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A comparative study on usage of Durov and Piper diagrams to interpret hydrochemical processes in groundwater from SRLIS river basin, Karnataka, India

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ABSTRACT

In the present study, an attempt was made to evaluate and identify hydrogeochemistry of water and the involved chemical processes using Durov and Piper diagrams. The prominent hydrochemical facies was Ca^{2+}-Mg^{2+}-Cl^{-}-SO_4^{2-} in both methods although slight variation in terms of Ca^{2+}-Mg^{2+}-HCO_3^{-} was also observed in few water samples. Piper diagrams indicated the dominance of mixed water type (70.84%) having no one cation-anion pair exceeds 50%, while Durov specified the dominance of simple dissolution or mixing (83.34 %) with no dominant major anion or cation. Thus, both the diagrams signify non-identification of the water types with neither anions dominant nor cations dominant. Piper diagram, Durov plot and chloroalkaline indices indicated the dominance of alkaline earth elements were over alkalies in majority of samples due to direct exchange of Ca^{2+} and Mg^{2+} from the Aquifer matrix with Na^{+} and K^{+} from the groundwater. Further, SAR (0.41>SAR< 2.78), percent sodium (7.3 > %Na < 42.4) and WQI (13.56 >WQI < 112.99) values recommended the suitability of 100, 91.67 and 62.5% of samples for domestic and irrigation purposes.

Introduction

Groundwater is the primary source of water for domestic, agricultural and industrial uses in many countries, and its contamination has been recognized as one of the most serious problems (Belkhiri *et al.*, 2010). Groundwater quality is dependent on nature of bedrock, topography, geology, soils, climate, atmospheric precipitation and quality of the recharged water in addition to anthropogenic pollution sources in terms of agricultural and industrial activities. Further, groundwater quality could be affected by means of subsurface geochemical reactions such as weathering, dissolution, precipitation, ion exchange and various biological processes (Todd, 1980; Sakram et al., 2013). The concept of hydrochemical facies can be used to denote the diagnostic chemical character of water in hydrologic systems. The facies reflect the effect of complex hydrochemical chemical processes in the subsurface (Sajil Kumar, 2013) occurring between the minerals of lithologic formation and groundwater to investigate the spatial variability of groundwater chemistry in terms of hydrochemical evolution. Piper trilinear diagram (Piper, 1944) evaluate the evolution of the river water and relationship between rock types and water composition while Durov diagram is advantageous over the Piper diagram in revealing some geochemical processes that could affect groundwater genesis (Lloyd and Heathcoat, 1985). Hence, the present study aimed at hydrogeochemical study involving presentation of geochemical data in the form of graphical charts like Piper and Durov diagrams to assess the geochemical processes controlling the water chemistry and to delineate variation in hydrochemical facies. Further, suitability of water for drinking and irrigation purpose was evaluated using parameters like Water quality index, sodium absorption ratio and percent sodium.

Study area

The SRLIS (Sri Rameshwara nala lift irrigation scheme) river basin is located near Aralimatti, a small village situated towards north to Koujalgi in Gokak Taluk, Belgaum District, which forms a part of the Ghataprabha sub-catchment in main Krishna above the confluence of Bhima catchment of Krishna basin. The dam site (intake structure) of SRLIS river basin is constructed across Ghataprabha river, which is geographically located at 75^{0} 04’ 15” E Longitude and 16^{0} 19’ 30” N latitude. Ghataprabha river originates in Sundergad of Western Ghats and major tributaries joining it are Tamraparani near Shedihal, Hiranyakeshi in Chikodi taluk and Markandeya near Gokak town. The gross command area of SRLIS is 180.23 km^2 (18022.73 ha) and the net command area is 138.0 km^2 (13800 ha) stretching to 59.31 km^2 (5930.81 ha) in Gokak, 58.83 km^2 (5883.02 ha) in Ramdurg and 19.94 km^2 (1993.73 ha) in Saudatti Taluks of Belgaum District (Fig 1). The study area comes under the northern dry zone of the tenfold agro-climatic zone of Karnataka. The climate is healthy, agreeable and is characterized by a general dryness, excepting during monsoon season. The summer season between March and May is dry, dusty and very hot with maximum temperature reaching up to 42^{0} C. December to February is the cold season when the minimum temperature falls to 18^{0}C. On an average, there are about 50 rainy days in a year with an average annual rainfall of 503 mm, with most of the rainfall received during southwest monsoon period. Generally humidity varies from less than 20% during summer to 85% during monsoon period (June to September). The winds are generally mild in nature with slightly increased velocity, as observed during the late summer and monsoon season. The oldest rock formations exposed in the area are the granite gneisses and migmatites belonging to the Peninsular Gneissic complex of Archaean age.

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The geological formations found in the area are the rocks belonging to Kaladgi series of Precambrian age overlaid by the basaltic rocks of Deccan traps. The major part of the study area is almost a gentle undulating landscape with a linear strap of hills running in almost east- west direction dividing the region into equal halves. The region has a gentle easterly slope forming largely a plain interspersed with isolated low hills.

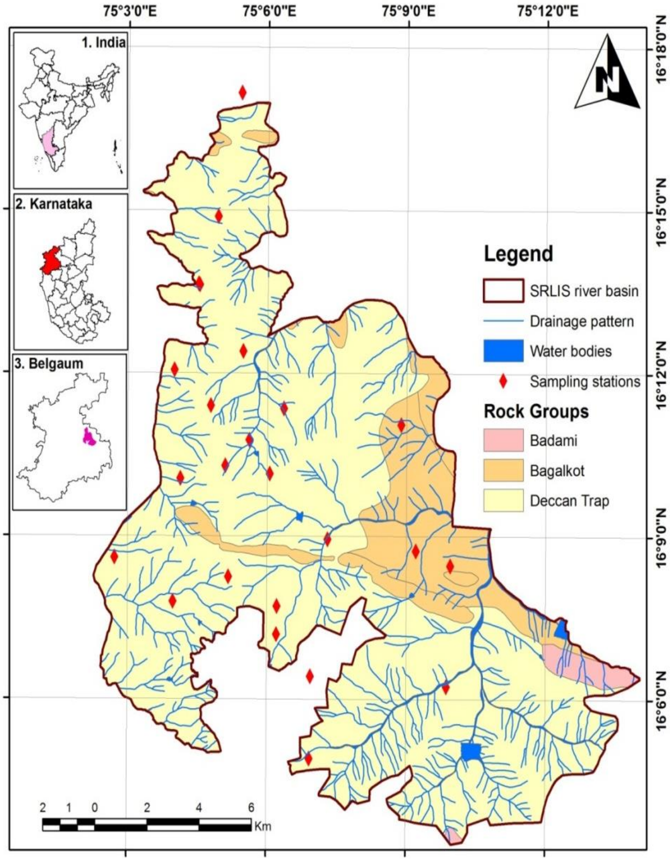


Fig 1. Location map of SRLIS river basin with sampling wells

Materials and Methods

A total of 24 water samples (i.e., 19 groundwater and 5 surface water) were collected in polyethylene bottles from the tube wells and river water and sequentially numbered during pre-monsoon season of the year 2006 (Fig 1). To avoid cross contamination, bottles are rinsed with the same water which has to be taken as samples. Electrical conductivity (EC) and total dissolved solids and pH were measured using digital meters immediately after sampling. Water samples have been analyzed for chemical constituents such as major ions in the laboratory using the standard methods as suggested by the APHA (2005). The ground and surface water quality was assessed with respect to BIS (2003) standards. Physico-chemical data of the area are subjected to graphical treatment by plotting them in a Piper Trilinear and Durov diagrams using Aquachem v3.7 software for better understanding of hydrochemistry, water quality and its evaluation by comparing the water types and to interpret variation in hydrochemical processes in the study area

Water quality index (WQI)

Water quality index (WQI) is defined as a rating reflecting the composite influence of different water quality parameters on the overall quality of water. WQI was calculated by adopting Weighted Arithmetical Index method (Table 1) considering thirteen water quality parameters (ie., pH, EC, TDS, total alkalinity, total hardness, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, F^{-}) in order to assess the degree of groundwater contamination and suitability. WQI is given by the equation

$$\mathbf{WQI} = \frac{\sum_{i=1}^{n} w_i q_i}{\sum_{i=1}^{n} w_i}$$

Where unit weight /weightage factor of ith parameter, $\mathbf{w_i = K/S_n}$; constant for proportionality, $\boldsymbol{K = 1 / (\sum_{i=1}^{n} 1/S_n)}$; V_{actual} = estimated value of the ith parameter from the laboratory analysis; Sn and $V_{standard}$ = BIS prescribed standard permissible value of the i^{th} parameter. V_{ideal} = ideal value of ith parameter in pure water (pH = 7and for the other parameters it is equivalent to zero. Sub index or Quality rating of the ith water quality parameter,

$$\mathbf{q_i = [(V_{actual} - V_{ideal})/(V_{standard} - V_{ideal})] \times 100}.$$

Chloroalkaline indices and Irrigational quality parameters

Chloroalkaline indices, Sodium absorption ration (SAR), Percent sodium (%Na) and were calculated using equation using Eq. 1 (Schoeller, 1977), Eq. 2 (Richards, 1954) and Eq. 3 (Todd 1980):

$$\text{Chloro Alkaline Indices (CAI-1)} = [\mathrm{Cl}-(\mathrm{Na}+\mathrm{K})]/\mathrm{Cl}$$

$$\text{Chloro Alkaline Indices (CAI-2)} \\ = [\mathrm{Cl}-(\mathrm{Na}+\mathrm{K})]/(\mathrm{SO_4}+\mathrm{HCO_3}+\mathrm{CO_3}+\mathrm{NO_3})$$

$$\mathrm{SAR} = \mathrm{Na}/\sqrt{(\mathrm{Ca}+\mathrm{Mg})/2}$$

$$\%\,\mathrm{Na} = \frac{(\mathrm{Na}^{+}+\mathrm{K}^{+}) \times 100}{(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}+\mathrm{Na}^{+}+\mathrm{K}^{+})}$$

Where all cationic concentrations are expressed in meq/L.

Results and discussion

Ground and Surface water quality

The pH value varied from 6.52 to 8.55 and 7.15 to 7.5 respectively in ground and surface water samples, showing slightly acidic to alkaline nature which is preferred for drinking. In ground and surface water samples, the electrical conductivity was in range of 510.7 to 2616.3 and 316 to 823.7 µS/cm; the total dissolved solids in the range of 318.7 to 1632.6 mg/L and 197.2 to 514 mg/L; Total alkalinity 204.8 to 435.9 mg/L and 77.4 to 195.7 mg/L; total hardness 230 to 760 mg/L and 140 to 338 mg/L respectively.

Among cations, the concentration of Ca, Mg, Na and K ranged from 44-186, 28.06-87.84, 24.7-168, 0.2-22.1 mg/L respectively in groundwater; and 26-72, 18.3-38.56, 11.1-55.9, 0.8-4.3 mg/L respectively in surface water. Among anions, Cl, HCO_3, NO_3, SO_4, F and PO_4 contents were in the range of 72.7-572.5, 249.9-531.8, 0.62-13.42, 17.1-258.8, 0.27-2.3 and 0.01-0.08 mg/L respectively in groundwater. In contrast, these values were 41.5-115.9, 94.4-238.8, 0.12-2.65, 1.3-113, 0.21-2.12 and 0.03-0.48 mg/L respectively in surface water.

Some of the groundwater samples did not meet the permissible limit for domestic purposes based on electrical conductivity and total hardness as their respective concentration was above 2000 µS/cm and 300 mg/L.

Hydrogeochemical facies

The geochemical evolution of water in general (groundwater in particular) can be understood by constructing Piper (1944) trilinear diagram and Durov (1948) plot. In the present study, Aquachem Scientific software version 3.7 was used to plot these diagrams. Piper diagram is a multifaceted plot wherein milliequivalents percentage concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (HCO_3^{-}, SO_4^{2-}, and Cl^{-}) are plotted in two triangular fields, which were then projected further into the central diamond field. In contrast, Durov diagram is a composite plot consisting of 2 ternary diagrams where the milliequivalents percentages of the cations of interest were plotted against that of anions of interest; sides form a central rectangular, binary plot of total cation vs. total anion concentrations. Both the diagrams reveals similarities and differences among water samples because those with similar qualities will tend to plot together as groups (Todd, 2001). But, in Piper diagram, it is the data plotted on the subdivisions of diamond-shaped field which decides the water type / hydrochemical facies in a water sample. Contrast to this, intersection of lines extended from the points in ternary diagrams and projected on the sub-divisions of binary plot of Durov diagram define the hydrochemical processes involved along with water type.

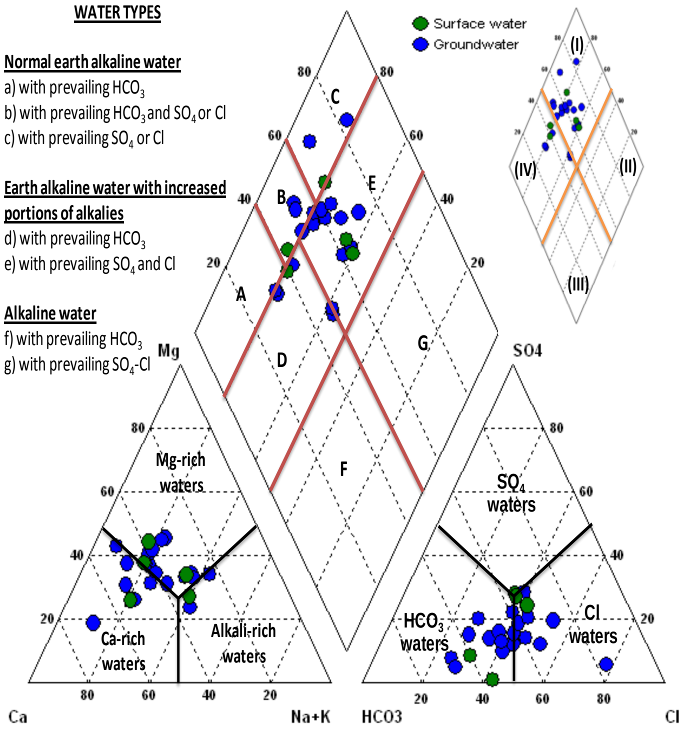


Fig 3. Piper Trilinear diagram classifying major hydrochemical facies (Langguth, 1966)

From the Piper trilinear diagram, it is apparent that majority of the samples (70.84%; 14 GW and 3 SW samples) belong to Ca^{2+}-Mg^{2+}-Cl^{-}-SO_4^{2-} (field I) demonstrating the dominance of alkaline earths over alkali (viz., Ca+Mg > Na+K) and strong acidic anions over weak acidic anions (i.e., $Cl+SO_4 > HCO_3$). Only few samples (29.16%; 5 GW and 2 SW samples) plotted under field (IV) belong to Ca^{2+}–Mg^{2+}–HCO_3^{-} signifying the dominance of alkaline earths over alkali and weak acidic anions over strong acidic anions. None of the samples represented fields (II) and (III) and hence Na^{+}–K^{+}–Cl^{-}–SO_4^{2-} and Na^{+}–K^{+}–HCO_3^{-} hydrochemical facies area absent. Among chloroalkaline indices, CAI-1 varied from (-0.02) to 0.85 and CAI-2 ranged from (-0.084) to 1.931, which were positive in the majority of the samples (91.67%) suggesting inverse / reverse ion exchange process occurring due to direct exchange of Ca^{2+} and Mg^{2+} from the Aquifer matrix with Na^{+} and K^{+} from the groundwater. This supports the fact that alkaline earth elements were abundant. Further, samples points plotted in diamond shape of piper diagram can further be classified into seven fields (designated with alphabets from A to G) using Langguth (1996) classification for Piper diagram of the analysis (Figure 3). Using this classification, the water from the study area were distinguished into four categories designated by B,C,D and E (Table 2); the first category is characterized by normal earth alkaline water with prevailing bicarbonate and sulfate or chloride (12.5 %); the second characterized by normal earth alkaline water with prevailing sulfate or chloride (12.5 %); the third characterized by alkaline earth water with increased portions of alkalis with prevailing bicarbonate (16.67 %) and, the fourth is characterized by the alkaline earth water with increased alkalis and prevailing sulfate and chloride ions (58.33 %). It is also apparent from the diagram that majority of the samples (79.17%) belong to mixed water type where water types cannot be identified as neither anions nor cations are dominant (having no one cation-anion pair exceeds 50%).

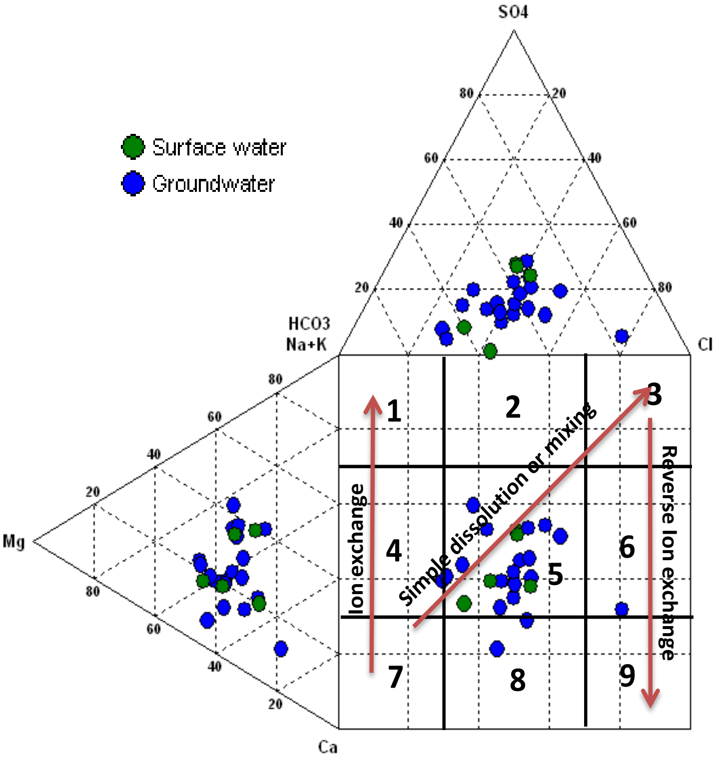


Fig 4. Durov plot depicting hydrochemical processes involved (Lloyd and Heathcoat (1985)

The fact that mixed water type prevail in the study area was supported by data plotted on Durov diagram (Fig 4) that 83.34 % of the samples plot in the field 5 of Durov plot along the dissolution or mixing line. Based on the classification of Lloyd and Heathcoat (1985), this trend can be attributed to fresh recent recharge water exhibiting simple dissolution or mixing with no dominant major anion or cation (Table 3). Addition to this, few samples (8.34%) showing Cl and Na as dominant anion / cation, indicated that the ground waters be related to reverse ion exchange of Na-Cl waters. Of the remaining samples, in one set of 4.16 % samples SO_4 dominates, or anion discriminant and Ca dominant, Ca and SO_4 dominant while the other set of 4.16 % showed SO_4 dominant or anion discriminate and Na dominant.

Mechanism controlling geochemistry

The distribution of sample points residing in the central part of Gibbs (1970) plot based on ratios of (Na+K)/(Na+K+Ca) and Cl/(Cl+HCO3) as a function of TDS, reflected the supremacy of weathering of rocks with some influence of evaporation-crystallization in controlling geochemistry of water samples from the study area (Fig 5). None of the data points lie in the lower-right side of the boomerang, where water composition is dominated by atmospheric precipitation process.

Water quality index

WQI is defined as a rating reflecting the composite influence of different water quality parameters on the overall quality of water.

Table 1.Computation methodology of WQI

Parameters	pH	EC	TDS	Total alkalinity	Total hardness	Ca	Mg	Na	K	Cl	SO_4	NO_3	F
Standard value (S_n and Vs)	8.5	3000	2000	600	600	200	100	200	10	1000	400	45	1.5
Ideal Standard (V_i)	7.0	0.0											
Weight factor (w_i)	0.1259	0.0004	0.0005	0.0018	0.0018	0.0054	0.0107	0.0054	0.1070	0.0011	0.0027	0.0238	0.7136

Table 2.Classification of water based on Piper diagram (Langguth, 1966)

Sl. No.	Water Types	No. of samples (GW=19; SW=5)	%
A	Normal earth alkaline water with prevailing bicarbonate	----	---
B	Normal earth alkaline water with prevailing bicarbonate and sulfate or chloride	03 (2 GW; 1 SW)	12.5
C	Normal earth alkaline water with prevailing sulfate or chloride	03 (2 GW; 1 SW)	12.5
D	Earth alkaline water with increased portions of alkalis with prevailing bicarbonate	04 (3 GW; 1 SW)	16.67
E	Earth alkaline water with increased portions of alkalis with prevailing sulfate and chloride	14 (12 GW; 2 SW)	58.33
F	Alkaline water with prevailing bicarbonate	----	---
G	Alkaline water with prevailing sulfate or chloride	----	---

Table 3. Classification of water based on Durov diagram (Lloyd and Heathcoat, 1985)

Sl. No	Water Types	No. of samples (GW=19; SW=5)	%
1	HCO_3 and Ca dominant, frequently indicates recharging waters in limestone, sandstone, and many other aquifers	----	---
2	This water type is dominated by Ca and HCO_3 ions. Association with dolomite is presumed if Mg is significant. However, those samples in which Na is significant, an important ion exchange is presumed	----	---
3	HCO_3 and Na are dominant, normally indicates ion exchanged water, although the generation of CO_2 at depth can produce HCO_3 where Na is dominant under certain circumstances	----	---
4	SO_4 dominates, or anion discriminant and Ca dominant, Ca and SO_4 dominant, frequently indicates recharge water in lava and gypsiferous deposits, otherwise mixed water or water exhibiting simple dissolution may be indicated.	01 (1 GW; 0 SW)	4.16
5	No dominant anion or cation, indicates water exhibiting simple dissolution or mixing.	20 (15 GW; 5 SW)	83.34
6	SO_4 dominant or anion discriminate and Na dominant; is a water type that is not frequently encountered and indicates probable mixing or uncommon dissolution influences.	01 (1 GW; 0 SW)	4.16
7	Cl and Na dominant is frequently encountered unless cement pollution is present. Otherwise the water may result from reverse ion exchange of Na-Cl waters.	----	---
8	Cl dominant anion and Na dominant cation, indicate that the ground waters be related to reverse ion exchange of Na-Cl waters.	02 (2 GW; 0 SW)	8.34
9	Cl and Na dominant frequently indicate end-point down gradient waters through dissolution	----	---

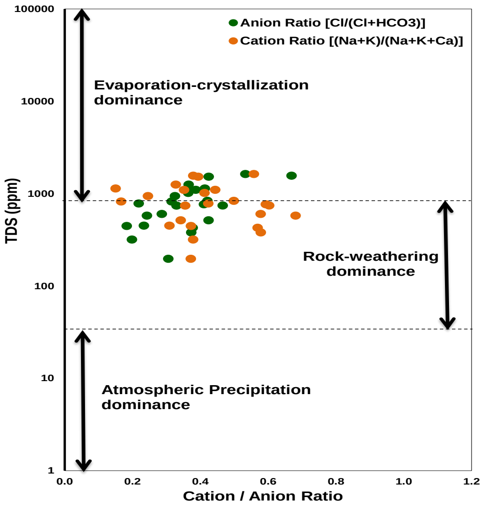
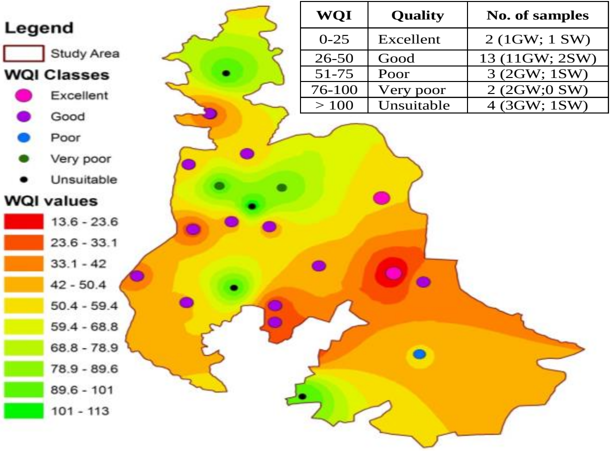


Fig 5. Gibb's diagram



WQI	Quality	No. of samples
0-25	Excellent	2 (1GW; 1 SW)
26-50	Good	13 (11GW; 2SW)
51-75	Poor	3 (2GW; 1SW)
76-100	Very poor	2 (2GW;0 SW)
> 100	Unsuitable	4 (3GW; 1SW)

Fig 6.Spatial distribution in WQI values in SRLIS river basin and their classification

It indicates the quality by an index number, which represents the overall quality of water for any intended use (Sisodia and Moundiotiya, 2006). Spatial distribution of WQI values is presented in Fig 6. The WQI values ranged from 13.56 to 112.99 water samples and 62.5% of the water samples can be considered suitable for domestic and other utilitarian purposes as they belong to excellent to good water quality classes. Remaining 37.5% of the samples were said to be unfit for consumption as they belong to poor, very poor and unsuitable classes.

Irrigational quality parameters

The classification of the water samples (Richards, 1954) from the study with respect to SAR value (0.41>SAR< 2.78) revealed that the water is excellent irrigation water (S1 type; SAR <10). Percent sodium values ranged from 7.3 to 42.4 and classification of water samples on its basis (Wilcox, 1955) demonstrated that 91.67% the samples are safe for irrigation purpose as its value was below 40 (viz., excellent to good quality). Only two samples belong to permissible category (40-60).

Conclusion

Results of the hydrochemistry suggest that all the water samples are alkaline in nature, with very few samples having electrical conductivity and total hardness above their standard limit. The alkaline earths were dominant over alkali and strong acidic anions over weak acidic anions in the present study due to reverse ion exchange processes. The dominant hydrochemical facies in the study area is Ca^{2+}-Mg^{2+}-Cl^{-}-SO_4^{2-} (70.83%) and Ca^{2+}–Mg^{2+}–HCO_3^{-} (29.17%). Groundwater types assessed and compared with Durov and Piper diagrams illustrated that simple mineral dissolution or mixing processes is mainly responsible for variation in hydrogeochemistry of ground / surface water in the study area. The positive chloroalkaline indices indicated direct ion exchange between the groundwater and its host environment during residence or travel. Gibbs diagram also indicated that the major process controlling the water quality as weathering of rocks with some influence of evaporation-crystallization. Finally, WQI based assessment revealed that majority of the samples (62.5%) were of excellent to good quality for domestic and irrigation purposes. Overall the results conclude suitability of all water samples for drinking and irrigation purpose.

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