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Hydrochemical evaluation of groundwater suitability for irrigation in lower Sindh, Pakistan

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Abstract

Regular monitoring of groundwater quality is the key component for sustainable agriculture. In this study, 40 tube well water samples were collected from two districts (Hyderabad and Tando Allahyar) of lower Sindh to assess the water quality for irrigation. Collected water samples were used for the measurement of electrical conductivity (EC), total dissolved solids (TDS), pH, cations i.e., potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{2+}) and sodium (Na^+) and anions including bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), chloride (Cl^-), nitrate (NO_3^-) and sulphates (SO^{-2}). Residual sodium carbonate (RSC) and bicarbonate (RSBC), sodium adsorption ratio (SAR), permeability index (PI), magnesium adsorption ratio (MAR) and Kelly's Ratio (KR) were also calculated. Data was interpreted based on Food and Agriculture Organization (FAO) criteria. Piper plot, Wilcox diagrams and United States Salinity Laboratory (USSL) plots were used for water quality assessment. When compared to the permissible limits, around 77.5% samples for Na^+, 72.25% for Mg^{2+}, 57.5% for SO_4^{2-},50% for Cl^-, 42.5 % for KR, 32.5% in Ca^{2+}, 15% in RSBC, 10% in EC and TDS, 2.5% in pH, RSC, SAR and PI were not suitable for irrigation purpose. As per Piper diagram, predominantly underground water found neither anion nor cation dominant, but it was found (35% samples) in mixed zone (Na-Cl type). Wilcox diagram revealed that 22.2% samples were doubtful to be unsuitable for irrigation. The USSL plot demonstrated that 35% samples were in C1S1 category of water (Low Sodium-Low salinity). Overall results indicated that mixed ions were dominant in collected samples. Thus, cyclic or mixing of tube well and canal water should be encouraged for agriculture in lower Sindh.

Keywords: Tube well water quality**,** piper diagram, wilcox diagram, USSL plot, irrigation, Lower Sindh

Introduction

Groundwater is a key input for every life form existing on earth (Hassan and Hassan, 2017) and used for many purposes specially for domestic, irrigation, and industrial purposes (Nickson *et al*., 2005). Globally, about 70% of fresh water is consumed for irrigation that is 90% of the total water used for all other domestic and industrial purposes (FAO, 2010). During last two to three decades, the use of groundwater for irrigation has increased due to changing climate (Llamas and Martinez-Santos, 2005). According to estimates, about 3×10^{12} m^2 is under irrigation globally and 38% of these lands are irrigated with 545 km^3 of groundwater every year (Siebert *et al*., 2010). In some countries like India, China and USA 39, 19 and 17 Mha, respectively, of land is irrigated through groundwater (Madramootoo, 2012). By 2050, groundwater requirement is expected to increase to 70% for increasing food requirements of the population (World Bank, 2020).

The groundwater is the 2nd biggest source of irrigation in Pakistan after canal water (Sabeen *et al*., 2020). The dependency on groundwater has been increased during past few years to feed the growing population and limited availability of fresh water (Qureshi, 2020). The increasing use of groundwater has decreased the quality of groundwater for irrigation due to increasing soil salinity and resultantly deteriorates the quality of soil directly or indirectly affecting the plant growth as well as food productivity (Irfan *et al*., 2014). There are many factors including physical and chemical that alter quality of groundwater in any area which are largely affected by geological formation (Magesh and Chandrasekar, 2011), mineralogy of the aquifer, underground recharge pathways and other factors including

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Table 1: Equations used for calculating different water quality parameters

Paramter	Formula	Reference
Sodium Adsorption Ratio	$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$	USSL, 1954
Residual Sodium Carbonate	$RSC = (CO_3 + HCO_3) - (Ca^{2+} + Mg^{2+})$	USSL, 1954
Kelly's Ratio	$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$	Kelley, 1940
Magnesium Adsorption Ratio	$MAR = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100$	Raghunath, 1987
Sodium %	$Na\% = \frac{(Na^{+} + K^{+}) \times 100}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})}$	Todd, 1995
Residual Sodium Bicarbonate	$RSBC = HCO_3 - Ca^{2+}$	Gupta and Gupta, 1987
PI = Permeability index	$PI = \frac{(Na^{+} + \sqrt{HCO_3})}{(Ca^{2+} + Mg^{2+} + Na^{+})} \times 100$	Doneen, 1964

type of rock and climatic changes (Elhag, 2016). Due to stress on natural resources, especially water, the conservation and proper use of such resources has become major challenge for human beings in recent years (Abbasnia *et al*., 2018). According to FAO (2012), Pakistan is expected to face acute shortage of water by 2035 and it likely will be included in the list of water scarce countries. So, it should be of paramount priority to monitor regularly and conserve groundwater (Suthar *et al.*, 2019).

Sindh is the 2nd most thickly populated province in Pakistan, divided in three regions including upper, central and lower Sindh. Lower Sindh is considered as fertile region of Sindh and mainly relies on freshwater resources (Talib *et al.*, 2019). However, in this region, agriculture is severely affected due to shortage of freshwater (Mari *et al.*, 2017). Thus, alternate water bodies such as groundwater use are increased for irrigation purpose. Some studies conducted at different parts of lower Sindh showed that quality of groundwater is unsuitable for irrigation (Talib *et al.*, 2019). For this purpose, the time-to-time evaluation of groundwater for quality assessment is a vital tool to manage the available water sources for their utilization for improving crop production (Mohamed *et al*., 2019). In view of above facts, the present study was proposed and conducted in two major agricultural districts, Hyderabad and Tando Allahyar of lower Sindh where crops like, cotton, wheat, sugarcane, maize and vegetables and fruits are grown at large area and extensively irrigated by groundwater due to limited availability of canal water in the area (Qureshi *et al.*, 2008). The results of this study are expected to characterize groundwater hydrochemically for irrigation use. Furthermore, findings of the study will facilitate to understand adverse effects associated with use of poor groundwater and its management for irrigation purpose in lower Sindh.

Materials and Methods

Site description and water sampling strategy

The study took place in two districts of Sindh province including Hyderabad and Tando Allahyar. The area is under high influence of tube well water irrigation during shortage of water. The district Hyderabad has population of 2,199,463 persons and district Tando Allahyar has estimated population of 836,887 people (Pakistan Bureau of Statistics, 2017). Most people living in rural areas of both districts depend upon the agriculture. The climate of study area often remains hot during summer (average temperature 40 °C) and cold in winter (average temperature 27 °C). The average precipitation is around 136 mm (Pak Met, 2021). The study area is lying in alluvial plain, and soils are medium to coarse textured and calcareous in nature.

From each district, ten (10) villages, having large population, were selected for water sampling during May and June, 2019 and the geological locations were recorded through coordination device and area map was created using Google application. Before water sampling, tube wells were operated to remove stagnant water from pipes for two minutes. Two water samples from each location were collected in 500 mL clean plastic bottles. The samples were transported and brought to Laboratory at Drainage and Reclamation Institute of Pakistan (DRIP) Tandojam for analysis.

Characterization of groundwater

Different water quality parameters including electrical conductivity (mS cm^{-1}), pH, cations (mg L^{-1}) potassium (K^{+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}) and anions (mg L^{-1}), bicarbonate (HCO_3^-), carbonate (CO_3^{-2}), chloride (Cl^-), nitrate (NO_3^-) and sulfate (SO_4^{-2}) were determined. The standard methods for cations and anions analysis were followed (APHA, 1995). The RSC (meq L^{-1}), SAR, soluble Na (%), RSBC (meq L^{-1}), PI, MAR and KR were calculated to determine the water quality according to standard equations (Table 1). The Piper's diagram (Piper, 1944) was constructed by using MODFLOW, Version 4. U.S. to describe the hydrogeochemical facies of the study area. Quality of groundwater was categorized according to standards of Food and Agriculture Organization (FAO, 1989), USSL (1954) and Wilcox (1955) for measuring concentration of cations, anions; salinity and Na^+ hazards and total salt concentration, respectively. The descriptive statistics (mean, minimum, maximum, median and mode) was calculated using Microsoft Excel.

Table 2: Descriptive statistics of measured parameters for water suitability for irrigation on the basis of cations and anions

Parameter	Unit	Min	Max	Mean	Std Dev	Median	Mode	Permissible limits *	Unsuitable Samples	Suitable Samples (%)
Bicarbonate	(mg L^{-1})	190.0	500.00	347.75	83.16	350.00	350.0	500	0	100
Carbonate	(mg L^{-1})	0.00	30.00	0.75	4.74	30.00	-	90	0	100
Chloride	(mg L^{-1})	18.0	900.00	176.93	186.45	109.50	60.0	106	20	50
Nitrate	(mg L^{-1})	0.00	2.30	0.80	0.56	0.80	0.50	30	0	100
Sulfate	(mg L^{-1})	8.0	970.00	279.53	226.75	205.00	305.0	180	23	43
Calcium	(mg L^{-1})	4.00	220.00	70.70	49.58	60.00	80.0	80	13	68
Iron	(mg L^{-1})	0.01	10.10	0.45	1.60	0.13	0.03	5	1	97.5
Magnesium	(mg L^{-1})	7.75	315.00	60.48	55.68	52.25	55.89	35	29	28
Potassium	(mg L^{-1})	1.30	14.10	6.21	2.74	5.750	5.50	30	0	100
Sodium	(mg L^{-1})	0.30	620.0	208.18	161.85	139.00	70.0	69	31	23

*The permissibility of cations and anions are given according to (McKee and Wolf 1963; Ayers and Westcot 1985; Duncan *et al*., 2000; Sharifi and Safari Sinegani 2012; Nagaraju *et al*., 2014)

Results and Discussion

Cations and anions concentration in ground water

The descriptive analysis of anions and cations is presented in Table 2. The minimum and maximum HCO_3^- concentration was 190 and 500 mg L^{-1}, respectively, with mean of 348 mg L^1. Among all the samples collected during the study, CO_3^{-2} was detected at the rate of 30 mg L^{-1} only in one sample. The other anions such as Cl^-, NO_3^-, and SO_4^{-2} ranged from 18-900, 0.00-2.30 and 8.0-970 mg L^{-1} with the mean of 176.93, 0.80 and 279.53 mg L^{-1}, respectively. The maximum permissible limits of anions such as HCO_3^-, CO_3^{-2}, Cl^-, NO_3^-, and SO_4^{-2} for irrigation were 500, 90, 106, 30 and 180 mg L^{-1}, respectively (Ayers and Westcot 1985; Duncan *et al.*, 2000; Sharifi and Sinegani, 2012). According to the standard limits, 50% of the samples were unfit for irrigation on the basis of Cl^- concentration, whereas 57% samples were not suitable on the basis of SO_4^{2-}. As per previous studies, waters high in CO_3^{2-}, can enhance the Na^+ hazard in soil solution concentration through evapotranspiration which ultimately affects the quality of soil (Zaman *et al*., 2018). Further, sea intrusion can increase Cl^- occurrence in groundwater (Satheeskumar and Subramani, 2016).

The Ca^{2+} ranged from 4 to 220 with the mean of 70.70 mg L^{-1}. The Fe^{2+} was present in traces and ranged 0.01 to 10.1 mg L^{-1} in all the tested samples with the mean of 0.4498 mg L^{-1}. The mean Mg concentration 131.58 mg L^{-1} was measured in all the samples, that ranged from 7.75 to 315 mg L^{-1}. The results further revealed that the minimum and maximum concentration of K was 1.30 mg L^{-1} and 14.1 mg L^{-1}, respectively. The Na level in the collected water samples ranged from 0.30-620.0 mg L^{-1}. The maximum permissible limits of measured cations for irrigation were 80, 5, 35, 30, 69 mg L^{-1} for Ca^{2+}, Fe^{2+}, Mg^{2+}, K^+ and Na^+, respectively (Duncan *et al*., 2000; Sharifi and Sinegani 2012; Nagaraju *et al*., 2014). As per standard permissible limits, 13 (32%), 1 (2.5%), 29 (72%) and 31 (77%) samples were unfit for irrigation on the basis of excess amount of Ca^{2+}, Fe^{2+}, Mg^{2+} and Na^+, respectively. The Fe in water is present mainly in ferric (Fe^{3+}) and ferrous (Fe^{2+}) states particularly in well aerated conditions. The Fe concentration in groundwater is largely affected by rock and mineral dissolution, acid mine drainage and sewage water of Fe related industries (Okun, 1983). K is one of the essential nutrients for the development of plants. The K mobility in soil largely depends on the soil texture (Neves *et al*., 2009), cation exchange capacity (CEC) and solubility of the used

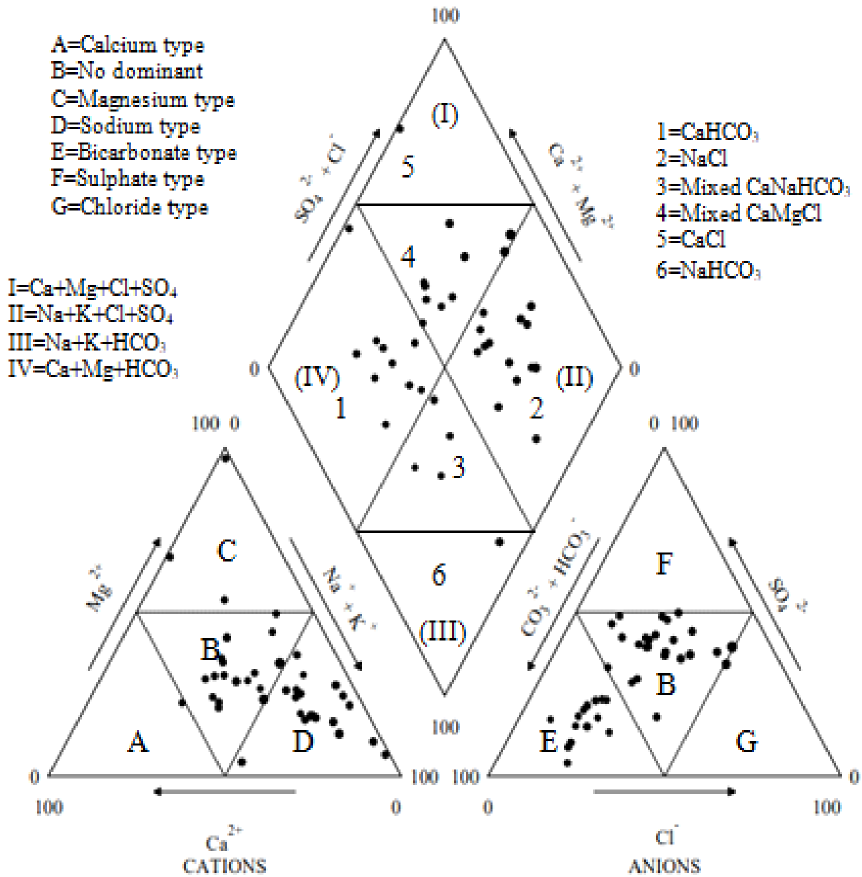

Figure 1: The hydrochemical facies of groundwater are presented (Piper's diagram)

fertilizer (Rosolem *et al*., 2006). The Na^+ is considered to be hazardous when Na^+ contaminated water is used for irrigation, especially, to fine texture soils as it deteriorates soil structure and causes sodicity. The Ca and Mg counteract sodicity if Na contaminated water is used for irrigation (Gupta and Gupta, 1987).

Groundwater hydrochemical facies

Piper diagram is an important tool to measure geochemical changes in groundwater (Piper, 1944). The Figure 1 showed that the dominant cations i.e., Na^+ and K^+ were found in right lower part of the cation triangle. The second most area where the samples are falling is non dominant region. Further, anion triangle indicated that most of the samples were mixed type. The diamond shaped field of piper diagram revealed that one sample was in type I ($Ca+Mg+Cl+SO_4$) area, fourteen samples were in type II area which is comprised of $Na+K+Cl+SO_4$, one sample in type III ($Na+K+HCO_3$) area and nine samples were in type IV area that is group of $Ca+Mg+HCO_3$. Furthermore, ten samples were in the category of mixed Ca-Mg-Cl whereas; four samples were in mixed Ca-Na-HCO_3 category. The mixed zones (3 and 4) showed that the groundwater found neither anion dominant nor cation dominant, but it was noticed as mixed zone having Na-Cl type (Todd and Mays, 2005). These results associated likely to the fact that groundwater of study area might be influenced by fresh recent recharge of groundwater with dominant dissolution process or water mixing with no dominant ion either cation or anion and flow of irrigation return (Vasilache *et al.*, 2020). Generally, piper diagrams are believed as suitable strategy to classify groundwater bodies, based on the ionic composition (Al-Omran *et al.*, 2012). The groundwater is one of the most important sources of irrigation water. The demand of water for agriculture is increasing day by day due to growing global population and climate changes (Qureshi, 2020).

Groundwater suitability based on pH, TDS and Na+ (%) and some calculated indices for irrigation purpose

The pH of water samples ranged from 6.9 to 8.5. Moreover, the mean of pH (7.38) of all the groundwater samples was alkaline in nature (pH: 7.10 to 8.50) and found within the safe limit i.e 7.0 to 8.5 (Ayers and Westcot, 1985) as indicated in Table 3. The maximum TDS was recorded as 3353 mg L^{-1} while minimum was 4.9 mg L^{-1} with mean value of 1113 mg L^{-1}. According to classification of TDS (Ayers and Westcot, 1985), only 4 samples were classified as severe saline water and 36 of samples were suitable for irrigation. For evaluating irrigation water quality, these parameters are widely used (Ayers and Westcot, 1985).

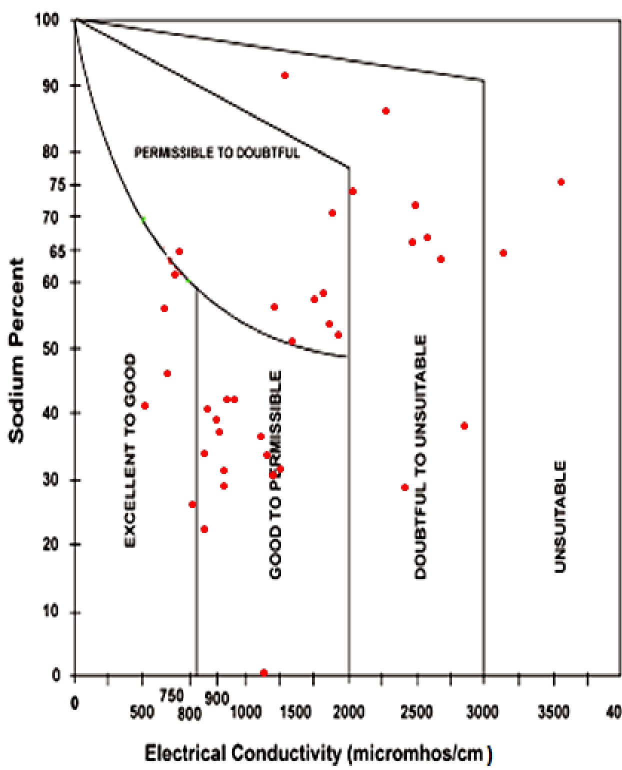

Figure 2: USSL diagram. Irrigation water quality classification on the basis of total salt concentration and sodium percent

Soluble Na(%)

The soluble Na (%) is common indicator for water quality assessment for irrigation (Wilcox, 1955). The results in Figure 2 revealed that 50% of the water samples were in good category for irrigation. Moreover, 20% water samples in permissible to doubtful range, 22.2% was under doubtful unsuitable category and rest of the samples were unsuitable. The collected samples were subject to test and found that the maximum soluble Na^+ (%) was 92.09, whereas minimum percentage of soluble Na^+ was 1.10. It is revealed that water with high Na^+ can retard the growth of plants and impede permeability of soil (Joshi *et al*., 2009; Bhat *et al.*, 2018). Further, higher Na^+ (%) may accumulate Na^+ in soil and may cause destruction of soil structure and reduction in infiltration rate and aeration in soil (Naseem *et al.*, 2010). Higher Na^+ (%) in some water samples might also be linked to (a) long residence time of water, (b) dissolution of minerals and (c) contamination of irrigation water through chemical fertilizers (Bhat *et al.*, 2016). According to Wilcox (1955), water is considered as excellent if the soluble Na^+ is less than 20%, good if it ranges from 20-40, fair when it is between 40-80 and poor if it exceeds 80%. As per these criteria, one sample was fallen in excellent category, 14 in good, 24 in fair and only two samples were in poor category. Regarding Cl^- concentration in ground water, around 50% samples were unfit for irrigation in this study. The Cl^- is known as the most vulnerable ion than the SO_4^{2-} in irrigation water (Verma *et al.*, 2007) due to its inherited property that Cl^- is not adsorbed to clay colloids and easily leached and moves to root zone. Upon arrival in root zone, Cl^- is easily up taken by the plant and can cause leaf burn or develop injury symptoms if its concentration increases beyond tolerance limit (Ayers and Westcot, 1985; Bhat *et al.*, 2018). Increase in Cl^- and SO_4^{2-} concentrations in groundwater in this study was likely due to dissolution of halite (NaCl) or gypsum ($CaSO_4$) mineral containing rocks and ion exchange of Ca-Mg (Mazor *et al*., 1993). The TDS expressed in terms of EC, which reduces the osmotic potential of soil resultantly decrease availability of water and nutrients in soil for plants (Saleh *et al*., 1999). High TDS in few water samples in this study might be linked to high concentration of some cations and anions in groundwater (Khemani *et al.*, 2012).

Sodium adsorption ratio

Sodium adsorption ratio (SAR) was found between 0.01 and 18.09. Out of 40 samples, 37 were excellent for the use of irrigation (Table 3). Moreover, two samples were under the category of marginal suitable water. Only one sample with the SAR value of 18.09 was unsuitable. The USSL (1954) plot demonstrated (Figure 3) that most of the samples (35%) under the category of C1S1 (Low Sodium-Low salinity) followed by C2S1 (Low sodium-medium salinity type) with 30% of total analyzed samples. Five (12.5%) samples were observed to be related to C2S2 region (Medium sodium-medium salinity) and two samples were in C2S3 and C3S2 regions. Furthermore, only one sample was in C3S1, C3S3, C4S2 and C4S3. Previous studies indicated that the water which falls under C1S1 and the C2S1 categories can be used on all type of soils, whereas; the water classes C3S1 and C3S2 can be considered for irrigation of only semi-salt tolerant and salt tolerant crops where proper drainage facilities are available (Prasanth *et al*., 2012).

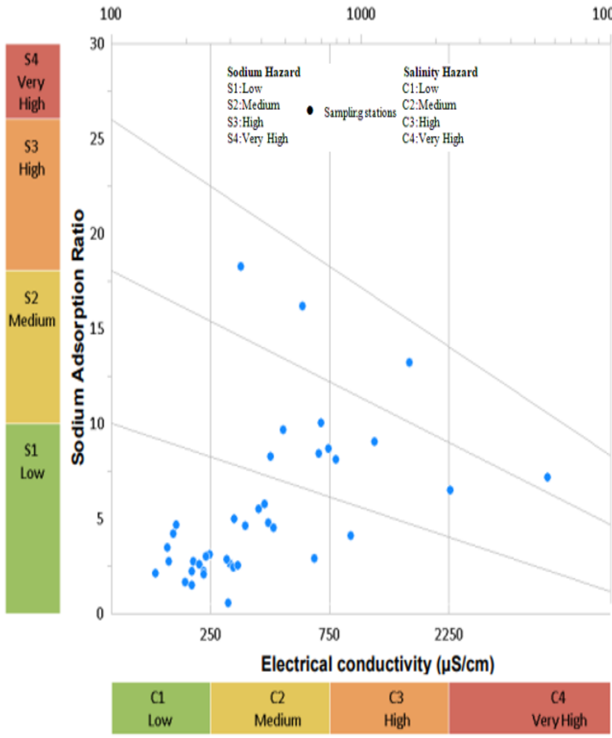

Figure 3: Wilcox diagram. Irrigation water quality classification on the basis of salinity hazard and sodium hazard

In hydrochemistry, SAR represents the Na hazard in the irrigation water and indicates how much Na will be expected to be adsorbed by the soil (Sattari *et al*., 2020). The high values of SAR indicated that the Na would increase the dispersion of clay colloids when they come in contact with soil (Temizel and Tok, 2019). This resulted in the replacement of Ca and Mg ions in the soil which might have damaged the soil structure (Lloyd, 1985). The increase in SAR up to 30 may lead to increase in crusting of soil, poor seedling emergence and poor soil aeration (Shah and Mistry, 2013).

Residual sodium carbonate (RSC)

The RSC ranged between -14.45 to 7.49 me L^{-1} (Table 3). Among all the samples collected in this study, 97.5% samples were found to be good for irrigation. Moreover, one sample have found unsuitable for irrigation. According to USSL (1954) and Sadashivaiah *et al*. (2008) the water is considered good when the RSC values are less than 1.25 me L^{-1}. Similarly, the water samples are grouped as doubtful/marginal when the RSC ranges from 1.25 to 2.5 me L^{-1} and unsuitable if the values are more than 2.5 me L^{-1}. The irrigation water with high RSC value need special irrigation management strategy and regular monitoring is needed for soil salinity (Nishanthiny *et al*., 2010).

Magnesium adsorption ratio (MAR)

During this study, the maximum calculated MAR value ranged between -0.21-51.58 (Table 3). It is measure of Mg hazard which was introduced by Paliwal (1972). According

Table 3: Different quality parameters of collected samples analyzed for irrigation purpose

Indices	Min	Max	Mean	Sd Dev	Permissible limit	Unsuitable Samples	Suitable Sample %	Reference
EC	500.	5240	1755.70	1009.34	3000 micro-S cm^{-1}	4	90	FAO, 1989
TDS	4.90	3353	1113	660.40	450-2000 mg L^{-1}	4	90	FAO, 1989
pH	6.90	8.50	7.3750	0.2844	6.5 - 8.4	1	97.5	FAO, 1989
RSC	-21.49	7.49	-2.26	4.95	≤2.5 meq L^{-1}	1	97.5	USSL, 1954
SAR	0.01	18.09	4.89	4.07	≤18 meq L^{-1}	1	97.5	Todd 1995; USSL, 1954
SSP	1.10	92.09	49.73	18.81	≤60 meq L^{-1}	12	70	Todd (1995)
RSBC	-4.93	7.50	2.17	2.61	≤5 meq L^{-1}	6	85	Gupta 1987; Oladeji *et. al*., 2012
PI	20.11	110.22	66.95	17.62	>25 meq L^{-1}	1	97.5	Doneen (1964)
MAR	-2.00	51.58	4.70	8.55	≤50 meq L^{-1}	0	100	Ayers and West cot, 1985
KR	0.00	11.62	1.51	1.99	≤1 meq L^{-1}	17	57.5	Kelly (1963)

to MAR index, if Mg hazard value (>50%) increases, crop yield will be decreased and soil will become alkaline (Joshi *et al*., 2009). Based on the results, only one sample was found to be beyond acceptable level of MAR. The acceptable MAR in the irrigation water is 50% (Ayers and Westcot, 1985) when it is calculated in percentage.

Residual sodium bicarbonate (RSBC)

In the collected samples, the calculated RSBC was in the range of -0.28 me L^{-1} to 6.78 me L^{-1} (Table 3). According to worldwide irrigation water quality guidelines, the RSBC value should not cross 3.0 me L^{-1} and if exceeded the water will not be considered as suitable for irrigation purpose (Jadhao, 2016). As per obtained results of the present study, 13 out of 40 samples were found to have more RSBC ratio as compared to standard allowable value.

Permeability index

The permeability index (PI) of measured samples was found between 20.11 to 110.22 % (Table 3). Out of 40, 29 samples were under the Class I and Class II with 75% of permeability as per Doneen's chart (Domenico and Schwartz, 1990). However, 11 water sources were found unsuitable for irrigation purpose. The PI is one of the most important parameters and it is used to assess the chemical composition of groundwater with its mobility in aquifer (Saraswat *et al.*, 2019). From ecological perspective, high PI measure would indicate extensive contamination of groundwater from hazardous materials (Al-Tabbal *et al*., 2012).

Kelly's ratio (KR)

Among the total collected water samples (40), 21 samples were found fit for irrigation purpose as their Kelly's ration (KR) was less than 1. According to Kelly (1963), the KR should not be exceeded than 1. The remaining water samples ratio was above 1 so they were not fit for irrigation purpose. Moreover, Ramesh and Elango (2012) in their study indicated that groundwater is considered as suitable for irrigation if KR value would be less than 1 and beyond this groundwater is considered unsuitable for irrigation.

Conclusion

It is concluded that majority of the groundwater samples were not suitable for irrigation in Na^+ (77.5%), Mg^{2+} (72.5%), SO_4^{2-} (57.5%), Cl^- (50%), KR (42.%), Ca^{2+} (32.5%), RSBC (15%), EC (10%) and TDS (10%) based on FAO guidelines. As per Piper diagrams, groundwater was found in mixed zone ((Na-Cl type). Wilcox diagram indicated that around 22% water samples were doubtful for irrigation. Further, 35% were found in C1S1 (Low Sodium-Low salinity) category of water according to USSL plot. These results suggest that careful management of groundwater through mixing canal water should be employed in study area to avoid harmful effects of groundwater on soil as well as on crops. Further, regular monitoring program of groundwater should be designed to mitigate future consequences of poor groundwater use for irrigation in selected areas of lower Sindh.

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