Environment and Ecology 39 (1) : 109—128, January—March 2021 ISSN 0970-0420

Major Ion Chemistry and Water Quality Index for Surface Water Quality Characterization in Parts of Kinnaur District, Himachal Pradesh, India

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Received 13 July 2020, Accepted 7 December 2020, Published on 8 January 2021

ABSTRACT

Himalayan rivers are the main resource of water for the communities living in mountains and plains of India. Over the years, due to different developmental and other anthropogenic activities like unscientific dumping of effluents, unplanned sewerage and drainage pattern the surface water quality has been persistently deteriorating. The present study makes an effort to evaluate the suitability of surface water in parts of district Kinnaur, Himachal Pradesh for domestic and agricultural purposes. In the years 2015 and 2016 during pre and post-monsoon seasons 30 surface water samples from different locations were collected and analyzed for different water quality parameters. The immediate parameters like pH, EC and TDS were analyzed on the spot using portable soil and water analysis kit. The concentrations of major cation and anion like, $Ca^{2+} Mg^{2+}$, Na⁺, K⁺, HCO₃-,

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Cl-, F- and SO_4 ²⁻ of collected water samples were analyzed to check the level of contamination in the study area. Systematic outcomes don't demonstrate any deterioration in the surface water quality; all the parameters were under desrable limits recommended by earlier workers for domestic purposes. However, turbidity (55% and 56% samples) and fluoride (14% and 13% samples) contents were above the prescribed limit, which gives us cautions. According to the Piper trilinear diagram all water sample belongs to the $Ca^{2+} - Mg^{2+} - HCO_3$ - water type with temporary hardness. The plot of $(Ca^{2+} + Mg^{2+})$ versus Na+ was used to understand the ion exchange in the surface water. The plot confirms that reverse ion exchange is the controlling factors as the entire water sample are fall above the equiline. The value $\text{Na}^+\text{/Cl}$ - molar ratio ranged from 0.51 to 2.02. 46.67% samples have $\mathrm{Na^+}$ / Cl- value greater than 1, indicating that dissolution of silicate is the main process releasing $Na⁺$ ion in the river water and the role of evaporation is insignificant. According to the Sodium Adsorption Ratio (SAR), US Salinity hazard plot, Magnesium Content (MH), Sodium percent (% Na), Residual Sodium Carbonate (RSC), Doneen's Permeability Index plot and Kelly's Ratio, all the water samples were found to be suitable for irrigation purposes for most of the crops and soil. The results of WQI and IWQI conclude that surface water is fit for domestic and irrigation purposes.

Keywords: Surface water, Piper trillinear, Water quality index, Salinity hazard, Permeability index.

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INTRODUCTION

Development in different sectors such as agriculture, industry and urbanization and population cover have increased the overall water demand (Herojeet *et al.* 2017). In several countries, people rely mainly upon municipal household water supply to meet the water demands (Brindha and Kavitha 2015). Rivers and its tributaries are the major freshwater resource domestic, irrigation and other recreation purposes in Himalayan regions (Jarvie *et al.* 1998, Razmkhah *et al.* 2010, Varol *et al.* 2011). Though, rivers and streams in several developing nations are highly polluted because of different man-made activities (Jonnalagadda and Mgere 2001). Developing country like India encounters water contamination issues because of changing lifestyles, financial improvement, urban sprawl, landuse pattern and industrialization (Liao *et al.* 2007, Mahavi *et al.* 2005, Nouri *et al.* 2008, Herojeet *et al*. 2017). The securing water quality and quantity to fulfill the demands of the people and ecology is one of the difficult problems in the $21st$ century as sustainable social and economic growth are mainly reliant on water resources (Amangabara and Ejenma 2012). The water quality is amongst the main sensitive issues around the world which is impacted by numerous regular and man made activities that includes origin of water, the level of its evaporation, kind of rock and mineral it has came across, topographical processes in the aquifer system, rate and direction of water flow and the residence time (Herojeet *et al.* 2016, Freeze and Cherry 1979, Sati and Paliwal 2008, Desai and Tank 2010, Shrivastava *et al.* 2013). It is also influenced by other outer contaminating agencies like, agricultural, industrial and household effluents (Srinivasamoorthy *et al.* 2012). Over the years, looking for better living conditions man has over exploited the water resource through different developmental and other anthropogenic activities to a large degree. Today, water resources have become the backbone for the present day society (Lata *et al.* 2014, Herojeet *et al.* 2017, Singh *et al.* 2004).

 Rivers and streams play the main role in absorption or carrying off the domestic and industrial effluents and run-off from the farm lands (Singh *et al.* 2004). Lately, in many countries, the assessment of water quality has become a serious concern (Varol *et al.*

2011, Bengraine and Marthaba 2003, Koklu *et al.* 2010). Usually, the quality evaluation of water is done by comparing calculated physico-chemical parameters with the suggested permissible and desirable limits prescribed by national or international organizations (Bhuiyan *et al.* 2011). A monitoring plan is required to supply a representative and reliable assessment of the surface water quality as a result of spatial and temporal differences in water chemistry (Anny *et al.* 2017).

 Sorang Khad is one of the main tributary of Satluj river originated at an altitude of 5625 meters of Kokshane mountain in the Himalayas. The stream current is powerful due to steep slope with series of rapids falls and flowing on the right side of river Satluj opposite the Nigulsari village of Kinnaur district. Thus, the Sorang Hydroelectric Power Project (HEP) is constructed on Sorang Khad to harness the electricity for societal development. Dam construction is an infrastructural development projects that have numerous long term impacts on the environment and social life. The large areas of land namely, forests, towns and villages are submerged due to accumulation of water by dam reservoirs. It results in the resettlement of local people leaving no option to change their lifestyles connected to livelihood issues. Further, the impact of such project have always associated with loss of terrestrial and aquatic biodiversity and changing hydrology of the lotic ecosystem (Lata *et al.* 2017). The study area lacks proper municipal pipeline water system where local people entirely depend on perennial streams and springs. It is noted during field study and interaction with local people that drying up of many springs in lower reaches of foothills due to construction of dam through cutting and blasting of project site. It clearly indicates that the water movement in subsurface strata is affected by changing the geomorphology of mountain. However, the adverse effects of hydroelectric projects have been overlooked by certain advantages in terms of electricity, employment, economy and water for irrigations, industries and domestic consumptions (Lata *et al.* 2017). The vital aim of HEPs are to assure better life for the people but difficult to anticipate in reality. So, developing country like India is facing extreme difficulty to support sustainable development with weak policies, less awareness, poor knowledge and limited financial resources.

 The study area is located at the high altitude rocky hilly terrain of Himachal Pradesh where surface water becomes the vital source for overall domestic and agricultural purposes. At this point of time, the impact of such development project during construction on the inland water quality need to be addressed. Also, till date there are very limited and sound water quality data published from the study area. The objective of the paper is to characterize the suitability of surface water for different utilities and extract probable hidden factor controlling the hydrochemistry using various water quality indices, hydrochemical facies and enviromentric modeling. The finding of the present study will be baseline asset for water quality in such fragile ecosystem area of Himachal Pradesh. machal Pradesh. It is situated on the Indo-Tibetan border and is surrounded by the Tibet on east, Garhwal Himalaya on South, Spiti Valley on North and Kullu on West. It lies between North latitude 31°35'40" to 31°34'42" and East longitude 77°52'38" to 78°51'28". Total population of Kinnaur is 84,121 of which male and female were 46,249 and 37,872 respectively.

Genaral description about the sorang hydroelectric power project (SHEP)

Sorang Hydroelectric Power Project (SHEP) is located on Sorang Khad a tributary of river Satluj near the village Nigulsari, which is about 170 kilometers from Shimla, the State Capital of Himachal Pradesh. Sorang Khad is on right bank of river Satluj, opposite village Nigulsari that falls along NH-22 and it originates at an altitude of 5625 meters in the high reaches of Kokshane Mountain in the Himalayas (Fig.1).

Study area

Kinnaur is very scenic but, less known district of Hi-

Fig.1. . Location of the study area, district Kinnaur

 SHEP is congenial by means of the Kucha Chaura-Bara Khamba interface street, which has been built upto Chhota Khamba town and is under development upto the admission site close Sorang village (Lata *et al.* 2013). Around 3 kilometers downstream of this point (in a south heading) the Sorang Khad joins the Satluj river on its north eastern bank near Nigulsari village. The powerhouse is on the correct bank, only upstream of conjunction of Tikada Khad with Satluj stream, close Nyole town in Kinnaur area. The water goes into the Satluj stream through tail race burrow downstream from the powerhouse site.

SHEP is accessible via the Kucha Chaura-Bara Khamba connecting road, which has been built upto the intake site near Sorang village (Lata *et al.* 2013). The powerhouse is on the right bank, just upstream of confluence of Tikada Khad with Satluj river, near Nyole village in Kinnaur district. The water enters into the Satluj river through tail race tunnel downstream from the powerhouse site.

Geological settings of the study area

Himalaya is one of the most fragile and youngest

orogenic beds in the world which lies in the suture of the Indian and Chinese tectonic plates. In the regional overview, Kinnaur district occupies a position as harbinger between the Kumaon and Punjab Himalaya with Satluj river forming the divide . Most of the area studied is composed of low and high grade metasediments presumably belonging to middle Haimanta group of rock formation of Precambrian age. The major rock types found are metapsummites, calcareous rocks and metapelites (Bassi and Chopra 1983, Bhargava and Bassi 1998, Sharma 1976, Srikantia and Bhargava 1998, Tiwari *et al.* 1978). The geological succession of the district is given in Table 1.

Rocks found in the study area are mainly granite, slates, schists, gneisses, phyllite, quartzite and limestone. Study area is rich in minerals like copper, pyrite, mica and silver (Srikantia and Bhargava 1998).

MATERIALS AND METHODS

The surface water samples (30) were collected from the different locations from Sorang Khad and its main tributaries and drinking water supply sources in the adjoining villages during pre-monsoon (May) and

Table 1. Geological succession in Kinnaur. (Source: after CGWB 2013)

Fig. 2. Water sampling locations in the study area.

post-monsoon (October) seasons for two years 2015 and 2016 shown in (Fig.2). The samples were stored in clean HDP bottles with screw caps. The plastic bottles were rinsed twice with the surface water samples to ensure the compositional originality of collected water samples. The immediate parameters like Temperature, pH, EC and TDS were analyzed on the spot using potable water and soil analysis kit. Chemical analysis of major cations (Na⁺, K⁺, Ca²⁺, Mg^{2+}) and anions (SO₄², Cl-, HCO₃-, F- and NO₃) for the assessment of water samples using standard method (APHA 2012) was carried out. Ca^{2+} , Mg^{2+,} CO_3^2 and HCO³ were analyzed by titration. Na⁺ and K^+ were measured by flame photometry and NO³-, SO₄²- and F- by UV Spectrophotometer. Maps were prepared using Mapinfo 6.5 and Vertical Mapper 3.0 and Piper trillinear diagram were plotted using Rock Works 15. The statistical software Minitab 16 and Microsoft Excel software were utilized for the calculation and interpretation of generated data.

RESULTS AND DISCUSSION

Physico-chemical compositions of the surface water samples are presented in S_1 and S_2 . The statistical description of water quality parameters indicating minimum, maximum, mean, median and standard deviation for both the years 2015 and 2016 (pre-monsoon and post-monsoon) respectively are presented in (Tables 2a and 2b). Temperature value ranged from 17.00 to 35.00 and 16.00 to 32.00 for both pre-monsoon and post-monsoon seasons. Turbidity values varied between 0.5 and 4.90 NTU with a mean \pm standard deviation (SD) of 2.67 ± 1.24 in pre-monsoon season and 0.7 and 4.8 with a mean \pm SD of 2.53 \pm 1.19 during post-monsoon season. Minimum, maximum, average, median and standard deviation values of the various parameters are shown in box plot (Fig. 3). The concentration of various physico-chemical parameters were compared with the threshold values given by Bureau of Indian Standards (BIS 2012) and World Health Organization (WHO 2011) for domestic purposes (Tables 2a and 2b). All the analyzed parameters fall within the desirable to permissible limit except for turbidity and fluoride. The turbidity values of 55 % samples in pre-monsoon and 56 % in post-monsoon were beyond the prescribed limit (1 NTU) of BIS (2012). Fluoride concentration of 14 % samples in pre-monsoon and 13 % in post-monsoon are above the prescribed limit (1 mg/L) of BIS (2012).

Drinking and irrigation water quality analysis

Drinking water quality analysis

Water Quality Index (WQI) reflects the combined

Water quality parametrs		Indian standards Desirable Permissible	Minimum	Maximum	Mean	Median		Std.devation	No. of samples beyond Desirable	Permissible
	limit	limit							limit $(\% \text{ of sample})$	limit $(\% \text{ of sample})$
Temperature			17.00	35.00	24.68	24.00		4.22		
Turbidity	1	5	0.5	4.90	2.67	2.60		1.24	55	NIL
pH		$6.5 - 8.5$	6.98	8.60	7.83	7.90		0.42	2	$\overline{2}$
EС		1500 ^a	50.89	219.00	84.81	66.54		39.33	NIL	NIL
TDS	500	2000	33.91	143.01	55.34	43.13		25.80	NIL	NIL
TH as CaCO ₂	200	600	26.00	96.00	55.62	52.5		19.30	NIL	NIL
Ca^{2+}	75	200	11.20	69.40	34.83	29.85		15.39	NIL	NIL
Mg^{2+}	30	100	2.00	9.45	5.20	4.85		1.89	NIL	NIL
$Na+$	200 ^a		6.20	16.90	9.74	9.30		2.41	NIL	NIL
$\mathrm{K}^{\scriptscriptstyle{+}}$	12a		0.80	2.60	1.58	1.5		0.45	NIL	NIL
$Cl-$	250	1000	8.40	27.20	15.94		16.10	4.11	NIL	NIL
$HCO3$ -	500 ^a	500 ^a	24.90	180.00	95.28	99.59		37.82	NIL	NIL
$F-$		1.5	0.02	1.40	0.62	0.65		0.40	14	NIL
SO_4^2	200	400	1.19	41.30	16.58		14.20	9.27	NIL	NIL
NO ₃	45	45	0.00	2.70	0.87	0.62		0.70	NIL	NIL
DO.			0.90	5.40	4.00	4.20		0.97		
COD			12.90	37.10	26.68	28.18		5.35		
BOD			0.20	2.00	1.32	1.50		0.46958		

Table 2 (a). Statistical summary of physico-chemical analysis of surface water samples (premonsoon year 2015-2016). a denotes WHO guidelines 2011. All parameters are in mg/l, except pH and EC (expressed in μ S/cm at 25^oC). EC electrical conductivity, TDS total dissolved solids, TH total hardness.

Table 2 (b). Statistical summary of physico-chemical analysis of surface water samples (postmonsoon year 2015-2016). a denotes WHO guidelines 2011. All parameters are in mg/l, except pH and EC (expressed in μ S/cm at 25°C). EC electrical conductivity, TDS total dissolved solids, TH total hardness.

Fig. 3. Box plot of concentration on cations and anions in the study area.

influence of different water quality parameters. The concept of WQI was first used in the year 1965 (Singh and Hussain 2016). The WQI takes the intricate scientific data into a single range (Rana *et al.* 2018). It is among most successful methods to know the quality of any water body (Stambuk-Giljanovic 1999, Herojeet *et al.* 2016). WQI provides comprehensive analysis of both the surface and ground quality and its suitability for domestic use (Seth *et al.* 2014, Tiwari and Mishra 1985, Rao 1997, Mishra and Patel 2001). For analyzing the WQI, BIS (2012) water standard for every analyzed parameter in mg/l have been considered. The index prepared by Tiwari and Mishra (1985) was used. 10 water quality parameters, like, pH, EC, TDS, Total hardness, calcium, magnesium, alkalinity, chloride, nitrate and sulfate were considered for analyzing the WQI in the current study.

The first step involved in calculation of WQI is calculating the relative weight (wi) of every parameter using the following equation. The unit weight (wi) for different water quality parameters

Table 3. Unit weightage of parameters.

Parameters	Highest permitted values of water (Si)	Unit weightage (W _i)
pH	8.5	0.577026
EC	1500a	0.003324
TDS	300	0.009728
TH	300	0.016563
Ca^{2+}	75	0.066502
Mg^{2+}	30	0.164631
$Cl-$	250	0.019466
HCO ₃	500a	0.009876
SO_4^2	200	0.024522
NO ₃	45	0.108246

is assumed to be inversely proportional to the suggested values for the related parameter (Table 3).

$$
wi (unit weight) ∞ 1/Sn
$$

\n→ $wi = K/Sn$

Where, K

 (Constant) = –––––––––––––––––––––––– and $1/\mathrm{v}_{\mathrm{s}1} + 1/\mathrm{v}_{\mathrm{s}2} + 1/\mathrm{v}_{\mathrm{s}3} + \ldots + 1/\mathrm{v}_{\mathrm{sn}}$ S_n = suggested acceptable value.

Based on the Indian drinking water standards the calculated unit weight of every parameters are also shown in Table 2.

In the next step, water quality rating (qi) was analyzed for every parameter using the following equation.

$$
Q_i = 100 \times \frac{(v_a - v_i)}{(v_s - v_i)}
$$

where V_a = actual value present in the water sample,

Table 4. Water quality index classification. (Source: After Mishra and Patel 2001)

Sl. No.	Water quality	Status	
	$0 - 25$	Excellent	
$\overline{2}$	$26 - 50$	Good	
3	51-75	Poor	
$\overline{4}$	76-100	Very Poor	
5	>100	Unfit	

S1. No.	WO class	Status	Pre monsoon 2015-16 No. of Per- samples cent-		Post monsoon $(2015-16)$ No. of Per- samples cent-	
				age		age
	$0 - 2.5$	Excellent	21	70%	25	83.33%
2	$26 - 50$	Good	9	30%	5	16.67%
3	51-75	Poor	NIL.	NIL	NIL.	NIL.
4	76-100	Very Poor	NIL.	NIL	NIL	NIL.
5	>100	Unfit	NIL	NIL.	NIL.	NIL.

Table 5. Result of water quality index for surface water samples.

 V_i =ideal value (0 for all parameters except pH which is 7.0), and V_s = standard value.

Third step included the summation of these sub-indices in the overall index. WQI is then calculated by using equation given below.

Water quality index (WQI) = $\Sigma_{ni=1}(Q_iW_i) / \Sigma_{ni=1} W_i$

Where, Q_i is the sub index of ith parameter. W_i is the unit weightage for ith parameter, n is the number of parameters considered.

WQI is categorized into 5 different water quality groups as summarized in Table 4. The maximum threshold value is 100 and beyond this value the water is not fit for drinking purposes.

Table 5 shows the percentage of surface water

Table 6. Correlation matrix for the surface water samples.

samples falling in different water quality categories on the basis of WQI values. According to the WQI classification during pre monsoon season 70% and 30% samples fall in excellent and good type in both the years 2015 and 2016. Whereas during post monsoon seasons 83.33 % and 16.67% samples belong to excellent and good type. None of the water samples fall in poor, very poor and unfit type during both the years. Therefore, it can be concluded from the analyzed observations that all the water samples during both the seasons are fit for domestic use.

Correlation matrix

The correlation matrix is applied to observe the significant relationship between the analyzed parameters that influenced the water quality (Bhandari and Nayal 2008, Joshi *et al.* 2009). The correlation coefficient (r) values ranged between $+1$ to -1 , where r score > 0.8 is strong, 0.5-0.8 is moderate and <0.5 is weak. Table 6 shows that EC has a positive score (strong) with TDS. TDS signifies the presence of rich soluble minerals in water and directly reciprocal with the conductivity. The positive loading of TH and their excess content of Ca and Mg ions may depict hardness in water

Classification of surface water for designated use

CPCB (2007) classified the surface water using the measured values of the following parameters i.e.,

Table 7. Designated best use classification of surface water source: Guidelines for water quality monitoring, MINARS/2007–08 (CPCB 2007).

Designated best use	Water class	Primary water quality criteria	No. of samples Premonsoon	Postmonsoon
Drinking water source without conventional treatment but after				
disinfection	A	» pH between 6.5 to 8.5 » Dissolved Oxygen 6mg/l or more » Biochemical Oxygen Demand 5 days 20° C 2mg/l or less	NIL	NIL.
Outdoor bathing (Organised)	B	» pH between 6.5 to 8.5 » Dissolved Oxygen 5mg/l or more » Biochemical Oxygen Demand 5 days 20° C 3 mg/l or less	3	3
Drinking water source after conventional treatment and				
disinfection	C	» pH between 6 to 9 » Dissolved Oxygen 4mg/l or more » Biochemical Oxygen Demand 5 days 20° C 3mg/l or less	16	15
Propagation of Wildlife and				
Fisheries	D	» pH between 6.5 to 8.5 » Dissolved Oxygen 4mg/l or more	16	15
Irrigation, Industrial Cooling,				
Controlled Waste disposal	E	» pH between 6.0 to 8.5 » Electrical Conductivity at 25° C $(\mu s/cm)$ Max. 2250 » Sodium adsorption ratio Max. 26	30	30

TC, DO, BOD, pH and EC for specific application (Table 7). The assessment of water quality based on multi-constituent parameter provides more reliable results rather than individual parameter. CGWB (2013) water quality criteria are used to evaluate surface water for both seasons.

Fig. 4. Geochemical classification of surface water (after Piper 1944).

Perusal of Table 7, ellustrates the number of samples fall in class A, B, C, D and E, respectively. are 0, 3, 16, 16, 30 for pre-monsoon and 0, 3, 15, 15, 30 for post-monsoon indicates that maximum number of the water samples are suitable for propagation of wildlife and fisher and irrigation, industrial cooling and controlled disposal. However, 50% sample fall in C class where the water source can easily used for drinking purpose after boiling and disinfection. It is clear that there are no significant temporal differences of surface water quality for both pre and post monsoon seasons as per the criteria of water quality guidelines (CPCB 2007).

Hydrochemical facies

Piper diagram is used to appraise the hydrochemical characteristics of surface water resources in the study area Fig. 4. Different major cations like $\rm Na^+, K^+, Ca^{2+}$ and Mg^{2+} and major anions like Cl, SO_4^2 , CO_3^2 and HCO₃ is used to prepare the piper diagram consisting of two outer triangles and a middle or inner diamond shaped quadrilateral (Pradhan and Pirasteh 2011). The left and right triangle confirms the dominant cation and anion in the water system. The central diamond-like quadrilateral structure indicates the overall characteristics of the water and hydrochemical facies. In the present study, piper diagram of water samples from the study area are presented (Figs.5, 6). Among the major cations and anions in water samples, triangle plot shows calcium and bicarbonate are the dominant ions in the study area. The diamond plots revealed that alkali earth metal elements $(Ca^{2+} +$ Mg^{2+}) are higher than alkali elements (Na⁺ + K⁺) and

weak acids $(CO_3^2 + HCO_3)$ are higher than strong acids $(Cl + SO₄²)$. The hydrochemical facies shows that all the water samples fall in the field $(Ca^{2+}$ – Mg^{2+} – HCO₂) type, indicating temporary hardness. The chemical composition of the water in the study area is influenced by rainfall, climate, rock type, (Cruz and Amaral 2004).

Base exchange indices (r_1) and meteoric genesis indices (r₂)

Developed the base exchange indices to study the dominant chemical constituent in water body and calculated using the eqn 1:

$$
r_1 = \frac{(Na^+ - Cl^-)}{So_4^{2}}
$$
 (1)

where, Na^+ , Cl and SO₄² concentrations are expressed in meq/L. The value of $r_1 < 1$ indicate Na⁺ SO₄² type, and $r_1 > 1$, Na⁺ HCO₃ type of water sources. Figure 5 indicates that reverse ion exchange is the controlling factor as majority of water samples are Na⁺- SO₄² type. However, 1(one) sample from pre- monsoon and 3(three) samples from post- monsoon shows Na⁺- HCO₃ type which depicts ion exchange.

The classified water source on the basis of meteoric genesis index (r_2) into two types and calculated using the eqn (2):

$$
r_2 = \frac{(Na^+ + K^+) - Cl^2}{So_4^{2}}
$$
 (2)

Fig. 5. Base exchange indices (r_1) and meteoric genesis indices (r_2) of the analyzed water samples.

Fig. 6. Gibbs's diagram for the surface water samples.

where, Na^+ , K^+ , Cl and SO_4^2 are the concentration of water sample in meq/L. If the value of $r₂$ indicates the deep meteoric water percolation type, whereas r_2 1 indicates shallow meteoric water percolation type. Figure 5 depicts that the majority of different surface water sources are influenced by deep meteoric water percolating type. Only one sample from pre-monsoon and three samples from post-monsoon are identified as shallow meteoric water percolating type. Thus, the water samples classified as Na^+ -SO₄² type are also belong to the deep meteoric water percolation type.

Gibb's diagram

The mechanism controlling hydrochemistry can be ascertained by the relationship between chemical constituent and lithological characteristics (Gibbs 1970). The Gibbs equations used to calculate majorcations and anions are given below.

Gibbs ratio I (cation) =
$$
\frac{(Na^+ + K^+)}{(Na^+ + K^+ + Ca^{2+})}
$$
 (3)

Gibbs ratio II (anion) =
$$
\frac{Cl}{(Cl^+ + HCO_3)}
$$
(4)

where all the ion concentrations are expressed in meq/L.

Gibbs diagram are plotted between the ionic ratios (cations and anions) versus TDS represent three distinct fields such as 1) evaporation dominance, 2) rock dominance and 3) precipitation dominance. Figure 6 shows that the maximum surface water samples are controlled by interaction between rock strata and percolating recharge water.

Process controlling the water chemistry

Satluj river and its tributaries crosses different geological formations in the study area. Thus, dissolution of different parent materials leads to different groups of ions to river water. For instance, generally Ca^{2+} and Mg^{2+} mainly originate from the weathering of carbonates, silicates, and evaporites, Na^+ and K^+ from the weathering of evaporites and silicates, HCO₃ from carbonates and silicates and SO_4^2 and Cl-from evaporites (Barzegar *et al.* 2016, Jiang *et al.* 2015). Previous studies (Datta and Tyagi 1996, Kumar *et al.* 2006 , Venugopal *et al.* 2009), the scatter plot of $Ca^{2+} + Mg^{2+}$ vs $SO_4^2 + HCO_3$ is a major indicator to identify rock minerals related ion exchange process (Fig. 7).

The silicate weathering indicates the dominance

Fig. 7. Scatter plot of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_{3} + SO_4^{-2-})$.

of $(HCO_{3}^2 + SO_4^2)$ over $(Ca^{2+} + Mg^{2+})$, whereas the abundance of $Ca^{2+} + Mg^{2+}$ suggest reverse ion exchange (Elango and Kannan 2007, Barzegar *et al.* 2016). In the present study, the entire samples fall below the 1:1 equiline indicates the silicate weathering influences the surface water chemistry. The plot of $(Ca^{2+} + Mg^{2+})$ versus Na⁺ (Fig. 8) was used to understand the ion exchange in the surface water.

The plot confirms that reverse ion exchange is the controlling factors as the entire water sample are fall above the aquiline.

The value Na+ /Cl- molar ratio ranged from 0.51 to 2.02. 46.67% samples have Na+ /Cl- value greater than 1, indicating that dissolution of silicate is the

Fig. 8. Plot of different ions indicating ion exchange on the chemistry of river water.

Fig. 9. Plot of Na vs Cl indicating silicate weathering.

main process releasing $Na⁺$ ion in the river water and the role of evaporation is insignificant (Fig. 9).

Table 8. Suitability of surface water for irrigation based on different classifications.

Irrigation water quality analysis

The quality of water for agriculture purposes varies substantially, depending principally upon the salinity, soil permeability, toxicity and some miscellaneous concerns such as excess nitrogen content and variation in water pH. The appraisal of water for irrigation relies on the presence of essential soluble minerals to enhance crop productivity (Gupta 1989). The different irrigation water quality indices like Electrical Conductivity, Percent Sodium (% Na+), Sodium Adsorption Ratio (SAR), Magnesium hazard (MH), Salinity hazard, Residual Sodium Carbonate (RSC), Permeability Index (PI), Kelley's Ratio, were used for the present study. Ionic balance was calculated by converting the mg/l value to milli equivalent/liter (meq/l) (Table 8).

Sodium adsorption ratio (SAR): SAR is an irrigation index used to evaluate the relative proportion of Na+ to Ca^{2+} and Mg^{2+} ions in a sample. The SAR value of each water sample was calculated using the following equation 5 (Hem 1991):

Fig. 10. USSL classification of surface water quality for irrigation (after USSL 1954).

Irrigation water having high Na⁺ content and low in Ca^{2+} ions may destroys the soil structure due to saturation of Na⁺ ions and affects plant growth (Todd 1980). Table 6 represented the water samples based on the SAR classification. In the study area, SAR values are very low ranging from -3.26 to 1.20 with mean value 0.45 meq/l indicates the surface water samples fall in excellent class for irrigation with no danger of ion exchange between Na⁺ and clay particles (Fetter 1994).

Magnesium hazard: Magnesium and calcium ions are essential for plant growth although these ions may be added with the soil aggregation and cause friability of soil. High concentration of calcium and magnesium of irrigation water can increase the pH of soil that may cause loss of phosphorus. Magnesium ions are also important for the productivity of soil. The water is safe and suitable for irrigation if the numerical value of magnesium hazard (MH) is less than 50% (Szabolcs and Darab 1964). Szabolcs and Darab (1964) proposed magnesium hazard and calculated by using the following eqn 6:

$$
MH=Mg^{2+}/(Ca^{2+}+Mg^{2+})*100
$$
 (6)

where all the concentrations are in meq/l The entire surface water samples were less than 50% in both the years and thus suitable for irrigation purposes for the all types of crops.

Salinity hazard: Salinity hazard depend on the overall content of soluble mineral ions present in water body. Water having high conductivity reduces osmotic potential of plants and renders incapable for plant to compete with the ions present in soil for water (Subramani *et al*. 2005). The US Salinity Laboratory categorized the suitability of water for irrigation purposes based on different classifications (Table 8). As per US Salinity diagram (USSL 1954) all the surface water samples in both the pre and post-monsoon seasons (2015-16) falls in the field of C1-S1 (Fig. 10), indicates irrigation suitability on all soil types.

*Percent sodium (%Na)***:** % Na is an important factor for the classification of irrigation water. A certain ratio of air water in the pore spaces of the soil is essential for the proper nutrition and growth of the plants. The water containing sodium reacts with the soil, accumulates in the void spaces the soil and reduces the permeability of the soil. The sodium concentration is expressed in terms of soluble sodium percent. The maximum permissible limit of SSP is 60% for irrigation water. Wilcox (1955) developed % Na, where the excessive content of Na⁺ ions relative to Ca^{2+} and Mg^{2+} ions reduces soil permeability. Irrigation water having high Na⁺ ions exchanged Ca^{2+} and Mg²⁺ ions, thereby get absorbed onto clay minerals and inhibits the water supply penetrating the plant roots. % Na is calculated using the following formula given eqn 7:

% Na = [(Na⁺ + K+)] × 100 / (Ca2+ +Mg2+ + Na+ + K+) (all units in meq/l) (7)

% Na values in the study area varied from 11.65% to 35.95% with mean value of 19.42%. The calculated % Na versus EC is plotted in Wilcox diagram. Perusal of Wilcox diagram (Fig. 11) reveals that the entire water samples in both the pre- monsoon (2015-16) and post- monsoon (2015-16) belongs to excellent to good water class, thus suitable for irrigation purposes for all types of crops (Table 8).

*Residual Sodium Carbonate (RSC)***:** The sum difference between weak acids (carbonate and bicarbonate) and alkaline earth metals (calcium and magnesium) influences water suitability for irrigation purpose. Excess of sodium bicarbonate and carbonate is considered to be detrimental to the physical properties of soils, as it causes dissolution of organic matter in the soil, which in turn leaves a black stain on the soil surface on drying. High exchangeable sodium causes

dispersion of soil particle and specific ion toxicity some plants also. The precipitation of Ca^{2+} and Mg^{2+} ions in soil depend on the concentration of bicarbonate content in water. As a result, the content of sodium increases in water as sodium carbonate. RSC is calculated using the following equ 8 (Eaton 1950):

$$
RSC \text{ (meq/l)} = (CO_3^{2+} + HCO_3^-) - (Ca^{2+} + Mg^{2+})
$$

(all units in meq/l) (8)

The study area have RSC value range from -3.23 to 1.35 meq/l. According to Richard's classification (Richards 1954), 98.3% water sample have RSC values less than 1.25 meq/l, except for one sample in pre- monsoon season, thus, safe for irrigation purpose (Table 8).

Permeability Index (PI): The method for determining the permeability of water in soil is developed by Doneen (1964). The permeability of the soil is affected by the lasting irrigation and accumulation of soluble minerals by Na^+ , Ca^{2+} , Mg^{2+} and HCO_3 . concentrations in soil (Chandu *et al.* 1995). PI is calculated using the following eqn 9:

Fig. 11. Classification of surface water quality for irrigation (after Wilcox 1955).

$$
PI = \frac{Na^{+}\sqrt{HCO_{3}}}{Ca^{2+} + Mg^{2+} + Na}
$$
 (all units in meq/l) (9)

PI values ranged from 18.4% to 60.1% with average value of 38.8% in the study area. Doneen's chart (Domenico and Schwartz 1990) show that all the surface water samples in both the seasons year 2015-16 falls in Class - I which is fit for irrigation use $(Fig. 12)$.

Kelley's Ratio: Kelley's ratio is calculated by the ratio of Na⁺ content against Ca²⁺ and Mg²⁺ concentration in particular water samples (Kelly 1957). Kelly's ratio value more

than 1 indicates an excess level of Na+ in water. It is

calculated using the following eqn 10:

Kelley's ratio= $\text{Na}^{+}/\left(\text{Ca}^{2+} + \text{Mg}^{2+}\right)$ (all units in meq/l) (10)

If, Kelly's ratio is <1 indicate suitable for irrigation, while $KI > 3$ means not suitable for agricultural purposes. Kelly's ratio of surface water varies from $0.07 - 0.572$ (KI <1), indicates irrigational suitability and free from salanity hazard.

Irrigation water quality index (IWQI)

Like water quality index for domestic purpose, water quality was used to assess for irrigation purpose. Irrigation water quality index (IWQI) was calculated using the following indices namely, MH, RSC, Na %,

Fig. 12. Permeability index showing surface water quality (after Domenico and Schwartz 1990).

Table 9. Weight of each parameter and the suitable limit for irrigation.

Para meter	unit	Suitable Unit irrigation (wn)	limit for weight	Reference
MН	No unit	50.0	0.110	Szabolcs and Darab (1964)
RSC	meq/l	2.5	0.793	Eaton (1950)
$Na\%$	$\frac{0}{0}$	60.0	0.040	Wilcox (1955)
SAR	No unit	18.0	0.033	Richard (1954)
EC	μ S/cm	2250.0	0.023	Freeze and Cherry (1979)
ΡI	No unit	85.0	0.001	Doneen (1964)

SAR, PI and salinity hazard as discussed in above section. Table 9 provides the unit weightage assigned each indices. Table 10 shows the percentage of surface water samples falling in different water quality status on the basis of IWQI values.

According to the IWQI classification during pre-monsoon season 23 out of 30 Surface water samples which is 76.6% falls in excellent category. Also 7 out of 30 Surface water samples i.e. 23.3% samples fall under good category in both the years 2015 and 2016. Whereas during post-monsoon seasons 24 Surface water samples that is 80 % fall in excellent category and 6 i.e. 20 % fall under good category class. None of the water samples fall in poor category in both the years.

Thus, IWQI classification indicates that all the surface water samples both in pre and post-monsoons seasons (2015-16) falls under excellent to good category and thus water is suitable for irrigation purposes.

Irrigated crops in the study area

Kinnaur district is largely located in the dry zone where the temperature is very low throughout the year. The crops grown take much time to, mature as compared to other parts of the State. Most of the area remains covered under snow for a long period and hence, the farmers grow only one crop. The climate of Kinnaur is cold and dry and is ideally suited for the production of temperate fruits and dry fruits. The agro-conditions of Kinnaur are very suitable for the cultivation of fruits and vegetables . Apples, apricot, almond, walnut are found almost all over the district. The upper region of the district is famous for production of apple, chilgoza, almonds and walnut whereas, the lower region i.e. Sangla block and Nichar block is famous for production of apple, cherry, hazelnut, pears, peaches and grapes.

In Kinnaur district, about 90% area of total cropped area was under cereal crops. The area under cash crop like fruits, potato and vegetables was about 14% in this district. During the decade of seventy to ninety (1970-90) the pattern of commercial crops has seen some changes as a lot of area has been shifted from non-commercial to commercial crops towards wheat, fruits, potato and vegetables. This changed trend towards commercialization of agriculture which has been more suitable. It is due to favorable agro-climate conditions that assured irrigation, better input supply road network the percentage of area under fruits and vegetables is the highest in Kinnaur i.e. about 25% in the district. The change in cropping pattern thus suggests a movement in favor of commercial crops as against persistence of traditional agriculture.

Sl. No.	WOI		Pre monsoon $(2015-16)$		Post monsoon $(2015-16)$	
	class	Status	No. of samples	Percentage	No. of samples	Percentage
	$0 - 25$	Excellent	23	76.6%	24	80%
2	$26 - 50$	Good		23.3%	6	20%
3	$51 - 75$	Poor	NIL.	NIL	NIL.	NIL
$\overline{4}$	76-100	Very Poor	NIL	NIL	NIL	NIL
5	>100	Unfit	NIL	NIL	NIL	NIL

Table 10. Result of irrigation water quality index for surface water samples.

Sl. No.	Horticulture crops vegetables	Major field crops
1.	Apple	Maize
2.	Nuts and Dry Fruits	Wheat
3.	Peas	Barley
$\overline{4}$.	Cabbage	Pulses
5.	Beans	Potato
6.	Capsicum	Vegetables
7.	Chillies	Millets (Ogla/ Phaphra)
8.	Other Temperate Fruits	

Table 11. Lists of the irrigated crops in the study area.

and the constant scarcity of rains have led people to improvise possibilities and methods of irrigating almost all their cultivated lands through the Kuhl system. By and large, when water through Kuhls is available, all the lands receive their share, whereas, during the months when water is not so available, only such crops are grown, which do not need constant supply of water (Table 11).

CONCLUSION

The assessment of surface water quality in parts of Kinnaur district using various indices approach for drinking and irrigation purposes. Analytical result shows that all the parameters were well within the threshold value given by BIS (2012) and WHO (2011) for drinking purpose except for turbidity and fluoride which gives us caution. Based on the hydrochemical most water type dominates in the study area is Ca^{2+} – Mg^{2+} – HCO₂ facies with temporary hardness. Gibb's diagram reveals that most of the surface water samples are controlled by interaction between rock strata and percolating recharge water. On the basis of SAR water quality of the study area falls under excellent category for agriculture purposes. Salinity and sodicity falls under C1-S1 category indicating low salinity and sodium hazard which is fit for irrigation to all soil types. As per RSC, % Na, Kelley's ratio and Permeability Index, surface water is fit for agricultural human purposes. Based on WQI and IWQI classification, all the water samples fall under excellent to good classes during both pre and post-monsoon seasons, which is ideally fit for consumption and irrigation purpose. The study area is highly geologically sensitive and eco-fragile area which requires indepth anticipation about the infrastructural advancement and other development activities. It is also recommended that adequate knowledge and awareness should be provided to the local villagers and their vital role to maintain the virgin water quality and environment sancity.

ACKNOWLEDGEMENT

The authors are grateful to the Director, GBPNIHE, Kosi-Katarmal, Almora, Uttarakhand, India for providing necessary facilities which could make this study possible. Authors are also thankful to UGC, Irrigation due to peculiar topography of Kinnaur New Delhi for providing financial assistance.

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