

EVALUATION OF HYDROGEOCHEMICAL PROCESSES AND CHEMOMETRICS OF THE GROUNDWATER IN VIJAYPUR BLOCK OF SAMBA DISTRICT, J&K, INDIA

Anjali Bala¹, Umesh Kumar Singh², Pankaj Mehta^{1*}, Sunil Dhar¹, Deepak Pathania¹
Department of Environmental Sciences, Central University of Jammu, Jammu, District Samba -
181143 J&K, India¹

Department of Integrated Science Education and Research (DISER), Institute of
Science, Visva-Bharati, Santiniketan-731235, West Bengal, India²
Corresponding author: drpankajmehta79@gmail.com*

ABSTRACT

Hydrogeochemical study of groundwater and possible source of major constituents were carried out in the part of Samba district, in the region of Jammu and Kashmir, India. This study, thoroughly discusses the geochemical processes that play a role in controlling the groundwater chemometrics in the study area. Twenty groundwater samples were collected in two seasons (Pre-monsoon and Post-monsoon) and all samples were analyzed for the physico-chemical parameters and major ions. Majority of the parameters were found well within permissible limit but above the acceptable limits of the Indian Standards IS10500:2012, excepting few chemical parameters such as pH, TDS and Total alkalinity at some locations. High concentration of major ions was found in the pre-monsoon, which may be due to high evaporation rate and low water table during this period. Carbonate weathering and cation exchange capacity are important geochemical processes which are controlling the major ion distribution in this area. Study of hydrochemical facies reveals the $Ca^{2+}-Mg^{2+}-HCO_3^-$ followed by $Na^+-K^+-Cl^- -SO_4^{2-}$ water types present in the study area. Cluster analysis (CA) classified ten sites into three category based on the analytical data. Further, PCA suggests that geogenic activities influence the majority of the parameters whereas source of NO_3^- , Cl and turbidity identified as leaching of subsurface contaminants from agriculture and industries. Groundwater quality is suitable for drinking and irrigation purposes after treatment because of the presence of high TDS, pH and carbonate components in the study area.

Key words: Groundwater, Hydrogeochemistry, Weathering, Ion Exchange Reaction, TDS

Introduction

Water is the most important life- sustaining natural resource on earth that plays a vital role to all life forms (Mir et al. 2016). Groundwater is one of the most precious natural freshwater sources,

which is easily accessible to human beings (Kumar et al. 2011). Around 1.5 billion people directly depend on the ground water resources and approximately $\approx 700 \times 10^3$ million m^3 water is consumed every year, which is 20% of worldwide water withdrawals (Mukherjee and Singh 2012). In India, about 80% rural and 50 % urban population is directly dependent on the ground water resource for domestic needs (Pemmaraju and Rao 2011). Approximately, 56 % rural Indian access to potable water from tube wells, about 14% from open wells and about 25% supplied water system depend on groundwater, which is on an average 90% of total rural water supply (NSSO 2006). The reasons for high dependency on groundwater is due to their less susceptibility to surface pollution as various pollutants get either diluted or chemically and biologically degraded in the unsaturated zone before reaching the groundwater table. Rock weathering plays a role in controlling the groundwater chemistry (Mehta, 2013). However, intensive use of groundwater and increased inputs from anthropogenic actions are posing a greater threat to the groundwater resources in terms of both quantity and quality (Foster, 1995). Groundwater is used for many purposes such as industrial water supply, irrigation, domestic uses and propagation of fish etc. However, rapid population growth, rising living standards in urban areas and industrialization has imposed further pressure on water resources. There are several natural and anthropogenic pathways of contaminants to enter drinking water resources (Ghosh et al. 2013). The quality of groundwater is generally controlled by geology, climate, topography, surface activities, mobility of soil and groundwater. However, extensive use of water in various sectors is resulting in water pollution with numerous contaminants such as municipal waste, biodegradable and ionised substances etc. (Han et al. 2015). These contaminants leached from effluent bearing water bodies are responsible for groundwater pollution. Therefore, considering the effects of groundwater pollution on human health, it becomes immensely important to understand the chemistry of water before its use for domestic, irrigation or industrial purposes (Reghunath et al. 2002; Han et al. 2015).

For the evaluation of the groundwater chemistry and numerous hydrogeochemical processes, several researchers have attempted different graphical, statistical and geochemical indices in the recent past (Reddy and Kumar 2010; Singh et al. 2012; Kumar and James 2013; Kumar et al. 2014; Thivya et al. 2015; Gouri et al. 2016). There are some techniques such as Geochemical Indices and geo-statistical techniques that could help to identify the characteristics of water

quality from monitored data. Cluster analysis (CA) is a useful technique to develop reliable and dependable classification of water. CA provides cluster of relationship and group of segregated stations in the entire data set, which can help to identify prominent polluted stations. Therefore, it can reduce the number of sampling sites in future investigations. CA also provides grouping of samples by linking up similar samples and indicates the interrelationship of variables in a data set (Massart and Kaufman 1983; Vega et al. 1998). Principal component analysis (PCA) is a statistical tool, which is helpful to reduce the dimensions of multivariate data and its problem (Johnson and Wichern 1992; Petersenet al. 2001). It also provides information about important parameters present in the whole data set, which is helpful to reduce insignificant parameters from monitoring stations (Helena et al. 2000; Shreshtha and Kazama 2007). The output of these tools is very helpful to identify groups, correlation and critical parameters present in the whole data set (Singh et al. 2005; Zhou et al., 2007; Kumar and Dua 2009). There are some relevant studies that have been carried out with reference to hydrogeochemical studies in Jammu and Kashmir. Kaur et al. (2018) conducted a study for assessing the hydrogeochemistry of groundwater samples of some locations in Poonch District of J&K State. Gibbs ratios in the study revealed that the Rock weathering is primarily controlling the groundwater chemistry. Jehangir et al. (2011) also attempted a study on groundwater hydrogeochemistry along the river Jhelum in the southern part of Kashmir, J&K. Authors suggested that the groundwater chemistry is predominantly controlled by geological processes where carbonate dissolution and silicate weathering are found as major dominant factors. Kanwar and Khanna (2015) carried out the study on the Bari Brahmna industrial area, Samba district. The authors concluded that the water quality parameters are highly influenced by anthropogenic causes due to leaching of contaminated waste due to surface activities. However, the evaluation of hydrogeochemistry of groundwater in Samba district, Jammu and Kashmir has largely been untouched. Therefore, present study is focused on the comprehensive assessment of hydrogeology and geochemistry to examine pathways and chemometrics of the groundwater in this area. The aim of the present study is to apply geochemical indices and multivariate techniques for the evaluation of sources, pathways and better interpretation of the analytical data.

Study area

Samba district is situated on the foothills of Siwalik hill range at an elevation of 384 meters above sea level and lies within the geographical coordinates of 32°34'N and 75°07'E latitudes and 32°57' N and 75°12'E longitudes. About 2/3rd of the area of the Samba district is kandi belt and rain fed. Being sub-tropical zone, the area witnesses hot and dry summers and cold winters. The temperature ranges between 6°C to 47°C. Groundwater potential in the area can be described into three belts on the basis of nature of the underlying sediments and the hydrological conditions as the Siwalik hill range, the Kandi belt and the Sirowal belt. In Siwalik hill range a little amount of rainwater finds the way to percolate down due to the steep dip and the compaction of the formation of the Siwalik of the hill range. Sediments found in the Kandi range are of the nature of boulders, pebbles and gravel with minor partings made the zone of saturation lie at great depths. Sirowal belt, on the other hand, contains very fine sediments and groundwater in this belt occurs both under water table and confined conditions. For the present study a total of ten sites were selected of the Vijaypur Block of Samba district.

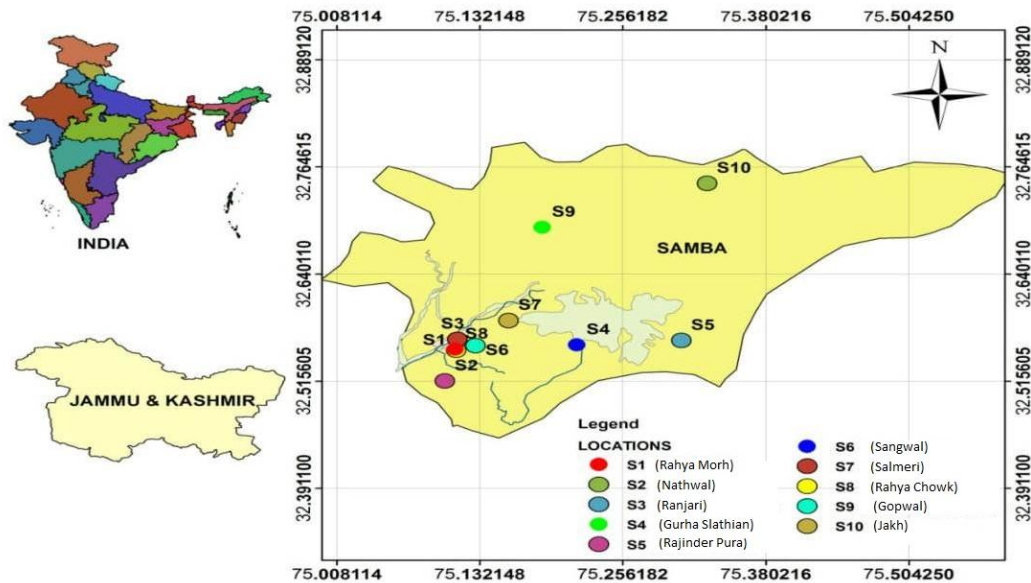


Fig. 1 Geographical location of study area and sampling sites

Methodology

Twenty water samples were collected in two consecutive seasons, which are Pre-monsoon, and Post-monsoon. All collected water samples were transported in laboratory after preservation as per standard procedures described by APHA (2012). Approximately 90% of groundwater

samples were collected from maximum usable tube-wells. The groundwater samples were collected from both shallow hand tube-wells (70 ± 10 ft deep) and deep tube-wells (140 ± 10 ft). The geochemical characteristics of groundwater and water quality were acquired from physicochemical analysis. All acidified groundwater samples were filtered with 0.45 mm before analysis. The collected water samples were estimated for the physico-chemical and as per standard procedure of APHA (2012). pH and Electrical Conductivity (EC) were analyzed in field by digital instrument. Total alkalinity and Total Hardness were analyzed in the Laboratory by titrimetric methods. Total Dissolved Solid (TDS) and Total Soluble Solids (TSS) are measured by gravimetric methods. After determination of physical parameters, all samples were preserved by 1:1 HNO₃ solution for further analysis in the laboratory. In the laboratory, Calcium (Ca²⁺), Magnesium (Mg²⁺), Nitrate (NO₃⁻), Chloride (Cl⁻), Sodium (Na⁺), Sulfate (SO₄²⁻) Potassium (K⁺), Fluoride (F⁻), Carbonate (CO₃⁻) and Bi-carbonate (HCO₃⁻) were analyzed by Ion Chromatograph (IC-Plus, 5: Metrohm). Analytical data was normalized by data standardization process (Z score) using IBM- SPSS V. (20) software before applying the statistical techniques. ArcGIS-10.3 and Surfer-11.0 software were employed for the formation of maps of sampling sites and contouring. Geochemical indices and diagrams for analytical values have been developed by Aqua-Chem V-2010.1 and OriginPro V-8 software respectively.

Results and discussion

The spatial and temporal variation in the mean values of chemical parameters is shown in Table 1. The statistical summary of water quality parameters is given in Table 2. Table 2 illustrates the seasonal values of analytical data in the expression of minimum, maximum, mean and standard deviation (SD).

General Geochemistry

Groundwater samples of the study area are alkaline in both seasons where pH ranging between 8.08 to 8.76 with an average value of 8.34 in pre-monsoon and 8.11 to 8.78 with an average value of 8.34 respectively. The high mean value of pH in the study area reveals the presence of carbonate host rocks that enhances the dissolution of limestone and dolomite in groundwater. EC values vary from 645.0 to 912 uS/cm with an average value of 823.26 uS/cm in pre-monsoon and 635.5 to 896.4 uS/cm with an average value of 813.26 uS/cm in post-monsoon respectively. Similarly, TDS ranges between 430.0 to 555.0 mg/L with an average value of 512.6 mg/L in pre-

monsoon and 428 to 548 mg/l with an average value of 507.0 mg/L in post-monsoon respectively. EC and TDS show large variation in the studied samples and express high SD in both the seasons demonstrates that the water quality of the study area is influenced by numerous geochemical process and anthropogenic sources. In addition, the mean values of both parameters are higher in pre-monsoon as compared to post-monsoon, which apparently indicates the enhancement of major ion constituents in the aquifer during this period. The enhancement of major ion in the pre-monsoon may be to due high evaporation rate and low water table during this period.

The variation of major ion (anion and cation) and their distribution patterns in twenty ground water samples are shown in (Fig. 2). The overall water is characterised by $\text{HCO}_3^- > \text{Na}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Cl}^- > \text{K}^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{F}^-$ facies. The figure illustrates that the HCO_3^- is the dominant anion for all groundwater samples, ranging from 230 to 400 mg/L with an average value of 293.5 mg/L in pre-monsoon and 225 to 392 mg/L with an average value of 285.6 mg/L in post-monsoon respectively. Result suggests that the water is highly influenced by carbonates and silicate weathering. Furthermore, Na^+ , SO_4^{2-} and Ca^{2+} are found to be representing second higher major ions in all the groundwater samples. The value of Na^+ ranging from 28.40 to 98.25 mg/L with mean value of 52.40 mg/L in pre-monsoon and 26.52 to 96.41 mg/L with mean value of 50.07 mg/L respectively is visible in the study. The considerable amount of Na^+ in the samples suggest that the groundwater is highly influenced by weathering of sodium feldspar whereas soil water interaction also enhanced Na^+ in ground water. The presence of SO_4^{2-} in the groundwater samples indicate gypsum containing rock whereas leaching of sulphur containing contaminates are also responsible for availability SO_4^{2-} in water table. Rest of the ion such as NO_3^- , Cl^- , Mg^{2+} , K^+ and F^- are third dominant ions in the groundwater samples. However, presence of elevated NO_3^- and Cl^- in the groundwater exposes the leaching of surface contaminants whereas elevated level of HCO_3^- , Total Alkalinity (TA), Total hardness (TH) and F^- strongly indicates that these are predominantly derived from rock water interaction.

In this area, groundwater is mostly applied for domestic, drinking and irrigational purposes. Therefore, it is necessary to evaluate suitability of water in terms of drinking and agricultural uses. The analytical data were compared with international and national water quality guidelines viz. World Health Organization (WHO, 2006) and Bureau of Indian Standard (BIS, 1991) respectively. The analytical data thus obtained showed that the majority of parameters are within

the permissible limits except total alkalinity and HCO_3^- and high pH value. The value of EC and TDS also exceeded the permissible limit in some groundwater samples. The elevated level of these parameters may be due to presence of carbon-based minerals in the water that mainly derived from dissolution of limestone and dolomite. Higher level of these parameters can cause human health problem as well as reduce fertility of soil. Further, sodium absorption ratio (SAR), percentage sodium (%Na) and permeability index (PI) showed that the water quality of the study area is quite suitable for agriculture purposes. However, result indicates that the groundwater is suitable for irrigation and drinking purposes after conventional treatment.

	Sites	Turbidity (NTU)	pH	TDS (mg/L)	Electrical Conductivity ($\mu\text{S}/\text{cm}$)	Total Hardness (as CaCO_3) (mg/L)	Ca (as Ca) (mg/L)	Mg (as Mg) (mg/L)	Alkalinity (as CaCO_3) (mg/L)	Carbonates (CO_3^{2-}) (mg/L)	Bicarbonates (HCO_3^-) (mg/L)	Chloride (as Cl) (mg/L)	Nitrate (as NO_3^-) (mg/L)	Fluoride (as F) (mg/L)	Sodium (Na) (mg/L)	Potassium (K) (mg/L)	Sulphate (as SO_4) (mg/L)	Sodium Absorption Ratio (SAR)	Percentage Sodium (%Na)	Permeability Index (PI)
Pre-monsoon	S1	0.3	8.76	520	882.4	275	84.3	20.66	345	20	325	14.2	19.76	00.1	36.2	18.5	45.6	0.70	25.70	45.78
	S2	0.4	8.21	460	655.8	295	84.4	20.66	370	20	350	21.3	19.95	0.66	32.2	15.42	55.2	0.62	23.27	45.39
	S3	0.4	8.08	524	822.7	325	76.6	32.81	420	20	400	14.2	13.39	0.68	78.52	32.5	68.5	1.50	39.39	54.92
	S4	0.6	8.63	430	645.2	240	66.3	18.26	250	20	230	10.65	15.27	0.40	28.4	12.2	72.5	0.61	24.30	46.49
	S5	0.5	8.13	525	866.9	320	86.2	25.52	325	20	305	10.65	21.64	0.13	44.1	14.6	55.2	0.83	26.29	44.58
	S6	0.5	8.31	530	895.3	315	76.7	30.36	330	20	305	10.65	19.19	00.1	59.62	22.54	60.8	1.15	33.37	49.41
	S7	0.6	8.46	542	896.2	260	98.8	3.65	290	20	270	31.95	22.95	0.01	98.25	44.2	75.2	1.90	50.95	63.05
	S8	0.7	8.13	555	912.3	270	98.6	6.08	265	10	255	35.5	29.4	0.53	55.78	26.3	74.4	1.07	36.44	51.75
	S9	0.4	8.37	515	823.6	235	80.5	8.51	270	20	250	14.2	21.23	00.1	42.45	21.5	73.5	0.88	33.73	53.23
	S10	0.3	8.37	525	832.2	235	76.1	10.94	265	20	245	14.2	21.64	00.1	48.5	24.5	79.8	1.02	36.74	54.79
Post-monsoon	S1	0.3	8.78	518	876.8	272	82.0	18.2	332	20	319	19.5	20.3	0.1	32.4	17.5	43.5	0.64	24.85	45.99
	S2	0.4	8.23	455	645.4	286	83.4	19.3	364	20	342	25.3	22.1	0.59	31.2	14.6	48.3	0.61	23.05	45.75
	S3	0.4	8.12	512	812.6	322	72.4	28.4	412	10	392	18.2	14.8	0.62	76.5	29.5	62.5	1.52	40.54	57.51
	S4	0.5	8.52	428	635.5	238	62.5	15.2	142	20	225	15.4	16.2	0.38	26.52	11.23	68.4	0.59	24.71	42.29
	S5	0.5	8.18	522	856.1	319	82.9	22.5	319	10	296	13.6	22.12	0.12	42.12	12.45	53.2	0.81	26.32	46.07
	S6	0.5	8.35	528	886.6	312	7.42	29.2	322	20	295	14.2	18.5	0.1	56.23	19.86	56.4	1.94	51.30	80.76
	S7	0.6	8.51	538	883.4	245	95.6	3.1	286	20	264	34.5	24.52	0.1	96.41	43.56	73.5	1.89	51.31	63.74
	S8	0.6	8.11	548	896.4	266	92.4	5.8	255	10	244	38.2	31.24	0.48	52.81	24.62	71.6	1.04	36.45	52.61
	S9	0.4	8.35	502	813.2	231	74.5	7.4	264	20	241	16.5	23.65	0.1	40.38	20.58	70.2	0.87	34.47	55.44
	S10	0.3	8.32	519	826.6	228	71.8	9.2	259	20	238	17.2	22.41	0.1	46.17	23.45	74.2	1.10	37.45	56.83

Table 1 Spatial and temporal changes in environmental parameters of examined groundwater samples

Parameters	Unit	Pre-monsoon				Post-monsoon				IS:10500(2012)	WHO(2006)
		Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD		
Turbidity	NTU	0.30	0.70	0.47	0.13	0.30	0.60	0.45	0.10	5	-
pH	-	8.08	8.76	8.34	0.22	8.11	8.78	8.34	0.20	6.5-8.5	6.5-8.5
TDS	mg/L	430.00	555.00	512.60	38.08	428.00	548.00	507.00	37.36	500	1500
Electrical Conductivity	mg/L	645.20	912.30	823.26	96.41	635.50	896.40	813.26	96.05	-	1400
Total Hardness(as CaCO ₃)	mg/L	235.00	325.00	277.00	35.21	228.00	322.00	271.90	36.58	300	-
Ca(as Ca)	mg/L	66.00	98.00	82.40	10.01	0.00	95.60	71.75	27.08	70	200
Mg(as Mg)	mg/L	3.65	32.81	17.74	10.16	3.10	29.20	15.83	9.29	30	150
Total Alkalinity(as CaCO ₃)	mg/L	250.00	420.00	313.00	54.88	142.00	412.00	295.50	73.38	200	-
Carbonates (CO ₃ ²⁻)	mg/L	10.00	20.00	19.00	3.16	10.00	20.00	17.00	4.83	-	-
Bicarbonates(HCO ₃ ⁻)	mg/L	230.00	400.00	293.50	53.85	225.00	392.00	285.60	53.68	300	-
Chloride (as Cl ⁻)	mg/L	10.65	35.50	17.75	9.01	13.60	38.20	21.26	8.64	250	500
Nitrate (as NO ₃ ⁻)	mg/L	13.39	29.40	20.44	4.33	14.80	31.24	21.58	4.63	45	40-70
Fluoride (as F ⁻)	mg/L	0.01	0.68	0.24	0.28	0.01	0.62	0.22	0.262	1.5	-
Sodium (as Na ⁺)	mg/L	28.40	98.25	52.40	21.80	26.52	96.41	50.07	21.82	-	500
Potassium (as K ⁺)	mg/L	12.20	44.20	23.22	9.54	11.23	43.56	21.73	9.53	-	50

Table 2 Statistical description of seasonal analytical data of examined groundwater water samples with minimum, maximum, mean and SD

Hydro-geochemistry of Groundwater

Hydrochemical facies

To define the hydrochemical processes and groundwater types, the hydrochemical facies were used for constructing Piper and Durov diagrams which is shown on Fig. 2a and 2b. Piper triangular plot diagram and Durov diagram was developed with hydrochemical data of twenty groundwater samples that were collected from ten different locations in two consecutive seasons. Both the diagrams were developed by using AquaChem Scientific Software to visualise concentrations of the different major ions in the particular water samples.

In the Piper, two major hydrochemical facies have been developed based on the chemometrics of the groundwater in the study area. Majority of the samples belong to the $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ type followed by $\text{Na}^+\text{-K}^+\text{-Cl}^-\text{-SO}_4^{2-}$ types in the study area. The composition of water clearly indicates the dissolution of carbonate rich rocks (limestone) such as weathering calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) whereas $\text{Na}^+\text{-K}^+\text{-Cl}^-\text{-SO}_4^{2-}$ is derived from weathering of Na^+ , K^+ and SO_4^{2-} minerals (ferro-magnesium, feldspar minerals and gypsum) in the groundwater. In addition, mixed water type in this region is the evidence of groundwater recharge from rainfall whereas dominance of cation in groundwater is the signature of enhanced weathering of subsurface material for a long time (Thomas et al. 2014). On the other hand, dominance of Cl^- suggests that the groundwater is slightly influenced by surface activity such as leaching of industrial effluent bearing water and agricultural waste. Durov diagram consisting of two ternary diagrams where cations are plotted against the anions and expanded with the addition of TDS (mg/l) and pH data to allow further comparisons (Durov, 1948). Approximately 90 % of the samples are plotted in the dissolution or mixing line according to classification of (Lloyd and Heathcoat, 1985). Result suggests that the majority of dominant ions come from geochemical sources.

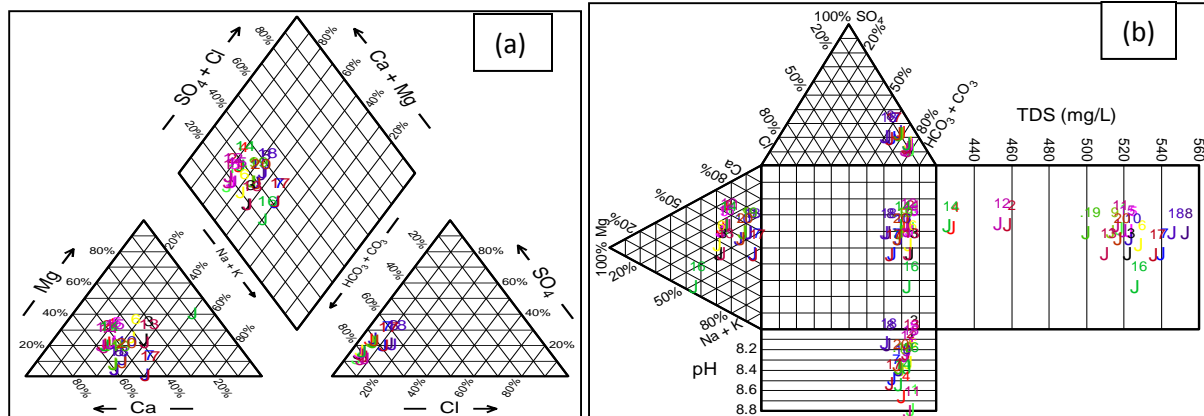


Fig. 2 Piper diagram **a** and Durov diagrams **b** showing the characterization of groundwater samples

Geochemical process

Groundwater aquifer materials play an important role in the water chemistry and are reveals the genesis of groundwater (Subramani et al. 2010). The understanding of hydrogeochemical process and role in groundwater chemistry Gibbs (1970) developed a water chemistry model based on the primary mechanism such as rock weathering, precipitation and evaporation. In this model, $Cl^- / (Cl + HCO_3^-)$ for anions, $(Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+})$ for cations and TDS as a function have been plotted to determine the chemometric of groundwater (Fig. 3a and 3b). Regional geology, weathering rate of minerals, water-rock interaction, precipitation and climatic condition are major factors that influence the water bodies (Li et al. 2015). The plot shows that all the data points are plotted in the rock dominance zone, which suggest that the groundwater chemistry of the study area is predominantly controlled by aquifer materials. However, the climatic condition of the study area is tropical climate that may reduce the rate of contribution of evaporation and precipitation in groundwater chemistry. In addition, general geology of the study area is characterized by following minerals such as limestone, gypsum, dolomite and quartzite which are play a major role in the groundwater chemistry.

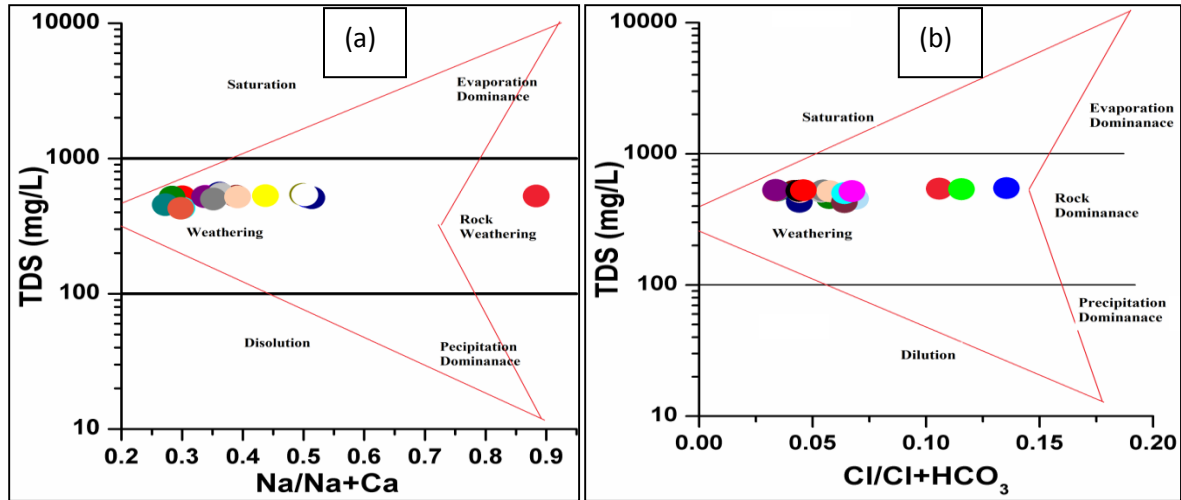


Fig. 3 Gibbs Diagram of **a** cations and **b** anions for groundwater samples
Carbonate weathering process

In this region, Ca^{2+} and Mg^{2+} are dominant cations present followed by Na^+ in the groundwater. Considerable amount of HCO_3^- is present in the groundwater, which reveals the presence of carbonate host rocks such as limestone, dolomite, gypsum and quartzite. These host rocks might be dissolved through the dissolution of weathered minerals and water rock interaction during groundwater movement. However, the evaluation of the carbonate weathering can be obtained through the explanation of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus HCO_3^- , $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus total cations and Na^++K^+ versus total cations relationship (Fig. 4a, 4b and 4c respectively). $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus HCO_3^- plot shows that all water samples are above the aquiline which indicate the dominance of $\text{Ca}^{2+}+\text{Mg}^{2+}$ in groundwater. Consequently, elevated $\text{Ca}^{2+}+\text{Mg}^{2+}$ ions in groundwater are mainly due to weathering of carbonate and silicate in this area. Further, $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus total cations and Na^++K^+ versus total cations plots indicate that all water samples fall below the aquiline which reveals the dominance of silicate weathering in the groundwater. Dissolution of silicate is one of the major sources of Na^+ in this region, because most of the ions are derived from silicate weathering where HCO_3^- is one of the most dominant ion present (Senthilkumar and Elango 2013). However, HCO_3^- ion releases may be due to reaction between feldspar minerals and carbonic acid in the presence of water (Elango et al. 2003). Therefore, these findings/observations clearly show that feldspars, limestones (calcite and dolomite) and amphiboles are major sources of cations and HCO_3^- in the groundwater.

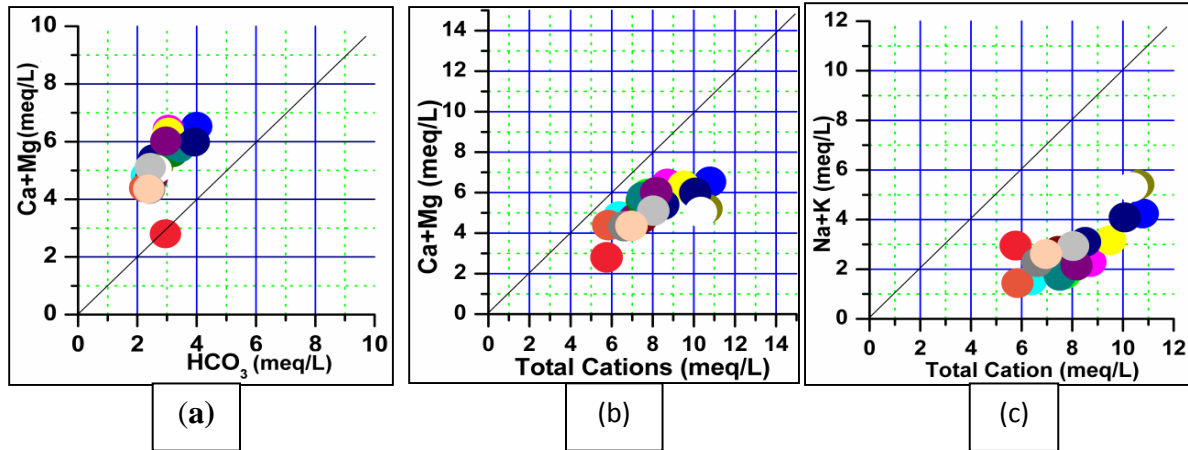


Fig. 4 Aquiline plot of (a) $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus HCO_3^- , (b) $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus total cations and (c) Na^++K^+ versus total cations for groundwater samples

Ion exchange reaction

The study of ion exchange reactions is very important to identify interrelationship between Na^+ versus Ca^{2+} and Na^+ versus Cl^- ion, which can be evaluated with the help of plotting of aquiline scatter diagram (Fig. 5a and 5b respectively). It plays a major role in geochemical reactions that directly or indirectly influences the concentration of ions in groundwater. Na^+ versus Ca^{2+} diagram shows that majority of the samples fall below the aquiline, which is revealing the silicate weathering. However, few samples are above the aquiline, which indicates the reduction of Ca^{2+} with respect to Na^+ in the groundwater. Therefore, the groundwater chemistry is predominantly controlled by cation exchange process in this region as one of the important geochemical process. Further, Na^+ versus Cl^- aquiline plot showed that all samples point fall above the aquiline because Cl^- is comparatively less than Na^+ , which indicates presence of silicate weathering in this region. However, the elevated level of Na^+ as compared to Cl^- in the groundwater is the major indication of cation exchange reactions (Salama 1993; Rajmohan and Elango 2004). On the other hand, higher concentration of Na^+ in the gneissic terrain would come from ion exchange process and leaching of industrial as well as agricultural contamination (Guo and Wang 2004).

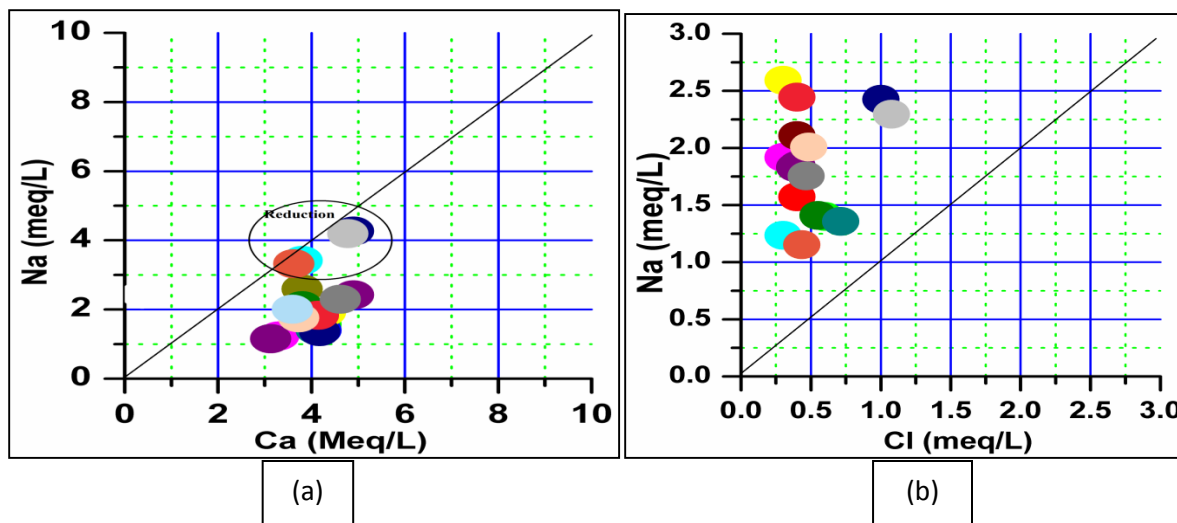


Fig. 5 Aquiline plot of (a) Na^+ versus Ca^{2+} and (b) Na^+ versus Cl^- ion for studied samples

Compositional Analysis

Cluster analysis (CA)

Cluster analysis (CA) displays clustering of sites based on the analytical data through ward method, which is displayed in dendrogram (Fig. 6). Three cluster groups are formed and further subdivided in sub group of the sites. In the 1st group site S1, S4, S9 and S10 are showing similar category which indicates these sites have comparable groundwater quality. This is because of the higher of ion concentration as observed at these sites which compose similar groundwater quality. Further, in the 2nd cluster group site S2, S3, S5 and S6 are showing similar characteristics which may be due to presence of comparable geology that controlled groundwater chemometrics in this region. Lastly, S7 and S8 show grouping in the cluster 3rd which may be due to presence of high concentration of Na^+ , K^+ and Cl^- in this region. In addition, due to presence of industrial and agricultural area in this region those contaminants/wastes may leach down in the groundwater, which enhance these ions in the groundwater and form similar water chemometrics.

Principle component analysis (PCA)

In this study, PCA was performed to chemometrics analysis of the analytical data. All data were standardised before multivariate analysis for reducing complex data into simple form (Singh et al. 2013). In this study, PCA was developed using Varimax rotation method, Kaiser Normalization technique and rotated factor solution. Five principle components (PCs) were

obtained to explain 87.9% of the variance in the variance in the dataset. The total variance of five PCs is as follows; 25.5% by PC1, 16.19 by PC2, 15.62% by PC3, 15.36% by PC4 and 15.21% by PC5.

In this study, PCs loading above the 0.6 are taken for the explanation of the input variables (Singh et al. 2013). The loadings of the PCs for variables are shown in Fig. 7. In the PC1, strong loading of HCO_3^- , alkalinity, total hardness and Mg^{2+} reveals the presence of carbonate host rocks (limestone, dolomite, gypsum and quartzite) in the aquifer which is responsible dissolution of silicate minerals in the ground water (Zheng et al. 2012). On the other hand, SO_4^{2-} shows negative strong loading in the PC1 which suggests the leaching of subsurface contaminants from agricultural area. Further, TDS and EC have strong loading with F^- negative strong loading in the PC2. The strong loading of TDS and EC reveals the groundwater is primarily mineralized through geochemical process. The negative loading of pH with CO_3^{2-} in the PC4 indicates weathering and dissolution of silicate minerals in the study area. Further, positive loading of Cl^- with NO_3^- and Ca^{2+} in the PC5 reveals the leaching of industrial and domestic effluent bearing water, as well as agriculture wastes in the study area, which enhances these ions in the groundwater (Osei et al. 2010). However, negative loading of Mg^{2+} in the PC5 presence of Mg^{2+} containing rocks such as feldspar and ferro-magnesium minerals demonstrates presence in this area (Bhardwaj et al. 2010).

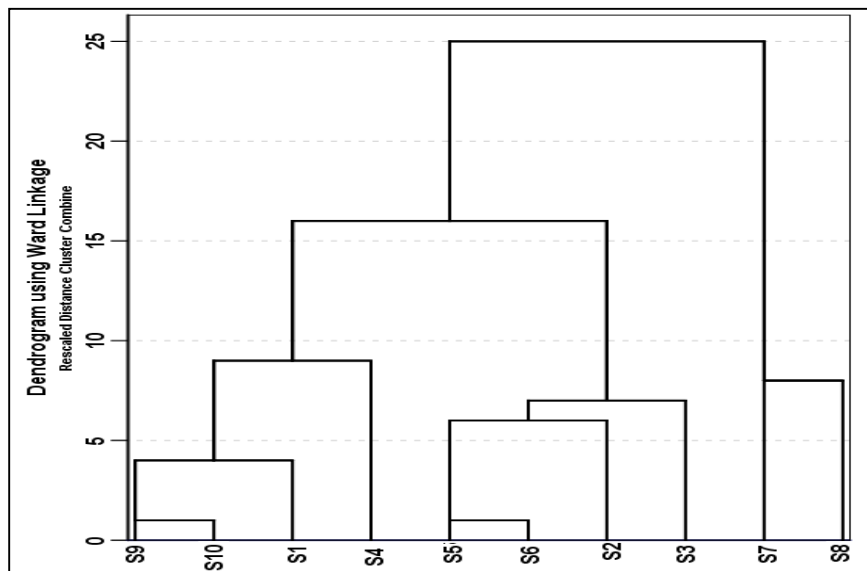


Fig. 6 Cluster analyses of water quality parameters for classification of sites

Conclusion

The present study has covered Vijaypur block, Samba district, Jammu and Kashmir, (India) with respect to the evaluation of hydro-geochemistry and chemometric of the groundwater via multiple approaches. Geochemical indices and multivariate techniques were applied to assess the groundwater chemistry and potability of the water present in the study area. The study area is dominated by Ca^{2+} , Mg^{2+} and HCO_3^- ion followed by Na^+ which is mostly derived from geogenic sources. Groundwater chemistry of the study area are predominantly controlled by mineral dissolution with following geochemical process viz. weathering carbonate, limestone, calcite, gypsum and dolomite, cation exchange process and precipitation of minerals. In addition, some ions like Cl^- and NO_3^- also reflected there presence through leaching of subsurface wastes from agricultural practices in the study area. However, groundwater quality of this area is suitable for drinking and irrigational purposes after conventional treatment because most parts of the study area have high pH, TDS and total alkalinity, which make it unsafe for drinking and irrigation purposes. Therefore, the present study recommends conventional treatment methods for treating Drinking water of the study area.

Acknowledgement

Authors are thankful to UGC and Central University of Jammu, for providing Research Grant and to Institute of Science, Visva-Bharati, Santiniketan, West Bengal for providing necessary infrastructure and support.

References:

- American Public Health Association (APHA) (2012) Standard methods for the examination of water and wastewater, 22nd edition, APHA, AWWA, WPCF, Washington DC, USA
- Bhardwaj V, Singh DS, Singh AK (2010) Water quality of the Chhoti Gandak River using principal component analysis, Ganga Plain, India. *J Earth Syst Sci* 1199(1):117-127
- Bureau of Indian Standards (BIS, 10500) (2012) Indian Standard Specification for Drinking Water
- Durov SA (1948) Classification of natural waters and graphical representation of their composition. *Dokl. Akad. Nauk. USSR*, 59(1): 87-90

- Elango L, Kannan R, Senthil Kumar M (2003) Major ion chemistry and identification of hydrogeochemical processes of groundwater in a part of Kancheepuram district, Tamil Nadu, India. *Journal of Environmental Geoscience*, 10:157–166
- Foster, S.S.D., 1995. Groundwater for development – an overview of quality constraints. In: Nash, H., McCall, G.J.H., (Eds.), *Groundwater Quality*. 17th Special Report (pp. 1–3). London United, Chapman Hall.
- Geological Survey of India (GSI) (2012) Geological and mineral resource of Jammu and Kashmir, India, 3rd edition ‘‘D.D. Bhattacharya, C. Sensarma and S.S. Hasan’’ ed. P.C Banopadhye, published by GSI, Nehru road Kolkata, India.
- Ghosh A, Mukherjee K , Gosh SK, Saha B (2013) Sources and toxicity of fluoride in the environment. *Research on Chemical Intermediates*, 2881–2915. doi: 10.1007/s11164-012-0841-1
- Gibbs RJ (1970) Mechanisms controlling world water chemistry. *Science*, (170): 1088–1090
- Gouri DKV, Bhunia S, Kumar P, Kumar SS (2016) Spatial variability of groundwater quality of Sabour block, Bhagalpur district, Bihar, India. *Applied Water Science*, doi: 10.1007/s13201-016-0380-9
- Guo H and Wang Y (2004) Hydrogeochemical processes in shallow quaternary aquifers from the northern part of the Datong Basin, China. *Applied Geochemistry*, 19(1) 19–27
- Han D, Song X, Currell MJ (2015) Identification of anthropogenic and natural inputs of sulfate into a karstic coastal groundwater system in northeast China : evidence from major ions , $\delta^{13}C$ DIC and $\delta^{34}S$ SO₄. doi: 10.5194/hessd-12-11331-2015
- Helena B, Pardo R, Vega M, Barrado E, Farnandeez, JM, Farnandeez L (2000) Temporal evolution of ground water composition in an alluvial aquifer (Pisuerga river Spain) by principal component analysis. *Water Research*, 34: 807-816
- Jasrotia AS and Kumar A (2014) Groundwater Quality Mapping Based on the Geographical Information System (GIS) of Jammu District, Jammu and Kashmir India. *Journal of Spatial Hydrology*, 12(1): 1-21
- Jehangir A, Tanveer A, Yousuf, AR, Masood A, Naqash AH (2011) Geochemistry and irrigation quality of groundwater along river Jhelum in south Kashmir, India; *Recent Research Science and Technology* 3(6) 57-63

- Johnson RA and Wichern DW (1992) Applied Multivariate Statistical Analysis, 3rd edition. Prentice Hall, Englewood Cliffs, NJ
- Kanwar P and Khanna P (2015) Impact of Industrial Waste on Ground Water in and Around Bari Brahmna Industrial Area, Samba District, Jammu and Kashmir, India, I.J.A.B.R, 5(2):143–149
- Kaur, J., Gorka, R., Kumar, R. (2018) Hydrogeochemistry and groundwater assessment of Poonch District, Jammu and Kashmir, India. Journal of applied Geochemistry, 20(2), 192-204.
- Krishna KS, Logeshkumaran A, Magesh NS, Godson PS, Chandrasekar N (2014) Hydrogeochemistry and application of water quality index (WQI) for groundwater quality assessment, Anna Nagar, part of Chennai City, Tamil Nadu, India. Applied Water Science, 335–343. doi: 10.1007/s13201-014-0196-4
- Kumar A and Dua A (2009) Water Quality Index for Assessment of Water Quality of River Ravi at Madhopur (India). Global Journal of Environmental Science, 8(1):49 – 57
- Kumar PJS and James KEJ (2013) Physicochemical parameters and their sources in groundwater in the Thirupathur region, Tamil Nadu, South India. Applied Water Science, 219–228. doi: 10.1007/s13201-012-0074-x
- Kumar R, Singh PVS, Banerjee SKGKP (2011) Application of drastic model and GIS: for assessing vulnerability in hard rock granitic aquifer. Environment and Monitoring Assessment, 143–155. doi: 10.1007/s10661-010-1572-7
- Massart DL and Kaufman L (1983) The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis. Wiley, New York
- Mehta P. (2013) Rock Weathering and Farmland Formation: It's Geology that determines Biology, Earth Science India, Popular Issue VI(III), July 2013, pp1-3, eISSN No. :0974-8350
- Mir RA, Jeelani GH, Dar AD (2016) Spatio-temporal patterns and factors controlling the hydrogeochemistry of the river Jhelum basin, Kashmir, Himalaya. Environment and Monitoring Assessment 118(438):1-24
- Mukherjee P, Singh CK (2012) Delineation of Groundwater Potential Zones in Arid Region of India - A Remote Sensing and GIS Approach. Water Resource Management, 2643–2672. doi: 10.1007/s11269-012-0038-9

- NSSO (2006): Morbidity, Health Care and the Condition of the Aged, National Sample Survey, 60th Round, Ministry of Statistics and Programme Implementation, Government of India, New Delhi
- Osei J, Nyame FK, Armah TK, Osae SK, Dampare SB, Fianko JR, Adomako D, Bentzi N (2010) Application of multivariate analysis for identification of pollution sources in the densu delta wetland in the vicinity of a landfill site in Ghana. *Journal of Water Resource Protection* 2:1020-1029
- Pemmaraju M, Rao SM (2011) Defluoridation of groundwater using magnesium oxide. *Environmentalist*, 39–53. doi: 10.1007/s10669-010-9299-0
- Petersen W, Bertino L, Callies U, Zorita E (2001) Process identification by principal component analysis of river water-quality data. *Ecological Modelling*, 138: 193–213
- Rajmohan N and Elango L (2004) Identification and evolution of hydrogeochemical processes in an area of the Palar and Cheyyar River Basin, Southern India. *Environmental Geology* 46 47–61
- Rao R, Agarwal A, Sharma RP, Bhalla UN, Nanda, A.C. (1988) Magnetic polarity stratigraphy and vertebrate paleontology of the Upper Siwalik sub group of Jammu hills, India, *Journal of the Geological Society of India*, 31(4),361-385.
- Reddy AGS, Kumar KN (2010) Identification of the hydrogeochemical processes in groundwater using major ion chemistry: A case study of Penna-Chitravathi river basins in Southern India. *Environmental Monitoring and Assessment*, 170:365–382. doi: 10.1007/s10661-009-1239-4
- Reghunath R, Murthy TRS, Raghavan BR (2002) The utility of multivariate statistical techniques in hydrogeochemical studies: An example from Karnataka, India. *Water Research* 36:2437–2442. doi: 10.1016/S0043-1354(01)00490-0
- Salama R B (1993) The chemical evolution of groundwater in a first-order catchment and the process of salt accumulation in the soil profile. *Journal of Hydrology*, 143 233–258
- Senthilkumar M, Elango L (2013) Geochemical processes controlling the groundwater quality in lower Palar river basin, southern India. *Journal of earth system science* 419–432
- Shreshtha S and Kazama F (2007) Assessment of surface water quality using multivariate statistical technique: A case study of Fuji River basin, Japan. *Environment Modelling Software*, 22: 464-475

- Singh AK, Mondal GC, Singh TB, Singh S, Tewary BK, Sinha A (2012) Hydrogeochemical processes and quality assessment of groundwater in Dumka and Jamtara districts. *Environmental Earth Science*, 2175–2191. doi: 10.1007/s12665-012-1658-3
- Singh CK, Shashtri S, Rina K, Mukherjee S (2013) Chemometric analysis to infer hydrogeochemical processes in a semi-arid region of India. *Arabian Journal of Geoscience*, 2915–2932. doi: 10.1007/s12517-012-0597-3
- Singh KP, Malik A, Mohan D, Sinha S, Singh VK (2005) Chemometric data analysis of pollutants in wastewater – A case study. *Analytica chimica acta*, 532: 15-25
- Subramani T, Rajmohan N, Elango L (2010) Groundwater geochemistry and identification of hydrogeochemical processes in a hard rock region, Southern India. *Environment and Monitoring Assessment* 162:123–137. doi: 10.1007/s10661-009-0781-4
- Thivya C, Chidambaram S, Rao MS, Thilagavathi R, Prasanna MV, Manikandan S (2015) Assessment of fluoride contaminations in groundwater of hard rock aquifers in Madurai district, Tamil Nadu (India). *Applied Water Science*, doi: 10.1007/s13201-015-0312-0
- Thomas J, Joseph S, Thirvikramji KP, Mukherjee TM, Arunkumar KS (2014) Seasonal variation in major ion chemistry of a tropical mountain river, the southern Western Ghats, Kerala, India. *Environmental Earth Science*, 71:2333–2351. doi: 10.1007/s12665-013-2634-2
- Vega M, Pardo R, Barrado ME, Debaân L (1998) Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research*, 32 (12) 3581-3592
- World Health Organization (WHO) Standard (2006) *Drinking Water Guidelines*, Geneva, pp 6
- Kakouros WN, Trautz E, Robert C (2012) Geochemical modeling of changes in shallow groundwater chemistry observed during the MSU-ZERT CO₂ injection experiment. *International Journal of Greenhouse Gas Control* 7:202–217. doi: 10.1016/j.ijggc.2011.10.003
- Zhou F, Liu Y, Guo H (2007) Application of Multivariate Statistical Methods to Water Quality Assessment of the Watercourses in North-western New Territories, Hong Kong. *Environment and Monitoring Assessment*, 132:1–13