

Spatial and seasonal variability in the water chemistry of Kabar Tal wetland (Ramsar site), Bihar, India: multivariate statistical techniques and GIS approach

Deepak Gupta, Rajesh Kumar Ranjan, Purushothaman Parthasarathy and Afroz Ansari

ABSTRACT

This study was performed to evaluate the spatial and temporal distribution of major ions in water samples of a newly designated Ramsar site, namely Kabar Tal (KT) wetland of Bihar. Samples were collected during summer, monsoon, and winter seasons. The analytical and GIS results show that concentration of electrical conductivity, chloride, and nitrate are higher in summer than monsoon and winter. However, the concentration of major cations such as sodium, potassium, calcium, and magnesium are higher in winter than monsoon and summer. In addition, major anions like sulphate and phosphate concentration is higher during monsoon than summer and winter. Multivariate statistical tool (discriminant analysis) results suggest that temperature, pH, electrical conductivity, sulphate, and potassium are the major parameters distinguishing the water quality in different seasons. The study confirms that seasonal variations are playing a major role in the hydrochemistry of KT wetland. Overall, this work outlines the approach towards proper conservation and utilization of wetlands and to assess the quality of surface water for determining its suitability for agricultural purposes. Overall, this work highlights the approach towards estimating the seasonal dynamics of chemical species in KT wetland and its suitability for irrigation purposes.

Key words | GIS, hydrochemistry, Kabar Tal, multivariate, Ramsar site, wetland

HIGHLIGHTS

- Spatiotemporal assessment of surface water has been characterized through hydrochemical studies.
- Temperature, pH, EC, sulphate, and potassium, influences water chemistry.
- Hydrochemical facies of surface water is of Ca^{2+} and Cl^- ; Ca^{2+} - Mg^{2+} - SO_4^{2-} and Cl^- type.
- The surface water of the wetland is of good quality for irrigation.
- Detailed exploration for the water chemistry has been studied through statistical methods.

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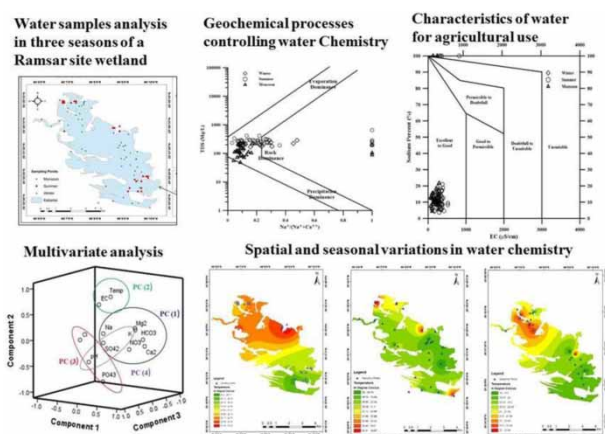
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GRAPHICAL ABSTRACT



INTRODUCTION

Freshwater is one of the most important constituents of life. Human interactions with water resources involve fresh streams, marshes, lakes, and groundwater. The rapid population growth, agriculture, and industrialization have forced environmentalists to determine the chemical, physical and biological characteristics of natural water resources (Regina & Nabi 2003). Wetlands are most productive ecosystems and play a very important role in the biogeochemical cycling of nutrients (Sánchez-Carrillo *et al.* 2014). In wetlands, nutrient dynamics is generally influenced by many processes like transport, transformation, storage, release, and removal of the inflow regime of wetlands (Shardendu *et al.* 2012). Wetlands function as water purification systems, helps in flood control, acts as sinks for pollutants as well as for organic carbon and therefore performs a vital role as climate stabilizers (Suhani *et al.* 2020). Wetlands are under increasing threat due to both point sources such as municipal and industrial wastewater and non-point sources like urban and agricultural run-off. Nitrate and phosphate are the major nutrients in the aquatic ecosystem which promote the productivity in an aquatic ecosystem (Weigelhofer *et al.* 2018). Phosphorous is an essential promoter of aquatic plant growth and a limiting nutrient for eutrophication in the lake ecosystem (Conley *et al.* 2009).

The use of various statistical techniques viz., principal component analysis (PCA), and discriminant analysis (DA) has been used by several researchers (Dash *et al.* 2018; Kaushik *et al.* 2021) to identify those parameters which

govern the water quality and determine the geochemical processes. It helps in sorting out samples having similar properties or a particular group or cluster (may be seasonal or restricted to a particular site) (Singh *et al.* 2004). Geographic information system (GIS) is one of the best intensive tools for processing, analyzing, storing, and displaying spatial distribution of data which improves the decision making ability of the conservation experts. Similar studies using the GIS tool has been conducted on Deepor Beel, by Dash & Kalamdhad (2021), for spatial mapping of water quality parameters.

Kabar Tal (KT) is one of the most important floodplain wetlands of Bihar (India) as it serves as a habitat for various migratory birds and plays important ecological functions for the regional hydrological balance. Recently, KT wetland has been designated as Ramsar sites (no. 2436) making it 'Wetlands of international importance' (Ramsar 2020). The wetland is shrinking at an alarming rate due to encroachment for agricultural practices (Ghosh *et al.* 2004; WISA 2016). Besides, it is also being used as a domestic wastewater drainage system by surrounding villages (Ambastha *et al.* 2007) resulting in the deterioration of water quality. Many researchers (Singh & Roy 1990; Siddiqui & Ramakrishna 2002; Ranjan & Kumari 2018) consider KT wetland to be at the initial stage of eutrophication.

The physicochemical characteristics of water alter seasonally; therefore it is very important to highlight its influence on the hydrochemistry of the wetland. Very few studies related to water quality have been carried on KT

wetland related to water quality, which includes Siddiqui & Ramakrishna (2002), Singh & Jayakumar (2016), Ranjan *et al.* (2017), Ranjan & Kumari (2018) and Singh *et al.* (2020). However, all earlier studies are based on either one-time sampling during winter season (e.g., Ranjan *et al.* 2017) or a very small sample size. In addition, previous findings by Singh & Jayakumar 2016 and Singh *et al.* 2020, etc; have not focused on hydrochemical characterization and identification of water types (such as by using piper plot, etc.) and have also not evaluated the water quality for irrigation purpose.

Therefore, the present study was undertaken to assess the hydrochemistry of KT wetland to understand the influence of seasons (i.e., summer, monsoon, and winter) on water chemistry and also to delineate the sources of major ions and nutrients in the water. The literature survey shows that this study would be the first to address sources and processes along with influence of spatial and temporal variability in surface water chemistry of KT wetland.

MATERIALS AND METHODS

Study area

KT wetland (Figure 1) located at 86°05'E to 86°09'E, 25°30'N to 25°32'N, also known as Kabar Lake Bird Sanctuary or Kanwar Jheel is situated in the Begusarai district of Bihar, India. This wetland lies in the middle Gangetic plains, with alluvial landscape and has an elevation of 37–39 m above mean sea level (MSL). It is the largest wetland among the various wetlands found in the Kosi-Ganga inter-fluve in the northern plains (Singh & Sinha 2019). The site is one among 18 wetlands within an extensive floodplain complex; it floods during the monsoon season to a depth of 1.5 meters. It experiences three climatic seasons, i.e., summer (March to mid-June), monsoon (mid-June to October), and winter (November to February), and characterized by tropical monsoon type climate with an average annual rainfall of 1,200 mm. The average temperature ranges from 25 °C to 38 °C in summer and 8 °C to 25 °C in winter.

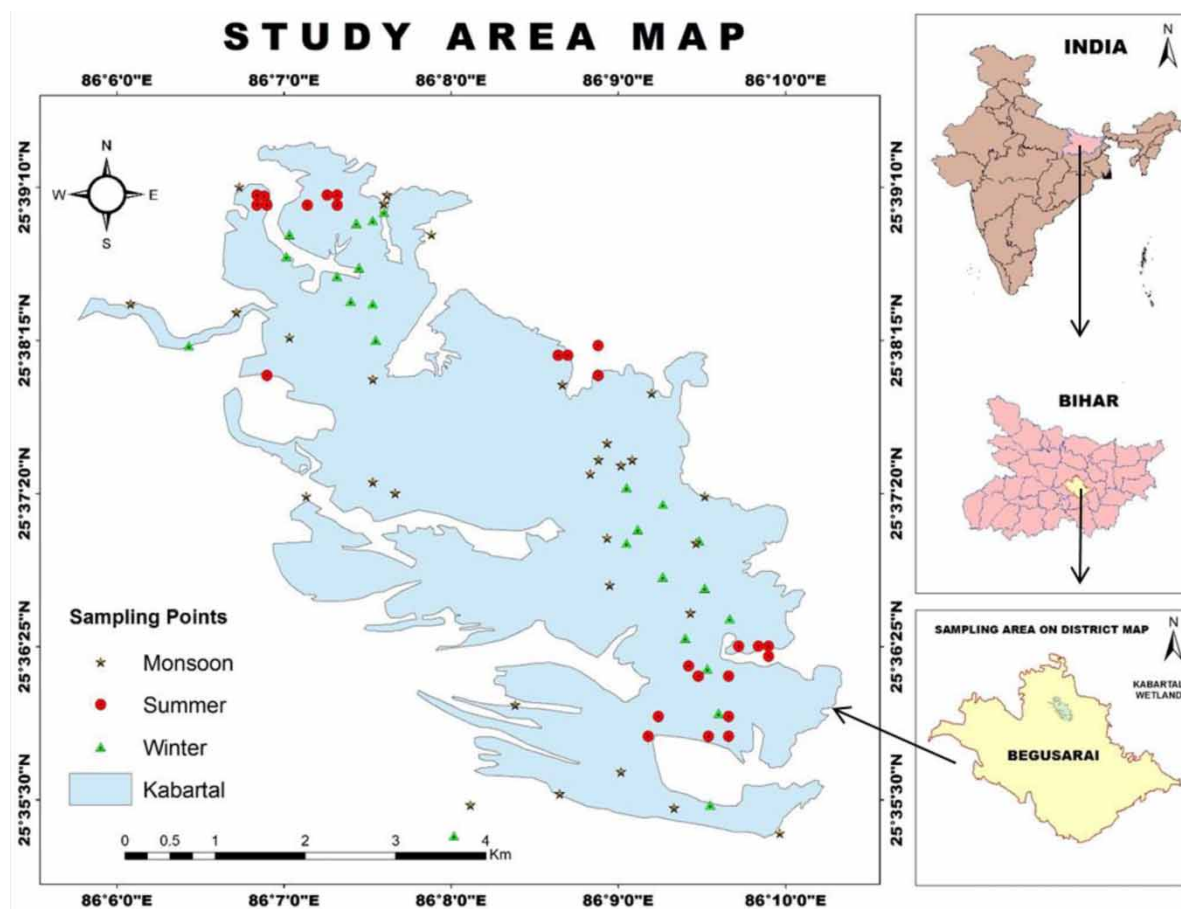


Figure 1 | Map of study area with sampling locations of all seasons.

The lake during dry season covers an area of 2600 hectares whereas; in monsoon, it expands up to an area of 7,400 ha. The Union Government of India has notified KT wetland as a wetland of national importance and also been declared as an IBA (Important Bird Area) site of Bihar and a Ramsar site. The wetland supports many waterfowl in the Gangetic plain along with a variety of species of migratory and resident avifauna; and an important stopover along the Central Asian Flyway, with 58 migratory water birds. Apart from this, the wetland is also a good source of fish varieties, paddy cultivation, and other resources like fodder (Irfan & Pasha 2013). Many varieties of aquatic flora is found in KT wetland, which includes *Pistia stratiotes*, *Hydrilla verticillata*, *Eleocharis plantaginea*, *Eichhornia crassipes*, *Myriophyllum spicatum*, *Zostera marina*, *Egeria densa*, *Lemna obscura*, *Phragmites australis*, *Typha* (Shardendu et al. 2012). KT inhabits three critically endangered species of vultures, namely the red-headed vulture (*Sarcogyps calvus*), white-rumped vulture (*Gyps bengalensis*) and Indian vulture (*Gyps indicus*), and two water birds, the sociable lapwing (*Vanellus gregarius*) and Baer's pochard (*Aythya baeri*) (Ramsar 2020).

Collection of samples and analysis

Overall 83 water samples, 29 samples each in summer (May 2015), and monsoon (July 2015), and 25 samples in winter (February 2016) were collected. Sampling points were fixed by using the portable Global Positioning System (GPS, Garmin Etrex-20). Water samples were collected based on water availability and possible sites for sampling. Samples were stored in an icebox and brought to the laboratory for analysis. The pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature were recorded on the field using a Thermo-Orion portable meter (Thermo Scientific Orion Star A329). Sodium and potassium were estimated by flame photometer; however, calcium and magnesium were analyzed by the EDTA complexometric titration method. Sulphate, nitrate, and phosphate were estimated by spectrophotometric method, chloride was analyzed by argentometric method and HCO_3^- by titrimetric methods (APHA 2012). The analytical data quality was controlled by standardization, procedure blank measurements. All observations were recorded in duplicate and average values were reported. The data used for doing all statistical analysis, as well as preparing contour map, were based on 29 samples each from summer and monsoon and 25 samples from winter season.

Statistical analysis and preparation of contour map

Correlation

Correlation analysis is a statistical method to know relations between variable pairs and given by formula:

$$r = \frac{N\Sigma(X_i Y_i) - (\Sigma X_i)(\Sigma Y_i)}{\sqrt{[N\Sigma X_i^2 - (\Sigma X_i)^2][N\Sigma Y_i^2 - (\Sigma Y_i)^2]}} \quad (1)$$

where r = correlation coefficient

X_i and Y_i represent two different parameters and N = the total number of observations.

Principal component analysis (PCA)

PCA overall is a mathematical approach which does not depend upon assumptions (Mazlum et al. 1999) and is used to decrease the number of the sample without losing on the original sample information (Helena et al. 2000; Singh et al. 2017). Eigen value plays a significant role in importing the variations of these observed data (Prau 2007). In the present study, principal component (PC) having Eigen value >1 is considered. The factor axis was varimax-rotated to extract and minimize the variations among the variables for each factor.

Discriminant analysis (DA)

DA is mostly used to identify the variables, by discriminating two or more naturally occurring groups. Prior understanding of the objects in a particular group/cluster is needed before proceeding with DA. It is applied to the raw data sets and is used to assist in the prediction of groups to which individual parameters belong (Singh et al. 2004), as shown in the equation below:

$$f(G_i) = k_i + \sum_{j=1}^n w_{ij} p_{ij} \quad (2)$$

where,

i represents the number of groups (G);

k_i = constant inherent to each group;

n = number of parameters used for classification of every parameter; and

w_j = the weighting coefficient assigned by DA to a particular parameter (p_j).

PCA, DA and correlation matrix for water samples was carried out by using 'Statistical Package for Social Sciences (SPSS), version-10.0'. Microsoft Excel 2013 was used for hydrochemical plotting.

Contour map

In this study, the contour map is prepared through interpolation, by Inverse Distance Weighted (IDW) method. IDW is the method, which implements the assumption that the things that are closer to one another are more alike than those farther apart. The data obtained through laboratory analysis were tabulated and interpolated using GIS tools. ArcGis 10.1 software was used for preparing contour map.

Calculation for classification of surface water quality for irrigation purpose

Classification of surface water quality (Table 1) for irrigation purpose is done on the basis of Na% [Sodium % = $[(Na + K) * 100] / [Ca + Mg + Na + K]$], Sodium adsorption Ratio (SAR) = $Na / [(Ca + Mg) / 2]^{1/2}$, Residual Sodium Carbonate (RSC)

$[RSC = (CO_3 + HCO_3) - (Ca + Mg)]$, and Salinity Hazard (EC) ($\mu S/cm$) (Richards 1954).

Sodium % <20; SAR <10; RSC < 1.25, indicates that the waters of the wetland is excellent for irrigation for all seasons, if RSC is >2.5 it indicates increased salt content which might lead to choking of soil pores and thereby reduce air passage (Inayathulla & Paul 2013).

RESULTS AND DISCUSSION

Spatial and seasonal variations in water chemistry

The change in temperature at different sampling points of KT wetland was analyzed during the summer, monsoon, and winter seasons are shown in Table 2. The results show that there is not much variation in temperature between summer (28.5 °C–34 °C) and monsoon (28 °C–35 °C) however, during winter temperature ranges between 18 °C and 23.5 °C. Temperature in the wetland varies at different segments with Northern part showing high temperature (~33 °C, ~23 °C) than southern part (~29 °C, 18 °C) during summer and winter, respectively. During monsoon (~30 °C) it is almost uniform showing

Table 1 | Classification of surface water on the basis of Na%, SAR, RSC and Salinity Hazard (EC) ($\mu S/cm$) (n = 29 summer and monsoon; n = 25 winter)

Parameters	Range	Water class	Summer	Monsoon	Winter
Na%	<20	Excellent	All	All	All
	20–40	Good	Nil	Nil	Nil
	40–60	Permissible	Nil	Nil	Nil
	60–80	Doubtful	Nil	Nil	Nil
SAR	<10	Excellent	All	All	All
	18	Good	Nil	Nil	Nil
	18–26	Doubtful	Nil	Nil	Nil
	>26	Unsuitable	Nil	Nil	Nil
RSC	<1.25	Good	All	All	All
	1.25–2.50	Doubtful	Nil	Nil	Nil
	>2.50	Unsuitable	Nil	Nil	Nil
Salinity Hazard (EC)($\mu S/cm$)	<250	Excellent	S3	M2,M3,M4,M5,M7,M8,M9,M10, M11,M13,M16,M17,M19,M20, M21,M22,M23,M24,M25,M26, M27,M28,M29	J5,J6,J7,J15,J24,J25
	250–750	Good	S1,S2,S4,S5,S6,S7,S8,S9,S10, S11,S12,S13,S14,S15,S17,S18, S19,S20,S21,S22,S23,S24,S25, S26,S27,S28,S29	M1,M6,M12,M14,M15,M18	J1,J2,J3,J4,J8,J9,J10, J11,J12,J13,J14,15, J16,J17,J18,J19,J20, J21,J22,J23
	750–2,000	Permissible	S16	Nil	Nil

Table 2 | Seasonal variations of different parameters at Kabar Tal wetland (n = 29 summer and monsoon; n = 25 winter)

	Temp(°C)	pH	EC (µS/cm)	SO ₄ ²⁻ (ppm)	PO ₄ ³⁻ (µ/l)	HCO ₃ (ppm)	NO ₃ (ppm)	Cl ⁻ (ppm)	Ca ²⁺ (ppm)	Mg ²⁺ (ppm)	K ⁺ (ppm)	Na ⁺ (ppm)
Summer												
Mean	31.4	7.1	371.0	18.4	47.5	11.2	1.1	86.5	13.7	5.7	0.5	3.2
Standard Error	0.3	0.1	19.6	3.3	3.6	1.3	0.1	14.9	1.4	0.7	0.1	0.3
Standard Deviation	1.7	0.3	105.3	18.0	19.1	6.9	0.5	80.2	7.7	3.7	0.3	1.8
Kurtosis	-1.2	1.7	11.8	1.7	0.3	-0.4	-0.1	-1.4	-0.5	0.7	4.8	0.5
Skewness	0.0	0.9	3.0	1.4	0.6	-0.4	0.6	0.6	-0.4	0.4	2.2	0.8
Minimum	28.5	6.5	240.0	0.4	10.6	0.0	0.2	2.3	0.0	0.0	0.2	0.7
Maximum	34.0	8.1	820.0	73.2	93.4	24.4	2.2	234.3	28.1	15.8	1.5	7.6
Monsoon												
Mean	30.2	6.8	164.8	59.0	63.3	11.2	0.6	34.4	17.1	5.5	2.4	2.7
Standard Error	0.4	0.1	12.7	4.0	11.9	1.0	0.1	5.5	1.9	0.9	0.3	0.3
Standard Deviation	1.9	0.3	68.2	21.8	64.2	5.6	0.3	29.9	10.0	4.8	1.6	1.6
Kurtosis	0.7	2.0	-0.9	2.5	4.1	-0.4	-0.7	7.5	0.0	2.1	3.4	10.0
Skewness	1.2	0.6	0.5	0.4	2.2	-0.5	-0.1	2.5	0.3	1.4	1.8	2.6
Minimum	28.0	6.1	60.0	0.1	16.3	0.0	0.1	2.3	0.0	0.0	0.5	0.2
Maximum	35.0	7.6	290.0	118.5	257.7	18.3	1.1	149.1	40.1	19.4	7.3	9.3
Winter												
Mean	20.7	7.9	257.2	47.7	28.9	17.4	0.8	37.8	22.7	12.9	4.8	4.1
Standard Error	0.3	0.1	10.2	3.3	2.5	1.1	0.1	8.2	2.3	1.2	0.4	0.4
Standard Deviation	1.5	0.3	51.0	16.7	12.7	5.4	0.3	40.8	11.5	6.0	1.8	1.9
Kurtosis	-0.7	-0.5	2.7	0.2	6.6	4.3	0.6	7.0	-1.0	-0.2	0.4	0.1
Skewness	0.5	0.6	-0.6	-0.1	2.6	-1.7	1.2	2.7	-0.3	0.6	0.6	-1.0
Minimum	18.0	7.4	110.0	16.0	17.7	0.0	0.5	7.1	0.0	2.4	1.4	0.0
Maximum	23.5	8.6	360.0	87.2	69.1	24.3	1.5	177.5	40.1	25.0	8.5	6.5

Standard Error, Standard Deviation, Kurtosis, and Skewness was calculated at 95% confidence level.

slight variation on the periphery of the northern, southern, and eastern region. It is observed that the temperature during winter is higher in the northeastern and northwestern regions (~23 °C) whereas the southern part has lower temperature (18 °C) (Figure 2(a)). The pH shows spatial variation during summer. It is highest at the southern side (~7.2) and lowest in the northwestern (~6.5) and northeastern region (~6.8). In monsoon, pH is highest at the south eastern side (~6.8) and lowest at the northern side (~6.5) whereas during winters, the pH is highest at the northern side (~7.97) as shown in Figure 2(b).

The seasonal variation of temperature in the water is due to the variability in water depth and its quantity (Ling et al. 2017). The temperature fluctuation of KT wetland at various seasons is less significant in areas where volume of water is greater.

The average value of pH during winter (7.9) is slightly more than in summer and monsoon, indicating the neutral to alkaline nature of water. pH value is affected by biological activities like photosynthetic and respiration rates in wetland (Weisse & Stadler 2006; Shah et al. 2019). Therefore, higher photosynthesis uptakes more CO₂ and thus increases pH in winter. The low value of pH in summer could be due to the decomposition of accumulated organic matter, and its biological oxidation, releasing CO₂ which in turn reduces the pH (Langmuir 1997). However, a low value in monsoon may be due to high turbidity of water and elevated temperatures which leads to less photosynthesis and accumulation of more free CO₂ (Adebisi 1981; Edoreh et al. 2019). A low rate of photosynthesis can also cause a decline in pH due to inefficiency of light-dependent reactions on a cloudy day during monsoon as temperatures hardly affect the light-dependent reactions of photosynthesis (Marra & Heinemann

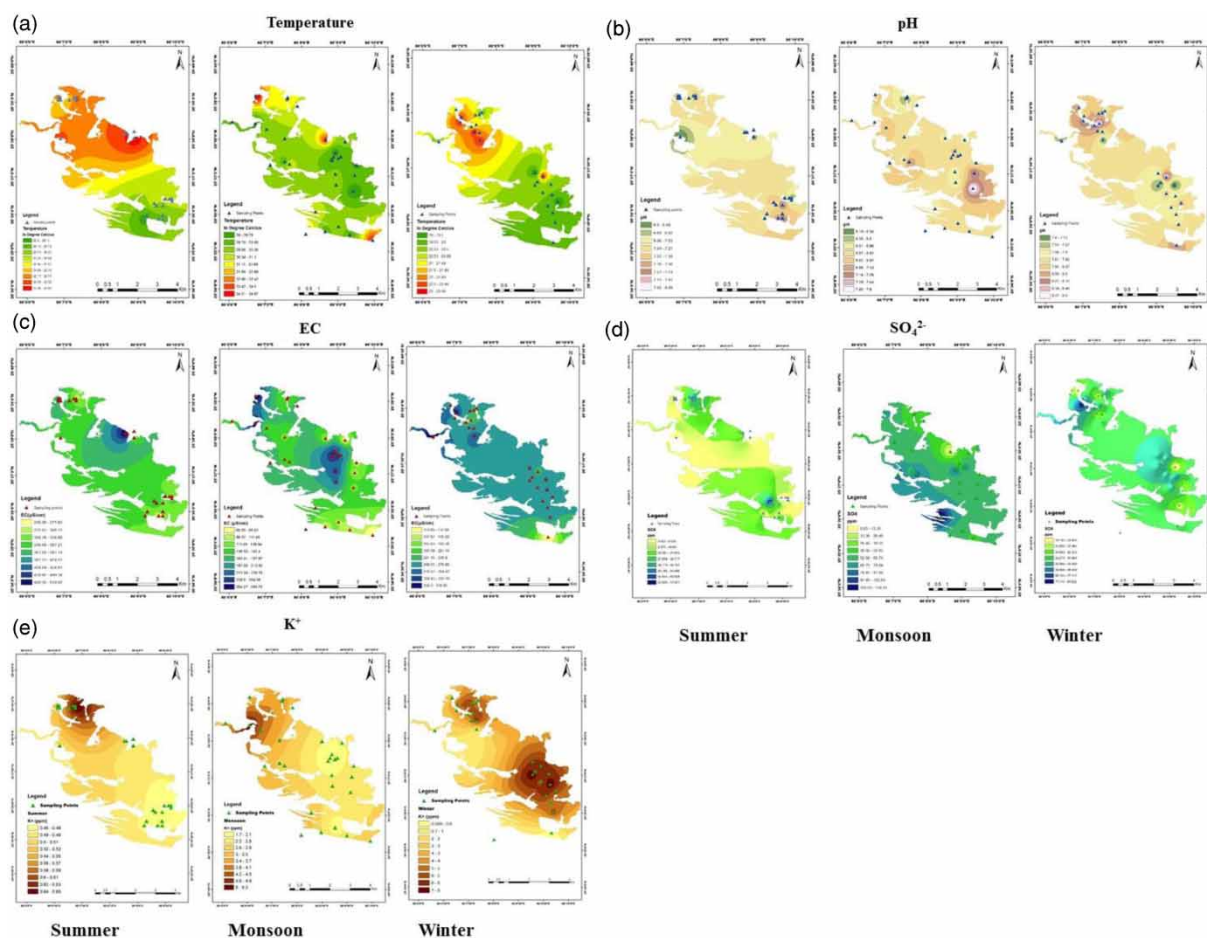


Figure 2 | Contour maps showing different parameters; (a) temperature, (b) pH, (c) EC, (d) SO_4^{2-} and (e) K^+ ; concentration in water samples of Kabar Tal wetland in different seasons (summer, monsoon and winter).

1982; Wu *et al.* 2017). Additionally, transport of humic and fulvic materials in colloidal suspension may also contribute to lower pH values (Langmuir 1997; Weng *et al.* 2002).

The electrical conductivity (EC) of water is a measure of dissolved ions which originates from the weathering processes and decaying plant matter (Sarwar & Majid 1997; Ray *et al.* 2021), and also input of organic and inorganic waste (Wright 1982; Dey & Dey 2015). During the present analysis, EC was found to be significantly higher in the summer ($371 \mu\text{S}/\text{cm}$) than monsoon and winter. The higher value of EC during summer shows the ions getting concentrated due to lesser water availability and temperature induced rapid evaporation (Gupta & Paul 2013; Singh *et al.* 2020). However, it was noticed to be least in monsoon due to dilutions of the wetland water through rainfall and runoff from its adjoining areas like agricultural lands and water bodies (Ambastha *et al.* 2007). Electrical conductivity during summer is maximum in the northeastern region by up to $850 (\mu\text{S}/\text{cm})$, reflecting the effect of an increase in

temperature over northeastern part (Figure 2(c)); and lowest at the southern part ($\sim 250 \mu\text{S}/\text{cm}$). EC shows the variation (from 110 to $360 \mu\text{S}/\text{cm}$) in winter as shown in Figure 2(c) whereas, during monsoon, EC is uniform and shows a slight increase in the northern region ($\sim 290 \mu\text{S}/\text{cm}$) and reduction at the southern region ($\sim 60 \mu\text{S}/\text{cm}$). This may be the case due to an increase in runoff at the northern region from the agricultural fields.

Anions

The seasonal variations shows (Table 2) that anions follows the trend $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{PO}_4^{3-}$ in monsoon and winter, whereas in summer its trend is $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{PO}_4^{3-}$. Chloride (Cl^-) occurs naturally in all types of water due to its high solubility. The higher concentration of chloride during summer may be associated with a high rate of evaporation as well as frequent run-off loaded with contaminated water from the surrounding

areas. Sources of chloride in surface water are both natural and anthropogenic, such as weathering, leaching from sedimentary rocks and soils, the use of inorganic fertilizers, animal feeds, industrial effluents, irrigation drainage, and organic wastes of animal origin. Chloride enters surface water through both natural (weathering, sedimentary rock and soil leaching) and anthropogenic (inorganic fertilizers, animal feed, agricultural waste, irrigation runoff) sources (Venkatasubramani & Meenambal 2007). The chloride distribution in the study area is found to be highest at the western (234 mg/L) and northern (139 mg/L) periphery of KT wetland during summer. During monsoon, a single patch of high concentration of chloride (149 mg/L) is observed at the northeastern region whereas the concentration of chloride is relatively high in patches during winter as shown in Supplementary Figure S1(a).

The concentration of HCO_3^- is higher (17.4 mg/L) in winter than summer and monsoon (11.2 mg/L). The source of HCO_3^- in the aquatic ecosystem is through the dissolution of gases, carbonate equilibrium, and weathering of carbonate rocks (Shah *et al.* 2019). The increase in HCO_3^- concentration in winter can be attributed to seasonal variability in the chemical weathering of carbonate and silicate minerals (Tipper *et al.* 2006). The higher presence of HCO_3^- pertains generally to the dissolution of minerals like calcite and dolomite (Cai *et al.* 2007). In the winter season, higher dissolution of CO_2 , due to the inverse relationship of dissolved CO_2 and temperature may induce a higher rate of carbonate weathering (Langmuir 1997). HCO_3^- is found to be higher at two patches at the northeastern and southern boundary of Kabar Tal during summer and monsoon; it has been vividly represented on the contour map, shown in Supplementary Figure S1(b). During winter, the bicarbonate concentration ranges from 12 to 24 (mg/L) but at the northeastern side wavering towards the center, it is 5.9 (mg/L) at a single patch.

Phosphorus is one of the key nutrients which limit primary productivity in many freshwater ecosystems, whereas nitrogen is a common limiting nutrient in marine ecosystems (Cloern 2001). However, in some freshwater environments, particularly in the tropics and subtropics, N is the primary limiting nutrient for phytoplankton production, owing to excessive P load and long growing seasons (e.g., Yang *et al.* 2008). The nitrogen in water is generally present in forms like nitrate, nitrite, ammonia and organic form sources are urea, amino acids, etc. The most significant source of NO_3^- in an aquatic ecosystem such as wetland and lake is the biological oxidation of nitrogen-rich organic matter such as domestic sewage, agricultural

runoff, and industrial effluents (Vrzel *et al.* 2016). The high concentration of nitrates is beneficial for irrigation, but it causes eutrophication which promotes the growth of algae and macrophytes (Trivedy & Goel 1984). NO_3^- concentration is greater in summer (0.5 ± 1.1 mg/L) than in monsoon (0.3 ± 0.6 mg/L) and winter (0.3 ± 0.8 mg/L). Similar trends in nitrate were also observed in many aquatic ecosystems (Garg *et al.* 2006; Sinha & Biswas 2011; Prabhakar *et al.* 2012; Singh & Jayakumar 2016; Singh & Deepika 2017). Nitrate concentration lies between 0.2 and 2.2 (mg/L), highest at the northern extreme, and two patches at the southeastern region during summers, and the distribution of nitrate is not found to be homogenous, especially during monsoons as nitrate cannot be attributed to a single source. Supplementary Figure S1(c) shows the heterogeneity of nitrate distribution in the wetland. Nitrate concentration gradually increases towards northern regions in winter.

The concentration of PO_4^{3-} in monsoon (63.3 ± 64.2 $\mu\text{g/L}$) is reported to be higher than in summer and winter. The source of PO_4^{3-} in the surface water comes mostly through anthropogenic sources. The high concentration of PO_4^{3-} and NO_3^- in monsoon may be due to the runoff from the agricultural area which contributes to both nitrate and phosphate (Desai *et al.* 1995; Bandela *et al.* 1999; Anshumali & Ramanathan 2007). In general, it is reported that 80% of lake and other reservoirs' eutrophication is controlled by phosphorus (Zhao 2004). The lowest values of phosphate were observed in summer and winter which may be due to low inflow of wastewater, biological utilization, and removal by absorption on to sediment and suspended particles (D'Sousa *et al.* 1981; Rajasegar 2003). PO_4^{3-} concentration is observed high in the northern region during monsoon (257.7 $\mu\text{g/L}$) and winter (69.1 $\mu\text{g/L}$), whereas during summers it is concentrated towards the southern part with maximum recorded value of 180 $\mu\text{g/L}$. Monsoon season also exhibits a very high concentration of PO_4^{3-} (~255 $\mu\text{g/L}$) towards the northern end of the KT wetland as shown in Supplementary Figure S1(d). The high concentration of phosphates in the northern part and some patches coupled with nitrate concentration depicts that the agricultural runoff (fertilizer) is contributing to the presence of excess ionic entities (Ambastha *et al.* 2007; Singh *et al.* 2020).

Sulphate is a naturally occurring substance constituting sulphur and oxygen and is present in various mineral salts that are found in soil. Sulphate may leach from the soil, fertilizers, decaying plant and animal matter commonly released into the water. The highest SO_4^{2-} concentrations were observed in monsoon (59 ± 21.8 mg/L). This could be attributed to the dissolution of SO_4^{2-} rich minerals, and

also by human interventions through the application of fertilizers (Grasby *et al.* 1997). The similar trends of seasonal variations in physicochemical characteristics of River Yamuna reported a higher sulphate concentration of 80 mg/L during the wet season than the in dry season (Ravindra *et al.* 2003). Sulphate concentration during monsoon reaches up to 118 (mg/L) in the southwestern region whereas during summer and winter it is confined 80 (mg/L) with variation at different sampling points as depicted in Figure 2(d). Ranjan *et al.* (2017) has analyzed sulphate concentration in KT area and reported concentration of 10.89 mg/L, which is lower than present study (47.7 mg/L). As this area is surrounded by agriculture field and the cropping patterns are variable, we can conclude that the application of fertilizers has increased in this area in a heterogeneous manner. Whereas, the elevation in SO_4^{2-} concentration might have occurred due to dissolution of SO_4^{2-} rich minerals with time (Grasby *et al.* 1997). Simultaneously Mg^{2+} and Cl^- is moderately increasing; by observing the pattern of increment in Mg^{2+} we can say that it is associated with SO_4^{2-} and Cl^- coupling when entering the system (Jhingran 1975).

Cations

The seasonal variations show (Table 2) that cations follow the trend $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ in summer and winter, whereas in monsoon its trend is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. Calcium is one of the most important nutrients for the aquatic organisms as it an essential element for the formation of the cell walls and is one of the important factors for physiological function (Yadav *et al.* 2013). The calcium ions are the dominant cations in the surface water. The mean value of calcium in KT wetland was found to be higher in the winter season (22.7 ± 11.5 mg/L) and lower during summer (13.7 ± 7.7 mg/L). Similar results were noted by (Munawar 1970; Singh & Jayakumar 2016). The high concentration of calcium ions may be due to the weathering of rocks such as limestone, marble, calcite, dolomite, gypsum, fluorite and apatite, etc. (Singh *et al.* 2011). Although calcium is found to be abundant in water naturally, as well as by induced weathering of rocks, still the addition of sewage waste from nearby residential areas of KT wetland may be accountable for its dominance (Angadi *et al.* 2005; Udhaya Kumar *et al.* 2006). Ca^{2+} during monsoon and winter reaches up to 40 (mg/L) and during summers they are confined to a maximum of 28 (mg/L). The distribution is shown in Supplementary Figure S1(e).

Magnesium is generally found in minerals and rocks linked up with calcium and iron compounds, but its concentration is always less than calcium (Tulsankar *et al.* 2020). It is a very essential macronutrient for the chlorophyll bearing autotrophs like algae and plants which manufacture their food (White & Brown 2010). For phytoplankton, the limiting factor for its growth is magnesium (Dijkstra *et al.* 2019). The mean concentration of magnesium recorded seasonally ranged between (12.9 ± 6 mg/L) to (5.5 ± 4.8 mg/L), maximum concentration was observed during winter (12.9 ± 6 mg/L) and minimum concentration during monsoon (5.5 ± 4.8 mg/L). A similar result was observed by Kumar *et al.* (2014) also. Magnesium also enters the system in association with anions like chloride and sulfate (Jhingran 1975). Mg^{2+} concentration show 1.2–15.8 (mg/L) variation during summers, maximum concentration was observed at the edges of the KT on the northeastern side. During monsoon, 2.4–19.4 (mg/L) concentration is observed with two patches recording high concentration in the northeastern and southeastern region. In winter season, a vivid patch of higher concentration is observed as shown in Supplementary Figure S1(f) ranging from 2.5 to 25 (mg/L).

The mean concentration of sodium ranges from 4.75 mg/L (± 1.8) to 2.40 mg/L (± 1.6), maximum during winter 4.75 mg/L (± 1.8) and minimum during monsoon 2.40 mg/L (± 1.6). However, mean concentration of potassium ranges from 4.1 mg/L (± 1.9) to 0.5 mg/L (± 0.3), maximum during winter 4.1 mg/L (± 1.9) and minimum during summer 0.5 mg/L (± 0.3). Sodium and potassium are naturally present in water, although its concentration may increase due to silicate weathering, application of potash fertilizers, precipitation runoff, and from detergents and soap (Kumar *et al.* 2014). The K^+ distribution in the study area is not homogenous as during summer and ranges from 0.2 to 1.49 (mg/L) with maximum value observed at the northern side of the KT wetland region (Figure 2(e)). During monsoon K^+ ranges from 0.22 to 9.25(mg/L), maximum concentration observed towards the northern side again but slightly moving towards the west. In winters, it is concentrated at two patches in the north and southeastern region.

Na^+ concentration ranges from 0.8 to 7.4 (mg/L) during summer. High concentration of Na^+ is observed in north side of KT wetland whereas southern region exhibits lower Na^+ concentration, 7.64 mg/L and 0.7 mg/L, respectively. However, during monsoon, Na^+ concentrations ranges from 0.52 to 7.2 (mg/L) and the highest value was noted to be at two patches at the center (7.2 mg/L) and northwestern (6.57 mg/L) part as shown in Supplementary

Figure S1(g). Winter shows the highest concentration of Na at northern extremes of KT wetland. Most of the dynamic ionic activity is thus seem to occur at the north and north-western patch of wetland. The presence of higher ionic concentrations can change the hydrogeochemical dynamics which leads to alteration in functionality of the wetlands. The occurrence of higher ionic presence could be due to the depression hydrology where all entities meet and form a dynamic system of alternating storage and release of ions.

Correlation among different parameters of Kabar Tal wetland

The correlation matrix (Supplementary Table S1(a)) plotted for the water samples collected in summer season shows good correlation between Ca^{2+} and HCO_3^- (0.671), Mg^{2+} and HCO_3^- (0.678). Its main source may occur due to natural death and the decaying process occurring in the wetland. During summer, the temperature and humidity are relatively high; hence the decaying process is also high in releasing gases like CO_2 , which dissolves in water. This helps in the formation of carbonic acid which leads to further breakdown resulting in an increased composition of bicarbonates.

The correlation matrix (Supplementary Table S1(b)) plotted for the monsoon water samples shows a good correlation between Na^+ and EC (0.717) as Na^+ ions are not generally up taken by the plants, thus, its concentration may have increased causing higher EC. Ca^{2+} and SO_4^{2-} show positive correlation (0.503). Similarly, Na^+ and Cl^- (0.537) and Ca^{2+} and HCO_3^- (0.692) pairs show high positive correlation. This may be present in the water samples due to weathering of sulphate minerals (e.g. gypsum) and transfer in the lake through agricultural runoffs.

The correlation matrix (Supplementary Table S1(c)) plotted for the winter NO_3^- and temperature (0.589), Na^+

and temperature (0.501), NO_3^- and pH (0.707), Mg^{2+} and EC (0.542), shows good correlation. These correlation values suggest that during winter, temperature governs the physicochemical character of the surface water of the wetland.

Classification of surface water chemistry

The surface water of the study area may have some similarities. To understand this, the study area has been classified hydrochemically using major cations and anions data by plotting Piper trilinear diagram (Piper 1944). Piper plot (Figure 3) shows that surface water during summer is dominated by Ca^{2+} and Cl^- but during the monsoon and winter period, the water shows the dominance of Ca^{2+} - Mg^{2+} - SO_4^{2-} and Cl^- types of ions, indicating possible runoff input of sulphur into the system. Excess input of sulphur into the system might be due to the agricultural runoff from the nearby agricultural fields. The presence of chloride type water during summer is mainly due to the evaporation of wetlands surface water. Overall, the hydrochemical facies in all the seasons indicates that strong acids exceed weak acids in the wetland and alkaline substances also dominate over alkalis.

Sodium percentage, SAR, RSC, and salinity hazard

The Wilcox plot, Figure 4(a), which uses sodium percentage and EC values helps in a better understanding of water usage for agricultural purposes pictorially. The study shows that wetland water in all seasons shows excellent nature for agricultural purposes except for few sampling locations in summer (S16, S17, S24, and S29) and monsoon (S11 and S21) where water quality falls in the group of unsuitable category. The unsuitable nature resulting from

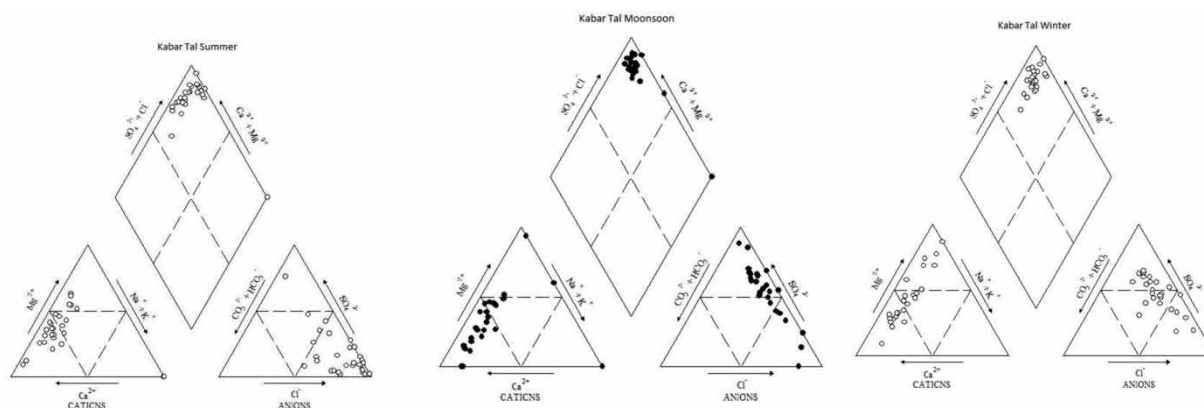


Figure 3 | Piper plot of the surface water at different locations in Kabar Tal during various season.

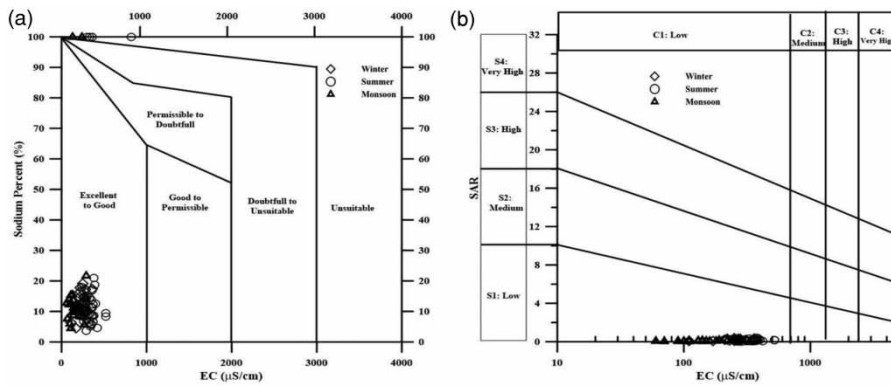


Figure 4 | (a) Wilcox classification of the surface water at different locations in Kabar Tal. (b) Water classification on the basis of sodium absorption ratio (SAR) and electrical conductivity (EC).

high sodium% during these seasons might be due to the influence of agricultural activity.

The SAR vs EC plot (Figure 4(b)) shows the usage of water for both drinking and agricultural purposes. The low EC (i.e. $<750 \mu\text{S/cm}$) indicates its suitability for drinking purposes and moderate EC value ($750\text{--}1,250 \mu\text{S/cm}$) indicate the acceptable nature of water. Low SAR values (<10) indicate its suitability for agricultural activity. The SAR vs EC plot shows that water in KT wetland in all seasons falls under the low-risk category (C1S1) indicating suitability for both drinking and agricultural purposes.

Provenance and water-rock interaction

The Gibbs plot (Gibbs 1970) helps to understand the dominant source of ions to the hydrological system. The low

values of total dissolved solids (TDS) and high Na/Cl content indicates precipitation source whereas, high TDS value indicates evaporation dominated source. The present study (Figure 5(a) and 5(b)) shows that all data lies within the rock dominance region indicating weathering as the main source of ions regulating the water chemistry. The Mg/Na and HCO_3^-/Na vs Ca/Na plot helps to find the dominance of weathering in the region (Figure 6(a) and 6(b)). It shows the dominance of carbonate weathering along with a minor amount of silicate weathering in the Kabar Tal wetland's water.

As depicted from the SO_4^{2-} vs Ca^{2+} plot (Figure 7(a)); HCO_3^- vs Ca^{2+} plot (Figure 7(b)); Na/Cl vs Cl^- plot (Figure 7(c)); $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs HCO_3^- plot (Figure 7(d)); it can be inferred that the dominance of ions in the study area is mainly due to weathering of both carbonate and silicate

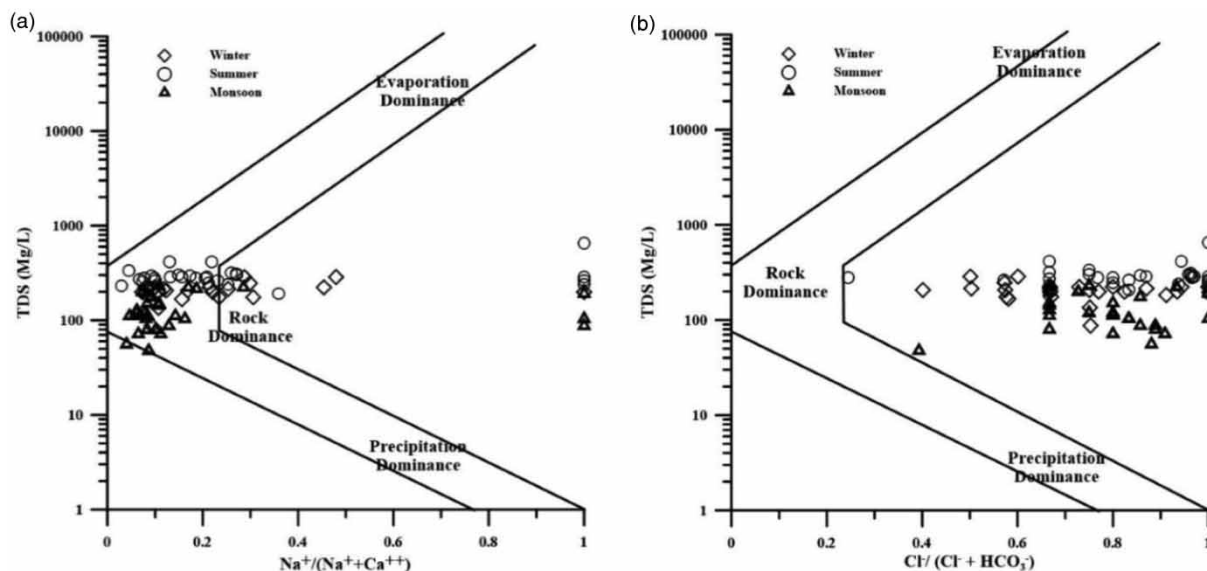


Figure 5 | (a) Log TDS vs $\text{Na}/(\text{Na}^{++} + \text{Ca}^{++})$; (b) log TDS vs $\text{Cl}/(\text{Cl} + \text{HCO}_3^-)$ plot showing dominant source of surface water chemistry in Kabar Tal.

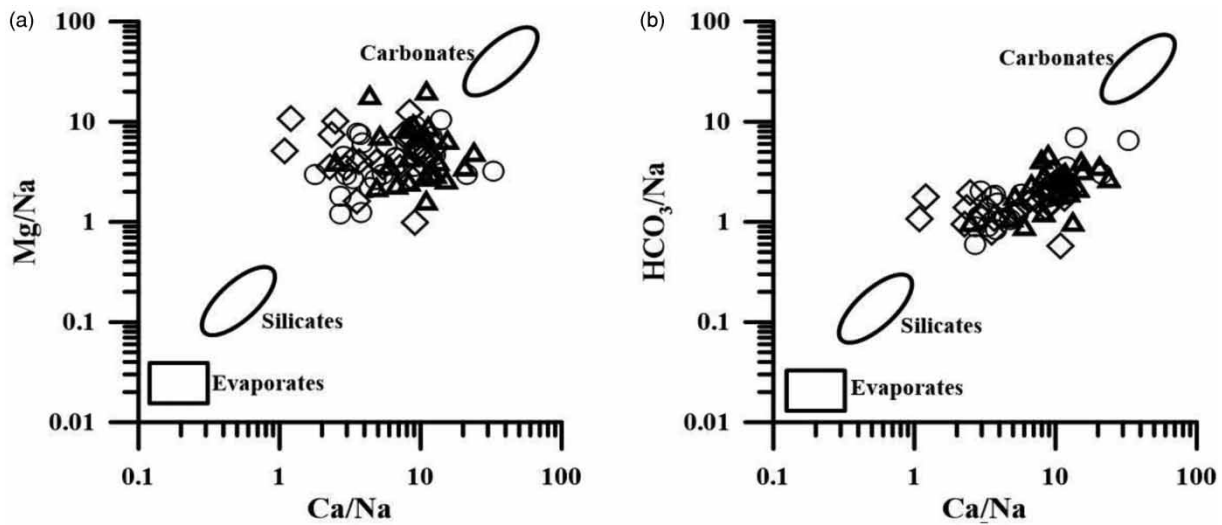


Figure 6 | (a) Mg/Na vs. Ca/Na; (b) HCO_3^-/Na vs. Ca/Na plot showing the major weathering source for surface water chemistry in Kabar Tal.

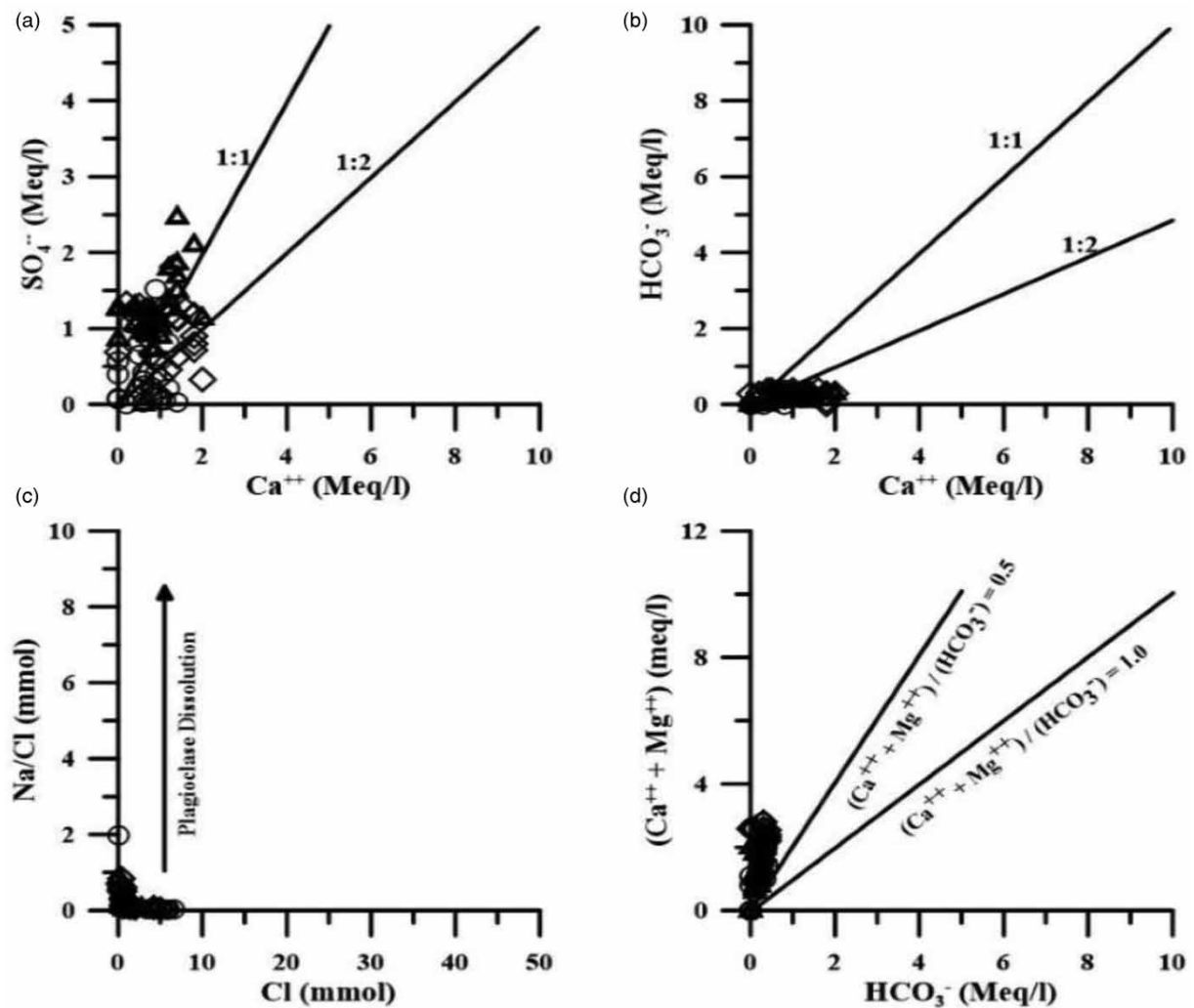


Figure 7 | Plots of (a) SO_4^{2-} vs. Ca^{2+} ; (b) HCO_3^- vs. Ca^{2+} ; (c) Na^+/Cl^- vs. Cl^- ; (d) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^- .

minerals. To understand the presence of dominant mineral, the biplots for various cations and anions were studied (Figure 7(a) and 7(d)). The Na^+/Cl^- vs Cl^- plot (Figure 7(c)) helps us decipher the dominance of evaporation over silicate weathering for Na^+ and Cl^- concentration in the water. The plot (Figure 7(c)) depicts that during summer, the evaporation dominates whereas during winter and monsoon silicate weathering dominates. The plots (Figure 7(b) and 7(d)) show that all the data points fall near to the Y-axis (Ca^{2+} and $\text{Ca}^{2+} + \text{Mg}^{2+}$) indicating Ca and Mg chemistry is dominated by the predominance of calcite and dolomite. The sulphate concentration in the region is derived from both natural (dissolution of sulphate minerals like gypsum) and anthropogenic (fertilizers) activities as the data plots scatter to large extent in the biplot (Figure 7(a)).

PRINCIPAL COMPONENT ANALYSIS (PCA) AND FACTOR ANALYSIS (FA)

PCA of the summer season

The first four PCs (Eigen value >1) are the most significant principal components, which represent 70.81% of the variance in water quality of KT wetland (Table 3). PC 1 explains 23.52% of the variation and is influenced highly by HCO_3^- , Ca^{2+} , and Mg^{2+} ; whereas the loading of Na^+ is very weak. This PC 1 suggest that carbonate weathering plays a major role in governing water chemistry in summer. PC 2 is responsible for 18.01% of the variation and is strongly influenced by temperature. The temperature in summer is relatively higher than winter and monsoon seasons and it is evident from the PC 2 that temperature is one of the determining factors which controls water chemistry. PC 3 contributes to 16.16% of the variation and is influenced highly by Cl^- and Na^+ ions. Since high evaporation rate in summer due to high temperature leads to an increase in concentration of Cl^- and Na^+ in water and controls the hydro geochemistry. However, PC 4 contributes to 13.13% of the variation and is highly influenced by SO_4^{2-} and is least influential in summer than other anions.

PCA of monsoon season

The first five PCs (Eigen value >1) are the most significant principals, which represent 75.57% of the variance in water quality of KT wetland (Table 3). PC 1 contributes to 20.19% of the variation and is highly loaded with Na^+ ,

and moderately loaded with nitrate and temperature. It is also observed that during a dry season Kabar Tal wetlands is used for agriculture purpose nitrogenous and phosphate-containing fertilizers are widely used (Ranjan et al. 2016). However, surface runoff from agricultural in monsoon increases concentration of nitrate which governs the water chemistry. PC 2 contributes to 18.76% of the variation with a high loading of Mg^{2+} and SO_4^{2-} . PC 3 contributes to 13.44% of the variation with a high loading of HCO_3^- . PC 4 contributes to 12.67% of the variation with high loading pH and EC. PC 5 contributes to 10.51% of the variation with a high loading of K^+ . The combined interpretation of PC2, PC3 and PC4 suggests that sulphate weathering plays the prominent role, followed by bicarbonate in monsoon.

PCA of the winter season

The first five PCs (Eigen value >1) are the most significant principals, which represent 80.35% of the variance in water quality of KT wetland (Table 3). PC 1 contributes to 20.69% of the variation with a high loading of Mg^{2+} and temperature. PC 2 contributes to 20.37% of the variation with a high loading of HCO_3^- , Ca^{2+} , and EC. PC 3 contributes to 15.05% of the variation with a high loading of Na^+ . PC 4 contributes to 13.85% of the variation with a high loading of NO_3^- and Cl^- . PC 5 contributes to 10.39% of the variation with a high loading of PO_4^{3-} . The overall analysis of PC suggest that carbonate/dolomite weathering plays a significant role in increasing HCO_3^- , Ca^{2+} and Mg^{2+} concentration in winter, which subsequently influences EC in winter season.

Discriminant analysis (DA)

Seasonal (summer, monsoon, and winter) water quality variations were evaluated using DA. Discriminant functions (DFs) and classification matrices (CMs) were obtained from standard, forward, and backward stepwise modes of DA (Table 4). In forward stepwise mode, parameters having more significant to no significant change are included by the step-by-step process. However, in backward stepwise mode, parameters with less significant to no significant change are obtained through removing the step-by-step process. The standard DA mode, constructed DFs including 12 parameters are shown in Table 4. All the standard, forward, and backward stepwise mode DFs using 12, 5, and 8 discriminant variables, respectively, rendered the corresponding CMs, assigning 100% cases correctly (Table 5). Forward stepwise and backward stepwise DA showed that

Table 3 | Rotated component matrix for different principal components of summer, monsoon and winter water samples (n = 29 summer and monsoon; n = 25 winter)

Parameters	Summer				Monsoon					Winter				
	PC (1)	PC (2)	PC (3)	PC (4)	PC(1)	PC (2)	PC (3)	PC (4)	PC (5)	PC(1)	PC (2)	PC (3)	PC (4)	PC (5)
HCO ₃ ⁻ (ppm)	0.845						0.830				0.810			
Ca ²⁺ (ppm)	0.845				-0.696			-0.324		-0.418	0.724			0.401
Mg ²⁺ (ppm)	0.734					0.775				0.870				
NO ₃ ⁻ (ppm)	0.690			-0.521	0.677		-0.522						0.871	
PO ₄ ³⁻ (ppb)		-0.830					0.585	0.316	0.461					0.921
Temp (°C)		0.829			0.618	0.474				0.722				
EC (µS/cm)		0.660					0.356	0.731			0.907			
Cl ⁻ (ppm)			0.850		-0.353	0.687			-0.300			0.309	0.797	
Na ⁺ (ppm)	0.427		0.784		0.893							0.888		
pH		-0.418	0.446	0.399				0.772		0.630	-0.316	-0.577		
SO ₄ ²⁻ (ppm)				0.860		0.862				0.643	0.521		0.314	
K ⁺ (ppm)	0.344		-0.479	0.540					0.914			0.667		
Eigenvalue	2.822	2.161	1.939	1.575	2.423	2.251	1.612	1.521	1.261	2.483	2.444	1.806	1.662	1.247
% of Variance	23.518	18.007	16.155	13.126	20.191	18.759	13.437	12.673	10.505	20.693	20.367	15.048	13.849	10.391
Cumulative %	23.518	41.525	57.680	70.806	20.191	38.950	52.387	65.060	75.565	20.693	41.060	56.107	69.956	80.348

Extraction Method: Principal Component Analysis & Rotation Method: Varimax with Kaiser Normalization.

Table 4 | Classification functions (Equation (3)) for discriminant analysis of temporal variation in Kabar Tal wetland (n = 29 summer and monsoon; n = 25 winter)

Parameters	Standard mode			Forward mode			Backward mode		
	Monsoon coefficient ^a	Summer coefficient ^a	Winter coefficient ^a	Monsoon coefficient ^a	Summer coefficient ^a	Winter coefficient ^a	Monsoon coefficient ^a	Summer coefficient ^a	Winter coefficient ^a
Temp (°C)	11.460	11.851	7.414	10.761	11.114	7.020	11.273	11.648	7.159
pH	79.431	85.467	93.549	67.190	73.504	78.629	67.966	73.710	79.446
EC (µS/cm)	0.051	0.105	0.071	0.051	0.101	0.076	0.056	0.109	0.079
SO ₄ ²⁻ (ppm)	-0.075	-0.174	-0.202	0.076	-0.041	-0.015	0.070	-0.030	-0.015
PO ₄ ³⁻ (µ/l)	0.070	0.065	0.081						
HCO ₃ ³⁻ (ppm)	0.410	0.589	0.381						
NO ₃ ³⁻ (ppm)	-19.195	-14.350	-20.762				-5.758	-1.024	-3.995
Cl ⁻ (ppm)	0.038	0.065	0.017				0.000	0.026	-0.030
Ca ²⁺ (ppm)	0.961	0.928	1.229						
Mg ²⁺ (ppm)	1.698	1.622	2.185						
K ⁺ (ppm)	-5.539	-8.503	-3.682	-3.951	-6.126	-2.153	-3.933	-6.678	-1.832
Na ⁺ (ppm)	-3.142	-3.899	-2.203				-1.606	-2.337	-0.330
Intercept	-446.938	-511.521	-463.146	-393.219	-453.849	-389.219	-399.917	-461.295	-392.042

Discriminant function coefficient for winter, summer and monsoon seasons correspond to w_{ij} as defined in Equation (2).

Table 5 | Classification matrix of DA of temporal variation in Kabar Tal wetland

Sampling seasons	% correct	Seasons assigned by DA		
		Monsoon	Summer	Winter
Standard DA mode				
Monsoon	100	29	0	0
Summer	100	0	29	0
Winter	100	0	0	25
Total	100	29	29	25
Forward stepwise DA mode				
Winter	100	29	0	0
Summer	100	0	29	0
Monsoon	100	0	0	25
Total	100	29	29	25
Backward stepwise DA mode				
Winter	100	29	0	0
Summer	100	0	29	0
Monsoon	100	0	0	25
Total	100	29	29	25

temperature, pH, EC, SO₄²⁻, and K⁺ are the major significant parameters followed by NO₃⁻, Cl⁻, Na⁺ (Table 4). Further, a less significant third group of the remaining four parameters, i.e., PO₄³⁻, HCO₃⁻, Ca²⁺, and Mg²⁺, is marked

from the standard mode. Thus, the temporal DA results explain that temperature, pH, EC, SO₄²⁻, and K⁺ are the most significant parameters to discriminate among the three different seasons, these five parameters justify most of the expected temporal variations in the water quality (Table 5).

CONCLUSIONS

In this study, SAR (sodium adsorption ratio) value of the study area is less than 10, favorable, and suitable for irrigation purposes. Based on RSC values, all the samples of the three seasons had values less than 1.25 which also supports its suitability criteria. Gibb's plot reveals that weathering processes are one of the major sources of ions in water. The statistical technique reveals that temperature, pH, EC, SO₄²⁻, and K⁺ are the most significant parameters which are governing the water quality. In summer season, the dry region of KT is utilized for agricultural purpose. Thus, application of fertilizers might occur to get good yield. Therefore, during monsoon these agricultural fields get flooded and change the water chemistry and deteriorate the water quality of the wetlands. The agricultural areas and villages around the wetland also contribute to the nutrient enrichment in the wetland. Overall results illustrate that seasonal variation is playing a

major role in nutrients dynamics and hydrochemistry of Kabar Tal wetland.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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