Spatio-temporal hydrochemistry of two selected Ramsar sites (Rara and Ghodaghodi) of west Nepal

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**ABSTRACT**

The present study was conducted in two Ramsar sites, Lake Rara and Lake Ghodaghodi, of the western Nepal covering pre-monsoon and post-monsoon seasons of 2019 to find out the dynamics of the hydrochemistry. A total of 11 major ions (Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4\)\(^{+}\), F\(^{-}\), Cl\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^{-}\), NO\(_2\)\(^{-}\), HCO\(_3\)\(^{-}\)) along with six on-site parameters (temperature, pH, electrical conductivity, total dissolved solids, dissolved oxygen, and turbidity) were sampled in replicates from 18 sites in Lake Rara and 13 sites in Lake Ghodaghodi. Major ions were analyzed using ion chromatography including field and procedural blanks to maintain quality standards, whereas on-site parameters were measured by using standard multi-meter probes. The most dominant cations and anions were Ca\(^{2+}\) and HCO\(_3\)\(^{-}\) in both lakes indicating rock dominance through carbonate weathering as the primary source of dissolved ions in the lake waters. Further analysis indicated that Rara belongs to Ca(Mg)HCO\(_3\) and Ghodaghodi belongs to Ca\(^{2+}\)HCO\(_3\) type. The higher concentrations of Na\(^{+}\) and Cl\(^{-}\) during the post-monsoon indicates a possibility of long-range marine transport through monsoon precipitation.

1. **Introduction**

Water quality is one of the major environmental concerns of the world today (Millennium Ecosystem Assessment, 2005) as majority of aquatic ecosystems are under a range of anthropogenic threats. The major threats that bring changes to aquatic bodies include a range of pollution such as chemical pollution, acidification, eutrophication (Herschy, 2012), heavy metal contamination (Mustapha, 2008), long-range transport of pollutants (Schlesinger, 2004; Tripathee et al., 2014b); alien plants and animal species (Herschy, 2012), and overharvesting of aquatic resources (Hasen et al., 2019). One of the major impacts of water pollution include environmental degradation (Briggs, 2003; Pandey, 2006; Yayñtas et al., 2007), such as reduced oxygen level leading to eutrophication and algal blooms (Kambole, 2003), accumulation of high quantities of toxins like mercury in the fishes (Sharma et al., 2013; Okereafor et al., 2020), and loss of biodiversity (Hanson and Butler, 1994; Argüelles et al., 2019). Lately published reports also indicate the geogenic and anthropogenic activities (Barbieri et al., 2018; Ricolfi et al., 2019) as well as climate change affects the water quality and quantity (Barbieri et al., 2021).

Estimation of seasonal changes in water parameters such as dissolved gases, ions, organic and inorganic molecules is vital for evaluating temporal variations of water bodies such as lakes, ponds, rivers, streams etc (McInnes et al., 1996; Garizi et al., 2011). Major ion studies of lake waters are important to know the geology of the catchments, to study the
material loads into the lakes, to understand the water chemistry and also the processes which influence water chemistry, such as rock-weathering, evaporation, crystallization and precipitation (Gibbs, 1970). Such types of studies help us to determine the water quality, water type, pollution level, local geology, climatic effects including long-range transport of pollutants (Xu et al., 2010; Bhatta et al., 2015; Mayanglambam and Neelam, 2020). Major ions present in fresh water include both cations (such as Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺) and anions (such as F⁻, Cl⁻, SO₄²⁻, NO₃⁻, NO₂⁻, HCO₃⁻) (Yao et al., 2002). The chemistry of lake water depends on the presence of chemical elements in rocks and soils of the catchment area (Gibbs, 1970), their solubility, atmospheric gases and aerosols, basin morphology, climate, native biota, and anthropogenic activities (Bhatta et al., 2019a,b; Mayanglambam and Neelam, 2020). Determination of water quality based on physico-chemical parameters of lakes and reservoirs have largely been used which gives an excellent idea of the status, productivity and sustainability of such water bodies (Khadam and Kaluarachchi, 2006; Garizi et al., 2011). In addition, understanding of geochemical evolution of natural water can help in its management.

In context of Nepal, there are sporadic studies regarding environmental status of the Himalayan range. These studies are mostly conducted in eastern and central region of Nepal. However, in the last two decades, studies related to water chemistry have increased. For example, Loewen et al. (2005) studied organic pollutants and mercury pollution in the Everest region, Sharma et al. (2012, 2015) published their findings on limnology of high-altitude lakes (Gokyo and Gosainkunda). Sharma et al. (2013) revealed the mercury pollution in fishes from Lake Phewa. Major ions in the Nepalese rivers and their water quality have been documented by Sharma et al. (2020) and Pant et al. (2021). In addition, the work of Tripathee et al. (2014a, 2014b), Kang et al. (2016), Paudyal et al. (2016), Pandey et al. (2017), Chalaune et al. (2020) were some other works related to the environmental pollution in the Himalayan region. Many of these studies have suggested that most of the freshwater bodies in the country are showing signs of pollution. For instance, lakes and streams have revealed increased salinity (Tuladhar et al., 2015); and nutrient concentrations (Ghimire et al., 2013; Gurung et al., 2021). Despite these studies, information on the status of water quality and pollution and spatio-temporal variations in hydrochemistry are still scant, particularly in western Nepal.

In present study, we have included two lakes, namely Lake Rara, a high mountain lake and Lake Ghodaghodi, a lowland lake, which are situated in western part of Nepal. These two lakes are very important wetlands and are listed as Ramsar sites (Kafle and Savillo, 2009).

The main aim of the present study is to discuss the water quality variations of lake Rara and Ghodaghodi in terms of major ions to identify the hydro-geochemical processes that control lake water chemistry.

2. Materials and methods

2.1. Study area

This study was conducted in two Ramsar sites of western Nepal, namely Lake Rara (Rara hereafter) and Lake Ghodaghodi (Ghodaghodi hereafter). Rara is the largest and deepest high mountain lake of Nepal (Lacoul and Freedman, 2005) situated in the Rara National Park, Mugu district, Karnali province. It was established as a Ramsar site in September 2007. Rara Lake (29°32′45″N, 82°05′35″E) (Kaphle et al., 2021) covers an area of 1583 ha at an elevation of 2990 m a.s.l (Ferro, 1978). It is 5.1 km in length, 2.7 km in width, and 167 m in depth (Okino and Satob, 1986). Geologically, Rara is situated within lesser Himalayan group of rocks as Galwa tectonic window of Chhal Nappe (Puchs, 1977) comprising of phyllite and quartzite rocks. The springs from the southern part of the lake accumulates waters from the dolomites composed of calcium magnesium carbonates (Dhital, 2015). The lake and its catchment area lie within the subalpine climatic zone, having a temperature range from -4 °C in winter to 27 °C in the summer. There are more than 30 small streams as inlets into the lake, and there is only one outlet the Khatyad Khol, on the western shore, which flows ultimately into the Karnali River (Okino and Satob, 1986). The lake has socio-economic and religious values. The tourism economy, particularly in recent years, is rising due to the growing number of domestic as well as international visitors to the lake (Gurung et al., 2018). The number of domestic visitors has increased recently with motorway access. Being one of the popular tourist destinations, pollution created by visitors and tourists is also one of the main threats to this wetland (Shrestha et al., 2020).

Ghodaghodi Lake Complex which lies between 28°41′17″N, 80°56′47″E, is situated in the Kailali district of Far Western plain in Nepal. It covers an area of 2,563 ha at an altitude of 205 m a.s.l on the lower slopes of the Siwalik Hills (Bhuj et al., 2007; Joshi and KC, 2017). It was established as a Ramsar site in August 2003. Ghodaghodi is situated on the Northern terai (Bhawar zone) on the southern lower slopes of the Siwalik Hills. This site consists of a shallow oxbow lakes and ponds within the thick alluvial deposit (Dhital, 2015).

The lake complex consists of a system of around 14 large and shallow oxbow lakes and ponds having finger-like projections with marshes and meadows, streams and swamps. It is surrounded by tropical deciduous mixed Shorea robusta forest in the lower slopes of Siwalik Hills. The area has a sub-tropical monsoonal type of climate with dry winter and rainy summer. Lake Ghodaghodi is one of the major lakes of the complex covering an area of 138 ha (Lamsal et al., 2014). It provides habitats and resting place for different rare and migratory birds, large turtles and marsh mugger crocodiles (Khatri and Baral, 2012). The lake is fed by atmospheric inputs and surface flows (Pant et al., 2020). It has two outlets along the Mahendra highway. The depth of Ghodaghodi varies from 1 to 2 m during the dry period to 3–4 m during the monsoon season (Siwakoti and Karki, 2009). According to the local people, during dry months, the lake water is pumped into the nearby lands for irrigation. The nearby people depend on this wetland for fishing, timber and other resources (Lamsal et al., 2015). Overexploitation of freshwater and wetland resources is one of the threats faced by the wetland (IUCN Nepal, 2004).

2.2. Sampling and analyses

Water samples were collected from 13 sites of Ghodaghodi and 18 sites of Rara (Figure 1) in early June (pre-monsoon season) and November (post-monsoon season) in 2019. The sampling sites were selected based on diverse land-use patterns, accessibility and stressors. Two replicate samples were collected from each site. Temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), and dissolved oxygen (DO) were measured on-site with a Multimeter probe (“Consort bvb” Parklan 36, B-2300 Turnhout, Belgium). Turbidity was also measured onsite using Wagtech turbidity meter (WAG-WE30200). The probes were calibrated prior to sampling.

Water samples were collected in 20 mL ultraclean HDPE (high-density polyethylene) vials through a 0.45 μm polypropylene membrane filter. The sampling vials were rinsed with lake water thrice before the samples were taken. The water samples were collected from a depth of nearly 0.25 m below the surface. All vials were labeled, packed inside polyethylene zip-lock bags and kept in a refrigerator at 4 °C until the laboratory analysis. The samples for major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, F⁻, Cl⁻, SO₄²⁻, NO₃⁻, NO₂⁻) were analyzed using ion chromatography. The major cations were analyzed by Dionex DX-600 ion chromatograph using an IonPac CS12A analytical column, IonPac CG12A guard column, 20 mmol/L methanesulfonic acid (MSA) eluent, and CSRS 300 continuous self-regeneration cation suppressor. Major anions were analyzed by Dionex ISC-2500 ion chromatograph using an IonPac AS11-HC analytical column, IonPac AG11-HC guard column, 20 mmol/L potassium hydroxide (KOH) eluent, and ASRS 300 continuous self-regeneration anion suppressor. Bicarbonate concentration was calculated using ion balance (Dhital et al., 2014a).

Non-powder vinyl clean room gloves and masks were used during sample collection and laboratory work for avoiding contamination. Field blanks were prepared with deionized water and taken in the field and were analyzed for major ions. Results of blank samples indicated...
negligible contamination during sampling, storage and transportation of the samples. During the laboratory analyses, distilled deionized water was used. Freshly prepared standards of known concentrations and procedural blanks were analyzed during analytical process and calibration curves were made. The detection limits for the different cations and anions are as follows: Na\(^+\) (0.0003 mg/L), K\(^+\) (0.0009 mg/L), Ca\(^{2+}\) (0.0006 mg/L), Mg\(^{2+}\) (0.0008 mg/L), NH\(_4\)\(^+\) (0.0009 mg/L), Cl\(^-\) (0.0006 mg/L), SO\(_4^{2-}\) (0.0006 mg/L), NO\(_3^−\) (0.0004 mg/L), NO\(_2^−\) (0.0006 mg/L).

2.3. Data analysis

Non-parametric Mann-Whitney tests (<0.05% significance level) were performed to compare the concentration of major ions between seasons and lakes. Piper plot was drawn using Origin 2016 software to classify the chemical water type and source of major ions of the lakes and also to compare relative proportions of the cations and anions of both the lakes. Other plots, such as Gibbs and Scatter, were also drawn using Origin 2016 software. The Gibbs plot were drawn to summarize the evolution of water chemistry that explains about evapo-crystallization, precipitation and water rock interaction as main governing processes. The scatter plots of major ions were used to identify the major sources and processes controlling the major ion chemistry.

Spearman’s correlation analysis was done using IBM SPSS Statistics 26.0.

3. Results and discussion

3.1. Seasonal variations of onsite parameters

The results of different onsite parameters (temperature, pH, EC, TDS, DO, Turbidity) and their seasonal variation of Ghodaghodi and Rara are given in Table 1. The surface water temperature of Ghodaghodi showed seasonal variation (U = 0.00; n\(_1\) = n\(_2\) = 13; p < 0.001), having an average value of 33.07 ± 2.52 °C in pre-monsoon and 25.44 ± 1.46 °C in post-monsoon, respectively.

Similarly, the surface water temperature of Rara showed seasonal variation (U = 17; n\(_1\) = 17, n\(_2\) = 18; p < 0.001), having average values of 17.87 ± 2.80 °C in pre-monsoon and 14.54 ± 1.02 °C in post-monsoon. Lake waters were alkaline in nature exceeding a value of pH 8, and it showed significant seasonal differences both in Ghodaghodi (U = 41; n\(_1\) = n\(_2\) = 13; p = 0.027) and Rara (U = 21.50; n\(_1\) = 17, n\(_2\) = 18; p < 0.001). The pH was recorded higher in pre-monsoon season in both the lakes. Electrical conductivity (EC) is the measure of concentration of ions in water and it depends on volume and mobility of different ionic species (Das and Kaur, 2001; Khadka and Ramanathan, 2021). The EC values were significantly higher in pre-monsoon than in post-monsoon in Ghodaghodi (U = 28.5; n\(_1\) = n\(_2\) = 13; p = 0.004). TDS showed significant seasonal variation in Rara with higher value in post-monsoon (U = 73; n\(_1\) = 15, n\(_2\) = 17; p = 0.041), however, no significant differences of TDS were observed in Ghodaghodi. DO values were significantly higher in pre-monsoon season in both the lakes. Turbidity was significantly higher in pre-monsoon season in Rara (U = 30; n\(_1\) = 14, n\(_2\) = 17; p < 0.001), but no significant seasonal difference was observed in Ghodaghodi although it was high in pre-monsoon (Table 1). Moreover, turbidity showed high variability in both seasons in both lakes (Table 1).

Summarizing the results of onsite parameters, the water temperature was found to be significantly higher in Ghodaghodi compared to Rara (U = 161; n\(_1\) = 35, n\(_2\) = 39; p < 0.001) due to altitudinal differences. Mean pH for Ghodaghodi was 8.41 ± 0.80 and that of Rara was 8.27 ± 0.30. Several surface water bodies in Nepal are known to have alkaline pH (Jones et al., 1989; Lacoul and Freedman, 2005). The probable reason for the higher pH values in pre-monsoon season, which was observed in our
study, could be due to the increased rate of photosynthesis by primary producers (Das et al., 2009; Khadka and Ramanathan, 2021). Furthermore, the range of pH was narrow in pre-monsoon and wider in the post-monsoon indicating higher variability in the post-monsoon. Similarly, alkaline pH was reported in Rara by previous studies too, e.g., 8.53 by Okino and Satoh (1986), 8.32–8.42 by Gurung et al. (2018), and 7.6–7.98 by Kapile et al. (2021). The significantly higher EC values in pre-monsoon than in post-monsoon in Ghodaghodi could be due to the dilution effect at the beginning of rainy season (Ross, 1998). Khadka and Ramanathan (2021) also observed similar trends in Lake Phewa. Significantly higher values were observed for both EC (U = 166; n₁ = 26, n₂ = 35; p < 0.001) and TDS (U = 136; n₁ = 26, n₂ = 32; p < 0.001) in Rara compared to Ghodaghodi.

Significantly higher DO values in pre-monsoon season in both lakes might be due to higher photosynthetic rate by primary producers (Das et al., 2009; Khadka and Ramanathan, 2021). DO values were significantly higher in Rara compared to Ghodaghodi (U = 61; n₁ = 26, n₂ = 29; p < 0.001). Nevertheless, the observed DO values are suitable for sustaining the aquatic biota in both the lakes (CBS, 2019). Turbidity value seems to be higher in Ghodaghodi (U = 246; n₁ = 25, n₂ = 31; p = 0.020), the average values being 6.99 ± 8.80 for Ghodaghodi and 3.82 ± 5.47 for Rara.

### 3.2. Major ion concentrations

The mean concentrations and ranges of major ions are given in Table 2. The most dominant cation and anion in both lakes were Ca²⁺ and HCO₃⁻ respectively in both seasons. The mean concentrations of major cations in Ghodaghodi during pre-monsoon and post-monsoon seasons were in the order of Ca²⁺ > Na⁺ > Mg²⁺ > K⁺ > NH₄⁺ and Ca²⁺ > K⁺ > Mg²⁺ > Na⁺ > NH₄⁺ respectively (Table 2), whereas the major anions follow the order HCO₃⁻ > Cl⁻ > NO₃⁻ > SO₄²⁻ > F⁻ > NO₂⁻ during pre-monsoon and HCO₃⁻ > Cl⁻ > SO₄²⁻ > F⁻ > NO₂⁻ during post-monsoon season, respectively. Moreover, NO₂⁻ was detected in pre-

### Table 2. Major ion concentrations in Lake Ghodaghodi and Lake Rara.

| Parameters | Lake Ghodaghodi | Lake Rara |
|------------|-----------------|-----------|
|            | Mean ± SD       | Range     | Mean ± SD       | Range     |
| Na⁺ (meq/L) | 4.84 ± 2.84     | 2.58-12.41| 0.68 ± 0.19    | 0.32-1.20 |
| K⁺ (meq/L)  | 2.52 ± 1.45     | 0.51-5.94 | 0.9 ± 0.27     | 0.42-1.66 |
| Ca²⁺ (meq/L)| 23.83 ± 11.96   | 14.31-55.09| 21.72 ± 3.17   | 12.69-19.25|
| Mg²⁺ (meq/L)| 3.05 ± 2.79     | 1.40-11.63| 10.38 ± 1.91   | 8.18-13.34 |
| NH₄⁺ (meq/L)| 0.29 ± 0.46     | 0.47-1.55 | 0.36 ± 0.72    | 0.05-0.95 |
| F⁻ (meq/L)  | 0.03 ± 0.01     | 0.02-0.04 | 0.01 ± 0.00    | 0.01-0.02 |
| Cl⁻ (meq/L) | 0.38 ± 0.19     | 0.09-0.68 | 0.26 ± 0.16    | 0.14-0.92 |
| SO₄²⁻ (meq/L)| 0.06 ± 0.14    | 0.01-0.54 | 0.35 ± 0.07    | 0.24-0.42 |
| NO₃⁻ (meq/L)| 0.01 ± 0.02    | 0.02-0.06 | ND             | ND         |
| NO₂⁻ (meq/L)| 0.28 ± 0.25    | 0.01-0.62 | 0.07 ± 0.07    | 0.00-0.01 |
| HCO₃⁻ (meq/L)| 104.63 ± 58.61| 61.76-267.59| 122.76 ± 19.65| 66.48-140.81|

ND, not detectable.

Values followed by a different letter differ significantly (p < 0.05).

### Table 3. Seasonal variations in ionic ratio in the Lake Ghodaghodi and Lake Rara.

| Parameters | Lake Ghodaghodi | Lake Rara |
|------------|-----------------|-----------|
|            | Mean ± SD       | Range     | Mean ± SD       | Range     |
| (Ca²⁺+Mg²⁺)/K⁺ | 0.84 ± 0.02 | 0.80-0.87 | 0.97 ± 0.00 | 0.96-0.97 |
| (Na⁺+K⁺)/K⁺   | 0.16 ± 0.02 | 0.13-0.20 | 0.03 ± 0.00 | 0.03-0.04 |
| (Ca²⁺+Mg²⁺)/(Na⁺+K⁺)| 5.22 ± 0.80| 4.11-8.66| 28.81 ± 2.90| 22.64-35.31|
| HCO₃⁻/(Ca²⁺+Mg²⁺) | 1.19 ± 0.92| 1.15-1.24| 1.04 ± 0.02| 1.02-1.10 |
| HCO₃⁻/SO₄²⁻   | 1.00 ± 0.00 | 1.00-1.00| 1.00 ± 0.00| 1.00-1.00 |
| HCO₃⁻/F⁻      | 0.99 ± 0.00 | 0.99-1.00| 0.99 ± 0.00| 0.99-0.99 |

ND, not detectable.

Values followed by a different letter differ significantly (p < 0.05).
Figure 2. Scatter diagram with regression line showing the relationships among major ions during pre-monsoon (red square) and post-monsoon (blue circle) in Lake Ghodaghodi. Panels 2a, 2b, 2c and 2d show scatter plots of (Ca$^{2+}$ + Mg$^{2+}$) vs (HCO$_3$ + SO$_4^{2-}$), (Ca$^{2+}$ + Mg$^{2+}$) vs total cation (Tz$^+$), (Ca$^{2+}$ + Mg$^{2+}$) vs HCO$_3^-$, and (Na$^+$ + K$^+$) vs total cation (Tz$^+$), respectively.

Figure 3. Scatter diagram with regression line showing the relationships among major ions during pre-monsoon (red square) and post-monsoon (blue circle) in Lake Rara. Panels 3a, 3b, 3c and 3d show scatter plots of (Ca$^{2+}$ + Mg$^{2+}$) vs (HCO$_3$ + SO$_4^{2-}$), (Ca$^{2+}$ + Mg$^{2+}$) vs total cation (Tz$^+$), (Ca$^{2+}$ + Mg$^{2+}$) vs HCO$_3^-$ and (Na$^+$ + K$^+$) vs total cation (Tz$^+$), respectively.
monsoon season only in Ghodaghodi. In Rara, the mean concentrations of the cations were in the order of Ca$^{2+}$ > Mg$^{2+}$ > K$^+$ > Na$^+$ > NH$_4^+$ in both the seasons, and for anions the order was HCO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ > NO$_3^-$ > F$^-$ for pre-monsoon and HCO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ > F$^-$ > NO$_3^-$ for post-monsoon season, respectively (Table 2). The water bodies across the country have been reported with the dominance of Ca$^{2+}$ and HCO$_3^-$ by various studies (Reynolds et al., 1995; Deka et al., 2015; Raut et al., 2015; Gurung et al., 2018).

Most of the ions showed higher concentrations in pre-monsoon season (except K$^+$ and Cl$^-$ in Ghodaghodi and Na$^+$, Mg$^{2+}$, and Cl$^-$ in Rara) and similar findings have been reported in number of lakes from Nepal and elsewhere (Deka et al., 2015; Mamun and An, 2017; Gurung et al., 2018; Mayanglambam and Neelam, 2020). Evaporative enrichment, snow melting and long-range transport through dry deposition may be the possible reasons for the increased concentration of ions during the pre-monsoon season (Deka et al., 2015; Gurung et al., 2018). In contrast, dilution effect due to monsoon could be attributed to lower concentrations of most of the ions during post-monsoon season because monsoon plays an important role in dilution of major ions in a large number of reservoirs in Asia (Mamun and An, 2017). In addition, ions like nitrate and ammonium show high concentration in some sites that may be due to some localized reasons like more human activity and cattle grazing sites.

The high ratio of (Ca$^{2+}$+Mg$^{2+}$)/Tz$^+$ throughout the study in both lakes (Table 3) indicates dominance of carbonate weathering that acts as a primary source of dissolved ions in lake waters. The Ca$^{2+}$+Mg$^{2+}$ vs Tz$^+$ scatter plots (Figures 2b & 3b) show distribution of points in a linear manner slightly below the equiline suggesting significant contribution of Ca$^{2+}$ and Mg$^{2+}$ ions to Tz$^+$. In contrast, (Na$^+$+K$^+$)/Tz$^+$ ratios were very low in both lakes throughout the study (Table 3, Figures 2 and 3). The (Na$^+$+K$^+$)/Tz$^+$ scatter plots (Figures 2d & 3d) show that points are not along the equiline and are scattered. Such a result indicates deficiency of Na$^+$ and K$^+$ and correspondingly lower contribution of aluminosilicate weathering to both lakes (Khadka and Ramanathan, 2021).

The (Ca$^{2+}$+Mg$^{2+}$)/(Na$^+$+K$^+$) ratio for pre-monsoon and post-monsoon seasons were 5.22 ± 0.80 and 7.41 ± 3.84, respectively in Ghodaghodi (Table 3) which indicates the dominance of Ca$^{2+}$ and Mg$^{2+}$ ions over Na$^+$ and K$^+$ ions. In Rara, the (Ca$^{2+}$+Mg$^{2+}$)/(Na$^+$+K$^+$) ratio for pre-monsoon and post-monsoon seasons were 28.81 ± 2.90 and 27.46 ± 4.12, respectively (Table 3) indicating even higher dominance of Ca$^{2+}$ and Mg$^{2+}$ ions over Na$^+$ and K$^+$ ions in comparison to Ghodaghodi.

The scatter plots of (Ca$^{2+}$+Mg$^{2+}$)/(HCO$_3^-$+SO$_4^{2-}$) in both lakes (Figures 2a & 3a) show that the samples spread near the equiline suggesting dominance of Ca$^{2+}$+Mg$^{2+}$ ions that is requiring very less portion of HCO$_3^-$ and SO$_4^{2-}$ to be balanced by alkali metal ions from silicate weathering. Similarly, the scatter plots of Ca$^{2+}$+Mg$^{2+}$ vs HCO$_3^-$ in both lakes (Figures 2c & 3c) also fall near equiline suggesting HCO$_3^-$ is balanced by Ca$^{2+}$ and Mg$^{2+}$. Furthermore, the HCO$_3^-$/Tz$^+$ ratio was high in both lakes (>0.99; Table 3) in both seasons indicating the dominance of HCO$_3^-$ anion in the lake water.

High (Ca$^{2+}$+Mg$^{2+}$)/Tz$^+$ ratio and a low (Na$^+$+K$^+$)/Tz$^+$ ratio in our study (Table 3) confirm the dominance of Ca$^{2+}$ and Mg$^{2+}$ resulting from carbonate weathering with very less input from silicate weathering. Similarly, the high ratio of HCO$_3^-$/Tz$^+$ indicates the dominance of bicarbonate in both lakes which is in accordance with a previous finding by Gurung et al. (2018) in Lake Rara. Similar trends were observed in the different Himalayan lakes from India and Nepal, for example, Pangchokhari (Raut et al., 2015), Begnas (Khadka and Ramanathan, 2013), Phewa (Khadka and Ramanathan, 2021), Pandoh (Ramanathan, 2007), Loktak (Mayanglambam and Neelam, 2020), Renuka (Das and Kaur, 2001), Tsokyo Tso, and Sella (Deka et al., 2015). According to Tranter et al. (1993), bicarbonate may be derived from two main sources, one from the dissociation of atmospheric CO$_2$ (Reaction – 1) and the other from the dissolution of carbonates, such as calcite (Reaction – 2).

\[
\text{CO}_2 (aq) + H_2O (aq) H^+ (aq) + HCO_3^- (aq)
\]

\[
\text{CaCO}_3 (s) + H_2O (aq) H^+ (aq) + HCO_3^- (aq) + CO_2 (aq)
\]

The ratio of HCO$_3^-$/(HCO$_3^-$+SO$_4^{2-}$) was 1.00 ± 0.001 for both seasons in both lakes (Table 3). According to Brown et al. (1996), for the weathering of carbonate rocks, proton sources are required. HCO$_3^-$ is the dominant anion where the dissolution and dissociation of atmospheric CO$_2$ provides protons for chemical weathering. This is supported by the C-ratio of 1 (Table 3) indicates weathering by carbonate reactions in both the lakes. This is also supported by the ratio of HCO$_3^-$/(Ca$^{2+}$+Mg$^{2+}$) which was slightly greater than unity in both the lakes during both seasons (Table 4).

We can describe the water type by plotting major ion on a piper trilinear diagram (Piper, 1944). The Piper diagram of Ghodaghodi (Figure 4) shows that the Ca$^{2+}$ and HCO$_3^-$ were the dominant cation and anion defining the water to be Ca-HCO$_3^-$ type. This illustrates that the
lake water was dominated by alkaline earth metal (Ca$^{2+}$) and weak acid (HCO$_3^-$), which is also evident from Table 2 (major ion composition) and Table 3 (ionic ratio). Similar findings were observed in different lakes of Nepal and India with Ca$^{2+}$ as dominant major cation and HCO$_3^-$ as dominant major anion [(Gokyo Lake by Lacoul and Freedman (2006); Pannchpokhari by Raut et al. (2015); Langtang valley by Tuladhar et al. (2015); Chandra Tal by Singh et al. (2016); Phewa lake by Khadka and Ramanathan (2021); Ghodaghodi lake by Pant et al. (2020)]. However, Rara shows the dominance of (Ca$^{2+}$ + Mg$^{2+}$) and HCO$_3^-$ defining the water to be Ca(Mg)HCO$_3$ type, i.e., alkaline earth metals and weak acid, also evident from Table 2 (major ion composition) and Table 3 (ionic ratios). The water collecting through several inlets to Rara flows over rocks like phyllite, quartzite and schist, especially the inlets which flows from the southern region accumulates surface water from dolomites composed of calcium magnesium carbonates (Dhital, 2015). Similar results were observed in some Himalayan lakes such as Renuka Lake (Das and Kaur, 2001), Pandoh Lake (Ramanathan, 2007), Begnas Lake (Khadka and Ramanathan, 2013), Tsokyo Tso Lake (Deka et al., 2015), Rara Lake (Kaphle et al., 2021), and Loktak Lake (Mayanglambam and Neelam, 2020).

Plots of TDS versus Na/Na$^{+}$+Ca$^{2+}$ and TDS versus Cl$^-$/Cl$^-$/HCO$_3^-$, known as Gibbs diagram (Gibbs, 1970), provides information regarding the importance of different major natural mechanisms that controls surface water chemistry, such as precipitation, rock dominance

Figure 4. Piper diagram showing the cations and anions of Lake Ghodaghodi and Rara. Panels 4a shows the cation triangle, 4b shows the anion triangle, and 4c is the diamond plot for both ions. Please note that the color differences are not obvious for anions (4b) because of the very close concentration values of HCO$_3^-$ of many readings.

Figure 5. Gibbs diagram showing ion source of Lake Ghodaghodi and Lake Rara in different seasons. Panel 5a shows plots of TDS vs. Na/Na$^{+}$+Ca$^{2+}$ and 5b shows plot of TDS vs. Cl$^-$/Cl$^-$/HCO$_3^-$. 
(weathering), or evaporation. Both lakes in the present study showed rock dominance as major source of ions through weathering (Figure 5). Many other studies in various lakes from different parts of world, including Nepal and India, also show the similar results where rock dominance prevails as the dominating source e.g., Begnas Lake (Khadka and Ramanathan, 2013), Lake Rara (Gurung et al., 2018; Kaphle et al., 2021), Loktak Lake (Mayanglambam and Neelam, 2020), Phewa Lake (Khadka and Ramanathan, 2021).
3.3. Correlation analysis

Spearman’s correlation coefficients among the various physicochemical parameters are given in Table 4 (for Ghodaghodi) and Table 5 (for Rara). In Ghodaghodi, the correlation coefficient between Ca\(^{2+}\) and HCO\(_3^-\) (0.98), Mg\(^{2+}\) and HCO\(_3^-\) (0.79), and Ca\(^{2+}\) and Mg\(^{2+}\) (0.74) suggest common origin of these ions, might be derived from carbonate weathering (Table 4). Furthermore, EC and TDS (0.68) as well as Na\(^+\) and EC (0.78) showed high correlation. Moreover, HCO\(_3^-\) shows moderate correlation with Na\(^+\) (0.55) and K\(^+\) (0.38).

The strong correlation of Cl\(^-\) ion with Mg\(^{2+}\) (0.73) and moderate correlation with K\(^+\) (0.55) might be due to common origin, in the form of chloride salt. A good correlation was also observed between Na\(^+\) and SO\(_4^{2-}\) (0.75), might be due to the presence of some sulphate salt like sodium sulphate.

In Rara, the correlation coefficient between Ca\(^{2+}\) and HCO\(_3^-\) (0.94), and Mg\(^{2+}\) and HCO\(_3^-\) (0.52) suggest the common origin of these ions, might be from carbonate weathering. HCO\(_3^-\) shows high to moderate correlation with K\(^+\) (0.79) and Na\(^+\) (0.53). Furthermore, we observed a strong correlation between Na\(^+\) and Cl\(^-\) (0.80), which indicated the ions are from local lithogenic source and an interaction of halite with stream water (Pant et al., 2018; Kapilie et al., 2021). The presence of NaCl could also be attributed to marine origin (Bhatt et al., 2007; Ramanathan, 2007; Deka et al., 2015; Ghimire et al., 2021) and Nepal being a country strongly affected by monsoon climate, marine transport could be one of the reasons behind the presence of these ions (Mamun and An, 2017). Additionally, Na\(^+\) ion shows high correlation with K\(^+\) (0.60) and Mg\(^{2+}\) (0.62). Likewise, K\(^+\) ion shows strong correlation with Ca\(^{2+}\) (0.73), Mg\(^{2+}\) (0.62), and SO\(_4^{2-}\) (0.72). Nonetheless, a good correlation was also observed between Na\(^+\) and SO\(_4^{2-}\) (0.69), Ca\(^{2+}\) and SO\(_4^{2-}\) (0.52), and Mg\(^{2+}\) and SO\(_4^{2-}\) (0.67) that might be due to the presence of some sulphate salts coming from contamination of some plant nutrients or from grazing horses (Kapilie et al., 2021).

3.4. Comparison to other lakes of the Himalayan region

Ghodaghodi and Rara in the present study indicated the dominance of Ca\(^{2+}\) and HCO\(_3^-\), an indication of crustal derived material (Wetzel, 2001). Bedrock geology is the most common source of different ions and minerals in water bodies (Das and Dhiman, 2003) although for some ions increasing anthropogenic activities also explain their elevated concentrations.

Calcium and bicarbonate are often the dominant cation and anion, respectively in most freshwater bodies across the earth (Wetzel, 2001); and several studies in Europe (Mosello et al., 2002; Torro et al., 2006) and America (Chapra et al., 2012) have also reported similar findings. Calcium and bicarbonate as the most dominant cation and anion have been reported from several water bodies from across the earth including India and Nepal (Table 6). Mg\(^{2+}\) ion was the second dominating ion in Lake Rara (present study, Jones et al., 1989; Gurung et al., 2018; Kapilie et al., 2021). This is in accordance with previous findings in other lakes as well (Table 6). In contrast, in Ghodaghodi (present study), Na\(^+\) was the second dominion. Similar findings have been reported from other lakes in Nepal and India (Table 6). Presences of sodium and chloride ions in freshwater bodies are often attributed to marine origin (Tartari et al., 1998; Bhatt et al., 2007).

Although bicarbonate is the most dominant anion in water bodies, in some lakes, chloride has been reported as the dominant anion (Raut et al., 2012). Presence of chloride ions in water is attributed to natural as well as anthropogenic sources. It is naturally associated with the processes of leaching from minerals, mainly from rocks (Nikanorov and Brazhnikova, 2009) and marine transport (Bhatt et al., 2007; Ramanathan, 2007; Deka et al., 2015; Pant et al., 2018; Ghimire et al., 2021). For instance, in Gosainkunda Lake – a high altitude lake in central Nepal, chloride concentration is attributed to marine transport (Tripathy et al., 2014b). On the other hand, untreated sewage, fertilizer run off has been identified as anthropogenic sources of chloride (Schlesinger, 2004).

4. Conclusions

The most dominant cation and anion were Ca\(^{2+}\) and HCO\(_3^-\) in both lakes indicating carbonate weathering as a primary source of dissolved ions in the lake waters. Further analysis indicated that Ghodaghodi belongs to Ca–HCO\(_3^-\) type and Rara belongs to Ca(Mg)HCO\(_3^-\) type. Majority of the ions showed strong seasonal variations, having higher concentration in pre-monsoon season in both lakes suggesting dilution effect of the monsoon. The presence of higher concentrations of Na\(^+\) and Cl\(^-\) during post-monsoon season could be attributed to marine transport – an indication of long-range transportation of pollutants.

Declarations

Author contribution statement

Rita Bhatta: Conceived and designed the experiments; Performed the experiment; Analyzed and interpreted the data; Wrote the paper.
Smriti Gurung: Conceived and designed the experiments; Performed the experiment; Analyzed and interpreted the data; Wrote the paper.
Rajendra Joshi; Shrija Tuladhar; Diksha Regmi; Babi Kumar Kafle; Bed Mani Dahal; Nani Raut; Kumud Raj Kafle; Rabindra Kayastha; Archana Prasad: Performed the experiment; Analyzed and interpreted the data.

Lekhendra Tripathee; Rukumesh Paudyal; Jumming Guo; Shichang Kang: Performed the experiment; Contributed reagents, materials, analysis tools or data.

Chhatra Mani Sharma: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest’s statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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