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The occurrence of geogenic fluoride in shallow aquifers of Kenya Rift Valley and its implications in groundwater management

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ABSTRACT

Widespread concerns about high-fluoride groundwater and their health risks have been raised worldwide. Weathering of volcanic minerals is regarded as a principal source of groundwater fluoride in regions with volcanic bedrocks. However, how does the volcanic minerals control fluoride occurrence, if it induces other hydrogeochemical processes participating in and how this relates to human health still remain unclear. This study takes Kenya Rift Valley, which has volcanic geological formations, as an example to delineate the occurrence and origins of high-fluoride shallow groundwater with analysis of hydrochemistry, graphical and multivariate statistical methods. Over 40% of shallow groundwater (F^-: up to 23.5 mg/L) show elevated fluoride values over the WHO standards of 1.5 mg/L. High fluoride groundwater are generally Na-rich and Ca-poor with high pH and HCO_3^- concentrations. Hydrogeochemical and principal component analysis indicate that weathering of hyper-alkaline volcanic rocks could release accumulated fluoride in melts and volatile fractions, as well as in clay minerals. Alkaline condition and high HCO_3^- contents lead to the competitive desorption of F^- from clay minerals and Fe-hydroxides into groundwater. Clay minerals also provide abundant exchange sites where cation exchange happens and promotes the release of F^- from the sediments by controlling the dissolution/precipitation of calcite and fluorite. Health risk assessment results show that chronic health risks by groundwater geogenic fluoride ingestion are identified to various individuals, with highest threats in children. Finally, a conceptual model has been developed to demonstrate the formations of high geogenic fluoride groundwater in regions with volcanic bedrocks and its relation with human health.

1. Introduction

With the explosion of population growth and expansion of economic activities worldwide, increasing water demand is occurring (Narsimha, 2020). Compared to surface water bodies, groundwater is generally considered to be less susceptible to contamination and pollution (Meffe and de Bustamante, 2014). Hence, groundwater is the most extracted water resource and intensively consumed to meet all major demands such as domestic, agricultural, and industrial (Li et al., 2019; Rashid et al., 2018). However, due to the unreasonable exploitation and utilization of groundwater resources, aquifer contamination is a growing problem in many parts of the world (Banerjee and Nagesh, 2018; Chaudhuri and Ale, 2014b; Narsimha, 2020; Vithanage and Prosun, 2015). Geogenic F^- contamination in groundwater is a representative major concern and being a challenge for safe water supply. Long-term intake of high fluoride groundwater can lead to maladies of water-borne disorders, such as dental fluorosis, skeletal fluorosis, and even tissue and organ carcinogenesis (Xiao et al., 2022). A guideline value of 1.5 mg/L is given by the World Health Organization (WHO) for long-term exposure (WHO, 2004). Studies have shown that regions that have low to high fluoride contamination in groundwater are mostly characterized by the presence of crystalline basement rocks or volcanic bedrocks during which the dissolution of F-containing minerals is promoted by arid/semi-arid climatic conditions (Kim and Jeong, 2005; Macdonald et al., 2011). Additionally, most high fluoride groundwater belongs to Ca^{2+} deficient Na-HCO_3 type water with higher residence time, and longer distance from the recharge areas (Banerjee, 2015; Lavanya et al., 2017).

Kenya Rift Valley is arid/semi-arid lands, where groundwater accounts for over 60% of water resources for domestic, agricultural, and industrial use and over 85% of the population depend entirely on groundwater. However, high concentrations of geogenic fluoride, up to 180 mg/L in groundwater, have been reported in Kenya (Ayenew et al., 2008; MacDonald et al., 2012). This elevated level of F^- has resulted in

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the prevalence of fluoride related health problems such as dental and skeletal fluorosis (García et al., 2012; Gevera et al., 2018; Fig. 1). Plenty of researches are focus on the extent of fluorine toxicity and levels of fluorosis through drinking high fluoride groundwater (Rango et al., 2012). Other regional studies have determined the hydrogeological characteristics and hydrogeochemical behavior of fluoride in natural waters (Tiwari et al., 2012). It is generally believed that the principal source of fluoride in groundwater of Kenyan relates to water interactions with rocks, especially volcanic minerals (Olaka et al., 2016). But it is more necessary to know not only the source but also how does the volcanic minerals weathering control fluoride occurrence, if it induces other hydrogeochemical processes taking part in and how this relates to human health. Without such knowledge, it is difficult to develop effective exploitation and management strategies for groundwater of the Kenya Rift Valley.

Therefore in the present study, the hydrogeochemistry of groundwater and geological formations for enrichment of F^- in groundwater of Kenya Rift Valley have been evaluated. The main objectives of this paper are as follows: (1) to delineate the occurrence of F in the groundwater, (2) to identify the origins of high geogenic fluoride groundwater, placing more emphasis on weathering of volcanic minerals and its induced hydrogeochemical processes participating in, and (3) to relate the geogenic fluoride with human health. Only by understanding these will it be possible to implement groundwater management strategies and reduce the health impact of fluoride in groundwater in places with similar geologic settings.

2. Study area

2.1. Location

The study area is located in the central upper region of the Kenya Rift Valley within the large Nakuru County in the Republic of Kenya (Fig. S1 and Fig. 2). It covers a total area of 7484 km^2 and extents between latitudes − 1.07 N and − 0.30 N, and longitudes 35.42 E and 36.6 E. The altitude of the area lies between 1642 m to 2302 m. According to Kenyan National Bureau of Statistics (KNBS) of 2019, there are 47 million people within the study area. Decades of population pressures have brought about changes in land use patterns from former highland areas to relatively large, intensive farms (Mutoko et al., 2014). However, farms within the Kenya are often integrated crop-livestock production systems, with stock farming thriving and maize being the main food crops (Herrero et al., 2014; Van de Steeg et al., 2010). Hence, the study area is still a zone with low agricultural activity intensity.

2.2. Climate

The study area belongs to equatorial climate influenced by the seasonal migrations of the Inter-tropical Convergence Zone (ITCZ), leading to a strongly bimodal annual cycle with seasonal precipitation concentrated in March/April and October/November. Due to the large differences in altitude, considerable variations in rainfall, temperature, and vegetation are observed throughout the catchment area. The average rainfall is about 650 mm/year, whereas the Aberdare range (Fig. S1) in the Eastern part of the catchment receives up to 2400 mm/year precipitation. The inter-annual variations in precipitation are linked to E-W adjustments in the zonal walker circulation associated with the Indian Ocean Dipole and the El Nino Southern Oscillation (Shaji et al., 2007). The average annual evapotranspiration reaches up to 1800 mm. The temperature varies in the study area, with a mean annual temperature of 28 °C at the rift floor and 18 °C at the escarpments (Winsemius et al., 2014; World Wide Fund for Nature, 2006).

2.3. Geology and hydrogeology

The catchment is bounded by high escarpments in the east (4000 masl), west (3080 masl) and south (2434 masl), with a significant drop to the Rift floor at 1880 masl. The lithology of Kenya, in general, varies from sand, clay, sandstone, shale, and limestone. The study area is comprised of Miocene phonolites in the east, welded and unwelded tuffs, minor rhyolites, trachyte, basalts tuffs, and pyroclastic in the west (Fig. 2). The most geological features are the faults and the Rift boundary that down faulted to form the central block of the Rift valley. It extends from NW-SE, and from N-S to NW-SW in the Rift floor. E-W trending faults are confined to the south area and associated with a strong fumarolic activity or geothermal activities (Omenda, 1998; Simiyu and Keller, 2000).

In general, the movement of groundwater is heavily dependent upon regional and local geology. The role of Rift and faults in the hydrodynamics and the understanding of the flow system have been approached

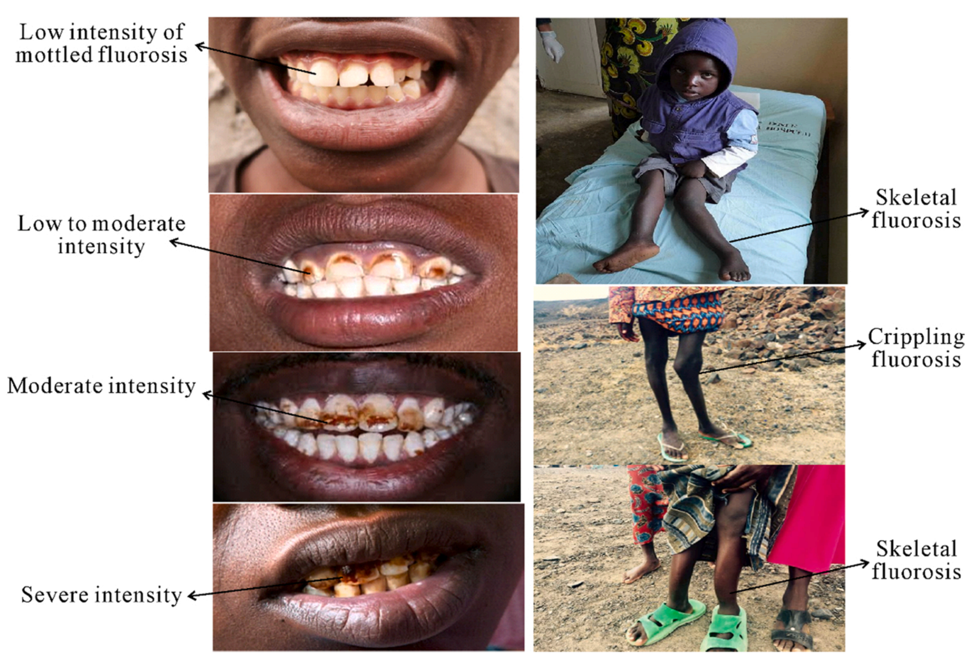

Fig. 1. Health disorder related to fluoride contaminated groundwater of study area.

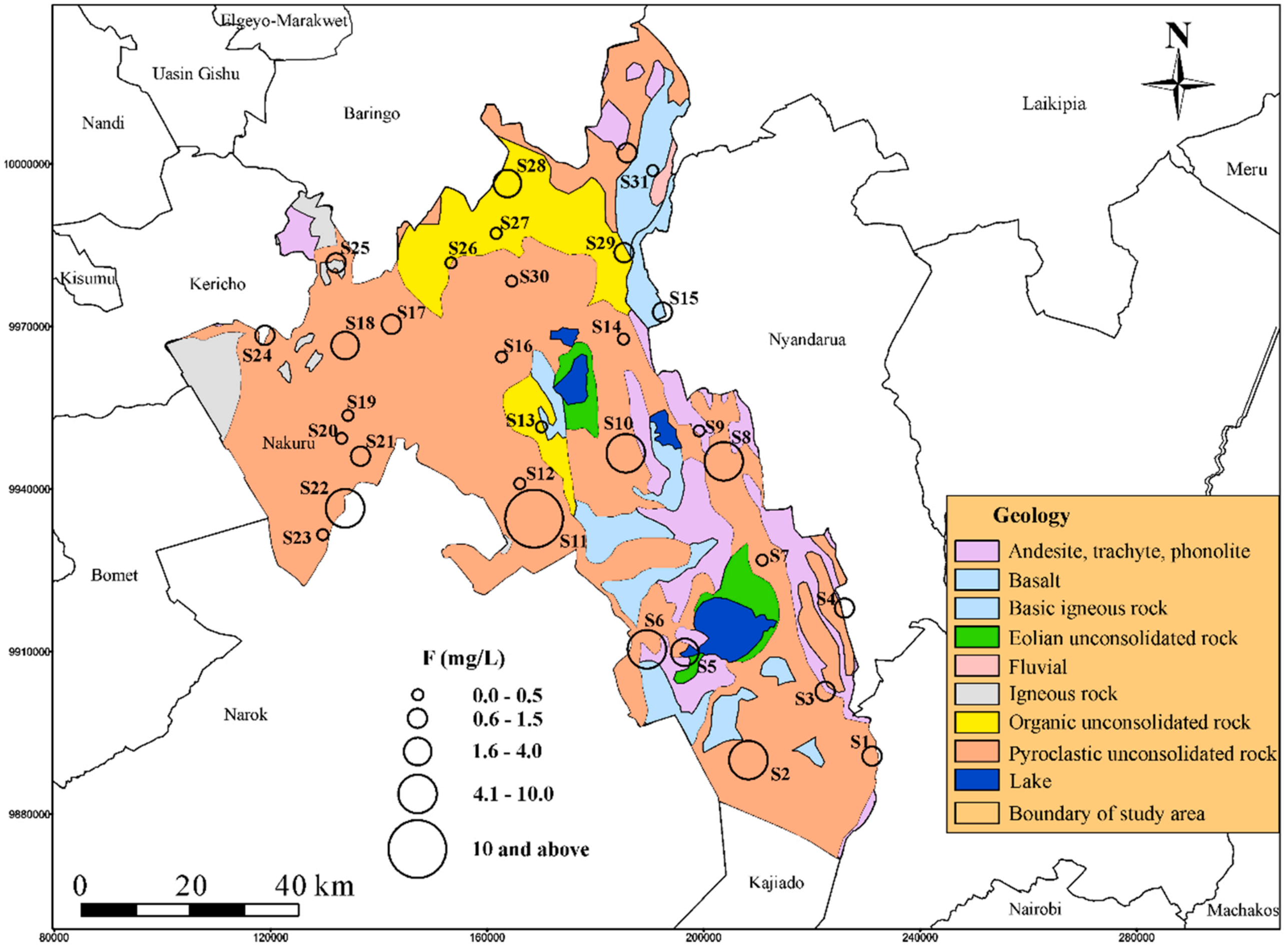

Fig. 2. Geology of the study area, with the fluoride concentration levels of the groundwater samples marked.

either solely or principally, using piezometric levels as the determinant for the flow pattern of groundwater (Chen et al., 2016). In the Kenya Rift Valley, the groundwater flow pattern is less complicated since the flow of groundwater often follows the topographic slope. The subsurface hydrology of the rift valley plays a greater role in groundwater balance than that of most lakes within the Rift (Kuria, 2013). Therefore, this signifies the importance of hydrogeological study with the movement and occurrence of groundwater and its relation with subsurface hydraulic interconnection (Didar et al., 2017; Macdonald et al., 2011). The volcanic and quaternary geological formations are rich in groundwater: shallow unconfined aquifer (<75 m) and intermediate confined aquifer (>75 m). Shallow aquifers have been extensively exploited within the study area for the provision of water. The groundwater is mainly replenished by atmospheric rainfall occurring in the highlands. Leakage of perennial and seasonal streams through river channels are additional sources of groundwater recharge (Bonetto et al., 2021). The rift floor represents the regional major discharge areas, with evapotranspiration and artificial abstraction being the other ways of groundwater discharge.

3. Methodology

3.1. Sampling and analysis

The identification and selection of the groundwater sampling locations were planned by taking into consideration of the previous geological, hydrogeological and geochemical studies of the entire Rift valley. A total of 32 groundwater samples from shallow aquifers was collected from the study area between 2018 and 2019 for hydrogeochemical analysis (Fig. S1 and Fig. 2). All the groundwater samples were collected from shallow active pumping wells with a depth of between 20 m and 75 m used for domestic purposes. Hydraulic head in each sampling point, as well as static water level and well depths, was recorded to establish the flow direction of the groundwater. Before sampling, the wells were pumped for 5–10 min. Samples were stored in new polyethylene bottles that have been rinsed two to three times with deionized water. Unstable parameters including EC, pH, and TDS were measured using Hanna HI 9811-5 multimeter in the field, which had been calibrated before. The alkalinity (HCO_3^- and CO_3^{2-}) was determined using the Gran titration method on the sampling day. The groundwater samples after collection were preserved according to the protocol designed by the American Public Health Association (APHA) of 1995 and 2003 standard methods. Within 2 weeks after sampling, the water samples were analyzed for other hydrochemical parameters, i.e., total hardness (TH) as $CaCO_3$, major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and NO_3^-), and fluoride (F^-) at the Ministry of Water Resources Management Central Laboratory in Nairobi Kenya. Total hardness was measured by the titrimetric method using a standard EDTA solution. Calcium and Magnesium were determined by titration with standard Ethylene Diamine Tetra Acetic acid solutions (EDTA). Chloride was analyzed by the titration method with silver nitrate. Sodium and Potassium were measured using the Model 130 Systronics Flame Photometer. Sulfate and nitrate ion concentrations were determined by the colorimetric method using a UV visible spectrophotometer. The fluoride concentration was analyzed electrochemically, using a fluoride ion-selective electrode (Orion fluoride electrode coupled with an Orion electrometer) according to the APHA standard method of 2003. Analytical precision for the measurements of cation and anion, expressed as the ionic charge balance error, was within the standard limit of ± 5% (Gao et al., 2020).

3.2. Health risk assessment

Human health risk assessment is an important tool to calculate risk exposure of fluoride through ingestion, dermal and inhalation pathways (Kaur et al., 2020). Oral ingestion of drinking groundwater is considered to be the prime exposure pathway in this study. Therefore, the fluoride concentration was chosen as the pollutant for risk assessment. Different input parameters and their respective values used for the estimation of average daily dose (ADD) were listed in Table S1 (Asante-Duah, 2002; Chen et al., 2021):

$$ADD_{\mathbf{Ingestion}} = \frac{CP * IR * EF * ED}{ABW * AAET} \quad (1)$$

where CP is the concentration of pollution, IR is ingestion rate, EF is exposure frequency, ED is exposure duration, ABW represents averaging body weight and AAET is age exposure time.

Usually, the lethal effects of F from the ingestion are measured through the following equation:

$$HQ_{\mathrm{Ingestion}} = \frac{ADD}{RfD} \quad (2)$$

Where HQ is the health hazard quotient and RfD is the oral reference dose representing the maximum permissible average daily intake (set as 0.06 mg/kg/day in this study). Generally human exposed by groundwater fluoride ingestion is safe if HQ > 1, otherwise is risky.

4. Results and discussion

4.1. Groundwater chemistry

The groundwater within the study area has a pH value of 6.38–9.5 (Table S2), indicating nearly neutral to weakly alkaline conditions. All the samples are colorless and odorless. Groundwater temperature (T) range between 28.3.3 °C and 36.2 °C. This high temperature would increase the rate of evaporation which subsequently enriches the water component concentrations. The physicochemical compositions of groundwater vary over a wide range, indicating that the groundwater in the study area is not uniform (Table S2). Sodium is the major abundant cation with concentrations up to 2390 mg/L, followed by calcium (0.8 mg/L – 1808 mg/L) and magnesium (0.4 mg/L - 613 mg/L) (Fig. 3 (a) and Table S2). Potassium has the least concentration of 0.79 mg/L-61.2 mg/L. Bicarbonate is the most dominant anion, varying from 102 mg/L to 4170 mg/L. The higher proportions of bicarbonate over other anions reflect weathering of primary silicate minerals and carbonates which tend to enrich bicarbonate and F^- contents in the groundwater. This concurs with other studies reporting that chemical weathering and dissolution of F-bearing minerals such as topaz, fluorite, fluorapatite, micas, amphiboles, cryolite, villiaumite and carbonates increase fluoride ions in groundwater (Mamatha and Rao, 2010; Rose, 2002; Todd and Mays, 2005). The concentration of Cl^- in the groundwater ranges between 0.1 mg/L and 8400 mg/L with a mean value of 1028 mg/L, falling above the WHO permissible limit of 250 mg/L. The content of SO_4^{2-} varies between 3.58 mg/L-2710 mg/L with a mean value of 348 mg/L.

The range of total dissolved solids (TDS) in the groundwater is quite wide, being 149 mg/L and 17,800 mg/L. The high mean value of TDS (2707 mg/L) indicates significant groundwater deterioration. According to the classification of Todd and Mays (2005) and Krishna et al. (2015), over 80% of groundwater samples within this study area fall under brackish category with TDS values between 1000–10,000 mg/L. Only 20% of samples are fresh groundwater with TDS less than 1000 mg/L. The hydrochemical types of water samples in the study area are diversified. Low fluoride groundwater normally belong to SO_4-Cl and Ca-Mg-HCO_3 types, while groundwater with high fluoride values are typical Na-HCO_3 type water (Fig. 3(b)).

4.2. Distribution of fluoride in groundwater

The F^- concentration in groundwater of the Kenya Rift Valley varies between 0.01 mg/L and 23.5 mg/L, with a mean value of 3.35 mg/L. Approximately 40% of the groundwater in shallow aquifers within the study area exhibits high fluoride values over the WHO/Kenya Standards (F: 1.5 mg/L). The distribution of F^- in groundwater within the study area shows wide spatial heterogeneity (Fig. 2) with samples from similar elevation demonstrating large fluoride content variations (Table S2). It is interesting to note that F^- concentrations in the upper zones of the study area are found to be relatively higher with similar spatial variation. In the upper zones, igneous geological formations render the leaching of fluoride-rich igneous rocks (e.g., fluorspar), thereby enriching the F^- contents. Hence in this case, geological condition plays a critical role.

4.3. Association of fluoride with other parameters of groundwater

To establish the relationship between fluoride and other physicochemical parameters in groundwater, correlation analysis is applied (Fig. 4 and Table S3). Positive correlations between F and pH, Mg, K, Na,

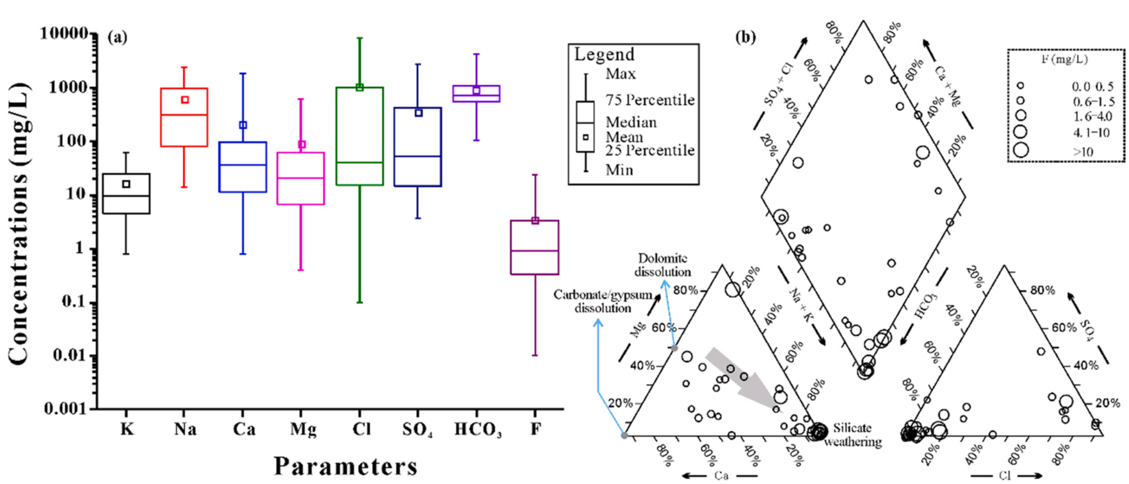

Fig. 3. (a) Box plot for the maximum, minimum, and average of the chemical constituents, including K, Na, Ca, Mg, Cl, SO_4, HCO_3 and F in groundwater of the study area; (b) Piper trilinear diagram showing groundwater facies.

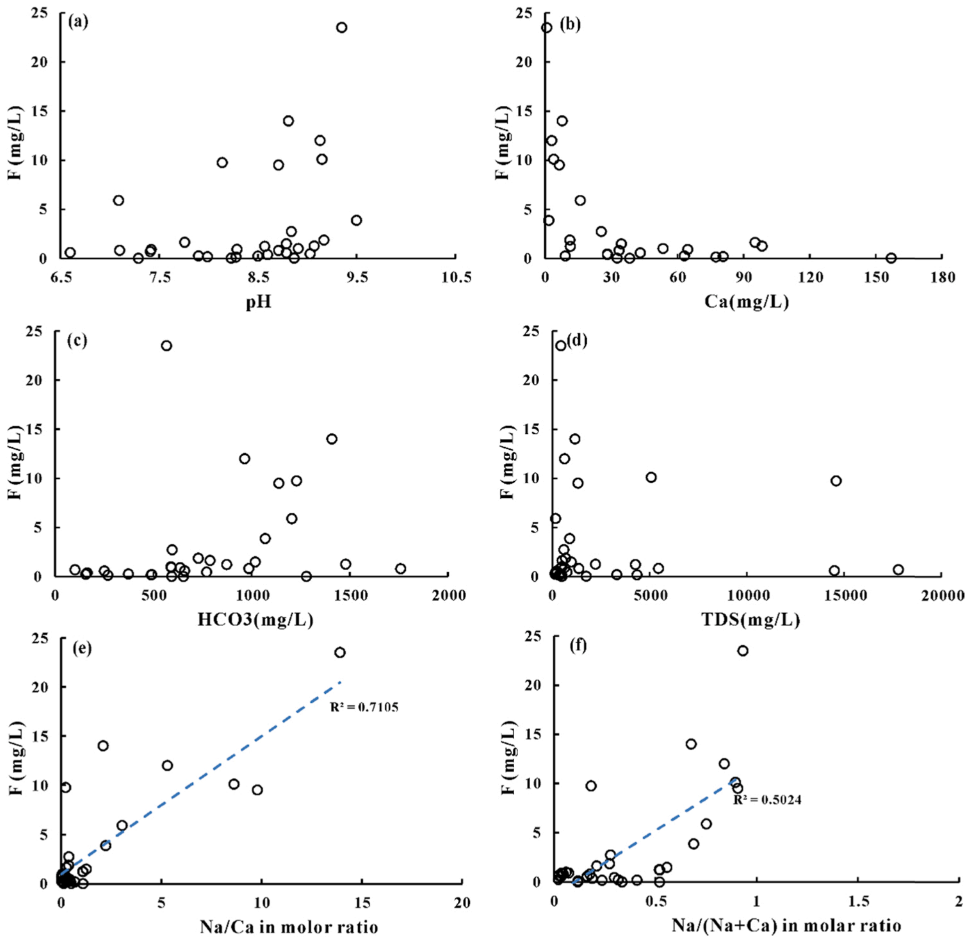

Fig. 4. Relationship between dominant chemical parameters (a) F vs pH, (b) F vs Ca, (c) F vs HCO_3, (d) F vs TDS, (e) F vs Na/Ca and (f) F vs Na/(Na +Ca).

and HCO_3 are observed, which are consistent with other studies from similar areas (Mondal et al., 2014). The study area is made up of volcanic rocks that contain clay minerals. These are capable of retaining F^- on the surfaces. At alkaline conditions (high pH), the F^- ions are usually released from water-bearing stratum into groundwater through the displacement by OH^- and the limitation of F^- sorption capacity (Fig. 4(a)). Groundwater with high F^- are generally characterized by low levels of calcium (Fig. 4(b)). This is mainly controlled by the dissolution equilibrium of fluorite (CaF_2), which brings about the antagonism between Ca^{2+} and F^- in groundwater. Due to the common ion effect of Ca^{2+}, solubility of calcite ($CaCO_3$) is of particular importance and controls the upper limit of dissolved F^- within the aquifer. Precipitation of calcite would lower the dissolved Ca^{2+} concentration and favor the dissolution of fluorite mineral in the groundwater. This signifies that groundwater F^- content is governed by the solubility of CaF_2 whereas solubility of calcite and fluorite together control contents of Ca^{2+} in groundwater (Kim et al., 2012). Unlike Ca^{2+} and Mg^{2+}, Na^+ does not undergo mineral precipitation reactions; hence, its appreciable dissolution makes it dominant in groundwater with perfect Na-TDS correlation (Table S3).

The TDS values exhibit a positive correlation with F^- within the study area (Fig. 4(d)), indicating that the enhancement of ionic strength increases solubility of F^- in groundwater (Sreedevi et al., 2006). Groundwater HCO_3^- contents positively correlate with F^- at HCO_3^- values less than 1200 mg/L, indicating the favorable F^- release at higher HCO_3^- contents. In the Kenya Rift Valley, the volcanic rocks contain largely clay minerals where F^- can be associated. Under the alkaline conditions with elevated HCO_3^- contents, HCO_3^- would compete with F^- for the sorption sites in the clay minerals and enable the adsorbed F^- to be desorbed and entered into groundwater (Gao et al., 2009; Su et al., 2013). It is also interesting to note that when the HCO_3^- values are over 1200 mg/L, there is a negative correlation between F^- and HCO_3^-. This is probably due to the fact that with the continuous increase of HCO_3^-, calcite would precipitate, leading to the co-precipitation of F^- and decrease of the F^- concentration in groundwater (Budyanto et al., 2015).

4.4. Interpretation of major hydrogeochemical processes by principal component analysis

The principal component analysis (PCA) is used to determine the main factors or processes responsible for the groundwater chemistry by analyzing 11 groundwater variables (TDS, pH, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^- and F^-). PCA is performed using varimax rotation method with Kaiser Normalization. Three significant PCs with eigenvalue >1, representing 73.88% of the total sample variances, are extracted and taken into account to infer the dominant hydrogeochemical processes in the study area (Table S4).

Factor 1 is associated with high loadings of TDS, Ca^{2+}, K^+, Na^+, Cl^-, accounting for 47.28% of the total variances. It exhibits significant correlation with TDS, Na and Cl (loading: 0.864, 0.805 and 0.8, respectively), indicating that the high salinity of the groundwater are attributed to the high factor loadings of Na and Cl. Therefore, the groundwater salinization is mostly influenced by the natural processes, mainly halite dissolution, that take place within the system in the study area. The highly involvement of main ion exchange elements Na and Ca in Factor 1, with loading of 0.805 and 0.663, respectively, demonstrates the participation of cation exchange reactions. Factor 2 is responsible for 15.94% of the total variances in the data set with high positive loadings of Mg^{2+} and SO_4^{2-}. Factor 3 is associated with highly loadings of Ca^{2+}, HCO_3^- and F^-, explaining 10.66% of the total variances. The highly positive correlation with F and negative correlation with Ca along this factor can be explained by the dissolution equilibrium of fluorite, which has been stated above. The positive correlations of pH and HCO_3 with F indicate the alkaline condition and competitive anion HCO_3 contribute to the release of F^- into the groundwater.

4.5. Hydrogeochemical processes and enrichment of fluoride

Gibbs diagram has been widely used to establish the hydrogeochemical processes taking place in the aquifers (Gibbs, 1970). Factors such as precipitation, evaporation, and rock-water interaction can be reflected. All the groundwater samples in the study area fall under rock-water interaction and evaporation dominance (Fig. 5), indicating the controlling role of water-rock interaction and evaporation process. It is found that high fluoride groundwater are characterized by medium to high TDS, high Na/(Na+Ca) and high Cl/(Cl+HCO_3) ratios. Parts of F-enriched groundwater, collected from the discharge areas of the Valley, are positioned in the evaporation dominant regions. Kenya Rift Valley belongs to semi-arid climate with low rainfall and high rate of evaporation, leading to the condensation of soluble components and the enrichment of F in groundwater as postulated by Guo et al. (2007). This is more pronounced in the discharge areas, where slow velocity of groundwater and weak permeability of the aquifer sediment promote the process of evaporation. Majority of high fluoride groundwater fall into the rock weathering dominance, reflecting the significance of water-rock interaction for the chemistry of these samples. Hyper-alkaline volcanic rocks, including nepheline and carbonatite magmas and associated ash deposits, are highly developed in the Rift valley zone (Ruggieri et al., 2010). These rocks are capable of accumulating large concentrations of fluoride in melts and volatile fractions. Hence, water bodies in the rift zone can accumulate fluoride directly as a result of rock weathering, as well as from high-fluoride geothermal solutions.

Groundwater with high fluoride values in Kenya Rift Valley are generally Na-rich and Ca-poor with relatively high pH and HCO_3^- concentrations. This is consistent with the studies of Muhammed et al. (2018) and Olago (2019), who report Na-HCO_3 type high fluoride groundwater in weathered or fractured granite bedrock. The relation between Na^+, Ca^{2+}, and F^- can be better explained by the plot between F^- and Na^+/Ca^{2+} in Fig. 4(e) where F^- concentration increases with an increase in the ratios of Na^+/Ca^{2+}. The positive correlation of F^- with Na/(Na+Ca) is associated with constant replacement of Ca^{2+} by Na^+ through cation exchange (Fig. 4(f)). The study area is rich in clay minerals, e.g., illite and kaolinite, which contain abundant exchange sites that may have already adsorbed large amounts of Na^+ when the clays were deposited. Cation exchange occurs during the preferential adsorption of Ca^{2+} and Mg^{2+} from groundwater and release of Na^+ into the groundwater, thereby leading to more dissolution of F^- from mineral phase. Hence, when Ca^{2+} type water changes to Na^+ type water in the system, weathered volcanic rock formation in the study area accelerates the dissolution of F-bearing minerals and therefore releases F^- into the groundwater.

The alkaline nature of groundwater contains OH^- ions that are capable of exchanging F^- ion present in F-bearing minerals such as biotite, fluorite, and amphiboles dissolution (Eq. (3); Sivasankar et al., 2016). This, as well as some spontaneous reactions (Eq. (4) and Eq. (5)), also contributes to an increase of groundwater F^- values. In such spontaneous reactions, the $NaHCO_3$ in weathered rock formation within the study area accelerates the displacement of F^- from F-enriched mineral to the groundwater (Banerjee, 2015; Li et al., 2015; Virendra and Shakeel, 2001). Therefore, ionic species (e.g., Na, Ca and HCO_3) and the pH play an important role in determining the F^- availability of groundwater within the study area.

$$KMg_3[AlSi_3O_{10}]F_2+2OH^- \leftrightarrow KMg[AlSi_3O_{10}][OH]_2+2\,F^- \quad (3)$$

$$CaF_2+H_2O+CO_2 \rightarrow CaCO_3+2\,F^-+2\,H^+ \quad (4)$$

$$CaF_2+\,2NaHCO_3 \rightarrow CaCO_3+2Na^++2\,F^-+\,H_2O+CO_2 \quad (5)$$

4.6. Influence of human activity on the availability of F^- in groundwater

Over times, enrichment of F in the groundwater system has been attributed to the anthropogenic activities that take place within the environment (Chaudhuri and Ale, 2014a; Jia et al., 2019; Li et al., 2018, 2019). Anthropogenic activities such as the addition of nitrogen/phosphate-containing fertilizers and wastewater that contain F^- contribute to an addition of F^- into groundwater (Li et al., 2019). However, it is noted that groundwater with high fluoride concentrations commonly have low NO_3, B and P contents (Fig. 6). The highest observed groundwater nitrate concentration of over 50 mg/L, highest boron concentration of over 50 μg/L and highest phosphate concentration of over 100 μg/L occur with a low F^- concentration (approximately less than 1.5 mg/L). These subtle correlations between F and NO_3, B and P indicate that the presence of F^- enrichment in groundwater is not related to anthropogenic activities, most likely to result from geogenic sources. The study area lies in the zone with low agricultural activities, hence, anthropogenic factors cannot be considered as the main contributor to high levels of fluoride in groundwater.

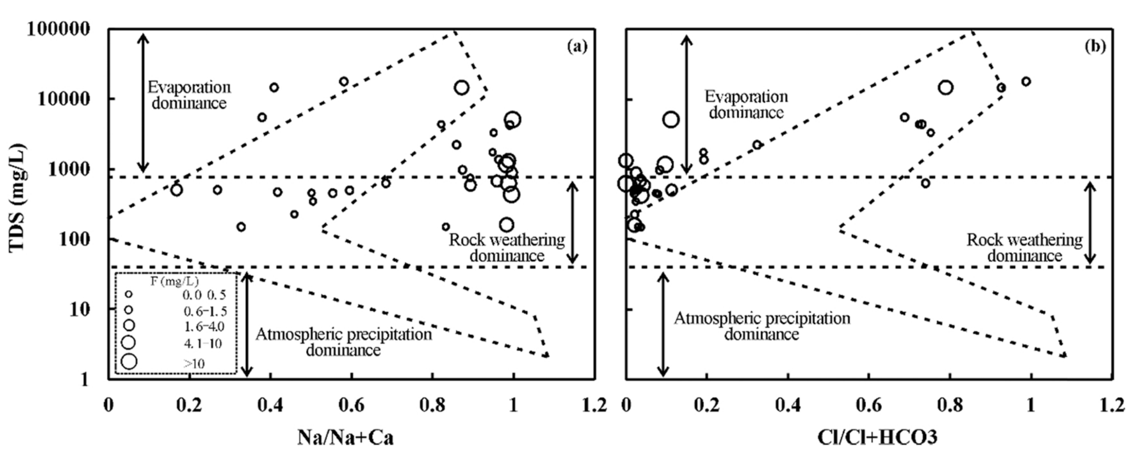

Fig. 5. Gibbs diagram showing the controlling mechanism of groundwater.

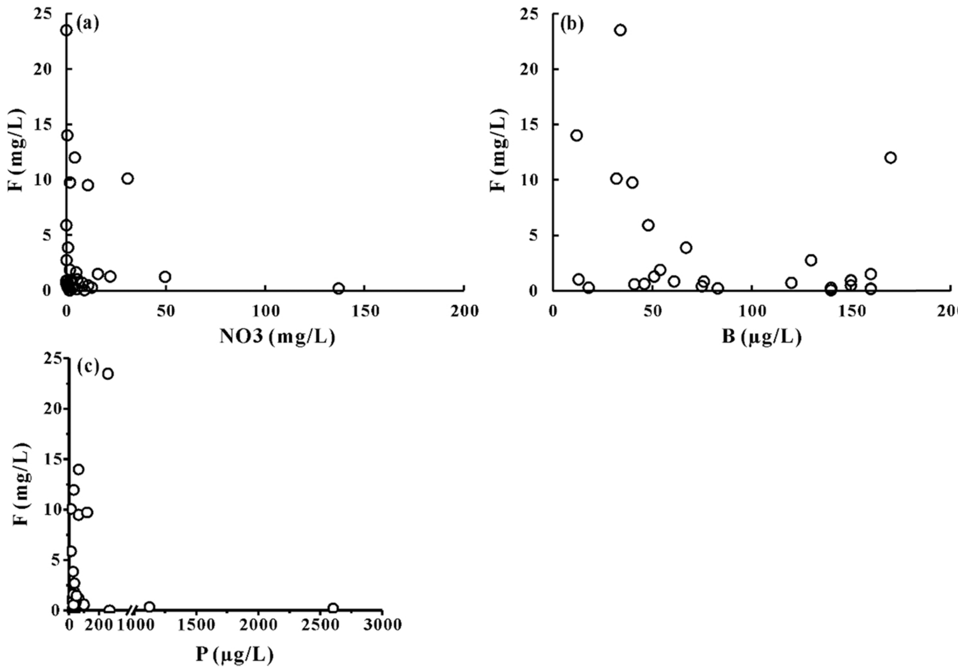

Fig. 6. The mutual relationship between F vs NO3 (a), F vs B (b) and F vs P (c).

4.7. Health risk exposure assessment

Consumption of fluoride-contaminated groundwater, with a potential to cause 80% of the diseases, has a notable impact on the exposing health (Narsimha and Sudarshan, 2017). Though fluoride is considered to be an important element for the developmental growth of human skeletal, and dental enamel formation, higher content of groundwater fluoride is responsible for dental and skeletal fluorosis. Therefore, the

Table 1
Health risk exposure assessment in the form of average daily ingestion (ADD), and hazard quotient (HQ) for children, and adults consuming fluoride contaminated groundwater of Kenya Rift Valley (n = 32).

Sample ID	F (mg/L)	ADD in child	ADD in male	ADD in female	HQ in child	HQ in male	HQ in female
S1	1.87	0.097	0.072	0.068	1.620	1.200	1.130
S2	9.51	0.495	0.366	0.346	8.240	6.100	5.760
S3	1.01	0.053	0.039	0.037	0.880	0.650	0.610
S4	0.81	0.042	0.031	0.029	0.700	0.520	0.490
S5	3.87	0.201	0.149	0.141	3.350	2.480	2.350
S6	10.1	0.525	0.388	0.367	8.750	6.470	6.120
S7	0.24	0.012	0.009	0.009	0.210	0.150	0.150
S8	14	0.728	0.538	0.509	12.130	8.970	8.480
S9	0.7	0.036	0.027	0.025	0.610	0.450	0.420
S10	12	0.624	0.462	0.436	10.400	7.690	7.270
S11	23.5	1.222	0.904	0.855	20.370	15.06	14.24
S12	0.2	0.01	0.008	0.007	0.170	0.130	0.120
S13	0.01	0.001	0.000	0.000	0.010	0.010	0.010
S14	0.26	0.014	0.010	0.009	0.230	0.170	0.160
S15	1.26	0.066	0.048	0.046	1.090	0.810	0.760
S16	0.03	0.002	0.001	0.001	0.030	0.020	0.020
S17	1.23	0.064	0.047	0.045	1.070	0.790	0.750
S18	2.74	0.142	0.105	0.100	2.370	1.760	1.660
S19	0.6	0.031	0.023	0.022	0.520	0.380	0.360
S20	0.39	0.02	0.015	0.014	0.340	0.250	0.240
S21	0.83	0.043	0.032	0.030	0.720	0.530	0.500
S22	9.75	0.507	0.375	0.355	8.450	6.250	5.910
S23	0.03	0.002	0.001	0.001	0.030	0.020	0.020
S24	0.92	0.048	0.035	0.033	0.800	0.590	0.560
S25	0.9	0.047	0.035	0.033	0.780	0.580	0.550
S26	0.14	0.007	0.005	0.005	0.120	0.090	0.080
S27	0.18	0.009	0.007	0.007	0.160	0.120	0.110
S28	5.9	0.307	0.227	0.215	5.110	3.780	3.580
S29	1.64	0.085	0.063	0.060	1.420	1.050	0.990
S30	0.46	0.024	0.018	0.017	0.400	0.290	0.280
S31	0.57	0.03	0.022	0.021	0.490	0.370	0.350
S32	1.49	0.077	0.057	0.054	1.290	0.960	0.900
Minimum	0.01	0.001	0.001	0.001	0.010	0.010	0.010
Maximum	23.5	1.222	0.904	0.855	20.37	15.060	14.24
Average	3.35	0.174	0.129	0.122	2.900	2.150	2.030

health risk assessment is conducted to calculate ADD and HQ values for children and adults in the study area.

Calculations indicate that the ranges of ADD ingestion for children, male and female in Kenya Rift Valley are observed to be 0.001–1.222, 0.001–0.904 and 0.001–0.855, with an average value of 0.174, 0.129 and 0.122, respectively (Table 1). The values of $HQ_{ingestion}$ span from 0.01 to 20.37, 0.01–15.06 and 0.01–14.24 for children, male and female respectively. It is noted that children top out for the maximum and average values of $ADD_{ingestion}$ and $HQ_{ingestion}$ in the study area, indicating that children are in the highest health risks by groundwater fluoride ingestion. The health risks for various individual are in the order of children > male > female. Generally, according to HQ values, health risks can be classified into three levels: low and negligible risk ($HQ<1$), medium risk ($1 < HQ<4$) and high risk ($HQ>4$). It is calculated that all the individuals are in health risks to some extent. Specifically, children suffer from low to high risk, with 56.3% in low chronic risk, 21.8% in medium chronic risk and 21.9% in high chronic risk. Large proportions of male and female are in low risk category. 15.6% of male and 12.5% of female fall in medium risk and 18.8% of male and 15.6% of female are in high risk category.

4.8. Implication for the sustainable management of groundwater resources

Fluoride is one of the essential elements (daily intake of 0.5 mg/L-1.5 mg/L) for the human formation of enamel and mineralization of bones (Raju et al., 2017; Ruchi and Anil, 2016). However, excess intake of fluoride (>1.5 mg/L) is considered to be harmful for human beings, including skeletal fluorosis, chronic joint pains, osteosclerosis (Gevera and Mouri, 2018; Lydia et al., 2016; Tekle-Haimanot et al., 2006) and cancer (Grimaldo et al., 1995; Nagaraju et al., 2014; Takahashi et al., 2001). This problem is further aggravated in the countries where lack of alternate water sources makes groundwater gaining increasing importance for cooking and drinking purposes and frequent droughts take place. Hence, it is extremely crucial to focus on monitoring and safe management of the existing groundwater resources to prevent further deterioration of groundwater and damage to human beings.

Our research recommends that water management authorities should take actions to establish comprehensive monitoring network of groundwater system. This can help realize real-time monitoring of groundwater quality and quantity and draw up plans to avoid aggravating the situation. Stronger and harsher measures to install safe drinking water wells should be urged by the local governments. Additionally, effective measures should be taken to improve the public awareness for sustainable and safe use of groundwater resources.

5. Conclusions

Integrated analysis of hydrogeochemistry, graphical and multivariate statistical methods provide important clues for understanding the occurrence and origins of high fluoride groundwater in shallow aquifers in Kenya Rift Valley, which has volcanic and quaternary geological formations. The main findings are as follows:

(1) High F^- groundwater (up to 23.5 mg/L) occurs in shallow aquifers, with over 40% showing elevated fluoride values over the WHO standards. Spatially, F^- contents are enriched in groundwater in the upper zones of the study area with igneous geological formations. Groundwater with high fluoride values are generally Na-rich and Ca-poor with relatively high pH and HCO_3^- concentrations, as indicated by hydrogeochemical and principal component analysis.

(2) Weathering and breakdown of hyper-alkaline volcanic rocks contribute most of F^- in groundwater, which were accumulated in melts, volatile fractions and clay minerals. Alkaline condition and competitive anion HCO_3^- promote the desorption of F^- from clay minerals and Fe-hydroxides into the aqueous phase. Clay minerals also provide abundant exchange sites where cation exchange takes place. The conversion of Ca-rich groundwater to Na-rich groundwater helps release F^- from sediments into groundwater, controlled by the dissolution-precipitation of calcite and fluorite.

(3) The health risks by groundwater geogenic fluoride ingestion for various individual are in the order of children > male > female. Although majority of groundwater samples pose low health risk to people, 43.7%, 34.4% and 28.1% of the sampled groundwater have potential medium to high chronic health threats to children, male and female, respectively.

(4) Our research recommends that monitoring and safe management of groundwater is required to meet the ever-increasing demand of population and economic activities without further deterioration of groundwater and damage to human beings. Local authorities should take actions to establish comprehensive monitoring network of groundwater system, as well as install safe drinking water wells. Public awareness for sustainable and safe use of groundwater resources should also be improved.

CRediT authorship contribution statement

Njagi Felix Mwiathi: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing – original draft. **Xubo Gao**: Methodology, Writing – review & editing, Funding acquisition. **Chengcheng Li**: Conceptualization, Methodology, Validation, Software, Formal analysis, Investigation, Writing – review & editing, Supervision, Funding acquisition, Project administration. **Abdur Rashid**: Software, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2021.113046.

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