Int. J. Econ. Environ. Geol. Vol. 10 (1) 05-15, 2019
Journal home page: www.econ-environ-geol.org

Open Access
ISSN: 2223-957X

Arsenic Contamination in Indus Alluvial Plain Sediments and Groundwater of Hyderabad and its Surroundings, Pakistan

Sadaf Naseem[1]*, Viqar Husain[1], Shella Bano[1]

[1] Department of Geology, University of Karachi, Pakistan

*E-mail: snaseem@uok.edu.pk

Received: *23 February, 2019* ***Accepted:*** *27 March, 2019*

Abstract: Alluvial aquifers are the main source of groundwater worldwide. In Hyderabad area of Sindh province, aquifers are naturally polluted by arsenic (As) like other alluvial aquifers of the world. Present study was carried out to decipher the mobilization mechanism of arsenic in Holocene aquifers of Indus river basin, where a large population is at the risk of arsenic ingested diseases. Fifty groundwater samples were collected from Hyderabad and its surrounding areas to examine their physical, chemical and microbiological characteristics. In 80% of the groundwater samples, TDS is above the WHO limit. Dominant (40%) hydrofacies in groundwater of study area is NaCl, which shows water-rock interaction and cation exchange mechanism. In order to investigate the source of arsenic, eleven near-surface soil samples were also collected and analyzed for elemental and mineral composition using XRD and AES techniques. Correlation Coefficient, Principal Component Analysis (PCA) and multivariate statistical analyses were used to interpret the data. Arsenic ranges between 10-150 µg/L in groundwater, while in soil samples it ranges from 77 and 137µg/kg. Findings showed that arsenic is mobilized in the alluvial aquifers of Indus river through dissolution/ leaching of iron oxyhydroxides under anoxic conditions. Arsenic is mainly leached from mica and phlogopite under reducing conditions. Meandering of Indus river through different historical time periods is an important factor for the distribution of redox zones created by mirco-biodegradation of organic matter rich with clayey sediments. Irrigation return flow, infiltration of sewerage in groundwater and unlined sanitation are also important anthropogenic factors for creating local anoxic conditions to mobilize arsenic in groundwater.

Keywords: Arsenic, groundwater quality, Indus, Hyderabad, Pakistan.

Introduction

In arid regions of the world, people mostly use groundwater from alluvial aquifers for drinking, irrigation and industrial purpose (Al-Ahmadi, 2013, Chen et al., 2017). Unfortunately, these aquifers are severely affected by geogenic and anthropogenic point and nonpoint sources of arsenic and other pollutants. It is estimated that 1 billion people consume polluted water all over the world (Farnsworth and Hering, 2011). A large number of studies on arsenic in groundwater have been carried out worldwide over the last decades and its elevated concentrations have been identified in 70 countries including South Asia (Mukherjee et al., 2001, Jiang et al., 2010, Bhattacharya et al., 1997, Acharya, 2000). In Pakistan Indus alluvial plain and deltaic plains (~150 km wide) aquifers are excellent groundwater source, which are severely affected by arsenic (Naseem and McArthur, 2018; Rasheed et al., 2017; Shrestha, 2002; Shah et al., 2009; Sarkar and Datta, 2004; Husain, 2009; Nickson, et al 2005; Husain, et al 2012; Khan and Husain, 2019). High concentrations of arsenic in ground water have been reported from various parts of Sindh province including Jamshoro, Matiari, Tando Allayar, Tando Muhammad Khan, Thatta, Hyderabad, Khairpur (Brahman et al., 2016, Arain et al., 2007, 2009, Rasool et al., 2016).

The study area comprised of Hyderabad and its neighboring rural areas (Fig.1). It is situated on the eastern side of the Indus river, which along with its tributaries are the main source of water but which are highly polluted due to unchecked dumping of liquid and solid wastes (Baig, et al., 2009). Due to low precipitation rate, high evapotranspiration and highly unpredictable flow of water in Indus river, local people depend on groundwater for domestic and agricultural uses. Hyderabad and its surrounding rural areas are mainly plain, highly fertile and dominant crops are sugarcane, wheat, vegetables and mango orchards mainly irrigated by groundwater. Aquifers in the area have variable thickness and hosted in grey silty and sandy friable layers. The depth of the water table varies from 10 to 30 m. Over-extraction of groundwater has resulted in groundwater quality degradation. Due to water table decline, fresh water has been replaced by brackish water (Latif et al., 1999; Samdani, 1995).

Previous studies show that groundwater in Hyderabad region of Sindh province is highly contaminated by arsenic and other contaminants. According to Khan et al. (2008) arsenic in the groundwater of Hyderabad city ranges from 25-1286 µg/L. According to Naseem and McArthur (2018) distribution of arsenic in Indus deltaic alluvial plain is highly heterogeneous caused by microbially-mediated reductive dissolution of sedimentary iron oxyhydroxides in groundwaters. Anoxic conditions in the aquifers are caused by biodegradation of organic matter, silty clay-rich oxbow lakes and meander scars of Indus river (Nickson et al.,

Table 1. Physical and microbiological characteristics of groundwater.

S.No.	Sample ID.	Coordinates		Depth m	Color	odour	Turb. NTU	pH	P.Colif. /100 ml	F.Colif. MPN/100 ml	E-coli
		Lat. N	Long. E								
1	HDR-2	251851	682527	24.3	UO	UO	4.8	7.2	Nil	Nil	-Ve
2	HDR-3	251846	682433	24.3	UO	UO	8.9	7.4	26	12	-Ve
3	HDR-4	251715	682513	13.7	UO	UO	4.6	7.4	17	9	-Ve
4	HDR-5	251707	682514	13.7	UO	UO	4	7.5	14	11	-Ve
5	HDR-6	251438	682641	26	UO	UO	3.2	7.8	7	4	-Ve
6	HDR-10	251446	682940	15.2	yellowish	unpleasant	10.6	7.1	14	7	-Ve
7	HDR-12	251451	683032	16.7	yellowish	UO	14	6.9	17	9	-Ve
8	H1	244647	675648	4.5	UO	UO	4.8	8.2	33	17	-Ve
9	H2	245844	680751	18.2	yellowish	UO	48	7.7	17	9	-Ve
10	H3	250207	681341	12.1	yellowish	UO	8.9	7.4	12	9	-Ve
11	H4	251719	681231	24.3	yellowish	UO	7.6	7.6	7	6	+Ve
12	H5	251442	682640	27.4	UO	unpleasant	8.5	7.6	17	9	-Ve
13	H6	251316	682804	24.3	UO	unpleasant	4.8	7.4	12	9	-Ve
14	H7	251316	682818	12.1	UO	UO	7.9	7.7	21	9	-Ve
15	H8	251222	682712	13.7	UO	unpleasant	8.7	7.2	7	6	-Ve
16	H9	251222	682712	30.4	UO	UO	4.3	7.2	Nil	Nil	-Ve
17	H10	251243	681216	16.7	UO	UO	3.9	7.5	9	4	-Ve
18	H11	251350	682739	13.7	UO	UO	4.6	7.6	12	9	-Ve
19	H12	252543	682107	16.7	UO	UO	4.6	8	11	7	-Ve
20	H13	252832	682356	19.8	UO	UO	18	7	Nil	Nil	-Ve
21	H14	253011	682532	21.3	UO	unpleasant	14	7.3	9	4	-Ve
22	H15	253014	682529	21.3	UO	UO	6.7	7.3	Nil	Nil	-Ve
23	H16	253010	682525	15.2	UO	UO	3.2	7.4	7	4	-Ve
24	H17	253013	682526	12.1	UO	unpleasant	4.6	7.3	21	14	-Ve
25	H18	253143	682601	15.2	UO	UO	4.1	7.4	17	9	-Ve
26	H19	253307	682608	21.3	UO	UO	5.8	7.3	Nil	Nil	-Ve
27	H20	253547	682622	9.1	yellowish	UO	10.6	6.9	26	14	-Ve
28	H21	253528	682631	21.3	UO	UO	4.5	7.2	7	4	-Ve
29	H22	253558	682718	21.3	UO	UO	27	6.9	9	4	-Ve
30	H23	253550	682739	21.3	UO	UO	3.6	7.3	21	14	-Ve
31	H24	253524	682836	15.2	UO	UO	3.8	7.1	12	9	-Ve
32	H25	253702	682821	18.2	UO	UO	4.2	7.2	7	4	-Ve
33	H26	253747	682925	13.7	UO	UO	6.8	7.6	21	14	-Ve
34	H27	253903	682953	21.3	UO	UO	19	7.4	Nil	Nil	-Ve
35	H28	253931	682956	30.5	UO	UO	22	7.3	Nil	Nil	-Ve
36	H29	253821	682940	30.5	UO	UO	4.3	7.1	Nil	Nil	-Ve
37	H30	253137	682601	18.2	UO	UO	4.6	6.9	9	4	-Ve
38	H31	252922	682518	16.7	UO	UO	5.4	6.9	11	7	-Ve
39	H32	252346	682435	16.7	UO	UO	3.8	6.8	7	4	-Ve
40	H33	252354	682451	13.7	UO	UO	23	7.2	26	14	-Ve
41	H34	252437	682803	21.3	UO	UO	6.3	6.9	7	6	-Ve
42	H35	252520	683108	21.3	yellowish	unpleasant	17	7	Nil	Nil	-Ve
43	H36	252639	683500	13.7	yellowish	unpleasant	7.3	7.2	21	14	-Ve
44	H37	252643	683606	24.3	UO	UO	4.7	7.3	Nil	Nil	-Ve
45	H38	252739	684159	21.3	UO	unpleasant	6.6	7	17	9	-Ve
46	H39	252805	684334	13.7	UO	UO	4.3	7	13	7	-Ve
47	H40	252834	684352	55	UO	UO	7.9	7.3	Nil	Nil	-Ve
48	H41	252700	683726	15.2	UO	UO	4.4	7.8	9	4	-Ve
49	H42	252632	683453	70	UO	UO	10.5	7.2	Nil	Nil	-Ve
50	H43	252519	683206	70	UO	UO	3.8	7.1	Nil	Nil	-Ve

2005; Husain et al., 2012a, b, Naseem and MacArthur, 2018, Naseem et al., 2018).

Present study focuses on multivariate statistical analyses, correlation coefficient and principal component analysis (PCA) to investigate hydrogeochemical processes, which would affect groundwater quality, distribution and relationship between arsenic and nature of aquifers. Therefore, that present study will help to elucidate water-rock interaction, groundwater mineralization process, distribution, occurrence and mobilization of arsenic in shallow alluvial aquifers of Hyderabad.

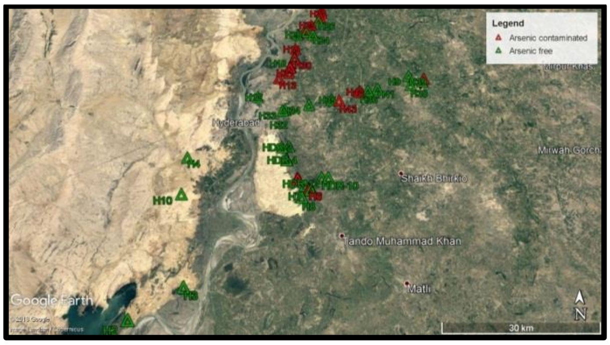

Fig. 1 Map of study area, showing groundwater samples collection points with arsenic polluted and As free wells.

Geology and Geomorphology of the Area

Hyderabad is the second largest city of Sindh province approximately 150 km away from Karachi and Arabian sea (Fig. 1). It lies at 25.367°N and 68.367°E with an average elevation of 13 m (43 ft). Phuleli canal is main canal in the area which originates from the left bank of Kotri barrage. It runs through the periphery of Hyderabad city and provides water for agricultural, industrial and domestic purposes to Hyderabad, Tando Muhammad Khan and Badin districts. This canal is non-perennial, but the water is released for domestic purpose in dry seasons (Kazmi and Jan, 1997; Giosan et al, 2006).

Hyderabad is located in the southern side of subdued relief alluvial and deltaic plain of Indus river. Indus Alluvial plain extends from the lower Punjab to the Arabian sea and filled with post-glacial sediments in Pleistocene incised-valley system (Kazmi, 1984; Giosan et al., 2006a Clift and Giosan, 2013; Kureshy, 1977; Kadri, 1995; Haq, 1999). Hyderabad lies at the starting point of Indus delta which extends upto Thatta district at the mouth of Arabian sea. Changing courses of the Indus river from east to west formed the present

Table 2. Chemical analysis of groundwater samples.

S.N.	Sample ID	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO$_3$ mg/l	Cl mg/l	SO$_4$ mg/l	Nitra. mg/l	Fe mg/l	Fl mg/l	Hard.	Alkal.	As	Cl/HCO$_3$	Na/Cl	SI	TDS mg/l	EC µ-S/cm	Water Type
1	HDR-2	120	58	106	8	340	223	108	0.3	0.03	0.37	540	6.8	0	0.68	0.47	0.36	988	1543	Ca-Cl
2	HDR-3	144	24	175	9	270	362	76	0.51	0.02	0.45	460	5.4	0	1.34	0.48	0.56	1107	1726	Na-Cl
3	HDR-4	140	29	137	5	280	286	88	1.2	0.03	0.58	470	5.6	0	1.02	0.47	0.57	1014	1584	Ca-Cl
4	HDR-5	168	85	219	6	300	472	260	0.84	0.04	1.1	770	6	0	1.57	0.46	0.76	1594	2490	Na-Cl
5	HDR-6	84	65	121	5	210	316	76	0.5	0.02	0.61	480	4.2	60	1.50	0.38	0.61	943	1473	Mg-CL
6	HDR10	160	112	447	6	540	674	324	0.5	3.44	0.99	860	10.8	0	1.24	0.66	0.48	493	770	Na-Cl
7	HDR-12	260	102	473	12	530	791	425	1.2	7.8	1	1070	10.6	0	1.49	0.59	0.43	2374	3710	Na-Cl
8	H1	88	46	442	8	290	691	115	0.411	0.04	0.79	410	5.8	5	2.38	0.07	1.15	2700	4220	Na-Cl
9	H2	76	39	104	3	230	152	126	0.614	0.01	0.89	350	4.6	5	2.66	0.68	0.56	1779	2780	Na-Cl
10	H3	220	49	210	9	250	167	700	0.33	0.01	1.61	750	5	5	0.66	0.25	0.64	744	1162	Ca-SO$_4$
11	H4	84	61	392	11	360	574	136	1.489	0.01	1.53	460	7.2	0	1.59	0.68	0.62	1568	2450	Na-Cl
12	H5	68	24	38	4	220	78	22	0.552	0.06	0.59	270	4.4	10	0.35	0.48	0.44	1702	2660	Ca-HCO$_3$
13	H6	40	27	33	5	200	53	12	0.491	0.5	0.27	210	4	100	0.26	0.62	-0.21	459	717	Mg-HCO$_3$
14	H7	64	19	71	4	160	106	78	1.047	0.05	0.54	240	3.2	5	0.66	1.66	0.37	370	578	Ca-Cl
15	H8	64	78	343	4	340	427	280	0.499	0.09	1.1	480	6.8	5	1.25	0.80	0.047	508	794	Na-Cl
16	H9	96	83	452	5	340	652	314	0.299	0.01	0.94	580	6.8	0	1.91	0.69	0.19	1587	2480	Na-Cl
17	H10	56	29	59	4	220	92	44	0.315	0.11	1.02	260	4.4	5	0.41	0.64	0.24	2048	3200	Ca-HCO$_3$
18	H11	60	24	47	3	210	64	54	0.295	0.02	0.63	250	4.2	5	0.30	0.73	0.36	509	796	Ca-HCO$_3$
19	H12	40	17	48	4	150	71	31	0.407	0.07	0.39	170	3	5	0.47	0.67	0.477	459	717	Na-HCO$_3$
20	H13	140	126	446	10	460	617	483	2.563	0.12	1.22	870	9.2	60	1.34	0.72	0.232	364	568	Na-Cl
21	H14	76	29	92	6	270	107	86	0.664	0.55	0.55	310	5.4	10	0.39	0.85	0.223	2381	3720	Na-HCO$_3$
22	H15	68	41	55	6	250	99	66	0.491	0.03	0.03	340	5	5	0.39	0.55	0.148	666	1040	Ca-HCO$_3$
23	H16	44	29	39	3	190	67	32	0.376	0.09	0.09	230	3.8	20	0.35	0.58	-0.015	589	921	Mg-HCO$_3$
24	H17	40	19	29	4	160	54	17	0.372	0.09	0.09	180	3.2	10	0.33	0.53	-0.219	410	641	Ca-HCO$_3$
25	H18	44	27	111	4	200	128	84	0.269	0.02	0.02	220	4	5	0.64	0.86	-0.023	327	511	Na-Cl
26	H19	76	46	127	4	300	177	104	0.411	0.03	0.03	380	6	60	0.59	0.71	0.245	600	938	Na-Cl
27	H20	236	112	217	7	260	720	248	0.529	0.01	0.01	1050	5.2	5	1.37	0.30	0.111	845	1320	Ca-Cl
28	H21	120	58	670	7	340	876	412	0.637	0.06	0.06	540	6.8	40	1.9	0.76	0.262	1971	3080	Na-Cl
29	H22	280	87	510	11	300	936	522	0.902	0.2	0.2	1060	6	10	1.6	0.54	0.262	2592	4050	Na-Cl
30	H23	68	36	61	3	260	89	61	0.506	0.03	0.03	320	5.2	5	0.27	0.68	0.169	2803	4380	Ca-HCO$_3$
31	H24	84	36	71	8	300	96	84	0.388	0.03	0.03	360	6	5	0.25	0.73	0.086	579	905	Ca-HCO$_3$
32	H25	76	39	66	5	270	89	81	0.533	0.09	0.09	350	5.4	30	0.25	0.74	0.114	669	1045	Ca-HCO$_3$
33	H26	44	22	28	5	160	54	28	0.388	0.1	0.1	200	3.2	5	0.26	0.51	0.135	643	1005	Ca-HCO$_3$
34	H27	92	44	49	6	240	131	98	0.556	0.13	0.13	410	4.8	150	0.39	0.37	0.353	340	532	Ca-Cl
35	H28	40	22	29	4	160	54	19	0.457	0.31	0.31	210	3.2	10	0.27	0.53	-0.225	675	1055	Ca-HCO$_3$
36	H29	136	29	123	7	350	178	122	0.905	0.53	0.53	460	7	10	0.36	0.69	0.329	333	521	Ca-Cl
37	H30	88	37	147	4	370	156	102	0.38	0.06	0.06	370	7.4	0	0.42	0.94	-0.059	943	1474	Na-HCO$_3$
38	H31	180	58	290	10	330	433	370	0.472	0.03	0.74	690	6.6	0	1.31	0.67	0.118	896	1400	Na-Cl
39	H32	480	136	620	14	350	1490	653	0.487	0.02	1.06	1760	7	5	4.25	0.41	0.331	1715	2680	Na-Cl
40	H33	180	102	542	6	320	745	640	0.867	0.06	0.96	870	6.4	0	2.32	0.72	0.395	4026	6290	Na-Cl
41	H34	68	78	217	6	440	217	205	0.43	0.7	0.57	490	8.8	0	0.49	1	-0.13	2650	4140	Na-Cl
42	H35	260	95	370	7	340	759	420	0.71	0.06	0.92	1040	6.8	0	0.23	0.48	0.366	1255	1961	Na-Cl
43	H36	60	29	60	4	230	78	50	0.418	0.03	0.41	270	4.6	5	0.33	0.76	-0.33	2394	3740	Ca-HCO$_3$
44	H37	52	24	43	3	180	64	45	0.422	0.05	0.53	230	3.6	0	0.35	0.63	-.074	518	810	Ca-HCO$_3$
45	H38	178	106	168	7	340	379	364	0.526	0.02	0.81	880	6.8	0	1.11	0.44	0.245	414	647	Ca-Cl
46	H39	92	49	148	7	320	167	190	0.771	0.02	0.65	430	6.4	0	0.52	0.88	0	1613	2520	Na-Cl
47	H40	48	46	140	4	290	138	130	5.414	0.06	0.85	310	5.8	30	0.47	1.01	0.040	982	1534	Na-HCO$_3$
48	H41	28	17	24	3	110	39	29	0.652	0.02	0.51	140	2.2	5	0.35	0.61	0.009	804	1256	Mg-HCO$_3$
49	H42	60	39	68	4	250	106	58	0.587	0.04	0.54	310	5	20	0.42	0.64	-0.01	252	394	Mg-HCO$_3$

delta (Wilhelmy, 1967; Holmes, 1968; Rubab et al., 2014). It constitutes a stream bed, superficial alluvium and extinct stream deposits. Most part of the study area consists of flood plain deposits of the extinct streams which consists of greenish grey to grey silt and clay with subordinate fine sand. The deposits are poorly sorted with fine to medium grained sand, silt and minute clay (Khan, 2014; Holmes, 1968). The Holocene alluvium of Indus constitutes organic matter bearing greyish brown sandy clay and grey sand brought by Indus river (Kidwai, 1963). In the southern part of Hyderabad, limestone hills (Ganjo Takkar) are the only elevated landforms (Ansari and Vink, 2007; Kazmi and Jan, 1997). The exposed cream to grey colored limestone in the study area with subordinate marl, calcareous shale, sandstone and lateritic clay belong to Laki Formation of Eocene age (Shah, 1977). However, another exposed white to grey colored limestone is mainly fossiliferous interbedded with subordinate shale and marl belonging to Kirthar Formation of Oligocene age (HSC, 1960).

Materials and Methods

Water Sampling and Analysis

Fifty groundwater samples were collected from Hyderabad city and its surrounding villages (Fig. 1). These water samples were analyzed for various microbiological and physicochemical parameters (Table 1, 2). The pH and temperature of the groundwater were measured in the field using an Adwa (AD111) Multimeter, while, Electrical conductivity was measured with Adwa ad330 conductivity meter. Well depths were obtained from well owners, which ranges from 4.5 to 70 meters. The well locations were marked with a handheld (Garmin eTrex 20x) Global Positioning System (GPS). Samples were collected in plastic bottles. Arsenic was measured in the field using a Merck test kit (0.01–0.5 mg/L) 1.17926.0001, Germany (Table 3).

For microbiological analysis, samples were collected in plastic bottles of 200ml capacity and were kept in the dark at 4°C in an ice box for analysis within 24 hours of sampling. Microbiological analysis for Total Coliforms, Fecal Coliforms and Escherichia Coli was done by Multiple-Tube Fermentation technique (MPN) (407D, Standard method, 1971). Inoculated tubes were incubated at 35 ± 0.5ºC and each tube was tested for presence of gas and acid after 24 hours of incubation and within 48±2 hours. Tubes showing acid and gas were marked as presumptive positive. Test tubes of BGLB of 10% of the positive were further shifted into the EC broth and incubated at 44 .5 ±0.2ºC for 24 hours. Positive test tubes with acid and gas production were noted. The presumptive and fecal coliforms per 100 ml of sample were calculated from the MPN standard table.

Soil Sample Collection and Analysis

Eleven topsoil samples were collected from 10 cm below the surface with the help of hand shovel. Soil color, grain size, shape and texture were also recorded (Table 4). The soil sample was dried in an oven at 110°C for 24 hours. After drying the sample was ground and sieved through a mesh -200 before digestion. For digestion 1 gm of soil sample was weighed into a 250ml beaker to which 7 ml concentrated hydrochloric acid and 3 ml nitric acid were added. The suspension was kept overnight in the beaker and it was refluxed for 2 hours, followed by dilution with deionized water to 50 ml, stirring for 5 minutes and filtering (0.80µm) after cooling. The filtrate was stored in a plastic bottle and was examined for total (aqua-regia extractable) concentration of arsenic, iron and manganese using Perkin-Elmer A Analyst 600 Graphite Furnace Atomic Absorption Spectrophotometer.

The XRD analysis of soil samples were conducted in Geoscience Laboratories, Islamabad. For XRD soil samples were dried in an oven at 110°C for 24 hours. Later, dried samples were pulverized and passed through mesh -200. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice were attained due to random orientation of the powdered material. The d-spacing of each peak is then obtained by solution of the Bragg equation for the appropriate value of λ.

Results and Discussion

Physicochemical Characteristics

Physico-chemical characteristics of groundwater were evaluated in order to check groundwater quality (Table 1, 2). About 50% of total groundwater samples were found to have turbidity higher (5.4-48 NTU) than the WHO permissible limit for drinking water. The pH of the groundwater ranges from 6.8 to 8.2. Groundwater geochemistry is characterized by high concentrations of bicarbonate, chloride, sulfate and sodium over other major ions and 80% were found with TDS above permissible limit of WHO (500 mg/L) in the area. The SO_4 content in groundwater of Hyderabad district shows great variability (12-700 mg/L). About half of groundwater samples contain SO_4 above the permissible limit (250 mg/L) for drinking water. Fifteen of the total 50 groundwater samples contain sodium above the WHO permissible limit of 200 mg/L for drinking water.

Multivariate Statistical Analysis

Electrical conductivity shows a strong correlation with calcium and negative correlation (-0.64) with pH suggests water-rock interaction phenomenon is dominant in the area (Table 5). In Hyderabad district chloride is dominant ion, which shows strong positive correlation with most of the major ions of sodium (r = 0.93), calcium (r = 0.84), sulfate (r = 0.78), potassium (r = 0.73) and magnesium (0.83). The plotting of Na versus Cl shows that most of the water samples fall away from 1:1 line. Na/Cl ratio, which is less than unit in most of the samples. It reflects the contribution of cation exchange phenomenon and consumption of sodium for the formation of clay minerals (Fig. 2). Low levels of Ca in water are caused by its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals (Zhu, et al., 2008). This is also indicated by saturation index as most of the groundwater samples are slightly supersaturated with respect to calcite indicating the consumption of calcium for the formation of secondary minerals (Table 2). Calcium shows a significant correlation (0.67) with sodium (Table 5) which also confirms cation exchange reaction (Edet and Okereke, 2001).

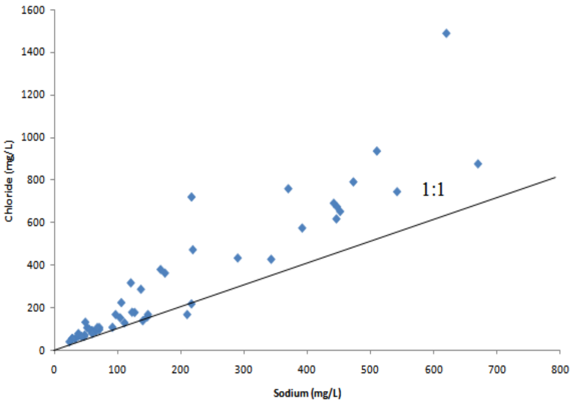

Fig. 2 Relationship between sodium and chloride in groundwater samples of Hyderabad district.

The plot of calcium and sulfate shows that about half of groundwater samples are plotted away from 1:1 gypsum dissolution line (Fig. 3). Low concentration of sulfate in rest of the water samples is due to aquifers in reducing Holocene alluvial sediments characterized by low NO_3^- and SO_4^{2-} levels (Nordstrom, 2002; Acharrya and Shah, 2007). High concentrations (160-540 mg/L) of bicarbonate in the study area indicate the weathering of carbonate minerals during recharge and to some extent in the aquifer matrix along with degradation of organic matter under local reducing conditions (Rowland et al., 2007; Mukherjee et al., 2009; Shamsudduha et al, 2008; Lang et al., 2006).

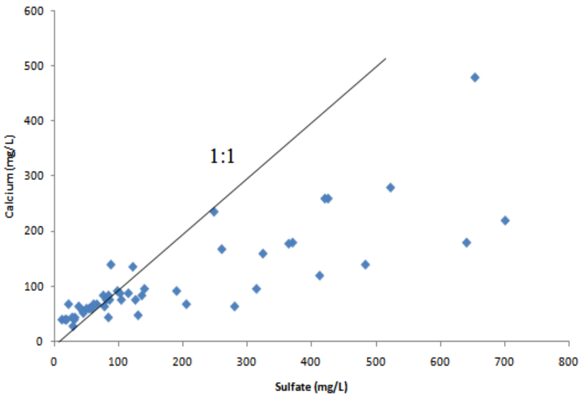

Fig. 3 Relationship between sulfate and calcium in groundwater samples of Hyderabad district.

Principal Component Analysis

PCA is used to establish a series of factorial variables that summarize all the hydrochemical information based on multivariate and complex information (Sanchez-Martozet et al., 2001). It expresses the relation or association between different chemical components in the groundwater (Mukherje-Goswami et al., 2008). Groundwater samples from different areas of Hyderabad were examined by PCA analysis which revealed 82.58% of total variance (Table 6). PCA analysis shows four principal components of which, PC1 and PC2 account for 58.76 and 9.45% of the total variance respectively. Most of the analyzed samples in the study area have strong loading (>0.78) of these two components. Further, strong positive loading (>0.78) of cations (Ca, Na, K, Mg) and anions (HCO_3, Cl, SO_4) associated TDS, alkalinity and hardness represent the main dissolved load of groundwater, which explains intense water-sediment interaction in a longer time. Strongly positive correlation of EC with HCO_3 and sulfate also indicates the phenomenon of mineral dissolution (Table 5).

The abundance of carbonate rocks in the study area, rapid weathering and erosion of these rocks may add significant amounts of Ca and Mg to the groundwater. In the study area, which is a part of Indus deltaic plain, influence of tectonic forces and Holocene eustatic changes have resulted in high sedimentation rate and rapid burial of large quantities of carbonates (Ansari and Vink 2007; Clift et al., 2008; Lee et al 2003; Clift and Blusztajn, 2005). Furthermore, dissolution of halite may be responsible for high sodium and chloride contents in the groundwater. The study area comprises of Holocene alluvial aquifers dominated by silt with variable quantities of sand, clay and micas (Kazmi, 1984; Khan et al., 1993). Furthermore, dissolution of gypsum from gypsiferous shale, belonging to Laki Formation of Eocene age is the source of SO_4 and additional Ca contents in groundwater of this area. Groundwater is highly saline, as most parts of this area are situated at offshoots of the Kirthar Range (Western High Lands) comprising of Laki, Tiyon, Kirthar and Nari formations of Eocene to Oligocene age. Dissolution of these rocks and its seepage in shallow alluvial aquifers also led to an increase in total dissolved solids in groundwater of the area (Kahlown et al, 2004; Malik, 2000). Indus River changed its course from east to west of Hyderabad and resulted in its present course within the delta (Wilhelmy, 1967). Due to the change in course, Indus River abandoned about 100 miles of its old channel in Matiari area (Holmes, 1968; Kazmi and Jan, 1997). Aquifers are located in the older river courses of Indus river, that must have left huge quantities of water, slowly turned saline, as the brackish water of the surrounding area encroached up to it (Panhwar, 1969). Over-extraction of groundwater causes the underlying highly saline water to mix with overlying freshwater and use of this poor quality water results in soil salinity problems in the area (Qureshi et al., 2008).

The NO_3 content in groundwater of Hyderabad district varies from 0.3-5.41mg/L (Table 2). Nitrate shows the absence of a significant correlation with all major ions in the study area. This indicates that agricultural pollution is unlikely in the area as in all groundwater samples the concentration of nitrate is quite low (0.3 to 5.4 mg/L). Lower concentrations of sulfate in few groundwater samples in the area may be due to the reduction of sulfate to sulfide by sulfate-reducing bacteria in the presence of organic matter. It is due to organic matter content in the groundwater, as shallow wells are more subjected to contamination, particularly in areas with porous and well-drained soils. Unlined sanitation and pit toilets are also common in the area which caused the mixing of anthropogenic organic waste with the groundwater resulting in microbial contamination of groundwater.

Hydrochemical Facies

The hydrofacies reflects the effects of chemical processes occurring between the minerals within the lithologic framework and the groundwater (Pulido-Leboeuf, 2004). According to Piper diagram, the dominant water type is NaCl (40%) in the study area (Fig. 4). Which generally indicates the influence of dissolution of aquifer material. In the study area, the occurrence of Na-Cl hydrofacies is an indication of input of terrestrial salts through the process of weathering and dissolution of rocks exposed in the area. The second predominant hydrofacies in the area is $CaHCO_3$ (fresh water) type, which occurs in 26% of the aquifers indicating highly recharged aquifer, through meteoric water. A large proportion of Ca-HCO_3 facies is found near the Indus river, where its tributaries play an important role in the aquifers recharge in the area. In addition, rest of the hydrofacies are Ca-Cl (16%), $MgHCO_3$ (8%) and $NaHCO_3$, (8%). It indicates strong water-aquifer interaction related to direct cation exchange between groundwater and the clay fraction of the aquifer material.

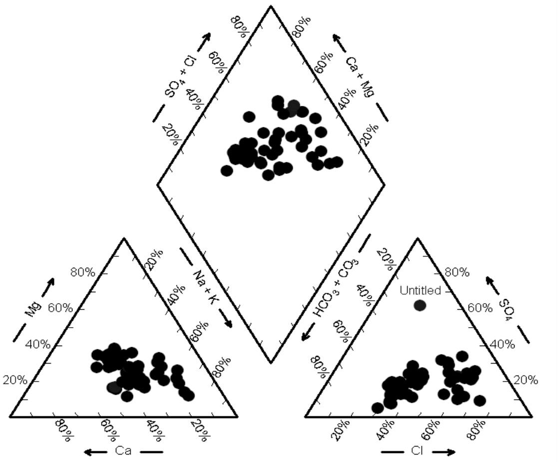

Fig. 4 Piper diagram showing hydrochemical characteristics of groundwater, Hyderabad district.

Due to the cation exchange, calcium which is absorbed on the surface of the clays is released in the saline water and in return sodium, which is a part of saline water is taken up by the clay of aquifer materials. Moreover, flushing of the freshwater aquifer by the saline water will thus result in uptake of Ca^{2+} with concomitant release of Na^{+}. This is reflected in an increase in the salinity and formation of the $NaHCO_3$ water type in the study area. Similarly, Mg-HCO_3 water type also indicates alteration of Ca-HCO_3 hydrofacies through the process of cation exchange in which magnesium is found on the surfaces of clays in the aquifer, where it exchanges with Ca and results in the creation of Mg-HCO_3 hydrofacies (Kelly, 1997).

Arsenic Distribution in Soil and Groundwater

In the groundwaters of Hyderabad As ranges between 10-150 µg/L. And most of the groundwater samples found were above the 10 µg/L permissible limit (WHO, 2011) for drinking water (Table 2). Moreover, As in soil samples ranges from 77 and 137 µg/kg while, Fe and Mn ranged between 82-121 mg/kg and 3.6 to 5.0 mg/kg respectively (Table 4). Organic matter in soil samples ranges from 1.26% to 7.20 %. In the Hyderabad district, most of the near-surface sediments are silty-clay to clayey in nature; their color ranges from yellowish brown to grey. Furthermore, the XRD analyses of selected soil sediment samples show that the sediments are dominated by quartz, calcite, dolomite, albite and phyllosilicates, phlogopite and muscovite. These minerals could be the possible source of arsenic in aquifers of the study area (Table 4). According to Chakraborty et al. (2007), silt-sized micas provide an effective adsorption site for arsenate and arsenite. In Hyderabad, high concentrations of As in groundwater occur due to the desorption/dissolution of As from phlogopite and mica under reducing conditions. Moreover, the presence of high contents of As (77-137 µg/kg) and Fe (82-121 mg/kg) in sediments of study area suggests that desorption process may occur, indicating that high arsenic in groundwater was released from Fe oxyhydroxides (Shamsudduha et al., 2008). As soil in the area is mostly clayey in nature, arsenic is concentrated in clay phases due to its adsorption onto Fe-oxyhydroxide. Consequently, the dissolution of Fe oxyhydroxide contributed to the leaching of arsenic in aquifers. According to Smedley, and Kinniburgh (2002) most of the areas with arsenic contaminated aquifers in the world are of Quaternary age. Aquifers in the study area also lie in Holocene fine-grained sediments. These late Holocene sediments (7000-1000 years B.P) were derived from Himalayan rocks and have been deposited primarily by the Indus river (Clift et al., 2008). Arsenic hot spots in the area include those through which Indus River passed during Holocene period depositing younger alluvium constituting inter-layered deposits of very fine sand, silt and clay (Husain, 2009; Husain, 2012; Kazmi and Jan, 1997).

Table 3. Water quality parameters and methods used for analysis.

S.No	**Parameters**	**Test Method**
1.	Alkalinity (m.mol/l as $CaCO_3$)	2320, Standard method (1992)
2.	Arsenic (mg/l)	Merck Test Kit (0.01–0.5 mg/L) 1.17926.0001, Germany
3.	Bicarbonate	2320, Standard method (1992)
4.	Calcium (mg/l)	3500-Ca-D, Standard Method (1992)
5.	Chloride (mg/l)	Titration (Silver Nitrate), Standard Method (1992)
6.	Electrical Conductivity (mS/cm)	Adwa ad330 conductivity meter
07.	Fluoride (mg/l)	8029, SPADNS Method (Hach) by Spectrophotometer
08.	Hardness (mg/l)	EDTA Titration, Standard Method (1992)
09.	Iron (mg/l)	TPTZ Method (Hach-8112) by Spectrophotometer
10.	Magnesium (mg/l)	2340-C, Standard Method (1992)
10.	Nitrate (mg/l)	Cd. Reduction (Hach-8171) by Spectrophotometer
12.	pH at 25ºC	Adwa (AD111) Multimeter
13.	Potassium (mg/l)	Flame photometer PFP7, UK
14.	Sodium (mg/l)	Flame photometer PFP7, UK
15.	Sulfate (mg/l)	Turbiditimetric Method ,UV-VIS Spectrophotometer (Analytik Jena)
16.	otal Coliforms PN/100ml)	407D, Standard method (1971)
17.	TDS (mg/l)	2540C, Standard method (1992)
18.	Turbidity (NTU)	Turbidity Meter, Lamotte, Model 2008, USA

Table 4. Mineralogical and trace elemens data of sediments collected near well sites of Hyderabad.

S.No.	Mineral	Sediment Characteristics	pH	Mn mg/kg	Fe mg/kg	As µg/kg	Organic matter %
3	Quartz, Calcite, Albite	Medium brown, sandy to Clayey in nature	7.8	4.1	120	100	2.29
6	Quartz, Dolomite, Phlogopite, Albite	Light brown, Sandy – Clay	7.4	3.6	94.3	76.9	1.35
8	Quartz, Phlogopite, Dolomite, Albite	Medium brown,	7.8	4.2	102.2	127.4	2.91

		Clayey						
7	Quartz, Albite, Muscovite	Dark brown to grayish brown, Clay	8.1	5.0	121.2	99.8	2.7
15	Quartz, Albite, Dolomite, Calcite	Dark grayish brown ,Sandy to Clayey	7.8	3.9	102.5	137.5	2.66
16	Quartz, Dolomite, Sylvite	Brown Sandy to Clayey	8.4	3.78	91.8	115.5	3.44
17	Quartz, Dolomite, Albite, Mg-Calcite Phlogopite	Medium brown sandy clay	7.4	3.6	104.9	77.56	7.20
22	Quartz, Dolomite, Phlogopite	Medium brown, Sandy to Clayey	7.7	4.17	103.2	117.1	1.73
27	Quartz, Calcite, Anorthite	Light brown, Silty Clay	7.9	4.1	104.4	98.3	2.35
29	Quartz, Calcite, Albite	Light brown, Silty Clay	8.0	4.3	82.4	117.9	2.84
43	Quartz, Dolomite, Albite	Medium brown, Clayey Shiny mica particles	8.2	3.6	94.14	132	1.26

Distribution of arsenic in the study area is heterogeneous may be related to the presence of a small scale redox zones in the aquifers controlled by quality, amount and distribution of natural organic matter within the aquifer (Wagener et al., 2005, Harvey, et al., 2002). These reducing zones are associated with oxbow lakes, meander scars and abandoned channels of Indus river, where degradation of organic matter creates an anoxic environment and results in the mobilization of As in the groundwater. After the formation of a new river course due to shifting of the Indus river (Holmes, 1968), the old channels turned into oxbow lakes in which high amount of fine-grained sediments and organic matter degradation created reducing environment (Halim et al., 2009). These redox conditions and processes are key factors in the variation of As concentrations in groundwater. In, addition, arsenic distribution is also controlled by agricultural activities, as it is shown by high concentration of arsenic in the soil, mostly collected from agricultural fields in the study area. Use of arsenic contaminated groundwater and subsequently its accumulation on the sediments leads to the formation of an iron-rich subsurface horizon, which favors the accumulation of arsenic (Zang and Gong 2003). Extensive groundwater irrigation accelerates the flow of groundwater that brought dissolved degraded organic matter in contact with arsenic-bearing sediments, enhancing reduction process and triggering the release of arsenic into groundwater (Acharrya et al., 2000). Throughout the study area of Hyderabad, the concentration of iron in groundwater is low ranging between 0.01 to 7.8 mg/L. Moreover, Fe concentrations do not correlate well with As throughout the area. Notably poor correlations between Fe and As may reflect a re-oxidation of Fe (II) due to subsurface distribution of redox potential, which mainly depends upon local lithological and biogeochemical conditions and distribution of redox zones (Yan et al., 2000).

In Hyderabad groundwater, the sulfate concentrations are highly variable and range from 12 to 700 mg/L. Extreme heterogeneity of sulfate indicates supply of sulfate through gypsum dissolution by freshwater recharge. While low concentrations of sulfate indicate decreased sulfate content due to micro biodegradation of organic matter which creates reducing conditions in the subsurface (Von Bromssen et al., 2007, Anawar et al., 2003). Furthermore, reducing conditions are also indicated by low nitrate concentration in the groundwater of the study area. This can be attributed to denitrification through nitrogen reducing bacteria causing redox conditions leading to the release of As into aquifers. Moreover, due to irrigation return flow, nitrate penetrates in the deeper parts of the aquifer along with organic matter, where it plays an important role for mobilization of arsenic in the groundwater (Acharyya et al., 2000). The study area is highly affected by bacteriological contamination, where 75% (n=50) wells show the presence of presumptive coliforms and fecal coliforms and E-coli. In Hyderabad city sewerage, industrial and domestic wastes are directly dumped in the Indus river and its distributary canals (Bano, 2003, Husain, 2009). Moreover, most of the handpump wells, installed on the canal banks at very shallow depths (<30 m) are severely contaminated by arsenic. The unlined sanitation in the area and presence of microbial organisms also contribute to microbial degradation of organic matter that enhances the reduction of iron oxy-hydroxides leading to release of arsenic to groundwater (Mc Arthur et al., 2001).

Acknowledgement

I am thankful to the Chairman, Department of Geology, University of Karachi for providing facilities to complete my research work. I am also grateful to my colleagues for their valuable suggestions and important discussions for the improvement of the manuscript.

Conclusion

- Aquifers in the areas are shallow, hosted in porous sediments and affected by surface and groundwater mixing, waste dumping and seepage from unlined canals as indicated by microbiological contamination in 75% water samples.
- Multivariate statistical analysis and PCA show that aquifers in Hyderabad show high salinity due to water-rock interaction, cation exchange, mineral dissolution and semi-arid climate.
- Dominant (40%) hydrofacies in the area is Na-Cl type, indicating halite dissolution, while the rest of the hydrofacies are fresh to mixed type.
- The soil in the area is fine grained silty clayey in nature and contains an appreciable amount of quartz, calcite, dolomite, albite, phlogopite, muscovite and desorption/dissolution of As from phlogopite and mica under reducing conditions plays an important role for arsenic mobilization.
- Presence of high contents of As (77-137 µg/kg), Fe (82-121 mg/kg) and Mn in (3.6-5.0 mg/kg) in sediments may indicate that high arsenic is released in groundwater by Fe oxyhydroxides desorption process.

- In Hyderabad districts, the arsenic mobilization seems to be controlled by geogenic factors particularly leaching of mica and Fe oxyhydroxides bearing sediments brought from the western Himalayas during the heavy monsoon of Holocene period. In addition, anthropogenic factors like poor drainage, waste dumps, unlined sanitation and flood irrigated crops promote the creation of local reducing zones by biodegradation of organic matter.
- High arsenic wells in the area are also associated with organic matter rich abandoned channels and oxbow lakes formed by Indus river during different historical periods during Holocene.

References

Acharyya, S. K., Lahiri, S., Raymahashay, B.C., Bhowmik, A. (2000). Arsenic toxicity of groundwater of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environ. Geol.*, **39**, 1127–1137.

Acharyya, S. K., Shah, B. A. (2007). Groundwater arsenic contamination affecting different geologic domains in India-a review: influence of geological setting fluvial geomorphology and Quaternary stratigraphy. *Environmental Science and Health part A*, **42**, 1795-1805.

Al-Ahmadi, M. E. (2013). Hydrochemical characterization of groundwater in wadi Sayyah, western Saudi Arabia. *Appl. Water Sci.*, **3**, p.721.

Anawar, H.M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Shizuka, T., Safiullah, S., Kato, K. (2003). Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *J. Geochem. Explore*, **77**, 109–131.

Ansari, M. H., Vink, A. (2007). Vegetation history and palaeoclimate of the past 30 kyr in Pakistan as inferred from the palynology of continental margin sediments off the Indus delta. *Review of Palaeobotany and Palynology*, **145,** 201–216.

Arain, M. B., Aslam, M., Majidano, S.A., Kuhawar, M.Y. (2007). A preliminary study on the arsenic contamination of underground water of Matiari and Khairpur districts, Sindh province, Pakistan. *Jour. Chem. Soc. Pakistan*, **29,** 463 – 467.

Arain, M. B., Kazi, T. G., Baig, J. A., Jamali, M. K., Afridi, H. I., Shah, A. Q., Jalbani, N., Sarfraz, R. A. (2009). Determination of arsenic levels in lake water, sediment, and food stuff from selected area of Sindh, Pakistan: estimation of daily dietary intake. *Food and Chemical Toxicology*, **47,** 242–248.

Baig, J. A., Kazi, T. G., Arain, M. B., Afridi, H.I., Kandhro, G.A., Sarfraz, R.A., Jamal, M.K., Shah, A. Q. (2009). Evaluation of arsenic and other physico-chemical parameters of surface and ground water of Jamshoro, Pakistan. *J. Hazard. Mater,* **166,** 662–669.

Bano, S. (2003). Water and health issues in Sindh. Islamabad, Pakistan: United Nations System in Pakistan, 81 pages.

Bhattacharya, P., Chatterjee, D., Jacks, G. (1997). Occurrence of arsenic contaminated groundwater in alluvial aquifers from the delta plains, eastern India: options for safe drinking water supply. *Water Resource Development,* **13,** 79-92.

Brahman, K. D., Kazi, T. G., Afridi, H. I., Baig, J. M., Arain, S. S, Talpur, F. N., Kazi, A. G., Ali, J., Panhwar, A. H., Arain, M. B. (2016). Exposure of children to arsenic in drinking water in the Tharparkar region of Sindh, Pakistan. *Sci. Total Environ.*, **544,** 653–660.

Chakraborty, S., Wolthers, M., Chatterjee, D., Charlet, L. (2007). Adsorption of arsenite and arsenate onto muscovite and biotite mica. *J. Colloid Interface Sci.*, **309,** 392-401.

Chen, Y., Marek, G.W., Marek, T.H., Brauer, D.K., Srinivasan, R. (2017). Assessing the efficacy of the SWAT auto-irrigation function to simulate irrigation, evapotranspiration and crop response to management strategies of the Texas high plains. *Water*, **9,** 509.

Claire, E., Farnsworth, J., Hering, G. (2011). Inorganic geochemistry and redox dynamics in bank filtration settings. *Environ. Sci. Technol.*, **45,** 5079–5087.

Clift, P. D., Blusztajn, J. S. (2005). Reorganization of the western Himalayan river system after five million years ago. *Nature*, **438** (7070): 1001–1003.

Clift, P.D., Giosan, L. (2013). Sediment fluxes and buffering in the post-glacial Indus basin. *Basin Research*, **25,** 1–18

Clift, P. D. (2002). A brief history of the Indus river. In: Clift, P.D., Kroon, D., Gaedicke, C., Craig, J. (eds), Tectonic and climatic evolution of the arabian sea region. London: *Geol. Soc., Spec. Pub.,* **195**, 237–258.

Clift, P. D., Giosan, L., Blusztajn, J., Campbell, I. H., Allen, C. M., Pringle, M., Tabrez, A., Danish, M., Rabbani, M. M., Carter, A., Leuckge, A. (2008). Holocene erosion of the lesser Himalaya triggered by intensified summer monsoon. *Geology*, **36**, 79–82.

Edet, A., Okereke, C. (2001). A regional study of salt water intrusion in southeastern Nigeria based on the analysis of geoelectrical and hydrochemical data. *Env. Geol.*, **40**, 1278.

Giosan. L., Constantinescu, S., Clift, P.D., Tabrez, A. R., Danish, M., Inam, A. (2006). Recent morphodynamics of the Indus delta shore and shelf. *Continental shelf research,* **26,** 1668–1684.

Halim, M.A., Majumder, R.K., Nessa, S.A., Hiroshiro, Y., Uddin, M.J., Shimada, J., Jinno, K. (2009). Hydrogeochemistry and arsenic contamination of groundwater in the Ganges delta plain, Bangladesh. *Journal of Hazardous Materials*, **164**, 1335–1345.

Haq, B.U. (1999). Past, present and future of the Indus delta. In: Meadows, A., Meadows, P.S. (eds.), Indus river, biodiversity, resources, humankind. Linnaean Society of London, Oxford University Press, Oxford, UK, 231–248.

Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F. (2002). Arsenic mobility and groundwater extraction in Bangladesh. *Science*, **298,** 1602–1606.

Holmes, D. A. (1968). The recent history of the Indus. *The Geographical Journal,* **134**(3), 367–382.

Hunting Survey Corporation, (1960). Reconnaissance geology of part of west Pakistan. Toronto, Canada: Hunting Survey Corporation, a Colombo Plan-Cooperative Project, 550 pages.

Husain, V. (2009). Drinking water quality component. (Report) sindh education reform program (SERP), A study for World Bank, 58 pages.

Husain, V., Nizam, H., Arain, G.M. (2012). Arsenic and fluoride mobilization mechanisms in groundwater of Indus Delta and Thar Desert, Sindh, Pakistan. *Int. Journ. Econ. Environ. Geol.,* **3**(1), 15-23.

Jiang, H., Ding, J.H., Chang, P., Chen, Z.X., Sun, G.F., (2010). Determination of the interaction of arsenic and human serum albumin by online microdialysis coupled to LC with hydride generation atomic fluorescence spectroscopy. *Chromatographia,* **71,** 1075–1079.

Kadri, I.B. (1995). Petroleum Geology of Pakistan. Pakistan Petroleum Limited, Ferozsons (Pvt) Limited, 275 pages.

Kahlown, M.A., Tahir, M.A., Sheikh, A.A. (2004). Water quality status in Pakistan: Second report (2002 – 2003), Pakistan Council of Research in Water Resources, Islamabad.

Kazmi, A.H. (1984). Geology of the Indus delta. In: Haq, B.U., Milliman, J.D. (eds.), Marine geology and oceanography of Arabian sea and coastal Pakistan, Van Nostrand, New York, 71-84.

Kazmi, A. H., Jan, M.Q. (1997). Geology and Tectonics of Pakistan, Graphic Publishers, Karachi 544 pages.

Kelly, W.R (1997). Heterogeneities in groundwater geochemistry in a sand aquifer beneath an irrigated field. *Journal of Hydrology,* **198**, 154-176.

Khan, A., Husain, V. (2019). Arsenic contamination in shallow aquifers of Holocene: A Case study from three union councils of Tando Muhammad Khan district, Sindh, Pakistan. *Int. J. of Ground Sediment & Water,* **8**, 383-404.

Khan, A., Husain, V., Hamid, G., Anjum, S. (2014). Arsenic contamination status in the Holocene alluvial aquifers of Indus deltaic flood plain: a case study of Tando Ghulam Hyder taluka, Sindh, Pakistan. *Int. Journ. Econ. Environ. Geol.*, **5**(2), 1-10.

Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, *China. Environ. Pollut.,* **152**, 686–692.

Khan, A.A., Memon, M.G., Danish, M., Inam, A. (1993). Distribution of surface sediments off Indus delta on the continental shelf of Pakistan. *Pakistan Journal of Marine Sciences,* **2**(1), 33–39.

Kidwai, Z.D. (1963). Geology of Rechna and Chaj Doabs, west Pakistan. West Pakistan Water and power Development Authority. *Water and soil investigation Div*. Bull., **5**.

Kureshy, K.U. (1977). A Geography of Pakistan, 4thed.

Lang, Y.C., Liu, C.Q., Zhao, Z.Q., Li, S.L., Han, G.L. (2006). Geochemistry of surface and groundwater in Guiyang, China: Water/rock interaction and pollution in a karst hydrological system. *Applied Geochemistry,* **21,** 887–903.

Latif, M., Akram, M., Altaf, S. (1999). Groundwater contamination from nitrates in irrigated areas of Pakistan. Proceedings on water resources achievements and issues in 20th century and challenges for next millennium, Pakistan Council of Research in Water Resources, Islamabad, Pakistan.

Lee, J. I., Clift, P. D., Layne G., Blum, J., Khan, A. A. (2003). Sediment influx in the modern Indus river inferred from the trace element composition of detrital amphibole grains. *Sedimentary Geology,* **160**, 243–257.

Malik, S.B. (2000). An overview of geothermal resources of Pakistan. In: Proceedings of the World Geothermal Congress, Kyushu, Tohoku, Japan.

McArthur, J.M., Ravenscroft, P., Safiullah, S., Thirlwall, M.F. (2001). Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh, *Water Resour. Res.,* **37,** 109–117.

Mukherjee, A., Fryar, A.E., Thomas, W. A. (2009). Geologic, geomorphic, and hydrologic framework and evolution of the Bengal basin, India and Bangladesh. *J. Asian Earth Sci.,* **34,** 227–244.

Mukherjee, A.B., Bhattacharya, P. (2001). Arsenic in groundwater in the Bengal delta plain: slow poisoning in Bangladesh. *Environmental Reviews,* **9,** 189–220.

Mukherjee-Goswami, A., Nath, B., Jana, J., Sahu, S. J., Sarkar, M. J., Jacks, G., Bhattacharya, P., Mukherjee, A., Polya, D.A., Jean, J.S., Chatterjee, D. (2008). Hydrogeochemical behavior of arsenic-enriched groundwater in the deltaic environment: Comparison between two study sites in West Bengal, India. *Journal of Contaminant Hydrology,* **99,** 22–30.

Naseem, S. McArthur, J.M. (2018). Arsenic in groundwater and other water-quality issues, Indus alluvial plain, Pakistan. *Hydrological Processes,* **32**, 1235-1253.

Naseem, S. Husain, V. Bano, S. (2018). Origin of salinity and other constituents in Indus deltaic plain groundwater, Thatta district, Pakistan, *Journal of Coastal, Research*, **34**, 883–891.

Nickson, R.T., McArthur, J.M., Shrestha, B.R., Kyaw-Myint, T.O., Lowry, D. (2005). Arsenic and other drinking water quality issues, Muzaffargarh district, Pakistan, *Applied Geochemistry,* **20**, 55-68.

Nordstrom, D.K., Ball, J.W., Donahoe, R.J., Whittemore, D. (1989). Groundwater chemistry and water–rock interactions at Stripa. *Geochimicaet Cosmochimica Acta,* **53** (8), 1727–1740.

Panhwar, M.H. (1969). Groundwater in Hyderabad and Khairpur divisions. Directorate of Agriculture, Hyderabad, region. 169 pages.

Qureshi, A.S., McCornick, P.G., Qadir, M., Aslam, Z. (2008). Managing salinity and waterlogging in the Indus basin of Pakistan. *Agricultural Water Management,* **9**(5), 1–10.

Rasheed, H. (2017). Human exposure assessment of different arsenic species in household water sources in a high risk arsenic area. *Science of Total Environment*, **584,** 10.1016/j.scitotenv.2017.01.089

Rasool, A., Xiao., T., Farooqi, A., Shafeeque, M., Masood, S., Ali, Fahad S., Naseem, W. (2016). Arsenic and heavy metal contaminations in the tube well water of Punjab, Pakistan and risk assessment: A case study. *Ecological Engineering,* **95**, 90-100.

Rowland, H.A.L., Pederick, R.L., Polya, D.A., Pancost, R.D., Van Dongen, B.E., Gault, A.G., loyd, J.R. (2007). The control of organic matter on microbially mediated iron reduction and arsenic release in shallow alluvial aquifers, Cambodia. *Geobiology,* **5**(3), 281–292.

Rubab, G., Naseem. S., Khan. A., Husain. V., Murtaza. G.M. (2014). Distribution and sources of arsenic contaminated groundwater in parts of Thatta district, Sindh. *Journal of Himalayan Earth Sciences,* **47**(2), 175-183.

Samdani, Z. (1995). LBOD: A futuristic project. Economic and Business Review. Daily Dawn Karachi, **III** (23-29/09/1995).

Sanchez-Martoz, F., Jimenez-espinosa, R., Pulido-Bosch, A. (2001). Mapping groundwater quality variables using PCA and geostatistics: A case study of Bajo Andarax, southeastern Spain. *Hydrological Sciences Journal-des Sciences Hydrologiques,* **46** (2), 227-242.

Sarkar, D., Datta, R. (2004). Arsenic fate and bioavailability in two soils contaminated with sodium arsenate pesticide: An incubation study. *Bulletin Environmental Contamination and Toxicology,* **72,** 240–247.

Shah, A.Q., Kazi, T.G., Arain, M.B., Jamali, M.K., Afridi, H.I., Jalbani, N., Baig, J.A., Kandhro, G.A. (2009). Accumulation of arsenic in different fresh water fish species potential contribution to high arsenic intakes. *Food Chem.,* **112,** 520–524.

Shamsudduha, M., Uddin, A., Saunders, J.A., Lee, M.K. (2008). Quaternary stratigraphy, sediment characteristics and geochemistry of arsenic contaminated alluvial aquifers in the Ganges–Brahmaputra floodplain in central Bangladesh. *J. Contam. Hydrol.,* **99,** 112–136.

Shrestha, B. (2002). Drinking water quality: Future directions for UNICEF in Pakistan. Consultancy report on water quality. UNICEF Pakistan, Islamabad, SWEET Project.

Smedley, P. L., Kinniburgh, D. G. (2002). A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.,* **17,** 517–568.

Von Bromssen, M., Jakariya, M., Bhattacharya, P. Ahmed, K.M., Hasan, M.A., Sracek, O. (2007). Targeting low-arsenic aquifers in groundwater of Matlab upazila, southeastern Bangladesh Sci. *Total Environ.,* **379,** 121-132.

Wagner, W.F., Berner, Z.A., Stuban, D. (2005). Arsenic in groundwater of the Bengal delta plan: geochemical evidences for small scale redox zonation in the aquifer. In Natural arsenic in groundwater, occurrence, remediation and management (eds.) J. Bundschuh, P. Bhattacharya and D. Chandra sekharam. Published by Taylor and Francis Group, London, 3-16.

Wilhelmy, H. (1967). The shifting river; studies in the history of the Indus valley. *Universities*,**10,** 53–68.

World Health Organization, (2011). Guidelines drinking water quality, Geneva. Switzerland, 564 pages.

Yan, X. P., Kerrich, R., Hendry, M. J. (2000). Distribution of arsenic (III), arsenic (V) and total inorganic arsenic in pore-waters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochim.Cosmochim.Acta*., **64,** 2637–2648.

Zhang, G. L., Gong, Z. T. (2003). Pedogenic evolution of paddy soils in different soil landscapes. *Geoderma*, **115,** 15–29.

Zhu, Y. G., Williams, P. N., Meharg, A. A. (2008). Exposure to inorganic arsenic from rice: a global health issue. *Environ. Pollut.*, **154**, 169–171.