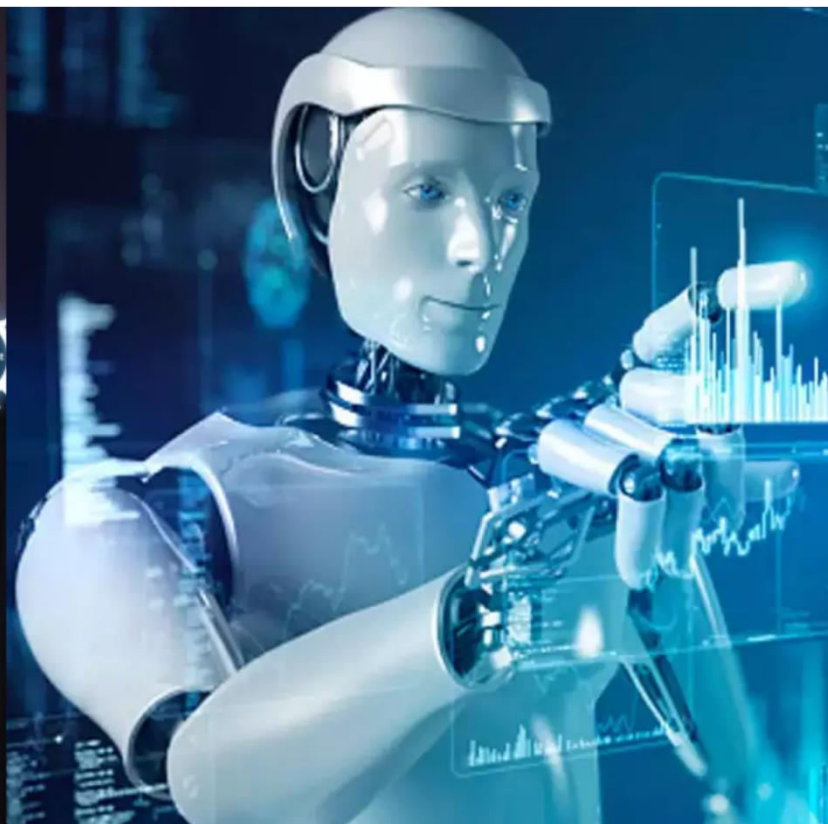




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Groundwater Fluoride in Wazirpur Tehsil, Rajasthan: A Hydrogeochemical and Analytical Chemistry Assessment Framework

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ABSTRACT: Fluoride in groundwater is governed by mineral dissolution, calcium activity, alkalinity, pH, ionic strength and aquifer residence time. This chemistry-focused paper examines plausible hydrogeochemical controls on dissolved fluoride in Wazirpur Tehsil, Rajasthan, and develops a testable laboratory and field strategy for source attribution and drinking-water evaluation. The Central Ground Water Board (CGWB) reported fluoride concentrations of 0.01–7.6 mg L⁻¹ in a 2021 study of the then–Sawai Madhopur district, with 36% of analyzed samples above 1.5 mg L⁻¹; these district-level observations must not be interpreted as Wazirpur-specific measurements. The proposed work integrates seasonal stratified sampling, fluoride ion-selective electrode (ISE) analysis with total ionic strength adjustment buffer, confirmatory ion chromatography, major-ion determinations, ionic charge-balance checks, mineral saturation calculations and multivariate hydrochemistry. Explicit quality-control criteria and an interpretable risk-classification scheme are specified. The central testable hypothesis is that relatively alkaline, calcium-depleted groundwaters with extended water–rock interaction will exhibit elevated dissolved fluoride where fluorine-bearing minerals are accessible. A well-executed investigation would distinguish equilibrium constraints from mixing, evaporation and anthropogenic contributions and support evidence-based drinking-water interventions.

Keywords: fluoride; groundwater chemistry; Wazirpur; fluorite saturation; ion-selective electrode; hydrogeochemistry; Rajasthan; analytical quality assurance

I. INTRODUCTION

Groundwater fluoride is an anionic contaminant of environmental and public-health significance at elevated concentrations. Dissolved fluorine occurs predominantly as F⁻ over the near-neutral to alkaline pH range of most fresh groundwaters. Its presence cannot be inferred from geology alone: mineral accessibility, thermodynamic driving force, flow paths and aqueous complexation jointly determine measured concentrations. Indian Standard IS 10500:2012 identifies 1.0 mg L⁻¹ as the acceptable fluoride concentration and 1.5 mg L⁻¹ as the permissible concentration in the absence of an alternate source; the WHO guideline value is 1.5 mg L⁻¹ [1–3].

A CGWB aquifer-mapping report for the then–Sawai Madhopur district lists substantial fluoride exceedance in the regional sample set and identifies heterogeneity among administrative blocks [4]. Administrative boundaries and current local hydrogeology must be verified before extrapolating those findings to Wazirpur. The scientific problem is thus a coupled analytical and geochemical one: quantify F⁻ robustly and determine the processes producing its spatial and seasonal variation.

II. RESEARCH AIMS AND FALSIFIABLE HYPOTHESES

The primary objective is to establish the distribution and chemical controls of groundwater fluoride in Wazirpur using an experimentally reproducible protocol. Secondary objectives are to characterize major-ion facies, assess compliance with drinking-water criteria, test seasonal consistency and distinguish likely geogenic drivers from non-geogenic indicators.

H1: F⁻ concentration increases with pH and alkalinity after accounting for depth and season. H2: F⁻ concentration tends to increase as free Ca²⁺ activity decreases where fluorite dissolution or saturation is influential. H3: fluoride-rich

waters show distinct ionic facies and mineral-saturation signatures rather than only increasing total dissolved solids. These are hypotheses, not results.

III. GEOCHEMICAL THEORY AND REACTION PATHWAYS

3.1 Mineral dissolution and equilibrium-

Fluorite dissolution is described by $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$, with the thermodynamic solubility product $K_{\text{sp}} = a(\text{Ca}^{2+}) \cdot a(\text{F}^{-})^2$. At a given fluorite saturation state, lower free Ca^{2+} activity permits higher fluoride activity. The measurable total dissolved concentrations differ from free-ion activities owing to ionic strength and complex formation. Fluoride can also be released through weathering of fluorapatite, biotite, amphiboles and other fluorine-bearing minerals where locally present; their actual roles require lithological or solid-phase confirmation [4–6].

Calcite precipitation may indirectly favor fluoride enrichment by decreasing dissolved calcium: $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{s})$. A working fluoride model should therefore consider alkalinity, carbonate speciation, calcite saturation and fluorite saturation together; a simple fluoride-versus-pH correlation alone cannot prove mechanism.

3.2 Ion exchange, complexation and evapoconcentration-

Cation exchange may reduce aqueous calcium when Na^{+} replaces exchangeable Ca^{2+} on clay surfaces, potentially changing fluoride mobility. Carbonate equilibria regulate both pH and Ca^{2+} availability. Evaporation can increase conservative-ion concentrations, but fluoride need not increase proportionally because mineral precipitation, adsorption and mixing may intervene. Consequently, $\text{Na}^{+}/\text{Ca}^{2+}$, $\text{HCO}_3^{-}/\text{Ca}^{2+}$, $\text{F}^{-}/\text{Cl}^{-}$ and saturation indices should be compared rather than attributing fluoride solely to evaporation.

3.3 Adsorption–desorption behavior-

Mineral surfaces such as aluminium and iron (oxyhydr)oxides can bind fluoride through ligand exchange. Adsorption is sensitive to pH, surface charge and competing anions such as bicarbonate and phosphate. Speciation modelling should be complemented by targeted sorption tests if surface reactions are hypothesized to dominate. Natural geochemical associations do not constitute proof of a causal source without mineralogical evidence.

IV. STUDY DESIGN AND SAMPLING STRATEGY

A defensible initial design is a stratified campaign across geographically distributed villages and water-source types. As an illustrative planning target, sample approximately 30–45 distinct groundwater sources across pre-monsoon and post-monsoon campaigns (60–90 observations if all sources are revisited). This is a proposed design, not a field count; final sample size must be justified by well inventory, terrain, pilot variance and statistical power. Record GPS coordinates, source type, well depth where verified, pumping history, recent rainfall, land use and water-treatment status. Do not combine treated tap water with untreated aquifer samples in geochemical interpretation.

Before collection, follow an approved site-specific purge/stabilization procedure and measure in situ pH, temperature, specific conductance and dissolved oxygen. Collect a fluoride/anion aliquot in a clean polymer bottle; use a separate filtered and appropriately acid-preserved aliquot for dissolved metals/cations where the validated method requires it. Fluoride should not be acidified by default. Refrigerate and analyze within the holding times stipulated by the selected accredited laboratory SOP. Include duplicate, blank and reference-material samples.

V. ANALYTICAL CHEMISTRY METHODS

5.1 Fluoride potentiometry-

Fluoride ion-selective electrode potentiometry is a primary quantitative method. Calibrate using matrix-appropriate fluoride standards bracketing the expected sample concentrations. Mix each standard and sample with the specified proportion of total ionic strength adjustment buffer (TISAB) to control ionic strength and pH and, where appropriate, complex interfering polyvalent ions. Record the stabilized electrode potential (mV). The ideal Nernst response for a monovalent anion is about -59.16 mV per tenfold increase in activity at 25°C ; actual slope acceptance follows electrode and method validation. Quantify by the standard calibration relation $E = E_0 - S \cdot \log_{10}(a\text{F}^{-})$, with the sign convention confirmed against instrument output. Run continuing calibration checks, and reanalyze out-of-range samples after validated dilution [7].

High Al^{3+} or Fe^{3+} can complex fluoride; elevated hydroxide activity and matrix mismatch may interfere with potentiometry. Matrix spikes and, for selected high-risk samples, standard addition or an orthogonal analytical method help diagnose bias. The detection limit, quantification limit and uncertainty must be determined experimentally, not assumed.

5.2 Ion chromatography and supporting ions-

Analyze anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) by validated ion chromatography for confirmation and hydrochemical interpretation. Quantify Ca^{2+} , Mg^{2+} , Na^+ and K^+ using validated ICP-OES, AAS or appropriate equivalent methods; assess HCO_3^-/CO_3^{2-} through alkalinity titration and measured pH. Record alkalinity units and convert consistently. Compare duplicate fluoride values using a predeclared agreement criterion determined from method precision. Do not report chromatographic or elemental measurements unless actually performed.

5.3 Quality assurance and charge-balance assessment-

Quality-control element	Proposed analytical rule / interpretation
Calibration	≥ 5 suitable levels where supported by SOP; verify residuals and working range
Calibration verification	Bracketing continuing check; use validated laboratory tolerance (e.g., $\pm 10\%$ as planning target)
Field duplicates	Target relative percent difference $\leq 10\%$ when concentrations are well above LOQ
Spike recovery	Set matrix-specific method acceptance range before sample analysis
Blanks	Below method reporting limit, or investigate source of contamination
Ionic charge balance	$CBE = \frac{100(\sum cations - \sum anions)}{(\sum cations + \sum anions)}, \text{ in meq L}^{-1}; \text{ flag } CBE > 5-10\% \text{ for review}$

The QC thresholds above are provisional planning values rather than claims of compliance with a particular standard. Ionic balance errors may reflect missing ions, analytical problems or incorrect chemical-unit conversions; all should be investigated before excluding measurements.

VI. HYDROGEOCHEMICAL DATA TREATMENT

Report pH, EC, TDS, alkalinity, major-ion concentrations and fluoride with units, detection limits and measurement uncertainty. Construct Piper and Gibbs diagrams to summarize facies and possible controls, while recognizing that such diagrams are descriptive rather than definitive causal tests. Calculate saturation indices $SI = \log_{10}(IAP/K)$ for fluorite and calcite using a specified thermodynamic database and a program such as PHREEQC. Explicitly document temperature assumptions, activity model and missing inputs. Conduct Spearman correlation tests and appropriately adjusted regression analyses, accounting for well clustering and season; do not infer source causation from bivariate correlations.

Spatial interpolations (e.g., inverse-distance weighting or kriging) should be attempted only after examining source density, clustering, anisotropy, variograms and cross-validation error. Display sampled-point values and map uncertainty, and avoid portraying unsampled villages as confirmed hotspots. Where feasible, measure fluoride content in representative aquifer solids with XRD-supported mineral identification and elemental analysis to evaluate proposed host phases.

VII. FLUORIDE CLASSIFICATION AND EXPOSURE INTERPRETATION

Measured fluoride (mg L ⁻¹)	Reporting category	Interpretive action
≤1.0	Within BIS acceptable concentration	Continue routine monitoring
>1.0 to ≤1.5	Above acceptable but not above permissible threshold	Confirm and investigate alternate supply context
>1.5	Exceeds BIS permissible concentration and WHO guideline value	Confirm promptly; notify responsible water-quality authority and prioritize safe-water response

These categories are chemical screening thresholds, not individual diagnoses. Fluoride intake depends on water consumption, diet and age, and health impacts depend on sustained exposure. Dental fluorosis and, at greater chronic exposures, skeletal fluorosis warrant public-health attention; epidemiological assessment would require ethics approval, clinical expertise and careful exposure histories [3].

VIII. INTERPRETATION OF EXISTING REGIONAL EVIDENCE

The 2021 CGWB aquifer-mapping report for the then–Sawai Madhopur district reported fluoride from 0.01 to 7.6 mg L⁻¹, with 44% of its analyzed samples at or below 1.0 mg L⁻¹, 20% between 1.0 and 1.5 mg L⁻¹, and 36% above 1.5 mg L⁻¹ [4]. The report names certain affected blocks; its sampling frame must be checked before assigning any of these proportions to present-day Wazirpur Tehsil. These values motivate a local study but are not its findings. Neither an inferred Wazirpur mean nor a local exposure prevalence can be responsibly calculated from the district percentages.

IX. DISCUSSION: MECHANISTIC TESTS, LIMITATIONS AND RESEARCH CONTRIBUTION

A strong chemistry study would triangulate three independent evidence streams: (i) robust fluoride quantification with matrix-specific QC, (ii) free-ion activities and mineral saturation constrained by complete major-ion chemistry, and (iii) aquifer lithology and seasonal hydraulic context. A consistent high-pH, low-calcium, near-fluorite-equilibrium pattern would support a mineral-equilibrium interpretation, but causality would remain conditional on mineral availability and flow-path evidence. Conversely, high fluoride together with high nitrate or agricultural tracers could justify investigations of additional human influences without treating these tracers as definitive proof.

The proposed design has limitations: sparse well coverage, unknown screened intervals, temporal pumping changes, mixing and inconsistent laboratory preservation can distort interpretation. Selection of sampling points should therefore be documented transparently. Health statements should remain at the level of exposure screening unless properly designed clinical or epidemiological evidence is acquired.

X. CONCLUSION

The principal scientific contribution is an analytical-chemistry framework connecting accurate F⁻ measurement to mechanistic aquifer interpretation in Wazirpur. Fluorite and carbonate equilibria, calcium depletion, ion exchange and surface reactions are competing or complementary hypotheses requiring field validation. The BIS acceptable and permissible thresholds (1.0 and 1.5 mg L⁻¹) provide operational screening categories; regional CGWB data justify investigation but cannot replace local measurements. The proposed ISE–IC confirmation workflow, ionic balance audit, major-ion facies assessment, PHREEQC saturation analysis and seasonal design provide a defensible foundation for a future original research article.

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