



## Assessment of Groundwater Quality in Coastal Region a Case Study of Qayyumabad, Karachi, Pakistan

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### Abstract

The aim of present study is to assess groundwater quality of Qayyumabad area for drinking purpose. Groundwater samples (n = 20) were collected from wellbores from variable depths (12-300 feet) occurring on both banks of the Malir River near study area. Water quality was assessed through estimation of physical parameters including, pH, Eh, TDS, EC, hardness, temperature, aesthetic character (taste, color and odor) and chemical parameters including major cations (Na, K, Ca, Mg), anions (Cl, NO<sub>3</sub>, SO<sub>4</sub>, HCO<sub>3</sub>) and minor/trace elements (Fe, As). Data revealed that groundwater of study area has very high TDS content (range: 805-40340 mg/l) and positive Eh (-180 to +125 mV), suggesting the recent recharge. The pH varies in the range of 6.55-7.75 which comply with WHO limit (6.5-8.5) for drinking water. Major solutes varied in the order of Na (mean: 2587 mg/l) > Mg (433mg/l) > Ca (231mg/l) > K (91 mg/l) while anions in the order of Cl (mean: 3385 mg/l) > SO<sub>4</sub> (mean: 580 mg/l) > HCO<sub>3</sub> (mean: 343 mg/l) > NO<sub>3</sub> (11.43 mg/l). Both arsenic and iron contents occur within the WHO permissible limits except two samples which showed elevated Fe (4950 ppb) and As (100 ppb) respectively. These results suggest that groundwater in study area is unfit for drinking purpose. Principal component analysis (PCA) explained four factors where F1 suggests the salts leaching mechanism and F2 indicated anoxia prevalence due to organic matter decomposition. On the other hand, F3 confirmed water rock interaction and F4 supported the prevalence arsenic release associated with anoxia.

**Keywords:** Groundwater, Shallow aquifers, Drinking quality, Coastal part, Karachi.

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### Contribution of this paper to the literature

This paper will integrate the knowledge of groundwater sources occurring in coastal parts of the world where dense population is a common demographic manifestation. It will also provide the insights about river systems occurring in the proximity of sea on groundwater characteristics.

## 1. Introduction

Water is fundamental need of each individual and it is a privilege of individual to approach drinking safe water. Life essentially depends on water and its quality being used on regular basis for different purposes. The water we use is either the river driven which is treated in different plants or the wellbore water which we directly suck from specific depth. However, recently the increasing population is resulting in the acute shortage of municipally supplied water. In order to overcome the demand of water, groundwater is used as an alternative. According to world health organization (WHO) about 80% diseases are water borne. Pakistan is becoming water stressed country and is likely to be water scarce in near future [1]. Pakistan positions at number 80 among 122 countries with respect to drinking water quality. Drinking water sources, both surface and groundwater are polluted with coliforms, dangerous metals and pesticides all through the nation.

Major factors of groundwater chemistry are regional geology, geochemical process and land use patterns [2]. The quality of water is greatly influenced by its composition. The major part of dissolved elements in groundwater comes from dissolved minerals in soil and sedimentary rocks. Natural filtration through soil and sediments makes the groundwater free from organic impurities [3]. On the other hand, seawater intrusion in coastal settings deteriorates the quality by increasing the salt content in groundwater. It becomes a menace where surface water is polluted and the municipal water supply is abandoned or irregular.

Like many big cities of developing countries, Karachi is a coastal city which is expanding every day. The city has a large number of industrial units generating approximately 1.3 million liters of effluents per day with only about 5% of the industrial and domestic waters receiving significant treatment and the rest untreated waste is discharged directly into Malir and Lyari rivers [4]. Coastal part of Karachi is by far, the most populous (~10 million inhabitants, as per 1998 census) and the largest industrial (more than 1000 large industrial units) base of Pakistan, with a coastline extending up to about 80 km.

Geomorphically, Karachi city lies on Hub and Malir River basins. Shallow aquifers of Karachi are mainly recharged by these two rivers. Presently, drinking water supply to the Metropolitan Karachi is maintained through three main sources including (i) Indus River (Keenjhar Lake) (ii) Hub River (Hub Dam) and (iii) groundwater through boring wells. However, increasing population, over-exploitation of groundwater and limited recharge of aquifer system has caused severe decline in water table during the last two decades. The three large industrial areas known as Sindh Industrial Trading Estate (SITE), Korangi Industrial Trading Estate (KITE) and Landhi Industrial Trading Estate (LITE) are discharging huge quantities of effluents comprising of organic matter, heavy metals, oil, greases, liquid and solid wastes into Malir and Lyari rivers. This malpractice is causing severe environmental degradation in various ecosystems of the city. The toxic metals and organic dye containing waste is directly poured into the Lyari and Malir rivers without any treatment. Malir River basin is very important in terms of agricultural activity, transporting municipal and industrial waste to the sea. Besides, Malir River is main water source recharging the shallow aquifers occurring in its surroundings. It is hypothesized that industrial effluents and municipal wastes being disposed off through Mali River is causing the contamination of shallow groundwater by infiltration through aquifer depths. This may lead to hamper the health of resident around Mali River. Therefore, it is imperative to screen the groundwater around Malir River for its quality determination. For this purpose, Qayyumabad area was selected as study site due to the fact that it lies at the terminus of Malir River where high accumulation of trace elements and other contaminates is expected as compared to the corresponding concentration upstream. Moreover, seawater intrusion is also likely to reduce groundwater potability due to excessive salt content.

## 2. Materials and Methods

### 2.1. Study Area

Qayyumabad is located (latitude: 24° 49' 32'' N, longitude: 67° 05' 02'' E) on the western bank of Malir River in Korangi creek area Figure 1. It is a suburb of Korangi which is spread over an area of about 109 Acre with a dense population (more than 7000 people) of multiple ethnic backgrounds. The residents are provided with municipally supplied water through pipelines but water supply is sporadic and occasionally available. Due to over population and damage to water supply line and water theft the problem of fresh water availability is aggravating. As a result, people have switched over to groundwater sources for domestic uses. The area under study lies on south eastern corner of Karachi Figure 1. Geologically, it is marking the southernmost extension of the Pab Range. Gaj Formation of Miocene age is exposed in study area. The catchment area of Malir River is situated in the north of study area [5]. Generally water is present at very shallow depth (12-40 feet) due to the fact that water-saturated zones are present within the weathered profile of the rocks or in the recent windblown sands. Stable aquifers are present in the terrace deposits of Mali River which are 150-200 meters thick.

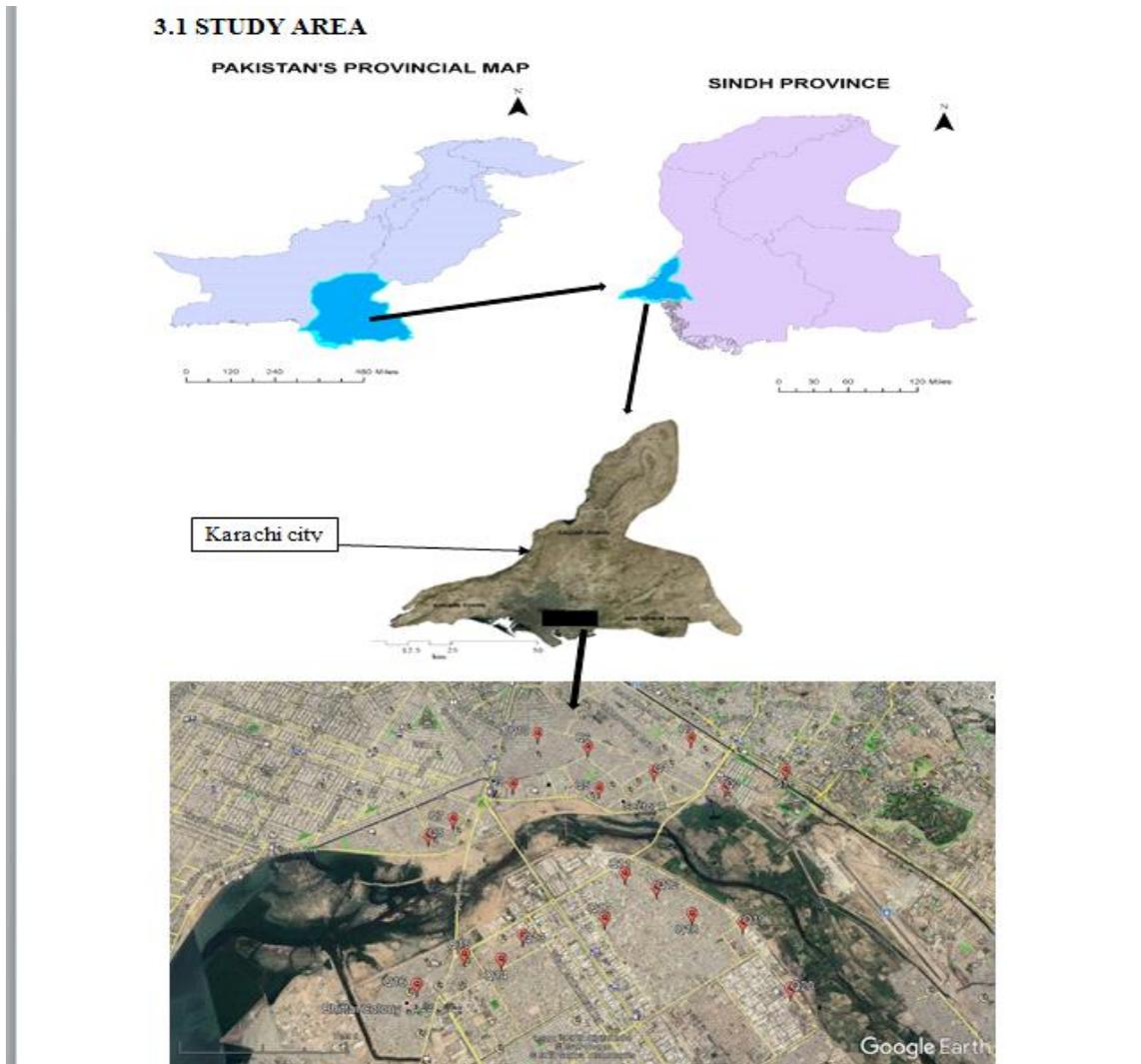


Figure 1. Sample location map of study area.

### 2.2. Sample Collection

Groundwater samples ( $n=20$ ) were collected from boring wells at variable depth range (12-300 feet). Water samples were collected in plastic bottles of about 1.5 liter by using electrical pumps to run water for 1-2 minutes to get fresh samples of the groundwater for physicochemical analysis. Bottles were properly washed and rinsed thoroughly with distilled water and then with groundwater at sampling site to minimize any impurity. Locations of the wells were marked on the map with the help of Global Positioning System (GPS).

### 2.3. Sample Analysis

Aesthetic characters (color, taste, odor,) and physical parameters including temperature, and turbidity were measured by thermometer and turbidity meter respectively. The pH and Eh of collected samples were measured by using pH meter (ADWA AD 111) while TDS and EC were determined by using EC meter (ADWA AD 330). Sodium and potassium were estimated by flame photometer (JENWAY EFP7) while calcium, magnesium, chloride, and bi-carbonate were determined by standard titration method. Gravimetric method was used for sulphate determination. Nitrate content was estimated by using spectrophotometer (HACH-8171) and iron by atomic absorption spectrometer (Analyst 400, Perkin Elmer). Arsenic content was determined by colorimetric method using arsenic testing Kit (Merck). Statistical analysis was carried out by using SPSS software (Version 16.00). PCA analysis was employed on data set of groundwater parameters including well depth, temperature, pH, Eh, TDS, EC, hardness, Na, K, Ca, Mg, Cl,  $\text{NO}_3$ ,  $\text{SO}_4$ ,  $\text{HCO}_3$ , Fe, and As.

## 3. Results and Discussion

### 3.1. Physical Parameters

Physical characteristics of collected groundwater samples have been summarized in Table 1. Well depth of collected samples ranges between 12-300 feet with a mean of 90 feet Table 1. Tapping the water from such variable depths is due to various factors including affordability, geological variation of aquifers characteristics and recharging tendency of aquifers. Data revealed that a few samples have shown light yellow to brown color, which suggest presence of organic matter or metals such as iron in those groundwater samples. The color of water is also dependent on the degree of oxidation i.e. darker the color of groundwater, higher the degree of oxidation. All samples are saline to highly saline in taste which is due to high TDS content (range: 805-40340 mean; 7820 ppm). Saline taste of groundwater is reported from all depth ranges (12-300 feet) which suggest that salinity of groundwater in study area is free from depth variation. Generally, it is observed that high TDS is found in both shallow and deeper wells, but wells with more depth have relatively low TDS content. It suggests that saline source is transmitting its salt content from shallow to deeper wells. Water is not considered suitable for drinking if the quantity of dissolved minerals exceeds 1,000 mg/L [6]. The groundwater temperature of collected samples ranges between 26-32°C with a mean of 30°C Table 4, but most of the samples ( $n=15$ ) have 30°C or above suggesting that water is infiltrating from surface runoffs.

The pH of groundwater in study area varies from 6.55 to 7.75 with a mean of 7.03 Table 4. The suitable pH for drinking water ranges between 6.5–8.5 [6]. About half of the collected samples are acidic making these water wells unfit for drinking due to possible chemical reactivity. Though pH has no direct effect on human health, its higher range accelerates the scale formations in water heating apparatus [7]. On the other hand it indirectly affects water quality and its parameters such as metal ion solubility and pathogen existence [8]. TDS content of the collected samples ranges between 800-40340 ppm with a mean value of 7820 ppm Table 4. All the samples have TDS above desirable limit of WHO (500 ppm) for drinking purpose. TDS content from natural sources vary from less than 30 mg/liter to as much as 6000 mg/liter [9] depending on the relative solubility of minerals in different geological regions. High TDS content in groundwater of study area may rise due to the influx of natural saline water such as sea water intrusion [10] which is consistent with the fact that study area lies in the proximity of Karachi coast where Malir River channel is invaded by sea water.

Table-1. Summary of physical parameters determined in collected groundwater samples of study area.

Physical Parameters												
Sample no	Well age	Well depth (ft)	Color	Taste	Temperature (°C)	Hardness mg/l	PH	Eh (mv)	TDS (ppm)	EC (µS/cm)	Latitude	Longitude
Q1	1 year	250	colorless	saline	32	600	6.91	76	3000	6000	24°52'16.19"N	67°5'31.21"E
Q2	15 years	22	light yellow	saline	32	1200	7.21	57	4210	8420	24°51'43.69"N	67°5'30.06"E
Q3	3 years	130	colorless	saline	29	1500	6.79	38	2100	4200	24°51'39.21"N	67°4'53.19"E
Q4	25 years	40	colorless	saline	30	800	6.9	97	3100	6200	24°51'13.67"N	67°5'7.19"E
Q5	20 years	12	colorless	saline	30	900	7.42	16	805	1610	24°50'44.04"N	67°5'7.44"E
Q6	3 years	20	light yellow	saline	31	1100	7.37	40	4100	8200	24°50'47.40"N	67°4'39.29"E
Q7	3 years	35	colorless	saline	30	3000	6.88	51	7830	1560	24°49'30.80"N	67°4'59.32"E
Q8	dna	dna	light yellow	saline	30	400	7.75	-70	1100	2300	24°49'16.89"N	67°5'5.03"E
Q9	3 years	180	light brown	saline	26	920	7.37	-120	4000	8000	24°50'4.58"N	67°4'48.80"E
Q10	dna	dna	light yellow	saline	26	620	6.8	125	1020	2040	24°50'26.05"N	67°4'20.96"E
Q11	6 months	150	colorless	saline	30.1	10000	6.57	-126	30200	60400	24°50'39.01"N	67°6'1.96"E
Q12	9 years	dna	light yellow	saline	30.5	900	7.3	-65	7230	14460	24°50'50.24"N	67°6'15.23"E
Q13	3 years	30	colorless	saline	30	10000	6.63	-180	40340	80680	24°49'43.45"N	67°6'17.55"E
Q14	5 years	16	colorless	saline	29.4	1000	7.1	-15	3600	7200	24°49'30.63"N	67°6'26.50"E
Q15	15 days	15	colorless	saline	31.3	1300	6.98	16	5310	10620	24°49'15.68"N	67°6'17.62"E
Q16	2 years	25	colorless	saline	30.1	1400	7.18	-101	1020	2040	24°48'51.63"N	67°6'25.30"E
Q17	7 years	100	colorless	saline	31.1	500	6.55	86	20340	40680	24°50'21.78"N	67°6'22.50"E
Q18	2 months	dna	smoky	saline	30	6000	6.83	33	11010	22020	24°51'0.50"N	67°6'35.46"E
Q19	6 months	117	colorless	saline	30.8	3000	7.23	38	2900	5800	24°51'20.87"N	67°6'48.72"E
Q20	7 months	300	colorless	saline	28	700	7.02	98	3180	6360	24°51'27.43"N	67°7'29.32"E
<b>WHO LIMITS</b>						500	6.5-8.5		500			

dna=data not available

Elevated content of TDS produces gastro-intestinal irritation in human body [11]. According to Prakash and Soma [12] classification only 5% of the total samples (n=20) are found non-saline, 30% are slightly saline, 45% are moderately saline and 20% are very saline Table 2 The variation in TDS of collected groundwater samples is quite higher (800-40340 ppm), which is mainly attributed to anthropogenic activities and to geochemical process [13] prevailing in the study area. The hardness of groundwater samples ranges between 400-10000 mg/L with a mean of 2292 mg/L Table 4. About 95% samples have hardness above permissible limit (500 mg/l) prescribed by World Health Organization (WHO) [6] for drinking purpose. The oxidation reduction potential of collected samples varies from -180 to +125 mV with a mean of +4.7 mV where about 65% samples showed positive Eh suggesting the recent recharge.

**Table 2.** TDS classification of study area groundwater (after Prakash and Soma [12]).

Classification	TDS in mg/l	No. of Samples
Non – saline	< 1000	1
Slightly saline	1000 – 3000	6
Moderately saline	3000 – 10000	9
Very saline	> 10000	4

Source: Prakash and Soma [12].

### 3.2. Chemical Characteristics

Chemical parameters include major cations (Na, K, Ca, Mg), anions (Cl, NO<sub>3</sub>, SO<sub>4</sub>, HCO<sub>3</sub>) and minor/trace elements (Fe, As) have been summarized in Table 3.

#### 3.2.1. Major Cations

Sodium is the major cation which has highly variable concentration (range: 205-14810 mg/L; mean 2587 mg/L). All samples have sodium concentration above permissible limit (200 mg/L) prescribed by WHO [14] for drinking purpose Table 3. High level of sodium in collected samples is due to the involvement of seawater as the study area lies in the proximity (8 km approximately) of Arabian Sea. Similar is true about potassium content (range 24-160 mg/L; mean: 90.7 mg/L). It is observed that all the collected samples are exceeding the safe limit of potassium (12 mg/L) Table 3. Main reason of increasing potassium in groundwater seems due to agricultural activities [15] and the sewage mixing. Moreover, K might have come from the weathering of feldspar and clay minerals from the aquifer matrix as feldspars are more susceptible to weathering and alteration than quartz in silicate rocks [16]. Calcium and magnesium contents range between 75-800 and 48.6-2217 mg/L respectively. The mean value of calcium (231 mg/L) is double of the permissible limit by WHO 100 mg/L Table 3. Likewise, the mean concentration of Mg is thrice the prescribed limit (150 mg/L). All samples have Mg concentration above the WHO limit for drinking purpose except four samples (Q3, Q5, Q12, and Q15). About 70% of the total samples show relatively high Mg concentration than Ca. Generally Ca dominates over Mg in groundwater but reverse occurs due groundwater interaction with dolomitic rocks [17] seawater intrusion or the cation exchange on clay surfaces.

**Table-3.** Summary of chemical parameters determined in collected groundwater samples of study area.

Chemical Parameters										
Sample no	Major Cations				Major Anions				Minor/trace elements	
	Na	K	Ca	Mg	Cl	NO <sub>3</sub>	SO <sub>4</sub>	HCO <sub>3</sub>	Fe	As
Q1	900	24	120	72.9	1100	8.03	230	290	8	bdl
Q2	1300	83	150	200.48	1700	13.8	980	200	bdl	5
Q3	560	35	350	151.88	460	4.01	660	380	4	bdl
Q4	1070	106	230	54.68	180	18.88	320	300	bdl	bdl
Q5	205	71	100	157.95	1600	4.6	106	490	bdl	5
Q6	1450	131	120	194.4	600	10	250	260	25	bdl
Q7	4500	125	90	674.32	190	9.06	650	224	35	5
Q8	220	79	80	48.6	200	12.9	190	220	102	bdl
Q9	1200	106	200	102.06	2100	8.48	120	550	4950	25
Q10	260	64	80	102.06	604	4.19	66	335	776	5
Q11	14810	144	350	2217.38	2000	8.66	2050	700	65	5
Q12	2830	100	100	157.95	3019	7.6	740	210	208	5
Q13	980	160	800	1944	30600	16	500	370	315	5
Q14	1170	82	150	151.87	1700	9.28	310	340	7	5
Q15	2616	96	160	218.7	1900	11.67	360	360	5	5
Q16	380	69	190	224.78	260	3.37	680	270	65	100
Q17	8620	142	600	85.05	12700	8.42	495	380	bdl	5
Q18	5850	109	400	1215	5600	16.78	210	390	194	5
Q19	1300	50	276	561.33	980	25.21	2010	280	4	bdl
Q20	1520	38	75	124.53	200	27.69	680	310	6	bdl
WHO LIMIT	200	12	75	150	250	10	250	300	300	10

All values are in (mg/l), except Fe & As which are in (µg/l)  
bdl=below detection level

#### 3.2.2. Major Anions

The concentration of chloride (range 180-30600 mg/L; mean: 3384.5 mg/L) and sulphate (range: 66-2050 mg/L; mean: 580.35 mg/L) are highly variable. About 80% of the total collected samples have chloride concentration above WHO standard (250 mg/L) for drinking water. Strong positive correlation of Cl with Ca ( $r^2 = 0.955$ ) followed by TDS and EC ( $r^2 = 0.786$ ) suggest that the evaporative concentration of major salts is increasing

in the study area due to aridity and sewage infiltration. Moreover, high concentrations of Cl<sup>-</sup> may be due to the effect of sea tides in the Qayyumabad area as suggested by Mashiatullah, et al. [18]. Luszczynski and Swarzenski [19] considers chloride content above 50 mg/L as an indication of salt water intrusion, the groundwater of study area contains chloride concentration far above the limits suggested by Luszczynski and Swarzenski [19] confirming the salt water intrusion. Similarly, mean concentration of sulphate is twice the permissible limit (250 mg/L) of WHO for drinking water Table 4. Very high sulphate content in the groundwater of study area suggests the gypsum dissolution, use of inorganic fertilizer and the recent recharge of saline water [20, 21]. High concentration of sulphate in study area is consistent with the study of Mashiatullah, et al. [18] in Ghizri creek which is 5.6 km away from Qayyumabad. It is also complimenting the seawater intrusion mechanism as an agent of high sulphate and chloride contents in groundwater of study area.

Nitrate concentration ranges between 3.37-27.69 mg/L with a mean of 11.43 mg/L Table 4. About 50% of total collected samples are unfit for drinking in terms of nitrate content as against WHO compliance (10 mg/L). It indicates that nitrate reducing bacteria are active in the groundwater of the study area, which is supported by exceptionally high bicarbonate content (mean: 346.9 mg/L) suggesting that organic matter decomposition is followed by nitrate reduction in the groundwater [22]. Bicarbonate content in collected groundwater samples ranges between 200-700 mg/L with a mean of 342.95 mg/L. About 55% of total collected samples have bicarbonate content above permissible limit (300 mg/l). Bicarbonate may be released from the dissolution of carbonate minerals via biodegradation of organic matter [23-25].

### 3.2.3. Minor and Trace Elements

Iron concentration in collected groundwater samples ranges between 4-4950 µg/L with a mean of 423 µg/L Table 4. It is observed that, all samples have iron concentration within permissible limit (300 µg/l) set by WHO except three samples (Q9, Q10 and Q13) which have high iron concentration (4950, 776 and 315 µg/l respectively). Iron in these samples may have come from some additional sources or due to prevalence of reducing conditions. Sample 9 contains rise value of both Fe and As but vice versa of this happens in sample 16 where extremely high value of arsenic As is present regardless of iron Fe. About 95% of the total samples (n=20) have very low correlation between Fe and As. It supports the notion that reduction of iron oxyhydroxide is necessary but not a sufficient condition for elevated arsenic concentration in groundwater of Holocene aquifers [26]. Arsenic content in collected samples varied between 5-100 µg/L with a mean of 13.84 µg/L Table 4. Only two samples (9 and 16) showed the abnormally high concentration of As i.e. 25 and 100 µg/l respectively, Arsenic is naturally occurring element available in the soil and sediments [27-29]. However Arsenic can be introduced to a groundwater system through various means, including surface water and precipitation as well as anthropogenic and naturally occurring sources [30, 31]. There is a relationship between the degree of reduction of the groundwater and the arsenic concentration; the more groundwater reduction, the more will be the arsenic concentration [32]. Since the groundwater of study area is mostly oxic as indicated by positive Eh values for most of the samples, the occurrence of low arsenic content is consistent with the redox rule.

Table-4. Statistics of physicochemical parameters.

Parameters	Minimum	Maximum	Mean	STD deviation
Hardness	400	10000	2292	2930.099
Well depth(ft)	12	300	90.12	90.88
Temperature (C)	76	37	79.86	1.619
pH	6.55	7.75	7.05	0.314
Eh (mv)	-180	+125	+4.7	+86.309
TDS (ppm)	805	40340	7819.8	105.18
EC	1610	80680	14939.5	21267.8
Na	205	14810	2587	3.58E+07
K	24	160	90.7	38.267
Ca	75	800	231.05	190.349
Mg	48.6	2217.38	432.99	629.069
Cl	180	30190	3384.65	7.01E+03
NO <sub>3</sub>	3.37	27.69	11.43	6.689
SO <sub>4</sub>	66	2050	580.35	554.697
HCO <sub>3</sub>	200	700	342.9	122.969
Fe	4	4950	423	1.22E+03
AS	5	100	13.84	26.46

### 3.3. Ionic Interrelationship

Strong positive correlation of well depth with bicarbonate ( $r = 0.851$ ) and iron ( $r = 0.731$ ) suggest that reducing conditions are increasing with depth Table 5. It is well established that bicarbonate may be released from dissolution of carbonate minerals via biodegradation of organic matter [23-25]. There is very weak negative relation of Na with Cl ( $r = -0.212$ ) Table 5 but this can be increases with time. The Na/Cl relation has often been used to identify the mechanism for salinity distribution and saline intrusion [33-35]. If Na and Cl ions enter in solution in equal quantity during the dissolution of halite, a linear relationship may be observed between these ions [36]. This relation is observed in our sample 17 and 18 Table 3. Abnormally high value of chloride concentration in sample Q13 (30600 mg/l) is observed regardless of sodium concentration. This concentration pattern suggests that sodium and chloride are not strongly correlated with each other. This pattern cannot rule out the same source of Na and Cl due to the fact that a part of Na is adsorbed onto the clays through cation exchange mechanism while chloride still remains in the mobile phase due to its conservative behavior.

Strong positive correlation of Na with SO<sub>4</sub>, Mg, and HCO<sub>3</sub> ( $r = 0.936$ ) ( $r = 0.666$ ) ( $r = 0.691$ ) Table 5 suggest that seawater intrusion. The negative correlation between nitrate and arsenic ( $r = -0.747$ ) Table 5 suggest that there is inverse relation between these two. Negative correlation between As and NO<sub>3</sub> does not exclude a common

source. Under anaerobic conditions  $\text{NO}_3$  is a very conservative ion whereas As is highly immobile at best in a near-neutral pH range. There is a relationship between the degree of reduction of the groundwater and the arsenic concentration; the more groundwater reduction, the more will be the arsenic concentration [32]. High concentration of nitrate in some samples suggests that the conditions are sub-oxic to anoxic. The reducing nature of the groundwater has led to the reduction of some of the arsenic to As (III) and possible desorption of arsenic since As (III) is normally less strongly sorbed by the iron oxides than As(V) under near-neutral pH conditions of groundwater [27, 37]. Further reduction will lead to the partial dissolution of the poorly crystallized ferric oxide with subsequent release of iron and additional arsenic [38].

**Table-5.** Correlation matrix of physicochemical parameters determined in collected Groundwater samples of study area.

Correlation matrix																	
	Well depth	Hardness	Temperature	PH	Eh	TDS	Ec	Na	K	Ca	Mg	Cl	$\text{NO}_3$	$\text{SO}_4$	$\text{HCO}_3$	Fe	As
Well depth	1																
Hardness	0.206	1															
Temperature	-0.707	0.257	1														
PH	0.093	-0.898	-0.593	1													
Eh	-0.45	-0.595	0.324	0.206	1												
TDS	0.147	0.975	0.211	-0.857	-0.624	1											
Ec	0.147	0.975	0.211	-0.857	-0.625	1	1										
Na	0.487	0.595	0.211	-0.634	-0.088	0.436	0.436	1									
K	0.286	0.879	0.058	-0.798	-0.407	0.902	0.902	0.481	1								
Ca	0.002	0.802	0.095	-0.606	-0.758	0.897	0.897	0.023	0.722	1							
Mg	0.232	0.995	0.274	-0.913	-0.546	0.952	0.951	0.666	0.872	0.74	1						
Cl	-0.18	0.646	0.094	-0.5	-0.598	0.786	0.786	-0.212	0.657	0.955	0.571	1					
$\text{NO}_3$	-0.161	0.505	0.167	-0.536	-0.157	0.661	0.661	-0.054	0.693	0.685	0.457	0.78	1				
$\text{SO}_4$	0.349	0.674	0.334	-0.683	-0.245	0.5	0.5	0.936	0.429	0.148	0.735	-0.11	-0.161	1			
$\text{HCO}_3$	0.851	0.468	-0.356	-0.239	-0.528	0.408	0.409	0.691	0.394	0.21	0.493	-0.029	0.053	0.582	1		
Fe	0.731	-0.278	-0.942	0.599	-0.312	-0.215	-0.215	-0.222	-0.037	-0.084	-0.3	-0.081	-0.083	-0.378	0.394	1	
As	-0.097	-0.339	-0.055	0.475	-0.231	-0.406	-0.406	-0.333	-0.594	-0.189	-0.351	-0.242	-0.747	-0.071	-0.27	0.04	1

This matrix is not positive definite

### 3.4. Principal Component Analysis (PCA)

To accurately identify the main processes governing the hydrochemistry of groundwater in the system, a factor analysis was performed using a subset of variables including the physical parameter (Well depth, Temperature, Hardness, pH, Eh, Total dissolved solids, Electrical conductivity) while chemical parameters (sodium, potassium, calcium, magnesium, chloride, nitrate, sulphate, bicarbonate), and minor/trace elements (Iron, Arsenic). Four factors were extracted which have Eigen values greater than 1 and these factors are discussed separately in detail. The PCA was performed on 20 groundwater samples where four principal components were extracted. The first four principal components together account for about 97.62% of the total variance in the data set, in which the first principal component explains 50.94% of the total data set variance, the second component explained the 20.43% while third component explained 16.89% and the fourth component explains the 9.37% Table 6.

**Table-6.** Principal components analysis (PCA).

Principle Component Matrix <sup>a</sup>				
	Component			
	F1	F2	F3	F4
TDS	0.99	-0.031	-0.121	0.062
EC	0.99	-0.03	-0.121	0.062
Hardness	0.986	0.017	0.082	0.124
Mg	0.975	0.034	0.172	0.099
K	0.914	0.069	-0.106	-0.247
PH	-0.896	0.319	-0.297	0.061
Ca	0.829	-0.087	-0.489	0.248
Cl	0.698	-0.249	-0.659	0.131
$\text{NO}_3$	0.632	-0.301	-0.498	-0.481
Eh	-0.566	-0.461	0.373	-0.553
Well depth	0.197	0.965	0.093	-0.111
Fe	-0.238	0.818	-0.474	-0.165
Temperature	0.241	-0.816	0.441	0.113
$\text{HCO}_3$	0.476	0.768	0.239	-0.1
Na	0.552	0.301	0.765	-0.14
$\text{SO}_4$	0.591	0.191	0.759	0.194
As	-0.459	0.076	0.023	0.871
Eigen values	8.66	3.474	2.871	1.592
Variance %	50.939	20.435	16.888	9.365
Cumulative	50.939	71.374	88.262	97.626

Extraction Method: Principal Component Analysis.

### 3.4.1. Factor 1 (F1)

F1 accounts for 50.94% of the total variance and strongly positive loaded with TDS (0.99), EC (0.99), hardness (0.98), magnesium (0.97), potassium (0.91), calcium (0.83), chloride (0.7), nitrate (0.63), sodium (0.55) and sulphate (0.59) while strong negatively loaded with pH (-0.89) and Eh (-0.56) Table 6. This clustering of variables associated with F1 suggest that the conditions are reducing with acidic pH which is leading to dissolve higher amount of salts and minerals in the groundwater of the area. Comparing the role of pH and Eh, it is observed that pH has dominating role in mineral dissolution and leaching of ions from their corresponding salts. About 50% of total samples have pH value less than 7 which are considered acidic Table 1.

### 3.4.2. Factor 2 (F2)

F2 accounts for 20.43% of total variance and strongly positive loaded with well depth (0.96), Iron Fe (0.82) and bicarbonate  $\text{HCO}_3$  (0.77) while negatively loaded with temperature (-0.82) Table 6. This clustering of variables associated with F2 suggests that Fe and  $\text{HCO}_3$  are increases with increasing depth. Due to the reducing condition leading to increase in concentration of  $\text{HCO}_3$  and Fe in groundwater of study area. The correlation of concentration of bicarbonate and iron is ( $r = 0.4$ ) Table 5 though the relationship between these two is not very significant because decomposition of oxygen by bacteria is not reach the stage of iron but as far as the bacterial activity present in the groundwater relationship between these two becomes stronger and stronger.

### 3.4.3. Factor 3 (F3)

F3 accounts for 16.88% of total variance which shows strong positive loading with sodium (0.76), sulphate (0.76) while negative with chloride (-0.66) Table 6. This cluster pattern of variables suggests that ion exchange of sodium is happening in groundwater of study area. Generally the source of sodium and chloride is same, but sodium has a tendency to ion exchange, so when the saline source transmit its concentration towards the depth sodium replace itself with available cation while the chloride concentration were kept constant because it is conservative and thereby reported in groundwater samples regardless of Na.

### 3.4.4. Factor 4 (F4)

F4 accounts for 9.36% of the total variance and showing strong positive loading with arsenic As (0.87) while negatively loaded with nitrate  $\text{NO}_3$  (-0.48) and Eh (-0.55) Table 6. This cluster of variable loadings clearly shows that the nitrate reducing bacteria are responsible for arsenic dissolution as arsenic is mobilized in reducing conditions [39]. Under anoxic conditions, nitrate reducing bacteria use nitrate instead of oxygen to oxidize organic material. This process of denitrification results in decrease of nitrate concentration in groundwater [40]. Reducing condition is very important for arsenic mobilization [39], but in present study the weak correlation of ORP with the arsenic indicates that there is recent inflow of nitrate in the system. On the other hand the principal component analysis has shown the Factor 4 as important one which caters the major role of reducing conditions, nitrate and arsenic.

## 4. Conclusion

The groundwater of study area is physically, chemically and biologically contaminated. Both natural process and anthropogenic activities are responsible for polluting the groundwater. High salinity, hardness and bacterial contamination are major water quality deteriorating factors. Most of the physiochemical parameters are against WHO compliance. The main parameters deteriorating the quality of groundwater are TDS, Na, K, Ca, Mg, Cl,  $\text{NO}_3$ ,  $\text{SO}_4$  and  $\text{HCO}_3$ . Water rock interaction is prime driver in study area which is leading to salt leaching followed by anoxia prevalence due to sewage mixing. Reducing environment is responsible for leaching of As from river bed sediments and alluvium forming the similar to aquifers in other river basins of the world. Seawater intrusion is also evident in the groundwater of study area. It is concluded that groundwater of Qayyumabad is unfit for drinking purpose and its long term intake may cause serious health consequences.

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