO	GPS LOCATION	ALTITUDE	NAME	DEPTH
1	-0.362,35.907	2450	Beeston-Rurii	130 m
2	-0.3866,35.888	2485	Nesuit sec school	180 m
3	-0.397,35.945	2307	Egerton Sunrise	172 m
4	-0.362,35.987	2142	Kikapu community	114 m
5	-0.367,35.942	2160	Njoro canning	230 m
6	-0.367,35.992	2156	Kwa Annah	207 m
7	-0.305,35.988	2043	Ngata Ndaruk	127 m
8	-0.304,36.033	1860	Ainabtich community	130 m
9	-0.270,36.037	1947	Kiamunyi	212 m
10	-0.302,36.062	1819	Pistis	180 m
11	-0.304,36.050	1794	Mother Kelvin	110 m
12	-0.320,36.022	1935	Mogon Community	140 m

3.2.4 GIS Data and Geostatistics

a) Catchment Delineation

A Digital Elevation Model (DEM) with a 90 m resolution was obtained by the Shuttle Radar Topography Mission (SRTM) and downloaded from the Global Land Cover Facility (GLCF). A DEM is a representation of the continuous spatial variation of relief that assists in assessing landscape characteristics along with topography and has a wide application in hydrological modeling. The Hydrology Tools of ArcGIS software was used to delineate the River Njoro catchment. Thereafter the process of catchment delineation in ArcGis which involved the filling of the sinks, the determination of the flow direction, accumulation and creation of the stream links was followed. The point at which River Njoro enters into the Nakuru National Park a protected area was used as the end of River Njoro and helped in delineating the watershed.

b) Geostatistics Data

In this study, Geostatistical data included: GPS locations of the boreholes, fluoride levels and depths of the sampled boreholes. The main elements of the geostatistics data collecting and analysis included: data input, data pre-processing and estimation of distance between boreholes to depict spatial variability between the sampled boreholes. The other elements included average fluoride levels of the sampled and neighbouring boreholes, scenario analysis at the diagnostic stage and if the scenario analysis depicts the picture of fluoride distribution the River Njoro catchment then fluoride prediction will be represented by a fluoride spatial distribution map. The procedure of geostatistics data collecting and analysis is represented in Figure 3.4.

The GPS locations and elevations of the 12 boreholes situated upstream, midstream and downstream were obtained using a hand held Germin (model GTN 635) Global Positioning System (GPS) receiver. Thereafter ArcGIS 10.1 GIS software packages and ArcGIS Geostatistical Analyst extension were adopted to derive the ordinary Kriging projections. Kriging is a geostatistical term depicting optimal linear prediction of spatial processes. Kriging is used to interpolate spatial data in the fields of geology, hydrology and environmental monitoring. Interpolation procedures simplify mathematical models by taking the form of inverse distance weighting, trend surface analysis and Thiessen polygon (Ninyerola *et al.* 2000). In this study Kriging Geostatistical interpolation technique utilized both the mathematical and the statistical properties of the fluoride levels in the sampled boreholes to project fluoride distribution in the boreholes in River Njoro catchment.

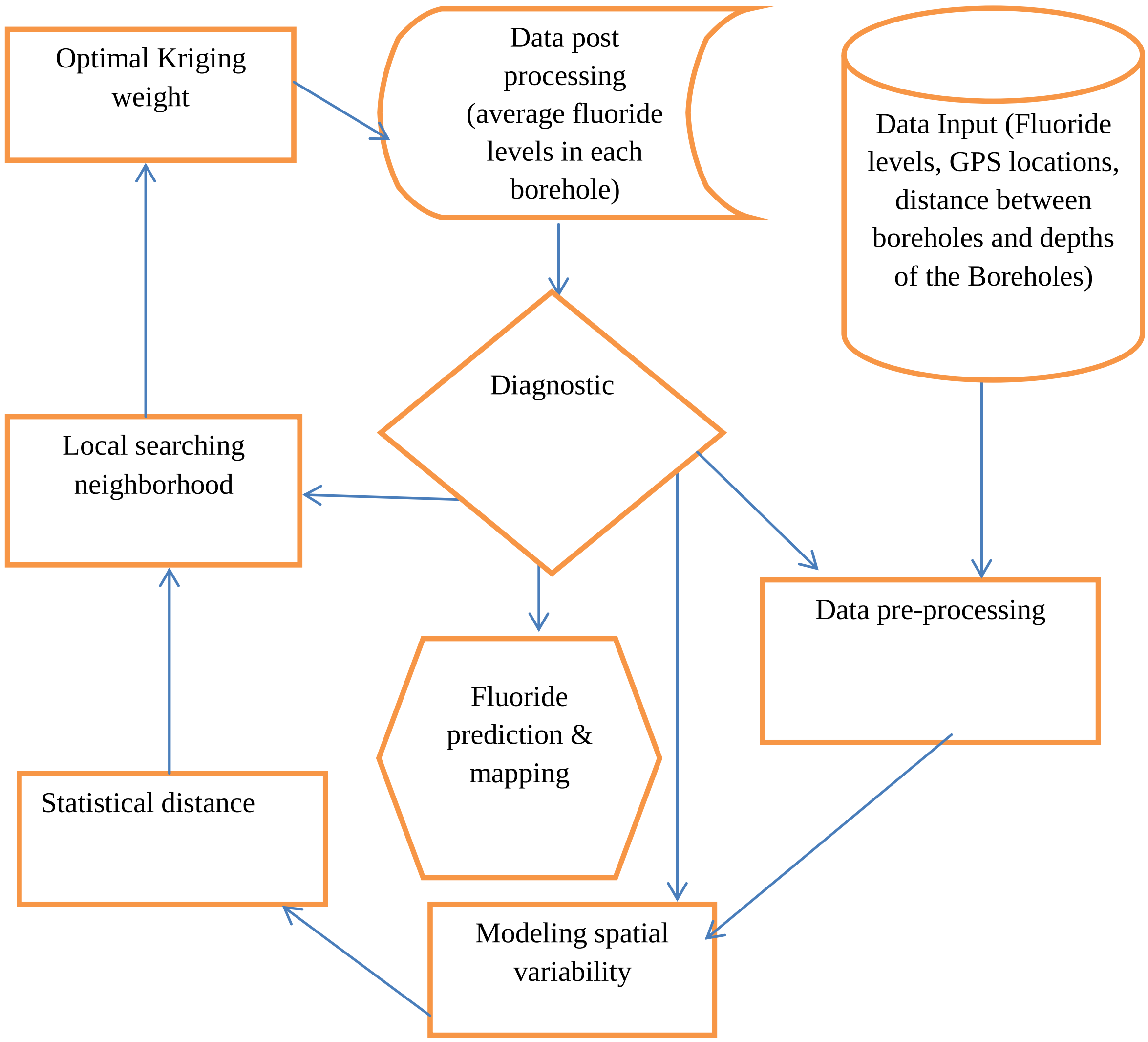

Figure 3.3: The Geostatistical process

The Geostatistical technique quantified the spatial autocorrelation of fluoride levels in the borehole sampling points and accounted for the spatial alignment of the sample points around the prediction areas. Kriging is a stochastic interpolation method useful in the prediction of phenomena in the spatial surface. Kriging is flexible and allows the investigation of spatial autocorrelation of the data by using statistical models. In

Kirging the basic assumption is that the data for modelling comes from a static stochastic process and the data should be normally distributed as observed by Arangi *et al*. (2005).

In using Kriging Interpolation in this study, the fluoride levels in the borehole data were quantified and later used to produce a predicted fluoride distribution surface in River Njoro catchment. In order to predict the unknown fluoride values neighbouring the sampled boreholes, Kriging was used to fit the model from the values of fluoride from the measured sample points around the prediction areas. Kriging uses statistical models and therefore in this study it allowed the production of borehole fluoride distribution prediction map in the River Njoro catchment. GIS provided a platform for multiple layers of topographical, geological and hydrological maps of the River Njoro catchment where analyses were done to locate the spatial locations of the boreholes. The topographical map of Njoro (Topographical Sheet Number 118 1:50,000) was used to digitalize the River Njoro catchment using ArcGIS. Selection of training samples was based on information from available past maps of the River Njoro catchment, Google Earth images and field surveys were carried out between January 2017 and April 2017.

The Hydrology Tools of ArcGIS software was used to delineate the Njoro watershed and to indicate the borehole sampling sites. Groundtruthing survey was undertaken in the area of study so as to confirm the location of the sampling boreholes. Finally to validate the fluoride distribution as projected by Kirging modelling, six neighbouring boreholes in the study area were identified for statistical interpolation purposes. The six neighbouring boreholes were selected purposely with two boreholes in each case representing upstream (Ogiek Primary and Bontana flowers boreholes), midstream

Tumaini Schools and Egerton University boreholes) and downstream (Mustard seed and Rift Valley Institute of Science and Technology-RVIST boreholes) of the River Njoro catchment. The secondary data on the predictor boreholes was collected from WRA offices in Nakuru.

3.3 Secondary data

The secondary data that was used in this research comprised of Meteorological, Geology and Borehole stratigraphy formations.

3.3.1 Meteorological data

Meteorological data for this study was provided by the Egerton University and Nakuru County meteorological stations. The Egerton University meteorological station is located at 35°94'E and 0°36'S upstream of the River Njoro catchment while Nakuru County meteorological station is located at 36°06 and 0°16'S downstream of the Njoro catchment. The Njoro University meteorological station is located upstream while the Nakuru County Meteorological station is located downstream of the study area at altitude 1901 metres above sea level. The data collected from the two meteorological stations as presented in figures 3.5 and 3.6 included: Total annual and average rainfalls, maximum and minimum temperatures.

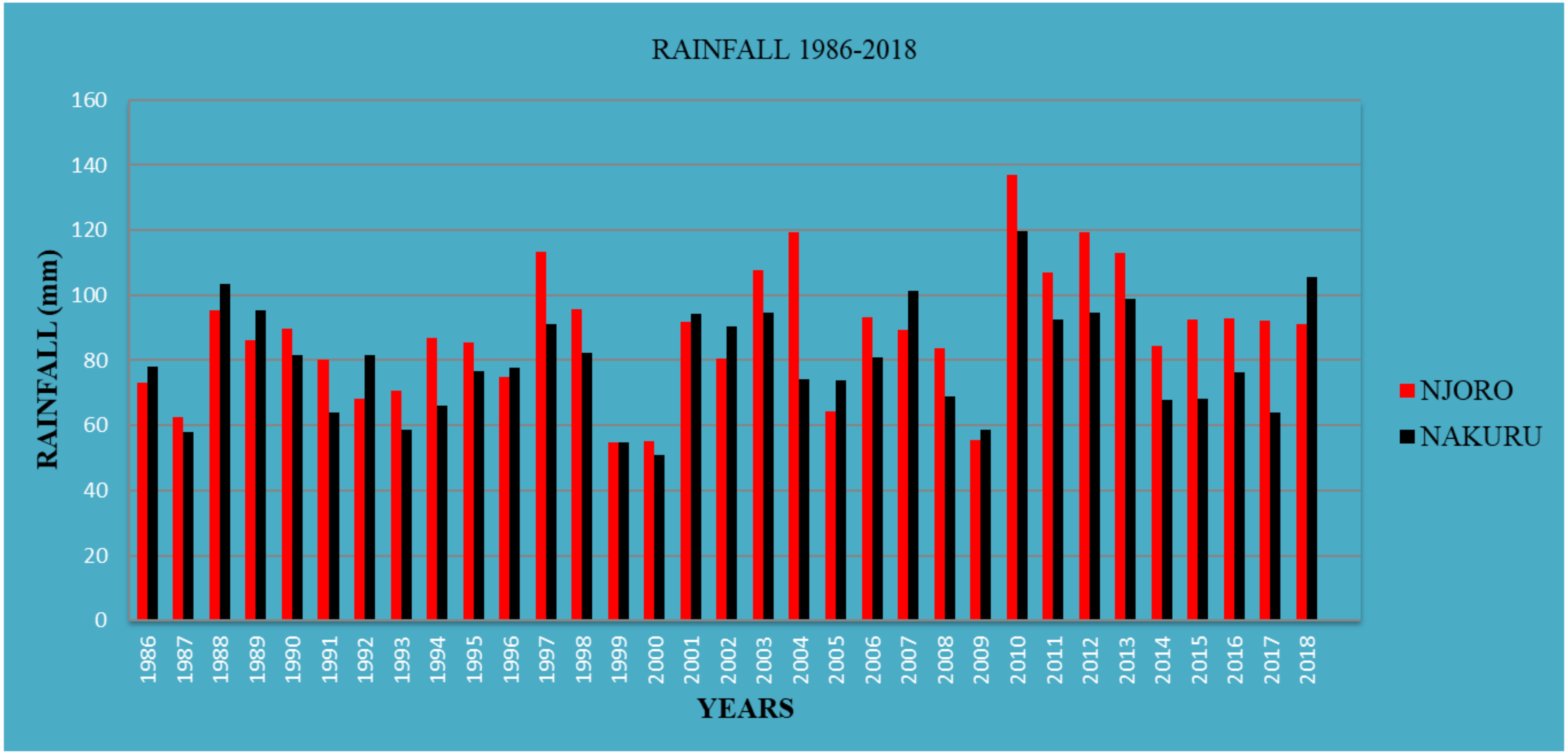

Figure 3.4: Total Annual Rainfall data for Egerton & Nakuru weather stations

Source: Egerton University and Nakuru County Meteorological Stations (2019)

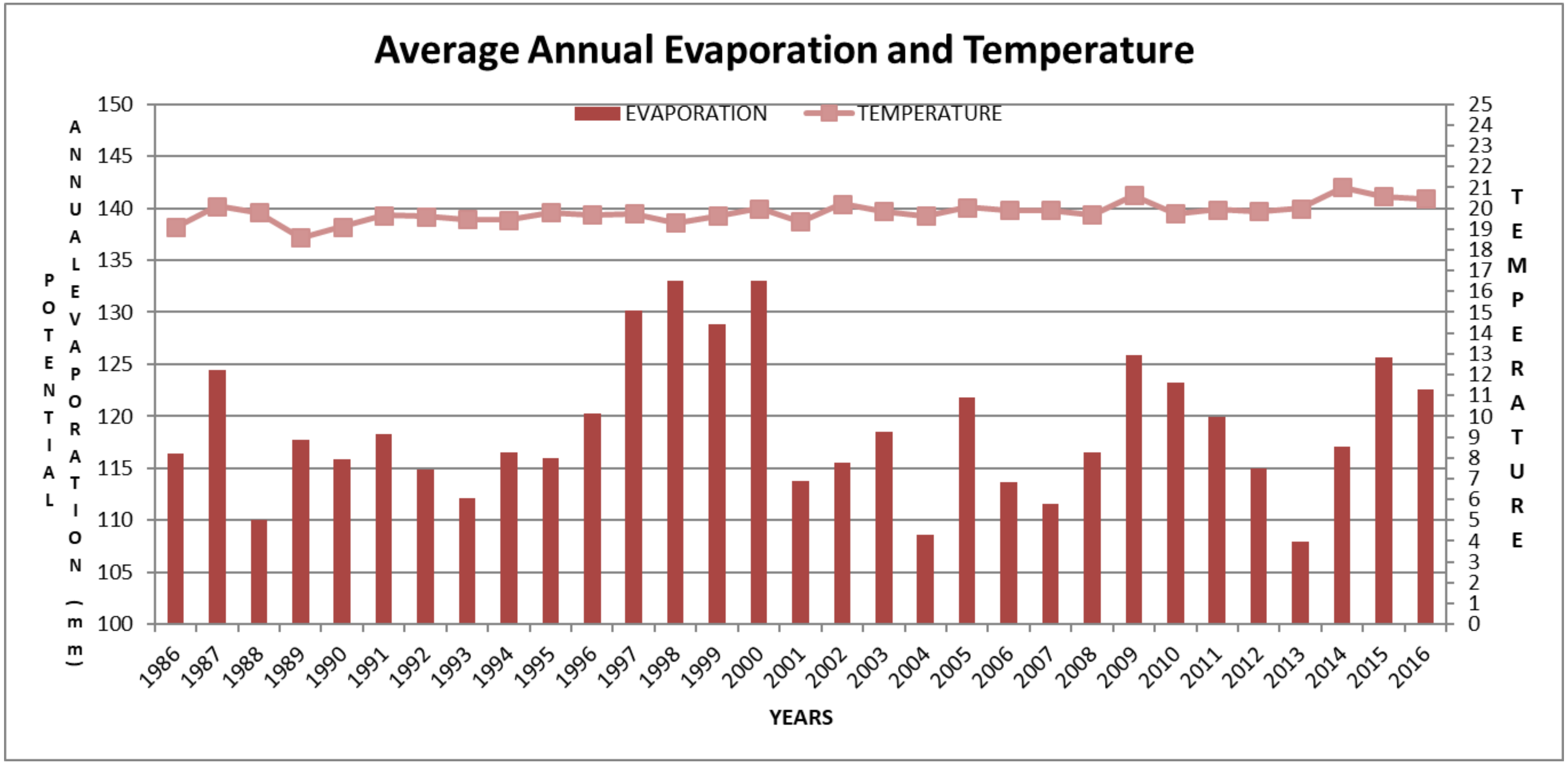

Figure 3.5: Average annual evaporation and temperature at Njoro University meteorological station

Source: Egerton University

3.3.2 Geological data

The geological information was extracted from the studies of past researchers who have mapped the Njoro area with a view to providing a more detailed local study. The geological map of Njoro catchment was generated by digitizing the geological maps of Nakuru (Sheet 119), Molo (Sheet 118) and Mau (Sheet 132) that were provided by the Department of Mines and Geology using ArcGIS. The data on the geological structure of the study area was gathered from content analysis of the geological map of the Njoro catchment and the literature on the geology of Rift Valley available from the Department of Mines and Geology in the Nakuru County Office.

Further information on geology was also gathered through observations made at some areas during groundtruthing survey. The geological data comprising the rock/geological formations of River Njoro catchment was analysed from the geological reports of Nakuru by McCall, (2007) area and other geological reports provided by the Department of Mines and Geology, Nakuru County.

3.3.3 Borehole Stratigraphy

Drillers' logs records were used to assess borehole lithologies in sampled boreholes. The borehole lithologies from the sampled 12 boreholes were obtained from the drilling company's borehole logs which were in possession of the owners or management committee officials for both private and community boreholes respectively. The information provided included: owner, date drilled, and location, total drilled depth, type of aquifer encountered, yield, and water quality remarks at the time of drilling.

In some boreholes their lithologies were supported by the geological surveys and the vertical electrical sounding (VES) tests that had been done prior to the drilling. The past fluoride levels were provided by owners of the boreholes from the earlier water quality analysis tests with the researcher giving emphasis to tests carried in out 2010. The Water Resource Authority (WRA) Nakuru office also provided data on the fluoride levels for the quality monitoring points along the River Njoro.

3.4 Sample and statistical data analysis

Sample analysis outlines the protocol that was adopted in the laboratory sample preparation and analysis. On the other hand, data analysis was the procedure of evaluating data either by use of analytical or statistical tools to discover useful information about research that was undertaken. Data from various sources was gathered, reviewed, and then analysed to form a basis to support conclusion. Data analysis for this study involved quantitative and qualitative analysis.

3.4.1 Sample analysis

Sample analysis in this study involved analysis of rock, soil and water samples.

a) Rock and Soil Samples

The rock samples were preserved in laboratory and the researcher used analytical techniques that are compliant to the standard methods from American Public Health Association (Neidell *et al.,* 2010) using a fluoride ion-selective electrode (ISE) method. American Public Health Association method is used to measure total fluoride solubilized in water meant for drinking, natural surface waters, and in soil and rock extracts. The rock sampled rocks were collected from specific sampling sites in the study area and crushed into powder using the geological hammer as shown in plate

3.5. Thereafter the air dried rock powder crushed from the sampled rock samples were sieved to<2mm and shaken in deionized water (20 ml) in a 50mL conical centrifuge tube for 16-18 hours. After the agitation period of 48 hours the extraction fluid/sample mixture was centrifuged and filtered. The rock filtrate was collected, preserved and analysed for fluoride levels.

Total fluoride soluble was then determined potentiometrically by use of a fluoride ion-selective electrode (ISE) together with a standard single-junction reference electrode, or a fluoride combination ISE, and a pH meter with an expanded millivolt scale or an ISE meter capable of being calibrated directly in terms of fluoride concentration. Standards and samples were mixed in the ratio of 1:1 with a total ionic strength adjustment buffer (TISAB). TISAB helped in adjusting ionic strength, buffers pH to 5-5.5, and contained a chelating agent to break up metal-fluoride complexes. Calibration was performed by analysing a series of standards and plotting mV vs. fluoride concentration on semi log paper or by calibrating the ion meter directly in terms of fluoride concentration. Descriptive statistics was used in data analysis where data were tabulated indicating the sampling sites, identified rock type, and fluoride level in the sampled rocks. The tabular presentation gave the types of rocks as identified on the geological map and the quantities of fluoride in the rocks as determined in the laboratory analysis.

b) Water and Rock Samples Quality Assurance and Control

This is the water and rock sampling protocol where double-distilled water was used to rinse the instruments and apparatus so that they were fluoride free before use. Laboratory instruments were rinsed thrice with double-distilled water to ensure no traces of fluoride outside the rocks and water samples before another consecutive measurement was done. The glass electrode was also cleaned by immersing it in a beaker containing distilled water, and its cleaners measured for fluoride-free ions. Finally TISAB solution was measured for any traces of fluoride to assess its purity before measurement of the solute of the sample.

To assess the precision and accuracy of water and rock sample results, replicate analysis of blank, standard, and samples was carried out. The relative standard deviations were determined to find the precision of the analysis. Recovery results were calculated for the determination of their accuracy. Experiments were repeated till an accuracy of 95–105 % and precision of ±5 % were obtained. Certified standards were used for the calibration of the instrument.

c) Water samples

The water samples were collected in clean 50 ml plastic bottles, transported in a cooling box to the University of Eldoret Chemistry Laboratory, and then stored at negative $20^{o}C$ before analysis. Fluoride was determined using an Orion® model 94-09 and model 96-09 combination fluoride electrodes. An amount of 10.0 ml of each water sample was measured and then mixed with an equal volume of TiSAB solution in a 100 ml beaker. Thereafter the fluoride activity of the solution was measured using a Jenway® fluoride ion specific electrode (ISE). During the measurements, magnetic stirrer was used to homogenize the solutions by steady continuous agitation during the fluoride measurements.

The values of fluoride quantities were recorded in millivolts (mV). Fluoride concentration in the solution was then determined based on a calibration curve constructed using five fluoride standards in the range 0.1-10 mg/l. To determine the variation in fluoride levels, means of all measured quantities were calculated for all the sampled points along River Njoro.

3.4.2 Statistical data Analysis

Statistical analyses were done using correlation coefficient to comprehend the fluoride levels and physical water quality parameters dataset obtained from the study area using IBM Statistical Package of Social Sciences (SPSS) version 21. The Pearson correlation coefficient method was used to generate the bivariate correlation coefficient matrix with a two-tailed test of significance, and significant correlations between the physical parameters and fluoride levels in the sampled boreholes were flagged based on 99% ($p<0.01$) and 95% ($p<0.05$:) confidence level. This statistical technique assisted in ascertaining the association of analysed physical parameters of water quality and fluoride levels for better data interpretation. Some other general statistical data analysis was performed using Microsoft Excel 2007 to determine the mean and standard deviation of the physical parameters.

a) Meteorological data

The interpretation of meteorological data involved spatial and temporal comparisons of total rainfall, temperature and evaporation of the Egerton University and the Nakuru County meteorological stations. The Meteorological data from Nakuru County and Egerton University Meteorological Stations were analysed by descriptive statistics. Bar graphs were drawn to represent the evaporation and rainfall. The data was plotted on graphs as presented in figures 3.5 and 3.6 and entered in tables and thereafter inferences of mean and annual values on the various weather elements made from the data.

b) Geological Data

The geological data in this study included data on rock and soil samples and data on borehole stratigraphy. The secondary data on the rock/geological structure was descriptively analysed in tables showing the water sampling points within the catchment and their corresponding rock types. The area under different geological formations and respective fluoride levels in the sampled rocks at water sampling points were tabulated. A cross section from upstream to downstream of the sampling points was drawn and helped in identifying the different rock types along River Njoro. Finally the area under different rocks and corresponding fluoride quantities was mapped in a geological map.

c) Rock and Soil Samples

Descriptive statistics was used in data analysis where data were tabulated indicating the sampling sites, identified rock type, and fluoride level in the sampled rocks. The tabular presentation gave the types of rocks as identified on the geological map and the quantities of fluoride in the corresponding rocks as determined in the laboratory analysis.

d) Water samples

Descriptive statistics in form of tables and figures were also used to explain the variation of the fluoride levels in the sampled boreholes and along the different river sampling points and the fluoride levels in the rocks from the sampled points. Tables were also drawn to present the maximum and minimum values of the measured water quality parameters the upstream, midstream and downstream boreholes.

e) Borehole Stratigraphy

Borehole stratigraphy for the sampled 12 boreholes was analysed to determine lithology and geological characteristics of the aquifers. Aquifer material was determined by examining entire borehole matrices and strata of the borehole as shown in the driller's logs. Stratigraphy of the boreholes was analysed descriptively by schematic diagrams of the borehole's strata. Stratigraphy analysis helped in deducing the types of rock that were in contact with groundwater and hence relate to levels of fluoride. Schematic formations for the individual sampled boreholes at upstream, midstream and downstream were representative of various locations in the longitudinal profile of the River Njoro catchment. The fluoride levels in the sampled boreholes were also qualitatively correlated to the nature of the stratigraphy matrices and formations. Finally schematic diagrams were drawn to describe the lithological variations of the boreholes where the water samples were collected while projected fluoride levels in the study area was presented in a fluoride distribution map.

3.4.3 Geostatistical modeling and mapping

Interpolation technique by Kriging, provide the ''best'' impartial, linear estimate of a regionalized variable in a location that was not sampled. In this scenario ''best'' is used to refer to a least-squares sense. The emphasis in Kriging interpolation is set on local accuracy, with the actual being close to the estimate value without any regard to the global statistical characteristics of the estimates. Geostatistics in this research provided a set of statistical tools that analyzed the spatial variability and spatial interpolation of fluoride in ground water in the River Njoro catchment. Geostatistical analysis tool was employed in establishing groundwater and surface fluoride spatial variation.

The average fluoride levels for the sampled and predictor boreholes were presented in a table. The average mean variation between the fluoride levels of the sampled and predictor boreholes was calculated to assist in geostatistical modeling and mapping. Geostatistical estimation consisted of two stages. The first stage consisted of identifying and modeling spatial structure of fluoride that was being investigated by semi variogram analysis, while the second phase was the estimation and interpolation of data using the Kriging method. The reason behind using Geostatistical methods was stationarity that was tested using semi variogram and independence and stationarity tests. Secondly the distribution of the fluoride data from the boreholes was close to a normal distribution. The Kriging model was used to interpolate the fluoride concentration of the sampled wells in the study area. The fluoride data from the boreholes helped in building a valid Kriging model by sub-setting and simulating the observed data. The predictions and their respective standard errors were generated during this process at un sampled neighbouring boreholes, and finally these repeated processes from each sampling stations created a spectrum of semi variogram to generate the model on the prediction of fluoride distribution. The procedure on the fluoride prediction map preparation is presented in Figure 3.7.

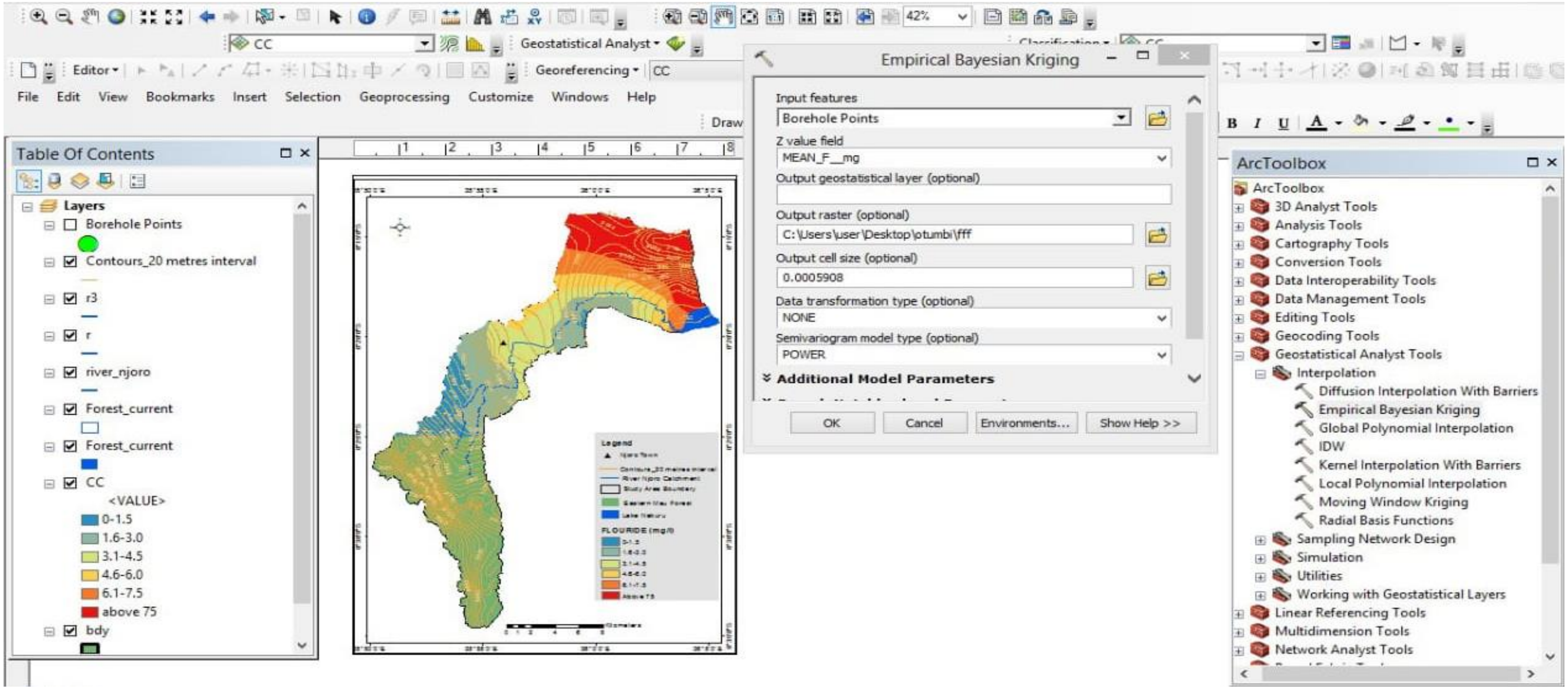

Figure 3.6: The data view of the River Njoro catchment Kirging model

3.4.5 GIS and Interpolation

Arangi (2005) observes that in Geostatistical analysis the first step is exploratory data analysis by using histogram, normality, trend of data, semi variogram cloud and cross covariance cloud of the observed raw data. The data on the water samples in this study had normal distribution in the upper, middle and downstream of the Njoro catchment which was sampled covering the wet and dry seasons and resulting in the adoption of Kriging technique (Johnston *et al*, 2001). Transformation was used to make the data normally distributed so as to confirm similarity for the borehole fluoride data. The histogram was used in ArcGIS Geostatistical Analyst, to see the need for transformations subsequently making the data more normally distributed. Prediction performances were assessed by cross validation of the secondary borehole data from the neighbouring boreholes.

3.4.6 Assumptions Underlying the Application of Interpolation by Kirging

Assumptions were user defined parameters that were used in the development of the Kirging model in the production of the fluoride distribution map. The use of assumptions was important because the model was adopted to be used in a catchment that had near similar characteristics in geology coverage and the depths of the sampled and neighboring boreholes ranged between 130M and 200M. The interpolation and mapping of the final prediction fluoride spatial distribution map was based on the following assumptions:

i) The stratigraphy in majority of the boreholes in the Njoro catchment displays almost a similar matrix.

ii) The rock types in River Njoro catchment area are of the same nature and type.

iii) There was equal variability for the borehole fluoride data.

iv) The distribution of fluoride levels Upstream, Downstream and Midstream boreholes did not show great variation in each of the segments.

3.4.7 Geostatistical Model Calibration and Validation

Calibration of the geostatistically interpolated results of the Kirging model was done by using the data for the current scenario and comparing the Kirging output to the recorded fluoride levels in the boreholes. Moriasi *et al*. (2007) observes that Proper model calibration is in modeling because it helps in minimizing model simulation uncertainty. Calibration of model gives the model parameter estimation by giving the appraisal of output of model within a given set with observed data having conditions that are similar. In this research, fluoride levels that were measured in sampled boreholes in River Njoro catchment were compared with the fluoride levels in the neighboring boreholes with equal depths to generate the fluoride prediction of the catchment.

Therefore the calibration process helped in minimizing the difference between predicted and measured fluoride levels. However, in all the model projections variations between the model and observed data are always anticipated. Model validation is the process of demonstrating that a given specific situation model is capable of making enough accurate projections (Refsgaard and Knudsen 1996). Model validation involves running a model using input parameters measured or determined during the calibration process.

The greatest limitation of this study was the availability of continuous fluoride data of the boreholes. Much of the data on fluoride levels were measured after drilling and therefore fluoride levels after operation of the boreholes were not available. The issues of unavailability and incompleteness of fluoride levels were addressed by spatial interpolation and extrapolation. In this study Cross validation was used for testing “moving neighborhood”. In this study validation of the predicted fluoride distribution in groundwater map of River Njoro catchment was done by comparing fluoride levels of sampled boreholes with the neighboring boreholes. After the prediction by Kriging, the researcher compared fluoride data available at WRA Nakuru office of the neighboring boreholes with almost similar characteristics of borehole depths and elevations. The boreholes that were used to validate the Kirging model included: Rift Valley Institute of Science and Technology (downstream), Ogiek Primary School and Bontana Flowers and finally Tumaini School and Egerton University boreholes to represent downstream boreholes as represented in Figure 3.3. The data of these boreholes were used as predictor boreholes to assist in the validation of the predicted fluoride distribution in the Njoro catchment. Therefore, each unknown value on fluoride levels was validated from fluoride levels data of the surrounding boreholes.

Cross validation allowed the acceptance of the Kirging model because it provided the best predictions. ARCGIS was used to draw and overlay the predicted fluoride distribution map on the digitized map of River Njoro catchment. Fluoride concentration and distribution mapping was done by graduated symbols proportional to values using ArcMap version 10.1. The fluoride concentration ranges in borehole water were grouped based on WHO (0.0–1.5 mg/l) standards simply for the purpose of assessing the status of the borehole water according to WHO requirements.

CHAPTER FOUR

RESULTS

Introduction

This chapter presents results that were guided by the objectives of the study. The study sought to: determine the relationship between fluoride levels and surface geology in River Njoro catchment, establish the variation of fluoride levels in surface geology, soils, surface water and ground water in River Njoro catchment, determine the relationship between stratigraphy and fluoride levels in ground water in River Njoro catchment, determine the relationship between selected physical parameters of water and fluoride levels in River Njoro catchment, and finally model spatial variation and distribution of fluoride levels in ground water in the River Njoro catchment.

4.1 Relationship between Fluoride Levels and Surface Geology in River Njoro

The results of fluoride analysis in the rocks sampled at the designated water sampling points along River Njoro are presented in table 4.1, while figure 4.1 presents the fluoride levels at the corresponding water sampling points. The designated water and rock outcrop sampling points along River Njoro were: Kwa Rhoda Bridge, Tumaini Bridge, KERMA Bridge, KARLO Bridge, Kwa Maisori Spring, Nesuit Centre Bridge, Ndarogo Bridge, Sigaon River, Sugutek River, Confluence of Sigaon and Sugutek Rivers and at the Kipkogo Spring. Finally, the geological map of the River Njoro catchment is presented in figure 4.2.

The rocks at the designated water sampling points were identified from the geological map of the River Njoro catchment that was a representative of the catchment. The sampled rocks identified from rocks of their sampling areas in the Njoro catchment included: Superficial deposits of volcanic soils at Kwa Rhoda Bridge and Tumaini Bridge, black ashes of Rongai at Njoro KERMA and KARLO Bridge and while Pyroclasic and sediments of Rongai were sampled at Kwa Maisori spring. Similarly black ashes of Rongai were sampled Nesuit Bridge, Ndarogo Bridge and Sugutek and finally Eutracite welded tuff were sampled at Sugutek/Sigaoni and Kipkogo spring sampling points. The analysis of fluoride levels in the rocks realised that the Black ashes of Rongai and Menengai Pumice recorded the highest fluoride levels of 1.70 mg/l while generally superficial deposits of volcanic soils recorded highest average fluoride levels at various sampling points and conversely Eutracite welded tuffs contained the lowest average levels of fluoride (0.79 mg/l).

The geological map of River Njoro catchment indicating the various types of rocks was used to project a schematic geomorphological cross section of the study area from upstream point at elevation 2532 metres above sea level to downstream point at Kwa Rhoda at the elevation of 1775 metres above sea level. The main rocks identified along the geomorphological profile section of River Njoro were: Eutracite welded tuffs, black ashes of Elburgon, Menegai pumice, Black ashes of Rongai and

Njoro, Pyroclastic and sediments of Rongi plain and Mau slope, volcanic soil and finally Superficial deposits.

Table 4.1: Rock Types at Sampling Points and levels of Fluorides in the Rocks

S/N	ROCK SAMPLING POINT	GPS LOCATION	ROCK TYPE	F mg/l
1	KWA RHODA BRIDGE	-0.367,35.992	Superficial Deposits of Volcanic Soils	1.575
2	TUMAINI BRIDGE	-0.297,36.009	Superficial Deposits of Volcanic Soils	1.563
3	NJORO BRIDGE KERMA	-0.333,35.943	Black Ashes of Rongai and Menengai Pumice	1.70
4	NJORO BRIDGE KARLO	-0.338,35.944	Black Ashes of Rongai	0.870
5	KWA MAISORI SPRING	-0.378,35.879	Pyroclasic and Sediments of Rongai	0.935
6	NESUIT CENTRE BRIDGE	-0.396,35.898	Black Ashes of Rongai	1.436
7	NDAROGO BRIDGE	-0.379,35.899	Black Ashes of Elburgon	0.905
8	SIGAON RIVER	-0.417,38.881	Lurmudiak Tuff	0.999
9	SUGUTEK RIVER	-0.416,35.881	Black Ashes of Elburgon	1.094
10	CONFLUENCE (SUGUTEK/ SIGAON	-0.417,35.880	Eutracite Welded Tuffs	0.678
11	SPRING KIPKOGO	-0.418,35.883	Eutracite Weded Tuffs	0.892

Source: Author (2019)

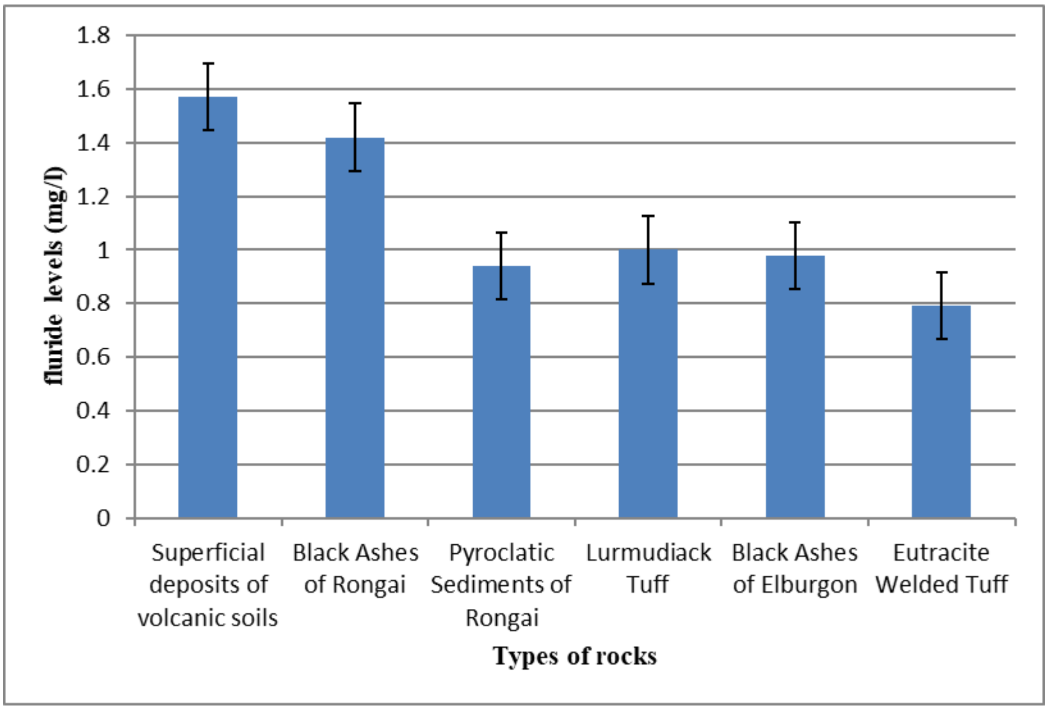

Table 4.1: Fluoride levels in different sampled rocks

4.2 Average fluoride levels in soil samples

Fluoride levels were analysed in both the top and sub soils which were sampled in the depths of 15 to 20 cm and of 30 to 40 cm respectively. Different soil samples were sampled from: forests, shrub land, agriculture and commercial settlement during the period of research. The average fluoride represents the average of fluoride levels of top and sub soils analysed from sampling areas during the dry and wet seasons. However, the soils samples were not taken from the residential settlement areas because the soils in these areas had been interfered with by the introduction of foreign soil types from different areas and in some cases the earth surface was paved. The average levels of fluoride from the sampling points in different land uses are presented in Table 4.2

The fluoride levels in soils under commercial settlement recorded highest levels of fluoride in both the top soils and sub soils sampled measuring 0.976 mg/l and 1.391 mg/l respectively. Conversely the top soils and sub soils sampled under the forest and shrub land uses recorded the lowest fluoride levels measuring 0.216 mg/l (top soils) and 0.188 mg/l (sub soils) and 0.207 mg/l (top soil) and 0.326 mg/l (sub soil) respectively.

Table 4.2: Fluoride levels in Soil under different Land Use/Cover

S/N	Land use/cover type	Average Fluoride (mg/l) sub soils	Average Fluoride (mg/l) top soils
1	Forests	0.216	0.188
2	Shrubs	0.207	0.302
3	Agriculture	0.262	0.342
4	Commercial settlement	0.976	1.391

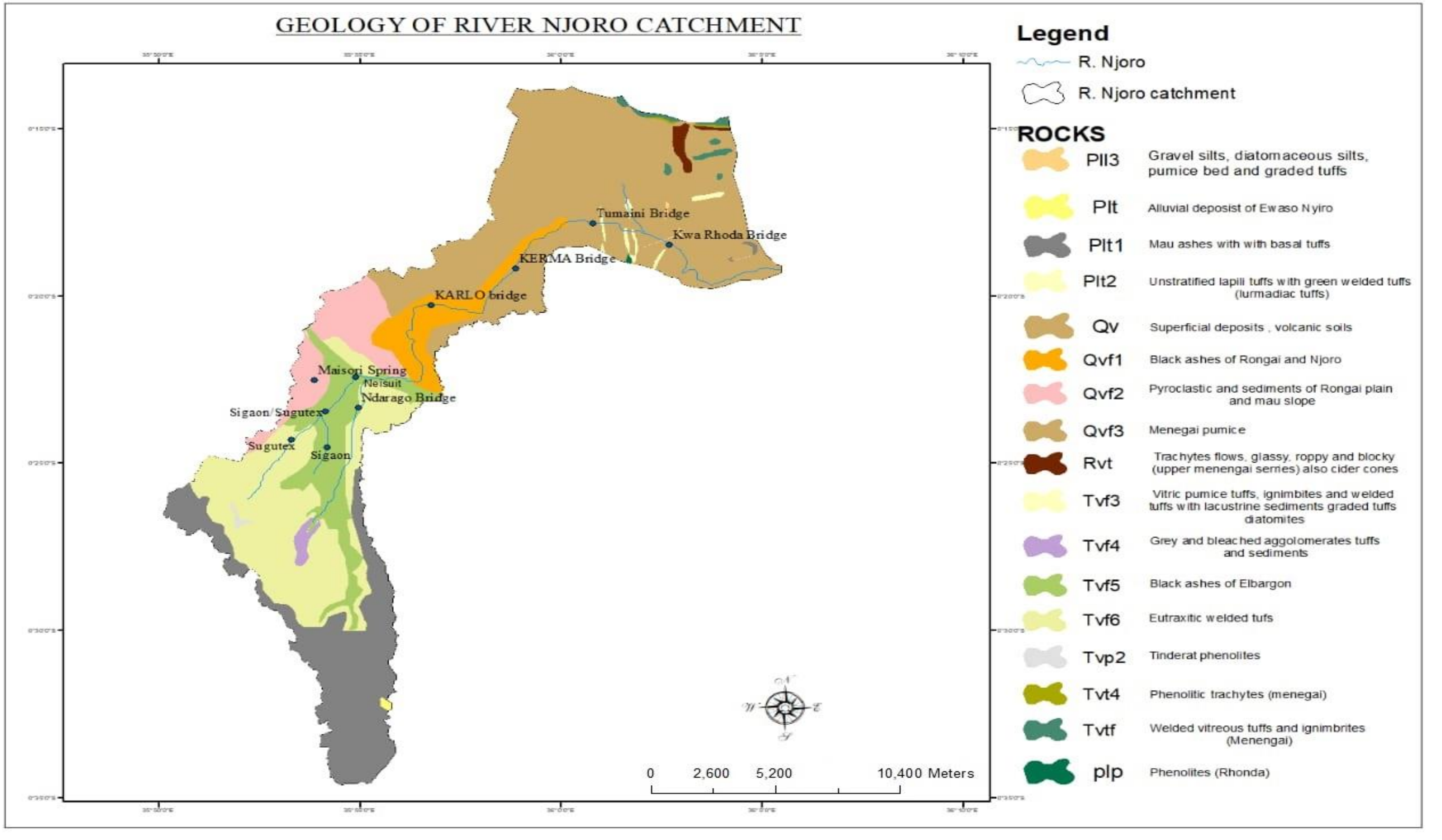

Figure 4.1: Geological map of River Njoro catchment

4.3 Relationship between Stratigraphy and Fluoride levels in borehole water in River Njoro catchment

This objective was achieved by analysing fluoride at different soils depths to justify infiltration of fluoride ions in soils at different soil depths at identified points and also analyse the relationship between the borehole stratigraphy and recorded average fluoride levels of the boreholes in River Njoro catchment. The wells' strata as provided by the drillers' logs assisted in the description of the stratigraphy formations. The sampled boreholes were located upstream, downstream and midstream in the River Njoro catchment.

4.3.1 Schematic Presentation of Borehole Stratigraphy

Geological formations of the boreholes in River Njoro catchment were obtained from the driller's logs and in some cases compared with available geological surveys that were done before the boreholes were drilled. Schematic stratification representations of individual boreholes sampled downstream in River Njoro and their corresponding depths are presented in Figure 4.3. The schematic stratigraphy shows the sequence of the possible aquifers of the boreholes. The lithological analyses identified four types of aquifer matrices: sediments (including volcanic ashes), trachyte, phonolites and tuffs.

The four downstream boreholes: Pistis, Mother Kelvin, Ainabtich and Mogon varied in depth and stratification. The stratigraphy analysis indicated that the aquifer distributions varied from sixteen to eighteen aquifer systems with eight major aquifer strata. The major lithologies included: Phonolites, Tuffs, Trachytes, Pumice, Volcanic Ash and Volcanic rock. Lithological logs analyses showed aquifer thickness variation that ranged from 2 to 46 meters. The aquifer matrix of Mogon and Pistis boreholes were made up of Tuff, Lava, Phonolites and Pumice rocks matrix. On the contrary the Mother Kelvin and Ainabtich boreholes had the Clay, Tuff and Phonolite rock matrix. Moreover, Mogon and Pistis boreholes recorded higher levels of fluoride of 8.798 mg/l and 19.369 mg/l respectively as compared to the Mother Kelvin and Ainabtich which recorded low levels of fluoride of 3.72 mg/l and 5.53 mg/l respectively.

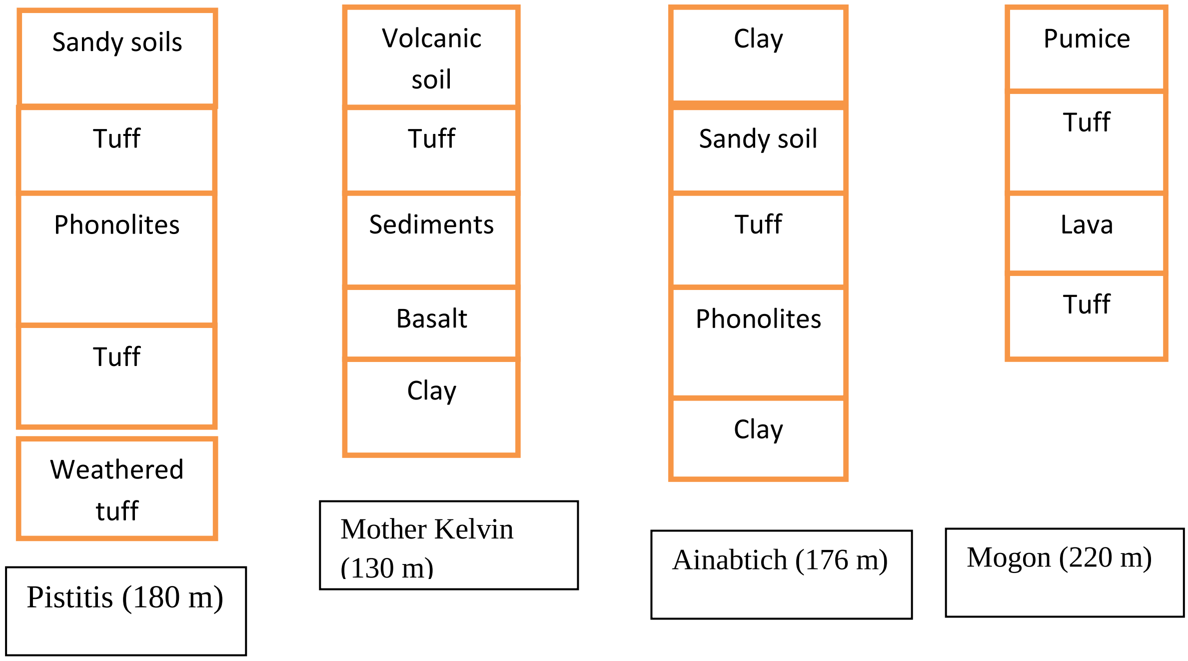

Figure 4.1: Stratigraphic Formations for Downstream Boreholes

Source: Author (Note: The Figure is not drawn to Scale)

The four midstream boreholes: Kwa Annah, Umoja Kikapu, Ngata Mbaruk and Kiamunyi had different depths. The borehole stratigraphy and corresponding depths of the midstream boreholes are presented in figure 4.4. The stratigraphy analysis of the midstream boreholes indicated that aquifer distribution varied from four to nine aquifer strata with nine major aquifer strata. The major lithologies included: Clay, Tuffs, Volcanic Soil, Sandy Soil, Black Top Soil, Pumice, Phonolites and Trachytes occurring at varied intervals and depths. The analyses showed aquifer thickness variation that ranged from 2 to 46 meters. The average levels of fluoride in the borehole water ranged from 18.59 mg/l at the Kiamunyi borehole being the highest to 1.74 mg/l at the Ngata Mbaruk borehole being the lowest. The Umoja Kikapu and Kwa Annah boreholes recorded 2.91 and 3.32 mg/l of fluoride levels respectively. Kiamunyi borehole has many layers composed of Pumice, Tuff and Trachyte.

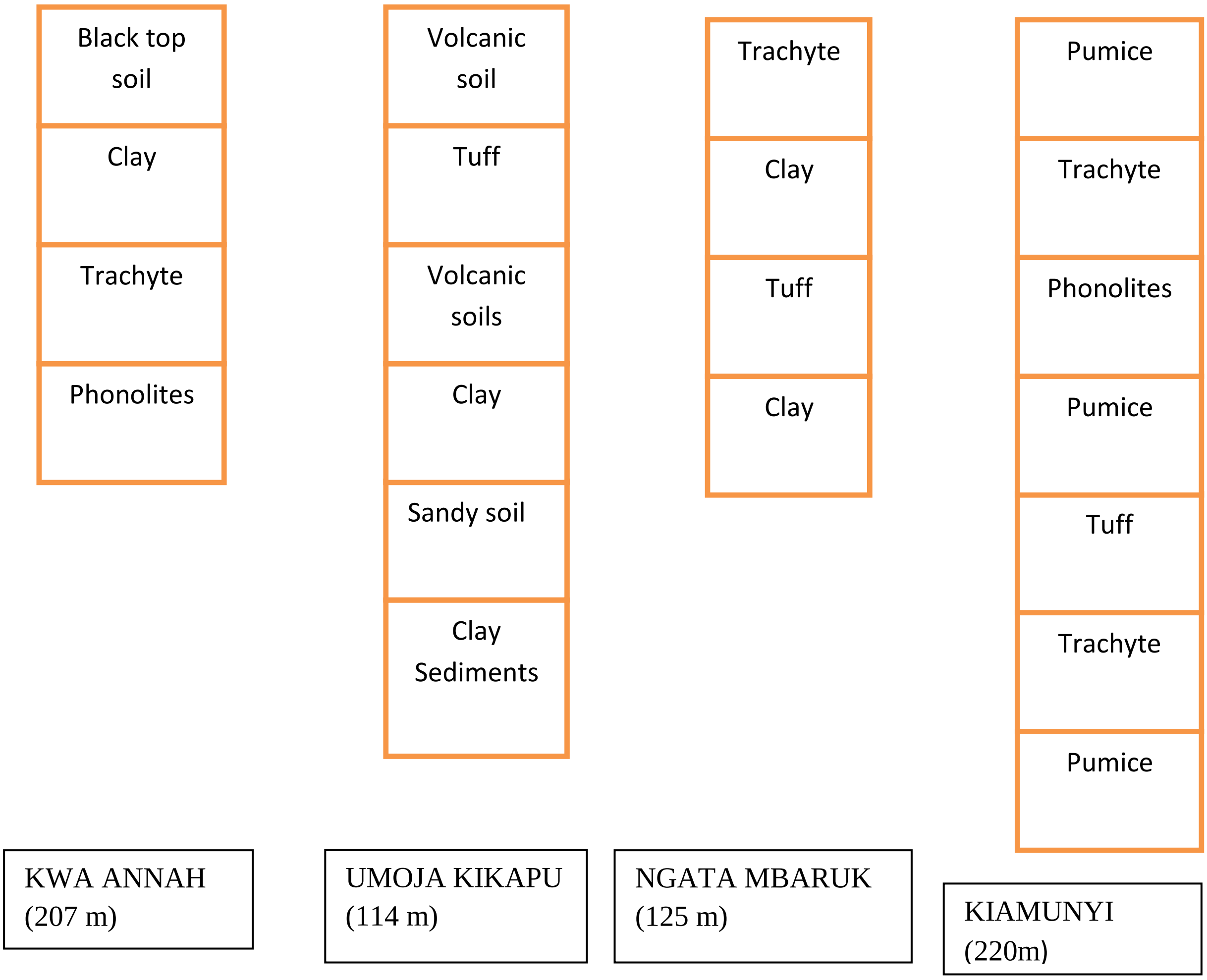

Figure 4.2: Stratigraphic Formations for Midstream Boreholes

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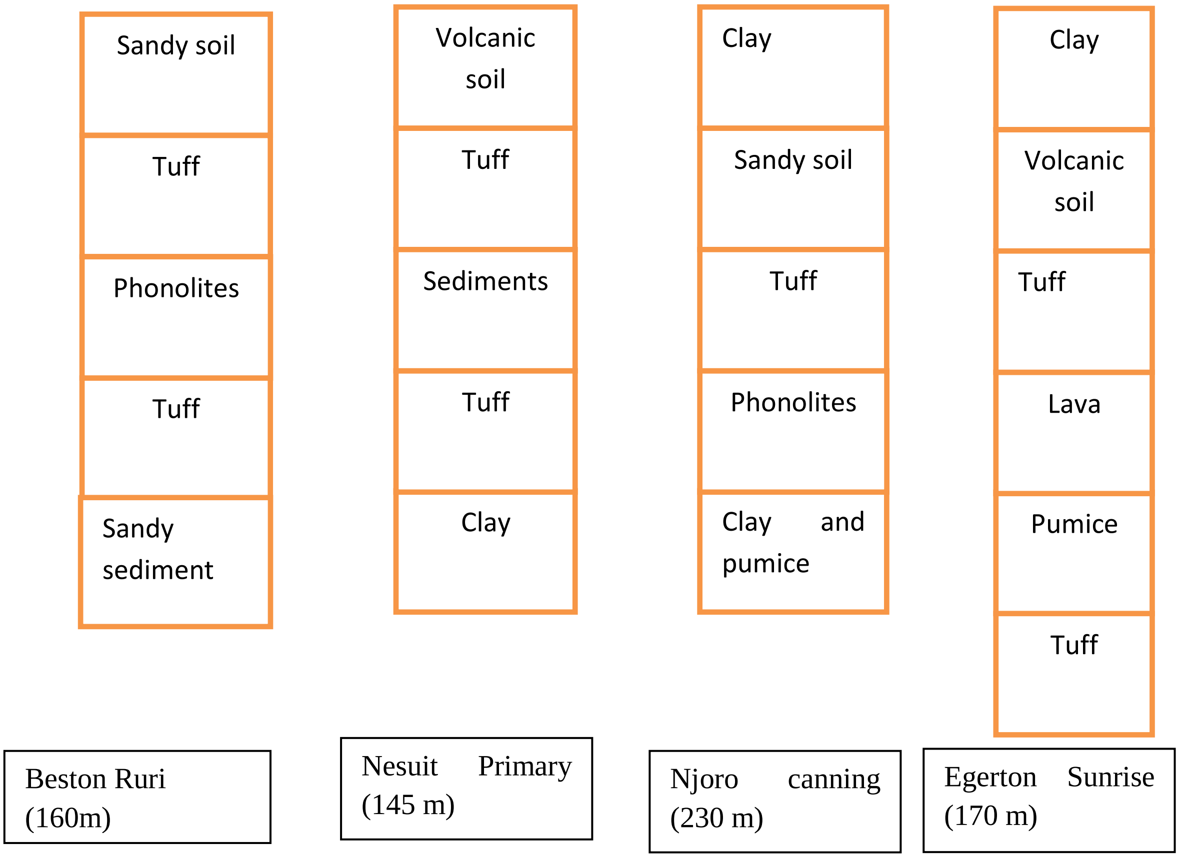

Figure 4.3: Stratigraphic formations for upstream Boreholes

(Note: The figure is not drawn to scale)

The four upstream boreholes: Egerton sunrise, Njoro canning, Biston Ruri community and Nesuit primary school borehole varied in depth. Stratigraphy analysis indicated that aquifer distribution varied from nine to eighteen aquifer systems with seven major aquifer strata as presented in Figure 4.5. The major lithologies included: Clay, Tuffs, Basalts, Volcanic, Pumice, Phonolites and Trachytes occurring at varied intervals and depths. The analyses showed that aquifer had variation in aquifer strata. Pyroclastics formed the top most part of the stratigraphy. The aquifer of Njoro Sunrise and Njoro canning boreholes was made up of Tuff, Lava and Pumice rocks matrix. On the contrary the Beeston Ruri and Nesuit school boreholes had the Clay, Tuff, Sediments and Phonolite rocks matrix. Moreover, Njoro sunrise and Njoro canning boreholes recorded higher levels of fluoride of 4.00 mg/l and 5.89 mg/l respectively as compared to the Beston Ruri and Nesuit School which recorded low levels of fluoride of 3.41mg/l and 3.00 mg/l respectively.

4.3.2 Depths of sampled boreholes and average fluoride levels

The boreholes where water samples were collected from are represented in table 4.3. The boreholes in the downstream of River Njoro catchment included: Pistis School, Mother Kelvin, Mogon community and Ainabtich Community boreholes. The four boreholes varied in depth with Mogon borehole being the deepest at 220 m and Mother Kelvin the shallow most at 130 m. The Ainabtich and Pistis boreholes were 160 m and 180 m respectively. The average levels of fluoride in the borehole water ranged from: Pistis (19.37 mg/l), Mogon community (8.80 mg/l), Mother Kelvin (3.72 mg/l) and finally Ainabtich (5.53 mg/l).

The boreholes in Midstream of the River Njoro catchment included: Ngata Ndaruk, Umoja Kikapu Community, Kwa Annah and Kiamunyi. The four boreholes varied in depth with Kiamunyi borehole being the deepest at 220 m and Umoja Kikapu the shallow most at 114 m. The Ngata Ndaruk and Kwa Annah boreholes were 125 m and 207 m respectively. The average levels of fluoride in the borehole water ranged from: Kiamunyi (18.59 mg/l), Kwa Annah (3.32 mg/l), Umoja Kikapu (2.91 mg/l) and finally Ngata Ndaruk (1.74 mg/l).

The boreholes Upstream of the River Njoro catchment included: Njoro Canning, Egerton Sunrise, Beston and Nesuit Primary boreholes. The upstream catchment boreholes varied in depth with Njoro Canning borehole being the deepest at 230 m and Nesuit Primary the shallow most at 145 m. The Egerton Sunrise and Biston

Community boreholes were 170 m and 160 m respectively. The average levels of fluoride in the borehole water ranged from: Njoro Canning (5.90 mg/l), Egerton Sunrise (4.00 mg/l), Biston Community (3.40 mg/l) and finally Nesuit Primary (3.00 mg/l).

Table 4.3: Average fluoride levels of the sampled boreholes

S/N	BOREHOLE NAME	GPS POINTS	Aver F(mg/l)	Depth (m)
Downstream boreholes				
1	MOGON COMM.	-0.320,36.022	8.798	220
2	PISTIS SCHOOL	-0.302,36.062	19.369	180
3	MOTHER KELVIN	-0.304,36.050	3.72	130
4	AINABTICH	-0.304,36.033	5.533	176
Midstream boreholes				
5	KIAMUNYI ESTATE	-0.270,36.037	18.591	220
6	NGATA MBARUK	-0.305,35.988	1.737	125
7	UMOJA KIKAPU	-0.362,35.987	2.907	114
8	KWA ANNAH	-0.367,35.992	3.315	207
Upstream boreholes				
9	EGERTON SUNRISE	-0.397,35.945	4.000	170
10	NJORO CANNING	-0.367,35.942	5.896	230
11	BESTON	-0.362,35.907	3.414	160
12	NESUIT PRI SCH	-0.3866,35.888	3.000	145

4.4 Relationship between selected Physical Parameters and Fluoride Levels in River Njoro Catchment

The statistical relationships and analysis between selected Physical Parameters and Fluoride Levels along River Njoro Catchment and relationship between selected Physical Parameters and Fluoride Levels in ground water in River Njoro Catchment is discussed in 4.4.2 and 4.4.2

4.4.1 Relationship between selected Physical Parameters and Fluoride Levels along River Njoro Catchment

Table 4.4 presents the description of temperature, pH, and Electrical conductivity and fluoride levels of water samples from River Njoro while Appendix II gives the maximum, minimum and average values of the Insitu parameters in the field during the period of study. The mean of temperature was 18.4 ºc: average pH was 7.3 while the means of Electrical conductivity and fluoride were 255.7µ and fluoride was 1.1 mg/l for each of the 80 samples per parameter sampled during the wet and dry seasons along River Njoro. The mean alkalinity of the water in River Njoro was 7.3 implying that the water was slightly neutral. Generally, in situ parameters showed a minimal spatial variation in all the sampling points. Low quantities and levels of electrical conductivity and temperature were recorded upstream while high quantities and levels of electrical conductivity and temperature were recorded downstream. Electrical conductivity had a large standard deviation of 90.276 while pH has the smallest standard deviation with value of 0.441. Therefore, the values of electrical conductivity in all the sampling sites along River Njoro had a large variation from the mean value of the measured pH values.

Table 4.4: Descriptive Statistics of Temperature, pH and Electrical conductivity and Fluoride levels

Parameter	Mean	Std. Deviation	N
Temperature	18.3636	2.34666	80
Electrical conductivity	255.7299	90.27649	80
pH	7.2897	.44162	80
Fluoride	1.0720	.39752	80

Table 4.5 shows the correlation relationship of Fluoride levels, Temperature, pH, and Electrical Conductivity at the designated river sampling points along River Njoro. The correlations between fluoride levels and temperature and electrical conductivity had a weak positive correlation in River Njoro. Conversely the correlation between fluoride levels and pH had a strong positive correlation with fluoride levels in River Njoro. Amongst the water quality parameters measured insitu, there was a positive correlation relationship between temperature and electrical conductivity and pH and electrical conductivity while on the other hand there was a negative correlation relationship between temperature and pH. Finally, there was a statistically significant association ($P<0.05$) between fluoride levels on one hand and electrical conductivity, temperature and pH on the other hand in the water sampled in River Njoro

Table 4. 5: Correlation of Temperature, pH and Electrical conductivity and Fluoride levels

PARAMETER		TEMP	EC	pH	FLUORIDE
TEMP	Pearson Correlation	1	.336	-.036	.274
	Sig. (2-tailed)		.003	.756	.016
	N	80	80	80	80
EC	Pearson Correlation	.336	1	-.337	.366
	Sig. (2-tailed)	.003		.003	.001
	N	80	80	80	80
pH	Pearson Correlation	-.036	-.337	1	.022
	Sig. (2-tailed)	.756	.003		.851
	N	80	80	80	80
FLUORIDE	Pearson Correlation	.274	.366	.022	1
	Sig. (2-tailed)	.016	.001	.851	
	N	80	80	80	80

4.4.2 Relationship between selected Physical Parameters and Fluoride Levels in Ground water in River Njoro Catchment

The selected physical quality parameters of water in this research were pH, temperature and electrical conductivity. The mean values for temperature, electrical conductivity and pH from 84 samples of water were: 26.2^{0}c, 797µ and 0.63 respectively in the samples as indicated in table 4.6. The mean alkalinity of the water sampled in the boreholes in River Njoro catchment was 7.3 implying that the water was slightly neutral. Generally, Insitu parameters: temperature and pH showed a minimal spatial variation in all the sampled boreholes while electrical conductivity had great variations in the sampled boreholes.

Table 4.6: Insitu Descriptive Statistics of Physical Water Quality Parameters

Parameter	Mean	Std. Deviation	N
Temperature	26.247	4.385	84
Electrical Conductivity	735.042	797.435	84
PH	7.328	.626	84
Fluoride	5.195	5.470	84

Table 4.7 shows the correlation of fluoride levels with respect to temperature, pH, and electrical conductivity. Fluoride levels indicated positive Pearson correlation relationship with pH, electrical conductivity and temperature. However pH singly had a very strong Pearson correlation coefficient of 0.725 with fluoride levels. Temperature had a moderately positive Pearson correlation relationship of 0.585 electrical conductivity was slightly correlated with fluoride levels with value of r being 0.414.

The correlation table 4.7 also shows that there was a statistical significance (p=0.00) at significant level of 0.01 between fluoride levels and the physical parameters in River Njoro. On the other hand, among the physical parameters in River Njoro, there was no statistically significant relationship between fluoride levels and electrical conductivity (p=0.975) in the sampled boreholes in River Njoro. However, there was a significant association (p=0.00) between pH and temperature of the water sampled from the boreholes in river catchment.

Table 4.7: Correlation Relationship of the Physical Water Quality Parameters

Correlation Results					
		TEMP	EC	PH	FLOURIDE
TEMP	Pearson Correlation	1	-.004	.396**	.414**
	Sig. (2-tailed)		.973	.000	.000
	N	84	84	84	84
EC	Pearson Correlation	-.004	1	.646**	.585**
	Sig. (2-tailed)	.973		.000	.000
	N	84	84	84	84
pH	Pearson Correlation	.396**	.646**	1	.725**
	Sig. (2-tailed)	.000	.000		.000
	N	84	84	84	84
FLOURIDE	Pearson Correlation	.414**	.585**	.725**	1
	Sig. (2-tailed)	.000	.000	.000	
	N	84	84	84	84

**. Correlation is significant at the 0.01 level (2-tailed).

4.5 Spatial Variation and Distribution of Fluorides in Ground water in River Njoro Catchment

To compare variation of fluoride levels in ground water in River Njoro catchment the fluoride levels were geostatistically analysed and interpolated by Kirging. To validate the fluoride prediction the researcher supplemented the primary data of sampled boreholes with secondary data of fluoride levels of the boreholes neighbouring the sampled boreholes (predictor boreholes).

The neighbouring boreholes that were used as predictor boreholes included: Rift Valley Technical Institute of Science and Technology and Mustard Seed boreholes at downstream, Ogiek Primary School and bontana flowers at upstream of the study area. The other boreholes were: Tumaini School and Egerton University boreholes at midstream. The analysis helped in predicting the contribution of: surface geology, borehole stratigraphy and physical parameters of water quality on the fluoride levels in ground water of River Njoro Catchment based on the analysis of fluoride levels of the sampled boreholes.

The average fluoride levels for the sampled and predictor boreholes upstream, midstream and downstream of the catchment are presented in table 4.8. The concentration of fluoride in the study area varied from 1.7 mg/l at the Ngata M'baruk borehole to 18.6 mg/l at the Kiamunyi borehole. The area upstream of River Njoro catchment around Nesuit Primary is predicted to have fluoride level ranges of between 0-1.5 mg/l and 1.6-3.0 mg/l. These are areas or zones of low fluoride concentrations. On the other hand, areas midstream of the study area has fluoride ranges of between 1.6-3.0 mg/l and 3.1-4.5 mg/l. This is the area around Njoro Township and its environment. Finally higher levels are predicted to occur in the boreholes downstream of the study area and its environment. Kiamunyi area, Pistis which is located extreme downstream and Mogon areas are some of the predicted high fluoride areas.

The fluoride levels along River Njoro sampling points showed that: Kwa Rhodah, KERMA and Tumaini Bridge points showed highest fluoride levels while the upstream points at Ndarogo, Sigaoni and Kwa Maisori to the contrary showed low levels of fluorides in the water. Generally majority of the sampling points within the

River Njoro had fluoride levels in the range of 0-1.5 mg/l. On the other hand boreholes with high fluoride levels in the category of 9.5 mg/l and above were recorded at Kiamunyi and Pistis boreholes while average fluoride levels in the classes between 3.00 mg/l and 9.5 mg/l were recorded at Beston, Mogon, and Njoro Canning, Njoro sunrise, Kwa Annah, Mother Kelvin, and Ainabtich Mogon boreholes. Finally low levels in the class of below 3mg/l were recorded at Ngata Mbaruk, Nesuit Primary and Umoja Kikapu. Finally, the validation by the Kriging model on fluoride distribution confirmed that the fluoride levels from the neighbouring boreholes were within the ranges of the model prediction. In comparison to the average fluoride levels in sampled boreholes and the average recorded fluoride levels in the predictor boreholes there was a mean variation of 0.382 mg/l, -0.401 mg/l and 0.395 mg/l in the downstream, midstream upstream catchments respectively.

Table 4.8: Average fluoride levels for the sampled and predictor boreholes

Borehole name	Type of Borehole	Average F(mg/l)
	Downstream catchment	
Mogon Community	Sampled	8.798
Pistis School	Sampled	19.369
Mother Kelvin	Sampled	3.72
Ainabtich	Sampled	5.533
Mustard Seed	**Predictor**	**7.732**
RVIST	**Predictor**	**8.000**
	Midstream catchment	
Kiamunyi Estate	Sampled	18.591
Ngata Mbaruk	Sampled	1.737
Umoja Kikapu	Sampled	2.907
Kwa Annah	Sampled	3.315
Tumaini Schools	**Predictor**	**4.672**
Egerton University	**Predictor**	**3.820**
	Upstream catchment	
Egerton Sunrise	Sampled	4.000
Njoro Canning	Sampled	5.896
Beston	Sampled	3.414
Nesuit Pri School	Sampled	3.000
Bontana Flowers	**Predictor**	**4.100**
Ogiek Primary sch.	**Predictor**	**3.210**

N/B: the type of borehole refers to data from the sampled boreholes or data for the predictor boreholes.

The average fluoride levels of both the predictor and sampled boreholes located downstream was 8.859 mg/l, while the average midstream was 5.851 mg/l and upstream catchment recorded 3.936 mg/l. The average fluoride level results for both types of boreholes were used in geostatistical analysis and prediction of fluoride spatial distribution. The results of Geostatistical analysis helped in the production of the ground water fluoride prediction map of River Njoro Catchment presented in figure 4.6. The simulation of spatial fluoride distribution data of the sampled and predictor boreholes in River Njoro catchment using the Kirging model achieved 79.2

% similarity. Therefore, there was no great variation in the mean and the covariance of the predictor and sampled boreholes.

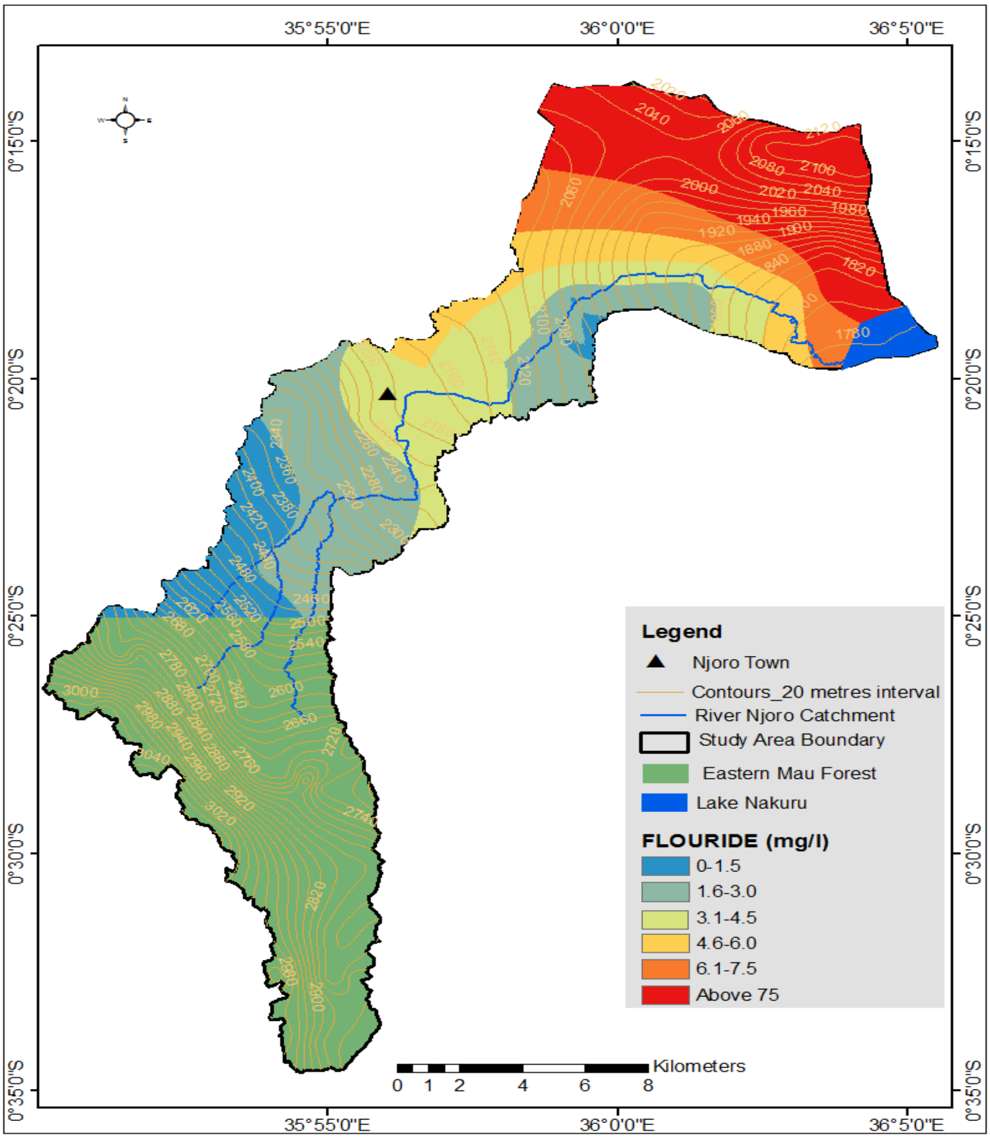

Figure 4.4: Groundwater Fluoride Prediction Map of River Njoro Catchment

CHAPTER FIVE

DISCUSSION

Introduction

This chapter is a discussion of the research as per the objectives and outcomes of the research. The objectives of the study were: to establish the relationship between surface geology and fluoride levels in River Njoro catchment, determine the relationship between stratigraphy and fluoride levels in ground water in River Njoro catchment. The research also sought to determine the relationship between temperature, pH and electrical conductivity of groundwater and fluoride levels in groundwater in River Njoro catchment and finally model spatial variation and distribution of fluoride levels in ground water in the River Njoro catchment.

5.1 Relationship between Fluoride Levels and Surface Geology in River Njoro Catchment

The results of this objective are discussed under: Geology and fluoride levels and fluoride in rocks and fluoride in water sampling points.

5.1.1 Geology and Fluoride Levels

According to the outcome of this study, concentration and quantities of fluoride occurring in different rock types is varied. The presence of fluoride minerals is associated with volcanic processes. These active volcanic areas are the geologically unstable areas which witnessed rifting and the rise of fluorine from the lower lithosphere or sections of the upper asthenosphere. In this study River Njoro Catchment is among the areas that experienced volcanicity and therefore presence of elevated fluoride quantities would be associated with the volcanic processes in this catchment.

Apart from volcanic rocks, high fluoride levels in major levels are associated with rocks of the Pre-Cambrian age and young sediments deposited on land as witnessed by the River Njoro catchment. The East African Rift System's volcanic rocks where River Njoro Catchment is located have higher quantities of fluoride. Similarly Kloos & Haimanot (1999) observed that incidences of highest fluoride concentration levels were recorded in boreholes located within the Rift system where the top values recorded in areas surrounding Lake Nakuru.

This study identified major rocks as: Eutracite Welded Tuffs, Black Ashes, Pyroclastic and Sediments of Rongi plain and Mau slope, volcanic soil and finally superficial deposits all of which are volcanic rocks in nature. These identified rocks were also identified by McCall (1957) who documented those volcanic rocks exposed in the Mau Escarpments are the oldest volcanic rocks locally exposed. Therefore, majority of the volcanic rocks in Mau consist of a series of greenish-grey welded tuffs, yellow pumice, tuffs, sedimentary intercalations, and reworked tuffs and clay. Finally, the findings of this study agreed with McCall's study who observed that the Njoro area has older faulted lavas and tuffs which are covered by compact black ash from Menengai, which is concentrated along the River Njoro valley. River Njoro is cut down through superimposed unconsolidated pumice and ash and runs over the hard upper surface of the black ash.

The magmatic related rocks in the Njoro catchment identified during the research consist of basalts, Trachytes, phonolites, ashes tuffs, agglomerates and acid lavas rhyolite and obsidian. Olaka (2016) similarily identifies these rocks as the main rock types in the River Njoro catchment. Much of the eastern highland areas are composed of a varied assortment of vitric pumice tuffs, Rumuruti phonolites, Mbaruk porphyritic olivine basalt and Gilgil trachyte (McCall, 1967). The regional geology of River Njoro catchment is characterized by volcanic rocks and Quartenary lucustrine from volcanicity. The volcanic rocks consist of tephrites, basalts, trachytes, phonolites, ashes tuffs, agglomerates and acid lavas rhyolite comendite and obsidian (Thompson and Dodson, 1963). Volcanic rocks especially amorphous rocks like pumice, tuffs, pyroclastics and porphyry and other easily weathered materials like volcanic ash or sediments of salt lakes are concerned with washing out the fluoride component into the surface and groundwater.

5.1.2 Fluoride levels, fluoride in rocks and fluoride in water sampling points

In this study volcanic rocks were identified as the main types of rocks contributing to elevated fluoride levels in the River Njoro catchment. Similarly Ramadan and Hilmi (2014) also agree in their study when they observed that in African rivers occurrence of fluoride has relationship with magmatic events, availability of hot alkaline waters, granitic and gneissic rocks. Equally the elevated concentrations of fluoride in water have been observed as the outcome of water rock interaction through chemical disintegration of fluoride bearing rocks and percolation of water in the ground (Brindha and Elango (2011).

The type of rock formation in areas with high fluoride concentrations is mostly volcanic and the River Njoro Catchment is within this location. Therefore, fluoride levels in the River Njoro catchment vary significantly based on the nature and type of rocks. Further, Abdulrahman *et al.* (2013) also concurs with the results of this research by observing that fluoride in water is a result of the dissolution of naturally occurring minerals in the rocks and soils facilitated by water interactions. Further Abdulrahman *et al.* (2013) alludes that the most common fluorine-bearing minerals are fluorite, apatite and micas. Similarly, Aldo *et al*. (2018) seems to agree by their observations that water that is rich in fluoride has strong relationship with volcanic, granitic, and gneissic rocks. Therefore Aldo *et al*. (2018) therefore agrees that elevated fluoride concentration in water is contributed by evaporation, weathering of volcanic rocks and hot magmatic activities in the rift valley system.

In the Midstream near Egerton University, River Njoro meanders following the line of north-south fault zones and cutting East wards across the area between the fault zones. Thereafter in the Njoro area along the river course the older faulted lavas and tuffs are covered by compact black ash (building stone) from Menengai. At this point the river is cut down through overlying unconsolidated pumice and Volcanic Ash and runs over the hard upper surface of the black ash. The high fluoride levels at the KERMA bridge sampling point is be attributed to contact of water with the unconsolidated pumice and volcanic ash. These findings agree with Chelangat, (2015) who observes that high fluoride concentrations are associated with rocks that are volcanic in nature, granites and layers of salt deposits in waters.

5.2 Stratigraphy matrices and Fluoride levels in ground water in River Njoro Catchment

The discussion is explained under the sections of: soils and fluoride levels, borehole stratigraphy and fluoride levels, and Borehole depths and fluoride levels.

5.2.1 Soils and fluoride levels

The processes of weathering and percolating which are activated by water infiltration result in high fluoride levels in soils. Chemical composition of water, presence and infiltration of water rich in fluoride minerals and the contact time between the source minerals are responsible for variation in fluoride levels in soils. The extent that weathering and dissolution of fluoride rich minerals occurs is significant and responsible for elevated fluoride levels in the soil which have been be interfered by human activities. This is evidenced by low fluoride levels in areas that are covered by Forests and Shrubs in River Njoro Catchment.

Human activities have an influence on fluoride levels in soils as evidenced by varied fluoride levels in areas under different Land Use/Cover in Njoro Catchment in this research. Similarly, these results concur with Ghosh *et al*. (2013) who observe that the emission of hydrogen fluoride is some of the human activities that increase fluoride into water. Further Ghosh *et al*. (2013 assert that fluoridation of drinking water supplies, industrialization, and use of fluoride rich pesticides increase levels of fluoride into the environment. Production and use of phosphate fertilizers is a main industrial source of fluoride as observed by Bhat *et al.* (2015).

The processes of weathering and aqueous leaching that occur in soils play a significant role by determining the quantities of fluoride that finally infiltrates into the soil. The release of fluoride into the water from fluoride-bearing minerals is determined by are the chemical composition of the water, the presence and accessibility of fluoride minerals to water. However, according to Meenakshi *et al.* 2004 and Raju *et al.* 2009) the general water quality plays an important role by influencing mineral solubility, complexion and sorption/exchange reactions.

Dissolution of fluoride types in the natural water is influenced by calcium and through the thermodynamic principles when chemical weathering takes place. The calcium ion reaction in nature is mainly influenced by carbonate ions, which contributes to insoluble calcite. The water moving through the ground react at varying degrees with minerals in the neighbourhood and other components give the water its characteristic chemistry on fluoride concentrations. This is equally confirmed in this research where the area under agriculture displayed high levels of fluoride as compared to Shrubs and forests.

5.2.2 Borehole Stratigraphy and Fluoride levels

In this study the sampled boreholes had different lithologies. Similarly, despite their relative physical locations the boreholes recorded varying levels of fluoride. The higher concentrations are associated with boreholes which have varied stratigraphic formations whose origin is volcanic of type as depicted in the borehole stratigraphic formations. The same observations were made by Nyamboge *et al.* (2018) who asserted that high fluoride concentrations are influenced more by lithology of the aquifer. Further also Ghiglieri *et al.* (2010) observes that levels of fluoride in the aquifers of boreholes depend on the mineralogy and lithology. Therefore, interaction between groundwater and different geological units of variable mineralogy results in different fluoride levels in boreholes as a result of a number of reactions. The reactions include: dissolution-precipitation, ion exchange, oxidation-reduction and absorption which can change water chemistry. Majority of the boreholes in the River Njoro Catchment have higher fluoride levels than river water as justified by Kiamunyi having 18.591mg/l, Pistis School 19.369 mg/l and Mogon Community having 8.798 mg/l.

The levels of fluoride in the Rift System groundwater vary significantly from place to place depending on the influence exerted by local geology within the Rift Valley. Moreover, it is generally accepted that prolonged contact of the water with the rock fluoride build-up in groundwater results in high fluoride levels. Lithology therefore becomes an important determinant of groundwater fluoride concentration. Sankar and Dar (2011) observes that bedrock aquifers in alkaline magmatic rocks and metamorphic rocks are particularly associated with fluoride contaminated groundwater with fluorspar, fluorapatite, amphiboles and certain micas being the minerals directly responsible for its release.

The geogenic contamination of ground water results in occurrence of high fluoride in groundwater. The sampled boreholes in River Njoro in this study equally displayed varied geological formations and varied fluoride levels. Geogenic contamination equally depends on the stratigraphic formations of an area. As rainwater infiltrates through the soil and reaches the water table, it dissolves components of bedrock. Consequently, therefore fluoride in groundwater originates from dissolution of fluorine bearing minerals in the bedrock (Chae *et al.,* 2007). The fluoride high levels in ground water in Njoro catchment would be attributed to percolation of groundwater through the weathered rock in the aquifers, where it dissolves fluoride-bearing minerals thereby releasing fluoride in solution form into the boreholes. Similarly, Saxena and Ahmed, (2003) observes that long residence with fluoride bearing rocks results in high fluoride levels in the boreholes.

In all the sampled borehole in this study there was a significant variation in the levels of fluoride recorded with the Kiamunyi recording the highest while the borehole at Umoja Kikapu recorded the lowest levels. Similarly, WHO (1994) alludes that due to the large number of variables, fluoride concentrations in groundwater can vary from well under 1 mg/l to more than 35 mg/l. In Tanzania studies have shown that the problem of high fluoride content in groundwater is very acute in mainland Tanzania (Mjengera and Mkongo, 2002). In Tanzania the high fluoride level is contributed by geological processes such as volcanic activities, thermal springs and the presence of minerals such as fluorite and apatite in rocks. Mjengera and Mkongo (2002) found that borehole water in South Sanya corridor contained up to 96 mg/l fluoride whereas the area west of Ngorongoro Crater had fluoride content of between 40 and 140 mg/l in spring water.

Fawell *et al*. (2006) documented that the fluoride concentration levels in groundwater are affected by: availability and solubility of fluoride containing materials, porosity of the rocks or soil through which water passes, residence time and temperature, the hydrogen ion concentration of the water and the presence of other elements which may combine with fluoride ions. The origin of the trachytes and pyroclastics are believed to arise from a number of volcanic centers within the catchment which are the main eruption centers. Prajapati *et al.* (2017) on spatial distribution of fluoride levels observes that the main reason for fluoride enrichment in groundwater is considered to be the existence of fluoride-bearing minerals in the host rocks and their interaction with water. Further Prajapati *et al.* (2017) concludes that the key chemical processes responsible for movement and transport of fluoride into groundwater are decomposition, dissociation, and dissolution of fluoride rich rocks such as basalt, dolerites, rhyolites, basalt dykes present in the study area.

Trachytes, Tuff and Pumice strata matrix at Kiamunyi and Mogon boreholes recorded high fluoride levels in River Njoro catchment. Similar findings were presented by

Kanda & Suwai (2013) who observed that Trachytes are fine-grained lava with an alkaline composition, typically with prominent large alkali feldspar crystals. Further Kanda & Suwai (2013) observe that Trachytes together with tuffs were deposited at the edges of rift escarpments were associated with elevated fluoride levels. Unconsolidated fragmentary deposits are eroded from volcano, reworked and deposited on land. Subsequently the compositions of these volcano sediments are related to the parent rock and therefore after weathering contribute to higher fluoride levels.

5.3.3 Borehole Depths and Fluoride Levels

The sampled boreholes in this study in River Njoro Catchment had varying depths traversing through various lithological formations. The deeper boreholes: Pistitis with depth of 180 metres had 19.369 mg/l and Kiamunyi with depth of 220 metres had 18.591 mg/l recorded higher levels of fluoride. Conversely, shallow boreholes Ngata Mbaruk 125 metres and Umoja Kikapu 114 metres recorded averagely low fluoride levels of 1.737 mg/l and 2.907 mg/l respectively. The ionic activity in deep boreholes would have contributed to higher fluoride levels than in shallow aquifers because of rock-water interaction. These findings are supported by Beg (2009) who observed that deeper boreholes with long residence time are likely to have high concentration of fluoride.

The depth of boreholes in the River Njoro Catchment in this study ranged from 114 metres at Kikapu to 220 metres at Kiamunyi and Mogon. The depth of boreholes and fluoride levels is supported by Beg (2009) on the research work titled Geospatial analysis of fluoride contamination in ground water of Tamnar area who observed that: most of the boreholes with high concentration of fluoride were in the depth range of

110 to 150 m. On the contrary low fluoride levels in shallow boreholes would be attributed to fast replenishment of ground by infiltrating rainwater. The Njoro catchment lies within the inner graben of the central Kenya rift valley and has experienced continual outpourings of trachyte magma. Basalts are rare, and volcanic rocks of intermediate composition are not exposed. Sedimentary rocks are intercalated with the volcanic rocks. Volcanic rocks older and underlie the area, contributing to the total volcanic and sedimentary rift fill.

The various eruptive styles of trachyte can be explained by eruption from relatively large magma chambers, capped by trachytic magmas and emplaced in the upper crust, like that thought to exist below the recent volcano Menengai. Similarly, Redda *et al*. (2006) observes that there are significant variations in the fluoride levels of the deep wells within the Rift Valley and this is confirmed by the deep Kiamunyi and Pistitis boreholes. The variation is related to the geophysical and geochemical characteristics in the Rift Valley. The principal processes that control the groundwater quality variations are the influence of silicate rocks weathering and anthropogenic contribution which is also significant.

According to Brindha and Elango (2011), Most of the fluoride in groundwater is naturally present due to weathering of rocks rich in fluoride. Fluoride occurs in almost all waters from trace to high concentrations however its concentration depends on temperature, pH, solubility of fluorine-bearing minerals, and the nature of geological formations drained by water and contact time of water with a particular formation. However, minerals which have the greatest effect on the hydro geochemistry of fluoride are fluorite, apatite, mica, amphiboles, certain clays and villiamite.

Levels of fluoride in groundwater would be attributed to natural or anthropogenic causes and sometimes a combination of both. Geological conditions of an area are attributed to natural sources. Several rocks like apatite, fluorite, biotite and hornblende within the geological formations have fluoride bearing minerals. The weathering of these rocks in conjunction with the process of infiltration of rainfall increases fluoride concentration in groundwater. Conversely fluoride which is present in high concentration in volcanic ash is readily soluble in water and thereby forming another natural source.

Volcanic rocks are enriched with fluoride. The high levels are contributed by hydrogen fluorine which is one of the most soluble gases in magmas and comes out partially during eruptive activity as observed by D'Alessandro *et al.* (2008). The aerial emission of fluoride in the form of volcanic ash during volcanic eruption reaches the surface by fall out of particulate fluorides and during rainfall. This fluoride from the soil surface finally reaches the groundwater zone along with percolating rainwater. Volcanic ash is readily soluble and thus the risk of fluoride contamination in groundwater is very high. Similar sentiments on volcanic ash and fluoride levels are held by Brindha and Elango (2011), who asserted that in Kenya volcanic sources have been found to cause fluoride contamination in groundwater. Further Francisca, (2017), fluoride is a common constitute of ground water where natural sources are connected to various types of rocks and to volcanic activities.

In the world today fluoride contamination in groundwater is a growing problem. High concentration of fluoride is reported both from hard rock (granites & gneisses) and alluvial aquifers. The cause of high fluoride in ground water is geogenic being a result of the dissolution of fluoride bearing minerals. Fluoride in ground water is mainly influenced by the local and regional geological setting and hydro geological conditions. However, soil consisting of clay minerals and the influence of local lithology, would be responsible for higher concentration of fluoride in the groundwater of an area. It is further observed that fluoride is found in large quantities in boreholes that have natural fluoride-carrying minerals at certain depths. Therefore, high fluoride concentrations are expected from calcium-poor aquifers where there is occurrence of cation exchange of sodium for calcium as observed by AbuZeid & Elhatow (2007).

Abdulrahman *et al.* (2013) while discussing Correlation of fluoride concentration with depth of the sampled wells observed that fluoride concentrations versus well depths in different regions in Arabia varied. Higher levels of fluoride that were found in deep wells would have been attributed to the geological factors. Similarly, Fawell *et al*. (2006) observes that fluoride levels in water are limited by fluoride solubility. Consequently, high fluoride levels may be expected in groundwater from calcium-poor aquifers and in areas where fluoride-containing minerals are common. Deeper groundwater has the higher fluoride concentration levels because the levels increase where cation exchange between sodium and calcium occurs.

5.4 Relationship between selected Physical Parameters and Fluoride Levels in Groundwater in River Njoro catchment

In the River Njoro during the period of study, pH, temperature and electrical conductivity in the in the river sampling points varied. Similarly, during the period, levels of fluoride recorded at the river sampling points also varied. Temperature and pH at the sampling points had an influence on the fluoride levels while the levels of electrical conductivity had no influence on the levels of fluoride levels recorded.

Similar observations on the influence of pH on fluoride levels in rivers were made by Aldo *et al.* (2018) who asserted that: there is spatial variation of fluoride in rivers attributed to chemical reaction that result in changes in the pH of the environment thereby influencing the amount of fluoride present. Further Aldo *et al.* (2018) observes that fluoride availability in water is affected highly by pH making it more favored in environments that are alkaline. Finally, Ramadan and Hilmi (2014) on the influence of climate as a determinant of the upper permissible fluoride quantities in water meant for domestic use in Sudan concurred that fluoride concentration and occurrence of severe of fluorosis seemed to increase as average daily temperature increased.

In the River Njoro catchment during the period of study, the physical attributes of water quality in the sampled boreholes varied. Similarly during the period of research, levels of fluoride recorded in these boreholes varied. pH and electrical conductivity of the water in the boreholes had a strong influence on fluoride levels in the sampled boreholes. The high electrical conductivity of the water would imply that the fluoride concentrations levels present in groundwater was a result of high concentrations of bicarbonate ions attributed to the process of change of the silicates depending on residence time of the water. Therefore, strong positive relationship between high pH and concentration of fluoride could be attributed to the presence of calcium salts which are associated with volcanic rocks and their control by ion exchange as concurred by Ortega (2009) and Alvarez *et al.* (2018).

High fluoride levels in the boreholes averaging 9.350 mg/l downstream, 6.637 mg/l Midstream and 4.078 mg/l upstream in the River Njoro catchment had a strong association with high pH and moderately correlated to temperatures and electrical conductivity. Past studies (Ghiglieri *et al*., 2012 and Srinivasamoorthy *et al.*, 2012) similarly tend to concur with results of this study. Ghiglieri *et al*. (2012) and Srinivasamoorthy *et al.* (2012) observed that alkaline nature of groundwater enhances and accelerates leaching of fluoride into the ground thereby resulting in elevated fluoride levels in boreholes. From this study high alkalinity of the borehole water was responsible for the levels and rate of fluoride release entering into the groundwater system. These observations were similarly observed by Saxena and Ahmed (2001) in experimental observations carried in controlled room temperature and asserted that fluoride was easily released from original rock formations having pH variations from 7.6–8.6.

5.5 Spatial Variation and Distribution of Fluoride levels in Ground water in the River Njoro Catchment

Despite water sampling for fluoride analysis in this study being done during the rainy and dry periods as guided by the research design, fluoride levels in the boreholes remained higher beyond the WHO recommended levels. In the River Njoro catchment, this study observed that the spatial distribution of fluoride concentrations showed that there were high fluoride levels of 19.369 mg/l at Pistitis and its environment which is located downstream of River Njoro catchment. Fluoride distribution in this study helped in identifying and delineating areas with less fluoride levels as per the WHO standards. Elevated fluoride levels that are beyond the WHO limits in catchment of River Njoro catchment would be attributed to the presence of basaltic rock formations and volcanic materials which contain high fluoride concentrations. Volcanic ash is one of the fluoride rich rocks which emanated from the eruption of Menengai crater in the neighborhood of the study area. The released volcanic rocks from the crater contaminated groundwater in the Njoro catchment with elevated fluoride levels.

Findings of this study pointed those high levels of fluoride would be attributed to weathering and percolating of minerals whose origin would be traced rocks whose origin is volcanic in nature with high fluoride concentrations. The floor of the Rift Valley is where majority of the boreholes recorded high fluoride levels are regions experiencing active volcanism. The high levels of fluoride in the boreholes would be associated with the contact of the water with high fluoride volcanic bearing rocks which formed the aquifer matrix of the boreholes. The main rocks that formed the aquifer of the sampled boreholes in the River Njoro catchment with high fluoride levels included: volcanic soils, tuff and trachytes. These sentiments are supported by Chae *et al*, (2007) who asserts that majority of the world zones associated with fluoride contamination occur in granite dominated terrains or in fluoride dominated sedimentary aquifers.

Like in the scenario in the River Njoro catchment, Aldo *et al.* (2017) on their study in Tanzania observed that the spatial variation of fluoride in river catchments is varied. The distribution is a function of levels of fluoride underlying the river channels and several other chemical reactions which result in alterations in the pH in the environment. Further Aldo *et al.* (2017) asserts that interaction of groundwater and surface water patterns and external inputs such as surface runoff, salinity, and climate change also determine levels of fluoride. Additionally, studies on surface water reported the occurrence of fluoride levels of 12-13 mg/l in Maji ya Chai and 690 mg/l in Engare Nanyuki Rivers (Nanyaro, 1984 & Mungure, 1984).

The study by Aldo *et al.* (2017) is a clear justification of varied distribution of fluoride levels in the environment. Odiyo & Makungo (2012) observe that high pH, varied levels of calcium, groundwater having high temperatures and desert like climatic conditions of an area increase make fluoride bearing rocks to dissolve thereby resulting in high fluoride concentrations. In this study water samples from areas having minerals bearing elevated fluoride levels had high levels of fluoride. The results have similarity with past researches. Ghiglieri e*t al.* (2012) observed that areas dominated by: fluorapatite, fluorite, topaz, phlogopite, and lepidolite minerals dominate places with fluoride contaminated water. These minerals are water-insoluble making them to discharge fluoride ions to the river and borehole water sources depending on variations in temperature and alkalinity which contribute to their solubility (Ghiglieri e*t al.*, 2012)

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The study focused on analysing effects of geological variability and selected physical parameters of water on fluoride levels in ground water in River Njoro catchment, Kenya. Later the entire study was guided by specific objectives. These specific objectives included: determining the connection between fluoride levels and surface geology in River Njoro catchment, determining the relationship between selected physical parameters of water and fluoride levels in River Njoro catchment. Additionally, also the study sought to determine how the borehole stratigraphy impacted on the fluoride levels in ground water in the catchment of River Njoro catchment. Ultimately the study focused in developing a model to account for areal variability and distribution of fluoride concentrations levels in ground water in the catchment under study.

In the study, the source of fluoride in waters in the River Njoro catchment was attributed to disintegration of fluorine rich minerals in rocks, magmatic and or volcanic related eruption activities. The concentration levels of Fluoride in water in the boreholes in River Njoro had a positive relationship pH, temperature and electrical conductivity which would have influenced the geochemical processes thereby resulting in variability of fluoride levels concentrations in the ground water sources. The levels of fluoride in the River Njoro catchment vary markedly from upstream to downstream on the influence exerted by variation of the nature of the underlying rocks.

The rocks covering River Njoro catchment are characterized by varied volcanic materials. The main volcanic rocks are: pyroclastic materials, tuffs, pumice and basalts. Therefore, the study concludes that high fluoride levels in the boreholes located in the River Njoro Catchment: Pistis 19.369 mg/l, Kiamunyi 18.591 mg/l and Mogon 8.0798 mg/l are results of contact of the water with fluoride rich rocks which form aquifers of the boreholes. The contribution of volcanic rocks on fluoride levels in boreholes was justified by the drillers' logs which identified four major dominant aquifer matrices as: sediments, trachyte, tuffs and pyroclastics. Geological formations of the boreholes within the River Njoro catchment is multi lithological formation of volcanic rocks, comprising of trachytes, basalts, phonolites, tuffs and volcanic sediments.

Fluoride enrichment in boreholes within the study area would be associated with the presence of minerals rich fluoride in the original parental rocks besides their connection and interaction with the water. Decomposition, dissociation, and dissolution of fluoride bearing rock minerals are the key chemical processes which account for fluoride movement and finally movement into the boreholes. Additionally, the high fluoride levels in borehole water may also be contributed by the disintegration of rocks chemically and solution percolating routes, fairly elevated alkaline conditions and lengthy period in interactions. While agriculture is one of the land uses in the River Njoro catchment fluoride levels in the boreholes during the wet and dry seasons remained high with little variations across the seasons. Therefore the enrichment of fluoride in the boreholes by the fluoride bearing fertilisers has no contribution to the high fluoride levels in borehole water in River Njoro catchment. Finally, the borehole lithology and depths of boreholes are important determinants of borehole fluoride concentration in the River Njoro Catchment.

6.2 Recommendations

Based on the study findings: the following recommendations are made:

i. The levels of fluoride along River Njoro are within the W.H.O limits and therefore suitable for human use unless the other physical-chemical parameters of River Njoro's water are not within the W.H.O acceptable limits. However there is need to disseminate information to the residents of Njoro on the causes of fluorosis, and advocate rainwater harvesting.

ii. The suitable sources of ground water within River Njoro catchment are found Midstream and Upstream of the River Catchment. These areas are located from Ndaruk Midstream to Nesuit Upstream with fluoride levels being within or slightly higher than the W.H.O permissible levels.

iii. An integrated active play of roles ought to be exercised by all partners on water matters to ensure that water is monitored and well-managed from the catchment groundwater feeding sources, water in aquifers, water withdrawal sites (boreholes), as well as delivery to the consumer. This should accommodate qualitative aspects related to fluoride contamination within the River Njoro Catchment. The qualitative aspect should focus on the health-based targets specified by W.H.O, whereas quantitative aspects should give emphasis to the rate of water withdrawal, source and recharge rates of water within the River Njoro catchment.

6.3 Areas for Further research

Geology and borehole stratigraphic variations are not the only sources of elevated fluoride levels in River Njoro. Therefore, to identify other potential sources of fluoride in ground and river water, the study recommends isotopic analysis of water samples from different sources of water in River Njoro catchment so as to trace the origin, and fluoride enrichment pathways and water quality alteration within the River Njoro catchment.

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APPENDICES

APPENDIX I: BOREHOLE WATER INSITU PHYSICAL PARAMETERS

Report				
BOREHOLE		TEMP(^{0}c)	EC(μ)	pH
NESUIT	Mean	20.6875	396.1250	6.1550
	Minimum	19.80	246.00	6.01
	Maximum	21.70	476.00	6.42
BISTON CENTRE	Mean	23.8000	441.1429	7.2686
	Minimum	21.50	413.00	6.72
	Maximum	26.30	463.00	8.20
EGERTON SUNRISE	Mean	25.3250	457.3750	7.3313
	Minimum	22.60	428.00	7.03
	Maximum	32.70	531.00	7.62
UMOJA KIKAPU	Mean	22.4500	406.0000	7.4083
	Minimum	20.70	354.00	7.26
	Maximum	24.50	531.00	7.52
KWA ANNAH	Mean	24.2600	439.4000	7.1040
	Minimum	21.80	318.00	6.85
	Maximum	26.60	852.00	7.34
NGATA NDARUK	Mean	22.5375	281.0000	6.9987
	Minimum	21.80	259.00	6.72
	Maximum	23.70	314.00	7.42
AINABTICH	Mean	29.9250	474.0000	7.4338
	Minimum	27.70	455.00	7.16
	Maximum	31.60	482.00	7.69
KIAMUNYI	Mean	29.8000	760.7143	7.8929
	Minimum	23.50	728.00	7.51
	Maximum	36.20	786.00	8.12
PISTIS	Mean	26.0500	3299.5000	8.7917
	Minimum	25.00	3220.00	8.66
	Maximum	27.20	3416.00	8.92
MOTHER KELVIN	Mean	23.4800	1837.4000	7.2620
	Minimum	20.80	1796.00	6.80
	Maximum	25.10	1867.00	7.55
NJORO CANNING	Mean	31.9667	436.1667	7.6233
	Minimum	30.40	428.00	7.51
	Maximum	32.80	443.00	7.80
MOGON COMMUNITY	Mean	32.2000	421.0000	7.0250
	Minimum	30.60	415.00	6.81
	Maximum	33.40	428.00	7.32
Total	Mean	25.9501	746.6716	7.3272
	Minimum	19.80	246.00	6.01
	Maximum	36.20	3416.00	8.92

APPENDIX II: RIVER SAMPLING WATER INSITU PHYSICAL PARAMETERS

Report				
POINT		TEMP(^{0}c)	pH	EC (µS/cm)
SIGAONI	Mean	14.1333	7.537	222.5000
	Minimum	13.80	6.46	97.00
	Maximum	14.60	8.15	268.00
SIGAONI/SUGUTEK	Mean	16.4800	7.280	164.4000
	Minimum	14.60	6.70	87.00
	Maximum	19.10	7.64	212.00
KIPKOGO	Mean	21.5250	7.435	213.5000
	Minimum	19.10	7.25	211.00
	Maximum	25.50	7.62	216.00
NESUIT	Mean	18.0875	7.236	268.8750
	Minimum	16.80	6.80	140.00
	Maximum	19.80	7.90	328.00
NDAROGO	Mean	19.7333	7.463	172.1111
	Minimum	17.90	6.90	86.00
	Maximum	21.00	7.82	233.00
KWA MAISORI	Mean	18.9429	6.784	341.0000
	Minimum	18.20	5.85	312.00
	Maximum	19.70	7.64	397.00
SUGUTEK	Mean	14.1200	7.520	213.4000
	Minimum	13.80	6.46	97.00
	Maximum	14.60	8.15	264.00
KARLO	Mean	17.3111	7.086	295.8889
	Minimum	15.30	6.27	136.00
	Maximum	18.60	7.87	397.00
KERMA	Mean	19.7625	7.418	316.3750
	Minimum	17.90	7.05	138.00
	Maximum	21.80	8.14	407.00
TUMAINI	Mean	20.0714	7.543	294.5714
	Minimum	17.60	6.68	138.00
	Maximum	23.30	8.32	425.00
KWA RHODA	Mean	20.2250	7.341	278.7500
	Minimum	17.80	7.02	136.00
	Maximum	24.30	8.07	330.00
Total	Mean	18.3309	7.3173	257.3429
	Minimum	13.80	5.85	86.00
	Maximum	25.50	8.32	425.00

APPENDIX III: DESCRIPTIVE TABLE: FLUORIDE LEVELS IN RIVER NJORO IN DIFFERENT ROCK TYPES

	N	Mean	Std. Error	95% Confidence Interval for Mean		Min	Max
				Lower Bound	Upper Bound		
SUPERFICIAL DEPOSITS	15	1.387	.0669	1.2440	1.5307	.81	1.82
BLACK OF RONGAI	25	1.170	.0714	1.0232	1.3177	.61	1.86
BLACK ASHES OF ELBURGON	15	1.0395	.09415	.8376	1.2415	.34	1.74
PYROCLASTS	7	1.042	.1311	.7215	1.3634	.57	1.43
LURMUDIAK TUFF	6	.7002	.1429	.3328	1.0676	.28	1.32
EUTRACITE TUFF	10	.6091	.0849	.4171	.8011	.25	1.28
Total	78	1.067	.0457	.9763	1.1584	.25	1.86

APPENDIX IV: CATCHMENT

Descriptives								
LUORIDE B								
	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Min	Max
					Lower Bound	Upper Bound		
UMOJA KIKAPU	5	3.0206	.64438	.2881	2.2205	3.820	2.04	3.78
NGATA NDARUK	8	1.7676	.24234	.0856	1.5650	1.970	1.29	2.05
AINABTICH	8	1.7229	.18486	.0653	1.5683	1.877	1.48	2.03
MOTHER KELVIN	5	1.6260	.17444	.0780	1.4094	1.842	1.42	1.81
NESUIT	8	.9610	.19375	.0685	.7990	1.123	.77	1.36
BISTON COMMUNITY	7	3.6641	1.0047	.3797	2.7349	4.593	2.94	5.87
NJORO SUNRISE	8	4.1750	.85451	.3021	3.4606	4.889	2.87	5.32
PISTIS SCHOOL	6	16.9772	1.0509	.4290	15.874	18.08	15.82	18.29
KWA ANNAH	5	3.0882	1.2918	.5777	1.4842	4.692	1.64	4.99
MOGON COMMUNITY	6	3.8445	.50013	.2041	3.3197	4.369	3.11	4.68
KIAMUNYI	7	17.5604	2.2021	.8323	15.523	19.59	14.66	20.83
NJORO CANNING	6	5.7140	.73565	.3003	4.9420	6.486	4.76	6.77
Total	79	5.2591	5.5961	.6296	4.0057	6.512	.77	20.88

APPENDIX V: NACOSTI PERMIT

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Ref. No.

Date: 22nd August, 2018

NACOSTJ/P/18/9989/1799

George Morara Ontumbi
University of Eldoret
P.o Box 1125-30100
ELDORET.

RE: RESEARCH AUTHORIZATION

Following your application for authority out research on "***Effects of geological variability and selected physical parameters of water quality on fluoride levels in river Njoro catchment Kenya***"

I am pleased to inform you that you have been authorized to undertake research in **Nakuru County** for a period ending **2nd October 2019**.

You are advised to report to the **County Commissioner and the County Director of Education, Nakuru County** before embarking on the research project.

On completion of the research, you are expected to submit **two hard copies and one soft copy in pdf** of the research report/Thesis to our office.

DR. M.K. RUGUTT, PhD, HSC.
SECRETARY/CEO

Copy to:

The County Commissioner
The County Director of Education
Nakuru County

APPENDIX VI: COUNTY COMMISSIONER'S AUTHORIZATION

THE PRESIDENCY
Ministry of Interior and Coordination of National Government

Telegram: "DISTRICTER" Nakuru
Telephone: Nakuru 051-2212515
When replying please quote

COUNTY COMMISSIONER
NAKURU COUNTY
P.O. BOX 81
NAKURU

Ref No CC.SR.EDU.12/1/2 VOL.11/263

22nd January 2018

TO WHOM IT MAY CONCERN

RE:- RESEARCH AUTHORIZATION

The following members of the University of Eldoret have been authorized to collect water samples for fluoride testing from boreholes in Nakuru County for a period ending 30th May 2019:-

- Douglas M. Wopicho
- George M. Ontumbi
- Jacob Kiptoo Sanga

Please accord them all the necessary support to facilitate the success of their research

VICTOR GITONGA
FOR COUNTY COMMISSIONER
NAKURU COUNTY

APPENDIX VII: SIMILARITY REPORT

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