

# Groundwater Geochemistry of Winder Agricultural Farms, Balochistan, Pakistan and Assessment for Irrigation Water Quality

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**Abstract:** The Winder agriculture farms are situated over the Bela Ophiolite of Cretaceous age, and lies west of Mor (Jurassic) and Pab (Cretaceous) ranges. Irrigation water availability is the crucial problem in the region due to arid climate. The main sources of irrigation water are deep tube wells and Winder River. Representative 33 groundwater samples were analyzed for important physical, chemical and irrigation water parameters. The abundance of major ions revealed  $\text{HCO}_3 > \text{Cl} > \text{SO}_4$  and  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  trend. The dominant hydrochemical facies of groundwater is CaMgCl-type with few NaCl-types. Various estimated parameters; Ca+Mg-HCO<sub>3</sub>, K/Na, Ca/SO<sub>4</sub> and Mg/Ca vs. Na/Ca ratios of the studied samples reflected its origin from incongruent dissolution of ophiolitic rocks with impact of sedimentary rocks and sulphide minerals. The PCA analysis and positive correlation matrix of Na-Cl, Ca-HCO<sub>3</sub>, Mg-SO<sub>4</sub> and Ca-SO<sub>4</sub> deduced a common source of origin. The positive chloro-alkaline indices revealed that the groundwater has suffered ion exchange between Na and K of water with Ca and Mg of soil during its flow. The Residue Sodium Carbonate, Sodium Adsorption Ratio, Permeability Index and Kelley's Ratio signified good quality, while Magnesium Absorption Ratio and Na% vs. EC are indicative of moderately suitable groundwater for irrigation purposes.

**Keywords:** Bela Ophiolite, water-rock interaction, irrigation water quality, Pakistan, Winder.

## 1. INTRODUCTION

Japanese Government in collaboration with the Department of Agriculture, Balochistan in 1993-94 has established agriculture farms in the surrounding of Winder Town, Balochistan (Fig. 1). Irrigation water resources are limited due to arid climate of the region. It is mainly obtained through deep tube wells. Farmers also utilize Winder River water, a stream with limited perennial flow (Bashir et al., 2007). These farms are situated over the ophiolitic rocks of Cretaceous age concealed by windblown sediments (Fig. 1). Pillow basalts in association with pelagic sediments are exposed in a strip striking NS in the eastern part of the area (Naseem et al., 2002). Ferozabad Group of Jurassic age is exposed in the Mor Range, and other sedimentary rocks belong to Cretaceous and Tertiary ages are exposed in the Pab Range.

The weathering of igneous and sedimentary rocks brought ions in the groundwater (Yousef et al., 2009). The dissolution of ophiolites contributes a very discrete assemblage of ions (Neal and Shand, 2002). The abundance of major ions largely depends upon the nature of bedrocks, climatic conditions and mobility. The ion distribution is also influenced by the infinite complex surface and subsurface physicochemical environments (Aghazadeh and Mogaddam, 2010).

The physical and chemical parameters of groundwater play a significant role in classifying and assessing water quality for irrigation purpose (Abou El-Hassan et al., 2009 and Hakim et al., 2009). The suitability of groundwater for irrigation is contingent on the effects of the mineral constituents of the water on both the fruit plant and the soil (Raihan and Alam, 2008).

The aim of this paper is to present a systematic approach to establish relation between rocks and major ions of the groundwater in the vicinity of Winder Town. Prime irrigation qualities are elaborated to appraise its suitability for irrigation in the Winder Agriculture Farms. Possibly present study helps farmers of the area for better irrigation planning.

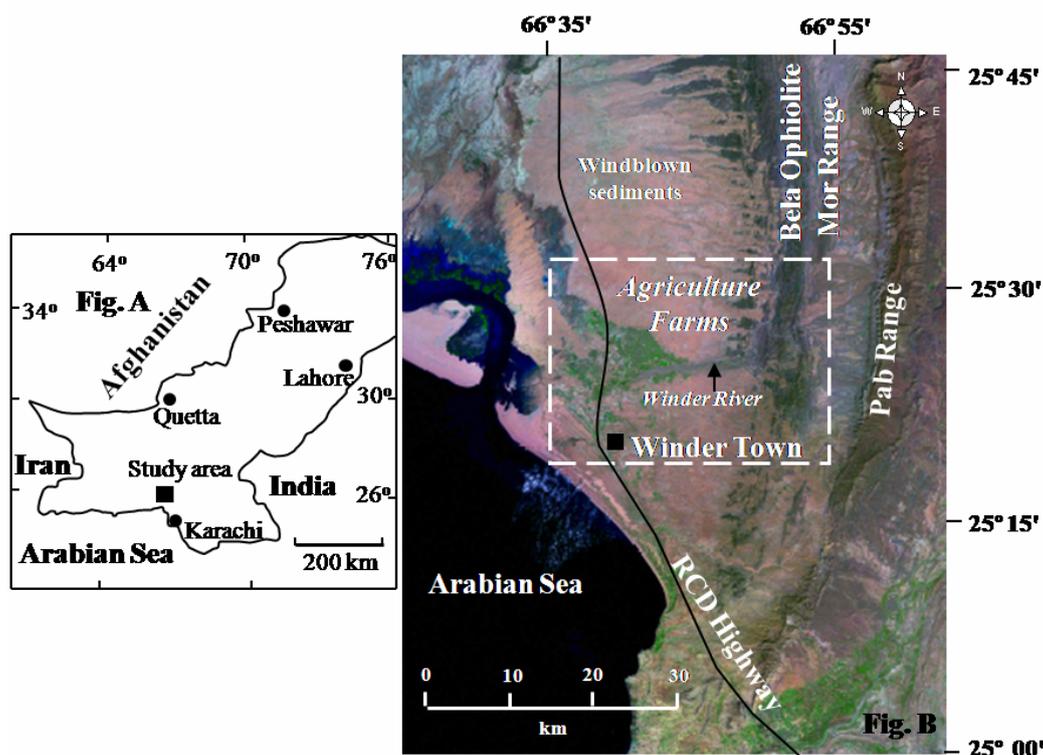


Figure 1: A. Map of Pakistan showing study area. B. Satellite image of the study area showing exposure of rock types and Winder Agriculture Farms.

## 2. METHODS AND MATERIAL

Groundwater samples were collected from 33 different localities of agriculture farms of the Winder area (Fig. 1). The electrical conductivity (EC), pH and Total Dissolved Solids (TDS) were determined by means of Denver Instrument, Model 50. Titrimetric methods were used for the determination of  $\text{HCO}_3$  and  $\text{Cl}$ , whereas  $\text{SO}_4$  was determined gravimetrically. Ca, Mg, Na and K were measured by AAS Hitachi-5000.

## 3. GEOLOGY

The study area lies in the southern extremity of the western fold belt. The Bela Ophiolite in association with sedimentary rocks of Jurassic (Mor Range) and Cretaceous (Pab Range) are exposed in the east of the study area in parallel belts (Fig. 1). Low-laying ophiolitic rocks of Cretaceous age are gradually concealed by the windblown sediments in the west. Rocks of the Mor Range consists of Ferozabad Group, comprised of Kharrari, Malikhor and Anjira formations (Shah, 2009). The stratabound replacement type (MVT) deposit is confined to the allochemical limestone beds of the Kharrari and Malikhor formations. Sedimentary exhalative mineralization (Sedex) is common in the topmost Anjira Formation. Sulphide mineralization comprises sphalerite, galena, pyrite and marcasite with minor chalcopyrite (Ahsan and Mallick, 1999). Outcrops of Sembar, Goru, Parh, Fort Munro, Mughal Kot and Pab formations are present in the Pab Range (Kazmi and Abbasi, 2008).

The Bela Ophiolite is linked with Alpine-Himalayan Mesozoic Ophiolite Belt. It is a harzburgite sub-type ophiolite, which is common in Tethyan Domain. It has characteristics of both suprasubduction zone and mid-ocean ridge settings and is also intruded by hotspot-derived magmas (Sheth, 2008 and Khan et al., 2007). It is represented by tholeiitic basalts, mafics and ultramafics. The study area is the part of lower unit of Bela Ophiolite in which ophiolite accretionary wedge and

trench sediments are common (Gnos et al., 1998) and intermittently exposed along the western contact of Mor Range.

## 4. RESULTS AND DISCUSSIONS

### 4.1 Water-Rock Interaction

#### 4.1.1 Composition

During weathering and circulation of water in rocks and soils, ions leached out and dissolve in groundwater. The geological formations, water-rock interaction and relative mobility of ions are the prime factors influencing the geochemistry of the groundwater (Yousef et al., 2009). Major ions and their ratios are significant to infer impact of rock chemistry on the composition of groundwater. Furthermore, principal component analysis (PCA) provides more robust technique for determining key variables in a multidimensional data set that shed some light on the origin of the elements (Zhou et al., 2009).

Geochemistry of groundwater is discussed by means of its major ions. Schoeller (1977) diagram provides a convenient way to present chemical composition of groundwater of a region. Plots of average composition, both in mg/l and epm/l are presented in Figure 2. The relative tendency of ions in mg/l shows  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  and  $\text{HCO}_3 > \text{Cl} > \text{SO}_4$ . The average ionic composition of groundwater is also represented by Stiff diagram (Fig. 2). The shape analysis of stiff diagram signifies dominance of Na-Cl (60%), while Ca-HCO<sub>3</sub> and Mg-SO<sub>4</sub> are nearly equal in proportion. Major ions in the rotated space diagram (Fig. 3) indicate their genetic affiliation.

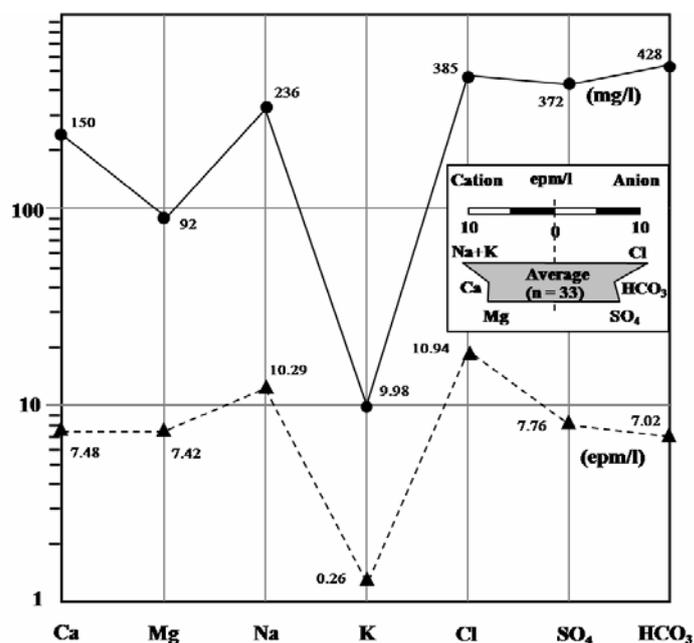


Figure 2: Schoeller diagram showing average composition in mg/l and epm of the groundwaters of Winder area. Stiff diagram is shown in inset.

#### 4.1.2 Sodium (Na) and Potassium (K)

The Na concentration in studied samples (50-665mg/l) is slightly higher than the permissible limit for agriculture purpose. In contrast to Na, K is very low and the K/Na ratio is 0.04. The low K in the groundwater shows good agreement with tholeiitic pillow basalt (Naseem et al., 1997). It is

also supported by low correlation matrix (Fig. 4) and both of them on PCA are plotted apart, indicating diverse behavior (Fig. 3). The very strong correlation matrix between Na and Cl (0.993) and overlapped plotting on rotated space diagram are valuable to appraise relation with seawater. The average Na/Cl ratio of the studied samples is 0.62 which is close to average oceanic water (0.55), indicating that NaCl is probably imparted from Arabian Sea, present in the west of study area (Fig. 1), but disturbed due to different magnitude of ion exchange. The molar Na/Na+Cl and Ca/Ca+SO<sub>4</sub> ratios are imperative to relate the genetic relationship (Hounslow, 1995). Groundwater of the study area show that majority of the samples are in the alignment from seawater to domain of evaporation (Fig. 5). The influence of evaporation in the study area also show compatibility with Jones et al. (2009) work, indicating high ionic Cl+SO<sub>4</sub> balance (760 mg/l) in contrast to HCO<sub>3</sub> (428 mg/l) in the groundwater (Table1).

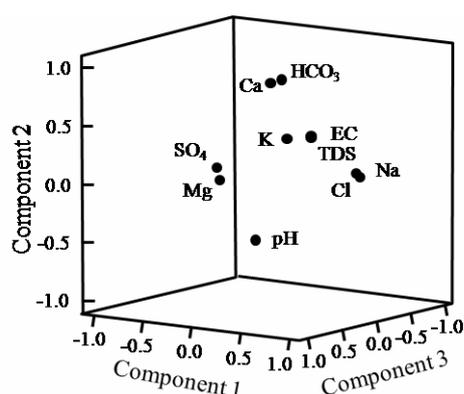


Figure 3: Rotated space diagram (PCA) showing the genetic affiliation of major ions in the water of the study area.

	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>
Ca	0.405 ■	0.356 ■	0.216 ■	0.969 ■■■	0.400 ■	0.715 ■
Mg		0.230 ■	0.001	0.340 ■	0.295 ■	0.96 ■■■
Na			0.225 ■	0.410 ■	0.993 ■■■	0.223 ■
K				0.258 ■	0.208 ■	0.029
HCO <sub>3</sub>					0.440 ■	0.430 ■
Cl						0.284 ■

**Key  
Correlation  
Matrix**  
 $r = 1.000$   
■■■■

Figure 4: Correlation matrix of major ions of groundwater of Winder Fruit Farms.

#### 4.1.3 Calcium (Ca) and Magnesium (Mg)

The Ca and Mg ions are significant to appraise the magnitude of seawater contribution. The low Ca/Mg ratio (0.3) may indicate seawater influence (Hem, 1989). The estimated av. values of Ca/Mg ratio is 1.63, indicating complexity in the budget of Ca and Mg of groundwater due to interaction with rocks and the arid climate of the study area. The Ca+Mg-HCO<sub>3</sub> of the study area range between 2.13 to 18.45 with a mean of 7.88 indicating that Ca and Mg are mainly driven from the weathering of ophiolites with influence of carbonate rocks. Han and Liu (2004) have used the variations in the composition of water (Mg/Ca versus Na/Ca) to distinguish limestone, dolomite and silicate rock sources of ions. The samples of the Winder area plots close to igneous rocks with influence of carbonate rocks of the area (Fig. 6).

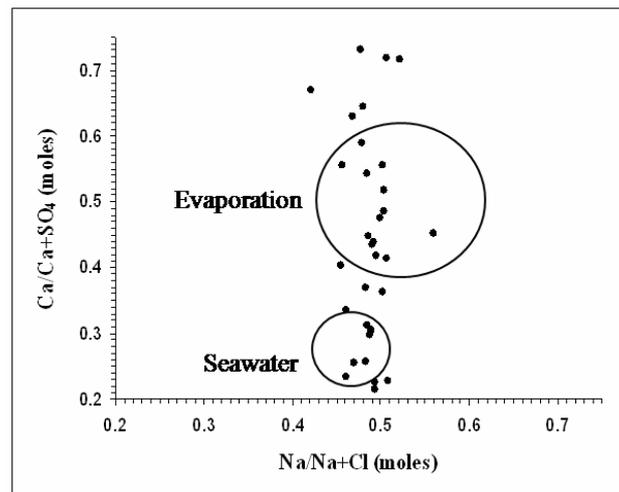


Figure 5: Molar  $\text{Ca}/\text{Ca}+\text{SO}_4$  and  $\text{Na}/\text{Na}+\text{Cl}$  to differentiate water of different origin. Domains for seawater and evaporation are after (Hounslow, 1995).

Aghazadeh and Mogaddam (2010) describe Chloro-alkaline Indices (CAI) to show the changes in chemical composition of groundwater during its travel in the subsurface. In case of ion exchange of Na and K from water with Ca and Mg from the soil, the indices are positive while if the exchange is reverse then the indices are negative. The statistics of CAI 1, 2 of the study area indicates 66% of the groundwater samples have positive and 34% negative values. It simply implies that the groundwater of Winder area has suffered ion exchange between alkali and alkaline earth metals. The process of ion exchange is further supported from low (av. 0.44)  $\text{Ca}/(\text{Ca}+\text{SO}_4)$  ratio (Hounslow, 1995).

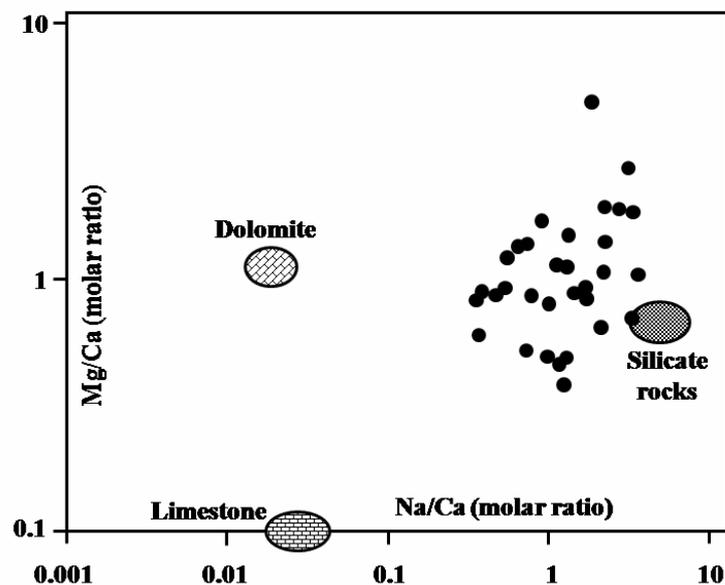


Figure 6: Plots of  $\text{Na}/\text{Ca}$  versus  $\text{Mg}/\text{Ca}$  ratios of groundwater of Winder area (Fields after Han and Liu, 2004).

#### 4.1.4 Chloride (Cl)

Chloride ion up to 70mg/l is considered safe. It cause severe problem in the crops at concentration  $>350\text{mg/l}$  (Hopkins et al., 2007). The content of Cl in the groundwater is best to study water-rock interaction. The basaltic aquifer has higher Na/Cl molar ratio in contrast to typical

rainfall values of 0.8 (Langmuir 1997). The studied samples have 0.72 to 1.27, suggesting some Na is derived from Na-bearing rocks or exchange with Ca. Groundwater having more HCO<sub>3</sub> and less Cl ions is the indication of natural water with no influx of pollution (Gholami and Srikantaswamy, 2009). The studied samples show Cl values ranges from 75 to 1200mg/l with a mean concentration of 388mg/l (Table 1). Mutual relationship of TDS vs. Cl/Cl+HCO<sub>3</sub> in form of Gibbs (1970) diagram also signifies dominance of rock weathering on some of the samples of the study area (Fig. 7). The average HCO<sub>3</sub>/Cl ratio is valuable to discriminate either seawater intrusion or rock weathering (El-Fiky, 2010). It is noteworthy that HCO<sub>3</sub>/Cl ratio of study area is 0.64, which is much higher than the average seawater ratio (0.004). Probably the high ratio is due to the weathering of carbonate rocks, exposed in the east of the area. The contrast behavior is also observed from PCA on rotated space diagram (Fig. 3).

Table 1: Statistical analysis of ions and important irrigation water parameters of Winder area.

	Minimum	Maximum	Average	SD	Median
<b>pH</b>	6.62	8.23	7.41	0.43	7.43
<b>EC dS/cm</b>	1.44	7.04	2.79	1.81	2.49
<b>TDS mg/l</b>	900	5400	2507	1326	2230
<b>Ca mg/l</b>	60	385	150	77.35	115
<b>Mg mg/l</b>	25	200	92	41.67	80
<b>Na mg/l</b>	50	665	236	166.14	160
<b>K mg/l</b>	2	24	9.98	5.43	10
<b>HCO<sub>3</sub> mg/l</b>	140	1050	428	216.84	365
<b>Cl mg/l</b>	75	1200	388	278.91	285
<b>SO<sub>4</sub> mg/l</b>	100	845	372	169.78	330
<b>RSC</b>	-18.45	-2.13	-7.88	3.84	-7.11
<b>Na %</b>	16.82	66.65	38.37	14.01	40.03
<b>SAR</b>	0.94	10.84	3.76	2.38	3.27
<b>PS</b>	4.45	42.64	14.82	8.53	12.13
<b>PI</b>	27.82	73.77	50.07	12.81	52.24
<b>MAR</b>	27.25	82.78	49.89	12.7	47.34
<b>KR</b>	0.2	2.03	0.73	0.44	0.68
<b>LDP</b>	1.00	2.68	1.75	0.46	1.75
<b>CAI1</b>	-0.344	0.267	0.012	0.10	0.02
<b>CAI2</b>	-0.117	0.152	0.189	0.06	0.02

#### 4.1.5 Sulfate (SO<sub>4</sub>)

Water containing more than 1000mg/l sulfate are harmful for plants (Sagnak, 2010). The concentration of SO<sub>4</sub> in the study area ranges from 100 to 845 with a mean concentration of 372mg/l. Sulfate ions have very strong correlation matrix ( $r = 960$ ) with Mg. The MVT/Sedex deposits of sulphide minerals within Ferozabad Group (Ahsan and Mallick, 1999) and MVS deposits of Bela Ophiolite are mainly responsible for the sympathetic relationship between Mg and SO<sub>4</sub> ions. The assumption also gets support from high Ca/SO<sub>4</sub> ratio (0.96), which is exceeding that

of seawater (0.40) and approaching a value of 1.0 which is probably resulting from dissolution of sulfate/sulphide minerals. In order to discriminate sulfate dissolution from sedimentary and igneous sources, molar ratio of  $\text{SO}_4+\text{HCO}_3$  is compared to  $\text{Ca}+\text{Mg}$  (Han and Liu, 2004). Nearly 50% of the samples of the study area show an excess of  $(\text{HCO}_3+\text{SO}_4)$  over  $(\text{Ca}+\text{Mg})$  indicates dissolution of silicate rocks, most probably from massive volcanic sulphides.

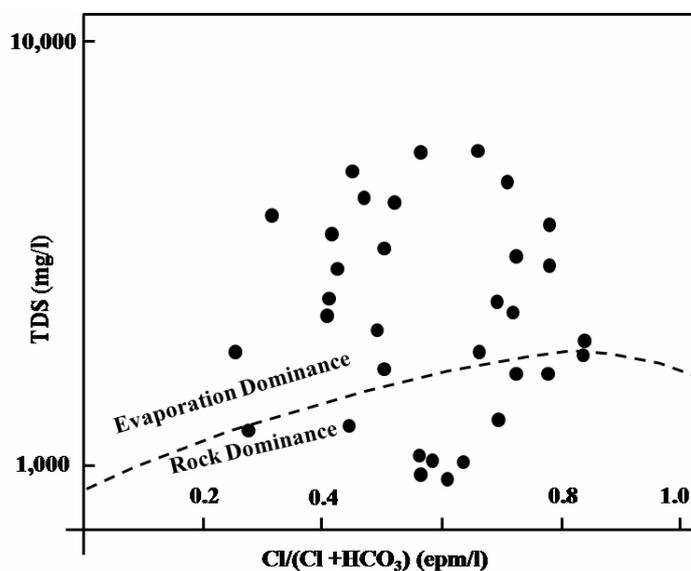


Figure 7: Dominance of rock and evaporation on log TDS vs.  $\text{Cl}/\text{Cl}+\text{HCO}_3$  of the study area (demarcation line after Gibbs, 1970).

#### 4.1.6 pH and Alkalinity

The pH and alkalinity are important factors influencing the suitability of water for irrigation purpose. The normal pH range for irrigation water is 6.5-8.4 (Bauder et al., 2010). The water samples of the study area having pH range from 6.62 to 8.23, indicating its suitability for irrigation purpose. The alkalinity is imparted due to  $\text{CO}_3$  and  $\text{HCO}_3$  ions in the ground water. The mean content of  $\text{HCO}_3$  is 428 mg/l, which is much higher than the maximum permissible limit of 244mg/l for crops (SAI, 2010). High  $\text{HCO}_3$  ions combined with Ca or Mg will precipitate as carbonate when the soil solution concentrates in drying conditions.

#### 4.1.7 Electrical Conductivity (EC)

The most significant water quality guideline on crop productivity is the water salinity hazard as measured by electrical conductivity (Johnson and Zhang, 1990). The samples of the study area indicates that 15% samples are in the range of medium salinity hazard, 55% are in the zone of high salinity while rest 30% samples show very high salinity hazard. The primary effect of high EC water is the inability of the plant to compete with ions in the soil (physiological drought).

#### 4.1.8 Classification

Piper (1953) classifies water types and hydrogeochemical facies on the basis of major ion chemistry in groundwater flow systems. Approximately 82% groundwater samples of study area show distribution of mixed-type cations, 15% are Na+K-type, while only one sample has influence of Mg-type water on piper diagram (Fig. 8). Among the major anions, 63% samples are plotted within the mixed-type and 33 % are decline towards Cl-type. The hydrofacies analysis of the study area reflects that water originates in the close geological environment. Majority of the studied

samples are plotted in the CaMgCl-type of water. According to Nagaraju et al. (2006), in this part of the trilinear diagram no ions are exceeded 50%. However few of them are NaCl-type (Fig. 8).

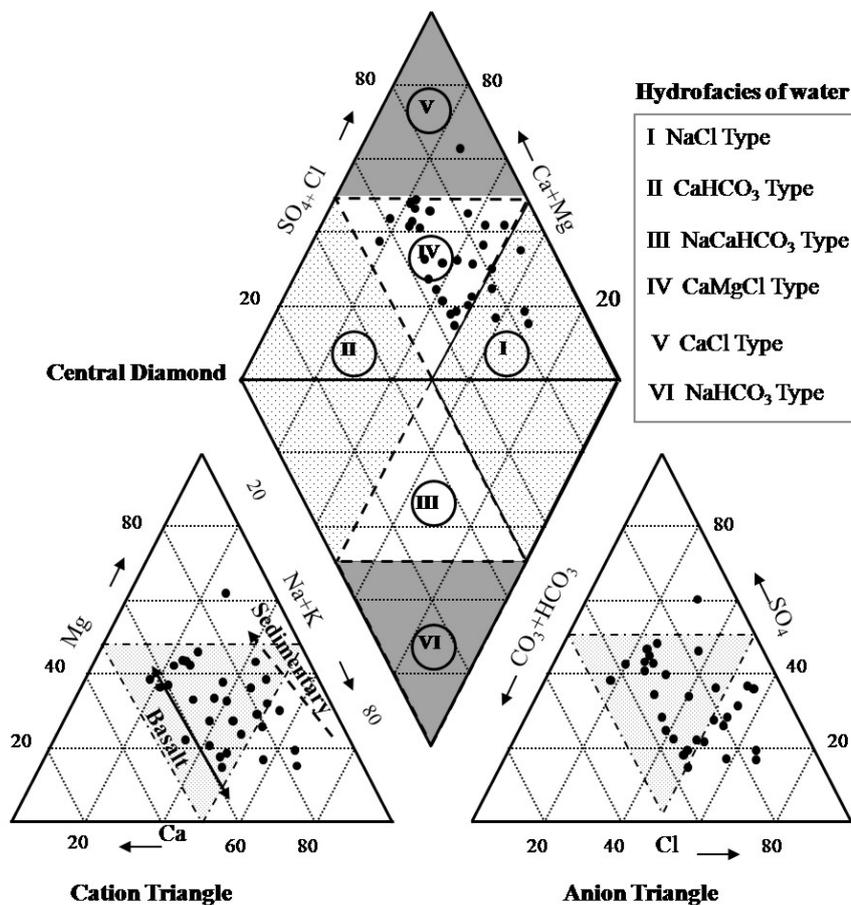


Figure 8: Piper diagram of groundwater chemistry in the study area. Arrows marked in the cation triangle is after Tweed et al., (2005).

## 4.2 Irrigation Water Quality

### 4.2.1 Residue Sodium Carbonate (RSC)

The RSC is a valuable parameter that has a great influence on the suitability of irrigation water (Bokhari and Khan, 1992). The RSC significantly influence the pH, EC and SAR of the irrigation water. The samples of the study area have RSC between -18.45 to -2.13, indicating good quality water for irrigation purpose. Continuous use of waters having RSC more than 2.5 meq/l leads to salt build up which may hinder the air and water movement by clogging the soil pores (Nishanthiny et al., 2010).

### 4.2.2 Sodium Percent (Na %)

It is the ratio of Na in epm in water to the total cations epm multiplied by 100. Irrigation water with Na% >60% may result in Na accumulation and possibly a deterioration of soil structure, infiltration, and aeration (Hakim et al., 2009). The values of the collected water samples ranged from 16.84 to 66.65 with an av. 38.37. The Na% and EC is important to categorize groundwater samples with respect to suitability as irrigation water (Khodapanah et al., 2009). The binary plot (Fig. 9) indicates that 16 samples are within the fair range, 14 samples are poor while 3 are in the

very poor water-type. Another important Na-bearing parameter is potential salinity ( $Cl+SO_4/2$ ). The estimated PS values of the Winder Agriculture Farm and surrounding is 4.45-42.64, with an average of 14.82. It is the amount of salt that gradually accumulate in the soil during repeated irrigation (Nagaraju et al., 2006 and Doneen, 1964).

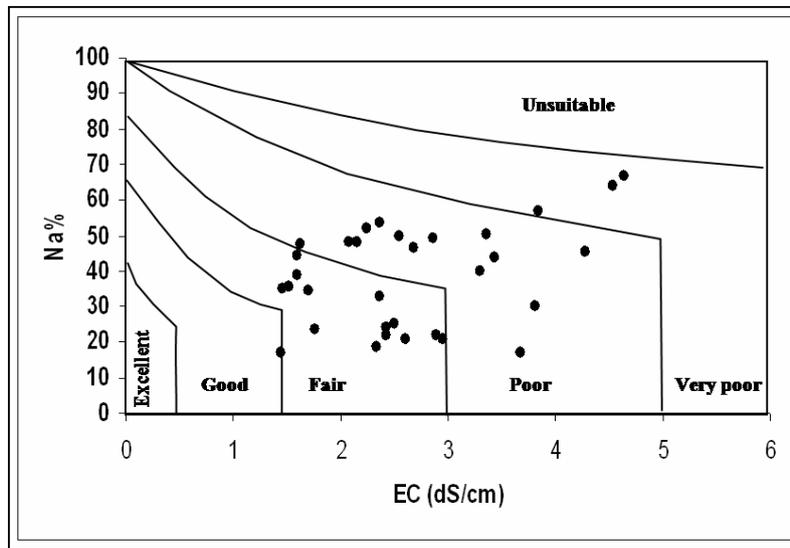


Figure 9: Na% vs. EC plots of the water samples of the study area and its suitability for irrigation.

#### 4.2.3 Sodium Absorption Ratio (SAR)

The Na or alkali hazard is expressed in terms of sodium adsorption ratio (Gholami and Srikantaswamy, 2009). The SAR values <10 is classified as excellent for irrigation. Values 10-28 are moderate and >28 are hazardous. The average SAR value of present study is 3.76 (Table 1), indicating water suitability for agricultural farms in the Winder area. Ramkumar et al. (2010) used Wilcox plot (SAR vs. EC) to develop the suitability of water for irrigation purpose. In the study area, nearly 30% groundwater samples fall in the each field of S1C3, S1C4 and S2C4, indicating low to medium SAR and medium to high salinity (Fig. 10). It is moderately suitable for irrigation purposes; however only 6% samples (2) occupies high hazard water-type (S3C4).

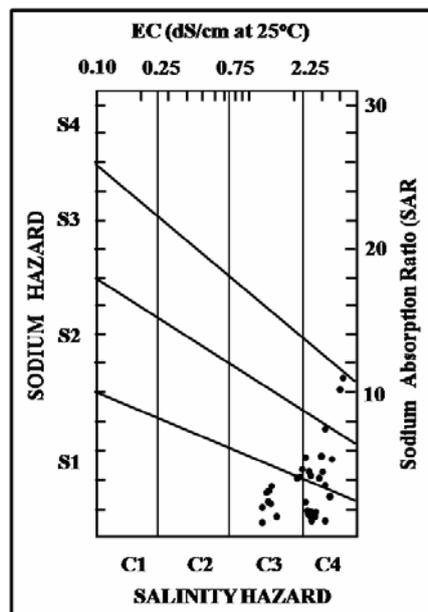


Figure 10: Classification of groundwater samples in relation to salinity and sodium hazard.

#### 4.2.4 Magnesium Absorption Ratio (MAR)

In natural waters, Mg in equilibrium state will adversely affect crop yields (Nagaraju et al., 2006). The magnesium hazard (MAR) of irrigation water is proposed by Szabolcs and Darab (1964) and redefined by Raghunath (1987). The MAR values exceeding 50 is considered harmful and unsuitable for irrigation use. In the analyzed groundwater samples, it is found between 27 and 82 (Table 1). The average is nearly 50, indicating that the groundwater is marginal for irrigation use with little harm with reference to Mg in the groundwater. Possibly high Mg in the water of study area is the reflection of pillow basalts, which contains more Mg.

#### 4.2.5 Permeability index (PI)

Doneen (1964) has assessed the suitability of water for irrigation, based on the permeability index. According to this classification, Class I and II possess maximum permeability >75% are classified good for irrigation while third category (Class III) having 25% maximum permeability are unsuitable for irrigation purpose (Nagaraju et al., 2006). In the present study, PI values vary from 27.82 to 73.77 (Table 1). On the basis of PI classification, the groundwater in the study area falls under class II and hence the water is considered suitable for irrigation.

#### 4.2.6 Kelley's Ratio (KR)

Kelley (1940) and Paliwal (1967) introduced an important parameter to evaluate irrigation water quality based on the level of Na measured against Ca and Mg. Waters with Kelley's ratio <1 are suitable for irrigation. The KR value of groundwater samples of Winder area are within the range of 0.2 to 2.03 with an average of 0.73, indicating the good quality of the groundwater for irrigation purpose (Table 1) Only 7 samples have KR values >1.

#### 4.2.7 Lime Deposition Potential (LDP)

A special parameter, called as Lime Deposition Potential (LDP) is assessed to evaluate LDP from the composition of cooling water (IFS, 1995). Water with high LDP usually leaves a spot of lime on fruits, which detract the value of the crop (SAI, 2010). The samples of the study area have LDP between 1.00 to 2.68 with a mean of 1.75 (Table 1), this value is more than the unit value of pH, it is likely that lime deposits will form on the fruit as a result of crop cooling.

## 5. CONCLUSIONS

Geochemistry of groundwater of Winder Agriculture Farms displays Na>Ca>Mg>K and HCO<sub>3</sub>>Cl>SO<sub>4</sub> trend. The type of water that predominates in the study area is Ca-Mg-Cl type, which is the best reflection of geology and climate of the area. The plots of studied samples on Gibbs diagram supports influence of rock weathering. The Mg/Ca versus Na/Ca diagram demonstrates major ionic contribution through igneous rocks with minor control of carbonate rocks. It is further established from cationic triangle of Piper diagram. High Na and very low K reflect genetic association with tholeiitic rocks of Bela Ophiolite. The Ca/SO<sub>4</sub> and Ca/Mg ratios of studied water samples are indicative of influence of MVS/MVT/Sedex deposits. The Chloro-alkaline Indices also suggestive for ion exchange mechanism. The Principal Component Analysis and strong correlation matrix portray genetic source of origin.

The pH, TDS and other major ions are within the specified limit for irrigation purpose except Na, which is at the margin. Important parameters such as RSC, SAR, PI and KR reveal as good quality water for irrigation purposes, while MAR is slightly higher for crops.

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