

# Hydro-Geochemical Conditions under Projected Climate Change Scenarios of Marshyangdi River, Nepal

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## Research Article

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# Abstract

Assessment of hydro-geochemical processes in a Himalayan River fed by snow and glaciers in the context of global climate change is crucial to understanding the changes in water quality due to natural and anthropogenic influences. Thus, the hydro-geochemical status of water quality was analyzed in a snow-fed Himalayan Watershed, Marshyangdi located in western Nepal for current and future scenarios under the medium (RCP 4.5) and pessimistic (RCP 8.5) representative concentration pathways (RCPs) for two seasons (pre-and post-monsoon, 2019) based on multiple regional climate models. Flow at each sampling site of a total of twenty-one sites was estimated from a soil and water assessment tool (SWAT) hydrological model and then the concentration of water quality for the future was determined. A descriptive analysis of water quality was carried and a Piper plot diagram for evaluating the spatiotemporal variation as well as the hydro-geochemical status of water for the current and future scenarios. The results reveal alkaline water in the watershed based on pH values that follow the pattern of average ionic dominance  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$  for cations and  $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-$  for anions indicating the carbonate-dominated lithology in the Marshyangdi Watershed for the current scenarios. However, for future scenarios dominance of cations is different for the respective seasons  $\text{Ca}^{2+} > \text{Na}^+ + \text{K}^+ > \text{Mg}^{2+}$  and  $\text{Na}^+ + \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$  with similar anion composition with respect to current scenarios under both RCPs.

## 1. Introduction

Many water resource challenges are rooted in hydrogeochemistry, a field that combines hydrology and mineral/rock chemistry (Zhu and Schwartz 2011). Therefore, future changes to hydrogeochemical processes that affect water quality must be considered in efforts to solve issues related to global warming. Furthermore, the demand for water is increasing rapidly due to population increase, industrialization, urbanization, and mechanization, which causes water supplies to be depleted thereby causing pollution (Falkenmark, 1994). Though water can be recycled and treated for both industrial and domestic usage, the expense of managing and treating it may be substantial (Eyankware et al., 2014). Hence, in order to manage water resources sustainably meeting human requirements, hydrogeochemical data on water resources are crucial.

The world's surface water chemistry is mainly controlled by three major mechanisms; atmospheric precipitation, rock dominance, and the evaporation-crystallization process (Gibbs et al., 1970). The hydrogeochemical processes reveal the zones and the suitability of the water quality for different uses, including drinking, farming, and industry. It also helps to understand the changes in water quality due to rock-water interaction as well as anthropogenic influences (Kumar et al., 2006). The hydrochemistry of river water is impacted by a number of anthropogenic activities, such as mining, quarrying, and dumping, as well as natural processes like weathering, precipitation, and ion exchange. As a result, water pollution has emerged as one of the world's most significant environmental issues today (Edet Okereke, 2014; Pasquini et al., 2012; Nganje, et al., 2010; Singh et al., 2008). Hence, to manage water resources

sustainably and meet human requirements, hydro-geochemical data on water resources and fluxes are crucial (Zhu et al., 2011). Hydrogeochemical studies have been carried out around the globe by several researchers. Kumar et al. (2008) studied the chemical characteristics of the surface, groundwater, and mine water at the upper catchment of the Damodar River Basin, India to evaluate the major ion chemistry and the geochemical processes controlling water composition and suitability of water for domestic, industrial and irrigation uses. The research showed that the water was acceptable for irrigation as well as domestic usage. Similarly, Gupta et al. (2016) focused on the hydrogeochemical investigation of water samples from the Rangit River, Sikkim, India for human consumption and agricultural purposes. The study visualized that the major hydrogeochemical facies in upstream river water as  $(K^+ - Ca^{2+} - Mg^{2+} - HCO_3^-)$ , whereas  $(Ca^{2+} - K^+ - HCO_3^-)$  predominated in downstream sections of the river. The high equivalent ratios of  $(Ca^{2+} - Mg^{2+}) / (Na^+ - K^+)$  and the low ratio of  $(Na^+ - K^+)$  in the study evidenced that the chemical composition of river water is mostly influenced by carbonate weathering, with partial contribution from silicate weathering. Further, Eyankware et al. (2016) assessed the anthropogenic activities on the hydrogeochemical quality of water resources of Ekaeru Inyimagu and its environs at Ebonyi State of Nigeria. The study reveals that a decline in water quality poses a major health challenge to the inhabitant of the study area. In addition, similar studies on the hydrogeochemical composition of ChuTalas River basin located in Central Asia revealed the dominance of calcium bicarbonate as the major ion (Ma et al., 2020). Similar composition  $(CaMg - HCO_3^-)$  was also observed in the Shiyang River of China mainly from the weathering of silicates and carbonates (Zhang et al., 2021).

However, there were very few hydrogeochemical investigations conducted in Nepal, most of which were on rivers and lakes that were situated at high altitudes. For example, in the Khumbu and Imja Khola at elevations ranging from 4530 to 5480 m, Tartari et al. (1998) examined the chemistry of 31 lakes while taking atmospheric loads, the geo-lithological and morphometric properties of the watershed, and surface waters into account. According to the study, the ionic content of the water in those lakes was mostly caused by the weathering of the rocks in the watershed. The study also revealed a direct connection between weathering events and the existence of glaciers, indicating that global atmospheric warming may have decreased the length of snow cover, increasing the contact time between precipitation and rocks, causing rapid ice melting and glacial formation. Raut et al. (2012) analyzed some major cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  &  $K^+$ ) and anions ( $Cl^-$ ,  $SO_4^{2-}$  &  $HCO_3^-$ ) on high altitude Himalayan Lake Gosainkunda in the Langtang National Park and their research revealed that the lake was predominant with calcium ( $Ca^{2+}$ ) and chloride ( $Cl^-$ ).

Similarly, the studies on water quality and solute sources of the Marshyangdi River reflect sulfide, silicate, and carbonate weathering in the watershed. Based on the geochemical analysis the surface waters located in different segments from different watersheds in the Tethyan Himalayan Sequence (THS) and Greater Himalayan Sequence (GHS) segments of the upper Marshyangdi drainage basin were characterized by a marked contrast in terms of solute load, and belong to different hydrofacies (Ghezzi et al., 2019).

Further studies on hydrogeochemical studies on snow-fed watersheds are few, for example, Pant et al. (2018) studied the hydrogeochemical variations in the Gandaki River Basin, and Sharma et al. (2021) studied major ions and water quality for irrigation of Nepalese Himalayan rivers. As snow-fed Himalayan rivers are more vulnerable to climate change because of the region's rapid warming which is nearly three times higher than the global average (Kulkarni et al., 2013; Shrestha & Aryal, 2011) hydrogeochemical studies play an important role in such watersheds. Thus, due to limited hydrogeochemical studies on such watersheds, this study aims to assess the spatio-temporal composition of major ion chemistry along with the assessment of the water quality based on physicochemical characteristics with respect to cations and anions in current and future contexts in a snow-fed Himalayan River Marshyangdi. In addition to this, other stressors such as the alteration of the flow regime, particularly as a result of the development of hydropower may also impact the hydrogeochemical process in a Marshyangdi Watershed. There are 47 hydropower plants in the various phases of operation in the Marshyangdi Watershed (DOED, 2020), where three major hydropower plants are already in operation. So, there might be a possibility of changing the hydrology of rivers impacting water quality.

## **2. Materials And Method**

### **2.1 Study Area**

Marshyangdi Watershed is a snow-fed perennial river that originated from the Tethyan Himalayan Sequence THS located in West-Central Nepal. It covers four districts namely Manang, Gorkha, Tanahu and Lamjung. The river is around 150 km long and it extends from 27°50 '42" to 28°54' 11" N latitudes and from 83°47'24" to 84°48'0 " E longitudes covering an area of 4,748 km<sup>2</sup> (Fig. 1). The elevation of this basin varies from 274 to 8,042 m. This river rises on the northern slopes of the Annapurna Himalaya, flows east through the arid valley around Manang, and then swings south to join the Trisuli River at Mugling. The major source of this river is the glaciers of Annapurna Himalaya range, Manaslu Himalaya range, and Larkya Himalayan sub range. The general climate varies from sub-tropical in the lower belt to arctic frost in the higher altitudes (Karki et al., 2016)

### **2.2 Sampling Sites and Analytic Methods**

A total of 21 sampling sites (M1-M21) were identified covering the mainstream and its tributaries (Fig. 1). Detail characteristics of the sampling sites are provided in Table 1.

The surface water samples with three replicates were collected, composited, and stored in a clean 500 mL polyethylene bottle. Then, the sample bottles were sealed, labeled properly, and transported to the laboratory in an ice box maintaining a temperature of 4°C. Before the collection of the water sample, each sample bottle was rinsed twice with the same river water and then washed with nitric acid for cations. For the analysis of chemical oxygen demand (COD), sample was preserved with a few drops of conc sulphuric acid in a separate sample bottle of 200 mL. Water quality parameters like pH, temperature (T), Total dissolved solids (TDS), and electrical conductivity (EC) were measured using the multipurpose

meter (HANNA; HI98129). Dissolved oxygen (DO) was directly measured in the field using the portable digital meter (EcosenseDO200A). These probes were immersed in composite water in a beaker and the parameter was noted after the stabilization of the instrument. The major cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  were analyzed using Flamephotometer (JENWAYPFP7) and anions like bicarbonate ( $\text{HCO}_3^-$ ), chloride ( $\text{Cl}^-$ ), were measured at the site while sulphate ( $\text{SO}_4^{2-}$ ), phosphate ( $\text{PO}_4^{3-}$ ), nitrate ( $\text{NO}_3^-$ ) and ammonia ( $\text{NH}_3\text{-N}$ ) was analyzed by adopting standard procedures as per APHA, 2005 at the laboratory. Finally, data were analysed using IBM SPSS 26, Origin 2019, Descriptive statistics were calculated to evaluate and interpret the temporal and spatial variations of the dataset.

Table 1  
Description of the sampling sites within Marshyangdi Watershed

Site Name	Site Code	Latitude (°N)	Longitude (°E)	Altitude (masl)	Description of sites
Kangsar	M1	83°56'55.12"	28° 40' 28.23"	3714	• Undisturbed site (M)
Dhukurpokhari	M2	84°09'36.5"	28° 36' 29.33"	3156	• Undisturbed site (M)
Chame	M3	84°15'30.61"	28° 33' 11.53"	2604	• Below Chame Bazar and Hotspring (M)
Dharapani	M4	84°21'31.08"	28° 30' 25.20"	1813	• Cross-sectional point, the site after mixing with Dudh Khola (M)
Tal Bazaar	M5	84°22'24.57"	28° 27' 56.54"	1675	• Settlement; tourism area (M)
Upper Marshyangdi U/S	M6	84°23'58.86"	28° 19' 52.52"	861	• Upstream to Upper Marshyangdi HP (M)
Upper Marshyangdi D/S	M7	84°23'18.67"	28° 18' 12.39"	851	• Downstream to Upper Marshyangdi HP (M)
Khudi	M8	84°21'15.90"	28° 16' 58.55"	798	• Tributary
Middle Marshyangdi U/S	M9	84°24'05.40"	28° 12' 13.11"	610	• Upstream to Middle Marshyangdi HP (M)
Middle Marshyangdi D/S	M10	84°25'58.00"	28° 10'59.70 "	582	• Downstream to Middle Marshyangdi HP (M)
Dordi	M11	84°27'24.89"	28° 11' 22.33"	640	• Tributary
Bhoteodar	M12	84°26'14.88"	28° 07' 49.52"	492	• Upstream of Paudi River (M)
Paudi	M13	84°25'40.28"	28° 06'42.16"	477	• Tributary
Chepe	M14	84°28'48.69"	28° 03' 23.90"	490	• Tributary
Turture	M15	84°27'47.59"	28° 02' 06.57"	368	• Downstream to the confluence of Tributary River Chepe to Marshyangdi (M)

Site Name	Site Code	Latitude (°N)	Longitude (°E)	Altitude (masl)	Description of sites
Chudi	M16	84°24'53.67"	27° 57' 33.00"	378	• Tributary river, dominated by human activities (washing, bathing)
Marshyangdi D/S	M17	84°27'59.37"	27° 56' 59.13"	335	• Upstream of Marshyangdi HP
Marshyangdi D/S	M18	84°30'53.17"	27° 54' 55.25"	286	• Downstream from Marshyangdi HP
Daraudi	M19	84°33'06.11"	27° 54' 54.68"	271	• Tributary
Lower Marshyangdi	M20	84°32'25.58"	27° 53' 20.80"	227	• Below the confluence point after mixing of Daraudi River with Marshyangdi (M)
Mugling	M21	84° 33'22.21"	27° 51' 26.67"	216	• Downstream of the river, before mixing with Trisuli River (M)

## 2.3 Climate change impacts on hydrogeochemical conditions

For the assessment of climate change's impact on hydrogeochemical status, the climate was projected at the watershed with the help of dynamic downscaling using three RCMS as described in Singh et al. (2020) at four climatic stations for two RCPs scenarios and two future periods (near future - NF: 2014–2033 and mid-future - MF: 2034–2053).

Further, the Soil and Water Assessment (SWAT) model was set up then calibrated and validated with acceptable statistics at three hydrological stations to study the impact of climate change on hydrogeochemical conditions within the watershed (Singh et al., 2022). After the development of the model, projected time series data of flow (Q) at each sampling site was calculated by using the drainage-area ratio method and then using Eq. 1. The concentration of water quality was calculated for two future periods and under two RCPs (4.5 and 8.5) scenarios.

### 2.3.1 Prediction of water quality condition

The water quality component was predicted by using Eq. 1, assuming the types and quantities of pollutants from human settlements remain constant (Zhao et al., 2019). Pollution and runoff concentrations is stated as:

$$\text{Vol} = \int (F \cdot C) dt$$

$$F' \cdot C' = F \cdot C / C' = 1 / F' \cdot d\text{Vol}/dt = F \cdot C / F' \dots\dots\dots(1)$$

where, F is the measured runoff, C is the measured concentration of pollutants, F' is the predicted future runoff, and C' is the concentration of pollutants.

### 3. Results And Discussion

## 3.1 Characterization of physico-chemical processes

### Current scenarios

The status of water quality based on the statistical summary of physico-chemical parameters among the 21 studied sites within the Marshyangdi Watershed has been explained briefly and presented in (Table 2) by categorizing them into physical, chemical, and nutrient parameters.

River temperature is a key physical parameter that influences river ecology (Medupi 2016; Webb & Walsh 2004) indirectly influencing the mobilization as well as the toxicity of pollutants. The temperature in the basin ranges from 4.9 to  $30.3 \pm 6.5$  (Table 2) in pre-monsoon whereas in post-monsoon  $3.3$  to  $25.1 \pm 5.6$  which might be due to the altitudinal variations within the watershed (Table 1). However, a number of factors, including diurnal daylight, weather, terrain, slope, aspects, different sampling times, altitudinal and seasonal change, flow of water, numerous biotic and abiotic components, and surface radiation (as well) may have an impact on the temperature of the surface water (Trivedi & Goel, 1986; Singh *et al.*, 2017). The overall temperature is crucial for regulating freshwater's physical, chemical, and biological processes.

All the water quality parameters representing physical status (pH, EC, TDS) are within the range of permissible limits for the sustenance of the aquatic life within the watershed (Table A1). In current scenarios, the mean pH values for both seasons show that the water is naturally alkaline. This pH parameter significantly impacts the composition of aquatic macroinvertebrates as well as their metabolic and physicochemical characteristics (Tadesse *et al.*, 2018). Similarly, mean values of all the parameters represent water chemical status (DO,  $\text{Cl}^-$ , COD, BOD,  $\text{NH}_3\text{-N}$  &  $\text{SO}_4^{2-}$ ). For the case of TH, water is very hard ( $> 180$  mg/L) in pre-monsoon and hard in post-monsoon. In addition, for alkalinity, it exceeded its permissible limit for the sustenance of aquatic life ( $> 200$ mg/L) in the post-monsoon season (Table 2). Finally, nutrient parameters ( $\text{NO}_3^-$  &  $\text{PO}_4^{3-}$ ) were also within the permissible level for the survival of aquatic organisms (Table A1) except total phosphate whose both maximum and mean values exceeded their limits for both studied seasons ( $> 0.1$ mg/L) (Table 2). Such exceedance in total phosphate might be due to non-point sources in the watershed, which might cause the problem of eutrophication in the fuMean values of cations like ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) are also within the acceptable limits for the survival of aquatic life in current scenarios.



Table 2  
Statistical summary of current physicochemical condition for pre- and post-monsoon

Pre-monsoon					Post-monsoon			
Parameters	Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD
<b>Physical</b>								
Temp	4.9	30.3	21.1	6.5	3.3	25.1	15.6	5.6
pH	8.3	9.0	8.7	0.2	8.1	8.9	8.5	0.2
TDS	39.9	175.5	122.3	42.0	39.5	246.5	137	49.2
EC	100	360	259	80	77.0	469.0	258	97.1
<b>Chemical</b>								
DO	5.1	7.4	6.4	0.7	5.1	6.9	6.1	0.6
Cl <sup>-</sup>	7.1	35.9	17.3	7.5	8.5	32.0	20.1	7.2
COD	2.0	23.1	6.3	4.7	2.9	26.6	12.6	6.3
BOD	1.2	13.9	3.8	2.8	1.7	16.0	7.5	3.8
Ca <sup>2+</sup>	15.8	56.0	26.6	10.0	26.9	73.5	64.3	14.4
Na <sup>+</sup>	1.0	28.0	10.6	8.8	14.3	33.0	19.7	3.8
K <sup>+</sup>	0.8	24.0	7.0	7.3	0.8	9.5	4.3	3.0
HCO <sub>3</sub> <sup>-</sup>	45	205	108	36	111.3	421.0	267	73.7
Mg <sup>2+</sup>	3.1	18	9.7	4.3	6.9	27.7	16.7	5.5
TH	60	366	187	100	35.0	292.5	128	63.5
SO <sub>4</sub> <sup>2-</sup>	3.4	4.7	4.0	0.3	3.7	4.6	3.9	0.2
NH <sub>3</sub> -N	0.03	0.18	0.05	0.04	0.03	0.27	0.08	0.05
<b>Nutrients</b>								
NO <sub>3</sub> <sup>-</sup>	0.03	1.41	0.94	0.35	0.37	1.10	0.81	0.18
TP	0.06	0.55	0.21	0.14	0.04	1.38	0.28	0.35
PO <sub>4</sub> <sup>3-</sup>	0.01	0.10	0.03	0.02	0.01	0.13	0.05	0.04
<i>Note: All values are expressed in mg/L except Temp (°C), EC (µS/cm), and Turbidity (NTU); SD is the Standard deviation</i>								

## Future scenarios (Near future, RCPs 4.5 and 8.5)

The descriptive statistics have been calculated and presented for both seasons under both RCPs scenarios for the near future (Table 3a and Table 3b) and for the mid-future (Table A2a and Table A2b). Mean pH values in both seasons indicate a continuation of alkaline water in the near future under both RCPs. All the physical parameters (pH, EC, and TDS) are within acceptable limits for the sustenance of aquatic organisms (Table A1). Likewise, chemical parameters (DO,  $\text{Cl}^-$ , COD, BOD, TH, TA,  $\text{NH}_3\text{-N}$  &  $\text{SO}_4^{2-}$ ) have been also predicted and within the standard limits for the sustenance of aquatic life in both seasons under both RCPs. Furthermore, nutrient parameters have been also predicted and are within the permissible limits (Table A1) for both seasons under both RCPs. Similarly, predicted mean values of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , &  $\text{Na}^+$ ) have also fallen within acceptable limits for the survival of aquatic life.

Table 3a

Characterization of seasonal variations in physicochemical conditions in near-future (RCP 4.5)

Pre-monsoon					Post-monsoon			
Parameters	Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD
<b>Physical</b>								
pH	6.2	13.1	8.3	7.6	5.9	12.5	8.1	1.8
TDS	88	428	241	247.0	43	257	127	51.5
EC	39	215	114	115.0	83	489	241	102.0
<b>Chemical</b>								
DO	3.8	10.6	6.1	6.1	3.9	10	6	1.7
Cl <sup>-</sup>	7.2	48.8	16.5	13.6	8.4	47.8	18.8	8.1
COD	1.5	20.0	6.0	5.3	3.2	26.8	11.9	6.7
BOD	0.9	12.0	3.6	3.2	1.9	16.1	7.1	4.0
Ca <sup>2+</sup>	15.8	56.4	25.0	20.5	29.4	105.0	60.3	18.2
Na <sup>+</sup>	1.0	28.2	9.5	9.1	12.9	37.2	19.0	6.8
K <sup>+</sup>	0.6	25.3	7.0	3.8	0.6	11.9	4.3	3.5
HCO <sub>3</sub> <sup>-</sup>	45	214	101	90.7	102	301	171	53.9
Mg <sup>2+</sup>	2.3	15	9.2	4.0	7.6	26.6	15.5	5.2
TH	60	381	168	172.5	38	305	119	64.5
NH <sub>3</sub> -N	0.02	0.15	0.05	0.14	0.02	0.32	0.08	0.07
<b>Nutrients</b>								
SO <sub>4</sub> <sup>2-</sup>	2.82	5.68	3.78	88.7	2.84	5.66	3.71	0.85
NO <sub>3</sub> <sup>-</sup>	0.03	1.60	0.87	0.70	0.41	1.31	0.75	0.17
TP	0.05	0.49	0.20	0.35	0.03	1.21	0.26	0.30
PO <sub>4</sub> <sup>3-</sup>	0.01	0.09	0.03	0.03	0.01	0.16	0.05	0.04

Table 3b

Characterization of seasonal variations in physicochemical conditions in near-future (RCP 8.5)

Pre-monsoon					Post-monsoon			
Parameters	Minimum	Maximum	Mean	SD	Minimum	Maximum	Mean	SD
<b>Physical</b>								
pH	6.0	49.8	9.6	9.0	5.9	48.6	9.3	8.8
TDS	88.8	1744.1	289.2	330	42	973	155	187
EC	38.8	855.3	137.8	163	81	1856	293	357
<b>Chemical</b>								
DO	3.4	31.3	6.8	5.5	3.6	34.7	6.7	6.3
Cl <sup>-</sup>	7.0	67.2	17.3	12.4	7.5	62.6	19.7	11.0
COD	1.5	46.4	7.3	9.6	3.1	28.5	12.2	7.0
BOD	0.9	27.8	4.4	5.8	1.9	17.1	7.3	4.2
Ca <sup>2+</sup>	15.2	195.6	31.1	38.0	28.8	408.1	71.2	76.0
Na <sup>+</sup>	0.9	100.6	13.2	20.9	11.6	98.4	21.1	17.8
K <sup>+</sup>	0.8	24.7	6.7	7.5	0.8	9.8	4.1	2.9
Mg <sup>2+</sup>	2.5	17.3	9.3	4.2	7.4	68.8	17	12.2
HCO <sub>3</sub> <sup>-</sup>	45	671	119	127	98	995	196	182
TH	60	1526	217	303	37	1118	153	222
SO <sub>4</sub> <sup>2-</sup>	2.63	21.24	4.34	3.80	2.73	22.47	4.30	4.09
NH <sub>3</sub> -N	0.02	0.17	0.05	0.04	0.02	0.47	0.11	0.10
<b>Nutrients</b>								
NO <sub>3</sub> <sup>-</sup>	0.03	7.66	1.11	1.49	0.44	1.69	1.16	0.33
TP	0.05	0.46	0.19	0.12	0.03	1.59	0.39	0.45
PO <sub>4</sub> <sup>3-</sup>	0.01	0.22	0.03	0.05	0.01	0.18	0.07	0.05

## Mid-Future (RCP 4.5 and 8.5)

The mid-future descriptive statistics under both RCPs are presented in Table A2a and Table A2b. For the mid-future also mean values of all the physical parameters, were within the acceptable limits for both seasons under both RCPs. For the case of chemical parameters, their mean values have been predicted to be their acceptable limits (Table A2a) for both RCPs. Similarly, nutrient parameters of water quality have been predicted as within the acceptable limits except for total phosphate whose both maximum as well as mean values exceeded their permissible level ( $> 0.05\text{mg/L}$ ) (Table A2a) for both seasons under both RCPs. For the case of cations, all of them have been predicted to be within the acceptable levels for the survival of aquatic life for both seasons under both RCPs (Table A1)

## 3.2 Composition of major ion chemistry with respect to cations and anions

### Current scenarios

The hydro-chemical characteristics of the Marshyangdi Watershed were analyzed for two seasons (pre and post-monsoon) from headwater to the mouth along the 21 sampling sites based on a piper trilinear diagram (Piper, 1944).

In pre-monsoon, based on mean values of cations,  $\text{Ca-HCO}_3$  mg/L was dominant (Fig. 2a) revealing the dominance of calcium in the river water followed by magnesium ( $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ + \text{K}^+$ ). The dominance of calcium and magnesium ions exhibited 44 and 58 percent, respectively more than the global mean (Gaillardet et al., 1999; Meybeck 2003,) which reflects the predominance of carbonate weathering in the watershed. The anion plot reveals that most samples fall on the left corner indicating the  $\text{HCO}_3$  type, and very few samples towards  $\text{SO}_4^{2-}$  indicate much less of sulfate dominance ( $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ ). The dominance of calcium and bicarbonate in the water might be due to the result of the dissolution of limestone and calcium-bicarbonate rock in the watershed (Nguyet and Goldscheider, 2006; Singh, 2009). Bicarbonate was also an abundant anion in this watershed indicating weathering of carbonate rock (Evans et al., 2004; Wolff-Boenish et al., 2009). High concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the water could be related to the weathering of crystalline dolomitic limestones. A similar  $\text{Ca}^{2+}$  dominance also has been observed in a snow-fed Himalayan Gandaki River Basin (Pant et al., 2018). The studied major ions in the Marshyangdi Watershed indicate that the observed chemical species are of natural origin.

The results of this study resemble the trend of ions in the Tethyan series (predominance of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration) reflecting carbonate weathering. Since carbonate has higher solubility, it produces more calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) than silicate under natural conditions. Similarly, based on the ternary plot, Wolff-Boenish et al. (2009) also observed the predominance of calcium and magnesium in TSS and GHS-drained watersheds, which was supported by Ghezzi et al. (2019) on the basis of the dominance of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and, to a lesser extent,  $\text{HCO}_3^-$  at superficial water sites of THS and GHS domain except at two sites in THS domain ( $\text{Mg-Ca-HCO}_3\text{-SO}_4$ ).

The overall characteristics of the water chemistry reveal the dominance of the alkaline earth metals ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) over the alkalis ( $\text{Na}^+$  +  $\text{K}^+$ ) and the weak acids ( $\text{HCO}_3^-$ ) over the strong acids ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) in pre-monsoon (Fig. 2a). In general, the sampling points in the piper diagram can be classified into six fields. The types are 1. Ca- $\text{HCO}_3$ , 2. Na-Cl, 3. Mixed: Ca-Mg-Cl, 4. Mixed: Ca-Na- $\text{HCO}_3$ , 5. Ca-Cl and 6. Na- $\text{HCO}_3$  (Khadka and Ramanathan 2012). The percentage reacting values at the three cation groups i.e.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and ( $\text{Na}^+$ + $\text{K}^+$ ) are plotted in the left triangular field. Similarly, the percentage reacting values at the three anion groups i.e., ( $\text{HCO}_3^- + \text{CO}_3^{2-}$ ),  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  in the right triangular field. In this season water type falls in class 1( $\text{Ca}^{2+} \text{HCO}_3^-$ ).

However, in post-monsoon (Fig. 2b), sodium and potassium ions predominate the water chemistry followed by calcium and magnesium ( $\text{Na}^+$ + $\text{K}^+$ > $\text{Ca}^{2+}$ > $\text{Mg}^{2+}$ ), whereas in the case of anions bicarbonate dominates the water chemistry followed by chloride and sulphate ( $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ ). As the basin is geologically carbonate-dominated, concentrations of bicarbonate are much higher than the other anions which is true for other basins like Gandaki (Pant et al., 2018). The diamond plot reveals the water type falls in class 1(Ca- $\text{HCO}_3$ ) and 3(Ca-Mg-Cl) for this season too.

## Future scenarios (RCP 4.5 and RCP 8.5)

In future scenarios based on the concentration of pre-monsoon water quality, cations composition in trilinear diagram (Fig. 3a) follows the pattern i.e.,  $\text{Ca}^{2+} > \text{Na}^+$ + $\text{K}^+ > \text{Mg}^{2+}$ , while anions follow the same pattern with respect to current scenarios ( $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ ). However, water type falls under a different category in the future based on RCP4.5NF water type is 1(Ca- $\text{HCO}_3$ ), while for the rest scenarios water type fall into classes class 1(Ca- $\text{HCO}_3$ ), 3(Ca-Mg-Cl), and 6 (Na- $\text{HCO}_3^-$ ).

Similarly, in post-monsoon, cations composition follows different patterns for RCP 4.5NF ( $\text{Ca}^{2+} > \text{Na}^+$ + $\text{K}^+ > \text{Mg}^{2+}$ ) and for the rest of the three scenarios  $\text{Na}^+$ + $\text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ . The domination of sodium and potassium ions could be due to the dissolution of evaporite and the weathering of silicates (Galy and France-Lanord, 1999). Water type falls in classes 3 and 6 for all scenarios in future periods based on the concentration of post-monsoon water quality data. For RCP8.5MF, sodium and potassium ions have shown many variations concerning current scenarios in both seasons. Also, for both seasons, it is interesting to note that in all scenarios and future periods anions composition of water is dominated by bicarbonate and follows the pattern for current scenarios ( $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ ).

## Conclusions

The water quality of the Marshyangdi Watershed has been analyzed based on the statistical summary of physicochemical and hydrogeochemical status for current and future scenarios for medium and pessimistic representative concentration pathways for two seasons (pre-and post-monsoon). All the physicochemical parameters were within the acceptable limit for the sustenance of aquatic life for current and future scenarios for both RCPs except total phosphate. The exceedance limit of this

parameter in current and future scenarios for both RCPs indicates the possibility of eutrophication in the watershed which could be managed with proper conservative measures on time. Further, hydrogeochemical analysis reveals that for the current scenarios, major ions follow the order of  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ , and for  $\text{catHCO}_3^- > \text{Cl}^- > \text{NO}_3^-$  for cations and anions, respectively, which indicate the carbonate-dominated lithology in the Marshyangdi Watershed. For future scenarios, the composition of cations based on the trilinear diagram follows the pattern  $\text{Ca}^{2+} > \text{Na}^+ + \text{K}^+ > \text{Mg}^{2+}$  in pre-monsoon while for post-monsoon except for NF4.5 it follows the same order for the rest of the scenarios  $\text{Na}^+ + \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ . However, for the current and future scenarios under both RCPs, anions concentration follows the same pattern i.e.,  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ ). Water type was dominated by class one from current to future scenarios under both RCPs indicating the dominance of calcium cations and bicarbonate anions in the watershed.

## Declarations

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### Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

### Author Contributions

All authors contributed to the study's conception and design. Material preparation and data collection from the field by Reeta Singh & Prof. Sadhana Pradhananga Kayastha, and analysis was performed by Suman Man Shrestha and Ramesh Prasad Sapkota. The first draft of the manuscript was written by Reeta Singh and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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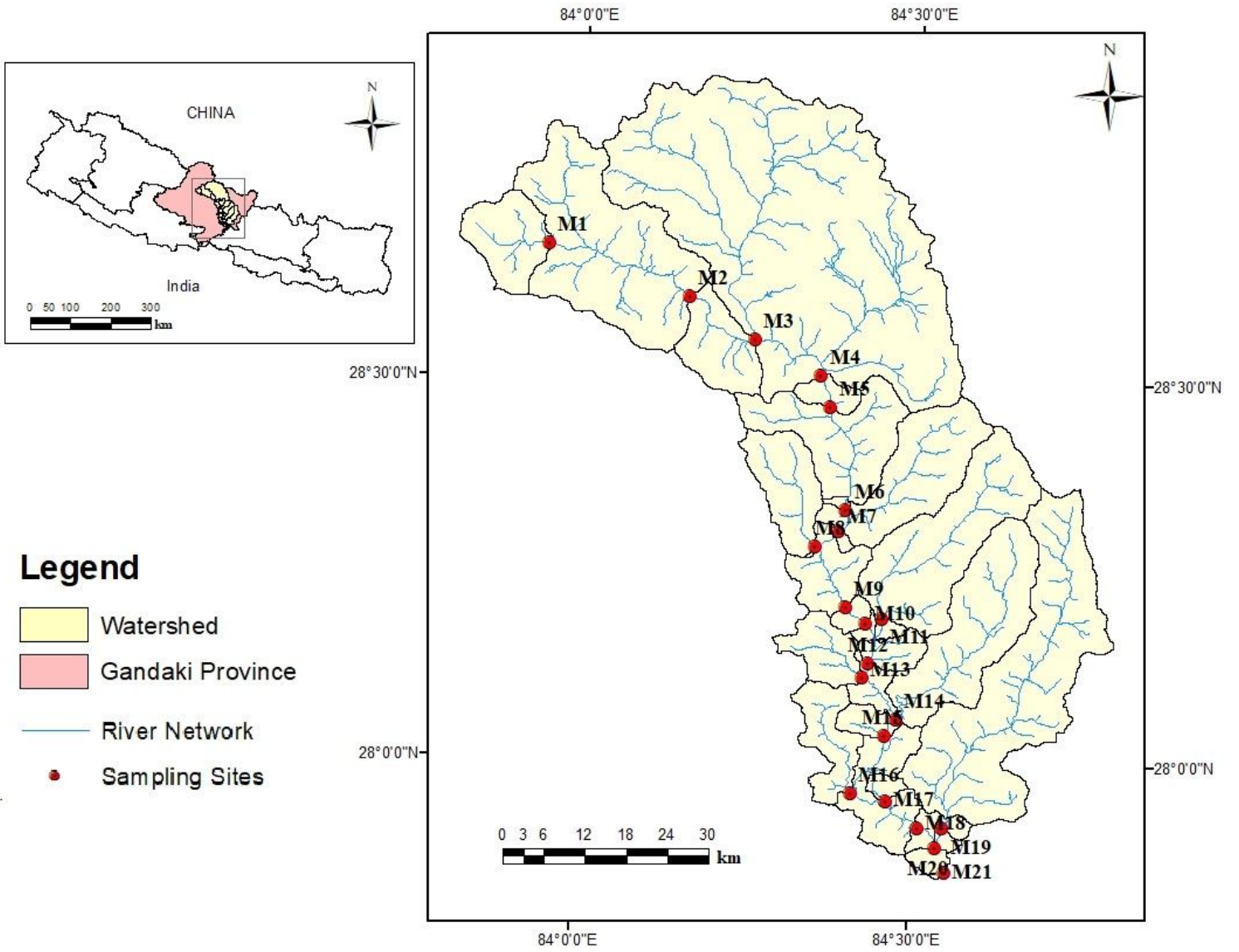
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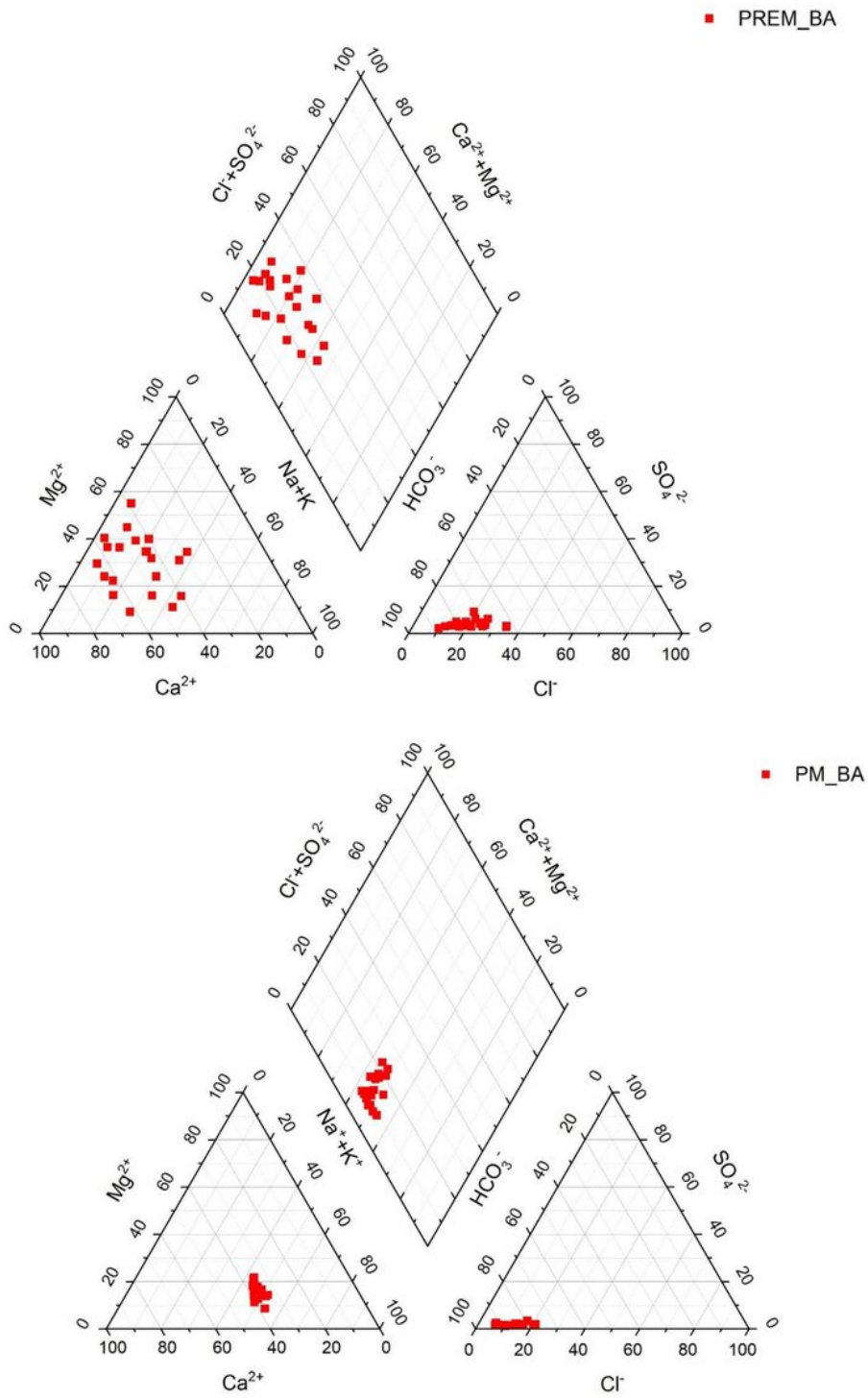
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## Figures



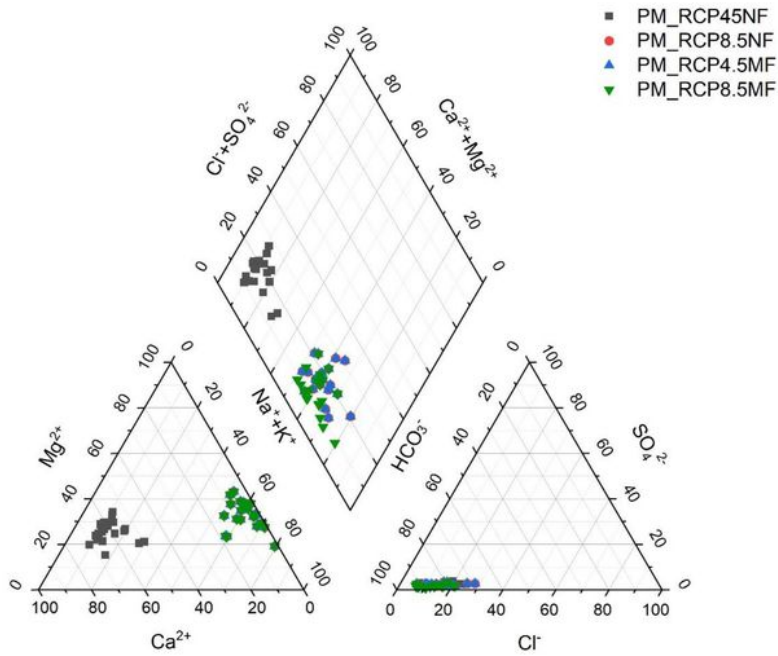
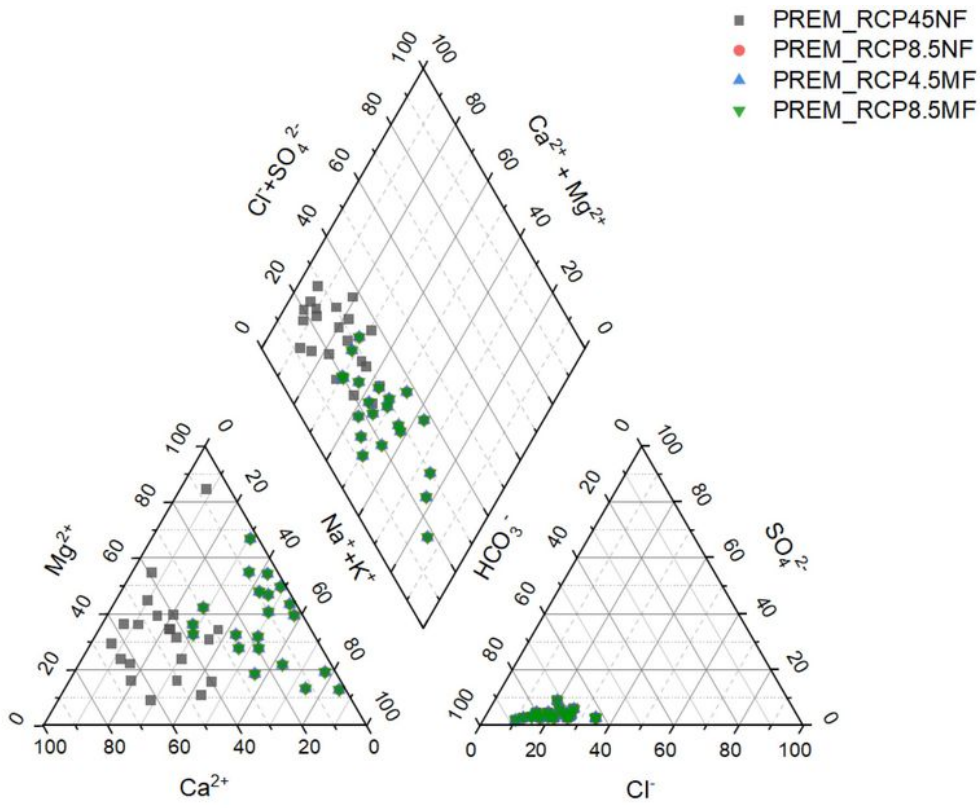
**Figure 1**

Sampling sites in the Marshyangdi Watershed



**Figure 2**

Current Scenarios of Piper Plot for a) pre-monsoon b) post-monsoon



**Figure 3**

Piper Plot for the future for both RCPs a) pre-monsoon b) post-monsoon

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