

FLUORIDE IONS IN GROUNDWATER
CASE STUDY;

BARINGO-BOGORIA GEOTHERMAL AREA IN KENYA Paper Title, Title Case

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ABSTRACT

The ground waters extend from the southern shores of Lake Bogoria to the northern shores of Lake Baringo, within the floor of the Kenyan Rift Valley have been examined in relation to the concentration of fluoride. The area is defined by co-ordinates 35° 45' - 36° 20' E, 10 00' - 0° 15' N, and covers approximately 6000 km². Fluoride concentrations as high as 50ppm had been reported and forced abandonment of some boreholes. Most of the members of the community in this area are suffering from the adverse effects of dental and skeletal fluorosis. The World Health Organization (WHO) recommends a maximum limit of 1.5ppm fluoride content in cooking or drinking water. WHO even recommends a lower limit value in an area with hot climate, where people drink more water. Kenya has adopted the WHO guideline of 1.5ppm fluoride limit. This however has been problematic due to the scarcity of water in most parts of the country and therefore people have been forced to take groundwater containing 8ppm fluoride, which is above the average.

Stratigraphically the formations underlying the study area are Tertiary sediments and volcanic; and quaternary sediments overlying the Precambrian basement system. Tertiary volcanics are represented by the Kapchererat basalts in the north and Samburu basalts on the Laikipia escarpment, while the phonolites cover large areas in the Tugen hills. The middle and Upper Pliocene volcanics represented by basalts phonolites and trachytes are found in extensive outcrops in the western slopes of the Tugen hills, unconsolidated or poorly indurated volcanic pyroclastic material/deposits cover large areas of the rift system. The average concentration of fluorine in igneous and volcanic rocks varies from 100mg/kg in ultra mafic rock to 1000mg/kg in alkali rocks. Ash ejected during quaternary volcanism has high fluoride with an estimated global flux of about 50-8600Gg/a. Evaporation and geothermal activity additionally increase fluoride concentrations especially in the lakes of closed basins such as Lake Bogoria.

Maps showing the distribution of the fluoride ions in the ground water were also drawn using ArcView 3. 2 and Surfer. The results showed that the ions are mainly concentrated within the central part of the study area, which lies on the rift valley. The concentrations are mainly controlled by geology. The groundwater samples were analysed for various ions which among others included; F⁻, Mg²⁺, Ca²⁺ HCO³⁻ ions, from the results of the analysis; A correlation of the fluoride concentration to that of Mg²⁺, Ca²⁺ and HCO³⁻ showed fluoride had negative linear relationship with Mg²⁺, and Ca²⁺ ions, however it has a general positive linear relationship with HCO³⁻. The pH of most waters sampled ranged from 7-10 on the pH scale. This means that waters with high concentrations of Mg²⁺, Ca²⁺ will generally have low concentrations of fluoride ions. The results of statistical analysis also indicate that Na⁺ has the highest mean for cat ions and HCO³⁻ has the highest mean for anions and that these ions have a very high positive correlation with fluoride ions.

The ground water fluoride concentration in the area exceeds the set standard limit of 1.5ppm fluoride. The prevalence of skeletal and dental fluorosis and low social economic standards of the community led the adoption of Bonechar defluoridation method. The

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efficiency of this technique rated at ninety percent. The findings in study will facilitate future planning and development of groundwater resource in this area by the various stake holders.

1. INTRODUCTION

It's the goal of every government to provide safe and clean water and for its entire people, to ensure a healthy and productive population. This however is not always possible. In the study, area development of institutions such as schools and dispensaries is

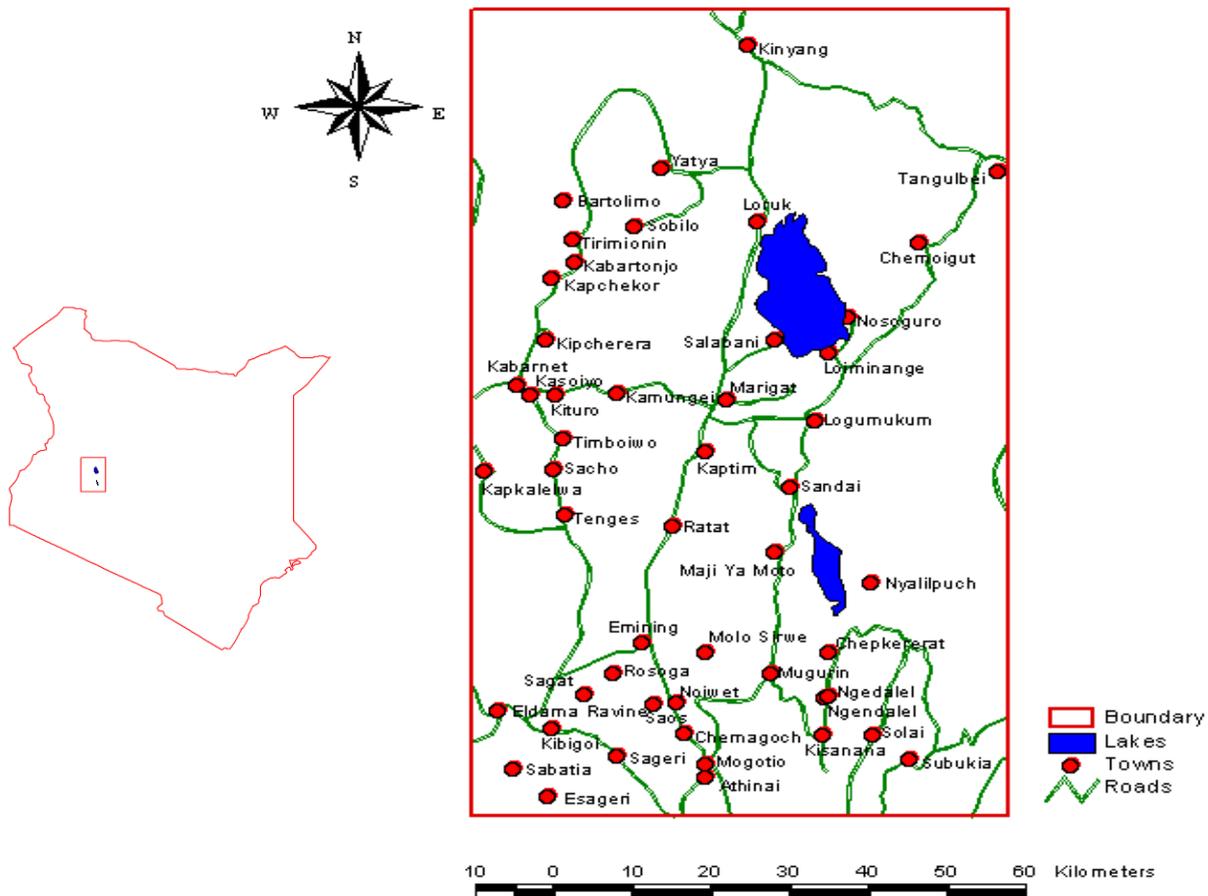


Figure 1: Map of the Baringo-Bogoria study area

hampered by unavailability of potable water. Provision of adequate and reliable supply of clean water within reasonable walking distance is key to stimulating economic growth, public health and thus poverty alleviation. In this regard, the government and non-governmental organization have been working with communities in drilling boreholes. Nevertheless, this is not enough; a further step has to be taken to ensure that the water is not only clean but also safe. This is especially true of the groundwaters from most parts of the East African Rift valley which extends from Syria and Jordan in the Middle East to Mozambique is associated with high fluoride levels in ground waters.

Fluoride is essential to living organisms at concentrations between 1-3mg/day Katsonu et.al.,(2013), when this limit is exceeded it poses a threat to human health due to its high affinity for Ca²⁺ 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 same area have been noted such that shifting the water supply from unsafe surface water to safe groundwater has introduced a fluoride poisoning (fluorosis). The study area had not received the much attention it deserved in relation to fluoride, most members of the community suffer from various degrees of dental and skeletal fluorosis. The study area extends from the southern shores of Lake Bogoria to the north of Lake

Baringo. The geographical co-ordinates are $35^{\circ} 45' - 36^{\circ} 20' E$, $1^{\circ} 00' - 0^{\circ} 15' N$ and the general elevation is on average 965 meters above sea level.

2. GEOLOGY

The geology of the study area is closely related to the formation of the East African rift valley system, which in the project area is bounded to the west by Elgeyo escarpment (over 3000m.a.s.l) and to the East by the Laikipia escarpment (over 2000m.a.s.l). The Tugen hills, which rise to almost 2,500m in the rift valley floor, separate the lowlands of the Kerio valley to the west and Lake Baringo basin on the eastern side. The altitudes of these parts of the study are fall below 1000m. There are numerous seasonal rivers in the district, most of whose bed contain massive boulders. The study area is covered by over 300m of 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 volcanics; Quaternary sediments. Basalts, phonolites and trachytes represent tertiary volcanics. The phonolites cover large areas in the Tugen hills. The middle and Upper Pliocene volcanic rocks are represented by basalts are found in extensive outcrops in the western slopes of the Tugen hills and north of Eldama Ravine.

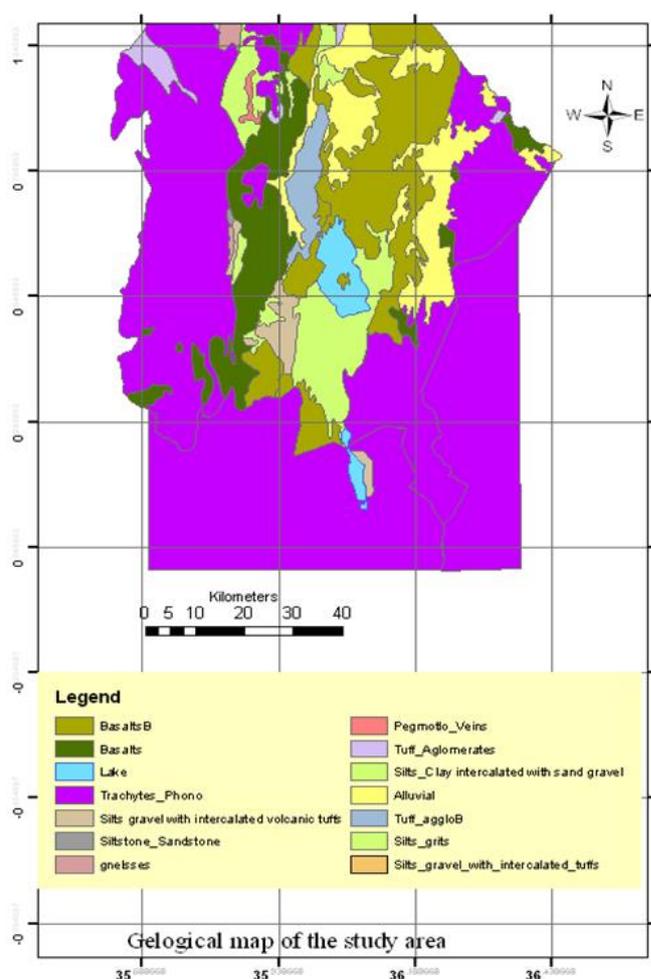


Figure 2 Simplified Geological map of the study area

Locally, piedmont deposits of silt and clay (Loboi plains sediment), occupy a large area between the lakes. The extension and thickness of the sediments is probably more than 1000m suggesting that Lake Baringo was formerly much bigger than at present.

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The rocks of the Basement system include various types of Gneisses, schist, quartzite and marbles. The only outcrop of the Basement rocks in the rest of the district is found along the foot of the Saimo escarpment in the Tugen Hills. Veins and dykes of coarse pegmatites locally occur along the escarpment. Structurally the tectonic events during the Rift formation produced faults of different magnitudes and trends.

3. MATERIALS AND METHODS

For this study random sampling was adopted (samples were taken from different boreholes and a few springs). More than 100 samples were collected. This was based on the geochemical principle that the more the samples and well distributed they are, the more representative they are of the study area (Hem 1959; Oguny 1973). Polyethylene bottle were preferred for the collection and storage of samples for analysis to;

- 1) prevent contamination of metals dissolved from the walls of the containers; a hazard that is always present in the case of glass vessels.
- 2) breakage during transport is minimized.

Stringent measures were also taken when cleaning the bottles to prevent contamination. These containers were cleaned with metal free nitric acid (HNO_3) then rinsed several times with distilled water and deionised water. While in the field each container was again rinsed atleast twice with the water about to be sampled. The geographic co-ordinates and altitude were also taken at the point of collection using a Geographic Positioning System (GPS). This was essential when it came to plotting the data points or relating any chemical constituents to a particular datum point using Arc view GIS or any other software. A review of the geology was also carried out hand in hand with sample collection to come up with a geological map that could be used to relate the fluoride concentration to the geological formation.

Most of the boreholes in this study are community owned and were drilled during the period 2003-2005 under the Belgium technical cooperation (BTC) with the government of Kenya. The main contractors are The Catholic Diocese of Nakuru; hence, the data collected is highly reliable. The total depth and water rest levels were also recorded in order to come up with a reliable groundwater contour map that could be used to delineate ground water discharge and recharge areas. This data was from contractors since most of the boreholes are sealed at the time the data is collected.

2.1 Chemical analysis

Chemical analyses carried out in this study area were nearly all on ground water, exceptions being the two lakes and some of the major rivers. It has been remarked (Hem, 1959; Powell in Ven te Chow, 1964) as sited in (Maina,1982) that a single sample from a groundwater source may represent closely the quality of water from that source for many years. The importance of groundwater quality has also been noted by Todd (1959) when he stated that quality of ground water is of nearly equal importance to quantity. Data obtained from such chemical analysis was subject to interpretation. Among the many methods suggested for the determination of fluorides are sometimes consuming, expensive and inaccurate due to interference by other ions causing problem of accuracy. Hence, the method chosen for analyzing fluoride must be of such sensitivity that even small quantities down to less than 1mg/l can be detected accurately. The ions selective method was therefore used to determine the concentration of fluoride in the samples. The table below shows the various methods used to analyze various constituents in this study.

Table.1 Parameters analyzed and Methods Used.

Methods of analysis used	Parameters
Ion selective Electrode	Na, F, NO_3 , K, Ca
Edta-Tritimertric Method	Hardness
Argentometric method	Cl
Calculation Method	Mg, HCO_3
Instrumental measurement	Conductivity
Turbidimetric Method	SO_4
Electrometric method	pH

2.2 Data Analyses

Data was first analyzed to show the mean relative to the WHO standards set for all the chemical characteristics tested. Linear regression analyses was used as a tool to determine whether two ranges of data correlated in order to find out whether large values of one set were associated with large values of the other (positive correlation), whether small values of one set are associated with large values of the other (negative correlation), or whether values in both sets are unrelated (correlation near zero). Trend lines were used to graphically display trends in data and to help in prediction.

Arc view GIS was used to show the spatial distribution of boreholes in the study area. Then show the various concentrations of fluoride Surfer 32 was used to come up with a contour map showing the spatial distribution fluoride ions.

4. RESULTS AND INTERPRETATION

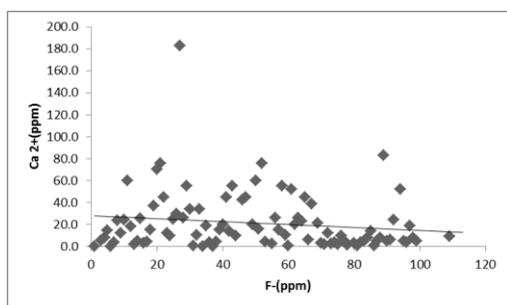


Figure 3: Ca²⁺ Vs F⁻(ppm)

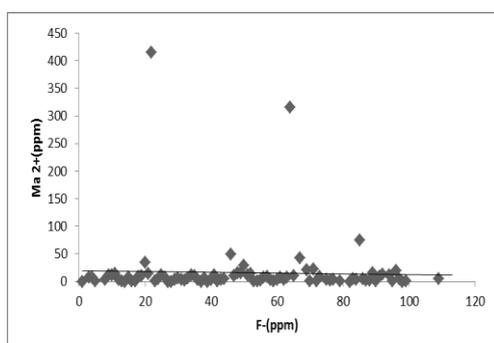


Figure 4: Mg²⁺ Vs F⁻(ppm)

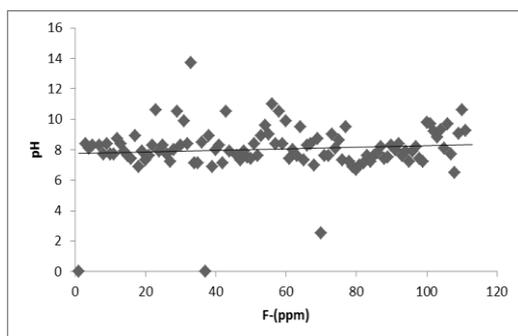


Figure 5: pH Vs F⁻(ppm)

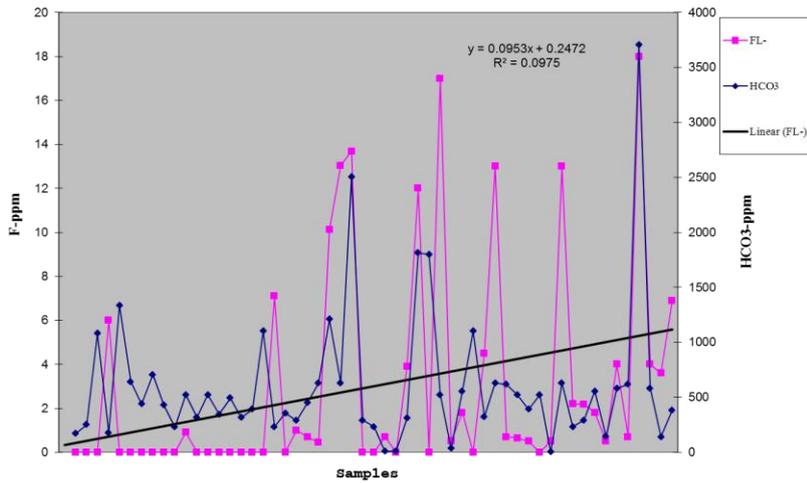


Figure 6: F⁻(ppm) VsHCO₃⁻ (ppm)

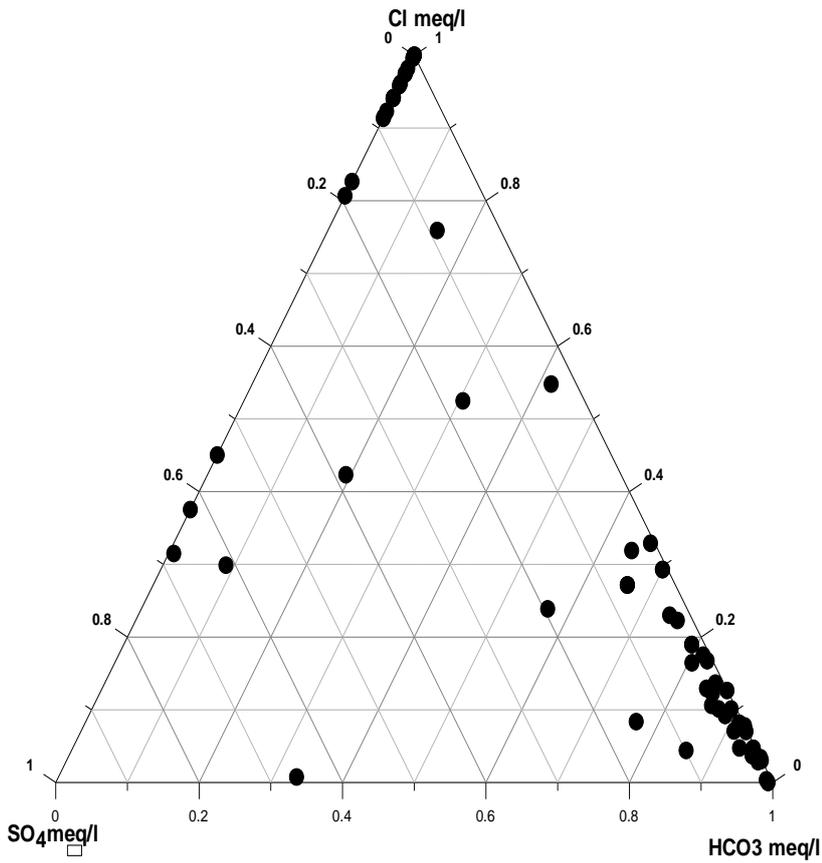


Figure 7: The SO₄⁻-CL⁻-HCO₃⁻ Ternary Diagram for the Baringo-Bogoria Geothermal area

The diagrams above indicate chemical characteristics of groundwaters containing fluoride ions in the study area as follows;

- Fluoride ions have a general negative linear relationship with Ca and Mg ions.
- Most samples pH fall in the range of 7-9ppm
- Most of the waters plot on the HCO₃⁻ side implying that most fluorotic waters are highly bicarbonate

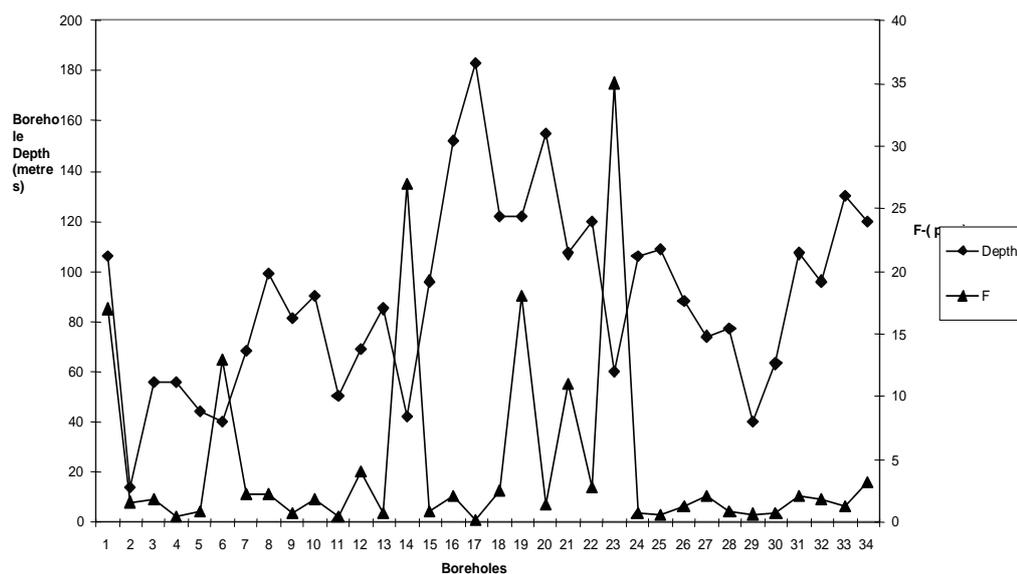


Figure 8: Relationship between Fluoride concentrations in Relation to depth

No relationship could be established between fluoride concentration and depth of the boreholes. Wide differences were noticed in the concentration of the ion in the samples from boreholes having approximately equal depth and situated in the same vicinity. As shown

4.1 Occurrence of fluorides

It occurs notably as fluorspar (CaF_2), Cryolite (Na_3AlF_6), Fluoroapatite, ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), as fluorapatites found in sedimentary rocks (limestone and sandstone) and as Cryolite in igneous rocks (granite). It's generally concentrated in the later stages of crystallizing magmas and in the residual solutions and vapors. Higher concentrations are encountered in siliceous igneous rocks (750ppm), alkali rocks (950ppm) and hydrothermal solutions (400ppm), (Frencken, 1992).

1. Fluorite CaF_2 with 49% F
2. Fluoroapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ with 13,500-26,000ppm F
3. Topaz $\text{Al}_2\text{FeSiO}_4$ 21% F

Some micas may reach a concentration level of 68,000 ppm F

Fluoride in water usually originates from different types of minerals as mentioned. These fluoride minerals are nearly insoluble in water. Hence fluorides will be present in ground water only when conditions favor their solution. It's also present in sea water (0.8-1.4ppm), in mica, and in many drinking water supplies. The Fluoride content in mica's varies considerably Table.2 (Frencken, 1992).

According to (Allmann and Koritnig, 1974) "The fluoride excess, which cannot be incorporated in the crystalline phases during magma differentiation, is accumulated in hydrothermal solutions." hydrothermal fluorite deposits and veins are formed by these fluids. It has also been noted (Rosi et al., 2003) that fluoride transport in aqueous solutions is controlled mainly by the solubility of CaF_2 (Additionally, the (calc-) alkaline volcanoes, typical of continental rift (East Africa), hot spot, continental margin (Andes) or island arc (Japan), produce relatively fluorine-rich lavas

Table.2 Fluoride content in Mica's

Mica	Concentration
Biotites	70-500ppm
Phlogopite	3300-37000ppm
Lepidolite	19000-68000ppm
Muscovite	170-14800ppm

Fluoride is generally concentrated in the later stages of crystallizing magmas and in the residual solutions and vapors. These juvenile sources can escape as gases and fumaroles and get dissolved in the ground water. Higher concentrations are encountered in siliceous igneous rocks (750ppm), alkali rocks (950ppm) and hydrothermal solutions(400ppm).

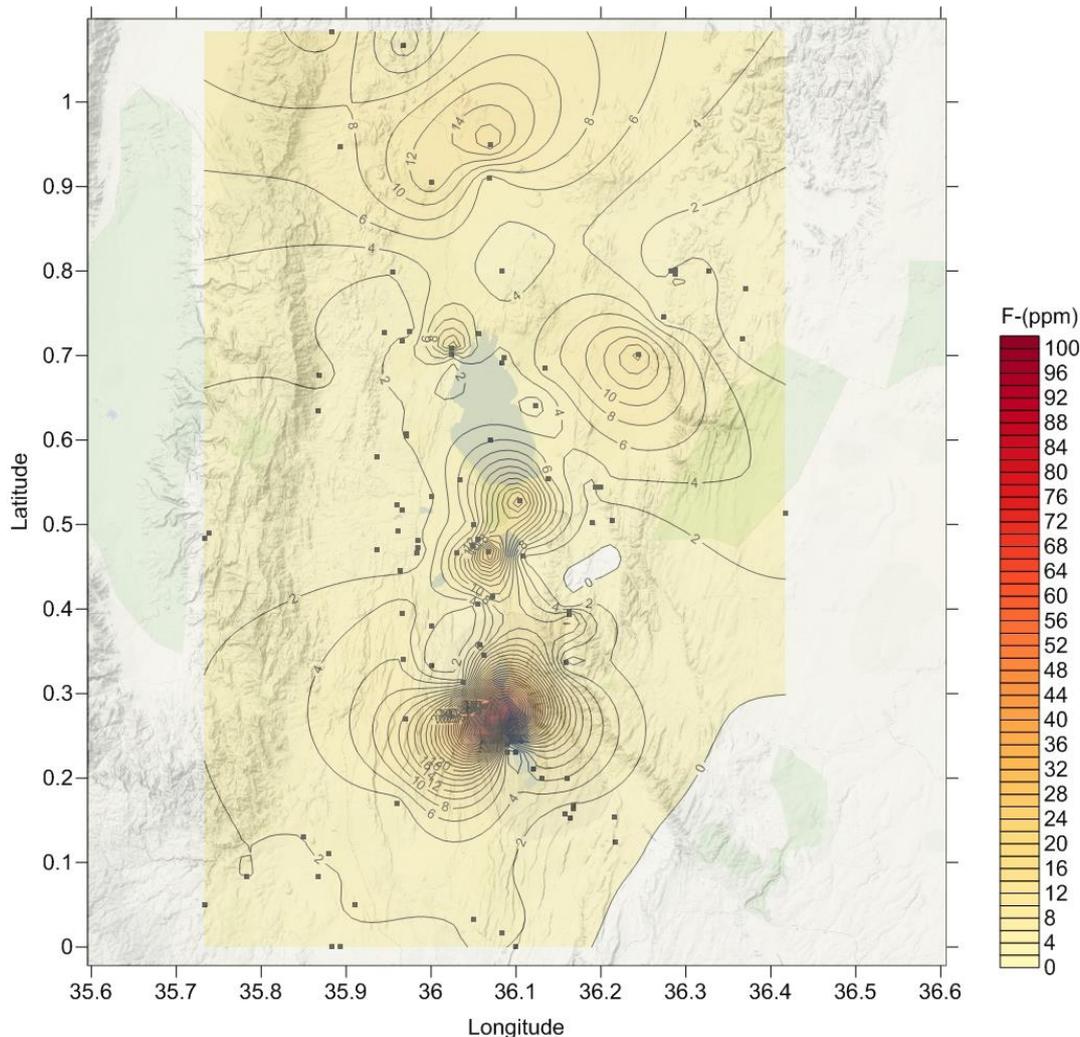


Figure. 9 The Distribution of fluoride ions in the Lake Baringo-Bogoria Geothermal area.

The contour map delineates fluoride distribution in the Baringo-Bogoria Geothermal area. The fluoride concentrations are highest in the central part of the study area with the lowest elevation and around Lake Baringo and Lake Bogoria with concentrations varying from 108ppm in the Bogoria springs to an average of 6.0ppm for the groundwater samples from boreholes drilled in the area. In the central part around Lake Baringo and Lake Bogoria we have highly unconsolidated or poorly indurated volcanic pyroclastic material and sediments that cover a large area that is generally flat, with the ultimate fluoride content in groundwater highly dependent on the residence time. It is possible that these are easily decomposed and leached in the Lobo plains where water is slow moving and has long residence times hence the high concentrations in the groundwaters. The high concentrations could also be attributed to high temperatures increasing solubility and mobility of the ions which could be attributed to the elevated temperatures as a result of hydrothermal alteration, the area is known to be geothermally active as evidenced by the presence of fumaroles and hot springs.

4.2 Hydrogeology

Ground water occurrence is controlled by the available geological conditions. The project area is situated in a zone with low-medium to high ground water potential. Ground water occurs in weathered and fractured zones in volcanic rocks; sediments interbedded between volcanic rocks; and alluvial and torrent wash deposits. Fresh volcanic rocks are known to be virtually compact and with no intergranular or primary porosities and thus their storage and transmitting capacities are limited. Large

variations in rainfall are related to the physiography of the area which influences the distribution of available recharge. Furthermore, rainfall and availability of permanent river water, away from Lake Baringo decreases generally towards the north.

The Lobi Plains occupy the flat area of approximate elevation, 1000 m.a.s.l between Lake Bogoria and Lake Baringo. The area is largely covered with fluvio-lacustrine deposits, which at some places exceed a thickness of 600m. No faults have been detected in the area. The ground water potential of the Lobi plains is low because of the low transmissivity of the sediments and presence of saline water at depth. The shore of the northern half of lake Baringo and the area north of it are covered with Quaternary volcanics (trachytes, basalts and pyroclastics) and sediments. The recharge conditions in this area are favorable due to expected higher permeability of the volcanic rocks. However, the aquifers are quite to be deep at about 100m

The Mukutan-Tangulbei basin is characterized by trachytes overlain by alluvial deposits in some parts underlain by basalts and phonolites. The area is considerably fractured with elongated faults running north south, which form good recharge elements. A major escarpment runs from the area near Tangulbei to the south near Lake Bogoria. On the down throw side, which is to the west of Laikipia Plateau infiltration of rainwater occurs through the faults and fractures and therefore the aquifers here are largely controlled by these structures. Some of the sediments have substantial thickness and form good aquifers.

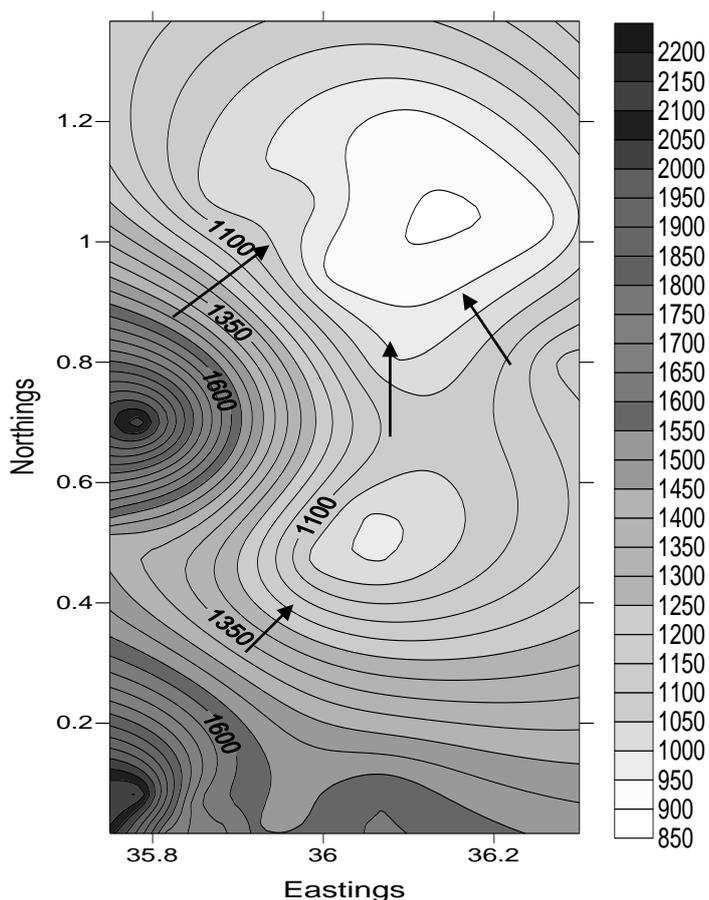


Figure 10: Map Showing possible flow direction of ground water.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Fluoride concentration in ground water in the Baringo-Bogoria Geothermal area exceeds the limit of 1.5ppm for portable drinking water that is recommended by WHO. The geology of this area is large composed of igneous rocks e.g. trachytes, trachyphonolites and sediments with some volcanic origin i.e. ash from volcanic eruptions that occurred at different time periods serving as clear indications of hydrothermal activities. The area is known to be geothermally active with some surface manifestations serving as evidence of hydrothermal activity. According to (Frenken,1992) higher concentrations of fluoride are encountered in siliceous igneous rocks (750ppm), alkali rocks (950ppm) and hydrothermal solutions (400ppm). When conditions allow fluoride will be implying that fluoride concentrations in natural waters depends on;

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- Availability and solubility of the parent fluoride minerals with which the water interacts,
- Porosity of the rocks or soils through which the water passes.
- The concentration of calcium and magnesium ions in water.
- The temperature of interaction between rock and water
- The hydrogen ion concentration of the water i.e. pH
- and the residence time

This area is ranked as water scarce area, therefore since it's impossible to avoid groundwater as the only source of portable water its paramount that ways of defluoridating water are sort, from the analysis of data its evident that the fluoride ions have a high affinity for Ca^{2+} ions in the bone and teeth. Therefore the defluoridation using bonechar as the filter medium, should be considered as it has already been applied successfully in Kenya.

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