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Hydrogeochemical Characterisation of Groundwater in Transboundary Aquifers of Gurdaspur District, Punjab, India

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Abstract: **Interpretation of spatial variations in chemistry of groundwater is necessary to appraise the pathways of groundwater and ascertain the most valuable strategies for the conservation and sustainable use of groundwater resources. Multivariate statistics and, in particular, factor analysis can efficiently support spatial variations in hydrogeochemical data providing an understanding of natural and anthropogenic effects on quality of groundwater. The present paper illustrates the integrated approach of hydrogeochemical methods and multivariate statistical investigation of the groundwater along transboundary aquifers in 5 blocks of Gurdaspur District, Punjab, India. Assessment of hydrochemistry diagrams indicated that the foremost water categories were Ca, Mg-HCO_3. Outcomes of factor evaluation indicated that the weathering activities and agricultural practices were the dominant controlling factors in the study area. Even though, maximum of the groundwater samples was within the permitted limits of drinking standards, few of the samples cross them and some of the samples were quite close to permissible limits representing that the groundwater quality may deteriorate in immediate future. This infers the necessity of appropriate monitoring of quality of water for the sustainable protection and safeguarding of groundwater resources in the region.**

***Keywords*: Spatial variations • Multivariate statistics • Hydrogeochemical processes • Transboundary aquifers • Sustainable**

I. INTRODUCTION

Water is one of the extreme substantial natural resources and is an imperative component for the socio-economic development of a country. Groundwater endures about two-thirds of the total world's populace for drinking, agricultural and extra household practices ([1], [2], [3]). Agriculture is the prime source of water demand in any agrarian country like India which consumes 40% of the overall groundwater abstraction universally ([4], [5], [6]) and contribute 46% of the gross national output [7]. Over-exploitation of water resources so as to encounter the agricultural demands with the bulging population, urbanization and industrialization put the resources of groundwater under great threat in terms of quality degradation. Dilution of fertilisers in water, change in land use, mixing of sewage in drinking water, leakages of petroleum products, industrial waste throw and invasion of saline water in aquifers are the causes behind the deteriorated groundwater quality ([8], [9]). It is approximated that out of the total world's population, 40% depend upon transboundary groundwater as their main drinking water supply [10].

Studies focusing on groundwater quality in transboundary aquifers of Gurdaspur district are either not stated or inadequately apprehended and has never been addressed to a suitable level for sustainable administration in any previous research. This paper signifies the reference line integrated approach of hydrogeochemical investigation and multivariate statistical methods for the characterization of the spatiotemporal variability of groundwater quality along transboundary aquifers in the study region. Five blocks namely Dinanagar (195 km^2), Dorangla (114 km^2), Gurdaspur (295 km^2), Kalanaur (178 km^2) and Dera Baba Nanak (303 km^2) are chosen for the contemporary study situated in the Gurdaspur district of Punjab in which all blocks are over exploited except Gurdaspur block which is semi critical [11]. This signifies the problem of over development of the groundwater in the area under investigation. Further, quality of groundwater in this region is affected by water swamping, runoffs from thermal trades, brick glaze and further minor and major scale trades. Hence repeated observation of quality of water is critical to comprehend the groundwater quality deprivation.

II. MATERIALS AND METHODS

Study Area

The area extends between north latitude 31°-40′ and 32°-16′ and east longitude 74°-56′ and 75°-24′ (Fig. 1). It covers an area of 1085 km^2 where river Ravi is also flowing across the borders. The present study area partakes mutual borders with Pathankot district in the north, Kangra and Chamba district in the north-east, Hoshiarpur district in the south-east, Kapurthala district in the south, Amritsar district in the south west and Pakistan in the north west. The climate of the region under investigation is tropical type. The average annual rainfall of the region is 1113 mm. The perennial rivers Ravi and Beas along with their tributaries provides the major drainage of the area.

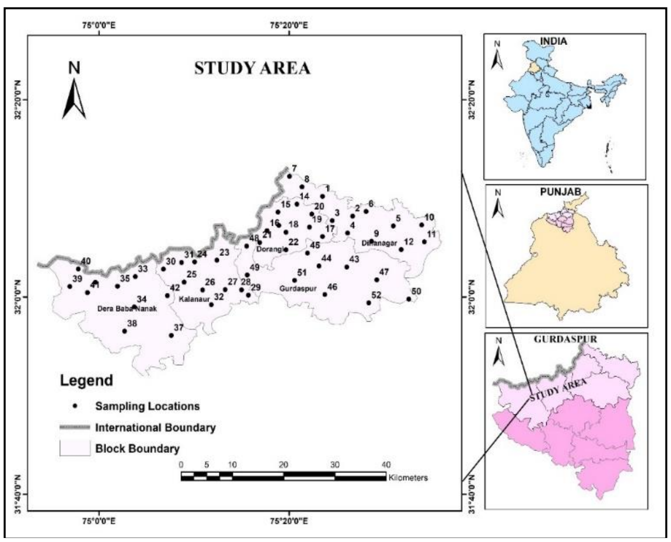

Fig. 1: Location map of the research area indicating groundwater sampling stations

Sampling and Analysis

Groundwater samples from 52 locations covering 5 blocks (Dinanagar, Dorangla, Kalanaur, Dera Baba Nanak and Gurdaspur) of the different parts of the district were collected in pre-monsoon period (May 2019) and the same number of samples were collected in post-monsoon period (October 2019) so as to analyse the seasonal variations. The samples were collected after 10 min pumping from borewells and handpumps which were mostly installed in the inhabitant's houses and agricultural fields and were being consumed for drinking and irrigational purpose. The collected samples were stored in the precleaned high-density polyethylene (HDPE) bottles with 10% nitric acid and then rinsed with distilled water. The bottles were thoroughly rinsed three times with the water sample to be collected before storing the samples in the pre-processed bottles so as to reduce the possibility of contamination. Physical parameters like pH, EC, TDS were determined onsite through Hanna (HI 98194) multiparameter portable water analysis kit. Chemical analysis of main cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, F^-) was carried out by using standard method given by APHA ([12]).

The precision of analysed ions was calculated by means of Charge Balance Error (CBE) as given below and results were well within the ± 5% of acceptable limit [13].

$$\text{CBE (\%)} = \frac{\frac{\text{meq}}{\text{L}}(\text{Cations}) - \frac{\text{meq}}{\text{L}}(\text{Anions})}{\frac{\text{meq}}{\text{L}}(\text{Cations}) + \frac{\text{meq}}{\text{L}}(\text{Anions})} \cdot 100 \qquad \ldots\ldots(1)$$

III. RESULTS AND DISCUSSION

Physicochemical Parameters of Groundwater

Statistical summary of groundwater samples is given in Table 1 and distribution of parameters are shown in Fig. 2, 3, 4 and 5 (supplementary files). The concentrations of major ions for Pre-monsoon and Post-monsoon seasons were correlated with drinking water standards Bureau of Indian Standards (BIS, 2012) [14] and World Health Organization (WHO, 2011) [15] and are displayed in Table 2.

The abundance of major cations followed $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ trend whereas major anions followed $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ trend. The pH value of groundwater showed a variation from 7.2-8.6 to 7.1-8.6 through pre-monsoon and post-monsoon period respectively. Furthermore, 11% of the groundwater samples exceeded the permitted limit of 6.5-8.5 as given by BIS (2012) and WHO (2011) during both the seasons indicating alkaline nature. More values of pH might be due to the soil and rain water interactions.

The levels of TDS varied from 174-1455.9 mg/L (pre-monsoon) to 234-1096.9 mg/L (post-monsoon). Therefore, 7.6% (pre-monsoon) and 5.7% (post-monsoon) of the groundwater samples were found above than the permissible limits of 1000 mg/L prescribed by the WHO (2011). Consumption of groundwater with high TDS may cause gastrointestinal irritation in humans. The concentration of the Mg^{2+} in the area under investigation ranged from 28.7 to 122.7 mg/L (pre-monsoon period), while it ranged from 29.7 to 131.5 mg/L during post-monsoon period. A total of 7.6% (pre-monsoon) and 11.5% (post-monsoon) of groundwater samples surpassed the permissible limit of 100 mg/L (BIS, 2012; WHO, 2011).

TABLE 1

Descriptive statistics of groundwater quality

WQP	Pre-monsoon				Post-monsoon			
	Range		Mean	SD	Range		Mean	SD
	Minimum	Maximum			Minimum	Maximum		
pH	7.2	8.68	8.06	0.44	7.1	8.67	7.81	0.38
TDS	174.2	1455.9	472.8	281.6	234	1096.9	592.6	233
EC	264	2206	716.5	426.7	355	1662	897.9	353
TH	160	561	291	87	174	681.5	409	103.7
Mg^{2+}	28.7	122.7	55	21	29.7	131.5	74.6	20.6
Ca^{2+}	10	42.6	25.5	8.7	11	82	40.7	19
Na^{+}	2.6	101.7	21.7	20	5.6	68	18	13
K^{+}	0.1	64.7	6.8	13	0.1	69.8	8.3	14.7
HCO_3^-	180	620	317.6	98.7	200	615	387	97
NO_3^-	0	6.95	0.96	1.58	1	29	7	6.8
SO_4^{2-}	2	18	6	3	4	22.5	12	5
Cl^-	15	115	48	23.7	28	175.5	73.9	33
F^-	0.1	0.4	0.2	0.09	0.1	0.4	0.3	0.05

TDS total dissolved salts, EC electrical conductivity, TH total hardness, all the units are in mg/L except EC (µS/cm), pH. WQP, water quality parameter, SD standard deviation.

TABLE 2

Percentage of groundwater samples surpassing limits for drinking purpose as per BIS (2012) and WHO (2011)

WQP	BIS (2012)		WHO (2011)	% of Sample above BIS (2012)				% of Sample above WHO (2011)	
				Pre-monsoon		Post-monsoon		Pre-monsoon	Post-monsoon
	DL	PL	Standard Value	DL	PL	DL	PL	DL	DL
pH	6.5-8.5		6.5-8.5	21		11		21	11
TDS	500	2000	1000	32.6	Nil	59	Nil	7.6	5.7
EC	-	1500	1500	-	7.6	-	5.7	7.6	5.7
TH	200	600	500	94	Nil	98	3.8	3.8	17.3
Mg^{2+}	30	100	100	96	7.6	98	11.5	7.6	11.5
Ca^{2+}	75	200	300	Nil	Nil	5	Nil	Nil	Nil
Na^{+}	-	200	200	-	Nil	-	Nil	Nil	Nil
K^{+}	-	12	12	-	17.3	-	21	17.3	21
HCO_3^-	-	-	500	-	-	-	-	5.7	7.6
NO_3^-	45	-	50	Nil	Nil	Nil	Nil	Nil	Nil
SO_4^{2-}	200	400	250	Nil	Nil	Nil	Nil	Nil	Nil
Cl^-	250	1000	250	Nil	Nil	Nil	Nil	Nil	Nil
F^-	1	1.5	1.5	Nil	Nil	Nil	Nil	Nil	Nil

All the units are in mg/L except EC (µS/cm), pH. WQP water quality parameter, DL desirable limit, PL permissible limit.

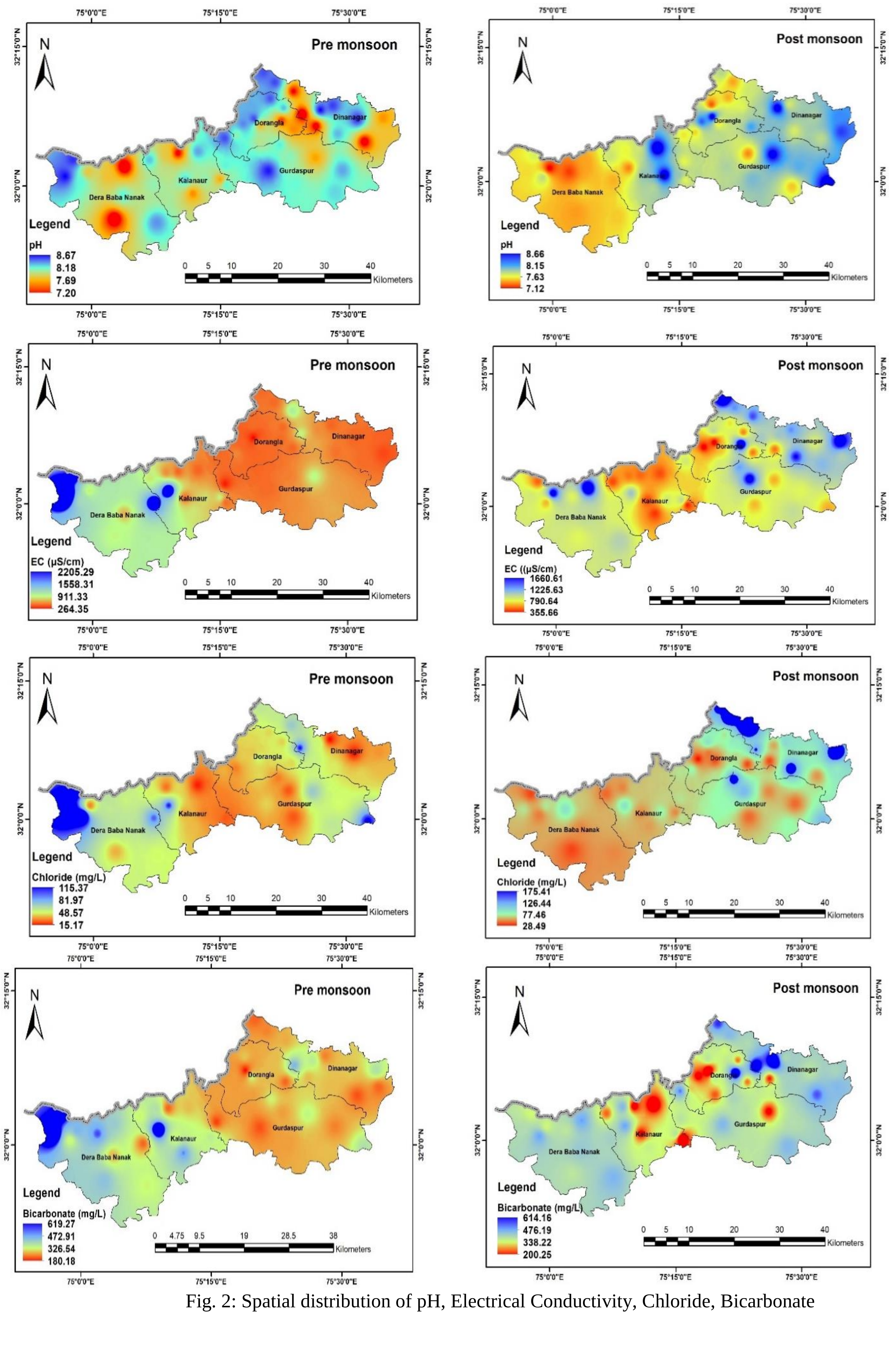

Fig. 2: Spatial distribution of pH, Electrical Conductivity, Chloride, Bicarbonate

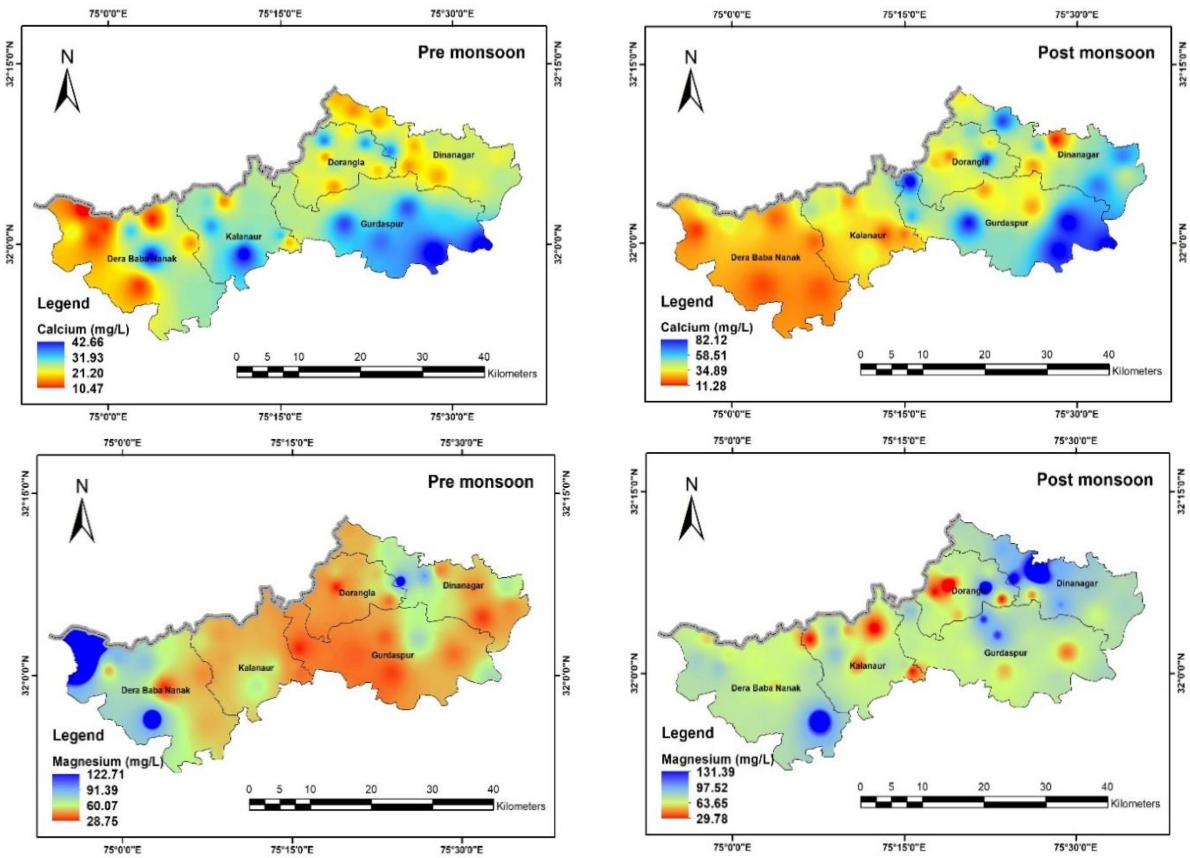

Fig. 3: Spatial distribution of Calcium and Magnesium

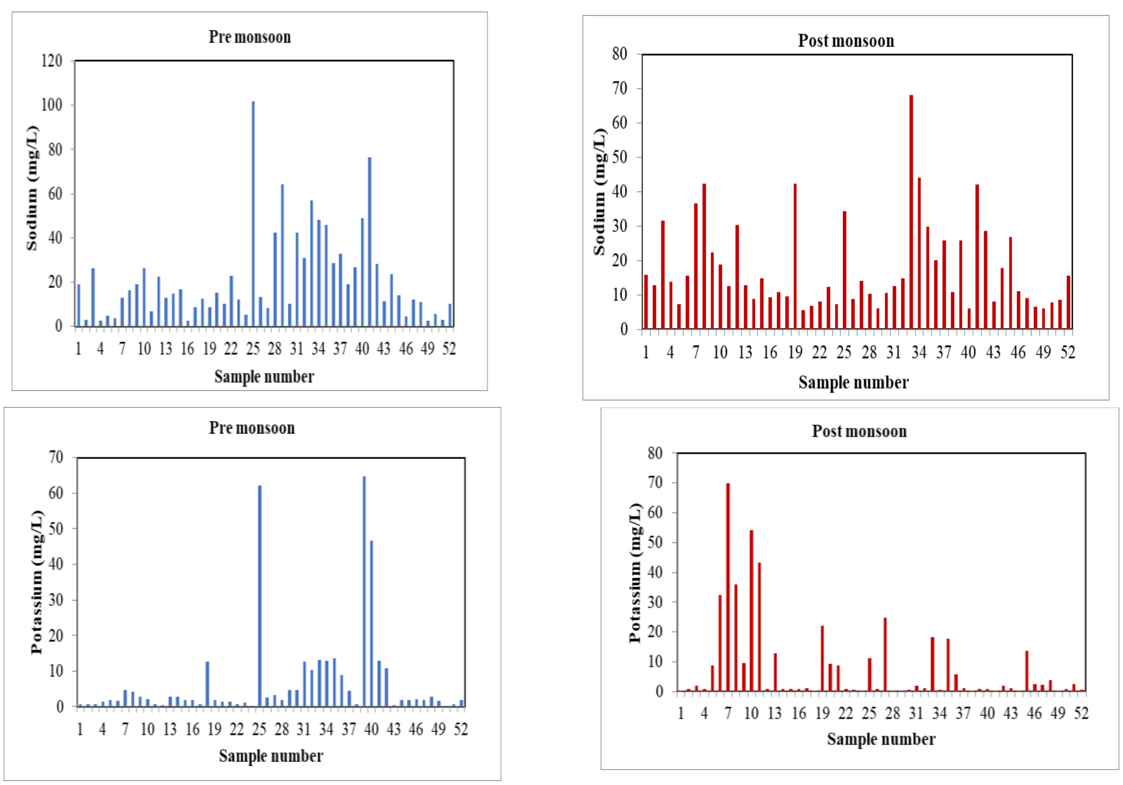

Fig. 4. Distribution of Sodium and Potassium

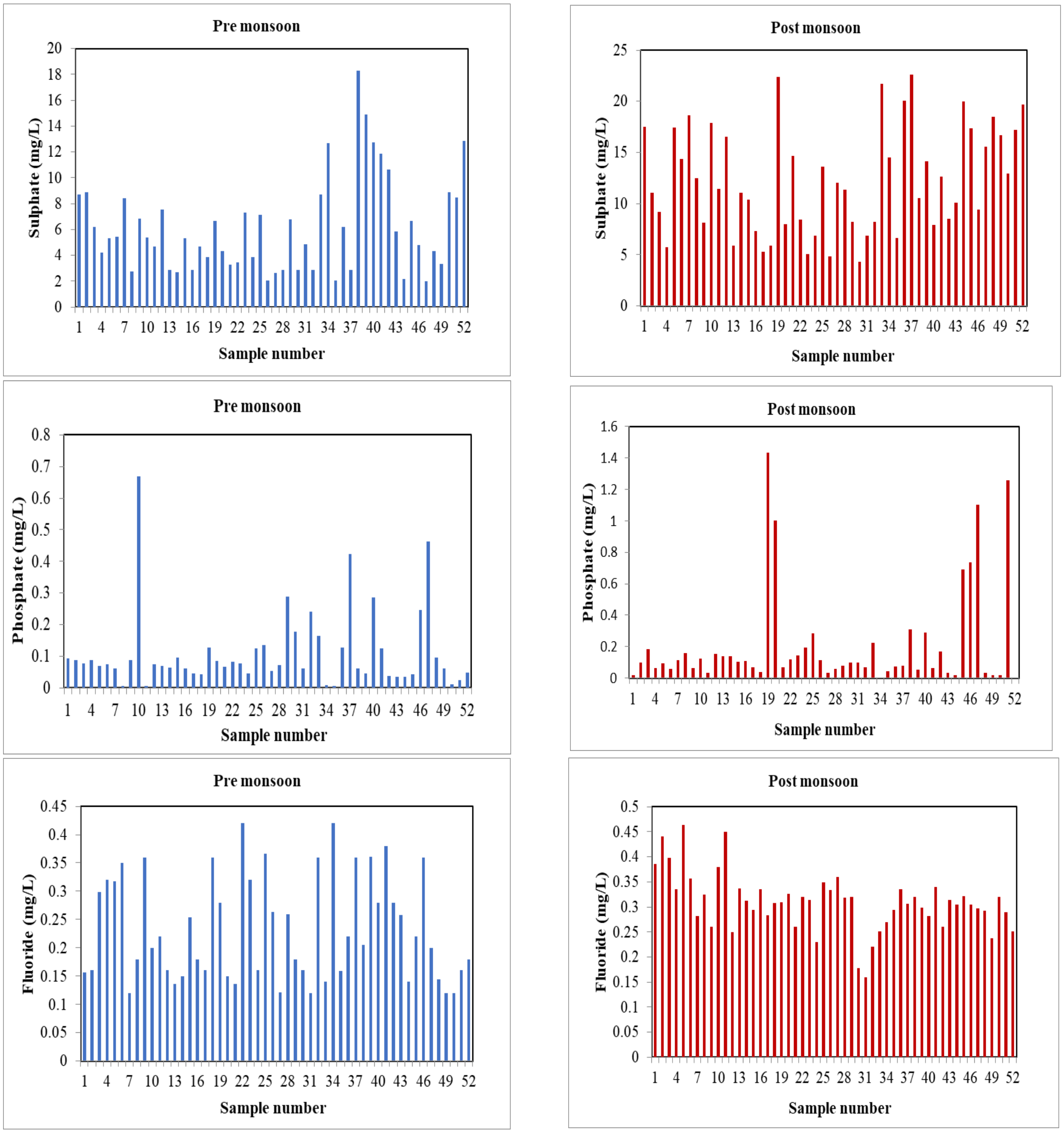

Fig. 5: Distribution of Sulphate, Phosphate and Fluoride

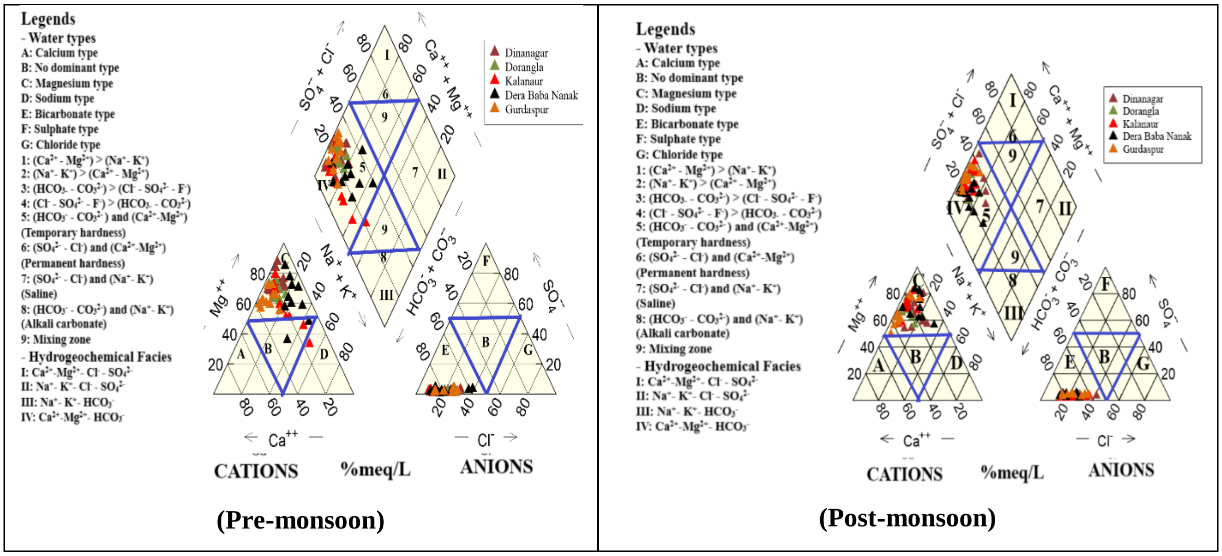

Fig. 6: Piper diagram illustrating the hydrogeochemical facies variation of groundwater.

Ca^{2+} concentration varied from 10 to 42.6 mg/L (pre-monsoon) and 11 to 82 mg/L (post-monsoon). All the groundwater samples were within the permissible limit during both the seasons. The concentration of K^+ in 17.3% and 21% of the samples in pre-monsoon and post-monsoon seasons respectively were above the permissible limit of 12 mg/L (BIS, 2012; WHO, 2011). The higher concentration of K^+ might be due to the fertilizer usages and may lead to the damage of nervous system. The mean concentration of Na^+ was 21.7 mg/L (pre-monsoon) and 18 mg/L (post-monsoon), where all the samples were within the permissible limit of 200 mg/L prescribed by the BIS (2012), WHO (2011) during both the seasons. The HCO_3^- ion concentration varied from 180 to 620 mg/l and 200 to 615 mg/l during pre-monsoon and post-monsoon season respectively. A total of 5.7% of the groundwater samples during pre-monsoon and 7.6% of the samples during post-monsoon surpassed the permissible limit of 500 mg/L (WHO, 2011). The values of SO_4^{2-}, Cl^- and NO_3^- were within the permissible limit (BIS, 2012; WHO, 2011).

Hydrogeochemical Facies

To understand the hydrogeochemical regime of an area under investigation, the experimental values attained from groundwater samples were plotted on the widely used Piper's tri-linear diagram (Piper, 1944) [16].The results of the piper diagram (Fig. 6 in supplementary files) affirmed that the majority of the groundwater samples fall under Ca^{2+}-Mg^{2+}-HCO_3^- type during pre-monsoon (98%) and post-monsoon (100%) period representing temporary hardness, Ca^{2+} - Mg^{2+} (Alkaline earths) exceeds Na^+- K^+ (Alkalies) and HCO_3^- - CO_3^{2-} (Weak acids) exceeds Cl^- - SO_4^{2-} - F^- (Strong acids). Only 1 sample fall under Na^+- K^+- HCO_3^- type during pre-monsoon period. Further, cation triangle shows that the Mg^{2+} (92.3, 100%) is the principal ion in both seasons and might be due to the occurrence of evaporite deposits and dolomitic rocks. Only 3 samples fall under no dominant type in pre-monsoon whereas, one sample fall under sodium type during pre-monsoon. Anions triangle represents that the HCO_3^- (100%, 100%) is the dominant anion in both the seasons. The enhanced concentration of HCO_3^- in the study region is might be due to the agricultural return flow and bacterial oxidation of organic matter.

Factor Analysis

Factor analysis is an extensively used statistical technique in groundwater related studies as it decreases the variable quantity and allows the revelation of structure in the associations between the variables. The factor analysis for two seasons (pre-monsoon and post-monsoon) was carried out *using rotated varimax method* and the outcomes are shown in table 3. A total of 4 factors were extracted representing 72% and 75% of entire data variability during pre-monsoon and post-monsoon period respectively. The factor scores were estimated to find out the spatial variability of the foremost factors in the study region. Extraction of factor scores was done by multiplying a coefficient matrix of factor score with standardised data for each groundwater sample. The zone whose factor score is positive indicates the dominance of that specific factor (hydrogeochemical regime) (Fig. 7 in supplementary files).

The first factor defined total variance of 30.02 % and 27.19% during both the seasons respectively and showed significant strong positive loading (>0.75) with TDS, EC, *Na^+ and K^+ in pre-monsoon reflecting lithogenic and several hydrogeochemical processes. The positive loading with HCO_3^-, Mg^{2+} and TH in post-monsoon indicates the dissolution of Mg^{2+} rich rocks by weathering process. Rotated varimax factor 2 explained 21.63% (pre-monsoon) and 26.13% (post-monsoon) of total variance and showed strong positive loadings with Mg^{2+} and TH (pre-monsoon) indicating the contribution of Mg^{2+} to the total hardness of groundwater. While, the strong positive loading for EC, TDS, K^+ (post-monsoon) indicates domestic activities and applications of fertilisers.*

The third factor defined total variance of 11.4% and 12.5 % during both the seasons respectively. The third factor with strong positive loading for Ca^{2+} (pre-monsoon) indicates the cation exchange reaction. However, the strong positive loading for pH (post-monsoon) reflects the oxidation of organic matter related to anthropogenic activities. The fourth factor described moderate positive loading (0.50 – 0.75) for pH and PO_4^{2-} indicating the anthropogenic impacts from agricultural activities during pre-monsoon. On the contrary, the post-monsoon period showed the strong positive loading for PO_4^{2-} with factor 4 reflecting utilization of phosphate rich fertilizers and irrigational return flow from agronomical area.

IV. Conclusion

The substantial purpose of the research was to know the factors governing the hydrochemistry of groundwater using multivariate statistical approach. The dominance of magnesium and calcium as major cations whereas bicarbonate and chloride as major anions, revealed that weathering of silicate minerals and ion exchange processes were prevalent activities in the area under investigation. Among various parameters of water quality only pH, EC, TDS, TH, Mg^{2+}, HCO_3^-, K^+ were found to be above the permissible limit in a few of the groundwater samples although rest of the parameters were totally between the limits stipulated by BIS (2012) and WHO (2011). Piper's plot revealed that the major part of the groundwater samples exhibited $MgHCO_3$ water type. The outcomes of the factor analysis exhibited that *the* lithogenic processes, ion exchange, weathering of aquifer material and anthropogenic influx from agricultural activities were the dominant controlling processes in the study region. The contemporary study reveals the main hydrogeochemical and human caused activities responsible for transboundary aquifers chemistry which in turn might support in the management of groundwater quality, strategy formulation and making governance in the research area.

TABLE 3
Factor analysis for the groundwater quality parameters

Variable	Factor 1	Factor 2	Factor3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
Varimax rotated (n= 52)								
pH	.118	-.226	-.350	-.525	-.181	-.046	.802	.149
TDS	.868	.355	.103	-.059	.515	.790	-.213	.041
EC	.868	.355	.103	-.059	.515	.790	-.213	.041
Cl^-	.647	.383	.158	-.296	.439	.560	.174	-.114
F^-	.522	-.033	-.171	.106	.234	.321	.675	-.203
SO_4^{2-}	.395	.350	.447	-.362	.559	.456	-.277	.225
PO_4^{2-}	.145	-.019	-.098	.734	.006	.133	-.031	.868
NO_3^-	-.034	.369	.714	.005	.378	.673	.148	.108
HCO_3^-	.592	.668	-.023	.286	.763	.327	-.240	.137
Ca^{2+}	-.064	.162	-.788	-.038	.535	-.199	.181	.609
Mg^{2+}	.217	.918	.194	.017	.861	.293	.003	-.138
Na^+	.785	-.078	.182	.333	.104	.618	-.552	-.073
K^+	.867	.242	-.021	-.083	-.062	.824	.185	.028
TH	.204	.968	-.002	.008	.957	.147	.087	.172
Eigen value	4.203	3.028	1.609	1.253	3.807	3.658	1.756	1.341
Variance (%)	30.023	21.630	11.493	8.952	27.191	26.132	12.541	9.578
Cumulative (%)	30.023	51.653	63.147	72.099	27.191	53.323	65.863	75.442

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