Seasonal Assessment of Water Quality by Statistical Analysis in the Coastal Area of Sindh, Pakistan

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Abstract. Monitoring of groundwater is very important because of climatic and demographic patterns along the coastline of Sindh Province, Pakistan. Seventy representative groundwater samples were collected during pre-monsoon and post-monsoon seasons for the investigation of physico-chemical variables to understand the groundwater chemistry of the coastal belt. Multivariate statistical techniques were applied to interpret the data to reveal the pollution sources in the groundwater samples. The normalized charge balance index (NCBI) was computed on the data set and the ΣTz^- and ΣTz^+ were analyzed in the collected groundwater samples. Cations were in excess and alkalinity in the aquifer of the study area was balanced by $Ca^+ + Mg^+$ ions. The contribution of ions was insignificant for charge balance. Mg^{+2} and Ca^{+2} were in huge concentration and alkaline hardness was maintained by the alkaline rocks formation. Majority of the charge was balanced by SO_4^{-2} and CI^- . In groundwater ionic composition is used to categorize it into ionic types of groundwater based on the dissolved cation and anion. The ionic reaction is likely regulated by domestic geological formation. The sample location illustrates $Na^+ - SO_4^{-2}$ and $Na^+ - CI^-$ nature of groundwater. The groundwater with $Na^+ - SO_4^{-2}$ and $Na^+ - CI^-$ dominancy generally shows saline characteristics that make groundwater unfit to use for irrigation and drinking purposes.

Keywords: salinity, groundwater, NCBI, multivariate

Introduction

The only significant level of urbanization along the Pakistan coast is found in Karachi city, with a population of about 16 million (Qureshi *et al.*, 2010). Around 17% of the industries of the country is situated in Karachi, which includes textile, chemical, pharmaceutical, electronic, tanneries, oil refineries, food, iron and steel, etc. (Zeb *et al.*, 2017). Whereas, district Thatta was previously considered as the most important agriculture centre along the coast of Pakistan (Alamgir *et al.*, 2016). However, since the district is positioned at the tail end of the irrigation systems and there is a perpetual shortage of freshwater, agriculture has deteriorated.

Monitoring of groundwater on the coastal belt of Sindh Province, Pakistan is very important because of its climatic pattern and demographic pressure in this region (Qureshi, 2010). A large population of the area consumes groundwater for different uses (Yu *et al.*, 2013), and over-exploitation causes deterioration in groundwater quality (Khuhawar *et al.*, 2018; Bashir *et al.*, 2017; Daud *et al.*, 2017; Memon *et al.*, 2011; Qureshi *et al.*, 2008; Mastoi *et al.*, 2008). On the other hand, the composition of groundwater modified as it added different

soluble material along its flow path and the behaviour and deviations leading to anomalous of specific elements in the groundwater. The configuration of groundwater differs at the lowest point of a constant stream. The variation of pH, soil and rock constitutes, the resident time of groundwater inside the formation and landscape and seawater intrusion is also a significant factor in groundwater of coastal area. The overall outcome is that groundwater geochemistry is regulated in response to its flow path (Malott *et al.*, 2016).

The study was conducted in the coastal belt of Province Sindh, Pakistan (Fig. 1). The coastal belt of Sindh covered total area of about 140,915 km², while, sampling area was positioned between 24°4′–28°7′ N and 66°8′–71° E. The Province Sindh comprises arid and hottest climate with an average annual rainfall less than 200 mm, whereas, summer and winter average temperature reaches above 40 and 16 °C, respectively (Rasul *et al.*, 2012). High evaporation, low precipitation, and canal irrigation network is the main characteristic of the study area (Steenbergen *et al.*, 2015).

The Indus belt predominantly consists of alluvium, along with middle to upper tertiary rocks having lithology of sand, shale, and limestone. Nari formation in

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Oligocene age showing in the area having interlaying of limestone, shale, and siltstone. Gaj formation of Miocene age overlies Nari formation, having shale and sandstone with subordinate limestone. The conglomerate of Manchar formation Quaternary in age covers Gaj formation (Malkani, 2010). Mangho Pir, Dirgh Road/PECHS, Landhi, and Korangi anticline marks the structural features of the area controls the water discharge from the effluent and seasonal rivers (Malir and Lyari) into the Arabian sea. Groundwater structure can be originated in fine channels through the river having the meander belt and streambed deposits. River Indus is the main source of irrigation network and aquifer recharge.

The Multivariate analysis methods of groundwater samples have been successfully used for chemical evaluation and data can be easily interpreted. In the current study, groundwater chemistry was evaluated using statistical applications. The study area is vulnerable to groundwater contamination which would ultimately risk the utilization of groundwater for different uses. There have been several studies on groundwater quality in the study area and had a focus on basic evaluation (Rubab et al., 2014; Husain et al., 2012; Zubair et al., 2010). The aim of the present study was to assess the groundwater quality in coastal areas of Sindh by using statistical analysis. The current study will be helpful for the identification of hydrogeochemical processes and characteristics controlling the chemistry of groundwater. Moreover, the results may help a clear understanding of adverse effects, and the solution. Concerning groundwater quality in the study area. This study is useful to determine the environmental impact of industrialization and urbanization on the coastal belt.

Material and Methods

A total of seventy representative groundwater samples were collected during each pre-monsoon and post-monsoon seasons to monitor the contamination and tried to identify the source, behaviour, distribution and transport pattern of contaminants along the coastal belt of Sindh Province, Pakistan. The variability in the groundwater composition is associated with the groundwater table that fluctuates during pre and post-monsoon seasons. Each of the groundwater samples was obtained during the month of March (pre-monsoon) and September (post-monsoon), respectively. The fresh bottles were washed with distilled water and then rinsed twice with groundwater being sampled before filling.

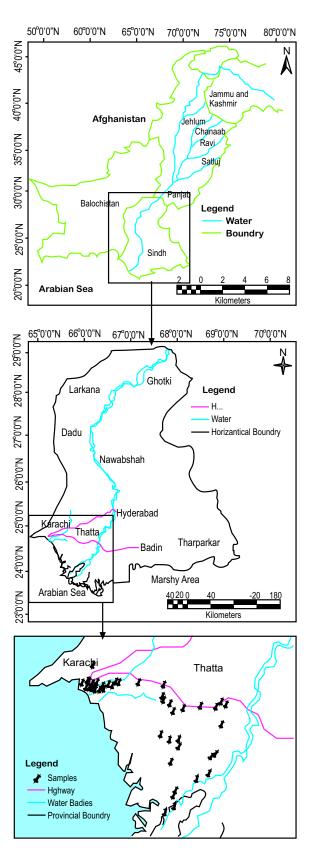


Fig. 1. Map showing the sampling locations in the present study.

Samples were carefully collected to avoid any contamination which can deteriorate the sampled water quality; therefore, it was sampled from the well after the well was pumped long enough to ensure that temperature, pH and conductivity stabilize.

Field measurement was made for physical parameters. Multimeter, Sension 156 HACH, USA were used to check conductivity, dissolved oxygen (DO), pH, total dissolved solids (TDS), salinity and turbidity at sampling sites (APHA, 2005). Chemical analysis for major ions was performed in the laboratory by standard methods (Mitra and Kebbekus, 2018). Total hardness, alkalinity, and chloride (Cl⁻) analysis were measured with the help of titrimetric method. Additionally, sulfate (SO₄⁻²), nitrate NO₃, and chemical oxygen demand (COD) calculated by performing spectrophotometry, while flame-photometry was performed to determine sodium (Na) and potassium (K). Minitab version (11.12) and SPSS (IBM SPSS 20) software were used for graphs and statistical analysis. Specific conductance methods (Laxen, 1977) were used to monitor the accuracy of analytical work that relies on tentatively determined and associations among specific conductance and ionic strength.

Results and Discussion

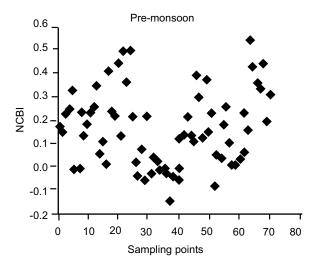
Geochemical evolution. Normalized charge balance index (NCBI) was calculated using the formula described by (Mor *et al.*, 2009; Kumar *et al.*, 2007):

$$NCBI = \frac{\sum TZ^{-} - \sum TZ^{+}}{\sum TZ^{-} + \sum TZ^{+}}$$

The sum of total anions ($\Sigma^{TZ'}$) and the sum of the total cations (Σ^{TZ^+}) in milliequivalent were analyzed in groundwater samples. Statistical analysis of the total cation and total anions in pre-monsoon and post-monsoon seasons are significantly correlated (Fig. 2). It has been revealed from the observations that most of the samples were in the range of 10% error (charge balance equation) and balance is in support of cations. Fig. 3 shows the relation between Hardness (Ca+Mg) and Alkalinity (HCO₃+CO₃). Cations are in excess and alkalinity of the earth metals in aquafer of the study area is balanced by Ca + Mg cations. Further, it can be seen that the overall equilibrium of charge is maintained with cations dominancy.

It is implicated that the contribution of ions other than measured ions is insignificant for the total charge balance (Maharana *et al.*, 2015). As shown in Fig. 3, Mg⁺² and Ca⁺² ions were in excess while the alkalinity of the groundwater (hardness) was balanced by the alkaline earth metals in the aquifers of the coastal region of Sindh in both seasons. Most of the samples displayed a similar trend and are influenced by local geology of the area (Sajil *et al.*, 2019; Chacha *et al.*, 2018; Elmahdy and Mohamed, 2013). This is further demonstrated that most of the points fall near the aquiline. Fig. 4 reveals that most of the samples fall along the aquiline, signifying the balanced contribution towards the charge equilibrium.

In spite of the control of evaporation/crystallization process occurrence in the groundwater, the ion chemistry



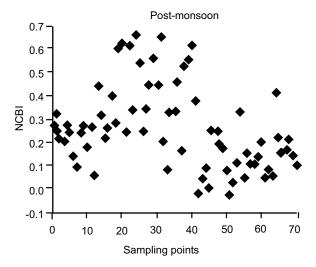


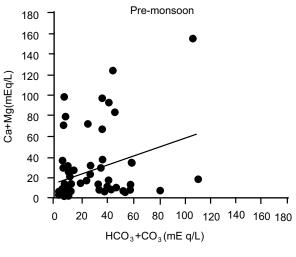
Fig. 2. Normalized charge balance index (NCBI) of the groundwater samples.

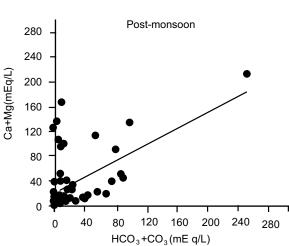
was generally controlled by alkaline earth metals (Puntoriero *et al.*, 2015). The same is being demonstrated by Gibb's plot (Fig. 5), which demonstrates the 40% variables fall in the rock control and 60% towards crystalline evaporation dominance and consequence from the weathering process of dolomite, gypsum and calcite rocks. Sodium is the leading cation in the groundwater and is governed by the alkaline earth metals (M_g^{+2} and C_a^{+2}).

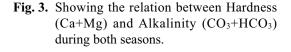
It is apparent that groundwater with high TDS is due to Gaj formation which is more clay formation than Nari formation of Oligocene age (Rahman *et al.*, 2018). The ion exchange reaction between rock and groundwater is high in Gaj formation due to mobile ions and

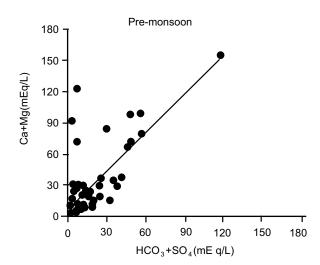
Hydrophiles such as sodium, potassium, and calcium. The Gibbs plot also represents a major contribution of rock because of recharge during monsoon lowers the ions concentration due to the increase in groundwater columns and dilution (Mondal *et al.*, 2010).

The present study shows that the contribution of ions is predominantly by the rocks belonging to Miocene in age (Fig. 6). The hydrogeochemical evaluation in the current study area (Fig. 7) demonstrates that many of the groundwater samples drop in the rock governance area that results from the weathering of gypsum, dolomite and calcite rocks. Even though Na⁺ is the most governing cation and groundwater chemistry is governed by Mg⁺² and Ca⁺² ions (Chang and Wang, 2010).









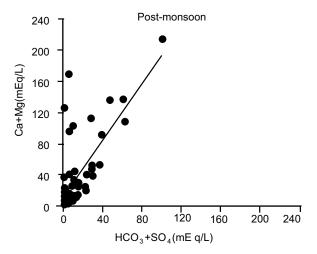


Fig. 4. Showing the relation between hardness (Ca+Mg) and acidic anion (HCO₃+SO₄).

It is obvious that alkali metal has control over alkaline earth metals while weak acidic anions were controlled by strong acidic anions (Essington, 2015). Both alkaline earth and alkali metal were controlled by the geochemistry of the aquifer in the study area.

Correlation analysis. Correlation analysis (bivariate method) was adopted to explain the extent of the relation between two hydro-chemical variables. The outcome of the correlation analysis was considered in the succeeding interpretation. A positive and negative correlation was observed among many variables. Standard normal distribution was assumed by correlation of the used parameters that must be analyzed for the

pre-established significance level (Vasanthavigar *et al.*, 2010).

The correlation of all parameters during the pre-monsoon season is shown in Table 1. It is apparent in the table that pH has a positive correlation with dissolved oxygen and negatively correlated with potassium. Conductivity showed a positive correlation with TDS, Salinity, sodium, calcium, chloride, nitrate, and bicarbonate. Dissolved oxygen showed a negative correlation with potassium while positively correlated with carbonate. Sodium showed a positive correlation with magnesium, calcium, chloride and bicarbonate variables. Potassium was positively correlated with nitrate only. Calcium showed

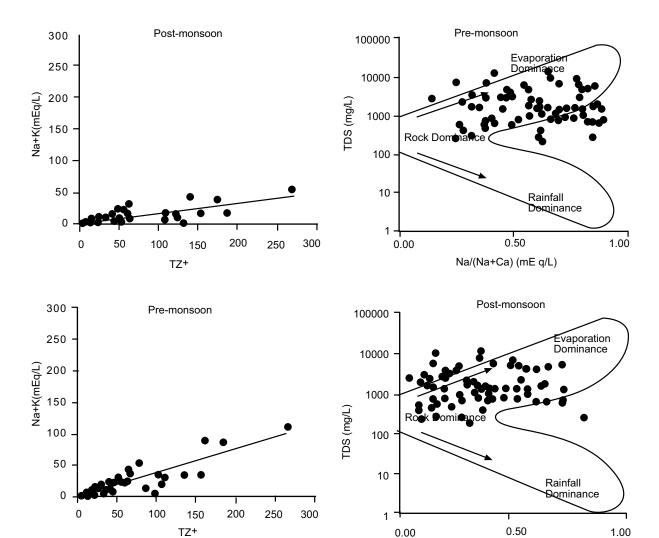


Fig. 5. Showing the relation between alkali metals (K+Na) and total cations (TZ⁺) during premonsoon and post-monsoon seasons.

Fig. 6. Gibb's plot showing hydrogeochemical processes in groundwater.

Na/(Na+Ca) (mE q/L)

a negative correlation with fluoride whereas positively correlated with magnesium, chloride, sulphate and bicarbonate. Magnesium showed a positive correlation with sulfate, bicarbonate, and repeat. Chloride showed a positive correlation with sulfate, bicarbonate and nitrate.

The correlation of all variables during post-monsoon presented in Table 2. The pH negatively correlated with potassium and showed a positive correlation with dissolved oxygen. Conductivity was highly significantly correlated with TDS (p<0.001) and showed a strong positive correlation with TDS, salinity, sodium, calcium,

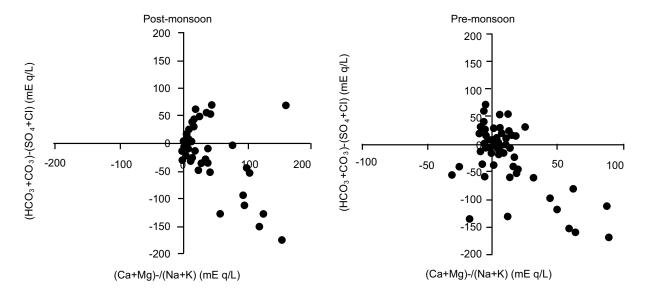


Fig. 7. Hydrogeochemical evaluation of ground-water of the study area.

Table 1. Correlation matrix of mean values of water samples during pre-monsoon season

	pН	Con.	TDS	Salinity	DO	Na	K	Ca	Mg	F	Cl	NO ₃	HCO ₃	CO ₃	PO ₄
Con.	-0.199														
TDS	-0.190	0.995													
Salinity	-0.202	0.483	0.504												
DO	0.354	-0.179	-0.196	-0.133											
Na	-0.064	0.759	0.764	0.458	-0.086										
K	-0.494	0.276	0.279	0.156	-0.388	0.190									
Ca	-0.043	0.684	0.697	0.583	-0.005	0.704	0.007								
Mg	-0.032	0.722	0.735	0.609	-0.053	0.731	0.080	0.940							
F	-0.167	-0.251	-0.253	-0.234	-0.254	-0.231	0.018	-0.387	-0.311						
C1	-0.062	0.748	0.760	0.542	0.014	0.746	0.169	0.919	0.945	-0.331					
NO_3	-0.227	0.396	0.417	0.238	-0.164	0.293	0.391	0.193	0.281	-0.124	0.360				
HCO_3	0.156	0.444	0.465	0.196	-0.266	0.572	-0.091	0.544	0.517	-0.199	0.368	-0.051			
CO_3	0.254	-0.001	-0.011	-0.121	0.436	-0.006	-0.055	-0.054	0.017	0.004	0.067	0.201	-0.176		
PO ₄	-0.067	0.176	0.148	0.044	0.243	0.094	-0.067	0.112	0.067	-0.052	0.066	-0.079	-0.126	0.198	
SO_4	-0.274	0.321	0.321	0.670	0.016	0.340	0.054	0.577	0.536	-0.217	0.435	0.064	0.107	-0.186	0.151

Here, Con. = Conductivity; TDS = Total Dissolve Solids; DO = Dissolve Oxygen; Na = Sodium; K = Potassium; Ca = Calcium; Mg = Magnesium; F = Fluoride; Cl = Chloride; NO₃ = Nitrate; HCO₃ = Bicarbonate; CO₃ = Carbonate; PO₄ = Phosphate; SO₄ = Sulfate; Values greater than 0.250 and less than 0.324 (p<0.05) significant; Values greater than 0.324 and less than 0.407 (p<0.01) more significant; Values greater than 0.407 (p<0.001) highly significant; Significance level for degree of freedom 68 was checked by using r table in sequence order; Bold face numbers indicate statistically significant correlation coefficient.

Table 2. Correlation matrix of mean values of water samples during post-monsoon season

	pН	Con.	TDS	Salinity	DO	Na	K	Ca	Mg	F	C1	NO ₃	HCO ₃	CO ₃	PO ₄
Con.	-0.169														
TDS	-0.172	0.996													
Salinity	-0.191	0.446	0.496												
DO	0.393	-0.242	-0.263	-0.143											
Na	-0.070	0.773	0.789	0.478	-0.194										
K	-0.494	0.271	0.279	0.146	-0.408	0.214									
Ca	-0.017	0.682	0.706	0.585	-0.052	0.700	0.006								
Mg	-0.006	0.717	0.742	0.615	-0.100	0.715	0.081	0.944							
F	-0.219	-0.326	-0.341	-0.292	-0.132	-0.312	-0.007	-0.506	-0.427						
Cl	-0.028	0.742	0.762	0.537	-0.054	0.748	0.162	0.922	0.948	-0.432					
NO_3	-0.202	0.405	0.426	0.234	-0.189	0.324	0.376	0.191	0.262	-0.147	0.346				
HCO_3	0.151	0.460	0.477	0.205	-0.303	0.586	-0.082	0.553	0.528	-0.272	0.397	-0.044			
CO_3	0.274	0.028	0.011	-0.119	0.412	-0.008	-0.052	-0.048	0.010	0.054	0.070	0.219	-0.181		
PO_4	-0.050	0.207	0.179	0.084	0.212	0.102	-0.059	0.118	0.081	-0.048	0.071	-0.086	-0.127	0.228	
SO_4	-0.245	0.344	0.364	0.715	-0.059	0.374	0.076	0.522	0.530	-0.264	0.367	0.067	0.136	-0.180	0.188

Here, Con. = Conductivity; TDS = Total Dissolve Solids; DO = Dissolve Oxygen; Na = Sodium; K = Potassium; Ca = Calcium; Mg = Magnesium; F = Fluoride; Cl = Chloride; NO₃ = Nitrate; HCO₃ = Bicarbonate; CO₃ = Carbonate; PO₄ = Phosphate; SO₄ = Sulfate; Values greater than 0.250 and less than 0.324 (p<0.05) significant; Values greater than 0.324 and less than 0.407 (p<0.01) more significant; Values greater than 0.407 (p<0.001) highly significant; Significance level for degree of freedom 68 was checked by using r table in sequence order; Bold face numbers indicate statistically significant correlation coefficient.

magnesium, chloride, nitrate and bicarbonate. TDS showed a weak negative correlation with fluoride and positively correlated with salinity, sodium, calcium, magnesium, chloride, nitrate sulfate and bicarbonate. Salinity showed a positive correlation with sodium, calcium, magnesium, chloride, and sulfate. Dissolved Oxygen was negatively correlated with potassium while positively correlated with carbonate. Sodium showed a positive correlation with bicarbonate, sulfate, chloride, magnesium, and calcium. Calcium showed a negative correlation with fluoride while positively correlated with magnesium, chloride, bicarbonate, and sulfate. Magnesium was negatively correlated with fluoride and showed a positive correlation with chloride, sulfate and bicarbonate. Therefore, it can be assumed that the correlation studies of the groundwater quality parameters have great importance and the non-significant correlation between parameters, and they are independent to each other.

Conclusion

The present study revealed that the ion exchange reaction between rock and groundwater is high in Gaj formation due to mobile ions and hydrophiles such as sodium, potassium, calcium, magnesium, and chloride and characterizes the nature of groundwater in the study area. Precipitation directly impacts the groundwater quality and infiltration takes place at a high level during the post-monsoon period. During water flow through residual rocks formations, that affects groundwater quality by changing the concentration of ions. The major changes in the groundwater of the study area are found naturally during both seasons.

Conflict of Interest. The authors declare no conflict of interest.

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