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ORIGINAL ARTICLE

Hydrochemical evaluation of Rangit river, Sikkim, India: using Water Quality Index and multivariate statistics

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Abstract This study is aiming to focus on hydrogeochemical investigation of water samples from Rangit river basin and assessment of water quality for human consumption and agricultural purposes. River water is neutral to mildly alkaline, with dominance of K^+, Ca^{2+}, HCO_3^-, and SO_4^{2-} in ionic strength. K^+–Ca^{2+}–Mg^{2+}–HCO_3^- is the major hydrochemical facies in upstream river water, whereas Ca^{2+}–K^+–Mg^{2+}–HCO_3^- water-type dominates in downstream stretches of river. The weathering of rock-forming minerals mainly controls the solute acquisition process. The high equivalent ratios of $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ and the low ratio of $(Na^+ + K^+/TZ^+)$ reveal that the chemical composition of river water is mostly determined by carbonate weathering with partial contribution from silicate weathering. An evaluation of Water Quality Index of sampled river water indicates that the majority of the water samples are good–moderate for human consumption and domestic usages. Irrigation suitability of river water in relation to EC content, SAR, and RSC values suggests that river water is good–excellent type for agricultural applications.

Keywords Hydrogeochemistry · Multivariate statistics · Water Quality Index (WQI) · Irrigation suitability · Rangit river

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Introduction

Rivers play a vital role in human sustenance, because not only they constitute the main source of fresh water, but also they have been used for diverse purposes (Kazi et al. 2009; Pasquini et al. 2012). India has a large river network, which has been nurturing its vast fertile lands. The rapid urbanization, industrialization, intensive agriculture, and growing demand for energy have adversely affected the physicochemical parameters of ground and surface water. The river water chemistry is determined by several geological factors and many natural processes, such as temperature, precipitation rate, relief of the catchment, bedrock composition, ground water inflow, and vegetal cover (Stallard and Edmond 1987; Ahmed et al. 1998; Rajamani et al. 2009). The river water quality is highly sensitive to alterations to diverse anthropogenic activities, such as mining, industries, discharge of urban waste water, and fertilizers used in agriculture (Carpenter et al. 1998; Pasquini et al. 2012). Seasonal variation and surface runoff during the rainy season are also known to influence the composition and quality of river water.

Regional geology of the study area

Rangit river basin encompasses the western and southern district of Sikkim. The western portion is much higher in altitude, and deeply cuts into steep escarpments, while southern Sikkim is lower and fairly well cultivated. This configuration is partly due to the direction of the main drainage, which is southern. Rangit river is the dominant river of the West and South Sikkim, showing subdendentric drainage pattern. Rangit river originates from Talung glacier of Himalayan mountains in West Sikkim. This river is a perennial river, and is fed by the melting snow of the ice

caps in summer and the monsoon rains in July–August, as well as atmospheric precipitation that accumulates in the catchment areas during the monsoons. The valleys cut by the rivers are very deep and usually attain a steep gorge like structure. At the Rangit dam site near Legship, the catchment area drained about 979.02 km^2; of which rainfed catchment is 712 km^2, the balance area is snow fed. The annual inflow in the river at the dam site is estimated approximately 696,000 m^3. The Rangit river flows past the small towns, viz. Pelling, Legship (in West Sikkim), and Jorethang (in South Sikkim) before its termination to Teesta river at Melli (Choudhury 2006).

The climate of the Rangit river basin is cold and humid with mean temperature in the catchment area ranges from 5–8 °C to 22–26 °C. The intensity of annual average rainfall for the individual station at catchment area varies from 800 to 1500 mm. Major portion of the studied basin area (Fig. 1) is comprised of interbanded chlorite, sericite schist, phyllite, quartzite, and mica schist. In some sections of upstream stretches occurrence of dolostone, orthoquartzite, pebble, conglomerate, and interblended chlorite sericite are witnessed, whereas the middle section of the studied region is dominated with sandstone, shale, and carbonaceous shale. Recent alluvium of sandy loam, silty loam, and clayey material of varying thickness overlay the rock formations. The banks of the Rangit river depict silty clay sediments with large rock blocks. Many landslides are noted in the catchment area particularly in rainy season, which added siltation problems to the river (Choudhury 2006; Shroder 1989).

There is no previous record on the hydrogeochemical study of Rangit river basin to the best of our knowledge. The present research work aims to focus on (1) hydrochemical evaluation of river water and ion chemistry, (2) multivariate analysis, and (3) Water Quality Index (WQI) for domestic and agricultural uses.

Experimental methods

Collection and analysis of river water samples

Total 60 water samples were collected from 20 different sites of approximately 35-km stretch of Rangit river from Upper Legship to Melli following upstream to downstream flow during March–September, 2014. River water samples were collected in pre acid washed 1-L polythene containers, rinsed well with the sample water before filling it up to capacity, and immediately brought to the laboratory for further analysis of various physicochemical parameters. pH, EC, and TDS were measured on field by using hand analyzer (pH meter: Hanna HI 98121, and EC/TDS meter: Eutech con 510). The water parameters, viz. pH, EC, TDS, turbidity, combined CO_2, alkalinity (HCO_3^-), total hardness (TH), chloride, sulfate, phosphate, nitrate, sodium, and potassium, were analyzed as per Standard Methods (APHA 1998).

For estimation of heavy metals, water samples were collected in separated bottles and acidified with 1-ml conc. HNO_3 (Suprapure quality) immediately after collection to prevent the metals to precipitates. Concentrations of metals were analyzed by AAS (GBC Avanta).

Statistical interpretations and indices used

Conventional graphical methods were used, and multivariate statistical analyses [Pearson correlations, principal component analysis (PCA)] were performed (Microsoft XL Stat, version 12) to identify and interpret the relative behavior and interdependency of measured variables. WQI and other irrigation water quality indices were applied to assess the overall appraisal of river water for domestic and agricultural uses.
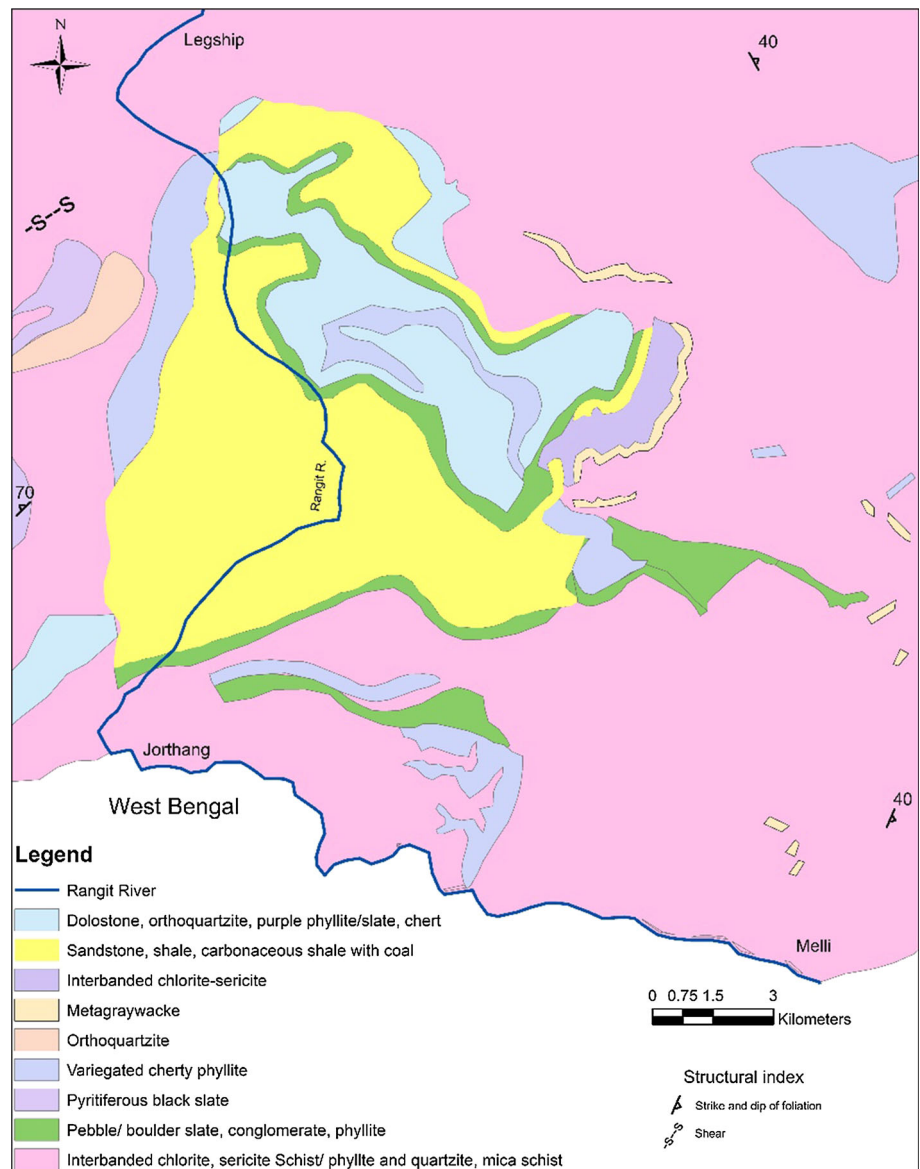
Quality control and assurance

Proper care has been taken during sample collection and preservation. Mark reagents (AR grade) and standard solutions were used for laboratory analysis and the preparation of intermediate standards. Each analysis for collected water samples was three times replicated to ensure the accuracy of analytical results. For metal analysis, each batch was consisting of blank (deionized water) and intermediate standard solutions. The R^2 values of standard curve for metals were Fe: 0.999, Pb: 0.996, Mn: 0.998, and Pb: 0.997, respectively. The precision and analytical accuracy were checked by using the standard reference material (NIST-SRM 1570) for water. Reproducibility of all experimental results was within 2 % standard error (SE) level of certified values for each metal.

Digital elevation model

Conceptually, a raster approach is ideal to represent surfaces. A raster surface is simply a grid of values in which each cell contains a single value representative of the observation on the earth that is covered by the cell. The raster surface that is generated by interpolating the available observations is known as digital elevation model (DEM). Here, a DEM is generated on the basis of each WQI sampling site. The interpolation process is based on an algorithm called distance transform. Interpolation is made between the source WQI and the WQI at equal-distance points from source locations. The output of the interpolated DEM is classified as a theme layer on the

Fig. 1 Geological map of Rangit river basin

Legend

— Rangit River

Dolostone, orthoquartzite, purple phyllite/slate, chert

Sandstone, shale, carbonaceous shale with coal

Interbanded chlorite-sericite

Metagraywacke

Orthoquartzite

Variegated cherty phyllite

Pyritiferous black slate

Pebble/ boulder slate, conglomerate, phyllite

Interbanded chlorite, sericite Schist/ phyllite and quartzite, mica schist

Structural index

Strike and dip of foliation

Shear

basis of WQI value. Entire work has been done on Geomatica V. 10.2 software.

Results and discussion

Hydrogeochemistry

The physicochemical analyses of river water sampled from various locations of the Rangit river basin along with the descriptive statistics of the analyzed data are shown in Tables 1 and 2.

The pH of water plays an important role in many types of geochemical equilibrium. The pH of analyzed river water samples varies between 7.02 and 7.95 mg/l with an average of 7.52 mg/l, indicating neutral to mildly alkaline nature of Rangit river basin water. Electrical conductivity denotes the capacity of substance or solution to conduct the electric current. In water, it is the property caused by the presence of ions. The average value of EC for water sample is 75 μS cm^{-1}. Total dissolved solid (TDS) indicates mainly the various kinds of minerals present in the water. TDS content in Rangit river waters varies from 50 to 200 mg/l, with the mean value of 64.5 mg/l. Total alkalinity of the water is its capacity to neutralize a strong acid and is characterized by the presence of all hydroxyl ions capable of combining with the hydrogen ion. Alkalinity of river water samples ranges from 40 to 130 mg/l with an average value is 56.5 mg/l. The hardness of water is due to the presence of alkaline earth, such as calcium and

Table 1 Hydrogeochemical characteristics of Rangit river water

Sampling station	pH	EC	TDS	TH	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Fe$_{Total}$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	PO$_4^{3-}$	NO$_3^-$	SiO$_2$	F$^-$	Water type
S1	7.95	80	90	48	5	25	10.08	5.56	1.36	61	4.99	19.44	0.36	0.987	0.91	0.145	K–Ca–Mg–HCO$_3$–SO$_4$
S2	7.88	90	80	44	6	25	10.08	4.58	1.39	85.4	4.99	20.19	0.06	1.594	0.93	0.144	K–Ca–HCO$_3$–SO$_4$
S3	7.68	90	80	44	6	26	10.08	4.58	3.02	73.2	9.99	19.64	0.125	1.391	0.92	0.142	K–Ca–Mg–HCO$_3$–SO$_4$
S4	7.52	90	80	48	6	27	11.76	5.56	3.76	85.4	9.99	18.96	0.1	1.78	0.93	0.145	K–Ca–Mg–HCO$_3$
S5	7.69	60	50	28	2	14	5.04	3.75	0.08	61	9.99	22.709	0.08	0.088	0.96	0.132	K–Mg–HCO$_3$–SO$_4$–Cl
S6	7.6	60	50	28	2	15	5.04	3.75	0	48.8	4.99	18.32	0.1	0.234	0.91	0.128	K–Mg–Ca–HCO$_3$–SO$_4$
S7	7.02	160	200	72	32	52	16.8	7.32	1.2	158.6	24.9	42.98	0.08	0.42	1.19	0.413	Na–K–HCO$_3$–SO$_4$
S8	7.7	60	50	28	2	14	5.04	3.75	0	48.8	24.9	9.44	0.05	0.478	0.9	0.134	K–Mg–HCO$_3$–Cl
S9	7.8	60	50	28	3	14	5.04	3.75	0.82	48.8	4.99	18.805	0.03	0.066	0.93	0.129	K–Mg–Ca–HCO$_3$–SO$_4$
S10	7.6	60	50	32	3	15	3.36	5.75	0.06	48.8	4.99	15.29	0.13	0.434	0.83	0.126	Mg–K–HCO$_3$–SO$_4$
S11	7.6	70	50	32	2	15	6.72	3.7	2.19	73.2	9.99	10.43	0.16	0.886	0.84	0.128	K–Ca–Mg–HCO$_3$
S12	7.6	60	50	32	3	15	8.4	2.68	0.61	73.2	9.99	18.64	0.08	0.522	0.93	0.125	Ca–K–HCO$_3$–SO4
S13	7.4	70	50	36	3	15	10.08	2.63	2.92	73.2	4.99	16.45	0.01	0.318	0.87	0.131	Ca–K–HCO$_3$–SO$_4$
S14	7.5	70	50	32	3	16	5.04	4.73	0	61	4.99	14.502	0.02	0.509	0.85	0.127	K–Mg–HCO$_3$–SO$_4$
S15	7.4	70	50	44	3	15	6.72	0.78	0	61	14.9	10.99	0.03	0.544	0.87	0.119	K–Ca–HCO$_3$–Cl
S16	7.4	70	50	32	3	15	8.4	0.73	0.2	73.2	9.99	8.64	0.025	0.925	0.89	0.116	Ca–K–HCO$_3$–Cl
S17	7.4	70	50	40	3	15	8.4	4.63	1.48	61	4.99	15.17	0.01	1.342	1.14	0.115	Ca–K–Mg–HCO$_3$–SO$_4$
S18	7.3	70	50	40	3	15	8.4	4.63	0.79	61	14.9	14.22	0.03	0.93	0.91	0.117	Ca–K–Mg–HCO$_3$–Cl
S19	7.2	70	60	40	3	16	10.08	3.61	0.27	61	9.99	11.79	0.16	1.696	0.89	0.106	Ca–K–Mg–HCO$_3$
S20	7.2	70	50	44	3	16	8.4	4.63	0.5	61	4.99	7.21	0.01	2.591	0.81	0.108	Ca–K–Mg–HCO$_3$

EC = μs/cm, except pH, rest all measured water parameters are expressed in mg/L^{-1}

Table 2 Range of values of chemical parameters in surface water of Rangit river water basin, WHO (1997), Indian Standards IS: 10500 (BIS 1991) for drinking water

Parameters	Min	Max	Mean	SD	WHO (1997)	BIS (1991)
pH	6.75	8.46	7.49	0.345	7–9.5	6.5–8.5
EC	50	160	73.21	20.009	–	–
TDS	40	200	63.92	30.591	1200	500–2000
Alkalinity	30	130	27.11	20.171	–	
HCO_3^-	48.80	158.60	68.93	23.84	–	200–600
Total hardness (TH)	28	72	37.48	9.504	500	300–600
Ca^{2+}	3.36	16.8	8.58	2.831	–	75–200
Mg^{2+}	0.73	7.32	3.61	1.520	–	30–100
Na^+	2	32	4.42	5.567	200	–
K^+	14	52	18.25	7.710	–	–
Cl^-	4.99	24.9	8.54	5.559	250	250–1000
SO_4^{2-}	7.21.	42.98	16.69	7.58	250	200–400
PO_4^{3-}	0.01	0.16	0.08	0.070	–	
NO_3^-	0.06	2.59	0.88	0.66	50	45–100
SiO_2	0.81	1.19	0.921	0.092	–	
F^-	0.160	0.153	0.142	0.054	1.5	1.0–1.5
Cu	0.0049	0.0098	0.0074	0.0014	1.0	1.5
Pb	0.039	0.054	0.047	0.005	0.1	0.1
Mn	0.00011	0.00020	0.000015	2.94	0.5	0.5
Fe_{Total}	0.04	3.76	1.06	1.02	0.3	0.3

magnesium. TH ranges from 28 to 72 mg/l, and the mean value is 38.6 mg/l. Therefore, the river water is of soft category (TH <75 mg/l).

The major anions constitute 75 % of the TDS. The anion chemistry of Rangit river basin is dominated by HCO_3^- followed by SO_4^{2-} and Cl^-. Bicarbonate alone comprises 68.93 % of the TDS, and its concentration ranges from 48.80 to 158.6 mg/l with an average of 68.33 mg/l. The plotted points on anion diagram shows that the sampled river water falls in the HCO_3^- field. Bicarbonate may be derived from the dissolution of carbonate and/or silicate minerals by carbonic acid. Sulfate (SO_4^{2-}) ions present in all surface water, and their concentrations are limited by the presence of Ca^{2+} ions with which they formed a slightly soluble. The main source of sulfate in surface water is due to the presence of sedimentary rock, which includes gypsum and anhydride. Sulfate concentration in the study area of river basin varies from 7.21 to 42.98 mg/l with an average value of 16.69 mg/l. SO_4^{2-} contributes 16.69 % of anionic strength. SO_4^{2-} content is notably high at sampling point S7 of Rangit river basin, which can be explained due to mixing of sulfur rich hot spring water to river at this site. Cl^- constitutes 9.72 % of total anions (TZ^-), and its concentration varies from 4.99 to 24.9 mg/l in river water with an average of 9.72 mg/l. The presence of low concentration of the Cl^- suggests that there is no anthropogenic contribution, such as domestic wastewater and industrial discharge. Concentration of nitrate in river water is relatively low (ranges from 0.06 to 2.59 mg/l with

average of 0.88 mg/l), while very less amount of phosphate is observed (average 0.8 mg/l) in the sampled river water. Fluoride content in the sampled water contributing less than 1 % to the anionic balance (ranges 0.10 to 0.41 mg/l with average 0.14 mg/l), and its source in the river water can be attributed to weathering of F^- bearing rock-forming minerals. Dissolved silica in the river water varies from 0.38 to 2.28 mg/l with an average value of 1.48 mg/l, accounting less than 1 % of the TDS. The average concentration of the silica is much lower than Indian rivers (7 mg/l) average. The low amount of dissolved silica in the river waters signifies limited contribution from silicate weathering.

The major cation constitute 25 % of the TDS with predominance of K^+ (0.49) and Ca^{2+} (0.05) followed by Na^+ (0.21) and Mg^{2+} (0.33). The concentration of K^+ in the river water samples ranges from 14 to 52 mg/l, with an average value of 18.25 mg/l. Major sources of K^+ in the river water are feldspar and mica rich rock occur within the river basin. Calcium is one of the most abundant elements found in the natural water. It is important ion imparting the hardness to the water. At high pH, much of its quantities may get precipitated as $CaCO_3$. The concentration of Ca^{2+} ion in the Rangit river basin varies from 3.36 to 16.8 mg/l, with an average concentration of 8.14 mg/l. The sources of Na^+ are various rocks, weathering products of silicate rocks and its displacement from the absorbed complex of rocks and soil by calcium and magnesium. In the study area, Na^+ varies from 2 to 32 mg/l the (average 4.42 mg/l).

Potassium (K^+) is an important parameter for water quality. Sources of potassium are potash feldspar ($KAlSi_3O_8$), mica (KAl_2) $(AlSi_3O_{10})(F,OH)_2$, and less commonly sylvite (KCl). The low level of K^+ in natural waters is a consequence of its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals. This study reveals that K^+ concentrations in river water samples range from 14 to 52 mg/l and mean value is 19 mg/l. Magnesium (Mg^{2+}) occurs in all kinds of natural waters, but its concentration remains generally lower than the calcium (Ca^{2+}). The concentration of Mg^{2+} ranges from 0.73 to 7.32 mg/l, with an average value of 4.05 mg/l.

Spatial distribution of heavy metals

Heavy metals are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity, and ability to be incorporated into food chains. Their occurrence in the environment results primarily from anthropogenic activities, though natural processes that may enrich waters with trace elements also play a noticeable role (Loska and Wiechuła 2003). The water quality of Rangit river is affected by factors, viz. weathering of rocks and ongoing road construction activities, agricultural drainage water, industrial, and domestic waste discharges directed into the river water.

Figure 2 shows the spatial variation heavy metals (Fig. a—Cu, Fig. b—Pd, Fig. c—Mn, and Fig. d—Fe) along the stretch of Rangit river. The Cu values ranges from 4.9 to 9.8 µg/l with an average value of 7.4 µg/l. Station 8 shows high Cu content (Table 2), where extensive farming is practiced, and it is expected that Cu may enter into the aquifers through agrochemicals. Pb value ranges from 0.04 to 0.06 mg/l with an average value of 0.05 mg/l. The Mn content ranges from 0.003 to 0.006 mg/l with the mean value of 0.004 mg/l (Table 2), while the concentration of Fe varies from 0.3 to 3.76 mg/l with an average value of 1.06 mg/l. The high Fe concentration in these waters may be assigned to the soil–water interaction, especially in the middle part of the river (Fig. d).

Since the concentrations of metals are very low (in comparison with those of major ions and as well as with reference to WHO standards), therefore, they were not included in multivariate statistical analysis and computation of WQI.
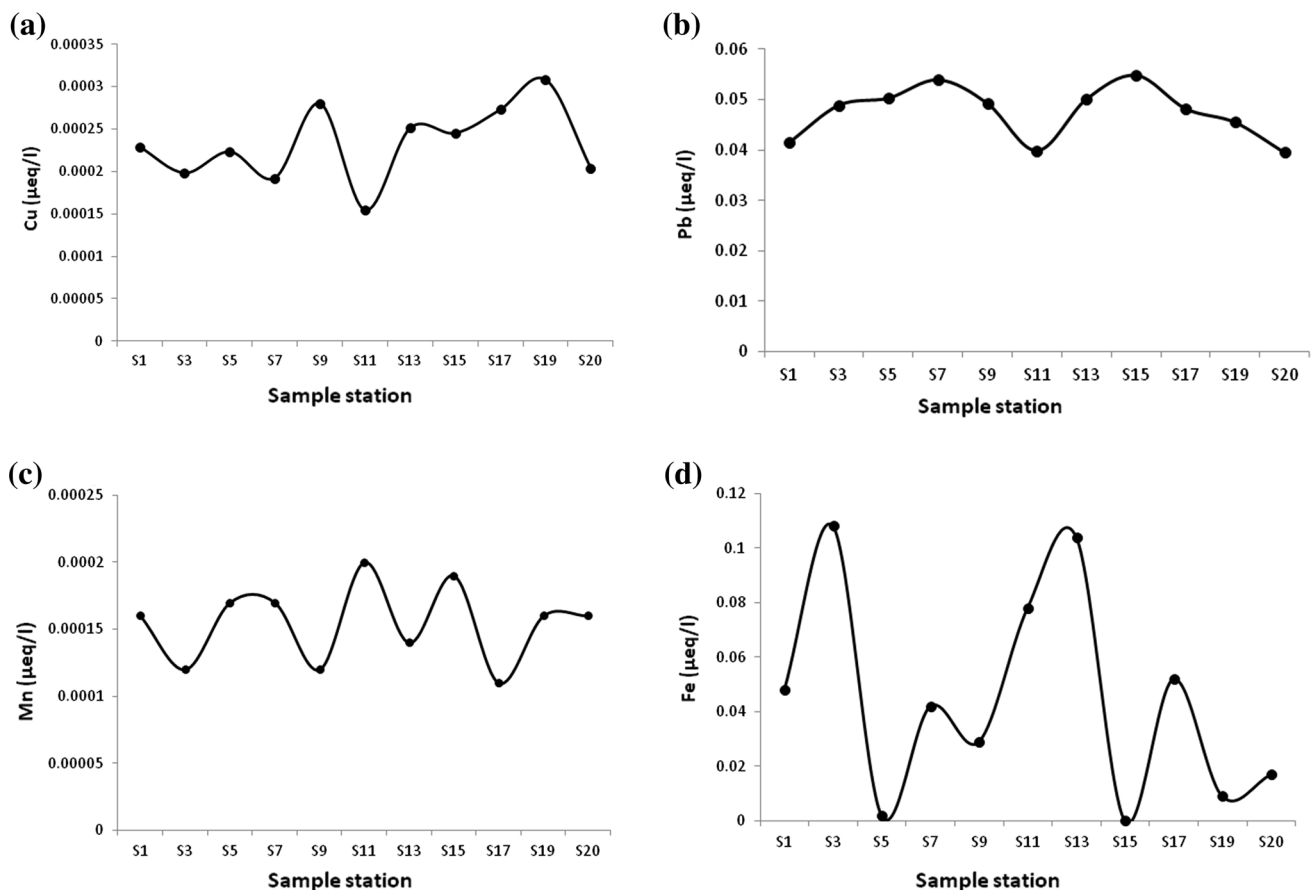

Fig. 2 Spatial variations in concentrations of heavy metals Cu (**a**), Pb (**b**), Mn (**c**), and Fe (**d**) along the stretch of Rangit river
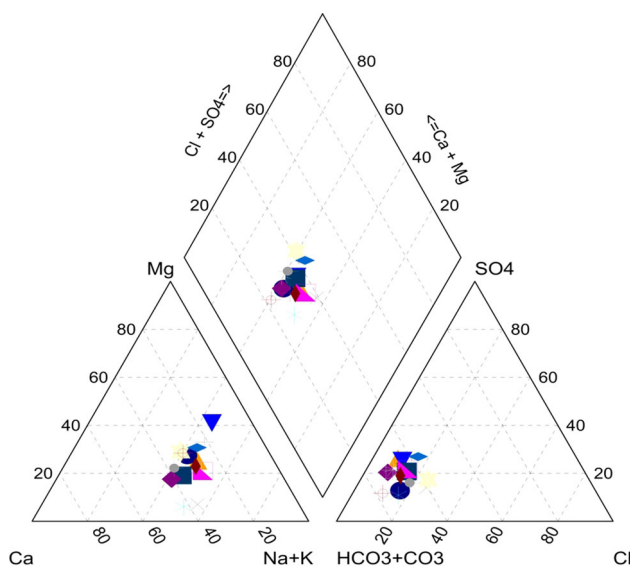
Fig. 3 Piper trilinear diagram showing hydrogeochemical facies of river water

Hydrogeochemical facies

From trilinear diagram analysis (Piper 1944; Fig. 3) and analyzed river water samples (Table 1), it is observed that Ca–K–Mg HCO₃ and K–Ca–Mg–HCO₃ types are the dominant hydrogeochemical facies in the study area of Rangit river basin. The 35 % of examined river water samples fall under Ca–K–Mg HCO₃ category, and are

dominant water-type in downstream stretches of the river, whereas 30 % of the samples are of the K–Ca–Mg–HCO₃ type and the principal water-type in upstream stretches of river. This situation can be corresponded with the prevailing rock-type (Fig. 1) at upstream and downstream stretches of Rangit river basin. Predominance of K^+ and Ca^{2+} in both upstream and downstream stretches of river can be attributed to release of K^+ and Ca^{2+} due to weathering of phyllite and mica schist, while major anionic component HCO_3^- can be corresponded with carbonate weathering at river basin.

Hydrogeochemical process

The hydrogeochemistry of river water is mainly controlled by the chemical composition of rain water, water–rock interaction phenomena, and anthropogenic activities in the river basin (Singh et al. 2008). The average low Na/Cl (0.49) in comparison with marine aerosols indicates higher contribution to dissolved salt from atmospheric precipitation, whereas high K/Cl ratios (1.95) are most likely due to the weathering of rock forming minerals. Similar kind of phenomena is also reported by (Sarin et al. 1989; Singh et al. 2005). Gibbs (1970) plot (Fig. 4) also emphasizes weathering as a dominant factor in controlling the river water chemistry of the study area. Both the scatter plots, i.e., $(Ca^{2+} + Mg^{2+})$ vs $(HCO_3^- + SO_4^{2-})$ and $(Ca^{2+} + Mg^{2+})$ vs HCO_3^-, suggest significant contribution

(a)

(b)
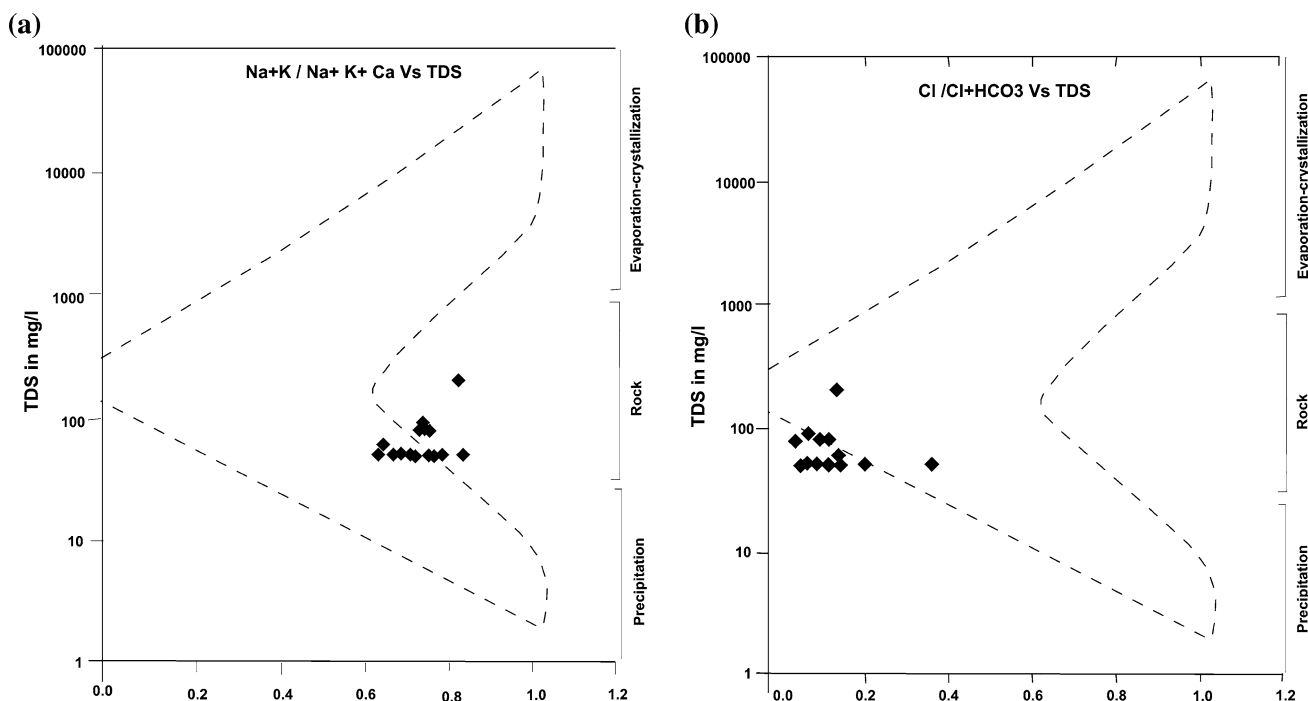
Fig. 4 Gibbs diagram representing the ratio of $Na^+ + K^+/(Na^+ + K^+ + Ca^{2+})$ (Fig. 3a) and $Cl^-/(Cl^- + HCO_3^-)$ (Fig. 3b) as a function of TDS (Gibbs 1970)

Fig. 5 Scatter plot of $HCO_3^- + SO_4$ vs $Ca^{2+} + Mg^{2+}$ (**a**), HCO_3^- vs $Ca^{2+} + Mg^{2+}$ (**b**), total cation vs $Ca^{2+} + Mg^{2+}$(**c**), Cl^- vs $Na^+ + K^+$ (**d**), total cation vs $Na^+ + K^+$ (**e**), and $Na^+ + K^+$ vs $Ca^{2+} + Mg^{2+}$ (**f**)
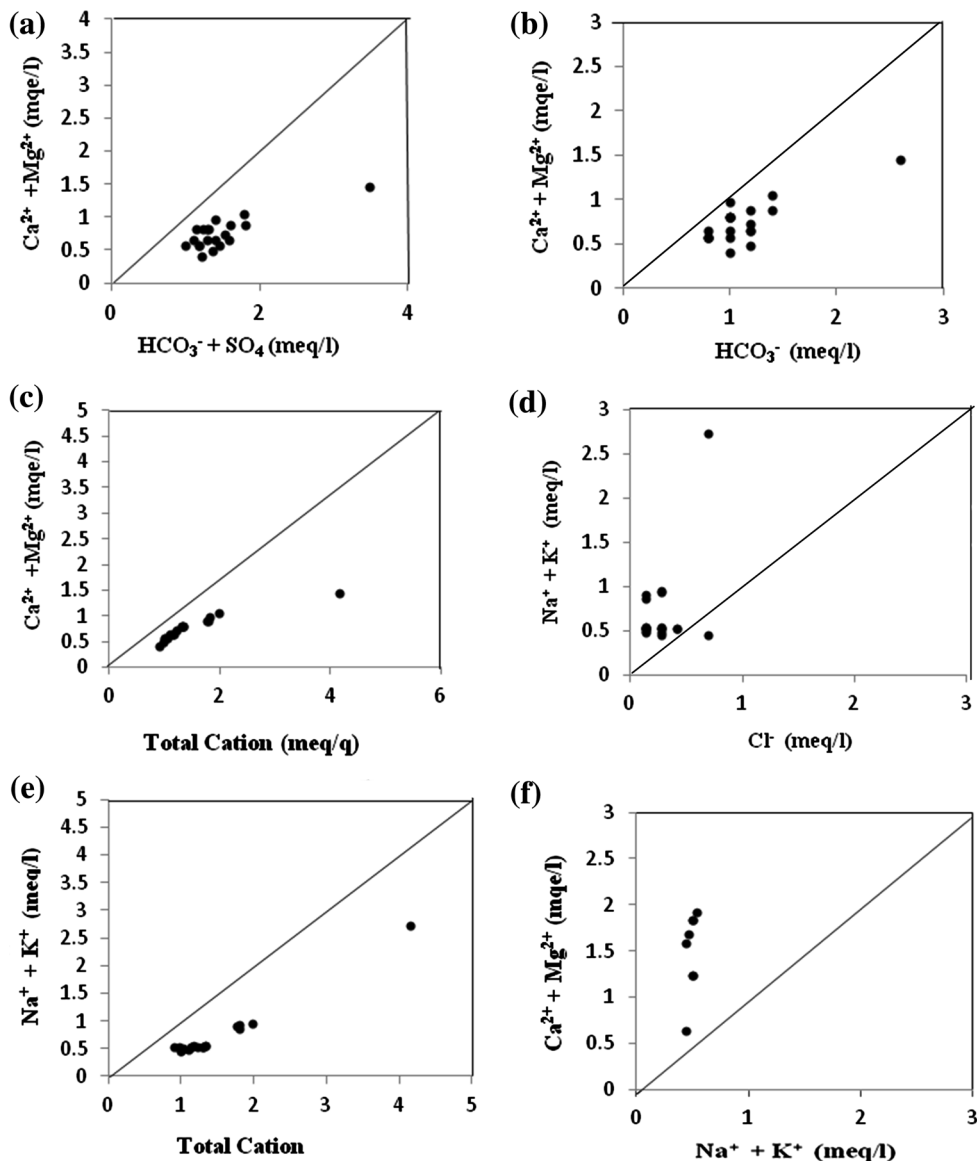
from noncarbonate source, and excess bicarbonate alkalinity should be balanced by the alkalis (Fig. 5a, b). In comparison with silicate breakdown, rapid dissolution of carbonate rocks is the major solute acquisition mechanism in the aquatic system (Sarin and Krishnaswami 1984). Furthermore, increasing contribution of Na^+ and K^+ with increasing dissolved solids (Fig. 5c) has been more pronounced in the river basin. The Na^+ and K^+ in aquatic systems are mainly derived from the atmospheric sources and/or from the weathering of alkaline silicates rich in Na^+ and K^+, but in the study area, significantly high $(Na^+ + K^+)/Cl^-$ ratio, i.e., 3.02 suggests that most of the alkalis originate from the weathering of silicates (Fig. 5d). High ratio of $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$, i.e., 10.57 and low ratio of $(Na^+ + K^+)/TZ$ (0.001) reveal that the chemical composition of the Rangit river water is largely

controlled by carbonate weathering with limited contribution of silicate weathering (Fig. 5e, f).

Saturation indices and water mineral equilibrium

Saturation Index (SI) is commonly used tool to determine the equilibrium state of river water (Garrels and Mackenzie 1971; Stumm and Morgan 1981). The SI is calculated as $SI = \log 10 (IAP/Ksp)$, where $IAP =$ ion activity product and $Ksp =$ solubility product at given temperature. In this study, the plot of calcite (SIc) vs dolomite (SId) signifies that sampled river waters are undersaturated with respect to dolomite and calcite (Fig. 6), and SIc values are higher than SId values. This undersaturation condition can be linked to dissolution of Ca–Mg carbonate under suitable physicotemporal condition.
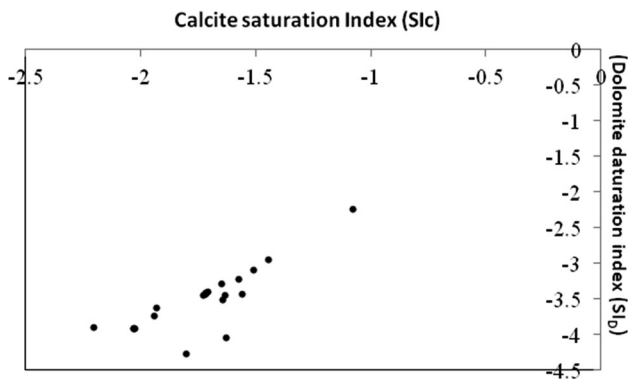
Fig. 6 Plot of saturation indices (SI) for calcite (SI_c) vs dolomite (SI_d)

Statistical interpretation

The chemical composition of the groundwater is characterized by major cations and anions, such as Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, PO_4^{3-}, SiO_2, and F. The correlation matrix of various water physical and chemical parameters is tabulated in Table 3. EC and TDS have a significant positive correlation ($p < 0.05$) with TA, TH, Na^+, K^+, Ca^{2+}, HCO_3^-, SO_4^{2-}, SiO_2, and F^-. Calcium has a significant positive correlation with HCO_3^-, whereas Mg^{2+} with SO_4^{2-}. This may suggest that carbonate weathering is the dominant weathering process in controlling river hydrogeochemistry.

Factor analysis (PCA) is a multivariate statistical method, which reproduces general relationship between measured variables by executing factor(s) and/or variable pattern that help to classify the original data set. The geological interpretation of factors gives an insight into the main hydrogeochemical process, which control the distribution of measured variables. PCA on the composite data sets resulted three factor (eigen values >1) that explained 86.19 % of the variability of data (Table 4). Result shows the factor loading of each variable within three selected factor representing possible sources of variation in the hydrochemistry of river water. Factor 1 shows loading of pH, TDS, TH, Ca^{2+}, Mg^{2+}, Cl^-, PO_4^{3-}, and NO_3^-; therefore, it can be attributed to anthropogenic origin/sources. Factor 2 shows the higher loading of Na^+, K^+, SO_4^{2-}, and F^-, while Factor 3 shows the higher loading of EC, alkalinity, and SiO_2. HCO_3^- ions execute higher loading for both Factor 2 and Factor 3. Factor 2 and Factor 3 together signifies geogenic attributes, viz. weathering of mineral bearing rocks, soil erosion, and surface runoff during rainy season. Hydrochemical process in studied river water is controlled by both SiO_2 and HCO_3^- weathering, of which HCO_3^- weathering appears to be the dominant.

Assessment of river water quality

Evaluation Water Quality Index)

The quality of sampled river water in relation to human consumption has been assessed by comparing with WHO (1997), and Indian standards (BIS 1991) for drinking water (Table 2), which shows that the surface water from Rangit basin is fit for drinking and domestic uses with a few exceptions.

WQI is a very useful technique frequently used by the researchers to assess the overall quality of surface and ground water samples for drinking and domestic uses (Sahu and Sikdar 2008; Yidana and Yidana 2010; Edet et al. 2013). WQI is defined as a rating that reflects the composite influence of various water quality parameters (Sahu and Sikdar 2008). For calculation of WQI, each water quality parameters were assigned a weight (W) based on their relative importance on water quality. Next, computation of relative weight (W_r) using the equation: $W_r = W/\sum W$, where W is the assigned weight of each parameters and $\sum W$ is sum of weights of all the parameters (Table 5). In this study, $\sum W$ is considered as 35.

In the third step, a quality rating scale Q_i was computed for each parameters:

$$Q_i = (C_i/S_i) \times 100$$

where C_i and S_i represent the measured concentrations of each parameter and WHO standard/World average for the same parameter, respectively.

Finally WQI was calculated as:

$$SI = Q_i \times W_r$$

$$WQI = \sum SI$$

The computed WQI was classified as: excellent (WQI <25), good (WQI: 25–50), moderate (WQI: 51–75), poor (WQI: 76–100), and very poor (WQI >100).

In this study, the calculated WQI value of sampled river water (Table 6) revealed that majority of water samples are of good to moderate category. 50 % water samples are classified as good, 20 % samples are of moderate type, and 30 % of samples are poor to very poor type category. Highest WQI value is observed in sampling points S3, S4, and S13.

On the basis of calculated WQI value at different sampling stations of examined stretch of Rangit river, a GIS-based river zonation map is constructed (Fig. 7). A poor water quality of Rangit river at Legship and Rishi (sampling points 2, 3, 4) and Nayabazar and Jorethang area (sampling points 11, 12, 13) can be attributed to the domestic waste discharge from the existing populated area and urban development at the bank of the river. Maximum

Table 3 Correlation matrix of physicochemical parameters

Variables	pH	EC	TDS	TA	TH	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Fe$_{Total}$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	PO$_4^{3-}$	NO$_3^-$	SiO$_2$	F$^-$
pH	1																
EC	−0.389	**1**															
TDS	−0.296	**0.970**	1														
TA	−0.437	**0.946**	**0.905**	1													
TH	**−0.445**	**0.911**	**0.872**	**0.817**	1												
Na$^+$	−0.424	**0.962**	**0.975**	**0.925**	**0.837**	1											
K$^+$	−0.256	**0.979**	**0.986**	**0.906**	**0.891**	**0.950**	1										
Ca^{2+}	−0.433	**0.853**	**0.798**	**0.850**	**0.883**	**0.755**	**0.823**	1									
Mg^{2+}	−0.031	**0.555**	**0.606**	0.404	**0.526**	**0.551**	**0.627**	0.364	1								
Fe	0.083	0.343	0.244	0.344	0.356	0.173	0.348	**0.534**	0.260	1							
HCO$_3^-$	−0.416	**0.902**	**0.882**	**0.944**	**0.746**	**0.901**	**0.881**	**0.778**	0.393	0.275	1						
Cl$^-$	−0.350	**0.467**	**0.487**	**0.473**	0.368	**0.533**	0.434	0.318	0.073	−0.115	0.417	1					
SO$_4$	−0.093	**0.788**	**0.858**	**0.772**	**0.626**	**0.852**	**0.837**	**0.588**	**0.586**	0.211	**0.797**	0.303	1				
PO$_4^{3-}$	0.386	0.139	0.255	0.041	0.237	0.081	0.250	0.199	0.335	0.206	−0.024	−0.057	0.142	1			
NO$_3^-$	−0.241	0.126	0.010	0.055	0.355	−0.057	0.098	0.377	0.183	0.318	−0.023	−0.192	−0.307	0.115	1		
SiO$_2$	−0.252	**0.639**	**0.663**	**0.627**	**0.549**	**0.687**	**0.625**	**0.555**	0.397	0.150	**0.625**	0.368	**0.730**	−0.069	−0.118	1	
F$^-$	−0.364	**0.919**	**0.955**	**0.899**	**0.756**	**0.984**	**0.915**	**0.672**	**0.541**	0.125	**0.892**	**0.569**	**0.872**	0.075	−0.195	**0.682**	1

Values in bold are different from 0 with a significance level alpha = 0.05

Table 4 Factor analysis with a factor pattern

	F1	F2	F3
pH	−0.752	−0.281	0.597
EC	0.165	0.441	0.882
TDS	0.813	0.425	0.398
Alkalinity	0.613	0.217	−0.760
TH	0.985	0.067	−0.160
Ca^{2+}	−0.830	0.495	−0.257
Mg^{2+}	−0.859	0.495	0.132
Na^{+}	−0.391	0.789	0.473
K^{+}	−0.423	0.859	0.288
HCO_3^{-}	0.283	0.674	−0.683
Cl^{-}	0.681	0.265	−0.090
SO_4^{-2}	0.380	0.901	0.208
PO_4^{-3}	0.790	0.389	0.473
NO_3^{-}	−0.810	0.554	−0.193
SiO_2	−0.285	0.498	−0.819
F^{-}	−0.045	0.977	−0.207
Eigen value	10.553	3.873	1.235
Variability (%)	47.968	17.603	5.612
Cumulative (%)	47.968	65.572	86.191

Table 5 Parameters, Standards, and Weights used for this study

Parameters	WHO (1993)	World average (Turekian 1977)	Assigned weights (W)	Relative weights (W_r)
pH	7.5	–	4	0.114
TDS	1000	–	4	0.114
Hardness	75	–	2	0.057
Ca^{2+}	100	13.40	2	0.057
Mg^{2+}	30	3.40	1	0.029
Na^{+}	200	5.20	1	0.029
K^{+}	12	1.30	1	0.029
HCO_3^{-}		52.00	3	0.086
NO_3^{-}	50	–	5	0.146
SO_4^{2-}	250	8.30	4	0.114
Cl^{-}	250	5.80	5	0.146
Fe (Total iron)	0.3	–	3	0.086
Total			35	1.00

deterioration of water quality has been observed at sampling point 4, which can be explained due to the presence of hot water spring at Rangit river basin at Rishi; high sulfur enriched hot spring water directly get mixed with the flowing river water due to gathering of local residents, visitors/tourist, and small human settlement at the bank of Rangit river. Moderate water quality at various sampling points (viz. 1, 9, 17, and 18) of Rangit river can be explained by soil erosion, fragmentation rocks and

Table 6 Water sample location, estimated WQI and water classification

Sample no	WQI value	Water category
SI	72.92	Moderate
S2	76.7	Poor
S3	121.91	Very Poor
S4	145.34	Very Poor
S5	30.91	Good
S6	26.57	Good
S7	50.02	Moderate
S8	27.18	Good
S9	28.53	Good
S10	48.16	Good
S11	93.02	Poor
S12	93.07	Poor
S13	114	Very Poor
S14	28.59	Good
S15	29.19	Good
S16	35.45	Good
S17	71.69	Moderate
S18	52.15	Moderate
S19	37.24	Good
S20	43.74	Good

minerals due to ongoing road construction activity along the stretch of Rangit river. River water quality at remaining of sampling stations and major stretch of river Rangit is noted as good quality.

Suitability for irrigation purposes

The FAO guidelines were used to interpret water quality for irrigation (Ayers and Westcot 1985). These guidelines emphasize the long-term influence of water quality on crop production and soil conditions. EC and Na^+ content are very useful parameters used to classify irrigation water. High salt content (high EC) in irrigation water results formation of saline soil, while high Na^+ content can be corresponded to the development of alkaline soil. EC value of sampled river water (Table 7) is very much within the permissible limit and categorized as 'excellent type' as recommended by Raghunath 1987. The high quantity of salts, especially Na^+ present in the water affects the soil structure, reduces permeability and aeration, and results alkaline soil, which indirectly affect the plant growth. The sodium or alkali hazard in the use of water for irrigation is determined by the absolute and relative concentration of cations and is expressed in terms of sodium adsorption ratio (SAR), which can be estimated as:

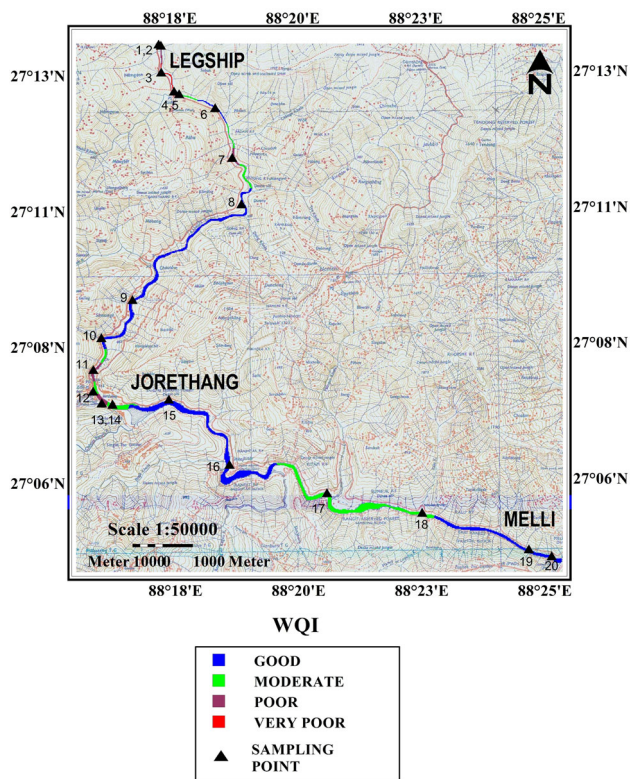$$SAR = Na^+ / \sqrt{(Ca^{2+} + Mg^{2+})/2}$$

Fig. 7 GIS-based schematic map showing Water Quality Index of stretch of Rangit river. Sampling points: *1* Upper Legship, *2* Legship Market, *3* Lower Legship, *4* Rishi-hot spring, *5* Rishi village, *6* Rayong, *7* Dumra, *8* Chautare, *9* Samsing, *10* Karfecter area, *11* Nayabazar Market, *12* Nayabazar Residential, *13* Jorethang, *14* Chirberey, *15* Salgari, *16* Mazitar, *17* Kitam, *18* Sumbuk, *19* Ralu, and *20* Melli Bazar

There is a significant relationship between SAR values of irrigation water and the extent to which sodium is absorbed by the soils. If water used for irrigation is high in sodium and low in calcium, the cation-exchange may become saturated with sodium. This can destroy the soil structure owing to the dispersion of the clay particles

(Richards 1954). In this study, SAR value ranges from 0.87 to 9.22, which shows that river water is of excellent type for irrigation (Table 7). The plot on data on the US Salinity diagram, in which that EC is taken as salinity hazards and SAR as alkalinity hazards, shows that all the river water samples are within C1S1 category (Fig. 8). This shows that the sampled river water with low salinity and low alkalinity is suitable for agricultural application with no risk of salinity and/or alkalinity hazards.

The presence of bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}) in excess of alkaline earths ($Ca^{2+} + Mg^{2+}$) may influence the suitability of irrigation water due to precipitation Ca^{2+} and Mg^{2+} in carbonate form (Karanth 1989), which is evaluated by calculating residual sodium carbonate (RSC):

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

The calculated RSC values of water samples from Rangit river basin ranging 0.019–0.42 meq/l, with an average of 0.193 meq/l suggests that river water is safe and is of excellent category for agricultural application.

Conclusion

The hydrogeochemical analysis of the collected water samples from the Rangit river reveals that the water is neutral to slightly alkaline; K^+ and Ca^{2+} are the dominant cations, and HCO_3^- and SO_4^{2-} are the dominant anions. The saturation indices for calcite (SI_c) and dolomite (SI_d) express that most of the water samples are undersaturated, thereby indicating more dissolution of calcium and magnesium. The concentration of low dissolved silica and higher ratios of ($Ca^{2+} + Mg^{2+}$)/($Na^+ + K^+$) along with a strong correlation of HCO_3^- with Ca^{2+} and Mg^{2+} signify carbonate weathering with limited contribution from silicate weathering. The river water chemistry is also

Table 7 Suitability of river water for irrigation purpose

Quality parameters	Reference/propose by	Range	Classification	Measured value	Examined water type
Electrical conductivity (EC: µs/cm)	Raghunath (1987)	<250	Excellent	50–160	Excellent
		250–750	Good		
		750–2000	Doubtful		
		>2000	Unsuitable		
Sodium adsorption ratio (SAR)	Richards (1954)	<10	Excellent	0.87–9.22	Excellent
		10–18	Good		
		18–26	Doubtful		
		>26	Unsuitable		
Residual sodium carbonate (RSC)	Karanth (1989)	<1.25	None	0.019–0.42	Excellent
		1.25–2.5	Slight-moderate		
		>2.5	Severe		

Fig. 8 US salinity diagram for classification of irrigation water (after Richards 1954)
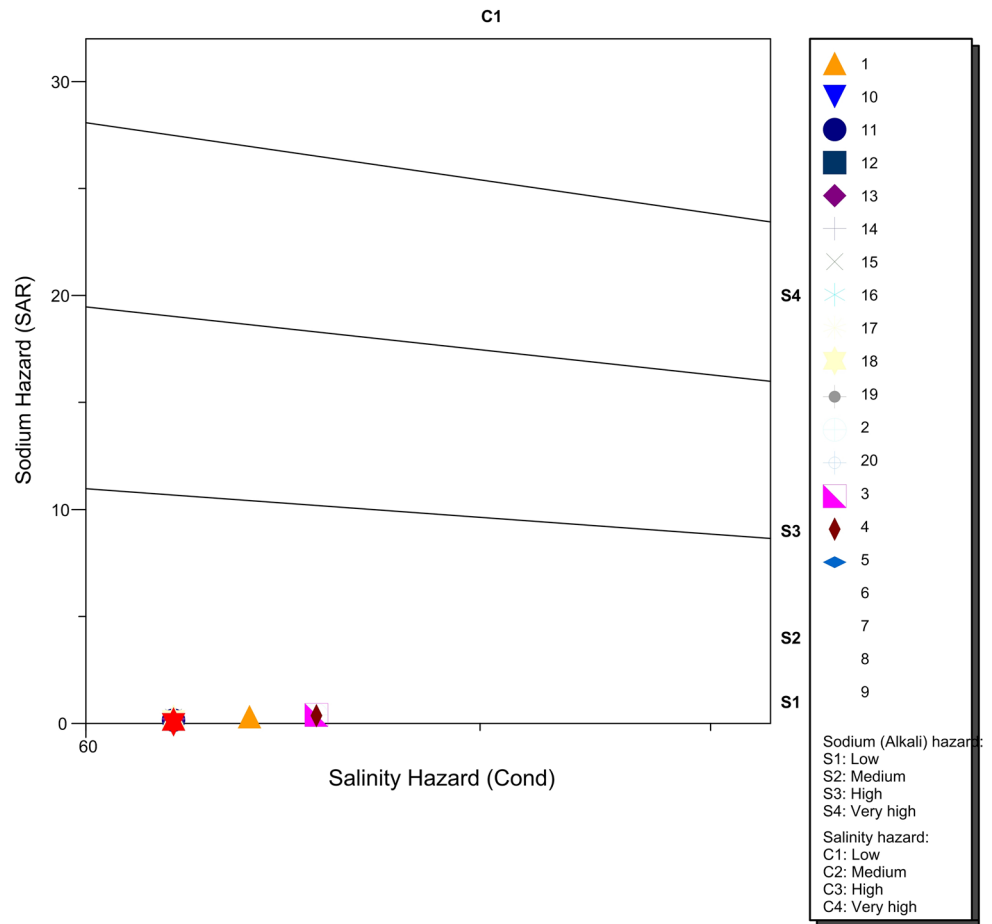
influenced by hot spring discharge at the upstream stretch of river at sampling station 4. WQI study of sampled water revealed that upstream stretch of Rangit river water is of poor quality in comparison with downstream river water samples. This situation is observed, because the upstream stretch of Rangit river is flowing by the edges of densely populated area, viz. Legship, Rishi, Nayabazar, and Jor-ethang, and subsequent discharges from residential and market areas coupled with other anthropogenic activity lead to decline in river water quality, whereas the down-stream stretch of Rangit river is mostly flowing through forests and sparsely populated areas, therefore exhibiting good–excellent quality of water. Overall investigation has shown that, except few exceptions Rangit river water is suitable for human consumption as well as domes-tic/household uses, and falls very much within the acceptable range for irrigation applications.

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