

# Evaluation of Hydrogeochemical Processes and Dissolve Ion Chemistry in Satopanth Tal, Garhwal Himalaya, India

Subhrajit Das

Annamalai University

Sivaprakasam Vasudevan (✉ [devansiva@gmail.com](mailto:devansiva@gmail.com))

Annamalai University <https://orcid.org/0000-0002-2434-9130>

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## Research Article

**Keywords:** Major ion chemistry, Hydrogeochemical processes, Himalayan Lake, Carbonate Weathering, Stable Isotope

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**Evaluation of hydrogeochemical processes and dissolve ion chemistry in Satopanth Tal, Garhwal Himalaya, India**

Subhrajit Das<sup>1</sup>, Sivaprakasam Vasudevan<sup>2\*</sup>

1, 2- Department of Earth Sciences, Annamalai University, Tamilnadu, India

1- subhrajitdas434@gmail.com, 2\*-Corresponding author: devansiva@gmail.com

ORCID ID: 1- 0000-0002-5074-7802, and 2- Orcid ID 0000-0002-2434-9130

**Abstract**

To grasp meltwater chemistry and geochemical processes influencing hydrogeochemistry, major ion chemistry of the glacial lake Satopanth Tal was carried out to provide relevant details on the dissolved ions sources, weathering, and hydrogeochemical processes as well as anthropogenic activities taking place throughout the lake setting. Twenty-one surficial water samples were collected and 12 different physicochemical parameters were analyzed to understand the hydrogeochemistry of the study area. The mean pH value was estimated to be 6.9 in the lake water, which indicates a marginally acidic. The ionic contribution through the organic matter decomposition has been indicated by the observation of dominancy of the total anions over the total cations. The most abundant anion was  $\text{Cl}^-$  in Satopanth Tal, while  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were significant cations in the water. The high ratios of  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{TZ}^+$ ,  $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ ,  $\text{HCO}_3^-/(\text{Ca}^{2+} + \text{Mg}^{2+})$ , and the higher  $\text{Ca}^+/\text{Na}^+$ ,  $\text{Mg}^+/\text{Na}^+$  and  $\text{HCO}_3^-/\text{Na}^+$  ratio indicate the supremacy of the weathering of carbonate as a significant source of dissolved ions in the study area's lake water. The lower equivalent ratios of  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  are measured and substantially comparable results are observed that have been expected from the Gibbs plot and the stable isotope analysis suggests a reasonably significant contribution to the chemical composition of the Satopanth Tal water by these ions from atmospheric precipitation. The correlation and factor analysis show that water chemistry at Satopanth Tal is primarily influenced by weathering processes such as weathering of carbonate and silicate, pyrite oxidation.

**Keyword:** Major ion chemistry, Hydrogeochemical processes, Himalayan Lake, Carbonate Weathering, Stable Isotope

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## Declarations

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## Introduction

Lakes are an imperative part of the cycling of components. The components brought to the lake are not principally fixed on the sediments and can be delivered back to the water-segment with the change in environmental conditions (Forstner et al., 1983; Håkanson, et al., 2004; Singh et al., 2005; Khadka and Ramanathan et al., 2021). “The investigational research of hydrogeochemistry is indispensable to decide the genesis of the chemical constitution of groundwater as well as surface water” (Zaporozec, 1972). Thus, estimating the lake water chemistry is crucial as it assists us with assessing the disintegration rate, and the geochemical changes of that specific area. Papatheodorou et al (2006) has suggested that besides several important natural processes like precipitation and weathering activities, other different activities such as industrial, rural, and urban activities are also the major parameters on which the quality of water depends, as the chemistry of water is a crucial index to understand the catchment lithology, soil erosion, and anthropogenic activities, etc. Vasudevan et al (2013) infer the different lithologies can alter the chemistry of surface water, as water passes through them. Therefore, precipitation water penetrates directly into the soil zones causing the dissolution of soil particles. Hence, during the flowing of water from the recharge point to the discharge point, several geochemical processes act to affect the water quality (Peiyue et al., 2014). “High altitudes lakes are endangered to atmosphere inputs than the lowland lakes due to different components like environment, shallow soil, little watershed, and so on” (Roshia et al., 2012).

Different water chemistry research has been carried out by several researchers on high-altitude lakes of the Indian Himalayas (Chakrapani 2002; Das 2005; Jeelani and Shah 2006; Dash et al. 2008; Saini et al. 2008; Sarah et al. 2011; Purushothaman et al. 2012; Najar and Khan 2012; Khan et al. 2012; Singh and Jain 2013; Sheikh et al. 2014; Singh et al. 2016; Khadka et al. 2021). However, no low down assessment has been done in the moraine-dammed lake Satopanth Tal in advance beside Bhambri et al. (2013) proposed the area type by using the satellite imageries and Kumar et al. (2017) on water quality index alone. Thus, the present study has attempted to assess the combined study on hydro-geochemical characteristics, and the stable isotopic investigation of The Garhwal Himalayan lake Satopanth Tal to understand the sources of dissolved ions and hydrogeochemical processes.



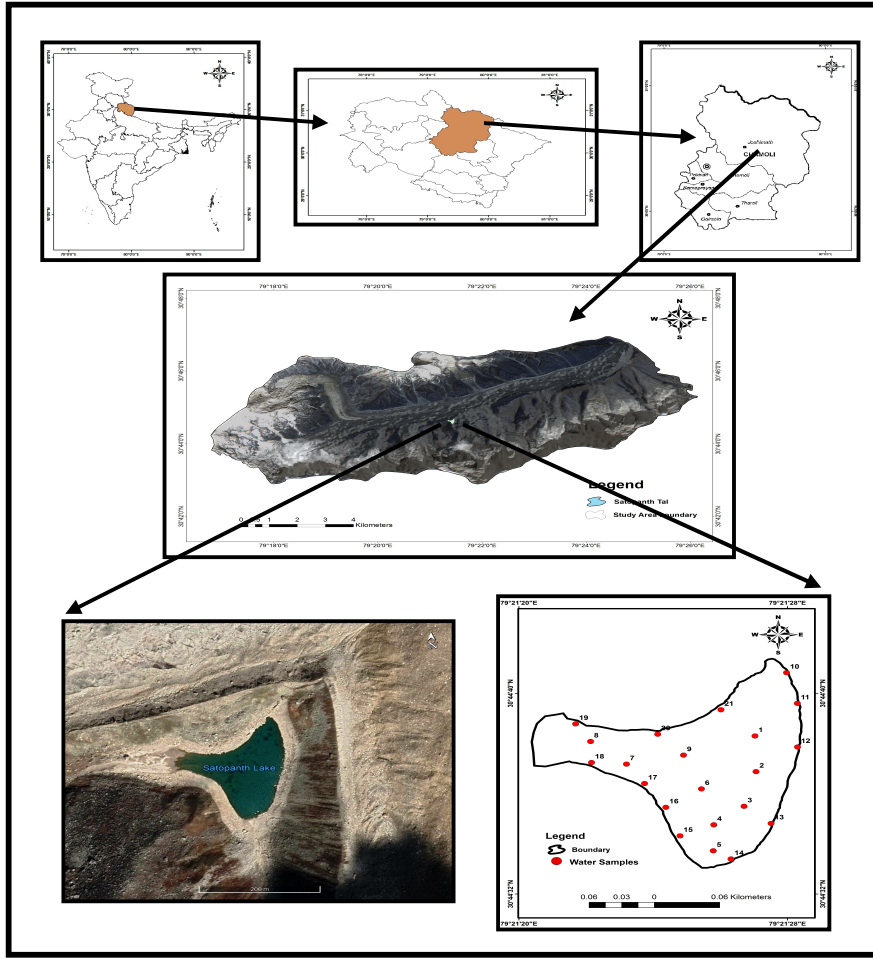
## Study area and its geological extent

The Satopanth Tal is situated in the Chamoli district of Uttarakhand, India (Fig. 1). This lake is drawn nearer from a distance of 25 km away from Badrinath in Garhwal Himalaya. Satopanth Tal is a triangular-shaped pristine lake located at 79°21'21.74"E and 30°44'38.30"N, occupying an area of 0.025 km<sup>2</sup> at an altitude of about 4600 m above mean sea level. The maximum length of the lake is 0.262 km; while the maximum width is 0.211 km with a maximum depth of 17.5 m. The climate in Satopanth Tal region is cooler throughout the year, as its summer temperature measured around 10<sup>0</sup> to 12<sup>0</sup> C during the day and 5<sup>0</sup> to –5<sup>0</sup> C during the night time, and the temperature drops to –20<sup>0</sup> to –25<sup>0</sup> C in the day hours, while between –30<sup>0</sup> to –35<sup>0</sup> C during night hours in winter. Geologically, the study area falls under Central Crystalline Zone. Lithologically, the study region is controlled by calc-silicate with sillimanite-kyanite-garnet-biotite gneiss and schist with tourmaline granite belonging to Pindari Formation (Valdiya, 1973 and 1999; Sharma, 2019). The Badrinath Granite nothing but the leucogranitic tourmaline bearing rocks and the crystalline rocks of metasediments and acidic intrusive are exposed in the study area grouped under Badrinath formation and Vaikrita group respectively.

## Material and methods

### Analytical Procedure

The 21 surficial water samples from Satopanth Tal were collected during post-monsoon in 500 ml narrow-necked, clean polyethylene bottles covering all parts of the lake. Parameters such as pH, EC, and TDS were analyzed by utilizing the multi-parameter meter Hanna instrument (HI98194) adopting the standard methods adopted by APHA (1995). Collected water samples were filtered by 0.45 µm Millipore membrane filter papers to remove the floating fine particles. Na<sup>+</sup> and K<sup>+</sup> were determined by using a flame photometer (CL-378), whereas Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>–</sup>, and Cl<sup>–</sup> were analyzed with the acid titration. SO<sub>4</sub><sup>2–</sup>, PO<sub>4</sub><sup>2–</sup> and H<sub>4</sub>SiO<sub>4</sub> were analyzed with a UV spectrophotometer (UV-1800). Software Aquachem (Version 5.1) software, best known for its water quality data analysis was used for plotting Piper diagram plotting, whereas pro chem software was used for other plots such as Gibbs. The Statistical Package for Social Sciences (SPSS) software (Version 22) was adopted for correlation matrix and principal component analysis (PCA).



**Fig.1** Study Area and Sample Location map for Satopanth Tal, Chamoli, Uttarakhand exhibiting a recent time image extracted from Google Earth Pro and 21 water samples location points

#### Stable isotope analysis

By utilizing the Continuous Flow Stable Isotope Ratio Mass Spectrometer (CF-IRMS) and the Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) respectively, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ( $\delta\text{D}$ ) of collected water samples were carried out to estimate the influence of precipitation or evaporation on lake water and required plots were performed using the Sigma Plot 14 software. Rozanski et al. (1993) derived Global Meteoric Water Line (GMWL), accessible dependent on precipitation and notify regarding the global distribution of stable isotope in precipitation mathematically as in Eq. (1);

$$\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10 \text{ ‰} \quad (1)$$

Whereas Dansgaard et al (1964) defined a parameter as a measure of the relative proportion of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in the water, Deuterium excess and derived mathematically as in Eq.(2)

$$D\text{-excess} = \delta^2\text{H} - 8 \times \delta^{18}\text{O} \quad (2)$$

## Result and Discussion

### Hydrogeochemistry

The study of water chemistry is one of the most vital investigations opted to evaluate the chemistry of water and the dominance of several cations and anions and their enrichment to recognize the geochemical processes. The physicochemical characteristics of the lake water are given in table 1. The order of concentration of major cations and anions was  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$  and  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{2-} > \text{H}_4\text{SiO}_4$  respectively (Table 1). Khadka and Ramanathan et al. (2021) infers that “pH is an important parameter controlling weathering patterns and availability of the dissolved solids in lakes”. The estimated pH values from Satopanth Tal water samples indicate that the lake water is of slightly acidic ( $6.4 \pm 0.2$ ) to little alkaline ( $7.1 \pm 0.2$ ) nature. The addition of all ions in water solution is termed total dissolved solids (TDS), which suggests the intensity of chemical weathering in the catchment (Singh and Hasnain, 1999). In Satopanth Tal, TDS ranged from  $7.3 \pm 3.5$  to  $20.4 \pm 3.5$  mg/L with an average of  $11.75 \pm 3.5$  mg/L, indicating freshwater (Table 1). “EC is an indirect measure of mineralization and ionic strength of natural water” (Chidambaram et al. 2011). In Satopanth Tal, EC values were recorded from  $14 \pm 7$  to  $42.2 \pm 7$   $\mu\text{S}/\text{cm}$  having a mean of  $21.02 \pm 7$   $\mu\text{S}/\text{cm}$  indicating the least amount of dissolution of minerals in the lake water.

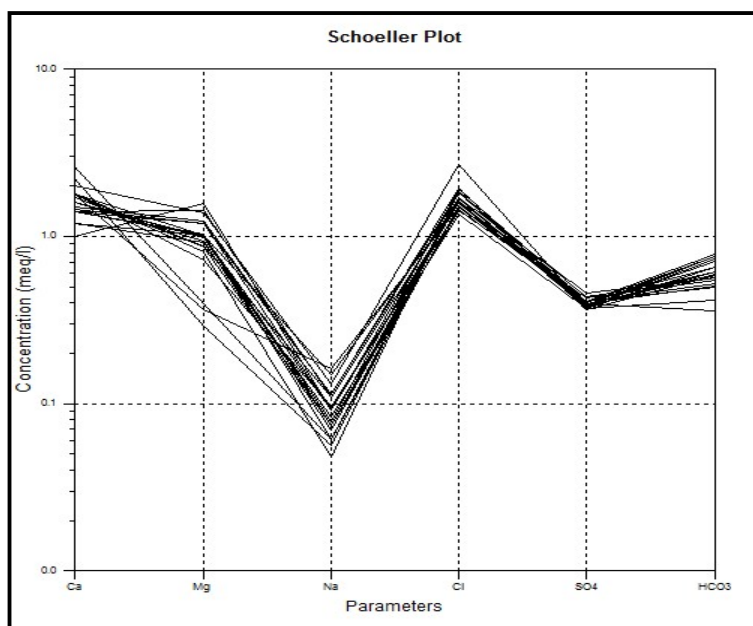
The average  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in the water of Satopanth Tal were observed to be  $32.9 \pm 7.2$  mg/L and  $11.7 \pm 4$  mg/L, respectively, whereas the  $\text{Na}^+$  and  $\text{K}^+$  ion concentration in the lake water was observed as an average of  $2.1 \pm 0.7$  mg/L and  $1.4 \pm 0.2$  mg/L respectively (Table 1). Generally, the dominance of  $\text{HCO}_3^-$  in water indicates intense chemical weathering, while the rich concentration of Chloride infers the anthropogenic sources (Meybeck, 1983). In Satopanth Tal, the average  $\text{HCO}_3^-$  and  $\text{Cl}^-$  concentrated was observed to be  $37.18 \pm 7.1$  mg/L and  $60.96 \pm 9.7$  mg/L respectively, which satisfy the permissible limit suggested by WHO(2011) (Table 1). Thus, the lower value of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  in Satopanth water might be accredited to the dilution effect of the meltwater. The calculated mean of  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{2-}$  as well as  $\text{H}_4\text{SiO}_4$  concentration in the lake water were found to be  $19.04 \pm 1.1$  mg/L,  $9.58 \pm 0.5$  mg/L, and  $5.1 \pm 3.97$  mg/L respectively. So the water sample collected from Satopanth Tal glacial lake were

analyzed and found to be fall under the advisable limit of WHO (2011) indicate the lake is holding pure and fresh water in it.

The use of semi-logarithmic graph paper to map anion and cation concentrations were suggested by Schoeller (1967) (Fig. 2). In milliequivalent per liter (meq/L), the concentration of dominant anions and cations are plotted on six evenly spaced logarithmic scales. This type of graph depicts not only the absolute value of each ion, but also the concentration differences (Khan and Jharia et al., 2018). As per the Schoeller diagram,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ , and  $\text{Cl}^-$  are the dominant ions in surface water.

**Table1** Physicochemical compositions of the water of Satopanth Tal water

Parameters	Min.	Max.	Mean	STDev	WHO (2011)
EC	14	42.2	21.6	7.0	500-1500
pH	6.4	7.1	6.9	0.2	6.5-8.5
TDS	7.3	20.4	11.9	3.5	500-1500
$\text{Na}^+$	1.1	3.7	2.1	0.7	50-200
$\text{K}^+$	1.1	1.9	1.4	0.2	10-12
$\text{Ca}^{2+}$	20	52	32.9	7.2	75-200
$\text{Mg}^{2+}$	3.5	19.2	11.7	4.0	30-150
$\text{Cl}^-$	48.1	95	61.9	9.7	250-600
$\text{HCO}_3^-$	22	47.6	37.0	7.1	200-500
$\text{SO}_4^{2-}$	17.5	22	19.1	1.1	250-400
$\text{PO}_4^{2-}$	8.9	11.1	9.6	0.5	10-20
$\text{H}_4\text{SiO}_4$	1.9	15.8	5.1	3.9	50-100



**Fig.2** Schoeller diagram representing the concentration of anions and cations

#### Hydrogeochemical processes on the lake water

The reaction within surface water and surrounding minerals plays a major role in the water quality and is also useful in understanding the genesis of surface water and its sources. To identify the hydrogeochemical processes operating in the Satopanth Tal region, the hydrogeochemical data is subjected to various conventional graphics plots.

#### *Major dissolved ions sources in water*

Rock weathering, precipitation, and anthropogenic activities are the important sources from which the ion got derived and dissolve in water. (Das and Kaur 2001; Jeelani and Shah 2006). The mean distribution of total cations ( $TZ^+$ ) and total anions ( $TZ^-$ ) in Satopanth Tal water were recorded as  $48.01 \pm 5.25$  and  $127.41 \pm 14.16$  (Table 2). The higher mean concentrations  $TZ^-$  than  $TZ^+$  indicate the contribution of total anions to the lake by the organic compound decompositions (Dalai et al. 2002). The second most abundant element in Earth's crust is Silicon, very much essential for life and available in the form of  $H_4SiO_4$  for phytoplankton and algae. The content of  $H_4SiO_4$  in the water of Satopanth Tal ranged from  $1.9 \pm 3.9$  to  $15.8 \pm 3.9$  meq/L. These high values indicate a significant

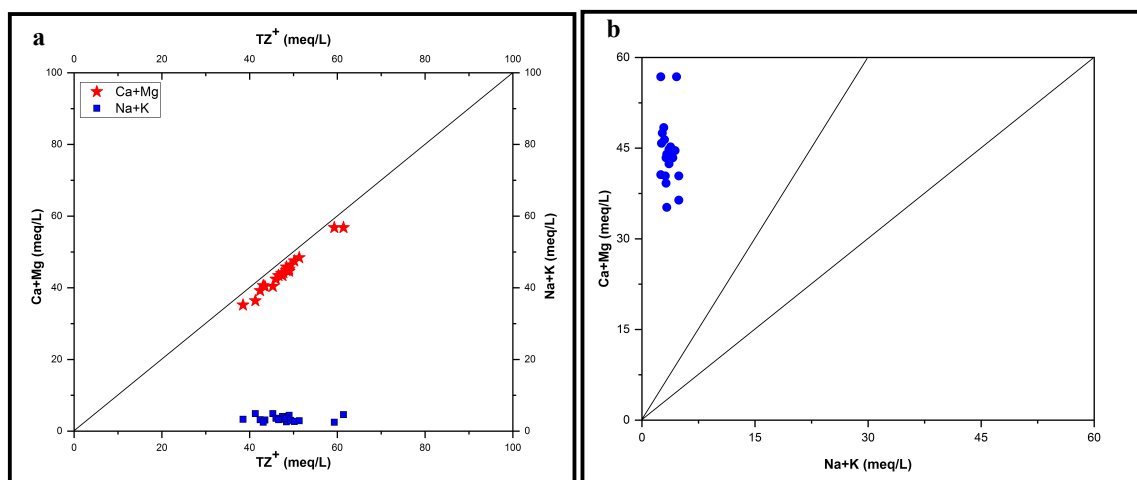
vertical gradient of temperature due to the mixing, which leads to the death and decomposition of diatoms, except the silicate weathering (Håkanson, 1984; Anshumali and Ramanathan, 2007). This argument is also supported by the high  $\text{H}_4\text{SiO}_4 / \text{Na}^+ + \text{K}^+$  ratio, as in Satopanth Tal water samples it is high with a mean of  $1.05 \pm 0.47$ . Subramanian et al (1979) classified the dissolved silica into two categories; the Indian Himalayan river average (9.6 meq/L) and the global average (12.0 meq/L). The present results show  $\text{H}_4\text{SiO}_4$  value ( $5.1 \pm 3.9$  meq/L) is substantially lower compared to the above said two classes indicates silicate minerals are resistant to the prevailing weathering conditions.

“The recorded  $(\text{Ca}^{2+} + \text{Mg}^{2+}) / (\text{Na}^+ + \text{K}^+)$  ratio in the silicates of the upper crust is 1.0” (Taylor and McLennan 1985). In the present study, this means the equivalent ratio is estimated as  $13.42 \pm 3.50$  (Table 2) and the scatter plot indicates all the points fall above 2:1 equiline, infers the dominance of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  over  $\text{Na}^+$  and  $\text{K}^+$  in the lake water (Fig 3a). The  $\text{Ca}^{2+} + \text{Mg}^{2+} / \text{TZ}^+$  scatter plot (Fig. 3a) for the lake water has a linear spread adjacent to the 1:1 equiline, suggesting that most of the cations are accounted by  $\text{Ca}^{2+} + \text{Mg}^{2+}$  with small contribution of silicate weathering derived alkali ( $\text{Na}^+ + \text{K}^+$ ). Several researchers have reported a similar trend in the Lesser Himalayan lakes such as Renuka Lake (Das and Kaur 2001), Pandoh Lake (Anshumali and Ramanathan 2007) of India, and Begnas lake, Nepal (Khadka and Ramanathan, 2012). The  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  is plotted versus  $\text{TZ}^+$  (Fig. 3b), exhibiting a strong correlation among the data set with a mean equivalent ratio of  $0.93 \pm 0.02$  infers the dominance of carbonate weathering act as a primary source of dissolved ions in the lake water. The average  $\text{Ca}^{2+} + \text{Mg}^{2+} / \text{TZ}^+$  ratio in the water of several Himalayan lakes such as Renuka, Begnas, Nainital, Bhimtal, Naukuchiyatal, Sattal, Chandra Tal, and Phewa was calculated as 0.97, 0.85, 0.90, 0.86, 0.84, 0.88, 0.97, 1.07 respectively which is very much similar to the current study ratio for Satopanth Tal (0.93), indicating carbonate weathering as a prevailing component governing the hydrogeochemistry of these Himalayan lakes (Das and Kaur 2001; Das 2005;; Singh et al. 2015a, b; Singh 2016; Khadka and Ramanathan, 2013 and 2021).

“Similarly, the  $(\text{Na}^+ + \text{K}^+) / \text{TZ}^+$  ratio is used as an index to assess the contribution of cations via silicate weathering” (Stallard and Edmond 1983). The  $(\text{Na}^+ + \text{K}^+)$  against  $\text{TZ}^+$  exhibits an average ratio of  $0.07 \pm 0.02$  (Table 2) indicating the silicate weathering contributes the least as a source for the dissolved ions in lake water. The plot of  $(\text{Na}^+ + \text{K}^+)$  versus  $\text{TZ}^+$  (Fig. 3b) shows all samples clustered just underneath the 1:1 line reflecting the deficiency of  $\text{Na}^+$  and  $\text{K}^+$  in the water.

**Table 2** Ionic ratios of Satopanth Tal water producing different hydrological processes

Parameters	Min.	Max.	Mean	STDev
$TZ^+$	38.50	61.40	48.01	5.25
$TZ^-$	100.60	167.70	127.41	14.16
C-ratio	0.54	0.72	0.65	0.05
$H_4SiO_4 / Na^+ + K^+$	0.52	2.25	1.05	0.47
$Ca^{2+} + Mg^{2+} / TZ^+$	0.88	0.96	0.93	0.02
$Na^+ + K^+ / TZ^+$	0.04	0.12	0.07	0.02
$Ca^{2+} + Mg^{2+} / Na^+ + K^+$	7.43	22.72	13.42	3.50
$Ca^{2+} + Mg^{2+} / HCO_3^- + SO_4^{2-}$	0.54	0.72	0.65	0.05
$HCO_3^- / Ca^{2+} + Mg^{2+}$	0.60	1.07	0.84	0.13
$HCO_3^- / TZ^+$	0.53	0.98	0.77	0.12
$HCO_3^- / Na^+$	6.47	35.69	19.61	7.22
$Ca^{2+} / Na^+$	7.06	37.14	17.79	8.21
$Mg^{2+} / Na^+$	1.19	9.14	5.80	2.09
$Na^+ / Cl^-$	0.02	0.07	0.04	0.01
$K^+ / Cl^-$	0.02	0.03	0.02	0.004
$Na^+ + K^+ / Cl^-$	0.04	0.09	0.06	0.01
$Ca^{2+} + Mg^{2+} / SO_4^{2-}$	1.91	3.14	2.35	0.30

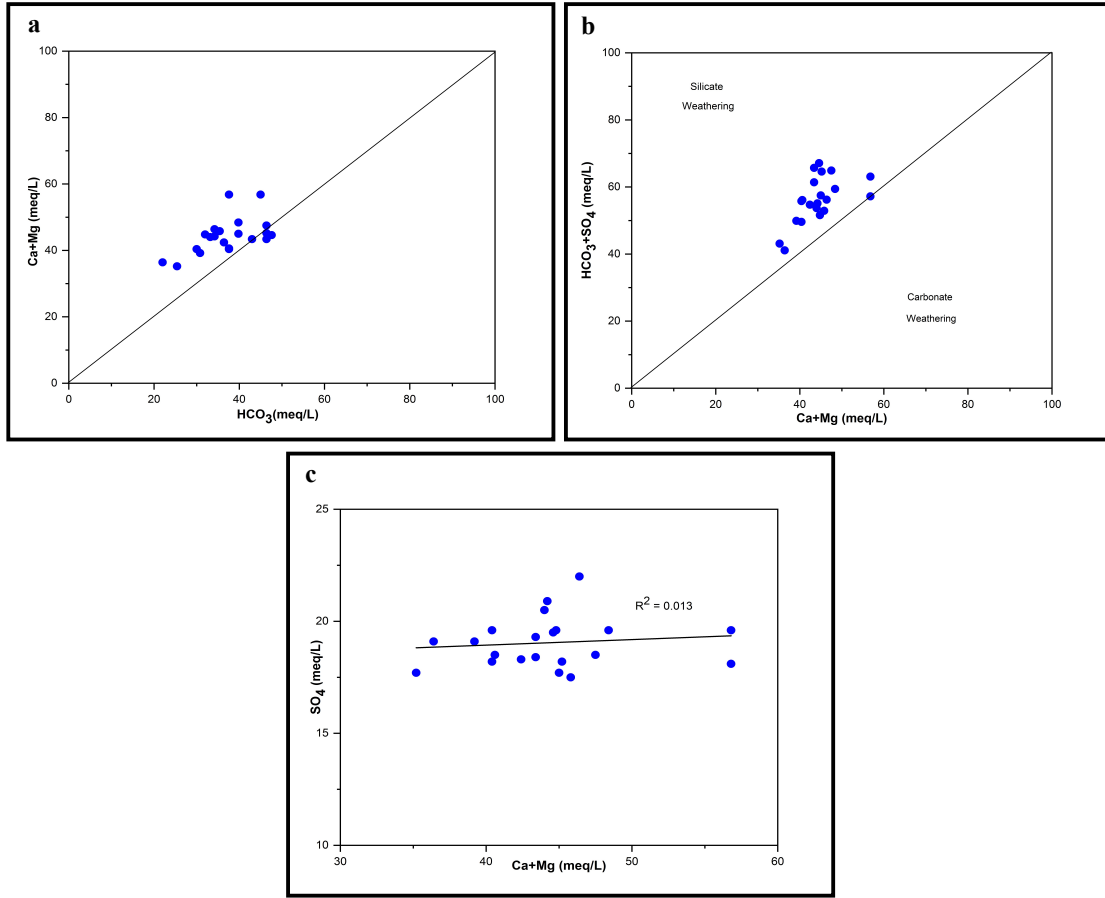


**Fig. 3** (a) showing the scatter plot of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  vs.  $\text{TZ}^{+}$  and  $(\text{Na}^{+} + \text{K}^{+})$  vs.  $\text{TZ}^{+}$ , (b) showing the scatter plot between  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  vs.  $(\text{Na}^{+} + \text{K}^{+})$  suggesting the dominancy of carbonate weathering

The high  $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^{+} + \text{K}^{+})$  and  $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{TZ}^{+}$  ratios and low  $(\text{Na}^{+} + \text{K}^{+})/\text{TZ}^{+}$  ratios of the water samples, therefore, suggest that the weathering of carbonates is the dominant mechanism and the negligible contribution of silicate weathering that regulates the Satopanth Tal's major ion chemistry. This weathering is carried out by the meltwater generated from the precipitation processes. The plot for  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  against  $\text{HCO}_3^{-}$  of lake water samples fall close to the equivalent of 1:1 indicating the predominance of alkali matter over bicarbonate, i.e.,  $\text{HCO}_3^{-}$  is balanced by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Fig 4a). The scatter plot of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  upon  $(\text{HCO}_3^{-} + \text{SO}_4^{2-})$  (Fig 4b) shows all the water sample points are clustered above 1:1 equiline needing apportion of the bicarbonate ( $\text{HCO}_3^{-}$ ) and Sulphate ( $\text{SO}_4^{2-}$ ) over Calcium (Ca) and Magnesium (Mg) to be balanced by Sodium ( $\text{Na}^{+}$ ) and Potassium ( $\text{K}^{+}$ ) from weathering of silicate rocks (Pandey et al 1999, Sharma et al. 2012). While,  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  versus  $\text{SO}_4^{2-}$  scatter plot (Fig. 4c) indicates a very weak correlation of  $R^2=0.013$  between  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  and  $\text{SO}_4^{2-}$  inferring negligible amount contribution from  $\text{CaSO}_4$  and  $\text{MgSO}_4$  to the meltwater of Satopanth glacier which feeds the lake Satopanth.

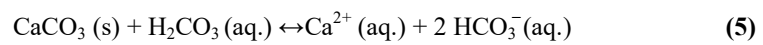
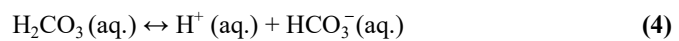
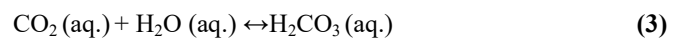
The carbonate dominant rocks through which water draining is characterized by high  $\text{Ca}^{+}/\text{Na}^{+}$ ,  $\text{Mg}^{+}/\text{Na}^{+}$  and  $\text{HCO}_3^{-}/\text{Na}^{+}$  by exhibiting  $\text{Ca}^{+}/\text{Na}^{+}$  nearly 50,  $\text{Mg}^{+}/\text{Na}^{+}$  nearly 10, and  $\text{HCO}_3^{-}/\text{Na}^{+}$  nearly 120 (Stallard et al. 1980; Meybeck et al. 1986; and Negrel et al. 1993). Whereas, in case of silicate dominant rocks low ratio of  $\text{Ca}^{+}/\text{Na}^{+}$  nearly  $0.35 \pm 0.12$ ,  $\text{Mg}^{+}/\text{Na}^{+}$  nearly  $0.24 \pm 0.12$  and  $\text{HCO}_3^{-}/\text{Na}^{+}$  nearly  $2 \pm 1$  (Gaillardet et al. 1999). The water samples from Satopanth Tal exhibit an average ratio of  $\text{Ca}^{+}/\text{Na}^{+} = 17.79 \pm 8.21$ ,  $\text{Mg}^{+}/\text{Na}^{+} = 5.80 \pm 2.09$ , and  $\text{HCO}_3^{-}/\text{Na}^{+} = 19.61 \pm 7.22$  (Table 2). The observed ratio in the Satopanth Tal water is lower than that of water draining out from carbonate lithology and much higher than that of from silicate rock type. These ratios therefore suggest that Satopanth Tal water's major ion chemistry is governed by carbonate weathering followed by silicate weathering as reported by other researchers for different Himalayan glacial feed lakes (Singh et al. 2012, 2015, and 2016). The  $\text{HCO}_3^{-}/\text{TZ}^{+}$  of the study area varied between  $0.53 \pm 0.12$  to  $0.98 \pm 0.12$ , with an average of  $0.77 \pm 0.12$  (Table 2). This high ratio indicates the dominancy of  $\text{HCO}_3^{-}$  anion in the water with a mean of  $37.0 \pm 7.1$  meq/L (Table 1).



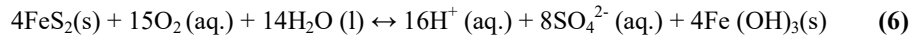


**Fig. 4** Showing the scatterplot between (a)  $(Ca^{2+}+Mg^{2+})$  vs.  $HCO_3^-$ , (b)  $(HCO_3^-+SO_4^{2-})$  vs.  $(Ca^{2+}+Mg^{2+})$ , and (c) regression plot between  $(Ca^{2+}+Mg^{2+})$  and  $SO_4^{2-}$  suggesting different weathering processes and contribution of sulphate to the water

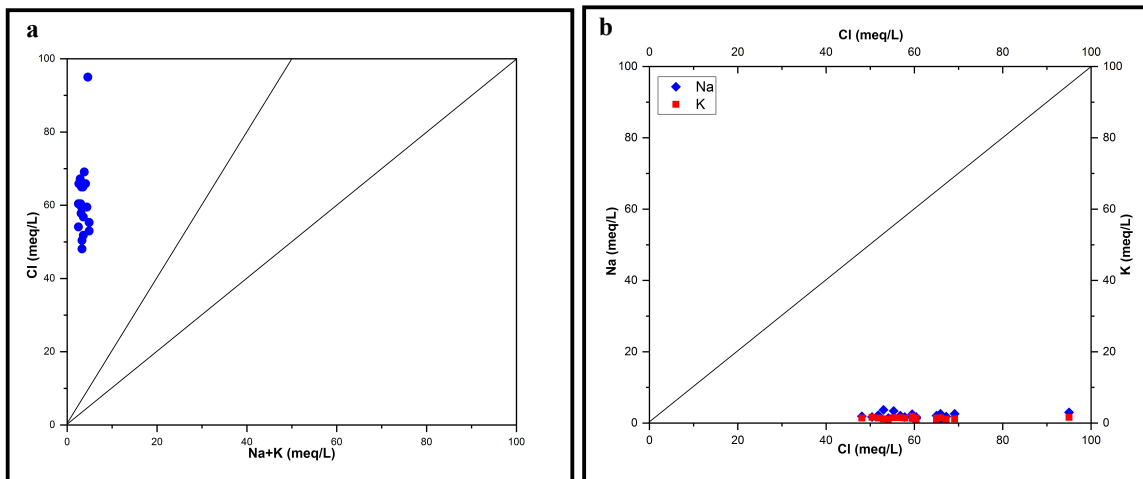
The proton sources are unavoidable parameters that influence carbonate weathering. Hence, to estimate these sources and to confirm its genesis whether from carbonation or oxidation, the C-ratio ( $HCO_3^- / HCO_3^- + SO_4^{2-}$ ) is adopted (Brown et al., 1996). Where the C-ratio of 1 implies weathering by carbonate reactions as shown in Eq. (3, 4, 5).



While, C-ratio of 0.5 suggests the coupled reaction involving weathering of carbonate rocks and derivation of protons from sulphide oxidation (Eq.6).



In Satopanth Tal, the C-ratio ranged between  $0.54 \pm 0.05$  to  $0.72 \pm 0.05$ , with an average of  $0.65 \pm 0$  (Table 2) suggesting the carbonate dissolution and derivation of a proton ( $\text{H}^+$ ) from sulphide oxidation as reported by other researchers on glacial domains (Panday et al. 1999; Singh, 2015a; Khadka and Ramanathan, 2013 and 2021). The major ions present in precipitation-dominated water are  $\text{Na}^+$  and  $\text{Cl}^-$  (Meybeck 2003). The scatter plot of  $(\text{Na}^+ + \text{K}^+)$  versus  $\text{Cl}^-$  indicates all sample points clusters above 2:1 line inferring concentration of  $\text{Cl}^-$  is much higher than the concentration of  $(\text{Na}^+ + \text{K}^+)$  in the water of Satopanth Tal (Fig.5a and b). The ratios of  $(\text{Na}^+ + \text{K}^+) / \text{Cl}^-$  is significantly lower with an average of  $0.06 \pm 0.01$ , and  $\text{Na}^+/\text{Cl}^-$  as well as  $\text{K}^+/\text{Cl}^-$  in the water of Satopanth Tal were ranged between  $0.02 \pm 0.01$  to  $0.07 \pm 0.01$ , with an average of  $0.04 \pm 0.01$  and  $0.02 \pm 0.03$ , mean of  $0.02 \pm 0.004$  (Table 2). This  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  of lake water can be compared with the ratio of  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  of marine aerosols to estimate the contribution of atmospheric precipitation to the chemical composition of the lake. The ratio of  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  for marine aerosols according to Singh et al. (2016) is 0.85 and 0.02 respectively. As the estimated  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  ratio for Satopanth Tal water are relatively lower than that of marine aerosols, this infers the chemical composition of the lake can be affected by the noticeable contribution from atmospheric precipitations.



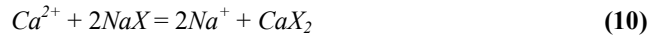
**Fig. 5** Scatter diagrams between (a)  $(\text{Na}^+ + \text{K}^+)$  vs.  $\text{Cl}^-$ , and (b)  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  suggests the contribution of atmospheric precipitations

Clark et al. (2015) proposed that one of the most significant geochemical processes that play an important role in regulating changes in water chemistry is cation exchange. Hence an index has been suggested by Schoeller et al. (1977) known as chloro-alkaline indices (CAI) to indicate the exchange of ions between the surface or groundwater and its source environment. The chloro-alkaline indices are calculated from the following relations as Eq. (7, 8);

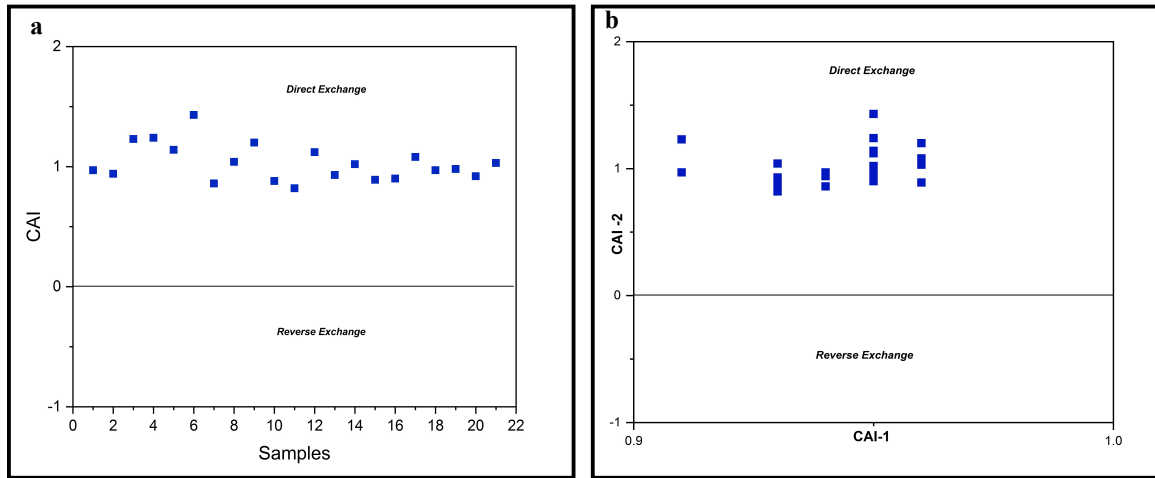
$$CAI\ 1 = [Cl^- - (Na^+ + K^+)] / Cl^- \quad (7)$$

$$CAI\ 2 = [Cl^- - (Na^+ + K^+)] / SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^- \quad (8)$$

If the indices values are positive as expressed in Eq. (9),  $Na^+$  and  $K^+$  ions in the water are exchanged with  $Ca^{2+}$  and  $Mg^{2+}$  ions, which indicating base-exchange reaction (direct exchange). While, the negative values infer  $Ca^{2+}$  and  $Mg^{2+}$  ions are exchanged with  $Na^+$  and  $K^+$  ions in the water, which indicates chloro-alkaline disequilibrium (reverse exchange) as expressed in Eq. (10) (Wang Q, 2020) (Fig.6a and b).



In the Satopanth Tal, CAI 1 value ranges from 0.91 to 0.96 with an average of 0.94 whereas CAI 2 value ranges from 0.82 to 1.43 with an average of 1.04. The predominantly positive CAI value of Satopanth Tal indicates that the  $Na^+$  and  $K^+$  ions from the water get exchanged with  $Ca^{2+}$  and  $Mg^{2+}$  ions from the rocks. Therefore, the most significant mechanism responsible for the water chemistry of Satopanth Tal is the cation exchange in the water

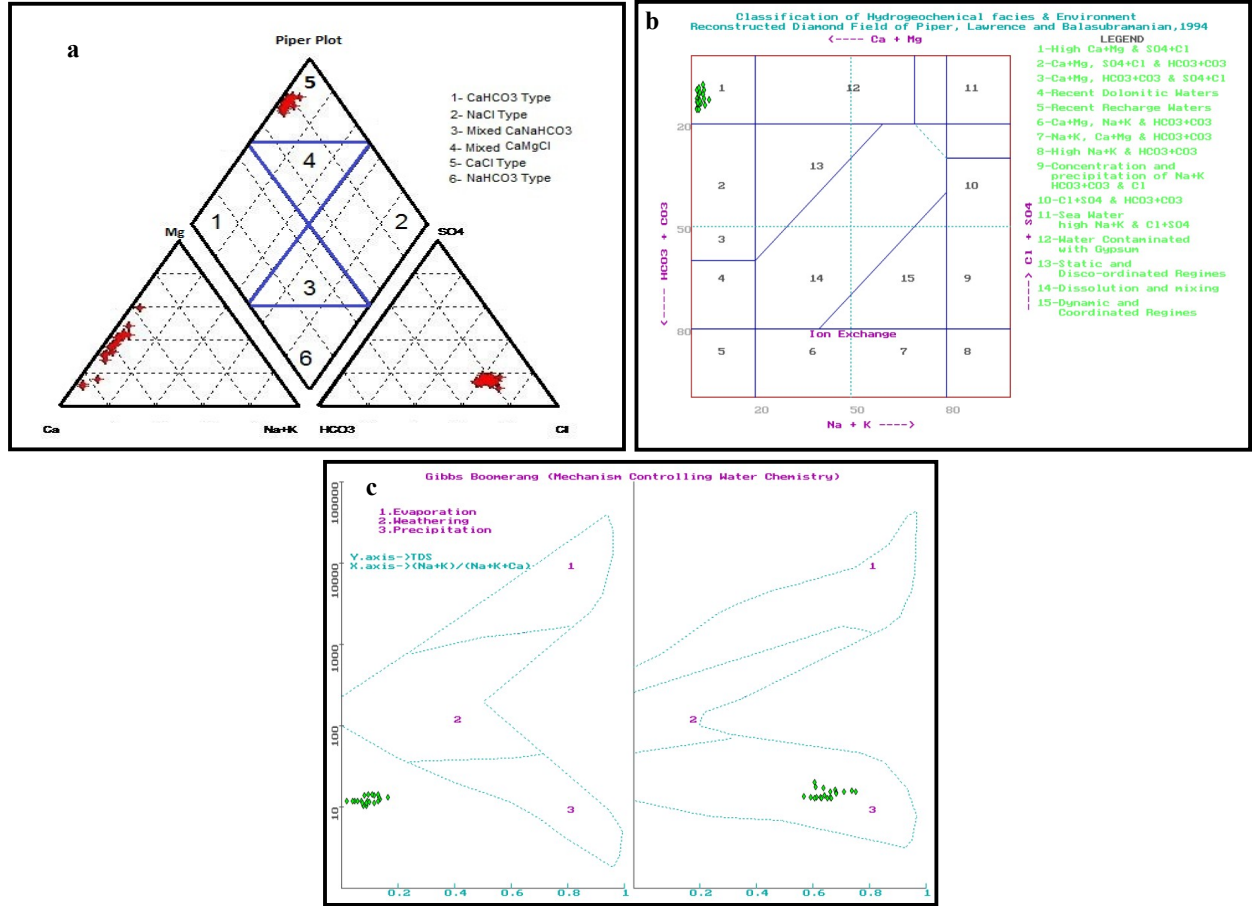


**Fig. 6** Relationship plot between (a) CAI vs. Samples and (b) CAI-1 vs. CAI-2 indicates the ion exchange processes in the lake water

#### *Hydrogeochemical facies*

To describe distinctive water type, Piper (1953) proposed a two based triangle plot where the cations and anions concentration in milliequivalent percentage, projected into a central diamond-shaped region further. The values of chemical data from the distinctive surface water samples in the study area are plotted on the Piper diagram (Fig. 7a), indicate that  $\text{Ca}^{+2} - \text{Cl}^-$  is the major hydrogeochemical facies, suggesting the dominance of alkali and strong acids, and as the percentage values of alkaline earth metal ( $\text{Ca}^{2+} + \text{Mg}^{2+} = 44.5 \pm 5.3$ ) significantly higher than the alkali metals ( $\text{Na}^+ + \text{K}^+ = 3.5 \pm 0.7$ ), inferring the dominance of carbonate weathering mechanism as well which regulating the hydrogeochemistry of Satopanth Tal. The piper plot was further modified (Fig 7b) by Johnson et al (1975), where all three components of the Piper trilinear plot are individually projected in rectangular coordinates to produce a pattern similar to the Piper plot to study and interpret the changes in water hydrogeochemical phases. Fig. 7b reveals that all samples fell into the class 1 suggesting high  $\text{Ca}^{2+} + \text{Mg}^{2+}$  and  $\text{SO}_4^{2-} + \text{Cl}^-$  indicates dominance of carbonate weathering in the study area with acidic to alkaline water type. To understand the dominance of several processes such as either precipitation, weathering, or evaporation in the geochemical evolution of water bodies, two semilog plots were being proposed by Gibbs (1970) widely known as the Gibbs diagrams (Fig. 7c). This simple boomerang plot provides information regarding the importance of different natural major mechanisms that

controlling surface water chemistry. In Satopanth Tal, the Gibbs diagram demonstrates that precipitation controls the major ion chemistry as estimated from  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  ratio study.



**Fig. 7** (a) Piper plot indication the different water type, (b) The modified Piper diamond plot, and (c) Gibbs plot showing the major ion sources of Satopanth Tal

Statistical approaches for various physicochemical parameters

Statistical analysis of the data has been tried to divulge the hidden relationship between every parameter (Singaraja et al. 2013). The correlation matrix is commonly used to explain the relationship between various ionic species (Mondal et al. 2011). Correlation matrices are applied to clarify the lake water samples and to use SPSS software to classify the geochemical processes controlling surface water geochemistry. The average value of all the variables is determined and tabulated as a matrix in Table 3. A very strong positive correlation of 0.73 has been obtained between  $\text{PO}_4^{2-}$  and  $\text{Na}^+$  and good positive correlations between  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  having values of

0.46 and 0.47, respectively indicating their common sources. Strong correlations were found between EC and TDS,  $\text{PO}_4^{2-}$ ,  $\text{Na}^+$  suggesting that dissolved solids,  $\text{Na}^+$  and  $\text{PO}_4^{2-}$  contribute to the EC of the lake water. Moreover, the positive correlation between EC and TDS ( $r = 0.58$ ) shows that electrical conductivity also increases as the concentration of dissolved constituents or ions increases (Singh and Ramanathan, 2014) and suggest that by snow melting, lake water originally receives much of the water. The low pH is due to a lower rate of silicate weathering, which is supported by the positive correlation between pH and  $\text{H}_4\text{SiO}_4$ . The positive correlation  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r = 0.68$ ) infers their similar sources.  $\text{Ca}^{2+}$  revealed a positive correlation with  $\text{HCO}_3^-$  ( $r = 0.36$ ), showing common provenance and may be due to carbonate weathering. A good correlation was found between  $\text{Na}^+$  and  $\text{K}^+$  ( $r = 0.13$ ),

while  $\text{H}_4\text{SiO}_4$  was significantly and negatively correlated with the  $\text{K}^+$  and  $\text{Na}^+$  indicating the absence of silicate weathering. A good correlation between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  indicates their similar origin like pyrite oxidation, sulphate minerals dissolution, and Sulphur compounds oxidation in the bottom sediment of the lake at the transition zone between aerobic and anaerobic environments (Singh et al 2016; Khadka et al. 2021).

**Table 3** Perason's Correlation matrix for SatopanthTal water samples

	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{PO}_4^{2-}$	$\text{SO}_4^{2-}$	$\text{H}_4\text{SiO}_4$	pH	EC	TDS
$\text{Ca}^{2+}$	1											
$\text{Mg}^{2+}$	0.68	1										
$\text{Na}^+$	-0.25	0.20	1									
$\text{K}^+$	-0.04	0.04	0.13	1								
$\text{Cl}^-$	0.15	0.46	0.17	0.07	1							
$\text{HCO}_3^-$	0.36	0.09	-0.16	0.25	0.47	1						
$\text{PO}_4^{2-}$	-0.35	0.11	0.73	-0.19	0.00	-0.39	1					
$\text{SO}_4^{2-}$	0.21	-0.22	0.03	-0.06	-0.20	-0.18	0.13	1				
$\text{H}_4\text{SiO}_4$	0.26	-0.23	-0.03	-0.18	-0.10	-0.07	-0.23	0.26	1			
pH	0.18	-0.17	-0.18	-0.09	0.03	-0.01	-0.41	-0.06	0.20	1		
EC	-0.05	-0.13	0.30	-0.20	-0.15	-0.29	0.45	0.18	-0.09	-0.10	1	
TDS	0.12	-0.23	0.12	-0.21	-0.15	-0.18	0.19	0.30	0.29	0.16	0.58	1

Correlation Significant at 0.01

The principal components analysis (PCA) is used to define trends in the data set and to explain the data in such a way that their similarities and differences are highlighted (Smith LI, 2002). With the assistance of main component analysis, which is responsible for explaining much of the intimation within the original data, the big data

matrix is reduced to two small ones (Ranjan, 2013). Eigenvalue more than one is recognized as an important contributing factor (Sharma, 2012 and Singh, 2014). Varimax rotation was utilized for factorial investigation (Gotelli and Ellison 2004) to amplify the amount of variance in factor coefficients, which ideally depicted the sources that influence the water system (Prasanna et al. 2012). The relationship level between each factor and each variable is shown by the load on that factor (Deka et al. 2015a). Table 4 displays the outcomes of the factor analysis of meltwater from Satopanth Tal. In factor analysis of meltwater samples, four factors were recognized as Eigenvalues of more than one. Around 65.01% of the overall variability in the data set was illustrated by these four variables. Factor 1 has strong loading for  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_4\text{SiO}_4$ , EC, and TDS and represents 23.16% variance in the data set. This factor suggests a lack of weathering of silicate in the meltwater as  $\text{Na}^+$  and  $\text{K}^+$  are null to a negligible amount of loading indicating an absence of silicate weathering. Factor 2 illustrates an 18.69% variance in the data matrix and demonstrates potential loading for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  suggesting that the carbonate weathering is the principal source for these ions. Factor 2 also infers sulphate dissolution and oxidation of pyrite. Factor 3 has good loading for  $\text{Cl}^-$  represents a variance in the data of 12.42%, this factor signifies the role of atmospheric precipitation in Satopanth Tal's meltwater. There is no notable variable in Factor 4, which illustrated about 10.74% except a higher variable at pH value inferring the lake water is acidic to slightly alkaline (Table 4).

**Table 4** Principal Component analysis for loading matrices of Satopanth Tal

Variables	Factor1	Factor 2	Factor 3	Factor 4
$\text{Ca}^{2+}$	0.402	0.761	0.294	-0.193
$\text{Mg}^{2+}$	-0.696	0.439	0.155	0.344
$\text{Na}^+$	-	-0.553	0.501	-0.153
$\text{K}^+$	-0.372	0.126	-	-0.619
$\text{Cl}^-$	-0.533	0.212	0.675	0.260
$\text{HCO}_3^-$	-0.419	0.611	0.428	-0.109
$\text{SO}_4^{2-}$	0.543	0.601	0.147	-0.307
$\text{H}_4\text{SiO}_4$	0.493	0.256	-	0.283
pH	0.228	0.354	-	0.580
EC	0.489	-0.547	0.382	-
TDS	0.685	-0.226	0.427	0.149
Eigen value	2.55	2.05	1.37	1.18
% of variance	23.16	18.69	12.42	10.74
Cumulative %	23.16	41.85	54.27	65.01

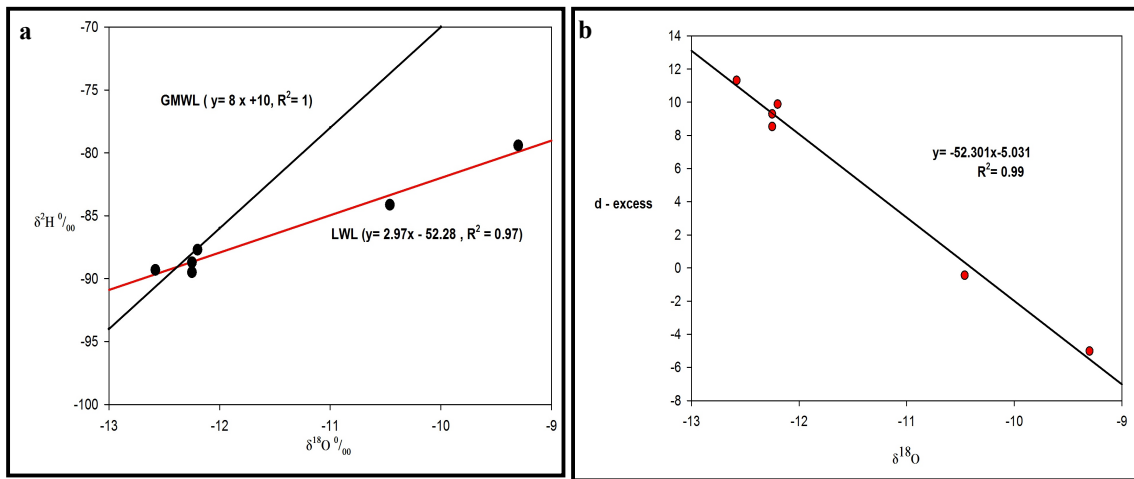
## Isotope geochemistry

Generally, two stable isotopes such as deuterium ( $\delta D$ ) and oxygen ( $\delta^{18}O$ ) were investigated for water samples to understand several geological processes includes streamflow, evaporation as well as precipitation which influence the chemical composition of water. Flaim et al (2013) infer that lower altitude regions were high isotopically enriched than higher and vice versa. Then the relation between  $\delta^{18}O$  and  $\delta D$  in global fresh surface waters has been established by Craig (1961) and termed as Global Meteoric Water Line (GMWL) (Eq. 4). GMWL line is the global application line and is a mean of various local or regional meteoric water lines known as Lake water line (LWL) which have different from GMWL in terms of slope and intercept (Clark and Fritz, 1997), due to different climatic and geographic parameters. Craig (1961) also inferred that waters associated with cold regions experience isotopically depletion, whereas water from warm regions exhibits isotopically enrichment. Hence, this variation in presence of stable isotopes in the water of different regions concerning their climatic conditions helps to emphasize the recharge environment of groundwater from the surface water. “Stable isotope study ( $\delta^{18}O$  and  $\delta^2H$ ) in the precipitation and glacial stored water of the study area allow us to demark how much these waters are moving away from GMWL and what the climatic processes are” (Giovanna et al., 2017). Fig. 8a shows that  $\delta^{18}O$  and  $\delta D$  values of the surface water samples distributed parallel to the LWL line, indicating an influence of precipitation as a major source to the lake. The correlation coefficient ( $R^2 = 0.97$ ) of the LWL is nearly the same as that of the correlation of GMWL ( $R^2 = 1$ ) nullified the probability of any anthropogenic activities, and the significant linear relationship between  $\delta^{18}O$  and  $\delta D$  suggests the dominancy of precipitation process in the lake (Zhu S et al. 2019). The slope of GMWL (8) is much higher than the slope of LWL (2.97), indicates the lake is fed employing precipitation and supplied by ice and snow meltwater from Satopanth glacier and plays a major role in ion exchange phenomenon as well as during their dissolution. Hence, exhibiting negative values (Fig. 8a).

Deuterium- excess, which is widely adopted for re-predicting of ancient climatic changes and several definite sources that influence the water by investigating the measure of relative proportions of  $\delta^{18}O$  and  $\delta D$  in the water has been proposed by Dansgaard, (1964) (Eq. 5). “It is an index of deviation from GMWL in which the values are usually close to 10‰ for the meteoric water line on a global scale” (Ayuba et al., 2019). High positive deuterium excess is characterized by precipitation (Yurtsever and Gat 1981; Pande et al., 2000), whereas evaporation by high



negative d-excess values. Negative d-excess values were reported in a few samples, while strong positive values were reported in the majority of the water samples, resulting in partial evaporation and heavy precipitation action either when the precipitation falls from the cloud or during storage (Ayuba et al., 2019). Nevertheless, Fig. 8b indicates that the gradual depletion of  $\delta^{18}\text{O}$  has contributed to the gradual enrichment of d-excess, reflecting the impact of precipitation on lake water. Therefore, the large difference in the d-excess with maximum positive values and only two negative values indicates that the characteristics of Satopanth Tal water are influenced by little evaporation and strong precipitation sources.



**Fig. 8** (a) Distribution of the values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  plotted on the global meteorological water line (GMWL), and (b) d-excess vs.  $\delta^{18}\text{O}$  of lake water showing the precipitation dominant

## Conclusion

This paper concentrates on several processes influencing the surface water. The hydrogeochemical study of Satopanth Tal indicates that water is slightly acidic to alkaline in nature. Among the anions,  $\text{Cl}^-$  is the major ion accounting for 57% followed by  $\text{HCO}_3^-$  of 27% of the whole anionic budget. While, from cations,  $\text{Ca}^{2+}$  is the dominant ion comprising 85% and  $\text{Mg}^{2+}$  constituting 31% of the total cationic budget. The high  $(\text{Ca}^{2+} + \text{Mg}^{2+}) / \text{TZ}^+$ , and  $(\text{Ca}^{2+} + \text{Mg}^{2+}) / (\text{Na}^+ + \text{K}^+)$  ratio, and strong positive correlation between  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and the low  $(\text{Na}^+ + \text{K}^+) / \text{TZ}^+$  ratio suggest that carbonate weathering is the dominant mechanism serving as the

critical source of ion dissolution in Satopanth Tal with comparison to silicate weathering. The higher  $\text{Ca}^+/\text{Na}^+$ ,  $\text{Mg}^+/\text{Na}^+$  and  $\text{HCO}_3^-/\text{Na}^+$  ratio than the highest ratio predicted for the silicate weathering suggest the exposure of carbonate weathering action. The trilinear plot indicates that the Satopanth Tal is influenced by the major hydrogeochemical facies of Ca-Cl type of water. The dominance of alkaline earth metal over alkali metals suggests the mechanism of carbonate weathering, which regulating the hydrogeochemistry of Satopanth Tal. Several investigations like Gibbs boomerang and stable isotopic analysis indicate that the predominant samples fall in the precipitation dominance zone, suggesting that precipitation is the dominant process that controls the lake water chemistry, which has been supported by the low ratio of  $\text{Na}^+/\text{Cl}^-$  and  $\text{K}^+/\text{Cl}^-$  concerning marine aerosols. The calculated C-ratio suggests the carbonate dissolution and derivation of the proton ( $\text{H}^+$ ) from sulphide oxidation in the Satopanth Tal region. The cation exchange study infers the processes influencing the direct exchange reaction rather than the reverse exchange in the study area. The PCA study suggests the carbonate weathering, sulphate mineral dissolution, and sulphide oxidation along with atmospheric precipitation contribution of atmospheric precipitation to govern the major ion chemistry.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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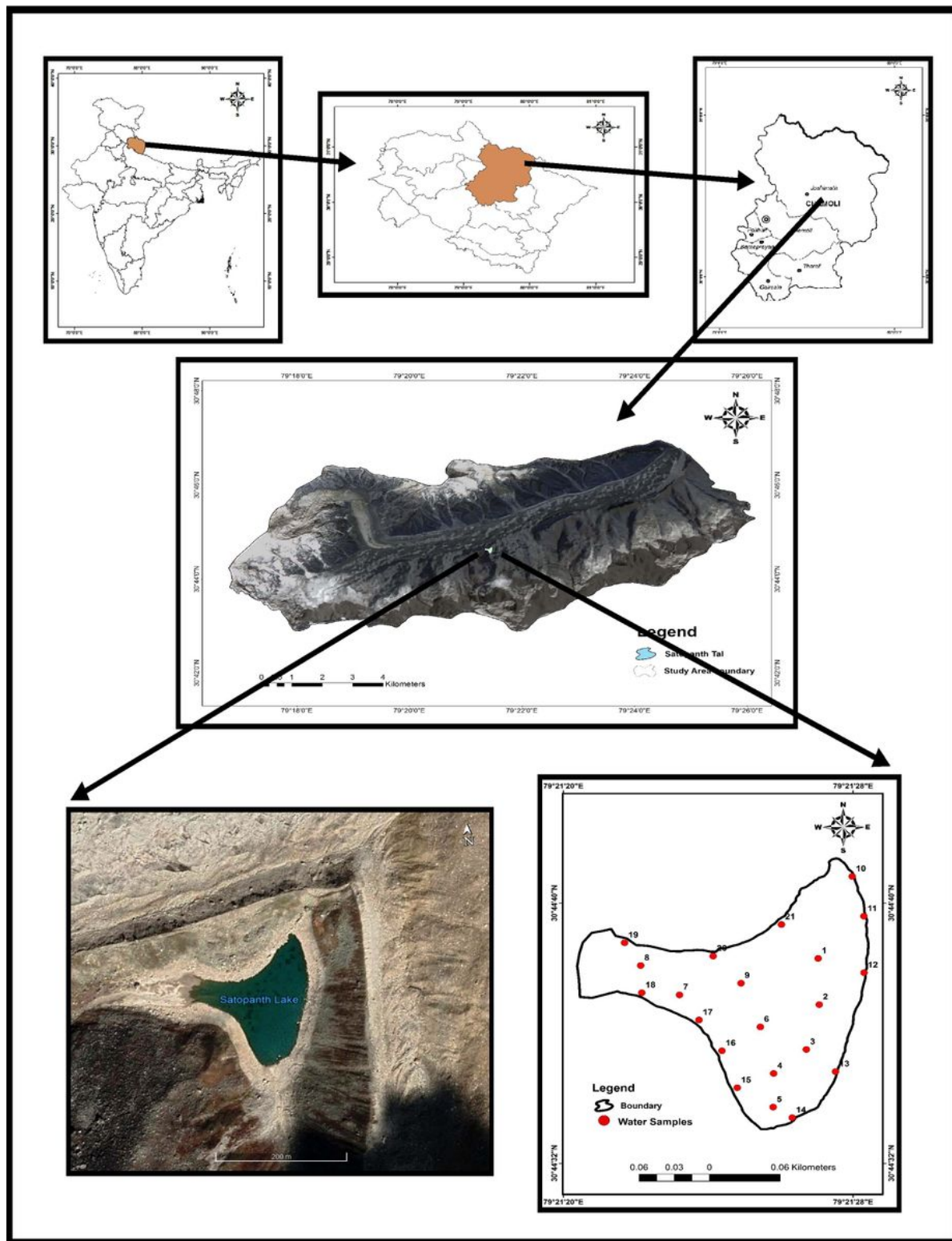
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**Highlights**

- The dataset helps to understand the processes affecting lake water geochemistry.
- Ionic ratios help to understand different hydrological and weathering processes.
- Piper trilinear and modified piper plot adopted to estimate the water type.
- Gibbs plots,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  utilized to dictate the major role of precipitation.

# Figures



**Figure 1**

Study Area and Sample Location map for Satopanth Tal, Chamoli, Uttarakhand exhibiting a recent time image extracted from Google Earth Pro and 21 water samples location points Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion



whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

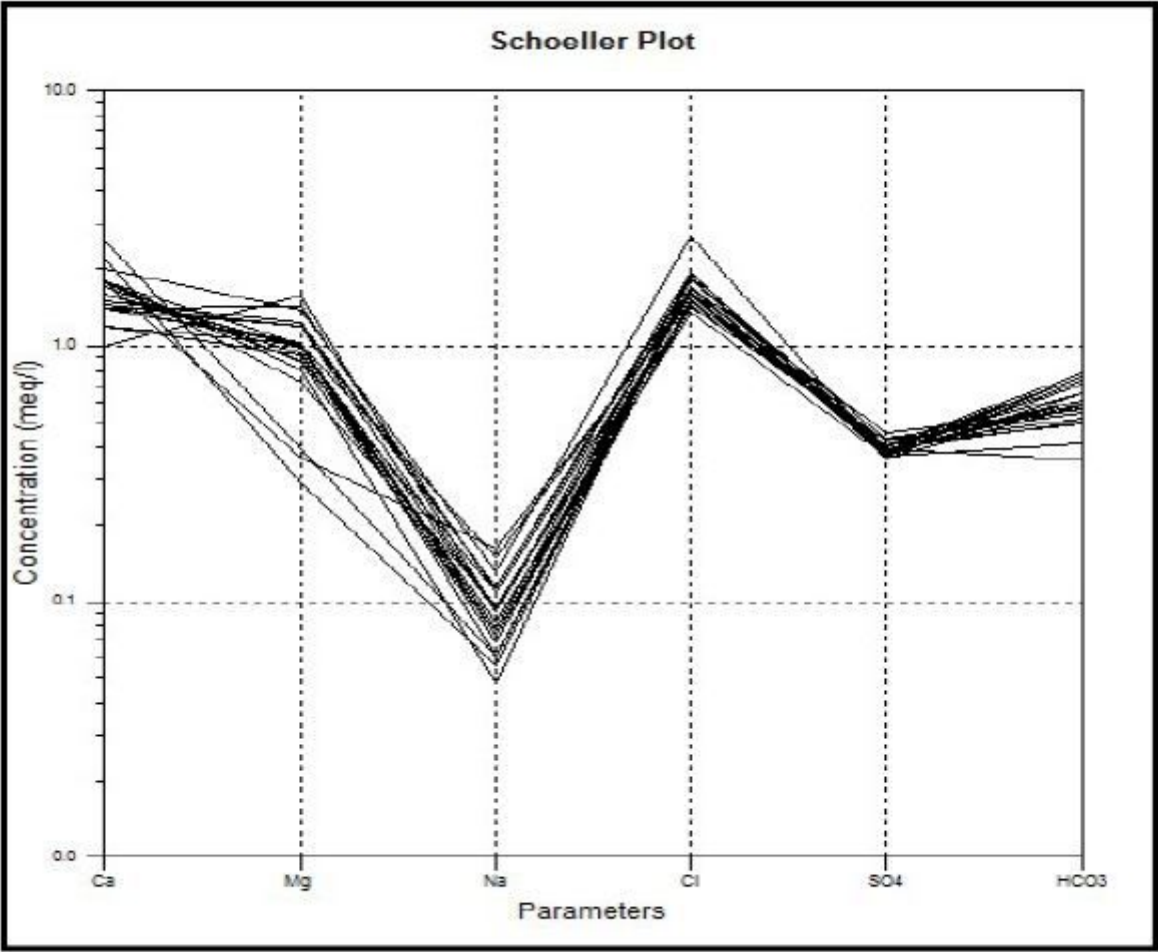
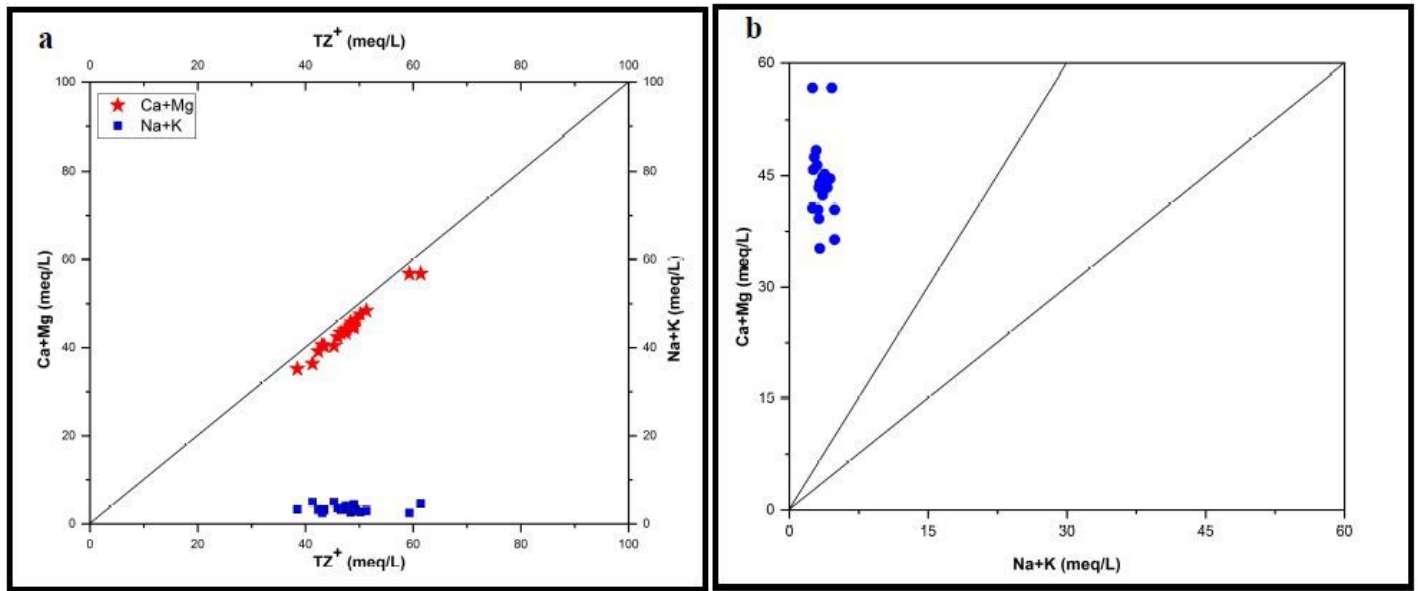


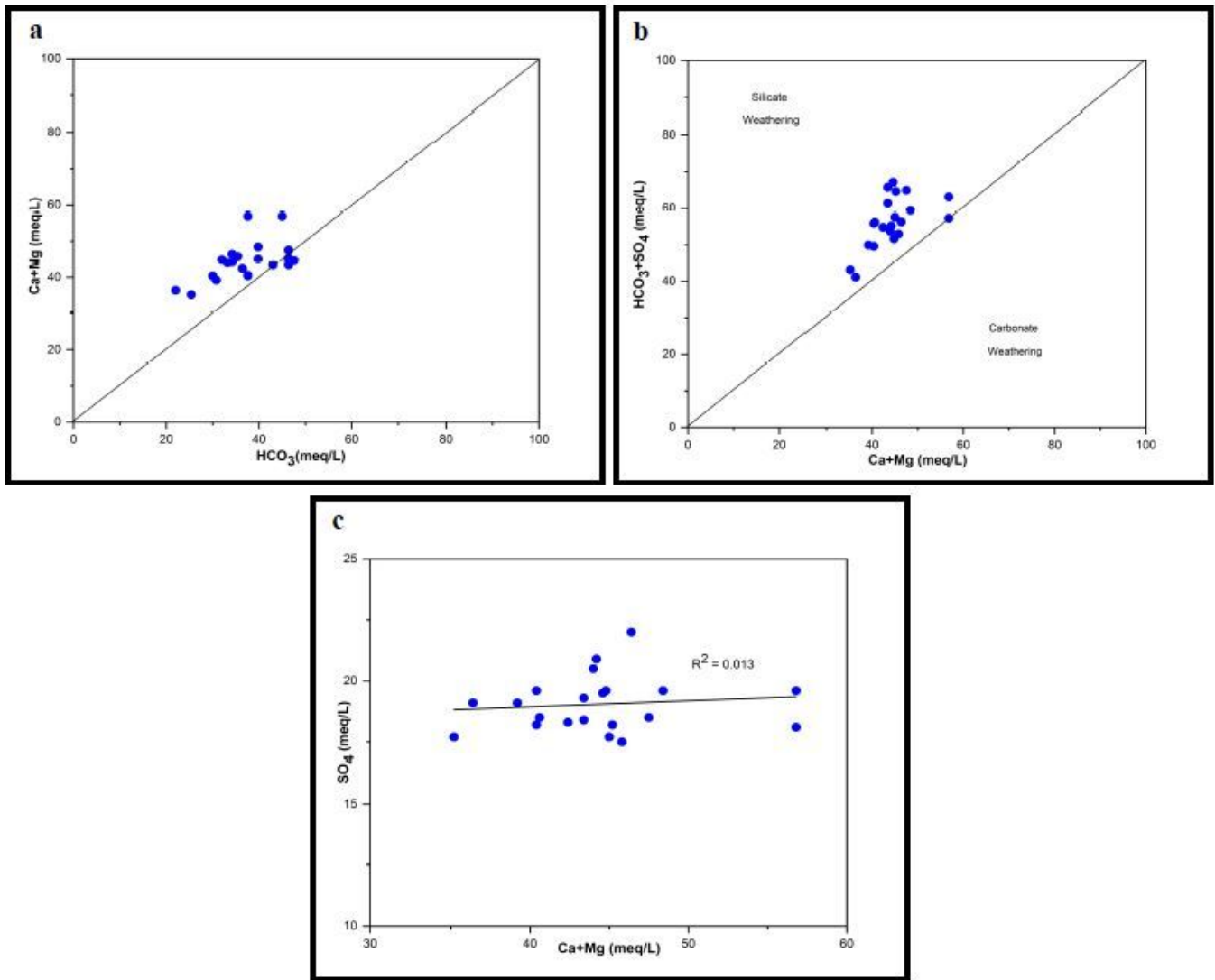
Figure 2

Schoeller diagram representing the concentration of anions and cations



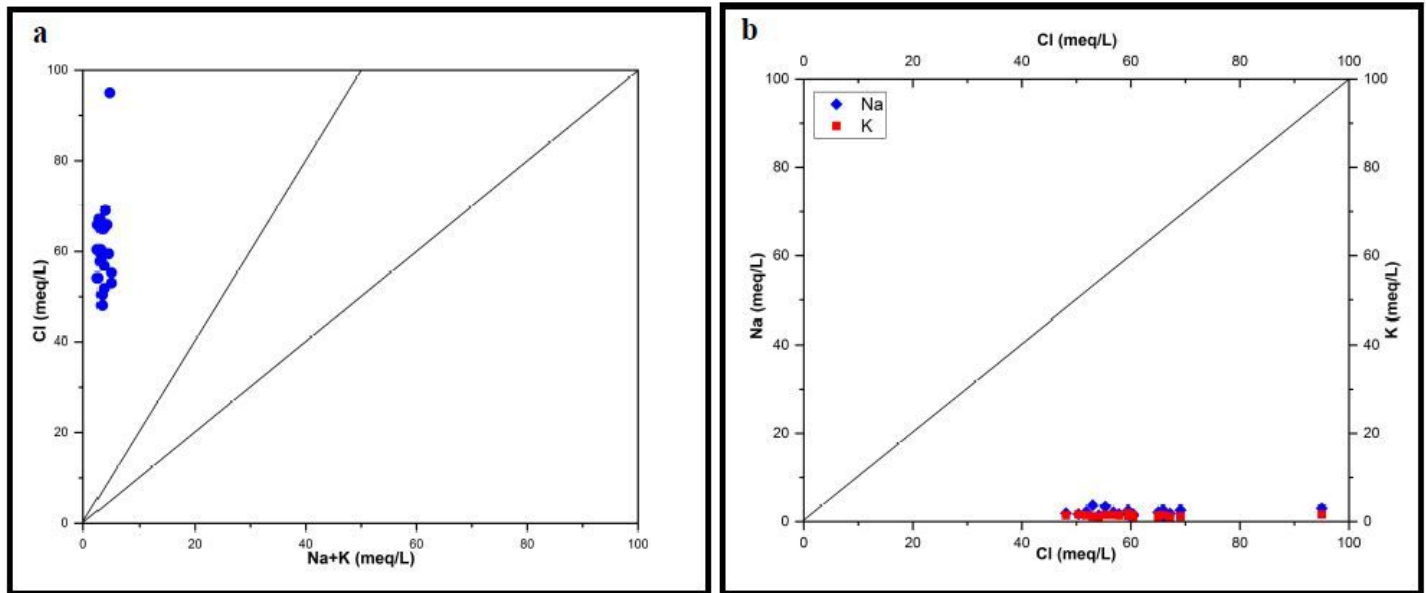
**Figure 3**

(a) showing the scatter plot of  $(\text{Ca}^{++}\text{Mg}^{+})$  vs.  $\text{TZ}^{+}$  and  $(\text{Na}^{+} + \text{K}^{+})$  vs.  $\text{TZ}^{+}$ , (b) showing the scatter plot between  $(\text{Ca}^{++}\text{Mg}^{+})$  vs.  $(\text{Na}^{+} + \text{K}^{+})$  suggesting the dominance of carbonate weathering



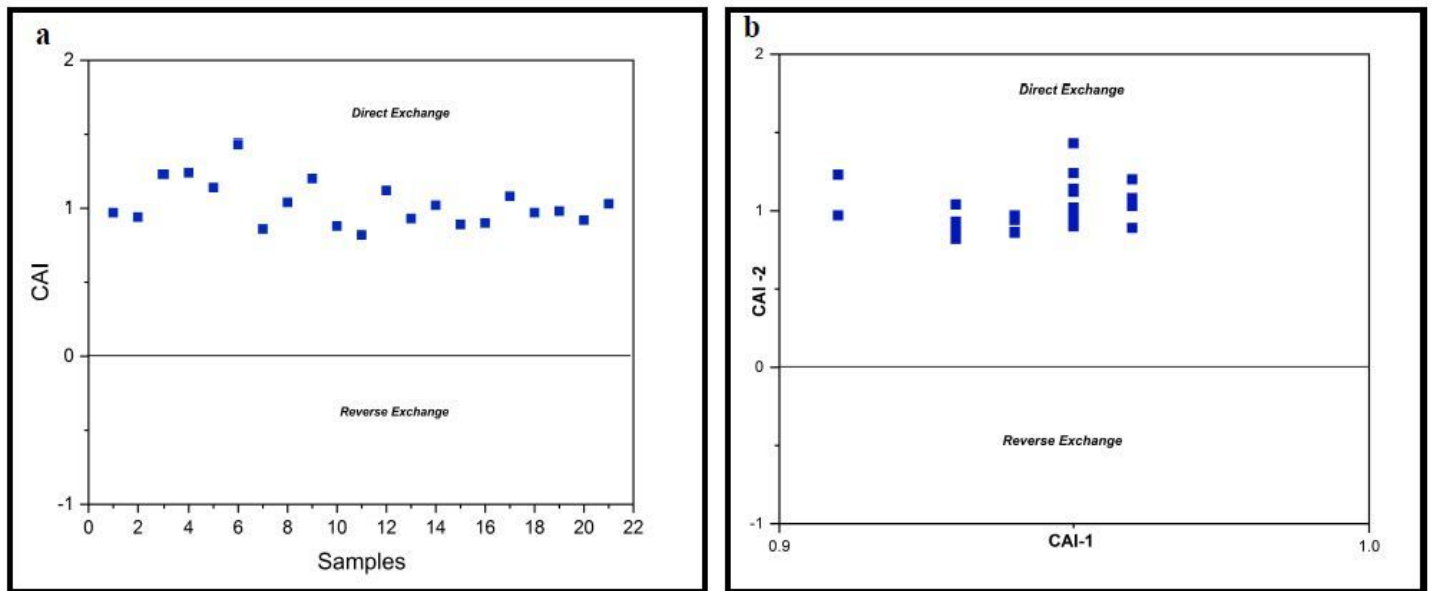
**Figure 4**

Showing the scatterplot between (a)  $(\text{Ca}^{2+}+\text{Mg}^{2+})$  vs.  $\text{HCO}_3^-$ , (b)  $(\text{HCO}_3^-+\text{SO}_4^{2-})$  vs.  $(\text{Ca}^{2+}+\text{Mg}^{2+})$ , and (c) regression plot between  $(\text{Ca}^{2+}+\text{Mg}^{2+})$  and  $\text{SO}_4^{2-}$  suggesting different weathering processes and contribution of sulphate to the water



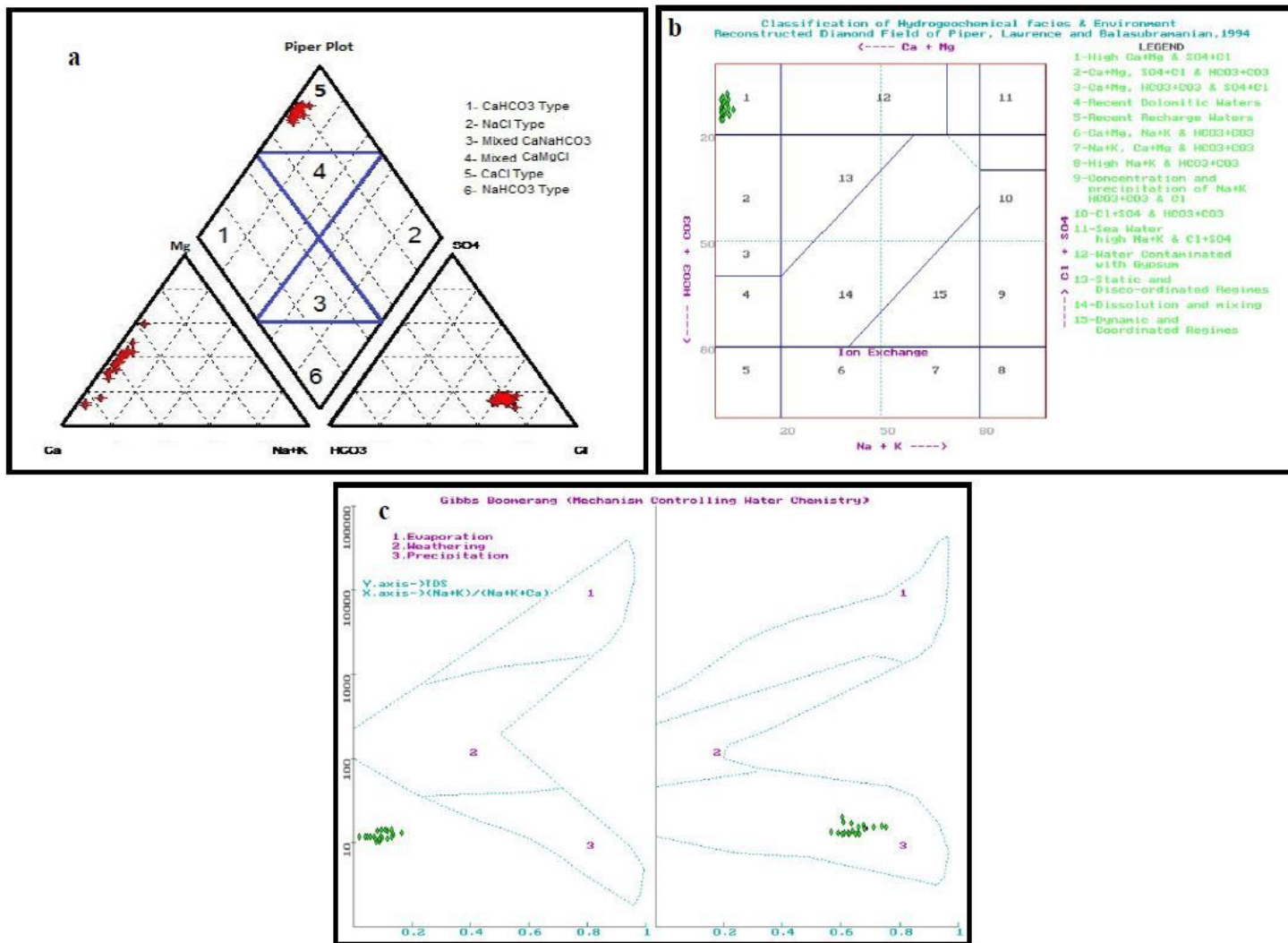
**Figure 5**

Scatter diagrams between (a) (Na++K+) vs. Cl<sup>-</sup>, and (b) Na+/Cl<sup>-</sup> and K+/Cl<sup>-</sup> suggests the contribution of atmospheric precipitations



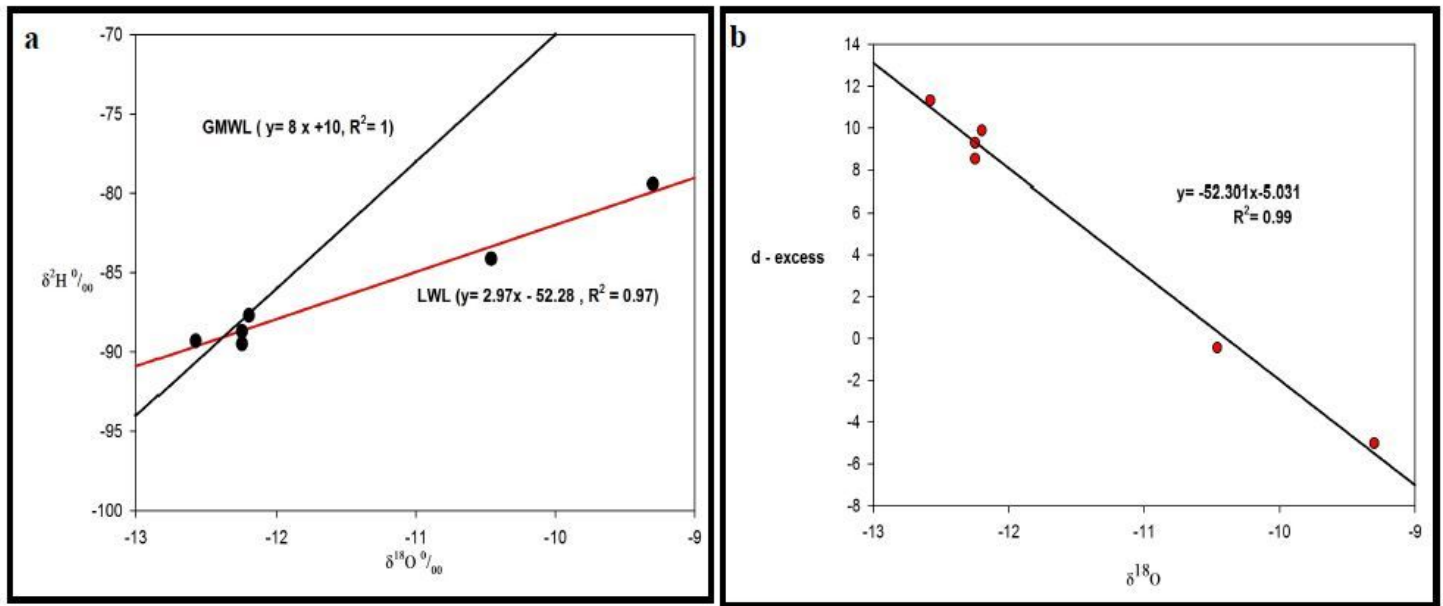
**Figure 6**

Relationship plot between (a) CAI vs. Samples and (b) CAI-1 vs. CAI-2 indicates the ion exchange processes in the lake water



**Figure 7**

(a) Piper plot indication the different water type, (b) The modified Piper diamond plot, and (c) Gibbs plot showing the major ion sources of Satopanth Tal



**Figure 8**

(a) Distribution of the values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  plotted on the global meteorological water line (GMWL), and (b) d-excess vs.  $\delta^{18}\text{O}$  of lake water showing the precipitation dominant