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Hydrogeochemical Investigation and Groundwater Quality Assessment of Pratapgarh District, Uttar Pradesh

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Abstract: Hydogrochemical investigation of groundwater resources of Paragraph district has been carried out to assess the solute acquisition processes and water quality for domestic and irrigation uses. Fifty-five groundwater samples were collected and analyzed for pH, electrical conductivity, total dissolved solids, hardness, major anions (F^-, Cl^-, NO_3, HCO_3^-, SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, K^+). Study results reveal that groundwater of the area is alkaline in nature and HCO_3^-, Cl^-, Mg^{2+}, Na^+ and Ca^{2+} are the major contributing ions to the dissolved solids. The hydrogeochemical data suggest that weathering of rock forming minerals along with secondary contributions from agricultural and anthropogenic sources are mainly controlling the groundwater composition of Pratapgarh district. Alkaline earth metals ($Ca^{2+}+Mg^{2+}$) exceed alkalis (Na^++K^+) and weak acid (HCO_3^-) dominate over strong acids ($Cl^-+SO_4^{2-}$) in majority of the groundwater samples. Ca-Mg-HCO_3 and Ca-Mg-Cl-HCO_3 are the dominant hydrogeochemical facies in the groundwater of the area. The computed saturation indices demonstrate oversaturated condition with respect to dolomite and calcite and undersaturated with gypsum and fluorite. A comparison of groundwater quality parameters in relation to specified limits for drinking water shows that concentrations of TDS, F^-, NO_3^- and total hardness exceed the desirable limits in many water samples. Quality assessment for irrigation uses reveal that the groundwater is good for irrigation. However, values of salinity, sodium adsorption ratio (SAR), residual sodium carbonate (RSC), %Na and Kelley index are exceeding the prescribed limit at some sites, demanding adequate drainage and water management plan for the area.

Keywords: Pratapgarh district, Groundwater quality, Hydrogeochemical processes, Sodium percent, Sodium adsorption ratio, Residual sodium carbonate, Kelley index, Uttar Pradesh.

INTRODUCTION

Water resource has played a critical and vital role throughout the history in the growth and development of human civilization. In modern times, water resources have critical importance in the economic growth of all contemporary societies. Therefore, water resource assessment and sustainability consideration are of utmost importance, especially, in the developing countries like India where water is commonly of economical and social significance. Access to safe drinking water remains an urgent necessity, as 30% of urban and 90% of rural Indian population still depend completely on untreated surface or groundwater resources (Kumar et al. 2005). Water quality plays an important role in promoting agricultural production and standard of human health. While access to drinking water in India has increased over the past decades but the tremendous adverse impact of unsafe water on health continues. Scarcity of clean and potable drinking water has emerged in recent years as one of the most serious developmental issues in many parts of West Bengal, Jharkahnd, Orissa, Western Uttar Pradesh, Andhra Pradesh, Rajasthan and Punjab. Public ignorance to environmental considerations, indiscriminate disposal of anthropogenic, agricultural and mining wastes, unplanned application of agrochemicals and fertilizers and overexploitation of groundwater resources caused excess accumulation of pollutants on the land and contamination of available surface and groundwater resources (Subramanian 2000; Singh 2000; CPCB 2008). The overdependecy on groundwater has led to 66 million people in 22 states at risk due to excessive fluoride and around 10 million at risk due to arsenic in six states (Ghosh 2007). This indicates endemic fluorosis has emerged as one of the most alarming public health problems in the country (Choubisa 2001; Susheela et al. 1993; Susheela 1999; Teotia and Teotia 1984). In addition, there are problems due to excessive salinity and hardness of groundwater in the coastal areas of Andhra Pradesh, Tamil Nadu, Gujrat, NCR (National Capital Region of Delhi) and Western Uttar Pradesh and higher concentration of iron and nitrate in the Andhra Pradesh, Rajasthan, Jharkhand, Goa and Orissa (Srikanth 2009). Many districts of Uttar Pradesh including Unnao, Agra, Mathura, Ghaziabad and Aligarh are facing the problem of inland salinity and excessive fluoride in groundwater (CGWB 2010). Understanding of the hydrogeochemical processes and pollutant source and regular monitoring of water quality are essential for sustainable development and effective management of groundwater resources of any region. Though, information on the groundwater quality status and impact of urban and industrial development on groundwater resources are available for some districts like Unnao, Ghaziabad, Sonbhadra, Varanasi and Deoria (Misra and Mishra 2007; Umar et al. 2006; Singh et al. 2012; Raju et al. 2009, 2011; Bhardwaz and Singh 2011), such information are lacking for many districts of Uttar Pradesh including Pratapgarh. In the present hydrogeochemical investigation, an attempt has been made to define the major ion chemistry and hydrogeochemical processes that control groundwater composition of the Pratapgarh district and to assess its suitability for domestic and irrigation uses. The study provides some basic hydro-geochemical data for rational exploitation and utilization of groundwater resources that may also help in future water resource planning for the area.

STUDY AREA

Pratapgarh is one of the oldest district of Uttar Pradesh, came into existence in the year 1858. It lies between 25°34' and 26°11'N latitudes and 81°19' and 82°27’E longitudes and covers a total area of 3,730 km^2 (Fig. 1). It has seventeen administrative blocks and total population of the district is 27,31,174 (India Census, 2001). Pratapgarh is bounded on the north by Sultanpur, on the south by Allahabad, on the east by Jaunpur, on the west by Fatehpur and northeast by Rae Bareli districts. In the south-west, the Ganga river forms the boundary of the district for about 50 km separating Pratapgarh from Fatehpur and Allahabad districts and in the extreme northeast, the Gomti river forms the boundary for about 6 km. The area has a tropical climate, characterized

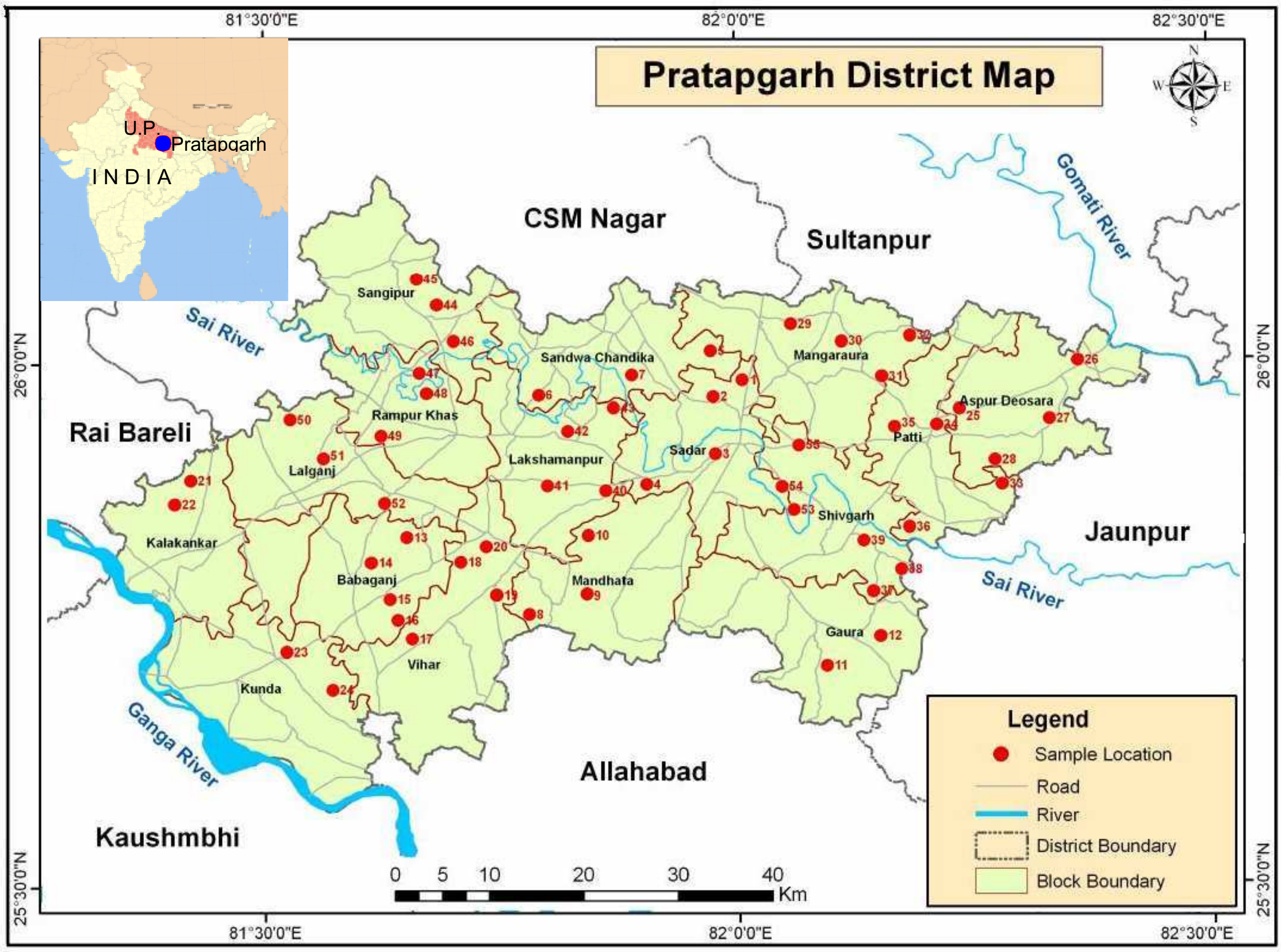


Fig.1. Location map of Pratapgarh district showing sampling sites.

by hot summer and cold winter. January is the coldest month of the year with the mean daily maximum and minimum temperature of 24.1°C and 7.5°C respectively. May is the hottest month with mean daily maximum temperature of 42.5°C and minimum of 26.4°C. The average annual rainfall is around 1000 mm and about 90% of the rainfall takes place from June to September months. Pratapgarh is primarily an agricultural district and ranked as the top producer of aonla fruit. Aonla also known as "Indian gooseberry" or *Embellica Officinalisis* is a multi-purpose fruit, extremely rich in vitamin C and used as a valuable ingredient of various Ayurvedic medicines in India.

The Ganga and Sai are the major rivers controlling the drainage pattern and natural slope of the area. Sai is the most important river flowing from west to east through heartland of the Pratapgarh district. This river irrigates northern and southern parts of Pratapgarh district and meets Gomti river at downstream in the Jaunpur district. Sixty-one percent of the total land area of Pratapgarh district is under cultivation followed by forest (5%), wasteland (6%), fallow land (17%) and other uses (11%). Saline, waterlogged and ravine lands are the major wasteland occurring in the area. The occurrence of salt affected wasteland is less; extensively occurs in the north of the Sai river than in the south. Saline wastelands are mostly barren and characterized by a salt encrustation of varying thickness. Most of the saline lands have a sub-surface layer of calcareous nodule at varying depth. Pratapgarh has no exploitable minerals except sand excavation along the rivers Ganga and Sai. *Kankar* (calcareous nodules) is available in the saline land and commonly used for road construction, while some poor people use saline soils (locally known as *Reh*) for washing clothes.

Geologically, unconsolidated sedimentary rock formations and Quaternary alluvium deposits covers the whole area. The formations are chiefly composed of sand, sandy clay, clay with varying amount of kankar (calcareous nodules). The older alluvium generally occupies a larger part of the area away from flood plains of the Ganga and Sai rivers, whereas, newer alluvium generally occupies the low-lying areas and is restricted to flood plains mainly in the narrow belt along the course of the rivers. The older alluvium is made up of massive beds of clay of pale reddish brown colour, very often yellowish clay layers with kankar (calcrete)in between. The newer alluvium is light coloured and poor in calcareous matter. The upper layer of alluvium is composed of sandy loam and clayey loam. The aquifer material is fine to medium grained sand and kankar variably occur with micaceous clay. Groundwater occurs under confined to semi-confined conditions (Kumar 2005). The clayey formations are dominate in the topographical low and waterlogged areas having shallow water table and sodic soils. The unlined irrigation canals aggravates sodic soil problem of the area and makes the land unfertile – the *Usar*.

Groundwater and canals are the main source of water for irrigation and dug wells and tube wells are the major source of water for drinking in the area. The depth of water level varies from 2.76 to 14.2 meter below the groundwater level (mbgl) during pre-monsoon and 2.10 to 12.07 mbgl in post-monsoon. The shallow water level occurs in canal command area and the deeper ones along the Ganga and Sai rivers. Depth of drinking water tube wells varies from 100 to 140 mbgl, while depth of the dug wells and hand pumps varies from 5-15 m and 35-60 m below the ground level respectively.

SAMPLING AND ANALYSIS

Fifty-five groundwater samples were collected from shallow (dug wells) and deep aquifers (tube well/hand pumps) at different locations of the Pratapgarh district during premonsoon (June 2009) season (Fig. 1). Groundwater samples were collected in pre-washed one-liter polyethylene narrow-mouth bottles after pumping the wells for 5-10 minutes and rinsing the bottles for 2-3 times with water to be sampled. Electrical conductivity (EC) and pH values were measured in the field using a portable conductivity and pH meter (Consort C831). Acid titration method was used to determine the concentration of bicarbonate (HCO_3^-) in unfiltered water samples. In the laboratory, water samples were filtered through 0.45 µm Millipore membrane filter to separate suspended particulate. Concentation of dissolved silica (SiO_2) was measured by molybdosilicate method with the help of UV-VIS spectrophotometer (APHA 1998). Major anions (F^-, Cl^-, SO_4^{2-}, NO_3^-) were analysed on ion chromatograph using anions AS12A/AG12 columns coupled to an anion self-regenerating suppressor (ASRS) in recycle mode. Major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were measured by Atomic Absorption Spectrophotometer (Varian 680FS) in flame mode after calibrating the instrument with known standards. Three replicates were run for each sample for cation analysis and the instrument recalibrated after every 15 samples. An overall precision, expressed as percent relative standard deviation (RSD), was obtained below 10% for the entire samples. Overall data reproducibility for anions was within ±10%. Cationic and anionic charge balance (<10%) is an added proof for the precision of the data.

RESULTS AND DISCUSSION

Table 1 presents the physico-chemical data of the

Table 1. Hydrogeochemical characteristics of groundwater of Pratapgarh district, Uttar Pradesh

S.No.	Site Name	Type	pH	EC	TDS	Turb.	F^-	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	Silica	Ca^{2+}	Mg^{2+}	Na^+	K^+	TH	pCO_2	CAI-I	CAI-II	SAR	%Na	RSC	KI
1	Godi	H.P	7.6	972	642	1.03	0.74	76.0	425	36.7	48.6	30.7	22.9	41.6	96.1	4.6	228	-1.9	-1.01	-0.25	2.77	48.5	2.39	0.92
2	Sonava	H.P	7.8	797	526	2.68	1.61	9.5	412	0.8	13.6	17.6	13.9	47.4	32.8	5.6	230	-2.2	-4.83	-0.19	0.94	25.4	2.16	0.31
3	Chilbila	H.P	7.5	3080	2033	0.84	0.41	743.0	458	48.1	58.5	17.6	115.4	127.5	213.6	10.4	812	-1.8	0.54	1.21	3.26	37.0	-8.74	0.57
4	Partapgarh city	S.P	8.2	2980	1967	0.24	2.42	690.0	455	159.1	0.8	11.8	27.4	17.6	685.0	3.5	141	-2.5	-0.54	-0.97	25.11	91.4	4.65	10.58
5	Dubeypur	H.P	7.9	1630	1076	0.57	1.93	166.5	616	170.6	11.5	12.4	25.9	70.4	211.3	4.5	354	-2.1	-0.98	-0.33	4.88	56.8	3.01	1.30
6	Ramnagar	W.W	7.8	670	442	0.48	1.23	16.1	325	7.3	19.0	13.8	37.7	26.8	31.9	3.1	204	-2.3	-2.22	-0.17	0.97	26.4	1.25	0.34
7	Bharopur	H.P	7.9	3300	2178	0.37	2.32	617.0	585	261.1	109.3	14.1	57.0	73.2	713.1	3.8	443	-2.1	-0.79	-0.82	14.73	77.8	0.73	3.50
8	Bachhua	W.W	7.6	1583	1045	0.50	1.00	259.9	348	49.7	170.2	14.6	87.6	84.6	64.7	3.7	567	-2.0	0.60	0.47	1.18	20.4	-5.62	0.25
9	Gokul	H.P	7.6	1006	664	0.28	0.83	146.0	302	34.9	13.2	14.1	51.6	61.6	42.9	2.9	382	-2.1	0.53	0.37	0.95	20.3	-2.68	0.24
10	Parvatpur	H.P	7.6	2830	1868	1.36	0.50	621.3	474	184.7	8.0	28.9	55.5	104.1	300.5	5.9	567	-1.9	0.25	0.37	5.49	53.8	-3.56	1.15
11	Ramapur	H.P	8.0	689	455	0.90	1.43	7.0	412	1.5	1.2	21.2	23.0	42.0	39.5	7.3	230	-2.4	-8.60	-0.25	1.13	29.3	2.15	0.37
12	Koyam	H.P	8.2	720	475	0.56	2.14	10.0	482	1.0	9.4	21.2	43.7	42.3	42.3	3.8	283	-2.5	-5.86	-0.20	1.09	25.5	2.24	0.32
13	Saray chaubain	W.W	7.8	941	621	0.47	0.49	112.0	354	9.2	5.2	23.0	52.8	43.1	32.8	3.3	309	-2.2	0.52	0.27	0.81	19.7	-0.38	0.23
14	Dulhapur	H.P	7.7	2440	1610	0.37	0.60	413.0	417	115.3	136.0	25.8	67.8	104.3	194.8	7.6	598	-2.0	0.26	0.26	3.46	42.0	-5.13	0.71
15	Pritampur	H.P	8.5	1578	1041	0.54	2.86	80.2	654	168.7	1.8	23.2	22.0	34.7	328.8	6.9	197	-2.6	-5.40	-0.86	10.18	78.6	6.77	3.62
16	Kusaha	H.P	7.8	797	526	0.30	1.72	29.0	413	7.9	8.0	24.6	33.9	43.7	32.6	3.8	264	-2.1	-0.85	-0.10	0.87	22.3	1.48	0.27
17	Galgali	H.P	7.9	570	376	0.30	3.75	21.6	314	2.5	10.7	16.5	25.6	43.6	33.7	6.9	243	-2.4	-1.70	-0.19	0.94	25.2	0.28	0.30
18	Badaipur	H.P	8.1	1667	1100	0.28	2.92	214.0	490	32.4	138.9	17.7	23.6	64.0	225.4	7.7	322	-2.4	-0.66	-0.36	5.46	60.8	1.58	1.52
19	Bhitara	W.W	7.9	618	408	0.30	1.82	13.6	324	4.1	23.7	33.4	34.9	35.6	20.6	2.8	234	-2.4	-1.53	-0.10	0.59	17.2	0.64	0.19
20	Kanupur	H.P	7.5	2520	1663	0.31	1.36	575.8	207	55.3	194.0	35.6	94.0	124.5	104.8	7.1	747	-2.1	0.71	1.50	1.67	24.1	-11.54	0.31
21	Chandpur	H.P	7.9	605	399	1.05	2.35	19.0	371	3.6	12.3	29.3	46.0	34.4	17.0	3.9	256	-2.3	-0.57	-0.05	0.46	14.1	0.96	0.14
22	Kushuvapur	H.P	7.7	778	513	0.17	3.10	78.0	279	29.5	4.2	28.7	52.8	29.7	32.3	2.1	254	-2.2	0.34	0.14	0.88	22.3	-0.50	0.28
23	Kajipur	H.P	8.1	813	537	2.20	2.11	44.0	387	17.4	1.2	27.8	24.6	48.1	29.6	7.3	259	-2.5	-0.19	-0.03	0.80	22.2	1.16	0.25
24	Amathi	H.P	7.9	720	475	0.67	2.35	36.0	367	13.5	5.7	31.1	41.7	29.9	30.1	2.0	227	-2.3	-0.34	-0.05	0.87	23.0	1.48	0.29
25	Bibipur	H.P	8.2	652	430	0.45	3.44	24.3	336	8.5	18.1	29.2	9.4	37.1	69.0	4.3	176	-2.6	-3.54	-0.41	2.26	46.9	1.99	0.85
26	Sujanpatee	H.P	7.7	878	579	0.93	2.97	17.1	413	9.2	9.8	23.0	16.8	47.7	47.8	3.1	238	-2.0	-3.48	-0.24	1.35	31.2	2.00	0.44
27	Amargarh	H.P	7.8	776	512	0.31	2.10	11.6	403	5.9	6.7	24.4	11.9	45.9	39.9	4.8	218	-2.2	-4.70	-0.22	1.17	29.8	2.24	0.40
28	Majhigava	H.P	7.8	1168	771	0.48	2.91	70.4	585	15.2	86.7	31.9	4.2	113.9	129.8	4.8	478	-2.0	-1.91	-0.33	2.58	37.6	0.02	0.59
29	Raigarh	H.P	7.6	880	581	0.32	2.63	114.0	283	15.1	32.7	33.5	58.3	47.2	23.1	7.0	340	-2.1	0.63	0.37	0.55	14.9	-2.14	0.15
30	Madhupur	H.P	7.7	660	436	0.26	1.54	56.0	221	9.8	36.5	32.5	23.9	32.8	20.7	4.7	195	-2.3	0.35	0.13	0.65	20.8	-0.27	0.23
31	Utarash	H.P	7.9	884	583	1.50	1.78	70.0	313	21.4	44.6	37.2	24.6	41.1	47.4	7.5	230	-2.4	-0.14	-0.04	1.36	32.9	0.53	0.45
32	Barikala	W.W	8.2	790	521	0.26	1.82	44.6	413	32.6	19.0	32.9	35.0	40.6	58.0	4.1	254	-2.5	-1.09	-0.18	1.58	34.1	1.69	0.50
33	Salahpur	H.P	7.9	810	535	1.01	1.61	15.4	483	7.4	1.2	33.6	23.2	41.8	59.7	4.0	230	-2.2	-5.24	-0.28	1.71	37.0	3.32	0.57
34	Sarsatpur	H.P	7.8	945	624	0.94	2.03	43.7	505	16.4	45.4	33.5	20.2	49.1	85.8	4.8	252	-2.1	-2.13	-0.28	2.35	43.3	3.23	0.74
35	Raypur	H.P	7.7	545	360	6.53	1.58	5.4	278	1.7	1.2	30.7	13.5	29.5	19.5	3.4	155	-2.2	-5.14	-0.17	0.68	23.2	1.46	0.27
36	Pritviganj	H.P	7.9	859	567	0.49	2.22	21.6	453	10.9	6.4	32.0	18.6	41.7	68.4	4.5	218	-2.2	-4.08	-0.32	2.02	41.5	3.07	0.68
37	Avadhanpur	H.P	8.0	672	444	1.57	1.69	10.9	394	3.9	1.1	18.5	12.9	35.0	53.0	5.2	176	-2.4	-6.96	-0.32	1.73	40.9	2.93	0.65
38	Jagadishpur	W.W	8.0	997	658	1.31	2.74	58.6	551	7.3	24.3	30.8	24.6	65.6	70.1	12.3	331	-2.2	-1.03	-0.18	1.67	33.7	2.40	0.46
39	Birapur	H.P	8.0	752	496	1.86	2.91	19.4	443	9.4	1.4	31.5	22.7	47.1	36.7	6.1	250	-2.3	-2.21	-0.16	1.01	25.9	2.25	0.32
40	Sarayannadet	B.W	7.9	2620	1729	0.53	3.05	486.0	532	110.0	14.7	38.9	92.4	111.6	239.8	30.8	690	-2.1	0.18	0.22	3.97	44.9	-5.07	0.76
41	Katvara	W.W	7.5	1746	1152	0.88	1.65	434.0	285	21.3	1.0	36.2	132.0	102.6	23.5	4.6	751	-2.0	0.91	2.16	0.37	7.1	-10.35	0.07
42	Leelapur	H.P	7.6	662	437	0.28	0.98	22.8	398	35.9	15.2	38.9	29.5	66.7	33.3	4.1	348	-2.0	-1.42	-0.12	0.78	18.3	-0.44	0.21
43	Nevada	W.W	7.7	2740	1808	0.46	0.84	551.8	451	90.0	49.2	38.1	160.0	73.3	141.9	11.5	701	-2.0	0.58	0.90	2.33	31.6	-6.61	0.44
44	Jagadishpur	H.P	7.9	725	479	0.27	1.68	26.3	405	1.8	14.7	37.5	21.6	49.4	23.6	3.5	257	-2.3	-0.51	-0.05	0.64	17.8	1.50	0.20
45	Lakhattpur	W.W	7.9	647	427	0.55	0.77	60.0	216	10.1	18.7	36.5	15.6	32.3	32.1	2.5	172	-2.5	0.14	0.06	1.07	29.8	0.11	0.41
46	Kamalpur	H.P	8.4	823	543	0.17	3.00	67.5	375	11.4	8.8	29.5	10.6	22.4	147.0	3.7	95	-2.8	-2.41	-0.70	6.56	77.4	4.25	3.37
47	Pichaura	H.P	7.6	665	439	0.56	0.64	9.1	328	4.1	11.8	28.0	28.6	24.9	40.0	3.0	174	-2.0	-6.11	-0.28	1.32	34.3	1.90	0.50
48	Devapur	W.W	7.9	1031	680	0.40	0.73	100.0	371	27.5	51.8	29.4	72.6	48.6	23.7	3.5	381	-2.3	0.60	0.23	0.53	12.8	-1.54	0.14
49	Betaha	H.P	7.8	598	395	0.56	0.76	4.8	348	1.9	12.0	28.8	19.5	34.8	27.8	4.2	192	-2.2	-8.81	-0.20	0.87	25.6	1.87	0.32
50	Beerbhadra	H.P	7.8	2810	1855	0.62	2.25	491.8	486	144.6	66.2	26.7	31.8	32.4	510.2	2.2	213	-2.1	-0.60	-0.70	15.22	84.0	3.71	5.22
51	Karimpur	H.P	7.9	647	427	0.29	2.74	13.4	360	9.9	10.9	38.8	23.5	46.1	21.1	4.0	248	-2.3	-1.69	-0.10	0.58	17.0	0.93	0.18
52	Maladhar	H.P	7.7	681	449	0.23	1.89	6.7	375	1.3	18.9	33.8	29.6	42.1	14.0	2.9	247	-2.1	-2.60	-0.08	0.39	12.1	1.21	0.12
53	Dilippur	H.P	8.1	975	644	0.55	3.36	148.0	245	10.2	38.8	32.8	11.5	60.1	57.6	7.5	251	-2.7	0.35	0.30	1.58	35.0	-1.00	0.50
54	Shivsat	H.P	7.1	1764	1164	0.20	3.16	403.9	229	32.7	2.1	39.6	98.9	102.4	73.7	13.8	668	-1.7	0.69	1.75	1.24	21.0	-9.60	0.24
55	Sarayganai	W.W	7.7	1778	1173	0.39	3.99	289.9	390	76.9	13.9	31.2	90.5	84.4	89.1	36.8	573	-2.1	0.41	0.41	1.62	29.6	-5.06	0.34

Unit: Concentrations are in mg L^{-1}, except EC (µS cm^{-1}), Turbidity (NTU) CIA (meq L^{-1}), SAR (meq L^{-1}), RSC (meq L^{-1}), %Na, pCO_2 and , pH

EC = Electrical Conductivity, TDS = Total Dissolved Solids, TH = Total hardness, CAI = Chloro-alkaline indices, SAR = Sodium adsorption ratio, RSC=Residual sodium carbonate, KI= Kelley index, H.P.= Hand pump, W.W.= Dugwell, Turb. = Turbidity, pCO_2= Partial pressure of CO_2

analysed groundwater samples of the Pratapgarh district. The computed values of chloroalkaline indices (CAI), sodium adsorption ratio (SAR), %Na, residual sodium carbonate (RSC) and Kelley index (KI) are also given in Table 1.

Hydrogeochemical Characterization

pH of the analysed water samples ranges from 7.1 to 8.5 with an average value of 7.84, suggesting neutral to alkaline nature of groundwater. Electrical conductivity (EC) measures the salt concentration and provides indication of ionic concentrations in the water. The measured EC of groundwater varies from 545 to 3300 µS cm^{-1} with an average value of 1227 µS cm^{-1}. Concentration of total dissolved solid (TDS) ranged from 360 mg L^{-1} to 2178 mg L^{-1} with an average value of 810 mg L^{-1}. Based on Freeze and Cherry (1979) classification, 71% of the groundwater samples of the study area are categorized as fresh water (TDS<1,000 mg L^{-1}), and remaining 29% as brackish water (TDS>1,000 mg L^{-1}). The higher standard deviations for EC (±778) and TDS (±514) values reflect vide spatial variability in ionic concentrations in groundwater of the area. The spatial variation shows higher TDS values at sites 3, 4, 7, 10, 14, 40, 43 and 50 (Fig. 2a). The large spatial differences between the values of TDS may be attributed to the lithological variations and local impact of agricultural and anthropogenic activities in the region.

The anion chemistry shows that HCO_3^- and Cl^- are the dominant anions followed by SO_4^{2-}, NO_3^- and F^-. The measured concentration of HCO_3^- in the groundwater samples varies from 207 mg L^{-1} to 654 mg L^{-1} (avg. 395 mg L^{-1}) and it accounts for 65% of the total anions (TZ^-) in equivalent unit. Weathering of carbonate and/or alumino-silicate minerals with a secondary contribution from dissolution of CO_2 gases are the primary source of HCO_3^- in the groundwater. The computed CO_2 partial pressure (pCO_2) in the groundwater samples varies between $10^{-2.8}$ and $10^{-1.7}$ with a mean value of $10^{-2.2}$ (atm). Throughout the data range, the pCO_2 values are significantly higher than that of the atmospheric ($10^{-3.5}$ atm) level (Table 1). This CO_2 can be produced by the oxidation of organic matter and by root respiration in the unsaturated zone, followed by the dissolution in the recharge water to form bicarbonate by the reaction:

$$CO_2 + H_2O = H^+ + HCO_3^-$$

In addition, bicarbonate is also be produced by the dissolution of carbonates and the weathering of silicate minerals (Njitchoua and Ngounou, 1997). The higher proportions of bicarbonate in relation to other anions indicate weathering of primary silicate minerals dominated by alkaline earths (Rose, 2002). The excess of F^-, Cl^- and NO_3^- in the groundwater are generally used as a tracer for groundwater contamination (Loizidou and Kapetanios 1993). Chloride (Cl^-) in groundwater may originate from both natural and anthropogenic sources. Atmospheric precipitation, dissolution of salt deposits and weathering of halite and evaporite are considered as the major lithogenic source of chloride in the groundwater. Possible anthropogenic source of chloride are septic, industrial and animal wastes, fertilizers and leachates from landfill and waste dumps (Appelo and Postama 1996). The chloride concentration in the groundwater of Pratapgarh district varied between 4.8 and 743 mg L^{-1} with an average value of 158 mg L^{-1}. In an equivalent unit, Cl^- constitutes about 25% of the total anions (TZ^-). The large lateral variations and high concentrations of chloride in some groundwater samples may be attributed to the local recharge and leaching of salt and saline residues in the soil and municipal, domestic and animal wastes. Concentration of sulphate varies from 0.8 to 261 mg L^{-1} (avg. 39.6 mg L^{-1}), contributing 4.8% to

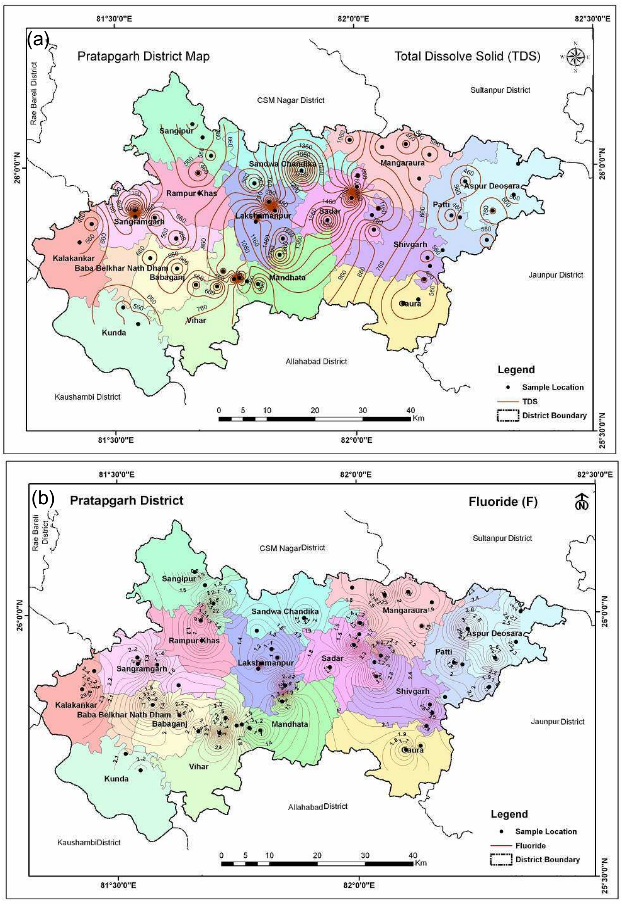


Fig.2. Spatial variation in concentrations (mg L^{-1}) of (a) Total Dissolved Solids and (b) Fluoride in the groundwater of Pratapgarh district

the total anionic charge balance. Sulphate concentration in natural water is usually found between 2 and 80 mg L^{-1} and higher concentration may be attributed to weathering of sulphide minerals or anthropogenic sources like industrial and agricultural effluents (Berner and Berner, 1987).

Concentration of nitrate (NO_3^-) in the analysed water samples varies between 0.10 and 194 mg L^{-1} (avg. 30.7 mg L^{-1}), constituting 3.8% of the total anionic mass balance (TZ^-). Nitrate is an important pollutant in the environment, generally derived from atmospheric precipitation, agricultural fertilizers, human and animal excreta, biological fixation and nitrification of organic N and NH_4 (Appelo and Postma 1996). The study area is under extensive agricultural acitivity and minimum two crops are cultivated annually. Chemical and organic fertilizers are indiscriminately used in agricultural practices for growing crops and to increase the agricultural productivity. Urea $(NH_2)_2CO$, ammonium nitrate (NH_4NO_3) and superphosphate are the most commonly used chemical fertilizers in this area. Nitrogen based fertilizers comprises 77% of the total annual used chemical fertilizer of 36,296 tons in the area (Yadav 2009). The observed higher concentration of NO_3^- in some groundwater samples could be attributed to leaching of organic and inorganic fertilizers from agricultural land by infiltration of rain and irrigation water. High nitrate level in the groundwater may also be due to leaching of the animal wastes especially in the rural areas. Most of the excreta of the domestic animals are not properly disposed and excreta, dung and urine produced by animal constitute a potential source of nitrate contamination in the groundwater (Reddy et al. 2011; Vidal et al. 2000). The main mechanism influencing the nitrate concentrations in the soil zone may be that ammonium, mineralised through organically bound nitrogen or releases from animal excreta and urine were sorbed by clays in the soil zones. This sorbed ammonium quickly nitrified in to nitrate, when it encountered with the infiltrating water. Studies shows that cations (positively charged ions) may readily sorbed or exchanged to negatively charged mineral surfaces (such as clays) but negatively charged anions (nitrate ions) were not sorbed on negatively charged sites on clay particles and rapidly migrate downward to the groundwater (Stumm 1992).

Fluoride (F^-) concentration varied from 0.41 to 3.99 mg L^{-1} (avg. 1.95 mg L^{-1}) in the groundwater samples of the area and it accounts 1.5% of the total anionic (TZ^-) charge balance. Concentration of fluoride marginally exceeds the permissible limit of drinking water (1.5 mg L^{-1}) in about 70% of the groundwater samples (Fig. 2b). Fluoride in groundwater is mainly derived from the weathering of fluoride bearing minerals like muscovite, biotite, fluorite, fluoro-apatite, besides industrial and agricultural sources (Appelo and Postma 1996). There is no major industrial setup in the study area that could cause fluoride contamination in the groundwater system. Therefore, occurrence of high F^- concentration in the groundwater of Pratapgarh district is either of geogenic origin or from percolation of phosphatic fertilizers from the irrigational runoff. The alkaline pH, positive correlation of F^- with pH (0.36) and HCO_3^- (0.22) and negative correlation with Ca^{2+} (-0.23) and Mg^{2+} (-0.08) suggest geogenic origin of fluoride (Table 2). Negative correlations of calcium and magnesium with fluoride may be expected due to the low solubility of fluoride in natural groundwater (Handa 1975; Hem 1991). The alkaline water helps in the mobilizing F^- from fluoride bearing minerals with the precipitation of calcium carbonate. The $NaHCO_3$ rich water accelerates the dissolution of fluoride bearing minerals and thereby releases fluoride into groundwater (Jacks et al. 2005; Saxena and Ahmed 2001). Higher concentration of HCO_3^- and Na^+, higher ratio of HCO_3^-/Ca^{2+} (5.03) and Na^+/Ca^{2+} (3.15) and alkaline nature of groundwater suggests favourable chemical conditions for fluoride dissolution (Saxena and Ahmed 2003). The sluggish movement of groundwater due to low hydraulic conductivity

Table 2. Inter-elemental correlation matrix of dissolved ions (n = 55)

	pH	EC	TDS	Turb	F^-	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	Silica	Ca^{2+}	Mg^{2+}	Na^+	K^+
pH	1.00													
EC	-0.20	1.00												
TDS	-0.07	0.97	1.00											
Turb.	-0.02	-0.16	-0.17	1.00										
F^-	0.36	-0.09	-0.03	-0.10	1.00									
Cl^-	-0.31	0.97	0.91	-0.15	-0.13	1.00								
HCO_3^-	0.40	0.36	0.51	-0.04	0.12	0.16	1.00							
SO_4^{2-}	0.05	0.81	0.88	-0.14	-0.01	0.71	0.53	1.00						
NO_3^-	-0.20	0.46	0.44	-0.18	-0.17	0.42	0.02	0.26	1.00					
Silica	-0.20	-0.17	-0.24	0.00	0.08	-0.11	-0.29	-0.29	-0.12	1.00				
Ca^{2+}	-0.53	0.60	0.48	-0.18	-0.23	0.68	-0.10	0.28	0.29	0.13	1.00			
Mg^{2+}	-0.49	0.62	0.56	-0.12	-0.08	0.65	0.15	0.32	0.50	0.12	0.63	1.00		
Na^+	0.20	0.79	0.88	-0.13	0.10	0.70	0.53	0.87	0.26	-0.38	0.10	0.15	1.00	
K^+	-0.11	0.34	0.29	-0.05	0.36	0.32	0.14	0.19	0.00	0.21	0.42	0.47	0.07	1.00
TH	-0.56	0.68	0.58	-0.16	-0.16	0.73	0.04	0.33	0.45	0.14	0.87	0.93	0.14	0.50

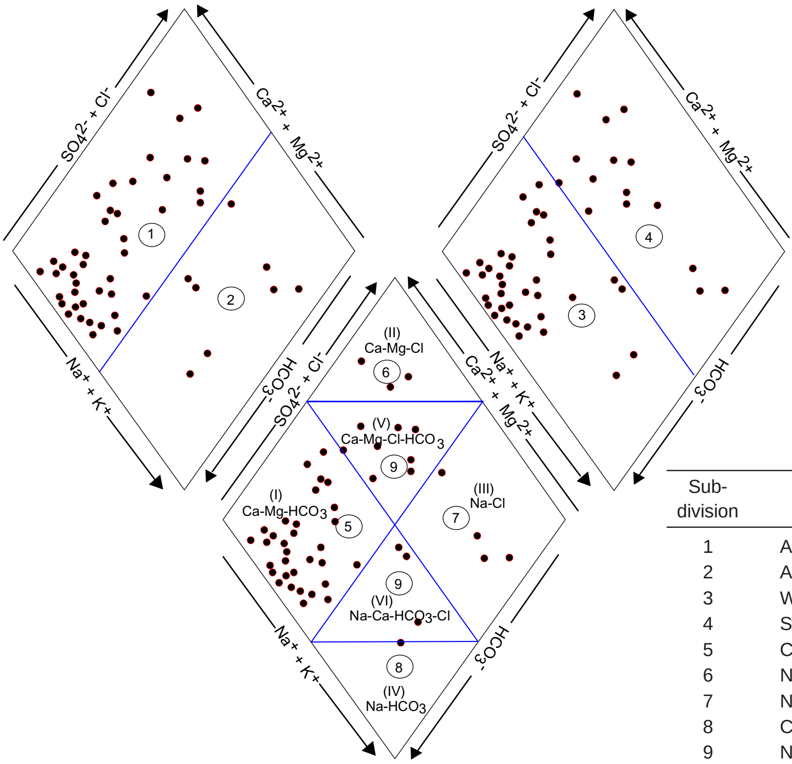
of clays provides higher residence time for interaction between groundwater and aquifer materials. This enables not only active dissolution of fluoride bearing minerals but also activates anion exchange between fluoride and hydroxyl ion in the weathered products (Rao 2003; Madhunure et al. 2007). Percolation of phosphatic fertilizers from the irrigational runoff from the nearby farming lands may also contribute fluoride concentration in the groundwater of the study area.

The concentration of Ca^{2+} varies from a minimum value of 9.4 mg L^{-1} to maximum of 160 mg L^{-1} with an average value of 41.4 mg L^{-1} and accounts for 20% of the total cationic mass balance (TZ^{+}). Concentration of Mg^{2+} varies between 17.6 mg L^{-1} and 127.5 mg L^{-1} (avg. 55 mg L^{-1}) and it exceeds Ca^{2+} concentration at many sites, denoting supply of magnesium from weathering of dolomite and/or mafic minerals and precipitation of calcium. Concentration of Na^{+} and K^{+} varies from 14.0 to 713.1 mg L^{-1} and 2.0 to 36.8 mg L^{-1} respectively in the groundwater of the study area with the average values of 107 and 6.2 mg L^{-1}. Sodium (32.5%) and potassium (1.6%) are together contributing about 34% of the total cationic charge balance. The concentration of dissolved silica varies from 11.8 to 39.6 mg L^{-1} with an average value of 27.9 mg L^{-1} and it accounts 4.6% of the total dissolved solids. Silica is negatively correlated (-0.20) with pH of the groundwater, suggesting sorption of silica by clay minerals (Siever and Woodward 1973; Subramanian 1974). It is likely that most of the dissolved silica in water originates from the chemical breakdown of silicates during weathering processes.

In order to understanding the chemical character of groundwater and relationships between dissolved ionic constituents, the hydrochemical data has been plotted on Piper diagram (Piper 1944). Figure 3 shows that the plotted points of the groundwater samples mainly fall in the sub-divisions 1, 3 and 5; indicating dominance of alkaline earth ($Ca^{2+}+Mg^{2+}$) over alkalis ($Na^{+}+K^{+}$) and weak acids (HCO_3^{-}) over strong acids ($SO_4^{2-}+Cl^{-}$). About 25% samples falls in the field 4, signifying the dominance of strong acid over weak acids and in 14% samples, alkali exceeds the alkaline earths (field 2). Plotted points of the majority of water samples fall in field 5, suggesting secondary alkalinity and carbonate hardness. Based on the dominance of different cations and anions in the groundwater, five hydrochemical water types can be defined as (I) Ca-Mg-$HCO_{3,}$ (II) Ca-Mg-Cl, (III) Na-Cl (IV) Ca-Mg-Cl-HCO_3 and (V) Na-Ca-Mg-HCO_3-Cl. Ca-Mg-HCO_3 and Ca-Mg-Cl-HCO_3.

Geochemical Evolution and Solute Acquisition Processes

A number of factors control chemical composition of groundwater and each groundwater system in any area has a unique chemistry due to chemical alteration of meteoric



Sub-division	Characteristics/Nature of water
1	Alkaline earths (Ca+Mg) exceeds alkalies (Na+K)
2	Alkalies exceeds alkaline earths
3	Weak acids (CO_3+HCO_3) exceeds strong acids (SO_4+Cl)
4	Strong acids exceed weak acid
5	Carbonate hardness (secondary alkalinity) exceeds 50%
6	Non-carbonate hardness (secondary salinity) exceeds 50%
7	Non-carbonate alkali (primary salinity) exceeds 50%
8	Carbonate alkali (primary alkalinity) exceeds 50%
9	None of the cation or anion pairs exceed 50%

Fig.3. Piper trilinear diagram showing hydrogeochemical character of groundwater

water recharging the aquifer system (Drever 1988; Hem 1991). The alterations in the chemical quality of meteoric water depends on composition of infiltrating rainwater, geological structure and mineralogical composition of aquifer, duration of water-rock interaction, dissolution and precipitation of mineral species and seawater and anthropogenic influences (Hounslow 1995; Andre et al. 2005; Datta and Tyagi 1996). Compositional relations among dissolved species can reveal origin of solutes and process that generated the observed water compositions (Jalali 2007, Singh et al. 2008). The stoichiometric relations of the dissolved ions have been evaluated in order to identify the main hydrogeochemical processes occurring in the aquifer. The relationship between Na^+ and Cl^- has often been used to identify the mechanism for acquiring salinity in semi-arid or arid regions and to quantify the atmospheric contribution (Sarin et al. 1989; Sami 1992; Singh et al. 2005). The observed higher Na^+/Cl^- ratio (avg. 2.54) in the groundwater as compared with marine aerosols (Na^+/Cl^- =0.85), suggests limited contribution from atmospheric precipitation and reveals that high levels of major ions are derived most likely by weathering of rock forming minerals and anthropogenic sources. The dissolution of halite in water releases equal concentrations of Na^+ and Cl^- into the solution and resulting Na^+/Cl^- molar ratio will be approximately one (Hounslow 1995). In the analysed groundwater samples, the molar ratio of Na^+/Cl^- ranges from 0.08 to 9.02 (avg. 2.54) and in majority of the samples (68%), sodium concentration exceeded over chloride content (Fig. 4a). The higher Na^+/Cl^- ratio (>1.0) indicate non-halite source and suggest silicate weathering as a possible source of Na^+. The lower molar ratio (Na^+/Cl^- <1.0) in some samples are probably result from ion exchange of Na^+ for Ca^{2+} and Mg^{2+} in clays. The positive correlations between Cl^--Na^+ (0.70), Cl^--TDS (0.91) and Na^+-TDS (0.88) indicate that Cl^- and part of the Na^+ are derived from anthropogenic sources (Table 2). The low levels of K^+ in the groundwater are a consequence of its tendency to be fixed by clay minerals and participate in the formation of secondary minerals.

The plot of (Ca^{2+}+Mg^{2+}) against (HCO_3^-+SO_4^{2-}) will be close to 1:1 line if the dissolution of calcite, dolomite and gypsum are the dominant reactions in a system (Cerling et al.1989; Fisher and Mulican 1997). The plotted points of the majority of the groundwater samples on the variation diagram relating (Ca^{2+}+Mg^{2+}) and (HCO_3^-+SO_4^{2-}) fall below the theoretical 1:1 equiline (Fig. 4b). The excess of (HCO_3^-+SO_4^{2-}) over (Ca^{2+}+Mg^{2+}) suggests significant contribution from non-carbonate source demanding the required portion of the (HCO_3^-+SO_4^{2-}) to be balanced by the alkalis (Na^++K^+). The plotted points of about 23% samples fall above the 1:1 line indicating some extra source of cations, which should be balanced by Cl^- and NO_3^-. The stoichiometry of carbonate weathering reactions demands that carbonate derived (Ca^{2+}+Mg^{2+}) should be equal to the carbonate derived HCO_3^-. The plot of (Ca^{2+}+Mg^{2+}) vs HCO_3^- shows a deficiency of Ca^{2+}+Mg^{2+} relative to HCO_3^- in majority of the samples (75%) and demands that excess negative charge of bicarbonate alkalinity should be balanced by the alkalis (Na^++K^+) provided through weathering of Na-K silicates. In some samples, (Ca^{2+}+Mg^{2+}) content is slightly in excess of HCO_3^- suggesting that excess (Ca^{2+}+Mg^{2+}) in these water should be balanced by SO_4^{2-} and Cl^- (Fig. 4c). The plotted points on (Ca^{2+}+Mg^{2+}) vs Total cations (TZ^+) scatter plot fall much below the equiline and the departure being more pronounced at higher concentration, reflecting an increasing contribution of Na^+ and K^+ with increasing dissolved solids (Fig. 4d). Sodium and potassium (Na^++K^+) shows much better correlation with the Total cations (TZ^+) especially at higher concentrations , signifying the role of silicate weathering in solute acquisition (Fig. 4e). The poor correlations of Ca^{2+} with HCO_3^- (0.10) and SO_4^{2-} (0.28) indicate that calcite and gypsum dissolution could not be the major contributor for the dissolved ions in the present case. Further, a relatively high (Na^++K^+)/TZ^+ i.e. 0.34 and low (Ca^{2+}+Mg^{2+})/(Na^++K^+) i.e. 2.8, ratios suggest that the chemical composition of the groundwater is largely controlled by silicate weathering with limited contribution by carbonate dissolution.

The ion exchange between the groundwater and its host environment during residence or in movement process are the important controlling factor for groundwater composition. Schoeller (1977) proposed chloro-alkaline indices (CAI) to understand the ion exchange between the groundwater and its host environment. The chloro-alkaline indices are expressed by the equations:

$$\text{CAI - I} = Cl^- - (Na^+ + K^+)/Cl^-$$
$$\text{CAI - II} = Cl^- \, (Na^+ + K^+)/SO_4^{2-} + HCO_3^- + NO_3^-$$

The chloro-alkaline indices can be either positive or negative depending on whether exchange of Na^+ and K^+ is from water with Mg^+ and Ca^+ in rock/soil or vice versa. If Na^+ and K^+ are exchanged in water with Mg^{2+} and Ca^{2+}, the value of the ratio will be positive, indicating a base-exchange phenomenon. The negative values of the ratio will indicate chloroalkaline disequilibrium and the reaction as a cation-anion exchange reaction. During this process, the host lithology is the primary source of dissolved solids in the water. In the present case, about 67% of the groundwater samples have negative values revealing chloro-alkaline disequilibrium and the reaction as a cation-anion exchange reaction. In 33% of the groundwater samples, the values

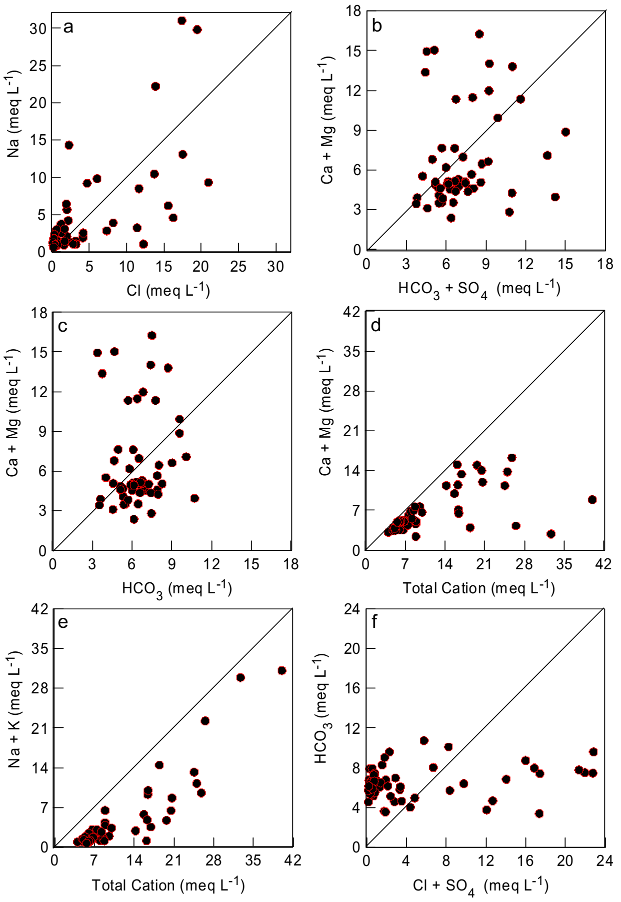


Fig.4. Scatter plot between (a) Na vs Cl (b) Ca+Mg vs HCO_3+SO_4, (c) Ca+Mg vs HCO_3, (d) Ca+Mg vs Total cations, (e) Na+K vs Total cations and (f) HCO_3 vs Cl+SO_4

are positive, indicating a base-exchange reaction (Table 1). Groundwater with a base-exchange reaction in which alkaline earths have been exchanged for Na^+ ion ($HCO_3^- > Ca^{2+}+Mg^{2+}$) may be referred as base-exchanged softened water, and those in which Na^+ ions have been exchanged for the alkaline earths ($Ca^{2+}+Mg^{2+} > HCO_3^-$) referred as base exchange hardened water. In the Pratapgarh district, 69% of the collected samples have higher HCO_3^- than alkaline earths ($HCO_3^- > Ca^{2+}+Mg^{2+}$) indicating exchange of Na^+ for alkaline earths and the water as base exchange softened water.

The evidence for cation exchange can also be verified by bivariate plot of $Ca^{2+}+Mg^{2+}-HCO_3^- -SO_4^{2-}$ as a function of $Na^++K^+-Cl^-$. $Na^++K^+-Cl^-$ represents the amount of Na^++K^+ gained or lost relative to that provided by chloride salt dissolution; while $Ca^{2+}+Mg^{2+}-HCO_3^- -SO_4^{2-}$ represents the amount of Ca^{2+} and Mg^{2+} gained or lost relative to that provided by gypsum, calcite and dolomite dissolution. If cation exchange were an important composition controlling process, the relation between these parameters would be linear with a slope of -1 (McLean et al. 2000). The bivariate plot for Pratapgarh groundwater indicates an increase in Na^++K^+ related to decrease in $Ca^{2+}+Mg^{2+}$ or an increase in $HCO_3^-+SO_4^{2-}$. The plotted points are close to a straight line (r^2=0.89) with a slope of -0.77 (Fig. 5). This indicates that almost all Na^+, Ca^{2+} and Mg^{2+} participate in the ion exchange reactions (Garcia et al. 2001).

Saturation Index (SI) and Mineral Equilibrium

Mineral equilibrium calculations are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity. By using saturation indices (SI), it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing mineralogy (Deutsch 1997). Saturation index (SI) is defined as the logarithm of the ratio of ion activity product (IAP) to the mineral equilibrium constant at a given temperature and expressed as:

$$SI = \log(IAP/Ksp)$$

where IAP is the ion activity product and Ksp is the solubility product of the mineral.

The saturation index (SI) describes the deviation of water from equilibrium with respect to dissolved minerals quantitatively (Garrels and Mackenzie 1971; Stumm and Morgan 1981). A negative saturation index (SI<0) indicates undersaturation conditions and dissolution of mineral phase. Such a value could reflect the character of water from a formation with insufficient amount of mineral for solution or short residence time. A positive index (SI>0) indicates that the water is supersaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral and under suitable physico-chemical

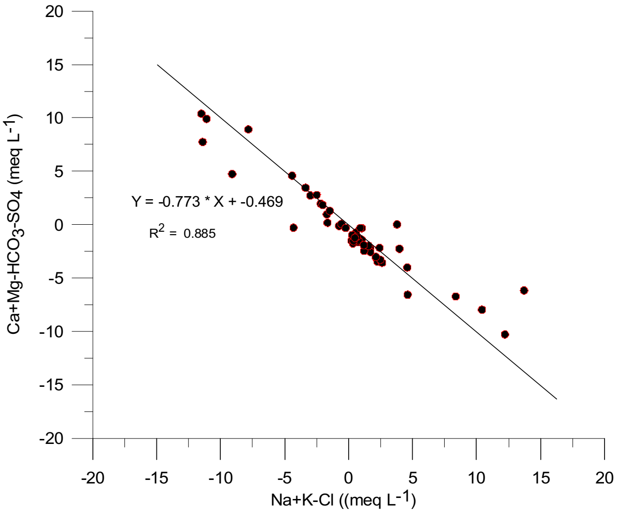


Fig.5. Bivariate plot between Ca+Mg-HCO_3-SO_4 vs Na+K-Cl

condition, the mineral phase in equilibrium may precipitate. Such an index value reflects groundwater discharging from an aquifer containing ample amount of mineral with sufficient resident time to reach equilibrium. A neutral SI (SI=0) is in equilibrium state with the particular mineral phase. The calculated saturation index values of calcite (SI_{cal}), dolomite (SI_{dol}), gypsum (SI_{gyp}) and fluorite (SI_{flu}) by PHREEQC software (Parkhurst and Applelo 1999) demonstrate that nearly all the groundwater samples are supersaturated with respect to dolomite and calcite and undersaturated with gypsum and fluorite throughout the data ranges (Fig 6). The supersaturation of carbonate phases may influenced the groundwater composition and leads to the precipitation of calcium as Ca and/or Ca-Mg carbonate under suitable physico-chemical conditions. This process explains the presence of calcareous nodules (kankar), which contain a mixture of calcite and/or dolomite in the sub-surface profile of the study area. The undersaturation of gypsum suggests that soluble sulphate mineral phases are absent in the host aquifer and the application of fertilizer through irrigation return flow may contributing sulphates to the groundwater.

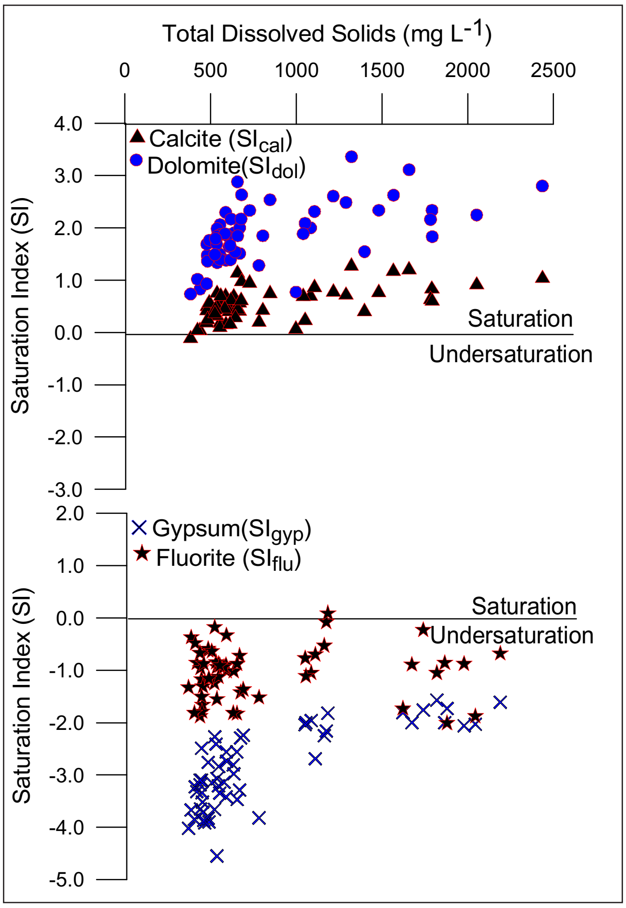


Fig.6. Plot of saturation indices of calcite (SI_{cal}), dolomite (SI_{dol}), gypsum (SI_{gyp}) and fluorite (SI_{flu}) against TDS

Water Quality Assessment

Understanding of the chemical quality of groundwater is important before its supply to the domestic, agricultural or industrial purposes. Data obtained by hydrogeochemical analyses of groundwater samples of Pratapgarh district have been evaluated in terms of its suitability for drinking and irrigation uses.

Potability of Goundwater for Dinking and Domestic Uses

To ascertain the potability of groundwater for drinking and domestic purposes, the analytical results have been compared with the standard guideline values recommended by the World Health Organisation (WHO 2006) and Bureau of Indian Standards (BIS 2003). Table 3 shows that pH of the groundwater samples (7.1-8.5) are well within the safe limit of 6.5-8.5, prescribed for drinking water (BIS 2003). The turbidity is one of the important physical parameter for water quality defining the presence of suspended solids in water and causes the muddy or turbid appearance of water body. The consumption of high turbid water may cause a health risk as excessive turbidity can protect pathogenic microorganisms from effects of disinfectants and stimulate the growth of bacteria during storage. In the study area, the turbidity ranges from 0.17 to 6.53 NTU and exceeds the recommended value of 5 NTU in only one groundwater sample. The total dissolved solid (TDS) exceeded the desirable limit (500 mg L^{-1}) in 64% of the groundwater samples and maximum permissible limit (1000 mg L^{-1}) in 29% samples. Hardness of the water is the property attributed to the presence of alkaline earths. Total hardness (TH) of the analysed sub-surface water varies between 95 mg L^{-1} and 812 mg L^{-1} with a mean value of 328 mg L^{-1}, indicating

Table 3. Statistical summary of measured parameters, compared to WHO and Indian standards for drinking water

Parameters Major ions (mg L^{-1})	Min.	Max.	Avg.	Std. Dev.	WHO (2006)	BIS (2003) IS:10500 *Maximum desirable*	BIS (2003) IS:10500 *Highest permissible*
pH	7.1	8.5	7.8	0.2	7.0-8.5	6.5-8.5	8.5-9.2
EC (µS cm^{-1})	545	3300	1227	778	750	-	-
TDS	360	2178	810	514	500	500	2000
Turbidity (NTU)	0.17	6.53	0.76	0.94	<5.0	<5.0	-
F^-	0.41	3.99	1.95	0.92	0.6-1.5	1.0	1.5
Cl^-	4.8	743	158.1	209.6	250	250	1000
HCO_3^-	207	654	395	100	200	200	600
SO_4^{2-}	0.80	261.1	39.6	57.1	200	200	400
NO_3^-	0.8	194.0	30.7	42.8	50	45	100
Silica	11.8	39.6	27.9	7.7	-	-	-
Ca^{2+}	9.4	160.0	41.4	33.7	75	75	200
Mg^{2+}	17.6	127.5	55.0	27.5	30	30	100
Na^+	14.0	713.1	107.0	148.0	200	-	-
K^+	2.0	36.8	6.2	5.8	-	-	-
TH	95	812	328	177	500	300	600

moderately hard to very hard types of groundwater (Sawyer and McCarty 1967). Hardness value exceeds the desirable limit of 300 mg L^{-1} in 36% of the groundwater samples and maximum permissible limit (600 mg L^{-1}) in 9% samples (BIS 2003). Hardness of water prevents lather formation with soap and increases the boiling point of the water. The high hardness may cause precipitation of calcium carbonate and encrustation on water supply distribution systems. The very hard water requires softening for household or commercial uses.

The content of HCO_3^- and Cl^- have no known adverse health effects, however it should not exceed the safe limits of 300 mg l^{-1} and 250 mg l^{-1} respectively in drinking water. The analytical data shows that HCO_3^- exceeds the desirable limit in about 80% and Cl^- in 24% of the groundwater samples. Higher concentration of Cl^- in drinking water gives a salty test and has a laxative effect for those who are not accustomed to it. Concentration of NO_3^- exceeds the recommended level of 45 mg L^{-1} in 20% of the groundwater samples. Excessive NO_3^- in drinking water can cause a number of disorders including methaemoglobinaemia in infants, gastric cancer, goiter, birth malformations and hypertensions (Majumdar and Gupta 2000). Fluoride is an essential element for maintaining normal development of healthy teeth and bones. However, higher F^- concentration causes dental and skeletal fluorosis such as mottling of teeth, deformation of ligaments and bending of spinal chord. Concentration of F^- marginally exceeds the permissible limit of 1.5 mg L^{-1} in about 70% of the groundwater samples.

Among the cations, Na^+ is most important ion for human health. A higher sodium intake may cause hypertension, congenial heart diseases, nervous disorder and kidney problems. The recommended limit for sodium concentration in drinking water is 200 mg L^{-1} (WHO 2006; BIS 2003). Concentrations of Na^+ exceed the recommended level in about 16% of the groundwater samples. Calcium and magnesium is an essential element for bone, nervous system and cell development. One possible adverse effect from ingesting high concentration of Ca^{2+} for long periods may be an increased risk of kidney stones (Maragella et al. 1996). Concentrations of Mg^{2+} are exceeding the maximum permissible limit of 100 mg L^{-1} in 14% groundwater samples. Calcium concentrations are well within the maximum permissible limit of 200 mg L^{-1}, though it exceeds the desirable limit of 75 mg L^{-1} in 15% samples (BIS 2003).

Suitability for Irrigation Uses

The total salt concentration, sodium percentage (%Na), residual sodium carbonate (RSC), sodium adsorption ratio (SAR) and Kelley index (KI) are the important parameters used for assessing the suitability of water for irrigation uses (Ayers and Westcot 1985). The computed values of these parameters calculated by the following equations are furnished in Table 1.

(a) Sodium percentage (%Na) = $Na^+ + K^+/(Ca^{2+} + Mg^{2+} + Na^+ + K^+)X100$

(b) Residual sodium carbonate (RSC) = $(CO_3^- + HCO_3^-) - (Ca^{2+} + Mg^{2+})$

(c) Sodium adsorption ratio (SAR) = $Na^+/(\sqrt{Ca^{2+} + Mg^{2+}})/2)$

(d) Kelley index (KI) = $Na^+/(Ca^{2+} + Mg^{2+})$

(All ionic concentrations used for calculation are expressed in epm)

Electrical conductivity (EC) and sodium concentration are very important parameters in the classification of the irrigation water. Water used for irrigation always contains measurable quantities of dissolved substances as salts. The salts, besides affecting the growth of the plants directly, also affect soil structure, permeability and aeration, which indirectly affect plant growth. Irrigation with high sodium water causes exchange of Na^+ in water for Ca^{2+} and Mg^{2+} in soil and reduces the permeability and eventually results in soil with poor internal drainage (Collins and Jenkins 1996). As per the Indian Standard, maximum sodium percent (%Na) of 60% in water is recommended for safe irrigation (BIS 2003). Sodium percent value in the analysed samples range between 8.87 and 91.4% (avg. 34%) and plot of analytical data on the Wilcox (1955) diagram shows that groundwater of the study area is excellent to good and good to permissible quality for irrigation uses. Out of 55 groundwater samples, seven samples fall in the zone of doubtful to unsuitable category and two in unsuitable category (Fig. 7).

Salinization is one of the most prolific adverse environmental impacts associated with irrigation. Saline condition severely limits the choice of crop, adversely affect seed germination and crop yields. Excessive solutes in irrigation water are a common problem in semi-arid areas where water loss through evaporation is high. Salinity problem encountered in irrigated agriculture area are most likely to arise when the drainage is poor. This allows the water table to rise close to the root zone of plants, causing the accumulation of sodium salts in the soil through capillary rise following surface evaporation of water. The total concentration of soluble salts in irrigation water can be expressed as low (EC = <250 µS cm^{-1}), medium (250-750 µS cm^{-1}), high (750-2250 µS cm^{-1}) and very high (>2250 µS cm^{-1}) and defined as C-1, C-2, C-3 and C-4 salinity zone respectively (USSL 1954). A high salt concentration in water leads to formation of saline soil and

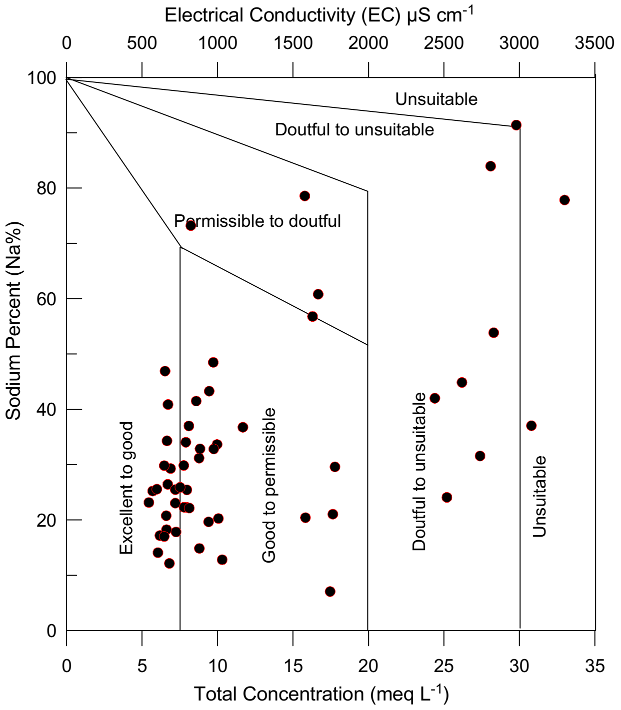


Fig.7. Wilcox diagram for classification of groundwater based on EC and %Na

high sodium concentration may cause the development of an alkaline soil. The sodium or alkali hazard in the irrigation water are expressed in terms of sodium adsorption ratio (SAR) and classified into four categories as S-1 (SAR<10), S-2 (10-18), S-3 (18-26) and S-4 (>26). There is a significant relationship between SAR values of irrigation water and the extent to which sodium adsorbed by the soils. If water used for irrigation is high in sodium and low in calcium, the cation-exchange complex may become saturated with sodium. This can destroy the soil structure due to dispersion of the clay particles. The plot of analysed data on the USSL (1954) diagram, in which the EC is taken as salinity hazard and SAR as alkalinity hazard, shows that most of the water samples fall in the category of C2S1 and C3S1 denoting good to moderate quality of water for irrigation (Fig. 8). The good water (C2S1) can be used for irrigation with little danger of harmful levels of exchangeable sodium and salinity. The moderate water (C3S1) may be used to irrigate salt tolerant and semi-tolerant crops under favorable drainage conditions. The bad water with high salinity and medium to high alkalinity (C4S3, C4S4) are generally undesirable for irrigation and such water should not be used on clayey soils of low permeability. Salt tolerant plants/crops should be selected for the high saline regions and the irrigation water must be applied in excess to provide considerable leaching (Karanth, 1989).

The quantity of bicarbonate and carbonate in excess of alkaline earth metal cations, expressed as residual sodium carbonate (RSC) are also influencing the water quality for irrigation purposes (Karanth 1989). The HCO_3^- and CO_3^- in the irrigation water tend to precipitate calcium and magnesium ions in the soil resulting in an increase in the proportion of the sodium ions. For this reason, RSC was considered as an indicative of the sodicity hazard of water. A high value of RSC in water leads to an increase in the adsorption of sodium on soil (Eaton 1950). Irrigation waters having RSC values greater than 5 meq L^{-1} have been considered harmful to the growth of plants, while waters with RSC values above 2.5 meq L^{-1} are unsuitable for irrigation. A RSC value between 1.25 and 2.5 meq L^{-1} is considered as the marginal quality and value <1.25 meq L^{-1} as the safe limit for irrigation. Table 1 shows that the calculated RSC values in 85% of the analysed groundwater samples were below 2.5 meq L^{-1}, indicating that in general groundwater is suitable to marginally suitable for irrigation purposes.

Kelley's index is the ratio of $Na^+/(Ca^{2+}+Mg^{2+})$ which is also used for the classification of water for irrigation. Water with >1.0 Kelley's ratio indicate an excess level of sodium and unsuitable for irrigation. Water with Kelley's ratio of <1.0 are only considered suitable for irrigation (Kelley 1946; Paliwal 1967). KI values in the groundwater of Pratapgarh district varied from 0.07 to 10.58 with an average of 0.88. The low KI value (KI<1.0) in most of the analyzed samples (86%), suggest that groundwater of the area is suitable for

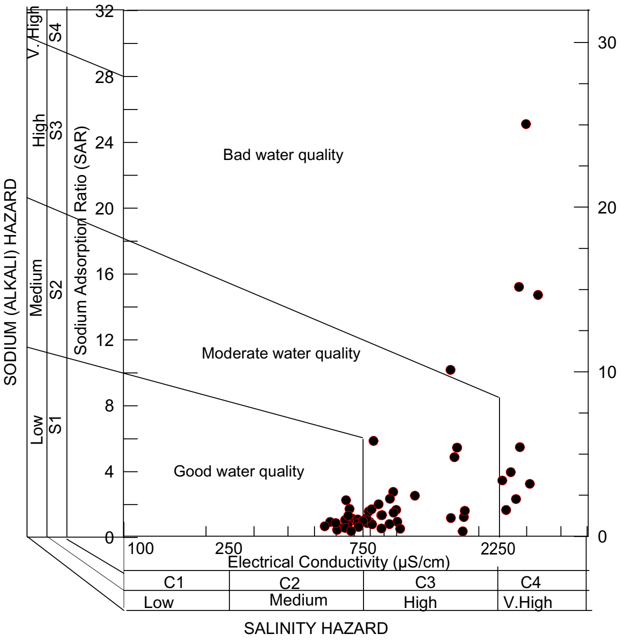


Fig.8. US salinity diagram (USSL) for classification of irrigation water

irrigation (Table 1). The KI value exceeded the specified limit (KI>1.0) in eight (14%) groundwater samples, making it unsuitable for irrigation.

CONCLUSIONS

The groundwater of the Pratapgarh district is alkaline in nature. Mg^{2+} and Na^{+} in cationic concentrations dominate the groundwater and HCO_3^- and Cl^- in anionic abundances. In majority of the groundwater samples, concentrations of alkaline earths (Ca^{2+}+Mg^{2+}) exceed alkali cations (Na^++K^+) and HCO_3^- dominate over (SO_4^{2-}+Cl^-). Ca-Mg-HCO_3 and Ca-Mg-Cl-HCO_3 are the dominant hydrogeochemical facies. Water chemistry of the study area strongly reflects the dominance of weathering of rock forming minerals with secondary inputs from agricultural and anthropogenic sources. The high contribution of (Ca^{2+}+Mg^{2+}) to the total cations, relatively high (Na^++K^+)/TZ^+ ratio (0.33) and low equivalent ratio of (Ca^{2+}+Mg^{2+})/(Na^++K^+) i.e. 2.8 suggest that the chemical composition of the water is largely controlled by silicate weathering with limited contribution bycarbonate weathering. The saturation indices of calcite (SIc) and dolomite (SI_d) demonstrate oversaturation condition and signify the presence of calcareous nodules in the sub-surface soil profile of the area. In majority of the samples, the analyzed parameters are well within the prescribed limits and water is potable for drinking purposes. However, concentrations of TDS, TH, NO_3^-, F^-, Ca^{2+}, and Mg^{2+} exceed the desirable limit in some samples and require treatment before its utilization. Suitable water treatment process such as water softening, ion exchange, demineralization and defluoridation should be applied to reduce the concentration of contaminants. Quality assessment for irrigation suitability shows that the groundwater of the area belongs good to moderate category and can be used for irrigation. High values of salinity, residual sodium carbonate, sodium adsorption ratio and sodium percent at some sites restricts the suitability of groundwater for agricultural purposes and demands special management plan for the area.

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