

## Variation of Fluoride Levels in Surface Geology: A Study of River Njoro Catchment, Kenya

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### Abstract

*Fluoride levels in water that is higher than the World Health Organization (WHO) recommended levels of 1.5mg/l have raised concerns to the health of human. Subsequently fluoride contamination in water is a pertinent matter that calls for concern by all people and government. This study sought to investigate variation of fluoride levels in surface geology in river Njoro catchment. This study adopted purposive longitudinal survey research designs. In this research, rock samples were collected from 11 purposively selected points along the river Njoro and its tributaries to analyse fluoride levels in the laboratory. The research adopted descriptive data analysis in evaluating fluoride changes as contained in the rocks. The study observed that despite different types of volcanic rock outcrops along Njoro River, there were minimal variations in the levels of fluoride in the river Njoro. The study identified Superficial Deposits of Volcanic Soils with highest fluoride levels (1.575 mg/l) while eutracite Welded Tuffs had the lowest fluoride levels (0.678 mg/l). In Conclusion the rocks within the River Njoro catchment have insignificant contribution to the known elevated fluoride levels contained in sub surface and water in the ground in Njoro River catchment.*

**Keywords:** Volcanicity, Defluoridation, Geology, Rock outcrops, Contamination

### INTRODUCTION

Natural occurrence of fluoride in volcanic rocks is associated with high levels in Precambrian rocks. With Fluorite (fluorspar,  $\text{CaF}_2$ ) being the abundant mineral bearing chemical. Soils with clay store high quantities of fluorite in groundwater and lakes in volcanic areas. In soils the decomposition and weathering of original geologic material is believed to result to elevated intensities of fluoride. Fluoride soluble in water attracts greatest interest because it may affect lives of plants and animals. 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 fluoride levels contained in soil. Subsurface water as observed by Marieta (2007) has the likelihood of having higher fluoride concentration than surface water.

River water quality would be linked to surface geology and affected by the type of aquifer where the source of the river is located as observed by Alberta Environment (2009). The hydrological processes of percolation and infiltration naturally therefore have the potential of causing contamination and thereby affecting both the surface and ground water quality. In the recent past concerns have been raised on the availability and quality of water in the developing countries. The woes regarding diminishing surface water resources and fluoride contamination are intertwined and associated to geology (Hassan & Nazem, 2016).

Fluoride contamination associated with surface water is related to presence of soluble fluorine-bearing mineral reserves, temperature, levels of pH, calcium concentration and ions of bicarbonate contained in the water samples. The significant role played by storage, transportation and quality of the surface water is played by geological and geomorphological characteristics of the area. Similarly, MacDonald et al. (2009) observed that geological and geomorphological characteristics of a place, would result to recharging varying between 10 and 50 mm of fluoride levels occurring in areas that receive an annual precipitation not exceeding 500 mm. Fluoride occurrence in water would be attributed to natural or geogenic contamination as observed by Saxena and Ahmad (2003) however, the specific source at a specific point cannot be identified. Contamination of water associated with geogenic processes is dependent majorly on the geology formations in particular places.

The elevated fluoride levels in river water would be attributed to natural and anthropogenic processes. Moreover, the natural causes are more responsible to degradation of the river's water through geological processes. The presence of fluorides in high concentration tends to pose health risks as observed by Chelangat (2015). The fluorosis of bone conditions is permanent with no treatment available. Therefore, the solution available to the adverse effects associated with elevated fluoride levels in portable water is prevented by an intake of fluoride quantities that are within the acceptable WHO limits. High fluoride levels become a case of concern because fluoride persists thereby becoming non-degradable substance and accruing in the ecosystem.

Percolation and dissolution of fluorine during weathering and water flowing within the rocks and soils contribute to fluoride occurrence in particular areas. Consequently, fluoride quantities in river water would fluctuate with variation on the geological formations which have association of; fluorite, apatite with micas being the common minerals that have fluorine. Subsequently the problems associated with high fluoride levels will be experienced where minerals of volcanic origin are in abundance in the rocks. 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 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 majorly depending how calcium fluorite would be soluble.

Edmunds & Smedley, (2013) observes that in parts of Indian sub-continent, Pakistan, parts of West Africa, Thailand, China, Sri Lanka, and South Africa have elevated sub surface fluoride quantities related to rocks of igneous and metamorphic nature. In the 28 provinces of China, widespread cases of fluorosis have been reported where wells that are shallow and deeper are affected with waters that are having higher concentrations. Hallett *et al.* (2015) observed that concentrations to high levels of 10 mg/l in borehole waters in the water deficient areas of Sri Lanka where cases of fluorosis associated with bones are severe. High quantities of rainfall and long-term leaching of fluoride and other minerals in the wet Zone of Sri Lanka possibly have relationship with bedrock crystals and hence contributing to reduced concentration levels of fluoride as observed by Dissanayake (1991).

The geology of Kenya as compared to the rest of the world makes it one of the countries worldwide where occurrence of fluoride has highest concentrations available in earth's lithosphere, river and bore water. The elevated fluoride in water occurs in some springs, wells, and Rift Valley lakes (Gikunju *et al.*, 2002). The documented areas associated with volcanic eruptions are situated in the countries traversed by the East African Rift. Majority of the lakes situated within the Rift Valley system, have extremely high fluoride concentrations which have levels ranging from 1,640 mg/l to 2,800 mg/l in Lakes of Elementaita and Nakuru respectively according to Nair *et al.* (1984). Further, Nair *et al.* (1984) asserted that in a survey involving more than 1,000 sub-surface water sources 61 per cent were higher than 1 mg/l, where 20 per cent surpassed 5 mg/l while those with 8 mg/l comprised of 12 per cent.

The government of Kenya in its vision 2030 blue print as observed by Ndungu & Otieno (2011) strives to provide water that is safe and clean for its whole population and emphasise a healthy and productive population. Primary sources of water for the rural populations in Njoro are; rivers, streams, springs, and boreholes. These communities in rural Njoro catchment area get their water from natural water points without treatment subsequently the significance of surface geology on fluoride levels are important. 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 on the levels of fluoride in the River Njoro catchment which is a major concern to the residents of Njoro.

The occurrence of elevated levels of fluoride in sub-surface and surface water resources has attracted worldwide attention attributed to the repercussions on human health. Depending on the levels fluoride in drinking water, the impacts have constructive and detrimental effects on the health of human beings. The geology of the Rift Valley makes it one of the vulnerable regions of the world with elevated fluoride levels in mineral rocks, soil, surface and ground water. Fluoride fluctuates in different sources of water with higher concentrations found in ground water. According to WHO (2004), 1.1 billion persons living in third world countries don't have accessibility to safe water for drinking and domestic uses. 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 thereby altering its physicochemical parameters. Therefore, the levels of fluoride 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 which are traversed by the geology of great East African Rift valley and yet rivers and boreholes are major sources of water in these Counties. Hence, the geology of River Njoro catchment would be a great potential risk to the region's fluoride levels in the river water in the catchment.

The problem of higher fluoride levels in Njoro catchment is not new as witnessed in the past research which placed emphasis on the justification of the elevated levels. Thus interrogating geology as the underlying factor determining the spatial distribution of fluoride levels becomes a pertinent research issue. Subsequently understanding the possible effects of the geological dynamics on elevated fluoride levels would form a

knowledge base and a requisite basis quality water supply in the River Njoro catchment.

## METHODOLOGY

### Study area

#### Climatic characteristics

Rainfall patterns within the River Njoro Catchment are extremely variable both spatially and temporal and in terms of rainfall intensities (Maina & Raude, 2016). This makes the natural flows of water in the river Njoro and its tributaries highly variable in space and time. The long term atmospheric conditions have characteristics of a trimodal pattern of rainfall: High and heavy rains are experienced from April through May; little and heavy rains in August; and shorter, less and strong rains experienced in November through to December. Total rainfall in the year is 956 mm while the mean annual temperature is 16.5°C, ranging from 9°C in July to 24°C in January for the minimum and maximum respectively.

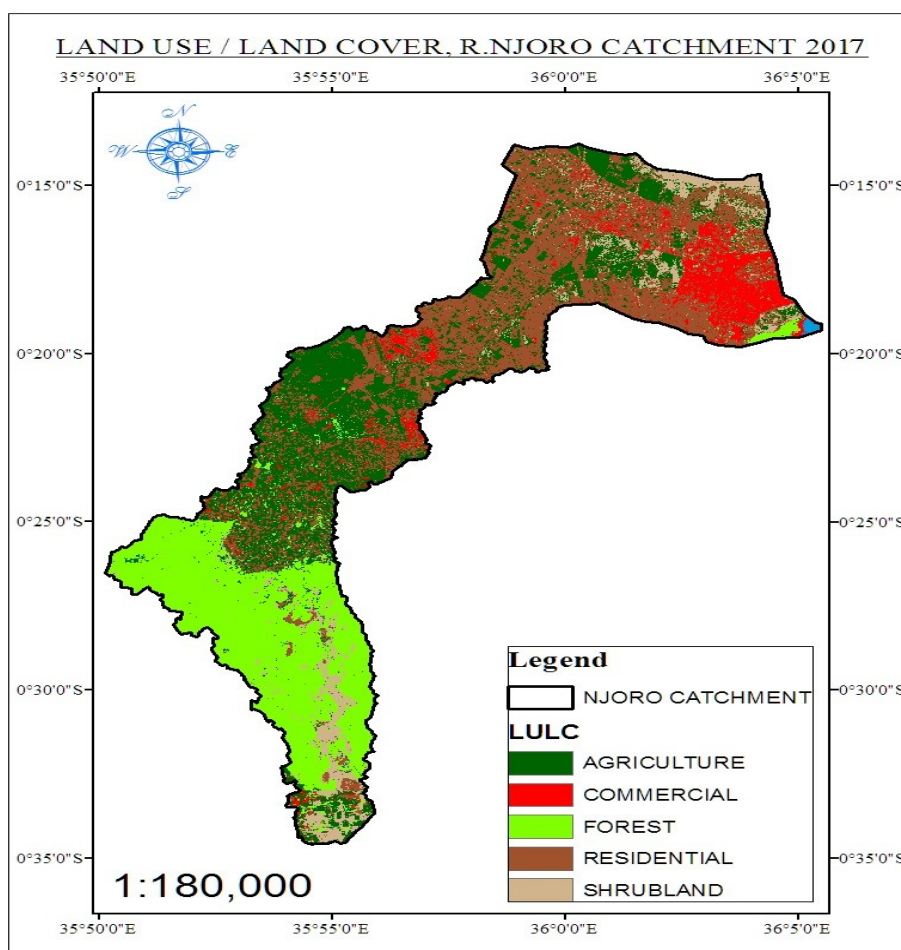
#### Land use/land cover

The dynamics of land cover in River Njoro catchment area has undergone alteration from the start of the 19<sup>th</sup> century attributed to large scale settlement in the upstream and midstream by colonialist and thereafter Kenyan settlers in the 1970's and 1980's. Njoro River 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 displays variation which is dependent greatly on the rainfall reliability. In the upper part of the catchment, forest clearance gave room for agriculture as main activities. The lower part of the Njoro River catchment comparatively receives low and unreliable rainfall as compared to the upper part. In this area, livestock keeping and crop farming is practiced together with irrigation to the land extending to the river banks. The agricultural practice in the steep slopes and near-stream areas draining within the catchment has contributed in the sediment transported out of the catchment. According to Yillia *et al.* (2008) the degradation of the Njoro river catchment has led to poor soil fertility which has eventually reduced the crop yields.

Over the last two decades, River Njoro Catchment has experienced fast changes in land utilisation and growth of population resulting in adverse effects on the water resources. The patterns in land use have been undergoing change dated to early 70's with increasing population which has resulted to increased conversion of forested land into crop cultivation, livestock rearing and settlement areas of Mau Escarpment upstream (Were *et al.*, 2013). Cumulatively four types of land uses would be identified which have subsequently led to the alteration of the hydrological characteristics of the catchment. Beginning upstream at the source of the river, the upstream portion is majorly occupied by forests of indigenous plant species. This gives way to recently emerging settlements on the deforested area which is characterized by settlement and small scale subsistence farms (Kibichii *et al.*, 2007).

Within the River Njoro catchment there are urban centres as another land use category occupying middle and lower streams, covering Egerton University, Njoro Township and parts of Nakuru Municipality. The middle stream and lower stream are areas with high population, industries and commercial activities. At the extreme downstream of the watershed there is Lake Nakuru National Park which border Lake Nakuru. The main categories of land covers within River Njoro catchment as shown in Figure 1 are: Agriculture, commercial and residential settlement, forest, grassland and water body. This has resulted to disparity in water allocations and therefore community involvement is vital to achieve refurbishment and preservation of the hydrologic resources within the Njoro watershed. Based on GIS and Land SAT images for analysing land use activities the main land use activities that were identified within 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: Land use/cover of Njoro River catchment**

### **Geological characteristics**

Geologically the Njoro area is majorly comprised of volcanic soils and rocks (lava and pyroclastics) whose age is Tertiary-Quaternary. These rocks have been affected by sequential faulting, and covered by latest sediments. The geology is distinguished by porous pumiceous formations. Soils as observed by Mainuri (2006) include; Humic Acrisols (Ultisols), Phaeozems (Mollisols), Andosols, Planosols (Aqualfs), Plinthosols, and Fluvisols. The soil textures are varied ranging from clay loams in downstream of the watershed to sandy clay upstream that is covered by indigenous forest areas. Maina & Laude (2016) observe that the watershed is also characterised by loam soils in the forests upstream and deep well drained to moderately deep loamy sandy clays in the downstream areas whose origin is erosive lacustrine.

### **Research design**

This study adopted purposive longitudinal survey and quasi experimental research designs. Rock and samples of water were collected at designated points along the river Njoro and its tributaries for laboratory analysis. The sampling sites in this study reflected variation in geological and topographic characteristics. The study area was stratified into upstream, midstream and downstream zones distinguished by the land use/ land cover variations, topographical and geological considerations for the purpose of rock and water sampling. Based on the criterion of sampling, the points identified included; Sigaoni, Sugutek, Nesuit Centre Bridge and Ndarogo Bridge (upstream), the midstream points were Kwa Maisori spring, KARLO Bridge and KERMA Bridge while the lower stream points were Tumaini Bridge and Kwa Rhoda Bridge. Later the rock and water samples were taken to University of Eldoret chemistry laboratory for analysis of fluorides levels. The sampling points in the study area are presented in Figure 2.

### **Field work**

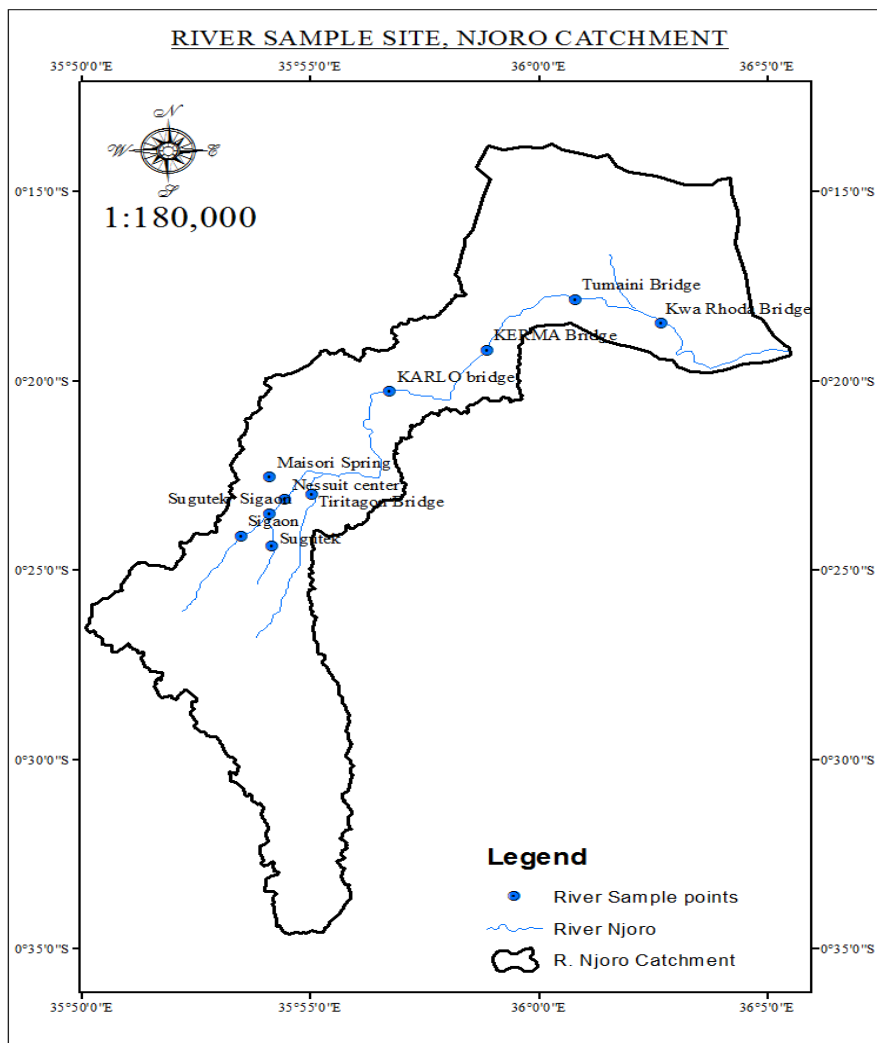
The rocks were sampled by breaking pieces of rock from the rock outcrops at the sampling points to determine the contribution of surface geology to levels of fluoride in the River Njoro catchment. The breaking and sampling of rocks from the rock outcrops and rocks underlying the River Njoro were broken with the help of the geological hammer as shown in plate 1 and packed in labelled in labelled bags as shown in plate 2 at the identified sampling points along river Njoro. The sampling points are shown in figure 2. Later the rock samples were packed into carrying bags which were labelled indicating the GPS and location details of the sampling sites. The rock outcrops were sampled at; 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.



**Plate 1: Breaking Rock samples from rock outcrops**



**Plate 2: Sampling the broken rock particles from the rock outcrops**



**Figure 1: Map of study area showing the rock sampling points**

## **Data analysis**

### **Laboratory data analysis**

Rock samples were analysed according to the American Public Health Association (Neidell *et al.*, 2010) using a fluoride ion-selective electrode (ISE) method. The American Public Health Association method is used to measure total solubilized fluoride available in water meant for drinking, naturally occurring water in the surface, and in soil and rock extracts. Samples were ground into powder using the geological hammer. Thereafter the air dried rock powder crushed from the sampled rock samples was sieved to 2mm and shaken in deionized water (20 ml) in a 50ml conical centrifuge tube for 16-18 hours. After the agitation period the extraction fluid/sample mixture was centrifuged and filtered. The filtrate was collected, preserved and subjected to fluoride levels analysis.

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.

### **Geological data analysis**

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 ground truthing survey. The geological data comprising of the rock/geological formations of river Njoro catchment was analysed from the geological reports of Nakuru by McCall, (1957) and other geological reports provided by the Department of Mines and Geology, Nakuru County. The types of rocks covering River Njoro catchment were also presented in a geological map and the map assisted in identifying the different rock types at the sampled points in the catchment. The surface rocks were descriptively analysed in reference to the geological map of the Njoro River catchment that was developed by the researcher as presented in figure 4.



## RESULTS

### Geological results

Rocks in river Njoro catchment were found to be comprised of Superficial deposits of volcanic soils, black ashes of Rongai, Pyroclastic and sediments of Rongai, Black ashes of Elburgon, Lurmudiack tuff and Eutracite welded tuffs as shown in table 1. Table 1 also gives the rock sampling points, rock types and fluoride levels in the sampled rocks. The black ashes of Rongai were sampled at three sampling points while the black ashes of Elburgon and Eutracite welded tuffs were sampled from two points along the river Njoro catchment. In average the black ashes of Rongai recorded the highest levels of fluoride while Eutracite welded tuffs recorded the lowest fluoride levels in the river Njoro catchment. The results of fluoride analysis in the rocks sampled at the designated water sampling points along river Njoro is also presented in figure 3.

Kwa Rhodah Bridge had Superficial Deposits of Volcanic Soils which recorded fluoride levels of 1.575 mg/l while Tumaini Bridge had Superficial Deposits of Volcanic Soils recording 1.563mg/l. The Njoro-KERMA Bridge had Black Ashes of Rongai and Menengai Pumice rocks which recorded 1.70 mg/l. Similarly, the Nesuit Centre Bridge recorded 1.436 mg/l with the dominant rocks being Black Ashes of Rongai. To the converse the Njoro Bridge, Kwa Maisori Spring, Sigaon River, Kipkogo Spring and the confluence of Sigaon/Sugetek rivers recorded fluoride levels of less than 1mg/l. The dominant rocks with fluoride levels of less than 1mg/l were; Black Ashes of Rongai, Black Ashes of Elburgon, Lurmudiack Tuff and Eutracite Welded Tuffs.

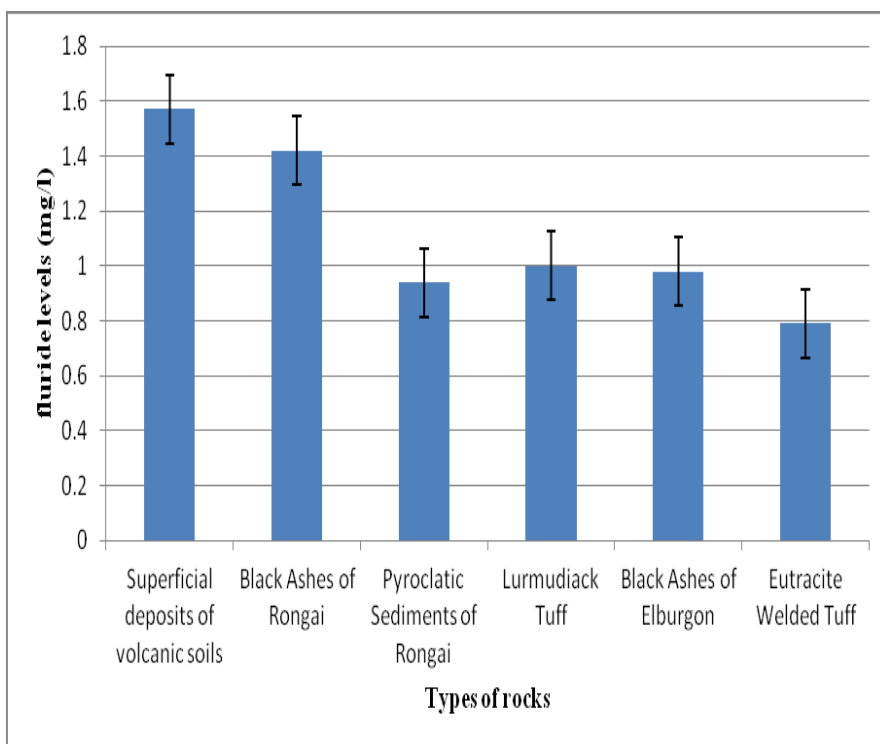


Figure 3: Fluoride levels in different sampled rocks

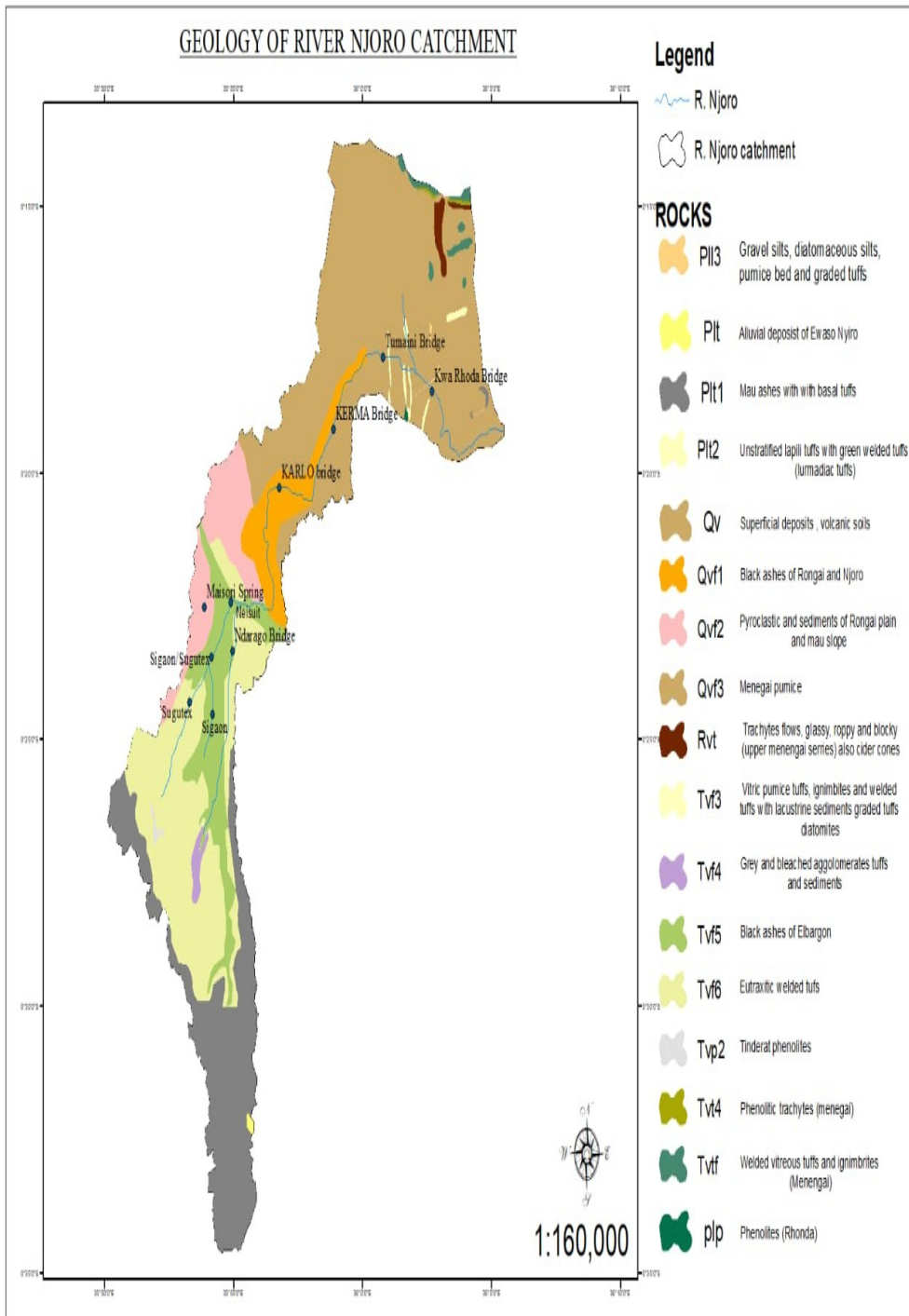
**Table 1: Rock sampling points with the corresponding fluoride levels in the samples**

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

## DISCUSSION

Fluoride was available in all rock types in different quantities in the river Njoro catchment. The varying fluoride levels of would be attributed to mineralization of different quantities of fluoride occurring in the different rock types. Apart from volcanic rocks, high fluoride concentration levels have also been found in Pre-Cambrian rocks and young marine sediments. The East African Rift System's volcanic rocks have higher quantities of fluoride than rocks that are analogous in nature found in other regions. Njoro catchment is situated within the rift valley and therefore geology is bound to have elevated fluoride levels.

This study identified the 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 findings concur with McCall (1957) who documented that volcanic rocks exposed in the Mau Escarpment where Njoro river catchment as the oldest volcanic rocks. 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. River Njoro is cut down through superimposed unconsolidated pumice and ash and runs over the hard upper surface of the black ash.



**Figure 4: Geology of river Njoro and rock sampling points**

In this study volcanic rocks were identified as the main types of rocks along the geomorphological section of river Njoro. Similarly, Ramadan and Hilmi (2014) also agree in their study when they observe that in African rivers occurrence of fluoride is associated with activities of volcanic nature, thermal waters of high pH, granitic and gneissic rocks. Equally the availability of fluoride in water would be attributed to water rock interaction through weathering would be attributed to rocks that are rich in fluoride rich and the process of circulation of water in soil and rock materials (Brindha and Elango, 2011). Further Abdulrahman *et al.* (2013) eludes that fluorite, apatite and micas are the common minerals that bear fluorine.

Important rocks that are associated with presence of fluoride minerals include rocks that are; volcanic, gneissic and granitic in nature. Moreover, fluoride is likely to occur in areas with abundant in fluor spar, cryolite, apatite and hornblende minerals. Chelangat, (2015) equally observes that high fluoride concentrations are associated with rocks that are volcanic in nature, granites and salt deposits that have originated from marine deposits. The types of rock formation in places of high concentrations of fluoride are mostly volcanic and the Njoro Catchment is within this location. Therefore, fluoride levels show variation that is dependent on the nature and rock types and these observations concur with Aldo *et al.* (2018).

## CONCLUSION

The natural sources of fluoride in waters in the Njoro river catchment is attributed to disintegration of rocks that bear fluorine in rocks and in places that have experienced eruption of volcanoes and fumaroles. Fluoride levels in the Njoro river catchment varies markedly from upstream to downstream on the influence exerted by local surface geology. The geology of Njoro catchment is dominated by varied volcanic materials

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