International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 24s, 2025
https://www.theaspd.com/ijes.php

Correlation Analysis of Heavy Metals (Zn, Cd, Cu, Pb) and Fluoride in Groundwater of Nawa Tehsil: Environmental and Health Implications

Lakha Ram[1], **Chanchal Kachhfawa**[2]
[1]Research Scholar, Department of Chemistry, Engineering College Bikaner, Maharaja Ganga Singh University, Bikaner, Rajasthan, India-334004. lakharamsaini@gmail.com
[2]Assistant Professor, Department of Chemistry, Engineering College Bikaner, Maharaja Ganga Singh University, Bikaner, Rajasthan, India-334004. drchanchalkachhawa@gmail.com

Abstract
This study investigates the correlation between heavy metals (Fe, Zn, Cd, Cu, Pb) and fluoride in groundwater of Nawa Tehsil, Nagaur District, Rajasthan, focusing on environmental and health implications. Groundwater samples from 12 hand pump locations were analyzed during pre-monsoon (May 2024) and post-monsoon (October 2024) seasons. Fluoride concentrations ranged from 1.3–4.5 mg/L (pre-monsoon) and 1.1–4.0 mg/L (post-monsoon), with 67% of sites exceeding WHO limits (1.5 mg/L), indicating severe geogenic contamination from fluoride-bearing minerals like fluorite and apatite under alkaline conditions (pH 7.5–8.5). Iron levels (0.10–0.45 mg/L pre-monsoon, 0.07–0.34 mg/L post-monsoon) exceeded WHO guidelines (0.3 mg/L) at 50% of sites pre-monsoon, while lead exceedances occurred at 42%. Total dissolved solids (1420–2320 mg/L pre-monsoon, 1210–2050 mg/L post-monsoon) and hardness (212–612 mg/L as $CaCO_3$ pre-monsoon) indicate poor water quality, unsuitable for direct consumption in most locations except Dalelpura and Govindi. Strong correlations between fluoride and pH (r=0.78), bicarbonate (r=0.72), and TDS (r=0.69) suggest geochemical controls via mineral dissolution and anion exchange. Moderate correlations between fluoride and iron (r=0.58) and zinc (r=0.52) indicate potential synergistic mobilization. Seasonal reductions (12–18% for TDS, 10–15% for fluoride) reflect monsoon dilution, yet contamination persists. These findings highlight significant health risks, including dental/skeletal fluorosis and heavy metal toxicity, necessitating integrated treatment strategies like reverse osmosis or activated alumina to ensure safe drinking water and sustainable agriculture in Nawa Tehsil.
Keywords: *groundwater quality, fluoride contamination, heavy metals, correlation analysis, Rajasthan, hydrogeochemistry, public health*

1. INTRODUCTION

Groundwater is the main source of drinking water among about 2.5 billion individuals around the world, and it is especially relied on in arid and semi-arid areas that have a limited amount of surface water (Scanlon et al., 2023). The quality of groundwater resources has become one of the burning issues because of the growing anthropogenic stress and natural geochemical processes that bring numerous contaminants to the aquifer systems (Mukherjee and Singh, 2018). Fluoride is one of the most outstanding naturally occurring contaminants of this group, as it affects more than 200 million individuals across the world by consuming fluoride-contaminated groundwater (Srivastava and Flora, 2020). The combination of heavy metals and fluoride in groundwater systems occurs concurrently, forming complex hydrogeochemical conditions that present multidimensional health hazards to the populations that rely on it. About 66 million people are at risk of fluorosis in India, and the western states of Rajasthan, Gujarat and Haryana are the most impacted (Choubisa, 2018). However, the state of Rajasthan, especially, is a case study that is crucial to comprehend the problem of groundwater contamination in arid settings where groundwater is extracted to supply around 80 percent of drinking water and 60 percent of irrigation needs (Central Ground Water Board, 2020). The dry climate of the state is semi-arid with unpredictable rainfall, average of 575 mm/year, and evapotranspiration is high, which makes the groundwater mineralized and prone to the accumulation of contaminants (Ahada & Suthar, 2018). Rajasthan is characterized by hydrogeological structure, which comprises different aquifer systems like alluvial deposits in the eastern plains and hard rock crystalline formation in the west and the central areas (Singh et al., 2014). These geological structures particularly fluoride bearing minerals such as fluorapatite, biotite and muscovite lead to high fluoride content in ground water due to natural weathering and dissolution (Brindha and Elango, 2011). These aquifers have high PH conditions, which further promote the fluoride mobility, as an exchange process where the hydroxide ions replace the fluoride on the surface of the clay minerals, increasing its bio availability (Chaudhary and Satheeshkumar, 2018).

The case of Nawa Tehsil, Nagaur District demonstrates the complexity of the situation with groundwater quality problem in the semi-arid regions of India. This occurs in the notorious Kubbad-Patti belt where severe instances of endemic fluorosis have been seen to afflict the residents in the region (Gautam et al., 2013). The geological background of the area, such as Quaternary alluvial deposits of the bottom of Proterozoic rocks of the Delhi Supergroup and Malani Igneous Suite, predetermines the presence of the conditions that enable the development of fluoride leaching by parent rocks formations (Patil et al., 2020). The semi-arid climate, whose coordinates are about 27.02 o N and 75o E, has extreme temperatures and uneven precipitation intensity which affect the dynamics of groundwater recharge and quality. Nawa Tehsil, similar to many other places in Rajasthan, is largely reliant on groundwater irrigation, and more than 90% of rural households use this resource both at home and in agriculture (Patel et al., 2020). Crop productivity, soil health, and food safety are directly dependent on the quality of irrigation water, and the assessment of groundwater quality is important in sustainable agricultural development (Darko et al., 2008). Crop yields, soil chemistry and possible contamination of the food chain can be lowered by high salinity, surplus fluoride, and heavy metal contamination of irrigation water (Psyllos et al., 2022).
Other heavy metals found in groundwater systems usually co-exist with fluoride as a result of comparable geochemical controls and mobilization (Rahman et al., 2002). Although the presence of heavy metals in the Ganga River of Rajasthan has been noted in several districts (Jhunjhunu and Sikar), where the arsenic levels are well beyond the recommended limits by WHO (Singh & Ramakrishna et al., 2015), the relationship between heavy metals and fluoride in the groundwater systems is not well understood. The overlapping of these contaminants produces synergistic effects, which can increase health risks more than the effects of the individual contaminants (Everett et al., 2002). Health effects of fluoride contamination are well documented, with dental fluorosis at a higher concentration of over 1.5 mg/L and skeletal fluorosis and non-skeletal effects such as thyroid dysfunction and neurological impairment at a higher concentration (Kabir et al., 2020). Even in relatively low levels, heavy metals have the ability to bioaccumulate in human tissues and have chronic health problems such as cardiovascular disease, neurological disorders, and cancer (Jarup, 2003). The joint exposure to fluoride and heavy metals can lead to either additive or synergistic toxicological effects which have not been well characterized in existing body of literature.
Physico-chemical parameters of groundwater are indicators of the appropriateness of the water in various uses and can provide information on the geochemical activities that occurred (Tiwari et al., 2014). Such parameters as pH, electrical conductivity (EC), total dissolved solids (TDS), and predominant ions reveal the level of interaction between the water and rocks, concentration of evaporation, and contamination source (Goren et al., 2022). The relationships of such parameters with the levels of contaminants are used in establishing the source of the pollution and in establishing the remediation strategies. The problem of poor groundwater quality is likely to be compounded by the problem of climate change and increasing water stress in arid regions like Rajasthan, which will raise evaporation and reduce recharge and groundwater availability at depths more likely to contain higher levels of contaminants (Wang et al., 2023). One needs to be aware of the current state of groundwater quality and the factors involved to derive adaptive management strategies that will ensure water security in the evolving climatic conditions. The gaps in the knowledge regarding the ground water quality in Nawa Tehsil are important ones that are addressed by the current research that offers a detailed analysis of the physicochemical and heavy metal.

2. MATERIALS AND METHODS

2.1 Study Area

The study was done in Nawa Tehsil, Nagaur District, Rajasthan, India. The Nagaur District is located at the center stage of the state of Rajasthan. The Tehsil of Nawa is located in the southeastern part of the district, which is located in the infamous Kubbad-Patti region that is known to have a population characterized by the high prevalence of fluorosis. The geographic location of the study area is around 27.02degN latitude, and 75degE longitude, which places the study area in the typical semi-arid weather of western Rajasthan. The topography in the region is moderately undulating with degraded hills, sand dunes and internally drained hydrological system without well-developed external drainage systems. The region has a semi-arid climate with drastic temperature changes, as the temperatures can reach 45degC during summer months, and almost freezing during the winter months. The annual rainfall is about 400-500mm, which is mainly during the southwest monsoon (June-September), interannual variability is high and drought is frequent (Gautam & Bhardwaj, 2010).

2.2 Geological and Hydrogeological Setting
The geological framework of Nawa Tehsil consists primarily of Quaternary alluvial and aeolian deposits overlying older Proterozoic rocks belonging to the Delhi Supergroup and Malani Igneous Suite (Dutta, Purohit, & Sharma, 2021). The major aquifer systems occur within unconsolidated Quaternary sediments comprising sand, silt, and clay layers with varying hydraulic conductivity values. Groundwater occurs under unconfined to semi-confined conditions throughout the region, with water table depths ranging from 15 to 80 meters below ground surface (Dutta, Purohit, & Sharma, 2021). The elevated fluoride concentrations characteristic of Nagaur District and Nawa Tehsil specifically can be attributed to the underlying geological formations. Primary natural fluoride sources in the groundwater system are associated with dissolution of fluoride-bearing minerals including fluorite (CaF_2), apatite ($Ca_5(PO_4)_3F$), topaz ($Al_2SiO_4(F,OH)_2$), and various mica minerals present in the granitic and metamorphic rock formations (Al Sabti et al., 2023). The alkaline conditions prevalent in these aquifers enhance fluoride mobility through anion exchange mechanisms and mineral dissolution processes.

2.3 Sampling Design and Site Selection
A stratified random sampling methodology was employed to ensure representative coverage of groundwater quality variations across Nawa Tehsil. Twelve groundwater sampling stations were identified and selected based on multiple criteria including proximity to known fluoride-affected areas, accessibility for repeated sampling, and representation of diverse hydrogeological conditions. The sampling sites encompassed groundwater extraction points as hand pumps which constitute the primary water supply infrastructure for domestic and household uses in the region. The spatial distribution of sampling sites was designed to provide comprehensive coverage of the entire tehsil area, enabling identification of contamination hotspots and regional trends in groundwater quality. Site selection considered factors such as depth to water table, surrounding land use patterns, and potential contamination sources.

Table 1: Groundwater Sampling Locations.

S. No.	Village/Location Name	Type of Source
1	Shimbhupura	Hand Pump
2	Devli	Hand Pump
3	Deola	Hand Pump
4	Minda	Hand Pump
5	Govindi	Hand Pump
6	Rajas	Hand Pump
7	Lohrana	Hand Pump
8	Khushiya	Hand Pump
9	Bhuni	Hand Pump
10	Dalelpura	Hand Pump
11	Rewasa	Hand Pump
12	Lichana	Hand Pump

2.4 Sample Collection and Preservation
Groundwater samples were collected during two distinct seasons to capture temporal variations in water quality: pre-monsoon period (May 2024) and post-monsoon period (October 2024). Water samples were collected in pre-cleaned 1-liter high-density polyethylene (HDPE) containers that had been acid-washed with 10% nitric acid and thoroughly rinsed with deionized water (APHA, 2017). Prior to sample collection, containers were rinsed three times with the groundwater sample to eliminate potential contamination from cleaning residues. The hand pump water sources were purged for 10-15 minutes before sampling to ensure collected samples reflected true aquifer water characteristics rather than stagnant water within casing or pump assemblies. This purging process also allowed stabilization of field parameters such as temperature and pH.

Field measurements were performed immediately upon sample collection for unstable parameters including temperature, pH, electrical conductivity, and total dissolved solids using calibrated portable instruments. All samples designated for laboratory analysis were immediately preserved according to parameter-specific requirements. Samples intended for cation and heavy metal analysis were acidified with 2 mL concentrated nitric acid (analytical grade) to achieve pH < 2, preventing precipitation and adsorption of metal ions onto container walls. All samples were stored at 4°C in insulated containers during transportation to prevent microbial activity and chemical alterations. Samples for dissolved oxygen and biochemical oxygen demand were collected in separate dark glass bottles and fixed immediately using standard Winkler method reagents to prevent oxygen exchange and microbial activity, respectively (APHA, 2017).

2.5 Analytical Methods

All laboratory analyses were conducted following standard methods prescribed by the American Public Health Association (APHA, 2017) and the National Environmental Engineering Research Institute (NEERI) to ensure methodological consistency and result comparability. Analytical reagent (AR) grade chemicals were used for all analyses, with deionized water (resistivity ≥18.2 MΩ·cm) employed for dilutions and reagent preparations.

2.5.1 Field Measurements

Temperature measurements were conducted using calibrated portable digital thermometers at sampling sources. pH determinations utilized high-precision portable digital pH meters calibrated daily with certified buffer solutions of pH 4.01, 7.01, and 10.01. Electrical conductivity was measured in-situ using portable conductivity meters calibrated with standard KCl solution (1413 µS/cm at 25°C). Total dissolved solids were determined using portable digital TDS meters, typically calculated from EC measurements using standard conversion factors.

2.5.2 Major Ion Analysis

Carbonate and bicarbonate concentrations were determined through volumetric titration using standard sulfuric acid solution (0.02N) with phenolphthalein and methyl orange indicators. To a 50 ml of water sample few drops of phenolphthalein solution were added, and the solution was titrated with 0.05M HCl. Few drops methyl orange indicator were added to titration flask and the titration was continued till the end point when the colour changes from yellow to red (APHA, 2017).

Chloride was measured by argentometric titration using standard $AgNO_3$ solution (0.0141N) with potassium chromate indicator. 50 ml of each sample were placed in a 250 ml conical flask, 1 ml of K2CrO4 indicator was added, the solution was then titrated with (0.014 M) AgNO3 solution until a reddish-brown silver chromate precipitate was produced (APHA, 2017).

Nitrate analysis employed ion chromatography using a Dionex ICS-5000 system equipped with AS19 column and NaOH eluent (Michalski, 2018).

Fluoride concentrations were measured using the Ion Selective Electrode (ISE) method with an Orion Star A214 pH/ISE meter equipped with fluoride combination electrode. Samples were buffered with Total Ionic Strength Adjustment Buffer (TISAB) to maintain consistent ionic strength and eliminate interference (Michalski, 2018).

Sulfate was determined using the turbidimetric method with spectrophotometric measurement at 420 nm following $BaCl_2$ addition (APHA, 2017).

Calcium and magnesium were determined by complexometric titration with EDTA (0.01M) using murexide indicator for calcium and Eriochrome Black T for total hardness determination. Total hardness was calculated as the sum of calcium and magnesium concentrations expressed as $CaCO_3$ equivalents (APHA, 2017).

2.5.3 Heavy Metal Analysis

Heavy metal concentrations were determined using Atomic Absorption Spectroscopy (AAS) with a Perkin Elmer PinAAcle 900F instrument. Sample preparation involved filtration through 0.45 µm membrane filters followed by acidification with concentrated HNO_3. Calibration curves were established for each target metal (Fe, Zn, Cd, Cu, Pb) using certified reference materials. Quality control measures included analysis of method blanks, duplicate samples, spiked samples, and certified reference materials to ensure analytical accuracy and precision. Background correction was applied for all measurements, and detection limits were established based on instrument specifications and method validation procedures.

2.6 Statistical Analysis

Pearson's correlation coefficients were calculated to evaluate relationships between physicochemical parameters, with particular emphasis on fluoride-heavy metal correlations. Correlation matrices were generated to identify significant relationships between parameters and understand underlying geochemical controls. Principal Component Analysis (PCA) was considered for data dimension reduction and identification of major factors controlling water quality variations. All statistical analyses were performed using XLSTAT software package.

3. RESULTS

3.1 General Physicochemical Parameters

The physicochemical analysis of groundwater samples from twelve villages in Nawa Tehsil revealed significant spatial and temporal variations across both pre-monsoon and post-monsoon periods. Temperature measurements ranged from 27.7°C to 29.3°C during pre-monsoon season and 25.2°C to 26.7°C during post-monsoon period, reflecting the typical seasonal thermal dynamics of semi-arid regions. The groundwater exhibited consistently alkaline conditions throughout the study area, with pH values ranging from 7.8 to 8.5 in pre-monsoon and 7.5 to 8.2 in post-monsoon periods. Minda village recorded the highest pH (8.5) during pre-monsoon, while Dalelpura showed the lowest values (7.8 pre-monsoon, 7.5 post-monsoon), indicating variations in aquifer geochemistry and mineral dissolution processes (**Table 2**).

Total dissolved solids (TDS) concentrations demonstrated considerable spatial heterogeneity, ranging from 1420 mg/L in Dalelpura to 2320 mg/L in Minda during pre-monsoon season. Post-monsoon TDS values showed a general decreasing trend, ranging from 1210 mg/L to 2050 mg/L, attributed to dilution effects from monsoon recharge. The highest TDS concentrations were consistently observed in Minda (2320 mg/L pre-monsoon, 2050 mg/L post-monsoon) and Shimbhupura (2180 mg/L pre-monsoon, 1940 mg/L post-monsoon), suggesting enhanced water-rock interaction and evaporation concentration in these localities. Electrical conductivity (EC) values paralleled TDS patterns, ranging from 2220-3620 μS/cm during pre-monsoon and 1890-3200 μS/cm during post-monsoon periods (**Table 2**). The strong positive correlation between TDS and EC ($r > 0.95$) confirms the reliability of field measurements and indicates that dissolved ionic content primarily controls electrical conductivity in the study area.

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	Shimbhupura	29	8.4	2180	3410	26.4	8.1	1940	3030
2	Devli	28.4	8.1	1800	2810	25.9	7.8	1580	2470
3	Deola	28.8	8.2	1960	3060	26.2	7.9	1720	2690
4	Minda	29.3	8.5	2320	3620	26.7	8.2	2050	3200
5	Govindi	28.2	7.9	1590	2480	25.8	7.6	1380	2160
6	Rajas	28.6	8.1	1840	2870	26.1	7.8	1610	2520
7	Lohrana	29.1	8.4	2110	3300	26.5	8.1	1870	2920
8	Khushiya	28.5	8	1750	2730	25.9	7.7	1520	2370
9	Bhuni	28.9	8.3	2080	3250	26.3	8	1840	2870
10	Dalelpura	27.7	7.8	1420	2220	25.2	7.5	1210	1890
11	Rewasa	28.7	8.2	1900	2970	26.1	7.9	1670	2610
12	Lichana	29.2	8.4	2150	3360	26.6	8.1	1910	2980

3.2 Major Ion Chemistry

The major anion composition revealed carbonate and bicarbonate as dominant species, with concentrations ranging from 325-605 mg/L for bicarbonate and 10-45 mg/L for carbonate during pre-monsoon conditions . Bicarbonate concentrations decreased to 280-535 mg/L post-monsoon, while carbonate levels reduced to 8-37 mg/L, reflecting seasonal dilution effects and altered carbonate equilibrium dynamics. The highest bicarbonate concentrations were observed in Minda (605 mg/L pre-monsoon) and Shimbhupura (565 mg/L pre-monsoon), corresponding to areas with elevated pH and enhanced carbonate mineral dissolution (**Table 3**). Chloride concentrations exhibited significant spatial variation, ranging from 205-445 mg/L during pre-monsoon and 172-385 mg/L during post-monsoon periods, with Minda consistently showing the highest levels (**Table 3**).

Nitrate concentrations remained relatively low across all sampling locations, ranging from 9.2-30.5 mg/L during pre-monsoon and 7.2-25.2 mg/L during post-monsoon seasons. The observed nitrate levels generally remained below WHO permissible limits (50 mg/L), indicating limited anthropogenic nitrogen pollution from agricultural activities or domestic waste sources. However, slight elevation in nitrate concentrations at Minda and Shimbhupura suggests potential localized inputs from fertilizer application or organic waste decomposition **(Table 3)**. Sulfate concentrations ranged from 88-205 mg/L during pre-monsoon and 75-182 mg/L during post-monsoon periods, with spatial distribution patterns similar to other major ions, indicating common geochemical controls **(Table 3)**.

Table 3: Major Anions and Cations concentrations.

S. No.	Village	Pre-monsoon				Post-monsoon			
		CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)
1	Shimbhupura	38	565	398	26.5	32	495	342	21.8
2	Devli	24	465	315	18.8	19	405	268	15.5
3	Deola	29	505	348	21.2	23	445	295	17.8
4	Minda	45	605	445	30.5	37	535	385	25.2
5	Govindi	16	395	258	13.8	13	340	218	10.8
6	Rajas	25	480	308	18.2	19	415	258	14.5
7	Lohrana	35	545	385	25.8	29	485	332	21.2
8	Khushiya	22	450	298	17.5	17	395	252	13.8
9	Bhuni	33	540	372	24.8	27	475	318	20.5
10	Dalelpura	10	325	205	9.2	8	280	172	7.2
11	Rewasa	27	500	335	20.5	22	445	285	16.8
12	Lichana	37	560	392	26.2	30	495	338	21.5

Table 4: Major Anions and Cations.

S. 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	Shimbhupura	3.9	182	128	62	3.5	158	108	52
2	Devli	2.7	142	92	41	2.4	125	78	34
3	Deola	3.1	158	108	48	2.8	138	92	40
4	Minda	4.5	205	148	72	4	182	125	61
5	Govindi	1.9	115	72	35	1.6	98	60	29
6	Rajas	2.7	140	94	42	2.4	122	78	35
7	Lohrana	3.8	175	122	59	3.4	155	102	50
8	Khushiya	2.5	135	88	40	2.2	118	74	33
9	Bhuni	3.7	170	118	56	3.3	148	98	47
10	Dalelpura	1.3	88	52	25	1.1	75	44	21
11	Rewasa	3	155	105	46	2.7	135	88	38
12	Lichana	3.8	180	130	61	3.4	158	110	52

3.3 Fluoride Contamination

Fluoride contamination emerged as a critical groundwater quality concern throughout the study area, with concentrations substantially exceeding WHO permissible limits (1.5 mg/L) in most sampling locations. Pre-monsoon fluoride levels ranged from 1.3 mg/L in Dalelpura to 4.5 mg/L in Minda, while post-monsoon concentrations varied from 1.1 mg/L to 4.0 mg/L respectively **(Table 4)**. Eight out of twelve villages recorded fluoride concentrations above WHO limits during both seasons, with Minda, Shimbhupura, Lohrana, and Lichana showing particularly elevated levels (>3.5 mg/L). The spatial distribution pattern reveals higher fluoride concentrations in the central and northern parts of the study area, correlating with alkaline pH conditions and specific geological formations. Seasonal variations in fluoride concentrations demonstrated a consistent decreasing trend from pre-monsoon to post-monsoon periods, with average reductions ranging from 10-15% across sampling locations. This temporal pattern reflects dilution effects from monsoon recharge and altered hydrogeochemical equilibrium conditions.

International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 24s, 2025
https://www.theaspd.com/ijes.php

The strong positive correlation observed between fluoride and pH (r = 0.78) confirms the influence of alkaline conditions in facilitating fluoride mobility through anion exchange mechanisms and enhanced dissolution of fluoride-bearing minerals present in the aquifer matrix.

3.4 Heavy Metal Concentrations

Heavy metal analysis revealed variable contamination levels across the study area, with iron showing the highest concentrations among analyzed metals. Iron concentrations ranged from 0.10-0.45 mg/L during pre-monsoon and 0.07-0.34 mg/L during post-monsoon periods, with several locations exceeding WHO guidelines (0.3 mg/L). Minda recorded the highest iron levels (0.45 mg/L pre-monsoon, 0.34 mg/L post-monsoon), while Dalelpura showed consistently low concentrations across both seasons (**Table 5**). Zinc concentrations varied from 0.03-0.16 mg/L during pre-monsoon and 0.02-0.12 mg/L during post-monsoon periods, remaining below WHO limits (3.0 mg/L) but showing spatial variability consistent with other contaminants (**Table 5**). Cadmium levels remained relatively low throughout the study area, ranging from 0.001-0.004 mg/L during pre-monsoon and 0.001-0.003 mg/L during post-monsoon seasons, staying within WHO permissible limits (0.003 mg/L) at most locations. However, slight exceedances were observed in Minda and Shimbhupura during pre-monsoon conditions, indicating potential localized sources or enhanced mobility under specific geochemical conditions (**Table 5**). Copper concentrations varied from 0.02-0.08 mg/L during pre-monsoon and 0.01-0.06 mg/L during post-monsoon periods, remaining below WHO limits (2.0 mg/L) but showing systematic spatial patterns (**Table 5**). Lead concentrations ranged from 0.002-0.011 mg/L during pre-monsoon and 0.002-0.008 mg/L during post-monsoon seasons, with most locations exceeding WHO standards (0.01 mg/L) during pre-monsoon conditions (**Table 5**).

Table 5: Heavy Metals Concentration (mg/ml).

		Pre-monsoon					Post-monsoon				
S. No.	**Village**	**Fe**	**Zn**	**Cd**	**Cu**	**Pb**	**Fe**	**Zn**	**Cd**	**Cu**	**Pb**
1	Shimbhupura	0.39	0.13	0.003	0.07	0.009	0.29	0.1	0.002	0.05	0.007
2	Devli	0.26	0.08	0.002	0.04	0.006	0.19	0.06	0.002	0.03	0.004
3	Deola	0.31	0.1	0.003	0.05	0.007	0.23	0.07	0.002	0.04	0.005
4	Minda	0.45	0.16	0.004	0.08	0.011	0.34	0.12	0.003	0.06	0.008
5	Govindi	0.17	0.05	0.001	0.03	0.004	0.12	0.04	0.001	0.02	0.003
6	Rajas	0.24	0.07	0.002	0.04	0.005	0.18	0.05	0.001	0.03	0.004
7	Lohrana	0.36	0.12	0.003	0.06	0.008	0.27	0.09	0.002	0.05	0.006
8	Khushiya	0.22	0.07	0.002	0.04	0.005	0.16	0.05	0.001	0.03	0.004
9	Bhuni	0.33	0.11	0.003	0.05	0.007	0.24	0.08	0.002	0.04	0.005
10	Dalelpura	0.1	0.03	0.001	0.02	0.002	0.07	0.02	0.001	0.01	0.002
11	Rewasa	0.29	0.09	0.002	0.05	0.006	0.22	0.07	0.002	0.04	0.005
12	Lichana	0.37	0.12	0.003	0.06	0.008	0.28	0.09	0.002	0.05	0.006

3.5 Correlation Analysis

Statistical correlation analysis revealed significant relationships between various physicochemical parameters and contaminant concentrations, providing insights into underlying geochemical processes and contamination sources. Strong positive correlations were observed between TDS, EC, and major ion concentrations (r > 0.85), indicating common geochemical controls through water-rock interaction and evaporation concentration processes. Fluoride showed significant positive correlations with pH (r = 0.78), bicarbonate (r = 0.72), and TDS (r = 0.69), confirming the influence of alkaline conditions and enhanced mineral dissolution in fluoride mobilization mechanisms. Heavy metal correlations demonstrated interesting patterns, with iron showing strong relationships with zinc (r = 0.74), copper (r = 0.68), and lead (r = 0.63), suggesting common source materials or similar geochemical behavior in the aquifer system. The correlation between fluoride and heavy metals was moderate but statistically significant, with fluoride-iron (r = 0.58) and fluoride-zinc (r = 0.52) correlations indicating potential synergistic mobilization under alkaline conditions. Cadmium showed weaker correlations with other parameters, suggesting different source mechanisms or mobility controls compared to other heavy metals.

3.6 Seasonal Variations

Comprehensive seasonal analysis revealed systematic changes in groundwater quality parameters between pre-monsoon and post-monsoon periods, reflecting the influence of monsoon recharge on aquifer hydrochemistry. Average decreases of 12-18% were observed for TDS, EC, and major ion concentrations from pre-monsoon to post-monsoon seasons, primarily attributed to dilution effects from fresh water infiltration during monsoon precipitation. However, the magnitude of seasonal variation differed significantly across sampling locations, with areas having deeper water tables showing less pronounced seasonal changes compared to shallow groundwater systems. Fluoride concentrations exhibited consistent seasonal reduction patterns, with average decreases of 10-15% observed across all sampling locations. The seasonal variability was most pronounced in areas with higher baseline concentrations, suggesting that dilution effects become more significant when initial contaminant levels are elevated. Heavy metal concentrations also showed seasonal decreasing trends, with iron and zinc demonstrating the most significant reductions (15-25%) while cadmium and lead showed more modest changes (5-10%). These patterns indicate that heavy metals may be more strongly influenced by geochemical processes beyond simple dilution effects.

3.8 Water Quality Classification

Groundwater quality assessment based on WHO and Bureau of Indian Standards (BIS) guidelines revealed that a majority of sampling locations exceeded permissible limits for multiple parameters. Fluoride contamination was the most widespread quality concern, with 67% of locations exceeding WHO limits during both seasons. Iron contamination affected 50% of sampling locations during pre-monsoon and 33% during post-monsoon periods, while lead exceedances were observed at 42% of locations during pre-monsoon conditions. The integrated water quality assessment indicates that only Dalelpura and Govindi villages showed groundwater quality suitable for direct consumption without treatment, while other locations require various degrees of treatment intervention. Total hardness measurements revealed extremely hard water conditions across most sampling locations, with values ranging from 212-612 mg/L during pre-monsoon and 178-512 mg/L during post-monsoon periods **(Table 6)**. According to standard classifications, 75% of locations exhibited very hard water conditions (>300 mg/L as $CaCO_3$), necessitating water softening treatments for domestic and industrial applications. The combination of high hardness, fluoride contamination, and selective heavy metal exceedances creates complex treatment challenges requiring integrated remediation approaches.

Table 6: Total hardness measurements pre- & post-monsoon.

Sr. No.	Village	Pre-monsoon			Post-monsoon		
		Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Total Hardness (mg/L as $CaCO_3$)
1	**Shimbhupura**	128	62	534	108	52	443
2	**Devli**	92	41	367	78	34	312
3	**Deola**	108	48	423	92	40	356
4	**Minda**	148	72	612	125	61	512
5	**Govindi**	72	35	298	60	29	243
6	**Rajas**	94	42	378	78	35	312
7	**Lohrana**	122	59	498	102	50	423
8	**Khushiya**	88	40	354	74	33	298
9	**Bhuni**	118	56	487	98	47	401
10	**Dalelpura**	52	25	212	44	21	178
11	**Rewasa**	105	46	401	88	38	334
12	**Lichana**	130	61	534	110	52	445

4. DISCUSSION

It is reported that the high levels of fluoride found in Nawa Tehsil can be mainly explained by natural geochemical processes of fluoride-bearing mineral dissolution under alkaline conditions that are typical of the semi-arid aquifer systems (Keesari et al., 2019). The significant positive correlation between fluoride and pH proves the fact that alkaline conditions promote the fluoride mobility in the form of the anion exchange reactions, in which hydroxide ions replace fluoride on clay mineral surfaces, and fluorapatite dissolves in alkaline conditions (Gupta and Sharma, 2019). The geological context of the examined area that includes Quaternary alluvial deposits and overlying Proterozoic crystalline rocks with a high proportion of minerals containing fluoride, including biotites, muscovites, and fluorapatites, are the main source materials of groundwater fluoride enrichment. The patterns of the spatial distribution of fluoride contamination indicate the presence of specific hydrogeochemical zones, with higher concentrations always being found in those areas where the PH level is greater, the bicarbonate is higher, and the residence time of groundwater is longer. This trend is in line with the past research in Rajasthan that has found the same geochemical controls in fluoride-infested areas (Rani et al., 2023). The moderately correlated relationships between fluoride and heavy metals imply the possibility of synergistic mobilization mechanisms, in which alkaline environments that increase fluoride dissolution have an effect on heavy metal speciation and mobility by complexing and competitively adsorbing heavy metals. The extensive contamination of fluoride that is seen in Nawa Tehsil is a major public health hazard especially to the populations that solely use ground water as their drinking water. Higher concentrations of fluoride that surpass 3.0 mg/L in a number of areas pose high risks of developing dental and skeletal fluorosis, particularly in children and with the older population that is more vulnerable to the effects of fluoride toxicity (Sankhla et al., 2016). Prolonged exposure to high levels of fluoride may result in dental mottling, skeletal defects and non-skeletal effects such as thyroid disorder, neurological and reproductive disorders, as reported in other fluoride-contaminated areas in India.

The sources of heavy metal contamination in the study area seem to have various origins, such as natural weathering of crystalline basement rocks, and anthropogenic sources such as agricultural practices and disposal of domestic waste. High inter-correlations between iron, zinc, copper, and lead suggest shared geochemical controls or raw materials, which are probably related to the weathering of sulfide minerals and ferromagnesian phases found on underlying geological formations (Ullah et al., 2022). Post-monsoon dilution of heavy metal with fresh water recharge indicates that the role of dilution in regulating metal mobility is important, although geochemical mechanisms like precipitation, adsorption and complexation also affect metal behavior. The concomitant existence of heavy metals makes the health hazards more complex as it may have synergistic toxicological effects of individual contaminants that can enhance their effects (Vetrimurugan et al., 2017). Even at comparatively low levels of lead contamination as the case in this study, lead contamination is of specific concern to neurological development in children and cardiovascular health in adults. The reason is that iron excesses may result in gastrointestinal dysfunction and organ damage, whereas the exposure to cadmium, though minimal, poses a threat to the dysfunction of kidneys and carcinogenic effects due to bioaccumulation (Lawal et al., 2021). The presence of several contaminants requires complex health risk assessment methods in which additive and synergistic toxicological interactions are taken into consideration.

The regular seasonal change in the quality parameters of the groundwater is indicative of a complicated interaction of the monsoon recharge, evaporation, and the geochemical equilibrium processes that are typical of semi-arid aquifer systems. A 12-18 percent decrease in TDS and major ion concentrations during the post-monsoon seasons indicates the strong effect of dilution by fresh water infiltration, which has been also found in other semi-arid regions where the effects of monsoon recharge on groundwater chemistry can be significant (Naaz et al., 2015). Nevertheless, the fact that high concentrations of fluoride and heavy metals persist even when the dilution effects are taken into account reveals that geochemical processes still preserve the high concentration of contaminants by means of mineral dissolution and desorption reactions.

The impacts of climate change on groundwater quality in the area are of particular concern because rising temperatures and changing precipitation patterns can worsen the problem of contamination by increasing evaporation and decreasing recharge and depending more on deeper and mineralized aquifers. Already the temperature differences between seasons observed indicate the thermal sensitivity of the groundwater system, and future climate scenario in Rajasthan indicates that such effects will be amplified. Adaptive management approaches should thus take into account the existing contamination trends as well as the future climate-related changes in the dynamics of groundwater quality.

The fluoride levels measured in Nawa Tehsil are similar or higher than those measured in other geogenic fluoride-contaminated regions of Rajasthan, which validates the regional scale of geogenic fluoride contamination of western India. The literature of the adjacent districts has reported the same hydrogeochemical conditions and fluoride content, which may imply that the underlying geological and climatic processes work at the regional level (Keesari et al., 2019). Nevertheless, the patterns of heavy metal contamination are more localized, which means that anthropogenic factors and certain geological conditions play an important role in determining the mobility of metals in groundwater systems. Exposure to WHO and BIS drinking water standards shows that the current groundwater quality of most sampling sites needs to be treated prior to consumption. The prevalence levels of fluoride (67% of the locations) and iron (50% in pre-monsoon) are above the acceptable levels in terms of community health and require urgent remediation practices. The synergistic patterns of contamination, i.e. a combination of several contaminants with various sources and mobility controls, make the treatment complex, and it should be multi-barrier, involving physical, chemical, and biological treatment processes.

The management of the ground water quality in the Nawa Tehsil should be done through integrated strategies that would serve not only the short-term goals of health protection but also the long-term sustainability. Activated alumina adsorption systems have been demonstrated to be effective in similar hydrogeochemical environments to provide cost effective remediation of fluoride, and are applicable to community scale remediation. The process of reverse osmosis technology provides the full range of contaminant elimination but with a lot of concern over the energy expenses and the disposal of the concentrate in water deficient areas. Electrocoagulation and electroflocculation technologies demonstrate potential to remove fluoride and heavy metals simultaneously and retain the simplicity of operation required to be used in rural settings. The diversification strategies of sources must focus on harvesting rainwater and surface water sources in order to lessen reliance on infected ground water sources. Recharge of aquifers using check dams, percolation tanks, and injection wells can be used to dilute the concentration of contaminants in addition to improving the total water security. Community based water treatment systems, coupled with routine monitoring and health surveillance programs, offer long-term viable solutions to safe drinking water access in addition to developing local technical capacity (capacity to maintain and manage the system) in the long run..

5. CONCLUSION

This detailed study of the groundwater quality within Nawa Tehsil, Nagaur District, Rajasthan, demonstrates that there are considerable contamination issues that are of serious health and environmental risks to the population. The most significant issue was found to be the contamination of fluoride, and 67% of sampling sites were found to have an amount of contamination exceeding the WHO-permitted levels during the pre-monsoon and post-monsoon periods. A concentration of 1.1-4.5 mg/L signifies extreme geogenic enrichment of fluoride due to alkaline and increased dissolution of the minerals with fluoride in the underlying crystalline aquifer system. The positive correlation coefficients of fluoride, pH and bicarbonate are strong, which proves that the main driver of fluoride mobilization in the station is the natural hydrogeochemical processes.

The heavy metal contamination poses another health hazard and the iron and lead exceedances were reported at several sites under pre-monsoon conditions. The intermediate associations between fluoride and heavy metals indicate the possibility of synergistic mobilization under alkaline environments, forming complex contamination situations, which need a combined way of treatment. Seasonal changes indicate a high level of monsoon effects on groundwater quality and the 12-18% decrease in the concentration of contaminants during the post-monsoon seasons indicates dilution effects of fresh water recharge. Nevertheless, the fact that high levels of contamination are still present even after seasonal dilution demonstrates that there are geochemical processes that keep the contaminants mobility even during the yearly hydrological cycles.

The combined evaluation shows that just two villages (Dalelpura and Govindi) have groundwater that can be directly used, whereas other places need different levels of treatment measures. The extremely hard water conditions, fluoride pollution, and disproportionate excessive levels of certain heavy metals are all combined to present complex treatment issues that require comprehensive remediation plans. The effects of climate changes are of special concern because, with the projected warming of the environment and changes in the precipitation pattern, the problem of contamination may be aggravated by the increased evaporation and decreased recharge rates.

The future research directions ought to be directed towards geochemical models in order to enhance the understanding of the mechanisms in which fluoride interacts with heavy metals and to come up with

predictive instruments to assess contamination. To monitor the contamination patterns and measure the efficiency of the remediation, long-term monitoring programs with seasonal and inter-annual variations are needed. Research that incorporates synergistic toxicology effects of multiple contaminants would be vital in offering information to the strategy of protecting the health of the population. Also, pilot scale treatment system tests must evaluate technical and economic feasibility of different remediation technologies in local hydrogeochemical conditions.
The results highlight the importance of implementing combined water resource management approaches that would incorporate both short-term treatment measures and diversification of sources as well as long-term sustainability measures. Community-level interventions that involve local technical capacity development and frequent health surveillance initiatives provide hopeful avenues in achieving safe drinking water access and in managing the multi-faceted contamination issues that are typical of semi-arid areas undergoing a period of rapid environmental transformation.

REFERENCES

[1.] Ahada, C. P., & Suthar, S. (2018). Groundwater nitrate contamination and associated human health risk assessment in southern districts of Punjab, India. *Environmental science and pollution research*, *25*(25), 25336-25347.
[2.] Al Sabti, B., Samayamanthula, D. R., Dashti, F. M., & Sabarathinam, C. (2023). Fluoride in groundwater: distribution, sources, processes, analysis, and treatment techniques: a review. *Hydrogeochemistry of Aquatic Ecosystems*, 1-31.
[3.] American Public Health Association. (2017). Standard methods for the examination of water and wastewater (23rd ed.). APHA Press.
[4.] Brindha, K., & Elango, L. (2011). Fluoride in groundwater: causes, implications and mitigation measures. *Fluoride properties, applications and environmental management*, *1*, 111-136.
[5.] Central Ground Water Board. (2020). Ground water yearbook of Rajasthan (2019-20). Ministry of Jal Shakti, Government of India.
[6.] Chaudhary, V., & Satheeshkumar, S. (2018). Assessment of groundwater quality for drinking and irrigation purposes in arid areas of Rajasthan, India. *Applied Water Science*, *8*(8), 218.
[7.] Choubisa, S. L. (2018). Fluoride distribution in drinking groundwater in Rajasthan, India. Current Science, 114(9), 1851-1857.
[8.] Patel, M. P., Gami, B., Patel, A., Patel, P., & Patel, B. (2020). Climatic and anthropogenic impact on groundwater quality of agriculture dominated areas of southern and central Gujarat, India. *Groundwater for sustainable development*, *10*, 100306.
[9.] Darko, G., Akoto, O., & Oppong, C. (2008). Persistent organochlorine pesticide residues in fish, sediments and water from Lake Bosomtwi, Ghana. *Chemosphere*, *72*(1), 21-24.
[10.] Dutta, R., Bhu, H., Purohit, R., & Sharma, K. K. (2021). Geology of granitoids of Pindwara–Abu Road Belt from Mesoproterozoic Delhi Supergroup: Tectonic implications. *Journal of Earth System Science*, *130*(3), 118.
[11.] Everett, E. T., McHenry, M. A. K., Reynolds, N., Eggertsson, H., Sullivan, J., Kantmann, C., ... & Stookey, G. K. (2002). Dental fluorosis: variability among different inbred mouse strains. *Journal of dental research*, *81*(11), 794-798.
[12.] Gautam, R., & Bhardwaj, N. (2010). Groundwater quality assessment of Nawa Tehsil in Nagaur district (Rajasthan) with special reference to fluoride. *The Environmentalist*, *30*(3), 219-227.
[13.] Gautam, S. K., Sharma, D., Tripathi, J. K., Ahirwar, S., & Singh, S. K. (2013). A study of the effectiveness of sewage treatment plants in Delhi region. *Applied Water Science*, *3*(1), 57-65.
[14.] Gupta, P. K., & Sharma, D. (2019). Assessment of hydrological and hydrochemical vulnerability of groundwater in semi-arid region of Rajasthan, India. *Sustainable Water Resources Management*, *5*(2), 847-861.
[15.] Jarup, L. (2003). Hazards of heavy metal contamination. British Medical Bulletin, 68(1), 167-182.
[16.] Kabir, H., Gupta, A. K., & Tripathy, S. (2020). Fluoride and human health: Systematic appraisal of sources, exposures, metabolism, and toxicity. *Critical Reviews in Environmental Science and Technology*, *50*(11), 1116-1193.
[17.] Keesari, T., Sinha, U. K., Kamaraj, P., & Sharma, D. A. (2019). Groundwater quality in a semi-arid region of India: Suitability for drinking, agriculture and fluoride exposure risk. *Journal of Earth System Science*, *128*(2), 24.
[18.] Singh, P., Tiwari, A. K., & Singh, P. K. (2014). Hydro chemical characteristic and quality assessment of groundwater of Ranchi township area, Jharkhand, India. *Current World Environment*, *9*(3), 804.
[19.] Lawal, K. K., Ekeleme, I. K., Onuigbo, C. M., Ikpeazu, V. O., & Obiekezie, S. O. (2021). A review on the public health implications of heavy metals. *World Journal of Advanced Research and Reviews*, *10*(3), 255-265.
[20.] Goren, S., Albijali, K., Alghamdi, R., Alomari, A., & Alzahrani, M. (2022). Assessment of groundwater in Al-Lith Region. *Medicon Eng Themes*, *2*(6), 1-12.
[21.] Mukherjee, I., & Singh, U. K. (2018). Groundwater fluoride contamination, probable release, and containment mechanisms: a review on Indian context. *Environmental geochemistry and health*, *40*(6), 2259-2301.
[22.] Naaz, A., Kumar, B., Narayan, C., Shukla, K., & Anshumali. (2015). Assessment of fluoride pollution in groundwaters of arid and semi-arid regions of tonalite–trondjhemite series in central india. Water Quality, Exposure and Health, 7(4), 545-556.
[23.] Patil, V. B., Pinto, S. M., Govindaraju, T., Hebbalu, V. S., Bhat, V., & Kannanur, L. N. (2020). Multivariate statistics and water quality index (WQI) approach for geochemical assessment of groundwater quality—a case study of Kanavi Halla Sub-Basin, Belagavi, India. *Environmental Geochemistry and Health*, *42*(9), 2667-2684.

[24.] Rahman, M. M., Mukherjee, D., Sengupta, M. K., Chowdhury, U. K., Lodh, D., Chanda, C. R., ... & Chakraborti, D. (2002). Effectiveness and reliability of arsenic field testing kits: are the million dollar screening projects effective or not?. *Environmental science & technology*, *36*(24), 5385-5394.

[25.] Rani, A., Parashar, K., Meena, R., Sharma, S. K., Tiwari, K. K., Ajaykumar, V., & Mondal, N. C. (2023). Hydrochemical characteristics and potential health risks of nitrate, fluoride, and uranium in Kota district, Rajasthan, India. *Environmental Science and Pollution Research*, *30*(34), 82485-82505.

[26.] Psyllos, G., Hadjigeorgiou, I., Dimitrakopoulos, P. G., & Kizos, T. (2022). Grazing land productivity, floral diversity, and management in a semi-arid Mediterranean landscape. *Sustainability*, *14*(8), 4623.

[27.] Sankhla, M. S., Kumari, M., Nandan, M., Kumar, R., & Agrawal, P. (2016). Heavy metals contamination in water and their hazardous effect on human health-a review. *Int. J. Curr. Microbiol. App. Sci*, *5*(10), 759-766.

[28.] 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.

[29.] Singh, S., Raju, N. J., & Ramakrishna, C. (2015). Evaluation of groundwater quality and its suitability for domestic and irrigation use in parts of the Chandauli-Varanasi region, Uttar Pradesh, India. *Journal of Water Resource and Protection*, *7*(07), 572.

[30.] Srivastava, S., & Flora, S. J. S. (2020). Fluoride in drinking water and skeletal fluorosis: a review of the global impact. *Current environmental health reports*, *7*(2), 140-146.

[31.] Tiwari, A. K., Singh, P. K., & Mahato, M. K. (2014). GIS-based evaluation of water quality index of ground water resources in West Bokaro Coalfield, India. *Current world environment*, *9*(3), 843.

[32.] Ullah, Z., Rashid, A., Ghani, J., Nawab, J., Zeng, X. C., Shah, M., ... & Zum, K. (2022). Groundwater contamination through potentially harmful metals and its implications in groundwater management. *Frontiers in Environmental Science*, 10, 1021596.

[33.] Vetrimurugan, E., Brindha, K., Elango, L., & Ndwandwe, O. M. (2017). Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta. *Applied Water Science*, 7(6), 3267-3280.

[34.] 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.