JOURNAL GEOLOGICAL SOCIETY OF INDIA
Vol.92, December 2018, pp.753-763

Geochemical Characterization and Controlling Factors of Chemical Composition of Spring Water in a Part of Eastern Himalaya

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ABSTRACT

This paper focuses on the suitability of spring water for drinking and irrigation purposes in a part of eastern Himalaya, south Sikkim. There are many anthropogenic and geogenic factors contributing as a source of major cations and anions in the spring water. The spring water chemistry show a variation in EC, pH, TDS, Temperature, Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Pb, Mn, Cu, HCO_3^-, Cl^-, PO_4^{3-}, NO_3^-, F^- and SO_4^{2-}. Mainly two types of water quality indexing has been used, one for suitability of spring water for drinking purposes and the other for irrigation purposes. For drinking purposes, Piper diagram used for determination of water type, water quality index (WQI) for quality monitoring and saturation index for mineral dissolution in water. % Na, RSC (Residual Sodium Carbon) and SAR (sodium absorption ratio) have been used for irrigation suitability. Piper diagram shows that $CaHCO_3$ type of water was dominant in the study area. The WQI depicted excellent category and SAR, percent sodium and RSC (Residual Sodium Carbon) depict excellent, good and permissible category for irrigation purposes. Principle component analysis (PCA) was used to determine the major influencing factor responsible for the variability in the parameters analysed of spring water.

INTRODUCTION

Sikkim is one of the smallest Indian states of Eastern Himalaya consisting of four districts namely East, West, North and South. Major region of the state is hilly with an elevation ranging from 230 to 8583 meters (Roy, 2009). The people of Himalayan region mainly depend on spring water for livelihood, drinking water, sanitation, and irrigation (Mahamuni and Kulkarni, 2012). Most of the rainfall flows off as surface runoff through kholas, streams, and intermittent spring due to the steep slope. Springs get recharged through infiltration of rainfall through fractures, joints, weathered zones of the rocks and through soil covers. Spring discharge increases by 2 to 6 times during the monsoon season as compared to the pre-monsoon season. It plays a very significant role for fulfilling the water security to nearly 80% of the rural households (Roy, 2009).

Although Sikkim is endowed with rich water resources but due to poor management, degradation in water quality has been observed in recent years. Being a tourist spot and a commercial hub, most of the towns in Sikkim are growing rapidly. Therefore, there is a need for proper management of water supply systems of these towns which can fulfill the water supply demands of consumers as well as tourist population. The state of Sikkim exclusively depends on surface water sources like streams, rivers, lakes and springs. The springs originate from the underground aquifers which are recharged with rainwater (P.H.E., 2012-2013).

The water quality of the study area is relatively good as it is a lowland area (Verghese, 1990). As discussed earlier, the spring water is the main source of livelihood and it comes through various geological structures like fractured and joints. The chemistry of groundwater affected by many factors like geology of the area, the extent of chemical weathering of various rock types and other anthropogenic factors (Singh et al., 2015). The chemical quality of groundwater is evaluated based on its suitability for agricultural and domestic purposes (Mukherjee, Kumar, & Koertvelyessy, 2005). All these factors are responsible for various water types which may vary from place and time (Ako et al., 2012). The run-off water interacts with weathered zone of schist, gneisses, quartzite and phyllite rocks (Tiwari, 2012). Due to gravity flow, the spring water reaches the household of lower areas. It is discussed that with increase in the run-off time, the surface-water interaction predisposes the water to microbial and mineral contamination present within rocks. Due to hydro-meteorological conditions, Sikkim receives the maximum rainfall amounting to more than 2500mm (P.H.E., 2012-2013). The precipitated water is responsible for weathering process. Therefore, the present study was carried with emphasis on the spring water hydro-geochemistry which helps in determination of the acquisition process of solute into water and primary and secondary minerals saturation states in groundwater. The chemical characteristics of groundwater were analyzed with the help of hydrogeochemical facies and hydrogeochemcial signatures such as dissolution, ion exchange process, precipitation and calcite buffering mechanism. Conventional graphical plots have been used to determine various hydrogeochemical processes controlling the hydrochemical characteristics of an aquifer in the study area (E. J. Singh, Gupta and Singh, 2013). Principal component analysis and correlation matrix are used in this study to identify the interaction between physico-chemical parameters of water and to understand the important variables which affect the quality of water (E. J. Singh et al., 2013).

STUDY AREA

The study area belongs to a part of south Sikkim extending from 88.271° E to 88.538° E longitude and 27.078° N to 27.336° N latitude (Fig. 1). Climatic condition in the study area can be broadly divided into tropical temperate and alpine zone. The climate and weather of the whole state is mainly governed by elevation which ranges from 230 to 8583 meters. The average annual rainfall in Sikkim is 2739 mm. The rainfall of pre-monsoon occurs in April to May and monsoon operates normally from the month of May and continues upto early October. South Sikkim has a lower elevation and is dominated by cultivated land. It is characterized by Himalayan topography with series of crisscross ridges and ravines (CGWB, 2017). This variation is due to the south direction of drainage pattern. Most part of the state is encompassed by Precambrian rocks (NIC, 2017).

0016-7622/2018-92-6-753/$ 1.00 © GEOL. SOC. INDIA | DOI: 10.1007/s12594-018-1098-0

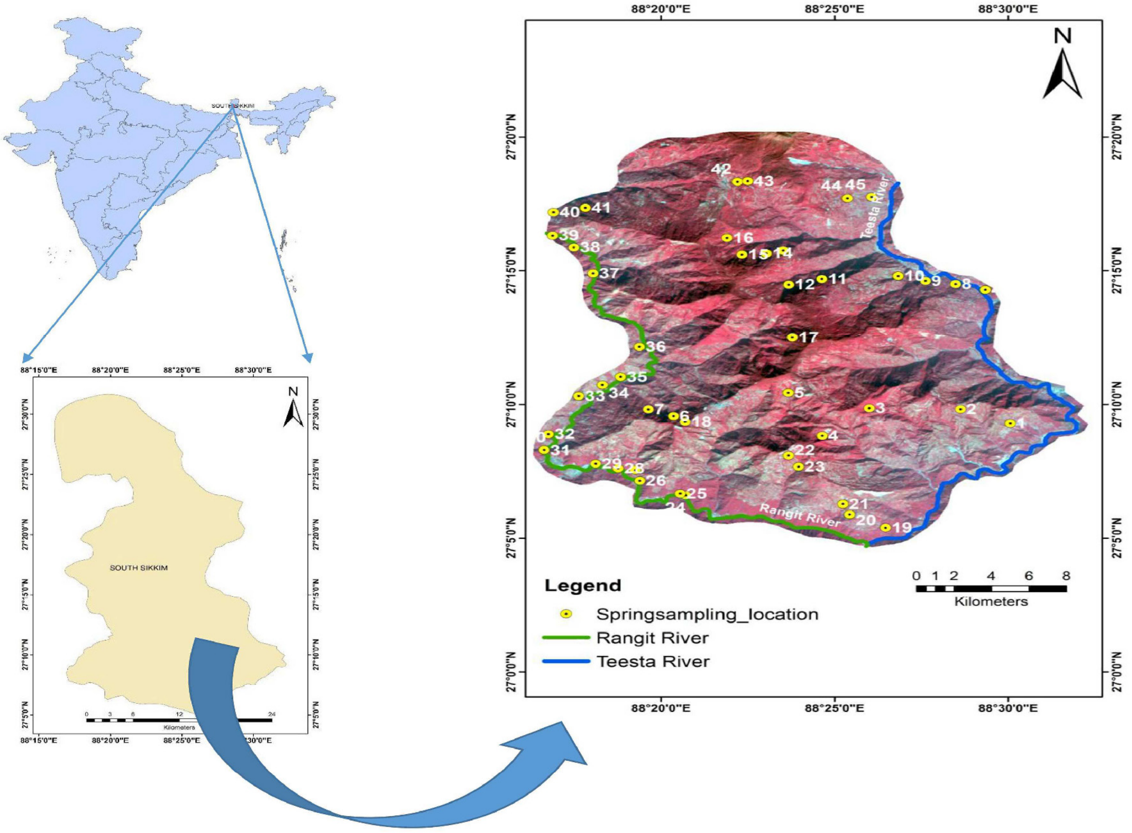

Fig.1. Location map of study area

The eastern, northern and western part of the state are constituted by hard massive gneissose rocks which is capable of resisting denudation; while the central and southern part of the state is cooperatively soft, thin, slaty and half-schistose rocks which denudes very easily (NIC, 2017).

Various lithological units exposed in Sikkim along with the surrounding area is mainly categorized as Darjeeling group of rocks, Daling group of rocks, Gondwana and Lingtse granite gneiss. Out of these, the Daling group of rocks is dominant in the study area. It comprises of dolostone, orthoquartzite, purple phyllite/slate, chert of Buxa formation, orthoquartzite, pyritiferrous black slate, variegated cherty phyllite, metagraywacke of Reyong formation and interbanded chlorite-sericite schist/phyllite and quartzite, pyritiferous black slate, biotite phyllite/mica schist, biotite quartzite, mica schist and chlorite quartzite of Gorubathan Formation (GSI, 2012). Amongst these, the Gorubathan Formation is the dominant rock formation in the study area (Fig. 2).

The storage of groundwater in the South district is within the fracture and joint plains. The presence of springs in various rock formations and weathered zone of phyllite, schist, gneisses and quartzite also suggest the occurrence of groundwater (CGWB, 2017). The Rangit and Teesta rivers are the two main drainage channels of Sikkim which flow from north to south direction (Fig. 1).

SAMPLING AND SAMPLE ANALYSIS

Forty-six water samples were collected from the springs from different altitudes (309m to 1987m) in the month of May, 2014. The location of the sampling points was recorded with handheld Garmin GPS. All the samples were collected into acid washed polypropylene bottles (Tarson: 250 and 125 ml). The samples were collected in 125 ml bottles for trace metal and heavy metal analysis and 250 ml bottles for anion analysis. The 125 ml bottle were acidified with HNO_3 to bring the pH<2 and 250 ml bottles were preserved without acidification (Rina, Singh, Datta, Singh, and Mukherjee, 2013; N. Singh, Singh, Kamal, Sen, & Mukherjee, 2015). The pH, EC, temperature and alkalinity were measured onsite using respective electrode (Hanna) and kit (Merck) (Jeelani, Bhat, Shivanna, and Bhat, 2011). After collection and onsite measurement, the samples were preserved in ice

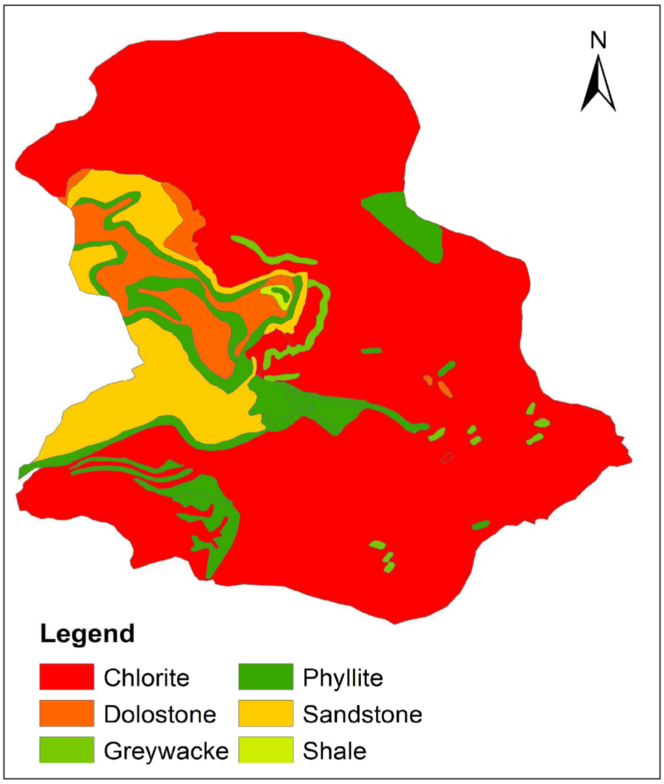

Fig.2. Geology map of study area

boxes. They were vacuum filtered using 0.45 µm Millipore filter paper and then stored at 4°C for further analysis.

All the physical and chemical parameters were analysed according to the standard methods given by American Public Health Association (APHA) (Federation & Association, 2005). Chloride was analyzed by titration method whereas other anions like fluoride, phosphate, sulphate and nitrate were analyzed using UV-Vis spectrophotometer (Perkin Elmer). The alkali and alkaline earth metals like sodium, potassium, magnesium and calcium were analyzed on flame photometer. The remaining cations including heavy metals were analyzed on AAS. The accuracy of analytical measurement was determined by calculating normalized charge balance index.

RESULT AND DISCUSSION

Hydrogeochemistry

The result of spring water quality is given in Table 1 with minimum, maximum and average values. The table shows that the spring water was slightly alkaline with pH range ranging from 5.9 to 9.2. Electrical conductivity varied from 15 to 360 µS/cm. Bicarbonate and chloride are dominant anions. The anionic dominance is in the order of HCO_3^- > Cl^-> NO_3^- >PO_4^{3-} > SO_{4-}^{2-} >F^-. To understand the existence of alkaline environment and dominance of silicate minerals in the area, the order of cations must be taken into consideration. The descending order of dominance of cations are Ca^{2+}> Na^+> Mg^{2+}> K^+ followed by trace metals. The dominance of bicarbonate mineral in the spring water is due to weathering of silicate minerals (Blum, Gazis, Jacobson and Chamberlain, 1998).

The elevation map of south district shows the variation in altitude from less than 1012m to 5728m (Fig. 3). Temperature of collected samples ranged from 15.1°C to 24.6°C. In general, the temperature of water sample decreased with increase in elevation (Jeelani et al., 2011). The same trend was found in the study area (Fig. 4). At the lowest altitude i.e. 306m, the temperature of spring water was 23.5°C while at highest altitude, 15.1°C temperature was recorded.

Solid particles which dissolve in water come from various sources such as mountain runoff, waste water stormflow and urban runoff (Kent and Belitz, 2004). It may contain mineral, salts, cations, anions and metals. TDS of spring water in this study ranges from 9 to 216 ppm which is below the BIS standard (500 ppm). In most of the samples the TDS decreased with elevation which might be attributed to less dissolution of minerals in water at low temperature and addition of the impurities in the stream water during its surface run-off through the slope. Erosion of sediments and organic matter such as leaf litter further add dissolved solids in water increasing the TDS value downstream. Figure 4 shows that the TDS of spring water sample at 1987m elevation was 9 ppm (sample no. 17) while at 347m elevation, it was 216 ppm (sample no. 29). Since the samples were collected in the month of May, the TDS of spring water remained low compared to other months due to melting of snow in the study area in this season (Jeelani et al., 2011).

Table 1. Minimum, maximum and average value of water quality parameters

Parameter	Min	Max	Avg.
pH	5.9	9.2	7.9
EC (µs)	15	360.0	121.3
TDS (ppm)	9	216.0	72.8
Temp. (°C)	15.1	24.6	20.7
Na^+ (mg/l)	1	23.0	5.9
K^+ (mg/l)	0.1	2.6	1.1
Mg^{2+} (mg/l)	0	6.7	3.5
Ca^{2+} (mg/l)	0.4	53.4	11.7
Fe^{2+} (mg/l)	0	0.8	0.1
Pb (ppm)	0	0.5	0.1
Mn (ppm)	0	0.3	0.1
Cu (ppm)	0	0.2	0.0
HCO_3^- (mg/l)	0.8	237.9	60.5
Cl^- (mg/L)	0.44	22.6	5.3
PO_4^{3-} (ppm)	0.13	1.2	0.6
NO_3^- (ppm)	0	48.4	1.8
SO_{4-}^{2-} (ppm)	0	17.17	0.46
F^- (ppm)	0	1.3	0.3
SiO_2 (mg/l)	5.25	36.45	18.45

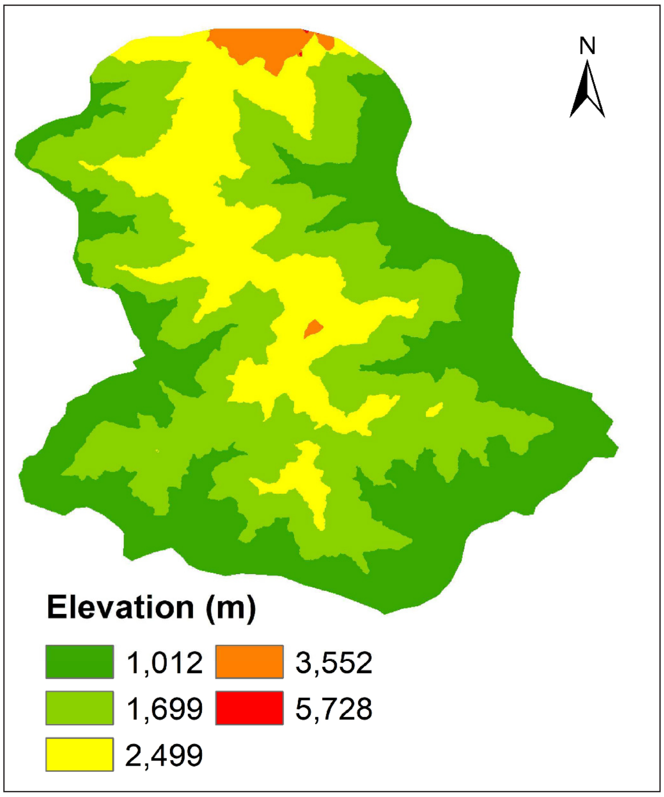

Fig.3. Elevation map of study area

Hydrochemical Facies

The chemical quality of water was interpreted using Durov and Piper diagram (Al Bassam, Awad and Al Alawi, 1997). The Schoeller diagram provides details about the hydrogeochemical facies (N. Singh et al., 2015).

The major cations and anions were plotted on left and right triangle respectively. All these points were projected on centrally located diamond-shaped area and represented total ionic distribution of spring water. The distribution of spring water samples into subdivision of diamond shaped field had some similarities and dissimilarities (Sakram, Sundaraiah, & Vishnu Bhoopathi, 2013). Based on percentage of chemical constituents shown in Piper Trilinear diagram, the spring water of the study area was classified into six different types. These were Ca-HCO_3, Mg-Cl, Mg-HCO_3, Na-Cl, Na-HCO_3 and Na-NO_3. Among them, Ca-HCO_3 type of water was dominant in the study area (Fig. 6).

Durov diagram provides a better display of hydrochemical facies along with pH and TDS. This diagram is based on the percentage of milliequivalent values of major ions. TDS values of the spring water samples ranges from 10 to 250 mg/L, which indicates primary type of groundwater having mainly bicarbonates of calcium and magnesium (Durov, 1949). Durov diagram (Fig. 7) shows the samples having higher concentration of bicarbonate, calcium and magnesium in the water sample with pH variation from 6.5 to 9.5.

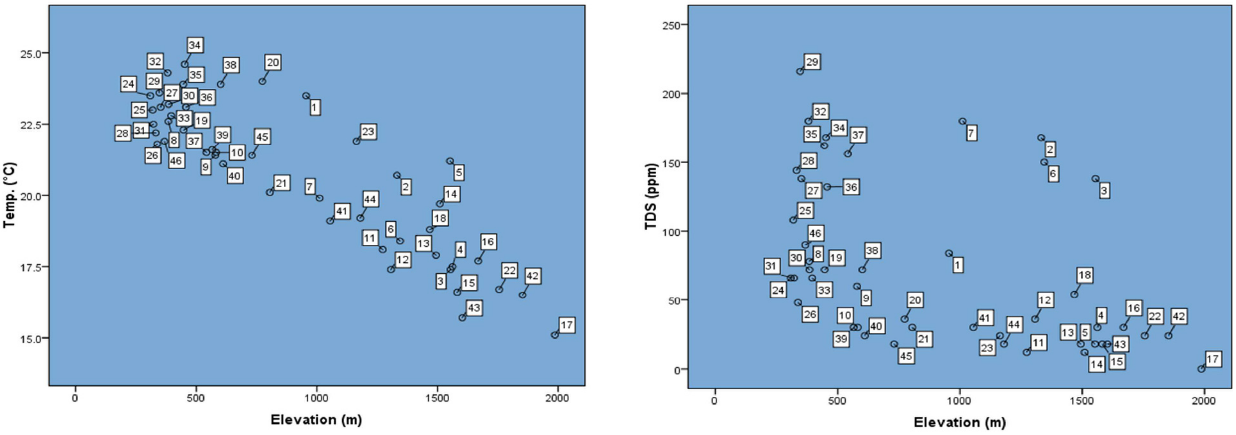

Fig.4. Graph showing the changes in spring water samples with **(a)** Temperature vs Elevation **(b)** TDS vs Elevation

Hydrochemical Processes

Saturation index (SI). The saturation index can be calculated by the following equation

$$SI = \log\left(\frac{IAP}{Ksp}\right)$$

The present data indicates that the saturation index of calcite, dolomite and goethite minerals is negative suggesting that, these minerals can dissolve further from surrounding rocks to reach its saturation point. The rock formations like Buxa Formation can be the source of dolomite and calcite in the spring water samples within the study area. Hematite, goethite and $Fe(OH)_3$ minerals were oversaturated which show the precipitation characteristic of these minerals into water samples. Pyretiferrous black slate mineral of Reyong Formation and Gorubathan Formation can be a source of iron in spring water samples (GSI, 2012).

The scatter plot between (Ca+Mg) vs (HCO_3 + SO_4) (Fig. 9) is used by various researchers to identify the dominant weathering process (Datta & Tyagi, 1996; Rina, Datta, Singh, & Mukherjee, 2012; N. Singh et al., 2015). If the samples fall above the equiline (1:1), carbonate weathering and reverse ion exchange is the dominant process. Whereas the samples falling below the equiline indicate silicate weathering and ion exchange as the dominant process. In this study, majority of the samples lie below the equiline due to an excess of bicarbonate ions. This excess of bicarbonate ions was released in spring water by the dissolution of albite mineral depicting that silicate weathering and ion exchange was the dominant process. Some of the samples were also found above the equiline which explain the carbonate weathering and reverse ion exchange process in the study area at these locations . Excess of bicarbonate anion within water samples might be balanced by some other cations. Following reaction are showing the possible process in spring water:

$$CO_2 + H_2O \xrightarrow{\textit{carbonic acid formation}} H_2CO_3$$

$$CaCO_3 + H_2CO_3 \xrightarrow{\textit{calcite dissolution}} Ca^{2+} + 2HCO_3^-$$

$$2NaAlSi_3O_8\ (albite) + 2H_2CO_3 + 9H_2O \xrightarrow{\textit{silicate weathering}} Al_2Si_2O_5\ (OH)_4\ (kaolinite) + 2Na^+ + 4H_4SiO_4 + 2HCO_3^-$$

Na^+ and K^+ ions are generally present in the form of NaCl and

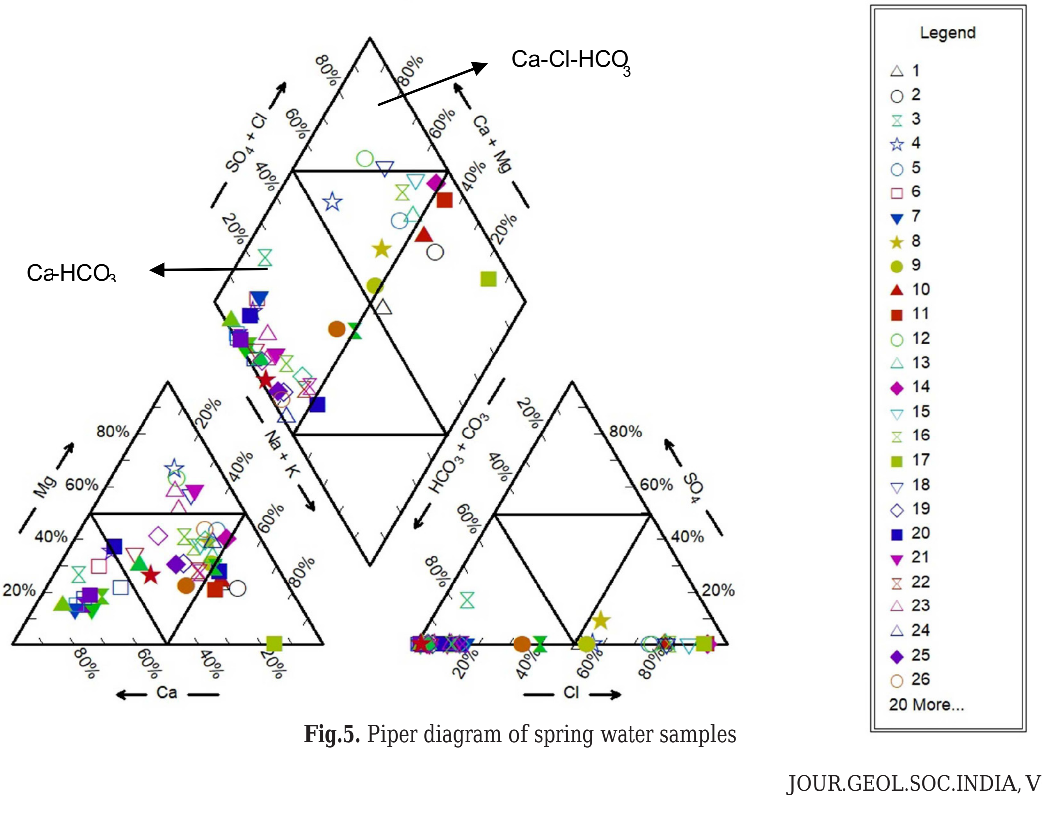

Fig.5. Piper diagram of spring water samples

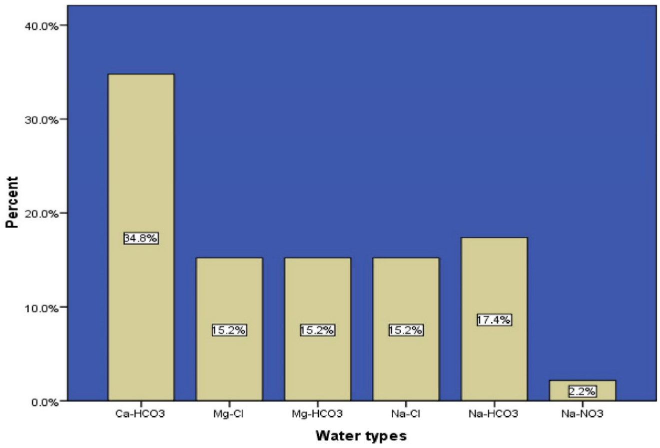

Fig.6. Percentage of water type of spring water samples.

KCl in water. Most of the samples lie above the equiline in scatter plot between Na+K vs. Cl^- (Fig. 9). It showed that the source of Na^+ and K^+ were away from NaCl and KCl respectively (WHO, 2009). The other sources of Na^+ and HCO_3^- in water might be from the dissolution of feldspar mineral such as albite (Rina et al., 2012). Silicate weathering can also be confirmed by this scatter plot. If the sample lies above the equiline, it depicts an excess of cations possibly due to silicate weathering (N. Singh et al., 2015). The excess of bicarbonate ions was due to silicate weathing confirmed by both the above plots indicating that silicate weathing is the source sodium and calcium within the spring water samples.

In the scatter plot of HCO_3^- vs Na^+, at some of the sampling locations, increased concentration of HCO_3^- compared to Na^+ indicate silicate weathering, while at some locations carbonate weathering is prevalent (Fig. 10a). This was inferred since the Na^+ concentration was lower than Ca^{2+} ion within the spring water. The reason behind this may be the ion exchange process where the Na^+ concentration reduced from spring water and Ca^{2+} ion concentration getting enhanced. The Na vs. Ca scatter plot (Fig. 10b) also supports this weathering process because the plot was found toward the calcium side (Lakshmanan, Kannan, & Kumar, 2003).

The source of calcium and bicarbonate ion in spring water was same. So, it can be interpreted that weathering of calcite is also important process in the study area. The R^2 value in between bicarbonate and calcium ion was 0.8655, which is showing a strong relationship between these ions (Fig. 11a).

Dolomite mineral might be the source of calcium ion along with calcite. Magnesium ion in the water sample was contributed by the dissolution of dolomite. The R^2 value between HCO_3 vs. (Ca+Mg) graph was 0.9009 depicting that dissolution of calcite and dolomite mineral is the source of calcium and magnesium ions (Fig. 11b).

The major cations in the water system are Na^+, K^+, Mg^{2+}, Ca^{2+} which govern most of the hydrogeochemcial processes of water. Most of the samples in the (Ca+Mg) vs total Cations plot (Fig. 11c) fall on the right side of the equiline which depicts the contribution of alkali ions by silicate weathering (Rao, 2008).

Chloroalkaline indices (CAI). Besides weathering, ion exchange during its subsurface flow governs the hydrochemistry. The chloro-alkaline indices CAI-1 and CAI-2 were described by Schoeller (Schoeller, 1965) to explain the ion exchange processes between the groundwater and its surrounding environment during the residence as well as travel time of groundwater. CAI-1 and CAI-2 were used to verify the ion exchange process in the aquifer of the study area calculated by following equation.

$$\text{Chloro Alkaline indices (CAI-1)} = [Cl-(Na+K)]/Cl$$

$$\text{Chloro Alkaline indices (CAI-2)} = [Cl-(Na+K)]/(SO_4 + HCO_3 + CO_3 + NO_3)$$

When the exchange of alkali ion i.e. Na^+ and K^+ ion present in groundwater takes place with alkaline earth ions i.e. Ca^{2+} and Mg^{2+} within rock material and both the indices are positive, the exchange is

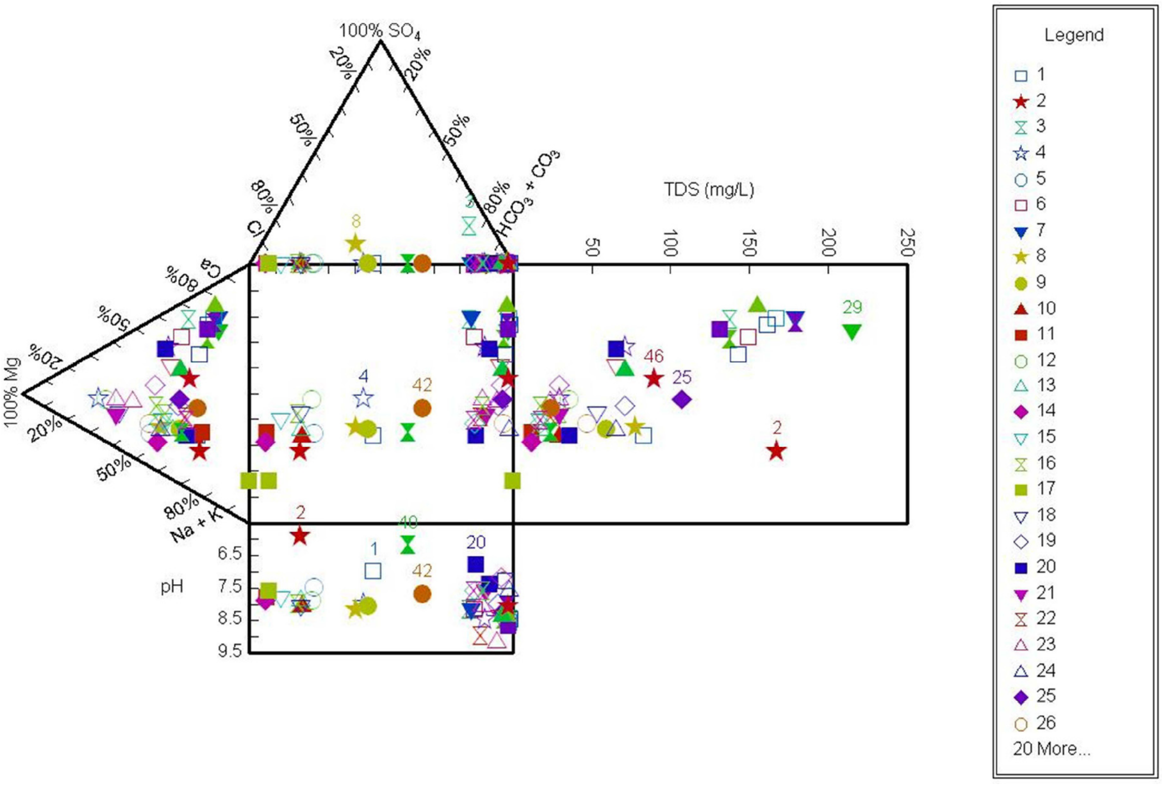

Fig.7. Durov diagram of spring water samples

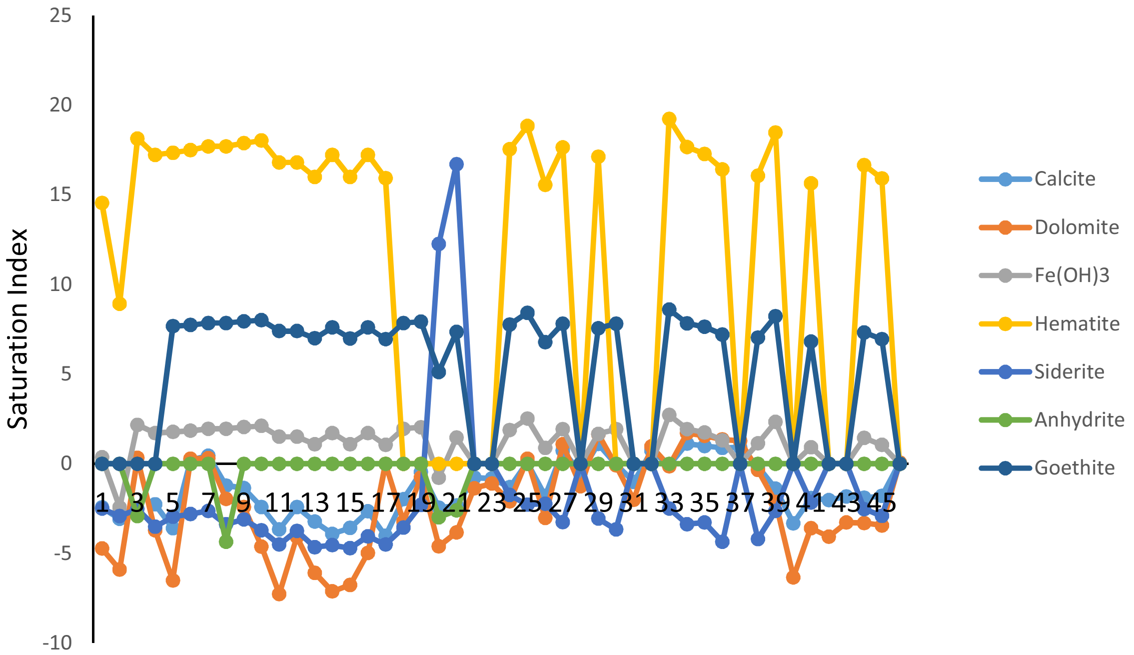

Fig.8. Plot showing the saturation index (SI) of minerals

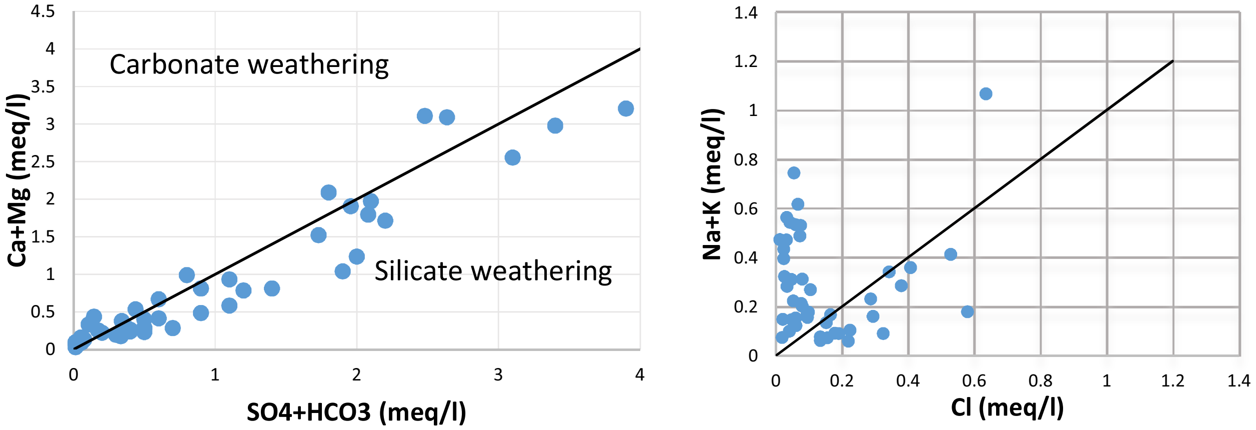

Fig.9. (a) Scatter diagram of (Ca+Mg) Vs. (SO_4+HCO_3) **(b)** Scatter diagram of (Na+K) Vs. Cl of spring water samples

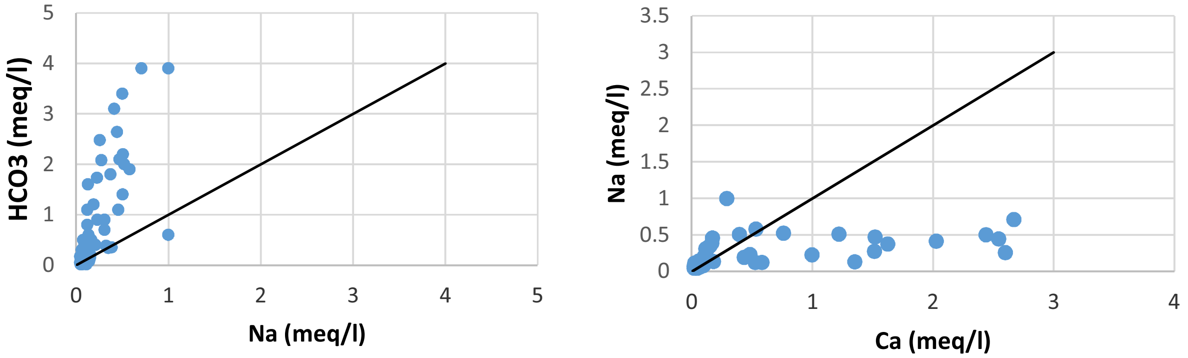

Fig.10. (a) Scatter plot of HCO_3 vs. Na **(b)** Scatter plot of Na vs. Ca

known reverse ion exchange. While, the case will be reversed when the exchange takes place between Ca^{2+} and Mg^{2+} ion of groundwater with Na^+ and K^+ ion of rock material and both the indices are negative, this type of exchange is known as indirect or ion exchange process (Aghazadeh & Mogaddam, 2010; Ako et al., 2012; Kumar, Kumari, Ramanathan, & Saxena, 2007; Rajmohan & Elango, 2004; N. Singh, Singh, Mukherjee, McDonald, & Reddy, 2014). In this study, CAI-1 and CAI-2 of 30 samples in spring water were found negative while rest of the value of the samples were found positive. Majority of samples showed ion exchange process which means the Ca^{2+} and Mg^{2+} ion of groundwater is replaced by Na^+ and K^+ ion of rock material. It also verifies the dominance of alkali metals in water over alkaline earth metals. The possibility of cation exchange is also enhanced due to availability of clay minerals (N. Singh et al., 2014). Clay minerals

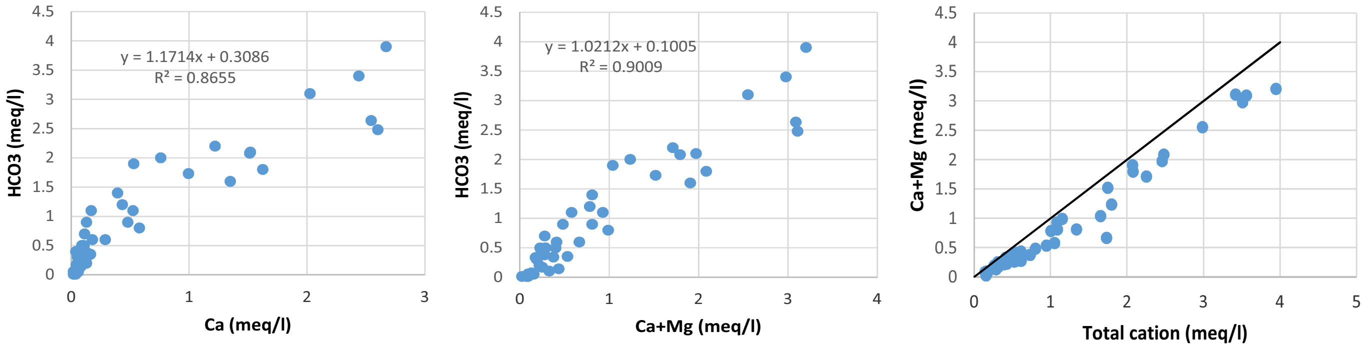

Fig.11. (a) Scatter plot of HCO_3 vs. Ca **(b)** Scatter plot of HCO_3 vs. (Ca+Mg) **(c)** Scatter plot between (Ca+Mg) vs Total cation showing the excess of alkalies.

are negatively charged particles which have a higher affinity to bind with large positively charge ions. Earlier equation shows that the clay minerals are the output of silicate weathering (Acheampong & Hess, 1998; Yidana, Ophori, & Banoeng-Yakubo, 2008) and therefore the ion exchange process is dominant in the study area.

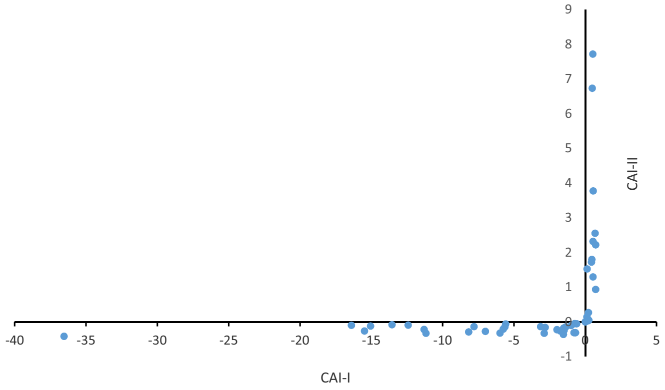

Fig.12. Scatter plot showing CAI-I vs CAI-II

Hardness: Table 2 shows that 76.1% of spring water samples is classified as soft water, 17.4% of samples are moderately hard and 6.5% are hard. None of the samples had hardness more than 300 mg/l. Majority of samples of south Sikkim were soft water.

Table 2. Hardness of spring water of South Sikkim

Hardness (as $CaCO_3$ in mg/l)	Water Classification	% of Samples
0-75	Soft	76.1
75-150	Moderately hard	17.4
150-300	Hard	6.5
>300	Very hard	0

Water quality index (WQI). WQI was initially developed by Horton (Horton, 1965) in United States by selecting the ten most common water quality parameters. Further, it was developed and modified by Brown in 1970 which was based on weights of individual water quality parameters (Tyagi, Sharma, Singh, & Dobhal, 2013).

The water quality index of an area is based on the significance of chemistry of water. Water quality index was used as an effective tool to obtain an overall scenario about the water. The importance of WQI has been explained by many researchers and scientists to provide a general idea about the water quality (Ramakrishnaiah, Sadashivaiah, & Ranganna, 2009; Ravikumar, Mehmood, & Somashekar, 2013; Sahu & Sikdar, 2008; N. Singh et al., 2015).

To calculate the WQI of spring water, fourteen important parameters were selected. Initially, weightage of all the water quality parameters was assigned from 1 to 5, depending on the relative importance which determine the overall quality of spring water in the study area. Next, the relative weight for all the parameters were calculated by following equation:

$$Wi = \frac{wi}{\Sigma_{i=1}^{n} wi}$$

The third step of WQI calculation was to calculate the quality rating scale (qi) for each of the parameters:

$$qi = \frac{Ci}{Si} \times 100$$

Where *Ci* is the concentration of each parameter of each sample and *Si* is the BIS standard of each parameters. And at final step, the WQI was calculated by sub-index (SI) of each chemical parameter by the following equation:

$$SIi = Wi \times qi$$

$$WQI = \Sigma\, SI_i$$

Where SI_i is the sub-index of *i*th parameters.

In this study, maximum weight was assigned to total dissolved solids (TDS) and chloride. The spring water is an open water source which emerges from surface aquifer. As it flows on the surface, more and more ions get dissolved from the surrounding rocks and soil. Therefore, maximum weightage was assigned to TDS with its relative significance. The lower weightage was given to those parameters which

Table 3. Water quality index calculating of spring water samples

Parameters	BIS desirable limit	Weight (wi)	Relative weight (Wi)
pH	6.5	4	0.091
TDS (ppm)	500	5	0.114
K^+ (ppm)	10	2	0.045
Mg^{2+} (ppm)	30	3	0.068
Ca^{2+} (ppm)	75	3	0.068
Fe (ppm)	0.3	2	0.045
Pb (ppm)	0.01	2	0.045
Mn (ppm)	0.1	3	0.068
Cu (ppm)	0.05	3	0.068
HCO_3^- (mg/l)	200	2	0.045
Cl^- (mg/l)	250	3	0.068
NO_3^- (ppm)	45	4	0.091
F^- (ppm)	1	4	0.091
SO_4 (ppm)	200	4	0.091
		ΣWi = 44	ΣWi = 1

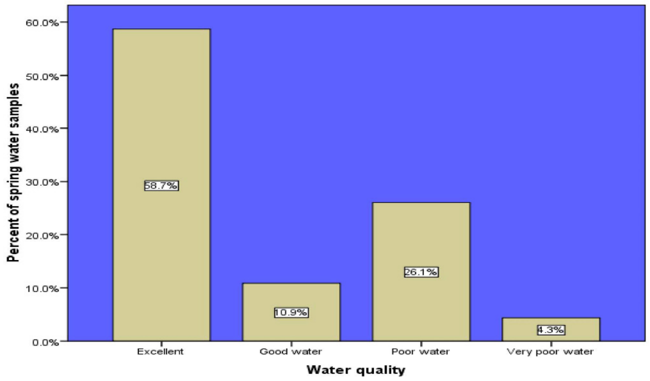

Fig.13. Percentage of spring water samples in WQI category

show less importance for spring water chemistry of the particular area. The pH of spring water varies from 5.9 to 9.2 which indicate slightly acidic to alkaline nature. This change in pH was due to surrounding geological formation (Abdulwahid, 2013).

The WQI of all the spring water samples were calculated. 58.70% samples belong to excellent category, 10.90% samples were of good category, 26.10% was of poor category and 4.3% came under very poor category of water (Fig. 13). WQI analysis showed that the spring water of South Sikkim was of excellent quality.

Sodium absorption ratio (SAR). The hazardous effect of irrigation water on soil can be seen by the reaction between soluble inorganic constituents of water with soils in the form of ions rather than molecules. This effect is determined by the absolute and relative concentration of the cations. If the sodium proportion is high among major cations, the alkali hazard is high. Whereas, the dominant calcium and magnesium proportion show low hazardous effect of irrigation water (Richards, 1954).

Richards (1954) explain the sodium absorption ratio of the soil solution as "it is simply related to the absorption of sodium by the soil; consequently, this ratio has certain advantages for use as an index of the sodium or alkali hazard of the water." This ratio can be defined by the following equation:

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{(\mathrm{CA} + \mathrm{Mg})} / 2}$$

Where the Na^+, Ca^{2+} and Mg^{2+} represent the concentration in milliequivalents per liter.

The SAR value of the spring water in this study was below 10 which falls under low sodium water class (S1) category representing excellent water type for irrigation. This type of water is suitable for all type of crops and soils but not suitable for sodium sensitive crops.

Residual sodium carbonate (RSC). The concentration of carbonate and bicarbonate ions play a significant role in determination of spring water for agricultural purposes. Water containing high concentration of these ions tends to precipitate out as calcium and magnesium carbonates. By getting precipitation of carbonates of calcium and magnesium from soil solution, the proportion of sodium is increased, as a result alkali hazard also increases. The excess concentration of bicarbonate and carbonate other than calcium and magnesium is considered as residual sodium carbonate (RSC) calculated by the following equation (N. Singh et al., 2015):

$$\mathrm{RSC} = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$$

Where, the concentration of all the ions is represented in meq/l

As per the above classification scheme, 93.5% of spring water samples had the RSC value less than 1.25 meq/l which fall under good or safe category, 4.3% of spring water sample had RSC value in between 1.25 to 2.5 meq/l which fall under doubtful category and 2.2% of spring water had RSC value above 2.5 meq/l which was unsuitable for irrigation purpose.

Table 4. Classification of irrigation water based on SAR value

SAR value	Types of water	Quality	Suitability for irrigation
0-10	Low sodium water (S1)	Excellent	Suitable for all types of crops and all types of soils, except for those crops, which are sensitive to sodium
10-18	Medium sodium water (S2)	Good	Suitable for coarse textured or organic soil with good permeability. Relatively unsuitable in fine texured soils
18-26	High sodium water (S3)	Fair	Harmful for almost all types of soil; Requires good drainage, high leaching gypsum addition
>26	Very high sodium water (S4)	Poor	Unsuitable for irrigation

Source: (Ravikumar et al., 2013)

Table 5. Classification of Water by RSC (Richards, 1954)

RSC	Quality
<1.25	Safe/Good
1.25-2.5	Marginal/Doubtful
>2.5	Unsuitable

Table 6. Water class by Sodium percent (Wilcox, 1955)

Sodium (%)	Water class
<20	Excellent
20-40	Good
40-60	Permissible
60-80	Doubtful
>80	Unsuitable

Percent sodium (%Na). Wilcox (Wilcox, 1955) explained the percent sodium as "a term used in connection with irrigation waters and soil extracts to indicate the proportion of sodium ions in solution in relation to the total cation concentration." The percent sodium can be calculated by following formula:

$$\%Na = \frac{Na}{(Ca + Mg + K + Na)} \times 100$$

Where, the concentration of Na^+, Ca^{2+}, Mg^{2+} and K^+ were in milliequivalents per litre (meq/l). On the basis of sodium percentage, the irrigation water can be categorized as given in Table 6

The sodium ions have tendency to get absorbed by clay particles. When the concentration of Na^+ increases in water, it gets absorbed onto clay particles displacing calcium and magnesium ions. Due to this ion exchange process, the soil reduces the permeability and as a result internal drainage becomes poor (Ako et al., 2012). The harmful effect of sodium percentage in water on soil should not exceed 50-60%. Above 60%, the water is considered unsuitable for irrigation purposes (Ravikumar et al., 2013).

The present study of spring water show that 34.8% of samples were within permissible water class for irrigation purpose. This means, majority of samples had >60% of sodium. Likewise, 32.6% came under good category, 28.3% under excellent category, 2.2% were doubtful and 2.2% were unsuitable for irrigation purposes.

Table 7. Correlation matrix of variables

	pH	TDS	Na	K	Mg	Ca	Fe	Pb	Mn	Cu	HCO_3	Cl	PO_4	NO_3	F	SiO_2
pH	1.00															
TDS	0.20	1.00														
Na	-0.16	**0.73**	1.00													
K	-0.23	0.16	0.27	1.00												
Mg	0.26	**0.83**	**0.63**	0.25	1.00											
Ca	0.38	**0.88**	0.48	0.16	**0.74**	1.00										
Fe	0.27	0.10	0.07	0.04	0.24	0.01	1.00									
Pb	-0.04	0.04	-0.21	-0.26	-0.20	-0.13	0.04	1.00								
Mn	0.38	0.12	-0.13	-0.10	0.18	0.27	**0.52**	-0.14	1.00							
Cu	0.26	-0.14	-0.03	-0.19	-0.14	-0.12	-0.07	-0.16	0.05	1.00						
HCO_3	0.30	**0.88**	**0.57**	0.11	**0.79**	**0.92**	0.13	-0.21	0.35	-0.07	1.00					
Cl	-0.25	0.06	0.12	-0.02	-0.13	-0.24	0.02	**0.64**	-0.47	-0.15	-0.29	1.00				
PO_4	0.00	**0.69**	**0.63**	0.22	**0.71**	**0.63**	0.18	-0.40	0.19	-0.08	**0.79**	-0.22	1.00			
NO_3	-0.45	0.24	**0.53**	0.40	0.07	-0.05	-0.06	0.09	-0.31	0.06	-0.03	0.42	0.11	1.00		
F	-0.06	-0.18	-0.24	-0.23	-0.39	-0.26	-0.04	**0.73**	-0.36	-0.19	-0.40	**0.71**	-0.50	0.02	1.00	
SiO_2	0.07	**0.64**	**0.74**	-0.02	**0.66**	**0.53**	0.08	-0.32	0.02	-0.06	**0.61**	-0.08	**0.74**	0.03	-0.32	1.00

Correlation between Variables

The correlation between variables is an important way to show the affinity of global coherence of the dataset. It provides the evidence of participation of individual water quality parameters which are affected by several hydrochemical processes (Helena et al., 2000).. The correlation coefficient varies from -1 to +1. The values which found over 0.5 was highlighted and considered for relationship study. If the correlation coefficient is in between 0.5 to 0.8, moderate strong relationship and above 0.8 the strong relationship were considered. The correlation matrix in Table 5 is showing the moderate relationship between TDS and Na$^+$ (r = 0.73), TDS and PO_4 (r = 0.69), TDS and Si (r = 0.64), Na$^+$ and Mg^{2+} (r = 0.63), Na$^+$ and HCO_3^- (r = 0.57), Na$^+$ and PO_4 (r = 0.63), Na$^+$ and NO_3^- (r = 0.53), Na$^+$ and Silica (r = 0.74), Mg^{2+} and Ca^{2+} (r =0.74), Mg^{2+} and HCO_3^- (r = 0.79), Mg^{2+} and PO_4 (r = 0.71), Mg^{2+} and Silica (r = 0.66), Ca^{2+} and PO_4 (r = 0.63), Ca and Silica (r = 0.53), Fe and Mn (r = 0.52), Pb and Cl (r = 0.64), Pb and F (0.73), HCO_3^- and PO_4 (r = 0.79), HCO_3^- and Silica (r = 0.61), Cl$^-$ and F$^-$ (r = 0.71), PO_4 and Silica (r = 0.74). The strong correlation was found between TDS and Mg^{2+} (r = 0.83), TDS and Ca^{2+} (r = 0.88), TDS and HCO_3^- (r = 0.88), Ca^{2+} and HCO_3^- (r = 0.92). The correlation between TDS with Na$^+$, Mg^{2+}, Ca^{2+}, HCO_3^- and Silica tells about the rock water interaction and natural weathering phenomenon. Very strong correlation between HCO_3^- and Ca^{2+} is due to $CaHCO_3$ type of water. This correlation is explained better with the help of principle component analysis.

Principle Component Analysis

The principle component analysis was done using statistical software Statistical Package for Social Sciences (SPSS 16.0). In groundwater system, the PCA is used in terms of principle component (PC) loadings and PC scores and these component are nothing but the chemical variables which relatively influence each other (Rao et al., 2017). PCA use to reduced the dimensionality of the data and present in less number of variables which express whole data. In present study, pH, TDS, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Fe, Pb, Mn, Cu, HCO_3^- , Cl$^-$, PO_4, NO_3^-, F$^-$ and Silica chemical variables are used in PCA (Table 8). Five principle component having eigen value greater than one are extracted which cover 80.85% of total variance of the chemical composition of spring water ranges from 39.954 to 7.344 for PC 1 to PC 4. The variation in PC loadings express the contribution of groundwater chemistry (Rao et al., 2017). In Table 8, the component loadings larger than 0.6 in taken into consideration for further interpretation of the result (Mazlum, ÖZER, & MAZLUM, 1999).

The first principal component PC-1 is dominated in the study area with 39.954% contribution in hydrogeochemistry of spring water. TDS, Na$^+$, Mg^{2+}, Ca^{2+}, HCO_3-, PO_4 and SiO_2 shows higher positive loading (Table 8). The input of Na$^+$, Ca^{2+}, HCO_3^- and Mg^{2+} is basically considered from rock water interaction and therefore the TDS of spring water is also dominant in this component. Chemically, the simplest component of silicate is silicon oxide which is also known as silica.

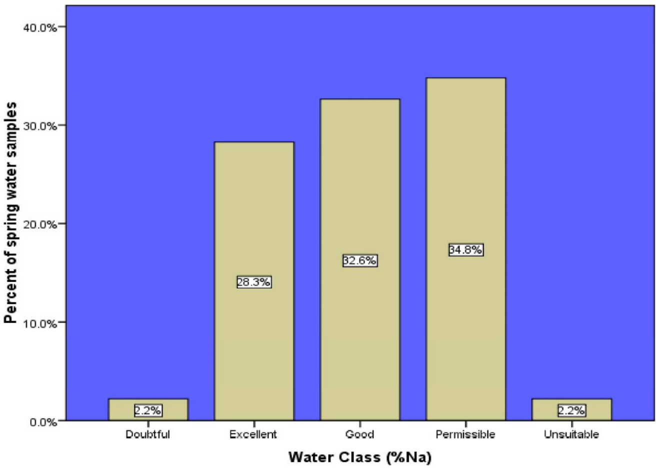

Fig.14. Classification of spring water on the basis of %Na

Table 8. The statistics after Principle component analysis

Parameters	Principle component loadings				
	1	**2**	**3**	**4**	**5**
pH	0.287	0.055	-0.594	0.36	0.419
TDS	**0.97**	0.109	0.087	0.067	-0.035
Na	**0.738**	-0.056	0.55	-0.083	0.119
K	0.179	-0.176	0.543	0.206	-0.401
Mg	**0.866**	-0.129	0.062	0.244	-0.059
Ca	**0.892**	-0.095	-0.218	0.05	-0.123
Fe	0.06	0.077	0.083	**0.91**	0.015
Pb	-0.084	**0.892**	-0.089	0.054	-0.072
Mn	0.099	-0.315	-0.315	**0.733**	-0.032
Cu	-0.111	-0.178	0.01	0.011	**0.909**
HCO_3	**0.928**	-0.237	-0.134	0.122	-0.059
Cl	-0.037	**0.839**	0.392	-0.089	0.007
NO_3	0.113	0.177	**0.867**	-0.096	0.132
F	-0.239	**0.872**	-0.079	-0.129	-0.095
SiO_2	**0.766**	-0.212	0.101	-0.105	0.086
Eigen value	6.282	2.801	2.109	1.682	1.248
Percentage of variables (%)	39.954	16.474	12.408	9.893	7.344
Cumulative percentage (%)	36.954	53.428	65.836	75.729	83.073

The silicate ions usually exist with the centrally located cations such as sodium, potassium, calcium magnesium and iron (Grotzinger, 2008). Therefore the above table is showing the positive and strong correlation with the cations. In this study, the concentration of HCO_3^- ion is higher, which indicates the dominance of mineral dissolution (Rao et al., 2017). As previously mentioned in Piper diagram, the spring water is $CaHCO_3$ type and the PC-1 is showing strong relationship between Ca^{2+} and HCO_3^- ion. PC-2 is contributing 16.474% in the total chemistry of spring water. Cl^- and F^- show strong positive correlation in PC-2 with loading of 0.913 and 0.840 respectively. The chloride ion has non-lithological source possibly through irrigation return flow with high rate of evaporation. Chloride is also derived from clay weathering products where drainage condition is poor. Fluoride is derived from F bearing minerals (hornblende, biotite, apatite) from surrounding country rocks (Rao et al., 2017). Third component, PC-3 contributes 12.408% of total hydrochemistry in spring water where positive correlation is found in NO_3^- ions. There is no known lithological source of NO_3^- ion in spring water therefore other sources like agriculture and domestic effluents can contribute as input of this ion. The forth component PC-4 is contributing to 9.893% of total hydrochemistry where positive correlation is found in Fe and Mn. These cations may come into water through geogenic source (shale and other clay minerals) (Penrose Jr, 1893). Fifth component PC-5 is contributing 7.344% in the hydrochemistry of spring water. Cu is only factor in this component with loading of 0.909. The state industrial report of Sikkim mentions that mining activity takes place in South Sikkim. The Pachekhani mine and Dikchu copper mine project was started during 9th five year plan from 1997-2002 (MSME, 2013-14). Therefore, fifth component in the study area may be due to mining activity.

CONCLUSION

The present study focusses on the assessment of spring water quality by hydrogeochemcial study and the suitability for drinking and irrigation purpose. The type of water was determined by Piper diagram. $CaHCO_3$ type of water was dominant in the study area along with the dominance of HCO_3^- ion. The saturation index of calcite, dolomite and goethite was negative which depicts the dissolution of these minerals into the water. The abundance of bicarbonate ion into samples was confirmed by the (Ca+Mg) vs. (SO_4+HCO_3) plot which showed the dominance of silicate weathering and ion exchange process in the study area. The chloro-alkaline indices were calculated and majority of samples have negative value which means the exchange of Ca^{2+} and Mg^{2+} ion of groundwater were replaced by Na^+ and K^+ ion of rock material. The drinking suitability of spring water was determined by calculation of hardness and water quality index of water. 76.1% of spring water samples were under soft water category and all the samples were under BIS standard limits. The water quality index of spring water samples was calculated which shows that 58.7% of water samples belong to excellent category. The irrigation suitability was determined by the Sodium absorption ration (SAR), Residual sodium carbonate (RSC) and percent sodium. The SAR value depicts the excellent category for spring water and RSC value explained the good category for irrigation purposes. The percent sodium explained that majority of samples had >60% of sodium which comes under excellent, good and permissible category for irrigation purposes.

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(Received: 22 December 2017; Revised form accepted: 15 February 2018)