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Hydrochemical evaluation of surface water quality of Sutlej river using multi-indices, multivariate statistics and GIS

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Abstract

The water quality of Sutlej river in Indian Punjab is getting deteriorated due to expansion of agricultural, industrial and recreational activities in the region. Many studies have evaluated the water quality of Sutlej river around the stretches of contaminated drains confluence with the river, but there are very few studies in which hydrochemistry of surface water of the river has been studied from the entry point of Sutlej river in Indian Punjab to its tail end when it leaves the country. Surface water samples ($n = 97$) were collected from the river during May 2019 and analyzed for pH, electrical conductivity, carbonate, bicarbonate, chloride, calcium, magnesium, sodium, potassium, nitrate and sulfate in the laboratory using the standard protocols. Results showed that total alkalinity, total hardness, sodium, potassium, chloride and nitrate were higher along the transboundary of the river. Water samples of the river are mainly $Ca–Mg–HCO_3$ and $Ca–Mg–Cl–SO_4$ types. Spatial distribution of all the parameters showed higher concentration of cations and anions along transboundary of the river. Principal component analysis, Heat map analysis and non-metric multidimensional scaling showed that water quality along the transboundary of the river are having different signature from the other zones of the river due to variations in chloride, sodium, total alkalinity and total hardness in water. Health risk assessment due to nitrate in water also showed that possibility of hazard was higher in the areas along transboundary of the river and children are more prone to health risks followed by women and men. Water quality along transboundary of the river followed by the area from the confluence of contaminated drain with river to transboundary along with localized spots in the river are not suitable for irrigation and drinking purposes. These results suggest that management of anthropogenic pressure, implementation of wastewater management and other strategies are required to improve the water quality of river.

Keywords Health risk · Hydrochemistry · Sutlej river · Water quality

Introduction

Rivers are the primary sources of water for domestic use, irrigation, industrial use and other purposes (Jiang et al. 2020). The quality of surface water is the result of interaction between abiotic (such as climate and temperature) and biotic factors (such as microorganisms) (Heinrichs et al. 2020). The biotic factors affect interrelationship among organisms and their relationship with surrounding environment (Matta et al. 2020a), whereas the abiotic factors affect ionic composition and the functions of water ecosystems (Harris and Vinobaba 2013). These abiotic factors regulate the hydrochemical characteristics of water which is the result of long-term interaction between the water body and the surrounding environment (Hamid et al. 2020). Besides climatic factors and weathering processes (Shrestha and Kazama 2007; Yegemova et al. 2018), anthropogenic aspects (such as urban growth and development, agronomic and industrial activities), chemical leak co-incidences and dam constructions affect the ion balance of river (Wang et al. 2013). The changes in water quality of the river have significant effect on its different trophic levels which determine the suitability of river water for drinking, irrigation and other purposes (Li et al. 2020).

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In general, water quality assessment of the river is based on analyzing the water samples for hydrochemistry (Zhang et al. 2018) which should be monitored on spatial scale at regular interval because water quality varies from one place to another (Sun et al. 2019). Generally, pH, electrical conductivity, cations (such as calcium, magnesium, sodium, and potassium) and anions (carbonate, bicarbonate, chloride, nitrate and sulfate) are used to study the hydrochemistry and river water quality (Matta et al. 2020b). To study the impact of all these hydrochemical parameters on the health of water body, water quality indices (WQIs) are used to find a single numeric quality rating scale (Ewaid et al. 2020; Sadiq et al. 2010; Wang et al. 2017) and these WQIs are based on different parameters, statistical techniques and weighting of parameters (Adimalla et al. 2018b; Jehan et al. 2020; Wagh et al. 2019a).

Many of natural occurring cations and anions (such as chloride, sodium, and potassium) are not of health concern for human, but these may affect the suitability of water for drinking purposes (Adimalla et al. 2018a; Jiang et al. 2020). The presence of excessive concentration of ions may result in quality induces water scarcity and associated health risks (Radu et al. 2020). According to Global Environment Monitoring System database, the concentration of nitrate–nitrogen (NO_3–N) of the most rivers in populated regions is seven times higher than it permissible limit of 10 mg L^{-1} as suggested by World Health Organization (He et al. 2011). The prolonged use of nitrate rich water may cause chronic poisoning linked to methemoglobinemia (Xue et al. 2016). However, the quality standards for surface water for drinking and irrigation purposes are different (Chigor et al. 2012). Electrical conductivity, sodium adsorption ratio and residual sodium carbonate are the main parameters used for assessing water quality for irrigation (Sappa et al. 2014). High sodium adsorption ratio cause high sodicity in soils which reduces infiltration rate and permeability of soils (Rengasamy and Olsson 1991). High residual sodium carbonate indicates that the bicarbonate and carbonate enrich water precipitate calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$), thereby increasing sodium concentration in soils (Prasad et al. 2001). Singh et al. (2014) found that anthropogenic activities beside ion exchange, dissolution activities are controlling the hydro-geochemistry of groundwater (Ca–Mg–HCO_3 type) in the parts of Sutlej river basin, but they did not study the hydrochemistry of surface water of the Sutlej river. In Punjab, Sutlej river is contaminated by domestic and industrial effluents, and agricultural runoff which are generally released into the river or neighboring areas (Jindal and Sharma 2011; Kaur et al. 2000; Khurana et al. 2014; Verma et al. 2013). Jindal and Sharma (2011) analyzed the water quality in different regions of Sutlej river in Punjab from November 2006 to October 2007, and stated that river was polluted by heavy metal contaminants.

Khurana et al. (2014) in another study on Sutlej river suggested that water of river in Ludhiana is contaminated due to discharge of effluents from industries. Most of these studies are limited to the stretches around contaminated drains which confluence with the river, but this is the first time in which hydrochemistry of surface water of the river has been studied from entry point of Sutlej river in Indian Punjab to its tail end when it leaves the country.

The Sutlej river is heterogeneous at different spatial scales as it is contaminated at selected points from various sources (Singh et al. 2014; Verma et al. 2013). Therefore, it is important to study the spatial variations in water quality of the river. Moreover, assessment of river water quality on spatial scale is important for framing the environmental protection policies. Multivariate statistical techniques (like principal component analysis and non-metric multidimensional scaling) are useful to find out the source apportionment in different rivers (El Najjar et al. 2019; Giri et al. 2019; Wagh et al. 2020) and the characteristics of hydrochemistry. There is no study in which spatial variations in hydrochemistry of Sutlej river and multivariate statistical techniques have been used to find the sources of contamination and number of latent factors affecting hydrochemistry of the river. Therefore, a study was carried out to assess the spatial variations in hydrochemistry of water of Sutlej river from its entry point in Indian Punjab to its tail end when it leaves the country. The specific objectives of the study were: (1) to investigate the spatial variations in major ion chemistry of water of Sutlej river flowing in Indian Punjab, (2) to evaluate the suitability of river water (for drinking and irrigation purposes) from water quality indices derived from physicochemical parameters of water, (3) to determine the factors controlling the surface water chemistry using multivariate statistical and geostatistical techniques, and (4) to assess the human health hazards associated with NO_3^- in water samples.

Materials and methods

Study area

The Sutlej river is one of the most important tributary of Indus river. It enters India nigh Shipki La Pass from where it navigates through several Himalayan valleys before it joins with Beas River in Punjab that in turn unites with Chenab in Pakistan before alighting into Indus. In Punjab, the river enters Nangal passes through Ropar, Ludhiana and merges with Beas at Harike and finally leaves the country and enters into Pakistan. The Sutlej river is polluted by industrial and domestic effluents and agricultural runoff which are generally released into the river or adjacent regions. The water samples were collected from the river and classified into

the four zones on the basis of variations in contamination of river water: Zone-I (Gobind Sagar), Zone-II (from Gobind Sagar to the confluence of Buddha Nullah and Sutlej river), Zone-III (from the confluence of Buddha Nullah and Sutlej river to the transboundary) and Zone-IV (Sutlej River along the transboundary).

The study area mainly lies in the sub-tropical belt with average annual rainfall of 580 mm. The major part (approximately 75%) of the rainfall occurs between July and September, and the rainfall is essential for growing Kharif crops (between May and October) and subsequent sowing of Rabi crops (November–April). The region experiences extreme type of climate as day temperature during summer season may exceed 45 °C whereas night time temperature during winter season may be as low as 0 °C.

Geologically, the river basin is comprised of three stratigraphic units from east to west: Siwaliks, piedmont and alluvial plain. The Siwalik hills are formed as a result of the latest phase of Himalayan orogeny. These composed of conglomerates and poor lithified, shales, soft and friable-sand stone. The age of these deposits vary from upper Miocene to lower Pleistocene. The piedmont plain is characterized by coarse textured, poorly sorted, gravel and pebbles and it is formed due to coalescence of alluvial fans and confined to narrow belt along the Siwalik foot hills. Barring the Siwaliks in the north eastern part, entire basin is covered with the Quaternary sediments deposited by the ancient river system forming a part of the vast Indus alluvial plain. The fluvial sediments are mostly represented by alternate beds of sand, silt and clay inter mixed with gravels and pebbles in varying proportion.

Water sampling and analysis for physiochemical parameters

Water samples ($n=97$) were collected from Sutlej river during May 2019 using stratified random sampling (Fig. 1). The samples were carried and stored in sterile polythene bottles in laboratory at (< 4 °C) temperature as per recommended protocols of American Public Health Association (APHA 1998). The water samples were analyzed for pH, electrical conductivity (EC), carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), chloride (Cl^-), total hardness, calcium (Ca^{+2}), sodium (Na^+) and potassium (K^+) using the standard procedure given in American Public Health Association (APHA 1998) within 24 h of sampling. The concentration of magnesium (Mg^{+2}) was calculated by subtracting Ca^{+2} from total hardness. Total alkalinity of water was calculated using the following formula equation:

$$\text{Total alkalinity as } CaCO_3 = 50.04 \times [(HCO_3^- \times 0.1639) + (CO_3^{2-} \times 0.03323)], \tag{1}$$

where all units are in mg L^{-1}.

The precision of all the physicochemical parameters was checked by analysis of duplicate samples. The accuracy of pH analysis of water samples was checked after every seven samples using standard buffer solutions of pH 7 and 9, whereas the accuracy of EC analysis was checked using standard EC solution of 1.414. These samples were also analyzed for nitrate and sulfate using UV–Visible spectrophotometer. As the water must be electrically neutral, the concentrations of cations and anions in the water should balance. The charge balance is expressed as follows:

$$\text{Electro - neutrality (E.N. in \%)} = \frac{\left(\sum \text{cations} - \sum \text{anions}\right)}{\left(\sum \text{cations} + \sum \text{anions}\right)} \times 100. \tag{2}$$

The concentration of cations in mg L^{-1} was converted to me L^{-1} and the E.N. of all the samples was within the acceptable limits of $\pm 5\%$ (Hounslow 1995). The spatial patterns in physicochemical parameters of water samples were studied using Inverse Distance weighted (IDW) method in ArcGIS 10.4.

Hydrochemical facies of surface water

The hydrochemical facies of surface water were demarcated using Piper diagram, and Durov plot. In Piper diagram, major cations and anions are plotted in a separate triangle. These plotted points in these diagrams are estimated further into the central diamond field, which gives the water characteristics. The triangular fields are plotted distinctly for cations, weak and strong acids, alkali earth metals and alkali. Durov plot is a composite plot consisting of two ternary diagrams where the milliequivalents percentages of the cations are plotted against that of anions. The intersection of lines extended from the points in ternary diagrams and projected on the sub-divisions of binary plot defines the hydrochemical processes involved along with the water type. In addition to this, Gibbs plot was used to find the source of chemical constituents in water related to the dominance of precipitation, rock, and evaporation (Gibbs 1970).

Assessment of surface water quality for irrigation

The suitability of surface water for irrigation purpose was evaluated based on the following indices:

Fig. 1 Sampling locations of water samples collected from Sutlej river in Indian Punjab during May 2019
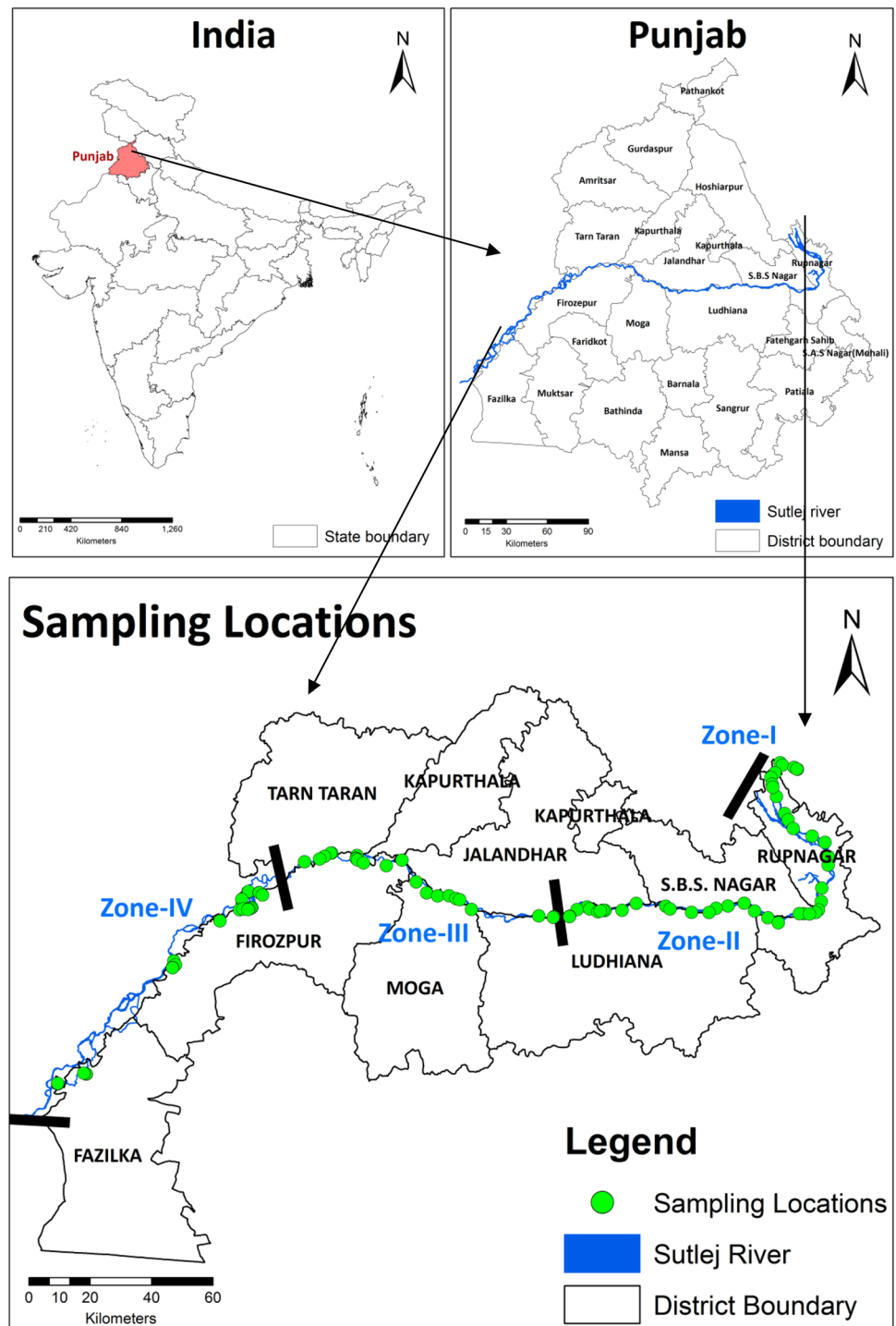
Sodium absorption ratio (SAR)

SAR determines the relative fraction of Na^+ ions to the Ca^{2+} and Mg^{2+} ions in the water samples. It signifies the Na hazard and calculated using the following equation:

$$SAR = \frac{Na^+}{\sqrt{\frac{Mg^{2+}+Ca^{2+}}{2}}}. \tag{3}$$

where, the concentration of these ions is expressed in $me\,L^{-1}$. On the basis of SAR values, Richards (1954)

categorized the water in four types: excellent (< 10), good (10–18), doubtful/fair poor (19–26), and unsuitable (> 26).

Sodium percentage (Na%)

Sodium percentage or soluble sodium percent is computed using the following equation (Wilcox 1955) in which the concentration of ions is expressed in meL^{-1}:

$$\% \, Na = \frac{Na^+ \times 2}{\left(Ca^{2+} + Mg^{2+} + Na^+ + K^+\right)}. \tag{4}$$

where, the concentration of these ions is expressed in meL^{-1}. If Na% < 60, water is classified as safe and trouble from excess Na will not occur on soil. If Na% > 60, water is classified as unsafe and the excess Na will affect soil physical fertility.

Residual sodium carbonate (RSC)

The amount of CO_3^{2-} and HCO_3^- in excess of alkaline earth metals (Ca^{2+} and Mg^{2+}) is represented by RSC which is calculated using the following equation in which the concentration of ions is expressed in meL^{-1}:

$$RSC = \left(CO_3^{2-} + HCO_3^-\right) - \left(Ca^{2+} + Mg^{2+}\right). \tag{5}$$

Residual sodium bicarbonate (RSBC)

Most of the water does not encompass CO_3^{-2} ions in substantial amount, and HCO_3^- ions do not precipitate Mg^{2+} ions, this alkalinity hazard is measured using RSBC suggested by Gupta and Gupta (1997). RSBC is calculated using the equation in which the concentration of ions is expressed in $me \, L^{-1}$:

$$RSBC = HCO_3^- - Ca^{2+}. \tag{6}$$

Assessment of surface water quality for drinking purposes and human health risk assessment

Water quality index (WQI)

The water quality index (WQI) is generally used to study the composite influence of all the ions into one parameter (Adimalla et al. 2018b; Sutadian et al. 2016). Water quality index (WQI) was calculated using the following steps:

(A) Calculation of relative weight (W_i) from the weights of different parameters given in Table S1 using the following equation:

$$W_i = \frac{w_i}{\sum_{n=1}^n w_i}. \tag{7}$$

(B) Calculation of quality rating scale (q_i) for each parameter: This was computed by dividing its concentration in each water sample by its acceptable limit (WHO 2011) followed by its multiplication by 100 using the following equation:

$$q_i = \frac{C_i}{S_i} \times 100. \tag{8}$$

(C) Calculation of WQI: Water quality sub-index (SI_i) for each chemical parameter was determined and SI_i was used to determine the WQI using the following equations:

$$SI_i = W_i \times q_i, \tag{9}$$

$$WQI = \sum_{i=1}^n SI_i, \tag{10}$$

where W_i is the relative weight of ith parameter, w_i is the weights of each water quality parameter, SI_i is the sub-index of ith parameter, q_i is the rating based on concentration of ith parameter, and n is the number of parameters.

In WQI, the higher weight is assigned to most importance parameters and the lesser weight to less important parameters. The standard permissible limit and unit weight of each parameter and index for drinking purposes is given in Table S1 (Supporting Information). The water was classified into five categories based on the WQI values: excellent water (< 50), good water (50–100), poor water (100–200), very poor water (200–300), and unsuitable for drinking (> 300).

Human health risk assessment

In the present study, health risk associated with NO_3^- was calculated using chronic daily intake (CDI) and hazard quotient (HQ) for children, men and women. The following equation was used to calculate CDI and HQ:

$$CDI = \frac{C \times WI \times EF \times ED}{BW \times T}, \tag{11}$$

$$HQ = \frac{CDI}{Rfd}, \tag{12}$$

where CDI is the chronic daily intake in mg/kg/day, C is the NO_3^- concentration in water (mg/L), WI is the average daily intake rate of water (L/day), EF is the exposure frequency (days/year), ED is the exposure duration (years), BW is the body weight (in kg), T is the average time (in days), and Rfd is the reference dose (mg/kg/day).

The values for calculation of CDI were taken from Rezaei et al (2019). USEPA (2013) recommends the Rfd value of 1.6 (mg/kg/day) for NO_3^-.

Statistical analyses

The descriptive statistics (such as minimum, maximum, mean, standard error, skewness, kurtosis and coefficient of variation) was calculated for all the parameters using PAST v.3.21. Box plots of different physiochemical parameters for different zones were made in Grapher v. 14.4 (LLC, Golden, Colorado). Pearson's correlation and heat map analysis was performed using R software v3.0 (Statistical Computing, Vienna, Austria). Principal component analysis was performed using SPSS v.16 software (IBM, USA). Non-metric multidimensional scaling was applied to different sampling sites using PAST v.3.21. Piper and Durov plots were prepared in RockWare.

Results and discussion

Descriptive statistics of physiochemical parameters of water quality

The descriptive statistics of different physiochemical parameters is given in Table 1. The pH of water samples ranged from 7.23 to 8.63 with average value of 7.79 indicating the alkaline nature of water in Sutlej river and these pH values were found within the acceptable limits for drinking water recommended by WHO (2011). Kumar et al. (2016) also found the pH range from 7.21 to 8.17 in the water samples of Beas river. Electrical conductivity (EC) varied from 0.21 to 4.0 dS m^{-1} with average value of 0.54 dS m^{-1}. According to WHO guidelines (2011), 9.3% samples surpassed their values for permissible limits. The average concentration of CO_3^{-2} and HCO_3^- were 29.6 mg L^{-1} and 31.3 mg L^{-1} and these values were below the desirable limit (300 mg L^{-1}) of WHO (2011) indicating no detrimental influence on human beings. The total alkalinity of water samples was lesser than the limit given by WHO (2011) and ranged from 25.0 to 165 mg L^{-1} with average value of 75.0 mg L^{-1}. The average concentration of Cl^- was 101 mg L^{-1} with range from 17.8 to 834 mg L^{-1} and 7.2% of the total samples exceeded the permissible limit defined by WHO (2011). The average concentration of Ca^{2+} in water samples was 37.2 mg L^{-1} with minimum and maximum values of 16.0 mg L^{-1} and 94.1 mg

L^{-1}, respectively. The concentration of Mg^{2+} in water ranged from 2.43 to 20.6 mg L^{-1} with mean value of 8.88 mg L^{-1} and all the sample were within the limits defined by WHO (2011). The average concentration of K^+ in surface water of the river was 4.8 mg L^{-1+} and only 9.2% of the samples exceeded the permissible limit of K in water for drinking purposes. The average concentration of Na^+ was 42.3 mg L^{-1} with the range from 4.9 to 513 mg L^{-1}. As per the guidelines of WHO (2011) for drinking water, only 9.3% samples surpassed their Na^+ concentration. It was found that 93.8% sampling sites exceeded the SO_4^{2-} concentration according to WHO (2011) guidelines and the average concentration was 6.81 mg L^{-1}. The concentration of NO_3^- ranged from 0.2 to 2.09 mg L^{-1} with an average value of 0.85 mg L^{-1} and all the samples were below the limits suggested by WHO. The total hardness of water samples varied from 50.0 to 285 mg L^{-1} with mean value of 130 mg L^{-1}, and 92.7% samples surpassed their values as per the WHO (2011) guidelines.

Distribution of cations and anions in different zones of Sutlej river

The concentration of cations and anions in the four zones of Sutlej river is given in Box plots (Fig. 2). Total alkalinity, total hardness, Na^+, K^+, NO_3^- and Cl^- was in the order: Zone-IV > Zone-III > Zone-II > Zone-I. EC, total hardness, Na^+ and SO_4^{2-} exceeded the desirable limits of WHO (2011) in the water samples collected from Zone-IV. In Zone-I, CO_3^{2-} and EC showed right handed skewness, whereas data were normally distributed for pH, HCO_3^-, alkalinity, Cl^-, total hardness, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-} and NO_3^-. The Kurtosis values for pH, EC, CO_3^{2-}, alkalinity, total hardness, Mg^{2+}, SO_4^{2-} and NO_3^- showed leptokurtic kurtosis. In Zone-II, pH and Na^+ showed right handed skewness, whereas other parameters having skewness values less than one indicating that data is normally distributed (Mendenhall et al. 2012). The kurtosis values of pH, total hardness, Ca^{2+}, Na^+ and SO_4^{2-} were found above one which signifies the leptokurtic kurtosis. In Zone-III, pH, EC, HCO_3^-, Na^+ and SO_4^{2-} showed kurtosis and skewness values greater than one which signifies leptokurtic and right handed skewness, respectively (Mendenhall et al. 2012). In Zone-IV, the skewness values of EC, CO_3^{2-}, alkalinity, Cl^-, Ca^{2+} and Na^+ showed right handed skewness, while the kurtosis values were greater than one (leptokurtic kurtosis) for CO_3^{2-}, Mg^{2+} and K^+, reflecting. Among all the parameters, EC, Cl^-, Na^+ and K^+ showed high coefficient of variation among the studied parameters, reflecting greater variations of these parameters in the Sutlej river.

The spatial distribution of all the parameters analyzed in water showed that pH and EC were higher in the water samples collected from Zone-IV (Fig S1 and S2, Supporting Information). There was high concentration of all other

Table 1 Descriptive statistical of physiochemical parameters of water samples collected from Sutlej river in Indian Punjab

Parameter	pH	EC (dS m⁻¹)	CO_3^{-2} (mg L⁻¹)	HCO_3^{-} (mg L⁻¹)	Total alkalinity (mg L⁻¹)	Cl^{-} (mg L⁻¹)	Total hardness (mg L⁻¹)	Ca^{2+} (mg L⁻¹)	Mg^{2+} (mg L⁻¹)	K^{+} (mg L⁻¹)	Na^{+} (mg L⁻¹)	SO_4^{-2} (mg L⁻¹)	NO_3^{-} (mg L⁻¹)
Minimum	7.23	0.21	0	0	25.0	17.8	50.0	16.0	2.43	2.00	4.90	0.30	0.20
Maximum	8.63	4.00	90	91.5	165	834	285	94.1	20.6	21.7	513	21.9	2.09
Mean	7.79	0.54	29.6	31.3	75.0	101	130	37.2	8.88	4.85	42.3	6.81	0.85
S.E.	0.03	0.09	1.58	1.88	2.55	19.2	4.18	1.51	0.35	0.47	11.4	0.32	0.05
Skewness	1.17	3.09	0.51	0.73	1.12	3.18	2.13	2.48	0.53	2.66	3.32	1.84	0.33
Kurtosis	1.72	8.0	2.31	0.12	2.69	8.70	4.57	5.97	0.98	5.83	9.78	8.07	-1.03
C.V.	3.20	160	52.5	59.0	33.4	187	31.8	40.0	38.8	94.7	264	46.6	53.6
Desirable limit	6.5–8.5	0.75	300	300	200	250	100	75	30	12	50	200	45
Permissible limit (WHO 2011)	9.2	1.50	–	–	–	600	500	200	150	–	200	600	–
% samples exceeding the permissible limit	–	8.3	–	–	–	7.2	–	–	–	–	9.3	–	–

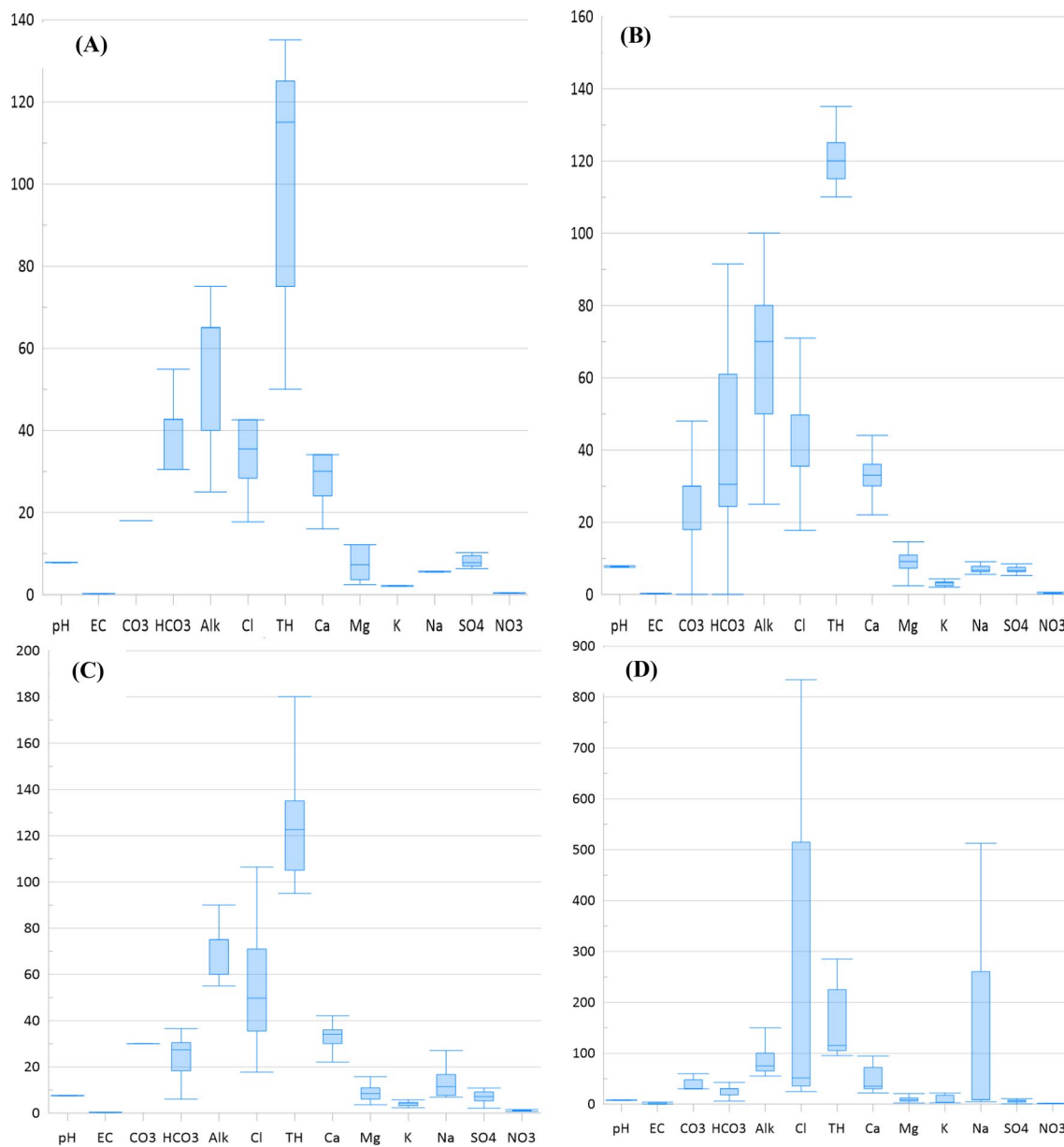The desirable and permissible limits are for drinking water only

Fig. 2 Boxplots of physiochemical parameters in water samples collected from different zones of Sutlej river: **A** Zone-I, **B** Zone-II, **C** Zone-III and **D** Zone-IV

parameters in water flowing along the Zone-IV and the parts of Zone-II (at the confluence of Sutlej river and Buddha Nullah) along with localized high concentration of these parameters in the other two zones (Fig S3-S12, Supporting Information). Spatially the higher concentration of Na, total alkalinity, total hardness, Cl^- and NO_3^- was prominent in the Zone-IV. The higher concentration of Cl^- in river water may be mainly attributed to industrial waste. Narsimha and Sudarshan (2017) also reported that higher concentration of Cl^- in river water is a signature of anthropogenic sources. Compared with Zone-I, the higher concentration of Na^+, K^+, NO_3^- and Cl^- in Zone-II was mainly due to industries (such as cement and

thermal) besides agricultural runoff. In Zone-III, heavy loads of pollutants are received in the river though Buddha Nulla drain which has many industries on its bank. The industrial and domestic effluents are discharged into the drain which results in increasing ion concentration in the river water. The Zone-IV is mainly transboundary of the river which is mainly separated by physical features, but transboundary aquifers are connected through a natural sub-surface path of groundwater. There are reports (Tabinda et al. 2013) that municipal and industrial wastewater drainage across transboundary to the river through wastewater drain also increased the concentration of ions in the Zone-IV of river.

Hydrogeochemical characterization of surface water

Piper (1944) plots are helpful in recognition of resemblances and dissimilarities in surface water as it divides the same qualities as groups (Todd 1980). In general, the sample points in the piper diagram are divided into six types: Ca–HCO$_3$, Na–Cl, Ca–Mg–Cl, Ca–Na–HCO$_3$, Ca–Cl and NaHCO$_3$. It was observed that water samples of all the four zones of Sutlej river are Ca–Mg–HCO$_3$ type which suggest the dominance of alkaline earths over alkali (Ca + Mg > Na + K) and weak acidic anions over strong acidic anions (HCO$_3$ > Cl + SO$_4$).In addition to this, water samples of all the four zones of Sutlej river samples are Ca–Mg–Cl–SO$_4$. Water samples of the Zone-II are Ca–Cl

Fig. 3 **A** Piper plot, and **B** Durov plot to describe the hydrochemical variations in the water samples of Sutlej river

type and of the Zone-IV near to transboundary are of Na–Cl type (Fig. 3A). The results of Durov plot indicated that most of the samples have no dominant anion or cation which indicates mixed water or exhibiting simple dissolution (Fig. 3B). In addition to this, water samples of Zone-II are recharging water (mainly Ca dominant frequently indicates recharging waters in limestone, sandstone, and many other aquifers) and of Zone-IV is also ion exchange water.

In Gibbs plot, the ratios for Na/(Na + Ca) and Cl-/(Cl + HCO$_3$) in the water samples are plotted against the relative values of TDS (Gibbs 1970). Gibbs plot showed that 8% of the samples were in the evaporation dominance and the remaining 92% of the samples were categorized in the rock dominance type (Fig. 4). The evaporation dominance is due to climate of the study region. However, most of the samples in rock dominance which indicates that rock forming minerals disintegrated by chemical weathering (water–rock interaction) are controlling the hydrochemistry of river water.

The ion exchange between water and its aquatic material during residence time can be estimated using chloro-alkaline indices (CAI) (Schoeller 1967) and the CAI values may be positive or negative. When there is an exchange between Ca and Mg in the water with Na and K, CAI values are negative, and if there is a reverse ion exchange, the CAI values will be positive which means ion exchange between Na and K with Ca and Mg (Schoeller 1967). The CAI-I of the river water samples varied from 0.01 to 0.85 and CAI-II from 0.05 to 2.73. The positive values of CAI-I and II in all the samples of river water indicate that sodium and potassium from river water are exchanged with magnesium and calcium in the host rocks during their period of residence and movement. This was also supported by Na/Cl ratio which was less than one in all the samples, however, it varied between 0.13 and 0.97 in the water samples. The higher Na/Cl ratio indicates the possible source of Na is silicate weathering and the Na/Cl ratio less than one suggests the possibility of ion exchanges of Na with for Ca and Mg in clay particles (Tiwari and Singh 2014; Wagh et al. 2019b).

Pearson's correlation analysis

The Pearson's correlation coefficients showed that pH is positively correlated with all the parameters except SO$_4^{2-}$. Among all the parameters, EC is significantly ($p < 0.05$) positively related with Cl$^-$, NO$_3^-$, total hardness, Ca^{2+}, K$^+$ and Na$^+$ (Fig. 5). A significant positive correlation between Ca and NO$_3^-$ suggest the origin of these ions in water is mainly from fertilizers. A significant positive correlation between Cl$^-$ and NO$_3^-$ indicate that surface water might be contributed from fertilizers which contribute Cl$^-$ followed by ion exchange of Cl$^-$ with NO$_3^-$ (Adimalla et al. 2018a). A significant positive correlation of Na$^+$ and Cl$^-$ is due to the fact
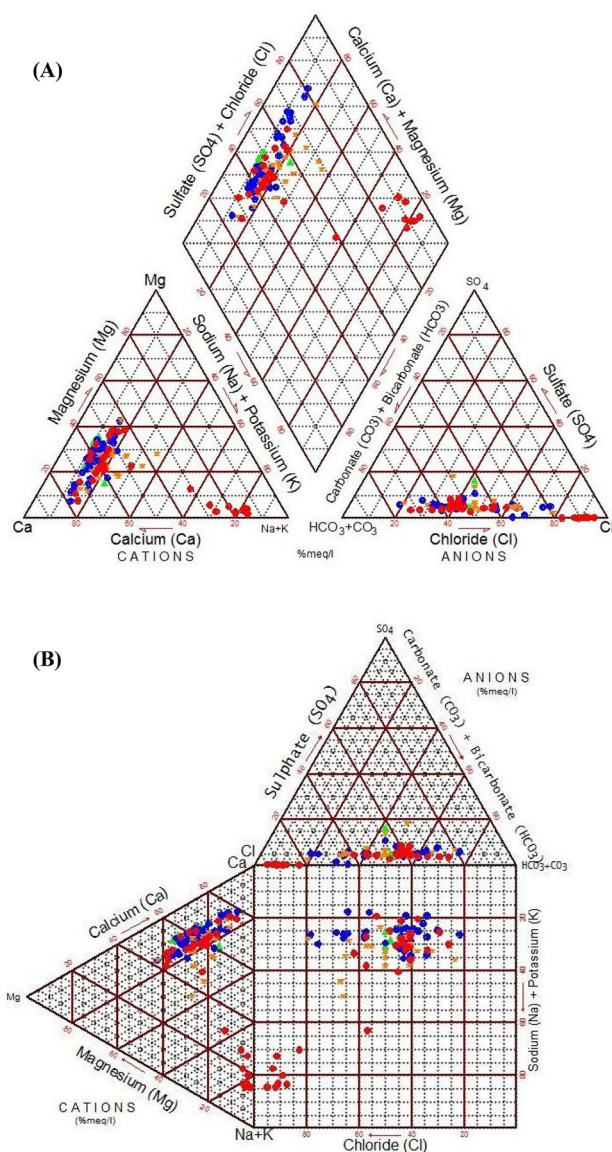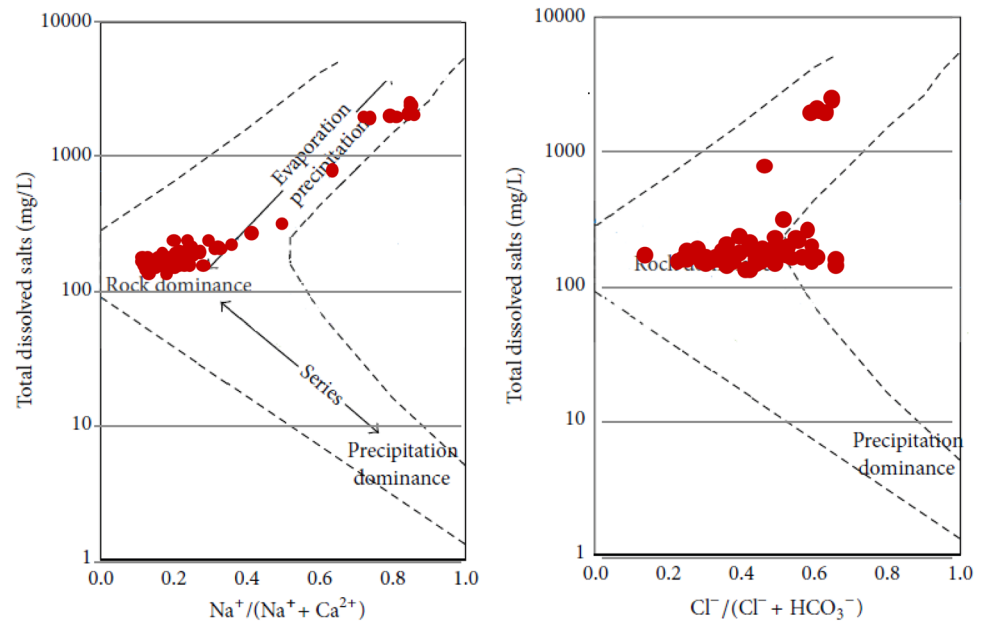
Fig. 4 Gibbs diagram

that NaCl salt is most abundant in water and imitative from the existence of halite minerals (Tiwari and Singh 2014). It was found that Ca^{2+} in water was significantly positively correlated with Cl^- and Na^+ (Fig. 5). There was a significant negative correlation among SO_4^{2-} and Ca^{2+}, K^+ and Na^+. Haque et al. (2019) also reported correlation of EC with NO_3^-, alkalinity and total hardness in the water samples of Padma River, Bangladesh. Nayak and Mohanty (2018) also reported the positive correlation of Ca^{2+}, Cl^- and Na^+ in the water samples collected from Brahmani River, India.

Multivariate statistical analysis of physiochemical parameters

Heatmap analysis was applied to physiochemical parameters in all the four zones (Fig. 6A). These results showed that Zone-II and Zone-III showed close proximities with each other which may be due to little variations in EC, NO_3^-, K^+, SO_4^{2-}, pH, Mg^{2+}, CO_3^{2-}, Ca^{2+}, alkalinity and total hardness (Fig. 6A). The Zone-I was associated with Zones-II and III. The Zone-IV formed separate group which may be due to Cl^-, total hardness, Na^+, alkalinity, HCO_3^- and Ca^{2+} showed higher variations in concentration of these parameters compared with the other zones (Fig. 6A). Among physiochemical parameters, Cl^- and total hardness, and Na^+ and alkalinity are included in the same group, HCO_3^+, CO_3^{2-} and Mg^{2+} formed same group, whereas EC, NO_3^-, K^+, SO_4^-, pH, and Mg^{2+} formed another similar group.

Principal component analysis (PCA) showed that first two components explained 96.2% of the total variance having Eigen values above one (Fig. 6B). The loadings of component matrix and after varimax rotation for different physiochemical parameters are given in Table 2. The loadings of component matrix for physiochemical parameters revealed that PC1 is dominated by pH, EC, CO_3^{2-}, HCO_3^-.Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+ and SO_4^{2-} with variance of 84.5%. PC2 has moderate loadings of EC, Cl^-, Na^+ and NO_3^- with 11.7% of the total variation (Table 2). To make sure that all the parameters and factors do not correlate with each other, varimax rotation was used and it produces orthogonal (uncorrelated) factor rotation. After varimax rotation, PC1 is influenced by pH, CO_3^{2-}, HCO_3^- and SO_4^{2-} with variance of 50.1% and it is mainly related to lithogenic factors which explain the dissolution of minerals from rock weathering. The PC2 accounted 46.1% of the total variation and dominated by EC, NO_3^-, Cl^-, Ca^{2+}, K^+ and Na^+ with higher loadings for NO_3^- and Cl^-. The higher loadings for NO_3^- and Cl^- may be mainly attributed to anthropogenic activities such as domestic and industrial waste besides runoff from agricultural fields. Jaiswal et al. (2019) also reported the loadings of EC, alkalinity, hardness, SO_4^{2-} and Cl^- on PC1 in the water samples of Yamuna river, India. They suggested that river water is affected by constituents of salts and minerals. Salt ions in water can arise due to atmospheric deposition, weathering of soils, rocks and minerals, and agronomic practices (Gholizadeh et al. 2016). Maji and Chaudhary (2019) reported that NO_3^- is influenced by PC1 in the water samples of Ganga river (India). Kumar and Thomas (2019) in another study on river Noyyal reported also dominance of alkalinity, Cl^- and NO_3^- on PC1, and pH on PC2.

Non-metric multidimensional scaling (NMDS) is an indirect gradient analysis method to produce an ordination based upon distance or dissimilarity matrix (Alamdar et al. 2019).
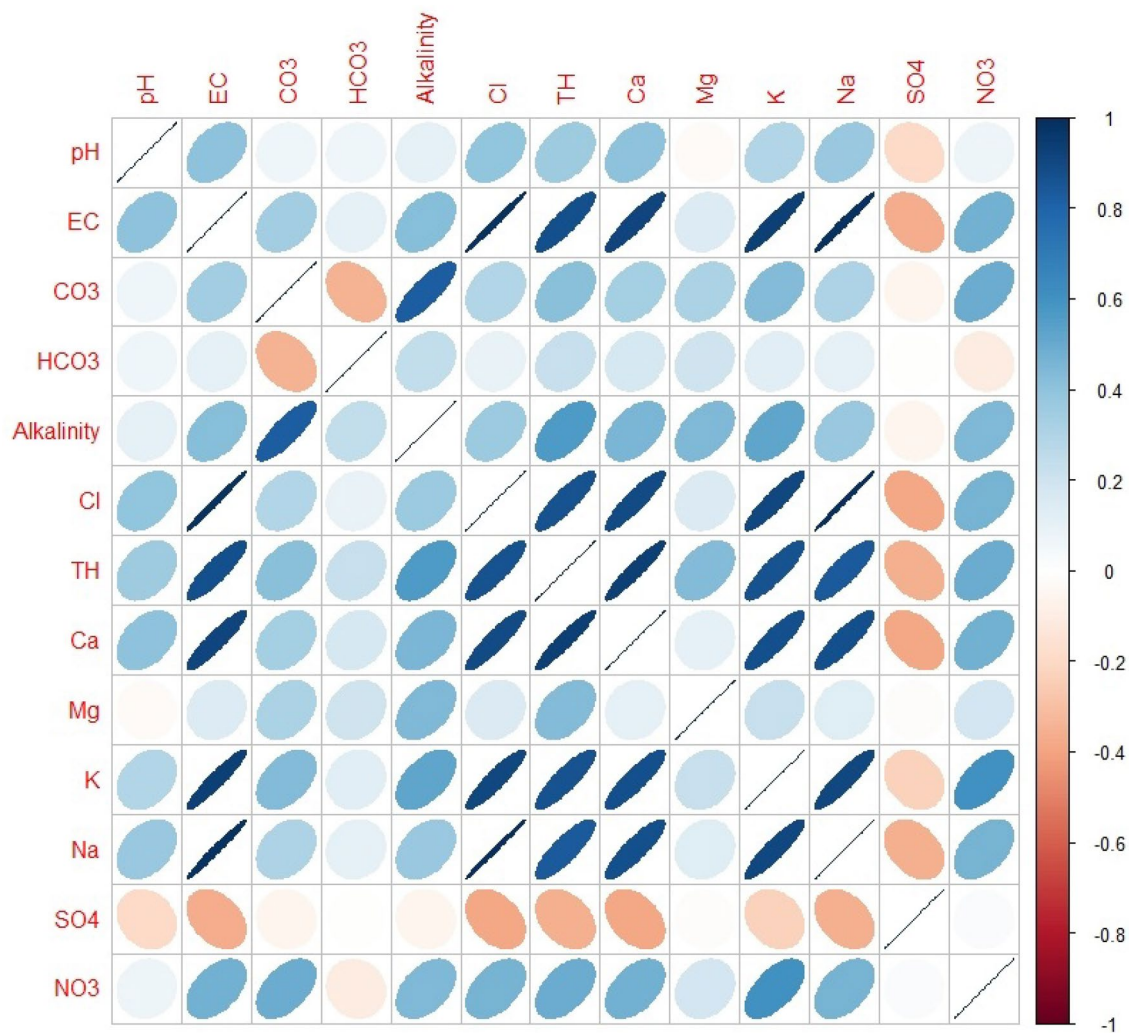
Fig. 5 Pearson's correlation analysis among physiochemical parameters in water samples of Sutlej river

Non-metric multidimensional scaling (NMDS) was applied on the sampling locations with all the physicochemical parameters and these results showed that 89.7% of the total samples were in the main group which indicates that these samples are of similar origin, whereas nine samples (87–94 and 97) of the Zone-IV are excluded from the main group (Fig. 6C). These nine location specific sample was taken from the point where there was a confluence of highly contaminated local drain with the river. The stress level 0.0351 ($p < 0.05$) was obtained in the present study indicating good fit of data to the NMDS model (Kaur et al. 2018).

Suitability of water for irrigational and agricultural purposes

Sawyer et al. (2003) classified the water into three categories for irrigation purposes on the basis of total hardness values and the results showed that 2.1% of the total samples were

in the category of less than 75 mg L^{-1} (safe for irrigational purposes), 83.5% samples were between 75 and 150 mg L^{-1} (moderate hard water), and 14.4% samples were between 150 and 300 mg L^{-1} (hard water). To determine the suitability of water for irrigation, three indices were computed: SAR, RSC and RSBC (Table 3). Based upon Richard's classification (Richards 1954), the values of SAR for all the zones belong to excellent category of water (Fig. 7A). In Zone-I, the SAR values showed ranged from 0.21 to 0.34 with mean value of 0.26. In Zone-II, the average SAR value was 0.29 with range from 0.22 to 0.53. In Zone-III, the SAR values ranged from 0.31 to 1.26 with mean value of 0.52, whereas in Zone-IV, the average SAR was 3.43 with range 0.20–10.9. Based on the classification of Richards (1954), the residual sodium carbonate (RSC) values were less than 1.25 which signifies the good category water of Sutlej river. According to classification given by Eaton (1950) to categorize the water on the basis of %Na values, it was found
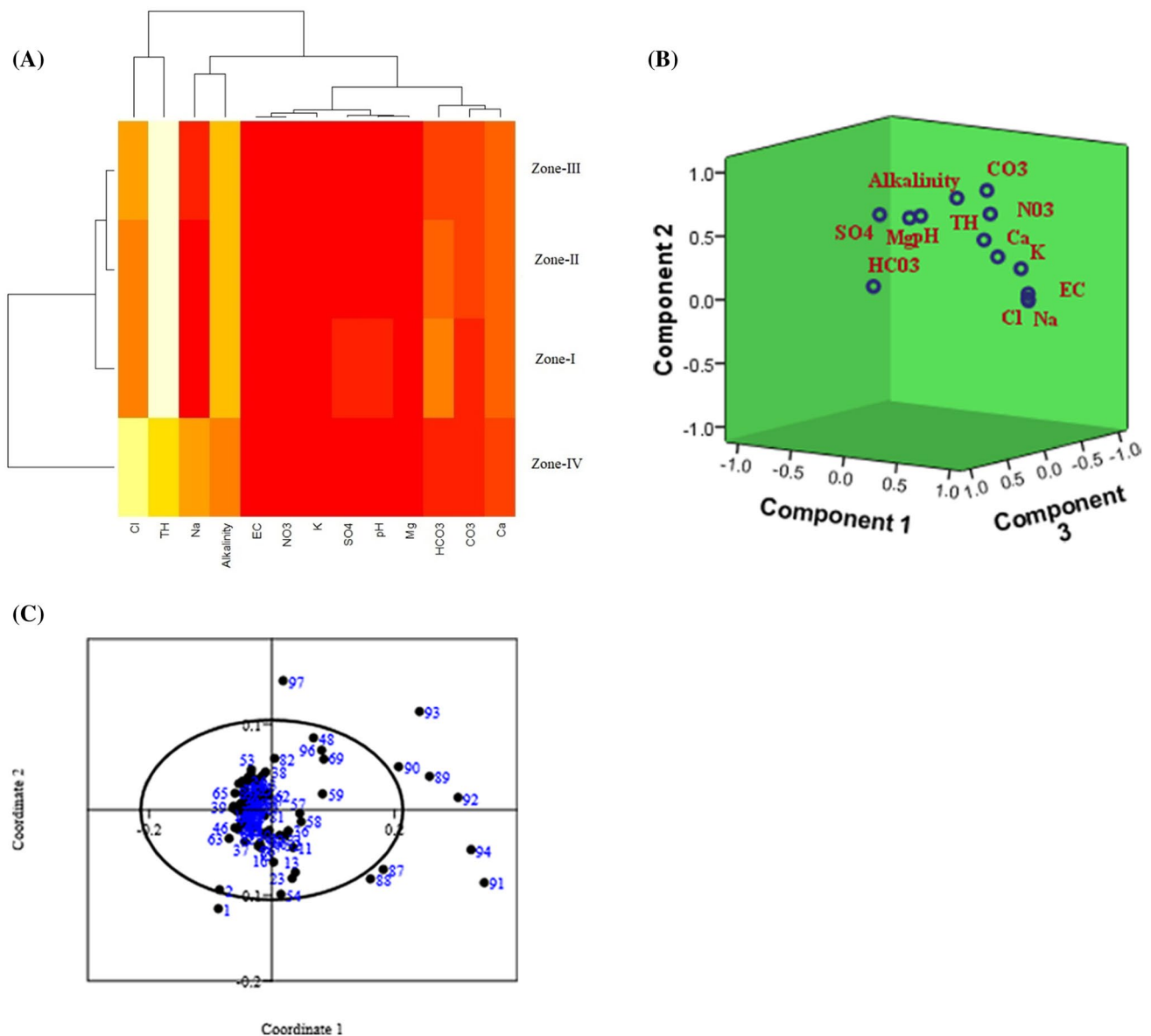
(A)

(B)

(C)

Fig. 6 **A** Heatmap analysis, **B** loading plot of principal component analysis and **C** non-metric multidimensional scaling scatter plot (95% eclipse) of physiochemical parameters in water samples of Sutlej river

that 8.24% samples in Zone-IV have values greater than 60 which signifies that water is unsafe for irrigation purposes, whereas all the samples in Zones-I, II and III have values less than 60 which shows that water is safe for irrigation purposes. The RSBC values were less than 5 meq L^{-1} in all the samples thereby indicating that that water is safe for irrigation purposes.

Assessment of water quality for drinking purposes

The results of WQI indicated that 86.5% of the total samples were of good quality, 4.1% of poor quality water, and 9.2% of the water samples are unsuitable for drinking. In Zone-I, the WQI varied from 32.9 to 36.3 with mean value of 34.3 (good category of water). In Zone-II, WQI ranged from 26.5 to 60.5 with mean value of 35.5, signifying good to poor quality of water in this zone (Table 3). The WQI in Zone-III ranged from 27.7 to 57.2 with average value of 37.0 and also water samples in this zone are good to poor quality of water (Fig. 7B). The average WQI in Zone-IV was 65.4 with range from 32.3 to 127 signifying that water is unsuitable for drinking. Kumar et al. (2017) reported that water of Beas river in Indian Punjab was of medium quality.

Table 2 Variance and loadings of principal components for physiochemical parameters in Sutlej river

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	9.29	84.52	84.52	9.29	84.52	84.52	5.52	50.18	50.18
2	1.29	11.75	96.28	1.29	11.75	96.28	5.07	46.10	96.28

Variables	Component matrix			Rotated component matrix	
	PC1	PC2		PC1	PC2
pH	0.975	− 0.170		0.826	0.546
EC	0.890	0.448		0.339	0.937
CO_3^{-2}	0.917	− 0.221		0.818	0.470
HCO_3^-	0.894	− 0.396		0.921	0.327
Cl^-	0.899	0.429		0.358	0.929
Ca^{2+}	0.982	0.170		0.597	0.798
Mg^{2+}	0.922	− 0.361		0.918	0.371
K^+	0.943	0.268		0.501	0.842
Na^+	0.881	0.461		0.323	0.941
SO_4^{-2}	0.940	− 0.182		0.808	0.513
NO_3^-	0.863	− 0.444		0.932	0.270

Table 3 Descriptive statistics of sodium adsorption ratio, sodium percent, residual sodium carbonate (RSC), residual sodium bicarbonate (RSBC), and Water Quality Index (WQI) in different zones of Sutlej river

Parameter	SAR	Na (%)	RSC (me L^{-1})	RSBC (me L^{-1})	WQI
Zone-I					
Minimum	0.21	10.4	− 1.21	− 0.39	32.9
Maximum	0.34	21.0	− 0.50	0.50	36.3
Mean	0.26	14.0	− 0.93	0.13	34.1
S.E.	0.03	2.03	0.14	0.15	0.68
Zone-II					
Minimum	0.22	11.0	− 1.80	− 1.58	26.5
Maximum	0.53	22.4	− 0.41	1.50	60.5
Mean	0.29	13.9	− 1.01	− 0.22	35.5
S.E.	0.01	0.42	0.06	0.12	1.04
Zone-III					
Minimum	0.31	14.5	− 1.61	− 1.78	27.7
Maximum	1.26	38.4	− 0.41	0.50	57.2
Mean	0.52	20.9	− 1.01	− 0.56	37.0
S.E.	0.05	1.28	0.08	0.09	1.91
Zone-IV					
Minimum	0.20	10.5	− 4.01	− 2.67	32.3
Maximum	10.9	82.8	− 0.12	0.01	127
Mean	3.43	33.7	− 1.35	− 0.81	65.4
S.E.	0.95	5.10	0.20	0.10	6.92

Health risk assessment of nitrate in surface water

The chronic daily intake (CDI) (mg/kg/day) and hazard quotient (HQ) for NO_3^- in surface water of Sutlej river are given in Table 4. The value of HQ varied from 0.0033 to 0.0336 for men, 0.0040–0.0404 for women and 0.0089–0.0904 for children and this implies that children are more prone to NO_3^- exposure followed by women and men for all the four zones. This is mainly due to lesser body weight of children and women than men. The trend HQ was in the order: Zone-IV > Zone-III > Zone-II > Zone-I. Spatially the concentration of NO_3^- was higher in Zone-IV followed by Zone-III (Fig. 7C). Though NO_3^- concentration was lesser than the acceptable limit in all the four zones, but the inhabitants living around the Zone-IV are may have health risks such as methemoglobinemia or "blue baby syndrome" (Pastén-Zapata et al. 2014) in near future due to movement of nitrate from nearby agricultural fields to river water followed by groundwater.

Conclusions

The results of this study showed that many sectors are contributing to Satluj's water quality challenges and the water quality data provides the evidence of sewage, agricultural, municipal and industrial sources of contamination. The water quality of Sutlej river typically deteriorates as the river flows downstream. The water samples of the river are mainly Ca–Mg–HCO_3 and Ca–Mg–Cl–SO_4 types. The water along transboundary may not potentially be used for drinking and irrigation purposes and the health risk associated with NO_3^- was higher in the areas along transboundary. Multivariate analyses showed that Zone-II

Fig. 7 Spatial distribution of **A** sodium adsorption ratio, **B** water quality index, and **C** nitrate concentration in water samples collected from Sutlej river in Indian Punjab
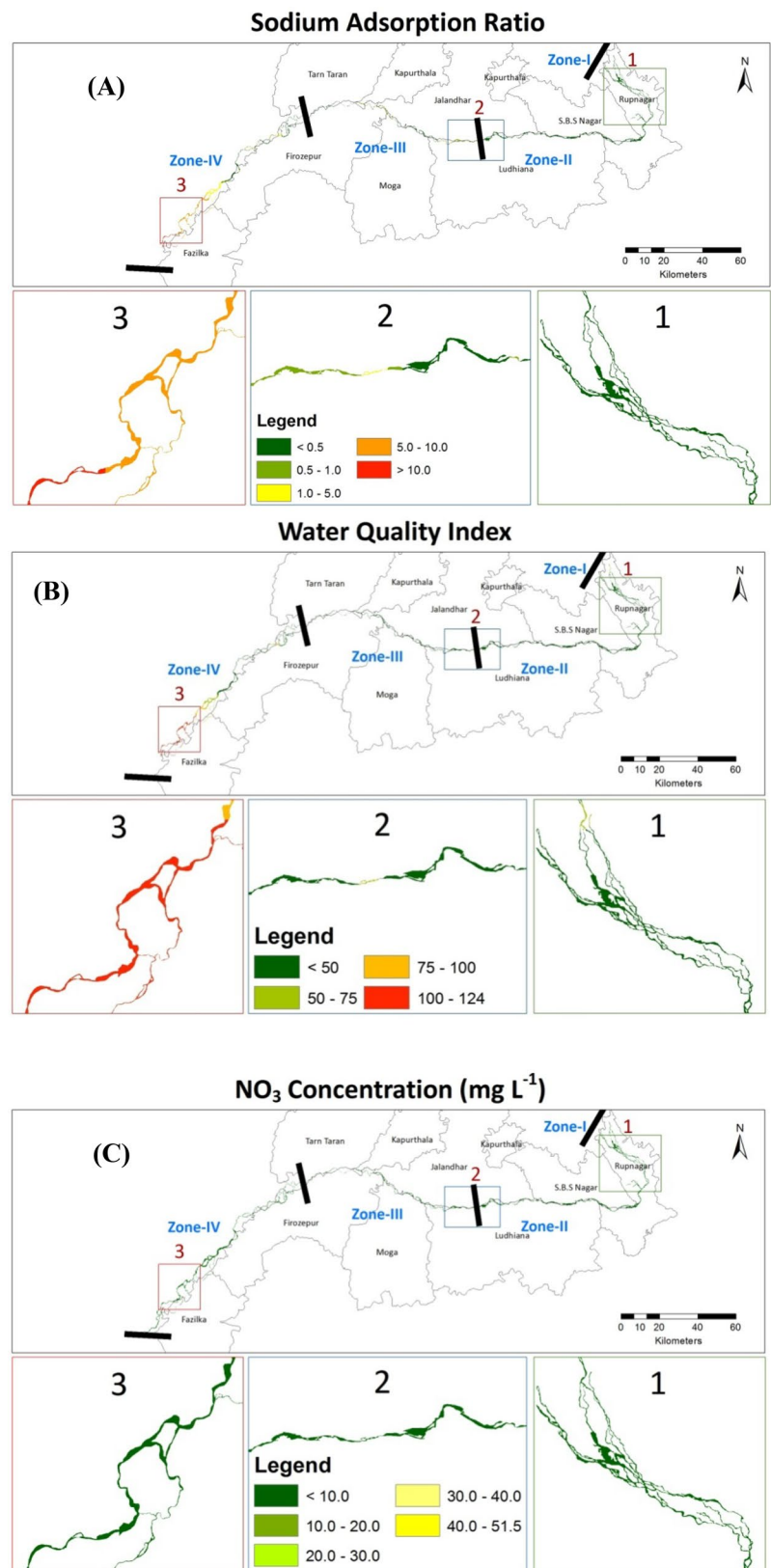
Table 4 Chronic daily intake and hazard quotient of nitrate in surface water of Sutlej river

Parameter	Chronic daily intake (CDI)			Hazard quotient (HQ)		
	Men	Women	Children	Men	Women	Children
Zone-I						
Minimum	0.0096	0.0116	0.0259	0.0060	0.0072	0.0162
Maximum	0.0117	0.0141	0.0315	0.0073	0.0088	0.0197
Mean	0.0108	0.0129	0.0290	0.0067	0.0081	0.0181
S.E.	0.0004	0.0005	0.0011	0.0003	0.0003	0.0007
Zone-II						
Minimum	0.0053	0.0064	0.0143	0.0033	0.0040	0.0089
Maximum	0.0229	0.0274	0.0615	0.0143	0.0171	0.0384
Mean	0.0113	0.0136	0.0304	0.0071	0.0085	0.0190
S.E.	0.0007	0.0009	0.0019	0.0005	0.0005	0.0012
Zone-III						
Minimum	0.0188	0.0226	0.0506	0.0118	0.0141	0.0316
Maximum	0.0409	0.0491	0.1100	0.0256	0.0307	0.0688
Mean	0.0286	0.0343	0.0768	0.0179	0.0214	0.0480
S.E.	0.0014	0.0016	0.0037	0.0009	0.0010	0.0023
Zone-IV						
Minimum	0.0175	0.0210	0.0470	0.0109	0.0131	0.0294
Maximum	0.0538	0.0646	0.1447	0.0336	0.0404	0.0904
Mean	0.0327	0.0393	0.0880	0.0205	0.0246	0.0550
S.E.	0.0015	0.0018	0.0040	0.0009	0.0011	0.0025

and Zone-III showed close proximities with each other but the Zone-IV was significantly different from the other three zones which may be due to larger variations in Cl^-, total hardness, Na^+, alkalinity, HCO_3^- and Ca^{2+} in water samples of Zone-IV and the remaining three Zones. The information on hydrochemistry of water samples would help to understand the water quality of Satluj river and take strategic management measures required to improve the water quality. The approaches for water quality management in the river are given below:

- Waste water treatment policy should be strictly implemented to check the flow of contaminants in the Sutlej river. This will help in restoring the ecological stability and economic viability of the river.
- Non-government and governments organizations must launch the mass awareness programme to stop the activities that contribute to contamination of surface water and restoring the health of the river.
- In India, the research on assessment of water quality using machine-learning techniques should be promoted. The integration of water chemistry, machine-learning techniques and GIS may help in developing algorithms to predict water quality and these results may be used by government for developing the water conservation projects.

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