

◆ Research Paper ◆

Groundwater arsenic contamination in shallow alluvial aquifers of Bhulri Shah Karim taluka, Tando Muhammad Khan district, Sindh, Pakistan

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Abstract: The aim of present study is to determine the groundwater arsenic contamination and identification of its possible sources through hydro-geochemistry in Bhulri Shah Karim Taluka which is part of Tando Muhammad Khan district, Sindh. For this purpose, 66 groundwater samples taken from shallow wells (depth < 30 meters) were analyzed to determine physicochemical and microbiological parameters including arsenic. Hydro-geochemical data reveal that groundwater is marginally saline (Mean TDS: 1166 mg/L) and slightly alkaline (Mean pH: 7.25). More than half of the groundwater wells (n = 25) are sewage impacted as indicated by the occurrence of pathogenic bacteria. Strong positive correlation of HCO₃ with SO₄ (r = 0.61), Cl⁻ (r = 0.54), F⁻ (r = 0.52) and NO₃ (r = 0.5) was observed which suggest that complex geochemical processes are operating in the study area. Hardness of groundwater showed the strong relationship with NO₃ (r = 0.57) and HCO₃ (r = 0.47) indicating the mineral and fertilizer contribution. On the other hand, weak but positive correlation of Fe with NO₃ (r = 0.22) suggests that denitrification process is active but slow in study area. In about 40% groundwater samples arsenic occurs in alarmingly high concentrations (up to 250 μg/L) against WHO permissible limit of 10 μg/L for drinking water. About one third of total sewage impacted wells show arsenic concentrations in the range of 10-200 μg/L suggesting that arsenic release is somehow linked with sanitation. Correlation of As with Fe (r = 0.21) is weak but positive and strong with PO₄ (r = 0.48) which suggest that as released from organic matter is followed by reductive dissolution of FeOOH through bacterial respiration in the groundwater of Bhulri Shah Karim.

Keywords: Groundwater, hydro-geochemistry, arsenic, pollution, Indus delta, Sindh

Introduction

In many flood plain aquifers of South Asia, widespread contamination of As is reported (Smedley and Kinniburgh, 2002; Farooqi et al., 2009) which is mainly restricted to sedimentary aquifers of Holocene age (Bhattacharya et al., 1997; Ishiga et al., 2000; Anawar et al., 2002, 2003). Generally accepted geochemical model for arsenic release into such aquifer waters is mobilization of arsenate absorbed to Fe (iii) oxyhydroxide coated sediments under reducing conditions. Inorganic As is considered a potent human carcinogen, with increased risk of lung, kidney, liver and skin cancer (NRC, 1999; Fatmi et al, 2009; IARC, 2004; Ramadan and Al-Ashkar, 2007). Since the source of arsenic appears to be both natural and anthropogenic (Acharyya et al., 1999; Chowdhury et al., 1999; Nickson et al., 2000; McArthur et al., 2001; Anawar et al., 2002; Harvey et al., 2002).

Although alarmingly high concentration of arsenic is reported in the groundwater of deltaic regions of the world, but very limited studies have been carried out in the Indus deltaic plain which are attempted to the arsenic toxicity in southern part of Sindh province (e.g. Arain et al., 2009; Kazi et al., 2009; Majidano et al., 2010). Elevated As concentration (up to 800 μ g/L) in Indus deltaic aquifers is reported to be caused by both Geogenic and anthropogenic (mainly sewage contamination) factors (Husain 2009; Naseem, 2012; Khan et al., 2014).

Study Area.

Bhulri Shah Karim (BSK) is Taluka of Tando Muhammad Khan district which is located between 68° 15' E-68° 45' E longitudes and 25° 00' N-25° 30' N latitudes, covering an area of 2600 km². The study area is 19 m above sea level and 58 km away from Hyderabad (Fig. 1). The main crops in the area are wheat, rice, cotton and sugarcane. Climate of this area is semi-arid subtropical with an average rainfall of about 220 cm. The average humidity of about 76% with mean annual temperature of 84.2 °F (Kureshy, 1977; Haq, 1999; Memon, 2005). Semi-arid climate and scarce rainfall in study area have constrained the irrigation system to switch from surface water source to groundwater.

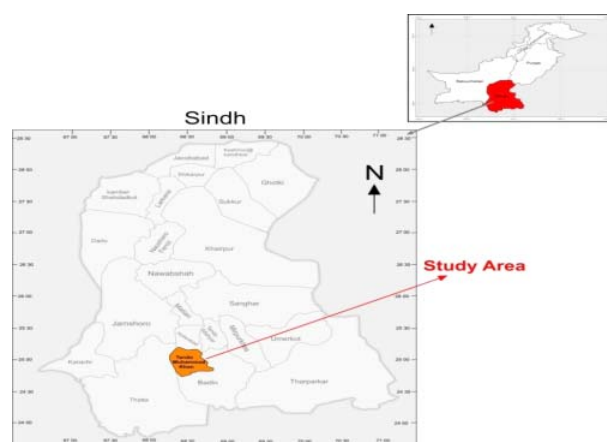


Fig. 1 Location map of Study area.

Study area lies in lower part of Indus flood plain which covers an area of about 34 million hectares (over 85 million acre). This plain is filled with very thick fluvial deposits brought by Indus River during Pleistocene to Recent time (Kazmi and Jan, 1997). BSK taluka mostly occupies cultivable land constituting the enormous amount of alluvium (up to > 200 meter depth) brought by the Indus River and its tributaries from Himalaya during Holocene period (Chauhan and Almedia, 1993). The subsurface sediments are underlain by Tertiary rocks, which are exposed on the western margin of this taluka (Fig. 2). Study area enjoys very simple topography where most of the area is flat with devoid of any prominent natural drainage both surface and subsurface (Qureshi et al, 2008). Surface sediments are very fine textured comprising silt and clay with relatively less amount of sand.

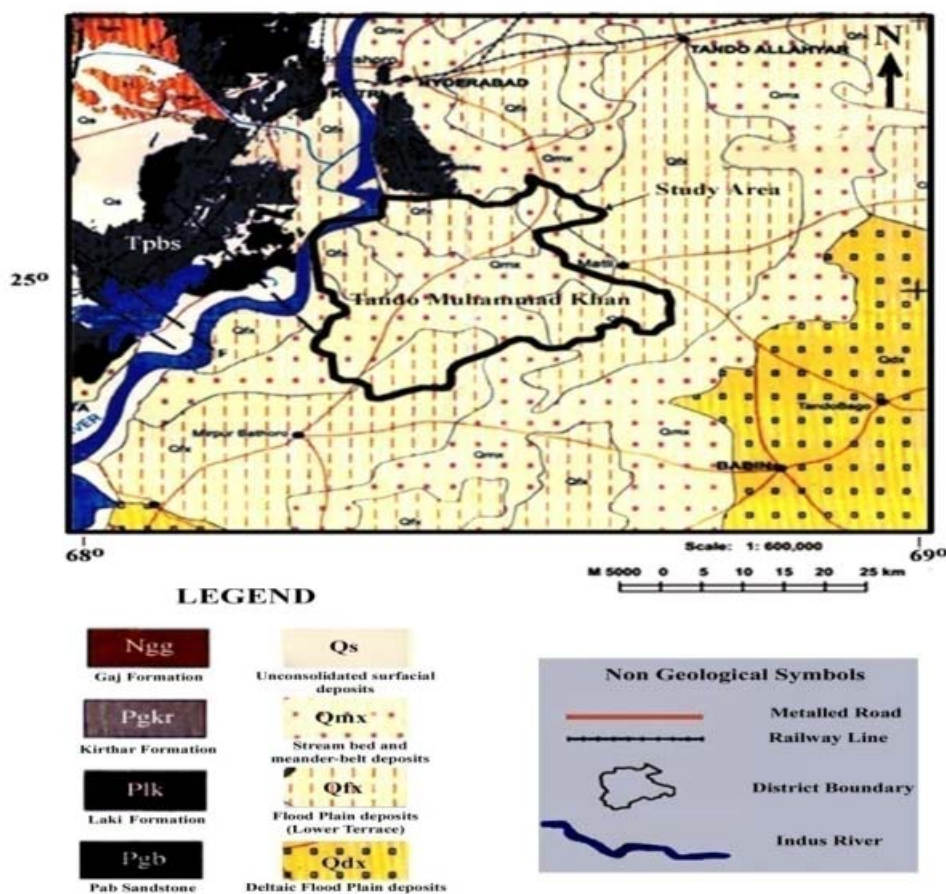


Fig. 2 Surface geology of study area (after Akhtar et al., 2012).

The fluvial landscape in the area is drained by Indus River (total length of 3180 km) which starts from Tibet and flows down along the transact of Pakistan and ultimately culminate the Arabian Sea in south. About 150 km wide alluvial valley of Indus plain is, formed by accumulation of enormous amount of sediments (600 million tons) in Indus Basin between Kirthar Range west in the and Thar Desert in the East (Fig.3). BSK and adjacent areas are characterized by active flood plain meanders and channel process. These Recent geomorphic signatures are rich in young and reactive organic matter. Indus River switched its channel from east to west of

Hyderabad in recent past and ultimately formed its present course in the vicinity of delta (Wilhelm, 1967). Hierarchical four main aggradational stages of Indus River are Jacobabad-Samaro, Shehdadkot-Jhudo, Qambar-Tando Allayar, Ghambat-Tando Muhammad Khan (Kazmi and Jan, 1997).

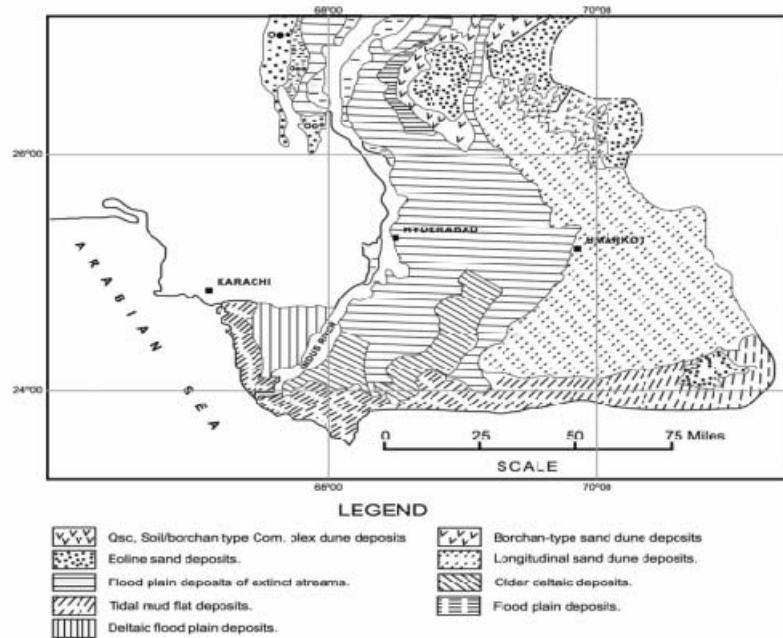


Fig. 3 Geomorphic distribution of Lower Indus plain (after Holmes, 1968).

The remnants of these major avulsions includes oxbow lakes, sand bars, swales and fresh channel scars which exists near Khairpur to Daulatpur, Matiari and Tando Muhammad Khan districts (Fig. 4). The land through which river Indus passed during Holocene is prone to be the worst arsenic affected part of Sindh province including the study area.



Fig. 4 oxbow lake in Tando Muhammad Khan district.

Materials and Methods

Sixty six groundwater samples were collected from shallow wells (depth >24 m) in sterile plastic bottles (0.5 and 1 liter) for the determination of physicochemical parameters including arsenic. Methods and equipments used to determine groundwater attributes are summarized in Table 1. For nitrate determination, groundwater samples were collected in 100 ml bottles and 1 ml boric acid solution was poured with syringe to cease any reaction which could alter the nitrate (NO₃) concentration. For pathogenic bacteria determination groundwater samples were directly poured into microbiological testing kits which were put in the incubator at 30° for 24 hours to get result.

Table 1. Equipment/methods used to analyze groundwater samples collected from Bhulri Shah Karim taluka, Sindh.

S. No.	Parameters	Equipments
	Turbidity	Turbidity meter, Lamotte, model 2008, USA
1	Electrical Conductivity/TDS	EC meter (Eutech Cyber Scan CON 11)
2	pH	pH meter (JENCO 6230N)
3	Alkalinity	2320 Standard Method (1992)
4	Carbonate mg/L	Titration Method, (USSL, 1954)
5	Bi-carbonate mg/L	Titration Method, (USSL, 1954)
6	Calcium mg/L	EDTA Titration Method
7	Chloride mg/L	Argenometric Titration Method
8	Magnesium mg/L	Titration Method
9	Potassium mg/L	Flame photometer (JENWAY PFP7)
10	Sodium mg/L	Flame photometer (JENWAY PFP7)
11	Sulphate mg/L	Spectrophotometer (DR 2800)
12	Nitrate mg/L	Spectrophotometer, HACH-8171
13	Hardness as CaCO ₃	EDTA titration standard method (1992)
14	iron	Spectrophotometer (Model: U-1100, HITACHI)
15	Fluoride	Spectrophotometer, SPADNS (HACH).
16	Arsenic	Perkin Elmer A Analyst 600 Graphite Furnace Atomic Absorption Spectrophotometer

Principal component analysis (PCA).

Statistical analysis was carried out by using PCA on data set of ground water parameters of Bulri Shah Karim taluka. The output of PCA was used to explain the variation of major data set of interrelated variables with small set of independent

variable (Simeonov et al, 2003) and to trace the factors which affect each other. Components with Eigen values <1 were not taken into account as these explain insignificant variation.

Results and Discussion

1. Groundwater characterization

1.1. Physical properties

Groundwater salinity is highly variable in Bhulri Shah Karim taluka where it ranges between 260-5312 mg/L with a mean of 1166 mg/L. The pH is marginally alkaline (range: 5.9-8.17, mean: 7.2) which is generally within the permissible limit (6.5-8.5) of WHO set for drinking water. Slight variation in the pH of groundwater of study area may be attributed to the heterogeneous soil alkalinity, reaction of silicate minerals, fertilizer use, human activities, water logging and evaporation (Shahid and Jenkins, 1994; Sharma et al. 2000; Vanlenza et al., 2000; Farooqi et al., 2009; Nicolli et al, 2010). Ground water is formed to be very hard (mean: 432 mg/c) where about 38% samples showed variable value of hardness ranging between 140-1480.

Table 2. Physicochemical parameters of groundwater in Bhulri Shah Karim Taluka.

S. No.	Sample No.	Coordinates		Well depth (meters)	pH	TDS (mg/L)	Micro +ve/-ve	Alk. (m. mol/l)	Hard (mg/l)
		Lat. °N	Long. °E						
1	TMK34	250653	682355	8	6.2	2342	+ve	9.2	810
2	TMK53	245147	681957	11	7.05	3104	+ve	5.2	980
3	TMK55	245132	682100	18	7.08	902	-ve	5.6	460
4	TMK56	245121	681939	7	7.08	881	-ve	7.2	410
5	TMK57	245144	681950	8	7.05	1085	-ve	4.8	550
6	TMK58	245204	682003	15	7.32	683	+ve	6	330
7	TMK120	245627	682123	24	7.49	753	-ve	7	380
8	TMK121	245622	682036	24	7.05	908	-ve	7.2	450
9	TMK122	245625	682017	9	6.9	1196	-ve	8	550
10	TMK123	245620	682017	8	6.69	5312	+ve	17.6	1480
11	TMK125	250218	682605	11	7.8	260	-ve	2.4	140
12	TMK188	245759	682700	8	7.21	605	-ve	6	330
13	TMK189	245636	682556	9	7.21	1009	-ve	6	410
14	TMK190	245620	682547	12	7.06	1100	+ve	4.8	490
15	TMK192	245653	682419	12	8.17	889	-ve	7.2	150
16	TMK193	245445	682301	9	7.4	513	-ve	3.2	240

17	TMK195	245220	681902	9	6.97	2176	+ve	9.2	610
18	TMK196	245322	681820	12	7.89	773	-ve	7.6	160
19	TMK66	245814	682410	15	7.37	746	-ve	5.8	370
20	TMK70	245729	682947	15	7.82	298	-ve	2.8	170
21	TMK79	245824	684552	9	7.66	626	+ve	3.6	320
22	TMK116	250111	682348	11	7.11	1523	+ve	7.2	650
23	TMK117	245954	682244	11	7.96	2009	-ve	12.8	350
24	TMK191	245809	682433	9	7.99	397	-ve	3	180
25	TMK202	245915	682350	12	7.37	986	+ve	4.6	380
26	TMK203	245953	682425	9	7.21	737	-ve	4.8	350
27	TMK59	245219	682030	20	7.85	1149	-ve	7	380
28	TMK60	245531	682115	18	8.03	1574	-ve	9.6	230
29	TMK61	245518	681944	8	7.29	643	-ve	6	350
30	TMK62	245522	681832	9	7.56	824	+ve	8	430
31	TMK63	245436	682152	8	7.49	839	-ve	6	410
32	TMK64	245612	682126	20	7.52	406	+ve	4.4	250
33	TMK65	245721	682106	9	7.53	480	-ve	4.4	260
34	TMK119	245749	682141	9	7.23	1670	+ve	10	580
35	TMK194	245428	682039	8	7.2	718	-ve	5.6	380
36	TMK197	245306	682027	8	7.31	795	-ve	4.8	330
37	TMK198	245357	681909	9	6.89	1754	-ve	4.2	680
38	TMK199	245319	682028	21	7.23	1016	-ve	4	460
39	TMK200	245416	682117	9	7.89	695	+ve	6.8	260
40	TMK201	245628	682144	9	7.28	795	-ve	4.2	380
41	TMK36	250648	682140	14	6.42	1266	+ve	9	460
42	TMK37	250648	682140	21	6.36	1271	-ve	9.4	450
43	TMK38	250638	682130	11	6.61	574	-ve	7	340
44	TMK39	250633	681808	11	6.5	1067	+ve	9	440
45	TMK40	250554	682013	11	6.6	993	-ve	7.6	450
46	TMK118	-----	-----	8	7.81	1077	-ve	8.2	310
47	TMK67	245736	682511	18	8.08	399	-ve	4.2	170
48	TMK68	245801	682600	9	7.55	870	-ve	6.4	300
49	TMK69	245759	682719	15	6.98	1862	+ve	4.4	880
50	TMK124	250004	682340	15	7.51	908	-ve	6.4	400
51	TMK186	250035	682739	14	7.95	593	-ve	5.4	280
52	TMK187	245840	682700	24	7.79	711	-ve	4.1	330
53	TMK28	250742	682951	21	6.84	2208	-ve	5.2	800

54	TMK29	250742	682951	8	6.29	1121	-ve	7.6	610
55	TMK30	250754	682601	9	7.47	454	+ve	4.2	180
56	TMK31	250857	682558	11	6.29	1160	+ve	10	660
57	TMK32	250857	682558	12	6.34	2374	+ve	7.6	920
58	TMK33	250757	682505	14	6.27	858	+ve	8.4	450
59	TMK35	250937	682258	7	6.09	1114	+ve	7.6	570
60	TMK52	250423	682840	15	8.15	3411	-ve	16.8	260
61	TMK114	250253	682538	11	6.86	2425	+ve	11	1070
62	TMK148	250140	682525	8	7.54	617	-ve	6	320
63	TMK149	250133	682533	8	6.83	1036	+ve	7.4	520
64	TMK185	250114	682645	8	7.4	708	-ve	4.8	300
65	TMK204	250134	682431	11	8.11	585	+ve	5	170
66	TMK205	250348	682843	15	7.57	2138	+ve	8.6	270

Table 3. Chemical characteristic of groundwater from Bhulri Shah Karim taluka.

S. No.	Sample No.	Ca (mg/L)	Mg(mg /L)	HCO ₃ (mg/L)	Cl(mg/ L)	SO ₄ (m g/L)	PO ₄ (m g/L)	NO ₃ (m g/L)	F ⁻ (mg/L)	Na (mg/L)	K(mg/ L)	Fe(mg/ L)	As µg/L
1	TMK34	180	87	460	587	510	-	0.64	0.91	462	9	0.05	0
2	TMK53	216	107	260	1446	107	0.27	1.46	0.41	676	11	0.87	100
3	TMK55	104	49	280	257	54	-	0.58	0.09	107	7.5	0.62	0
4	TMK56	76	53	360	156	96	-	0.58	0.34	128	6	0.07	0
5	TMK57	128	56	240	351	103	-	0.74	0.41	141	9.8	0.02	0
6	TMK58	80	32	300	139	36	0.58	0.62	0.33	91	4.8	0.45	80
7	TMK120	72	49	350	85	104	-	1.69	0.48	91	6.6	0.44	40
8	TMK121	108	44	360	173	96	0.12	1.07	0.48	113	7.4	0.08	60
9	TMK122	116	63	400	255	160	0.15	0.89	0.52	168	8.6	0.05	80
10	TMK123	472	73	880	1743	556	-	19.41	1.21	1020	216	0.89	0
11	TMK125	32	15	120	37	26	-	0.65	0.37	27	3.3	0.04	0
12	TMK188	92	24	300	67	70	0.82	0.70	0.58	63	4.2	1.15	250
13	TMK189	80	51	300	243	128	-	0.44	0.51	164	11	0.14	5
14	TMK190	104	56	240	344	124	0.21	0.60	0.41	170	6.2	0.28	200
15	TMK192	36	15	360	156	100	0.34	0.60	1.76	240	3	0.06	200
16	TMK193	54	26	160	109	81	-	0.37	0.52	71	4	0.09	0
17	TMK195	108	83	460	639	315	0.15	0.93	0.9	476	10.6	0.61	200
18	TMK196	28	22	380	110	61	-	0.50	1.28	198	4.1	0.02	0
19	TMK66	68	49	290	141	89	0.18	0.63	0.15	96	7.1	0.06	100
20	TMK70	36	19	140	42	30	-	0.58	0.44	29	4.7	0.04	0

21	TMK79	62	40	180	157	84	-	1.29	0.46	72	11.4	0.04	0
22	TMK116	116	87	360	386	270	-	0.91	0.57	230	8.7	0.06	0
23	TMK117	60	49	640	454	250	-	1.22	2.72	540	14.5	0.04	5
24	TMK191	40	19	150	67	59	-	0.39	0.57	56	3.9	0.03	0
25	TMK202	96	34	230	262	154	0.15	0.91	0.9	167	5	0.01	70
26	TMK203	88	32	240	140	126	0.22	0.68	0.45	93	14	0.4	25
27	TMK59	78	45	350	319	107	-	0.73	0.54	236	6.1	0.04	0
28	TMK60	44	29	480	489	45	0.87	1.29	0.94	448	6.2	0.23	150
29	TMK61	68	44	300	103	64	-	0.45	0.52	78	4.1	0.19	30
30	TMK62	84	53	400	117	74	-	0.72	0.3	97	6	0.02	0
31	TMK63	72	56	300	164	112	-	0.56	0.4	119	5.4	0.36	5
32	TMK64	44	34	220	39	46	0.02	0.57	0.03	33	3.8	0.04	100
33	TMK65	52	32	220	67	61	-	0.57	0.04	54	4	0.08	40
34	TMK119	112	73	500	390	230	-	1.27	0.75	322	9	0.01	5
35	TMK194	60	56	280	117	108	-	0.55	0.99	80	4.3	0.07	100
36	TMK197	92	24	240	159	138	-	0.46	0.57	134	4.1	0.45	100
37	TMK198	140	80	210	651	205	-	0.58	0.66	306	6.2	0.07	0
38	TMK199	96	53	200	315	130	0.23	0.76	0.68	144	10.6	0.04	5
39	TMK200	60	27	340	92	98	-	0.67	0.43	124	5.8	0.02	25
40	TMK201	90	40	210	166	161	0.19	0.63	0.79	97	8.7	0.55	30
41	TMK36	76	66	450	305	152	-	0.70	0.6	260	11	0.08	0
42	TMK37	96	51	470	312	132	-	0.93	0.6	258	12	0.05	5
43	TMK38	68	41	350	71	42	-	0.54	0.46	47	7	0.04	0
44	TMK39	76	61	450	195	178	-	0.53	0.97	234	7	0.15	0
45	TMK40	68	68	380	255	106	-	0.55	0.34	198	5	0.02	40
46	TMK118	60	39	410	248	75	0.08	0.86	0.54	233	13.4	0.02	10
47	TMK67	36	19	210	53	29	-	0.88	0.6	67	3.6	0.03	5
48	TMK68	48	44	320	219	56	-	1.49	0.31	169	6.4	0.53	20
49	TMK69	148	124	220	815	73	-	1.07	0.24	232	94.2	0.12	0
50	TMK124	72	53	320	192	110	-	0.65	1.15	135	10.6	0.05	0
51	TMK-186	56	34	270	74	81	-	0.5	0.67	82	4.3	0.05	0
52	TMK-187	78	33	260	138	88	-	0.71	0.49	103	3.7	0.06	100
53	TMK28	128	117	260	549	655	-	0.98	0.94	422	5	0.22	0
54	TMK29	124	73	380	269	186	-	0.37	0.8	184	6	0.04	5
55	TMK30	36	22	210	70	40	-	0.62	0.58	79	2	0.05	20
56	TMK31	112	92	500	237	178	-	0.45	1.38	198	6	0.23	5
57	TMK32	172	119	380	658	515	-	0.81	0.75	422	11	2.78	0

58	TMK33	80	61	420	103	100	-	0.43	0.22	102	6	0.09	5
59	TMK35	120	66	380	223	164	-	2.28	0.5	137	7	0.07	0
60	TMK52	68	22	840	823	615	-	0.61	2.21	1098	4.5	0.04	5
61	TMK114	288	85	550	593	455	-	1.17	0.76	368	9.5	0.07	0
62	TMK-148	52	46	300	77	66	-	0.76	0.43	70	5.5	0.02	0
63	TMK-149	140	41	370	193	151	-	0.77	0.29	127	5.6	0.03	0
64	TMK-185	72	29	240	167	84	-	0.41	0.72	114	3.3	0.04	5
65	TMK204	40	17	250	88	75	-	0.42	0.93	126	3.8	0.03	0
66	TMK205	36	44	430	616	332	-	0.57	3.16	627	4.2	0.05	0

1.2. Chemical characteristics of groundwater

Analytical results of groundwater samples (n=66) collected from Bhulri Shah Karim taluka have been given in Table 3. Both calcium and magnesium concentrations are highly variable which ranges between 28-472 mg/L and 15-124 mg/L respectively (Table 3). Although mean value (92.33 mg/L) of Ca is within the admissible limit of WHO (100 mg/L) for drinking water but 30% samples show Ca > 100 mg/L. On the other hand, 44% of total collected samples are very high in Mg concentration above WHO permissible value of 50 mg/L for drinking water. Interestingly, most of the samples high in their Ca content also exceed corresponding Mg concentration (Table 3). It suggests that the source of these ions is same which seems to be the dissolution of dolomitic limestone fragments occurring in the alluvium of study area. Moreover, elevated Ca concentration in groundwater of study area suggests feldspar dissolution which is assumed to be one of the main sources of this ion as feldspar is one of the most reactive minerals during chemical weathering (Mast and Drever, 1987). Similarly incongruent dissolution of plagioclase can release Ca (Saether et al, 2001) into the groundwater. Sodium and chloride concentrations ranged between 27-1098 mg/L and 37-1743 mg/L respectively. One third of total groundwater samples show very high sodium concentrations (> 200 mg/L) and about 40% wells have elevated chloride contents (> 250 mg/L) against the permissible limit of WHO for drinking water.

Generally very low nitrate content (< 1 mg/L) occurs in the groundwater of Bhulri Shah Karim taluka which is within the permissible guidelines of 10 mg/L for drinking water set by WHO, 2004. It suggests that nitrate reducing bacteria are very active in alluvial aquifers of study area. Nitrate generally moves in soil and groundwater with no transformation and volatilization and denitrification may reduce its concentration by denitrifying bacteria. Only one sample (TMK-123) collected from very shallow well (depth<8 meters) shows exceptionally high nitrate concentration (19.41 mg/L). This groundwater sample is also very high in its SO₄, Cl⁻, HCO₃ and iron contents which indicates that redox processes are taking place in aquifers (Lang et al 2006; Rowland et al., 2008; Shamsudduha et al, 2008; Nath et al., 2008; Mukherjee et al., 2009). High chloride coupled with high nitrate in this well suggests anthropogenic input (Gorski, 1989) which may be due to sewage disposal into nearby depression areas. Moreover, fertilizer application and subsequent irrigation is common in study area which in turn leads to high nitrate concentrations in shallow unconfined aquifers from recharge through soil (Spalding and Exner, 1993). Highly

varying occurrence of sulphate content (range: 29-655 mg/L; mean: 153 mg/L) suggested that bacterial respiration is patchy in the groundwater which creates small scale redox zonations in study area.

Table 4. Statistical description of physicochemical parameters of groundwater samples.

	Min	Max	Mean	SD
Hard.	140	1480	432.87	237.78
Mg	15	124	51.42	25.45
Ca	28	472	92.33	65.59
HCO ₃	120	880	338.03	140.37
Cl ⁻	37	1743	292.07	304.13
SO ₄	26	655	153.12	143.28
PO ₄	0.02	0.87	0.28	0.25
NO ₃	0.37	19.41	1.04	2.32
F ⁻	0.03	3.16	0.697	0.54
Na	27	1098	212.92	208.48
K	2	216	11.36	28.12
Fe	0.01	2.78	0.20	0.40
As	0	250	33.78	58.17
pH	6.09	8.17	7.25	0.54
TDS	260	5312	1166	836.36
EC	407	8300	1822	1306.87
Alkalinity	2.4	17.6	288.46	394.13

Bicarbonate varies from 120 to 880 mg/l with elevated mean (338 mg/l) value. It is known that high HCO₃ level generally indicates weathering of carbonates and degradation of organic matter under local reducing conditions (Chkirbene et al., 2009). Hence, both bicarbonate and dissolved organic carbon co-exist (Mukherjee-Goswami et al., 2008). Study area is comprises of many oxbow lakes which are rich in organic matter hence it is more close to decipher organic matter as source of bicarbonate in study area.

2. Principle Component Analysis (PCA)

Multivariate statistical analysis expresses the relation/association between different chemical components in the groundwater (Mukherjee-Goswami et al., 2008). Four components of PCA analysis revealed 80.28% of the total variance on data of 66 groundwater samples of Bulri Shah Karim (Table 5). First component (F1) encompasses 47.62% of the total variance in the data set of collected groundwater samples. Strong positive loading ($> \pm 0.5$) of cation (Na) and anions (HCO₃, SO₄, Cl⁻, F⁻) associated with TDS and alkalinity represent the main dissolved load of groundwater which explains intense water-sediment interaction in a longer time (Mukherjee-Goswami et al., 2008). The second component (F2) (13.27%) shows strong positive loading of hardness with Ca, Mg, Cl and Fe which suggests climate effects (Braman et al, 2013). The third (F3) component of PCA revealed 10.85% of the total variations with positive loading of Ca, NO₃, K, which clearly indicates the agricultural input or nutrient effect (Khan,2011;Simeonov et al, 2003; Zhang et al, 2011). Since the study area is an agricultural terrain the use of fertilizers is quite

common, which seems to be the main source of these ions (Ca, K, NO₃) in the groundwater.

Table 5. Factors loadings of different chemical parameters of groundwater from study area.

	F1	F2	F3	F4
Alkalinity	.816	.055	.328	-.031
Hardness	.245	.803	.494	-.075
Ca	.263	.600	.696	-.009
Mg	.153	.904	.050	-.158
HCO ₃	.816	.055	.328	-.031
Cl	.575	.535	.489	.056
SO ₄	.723	.495	.088	-.127
PO ₄	-.015	-.087	-.002	.914
NO ₃	.269	.077	.931	.007
F	.843	-.227	-.145	.000
Na	.890	.262	.270	.038
K	.204	.162	.919	-.051
Fe	.049	.558	.095	.418
pH	.087	-.698	-.113	.135
EC	.737	.477	.454	.007
TDS	.737	.477	.454	.007
As	-.041	-.040	-.059	.908
Variance%	47.62	13.27	10.85	8.54
Cumulative %	47.62	60.89	71.70	80.28
Eigen value	8.67	2.78	2.08	2.02

Strong affinity of As with PO₄ clearly indicates the role of organic matter decomposition coupled with concomitant release of arsenic (Hossain et al., 2013) into the aquifer. On the other hand FeOOH decomposition is also supplementing the groundwater by As content into the through bacteria mediated oxidation of organic carbon.

Factor 4 (8.54%) includes high loadings of PO₄ (0.91) and As (0.90) followed by Fe (0.41). The association of PO₄ with As void the competitive adsorption/desorption hypothesis rather favors the reductive dissolution of FeOOH theory (co-occurrence of As and Fe) for the release of arsenic in the groundwater (Mukherjee-Goswami et al., 2008).

3. Interrelationship of Major Ions

Very strong correlation between Na and Cl ($r^2 = 0.75$) is observed which suggests that same source is responsible for elevated concentration of these ions (Fig. 7). Weak correlation of SO₄ with Ca ($r^2 = 0.02$) and its positive relationship with chloride ($r^2 = 0.41$) as shown in Fig. 6 suggests evaporation and contamination due to agricultural

activities and leaching from contaminated fill sites (Appelo and Postma, 2005; Nicolli et al, 2010), which are responsible for high concentration of these ions in the study area. Strong positive correlation of EC with HCO_3 ($r^2 = 0.53$) indicates mineral dissolution (Montety, et al., 2008, Beaucaire, et al., 1999) causing elevated bicarbonate in the groundwater of study area. The possible sources of HCO_3 ion are carbonates and feldspar minerals which are frequently available in the sediments of study area (Khan, 2014). However, weak positive correlation of HCO_3 with Ca ($r^2 = 0.23$) and Mg ($r^2 = 0.06$) suggests that dissolution of carbonate minerals is not the major factor controlling high bicarbonate in the groundwater of study area. Contrary to this, good positive correlation ($r^2 = 0.43$) of hardness with HCO_3 (Fig. 8) confirms that organic matter decomposition is important factor in generating high HCO_3 water.

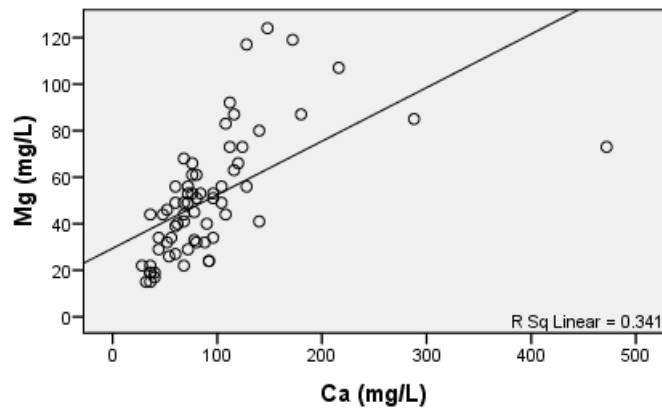
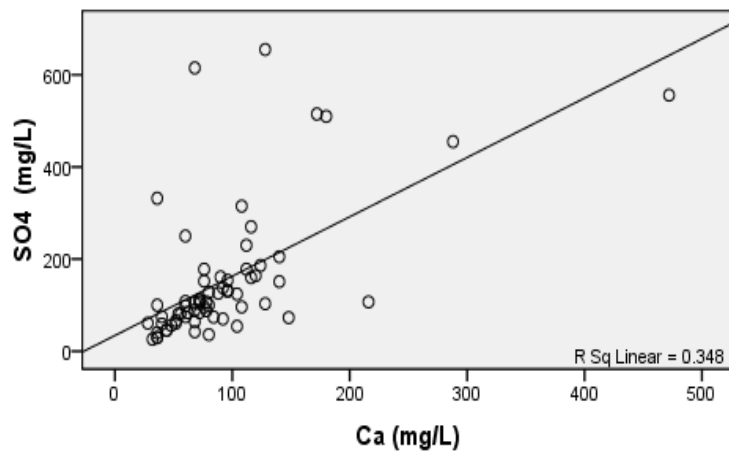


Fig. 5 Relationship between Ca and Mg in the groundwater of study area.



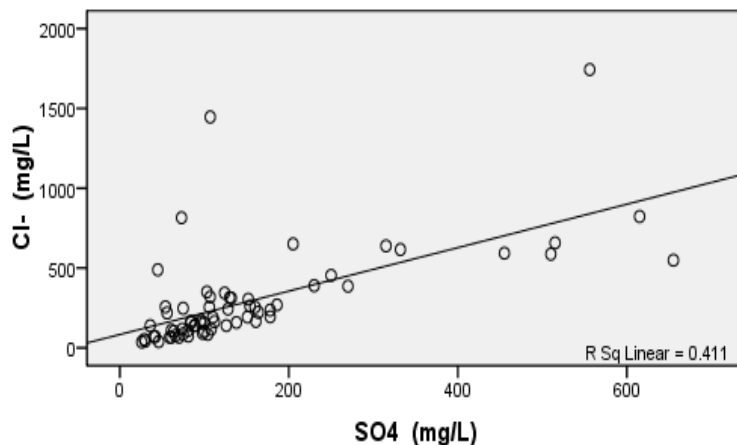


Fig 6. Relationship of SO_4 with Ca (a) and Cl^- (b) in the groundwater of study area.

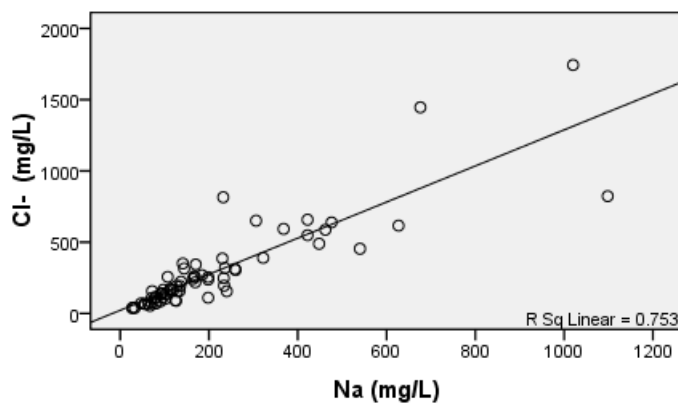


Fig. 7 Na-Cl relationship in the groundwater of study area.

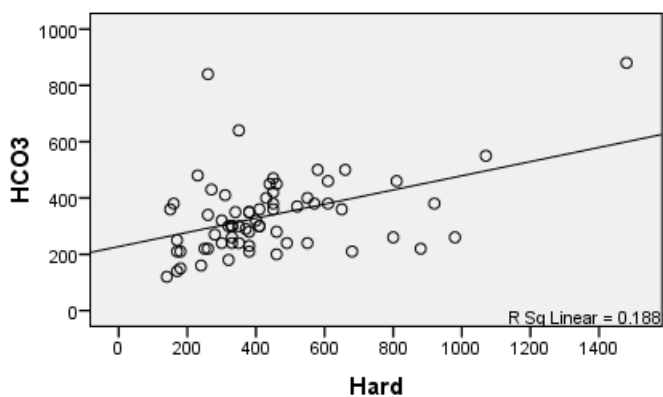


Fig. 8 Hardness - HCO_3 relationship in the groundwater of study area.

4. Arsenic distribution

Arsenic distribution is highly uneven in the groundwater (Fig. 9) suggesting the

prevalence of small scale redox zonation in study area. Out of total (h=66) only 29 wells are reported arsenic free. 12 wells have shown As content within the permissible guideline ($10\mu\text{g/L}$) of WHO set for drinking water. On the other hand, 56% wells suffered from arsenic contamination where it varied b/w 10-250 (Table 3). Out of these, 15 groundwater samples show $\text{As} > 50\mu\text{g/L}$ which fluctuated between 60-250 $\mu\text{g/L}$. Contrary to this, arsenic concentration ranged between 20- 40 $\mu\text{g/L}$ in nine wells.

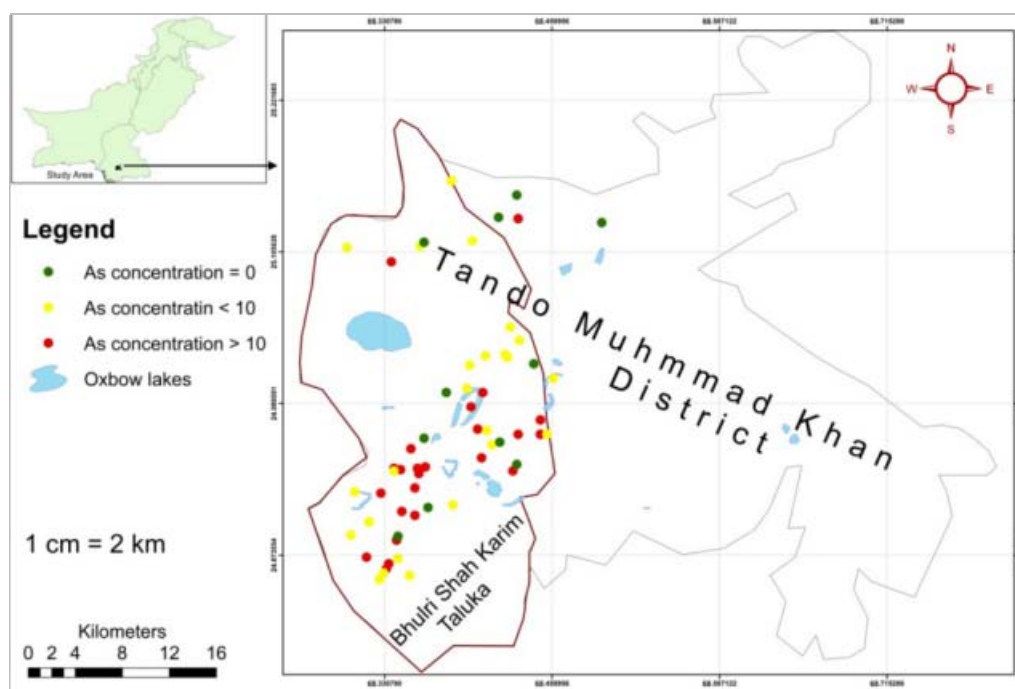


Fig. 9 Arsenic distribution in the groundwater of study area.

5. Arsenic Interrelationship

Pearson correlation is a measure of linear association among different variables which is used to observe the groundwater As relationship with the other parameters in study area (Table 6). Arsenic relationship with the quantifiable and qualitative parameters has been described below.

5.1. Arsenic and major ions

Arsenic demonstrated random relationship with Cl ($r = -0.011$; $p > 0.05$), SO_4 ($r = -0.153$; $p > 0.05$) and NO_3 ($r = -0.066$; $p > 0.05$). Nonlinear relationship of As with these ions is consistent with the fact that these anions (Cl , SO_4 , NO_3) appear to have minimal impacts on arsenic desorption from soil to aquifer water, yet these ions can contribute to ionic strength and salinization effects on As desorption from sediments (Smith et al, 1998; Gupta and Cher, 1978). Similarly, arsenic did not show any significant relationship with major cations (Na , K , Mg ,) suggesting that evaporative concentration is not the main mechanism controlling high arsenic in the groundwater of study area which is reported from other parts of country and other regions of the world (e.g. Farooqi et al., 2007; Nickson et al., 2005; Harvey et al., 2002).

5.2. Arsenic and redox conditions

Arsenic showed weak relationship with pH ($r = 0.12$) and HCO_3 ($r = 0.05$). It is known that combined role of pH and HCO_3 ion exert a significant effect on As leaching from sediments (Anawar et al., 2003). Weak relationship between As and HCO_3 in the groundwater of study area is due to patchy nature of small scale redox zonation which is evident by the fact that high arsenic wells are reported in the proximity of oxbow lakes where young and reactive organic matter occurs for degradation by bacteria. Degradation of organic matter through bacterial respiration releases the sorbed load of As from FeOOH and organic matter (Anawar et al., 2009).

5.3. Arsenic and FeOOH

About one third of high arsenic ($\text{As} > 10 \mu\text{g/L}$) groundwater has objectionable iron content (0.4- 1.15 mg/L) against WHO permissible guideline of 0.3 mg/L. The reduction of As rich FeOOH due to buried peat or other organic matter leads to As release to the aquifer (Bhattacharya et al., 1997; Nickson et al., 1998; 2000; 2005). Slightly positive correlation of As with Fe_{total} ($r = 0.12$; $p > 0.05$) suggests that reductive dissolution of FeOOH is taking place in the groundwater of study area which is consistent with the arsenic release mechanism in the alluvial aquifers of other deltaic regions (Bhattacharya et al, 1997; Nickson et al, 1998; 2000; Ahmed et al, 1998; McArthur et al, 2001; 2004; Dowling et al, 2002; Harvey et al, 2002; Smedley and Kinniburgh, 2002; Acheryya et al, 2002; Anawar et al, 2003; Bennett and Dudas, 2003; Islam et al, 2004; Zheng et al, 2004; Makhurjee, 2006).

However weak correlation of As with dissolved Fe_{total} is due to near neutral pH (mean = 7.2) in the groundwater of Bhulri Shah Karim taluka which is consistent with the fact that at $\text{pH} > 8$, desorption of As from metal oxides (especially Fe, Mn) leads to high As groundwater (Smedley and Kinniburgh, 2002, 2005). On the other hand, the occurrence of excessive Fe_{total} in 20% of the collected samples is due to reduction of iron driven by microbial action on sedimentary organic matter (Holloway et al., 2007) in study area. This young and reactive organic matter is abundantly available in the study area hosted by oxbow lakes and as burnt residue of crops which is common practice in the area (Fig. 10).





Fig. 10(a) In situ residue of burnt crop (b) oxbow lake in Gul Muhammad Sathyo Goth (c) flood irrigation showing the sources of organic matter and anoxia in Bhulri Shah Karim taluka.

Table 6. Arsenic interrelationship with various physicochemical parameters of groundwater.

Interrelationship	Pearson Correlation Value	P value (2tailed)
As- SO ₄	-0.153	0.220
As- Cl ⁻	-0.011	0.928
As-NO ₃	-0.066	0.600
As- Fe	0.211	0.088

As-HCO ₃	-0.073	0.562
As-PO ₄	0.480	0.060
As-pH	0.129	0.303
As-Depth	0.053	0.670
As-F ⁻	-0.027	0.831
As-Hardness	-0.0185	0.0138

5.4. Arsenic and PO₄

Phosphate content occurs only in 16 groundwater samples where its concentration varies from 0.02 to 0.87 mg/L in the groundwater of Bhulri Shah Karim taluka (Table 4). Phosphorus is highly reactive in soil hence its leaching is substantial (Magahud and Asio, 2009). In agricultural soils, the soil solution concentrations of PO₄ may reach as high as 6-8 mg/L after fertilization (Pierzynski, 1994b). However, its low concentration (PO₄ < 1 mg/L) in the groundwater of study area suggests that P is mainly fixed in the soil and crops cultivated in the area where phosphate fertilizer (Diammonium Phosphate) is applied as soil conditioner. Phosphate is sorbed strongly onto the solid phases, including Fe and Al oxides in the soil (Zahid et al., 2007) and amount of P released into water is related to the concentration of PO₄ that exceeds the capacity of Fe to create insoluble iron phosphate (Lijkalema 1980). Strong correlation of PO₄ (r = 0.49; p < 0.05) with Fe(total) suggest that phosphate is linked with iron due to its release from reductive dissolution of FeOOH (Sracek, 2005) in the groundwater of study area (Fig. 11).

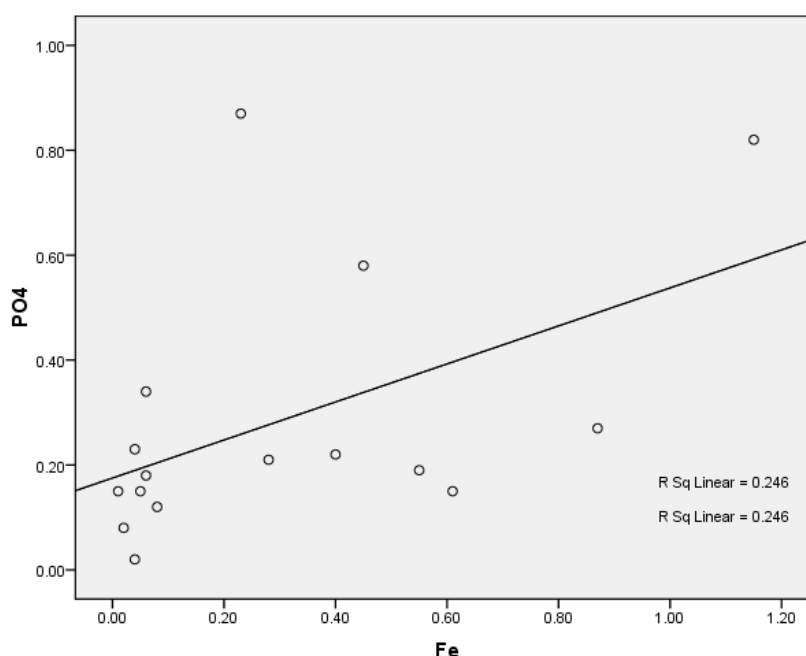


Fig. 11 Correlation between dissolved Fe and PO₄
Soil has significant sorption capacity for P thus minimizes its leaching loss and

availability (Davies et al., 1993). In most of the soils, PO_4 does not move in the soil water but becomes insoluble and subject to less leaching losses (Davies et al., 1993) which may be the reason of low PO_4 concentration in the groundwater of study area. Similarly, flood plain soil is other important factor which mainly comprises of silty-clay. This clayey soil is assumed to adsorb more PO_4 than sandy soils (Sawhney, 1997). Moreover, groundwater pH of Bhulri Shah Karim taluka is slightly alkaline (mean: 7.2) which further explains why low concentration of PO_4 occurs in the study area as phosphorous leaching is greatest in slightly acidic (pH: 6-6.5) conditions (Pierzynski, 1994b).

All the groundwater samples reported for PO_4 occurrence are concomitantly observed for arsenic presence where As ranged from 5 to 250 $\mu\text{g/L}$. Similarly, PO_4 showed positive correlation with As ($r = 0.48$; $p < 0.06$) in study area which suggests that arsenic is strongly linked with organic matter decomposition and agricultural fertilizer (Acharya et al., 1999, 2000; Young and Ross, 2001; BGS, DPHE, 2001; Bhattacharya et al., 2002) because land use of Bhulri Shah Karim taluka is mainly agriculture. As discussed earlier, low PO_4 content in the groundwater of study area void the role of agricultural fertilizer as main source of arsenic in the groundwater. Hence, organic matter seems to be the main source of PO_4 which is also releasing arsenic under local reducing conditions. Phosphorus movement occurs in heavily manured soils where organic matter together with other organic acids, iron and aluminum may accelerate its downward movement (Miller, 1979). A decrease in PO_4 adsorption capacity follows manure addition, increasing the possibility of leaching. This is due to the effect of organic matter which may enhance P mobility by coating the soil surfaces responsible for P adsorption (Magahud and Asio, 2009). Moreover, organic complexes of phosphorus have been shown to leach more rapidly and to greater depths than inorganic soluble PO_4 (Lal and Stewart, 1994). The latter usually accumulates after several years of fertilizer application (Davies et al., 1993). Similarly, Toor et al., (2003) observed that substantial amount of P that is leached from grassland soil occurs as organic P.

5.5. Arsenic and oxbow lakes

Meandering behavior of river Indus has established a number of oxbow lakes in the fluvial plain of study area (Fig. 10b). These oxbow lakes revealed that most of the high arsenic groundwater is strongly associated with these freshwater bodies (Fig. 9). It suggests significant role of these geomorphic expressions to serve as accumulating sites of arsenic hosted sediments (mainly clays) deposited in these micro basins which are rich in young and reactive organic matter. It is confirmed by study carried out by Khan (2014) which revealed that soil in Bhulri Shah Karim taluka is mainly comprised of clayey sediments as flood plain deposit. These flood plain and oxbow lake sediments are enriched in natural organic matter (Donselaar et al., 2013). Sediments below the oxbow lakes have low permeability due to its clay content leading to slower drainage after the rainy season. High water content in the oxbow lakes moves toward the sandy point bars adjoining the oxbow lakes due to hydraulic gradient. These organic rich sediments of oxbow lakes create reducing conditions which also shifts laterally to the sand bars where reaction takes place with solid state Fe-As oxides, leading to the release of As and control the distribution of arsenic concentration in the groundwater.

5.6. Arsenic and sewage

Twenty five groundwater wells are found to be sewage impacted as indicated by

the occurrence of pathogenic bacteria in such wells (Table 2). Since groundwater wells are very shallow (depth < 25 meters), sewage contamination is likely to occur in study area coupled with transport of other solutes including arsenic. About one third of these sewage impacted wells are also arsenic contaminated where arsenic ranged between 20 -200 µg/L. All these sewage impacted and arsenic contaminated groundwater samples were collected from rural areas where unlined sanitation is common. Free roaming animals and open air excretion is the common source of fecal material in the study area impact on arsenic release in groundwater (Cole et al., 2004). This organic excreta is rich in PO₄ and pathogenic bacteria (fecal coli forms) which reaches the groundwater through aquifer depth. The occurrence of this dissolved organic matter creates reducing conditions which ultimately mobilizes arsenic from the aquifer sediments into the groundwater. The co-occurrence of As and PO₄ is also supported by this mechanism.

6. Arsenic mobilization mechanism

Arsenic concentration in the groundwater of study area (part of Indus deltaic flood plain) is found to be highly variable on both local and regional scale. It supports the dispersed source of arsenic which negates the point source of arsenic (anthropogenic) in study area. In other words, the main source of arsenic in Indus deltaic aquifers is natural where release mechanism of arsenic is strongly influenced by the local factors as indicated by various researchers (e.g. Chatterjee et al., 2003; McArthur et al., 2004; Nath et al., 2008c). Many models have been put forwarded to explain the arsenic mobilization mechanism in reducing groundwaters (e.g. Mallick and Rajagopal, 1996; Das et al., 1996; Mandal et al., 1998; Chowdhuri et al., 1999; Nickson et al., 2000; Islam et al., 2004; McArthur et al., 2001; Bhattacharya et al., 2002; Bhattacharya et al., 2003a; Sracek et al., 2005; Charlet et al., 2007; Nath et al., 2008d) but reductive dissolution of FeOOH theory proposed by Bagla and Kaisar and Bhattacharya et al., (1997) earned more fame. According of this model, arsenic adsorbed on or co-precipitated with secondary iron phases like FeOOH is released into groundwater during reducing conditions.

The present study supports this model as one third of high arsenic (As > 10 µg/L) samples showed elevated iron content (0.4- 1.15 mg/L) indicating the prevalence of reducing conditions. Moreover, occurrence of very low nitrate (< 2 mg/L) content despite agricultural terrain, further support the prevalence of anoxia in the groundwater of study area. However, abundantly available SO₄ content (mean: 153 mg/L) and weak correlation of As with Fe_{total} ($r = 0.12$; $p > 0.05$) suggests that reduction process is still in early phases and not yet reached where bacteria respire through iron reduction intensively. This could be the reason of why more wells in the study area are still arsenic free or within the permissible limit (Table 3). The reductive dissolution model is further supported by the strong association (co-occurrence) of As with PO₄ in this study which is indicated by high loading (> ± 0.5) in factor 4 (8.54%) of PCA analysis. Phosphorus (Phosphate) is an important constituent of organic matter and essential for plant growth as well as an important component in the developmental processes of agricultural crops (Withers et al., 2008). The occurrence of organic matter from oxbow lakes and burnt residue of crops is common in the study area (Fig. 10). This organic matter is relatively young and reactive due to its proximal occurrence with river Indus. Thus, bacteria mediated decomposition of this organic matter is creating reducing conditions which trigger the release of arsenic into aquifer (Husain, 2009). Anoxia is prevailing further by flood irrigation practices in the study

area (Fig. 10c) which is triggering the arsenic release from agricultural soils and transporting up to the aquifer depth through infiltration.

Conclusion

Present study revealed that the source of arsenic in deltaic flood plain of Indus river is natural where arsenic is hosted by the fine fluvial sediments associated with young and reactive organic matter deposited in oxbow lakes and meander scars. Besides serving as source, organic matter is fueling the bacteria to create anoxia leading to the release of arsenic from its host sediments which are coated with FeOOH. Redox sensitive geochemical signatures (NO_3 , SO_4 , HCO_3 and Fe) indicates that prevalence of anoxia is in early phase which may increase arsenic release and its mobilization in the future if the rate of organic matter decomposition is triggered by anthropogenic activities like sewage contamination and flood irrigation practices. The role of geomorphic process is very important in controlling fine sediments as arsenic host and the organic matter accumulation in study area. Although this study highlighted the role of organic matter in arsenic mobilization but type and quality of organic matter is not determined which must be taken into account in future investigations to elaborate more explicitly the role of organic matter as source and arsenic releasing agent. Similarly, the role of sediment mineralogy and chemistry is important to investigate in further studies to elaborate more clear the source and mechanism involved in arsenic release in Indus deltaic aquifers of Holocene age.

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