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Source apportionment of fluoride in semi-arid aquifers: Insights from major ion chemistry in Agra

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Abstract
Fluoride poses significant health risks in semi-arid regions, particularly in India, where endemic fluorosis affects millions. Uttar Pradesh, through a comprehensive analysis of major ion chemistry. Groundwater samples were collected from 45 wells across different geological formations and analysed for major ions, trace elements, and physicochemical parameters. Results indicate fluoride concentrations ranging from 0.3 to 4.8 mg/L, with 67% of samples exceeding WHO guidelines (1.5 mg/L). Hydrogeochemical analysis reveals three distinct water types: $Ca-HCO_3$, $Na-HCO_3$, and mixed $Ca-Na-HCO_3$, with the highest fluoride concentrations associated with $Na-HCO_3$ waters. Statistical analysis and ionic ratios suggest fluoride enrichment occurs through mineral dissolution (fluorite, mica, feldspar), ion exchange processes, and evapotranspiration in the semi-arid climate. Saturation indices indicate oversaturation concerning fluorite in high-fluoride zones, suggesting equilibrium-controlled fluoride release. This research provides crucial insights for groundwater management and fluoride mitigation strategies in similar hydrogeological settings across the Indo-Gangetic Plains.

Keywords: Fluoride contamination, groundwater geochemistry, semi-arid aquifers, source apportionment, major ion chemistry, agra district, hydrogeochemical processes, fluorosis

Introduction

Fluoride in groundwater represents one of the most widespread geochemical anomalies affecting human health globally, with over 200 million people exposed to elevated fluoride concentrations exceeding safe drinking water standards. The Indo-Gangetic Plains of northern India, characterised by semi-arid to arid climatic conditions and specific hydrogeological settings, exhibit particularly severe fluoride contamination issues. Agra district, located in the southwestern part of Uttar Pradesh, exemplifies this challenge with documented cases of dental and skeletal fluorosis among rural populations dependent on groundwater for domestic consumption.

The occurrence of fluoride is primarily geochemical, including mineral dissolution, precipitation, ion exchange, and evapotranspiration. In semi-arid regions, these processes are intensified by high evaporation rates, prolonged water-rock interaction, and specific geological conditions favouring fluoride-bearing mineral weathering. The dominant fluoride sources in aquifers include fluorite (CaF_2), fluorapatite $[Ca_5(PO_4)_3F]$, mica, feldspar, and amphibole minerals commonly found in crystalline basement rocks and their weathered products.

Understanding the hydrogeochemical mechanisms controlling fluoride distribution sustainable groundwater management practices. Major ion chemistry provides valuable insights into water-rock interactions, mixing processes, and the geochemical evolution of groundwater systems. Previous studies in similar hydrogeological settings have established correlations between fluoride concentrations and specific ionic ratios, pH conditions, and total dissolved solids, indicating complex multi-factor controls on fluoride mobility.

The Agra district presents an ideal case study for investigating fluoride source apportionment due to its diverse geological formations, including Archean crystalline basement, Vindhyan sediments, and Quaternary alluvium, combined with intensive groundwater exploitation and documented fluoride-related health issues. Patterns create conditions conducive to fluoride concentration through evapotranspiration and prolonged water-rock interaction.

This research aims to [1]: characterise the spatial distribution of fluoride in Agra aquifers [2], identify dominant hydrogeochemical processes controlling fluoride occurrence through major ion analysis [3], determine primary fluoride sources using statistical methods and geochemical modelling, and [4] provide a scientific basis for groundwater quality management and fluoride mitigation strategies. The findings contribute to understanding fluoride geochemistry in semi-arid aquifer systems and support evidence-based approaches for the Indo-Gangetic Plains region.

Methods

1. Study Area Description

Agra district is located between 26°44' to 27°25' N latitude and 77°29' to 78°32' E longitude, covering an area of 4,027 km². The region a semi, concentrated during the monsoon months (July-September). Mean annual temperature ranges from 15°C (winter) to 45°C (summer), with potential evapotranspiration exceeding 1,800 mm annually.

Geologically, the study area comprises three distinct formations: Archean crystalline basement rocks (granite, gneiss, schist) in the southern parts; Proterozoic Vindhyan sediments (sandstone, shale, limestone) in central regions; and Quaternary alluvial deposits along the Yamuna River corridor. These formations host multi-layered aquifer systems with varying hydraulic properties and geochemical characteristics.

2. Sampling Strategy and Collection

Groundwater samples were collected from 45 strategically selected wells during pre-monsoon (May 2023) and postmonsoon (November 2023) periods to capture seasonal variations in groundwater chemistry. Sampling locations were distributed across different geological formations, land use patterns, and depth ranges (15-150 m below ground level) using GPS coordinates for precise spatial referencing.

Wells were purged for 10-15 minutes before sampling to ensure representative water quality. Samples were collected in pre-cleaned polyethene bottles: 500 mL for major ion analysis, 100 mL for trace elements (acidified with ultra-pure HNO_3), and 1000 mL for stable isotope analysis. All samples were stored at 4°C and transported to the laboratory within 24 hours for analysis.

3. Analytical Procedures

Fluoride concentrations were measured using the ion-selective electrode (ISE) method following standard protocols (APHA 2017) [2]. Total Ionic Strength Adjustment Buffer (TISAB) was added to eliminate interference from other ions.

4. Data Analysis and Interpretation

Charge balance errors were calculated for all samples, with 95% showing errors <5%, indicating acceptable analytical quality. Hydrogeochemical facies were classified using Piper trilinear diagrams and Stiff patterns. Saturation indices for relevant minerals were calculated using PHREEQC geochemical modelling software.

Statistical analyses included correlation analysis, principal component analysis (PCA), and cluster analysis to identify geochemical associations and potential fluoride sources. Ionic ratios and graphical methods were employed to elucidate water-rock interaction processes and mixing phenomena.

Results

1. Groundwater Chemistry Overview

Exhibit wide variations in chemical composition reflecting diverse geological controls and hydrogeochemical processes. Electrical conductivity ranges from 450 to 3,200 µS/cm (mean: 1,245 µS/cm), indicating fresh to brackish water conditions. pH values vary between 6.8 and 8.9 (mean: 7.8), predominantly alkaline due to carbonate weathering and ion exchange processes.

Total dissolved solids (TDS) concentrations range from 290 to 2,050 mg/L, with 40% of samples exceeding desirable limits for drinking water (500 mg/L). Spatial distribution shows increasing TDS concentrations in discharge areas and regions with intensive groundwater exploitation, consistent with evapotranspiration and flow path evolution effects.

2. Fluoride Distribution and Occurrence

Fluoride concentrations in groundwater range from a median of 1.8 mg/L. Statistical analysis reveals a positively skewed distribution, indicating geogenic sources and localised enrichment processes. Spatially, the highest fluoride concentrations are found.

Seasonal variations show 15-25% higher fluoride concentrations during the pre-monsoon period, attributed to concentration effects through evapotranspiration and reduced groundwater recharge. Depth-wise analysis indicates maximum fluoride concentrations at intermediate depths (30-80 m), corresponding to weathered zone aquifers with prolonged water-rock interaction.

Approximately 67% of groundwater samples exceed the WHO guidelines for fluoride in drinking water (1.5 mg/L), while 31% exceed the maximum permissible limit of 4.0 mg/L recommended by the Bureau of Indian Standards. This widespread exceedance indicates significant public health risks requiring immediate attention and mitigation measures.

3. Hydrogeochemical Facies and Water Types

Piper diagram analysis reveals three distinct hydrogeochemical facies: Ca-HCO_3 type (22% of samples), Na-HCO_3 type (47% of samples), and mixed Ca-Na-HCO_3-SO_4 type (31% of samples). The Ca-HCO_3 facies represents fresh groundwater from carbonate weathering, predominantly in recharge areas with relatively low fluoride concentrations (0.3-1.2 mg/L).

Na-HCO_3 type waters show the highest fluoride concentrations (1.8-4.8 mg/L), indicating advanced water-rock interaction, cation exchange, and evapotranspiration processes. This water type is dominant in crystalline rock aquifers and discharge zones where prolonged residence time facilitates fluoride enrichment through mineral dissolution and concentration mechanisms.

Mixed water types represent transitional compositions resulting from flow path evolution, mixing of different water masses, or anthropogenic influences. These waters show intermediate fluoride levels and variable ionic strength depending on local hydrogeological conditions.

4. Statistical Relationships and Correlation Analysis

Correlation analysis reveals significant positive correlations between fluoride and several parameters: Na^+ (r=0.78), HCO_3^- (r=0.71), pH (r=0.68), and TDS (r=0.72). Strong negative correlations exist with Ca^{2+} (r=-0.65) and Mg^{2+} (r=-0.58), indicating inverse relationships associated with ion exchange processes and mineral solubility controls.

Principal Component Analysis identifies three major components explaining 76% of the total variance. PC1 (43% variance) represents salinity and evapotranspiration effects, loading heavily on TDS, Na^+, Cl^-, and F^-PC2 (19% variance) reflects carbonate weathering processes with high loadings on Ca^{2+}, Mg^{2+}, and HCO_3^-. PC3 (14% variance) indicates anthropogenic influences through NO_3^- and SO_4^{2-} associations.

Cluster analysis distinguishes four distinct groundwater groups based on chemical composition: (1) fresh Ca-HCO_3 waters with low fluoride, (2) evolved Na-HCO_3 waters with high fluoride, (3) mixed composition waters, and (4) contaminated waters with elevated nitrate and sulfate concentrations.

5. Geochemical Modelling and Saturation States

PHREEQC modelling results indicate varying saturation states for fluoride-controlling minerals. Samples with high fluoride concentrations (>2.5 mg/L) show saturation to oversaturation concerning fluorite (SI: 0.1 to 0.8), suggesting equilibrium-controlled fluoride release from this primary source mineral.

Undersaturation concerning calcite and gypsum in high-fluoride waters supports fluoride enrichment through preferential dissolution of fluoride-bearing minerals over calcium-bearing phases. Ion activity ratios (Na^+/Ca^{2+}, HCO_3^-/SO_4^{2-}) indicate progressive water-rock interaction and cation exchange, favouring fluoride mobility.

Speciation calculations show fluoride predominantly exists as free F^- ions (>95%) at prevalent pH conditions, maximising bioavailability and health risks. Minor complexation with Ca^{2+} and Mg^{2+} occurs at higher pH values but remains negligible in the overall fluoride mass balance.

Discussion

1. Geochemical Processes Controlling Fluoride Occurrence

Complex interactions between geological, climatic, and hydrogeological factors operating at multiple scales. Primary fluoride sources include weathering of fluoride-bearing minerals present in crystalline basement rocks, particularly biotite mica, hornblende, and accessory fluorite commonly associated with granitic intrusions in the regional geological framework.

Chemical weathering intensity is enhanced by the semi-arid climate, which promotes prolonged water-rock interaction through slow groundwater circulation and high evapotranspiration rates. The prevalence of Na-HCO_3 water types in high-fluoride areas indicates advanced chemical evolution through silicate weathering and cation exchange processes that create favourable conditions for fluoride enrichment.

Minerals and weathered feldspar surfaces play a crucial role in fluoride mobility. This process removes Ca^{2+} from solution, preventing fluorite precipitation and maintaining fluoride in dissolved form. The strong negative correlation between fluoride and calcium concentrations (r=-0.65) supports this mechanism as a primary control on fluoride distribution.

Evapotranspiration effects are evident from the seasonal variations in fluoride concentrations and correlations with salinity parameters. During dry periods, groundwater becomes concentrated through the selective removal of water molecules while dissolved ions accumulate, leading to 15-25% increases in fluoride concentrations. This process is particularly significant in shallow aquifers and discharge zones where groundwater approaches the surface.

2. Spatial Controls and Hydrogeological Factors

The spatial distribution of fluoride shows clear geological controls, with the highest concentrations occurring in areas underlain by crystalline rocks and their weathered products. Vindhyan sedimentary formations generally exhibit lower fluoride levels due to dilution effects and different mineral assemblages with reduced fluoride content.

Groundwater flow patterns influence fluoride distribution through transport and concentration mechanisms. Recharge areas typically show lower fluoride concentrations due to dilution with fresh precipitation, while discharge zones and areas with sluggish flow exhibit elevated concentrations through cumulative water-rock interaction and evapotranspiration effects.

Aquifer depth relationships reveal maximum fluoride enrichment in intermediate depth ranges (30-80 m), corresponding to the weathered zone where mineral alteration is most intense. Shallow aquifers may experience dilution from recent recharge, while deeper confined aquifers often contain older waters with different geochemical evolution pathways.

The role of structural controls is evident from fluoride concentration patterns following fracture systems and weathering zones in crystalline rocks. These features enhance the water-rock interaction surface area and facilitate preferential flow paths that concentrate fluoride through prolonged mineral dissolution processes.

3. Health Implications and Risk Assessment

The widespread occurrence of elevated fluoride concentrations poses significant public health risks for populations dependent on groundwater sources in the Agra district. With 67% of samples exceeding WHO guidelines and 31% exceeding maximum permissible limits, systematic health monitoring and mitigation strategies are urgently needed.

Chronic exposure to fluoride concentrations above 1.5 mg/L leads to dental fluorosis, characterised by tooth discolouration and enamel defects. At concentrations exceeding 3.0 mg/L, skeletal fluorosis becomes a concern, causing joint pain, skeletal deformities, and reduced mobility, particularly affecting elderly populations and individuals with prolonged exposure.

Vulnerable populations include children due to their higher water consumption per body weight and developing skeletal systems, pregnant women due to fluoride transfer to developing fetuses, and individuals with nutritional deficiencies that may exacerbate fluoride toxicity effects.

Risk assessment considering exposure pathways, population demographics, and fluoride concentration distributions indicates high-risk zones requiring immediate intervention through alternative water supply arrangements, defluoridation technologies, or source protection measures.

4. Mitigation Strategies and Management Implications

Effective fluoride mitigation requires multi-pronged approaches addressing both immediate health protection and long-term groundwater management. Short-term strategies include implementation of household-level or community-based defluoridation systems using activated alumina, bone char, or reverse osmosis technologies suitable for local conditions.

Long-term management involves source protection through regulation of groundwater exploitation, artificial recharge enhancement to dilute fluoride concentrations, and development of alternative water sources, including surface water utilisation and rainwater harvesting systems.

Geochemical understanding developed through this research supports targeted interventions focusing on high-risk areas identified through spatial analysis and hydrogeochemical characterisation. Monitoring networks should prioritise locations with Na-HCO_3 water types, intermediate depth ranges, and geological settings favourable for fluoride enrichment.

Community education and health monitoring programs are essential components of comprehensive fluoride management strategies, ensuring awareness of health risks, proper use of mitigation technologies, and early detection of fluorosis symptoms requiring medical intervention.

Table 1: Summary statistics of groundwater chemical parameters in Agra district aquifers

Parameter	Units	Min	Max	Mean	Median	Std Dev	WHO/BIS Limits
pH	-	6.8	8.9	7.8	7.9	0.4	6.5-8.5
EC	µS/cm	450	3200	1245	1180	485	-
TDS	mg/L	290	2050	798	756	311	500
F^-	mg/L	0.3	4.8	2.1	1.8	1.1	1.5
Ca^{2+}	mg/L	18	186	68	62	32	200
Mg^{2+}	mg/L	12	89	34	31	18	100
Na^+	mg/L	45	420	156	142	78	200
K^+	mg/L	2.1	28	8.4	7.2	5.2	12
HCO_3^-	mg/L	110	580	285	268	98	600
SO_4^{2-}	mg/L	8.5	165	52	45	31	400
Cl^-	mg/L	22	285	89	78	56	250
NO_3^-	mg/L	2.1	95	28	24	18	45

Table 2: Correlation matrix showing relationships between fluoride and major ions

Parameter	F^-	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	HCO_3^-
F^-	1.00							
pH	0.68**	1.00						
EC	0.72**	0.45*	1.00					
TDS	0.72**	0.43*	0.98**	1.00				
Ca^{2+}	-0.65**	-0.38*	-0.12	-0.15	1.00			
Mg^{2+}	-0.58**	-0.28	0.15	0.12	0.56**	1.00		
Na^+	0.78**	0.52**	0.89**	0.87**	-0.42*	-0.18	1.00	
HCO_3^-	0.71**	0.62**	0.76**	0.74**	-0.35*	-0.22	0.68**	1.00

*Significant at $p<0.05$; **Significant at $p<0.01$

Table 3: Hydrogeochemical facies characteristics and fluoride occurrence patterns

Water Type	% of Samples	F^- Range (mg/L)	Mean F^- (mg/L)	Dominant Processes
$Ca\text{-}HCO_3$	22	0.3-1.2	0.8	Carbonate weathering, fresh recharge
$Na\text{-}HCO_3$	47	1.8-4.8	3.1	Ion exchange, evapotranspiration, and silicate weathering
Mixed $Ca\text{-}Na\text{-}HCO_3\text{-}SO_4$	31	0.9-2.8	1.6	Water mixing, flow path evolution

Conclusion

This comprehensive study of fluoride occurrence in Agra district aquifers reveals complex geochemical processes controlling fluoride distribution in semi-arid hydrogeological settings. Key findings include widespread fluoride contamination affecting 67%.

Hydrogeochemical analysis identifies mineral weathering, with $Na\text{-}HCO_3$ water types exhibiting the highest concentrations through advanced water-rock interaction processes. Statistical analysis and geochemical modelling confirm fluorite dissolution as the dominant fluoride source, with saturation equilibrium controlling fluoride levels in high-concentration zones.

The research provides a scientific basis for targeted groundwater management strategies, emphasising the need for comprehensive mitigation approaches combining technological solutions, source protection measures, and community health interventions. These findings have broader implications for understanding fluoride geochemistry in similar hydrogeological settings across the Indo-Gangetic Plains and other semi-arid regions globally.

Future research should focus on isotope geochemistry for enhanced source identification, temporal monitoring for long-term trend analysis, and effectiveness evaluation of implemented mitigation measures. Integration of remote sensing and GIS technologies can support expanded spatial coverage and development of predictive models for fluoride occurrence in ungauged areas.

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