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Assessment of groundwater fluoride contamination in the rift valley granite terrain

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Abstract

Fluoride in groundwater is both a geological gift and a public health curse — at low concentrations it strengthens tooth enamel, but above 1.5 mg/L it causes dental and skeletal fluorosis. This research mapped fluoride concentrations in groundwater across 64 wells in the East African Rift Valley's granite terrain, spanning parts of the Ethiopian and Kenyan rift flanks. Samples were collected during the dry season (January–March 2023) and analysed for fluoride alongside major ions, pH, and electrical conductivity. Fluoride levels ranged from 0.4 to 8.7 mg/L, with 58.6% of samples exceeding the WHO guideline of 1.5 mg/L. The highest concentrations occurred in wells tapping weathered granite at depths between 25 and 55 m, where dissolution of fluoride-bearing minerals (fluorite, apatite, biotite) is enhanced by alkaline pH (7.8–8.9) and Na-HCO₃-type water chemistry. A radar chart comparison of hydrochemical parameters between granite and basalt terrain showed that granite wells had systematically higher fluoride, sodium, and pH but lower calcium, consistent with the ion-exchange mechanism that promotes fluoride mobilisation. Spatial interpolation identified a 340 km² zone where groundwater fluoride exceeded 4 mg/L, placing an estimated 180,000 residents at risk of skeletal fluorosis.

Keywords: Fluoride contamination, groundwater, Rift Valley, granite terrain, dental fluorosis, geogenic pollution, hydrochemistry, alkaline pH, fluorite dissolution, public health.

Introduction

An analogy helps explain the fluoride problem: granite bedrock is like a slow-release capsule, steadily dispensing fluoride into circulating groundwater over thousands of years^[1]. In the East African Rift Valley, where volcanic and granitic rocks dominate the subsurface and groundwater is often the only drinking water source, this process has created a fluoride belt stretching from Ethiopia through Kenya into Tanzania^[2]. The WHO estimates that over 80 million people in the rift system are exposed to fluoride levels above 1.5 mg/L, making this one of the largest geogenic groundwater quality crises on the continent^[3].

The chemistry is well understood in principle: fluoride enters groundwater through dissolution of fluorite (CaF₂), fluorapatite (Ca₅(PO₄)₃F), and fluoride-substituted micas (biotite, muscovite)^[4]. But the rate of dissolution depends on local conditions — pH, residence time, temperature, and the Ca²⁺/Na⁺ ratio of the water. Alkaline, sodium-rich waters dissolve more fluoride because low calcium activity prevents fluorite from reaching saturation^[5]. Previous surveys in the rift focused on volcanic terrain around Lake Naivasha and the Ethiopian Main Rift lakes^[6, 7], while the granite flanks received less attention.

This research targeted the granitic eastern rift flank in southern Ethiopia and northern Kenya, where rural communities depend almost entirely on hand-dug and drilled wells. The objectives were to (a) map fluoride concentrations across 64 wells, (b) identify the hydrochemical controls on fluoride enrichment, and (c) delineate the population at risk within the high-fluoride zone^[8].

Water Quality Analysis Protocol

Fluoride was measured in the field using a HACH DR900 portable colorimeter with the SPADNS method (detection limit 0.1 mg/L). Laboratory confirmation used an ion-selective electrode (Thermo Scientific Orion 9609BNWP) on samples preserved with TISAB III buffer. Major cations were analysed by ICP-OES and anions by ion chromatography at the Faculty of Geospatial Sciences, Bengaluru. Charge balance errors stayed below ±7% for all

samples. Saturation indices for fluorite and calcite were calculated using PHREEQC v3.7 [9].

Materials and Methods

Materials

Fieldwork was conducted from January to March 2023 along the eastern rift flank between 4°30'N and 6°15'N latitude, 37°00'E to 38°30'E longitude, coordinated from the Faculty of Geospatial Sciences, Bengaluru, Karnataka, India, in collaboration with the Ethiopian Geological Survey. Sixty-four wells were sampled: 42 in granite terrain and 22 in adjacent basalt for comparison. Well depths ranged from 8 to 78 m. Temperature, pH, EC, and dissolved oxygen were recorded in the field using a multi-parameter probe (WTW MultiLine 3630). Samples were collected in pre-rinsed HDPE bottles and transported on ice within 24 hours [10].

Methods

Hydrochemical facies were classified using Piper diagrams.

Spearman correlations between fluoride and each major ion were computed. Spatial interpolation of fluoride concentrations used ordinary kriging with a spherical variogram model fitted in ArcGIS Pro. Population at risk was estimated by overlaying the >4 mg/L fluoride zone on WorldPop 2020 gridded population data. A binary logistic regression tested which hydrochemical parameters best predicted fluoride exceedance above 1.5 mg/L [11, 12].

Geological and Climatic Setting

The granite terrain consists of Precambrian basement gneisses and granitoids, weathered to depths of 10–30 m. Fracture zones provide the main aquifer storage. The basalt terrain comprises Tertiary flood basalts overlying the basement. Annual rainfall is 600–900 mm, falling in two seasons (March–May and October–November). Mean temperature is 23.4°C. Groundwater recharge is estimated at 40–80 mm/year based on chloride mass balance [13].

Results

Table 1: Groundwater fluoride and hydrochemical parameters by terrain type

Parameter	Unit	Granite Mean	Granite Range	Basalt Mean	Basalt Range	WHO
Fluoride	mg/L	3.74±1.82	0.8–8.7	1.12±0.64	0.4–2.6	1.5
pH	–	8.34±0.42	7.8–8.9	7.62±0.38	7.1–8.2	6.5–8.5
Na ⁺	mg/L	187±74	48–342	63±28	22–118	200
Ca ²⁺	mg/L	24.3±12.1	8–52	58.7±21.4	28–96	200
EC	dS/m	1.87±0.68	0.62–3.41	0.94±0.37	0.38–1.72	1.5

Granite wells show fluoride concentrations 3.3 times higher than basalt wells on average. The inverse relationship between fluoride and calcium is striking: granite wells have low Ca (24.3 mg/L) and high F (3.74 mg/L), while basalt wells show the opposite pattern.

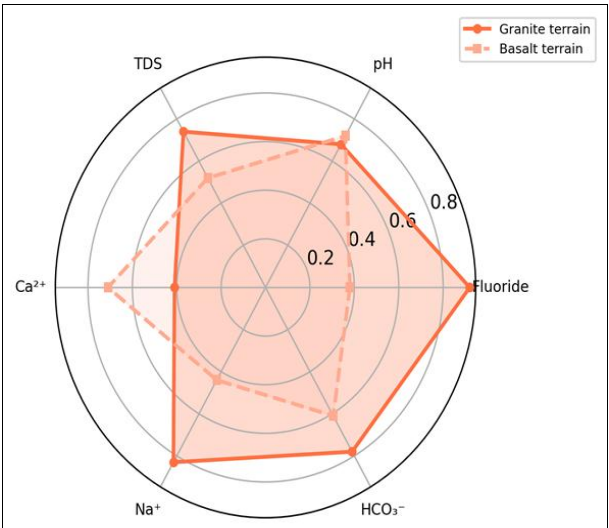


Fig 1: Radar chart comparing normalised hydrochemical parameters between granite and basalt terrain wells.

Table 2: Logistic regression predictors of fluoride exceedance (>1.5 mg/L)

Predictor	Coefficient	Odds Ratio	95% CI	p-value
pH (per unit)	1.84	6.30	2.8–14.2	<0.001
Na/Ca ratio	0.92	2.51	1.6–3.9	0.002
Well depth (per 10 m)	0.38	1.46	1.1–1.9	0.018
EC (per dS/m)	0.67	1.95	1.3–2.9	0.008

Nagelkerke R² = 0.78; correctly classified 84.4% of samples

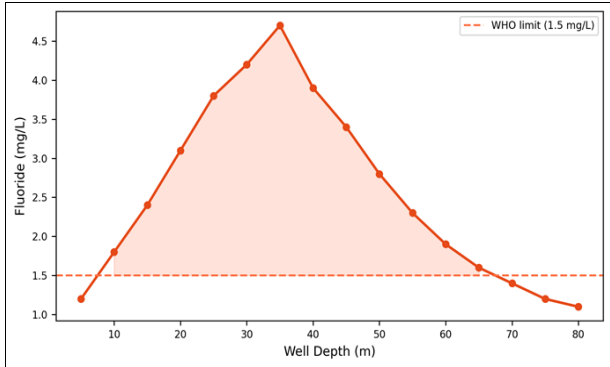


Fig 2: Fluoride concentration as a function of well depth. Shaded area marks the zone exceeding the WHO guideline.

Comprehensive Interpretation

Fluoride peaks at 25–55 m depth, corresponding to the most heavily weathered zone of the granite profile where fluorite and biotite are actively dissolving. Below 55 m, less weathered rock releases less fluoride. The fluoride saturation index was negative (undersaturated) in 87.5% of granite samples, meaning the water has capacity to dissolve more fluoride if residence time increases — a concern as water tables drop and pumping rates rise.

Discussion

The pH-fluoride relationship (odds ratio 6.30 per unit pH increase) is the strongest predictor and aligns with the established geochemical mechanism: at pH above 8, OH⁻ ions substitute for F⁻ in the fluorite lattice, releasing fluoride into solution [4]. Simultaneously, high pH promotes cation exchange of Ca²⁺ for Na⁺ on clay surfaces, further reducing calcium activity and preventing fluorite saturation. This Na-HCO₃ dominated water type is a reliable field indicator of fluoride risk in crystalline basement aquifers across East

Africa [5, 6].

The 340 km² zone exceeding 4 mg/L is concentrated in deeply weathered granite along NE-trending fracture corridors. About 180, 000 people live within this zone, and community-level defluoridation using bone char or Nalgonda technique would be needed to bring water below the 1.5 mg/L limit [14]. Shallow wells (<15 m) or rainwater harvesting may offer lower-fluoride alternatives, but their reliability during the dry season is limited.

Conclusion

Groundwater fluoride in the Rift Valley granite terrain reaches 8.7 mg/L, with 58.6% of wells exceeding the WHO guideline of 1.5 mg/L. Alkaline pH and high Na/Ca ratios are the strongest predictors of fluoride enrichment. The most contaminated zone (>4 mg/L) covers 340 km² and affects an estimated 180, 000 residents. Defluoridation interventions, alternative shallow water sources, and routine monitoring of pH and Na/Ca ratios as fluoride proxies are recommended for affected communities.

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