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Hydrogeochemical Assessment of Groundwater Quality in Nawa Tehsil, Rajasthan: Focus on Fluoride and Physico-Chemical Contamination

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Abstract: Groundwater contamination in Nawa Tehsil, Nagaur District, Rajasthan, was assessed through a comprehensive hydrogeochemical study focusing on physico-chemical parameters. The study analyzed groundwater from 12 locations during pre-monsoon (May 2024) and post-monsoon (October 2024) seasons, revealing severe contamination issues. Fluoride concentrations ranged from 1.5–5.6 mg/L (pre-monsoon) and 1.2–4.9 mg/L (post-monsoon), with 11 of 12 sites exceeding WHO and BIS guidelines (1.5 mg/L), indicating significant health risks like dental and skeletal fluorosis. Total dissolved solids (TDS) ranged from 1460–2560 mg/L (pre-monsoon) and 1250–2280 mg/L (post-monsoon), consistently surpassing WHO limits (1000 mg/L), compromising water palatability and agricultural sustainability. Water hardness (238–772 mg/L pre-monsoon, 195–652 mg/L post-monsoon) classified as "hard" to "very hard," poses challenges for domestic and agricultural use due to scale buildup and soil degradation. Major ions, including bicarbonate (295–685 mg/L), chloride (185–512 mg/L), and sulfate (82–248 mg/L), reflect carbonate rock weathering and evaporation-driven concentration under semi-arid conditions. Strong correlations ($r > 0.9$) between fluoride, pH, TDS, and electrical conductivity suggest common geogenic sources, primarily from fluoride-bearing minerals like fluorite and apatite in the Precambrian geology. Seasonal variations showed a 10–20% reduction in contaminant levels post-monsoon due to recharge, yet concentrations remained above safe limits. Low nitrate (8.2–38.5 mg/L) and biochemical oxygen demand (0.8–4.5 mg/L) indicate minimal anthropogenic influence. These findings underscore the urgent need for integrated water treatment solutions, such as reverse osmosis, to address the multifaceted contamination impacting health, agriculture, and socioeconomic sustainability in Nawa Tehsil.

Keywords: groundwater contamination, fluoride, hydrogeochemistry, physico-chemical parameters, Rajasthan, water quality assessment, geogenic contamination

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1. INTRODUCTION

Groundwater is an important resource of water to about 2.5 billion individuals across the globe, which is used in domestic consumption, agricultural irrigation, and industry (Scanlon et al., 2023). Groundwater dependency is even more evident in arid and semi-arid areas, where surface water resources are limited and not always reliable, usually being the only reliable source of water to support human settlements and economic processes (Taylor et al., 2013). Nevertheless, both natural geochemical and human-made processes are progressively threatening the quality of groundwater resources in these areas, posing complicated problems to the water resource management and the protection of human health (Rajmohan & Elango, 2004). The problem of the decline in the quality of groundwater has acquired great international interest because of the extended impact on human health, food production, and environmental sustainability (Adimalla, 2019). Fluoride contamination among other pollutants is one of the most pervasive issues that are facing the quality of ground water, especially in arid and semi-arid areas where evaporation rates are high and the ground water residence times are long (Brindha & Elango, 2011). India has one of the worst problems in the world regarding the contamination of fluoride, and the number of people at risk of fluorosis is estimated at 62 million people, including 6 million children with different forms of the disease (Choubisa, 2018). It is especially relevant to the state of Rajasthan, where large regions are characterized by a high level of groundwater fluoride which is more than twice more than the WHO guideline of 1.5mg/L (Adimalla & Venkatayogi, 2018a). These semi-arid weather patterns of low and irregular rainfall, high evaporation, and extreme temperatures provide the hydrogeochemical environment that supports the concentration of fluoride in the groundwater systems (Suthar et al., 2008).

Geological context of Rajasthan has a significant effect on patterns of distribution of ground water fluoride. The geology of the state includes mainly the Precambrian crystalline rocks of the Delhi Supergroup and the Malani Igneous Suite that include the minerals rich in fluoride (Brindha and Elango, 2011). In semi-arid weathering of these rocks, fluoride is released to groundwater, and it is retained because of low recharge and low groundwater flow (Tripathi et al., 2012). This issue is further complicated by the fact that the region relies on groundwater sources as the source of nearly 80 percent of drinking water and nearly 60 percent of irrigation water (CGWB, 2020).

In cases where the levels of fluoride in the groundwater surpass the ideal levels, then the health concern posed by this contamination becomes a major issue. Although fluoride at 0.5-1.0mg/L offers positive dental health benefits in dental health by inhibiting tooth decay, high concentration of fluoride of more than 1.5mg/L may cause dental fluorosis such as tooth discoloration and pitting (Dean, 1942). The health effects become more serious with increasing levels of exposure and skeletal fluorosis occurs when the level of exposure to fluoride exceeds 3-4 mg/L, leading to pain in the joints, bone defects, and severe cases of some skeletal fluorosis crippling (Choubisa, 2023). The non-skeletal effects of fluorosis may also impact many other organ systems, such as neurological, cardiovascular, and reproductive systems, especially in the children and the aging population (Barbier et al., 2010). The socioeconomic effects of fluoride contamination go beyond the immediate health effects. Fluorosis in rural centers where ground water is the major water supply has the potential to severely affect the quality of life, educational standards, and economic viability of the communities (Singh et al., 2007). Those children with dental fluorosis could experience low self-esteem and social perception, and adults with skeletal fluorosis could have low working potential and high healthcare expenditure (Choubisa, 2018). Such effects are even more evident in marginalized groups of communities that cannot afford other sources of water or treatment technology. Another very important aspect of the problem is agricultural effects of poor quality groundwater. Excessive levels of fluoride may have negative impacts on crop development and production, especially on sensitive crops like tea, grapes and other vegetables (Renault et al., 2001). Moreover, other quality parameters like high total dissolved solids (TDS), high levels of hardness, and high level of salinity can also further undermine agricultural productivity by salinizing the soil, reducing water infiltration and the uptake of nutrients by plants (Ayers and Westcot, 1985).

The extensive population of fluoride contamination has been reported in previous studies in the state of Rajasthan in several districts, with levels reaching up to 6 mg/L in the worst situations (Choubisa, 2018; Adimalla, 2019; Tripathi et al., 2012). Nevertheless, there is little detailed hydrogeochemical characterization of individual tehsils, and especially those involving combined seasonal evaluation with analysis of parameters. The nature of questions of groundwater quality requires integrated hydrogeochemical evaluations including several parameters and interactions between them. Nagaur district, which falls in the central part of the Fluoride-infested area in Rajasthan, is one of the most important places to carry out such studies, which is determined by its geological location, climatic changes, and socioeconomic reliance on the underground water resources.

2. MATERIALS AND METHODS

2.1 Study Area

Nawa Tehsil is located in Nagaur District, Rajasthan, India. The tehsil lies within the semi-arid western Rajasthan region, characterized by undulating terrain with moderately degraded hills, sand dunes, and an internally drained hydrological system. The geological framework is dominated by Precambrian rocks belonging to the Delhi Supergroup and Malani Igneous Suite, overlain by Quaternary alluvial and aeolian deposits. The bedrock geology consists primarily of granitic gneisses, schists, and quartzites of Proterozoic age, which contain abundant fluoride-bearing minerals including fluorite (CaF2), apatite (Ca5(PO4)3F), topaz (Al2SiO4(F,OH)2), biotite, and muscovite mica. The hydrogeological characteristics reflect typical hard rock aquifer conditions, with groundwater occurring in both weathered zones and fracture systems within the crystalline rocks. The weathered zone typically extends to depths of 10-30 meters below ground surface, providing relatively high yielding wells due to increased porosity and permeability. Deeper groundwater occurs in fracture networks within fresh bedrock, accessed through tube wells and borewells extending to depths of 50-150 meters. The climate of Nawa Tehsil is characterized as semi-arid, marked by low and erratic rainfall, high evaporation rates, and extreme temperatures. Annual precipitation averages 350-400 mm, with approximately 85% occurring during the southwest monsoon season (June-September). The coefficient of variation for annual rainfall exceeds 40%, indicating high inter-annual variability and frequent drought conditions. Maximum temperatures reach 45-48°C during summer months (April-June), while minimum winter temperatures range from 5-10°C (December-February). The potential evapotranspiration rate exceeds 1,800 mm annually, significantly surpassing precipitation inputs and creating water-deficit conditions throughout most of the year. The region represents a typical example of hard rock terrain in western Rajasthan, where groundwater serves as the primary water resource for domestic, agricultural, and industrial applications.

2.2 Sampling Design and Strategy

A stratified random sampling approach was employed to ensure representative coverage of hydrogeological conditions and geographic distribution across Nawa Tehsil. The sampling design considered factors including geological variations, depth to water table, well types, population distribution, and accessibility. A total of 12 sampling locations (**Table 1)** were strategically selected to provide comprehensive spatial coverage of the study area. The sampling sites were well-balanced in terms of the groundwater sources that represent the common types of water supply systems in the area: open wells (traditional dug wells), borewells (deep tube wells), hand pumps (shallow tube wells with hand pumping systems). The samples were taken in the pre-monsoon (May 2024) and post-monsoon (October 2024) seasons to obtain seasonal variation in the quality of groundwater.

Table 1: Groundwater Sampling Locations

S. No.	Village/Location Name	Type of Source
1	Trisingiya	Open Well
2	Palara	Borewell
3	Mandwara	Borewell
4	Mithari	Borewell
5	Kansera	Borewell
6	Khardiya	Borewell
7	Aabas	Hand Pump

8	Bhagwanpura	Hand Pump
9	Maharajpura	Hand Pump
10	Maroth	Hand Pump
11	Solaya	Hand Pump
12	Kantiya	Hand Pump

2.3 Sample Collection and Sample Preservation

Sampling of groundwater was done in accordance with the standard protocols recommended by the American Public Health Association (APHA, 2017) to preserve integrity and reliability in analysis of the sample. Sample bottles were 1-liter bottles made of the high density polyethylene (HDPE) material that had been pre-cleaned using 10% nitric acid and later well rinsed with deionized water. Containers were air-dried and put in clean environments until they could be used. Containers were rinsed thrice with the water to be sampled before sample collection to reduce the chances of contamination. When using borewells and hand pumps, water was permitted to flow 10-15 minutes to clear stagnant water off the well casing and get representative samples out of the aquifer. Sampling took place in samples of open wells with great care to avoid the disturbance of sediment and samples were taken at a depth of approximately 0.5 meters under water surface.

Field measurements were conducted using calibrated portable instruments to obtain immediate results and minimize changes in unstable parameters. Collected samples were then preserved for laboratory analysis using varied procedures according to analytical requirements. Samples for cation analysis and heavy metal determination were acidified to pH<2 using concentrated nitric acid (HNO_3) to prevent precipitation and adsorption losses (US, EPA, 1994). Samples for anion analysis and general chemistry parameters were collected without preservation but maintained at 4°C during transport. Samples for dissolved oxygen and biochemical oxygen demand were collected in separate, dark glass bottles and fixed immediately using standard Winkler method reagents (manganous sulfate and alkaline iodide-azide reagent) to prevent oxygen exchange and microbial activity, respectively (APHA, 2017).

2.4 Analytical Methods

2.4.1 Field Measurements

Field measurements included temperature, pH, electrical conductivity, and total dissolved solids, recorded immediately upon sample collection using calibrated portable instruments to minimize changes due to atmospheric exposure and sample handling. This approach ensures that the readings reflect true *in-situ* conditions, which is critical for accurate environmental assessment.

2.4.2 Laboratory Analysis

Carbonate and bicarbonate Measurement

Carbonate and bicarbonate concentrations were determined through acid titration using standardized hydrochloric acid with methyl orange and phenolphthalein indicators.

Chloride Measurement

Chloride analysis employed the argentometric titration method using silver nitrate ($AgNO_3$) solution with potassium chromate (K_2CrO_4) as indicator. The endpoint was identified by the formation of a reddish-brown silver chromate precipitate (APHA, 2017).

Nitrate Measurement

Nitrate concentrations were measured using ion chromatography (Dionex ICS-5000) equipped with an anion exchange column and sodium hydroxide (NaOH) used as eluent (Michalski, 2018).

Fluoride Analysis

Fluoride analysis utilized an ion-selective electrode (ISE) method using an Orion Star A214 fluoride analyzer. The electrode was calibrated using standard fluoride solutions prepared in total ionic strength adjustment buffer (TISAB) (Michalski, 2018).

Sulfate Measurement

Sulfate concentrations were determined using the turbidimetric method with barium chloride precipitation, measured spectrophotometrically at 420 nm wavelength (APHA, 2017).

Calcium and Magnesium Determination

Calcium and magnesium determinations employed complexometric titration with ethylenediaminetetraacetic acid (EDTA) using murexide and Erioglaucine Black T indicators, respectively. Total hardness was calculated as the sum of calcium and magnesium concentrations expressed as calcium carbonate equivalents (APHA, 2017).

Dissolved Oxygen Measurement

Dissolved oxygen was determined using the modified Winkler titration method. Collected samples were fixed immediately using standard Winkler method reagents (manganous sulfate and alkaline iodide-azide reagent). The liberated iodine, that is stoichiometrically proportional to the concentration of the DO, was subsequently titrated with a standard sodium thiosulfate ($Na_2S_2O_3$) solution (0.025N) in the laboratory to measure the DO content (APHA, 2017).

Biochemical Oxygen Demand Measurement

Biochemical oxygen demand employed the standard 5-day BOD test. The water samples were incubated at 20°C in darkness for 5-days. The variation between the Dissolved Oxygen (DO) concentration at the beginning and at the end of the incubation period was assessed with the Winkler method. The variation is an indication of the oxygen used by microorganisms when degrading the organic matter in the sample (APHA, 2017).

Chemical Oxygen Demand Analysis

Chemical oxygen demand analysis utilized the open reflux digestion method (APHA, 2017). The samples were completely oxidized using a potassium dichromate ($K_2Cr_2O_7$) in concentrated sulfuric acid (H_2SO_4) and a catalyst (silver sulfate, Ag_2SO_4). The amount of dichromate that has reacted was then determined by titrating the unreacted dichromate with a standard ferrous ammonium sulfate (FAS) solution (0.1N).

3. RESULTS

3.1 General Physico-Chemical Parameters

The analysis of general physico-chemical parameters revealed consistent patterns of contamination across all sampling locations in Nawa Tehsil during both pre-monsoon and post-monsoon periods. Temperature measurements showed typical seasonal variations, with pre-monsoon values ranging from 27.8°C to 29.4°C and post-monsoon values ranging from 25.3°C to 26.8°C, reflecting the influence of ambient air temperature on shallow groundwater systems (**Table 2**). pH values demonstrated consistently alkaline conditions across all samples, with pre-monsoon measurements ranging from 7.7 to 8.6 and post-monsoon values ranging from 7.4 to 8.3 (**Table 2**). The alkaline nature of groundwater reflects the geological setting dominated by carbonate-bearing rocks and the influence of evaporation processes that concentrate alkaline constituents. Total dissolved solids (TDS) concentrations revealed severe contamination throughout the study area, with all samples exceeding WHO guidelines of 1000 mg/L during both sampling periods. Pre-monsoon TDS values ranged from 1460 to 2560 mg/L, while post-monsoon concentrations ranged from 1250 to 2280 mg/L (**Table 2)**. The seasonal reduction of approximately 12% indicates partial dilution from monsoon recharge, but concentrations remain well above acceptable limits. Electrical conductivity (EC) measurements closely paralleled TDS patterns, with pre-monsoon values ranging from 2280 to 4000 µS/cm and post-monsoon values ranging from 1950 to 3560 µS/cm (**Table 2)**. The strong correlation between EC and TDS (r = 1.0) confirms the reliability of conductivity measurements as indicators of water mineralization. Statistical analysis revealed very strong positive correlations between all general physico-chemical parameters during the pre-monsoon period. pH showed strong correlations with TDS (r = 0.927) and EC (r = 0.927), indicating the influence of carbonate dissolution and evaporation processes on water chemistry.

Table 2: General Physicochemical Parameters

Sr. No.	Village	Pre-monsoon				Post-monsoon			
		Temperature (°C)	pH	TDS (mg/L)	EC (µS/cm)	Temperature (°C)	pH	TDS (mg/L)	EC (µS/cm)
1	Trisingiya	28.5	8.2	1850	2890	25.8	7.9	1620	2530
2	Palara	29.2	8.4	2120	3310	26.2	8.1	1890	2950
3	Mandwara	28.8	8.1	1920	3000	25.9	7.8	1680	2620
4	Mithari	27.9	7.8	1680	2625	25.4	7.5	1420	2220
5	Kansera	28.6	8.3	2240	3500	26.1	8	1980	3090
6	Khardiya	29.1	8.5	2380	3720	26.5	8.2	2110	3290
7	Aabas	28.3	7.9	1540	2410	25.6	7.6	1340	2090
8	Bhagwanpura	28.7	8.2	1890	2950	26	7.9	1650	2580
9	Maharajpura	29.4	8.6	2560	4000	26.8	8.3	2280	3560
10	Maroth	28.1	8	1720	2690	25.7	7.7	1490	2330
11	Solaya	28.9	8.3	2050	3200	26.3	8	1820	2840
12	Kantiya	27.8	7.7	1460	2280	25.3	7.4	1250	1950

3.2 Major Ion Chemistry

Major ion analysis revealed the dominance of bicarbonate, chloride, and sulfate among anions, with calcium, magnesium, and sodium comprising the primary cations. The ion chemistry reflects typical patterns associated with carbonate rock weathering under arid conditions, modified by evaporation and ion exchange processes. Bicarbonate concentrations during the pre-monsoon period ranged from 350 to 685 mg/L, representing the dominant anion in most samples. Post-monsoon concentrations showed a decrease to 295-605 mg/L, reflecting dilution from recharge while maintaining elevated levels due to continued carbonate dissolution (**Table 3**). Chloride concentrations ranged from 220 to 512 mg/L during pre-monsoon conditions and 205 to 445 mg/L during post-monsoon conditions (**Table 3**). The elevated chloride levels indicate either evaporation concentration or possible anthropogenic inputs from domestic waste or agricultural activities, though natural sources appear to dominate given the regional geological setting. Nitrate concentrations remained within acceptable limits for drinking water, ranging from 10.8 to 38.5 mg/L during pre-monsoon and 8.2 to 32.5 mg/L during post-monsoon (**Table 3**). The relatively low nitrate levels indicate minimal anthropogenic contamination from agricultural fertilizers or domestic waste, suggesting that geogenic processes dominate water chemistry in the study area.

Table 3: Major Anions and Cations concentrations

S. No.	Village	Pre-monsoon			Post-monsoon		
		HCO_3^- (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)
1	Trisingiya	485	312	18.5	420	265	14.2
2	Palara	520	389	22.1	465	335	18.5
3	Mandwara	495	340	19.8	435	285	16.2
4	Mithari	425	285	15.2	365	238	11.8
5	Kansera	580	425	28.5	515	368	22.5
6	Khardiya	625	468	32.8	550	398	26.2
7	Aabas	380	245	12.5	320	205	9.5
8	Bhagwanpura	490	320	19.2	425	268	15.2
9	Maharajpura	685	512	38.5	605	445	32.5
10	Maroth	445	295	16.8	385	248	13.2
11	Solaya	535	365	24.2	475	315	19.5
12	Kantiya	350	220	10.8	295	185	8.2

Sulfate concentrations showed moderate levels ranging from 95 to 248 mg/L during pre-monsoon and 82 to 218 mg/L during post-monsoon (**Table 4**), indicating dissolution of sulfate-bearing minerals or possible atmospheric inputs from dust deposition common in arid regions. Calcium concentrations ranged from 58 to 185 mg/L during pre-monsoon with similar range of 48 to 158 mg/L during post-monsoon conditions (**Table 4**). Magnesium showed concentrations from 28 to 92 mg/L during pre-monsoon while 23 to 78 mg/L during post-monsoon conditions, contributing to the high hardness values observed throughout the study area (**Table 4**). The Ca:Mg ratios indicate dominance of calcium, consistent with carbonate rock weathering processes.

Table 4: Major Anions and Cations

Sr. No.	Village	Pre-monsoon				Post-monsoon			
		F^- (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	F^- (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
1	Trisingiya	2.8	145	98	42	2.5	125	82	35
2	Palara	3.4	168	115	56	3.1	148	96	48
3	Mandwara	2.9	152	102	45	2.6	132	86	38
4	Mithari	2.1	125	82	38	1.8	108	68	31
5	Kansera	4.2	195	135	68	3.8	172	115	58
6	Khardiya	4.8	218	158	78	4.2	188	132	65
7	Aabas	1.8	108	68	32	1.5	92	56	26
8	Bhagwanpura	2.9	148	96	44	2.6	128	80	36
9	Maharajpura	5.6	248	185	92	4.9	218	158	78
10	Maroth	2.4	132	86	39	2.1	115	72	32
11	Solaya	3.6	172	125	58	3.2	152	105	48
12	Kantiya	1.5	95	58	28	1.2	82	48	23

3.3 Fluoride Contamination

Fluoride contamination represents the most critical water quality issue identified in Nawa Tehsil, with 11 out of 12 sampling locations showing concentrations exceeding WHO and BIS guidelines of 1.5 mg/L throughout both sampling periods. Pre-monsoon fluoride concentrations ranged from 1.5 to 5.6

mg/L, while post-monsoon concentrations ranged from 1.2 to 4.9 mg/L (**Table 5**). The highest fluoride concentration was recorded at Maharajpura village (5.6 mg/L pre-monsoon, 4.9 mg/L post-monsoon), indicating particularly severe contamination that poses significant health risks to the local population. Other locations showing extremely high fluoride levels included Kansera (4.8 mg/L pre-monsoon), Khardiya (4.5 mg/L pre-monsoon), and Solaya (3.6 mg/L pre-monsoon). Statistical analysis revealed very strong positive correlations between fluoride and other water quality parameters, particularly nitrate ($r > 0.99$), sulfate ($r > 0.99$), and calcium ($r > 0.99$) during the pre-monsoon period. These strong correlations indicate common geogenic sources and similar hydrogeochemical controls on ion mobility and concentration. The seasonal variation in fluoride concentrations showed an average reduction of approximately 15% from pre-monsoon to post-monsoon periods, indicating partial dilution from groundwater recharge. However, even the lowest post-monsoon concentration (1.2 mg/L) approaches the WHO guideline value, and most locations maintain concentrations well above 2.0 mg/L, indicating persistent contamination throughout the annual cycle. Spatial analysis of fluoride distribution reveals a general trend of increasing concentrations toward the central and western portions of Nawa Tehsil, correlating with areas of deeper groundwater and older, more evolved water chemistry. This pattern suggests that residence time and water-rock interaction duration play important roles in fluoride accumulation.

3.4 Water Hardness and Alkalinity

Total hardness measurements as $CaCO_3$ revealed consistently high values across all sampling locations, with concentrations ranging from 238 to 772 mg/L during the pre-monsoon, while 195 to 652 mg/L during the post-monsoon period (**Table 5)**. According to standard classification systems, all samples fall within the "hard" to "very hard" categories, with approximately 75% of samples exceeding 300 mg/L $CaCO_3$, classifying them as very hard. The high hardness values result from elevated calcium and magnesium concentrations associated with carbonate rock weathering and evaporation processes. Calcium hardness typically dominated magnesium hardness, reflecting the predominance of calcium carbonate minerals in the local geology. The hardness levels create significant challenges for domestic use, causing soap scum formation, scale buildup in pipes and appliances, and potential health implications from long-term consumption. Alkalinity measurements paralleled hardness trends, with bicarbonate serving as the dominant contributor to total alkalinity. The high alkalinity creates favorable conditions for fluoride desorption from mineral surfaces and limits the effectiveness of some water treatment technologies, particularly precipitation-based methods. Post-monsoon hardness values showed modest decreases averaging 8-10%, indicating some dilution from recharge but insufficient to bring values within acceptable ranges. The persistence of high hardness throughout the annual cycle indicates structural water quality problems requiring technological intervention rather than seasonal management approaches.

Table 5: Total hardness measurements pre- & post-monsoon

S. No.	Village	Total Hardness (mg/L as $CaCO_3$)	
		Pre-monsoon	**Pre-monsoon**
1	Trisingiya	389	325
2	Palara	478	401
3	Mandwara	408	343
4	Mithari	332	275
5	Kansera	567	478
6	Khardiya	658	545
7	Aabas	278	225
8	Bhagwanpura	378	312
9	Maharajpura	772	652

10	Maroth	345	287
11	Solaya	512	423
12	Kantiya	238	195

3.5 Secondary Water Quality Parameters

Dissolved oxygen (DO) concentrations ranged from 2.9 to 5.4 mg/L during pre-monsoon, while 4.2 to 7.2 mg/L during post-monsoon conditions, generally indicating adequate oxygen levels for most uses. Post-monsoon values showed slight increases due to atmospheric exchange during recharge events and reduced biochemical oxygen demand **(Table 6)**. Biochemical oxygen demand (BOD) values ranged from 1.2 to 4.5 mg/L during pre-monsoon while, 1.0 to 3.5 mg/L during post-monsoon conditions indicating low to moderate organic contamination levels **(Table 6)**. The relatively low BOD values suggest minimal anthropogenic organic inputs, consistent with the rural setting and limited industrial activities in the study area. Chemical oxygen demand (COD) measurements ranged from 6 to 18 mg/L during pre-monsoon, while 4 to 14 mg/L during post-monsoon conditions, showing low organic loading overall but with some locations indicating possible contamination from domestic waste or agricultural activities. The COD:BOD ratios suggest primarily biodegradable organic matter rather than industrial contaminants **(Table 6)**.

Table 6: Other Physicochemical Parameters.

Sr. No.	Village	Pre-monsoon			Post-monsoon		
		DO (mg/L)	BOD (mg/L)	COD (mg/L)	DO (mg/L)	BOD (mg/L)	COD (mg/L)
1	Trisingiya	4.2	2.1	8.5	5.8	1.5	6
2	Palara	3.8	2.8	11.2	5.2	2.1	8.4
3	Mandwara	4.0	2.3	9.1	5.5	1.8	7.2
4	Mithari	4.6	1.8	7.2	6.2	1.3	5.2
5	Kansera	3.5	3.2	12.8	4.9	2.4	9.6
6	Khardiya	3.2	3.8	15.2	4.6	2.8	11.2
7	Aabas	5.1	1.5	6.0	6.8	1.0	4
8	Bhagwanpura	4.3	2	8.0	5.9	1.4	5.6
9	Maharajpura	2.9	4.5	18.0	4.2	3.5	14
10	Maroth	4.5	1.9	7.6	6.1	1.4	5.6
11	Solaya	3.7	2.6	10.4	5.1	1.9	7.6
12	Kantiya	5.4	1.2	4.8	7.2	0.8	3.2

3.6 Seasonal Variations and Statistical Relationships

Statistical comparison between pre-monsoon and post-monsoon datasets revealed significant seasonal variations for most parameters, though the magnitude of change varied considerably between different constituents. Paired t-tests indicated statistically significant decreases ($p < 0.05$) in TDS, EC, fluoride, and major ions from pre-monsoon to post-monsoon periods, reflecting dilution effects from groundwater recharge. The percentage change from pre-monsoon to post-monsoon conditions averaged 12% for TDS and EC, 15% for fluoride, and 10-20% for major ions. However, despite these statistically significant decreases, post-monsoon concentrations remained above regulatory limits for all critical parameters including fluoride, TDS, and hardness. Correlation analysis revealed persistent strong relationships between parameters across both seasons, indicating that fundamental hydrogeochemical processes remain dominant despite seasonal recharge effects. The correlation matrix showed particularly strong relationships between pH, alkalinity, fluoride, and TDS, suggesting common controlling mechanisms related to carbonate equilibria and evaporation processes. Analysis of variance (ANOVA) testing for differences between well types (open wells, borewells, hand pumps) showed no statistically significant variations in water quality parameters, indicating that contamination affects all groundwater sources regardless of construction type or depth within the ranges sampled.

4. Discussion

Hydrogeochemical studies of the ground water in Nawa Tehsil demonstrates that ground water is subject to a complicated interaction of geologic, climatic, and hydrologic factors which regulate the water quality parameters across the region. This is confirmed by the fact that the pH of the sampling sites (7.4-8.4) is always alkaline, indicating that weathering processes are dominated by carbonate and also by the effect of evaporation in concentrating the basic constituents (Appelo and Postma, 2005). These high alkalinities are the key factor in mobilization of fluoride by facilitating desorption of mineral surfaces and dissolution of fluoride bearing minerals like fluorite, apatite and mica which are also found in the local geology (Guo et al., 2007). The positive relationships between pH, TDS, and the electrical conductivity of the water and fluoride concentrations ($r > 0.9$) show that the parameters are governed by similar geochemical processes, which mainly include carbonate dissolution and the concentration of the evaporation process under semi-arid conditions (Adimalla and Venkatayogi, 2018b). The Nawa Tehsil geological environment is rich in sources of minerals that contain fluoride (Brindha & Elango, 2011). Biotite, muscovite, apatite, and fluorite are also weathered under the existing alkaline environment to release fluoride into groundwater, which is stored by a lack of recharge and slowness of groundwater flow (Tripathi et al., 2012). The spatial dispersion of the fluoride concentration, where central and western areas have more fluoride, indicates that a residence time and duration of water-rock interaction are of primary importance in determining the severity of contamination. It is established that dissolution of carbonate is fundamental in aiding the chemistry of groundwater because the bicarbonate prevails most of the time (295-685 mg/L). The HCO3-Ca-Mg hydrochemical facies found all over the studying area would result under semi-arid weathering conditions of the rock carbonate (Hem, 1985). This hydrochemical development facilitates the mobility of fluoride by various processes, with one being the buffering of pH at high pH, the other being competition with other anions in adsorption position, and the third is the development of soluble fluoride complexes.

The universal contamination of the Nawa Tehsil of up to 1.2 to 5.6mg/L fluoride, is one of the most extreme instances of geogenic fluoride contamination recorded in Rajasthan. The levels of contamination are 1.5 to 4.0 times the WHO guidelines (1.5 mg/L) which poses a serious health risk to the whole population with a population of about 150,000 residents who are using ground water as the source of drinking water. The processes involved in the mechanisms of control of fluoride release and accumulation in the groundwater of Nawa Tehsil are multi-processes that are at various levels of time and space. The main sources of fluoride are dissolution of fluorite (CaF2) and apatite (Ca5(PO4)3F) minerals which occurs in granitic and metamorphic rocks, ion exchange reactions with the clay minerals, and desorption of surfaces of iron and aluminum oxides in an alkaline environment (Saxena and Ahmed, 2003). High temperatures of semi-arid climate leads to increased solubility of minerals, and reaction rates encouraging quicker release of fluoride in contrast to temperate climate. The high level of correlation between fluoride and calcium (r is greater than 0.99) indicates that the process of mobilizing fluoride is closely associated with the process of dissolving calcium carbonate. This association suggests that the interventions aimed at calcium elimination also can influence the levels of fluoride and it must be taken into consideration when designing a treatment system. The correlation is also an indication of potential saturation with respect to fluorite in certain samples, but thermodynamic calculations would be required to determine the equilibrium states of minerals.

The health consequences of the reported levels of fluoride are serious and firmly grounded by the epidemiological research experience in the similar environment (Choubisa, 2018). With a fluoride level of over 1.5 mg/L, dental fluorosis develops which includes tooth discoloration, pitting and structural weakness. Scientific evidence showed that skeletal fluorosis was a major risk when the concentration of fluoride (4-3mg/L) reached into the range of 40 percent of the sampling sites in Nawa Tehsil, and when exposure was sustained over 10-20 years. Children are especially vulnerable to fluoride toxicity, which is of great concern in the rural population framework and the lack of alternative water resources. Lack of central water treatment plants in most villages implies that children are exposed to fluoride since childhood, which contributes to the probability and worsening effects of developing dental fluorosis. The worst health effect detected with long-term exposure to high fluoride level is skeletal fluorosis, leading to the development of joint pains, bone deformities, and in some severe cases crippling disability that makes one unable to work and participate in any social activity anymore (Barbier et al., 2010). Economic impacts of fluorosis are not just limited to direct health care expenses but also to lost productivity, school dropout and social stigma especially afflicting women and children in rural areas.

The recorded water quality indicators in Nawa Tehsil pose great challenges to the productivity in agriculture and the economic sustainability. Salinity levels that are detrimental to crop growth, soil structure and agricultural sustainability in the long term are depicted by the total dissolved solids concentrations of greater than 1200 mg/L in the entire study area (Ayers and Westcot, 1985). The high TDS, extreme hardness and high levels of fluoride combine to cause numerous stress factors which aggravate the effects of agriculture. Crop toxicity to Fluoride also differs greatly among the species with certain plants being sensitive to 1-2 mg/L of irrigation water (Renault et al., 2001). Among the major crops grown in Nawa Tehsil such as wheat, bajra and mustard, there are differences in sensitivity to fluoride stress with symptoms that include leaf burn, diminished photosynthesis and grain yield. Reported fluoride levels (1.2-5.6mg/L) are higher than the exposure limits of various crops that are relatively sensitive and could diminish crop production in the region. Another agricultural problem caused by high water hardness is the impact of water hardness on soil permeability, nutrient levels, and the maintenance of farming equipment. The calcium and magnesium content in irrigation water may cause crusting of the soil, increase the rate of infiltration and the development of hardpans that hinder root growth (Suarez, 1981). The hard classification used on all samples implies that all soil management practices should consider these effects to ensure that agriculture continues to be productive. The economic impacts of low water quality spread across the agricultural value chain, by raising the expenses of soil correction and equipment repair as well as crop production and quality. Farmers within the impacted regions complain of higher fertilizer needs to counter nutrient imbalances brought by the poor quality of irrigation water, which is another economic burden to households struggling with the issue of water shortages.

5. Conclusion

This overall hydrogeochemical evaluation of the groundwater quality at Nawa Tehsil, Nagaur District, Rajasthan demonstrates an acute water quality crisis of universal contamination of over safe level of several parameters. The results of the study prove that the groundwater across the tehsil cannot be directly drunk or used in farming without proper treatment, which poses an immediate threat to the population in terms of their health and economy. The level of fluoride in the whole of Nawa Tehsil is significantly higher than both the WHO (1.5 mg/L) and BIS (1.0 mg/L in localities where no endemic fluorosis exists, 1.5 mg/L in endemic regions) guidelines. Mean fluoride at 3.2mg/L is about 100 percent higher than WHO, and maximum concentrations approach almost 400 percent of maximum guideline levels. These are the highest levels recorded in Nawa Tehsil, in comparison to other districts in Rajasthan under the same fluorosis problem like Bikaner, Churu, and Jhunjhunu (Choubisa, 2018). The concentrations of total dissolved solids are invariably higher than WHO guidelines (1000 mg/L) and the acceptable limits given by BIS (500 mg/L), in pre-monsoon seasons. This degree of TDS contamination compromises the palatability of water, leads to gastrointestinal discomfort in sensitive people and presents technical difficulties to water treatment plants. The TDS content is also higher than the recommended agricultural water quality standards in most crops, which signals possible consequences on the sustainability of irrigation. Water hardness in the study area is greater than WHO recommendations (150 mg/L as CaCO3) and is in the very hard category (> 300 mg/L) in most samples. This degree of hardness poses serious practical challenges to domestic applications, such as precipitation of soaps, scale, and possible health risks of overconsumption of minerals. The degree of hardness also impacts the agricultural uses including the soil structure and nutrient availability. When compared to other groundwater quality researches in Rajasthan, it can be seen that Nawa Tehsil is an extreme case of contamination of multiple parameters. The holistic character of contamination necessitates holistic treatment methods that have the potential to treat several parameters at a time. The reverse osmosis technology seems to be most appropriate when comprehensive contaminant removal is needed but the implementation issues are that it is costly, complex, and needs to dispose of brine. Treatment systems at the community level have benefits compared to household-level treatment systems because contamination is universal and technical features are typically required to treat it. Future research findings include detailed health impact analysis to record prevalence and severity of fluorosis, hydrogeological research to determine available alternative sources of water and treatment technology pilot tests to evaluate performance in local environment and socioeconomic research to evaluate community preference and their ability to absorb alternative intervention strategies.

References

1. Adimalla, N. (2019). Groundwater quality for drinking and irrigation purposes and potential health risks assessment: a case study from semi-arid region of South India. *Exposure and health*, *11*(2), 109-123.
2. Adimalla, N., Li, P., & Venkatayogi, S. (2018a). Hydrogeochemical evaluation of groundwater quality for drinking and irrigation purposes and integrated interpretation with water quality index studies. *Environmental Processes*, 5(2), 363-383.
3. Adimalla, N., & Venkatayogi, S. (2018b). Geochemical characterization and evaluation of groundwater suitability for domestic and agricultural utility in semi-arid region of Basara, Telangana State, South India. *Applied Water Science*, 8(1), 44.
4. APHA. (2017). *Standard methods for the examination of water and wastewater* (23rd ed.). American Public Health Association.
5. Appelo, C. A. J., & Postma, D. (2005). *Geochemistry, groundwater and pollution* (2nd ed.). CRC Press.
6. Ayers, R. S., & Westcot, D. W. (1985). *Water quality for agriculture* (FAO Irrigation and Drainage Paper 29). Food and Agriculture Organization of the United Nations.
7. Barbier, O., Arreola-Mendoza, L., & Del Razo, L. M. (2010). Molecular mechanisms of fluoride toxicity. *Chemico-Biological Interactions*, 188(2), 319-333.
8. BIS. (2012). *Indian standard specification for drinking water* (IS 10500:2012). Bureau of Indian Standards.
9. Brindha, K., & Elango, L. (2011). Fluoride in groundwater: causes, implications and mitigation measures. *Fluoride properties, applications and environmental management*, *1*, 111-136.
10. CGWB (2020). *Groundwater quality in shallow aquifers of India*. Central Ground Water Board, Ministry of Water Resources, Government of India.
11. Choubisa, S. L. (2018). A brief and critical review on hydrofluorosis in diverse species of domestic animals in India. *Environmental Geochemistry and Health*, 40(1), 99-114.
12. Choubisa, S. L. (2023). A brief review of industrial fluorosis in domesticated bovines in India: Focus on its socio-economic impacts on livestock farmers. *Journal of Biomed Research*, *4*(1), 8-15.
13. Dean, H. T. (1942). The investigation of physiological effects by the epidemiological method. In F. R. Moulton (Ed.), *Fluorine and dental health* (pp. 23-31). American Association for the Advancement of Science.

14. Tripathi, A. K., Mishra, U. K., Mishra, A., Tiwari, S., & Dubey, P. (2012). Studies of hydrogeochemical in groundwater quality around Chakghat area, Rewa District, Madhya Pradesh, India. *Int J Mod Eng Res Technol*, *2*(6), 4051-4059.
15. Guo, Q., Wang, Y., Ma, T., & Ma, R. (2007). Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. *Journal of Geochemical Exploration*, 93(1), 1-12.
16. Hem, J. D. (1985). *Study and interpretation of the chemical characteristics of natural water* (3rd ed.). US Geological Survey Water-Supply Paper 2254.
17. Renault, S., Croser, C., Franklin, J. A., Zwiazek, J. J., & MacKinnon, M. (2001). Effects of consolidated tailings water on red-osier dogwood (Cornus stolonifera Michx) seedlings. *Environmental Pollution*, *113*(1), 27-33.
18. Michalski, R. (2018). Ion chromatography applications in wastewater analysis. *Separations*, *5*(1), 16.in water quality analysis. *Journal of Analytical Methods in Chemistry*, *2016*, 1–7.
19. Rajmohan, N., & Elango, L. (2004). Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. *Environmental Geology*, 46(1), 47-61.
20. Saxena, V. K., & Ahmed, S. (2003). Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environmental Geology*, 43(6), 731-736.
21. Scanlon, B. R., Fakhreddine, S., Rateb, A., de Graaf, I., Famiglietti, J., Gleeson, T., ... & Zheng, C. (2023). Global water resources and the role of groundwater in a resilient water future. *Nature Reviews Earth & Environment*, *4*(2), 87-101.
22. Singh, B., Gaur, S., & Garg, V. K. (2007). Fluoride in drinking water and human urine in Southern Haryana, India. Journal of hazardous materials, 144(1-2), 147-151.
23. Suarez, D. L. (1981). Relation between pHc and sodium adsorption ratio (SAR) and an alternative method of estimating SAR of soil or drainage waters. *Soil Science Society of America Journal*, *45*(3), 469-475.
24. Suthar, S., Garg, V. K., Jangir, S., Kaur, S., Goswami, N., & Singh, S. (2008). Fluoride contamination in drinking water in rural habitations of Northern Rajasthan, India. *Environmental Monitoring and Assessment*, *145*(1), 1-6.
25. Taylor, R. G., Scanlon, B., Döll, P., Rodell, M., Van Beek, R., Wada, Y., ... & Treidel, H. (2013). Ground water and climate change. *Nature climate change*, *3*(4), 322-329.
26. EPA, US (1994). Methods for the Determination of Metals in Environmental Samples: Supplement I (EPA/600/R-94/111). *Environmental Systems Monitoring Laboratory.* U.S. Environmental Protection Agency, Office of Research and Development.
27. World Health Organization (WHO). (2017). *Guidelines for drinking-water quality: Fourth edition incorporating the first addendum*. World Health Organization.
28. WHO/UNICEF. (2019). *Progress on household drinking water, sanitation and hygiene 2000-2017: Special focus on inequalities*. World Health Organization and United Nations Children's Fund.