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Relationship between Lithology and Fluoride Contamination in Groundwater

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Abstract: *Fluoride contamination in groundwater is a significant hydrogeochemical and public-health concern in many arid and semi-arid regions. The concentration of fluoride in groundwater is controlled by a combination of geological, hydrogeological, geochemical and anthropogenic factors, among which lithology plays a particularly important role. The mineralogical composition of aquifer rocks determines the availability of fluoride-bearing minerals and influences groundwater–rock interaction, dissolution, ion exchange and geochemical evolution. Rocks containing fluoride-bearing minerals such as fluorite, apatite, mica and amphiboles may contribute fluoride to groundwater when subjected to prolonged weathering and water–rock interaction.*

Keywords: Fluoride, groundwater, lithology, hydro geochemistry, aquifer, water–rock interaction, fluorite, groundwater contamination.

I. INTRODUCTION

Groundwater represents one of the most important sources of drinking water, irrigation and domestic water supply, particularly in rural and semi-arid regions where surface-water resources are limited. Although groundwater is generally considered relatively protected from direct contamination, its chemical composition is strongly influenced by the geological materials through which it flows and with which it remains in contact. Among naturally occurring groundwater contaminants, fluoride is of particular importance because its concentration can increase substantially through natural geochemical processes. While fluoride at low concentrations is beneficial for dental health, prolonged consumption of groundwater containing excessive fluoride may result in dental and skeletal fluorosis.

The occurrence of fluoride in groundwater is closely associated with the mineralogical and lithological characteristics of aquifer systems. Lithology refers to the physical and mineralogical characteristics of rocks and sediments forming the geological framework of an area. Different rock types contain different proportions of fluoride-bearing minerals and therefore have different capacities to release fluoride into groundwater. Granitic and gneissic rocks, for example, may contain minerals such as biotite, muscovite, amphiboles and apatite that can act as sources of fluoride during weathering. Fluoride may also be associated with fluorite and certain clay minerals. Consequently, groundwater flowing through or stored within particular lithological formations may develop elevated fluoride concentrations.

The relationship between lithology and fluoride is not simply determined by the presence of fluoride-bearing minerals. Groundwater chemistry, pH, alkalinity, residence time, temperature, evaporation, calcium concentration and ion-exchange processes also affect fluoride mobility. Under alkaline conditions, fluoride can remain relatively mobile in groundwater. Similarly, low calcium concentrations may promote fluoride enrichment because fluoride removal through precipitation of calcium fluoride becomes less favorable. Thus, lithology provides the geological source, whereas hydrogeochemical conditions determine the extent to which fluoride is released and transported.

II. LITHOLOGICAL CONTROL OF FLUORIDE IN GROUNDWATER

The lithological control of fluoride contamination operates primarily through mineral dissolution and water–rock interaction. When groundwater infiltrates through weathered rocks and fractures, it reacts with minerals present within

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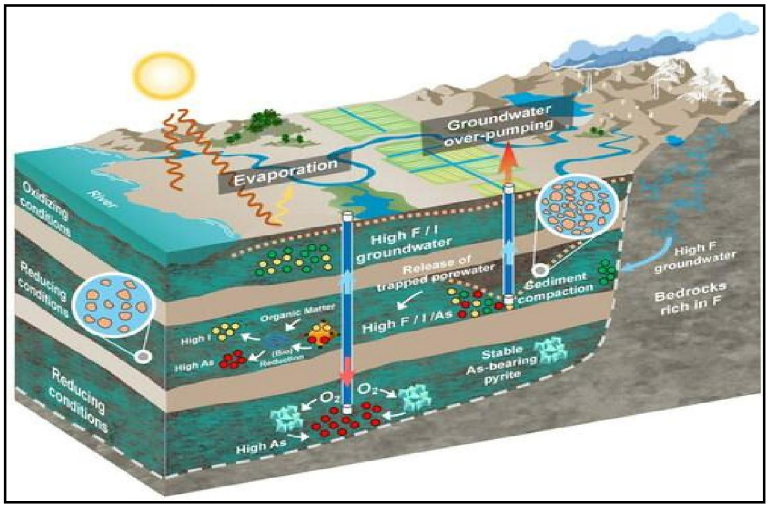
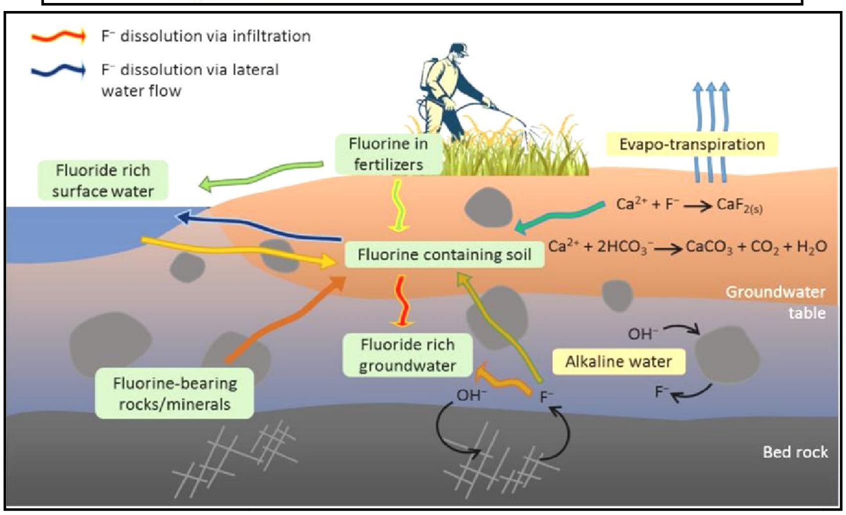
the geological formation. Over time, soluble components are released into the groundwater. Fluoride-bearing minerals can therefore contribute fluoride to groundwater depending on their abundance, stability and interaction with water.





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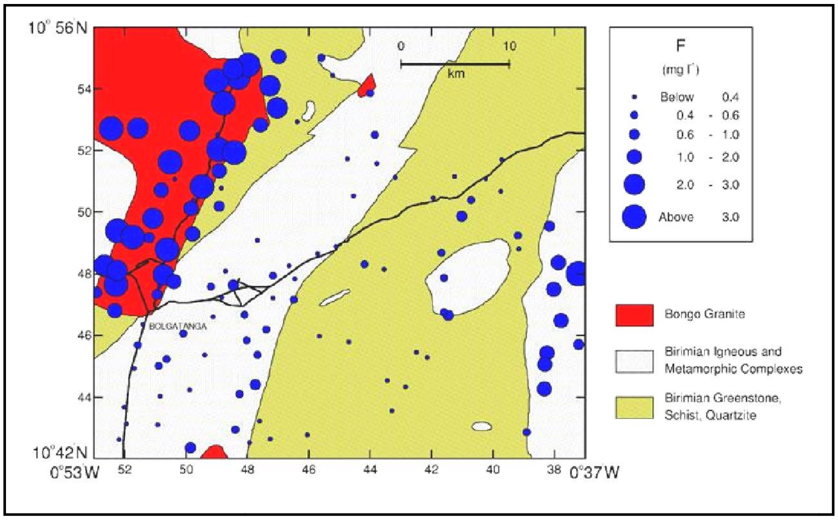

Granite and granitic gneiss are frequently associated with fluoride-rich groundwater because they may contain fluorine-bearing micas and amphiboles. Weathering of these minerals can release fluoride into groundwater. The intensity of weathering, fracture density and groundwater residence time can further determine fluoride concentrations. In crystalline-rock aquifers, groundwater may accumulate fluoride when circulation is relatively slow and water remains in contact with mineral surfaces for extended periods.

Sedimentary formations can also influence fluoride concentrations. Sandstone, shale and carbonate formations differ considerably in mineralogical composition and permeability. Clay-rich formations may participate in ion exchange and adsorption processes, while carbonate minerals can influence calcium availability and groundwater alkalinity. Therefore, two aquifers located in the same climatic region may exhibit substantially different fluoride concentrations because of differences in their lithological characteristics.

III. MAJOR LITHOLOGICAL SOURCES OF FLUORIDE

Lithological unit	Important fluoride-bearing minerals	Potential fluoride contribution	Typical hydrogeochemical influence
Granite	Biotite, muscovite, amphibole, apatite	High	Long residence time and weathering may enhance fluoride
Granitic gneiss	Biotite, amphibole, apatite	Moderate–high	Fracturing and weathering facilitate mineral–water interaction
Basalt	Apatite, amphibole and other accessory minerals	Low–moderate	Depends strongly on mineral assemblage and groundwater chemistry
Sandstone	Fluorite, mica, clay minerals in some formations	Variable	Depends on cement and mineral composition
Shale	Clay minerals, mica, phosphate minerals	Variable	Adsorption/desorption and ion exchange may influence fluoride
Limestone	Fluorite/apatite and secondary minerals	Variable	Calcium-rich water may restrict dissolved fluoride
Alluvium	Mixed mineral fragments	Low–high	Depends on sediments derived from surrounding rocks
Weathered crystalline rocks	Secondary clay minerals and residual primary minerals	Moderate–high	Enhanced interaction due to weathering

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The table demonstrates that lithology should not be interpreted solely according to broad rock classifications. Mineralogical composition is equally important. For example, two granite formations may have different fluoride-producing capacities because of differences in mica, amphibole and apatite content.

IV. MECHANISM OF FLUORIDE RELEASE

Fluoride enters groundwater predominantly through the dissolution and weathering of fluoride-bearing minerals. The simplified dissolution process can be represented as:

$$\textbf{Fluoride-bearing mineral} + H_2O \rightarrow \textbf{dissolved ions} + F^-$$

Fluorite dissolution is commonly represented by:

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

The equilibrium of this reaction is affected by calcium concentration. When calcium is abundant, fluoride may be removed from solution through mineral precipitation or other geochemical processes. Conversely, when calcium concentrations are low, fluoride can remain dissolved and become enriched.

Fluoride-bearing silicate minerals can also release fluoride during chemical weathering. The process is more complex because several reactions occur simultaneously, involving dissolution, hydrolysis, ion exchange and secondary-mineral formation. Elevated pH can increase fluoride mobility, while groundwater with high bicarbonate concentrations may facilitate desorption of fluoride from mineral surfaces.

V. RELATIONSHIP BETWEEN LITHOLOGY AND GROUNDWATER CHEMISTRY

The relationship between lithology and fluoride contamination can be assessed by comparing fluoride concentrations with parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), calcium, bicarbonate and sodium.

Table 2. Illustrative Hydrochemical Characteristics of Groundwater Under Different Lithologies

Lithology	**Mean F^- (mg/L)**	**Mean pH**	**Mean EC (µS/cm)**	**Mean Ca^{2+} (mg/L)**	**Mean HCO_3^- (mg/L)**	**Interpretation**
Granite	2.8	8.1	1,120	32	285	High water–rock interaction
Granitic gneiss	2.3	7.9	980	38	250	Moderate–high fluoride release
Sandstone	1.5	7.7	760	48	205	Moderate enrichment
Basalt	0.9	7.5	610	61	175	Comparatively lower fluoride
Alluvium	1.1	7.6	680	55	190	Variable mineral contribution

Note: Values are illustrative examples for demonstrating research-paper presentation and are not field observations.

The illustrative comparison indicates that groundwater associated with granite and granitic gneiss may exhibit comparatively higher fluoride concentrations. This can be explained by the presence of fluoride-bearing minerals and greater groundwater–rock interaction. However, lithology alone cannot explain all variations. Groundwater flow, well depth, recharge conditions and hydrochemical evolution must also be considered.

VI. INFLUENCE OF P_H AND ALKALINITY

pH is one of the most important factors affecting fluoride mobility. Fluoride generally becomes more mobile under alkaline groundwater conditions. In crystalline-rock aquifers, prolonged water–rock interaction can increase pH and alkalinity, creating conditions favorable for fluoride enrichment.

The bicarbonate ion may also influence fluoride behavior. High bicarbonate concentrations can promote competitive interactions between bicarbonate and fluoride at mineral surfaces, potentially increasing fluoride desorption. Consequently, groundwater characterized by relatively high pH, bicarbonate and sodium and comparatively low calcium may be particularly susceptible to fluoride enrichment.

VII. ROLE OF GROUNDWATER RESIDENCE TIME

Groundwater residence time represents the period during which water remains within the subsurface before discharge or extraction. Long residence times allow groundwater to interact extensively with minerals. In regions where recharge is limited and groundwater movement is slow, prolonged contact with fluoride-bearing minerals may increase dissolved fluoride concentrations.

In contrast, rapidly recharged aquifers with relatively short residence times may have lower fluoride concentrations because groundwater has less opportunity to interact with fluoride-bearing minerals. Therefore, the highest fluoride concentrations may occur in deeper groundwater systems where prolonged water–rock interaction, evaporation and geochemical evolution have taken place.

VIII. LITHOLOGY–FLUORIDE RELATIONSHIP: CONCEPTUAL INTERPRETATION

Factor	Effect on fluoride concentration	Relationship
Fluoride-bearing minerals	Provides fluoride source	Positive
Rock weathering	Releases fluoride-bearing components	Positive
Groundwater residence time	Increases mineral interaction	Positive
Alkaline pH	Enhances fluoride mobility	Positive
High bicarbonate	May promote fluoride desorption	Positive
High calcium	May reduce dissolved fluoride	Negative
Rapid recharge	Reduces residence time	Generally negative
Strong groundwater circulation	Limits prolonged mineral interaction	Generally negative
Evaporation	Concentrates dissolved ions	Positive
Fracturing	Enhances water–rock contact	Context-dependent

This conceptual relationship shows that fluoride contamination is a result of the interaction between geological source and hydrogeochemical conditions rather than a single controlling factor.

IX. STATISTICAL ASSESSMENT OF THE LITHOLOGY–FLUORIDE RELATIONSHIP

A research study can statistically evaluate the relationship between lithology and fluoride contamination using correlation, regression and analysis of variance. Pearson correlation can be used to assess associations between fluoride and continuous hydrochemical variables. One-way ANOVA can determine whether mean fluoride concentrations differ significantly among lithological groups. Multiple regression can then be used to determine the relative contribution of pH, TDS, calcium, bicarbonate and lithology to fluoride concentrations.

A conceptual regression model can be expressed as:

$$\mathbf{F = \beta_0 + \beta_1 pH + \beta_2 TDS + \beta_3 Ca + \beta_4 HCO_3 + \beta_5 Lithology + \varepsilon}$$

where **F** represents groundwater fluoride concentration, β_0 is the intercept, β_1–β_5 are regression coefficients and ε represents the error term.

Table 3. Suggested Statistical Framework

Research variable	Statistical technique	Purpose
Fluoride concentration	Mean, SD, minimum, maximum	Describe contamination levels
Fluoride vs. pH	Pearson correlation	Determine association
Fluoride vs. TDS	Pearson correlation	Assess mineralization relationship

Fluoride vs. Ca^{2+}	Pearson correlation	Examine calcium control
Fluoride among lithologies	One-way ANOVA	Compare lithological groups
Fluoride prediction	Multiple regression	Identify controlling factors
Spatial distribution	GIS mapping	Identify fluoride-prone zones
Hydrochemical facies	Piper diagram	Understand groundwater evolution

X. CONCLUSION

Lithology is a fundamental geological control on fluoride contamination in groundwater because it determines the availability of fluoride-bearing minerals and influences groundwater–rock interaction. Granite, granitic gneiss and other crystalline formations containing fluorine-bearing minerals can provide important sources of fluoride under favorable geochemical conditions. Nevertheless, fluoride enrichment is controlled by multiple interacting factors, including mineral dissolution, groundwater residence time, pH, bicarbonate, calcium, evaporation, recharge and groundwater circulation.

The relationship between lithology and fluoride is therefore best understood through an integrated hydrogeochemical approach. Combining geological mapping with groundwater sampling, statistical analysis and GIS-based spatial assessment can identify areas vulnerable to fluoride contamination. Such an approach is particularly useful for sustainable groundwater management because it enables fluoride-prone aquifers to be identified before extensive dependence on contaminated groundwater develops. Future investigations should incorporate mineralogical analysis, groundwater age, isotopic techniques and detailed spatial modelling to establish more precise links between geological formations and fluoride mobility.

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