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Assessment Of Ground Water Quality In Some Villages Of Shreemadhopur Tehsil Using Statistical Methods And Its Impact Of Human Health With Special Reference To Fluoride Contamination

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abstract:

The main aim of research work is to evaluate the quality of groundwater in some villages of shreemadhopur tehsil, District Sikar, Rajasthan, India for drinking and irrigation purposes. Assessment of groundwater quality is very important to estimate the contaminants to take preventive measures and predict future disasters. Groundwater contamination is a global problem that has a significant impact on human health and ecological services. Groundwater samples were collected from various locations in the study area during the pre and post-monsoon season and were analyzed for different physic chemical parameters including pH, Turbidity, Dissolved oxygen, Electrical conductivity, Total alkalinity, Total hardness, Calcium hardness, Magnesium hardness, Total dissolved solids, Fluoride, Nitrate, Sulphate, chloride, bicarbonate, Calcium, Magnesium, Sodium and Potassium. The results were then compared with the water quality standards of the World Health Organization (WHO). All the water samples in the study area are within the levels of pH but in most of samples fluoride, total hardness and total dissolved solids are found exceeded the permitted limit. Fluoride has positive correlation with electrical conductivity, total alkalinity, total dissolved solids, chloride, sodium and negative correlation with total hardness, calcium and magnesium. A positive correlation between fluoride and total alkalinity indicate the alkaline nature of groundwater, which promotes the leaching of fluoride and thus increasing the fluoride concentration groundwater. Piper diagram classified all groundwater samples into 'Mixed Na⁺-HCO₃ - Cl⁻ Ca²⁺ type. The results also suggest that the groundwater contamination problem is alarming at present and groundwater quality is deteriorating with time. Artificial recharge and rainwater harvesting practices should be adopted to improve the groundwater quality and the residents are advised to drink purified groundwater.

Keywords: Groundwater quality, physicochemical parameters and fluoride contamination.

INTRODUCTION: -

Groundwater is a critical source of drinking water, irrigation and industrial usage worldwide, especially for rural and semi-urban populations. Aquifers of the arid/ semi-arid regions are under tremendous stress due to the over extraction of groundwater or Increased water consumption, combined with rapid industrialization, urbanization and agricultural activities, has led to severe challenges in water quality worldwide and India is no exception. Because there are few surface water supplies, the majority of Indian locations rely on groundwater resources for domestic, industrial, and agricultural uses, including drinking water (Adimalla N, et al., 2020; Pasham H, et al., 2022; Chinthala K, et al., 2023). In India's most abundant and effective source of water for irrigation is groundwater (Krishna kumar P, et al., 2014; Jatwa P, et al., 2019).

A number of significant environmental issues have arisen as a result of the alarming rate of population expansion, the development of industrial society, technological advancements, and the current trend of groundwater resource depletion. For many decades, there have been growing concerns about the healthfulness of drinking water (Gowd S S, et al., 2005; Aly A A et al., 2015; Papazotos P, et al., 2019; Agarwal M, et al., 2020). Therefore, understanding the hydrochemistry of groundwater is crucial to evaluating the excellence of groundwater, particularly in rural regions, which affects its suitability for household, irrigational, and industrial requirements. Because of this, groundwater is a particularly valuable natural resource. Groundwater-related environmental issues vary in severity from location to location based on the local geology, hydrology, weather conditions, and geochemical considerations (Lakshmi R V, et al., 2021; Anusha B N et al., 2022; Kumar P R, et al., 2022).

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Fluoride concentrations in groundwater change due to various factors such as the solubility of F bearing minerals, ion exchange, residence time, dilution, temperature, pH, salinity, and evaporation-transpiration (Battaleb-Looie et al., 2012; Dehbandi R, et al., 2018). The major factors contributing to high fluoride concentrations in the ground water were found to be the dissolution of F containing minerals, alkaline conditions, and calciumremoving processes promoting the water-rock interactions. Different regions with different climate have different geological environments and groundwater chemical characteristics. Hence, there are different causes for the occurrence of fluoride containing groundwater (Borgnino L, et al., 2013; Cinti D, et al., 2019; Jia H, et al., 2019). The occurrences of fluoride in potable groundwater cause different types of dental and skeletal deformities (fluorosis) in humans including pitting and mottling of teeth, ligaments calcification, osteoporosis, osteosclerosis, crippling, abdominal pain, tingling sensations and calcification of blood vessels (Mukherjee I, and Singh U K,, 2018). Fluoride may get mobilized in groundwater from diverse geogenic sources (such as fluoride-bearing minerals, marine aerosols and volcanic eruptions) and anthropogenic sources (such as usage of fluoride containing irrigation water and application of phosphate fertilizers), and different geochemical processes (e.g., weathering of fluoride-containing minerals, ion exchange/reverse ion exchange, mixing and adsorption/desorption) and meteorological factors (e.g., evaporation and precipitation), drive the enrichment of fluoride in groundwater systems (Adimalla N and Li PY, et al., 2019; Li PY, et al., 2019, He XD, et al., 2020, Ji YJ, et al., 2020). Igneous (e.g., granitic-gneiss and pegmatite), sedimentary and metamorphic rocks usually contain significant amounts of fluoride-bearing minerals such as amphiboles, fluorite, muscovite, fluorapatite, topaz and hornblende. Several studies concluded that weathering of such host rocks is primarily responsible for mobilizing fluoride into the groundwater systems of most fluoride-endemic regions worldwide (Aravindan S, et al., 2011). Therefore, it is expected that local lithology, climatic conditions and anthropogenic influences control the groundwater hydrogeochemistry of the region.

MATERIAL AND METHODS:-

Shreemadhopur tehsil is located at north eastern part of Sikar districts headquarter. Its coordinates are 27.47° N and 75.60° E. The map of study area is shown in Fig.1.

For more focused, efficient investigation and better understanding of groundwater quality and quantity the entire study area is divided in eight zones so as to get representative samples as follows:- North zone:- [Kalyanpura- Gram panchayat office (TW), Jairampura- Post office (TW)], South zone:- [Jalpali -Bus Stand (OT), Bharni- Post office (TW)], East zone:- [Prithvipura -SBS Govt School (OT) Tilokpura -Bus stand (TW)], West zone:- [Vijaipura- Govt Se.sec.school (OT), Ranipura- Bus Stand (TW)], North- East zone:- [Rupawali-Raj.Se.Sec.School (TW), Hanspur- Post Office (TW)], South- East zone:- [Mau - Gopinath ji Temple (TW), Bagariawas- Bal Bharati School (OW)], South- West zone:- [Gopinath Ki Dhani- Govt. Hospital (TW), Patwari Ka Bass- Shiv ji Temple (TW)], North- West zone:- [Bashi- Bus Stand (TW), Shivpura- Ramdev ji Temple (TW)].

A total of thirty two (32) ground water samples were collected from tube wells, open wells and hand pumps of different sampling sites. The ground water samples were collected during the pre monsoon (May 2023) and post monsoon session (October 2023). The ground water samples were systematically collected in pre cleaned, dry and sterilized plastic bottles of one litre capacity. At the time of sampling, sample bottles are thoroughly raised 2-3 times using the ground water to be sampled. These water samples are collected after pumping the water for 10 minutes. The samples were stored at a temperature below 4 °C prior to analysis. The physico chemical analysis and Correlation analysis were carried out for various parameters. Analytical grade reagents were used for the assessment of samples and double distilled water was used for preparation of solutions. The analysis of water samples for various physicochemical parameters were carried out using standards methods recommended by American Public Health Association (APHA 2012). Temperature and pH were determined immediately at the place of collection while Turbidity, EC (electrical conductivity), TDS (total dissolved solids) and DO (dissolved oxygen) were determined at the same day of sampling using Water Analyzer (Systronic-371).

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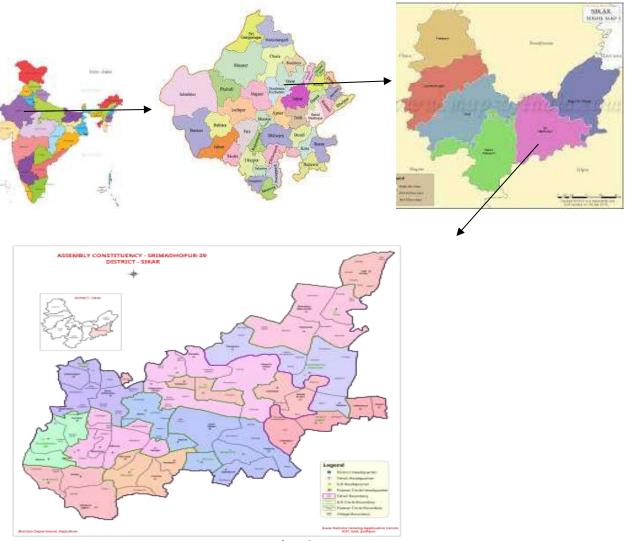


Fig.1:- Map of study are

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Table 1: Physical Parameters of Ground Water Samples of Some Villages of ShreeMadhopur Tehsil (Pre Monsoon - 2023)

S.N	Village	Sample Site	Code	Sample	Temp	DO	рН	EC	TA	TH	СаН	Mg H	TDS
٠				Source									
1	Kalyanpura	Gram panchayat											
		office	SMT_1	TW	21.9	4.9	7.96	1472	289	195	130	65	941
2	Jairampura	Post office	SMT_2	TW	22.4	4.7	8.14	1665	325	188	125	63	1065
3	Jalpali	Bus Stand	SMT_3	OT	21.6	5.3	7.71	1285	244	214	141	73	822
4	Bharni	Post office	SMT ₄	TW	21.8	5.2	7.76	1311	257	198	132	66	839
5	Prithvipura	SBS Govt School	SMT_5	OT	22.8	5.6	7.69	1137	223	255	170	85	727
6	Tilokpura	Bus stand	SMT_6	TW	21.9	4.6	7.85	1369	269	231	154	77	876
7	Vijaipura	Govt Se.sec.school	SMT ₇	OT	23.4	4.5	8.09	1818	317	275	183	92	1163
8	Ranipura	Bus Stand	SMT_8	TW	22.7	5.2	7.67	1434	265	210	140	70	918
9	Rupawali	Raj.Se.Sec.School	SMT ₉	TW	22.4	4.9	7.62	821	155	331	221	110	524
10	Hanspur	Post Office	SMT_{10}	TW	22.9	4.7	7.87	864	171	314	209	105	552
11	Mau	Bus Stand	SMT_{11}	TW	22.3	5.1	8.12	1267	268	289	193	96	811
12	Bagariawas	Bal Bharati School	SMT_{12}	OW	21.8	5.2	7.64	905	183	301	200	100	579
13	Gopinath Ki Dhani	Govt Hospital	SMT_{13}	TW	22.2	4.9	7.76	927	179	292	195	97	592
14	Patwari Ka Bass	Shiv ji Temple	SMT ₁₄	TW	22.7	4.8	7.89	1076	210	227	151	76	687
15	Bashi	Bus Stand	SMT ₁₅	TW	21.4	5.1	7.75	903	176	318	212	106	576
16	Shivpura	Ramdev ji Temple	SMT ₁₆	TW	22	5	7.83	1008	292	277	185	92	645

All values of parameters are expressed in mg/L, except of pH, Temperature (°C) and EC in µmhos/cm

Table 2: Chemical Parameters of Ground Water Samples of Some Villages of ShreeMadhopur Tehsil (Pre Monsoon - 2023)

S.N	Village	Sample Site	Code	Sample	F	NO_3	SO ₄ -2	Cl	CO_3^2	HCO ₃	Ca ⁺²	Mg ⁺²	Na⁺		%Na	SAR
				Source										K^{+}		
1	Kalyanpura	Gram panchayat office	SMT_1	TW	1.96	29	16	179	3.1	286	52.0	15.8	418	7.5	82.48	12.98
2	Jairampura	Post office	SMT_2	TW	2.37	31	20	211	0.0	325	50.0	15.3	504	8.2	84.47	15.99

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3	Jalpali	Bus Stand	SMT ₃	OT	1.89	24	17	167	6.1	238	56.4	17.7	360	4.1	78.63	10.72
4	Bharni	Post office	SMT ₄	TW	1.92	27	20	152	3.9	253	52.8	16.0	382	5.4	80.88	11.78
5	Prithvipura	SBS Govt School	SMT_5	OT	1.85	31	21	110	4.8	218	68.0	20.7	294	5.3	71.70	14.38
6	Tilokpura	Bus stand	SMT_6	TW	1.98	24	14	172	5.0	264	61.6	18.71	389	7.7	78.74	11.13
7	Vijaipura	Govt Se.sec.school	SMT ₇	OT	2.14	33	22	256	0.0	317	73.2	22.4	523	8.6	80.67	13.70
8	Ranipura	Bus Stand	SMT_8	TW	1.90	25	15	159	4.0	261	56.0	17.0	421	2.9	81.39	12.62
9	Rupawali	Raj.Se.Sec.School	SMT ₉	TW	1.16	12	8	96	6.9	148	88.4	26.7	154	2.6	50.56	3.68
10	Hanspur	Post Office	SMT ₁₀	TW	1.21	17	10	102	6.0	165	83.6	25.5	178	3.1	55.46	4.37
11	Mau	Bus Stand	SMT_{11}	TW	1.76	27	16	165	0.0	268	77.2	23.3	375	3.9	73.94	9.60
12	Bagariawas	Bal Bharati School	SMT ₁₂	OW	1.54	16	10	105	5.9	177	80.0	24.5	210	3.6	60.50	5.28
13	Gopinath Ki Dhani	Govt Hospital	SMT_{13}	TW	1.81	22	14	101	5.0	174	78.0	23.6	225	3.2	62.80	5.72
14	Patwari Ka Bass	Shiv ji Temple	SMT ₁₄	TW	1.97	31	19	114	4.1	206	60.4	18.5	296	3.8	74.07	8.52
15	Bashi	Bus Stand	SMT ₁₅	TW	1.49	18	13	105	3.1	173	84.8	25.8	204	3.0	57.85	4.86
16	Shivpura	Ramdev ji Temple	SMT ₁₆	TW	1.75	25	15	109	3.9	188	74.0	22.4	245	3.4	65.97	6.42

All values of parameters are expressed in mg/L, except of percentage sodium and SAR.

Table 3: Physical Parameters of Ground Water Samples of Some Villages of ShreeMadhopur Tehsil (Post Monsoon - 2023)

S.N	Village	Sample Site	Code	Sample	Temp	DO	рН	EC	TA	TH	СаН	MgH	TDS
				Source									
1	Kalyanpura	Gram panchayat											
		office	SMT_1	TW	19.5	5.2	7.98	1528	294	218	145	73	978
2	Jairampura	Post office	SMT_2	TW	20.4	4.8	8.1	1906	330	212	141	71	1220
3	Jalpali	Bus Stand	SMT_3	OT	18.6	5.5	7.91	1358	258	226	1561	75	863
4	Bharni	Post office	SMT ₄	TW	19.8	5.5	8.16	1447	272	205	137	68	926
5	Prithvipura	SBS Govt School	SMT_5	OT	19.4	5.8	7.93	1211	239	271	181	90	775
6	Tilokpura	Bus stand	SMT_6	TW	19.9	5.0	7.96	1502	285	244	163	81	961
7	Vijaipura	Govt Se.sec.school	SMT ₇	OT	20.2	5.1	8.12	1894	334	292	195	97	1212

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8	Ranipura	Bus Stand	SMT ₈	TW	19.7	5.4	7.94	1485	281	227	151	76	950
9	Rupawali	Raj.Se.Sec.School	SMT ₉	TW	18.8	5.1	7.91	1023	189	339	226	113	655
10	Hanspur	Post Office	SMT ₁₀	TW	18.4	5.6	7.02	959	176	352	235	117	614
11	Mau	Bus Stand	SMT ₁₁	TW	19.5	5.3	8.12	1472	296	296	197	99	942
12	Bagariawas	Bal Bharati School	SMT ₁₂	OW	18.9	5.5	7.90	1053	198	317	211	106	674
13	Gopinath Ki Dhani	Govt Hospital	SMT ₁₃	TW	19.3	5.2	7.92	1126	186	304	203	101	721
14	Patwari Ka Bass	Shiv ji Temple	SMT ₁₄	TW	19.5	5.0	7.95	1297	231	246	164	82	830
15	Bashi	Bus Stand	SMT ₁₅	TW	19	5.4	7.87	1070	193	327	218	109	685
16	Shivpura	Ramdev ji Temple	SMT ₁₆	TW	19.8	5.3	7.89	1175	214	293	195	98	752

Table 4: Chemical Parameters of Ground Water Samples of Some Villages of ShreeMadhopur Tehsil (Post Monsoon - 2023)

S.N	Village	Sample Site	Code	Sample	F	NO_3	SO ₄ -2	Cl	CO_3^2	HCO ₃	Ca ⁺²	Mg^{+2}	Na ⁺		%Na	SAR
				Source										K^{+}		
1	Kalyanpura	Gram panchayat office	SMT_1	TW	1.84	31	19	196	4.1	290	58	17.7	425	7.7	81.11	12.51
2	Jairampura	Post office	SMT_2	TW	1.91	34	22	285	0.0	330	56.4	17.3	580	9.3	85.29	16.68
3	Jalpali	Bus Stand	SMT ₃	OT	1.72	26	18	178	5.3	253	60.4	18.2	372	4.4	78.27	10.78
4	Bharni	Post office	SMT ₄	TW	1.95	30	21	191	0.0	272	54.8	16.5	398	5.7	80.97	12.10
5	Prithvipura	SBS Govt School	SMT_5	OT	1.69	35	23	129	5.5	233	72.4	21.9	310	5.9	71.55	8.17
6	Tilokpura	Bus stand	SMT_6	TW	1.78	27	17	198	5.1	280	65.2	19.7	412	7.8	78.77	11.48
7	Vijaipura	Govt Se.sec.school	SMT ₇	OT	1.91	35	24	267	0.0	334	78.0	23.6	531	8.9	79.96	13.50
8	Ranipura	Bus Stand	SMT_8	TW	1.86	28	18	182	5.5	275	60.4	18.5	425	3.3	80.35	12.24
9	Rupawali	Raj.Se.Sec.School	SMT ₉	TW	1.10	19	13	125	6.0	183	90.4	27.5	227	3.2	59.47	5.36
10	Hanspur	Post Office	SMT ₁₀	TW	1.06	22	14	112	6.2	170	94.0	28.4	196	3.4	55.02	4.53
11	Mau	Bus Stand	SMT_{11}	TW	1.55	29	19	179	0.0	296	78.8	24.0	392	4.1	74.33	9.91
12	Bagariawas	Bal Bharati School	SMT ₁₂	OW	1.41	18	11	134	5.6	192	84.4	25.8	241	3.9	62.53	5.89
13	Gopinath Ki Dhani	Govt Hospital	SMT ₁₃	TW	1.63	26	17	153	4.7	181	81.2	24.5	270	3.6	66.05	6.75
14	Patwari Ka Bass	Shiv ji Temple	SMT ₁₄	TW	1.75	37	24	160	4.2	227	65.6	19.9	355	4.4	75.95	9.83

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15	Bashi	Bus Stand	SMT ₁₅	TW	1.27	23	15	137	4.9	188	87.2	26.5	247	3.7	62.35	5.93
16	Shivpura	Ramdev ji Temple	SMT ₁₆	TW	1.62	29	18	149	4.0	210	78.0	23.8	294	3.9	68.73	7.47

Table 5: Correlation-Coefficient (r) of Various Groundwater Quality Parameters of Shree madhopur Tehsil (Pre monsoon 2023)

Parameters	рН	EC	ΤA	TH	TDS	F	NO ₃	Cl	HCO ₃	Ca ⁺²	Mg ⁺²	Na ⁺
рН	1											
EC	0.6267	1										
ΤA	0.6623	0.8870	1									
TH	-0.2428	0.6874	-0.6672	1								
TDS	0.6261	0.9999	0.8876	0.6876	1							
F	0.5410	0.8377	0.8190	-0.7964	-0.8376	1						
NO ₃	0.6083	0.7621	0.7704	-0.6821	0.7618	0.8775	1					
Cl	0.6818	0.9672	0.8363	-0.5410	0.9671	0.7402	0.6462	1				
HCO ₃	0.6477	0.8837	0.7790	-0.6410	0.8836	0.8688	0.7388	0.8455	1			
Ca ⁺²	-0.2403	0.6871	-0.6646	0.9998	-0.6872	-0.7953	-0.6798	-0.5422	-0.6385	1		
Mg ⁺²	-0.2461	0.6866	-0.6701	0.9996	-0.6868	-0.7952	-0.6824	-0.5378	-0.6444	0.9990	1	
Na ⁺	0.6295	0.9900	0.8930	-0.7427	0.9902	0.8743	0.7917	0.9433	0.9020	-0.7420	-0.7427	1

Table 6:- Correlation-Coefficient (r) of Various Groundwater Quality Parameters of Shreemadhopur Tehsil (Post monsoon 2023)

Parameters	рН	EC	ΤA	TH	TDS	F	NO´3	Cľ	HCO ₃	Ca ⁺²	Mg ⁺²	Na ⁺
pН	1											
EC	0.5914	1										
ΤA	0.6022	0.9704	1									
TH	-0.5404	-0.6628	-0.6943	1								
TDS	0.5914	0.9999	0.9699	-0.6605	1							
F	0.6752	0.8000	0.7905	-0.8744	-0.7991	1						
NO ₃	0.4386	0.6704	0.6473	-0.6011	0.6711	0.7584	1					

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Cl	0.5638	0.9730	0.8798	-0.6032	0.9731	0.7434	0.5770	1				
HCO ₃	0.6074	0.9722	0.9995	-0.6884	0.9718	0.7886	0.6505	0.9044	1			
Ca ⁺²	-0.3735	-0.3631	-0.3724	0.9448	-0.3617	-0.6314	-0.4715	-0.3367	-0.3719	1		
Mg ⁺²	-0.5350	-0.6598	-0.6911	0.9997	-0.6574	-0.8750	-0.6036	-0.6000	-0.6853	0.6406	1	
Na ⁺	0.6072	0.9933	0.9656	-0.7311	0.9930	0.8345	0.6932	0.9631	0.9963	-0.4197	-0.7276	1

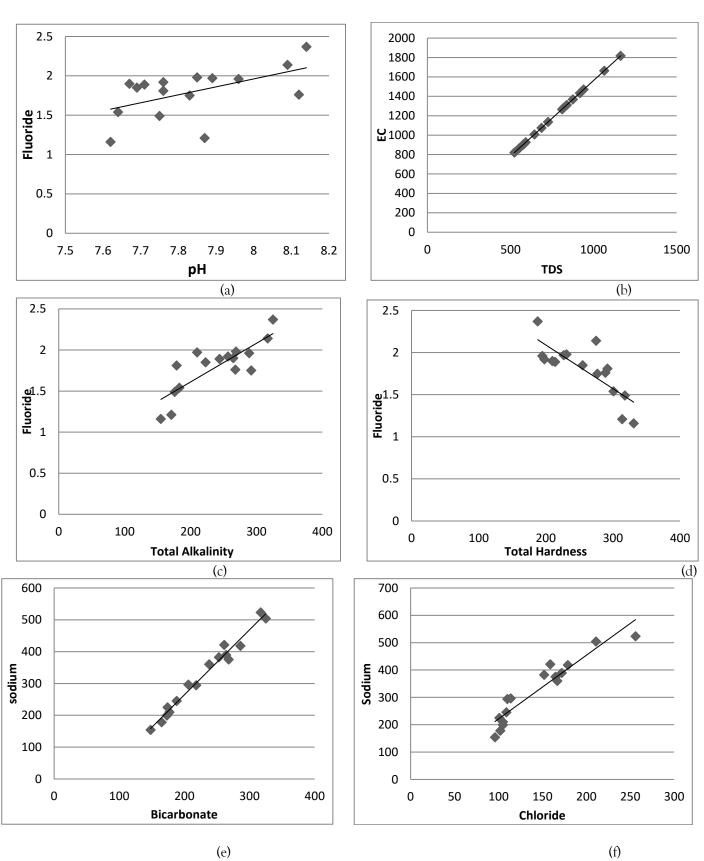
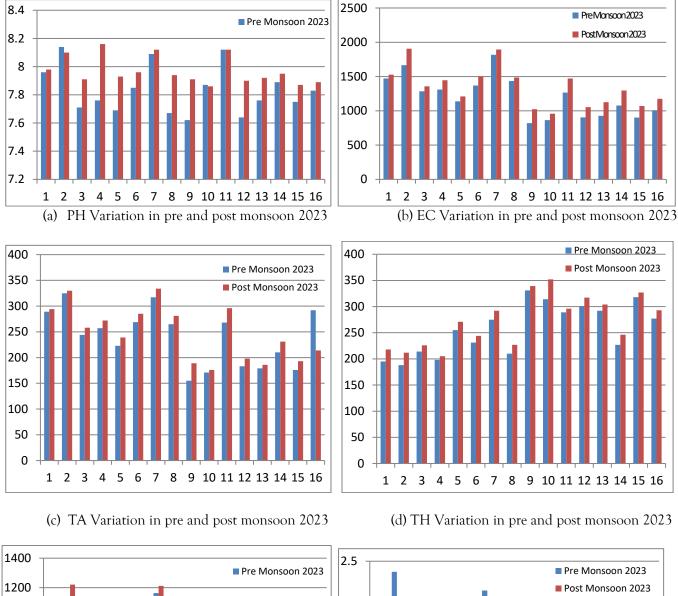
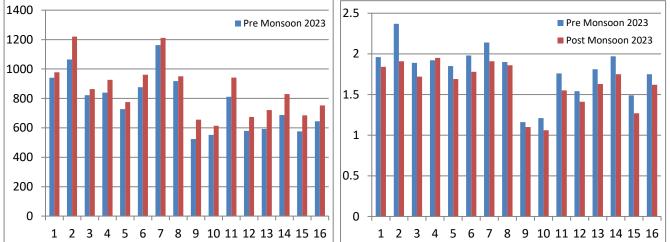


Fig.1. Scatter diagram showing correlation between various physicochemical parameters of groundwater in some villages of Shreemadhopur tehsil.

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- (e) TDS Variation in pre and post monsoon 2023
- (f) Fluoride Variation in pre and post monsoon 2023

Fig. 2. Comparison between various physicochemical parameters of groundwater in some villages of shreemadhopur tehsil during pre and post 2023.

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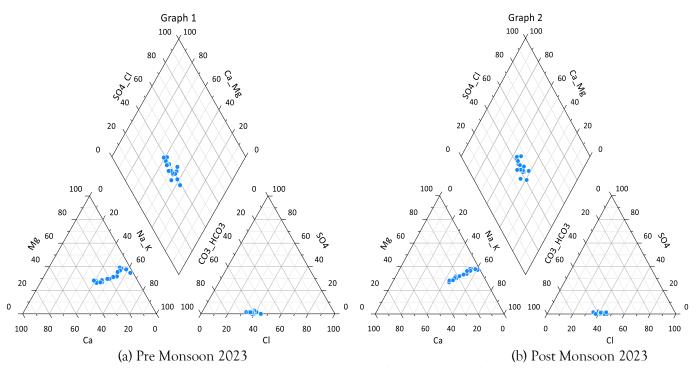


Fig.3. Piper trilinear diagram show the groundwater quality of some villages of shreemadhopur tehsil during pre and post monsoon.

RESULT AND DISCUSSION:

The respective values of all observed water quality physico-chemical parameters of ground water samples of some villages of Shreemadhopur tehsil in pre and post monsoon seasons during the study period (2023) are summarized in Table-1 to Table - 4. The data have been compared with World Health Organization (WHO) standard. Seasonal changes in physico-chemical parameters during pre monsoon and post monsoon season are showed in Fig.2.a to Fig.2.f.

pH

The pH of water is the most significant parameter and is valuable in estimating the overall quality of water. The pH level of the groundwater in the study area during pre monsoon ranged from 7.62 to 8.14 with an average value of 7.83 and in post monsoon ranged from 7.86 to 8.16 with an average value of 7.97, which indicating a slightly alkaline. All the water samples in the study area are within the recommended levels of 6.5–8.5 (WHO, 2012).

Electrical conductivity

Electrical conductivity is a measure of ion concentrations that depends on the temperature and type of ions and their concentrations in the water. The observed EC levels during pre monsoon ranged from 821 to 1818 μ mhos/cm with an average value of 1203.9 μ mhos/cm and in post monsoon ranged from 959 to 1906 μ mhos/cm with an average value of 1344 μ mhos/cm. High EC levels in groundwater suggest a higher concentration of dissolved salt content and greater attentiveness level. This also indicates the existence of multiple aquifer systems and regional differences in soil types.

Total Alkalinity (TA)

In study area total alkalinity during pre monsoon ranged from 155 to 325 mg/L with an average value of 238.9 mg/L, and in post monsoon ranged from 176 to 334 mg/L with an average value of 248.5 mg/L , Total alkalinity is the combined activity of the values of carbonates and bicarbonates in water.

Total hardness (TH)

Total hardness is determined by the quantity of magnesium and calcium-containing suspended particulates in the water. The total hardness during pre monsoon ranged from 188 to 331 mg/L with an average value of 257.2 mg/L and in post monsoon ranged from 205 to 352 mg/L with an average value of 273 mg/L. In pre monsoon 81.25 % and in post monsoon all samples exceeded the permitted limit recommended by WHO 2012 guidelines. Hard water is not

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recommended for home usage because it can cause metal dissolution, leading to abrasive coatings under pipelines, heaters, and drums. It may also lower the observed quality of water, putting human health at risk by producing disorders like kidney diseases, prenatal mortality, leukaemia, and cardiovascular problems.

Total dissolved solids (TDS)

TDS refers to the collective amount of soluble inorganic and organic ions present in water. TDS levels during pre monsoon ranged from 524 to 1163 mg/L with an average value of 769.8 mg/L and in post monsoon ranged from 614 to 1220 mg/L with an average value of 859.9 mg/L. The highest useful level for TDS was exceeded in several locations, making the water unfit for drinking. Based on groundwater categorization, during pre monsoon 31.25% of groundwater sources are safe to drink, while the other 68.75 % are not while in post monsoon all samples exceeded the WHO permitted limit.

Fluoride

Fluoride value varied from 1.16 to 2.37 mg/L with an average value of 1.79 mg/L in pre monsoon season and 1.06 to 1.95 mg/L with an average value of 1.63 mg/L in post monsoon season during the study period (2023). In pre monsoon 81.25 % and in post monsoon 75 % samples exceeded the permitted limit (<1.5 mg/L) recommended by WHO 2012 guidelines. Fluoride values are slightly decreased in post monsoon compare to pre monsoon season. Fluoride concentration decreases with the increase of total hardness, calcium and magnesium hardness.

Nitrate and Suphate

The nitrate content in pre monsoon ranged from 12 to 33 mg/L with an average value of 24.5 mg/L and in post monsoon ranged from 18 to 37 mg/L with an average value of 28 mg/L. All the water samples are within the recommended levels of nitrate by World Health Organisation. The sulphate content in pre monsoon varied from 8 to 22 mg/L with an average value of 15.6 mg/L and in post monsoon varied from 11 to 24 mg/L with an average value of 18.3 mg/L. All the water samples are within the recommended levels of sulphate by World Health Organisation.

Chloride

Chloride is a mineral that occurs naturally in water and is also found in salt and sometimes in combination with sodium, potassium and calcium. Chloride levels range from 96 mg/L to 256 mg/L with a mean of 143.6 mg/L and in post monsoon varied from 112 to 285 mg/L with an average value of 173.4 mg/L. In pre monsoon 6.25 % and in post monsoon 12.5 % samples are exceeded the permitted limit of chloride recommended by WHO 2012 guidelines which indicating a salty taste in the groundwater.

Bicarbonate

Bicarbonate concentration of the water samples in pre monsoon range from 148 mg/L to 325 mg/L with a mean of 228.8 mg/L and in post monsoon varied from 170 to 334 mg/L with an average value of 244.6 mg/L. Bicarbonate ions in the water can help neutralize any acidic substances present in the water, making it less acidic and more balanced in terms of pH.

Calcium and Magnesium

The acceptable range of calcium concentration in drinking water typically falls between 75 and 200 mg/L. Calcium levels in pre monsoon range from 50 mg/L to 88.4 mg/L with a mean of 68.5 mg/L and in post monsoon varied from 54.8 to 94 mg/L with an average value of 72.8 mg/L. Pre monsoon 37.5 % and in post monsoon 50 % of samples exceeding the permissible amount of 75 mg/L.Magnesium levels in pre monsoon range from 15.3 mg/L to 26.7 mg/L with a mean of 20.9 mg/L and in post monsoon varied from 16.5 to 28.4 mg/L with an average value of 22.1mg/L. All the water samples are within the recommended levels.

Sodium and Potassium

Due to the high solubility of sodium salts, sodium ions are present almost everywhere in water. Sodium levels in pre monsoon range from 154 mg/L to 523 mg/L with a mean of 323.3 mg/L and in post monsoon varied from 196 to 580 mg/L with an average value of 354.7 mg/L. Pre monsoon 87.5 % and in post monsoon 93.75 % of samples exceeding the permissible limit. Potassium levels in pre monsoon range from 2.6 mg/L to 8.6 mg/L with a mean of 4.8 mg/L and in post monsoon varied from 3.2 to 9.3 mg/L with an average value of 5.2 mg/L. All the water samples are within the recommended levels of potassium.

Percent sodium (%Na)

Sodium content is generally expressed in terms of percentage of sodium or soluble sodium percentage. The permeability of soil is reduced when sodium replaces calcium. Sodium combines with carbonates and chloride to produce alkaline and saline soils. Alkaline or saline soils are harmful to plant growth. Sodium content is frequently represented as

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a percentage of sodium (%Na). In pre monsoon percentage of sodium range from 50.56 to 85.47 with a mean of 71.3 and in post monsoon varied from 55.02 to 85.29 with an average value of 72.54.

Sodium adsorption ratio (SAR)

SAR is an important parameter for determination of soil alkalinity or alkali hazards in the use of ground water for agricultural applications. The value of SAR can be calculated by the formula

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)}}$$
 Where, all ionic concentrations are expressed in terms of meq/L.

The Sodium Adsorption Ratio (SAR) is a dimensionless parameter used to evaluate the sodium hazard in relation to calcium and magnesium concentrations (Sappa G, et al., 2014). This parameter is used as an index to evaluate groundwater suitability for the irrigation purposes in the study area (Shaki A, and Adeloye A, 2006). If water used for irrigation is high in sodium and low in calcium content, then exchangeable calcium in soil may replace sodium by base exchange reaction in water. This can destroy the soil structure owing to dispersion of the clay particles. The SAR values in pre monsoon range from 3.68 to 15.99 with a mean of 9.48 and in post monsoon varied from 4.53 to 16.68 with an average value of 9.57.

Correlation Analysis

Pearson's correlation matrices were used to find relationships between two or more variables and two sets of data (Bajpayee S, et al., 2012). It is a simplified statistical tool to show the degree of dependency of one variable to another. The correlation coefficients of various water quality parameters were calculated and the values of the correlation coefficients are given in Table-5 and Table-6. Based on the value of Pearson coefficient 'r', the correlation between two parameters plotted on a XY scatter diagram can be termed as a positive or negative (Das S and Nag S K, 2015). According to the Pearson's correlation, samples showing r > 0.7 are considered to be strongly correlated whereas r in the range of 0.45–0.7 shows moderate and $r \le 0.45$ shows weak correlation.

In the present study minimum, maximum, average, standard deviation, correlation coefficient (r) and regression coefficient (a & b) has been calculated for each pair of water quality parameters by using Excel spreadsheet for the experimental data.

The standard formulae were used in the calculation for statistical parameters are as follows:-

$$Mean(\mu) = \frac{\sum x}{N}$$
, Standard Deviation $(\sigma) = \frac{\sqrt{n\sum x^2 - (\sum x)^2}}{n(n-1)}$

x = values of parameter, N = Number of observations.

Karl Pearson Correlation coefficients (r) have been calculated between each pair of water quality parameter for the

experimental data. Let x and y be the two variables, then the correlation 'r' between the two variable are given by:
$$Karl\ Pearson\ Correlation\ coefficients\ \left(r\right) = \frac{n\sum xy - \sum x\sum y}{\sqrt{n\sum x^2} - (\sum x)^2\sqrt{n\sum y^2} - (\sum y)^2}\ ,\ \ n = \text{Number of observation}.$$

In the present study the Karl Pearson coefficient (r) among various water quality parameters have been calculated and the numerical values of correlation coefficients (r) for pre and post monsoon season

Fluoride has positive correlation with electrical conductivity, total alkalinity, total dissolved solids, chloride, sodium and negative correlation with total hardness, calcium and magnesium. A positive correlation between fluoride and total alkalinity indicate the alkaline nature of groundwater, which promotes the leaching of fluoride and thus increasing the fluoride concentration groundwater (Saxena V K and Ahmed S, 2001). HCO₃ ions is the dominant species of carbon in the intermediate pH of water. The positive correlation between fluoride and bicarbonate can be explained by considering the mass law equation relating to calcite and fluorite when both are in contact with water (Sharma S K, 2004).

$$CaF_2(s) + HCO_3^- \rightarrow CaCO_3(s) + H^+ + F^-$$

Electrical conductivity has positive correlation with total alkalinity, total dissolved solids, nitrate, sulphate, bicarbonate, chloride, sodium and negative correlation with total hardness, calcium and magnesium. High positive correlation of electrical conductivity with total dissolved solids and chloride indicates the high mobility of ions. EC indicates that these ions tend to increase in concentration as the salinity of the water increases. The salinization of the groundwater can be

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expected to result from the ionic concentrations increasing due to both evaporation of recharge water and to the effects of interactions between the groundwater and the geological formations (*Eviritt B S, et al.*, 2011).

Total alkalinity has positive correlation with total dissolved solids, bicarbonate, chloride and sodium and negative correlation with total hardness. Solubility of CaF_2 increased with the increase of total alkalinity.

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CaF_2 + CO_3^2 \rightarrow CaCO_3 + 2F^2

CaF_2 + HCO_3^2 \rightarrow CaCO_3 + 2F^2 + H_2O + CO_2
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High positive correlation of total hardness with calcium ion and magnesium ion exhibits that hardness is mainly due to presence of calcium and magnesium salts in water. Total dissolved solids has positive correlation with chloride, sodium, bicarbonate, fluoride, nitrate, sulphate and negative correlation with total hardness, calcium and magnesium.

Scatter diagram for highly significant positive correlation (F -pH, EC-TDS, F -TA, HCO₃ - Na⁺, Cl - Na⁺) and negative correlation (TH -F) in pre monsoon and post monsoon season are depicted in Fig.1.a to Fig.1.f.

Piper Trilinear Diagram

Piper's diagram was adopted to determine the overall characteristics of the groundwater systems. It is a graphical representation of relative abundance of cations and anions individually and also the combined representation as a whole of major cations and anions. Piper plot has been used to understand the hydrogeochemistry of the water and process involved with it. Along the groundwater flow path, it comes in contact with various materials and other fluids which affect its quality. This water quality depends upon various factors such as topography, nature of bedrock, and soil atmosphere. Some major ions determined in water samples were plotted on the Piper diagram and compared with other reported literature in order to classify and designate ionic nature of water (*Ravi kumar P, and Somashekar R K,* 2010). Classification of water types is displayed in Fig.3.a to Fig.3.b.This illustration of ionic signature helps in uncovering the principal ions trolling the water chemistry. Piper diagram classified all groundwater samples into 'Mixed Na*-HCO3--Classification's uggests geogenic activities are primarily responsible for the occurrence of above mentioned ions in groundwater, and which also indicates similar geogenic processes control the ionic signature of water bodies in study area.

CONCLUSION

Groundwater quality of study area is varies from place to place. All the water samples in the study area are within the levels of pH but in most of samples fluoride, total hardness and total dissolved solids are found exceeded the permitted limit recommended by WHO 2012 guidelines. From the above observation it is clear that the concentration of fluoride in groundwater increases as the carbonate and bicarbonate content of water increase and it decreases along with an increase in calcium and magnesium contents. Fluoride has positive correlation with electrical conductivity, total alkalinity, total dissolved solids, chloride, sodium and negative correlation with total hardness, calcium and magnesium. A positive correlation between fluoride and total alkalinity indicate the alkaline nature of groundwater, which promotes the leaching of fluoride and thus increasing the fluoride concentration groundwater. Sodium value of all groundwater samples in study area were found exceed WHO standard. Sodium values are slightly increased in post monsoon than pre monsoon season. Piper diagram classified all groundwater samples into 'Mixed Na*- HCO3*- Cl*- Ca²* type. This suggests geogenic activities are primarily responsible for the occurrence of above mentioned ions in groundwater. The results also suggest that the groundwater contamination problem is alarming at present and groundwater quality is deteriorating with time. Therefore proper care should be taken to avoid any groundwater contamination. Therefore, the study may be useful for groundwater management and to improve the public health of the study area.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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