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## Groundwater Quality Assessment in and Around Kalu Khuhar, Super Highway, Sindh, Pakistan

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**Abstract:** Twenty one representative groundwater samples were collected from Sari, Liari, Lang and other drainage basins. The samples were analyzed to elaborate geochemical characteristics, ionic composition and hydrofacies. Drinking and irrigation water quality were also assessed. Small seasonal aquifers were present within sub recent valley fills, above the folded rocks of tertiary period. However, permanent aquifers were located within the sandstone of Nari Formation of Oligocene age. The major ionic composition showed a wide variation in the hydrochemical properties of the groundwater of the area. The degree of correspondence among cations and anions has been estimated in order to evaluate their mutual relationships. Abundance of major elements was interpreted in relations to the composition of aquifer, bedrock and climatic conditions, which may contribute to the genetic affiliation. The important hydrogeophysical parameters have been estimated for reasonable assessment of groundwater quality for domestic and irrigation purposes. Ionic relationship is exhibited in the form of Stiff diagrams. Piper diagram has been used to classify the hydrofacies. Relationships between various elements have been identified from correlation coefficient, reflect genetic associations. Strong positive correlation exists between Na-K, Na-Cl, Na-SO<sub>4</sub> and K-SO<sub>4</sub>.

**Key words:** Kalu Khuhar, super highway, groundwater quality, Sindh, Pakistan

### INTRODUCTION

Water is very essential for human life especially in arid regions where the evaporation rates are high and the refilling resources are limited<sup>[1]</sup>. The climate of the Sindh is very arid and characterised by high temperatures and low precipitation. Furthermore, Sindh is facing a severe shortage of water since the last two decades. The exploration and evaluation of groundwater is crucial and required more work to meet the future demands. There has been limited published work on the groundwater of Sindh<sup>[2]</sup>.

In and around Kalu Khuhar, the water demand has drastically increased due to the expansion in the agriculture, poultry, dairy and other industries in the area. Groundwater is the potential source because the area has no river or canal system. The aim of this study was to present a systematic approach to evaluate the geochemistry of groundwater and to elaborate relation between bedrock and climatic conditions for the distribution of elements in the groundwater. It also aims to develop easier empirical relationship for use in determining the groundwater composition, quality and its suitability for domestic and irrigation purposes and possible health hazards.

### MATERIALS AND METHODS

Groundwater samples were collected from Kalu Khuhar and adjoining areas of Super Highway (Fig. 1), during the September to December, 2004. These water were obtained mainly from dug-wells, at a depth of ~ 200 ft. Total Dissolved Solids (TDS), pH and electrical conductivity were determined at site with the help of Denver Instrument Model 50. These samples were stored in pre-sterilized polyethylene bottles. Chloride meter (Jenway PCLM 3) was used for determination of chlorides. Sulphate was determined by barium chloride precipitation method and carbonate and bicarbonate were estimated by titration with 0.1 N hydrochloric acid. Calcium and magnesium were measured by EDTA titration. Alkalis were estimated using Gallenkamp FGA 350 L flame photometer.

**Geology and hydrogeology:** Area of study was located within southern most domain of Kirthar Fold Belt. In Sindh Province, Cretaceous to Recent sedimentary rocks are well exposed. The formations have been deposited in varieties of sedimentary environments which are the reflections of changing regional tectonics<sup>[3]</sup>. Laki Formation of Ypresian age is mainly developed in the

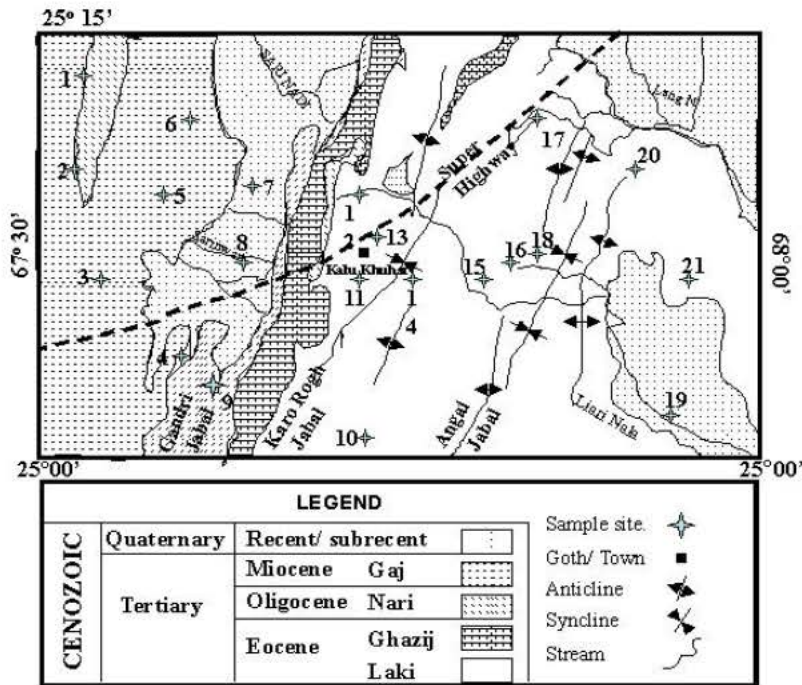


Fig. 1: Geological map of the study area showing sample locations

southern part of the Kirthar Province of Lower Indus Basin. It is confined to a stripe that extends from the Lakhi and Bhadra ranges in the north to hills near Thatta in the south<sup>[4]</sup>. The western stripe of the study area has Ghazij, Nari and Gaj formations of Eocene, Oligocene and Miocene ages respectively (Fig. 1). Hydrophile elements derived through the chemical weathering of above rocks are dispersed in ground and stream waters. The abundance and mobility of these elements largely depend upon the nature of bedrock, climatic conditions and other physicochemical environments<sup>[5]</sup>.

The area is intensively folded. The Surjan and Karo Rogh are prominent anticlinal structures (Fig. 1). These folds have high to gentle dips and are asymmetrical and plunging. The fold axes run nearly NS that plunge south and SW. In the study area, numerous normal faults are present but their displacement is not significant<sup>[6,7]</sup>. Western flank of Surjan anticline is bisected by a normal fault that is traceable along the strike for more than 30 km<sup>[8]</sup>.

The western areas have the influence of Mol and Sari streams whereas Lang and Liari streams are situated in the eastern part of the study area. In the major part of the area, water is present at variable depths. Stable aquifers are present in the Nari Formation which is present at 200 to 400 ft depth. The source of this subsurface water is percolating rain water.

## RESULTS

**Geochemistry:** The distribution pattern of major ions showed compositional variation in the groundwater samples (Table 1), the general trend among cations showed  $Na > Ca > Mg > K$ . Similarly, anions display  $Cl > SO_4 > HCO_3 > CO_3$  distribution pattern. The dispersion of ions in the groundwater of these drainage basins probably indicates nearly similar geochemical environment, climatic condition and pH, except few anomalies.

Sodium was the most abundant element found in the groundwater of study area. It ranged from 70 to 739 with a mean of 270 ppm (Table 1). It showed variable enrichments in the samples of the study area so that Na has high standard deviation (171). In contrast, K shows nearly consistent values 6-40 with an average of 16 ppm (Table 1), Na and K, both have good solubility and mobility and do not precipitate at any pH<sup>[9]</sup>. The geochemical environment does not much favour high Na or K addition in the groundwater. The possible source of contamination was the sea water. It is important to note that the mutual relation between Na and Cl is positive linear (Fig. 2A), indicating genetic relation with meteoric water<sup>[1]</sup>. The above statement gets support from the correlation coefficient, which is 0.910 for Na-K, 0.841 for Na-Cl and 0.780 for K-Cl (Table 3).

Table 1: Major ions distribution in the groundwater

Elements	Minimum (ppm)	Maximum (ppm)	Mean (ppm)	Median	S.D
Na <sup>+</sup>	70	739	270	224	171
K <sup>+</sup>	6	40	16	13	9
Ca <sup>++</sup>	35	345	144	133	85
Mg <sup>++</sup>	22	281	92	68	77
Cl <sup>-</sup>	72	1515	371	315	301
HCO <sub>3</sub> <sup>-</sup>	212	386	296	303	51
CO <sub>3</sub> <sup>-</sup>	1	43	11	6	11
SO <sub>4</sub> <sup>-</sup>	66	948	313	178	277

Table 2: Important hydrogeophysical parameters of groundwater

pH	TDS (ppm)	EC (mS/cm)	RSC	SAR
8.43	2.125	3.187	-5.588	9.68
8.39	1.415	2.122	-2.513	6.58
8.41	1.600	2.400	-2.138	6.29
8.53	2.800	4.200	-9.010	8.83
8.66	1.020	1.530	0.350	5.40
8.25	1.025	1.537	-1.585	5.51
8.19	2.410	3.615	-12.229	5.71
8.08	1.325	1.987	-7.209	2.52
8.17	1.310	1.965	-8.318	2.19
8.72	0.705	1.057	-0.037	2.14
8.45	1.068	1.602	-3.342	4.42
8.38	1.210	1.815	-0.950	5.54
8.53	0.830	1.245	-1.190	1.67
8.61	0.979	1.468	0.143	6.38
8.35	1.695	2.542	-2.405	8.37
8.52	0.670	1.005	0.612	4.50
8.42	0.935	1.402	-3.873	1.88
8.11	0.950	1.425	0.709	4.63
8.02	1.420	2.130	-3.360	6.21
8.17	2.565	3.847	-14.130	4.89
8.22	3.950	5.925	-26.905	7.89

Table 3: Correlation coefficient among major ions in the groundwater of the study area

	Na	K	Ca	Mg	Cl	HCO <sub>3</sub>	CO <sub>3</sub>
Na							
K	0.910						
Ca	0.220	0.184					
Mg	0.605	0.522	0.761				
Cl	0.841	0.780	0.433	0.797			
HCO <sub>3</sub>	0.309	0.360	0.139	0.158	0.221		
CO <sub>3</sub>	0.284	0.433	-0.250	-0.173	-0.027	0.241	
SO <sub>4</sub>	0.884	0.810	0.422	0.609	0.678	0.305	0.205

Calcium showed concentration between 35 to 345 ppm. Alkalinity was imparted by calcareous soil and limestone formations which were exposed in the study area. Bicarbonate ions showed distribution between 212 to 386 ppm. The samples exhibited two distinct clusters, one with majority of the samples, while five samples (No. 4, 7, 9, 20 and 21) have high amount of Ca (Fig. 2B). Bicarbonate demonstrates close spread (SD, 51) because the mean and median are 296 and 303, respectively (Table 1). The Mg-SO<sub>4</sub> ion relationship displayed dual characteristics (Fig. 2C). Majority of samples have low SO<sub>4</sub>, while few of them have high SO<sub>4</sub> concentration. The two fold character of Mg probably understood from the correlation coefficient of Mg. Magnesium has medium value for SO<sub>4</sub>(0.609) while it was

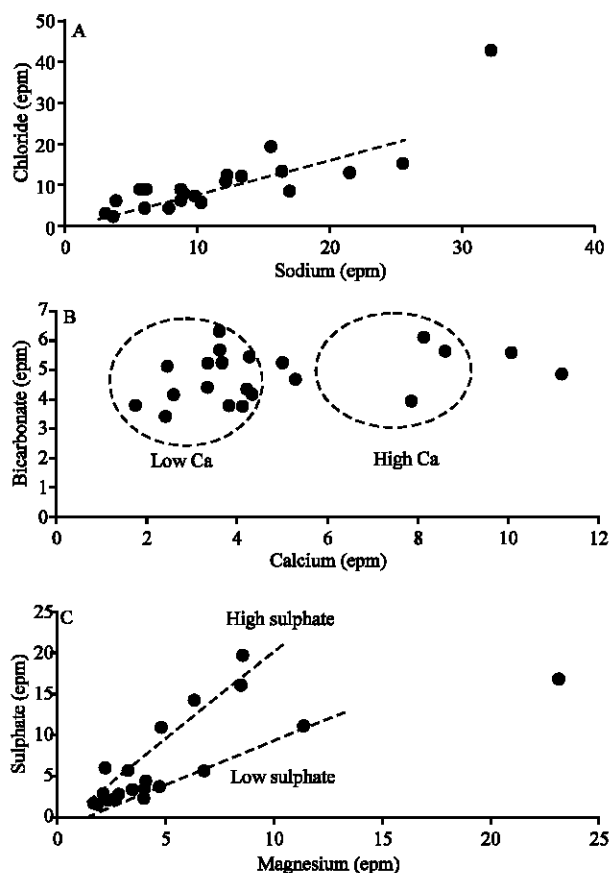


Fig. 2: Plots showing degree of corresponding among major elements

0.797 and 0.605 with Cl and Na, respectively (Table 3). Sample No. 20 and 21 have high amount of Mg, which was probably due to dolomitization in the Laki Formation<sup>[10]</sup>.

**Ionic composition:** In order to elaborate the composition of water, major ions were expressed in Milliequivalents Per Million (epm) and plotted in the form of closed patterns (Fig. 3) as suggested by Hem<sup>[11]</sup>. This figure revealed high sodium chloride, medium magnesium sulphate and low calcium bicarbonate, however in 9 samples, CaCO<sub>3</sub> >MgSO<sub>4</sub>. About 12 samples have low ionic composition (<10 epm). Five samples have epm less than 20, the rest of 4 samples have high contents (>20 epm) of dissolved salts. Calcium, Mg and HCO<sub>3</sub> ions were mainly derived from the weathering and erosion of carbonate rocks of Laki, Kirthar and Ghazij formations<sup>[10]</sup>. Sulphate ions were related with different gypsiferous shale units of these formations and partly from celestite deposits found in Laki and Tiyon formations<sup>[8]</sup>. The dominance of these ions was the best reflection of bed rock chemistry.

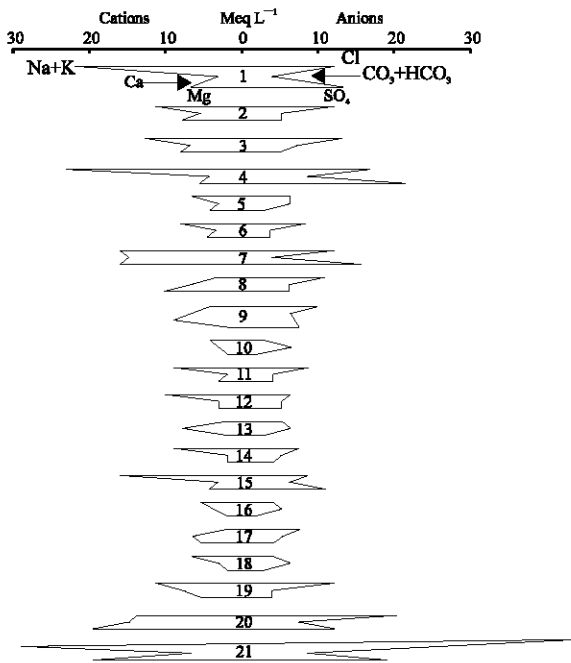


Fig. 3: Stiff diagrams for ionic composition of groundwater of study area

**Hydrofacies:** The hydrochemical facies analysis reflected the chemical processes operative in a certain lithological environment and under specific geochemical conditions. The general classification and trend of variation in the groundwater of the study area was exhibited in the Piper-diagram (Fig. 4). The diagram showed dominance of alkaline earth elements (Ca+Mg) over the alkaline metals (Na+K), that reflected good agreement in the carbonate rock terrain. The area has high Cl+SO<sub>4</sub> in contrast to HCO<sub>3</sub>+CO<sub>3</sub>, indicating an acidic environment<sup>[1]</sup>. In the cation triangle, majority of the samples were Na-type and have Na+K 85-55% with few exceptions-calcium was more than Mg, only sample 9 showed relatively high enrichment of Ca (58%). The anion triangle reflected a Cl-type with HCO<sub>3</sub>+CO<sub>3</sub> > SO<sub>4</sub>.

In order to determine salinization, the Ca/Mg and Na/Cl ratios were valuable<sup>[1]</sup>. The majority of the collected samples have Ca/Mg ratio ~1.0, except in few sample, indicating exposures of carbonate rocks in the area. Similarly Na/Cl ratio below 1.0 indicates fresh water existence. In the study area, collected samples have Na/Cl ratio between 0.412-1.289 with a mean of 0.801 indicating a fresh water source, however a few samples have high

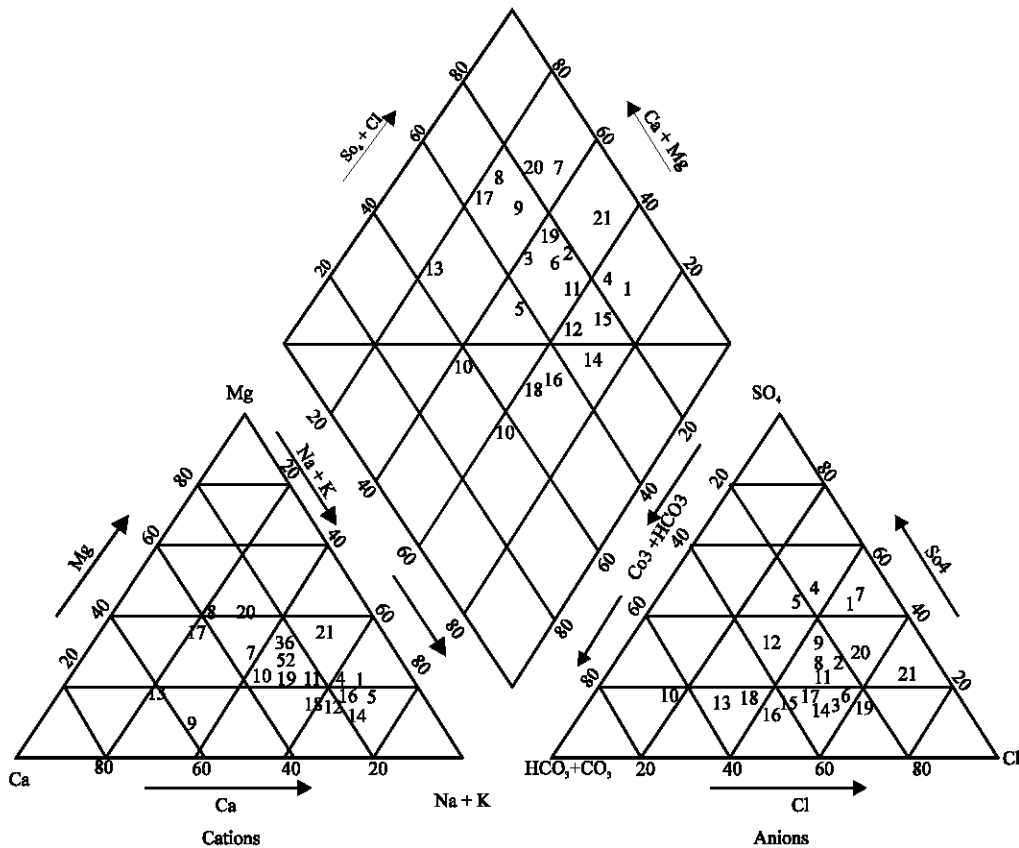


Fig. 4: Piper diagram for the chemical composition of the groundwater samples of the study area

Na/Cl ratio more than 1.0, suggesting evaporation and concentration<sup>[2]</sup>.

**Drinking water quality:** Quality of drinking water was evaluated according to the standards of WHO<sup>[12]</sup>. The pH of the collected samples were within safe limit (Table 2) but the Total Dissolved Solids (TDS) are more than the maximum permissible limit (>1500 ppm). Major constituents such as Na, Ca, Mg, Cl and SO<sub>4</sub> were within maximum permissible limit in those samples that have low TDS. Calcium was high in sample No. 7, 8, 9 and 20 in contrast to WHO recommended values 200 ppm. Four samples, namely 7, 8, 20 and 21 have more Mg (>150 ppm). It appears that nearly all samples were slightly above than the highest level of tolerance for Na and K. The anionic contaminations were within the permissible limit for drinking purpose. This situation indicated that the groundwater from Kalu Khuhar region was marginally suitable for drinking purpose.

**Irrigation water quality:** According to Bokhari and Khan the Residue Sodium Carbonate (RSC) has maximum influences on the suitability of water for irrigation purpose<sup>[13]</sup>. It is important to note that all the samples have very low RSC. The SAR values are also an important tool to evaluate the suitability of irrigation water. The calculated SAR values were between 1.67 and 9.68 with a mean of 5.83 (Table 2). These values were less than 10, indicating that the water have low sodium hazard.

Electrical Conductivity (EC) and SAR mutually can be used to evaluate irrigation water quality. Only seven samples (1, 3, 4, 7, 15, 20 and 21) have high salinity hazard and the rest of samples have low sodium and salinity hazard (Table 2). As a whole the groundwater of the Kalu Khuhar region were low in SAR and medium salinity hazard, therefore, they can be considered as medium quality irrigation water.

### CONCLUSIONS

- The bed rock chemistry, mobility, climate and contamination through water supply, sewerage, industries and other factors were responsible for fluctuation distribution of ions in the groundwater.
- Major ions demonstrated variable and resembling distribution pattern except few, indicating the influence of uniform geochemical environment. The general trend of major cation displayed Na>Ca>Mg>K, whereas anions were Cl>SO<sub>4</sub>>HCO<sub>3</sub>.
- Low Na/Cl ratio (0.76-0.96) of majority of the samples explicit their genetic relationship with the meteoric water, However few of them showed more concentration due to evaporation.

- The general ionic composition revealed high NaCl, medium CaHCO<sub>3</sub> and MgSO<sub>4</sub>. About 12 samples have low ionic composition whereas rest were high in salt. Their Stiff diagrams showed slight imbalance ionic relation conceivably due to arid climate and influence of bed rock.
- The hydrofacies analysis of major cations from Piper diagram clearly indicated Na- type and majority of the samples have Na+K 90-50% with few exemptions. The anions were mainly Cl-type with HCO<sub>3</sub>+CO<sub>3</sub>>SO<sub>4</sub>.
- On the basis of major ions, nearly all samples were slightly above the recommended range of WHO<sup>[12]</sup> standards for drinking water.
- Important hydrogeophysical parameters such as RSC, EC and SAR indicated that the groundwater of Kalu Khuhar region is marginally suitable for irrigation purposes.

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