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Original Article

Hydrochemistry of Rara Lake: A Ramsar lake from the southern slope of the central Himalayas, Nepal

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Abstract: High-altitude Himalayan lakes act as natural storage for environmental evidence related to climate change and environmental factors. A great number of lakes are distributed in the southern slope area of the central Himalayas; however, research concerning the hydrochemical processes of these lakes is still insufficient. Herein, we present a comprehensive study on the water chemistry of the lake waters and the inlet stream waters from Rara Lake in western Nepal based upon samples collected in November 2018. The pH, dissolved oxygen, chlorophyll-a concentration (chl-a), water temperature, electric conductivity (EC) and total dissolved solids (TDS) were measured in situ, and the concentrations of major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, and NO_3^-) were analyzed in the laboratory. The results revealed that the water in Rara Lake is slightly alkaline, with pH values ranging from 7.6-7.98. The cations, in decreasing order of concentration in the lake water, are $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ with average concentrations of 20.64 mg·L^{-1}, 11.78 mg·L^{-1}, 1.48 mg·L^{-1} and 0.72 mg·L^{-1}, respectively; the order and concentrations for the anions is $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$, with average concentrations of 122.15 mg·L^{-1}, 2.15 mg·L^{-1}, 0.46 mg·L^{-1} and 0.55 mg·L^{-1}, respectively. The dominant cation and anion in the lake water are Ca^{2+} and HCO_3^-, and they account for 48.14% and 71.8% of the totals, respectively. The range of lake water TDS is from 95 mg·L^{-1} to 98 mg·L^{-1}, with an average of 96.85 mg·L^{-1}. The high ratio of (Ca^{2+} + Mg^{2+}) to total cations and the low ratio of (Na^+ + K^+) to total cations indicate that Rara Lake receives ions from rock weathering,

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especially from carbonate rocks. Similarly, Gibbs boomerang diagrams and Piper diagrams also support the hydrochemistry of Rara Lake as being dominated by rock-weathering patterns. Likewise, other statistical analysis tools, such as Principal Component Analysis (PCA) and correlation strongly suggest the dominance of weathering of calcium and magnesium bicarbonate rocks as the major source of ions in Rara Lake. However, several traces of anthropogenic inputs into the lake were noticed, and the hypolimnion in the lake appears to be oxygen deficient, which may not be an issue at present but cannot be ignored in the future.

Keywords: Water quality profiling; Major ions; Rock weathering; Anthropogenic; Rara Lake; Himalayas

1 Introduction

Lakes are important wetland areas that support the lives of various of plants, animals and humans (Paudel et al. 2017). Freshwater lakes at higher altitudes are very important for balancing ecosystems and have been sources of drinking water for many generations (Liu et al. 2009). As high-altitude lakes are characteristically pristine i.e. pure and in natural conditions, with constricted terrestrial areas, diluted surface water and limited vegetation cover (Raut et al. 2012), they are sensitive to climate change and anthropogenic activities (Raut et al. 2012). The physiochemical features of water are controlled by bedrock weathering, local climate, land forms and other parameters (Zhu et al. 2009; Fang et al. 2012; Liu et al. 2019). Under natural conditions, the rate of bedrock weathering is slow in high-elevation lakes, and these lakes are distant from anthropogenic disturbances due to the remoteness and inaccessibility of these areas (Wang et al. 2010; Raut et al. 2012). However, the vulnerability i.e. susceptibility to be influenced by external factors and rate of climate change in high-elevation lands, especially those in the Himalayan region, are greater than those for other regions of the world (Gaire et al. 2017). The variations of lake water chemistry under great climate change should be carefully studied to help understand the geochemical processes in high-elevation areas (Ramanathan 2007).

Nepal is located in the central part of the great Himalayan range; several studies of lake water chemistry and water quality have been conducted in the Himalayan region, which have provided baseline datasets for tracing ion sources for the waters. The studies conducted by Lofler in 1969 in high-altitude lakes in the Khumbu Himalayan Region (4,500-5,600 m a.s.l) presented general information on lakes in Nepal and its physical characteristics and those conducted in Rara Lake (2,990 m a.s.l) by Okino and Satoh (1986) described physical features, productivity and composition of the lake biomes in a limited study samples were the first research attempts for high-elevation lakes in Nepal (Rai 2000; Sharma et al. 2005). The analysis of hydro-chemistry from Gosaikunda Lake, situated at 4,380 m a.s.l, revealed that, despite being influenced by human activities, the lake is still oligotrophic and pristine (Bhatt et al. 2014). However, Rupa Lake, situated at an altitude of 600 m a.s.l in western Nepal is highly altered and is currently a eutrophic lake due to high nutrient values in the lake water and higher biomass levels that were revealed in a study conducted by (Kunwar and Devkota 2012).

Rara Lake is the largest and deepest lake in Nepal (Yagi et al. 2009) and is also an important high-elevation Ramsar site located on the southern slope of the Himalayas. Rara Lake is a very favorable study site for the study of environmental changes because it lies in the Intertropical Convergence Zone (ITCZ) and is affected by westerlies and the Indian summer monsoon (Cannon et al. 2014; Nakamura et al. 2016). Since the lake is situated at a higher altitude, it provides information regarding environmental changes without any interference. The bathymetry of the lake was first described by Okino and Satoh (1986). Yagi et al (2009) discussed the bathymetry and origin of Rara Lake and found that the lake is of tectonic origin and is the largest and deepest lake in Nepal. Nakamura et al. (2016) and Ghazoui et al (2015) studied the variations of the Asian monsoon at this lake based on archives of the lake sediments. Gurung et al (2018) and Jüttner et al (2018) studied the lake water chemistry in the littoral areas and sampled from the middle of the lake but only focused on the surface water. The understanding of the ion chemistry is sufficiently comprehensive through the study of inlet streams and the environmental setting of the study area (Yao et al. 2015).

Rara Lake (29°32'45"N, 82°05'35"E) (Fig. 1(a)) is one of the largest lakes in the western region of Nepal on the southern slope of the Himalaya at an altitude of 2,990 m a.s.l (Fig. 1(b)) (Nakamura et al. 2012;

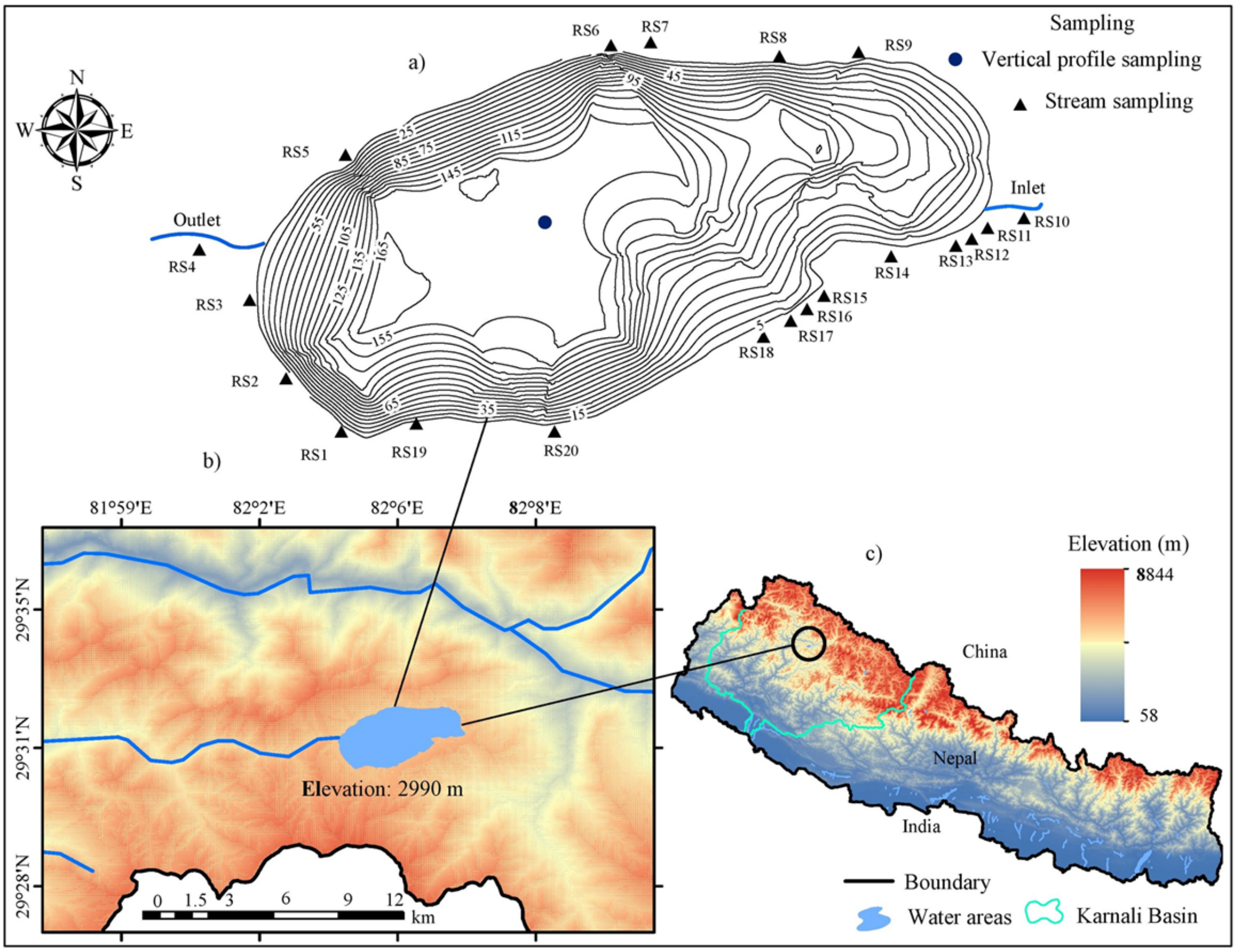

Fig.1 Bathymetric map of Rara Lake and sampling sites of water samples from streams and Lake (a) Location of Rara Lake and its elevation (b) Topographic map of Nepal showing Karnali River Basin and Rara Lake (c).

Jüttner et al. 2018). This lake is situated in the core of Rara National Park and is one of the important Ramsar sites, providing habitats for different plants and animal species and acting as the foundation for the lives of people living nearby. Rara Lake lies in the Karnali River basin (Fig. 1(c)), and only one outlet flows to join the Mugu Karnali River, which is a tributary of the Ganges River. The Rara Lake catchment is surrounded by mountains with elevations ranging from 3,200 m a.s.l in the south to 3,700-3,900 m a.s.l in the north and forms a wide rhomboid-shaped valley that opens to the east at the southwest part of the Lake (Gurung et al. 2018). Climatically, the lake lies within the temperate sub-Himalayan climatic zone with an annual mean temperature and precipitation of 11.5°C and 462 mm, respectively. The temperate forest around the catchment of Rara Lake consists of various species of conifers, namely, *Pinus wallichiana*, *Betula utilis* and *Abies spectabilis* (Yagi et al. 2009; Gurung et al. 2018). Some species, such as *Quercus semecarpifolia*, *Picea smithiana*, *Rhododendron*, *Juniperus*, *Alnus*, and *Cedrus* are also found near the northern part of the lake.

Rara Lake is approximately 5.1 km long and lies in a west to east direction with a maximum width of approximately 2.7 km in the eastern part of the lake. The lake has a surface area of 9.8 km² and a catchment area of 30 km² with a maximum depth of 168 m (Yagi et al. 2009; Nakamura et al. 2016; Gurung et al. 2018; Jüttner et al. 2018). More than 30 streams flow into the lake, while there is only one outlet along the western shore, which is known as Khater khola ("khola" means lake in the local language). Most of these streams drain into the west and south portions of the lake, while nearly all streams on the northern side of the lake dry up in the post-monsoon season. Agriculture is the main occupation of people living around the lake including cattle rearing and extraction of medicinal plants for their livelihood. The Northern part of the lake shore is occupied by human civilization that includes army post, national park office, and accommodating houses or hotels. Since, the lake is really far from the approachable zone, the human influence is minimal but the tourism industry especially domestic tourists seem to flourish since several years.

Table 1 Steam water sampling sites in Rara Lake catchment

ID	Position			Time
	Lat.	Long.	Elev. (m)	
RS-1	29°30'58"	82°4'22"	2984	10:53 AM
RS-2	29°31'12"	82°4'8"	2966	11:07 AM
RS-3	29°31'12"	82°4'8"	2966	11:29 AM
RS-4	29°31'44"	82°3'46"	2969	11:51 AM
RS-5	29°32'8"	82°4'23"	2976	12:24 PM
RS-6	29°32'34"	82°5'32"	2978	13:55 PM
RS-7	29°32'33"	82°5'38"	2976	14:08 PM
RS-8	29°32'33"	82°6'13"	2966	14:33 PM
RS-9	29°32'34"	82°6'33"	2981	14:50 PM
RS-10	29°31'51"	82°7'15"	2965	15:53 PM
RS-11	29°31'46"	82°7'11"	2970	16:00 PM
RS-12	29°31'45"	82°7'5"	2967	16:09 PM
RS-13	29°31'45"	82°7'0"	2980	16:15 PM
RS-14	29°31'44"	82°6'39"	2969	16:27 PM
RS-15	29°31'30"	82°6'22"	2989	16:49 PM
RS-16	29°31'29"	82°6'20"	2993	16:54 PM
RS-17	29°31'26"	82°6'17"	2997	16:57 PM
RS-18	29°31'22"	82°6'9"	2974	17:05 PM
RS-19	29°31'0"	82°4'41"	2960	17:34 PM
RS-20	29°30'58"	82°5'16"	2961	17:52 PM

The current research focuses on the study of streams flowing into the lake and emphasizes the vertical profiles of water chemistry, including all 3 zones present in a lentic body, e.g., the littoral (lake shore), benthic (deepest part of the lake) and profundal zones i.e vertical profile, which were lacking in the study of Gurung et al (2018) and in other studies in Nepal except for that of Tilitso Lake (Aizaki et al. 1987), which was conducted several decades ago. This research will be a novel one as there is no previous records of studies in the Himalayan lakes of Nepal. Despite harsh environmental conditions and difficult topography, the samples from streams and vertical profile from Rara lake were collected, which will be a great contribution to the future researchers and wave a path for researches in different fields.

The objectives of the present study are i) to investigate the vertical variations of the physical parameters and major ions in the water column, ii) to determine the causes of variations in the water column and their relationships with biological phenomena, iii) to outline the sources of major ions and the controlling factors for the water chemistry in Rara Lake, and iv) to study the contributions of the major ions from the streams into the lake. Since lakes at higher elevations are in ecologically marginal situations, they quickly react to changes occurring in the environment. The influences of high altitude and climate on the bio-geochemical properties of water are distinct in high-elevation lakes; therefore, these lakes are strongly preferred for comparative studies (Khadka et al. 2013; Rupakheti et al. 2017). Hence, this study provides baseline datasets for hydro-geochemical studies in Nepal and provides information to the government and stakeholders to maintain the policy and development of the study site.

2 Materials and Methods

2.1 Geological settings

In this study, the major ions from vertical water profile of the lake and stream samples from Rara Lake catchment were investigated (Fig. 1(a), Table 1). Most of these streams originated from the hills and mountains surrounding the lake catchment (Okino and Satoh 1986). Minimum sediment is contributed to the lake from the surrounding catchment area (Nakamura et al. 2012; Gurung et al. 2018). Previous study revealed two basins in Rara Lake. The bigger basin lies in the western part of the lake with a maximum depth of over 160 m and also covered about 80% of the total surface area, while maximum depth of about 127 m was revealed in the smaller basin in the east. A box shaped large basin with steep margins and a large flat area, and a "V"- shaped valley with smaller basin with gentler slopes and a small bottom area is present in the lake catchment (Okino and Satoh 1986; Yagi et al. 2009).

The catchment of the Rara Lake is mainly composed of Phyllite and Quartzite. The bed rock is highly weathered and covered with vegetation. The northern edge of the lake is composed of schist with quartz veins which contribute coarse sediments to the basin fill sediments. In the southern catchment dolomites are partly exposed. A drainage flowing from south collects surface water from dolomitic terrain while rest of the drainages coming to lake Rara collect the water flowing over the phyllite, quartzite and Schist (Fig. 2) (Dhital 2015).

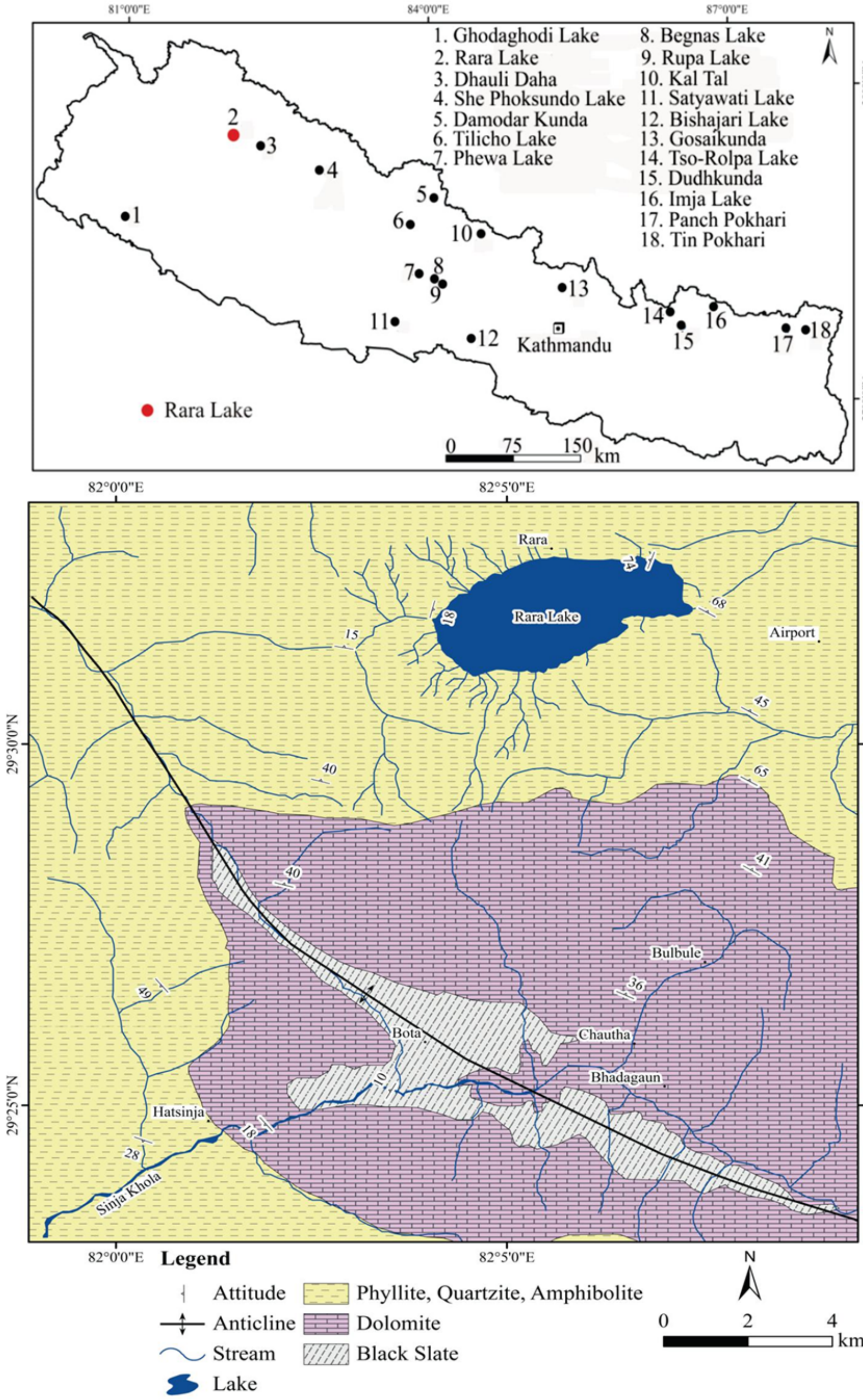

Fig. 2 Geological map of Rara Lake catchment with list of lakes in Nepal (modified after Dhital 2015).

2.2 Sampling and laboratory analysis

Post-monsoon water samples from the deepest point (29°31'51"N, 82°5'13"E) in the lake were collected on 6-7 November 2018 (Fig. 1(a)). A total of 14 vertical water samples from the lake were collected, and the water depths at the sampling sites varied from 0 m to 100 m. Water samples for determining temperature, dissolved oxygen and chlorophyll-a (chl-a) was measured with EXO2 multiparameter sonde (YSI Inc., USA) (measured at 1:50 PM, November 7, 2018) every 1 m interval till 160 m depths. While pH, EC and TDS were measured using a multi-parameter device (Hi-98129, HANNA, Romania) at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 80, 100 m depths. Water samples for determining the vertical changes of chemical characteristics were collected from 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 80, 100 m depth at the deepest point of the lake on November 7, 2018. Water samples were also collected from 20 stream sites flowing into the lake (Table 1) on 5 November 2018, and a total of 34 water samples were collected. The water samples were filtered using a 0.45-μm membrane filter. The water samples were kept in polyethylene vials and were stored in a refrigerator at 4°C until analysis. A bathymetric survey of the entire lake was completed with a narrow-beam parametric sub-bottom profiler (Innomar SES-2000, Germany) and with a Lowrance echosounder (Elite 7, USA). All stream sampling locations were recorded by a handheld GPS tracker, and the positions of the sampling sites in the lake were recorded by the Lowrance echosounder. A 20-cm Secchi disk was used to measure the lake transparency at different sites. The major ions in the water samples were analyzed in the laboratory at the Institute of Tibetan Plateau Research, CAS (Beijing) by use of ICS-2000 and ICS-2500 (Thermo Fisher Scientific, Waltham, MA, USA) ion chromatography.

2.3 Statistical analysis

The balance between anions and cations was used to calculate the bicarbonate concentrations in the water samples. As the HCO_3^- ion concentrations in the lake and stream waters were not measured, they were calculated using the ion-balance equation between cations and anions (Trower 2009; Pant et al. 2018; Adhikari et al. 2020).

Descriptive statistics, such as the means, medians and standard deviations were calculated for both stream samples and lake water samples. One-way ANOVA was performed to establish the contributions of the streams to the lake. Correlation analyses and principal component analyses (PCA) were performed to investigate the correlation coefficients between different parameters affecting the water chemistry of the lake. The correlation coefficients between the ions and other physical parameters were used to find possible similar sources between them, and PCA was useful for distinguishing the various contributions of ions originating in the stream sources. Further analyses for determining the controlling factors of the lake hydrochemistry were carried out using Piper plots and Gibbs boomerang diagrams.

3 Results and Discussion

3.1 Vertical fluctuations of the water quality profiles

The in situ measured surface water temperature, pH and electrical conductivity were 14.61°C, 7.78 and 193.85 μS·cm^{-1}, respectively, reflecting a slightly alkaline freshwater body. Similarly, the pH of the lake showed slight vertical variations ranging from 7.6-7.98, with changes in temperature and dissolved oxygen. The range of TDS was from 95 mg·L^{-1} to 98 mg·L^{-1}, with an average value of 96.85 mg·L^{-1}. Electric conductivity (EC) and total dissolved solids (TDS) had a similar pattern and exhibited no distinct variations. Other high altitude lakes in the southern Himalayas reported the conductivity values 49.5 μS·cm^{-1} in Gokyo Lake (Sharma et al. 2012), 83.36 μS·cm^{-1} in Dudkoshi (Gurung et al. 2018), whereas previous study by Okino and Satoh (1986) reported the EC of Rara Lake was 131.28 μS·cm^{-1}. Gurung et al (2018) reported increased of EC to 189.93 μS·cm^{-1} after 30 years in post-monsoon season. Our study also reported EC a little higher i.e. 193.85 μS·cm^{-1} in present findings.

The transparency of the lake at the deepest point was measured to be 19 m. In previous study, 18.9 m transparency was measured by Gurung et al (2018) in post-monsoon season. The vertical variations of the various physical parameters are shown in Fig. 3. Thermal stratification was observed (Fig. 3) in Rara Lake while measuring the physical parameters in situ. Lake stratification processes exert effects on the ecosystems within the lake (Wang et al. 2019). A record of three thermal strata in the lake and the fluctuations in lake water temperatures were also noted.

Epilimnion: The upper stratum of the lake, with circulation, uniformly warm temperatures, and the highest dissolved oxygen content, is termed the epilimnion. The epilimnion extended from the surface to approximately 27-29 m, with relatively homogeneous temperatures of approximately 14°C. Similarly, the dissolved oxygen concentrations appeared to increase with decreases in depth, since a decrease in temperature increases the dissolution of oxygen in water, to some extent.

Metalimnion: The metalimnion ranged from approximately 30 m to 50 m, with a distinct decrease in temperature of approximately 10°C that formed a thermocline and exhibited the highest dissolution of dissolved oxygen in this region. The phytoplanktonic biomass in the lake is indicated by the chlorophyll-a concentration (chl-a) (Parinet et al. 2004). The chlorophyll concentrations show slight to distinct increases at approximately 20-80 m, with a maximum at 50 m, suggesting high photosynthetic activity and increased phytoplankton in this zone, as these organisms need to adapt to low light conditions. This finding is also supported by the vertical profile of total nitrogen (TN) in Fig. 4. The epilimnion at around 40 m depth has increased TN i.e. the bio-productivity at that depth is higher than other depths. A study in Lake Puma Yum Co, located in the pre-Himalayas in Tibet, also recorded the highest dissolved oxygen values and high biological activity in the metalimnion (Ju et al. 2010).

Hypolimnion: With the trend of decreasing temperature, the hypolimnion, or the bottom stratum of the lake, was at approximately 8°C, with no distinct change in temperature from 60 m to 160 m, indicating a stable temperature gradient. The dissolved oxygen parameter shows stratification in the lake and has been decreasing in the depth. Okino and Satoh (1986) recorded well oxygenated vertical profile of the lake during 1982-1984 (58.2% saturation), but present research revealed that the oxygen saturation in the lake bottom is only (4.3% saturation). The dissolved oxygen concentration was nearly null at the bottom, indicating hypoxic conditions, and suggested a great risk for the aquatic ecosystem in the lake. The result revealed by this study is very important for further ecological research in the lake ecosystem. Low biological productivity or decreases in chlorophyll-a concentrations were also consistent with the oxygen decrease in the hypolimnion. There is a distinct decrease in TN concentration and NPOC (non-purgeable organic carbon) at the lake bottom, which suggests low nutrient and organic matter content responsible for reducing dissolved oxygen and making it unavailable at the lake bottom (Keller et al. 2008). NPOC and TN concentration of inflowing streams are similar to the lake values and are listed in Appendix 1.

Polymictic lakes, such as Taudaha with a 6 m depth, do not show stratification phenomena (Shrestha and Adhikari 2016). Similar stratification of Nam Co Lake was reported by Wang et al. (2009) with the epilimnion at 18-20 m, the metalimnion ranging from 20-60 m and the deepest and darker hypolimnion at the bottom of the lake. High dissolved oxygen concentrations from the top to bottom were found in Nam Co Lake, with the maximum dissolved oxygen at approximately 30-40 m (Wang et al.

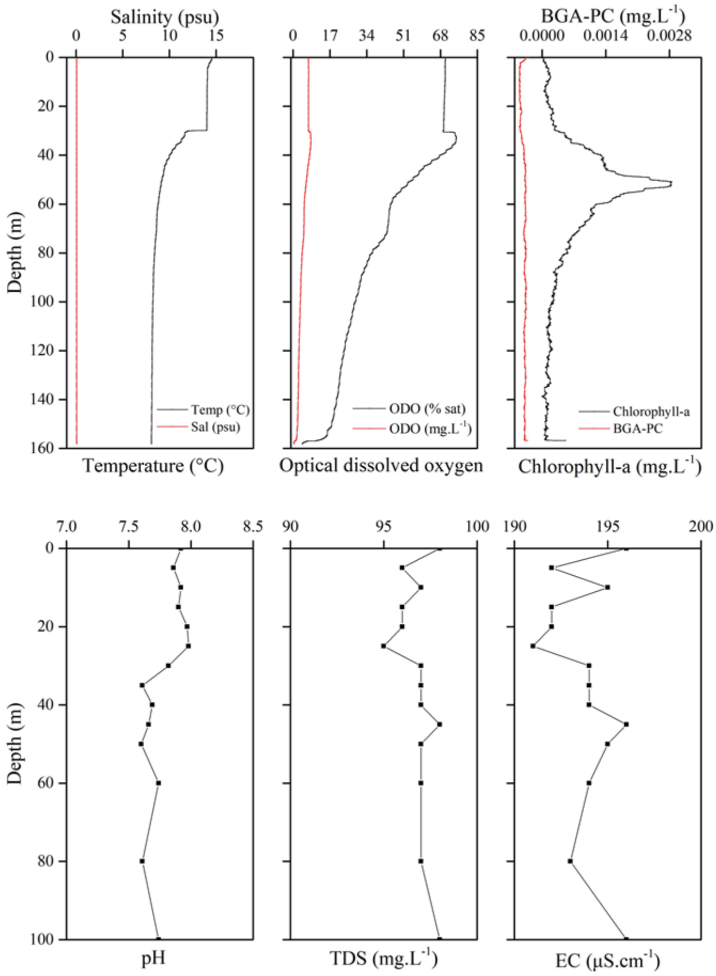

Fig. 3 Vertical variations of water quality parameters (measured at 1:50 PM, November 7, 2018) of Rara Lake. pH, electric conductivity (EC) and total dissolved solids (TDS) were measured in ITPCAS using pH/conductivity/TDS tester. Note: Sal-salinity, unit for salinity psu (practical salinity unit), ODO refers to optical dissolved oxygen, unit %sat (% saturation), BGA-PC refers to Blue Green Algae-phycocyanin.

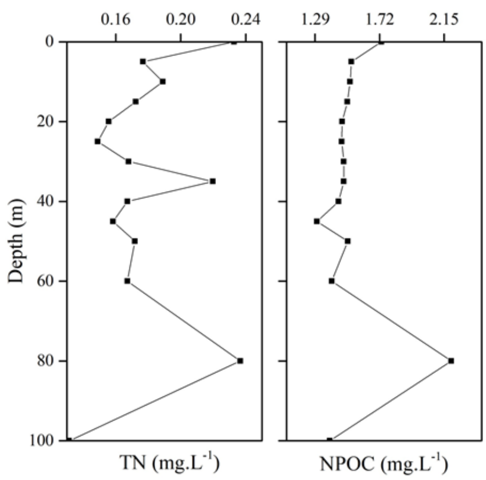

Fig. 4 Vertical profile of total nitrogen (TN) and non-purgeable organic carbon (NPOC) for Rara Lake.

2010) and sufficient dissolved oxygen in the hypolimnion of the lake. In contrast to the results for Rara Lake, Tilitso Lake, in the Himalayan region, showed an almost similar pattern of dissolved oxygen from the top to bottom of the lake except at 20 m, suggesting high biomass around that depth (Aizaki et al. 1987). The vertical profiles of sub-tropical lakes in Nepal, Fewa, Rupa and Begnas have also shown dissolved oxygen patterns similar to the lakes in the Tibetan Plateau (Nakanishi et al. 1988), which are in contrast to the results from Rara Lake.

For instance, the temperature profiles and dissolved oxygen contents strongly suggest that Rara Lake is a thermally stratified lake with a thin but distinct metalimnion, since the circulation of the thermocline to the surface seems unattainable because the bottom of the lake is highly deficient in dissolved oxygen. However due to lack of enough monitoring data, based on our vertical profile of in situ measured water parameters and ionic compositions and the fact that this is a freshwater lake, the mixing phenomenon can't be determined with sufficient evidences. Insufficient oxygen for aquatic plants and animals in the deeper waters and the distinct decrease of chl-a from the middle of the lake to the bottom suggest the occurrence of eutrophication in the lake. However, other parameters are yet to be studied. The overall pattern of mixing in the lake can be understood by studying the dynamics of thermal stratification (Elci 2008). The vertical temperature distribution in a large lake is greatly influenced by its geographic positioning and by its depth (Yang et al. 2018). Larger lakes with greater depths are highly prone to stratification more than are shallow lakes (Shrestha and Adhikari 2016). This phenomenon in a lake is a very important indicator that determines the water quality and aquatic ecosystem (Pal et al. 2014).

3.2 Vertical variations of the major ion compositions in lake water samples

Ca^{2+} and Mg^{2+} ions were found to be the major dominant cations, while HCO_3^- was the major dominant anion in Rara Lake. The cations, in decreasing order of concentration, were Ca^{2+} >Mg^{2+} >K^+ >Na^+ with averages of 20.64 mg·L^{-1}, 11.78 mg·L^{-1}, 1.48 mg·L^{-1} and 0.72 mg·L^{-1} respectively, while the order and concentrations of the anions were HCO_3^->SO_4^-> NO_3^- >Cl^-, with averages of 12 mg·L^{-1}, 2.15 mg·L^{-1}, 0.55 mg·L^{-1} and 0.46 mg·L^{-1}, respectively. Ca^{2+} and HCO_3^- were the dominant ions and accounted for 48.14% and 71.8% of total cations and anions, respectively.

Fig. 5 shows the vertical variations of anions (upper side) and cations (lower side) in the water column from 0-100 m in Rara Lake. The cation and anion concentrations show no obvious vertical variations. Cl^- and SO_4^{2-} seem to exhibit similar curves down to 20 m, suggesting that the source of these ions may be from a similar source. The anthropogenic sources of chlorine and sulphate could be agricultural fertilizers or from coal burning (Karthikeyan and Lakshmanan 2011). Mg^{2+}, Ca^{2+}, and K^+ show similar trends down to 5 m, and these trends suggest that the sources of these ions could be similar. The Mg^{2+}, Ca^{2+} and HCO_3^- concentrations seem to show similar trends down to the lake bottom, which may be evidence of carbonate weathering within the lake. According to the data from the vertical ion profiles, NH_4^+ ions showed different results. It was found that there were traces of NH_4^+ ions (0.06 mg·L^{-1}) at only 5 m and an absence at other depths, suggesting anthropogenic influences for the lake.

3.2.1 Major ion composition in stream water samples

Ca^{2+} and Mg^{2+} are the major dominant cations, while HCO_3^- is the major dominant anion in the inflowing streams in Rara Lake. The cations, in decreasing order of concentration in the inflowing waters were Ca^{2+} >Mg^{2+} > K^+> Na^+ >NH_4^+ , with averages of 16.78 mg·L^{-1}, 10.77 mg·L^{-1}, 1.67 mg·L^{-1}, 1.07 mg·L^{-1} and 0.04 mg·L^{-1}, respectively, and the concentrations for anions were HCO_3^->SO_4^{2-}> NO_3^-> Cl^-, with averages of 106.92 mg·L^{-1}, 1.68 mg·L^{-1}, 0.65 mg·L^{-1} and 0.59 mg·L^{-1}, respectively. Ca^{2+} and HCO_3^- are the major dominant ions and account for 55.32% and 97.34% of the total ions, respectively. The concentration of major ions in stream water samples has been listed in Appendix 2. The mean values of the concentrations of selected major ions are shown in Table 2.

The dominance of Ca^{2+}, Mg^{2+} and HCO_3^- have also been reported from other Himalayan lakes in Nepal which is shown in Table 3. The previous study in Rara Lake suggested that the pre-monsoon surface water has high concentration of major ions than in post-monsoon season (Gurung et al. 2018). Several factors like evaporative enrichment, dry deposition via long range transport and mixing of melting of

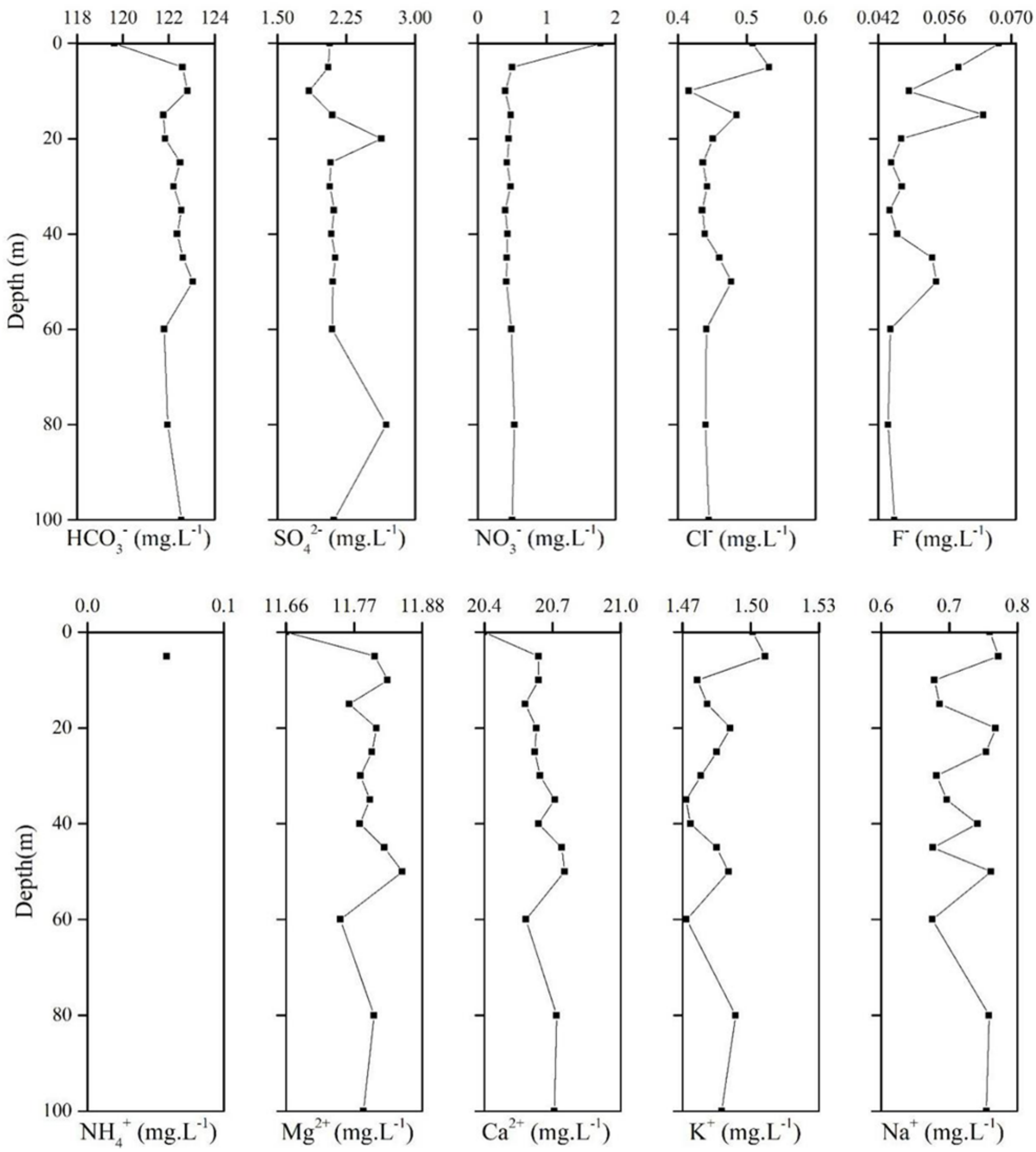

Fig. 5 Vertical profile of various anions (upper side) and cations (lower side) in Rara lake water.

Table 2 Major ionic composition of the 20 streams flowing into Rara Lake (mg·L^{-1})

Concentration	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Min.	6.20	0.25	0.12	0.23	0	0.26	0.14	0.57	1.08
Avg.	106.92	0.59	1.68	0.65	0.04	1.07	1.67	10.77	16.78
Max.	245.94	1.10	4.3	2.06	0.47	2.31	6.65	25.87	35.93

snow contribute in increase of ionic concentration in post-monsoon season (Deka et al. 2015; Gurung et al. 2018). Tilitso (Aizaki et al. 1987) a 95m deep lake in the higher Himalayas also reported similar ionic concentration as Rara Lake. Since, Tilitso is very far from human approach the lake was found to be very pristine and ultraoligotropic with low chlorophyll content. Panch Pokhari (Raut et al. 2017), Gokyo (Sharma et al. 2012), and Gosaikunda (Bhatt et al. 2014) lakes are also Himalayan lakes from the Southern Himalayas whose findings also reported that the lake water is dominance of HCO_3^- and Ca^{2+} ions.

3.3 Associations among the hydro-geochemical attributes

3.3.1 Correlation matrix

The relationship between two or more hydro-chemical parameters can be described by using correlation analysis. The degree of dependency of one variable on another is predicted by using a statistical tool known as the correlation matrix, which helps to establish the relationships between several hydro-geochemical parameters (Ramanathan 2007; Pant et al. 2018). Table 4 and Table 5 present correlation coefficient between parameters of stream and lake water respectively. There is a positive correlation between the Mg^{2+}-Ca^{2+} (r=0.88), Mg^{2+}-HCO_3^- (r=0.97) and Ca^{2+}-HCO_3^- (r=0.92) pairs, indicating strong carbonate weathering, while the Na^+ - K^+ (r=0.73) and F^--Cl^- (r=0.84) pairs with high positive correlations suggest evaporites weathering and anthropogenic inputs as the sources of these ions in the lake water. There is no correlation of SO_4^{2-} or TDS with the other parameters in the lake water samples. On the other hand, the positive correlations between the Mg^{2+}-Ca^{2+} (r=0.77), Mg^{2+}-HCO_3^- (r=0.80) and Ca^{2+}-HCO_3^- (r=0.99) pairs and the extremely low correlations between the Na^+-Ca^{2+} (r=0.008) and Na^+-K^+ (r=0.03) pairs and other ions suggest a common origin for Mg^{2+}, Ca^{2+} and HCO_3^-; however, the low correlation of Na^+ with the other parameters strongly suggests the absence of evaporites weathering and evaporation in the streams. The Na^+ - Cl^- (r=0.78) pair has a high positive correlation, which indicates that the ions are from a local lithogenic source and an interaction of halite with stream water (Jiang et al. 2015; Pant et al. 2018). Similarly, there is a high positive correlation between NH_4^+ and SO_4^{2-} (r=0.81), suggesting that the inflowing streams might have been contaminated with agricultural fertilizer and untreated industrial effluents and were also affected by grazing animals, such as horses (Paudyal et al. 2016). During the field investigation, several streams flowing into the lake were crossed with roads for transportation; also, sometimes horses walked through the streams, and their manure contaminated the streams. All cations and anions except Na^+, K^+ and Cl^- are highly positively correlated with TDS, which suggests that these cations and anions dissolved in the lake water and resulted in an increase in TDS (Liu et al. 2015).

3.3.2 Principal component analysis

Principal component analysis or multivariate analysis was applied for both lake and stream water samples to elaborate the principal components i.e. transformations of bigger number of correlated variables to smaller quantity of uncorrelated variables. The loading on the factor determines the intensity of relationship between each variables and eigenvalue>1 was considered as significant factor contributing to the sample data (Singh et al. 2015). The results of the principal component analysis, resulting variance and variable loadings for the lake water samples are shown in Fig. 6 right side. The three principal components explained 74.05% of the total variance. PC1 accounts for 35.50% and has strong loadings on Ca^{2+}, Mg^{2+}, and $HCO3^-$. The accumulation of these ions indicates carbonate rock weathering as the primary source of the ions with evaporate dissolution (Sun et al. 2010; Pant et al. 2018). PC2 accounted for 21.98% of the total variance and has strong loadings on the Na+, NH4+, F-, Cl- and SO42- ions. The aggregation of these particular parameters suggests that atmospheric inputs, mixed sources or silicate weathering may be the sources of these ions in the water. Similarly, PC3 accounts for 16.57% of the total variance and has strong loadings on NO_3^-, pH and temperature (T). The following loading of PC3 also suggests some influence from local anthropogenic inputs of NO_3^- in the lake water.

The results of the principal component analysis, resulting variance and variable loadings for the stream water samples are shown in Fig. 6 left side. The three principal components explained 86.51% of the total variance. PC1 accounts for 60.52% and has strong loadings on pH, Ca^{2+}, Mg^{2+}, HCO_3^-, K^+, SO_4^{2-}, F^-, and NO_3^-. The aggregation of Ca^{2+}, Mg^{2+}, and HCO_3^- suggests the weathering of carbonate rocks, while the association of NO_3^-, SO_4^{2-}, and F^- suggests that local anthropogenic inputs from agriculture and domestic animals may be the sources of these ions. These outcomes suggest that the deposition of these ions in the stream water causes the increase in TDS in the stream water samples. PC2 accounted for 16.44% of the total variance and has strong loadings on Na^+ and Cl^-. The following loading of PC2 suggests local weathering of halite rocks and evaporites as the source of ions in the stream water (Jiang et al. 2015). Similarly, PC3 accounts for 9.55% of the total variance and has loadings on NH_4^+ only. This result supports the fact that there are some anthropogenic influences in the stream water. The PCA of the lake and streams demonstrates similar kinds of loadings, which can be evidence of the influence of inflowing streams contributing to ion deposition in the lake, to some extent.

Table 3 Mean concentrations of major ions (mean±Standard deviation) in some high altitude mountain lakes in Nepal ($mg \cdot L^{-1}$)

Lake name	Studied by	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Type of water
Lake Rara (post-monsoon)	(Gurung et al. 2018)	0.35±0.19	5.89±3.65	0.80±0.51	9.17±2.67	0.10±0.05	0.14±0.09	54.02±23.5	Surface water
Lake Rara (pre-monsoon)		0.66±0.09	10.16±1.39	1.45±0.02	13.69±1.79	5.79±7.28	0.24±0.07	76.16±14.8	Surface water
Lake Rara (pre-monsoon)	Under study	0.73±0.03	20.64±0.91	1.48±0.06	24.79±0.04	0.43±0.03	1.51±0.07	180.89±6.25	Vertical Profile
Lake Rara	(Jones et al. 1989)	0.9	12	1.6	20	1.5	-	116	Surface water
Lake Gokyo	(Lacoul and Freedman 2006)	0.9±0.22	0.4±0.03	0.6±0.06	5.13±0.91	0.2±0.05	4.3±1.15	17±2.24	Surface water
Lake Gosaikunda	(Bhatt et al. 2014)	0.5±5.44	1.30±0.7	0.3±0.07	3.5±2.05	20.50±14	3.94±2.4	17.5±3.3	Surface water
Lake Tilitso	(Aizaki et al. 1987)	0.86±0.05	5.75±1.09	0.31±0.04	20.7±1.27	1.8±0.03	8.6±0.12	-	Vertical Profile
Lake Panch Pokhari	(Raut et al. 2017)	0.31±0.24	0.2±0.11	0.22±0.12	1±0.4	3.5±1.39	4.62±1.3	13.9±13	Surface water

Table 4 Correlation coefficients of different parameters in stream water for Rara Lake

Parameters	Na^+	Mg^{2+}	Ca^{2+}	NH_4^+	K^+	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}	TDS
Na^+	1										
Mg^{2+}	0.40*	1									
Ca^{2+}	0.008	0.77**	1								
NH_4^+	-0.04	0.70**	0.99**	1							
K^+	-0.03	-0.10	-0.14	-0.12	1						
HCO_3^-	0.05	0.80**	0.99**	0.98**	-0.13	1					
F^-	0.53**	0.70**	0.64**	0.60**	-0.27	0.66**	1				
Cl^-	0.78**	0.56**	0.25	0.19	0.07	0.27	0.55**	1			
NO_3^-	-0.03	0.49*	0.61**	0.60**	-0.06	0.61**	0.28	0.25	1		
SO_4^{2-}	0.22	0.89**	0.85**	0.81**	-0.10	0.86**	0.65**	0.36	0.50*	1	
TDS	0.02	0.76**	0.99**	0.99**	-0.08	0.99**	0.64**	0.26	0.60**	0.85**	1

Note: **means significance at 0.01 level, * means significance at 0.05 level.

Table 5 Correlation coefficients of different parameters in lake water

Parameters	Na^+	Mg^{2+}	Ca^{2+}	NH_4^+	K^+	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}	TDS
Na^+	1										
Mg^{2+}	-0.008	1									
Ca^{2+}	-0.057	0.88**	1								
NH_4^+	0.33	0.11	-0.01	1							
K^+	0.73**	-0.12	-0.20	0.57*	1						
HCO_3^-	0.009	0.97**	0.92**	0.18	-0.14	1					
F^-	0.09	-0.46	-0.55*	0.30	0.53*	-0.52	1				
Cl^-	0.40	-0.32	-0.37	0.66**	0.75**	-0.37	0.84**	1			
NO_3^-	0.27	-0.84**	-0.79**	-0.04	0.47	-0.90**	0.62*	0.48	1		
SO_4^{2-}	0.42	0.11	0.19	-0.13	0.28	-0.15	-0.26	-0.08	-0.06	1	
TDS	-0.20	-0.26	0.04	-0.28	-0.04	-0.22	0.09	-0.03	0.38	-0.12	1

Note: **means significance at 0.01 level, * means significance at 0.05 level.

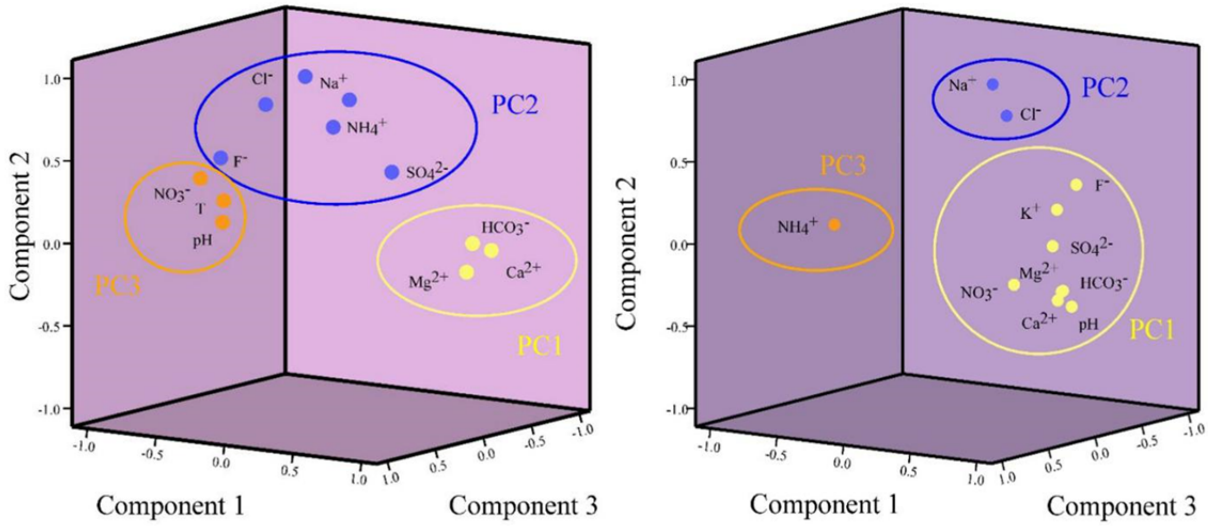

Fig. 6 Principal component analysis (PCA) of various physical and chemical parameters in Rara Lake (left side) water and Stream water (right side).

3.4 Mechanisms controlling hydro geochemistry of lake and stream water

3.4.1 Gibbs plot

Worldwide surface water chemistry is controlled by three different mechanisms, namely, rock dominance, atmospheric precipitation and evaporation-crystallization processes (Gibbs 1970; Wang et al. 2010; Pant et al. 2018). Calcium (Ca^{2+}) and sodium (Na^{+}) are considered as the major cations in fresh water bodies, and the weight ratio of $Na^{+}/(Na^{+} + Ca^{2+})$ on the x-axis and log(TDS) values on the y-axis are plotted to generate a Gibbs diagram (1970). According to the Gibbs boomerang envelope shown in Fig. 7, the ionic composition of Rara Lake and it's inflowing stream water is dominated by rock weathering. The TDS of lake water is nearly 100 mg·L^{-1} and is clustered in the rock dominance region of the Gibbs plot. Unlike the lake water samples, stream water samples show a different pattern. Among 20 stream samples, nine of them plot in the rock dominance region, and the remaining eleven samples fall into the partially precipitation dominant region. Of the eleven samples, four data samples plot outside of the Gibbs diagram due to very low TDS values and $Na^{+}/(Na^{+} + Ca^{2+})$ ratios. Sampling sites RS-10 to RS-18 (Fig. 1(a)) have relatively lower ion concentrations than the other sampling sites, since they are located in the southeast and southern parts of the lake, which have steeper slopes and larger coniferous forests that are surrounded by wet marshlands. The long distance transport of ions toward the lake and the influence of vegetation and other terrestrial factors can be a reason for low input of ions from these inflowing streams. These sampling sites consist of quartz and feldspar-rich rocks, which are very hard; due to this hardness, slow weathering of these rocks occurs. Sampling sites RS-15, RS-16, RS-17 and

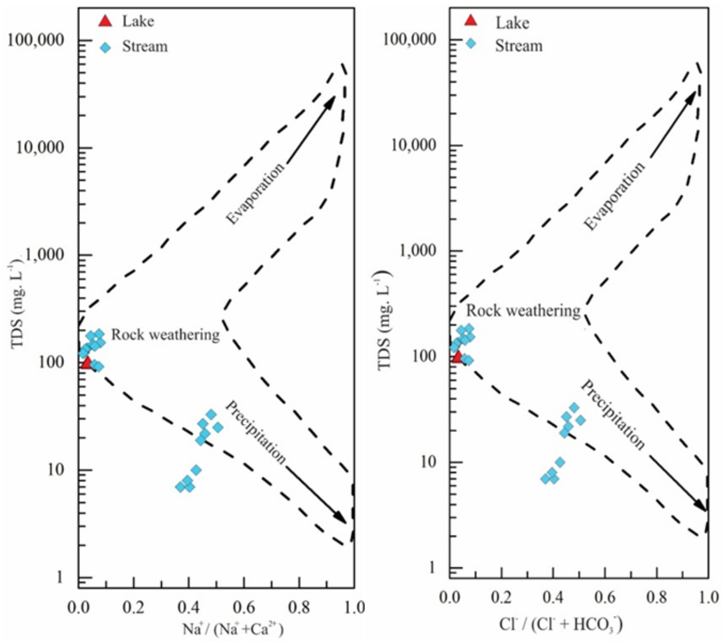

Fig. 7 Gibbs diagram showing rock dominance of water chemistry of Rara Lake. TDS: total dissolved solids.

RS-18, shown in Fig. 1(a), are in inflowing streams situated in the southern part of the Rara Lake and fall outside the Gibbs diagram due to lower TDS values and low concentrations of Na^+ and Cl^- ions. Since Rara Lake lies in the midland meta-sediment zone, the structure surrounding the lake is mostly comprised of metamorphic rocks. The geological structure also suggests that these sampling sites have black phyllite, quartz and feldspar (Fig. 2), all of which rarely weather. Similar reports were published by Wang et al. (2010) for Nam Co Lake, in which some samples from stream waters fell outside the Gibbs plot in a precipitation-dominant region, suggesting that these regions were influenced by precipitation; because of this result, the TDS levels were relatively low. Although Ca showed high concentrations, concentrations of Na were relatively low, leading to a very low ratio of $Na^+/ (Na^+ +Ca^{2+})$. The maximum TDS among the stream water samples was 185 $mg·L^{-1}$. The following result suggests that the water chemistry in Rara Lake has influences from local rock weathering and from long-range transport of ions into the lake. The weathering or dissolution of carbonate rocks is pretty quicker than the silicate rocks and thus mechanism of solute acquisition in aquatic systems is resulted by dissolution of carbonate rocks (Sharma et al. 2012). The low ratios of $Na^+/ (Na^+ +Ca^{2+})$ and $Cl^-/ (Cl^-+ HCO_3^-)$ along with low TDS levels suggest that Rara Lake and the inflowing streams fall in the rock dominance region, which is similar to the studies conducted by Qiao et al. (2017) for Tangra Yumco Lake. The source of ions in the stream waters was rock weathering, unlike Tangra Yumco Lake, which had a high ratio of Na/ (Na+Ca) and TDS levels similar to the ocean due to high rates of the evaporation and crystallization processes (Qiao et al. 2017). Similar results were published by a Canadian research team led by Ghesquière et al. (2015) that supported the above findings. The Gaerqu and Buqu Rivers in the Tibetan Plateau also showed low ratios of $Na^+/ (Na^+ +Ca^{2+})$ and $Cl^-/ (Cl^-+ HCO_3^-)$, with moderate concentrations of TDS, and plotted in the rock dominance region (Jiang et al. 2015).

As Rara Lake is surrounded by coniferous forests and hills in the southern part, it seems that the water flows from the hills and mixes with the lake water and that this area receives more filtered and cleaner water than is received by the other areas surrounding the lake. Rainfall occurred several days before and snowfall took place three days before the sample collection day. The locations of these streams seem to receive some water input from the Mugu Karnali River (see Fig.1(c)) and may be influenced by precipitation. Since the southern and southeast parts of Rara Lake are far from human settlement areas, during field investigation, the streams were clean and the presence of wetlands around that area represents evidence that these regions produce low TDS inputs and other factors into the lake from these stream waters.

3.4.2 Piper plot

All the data that were initially in units of milligrams per liter were converted to units of mill equivalents per liter, and a Piper plot was then created based on the work of Piper (1944). The Piper plot is a very important tool that is used to trace stream water compositions and process characteristics (Teng et al. 2016). The affinities of the alkaline earth metals (Ca^{2+} and Mg^{2+}) to the alkali metals (Na^+ and K^+) and of the weak acidic anion (HCO_3^-) to the strong acidic anions (SO_4^{2-} and Cl^-) shown in the Piper plot are found to be higher in Rara Lake. Research conducted by Gurung et al. (2018) also showed findings similar to those for Rara Lake. The Piper plot clearly demonstrates that the cations and anions in the water of Rara Lake and in the inflowing streams have a high affinity for the Ca^{2+}/Mg^{2+} and HCO_3^- junction as shown in Fig. 8.

3.4.3 Contribution of inlet streams to lake ion compositions

Because spatial variations of ions in the inflowing streams are of great significance i.e. very essential for lake system, they continuously supply water from their respective areas into the lake, resulting in notable variations in the lake water chemistry. Significant differences in the concentrations of some ions (e.g., Ca^{2+}, Mg^{2+}, HCO_3^-, NH_4^+, and K^+) suggest that there is some influence from the ions from the inflowing streams along the lake. Some major ion concentrations (e.g., Ca^{2+}, Mg^{2+}, NH_4^+, and K^+) from the east and northeast inlet stream sampling sites are higher than those for the southeast and south sides of the lake. Thus, the lack of sufficient water exchange between the inlet streams and some parts of the lake results in substantial variation between the ion concentrations. The higher pH value of the lake compared to the inlet streams suggests an increasing trend of pH in the lake due to mixing of water from upstream (Yao et al. 2015).

However, a major contribution to the water chemistry fluctuations from stream waters to the lake water was noticed. By comparing the mean values of the major ion concentrations and various physical parameters of streams with the lake water, as shown in Fig. 9, the tributaries seemed more likely to have some influence on the lake, since the major ion concentrations in the lake are relatively higher than in the inlet streams. On one hand, the mean concentrations of NH_4^+, Na^+, Cl^- and NO_3^- seemed to be higher in the stream waters than in the lake. The dissolution of Na^+ and Cl^- ions in the stream water occurred due to weathering of halite and evaporites in the stream locations, resulting in an increase of these ions (Wang et al. 2010; Stachnik et al. 2014), whereas the NH_4^+, NO_3^- and SO_4^{2-} ions were due to anthropogenic influences in the inlet streams as some of the streams in the study site were contaminated by animal dung and human transportation; therefore, the inflowing streams could contribute these components to the lake water. Hence, these ions flowed into the lake by deposition in the water column and resulted in the increase in TDS and contributed to the pH of the lake (Liu et al. 2015). The higher concentrations of HCO_3^-, Ca^{2+}, and Mg^{2+} in both the lake and stream waters suggest that catchment weathering of carbonate rocks is the source of ions in both the lake and stream sites with similar sources (Huang et al. 2009).

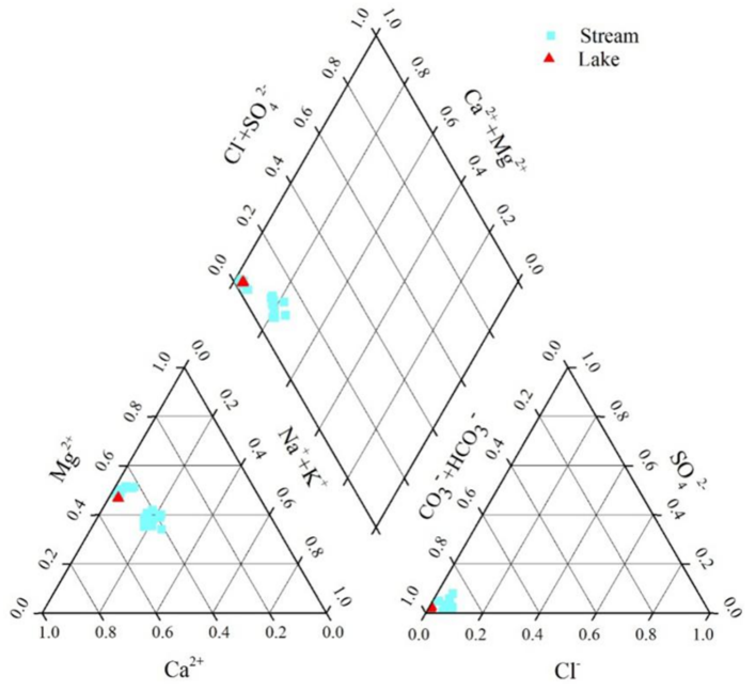

Fig. 8 Piper diagram showing rock dominance of water chemistry of Rara Lake.

The scatter diagram between $(Ca^{2+}+Mg^{2+})/Tz^+$ plots along a linear line, while the scatter diagram between $(Na^++K^+)/Tz^+$ plots away from the diagonal in Fig. 10, suggesting that the water chemistry is highly influenced by Ca^{2+} and Mg^{2+} and is less influenced by Na^+ and K^+. The smaller ratio of $(Na^++K^+)/Tz^+$ explains the Na^+ and K^+ deficiency and suggests a nominal contribution of cations through silicate weathering (Xu et al. 2010). Similar plots were derived by Khadka et al. (2013) for Begnas Lake in the Pokhara valley in the central Himalayas. Several rivers in the lesser Himalaya, Lake Nam Co (Wang et al. 2010) in the Tibetan plateau and Pandoh Lake in Himalchal Pradesh (Ramanathan 2007; Khadka et al. 2013) also showed similar results. Since the molar ratio between $(Ca^{2+}+Mg^{2+})$ and (Na^++K^+) is greater than 1, we can infer that the main source of ions in the Rara Lake water is carbonate weathering. These results also support the conclusion that the major source of ions in the inlet streams is weathering of carbonate rocks and that the resultant ions eventually contribute to the lake by deposition into the water column and may result in the increase of TDS and contribute to the lake pH.

4 Uncertainty and Recommendations

The major advantage of this paper is that we have focused on vertical water profiling and the inlet streams surrounding the lake. Previous studies of Rara Lake only focused on the surface water, so this research is very important for ecological studies of the southern slope of the Himalayas. Rara Lake lies in the Karnali River basin, which is very difficult to study due to the lack of meteorological stations and its rugged topography (Khatiwada et al. 2016). The topographic challenges in western Nepal have resulted in limited research in these areas. Due to this limitation, our paper presents data for only one season. In the monsoon season, there are disasters such as landslides and floods, causing access to high altitude lakes such as Rara to be very difficult.

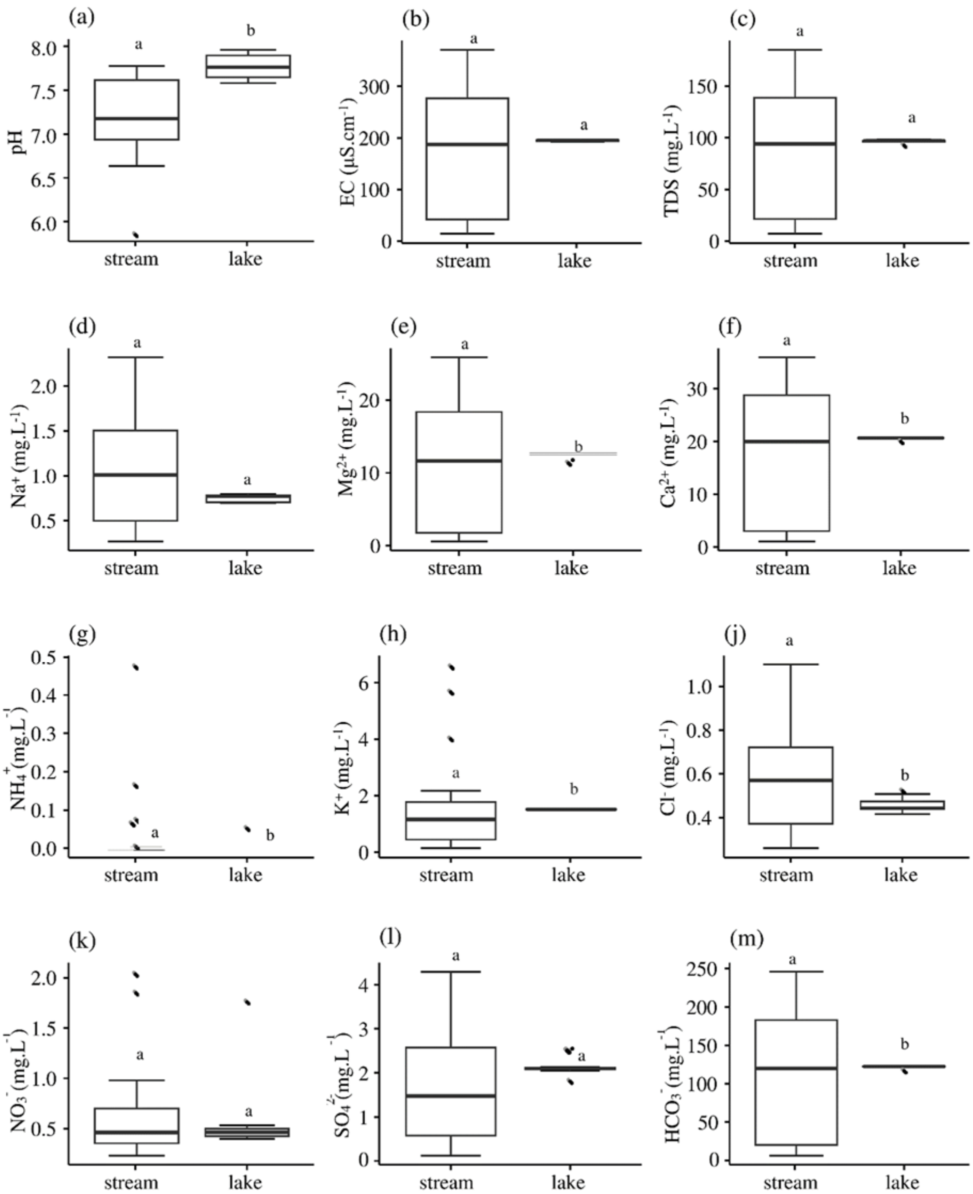

Fig. 9 Chemical quality of lake water and inlet-stream water given as mean values. Note: The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. Outliers are also shown where number of observations permit.

Bicarbonate levels were calculated using the charge balance equation with reference to previous publications (Trower 2009; Pant et al. 2018). It would have been much better if we had been able to calculate HCO_3^- levels using the titration method. However, due to insufficient equipment and time, we used the charge balance equation and proved our results by statistical analysis. For further improvement of this research, a seasonal study needs to be conducted to understand the long term changes and long range ion transport mechanisms resulting from the effects of westerlies and from the Indian summer monsoon. The vertical profiles of temperature and dissolved oxygen are not sufficient to demonstrate the stratification phenomena in the lake, so intensive study in this regard is necessary.

5 Conclusions

Rara Lake is located at high altitudes and is surrounded by hills and by the River Karnali, which is

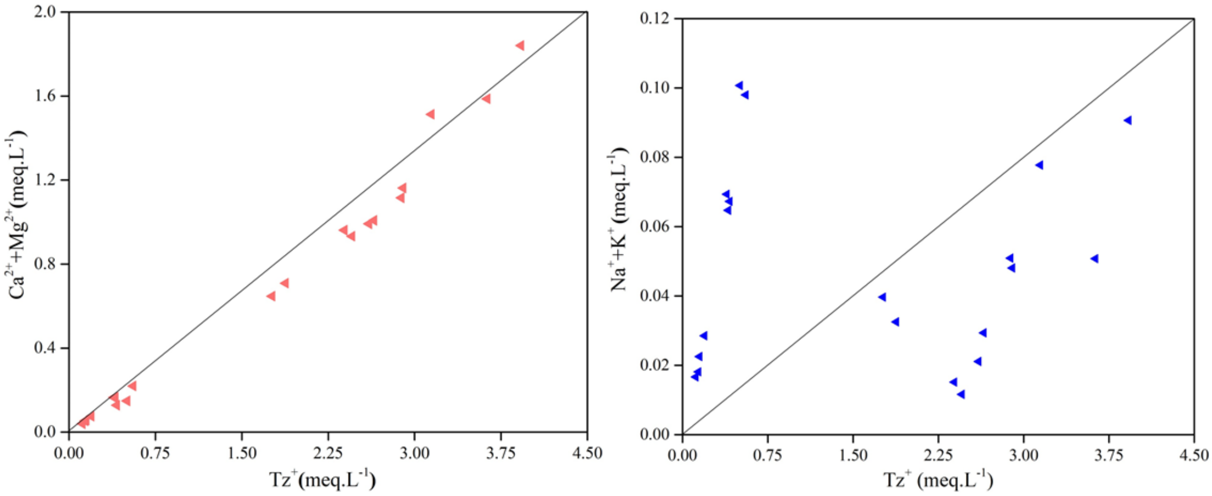

Fig. 10 Scatter diagrams showing (Ca^{2+} + Mg^{2+}) vs. total cations (Tz^+) and (Na^+ + K^+) vs. total cations (Tz^+) for Rara Lake water.

a tributary of the River Ganges, and its unique geographical features remain as an ideal study site for environmental and limnological studies. Our preliminary results from the present study show the following findings:

1) Ca^{2+} and Mg^{2+} ions are the major dominant ions in Rara Lake, averaging 20.64±0.08 mg·L^{-1} and 11.78±0.044 mg·L^{-1}, respectively, in the lake water. NH_4^+ and Ca^{2+} are the major cations that are dominant in the inflowing streams for Rara Lake, and average 16.78±13.68 mg·L^{-1}, and 10.77±9.27 mg·L^{-1}, respectively.

2) The results reveal that the water in Rara Lake is slightly alkaline, with a pH ranging from 7.6-7.98, is clear, and presents 19 m transparency. The lake has an average TDS level of 96.85 mg·L^{-1}, while the average TDS of the inlet streams is 83.55 mg·L^{-1}. Due to low concentrations of TDS and low ratios of Na^+/ (Na^+ +Ca^{2+}) and Cl^-/ (Cl^-+ HCO_3^-), the sampling sites fall in the rock weathering dominance region on the Gibbs plot, which is supported by other analyses, namely, Piper plots, PCA and correlations.

3) The oxygen concentration is an important parameter in deep and stratified lakes such as Rara, as it structures the biology in the water column. However, during thermal stratification, the hypolimnion appears to be deficient in dissolved oxygen, total nitrogen and dissolved organic carbon, while the metalimnion shows higher biological activity, i.e. chlorophyll a, which can pose a threat to the lake ecosystem.

4) The high occurrence of NH_4^+ ions in the streams appears to contribute traces of ammonium ions to the lake; this result is confirmed by the presence of NH_4^+ ions present at approximately 5 m depth and their absence at other depths.

5) Overall, the data from Rara Lake suggests that the source of ions in the lake is from the weathering of carbonate rocks. Since the lake and stream waters are dominated by Ca^{2+} and HCO_3^- ions, the chemical composition of the lake is highly controlled by rock weathering.

Our study presented vertical profile of chemical composition of the water column of Rara Lake and provided insights of differences and changes in chemical composition profile at different depths and its relationship with change in the environmental factors surrounding them. This is the first vertical profile study of such a deep lake in Nepal. This study provides insights into the deposition of major ions and their controlling environmental factors in Rara Lake, which will serve as baseline datasets for the water quality profiles of Rara Lake and other inflowing streams on the southern slope of the Himalayas. This vertical profile study should serve as a preliminary inventory survey for bacterial and diatom study i.e. functional ecology and metagenomics to establish a relationship between environmental parameters and biological community structure. Hence, the findings of the present study construct the baseline dataset for evaluating future anthropogenic influence on the lake and also pave a way for future lake management strategies.

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