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Physicochemical and Microbiological Characterization of Groundwater along the Banks of Malir River in Karachi, Pakistan

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INFORMATION

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ABSTRACT

The main objective of this study is to assess the groundwater quality beneath urban settlements along banks of Malir River in Karachi, which is major drainage of Karachi to transport domestic and industrial wastewater into the Arabian Sea. Due to discharging untreated domestic sewage and industrial wastewater, it has become highly polluted with undesired contents which may also cause an adverse impact on the quality of shallow groundwater along the banks. For this purpose, 20 and 24 groundwater samples each from Right Bank (RB) and Left Bank (LB) of Malir River were collected boring wells at various depths (12-300ft). The samples were analysed to determine physical (pH, ORP, total dissolve solid (TDS), electrical conductivity (EC), hardness, alkalinity, salinity, specific gravity, temperature, taste, colour and odour) and chemical parameters (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, HCO_3^{-} and F^{-}). Besides, Iron (as minor element) and faecal coliforms were estimated. Data revealed that groundwater salinity is very high along both banks of Malir River which varied in the order of Right bank (mean TDS=8983 mg/L) > Left bank (mean TDS=3163 mg/L). The groundwater from both banks was found contaminated, where the RB was found more polluted as compared to LB of Malir River. Microbiological analysis revealed that 50 and 60% samples each from RB and LB have pathogenic bacterial occurrence, which suggests that sewage infiltration is common in groundwater of study area. Principal Component Analysis (PCA) revealed five significant factors, which indicate that the both natural and anthropogenic factors are responsible to alter the groundwater characteristics of study area. It is concluded that the groundwater along Malir River on both banks is unfit for drinking purpose, and the situation is worst towards the right bank.

1. Introduction

Water quality for humans and ecosystems is as important as water quantity (UNESCO, 2015). The development of nations rests on the provision of safe and required amount of drinking water (Pritchard et al., 2007). Groundwater is an excellent source of freshwater but the key issue for policy makers is to sustain its utilization. There are many factors to control groundwater chemistry such as geology of the area, geochemical processes and different patterns of land use (Saha and Kumar, 2006). Hence, the composition of groundwater is mainly affected by both geogenic and anthropogenic actions in terms of measurable quantities of pollutants (Kumar et al., 2015). The demand of groundwater is increasing due to rapidly growing population, urbanisation, industrialization, excessive fertilizer and pesticides application (Babu et al., 2015). This increasing demand has convinced the researchers for studies on groundwater quality, which have received more importance in recent decades (Vetrimurugan et al., 2013). Therefore, the resources of groundwater are considered as most important reserves all over the world (Mohamadi et al., 2011).

The surface water and surrounding groundwater is always in interconnection with each other (Raksmey et al., 2009; Banning, 2010; Fardal, 2003; Griffin, 2004). Alteration of groundwater quality by infiltration of surface water bodies is most common factor in aquifer system (Orlikowski et al., 2002). Where the seasonal variation of surface water also dominantly takes a part in alteration of groundwater quality (Raksmey et al., 2009). In Cambodia on the Mekong River, the interaction between the river water and groundwater was confirmed. It was observed that groundwater aquifers supply water to the river in dry season and river water recharges the aquifer in rainy season (Raksmey et al., 2009). Similarly, Arikaree River in North America is also very detrimental and declination of water table levels are caused by groundwater pumping (Banning, 2010). There is an inverse relationship between Akira River stream and surrounding groundwater (Fardal, 2003; Griffin, 2004).

On the other hand, impacts of polluted water of Kham River (India) has also been evolved which penetrated through the soil and contaminated the groundwater of villages around Kham River (Shinde et al., 2016). Whereas, Orlikowski et al. (2002) evaluated the adverse impact of river water on groundwater quality of urban areas in Lobau in Vienna. In study area along the banks of Malir River various agricultural fields are irrigated by groundwater. Impacts of contaminated groundwater and Malir River water on some plant species have been reported (Farooq et al., 2010).

In view of these findings, it is assumed that the polluted water of Malir River may be possible source for contamination of groundwater along both banks. Unfortunately, along both banks of Malir River, low income people live who mainly depend on groundwater due to scanty supply of municipal water. The heavy dependence on these groundwater resources is leading to lowering of the groundwater table which will stress the river water to recharge the aquifers. The impacts of polluted water of Malir River have also been reported in the groundwater of some areas along Malir River (Siddique et al., 2012; Khattak and Khattak., 2013; Farooq et al., 2010).

However, the study area still lacks detailed study to give insights about the groundwater quality on both banks of Malir River which can also aggravate the health concerns of the public in near future. There is a dire need to carry out detailed work to assess the quality of groundwater occurring on banks of Malir River in Karachi. Therefore, present study is aimed to assess the groundwater quality using hydrogeochemical and microbiological characterization along both banks of Malir River.

2. Materials and Methods

2.1. The study area

Study area covers the urban settlements along left and right banks of Malir River in Karachi. The geographic coordinates of the study area lie between latitude: 24° 81’-91' N, longitude: 67° 04’-22’ E (Fig. 1a). Also, the location of collected groundwater samples in the study area were given in the Fig. 1b. The Malir River flows from northeast to the southernmost Karachi and drains out into the Arabian sea. Malir River nearly bisects the city into western and eastern parts after crossing a wide valley between the Drig road hills and the Ibrahim Haidari. Areas on the Right bank of Malir River are Landhi, Korangi, Qaidabad, Future colony and Mansahra colony, including two large industrial estates of the city i.e. Korangi Industrial Trading Estate (KITE) and Landhi Industrial Trading Estate (LITE). Malir River is receiving huge quantity of industrial effluent from these trading estates (Khattak and Khattak, 2013). Whereas, areas on the Left bank are Malir town, Shahfaisal town, Qayyumabad, DHA Phase VII, Manzoor, Akhtar and Kashmir colonies, which are highly populated pockets of Karachi city. Apart from industrial and domestic contamination from the Right and Left banks, Malir River also host the agricultural farms along its banks which are being irrigated by Malir River and groundwater near the banks.

Most of the study area is composed of Recent alluvium, which is underlain by Manchar Formation followed by Gaj Formation (exposed in the north and the west of the study area) Fig. 2. Manchar formation comprises sandstone, clay with subordinate conglomerate (JICA, 2013). Whereas the Nari and Gaj Formations consist of shale, sandstones, and limestone with some weathered supplies from older rocks. The composition of these Formations has great influence on the adoption of hazardous components in the soil, vegetation and groundwater of the region.

2.2. Groundwater sampling

Vernacular Groundwater samples were collected before monsoon rain during November 2018 to February 2019 to avoid alteration of groundwater chemistry by infiltration of rainwater. Forty-four groundwater samples were collected, twenty from RB and 24 from LB. Samples were collected from boring wells by running electrical pump for 2 to 3 minutes to get representative samples of the groundwater similarly hand pump wells were pumped for at least 50-80 times. Location of the wells was marked on google map by using Global Positioning System (GPS) to locate the sampling points on the map. Four samples from each well were collected separately for different parameters and marked with identification symbols as; (A) for physicochemical analysis, (B) for Bacterial analysis, (C) for Nitrate and (D) for Iron determination. Groundwater samples for physicochemical analysis were collected in 1 to 1.5-liters sterilized polystyrene bottles. Groundwater samples for bacterial (Coliform) detection were collected in 200 ml sterilized bottles and kept into ice box. To determine the nitrate content, samples were collected in plastic bottles of 200ml capacity and 2ml of boric acid solution was added in each sample. These samples were then placed in ice box to maintain temperature of about 4 °C. To determine the Iron concentration, samples were collected in 100ml clean plastic bottles and 2 to 3 drops of hydrochloric acid were added as preservative.

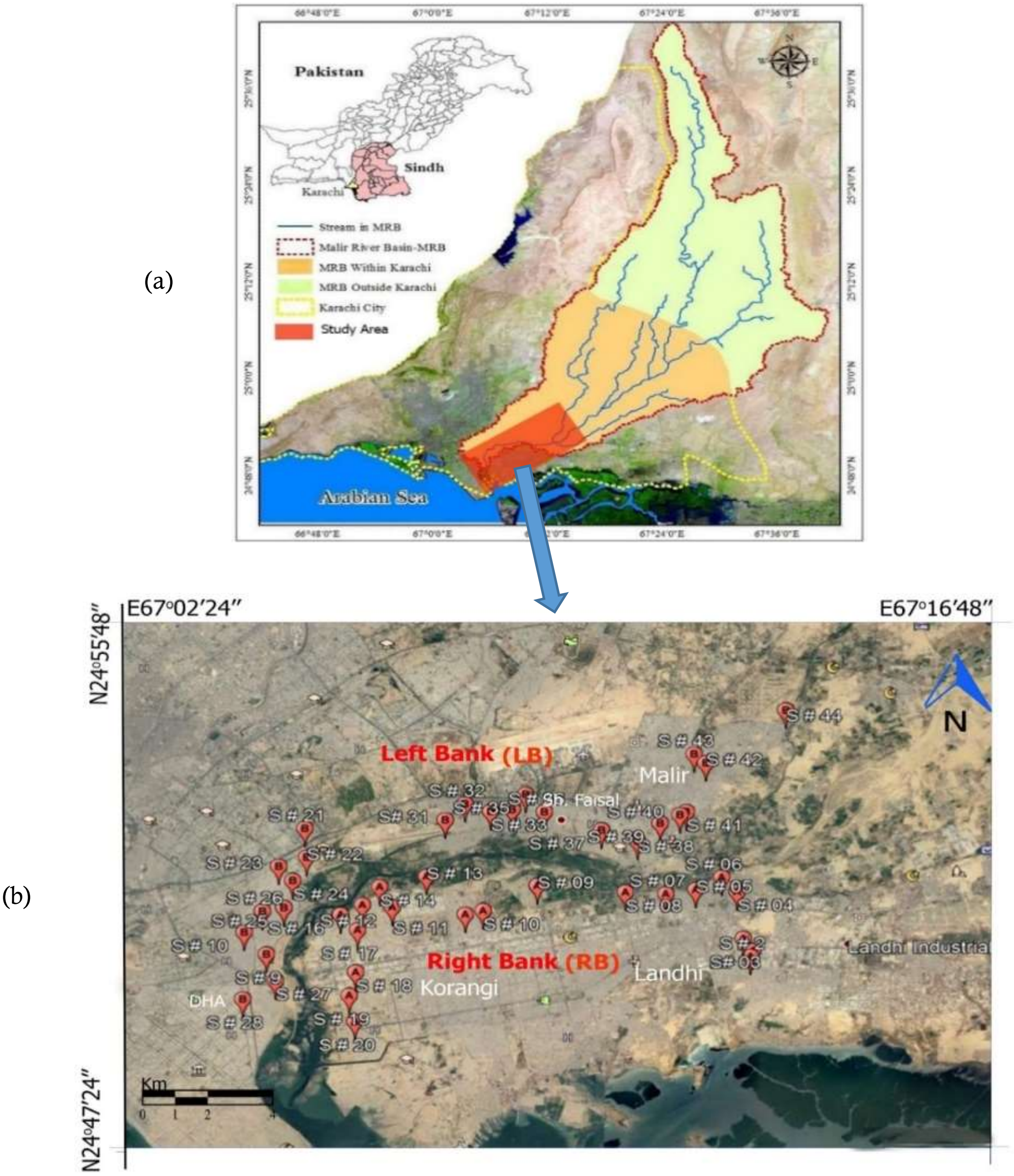

Fig. 1. Location map of study area (a) and collected groundwater samples (b)

2.3. Analytical methods

Analytical methods used for the determination of physicochemical parameters of collected groundwater samples have been summarized in Table 1. Physicochemical parameters of groundwater samples were determined in the laboratory of Department of Geology, University of Karachi. For fluoride determination, the samples were sent to the laboratory of Pakistan Council of Research in Water Resources (PCRWR).

2.4. Microbiological and statistical analysis

Membrane Filter (MF) technique was used to determine the presence or absence of E-coli in collected groundwater samples. SPSS software (Version 16.00) was used to evaluate Ionic correlation and PCA data.

3. Results and Discussion

3.1. Physical parameters

Quantitative estimation of physical parameters along RB and LB of Malir River have been summarized in Table 2 and 3, respectively.

3.1.1. Aesthetic characteristics (colour, taste and odour)

All samples from both banks of Malir River were found odourless and colourless except 1 and 5 samples from RB and LB respectively (Tables 2 and 3). Light yellow colour of these 6 samples is attributed to organic matter, dissolved iron and suspended solids (Kumar et al., 2015). In study area the source of these contaminant may be industrial, domestic effluents and domestic sewage. Based on taste, study area can be divided into two zones, i.e. salty (southern) and freshwater (northern) zone. Most of salty samples were found in areas near the coastal region i.e. DHA Phase VII, Manzoor colony, Akhtar colony, Kashmir colony and Qayyumabad along LB and southern Korangi along RB of Malir River.

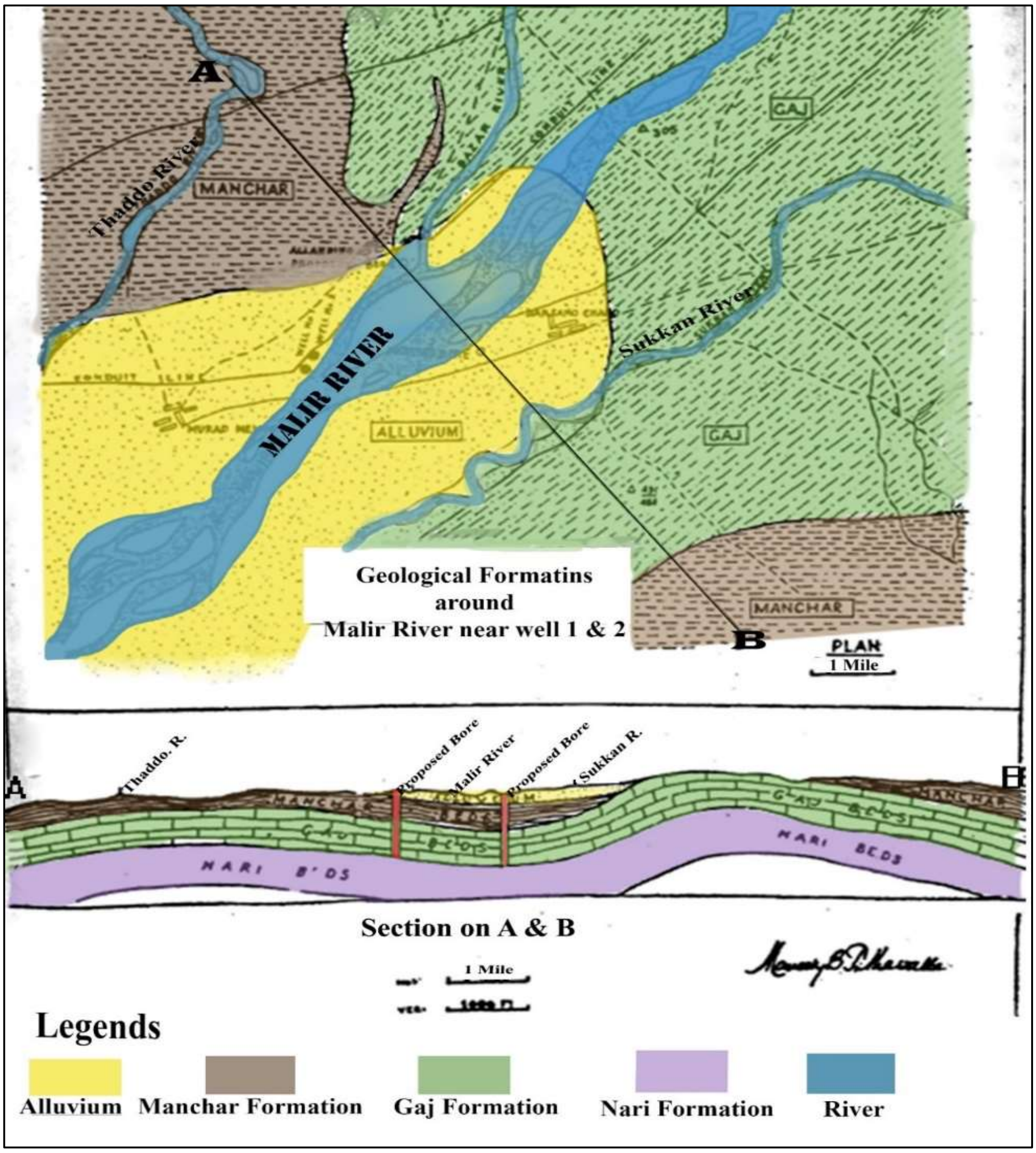

Fig. 2. Stratigraphy and cross section of study area (after Pithawala et al., 1946)

About 55% and 33% samples along RB and LB respectively were found salty to bitter in taste (Table 3). These samples were collected at variable depths (12-300ft), which shows that the salinity of these groundwaters in study area is free from depth variation. It implies that the saline source is spreading from shallow to deeper wells. The saline taste in these areas due to sea water intrusion, which is already reported by earlier workers (Khan and Bakhtiari, 2017; Mashiatullah et al., 2002). Moreover, high salinity may also be associated with the sewage mixing (Kass et al., 2005). The main source of sewage infiltration is Malir River, whereas the industrial contamination from KITE and LITE may also be the source for higher salinity in this area.

3.1.2. Physical parameters

Groundwater temperature varied in the range of 26-32°C along both sides of Malir River, where mean temperatures of 31°C and 29°C are reported along RB and LB of Malir River respectively. The temperature of groundwater is one of the most important parameters (Jones et al., 1999) that may cause many alterations of water such as bacterial growth, colour, taste, odour and corrosion problem (WHO, 2008). Many anthropogenic sources are responsible for higher temperature of groundwater on long-term basis (Gunawardhana and Kazama, 2009). The occurrence of high mean temperature on RB (+30°C) may be explained by the mixing of polluted water from Malir River.

The pH varies from acidic to basic (6.3 to 8) with a mean value of 7.3 and 7.4 along RB and LB respectively. Generally, groundwater pH is within the permissible range (6.5-8.5) of WHO, (2011). Most of groundwater samples were found neutral to slightly alkaline on both banks, while a few have shown acidic values. The pH of water has no direct impact on human health, but its greater values increase the scale formations in water heating apparatus (Narsimha et al., 2013). Moreover, the pH is an important parameter causing dissolution of minerals (Zhang et al., 2009). The sampling wells near the river showed slightly higher pH values compared to more distant points. This may be due to infiltration of sewage in shallow groundwater. The variation in pH values indirectly affects the quality of groundwater such as solubility of heavy metal ion and microbial growth (Mohamadi et al., 2011).

Table 1. Equipment/methods used to analyse physicochemical parameters of groundwater samples (after PCRWR, 2002).

Sample No	Parameters	Equipment /Methods
1	Color	Visual observation
2	Odor and Taste	Aesthetically
3	Temperature	Thermometer
4	pH and Eh	pH meter, ADWA (AD 111)
5	Turbidity	Turbidity meter, Lamotte, model 2008, USA
6	Electrical Conductivity/TDS	EC meter, ADWA (AD 330)
7	Salinity and Specific gravity	Portable Refractometer
8	Hardness as $CaCo_3$	EDTA Titration Standard Method (1992).
9	Alkalinity	APHA 2320 Standard Method (1992)
10	Bi-Carbonate	Titration Method (USSL, 1954)
11	Calcium	EDTA Titration Method
12	Chloride	Argenometric Titration Method
13	Carbonate	Titration Method, (USSL, 1954)
14	Fluoride	Spectrophotometer, SPADNS (HACH)
15	Iron	Atomic Absorption Spectrometer
16	Magnesium	Titration Method
17	Nitrate	Spectrophotometer, HACH-8171
18	Potassium	Flame photometer (JENWAY PFP7)
19	Sodium	Flame photometer (JENWAY PFP7)
20	Sulphate	Spectrophotometer (DR 2800)

Redox potential varied between -62 to +255 mV and -70 to +219 mV with mean of +74.45 mV and +96.3 mV along RB and LB respectively (Tables 2 and 3). Generally, the ORP values area positive on both banks. However, 4 and 3 samples each from right and LB have shown negative values (Tables 2 and 3). All samples with negative values showing inverse relationship with salinity except sample number 2 indicating the reducing environment in saline aquifers (Fig. 3). The landfills containing organic matter may impart great influence on the redox potential due to biological disintegration (Christensen et al., 2000; Atlas, 1981). Comparatively the groundwater samples from RB have greater values with mean difference of 21mV which indicates bacterial activity may be due to mixing of sewage either from local source or from Malir River.

Highly variable values of TDS content were determined along both banks of Malir River, range between 216-48442mg/L and 1242-9408mg/L with mean values of 8983mg/L and 3163mg/L (Tables 2 and 3) along RB and LB respectively. A greater value at RB with a mean difference of 5820mg/L is mainly due to sample number RB-16,17 and 18, which were collected from coastal parts of southern Korangi.

All the samples from both banks exceeded WHO and Pakistan guideline values of 500 and 1000mg/L for drinking purpose. However, the RB has higher TDS values than LB. Such wide variation in TDS content may be attributed to geochemical processes and human activities. TDS estimation is very important for suitability of water for drinking purpose, agriculture and industrial uses. Elevated TDS contents in groundwater of study area may be due to higher concentration of chemical parameters including major cations (Na, K, Ca, Mg), anions (Cl, NO_3, HCO_3) (Tables 4 and 5) coupled with the bacterial occurrence suggests that sewage water infiltration in groundwater aquifers results in high salt load (Cole et al., 2004). A very important source for higher values of TDS in collected groundwater samples may be due to the influx of natural saline water by sea water intrusion (Kass et al., 2005; Khan and Bakhtiari, 2017; Mashiatulla et al., 2002).

Turbidity of collected groundwater samples ranges between 0.7-4.9 NTU and 0.01-3.5 NTU along RB and LB (Tables 2 and 3) with the same mean value of 1.4 NTU. All samples were found under permissible limit <5 NTU by WHO (2011). The turbidity of water indicates the grade of pollution (Momba et al., 2006). As samples were collected during dry season, the turbidity is found low and siltation of soil and clay was also not found. Extremely variable content of hardness is reported from RB (range: 230-10000mg/L, mean: 1946mg/L) and LB (rang: 200-3000mg/L, mean: 872mg/L) (Tables 2 and 5). Hardness of about 60% and 84% samples along RB and LB are above WHO permissible limit (500 mg/L) for drinking purpose (Fig. 4). Sample number RB-16 and 18 are responsible for higher mean of hardness at right side of Malir River. These two samples are also high in calcium and magnesium contents (Table 4). In study area 97% samples are found very hard, it may be due to groundwater interaction with Ca and Mg rich minerals causing high concentration of these content along both banks of Malir River (Bhatnagar, 1999; Priya et al., 2015). Possible source of these two main responsible factors for hardness may cause dissolution of limestone of underlying Gaj Formation. Hard water may cause various health problems including calcification of arteries (Saleem et al., 2016).

Table 2. Summary of physical parameters along RB of Malir River

Sample No	**Coordinates**		**Locality**	**Place**	**Well dept (ft)**	**Well life**	**Color**	**Taste**	**Odor**	**pH**	**Eh (mv)**	**TDS (mg/L)**	**EC (mS/cm)**	**Temp. (˚C)**	**Turbidity (NTU)**	**Salinity (%)**	**Specific gravity (mm)**	**Hardness (mg/l)**	**Alkalinity as $CaCO_3$ (mg/l)**
	Latitude	**Longitude**																	
RB-01	24.83′66.572″	67°21′67.43″	Bilal Colony Landhi	House	40	3 years	Colorless	UO	UO	7.25	125	1216	1.90	29	0.8	0	1	370	250
RB-02	24.83′49.882″	67°21′61.15″	Bilal Colony Landhi	Street	35	10 months	Colorless	UO	UO	7.90	-62	1171	1.83	30	1.2	0	1	230	200
RB-03	24.84′03.36″	67°21′39.92″	Mehmood Nagar Landhi	Masjid	40	3 years	Colorless	UO	UO	7.34	164	1254	1.96	31	0.6	0	1	320	100
RB-04	24.84′43.02″	67°21′20.71″	Qaidabad	Masjid	120	>12 years	Colorless	UO	UO	7.14	157	979	1.53	30	0.8	0	1	410	150
RB-05	24.84′49.52″	67°20′10.61″	Future Colony	Shope	110	10 months	Colorless	UO	UO	7.25	151	928	1.45	30	1.2	0	1	420	250
RB-06	24.84′58.48″	67°20′76.98″	Murghi Khana	House	160	3 days	Colorless	UO	UO	7.33	128	1568	2.45	31	3.5	0	1	450	250
RB-07	24.51′11.9772″	67°11′31.68″	Korangi	Service station	120	+20 years	Colorless	UO	UO	8.00	255	1114	1.74	28	2.5	0	1	460	200
RB-08	24.51′12.808″	67°10′51.056″	Murtaza Chowrangi	Masjid	750	3-4 months	Colorless	Salty	UO	7.85	163	6611	10.33	27	1.9	2	1.002	1475	100
RB-09	24.51′18.910″	67°9′22.820″	Allah Bukhs Goat	Masjid	120	1 year	Colorless	UO	UO	7.77	181	3821	5.97	29	0.8	0	1	980	200
RB-10	24.50′50.64″	67°8′28.651″	Gulshane Bilal, Korangi	Masjid	180	1 year	Colorless	UO	UO	7.45	155	3392	5.3	30	0.5	0	1	910	500
RB-11	24.50′46.43″	67°8′10.94″	Bilal Colony, Kongari	Masjid	200	+15 years	Colorless	Bitter	UO	7.21	124	9856	15.4	30	0.6	15	1.012	3440	25
RB-12	24.50′52.95″	67°6′57.44″	Mehran Town, Kongari	Masjid	80	+5 years	Colorless	Salty	UO	7.33	120	10643	16.63	29	0.7	8	1.005	2020	100
RB-13	24.51′26.69″	67°7′31.20″	Kongari Sector 7A	Factory	300	7 months	Colorless	Salty	UO	7.03	98	3795	5.93	28	2	10	1.01	700	180
RB-14	24.51′14.71″	67°6′44.37″	Mehran Town, Kongari	Masjid	117	6 months	Light yellow	Salty	UO	7.11	38	3846	6.01	30.08	0.4	8	1.005	3000	170
RB-15	24.50′55.00″	67°6′27.40″	Kongari Sector 6	Masjid	88	9 years	Colorless	Bitter	UO	7.00	-65	9847	13.98	30.5	0.4	11	1.011	900	100
RB-16	24.50′43.96″	67°6′5.77″	Kongari Sector 5	Home	150	6 months	Colorless	Bitter	UO	6.77	-126	38784	60.6	30.1	1.1	20	1.015	10000	360
RB-17	24.50′27.78″	67°6′23.08″	Kongari Sector 6	Masjid	100	7 years	Colorless	Bitter	UO	6.38	86	25459	39.78	31.1	2.9	19	1.014	500	220
RB-18	24.49′42.22″	67°6′22.16″	Allahwala Town Sector A	Masjid	30	3 years	Colorless	Bitter	UO	6.51	-180	48442	75.69	30	0.7	25	1.024	10000	210
RB-19	24.49′16.92″	67°6′16.16″	Bhitai Colony	Masjid	15	15 days	Colorless	Bitter	UO	7.10	16	6394	9.99	31.3	0	8	1.005	1300	150
RB-20	24.48′49.00″	67°6′22.51″	Bhitai Colony	Home	25	2 years	Colorless	Bitter	UO	7.28	-101	1440	2.25	30.1	1.4	5	1.001	1400	190
Min	-	-	-	-	-	-	-	-	-	6,28	-180	928	1.45	27	0	0	1	230	25
Max	-	-	-	-	-	-	-	-	-	8	255	48442	75.69	31.3	4.9	25	1.024	10000	500
Mean	-	-	-	-	-	-	-	-	-	7,3	71.4	8983	14.0	29.8	1.4	6.6	1	1964.3	195.5
WHO	**-**	**-**	**-**	**-**	**-**	**-**	**Colorless**	**UO**	**UO**	**6.5-8.5**	**-**	**500**	**-**	**-**	**0**	**0**	**-**	**500**	**500**

Table 3. Summary of physical parameters along LB of Malir River

Sample No	**Coordinates**		**Locality**	**Place**	**Well dept (ft)**	**Well life**	**Color**	**Taste**	**Odor**	**pH**	**Eh (mv)**	**TDS (mg/L)**	**EC (mS/cm)**	**Temp. (˚C)**	**Turbidity (NTU)**	**Salinity (%)**	**Specific gravity (mm)**	**Hardness (mg/l)**	**Alkalinity as $CaCO_3$ (mg/l)**
	Latitude	**Longitude**																	
RB-21	24.52′16.42″	67°5′27.90″	Karsaz	Home	252	1 year	Colorless	Salty	UO	6.82	76	3904	6.1	32	0.8	10	1.01	600	150
RB-22	24.51′45.34″	67°5′30.34″	Falcon Complex Faisal	Masjid	25	15 years	Light yellow	Salty	UO	7.01	57	5325	8.3	32	0.72	5	1.001	1200	170
RB-23	24.51′35.14″	67°5′2.47″	KAEHS Block 8	Home	128	3 years	Colorless	UO	UO	6.45	38	2752	4.3	29	0.01	0	1	1500	200
RB-24	24.51′19.94″	67°5′16.85″	Manzor Colony Sec I	Masjid	43	25 years	Colorless	Salty	UO	6.32	97	4173	6.5	30	0.6	5	1.001	800	190
RB-25	24.50′50.60″	67°5′8.60″	Manzor Colony Sec E	Home	15	20 years	Colorless	Salty	UO	7.21	16	1126	1.8	30	1.2	5	1.001	900	260
RB-26	24.50′46.40″	67°4′47.18″	Junaijo Town	Home	26	3 years	Light yellow	UO	UO	7.52	40	5280	8.3	31	0.6	0	1	1100	100
RB-27	24.49′31.66″	67°5′1.80″	Qayyumabad	Masjid	37	3 years	Colorless	Salty	UO	6.91	51	9408	15	30	1.2	15	1.012	3000	100
RB-28	24.49′11.15″	67°4′29.35″	DHA phas 7	Masjid	25	dna	Light yellow	Salty	UO	7.42	-70	1613	2.5	30	1.6	15	1.012	400	110
RB-29	24.49′59.98″	67°4′52.01″	DVHS	House	102	dna	Light yellow	Salty	UO	7.62	-20	5107	8	26	2.01	5	1.001	920	230
RB-30	24.50′23.38″	67°4′29.22″	Akhtar Colony	House	36	dna	Light yellow	Salty	UO	6.50	125	1267	2	26	2.26	10	1.01	620	185
RB-31	24.52′28.3944″	67°7′65.52″	Shah Faisal No: 05	Masjid	110	3 years	Colorless	UO	UO	7.76	107	3014	4.7	29	1.2	0	1	440	50
RB-32	24.52′45.685″	67°8′8.196″	Shah Faisal No: 04	Masjid	100	3 years	Colorless	UO	UO	8.03	169	1242	1.9	29	0.8	0	1	200	150
RB-33	24.52′37.9164″	67°8′34.3284″	Shah Faisal No: 1 Rita Plot	Masjid	75	3 years	Colorless	UO	UO	7.70	109	3046	4.8	28	0.6	0	1	500	175
RB-34	24.52′40.1556″	67°8′55.8024″	Shah Faisal No: 2 Rita Plot	Masjid	90	4 years	Colorless	UO	UO	7.64	146	3130	4.9	30	0.7	0	1	540	500
RB-35	24.52′56.2416″	67°9′8.8992″	Shah Faisal No: 3	Masjid	75	10 years	Colorless	UO	UO	7.65	130	3846	6	30	1.1	0	1	1020	100
RB-36	24.52′38.0496″	67°9′27.342″	Shah Faisal No: 3	Masjid	120	1 month	Colorless	UO	UO	7.72	80	5069	7.9	29	1.2	0	1	1040	250
RB-37	24.52′19.8804″	67°10′25.9716″	Gulhane Ghazali	Home	140	2 years	Colorless	UO	UO	7.6	92	1888	3	28	1.5	0	1	580	250
RB-38	24.52′8.4864″	67°11′2.238″	Muhammad Ali Shaheed	Home	120	2 years	Colorless	UO	UO	7.57	100	1760	2.8	31	2.9	0	1	640	100
RB-39	24.52′28.0092″	67°11′24.8928″	Baghe Ibrahim	Home	150	3-4 months	Colorless	UO	UO	7.83	85	1869	2.9	30	3.5	0	1	700	40
RB-40	24.52′37.4088″	67°11′44.5776″	Chatai Ground, Asu Goth	Masjid	150	2 years	Colorless	UO	UO	7.40	160	1933	3	29	2.2	0	1	960	75
RB-41	24.52′40.7712″	67°11′50.8632″	Bakra Piri, Asu Goth	Masjid	120	10 years	Colorless	UO	UO	7.27	174	3174	5	30	2.6	0	1	1300	250
RB-42	24.53′34.2348″	67°12′09.1404″	Jafar-e-Tayyar	Masjid	150	16 years	Colorless	UO	UO	7.96	148	1536	2.4	27	1.5	0	1	300	20
RB-43	24.53′43.5372″	67°11′56.814″	Urdu Nagar, Malir Colony	Masjid	220	2 years	Colorless	UO	UO	7.35	219	2598	4.1	28	0.7	0	1	900	125
RB-44	24.54′32.0688″	67°13′28.2576″	Aram Goth	Masjid	130	6 years	Colorless	UO	UO	7.41	189	1862	2.9	31	1.1	0	1	780	100
Min	-	-	-	-	15	-	-	-	-	6,32	-70	1126	1.8	26	0.01	0	1	200	20
Max	-	-	-	-	252	-	-	-	-	8.03	219	9408	15	32	3.5	15	1.012	3000	500
Mean	-	-	-	-	-	-	-	-	-	7.4	96.3	3163	4.9	29.4	1.4	2.9	1	872.5	161.7
WHO	**-**	**-**	**-**	**-**	**-**	**-**	**Colorless**	**UO**	**UO**	**6.5-8.5**	**-**	**500**	**-**	**-**	**0**	**0**	**-**	**500**	**500**

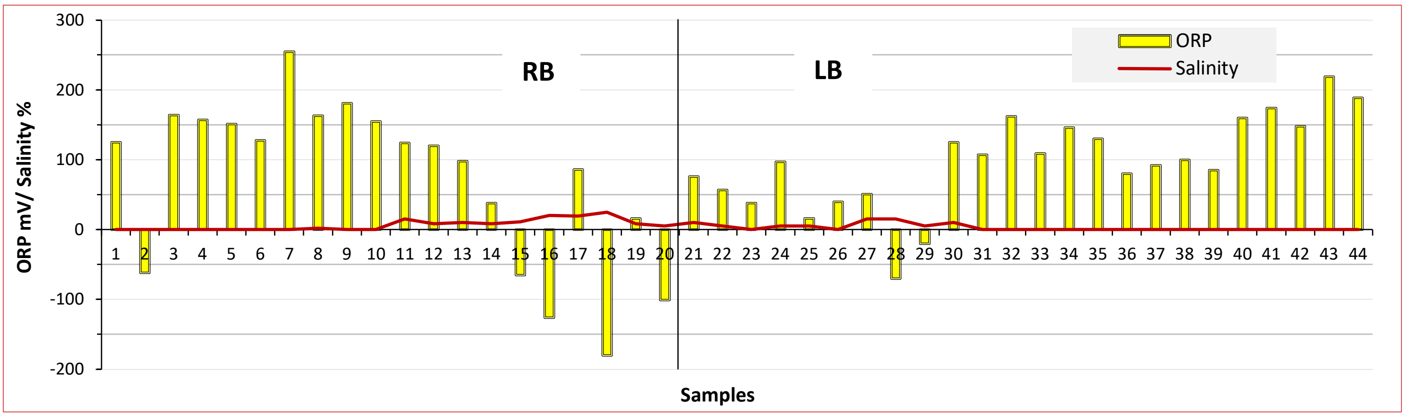

Fig. 3. Relationship between salinity and ORP of groundwater samples

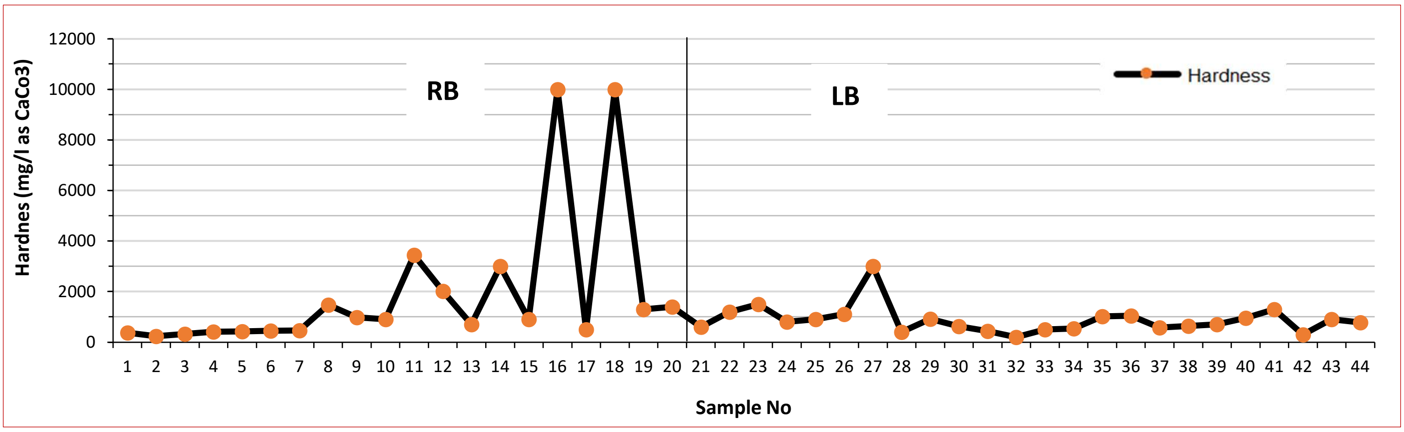

Fig.4. Distribution pattern of hardness of groundwater samples along banks of Malir River

A wide range of alkalinity on RB (25-500 mg/L) and LB (20-500 mg/L) (Tables 2 and 3). Although alkalinity varied within the guideline of (500mg/L) for drinking purpose on both the banks but alkalinity at RB is relatively higher (mean = 195 mg/L) than LB (mean = 165 mg/L).

Bicarbonate dominate over CO_3^{-2} and OH^- ions in groundwater within pH range of 6.5-8.5 (McDonald, 2006). Similar is true about groundwater of the Malir River basin (pH rang: 6.3-8) has shown direct relationship with HCO_3^- (Fig. 5).

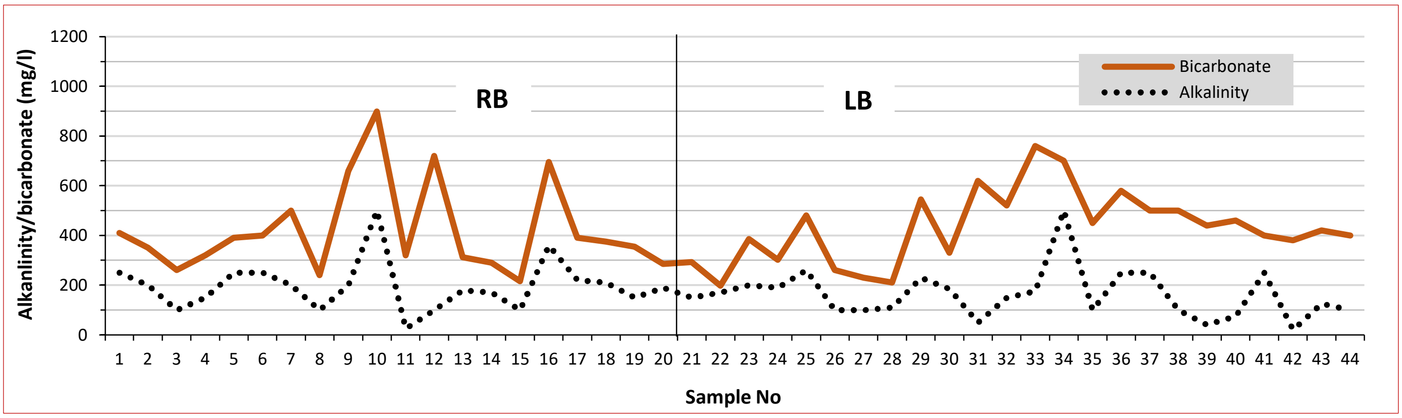

Fig. 5. Direct relationship between alkalinity and bicarbonate of groundwater samples along banks of Malir River

3.2. Chemical parameters

3.2.1. Major cations

The concentration of sodium in all collected samples from the both banks of Malir River found objectionable against permissible limit (200mg/L) prescribed by WHO (2011) for drinking purpose. Sodium content ranged at RB between 272-14809mg/L and along LF 2221mg/L and 986mg/L respectively. The RB showed two times higher sodium mean

(2221mg/L) than LB (986mg/L) (Tables 4 and 5). The higher values of sodium concentration were observed from sample number 8 to 27 which were collected in coastal proximity including southern side of Korangi along RB and DHA Phase VII, Manzoorr Colony, Akhtar Colony, Kashmir Colony and Qayyumabad at LB of Malir River. The higher salinity of groundwater in these areas has already been reported by seawater intrusion (Khan and Bakhtiari., 2017; Mashiatulla et al., 2002). The sources of high sodium include dissolution from subsurface strata or anthropogenic activity (Dieng et al, 2016; Hem, 1985). Interestingly a large mean difference of Na content occurs on both banks, where the concentration on RB is double than on LB is clear indication of industrial impact and seawater intrusion on RB.

A wide range of potassium concentration occurs on the RB (17-160mg/L) and LB (13-130mg/L) with mean of 71mg/L and 47mg/L respectively (Tables 4 and 5). Potassium in groundwater of RB is six and LB is four times higher than the WHO guidelines for drinking purpose. All the samples along both banks are found above the prescribed limit of potassium (12mg/L) for drinking purpose. The possible sources of potassium in groundwater include precipitation, weathering of existing minerals of potash silicate, excessive use of potash fertilizer (Jain et al., 2011; Deshpande and Aher, 2012). Since Malir River basin is an agriculture belt, so the high concentration of potassium in collected groundwater samples from both banks of Malir River may be attributed to agricultural effects on the groundwater of these areas.

Fig. 4. Summary of chemical parameters along RB of Malir River

Sample No	**Cations**					**Anions**				**Minor element**
	Calcium (Ca)	**Magnesium (Mg)**	**Sodium (Na)**	**Potassium (K)**	**Chloride (Cl)**	**Sulphate (SO4)**	**Bicarbonate (HCO3)**	**Nitrate NO3**	**Fluoride (F)**	**Iron (Fe)**
RB-01	72	46	440	32	355	342	410	2.5	1.01	BDL
RB-02	20	44	535	17	284	961	350	3.6	1.01	BDL
RB-03	68	36	272	32	177	814	260	3.88	1.02	BDL
RB-04	60	63	385	30	284	969	320	9.85	0.98	BDL
RB-05	80	53	341	57	213	1331	390	10.69	0.9	BDL
RB-06	70	67	547	23	567	1237	400	5.10	1.11	BDL
RB-07	72	68	418	69	319	794	500	11.97	1.25	BDL
RB-08	200	237	1282	30	3901	1729	240	9.34	1.35	BDL
RB-09	96	182	955	23	2021	1280	660	11.26	1.5	BDL
RB-10	84	170	907	62	1525	889	900	12.88	1.89	1
RB-11	720	399	5060	160	9574	1368	320	9.56	1.98	BDL
RB-12	84	440	1250	86	6737	2123	720	13.50	1.74	BDL
RB-13	74	125	1515	37	198	678	312	27.69	2.4	6
RB-14	275	562	1290	48	1002	2012	290	25.21	1.5	40
RB-15	104	156	1830	105	3020	739	215	7.6	1.9	46
RB-16	348	2219	14809	140	1998	2049	695	8.66	5.54	79
RB-17	590	237	8615	139	12720	490	390	8.42	5.51	260
RB-18	750	1974	979	158	30666	505	375	16	5.55	19
RB-19	159	219	2606	102	1998	370	355	11.67	2.52	90
RB-20	195	250	375	70	258	675	285	3.37	1.05	65
Min	20	36	272	17	177	342	215	2.5	0.9	1
Max	750	2219	14809	160	30666	2123	900	27.7	5.6	260
Mean	206	377	2221	71	3891	1068	419	11	2	30
St. Deviation	224	606	3568	48	7171	558	184	7	2	79
WHO	**75**	**150**	**200**	**12**	**250**	**250**	**300**	**10**	**1.5**	**300**
Samples above permissible limit	13	12	20	20	17	20	15	9	11	0

All values are in mg/l except Fe in (µg/l); BDL= Below detection limit

Like other ions, highly variable calcium concentration is also reported in groundwater of study area. The Ca content at RB ranges (201-750mg/L) and LB (8-348mg/L). The RB showed double mean value (206mg/L) as compared to LB (94mg/L). Only 35 and 45% samples are found with permissible limit of Ca content (75mg/L) by WHO (2011) for drinking water. The water, flowing through limestone may contain greater concentration of calcium ions (Shrivastava and Pandey, 2012). Silicate mineral group is also source of calcium in groundwater while shales and sandstone may contain calcium in the form of carbonate cement. The underlying rocks in study area constitute shale, sandstone (Manchar Formation) and limestone (Gaj Formation). Higher values of Ca on RB may due to limestone of underlying Gaj Formation. Contrary to this lower value of Ca on LB may due to underlying Manchar Formation.

Extremely variable magnesium concentration is found along both banks of Malir River varied between RB (36-2219 mg/L) and LB (44-669mg/L). Interestingly the mean Mg on RB is more than double (370mg/L) of its mean on LB (165 mg/L) (Tables 4 and 5). Where only 35 and 41% samples each from RB and LB respectively found under permissible limit for magnesium content (150mg/L) by WHO (2011) for drinking purpose. Similar to previously discussed factors, the concentration of Mg is also greater at the RB of Malir River as compared to LB.

Higher values of Mg may come from seawater intrusion. Groundwater along LB coastal part i.e. Qayyumabad, DHA Phase VII, Manzar colony and Akhtar colony are showing lower values, while on other side, southern Korangi are showing much higher values. Therefore, the factor of seawater intrusion may not be responsible for the higher concentration of Mg ions on the RB, rather it may be related to sewage mixing (Cole et al., 2004). The higher concentration in drinking water it is considered as laxative agent (Sarala and Ravi, 2012).

Fig. 5. Summary of chemical parameters along LB of Malir River

Sample No	**Cations**					**Anions**				**Minor element**
	Calcium (Ca)	**Magnesium (Mg)**	**Sodium (Na)**	**Potassium (K)**	**Chloride (Cl)**	**Sulphate (SO4)**	**Bicarbonate (HCO3)**	**Nitrate NO3**	**Fluoride (F)**	**Iron (Fe)**
LB-21	124	70	855	25	1098	220	292	8.03	1.6	10
LB-22	149	201	1305	85	1695	981	198	13.8	1.9	BDL
LB-23	348	153	561	38	458	659	385	4.01	1.7	6
LB-24	222	60	1069	110	175	321	302	18.88	2.7	BDL
LB-25	104	156	203	74	1650	105	480	4.6	1.86	BDL
LB-26	119	195	1449	130	598	255	261	10	2.62	20
LB-27	98	669	4350	129	195	645	230	9.06	3.1	10
LB-28	82	47	222	80	205	188	210	12.9	1.56	106
LB-29	201	101	1198	104	2108	121	545	8.48	2.55	2850
LB-30	79	103	258	69	599	69	330	4.19	1.23	776
LB-31	44	80	895	32	994	1250	620	11.22	2.99	10
LB-32	8	44	580	16	355	1371	520	10.56	1.4	BDL
LB-33	32	102	1000	24	1383	1273	760	11.50	3.1	BDL
LB-34	40	107	1010	25	1418	997	700	10.70	3.12	BDL
LB-35	48	219	1582	27	1950	806	450	11.12	2.9	BDL
LB-36	80	204	1620	23	3120	733	580	11.40	3.8	19
LB-37	60	104	600	21	745	512	500	11.42	1.33	BDL
LB-38	64	117	938	25	709	924	500	11.84	1.27	BDL
LB-39	52	139	1143	18	887	1319	440	10.88	1.79	BDL
LB-40	56	199	500	19	5851	558	460	9.15	2.1	BDL
LB-41	100	255	633	21	7801	830	400	9.50	1.08	16
LB-42	24	58	589	13	3014	711	380	2.38	1.01	BDL
LB-43	88	165	757	14	6028	941	420	10.13	1.85	BDL
LB-44	40	165	347	14	4078	1536	400	7.89	0.84	BDL
Min	8	44	203	13	175	69	198	2.4	0.8	6
Max	348	669	4350	130	7801.2	1536	760	18.9	3.8	2850
Mean	94	155	986	47	1963	722	432	10	2	159
St. Deviation	75	125	826	39	2057	439	147	4	1	899
WHO	**75**	**150**	**200**	**12**	**250**	**250**	**300**	**10**	**1.5**	**300**
Samples above permissible limit	13	11	24	24	21	20	20	12	16	2

All values are in mg/l except Fe in (µg/l); BDL= Below detection limit

3.2.2 Major anions

Very high variation in chloride concentration has been found along RB and LB of Malir River ranging between 177-30666mg/L and 175-7801mg/L with mean values 3891mg/L to 1963 mg/L respectively (Tables 4 and 5). Two samples (RB-7 and 8) showed exceptionally high values (1270 and 30666mg/L) at RB which are responsible for greater variation. Apart from these two samples both banks found with similar values. About 85% and 88% samples each from RB and LB are above WHO permissible limit. High concentrations of Cl$^-$ is because of sea water intrusion in the Qayyumabad area, near Ghizri Creek (Mashiatullah et al, 2002). Similar pattern of higher concentration of Cl on both banks except sample (8 to 18) may be the indication of seawater intrusion or anthropogenic activity as the chloride is a good indicator of anthropogenic inputs in groundwater system (CGWB, 1995).

High variation in sulphate content was determined on RB (342-2123mg/L) and LB (69-1536mg/L), (Tables 4 and 5). Mean value of sulphate is found 4 (RB) and 3 (LB) times higher than prescribed limit (250mg/L) by WHO (2011) including all samples form RB and 80 samples from LB. High sulphate content in the groundwater of study area suggests dissolution of gypsum from gypsiferrous shale of Gaj Formation, use of SO_4 fertilizer may increase sulphate content in groundwater (Nguyen and Itio, 2009; Anawar et al., 2013). Higher value of sulphate in groundwater is indicator of sewage mixing and industrial discharges (Kumar el al., 2015). Where high sulphate content in Qayyumabad and near Ghizri area has already been reported due to seawater intrusion (Mashiatullah et al, 2002). In urban areas the major source for sulphate in water is smoke from fossil fuel, Karachi is the densely populated city of the country, where huge amount of fossil fuel resulting in air pollution and smoke. This smoke by on interaction with rainfall may oxidize and infiltrate to the aquifer depth causing high sulphate. Intake of 8g of $NaSO_4$ and 7g of $MgSO_4$ may cause catharsis in adult males (Morris and Levy, 1983; Cocchetto and Levy, 1981)

Great variation is found in the range of nitrate concentration along RB (2.5-27.7mg/L) and LB (2.4-18.9mg/L) with mean 10mg/L and 11mg/L respectively (Tables 4 and 5). Above 40% samples each from RB and LB are found above permissible limit (10mg/L). About 52% samples of the total (n=44) are found with NO_3 concentration <10mg/L. Possibly the fecal bacteria are accelerating the nitrate reduction process by oxidation of organic matter, which results in decrease of nitrate content in groundwater and causing reducing conditions in the aquifer (Canters, 1997; McCreadie et al., 2000; Rowland et al., 2008; Mukherjee et al., 2009). Presence of fecal bacteria (47%) of total samples in study area and high bicarbonate concentration suggests that organic matter decay is followed by nitrate reduction in the groundwater of the study area (Davis and DeWiest, 1996).

Bicarbonate concentration along both banks of Malir River found in the range of 215-900 and 198-760mg/L along RB and LB with mean of 419 and 432 mg/L respectively. Total mean of both sides 425mg/l. About 80% samples along both banks are above the permissible limit 300mg/L (WHO, 2011). Naturally bicarbonate is mainly derived from soil zone CO_2 during weathering of parent rock (Kenneth et al., 2014). Dissolution of silicate minerals and reaction between feldspar minerals and carbonic acid in the presence of water are possible sources of HCO_3- (Elango et al., 2003). It can also come from dissolution of carbonate minerals along with biodegradation of organic matter under the reducing conditions (Shamsudduha et al., 2008; Jeong, 2001). In the study area bicarbonate has not shown significant correlation with any major ions suggesting that organic matter decomposition is main source to release HCO_3 into the groundwater (Jeong, 2001).

The concentration of fluoride content is found between the range 0.9-5.6 and 0.8 to 3.8mg/L along RB and LB respectively with same mean value of 2mg/l. About 45% and 67% samples along RB and LB, respectively exceeded the permissible limit of 1.5mg/L (WHO, 2008). Normally seawater contains 1.3mg/L (Slooff, et al., 1988) and areas which are rich in fluoride-containing minerals such as mica, amphibole, apatite and titanite (Sphene) etc, have fluoride contaminated groundwater up to 10 mg/L. Industrial discharge contains high concentration of fluoride and can contaminate the river system (Slooff et al., 1988). The higher concentration of fluoride indicates anthropogenic influx which contains huge industrial, domestic and agricultural wastes. Higher fluoride ingestion may have severe effects on skeletal tissues (skeletal fluorosis). Adverse impact on bone structure may be observed when drinking-water contains 3 to 6 mg/l of fluoride. Whereas over 10mg/L can cause crippling skeletal fluorosis (IPCS, 1984).

3.2.3. Trace element

Highly variable range of iron concentration found in groundwater along both banks of which span between 1-460 and 6-2850 μg/L along RB and LB respectively. Mean concentration of iron in groundwater along LB is three times higher than its content along RB (51 μg/L). This large variation on LB is due to anomalous concentration in sample LB-29 and 30 which also elevated the mean value (Tables 4 and 5). All samples along both banks except sample (RB-15, and LB-29, 30) are found under permissible limit of (300μg/l by WHO (2011). This low concentration of iron content indicates the oxidizing environment along both banks except three samples which may have high iron content from additional sources or reducing environment.

3.3. Microbiological analysis

Qualitative analysis of groundwater samples was done to evaluate the possible interaction of sewage water with the aquafer system of the study area. About 50% and 62% samples each from RB and LB of Malir River were found contaminated with positivity fecal coliform respectively (Table 6). The wells analysed with positive coliform also showed high concentration of Na, K, Cl, SO_4, F ions and shallow depth suggesting the impact of sewage infiltration (Husain, 2009; Cole et al., 2005; Hussain, 2009) possibly form Malir River in study area. Sewage infiltration of latrine is the common factor for fecal discharge that tends to leach from liquid to soil and decompose solid waste (Rao, et al., 2012) and causes unacceptable levels of nitrates contamination and *E. coli* bacteria in groundwater (Rao, et al.,2006).

3.4. Statistical analysis

3.4.1. Ionic correlation

The ionic correlation between physicochemical parameters including physical parameters, well depth, temperature, pH, Eh, salinity, specific gravity, TDS, EC, hardness and alkalinity while chemical parameters include major cations (Na, K, Ca, Mg), anion (Cl, NO_3, SO_4, HCO_3) of collected groundwater samples was done for RB and LB.

3.4.1.1. RB

There is strong correlation of TDS, salinity, specific gravity and EC exist with major cations (Ca, Mg, Na and K). It shows that the major cations are responsible for elevated TDS content and salinity of groundwater, (Table 7). Likewise, hardness also shows strong correlation with cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) where strongest correlation is shown by Mg (r=0.90) and Ca (r=0.6) which suggest that the hardness of groundwater along RB of Malir River is mainly influenced by Mg and Ca contents. High content of Mg in groundwater of study area is attributed to multiple sources including ion exchange processes and dissolution of limestone (Hem, 1985).

Strong correlation of hardness with Na (r =0.8) and K (r

=0.6) indicate the seawater intrusion in the groundwater of study area. Moderate correlation of SO_4 with Mg (0.4) suggests leaching from evaporitic sediments rich in gypsiferrous shale. It is consistent with the fact that gypsiferrous shales occurs in Gaj Formation. Among anions, HCO_3 showed strong correlation with alkalinity (r =0.67). It is well established that redox process in alluvial aquifers results in bacterial oxidation of organic matter (Nickson et al., 2008; Harvey et al., 2002; McArthur et al., 2001; 2004; Bhatacharya et al., 1997) resulting in generation of higher HCO_3 concentrations (Harvey et al., 2002; McArthur et al., 2001; 2004). Dissolution of biogenic CO_2 gas in the vadose zone causes the generation of bicarbonate in groundwater (Garrels, 1967). The other sources for higher bicarbonate in groundwater is weathering of carbonate and silicate minerals (Rao and Subba, 2002). Fluoride showed the strong correlation with TDS (r =0.9), salinity (r =0.8), hardness (r =0.7), EC (r =0.9), Ca (r =0.7), Mg (r =0.58), Na (r =0.94,) and K (r =0.7) suggesting the dissolution with major salts from sediments.

Table 6 Summary of microbiological characterization of groundwater samples of the study area

RB			LB			Total	
No. of Samples with +ve E. Coli	Samples	%age	No. of Samples with +ve E. Coli	Samples	%age	No Samples	%age
10	1, 2, 3, 4, 8, 11, 15, 18, 19 and 20	50%	11	21, 23, 24, 25, 26, 28, 30, 34, 35, 38 and 40	45%	21	47.5%

3.4.1.2. LB

TDS and pH have shown excellent correlation (r =1) with each other and strong to moderate correlation of TDS with Mg (r =0.9) and Na (r =0.6). It suggests that TDS is mainly controlled by these two parameters along LB and the pH variation is responsible for the solubility of Mg and Na ions (Table 8). The strong correlation of Na ions with TDS, salinity, specific gravity, EC and Mg indicates the impact of seawater intrusion in the study area. Many researchers have worked on seawater intrusion in study area (Khan and Bakhtiari., 2017; Mashiatullah et al., 2002).

Moreover, the negative correlation between Na and depth (r =-0.69) is also an indication of seawater intrusion in shallow aquifers of the study area as these aquifers occur in unconsolidated Recent alluvium which are more prone to seawater intrusion in coastal region (Rao, et al., 2006). The weakly negative correlation of temperature with TDS (r=-0.23) indicates that a part of salts is being contributed by sewage mixing. It is further supported by presence of faecal coliforms (Table 8) and the strong positive correlation between temperature and SO_4 (r =0.52). Strong positive correlation of fluoride with pH (r =0.61), TDS (r = 0.61) and Mg (r =0.57) ions suggest that fluoride is mainly contributed from clays and chemical weathering of mica minerals or may come from irrigation practices, and heavy use of fertilizers for cultivation (Rao and Devadas, 2003).

3.4.2. PCA

The PCA on dataset of groundwater parameters including physical parameters, well depth, temperature, pH, Eh, salinity, specific gravity, total dissolved solids (TDS), electrical conductivity (EC), hardness and alkalinity. Chemical parameters include major cations (Na, K, Ca, Mg), anions (Cl, NO_3, SO_4, HCO_3) (Tables 9 and 10). The output of PCA was used to explain the variation of major data set of interrelated variables with small set of independent variables and to trace the factors, which affect each other.

3.4.2.1. RB

Factor 1 explained 47.51% of the total variance where strong positive loading of TDS (0.96) with major cations including Ca (0.84), Na (0.97), Mg (0.77), K (0.89) and F (0.93) were observed. It is suggesting that the first principal component along RB is related with an interconnection of various hydrogeochemical processes that are responsible for higher mineralized water (TDS). The dissolution of Na+ ions from the subsurface soil in the area may be caused by high rate of mineral weathering, evapotranspiration and longer contact of water with the adjacent rock (Drever, 1988; Jankowski and Acworth 1997; Karanth 1997; Rao and Subba, 2002). Since the study areas occur along Malir River, which drains large amount of domestic and industrial waste, the organic acids upon contact with surrounding rocks, causes leaching of ions from soil and sediments resulting in increasing specific conductance of water (Halim et al., 2009).

Similarly, semi-arid climate causes high rate of evaporation, which results in elevated concentration of salts in the groundwater (Farooqi et al., 2007; Panhwar, 1969). The strong positive loading of fluoride is suggesting that leaching of F^-containing compounds, ionic exchange processes in the clay minerals, long residence time of water in the aquifer, high rate of evapotranspiration, intensively long-term irrigation practices in the area, and heavy use of fertilizers for cultivation responsible for elevated concentration of fluoride in groundwater (Jankowski and Acworth 1997; Rao and Devadas, 2003).

The second factor explained about 11.8% of total variance with positive loadings of depth (0.61), SO_4 (0.64), HCO3 (0.47), Mg (0.45) and NO_3^- (0.4). The moderate positive loading of NO_3, HCO_3 and SO_4 is indicates the effects of anthropogenic activities (fertilizers, irrigation return flow and sewage wastes). The combination of HCO_3 and NO_3 content indicates the effects of runoff leakage on the groundwater (Wang and Luo, 2001).

Table 7. Correlation coefficient among various groundwater parameters along RB of Malir River

Parameters	**Depth**	**Temp**	**pH**	**TDS**	**Salinity**	**Sp. Gravity**	**Hardness**	**Alkalinity**	**Turbidity**	**EC**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO4**	**HCO3**	**NO3**	**F**
Depth	1.00																		
Temp	**-0.65**	1.00																	
pH	0.29	**-0.51**	1.00																
TDS	-0.08	0.15	**-0.68**	1.00															
salinity	-0.09	0.22	**-0.79**	**0.89**	1.00														
Sp. Gravity	-0.05	0.16	**-0.77**	**0.89**	**0.98**	1.00													
Hardness	-0.05	0.08	**-0.50**	**0.88**	**0.76**	**0.76**	1.00												
Alkalinity	-0.12	0.10	-0.07	0.16	-0.08	-0.08	0.17	1.00											
Turbidity	0.20	0.02	-0.02	-0.10	-0.02	-0.06	-0.09	0.04	1.00										
EC	-0.08	0.15	**-0.68**	1.00	**0.89**	**0.89**	**0.88**	0.16	-0.10	1.00									
Ca	-0.01	0.21	**-0.62**	**0.76**	**0.84**	**0.82**	**0.66**	-0.14	0.04	**0.76**	1.00								
Mg	0.11	-0.07	-0.31	**0.76**	**0.67**	**0.66**	**0.90**	0.04	-0.18	**0.76**	0.65	1.00							
Na	-0.08	0.20	**-0.69**	**0.98**	**0.90**	**0.88**	**0.88**	0.19	-0.09	**0.98**	**0.77**	**0.76**	1.00						
K	-0.19	0.28	**-0.67**	**0.78**	**0.89**	**0.84**	**0.67**	-0.04	-0.19	**0.78**	**0.83**	**0.67**	**0.81**	1.00					
Cl	0.00	0.18	-0.30	0.17	0.37	0.39	-0.04	-0.32	-0.16	0.17	0.20	0.00	0.17	0.42	1.00				
SO_4	0.37	-0.13	0.11	0.08	0.07	0.00	0.30	-0.07	0.32	0.08	0.01	0.49	0.09	0.05	-0.04	1.00			
HCO_3	-0.11	-0.11	0.13	0.16	-0.05	-0.08	0.19	**0.67**	-0.21	0.16	-0.12	0.32	0.15	0.09	-0.20	0.20	1.00		
NO_3	0.20	-0.23	-0.21	0.12	0.29	0.32	0.20	0.00	0.36	0.12	0.14	0.16	0.09	0.08	-0.11	0.21	0.06	1.00	
F	-0.08	0.21	**-0.75**	**0.94**	**0.89**	0.87	**0.73**	0.24	-0.01	**0.94**	**0.73**	**0.59**	**0.94**	**0.78**	0.19	-0.04	0.19	0.19	1.00

Table 8. Correlation coefficient among various physicochemical parameters of groundwater along the LB of Malir River

Parameters	**Depth**	**Temp**	**pH**	**TDS**	**Salinity**	**Sp. Gravity**	**Hardness**	**Alkalinity**	**Turbidity**	**EC**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO4**	**HCO3**	**NO3**	**F**
Depth	1.000																		
Temp	0.179	1.000																	
pH	-0.233	-0.231	1.000																
TDS	-0.233	-0.231	1.000	1.000															
salinity	-0.183	**-0.446**	0.264	0.264	1.000														
Sp. Gravity	-0.228	**-0.418**	**0.778**	**0.778**	0.282	1.000													
Hardness	-0.152	-0.138	0.045	0.045	-0.108	-0.018	1.000												
Alkalinity	0.025	0.164	0.146	0.146	-0.039	-0.004	0.084	1.000											
Turbidity	-0.055	-0.140	0.222	0.222	0.052	0.197	-0.048	**-0.452**	1.000										
EC	-0.093	**-0.704**	0.298	0.298	0.048	0.385	0.176	0.216	0.034	1.000									
Ca	0.194	0.213	0.298	0.298	-0.187	**0.515**	-0.050	-0.138	0.126	-0.306	1.000								
Mg	-0.211	-0.068	**0.897**	**0.897**	0.285	**0.791**	-0.094	0.031	0.176	0.046	0.439	1.000							
Na	**-0.696**	**-0.446**	**0.610**	**0.610**	**0.415**	**0.493**	0.015	0.253	0.084	**0.453**	-0.288	**0.465**	1.000						
K	0.424	0.152	-0.126	-0.126	-0.340	0.057	0.004	0.060	-0.086	-0.170	**0.614**	-0.212	-0.424	1.000					
Cl	0.25	**0.49**	-0.13	-0.13	-0.48	-0.13	-0.17	-0.27	0.19	**-0.44**	0.38	0.04	**-0.58**	0.18	1.00				
SO_4	0.197	0.553	-0.269	-0.269	-0.548	-0.389	0.379	0.159	-0.357	-0.351	0.138	-0.179	-0.524	0.100	0.424	1.000			
HCO_3	-0.193	0.022	0.257	0.257	-0.107	-0.062	0.064	-0.085	0.378	-0.029	0.057	0.198	0.183	-0.151	0.185	0.007	1.000		
NO_3	-0.193	0.022	0.257	0.257	-0.107	-0.062	0.064	-0.085	0.378	-0.029	0.057	0.198	0.183	-0.151	0.185	0.007	1.000	1.000	
F	-0.266	0.092	0.617	0.617	-0.071	0.292	0.246	0.048	-0.003	0.052	0.201	**0.571**	0.298	-0.195	-0.005	0.364	0.387	0.387	1.000

Factor 3 explained 10.19% of total variance, which is similar to factor 2. This factor expressed positive loading of depth (0.53) with strongly negative loading of alkalinity (-0.79) and HCO_3 (-0.72) suggesting that the alkalinity is decreasing with depth indicating that the source of alkaline ions occur on the surface. It is consistent with the fact that flood plain area of Malir River is organic matter rich, which is both natural and sewage derived.

Table 9. Principle component's matrix of groundwater samples along RB of Malir River

Variables	Components				
	PC1	PC2	PC3	PC4	PC5
pH	**-0.76**	0.38	-0.01	-0.32	0.04
Depth	-0.11	**0.61**	**0.53**	-0.18	-0.23
Temperature	0.24	**-0.65**	-0.29	0.34	**0.48**
Sp. Gravity	**0.95**	-0.09	0.21	0.01	-0.14
Salinity	**0.96**	-0.09	0.18	0.05	-0.04
Turbidity	-0.08	0.23	0.34	**0.78**	0.15
Alkalinity	0.08	0.28	**-0.79**	0.29	-0.18
Conductivity	**0.96**	0.08	-0.09	-0.04	-0.07
Hardness	**0.87**	0.30	-0.11	-0.06	0.13
TDS	**0.96**	0.08	-0.09	-0.04	-0.07
Ca	**0.84**	-0.08	0.23	0.00	0.00
Mg	**0.77**	**0.45**	-0.02	-0.28	0.27
Na	0.97	0.06	-0.10	-0.03	-0.03
K	**0.89**	-0.17	0.04	-0.15	0.08
Cl	0.26	**-0.45**	0.37	-0.30	0.06
F	**0.93**	-0.01	-0.11	0.12	-0.19
HCO3	0.10	0.47	**-0.72**	-0.10	0.02
NO3	0.20	0.39	0.31	**0.52**	-0.28
SO4	0.10	**0.64**	0.23	0.04	**0.67**
Eigen Value	9.03	2.12	1.94	1.58	1.46
% of Variance	47.51	11.18	10.19	8.32	7.70
Cumulative %	47.51	58.69	68.88	77.20	84.90

Factor 4 explained 8.32% of total variance with essential positive loading of turbidity (0.78) and NO_3 (0.52) which clearly indicates the role of sewage mixing. It is widely believed that sewage mixing in groundwater is mainly responsible for higher values of turbidity and nitrate (Husain, 2009; McArthur et al., 2004; Cole et al., 2005; Nickson et al., 2004). The sewage mixing is further supported by the presence of coliform bacteria (50% samples) in the collected groundwater samples along RB of Malir River.

Factor 5 showed least percentage (7.70%) of total variance. It explained moderate positive loading of temperature (0.48) and SO_4 (0.67). The strong positive loading of SO_4 and temperature is the indication of gypsum dissolution from Gaj Formation. Substantial thickness of gypsiferrous shales is resting underneath the settlements along Malir River, which upon receiving the water infiltrated from surface or from the banks of Malir River causing the dissolution of gypsum and releasing sulphate ions into the groundwater.

Many researchers have reported the direct relationship between solubility of gypsum and temperature (Blount and Dickson, 1973; James, 1992; Liley et al., 1963; Cigna 1985).

3.4.2.1. LB

Along LB of Malir River, five factors explained about 77% of total variations (Table 10). Factor 1 explained 28.76% of the total variance and strong positive loading of pH (0.89) and TDS (0.89), Specific gravity (0.78), salinity (0.46), EC (0.46), sodium (0.83), magnesium (0.79), and fluoride (0.50) are negatively loaded with depth (-0.48), temperature (-0.50) and sulphate (-0.49). The factor is reflecting the influence of both climate and anthropogenic activity. The moderate negative loading of sulphate and temperature indicate that bacterial mediated sulphate reduction is causing organic soil degradation. Moderate positive loading of fluoride indicates the industrial and agricultural contamination in groundwater along LB of Malir River as the Industrial discharge contains high contents of fluorides (Slooff et al., 1988).

Table 10. Principle component's matrix of groundwater samples along LB of Malir River

Variables	Component				
	PC1	PC2	PC3	PC4	PC5
pH	**0.895**	0.311	0.182	0.113	-0.016
Depth	**-0.481**	0.158	0.399	-0.126	0.238
Temperature	**-0.505**	**0.548**	0.039	0.233	**-0.463**
Sp. Gravity	**0.781**	0.137	**0.520**	-0.070	0.103
Salinity	**0.462**	**-0.456**	0.094	-0.220	-0.361
Turbidity	0.275	0.226	-0.212	**-0.688**	0.184
Alkalinity	0.074	-0.134	-0.098	**0.686**	-0.021
Conductivity	**0.467**	**-0.457**	0.010	0.129	**0.582**
Alkalinity	**0.895**	0.311	0.182	0.113	-0.016
Hardness	0.046	0.024	-0.207	**0.466**	**0.525**
TDS	**0.895**	0.311	0.182	0.113	-0.016
Ca	0.079	**0.696**	**0.564**	-0.143	0.121
Mg	**0.790**	**0.426**	0.252	0.038	-0.268
Na	**0.831**	-0.329	-0.194	0.144	-0.127
K	-0.335	0.295	**0.553**	-0.063	**0.425**
Cl	-0.381	**0.687**	0.003	-0.238	-0.080
F	**0.503**	**0.520**	-0.205	**0.443**	-0.028
HCO3	0.293	**0.483**	**-0.694**	-0.188	0.176
NO3	0.293	**0.483**	**-0.694**	-0.188	0.176
SO4	**-0.497**	**0.489**	-0.132	**0.595**	0.037
Eigen Values	5.46	3.33	2.353	2.05	1.41
% of Variance	28.76	17.55	12.383	10.80	7.44
Alkalinity	28.76	46.31	58.689	69.49	76.93

The second factor showed variance of about 17.55% with positive loading of temperature (0.54), calcium (0.69), magnesium (0.42), Cl (0.687), fluoride (0.52), HCO_3 (0.483), NO_3 (0.483) and SO_4 (0.48). Positive loading of these ions suggesting water-rock interaction. The source of these ions is weathering of feldspar and ferromagnesium minerals. Besides, anthropogenic sources are also the contributors of these ions (Hem, 1991; Zhang et al., 1995). Moderate positive loading of HCO_3 (0.48) and pH (0.31) indicate the reaction of soil CO_2 with the dissolution of silicate minerals.

The dissolution of various minerals in groundwater during water-soil and water-rock interactions generally depend on the amount of CO_2, originating from H_2CO_3. Hence, decrease in CO2 and H_2CO_3 values during the outgassing of CO_2 results in an increase of HCO_3 and pH (Ozler, 2003).

Hence, Factor 3 explained variance percentage of about 12.3% with strong positive loading of specific gravity, calcium (0.52), potassium (0.55) and negative loadings of NO_3 (-0.69) and HCO_3 (-0.69). Positive loadings of Ca and K suggest the water rock interaction with dissolution of Ca and K feldspar. Whereas the negative loading of nitrate and bicarbonate representing the reduction in anthropogenic influence on the groundwater of the study area.

Factor 4 explained 12.3% of total variance with moderate positive loadings of alkalinity (0.68) and hardness (0.46), fluoride (0.44) and sulphate (0.59) whereas negative loading of turbidity (-0.68) suggest inter relationship of alkalinity and hardness, while positive loading of fluoride and sulphate indicate the possible source of groundwater contamination from industrial and agricultural wastes from Malir River. The high sulphate content in groundwater of the study area suggests the gypsum dissolution from weathering of gypsiferrous shales, use of inorganic fertilizer the recent recharge of saline water may also be the cause of higher concentration (Nguyen and Itio, 2009; Anawar et al., 2013).

The Factor 5 showed least of total variance (7.4%) with positive loadings EC (0.582), hardness (0.52) and potassium (0.42). Whereas, negative loading of temperature (-0.46) suggests the early phase of natural phenomenon, where decrease in temperature results in decrease of the thermal expansion of the water causing increase of the other parameters.

4. Conclusion

It is concluded that groundwater along both banks of Malir River is unfit for drinking purpose, but the situation is worst on the RB as compared to the LB. High salinity and hardness are the key factor in deteriorating the groundwater quality along both banks. Most of physicochemical parameters exceed the permissible limits of WHO. The main parameters in deteriorating the groundwater quality are TDS, Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, SO_4^{2-}, HCO_3^- , NO_3^-, F^- along both banks of the river. Major cation varied in the order of Na^+ (mean: 2221mg/L) > Mg^{2+} (376mg/L) > Ca^{2+} (206mg/L) > K^+ (71mg/L) and anions Cl^- (mean: 3891mg/1) > SO_4^{2-} (1068mg/L) > HCO_3^- (419mg/L) > NO_3^- (11mg/L)> F^- (2mg/L, 2mg/L) along RB while to the LB as Na^+ (mean: 986mg/L) > Mg^{2+} (155mg/L) > Ca^{2+} (94mg/L) > K^+ (47mg/L) and anions Cl^- (1963mg/L) > SO_4^{2-} (722mg/L) > HCO_3^- (432mg/L) > NO_3^- (10mg/L), F^- (2mg/L). About 50% and 60% samples each from RB and LB have pathogenic bacterial occurrence, which suggests the sewage contamination is common in ground waters of the study area. PCA revealed five significant factors which indicate that both geogenic and anthropogenic factors are responsible to alter the groundwater characteristic of the study area.

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