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Groundwater Arsenic Contamination in Semi-Urban Areas of Tando Muhammad Khan District: A Case Study from Deltaic Flood Plain of Sindh, Pakistan

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Abstract

An attempt has been made to assess the arsenic contamination and role of anthropogenic activities on its release in the groundwater of alluvial aquifers occurring on deltaic flood plain of Indus River. Groundwater collected from three semi-urban union councils of Tando Muhammad Khan district revealed that the groundwater has bad quality for drinking which varied in the order of UC-2 > UC-1 > UC-3. Anoxia is prevalent in the aquifers of study area which is indicated by high HCO_3 and low NO_3 and Fe contents. However, the natural concentration of sulphate (Mean range: 105-450 mg/L) in the groundwater of study area suggested that anoxia has not reached the stage where sulphate is consumed by SO_4 reducing bacteria for organic matter decomposition. On the other hand elevated content of Na and Cl coupled with pathogenic bacteria occurrence indicated that sewage mixing is common in the study area. Elevated arsenic is reported from all there union councils which varied in the order of UC2 > UC 1 > UC3. Arsenic is mobilized from host sediments (clays/biotite) due to the prevalence of reduced environment caused by organic matter decomposition and triggered by sewage mixing.

Keywords

semi-urban, deltaic aquifers, groundwater, arsenic, factors of As release

1. Introduction

The toxic concentration of arsenic in groundwater covered almost all deltaic regions of the world including Pakistan where widespread contamination is reported (Charlet & Polya, 2006; Smedley & Kinniburgh, 2002; Nickson et al., 2004; Haq et al., 2007; Farooqi et al., 2009; Malana & Khosa, 2011; Khan, 2014). Generally, the geochemical mechanism of arsenic mobilization under anoxic reducing condition is widely attributed to chemical and/or microbial reductive dissolution of arsenic bearing iron minerals in the sediments of aquifer (Nickson et al., 2000; Dowling et al., 2002; Harvey et al., 2002; Stuben et al., 2003; Horneman et al., 2004; Islam et al., 2004; Zheng et al., 2004; Charlet & Polya, 2006; Postma et al., 2007; Berg et al., 2008). However, arsenic may also be released from soil minerals at oxic-anoxic environments and could subsequently be drawn down from the near-surface through aquifer to well depths (Polizzotto et al., 2006). A few studies suggested the anthropogenic sources of arsenic concentration such as application of fertilizer, sewage disposal or coal combustion (Baig et al., 2009; Farooqi et al., 2009; Farooqi et al., 2007; Haq et al., 2007; Nikson et al., 2004).

Arsenic commonly pollutes the groundwater and damage the health of population settled along the rivers (Rabbani et al., 2016). Main factors increasing the arsenic concentration in groundwater along the river belts are 1. Clay in sediments 2. Iron (Fe^{+2} & Fe^{+3}) content and 3. Organic matter (Reza et al., 2010b). About 500 million people are at the risk of arsenicosis along Ganga-Meghna-Brahmaputra plains which are drained by the rivers originating from Himalaya (Sengupta, 1996). Similarly, about 13 million people are assumed to be at risk due to arsenic exposure in 27 districts of Pakistan along the transact of Indus River (Rabbani et al., 2016). In lower parts of the Indus River, including Indus delta, the arsenic toxicity have been reported by various workers (Khan, 2014; Majidano et al., 2010; Arain et al., 2009; Kazi et al., 2009; Naseem, 2012; Husain et al., 2012; Husain, 2009). Tando Muhammad Khan district is one of the worst arsenic affected areas of Pakistan where its concentration is reported up to 600 µg/L (Khan, 2014).

Tando Muhammad Khan district is mainly comprised of agricultural terrain with small pockets of semi-urban areas located in the central part of the district where population density is high. Up to now the arsenic toxicity is reported only from rural areas and agricultural sites by some workers (Khan et al., 2017; Khan, 2014; Husain, 2012). However, the semi-urban areas of Tando Muhammad Khan district have not been addressed in detail to understand the dynamics influencing the arsenic release in densely populated areas. Therefore, present study is aimed at identifying the factors controlling the arsenic release in three urban union councils of Tando Muhammad Khan district.

2. Study Area

Study sites are part of Tando Muhammad Khan district which lies in the south west of Sindh province about 35 km from Hyderabad on the Badin-Hyderabad National Highway between 68º15´E-68º45´E longitudes and 25º00´N-25º30´N latitudes, covering an area of 2600 sq. km (Figure 1). The climate of the area is moderate. However, April, May and June are very hot during the day time. December and January are the coldest months with maximum and minimum temperatures of 30 C and 10 C respectively. Rainfall is highly variable with an average of about 130 mm. The monsoon spans during July to September. Main crops grown in the district are: sugarcane, rice, wheat and cotton. Phuleli, Pinyari and Akram canal are the main source of water-reservoir for irrigation in this district. About 70% of the district population is engaged with agriculture. Study area is cultivated for rice, wheat, cotton, sugarcane followed by banana and mango plantations. It is extensively irrigated by groundwater where flood irrigation practice is common. Due to productivity of sugarcane crop sugar mills are common in Tando Muhammad Khan district.

Soil in the area is silty-clay which is calcareous and dark grey in color. Most of the farmers are poor and mainly dependent on groundwater for irrigation because of scanty supply of surface/canal water due to semiarid climate and scarce rainfall. Local population is generally poor, undernourished, inadequately hydrated, and using mostly contaminated groundwater for drinking purpose. Due to scarcity of fresh and clean water for drinking and other purposes people mainly rely on groundwater resources to meet domestic requirements. Unlined sanitation is common in study area where municipal waste water is generally drained in depressions or low lying areas due to lack of sewerage lines. Houses near by the canals dump the domestic sewage directly into it.

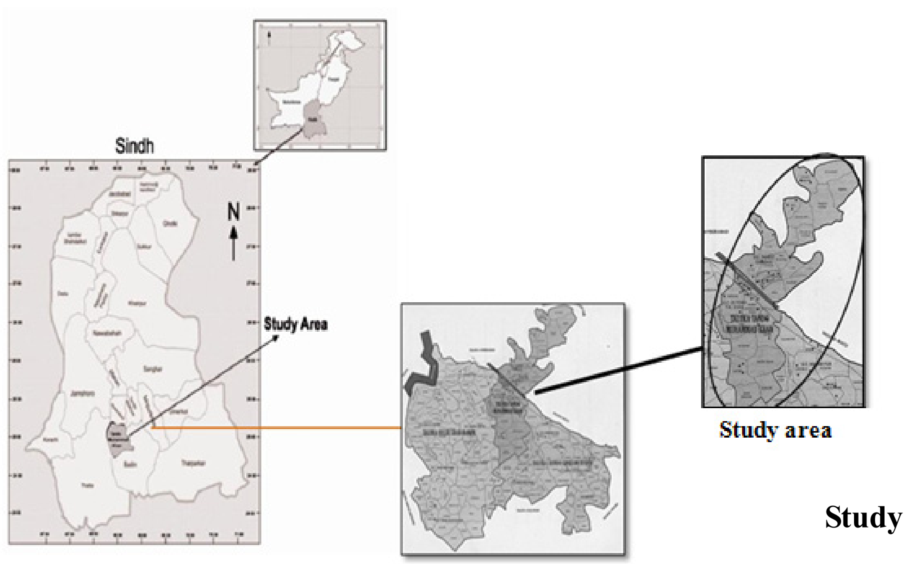

Figure 1. Location Map of Study Area

3. Materials and Methods

3.1 Groundwater Sampling

3.1.1 Sampling for Physicochemical Analysis

The groundwater sampling was carried out at the onset of dry season. Field studies included the collection of groundwater samples (n = 48) from shallow wells (depth<25m). Water samples were collected through hand pump wells after pumping for at least 5-10 minutes to get representative samples of groundwater. Locations of the wells were marked with the Global Positioning System (GPS) on the topographic survey sheet. Groundwater samples were collected in cleaned plastic bottles (0.5 and 1 liter capacity) for physicochemical analysis. The bottles were washed properly and rinsed thoroughly with distilled water and then with the groundwater. Electrical Conductivity (EC), Temperature (T) and pH were measured immediately after sampling at each site using a portable meter. Arsenic concentration in groundwater was determined at each site using Merk field testing kit (Cat No. 1.17926.0001, Germany, 0.01-0.5 mg/l). The concentration of arsenic was measured by visual comparison of the reaction zone of analytical test strip with the fields of color scale. This method gives semi-quantitative estimation of arsenic which was confirmed by checking 10% of the total collected samples on Atomic Absorption Spectrophotometer. For nitrate determination groundwater samples were separately collected in bottles of 100 ml capacity. One ml boric acid solution was injected with sterile syringe in each water sample. Water samples were kept in ice box (temperature: 4°C) to cease any reaction that could alter the concentration of nitrate in the collected samples.

3.1.2 Sampling for Microbiological Analysis

For bacteria detection, groundwater samples were directly poured into microbiological testing kits manufactured by Pakistan Council of Research for Water Resources (PCRWR). The sample kits were kept in incubator at 30°C for 24 hours to obtain the results. This method gives semi-quantitative determination of pathogenic bacteria by change in color from transparent to black.

3.2 Groundwater Analysis

Physicochemical tests were carried out to determine major, minor and trace elements including arsenic. The analytical data quality was ensured through careful standardization, procedural blank measurements and duplicate samples. Groundwater samples preserved in the boric acid were analyzed to determine the nitrate concentrations.

Nephelometric method was used to determine turbidity of groundwater samples. Turbidity meter (Lamotte, model 2008, USA) was used for this purpose and Formazin polymer was used as turbidity standard suspension for reference. The pH and electrical conductivity of collected groundwater samples (n = 24) were measured with the glass electrode pH meter (JENCO 6230N) and EC meter (Eutech Cyber Scan CON II) respectively. Alkalinity was determined by 2320 Standard Method (1992) while hardness was measured in terms of calcium carbonate by EDTA titration standard method (Guldager et al., 1992). Soluble Ca^{+2}, Mg^{+2}, CO_3^{-2}, HCO_3 and Cl^- in groundwater samples were measured by titration method (USSL, 1954).

Flame photometer (Model: PFP-7, JENWAY, UK) was used to determine concentration of Na^+ and K^+ while SO_4^{-2} by Turbidity Metric method. For nitrate determination Cadmium Reduction method (HACH-8171) by Spectrophotometer was used. Iron concentration was measured by Phenanthro line Photometric method using Spectrophotometer (Model: U-1100, HITACHI) at 510 nanometer. Field tests of arsenic detection in groundwater were cross checked by using 10% of total arsenic containing samples on Perkin Elmer A Analyst 600 Graphite Furnace Atomic Absorption Spectrophotometer. Fluoride concentration in the groundwater samples was determined by Spectrophotometer by the method of 8092, SPADNS (HACH).

4. Results and Discussion

Groundwater samples were randomly collected from 3 union councils of Tando Muhammad Khan district in the order of UC-1 (n = 27) > UC-2 (17) > UC-3 (n = 4). All the samples were collected from shallow wells (depth < 100 feet) through hand pump. The results of physicochemical data for groundwater samples collected from all three union councils have been summarized in Tables 1-6.

4.1 Physical Characteristics

Aesthetic characters (color, taste, odor) of all groundwater samples collected from 3 union councils are found to be acceptable except a few wells in UC-1 and 2 where a few samples showed objectionable color/taste and odor (Tables 1-3).Water temperature is found to be uniform in all union councils where it spans between 30-32°C. Groundwater pH is circum-neutral (mean range: 6.9-7.1) which is within the permissible limit of WHO (6.5-8.5) set for drinking water. Variation pattern of pH is found to be UC-2 (mean: 7.18) > UC-1 (7.0) > UC-3 (6.9). A few samples collected from UC-1 and 2 showed objectionable pH (< 6.5) which is due to sewage impact as these samples were collected from the wells installed near toilets. Since the study area lacks sanitation facilities, the sewage is directly dumped into the open pits which are dug nearby the washrooms. Similarly, people living nearby the lakes or ponds use to drain their sewerage directly into these surface water bodies. On the other hand, the settlements along canals are dumping garbage and sewage is such running water bodies.

Interestingly these wells low in pH are very high in TDS content (up to 1683 mg/L) which further supports the sewage mixing with groundwater (Cole, 2004). The occurrence of pathogenic bacteria in such wells confirmed the sewage mixing with groundwater (Tables 1, 2, 3). Turbidity of groundwater is generally within permissible guideline (< 5 NTU) but a few wells in all three union councils showed objectionable values (6.1-33 NTU). All these high turbidity samples showed bacterial occurrence (Tables 1, 2, 3) which may be the reason of high turbidity in such wells where it varied in the order of UC-2 > UC-1 > UC-3. TDS content is found to be very high in all three union councils which decreased in the order of UC-2 (mean: 1133 mg/L) > UC-1 (mean: 841 mg/L) > UC-3 (mean: 724 mg/L).

Table 1. Physical Parameters of Groundwater Samples Collected from UC 1 of Tando Muhammad Khan District

TMK UC-1												
S.No.	Sample No.	Coordinates		Locality	Color	Odor	Taste	Water Temp ^{0}C	pH	TDS (mg/L)	Turb. (NTU)	Micro (+ve/-e)
		Lat. N	Long. E									
1	TMK-1	250753	683201	Main T.M. Khan city	Colorless	O	O	31.4	6.34	621	<5	+ve
2	TMK-6	250719	683234	New Christian colony	Colorless	U	O	31.3	5.96	1651	<5	+ve
3	TMK-7	250725	683212	SAATH, welfare Trust	Colorless	U	U	31.2	6.54	301	<5	-ve
4	TMK-9	250737	683210	Gulshane Faiz Colony	Colorless	U	U	31.3	5.94	907	<5	+ve

5	TMK-10	250747	683207	Seerat un Nabi chawk	Colorless	U	U	31.3	6.44	934	<5	-ve
6	TMK-16	250750	683316	Masjid Usman Ghani	Colorless	O	O	31.5	6.31	1128	<5	+ve
7	TMK-17	250748	683323	Main T.M. Khan city	Colorless	U	U	31.6	6.53	506	<5	+ve
8	TMK-18	250740	683338	Main T.M. Khan city	Colorless	U	O	31.6	6.56	456	<5	-ve
9	TMK-87	250743	683351	Budhu Bhatti	Colorless	U	U	31.2	7.04	719	<5	+ve
10	TMK-94	250755	683159	Paleo humrani	Colorless	U	U	31.4	7.49	668	<5	-ve
11	TMK-95	250806	683214	Sachal Abad	Colorless	U	U	31.4	7.32	1088	<5	-ve
12	TMK-96	250742	683241	Sajawal Road	Colorless	U	U	31.4	7.42	846	6.1	+ve
13	TMK-97	250721	683311	Mir Mumtaz Farm	Colorless	U	U	31.4	7.27	806	<5	-ve
14	TMK-99	250627	683349	Khamiso Khan Halepoto	Colorless	U	U	31.5	7.27	733	<5	+ve
15	TMK-113	250742	683250	Gulam Husain, Talpur	Colorless	U	U	31.2	7.41	979	<5	-ve
16	TMK-141	250815	683317	Aziz Ali Khawaja	Colorless	U	U	31.4	7.24	631	<5	+ve
17	TMK-142	250738	683305	Mir Mazhar Farm	Colorless	U	U	31.5	7.21	672	<5	-ve
18	TMK-164	250738	683214	Mir Baher Mohalla	Colorless	U	U	30.7	7.93	315	<5	-ve
19	TMK-169	250242	683414	Mohammad Hassan Halo	Colorless	U	U	31.2	7.94	28	<5	+ve
20	TMK-172	250212	683406	Haji Mohd. Ibrahim khoso	Colorless	U	U	31.2	7.11	765	<5	-ve
21	TMK-49	250607	683450	Nabi Bakhsh Laghari	Colorless	U	U	24.5	7.15	683	<5	-ve
22	TMK-54	245139	681957	Khorwa Road	Colorless	U	U	24.5	7.36	760	<5	-ve
23	TMK-154	251056	683603	A. Hameed Nizamani	Turbid	U	O	31.5	6.56	4153	33	+ve
24	TMK-160	251405	684159	JaraWah Stop	Yellow	U	U	31.1	7.46	737	12.5	+ve
25	TMK-162	251318	683747	Haji Ashfaq Nizamani	Colorless	U	U	31.2	7.27	591	<5	-ve
26	TMK-112	250831	683534	Haji Nadeem Goth	Colorless	U	U	31.2	7.74	521	<5	-ve
27	TMK-128	----	-----	T.M. Khan city	Colorless	U	U	31.2	7.03	519	<5	-ve

Table 2. Physical Parameters of Groundwater Samples Collected from UC 2 of Tando Muhammad Khan District

TMK UC-2												
28	TMK-2	250743	683209	Seerat Nabi chawk	Colorless	U	U	31.3	5.95	1073	<5	-ve
29	TMK-5	250715	683145	Main T.M. Khan city	Colorless	U	U	31.3	6.22	1683	<5	+ve
30	TMK-15	250750	683248	Suberb of T.M. Khan city	Colorless	U	U	31.4	6.37	640	<5	+ve
31	TMK-27	250607	683217	Siddique Maachi Goth	Colorless	U	U	31.6	6.96	1946	<5	-ve
32	TMK-98	250636	683325	Durr M. Bhatti Farm	Colorless	U	U	31.4	7.65	868	<5	-ve
33	TMK-100	250557	683405	Khamiso Khan Laghari	Yellow	U	U	31.5	7.53	896	18.5	+ve
34	TMK-101	250538	683424	M. Khan Laghari Goth	Colorless	U	U	31.4	7.74	233	<5	-ve

35	TMK-102	250526	683452	Imam Wah Regulator	Colorless	U	U	31.3	7.88	362	<5	-ve
36	TMK-143	250658	683238	People Colony	Colorless	U	U	31.5	7.16	624	<5	-ve
37	TMK-144	250719	683236	People Colony	Colorless	U	U	31.4	7.03	2381	<5	+ve
38	TMK-145	250644	683244	Bhuro Thakar Village	Colorless	U	U	31.5	7.67	438	<5	-ve
39	TMK-146	250639	683258	Roshan	Colorless	U	U	31.5	7.52	817	<5	-ve
40	TMK-147	250709	683226	Talpur Colony	Colorless	U	U	31.2	7.45	707	<5	-ve
41	TMK-150	250541	683015	Saleh Abad	Colorless	U	U	31.6	7.05	1619	<5	-ve
42	TMK-151	250706	683212	Sun Flower Thresher Shop	Yellow	U	U	31.5	7.12	2572	32	+ve
43	TMK-165	250620	683215	Sardar Khan Khosa	Colorless	U	U	31.2	7.54	1632	<5	-ve
44	TMK-182	250759	683236	Talpur Colony	Colorless	U	U	31.2	7.22	774	<5	-ve

Table 3. Physical Parameters of Groundwater Samples Collected from UC 3 of Tando Muhammad Khan District

TMK UC-3												
45	TMK-4	250732	683150	Mir Mohallah	Colorless	U	U	31.2	6.52	351	<5	-ve
46	TMK-8	250727	683209	Govt. Girls High School	Colorless	U	U	31.3	6.52	498	<5	+ve
47	TMK-91	250839	683343	Khaspura	Turbid	U	U	31.5	7.39	1140	19.8	+ve
48	TMK-111	250804	683539	Sardar Khan Gujar Goth	Colorless	U	U	31.2	7.44	907	<5	-ve

4.2 Chemical Characteristics

4.2.1 Major Cations

Major solutes showed heterogeneous distribution in the groundwater of all three union councils of Tando Muhammad Khan district. Calcium concentration fluctuates in the order of UC-2 (mean: 113 mg/L) > UC-1 (mean: 81 mg/L) > UC-3 (mean: 69 mg/L). The same pattern is followed by the Mg and Na contents which varied between 38-50 and 106-166 mg/L respectively (Tables 4, 5, 6). On the other hand, only 3 wells showed elevated concentration (13-61 mg/L) of K only from UC-1 (Table 4). These samples with high K content are also sewage impacted as indicated by the occurrence of pathogenic bacteria in such wells.

4.2.2 Major Anions

Very high bicarbonate (> 250 mg/L) is reported from all three union councils where it varied in the order of UC-2 (mean: 289 mg/L) > UC-1(mean: 287 mg/L) > UC-3 (mean: 285 mg/L). Elevated Cl concentration (up to 297 mg/L) is reported from all union councils where seven and two wells each from UC-1 and 2 revealed objectionable chloride content. Generally sulphate content is found to be within the safe limit (< 250 mg/L) except four wells from UC-2 where it exceeded the guideline value up to 644 mg/L (Table 5). Nitrate occurs in very low quantity throughout the study sites where it rarely exceeded 1.5 mg/L in few wells. On the other hand two wells from UC-1 showed objectionable concentration (13-18 mg/L) of nitrate. High nitrate in such wells may be attributed to the sewage mixing (Cole & Ryan, 2005).

4.2.3 Minor Ions

Very low phosphate content (PO_4 < 1 mg/L) is reported which occurred in less than 50% of samples collected each from three union councils where it varied between 0.11-0.25 mg/L. Fluoride concentration vibrates between 0.02-1.4 where it declined in the order of UC-2 (mean: 0.5 mg/L) > UC-1 (mean: 0.4 mg/L) > UC-3 (mean: 0.3 mg/L). Only one sample from UC-2 showed objectionable concentration which was collected from sunflower cultivation field. Mean concentration of iron in all three union councils is found to be within safe limit (< 0.3 mg/L) but objectionable quantity is reported in some wells of all three union councils (Tables 4, 5, 6). Further, mean concentration of iron in UC-3 is almost double its content in other two union councils (Table 6). It suggests that anoxia is prevailing in all union councils of Tando Muhammad Khan district where it is more pronounced in UC-3.

Table 4. Chemical Characteristics of Groundwater Samples Collected from UC 1, Tando Muhammad Khan District

TMK-UC-1													
S. No.	Sample No.	Ca (mg/L)	Mg (mg/L)	HCO_3 (mg/L)	Cl- (mg/L)	SO_4 (mg/L)	PO_4 (mg/L)	NO_3 (mg/L)	F- (mg/L)	Na (mg/L)	K (mg/L)	Fe (mg/L)	As (μg/L)
1	TMK-1	52	37	310	81	93	0.45	0.66	0.3	122	4	0.44	100
2	TMK-6	140	80	400	436	204	-	13.86	0.3	267	19	0.13	0
3	TMK-7	52	15	220	35	10	-	0.48	0.15	33	4	0.12	20
4	TMK-9	80	97	360	280	58	-	0.73	0.21	76	8	0.42	0
5	TMK-10	92	37	270	245	112	-	0.82	0.34	186	7	0.04	10
6	TMK-16	96	44	400	248	102	0.43	1.52	0.68	168	61	1.99	450
7	TMK-17	72	27	250	85	70	-	0.46	0.24	78	4	0.13	5
8	TMK-18	64	29	280	39	56	0.2	0.57	0.13	66	3	0.64	120
9	TMK-87	84	39	330	106	74	-	0.83	0.46	88	4.8	0.03	5
10	TMK-94	52	32	290	92	102	-	0.81	0.57	111	4.4	0.07	10
11	TMK-95	100	56	310	198	185	-	18.6	0.57	157	11.3	0.01	0
12	TMK-96	92	39	300	149	110	0.17	2.7	0.35	112	8.9	0.06	100
13	TMK-97	96	41	320	117	128	0.16	0.64	0.49	93	13.2	0.62	60
14	TMK-99	124	19	130	238	90	0.18	1.82	0.52	80	7	0.05	80
15	TMK-113	96	51	330	202	134	-	2.13	0.47	138	10.7	0.02	0
16	TMK-141	52	32	220	123	90	0.17	0.86	0.68	102	5.1	0.09	20
17	TMK-142	80	41	350	67	76	-	0.78	0.46	63	7.2	0.04	0
18	TMK-164	36	10	110	50	58	-	0.34	0.42	51	4.5	0.01	0

19	TMK-169	28	12	260	124	50	0.24	1.02	0.51	167	3.5	0.04	50
20	TMK-172	92	34	300	131	102	-	1.44	0.56	104	4	0.03	0
21	TMK-49	78	38	260	131	87	0.19	0.57	0.28	77	10.4	0.05	100
22	TMK-54	78	45	340	128	77	-	0.6	0.17	97	5.9	0.91	20
23	TMK-154	78	194	380	1596	450	-	2.63	0.58	522	15.1	0.05	0
24	TMK-160	72	49	260	137	122	-	1.07	1.11	84	6.1	1.33	5
25	TMK-162	72	36	270	74	76	0.23	0.75	0.46	64	4.6	0.02	50
26	TMK-112	48	36	260	57	60	0.15	0.85	0.42	61	4	0.04	100
27	TMK-128	84	38	300	280	82	-	0.93	0.43	190	4.3	0.05	0

Table 5. Chemical Characteristics of Groundwater Samples Collected from UC 2, Tando Muhammad Khan District

TMK UC-2													
28	TMK-2	136	63	390	337	36	0.17	0.79	0.18	138	6	0.24	450
29	TMK-5	160	34	350	285	112	-	0.61	0.07	140	6	0.07	50
30	TMK-15	56	71	340	117	71	-	0.51	0.49	69	3	0.19	5
31	TMK-27	160	112	280	408	644	-	0.34	0.98	296	8	0.06	0
32	TMK-98	64	49	340	173	80	0.27	1.25	0.62	140	8.1	0.03	300
33	TMK-100	80	36	270	217	110	0.14	0.73	0.45	156	7.1	2.35	100
34	TMK-101	32	12	110	32	21	-	0.88	0.07	21	3.6	0.01	30
35	TMK-102	40	19	140	57	60	-	0.56	0.48	43	4.6	0.06	10
36	TMK-143	64	27	280	103	56	0.19	0.63	0.11	96	3.6	0.02	500
37	TMK-144	188	85	370	978	94	0.1	1.2	0.64	467	3.1	0.03	400
38	TMK-145	28	19	200	92	5	0.78	0.95	0.6	86	3.3	0.05	80
39	TMK-146	68	41	230	247	50	-	0.67	0.85	134	5.5	0.07	5
40	TMK-147	92	41	205	237	8	0.11	0.74	0.02	66	4.4	0.04	0
41	TMK-150	208	63	290	353	435	-	0.76	0.91	212	4.7	0.09	0
42	TMK-151	328	49	460	886	250	0.18	1.55	0.25	418	11.4	1.14	500
43	TMK-165	148	95	420	369	305	-	0.44	1.4	238	4.3	0.08	0
44	TMK-182	82	38	240	170	112	0.24	0.66	0.53	105	5.5	0.23	100

Table 6. Chemical Characteristics of Groundwater Samples Collected from UC 3, Tando Muhammad Khan District

TMK UC-3													
45	TMK-4	56	12	150	53	46	-	0.86	0.05	36	3	0.03	30
46	TMK-8	52	22	210	103	58	-	0.47	0.15	82	5	0.04	5

47	TMK-91	92	61	420	198	171	-	1.01	0.54	183	8.3	1.59	10
48	TMK-111	76	58	360	131	148	0.11	1.03	0.65	123	7.8	0.05	0

Table 7. Statistical Descriptive of the Groundwater Parameters from Three Union Councils of Tando Muhammad Khan District

Physicochemical	TMK UC-1				TMK UC-2				TMK UC-3			
Parameters	Min	Max	Mean	S.D	Min	Max	Mean	S.D	Min	Max	Mean	S.D
pH	5.94	7.94	7.03	0.55	5.95	7.88	7.18	0.55	6.52	7.44	6.96	0.51
TDS	28	4153	841.4	728.17	233	2572	1133.23	707.4	351	1140	724	363.66
Temperature	24.5	31.6	30.81	1.82	31.2	31.6	31.4	0.13	31.2	31.5	31.3	0.14
Ca	28	140	77.4	24.99	28	328	113.76	78.54	52	92	69	18.58
Mg	10	194	44.74	34.93	12	112	50.23	27.98	12	61	38.25	24.9
Na	33	522	124.33	95.01	21	476	166.17	125.53	36	183	106	62.43
K	3	61	9.07	11.1	3	11.4	5.42	2.22	3	8.3	6.02	2.48
HCO_3	110	400	289.25	68.6	110	460	289.11	96.08	150	420	285	126.09
SO_4	10	450	105.85	79.41	5	644	144.05	172.33	46	171	105.75	62.96
Cl-	35	1596	201.81	293.54	32	978	297.7	264.21	53	158	121.25	60.48
NO_3	0.34	18.6	2.16	4.15	0.34	1.55	0.78	0.31	0.47	1.03	0.84	0.25
PO_4	0.15	0.45	0.23	0.1	0.78	0.1	0.24	0.2	0.11	0.11	0.11	….
F-	0.13	1.11	0.43	0.2	0.02	1.4	0.5	0.37	0.05	0.65	0.34	0.29
Fe	0.01	1.99	0.27	0.47	0.01	2.35	0.28	0.59	0.03	1.59	0.42	0.77
As	5	450	48.33	89.93	5	500	148.82	194.6	5	30	11.25	13.14

5. Arsenic Distribution

Arsenic occurrence is reported in the groundwater of all three union councils where it varied in the order of UC-2 (5-500 µg/L) > UC-1 (5-450 µg/L) > UC-3 (5-30 µg/L). Although magnitude of arsenic contamination is almost same in both UC 1 and 2 (5-500 µg/L) but large fraction of samples (88%) is affected by arsenic toxicity in UC-2 as compared to UC 1 and 3 (Tables 4-6). Total 6 samples have arsenic in the range of 300-500 µg/L out of which only one is reported from UC-1 450 µg/L and rest belong to UC-2. It indicates that environment conducive for arsenic mobilization is more prevalent in UC-2 as compared to other two union councils of Tando Muhammad Khan district.

Table 8. Showing the Arsenic Toxicity Distribution in Three Union Councils of Study Area

Union council	Arsenic toxicity range	No. of arsenic contaminated samples	Arsenic contaminated samples in %
UC-1	5-450	15	55.55%
UC-2	5-500	11	88.2%

UC-3	5-30	02	50%

Meandering behavior of Indus River has created many oxbow lakes in the fluvial plain of Tando Muhammad Khan district as shown in Figure 2. These oxbow lakes are rich in organic matter associated with clayey sediments. Oxbow lakes are identified as one of the important hot spots hosting arsenic rich sediments which upon prevalence of anoxia release arsenic into the adjoining sand bars (Donselaar et al., 2017, 2013). Sediments occurring at the bottom of these oxbow lakes have poor permeability due to high clay content. During rainy season a hydraulic gradient is created due to poor drainage in oxbow lake. As a result, water from such lakes flow toward sand prone point bars which borders the oxbows. Since these lakes are rich in natural organic matter (Ravenscroft et al., 2001; Harvey et al., 2002, 2006; Islam et al., 2004; McArthur et al., 2004; Meharg et al., 2006; Postma et al., 2007; Neumann et al., 2010; Mailloux et al., 2013; Desbarats et al., 2014) anoxic condition is developed due to bacteria mediated organic matter decomposition and iron (FeOOH) reduction (Bauer & Blodau, 2006). Consequently, arsenic is released from the host sediments into the groundwater.

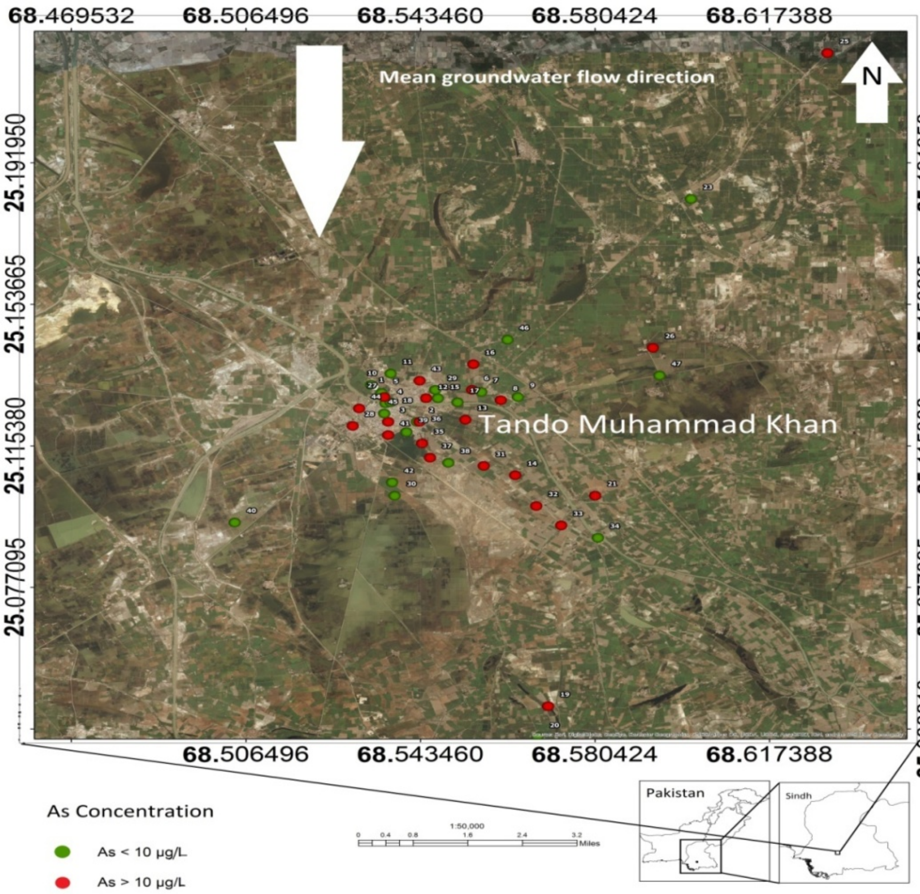

Figure 2. Arsenic Distribution Map of Study Area

A network of open channels in terms of canals and associated minors is passing through the study area where dense human settlements are occurring of both sides of the canal (Figure 2). The occurrence of high arsenic groundwater along the canal depicts that As is somehow linked with the canal water. Since these surface water bodies are artificial distributaries of Indus River, therefore occurrence of arsenic in these channels is linked with the Indus River load. Similarly, the industrial effluent including toxic metals and arsenic is also discharged into the river Indus upstream. Hence, this toxic dissolved load is transported to the canals which subsequently infiltrate into the shallow aquifers occurring along these water channels.

6. Prevalence of Anoxia

Redox sensitive ions including HCO_3, SO_4 and NO_3 from all three union councils showed the signature of sub-oxic environment prevailing in the aquifers of study area. Elevated bicarbonate (mean > 285) is reported from all three union councils where it is almost same (mean: 289 mg/L) in the UC-1 and 2 and relatively less in UC-3. Very high content of bicarbonate in the groundwater generally occur either due to carbonate mineral dissolution or organic matter decomposition (Anawar et al., 2013) in flood plain setting. Since the alluvial sediments brought by the Indus River are mainly comprised of silt and clay (non carbonate grains) the source of bicarbonate seems to be organic matter decomposition. Contrary to this, very low nitrate content (Mean < 3 mg/L) in the aquifers of all three union councils is reported despite of the fact that Tando Muhammad Khan district is agriculture dominated terrain. It clearly indicates that nitrate reducing bacteria are active in the aquifer sediments of study area.

Similarly, the occurrence of SO_4 in all three union councils is high although it is fluctuating widely in the groundwater of all three union councils. Sulphate content decreases in the order of UC-2 (144 mg/L) > UC-1 = UC3 (mean: 105 mg/L). It indicates that anoxia is not reached the threshold where sulphate reducing bacteria start consuming it for organic matter decomposition. Heterogeneous sulphate in the groundwater suggests that small scale redox zonation is being created in subsurface environment. Similarly very high concentration of Na and Cl in the groundwater of study area indicates sewage mixing which also trigger the reduction process. The distribution of these two ions is very high and uneven in UC-2 followed by UC-1 and 3 (Table 7). It suggests that human settlements are denser in UC-2 as compared to other two union councils.

7. Principle Component Analysis (PCA)

Four components of PCA analysis 74.5% of the total variance on data of 48 ground water samples from UC 1, 2, and 3 of Tando Muhammad Khan district as shown in Table 9. First component (F1) encompasses 37.7% of total variance in the data set of collected ground water samples. Strong positive loading of major ions and TDS explains intense water-sediment interaction. Similarly, significant loading of As and HCO_3 depicts organic matter decomposition due to which arsenic is being released both from organic matter itself and aquifer sediments (Anawar et al., 2013) in study area. Moreover, very strong loading of Cl, SO_4 and Na indicates sewage mixing with groundwater which is triggering the arsenic release process (Cole & Ryan, 2005).

Table 9. Principle Components Analysis of Samples from 3 Union Councils

Parameters	F1	F2	F3	F4
pH	-.352	**-.495**	-.281	**.473**
TDS	**.976**	-.059	-.104	.000
Temp	.161	.023	-.009	**.636**
Ca	**.889**	.014	-.230	-.026
Mg	**.798**	-.384	.221	-.158
Na	**.916**	-.017	-.197	.088
K	.214	**.603**	**.584**	.191
HCO_3	**.736**	.327	.131	-.110
Cl	**.885**	.050	-.357	.026
SO_4	**.648**	-.500	.327	.021
PO_4	-.326	**.589**	.097	.127
NO_3	.115	**.446**	-.356	**.565**
F	.376	**-.567**	**.451**	.380
Fe	.230	**.581**	**.439**	.161
As	**.435**	**.733**	-.235	-.156
Eigen value	5.6	2.8	1.4	1.2
Variance%	37.7	19	9.40	8.2
Cumulative %	37.7	56.8	66.2	74.5

The second component (F2) (19%) shows strong positive loadings of As, PO4, NO3, Fe, K coupled with strong negative association of pH, SO4 and F-. Negative loading of pH, SO4 and F- suggest that bacteria mediated sulphate reduction is causing organic soil degradation which in turn is decreasing the pH and releasing F- from sediments. Fluoride concentration in groundwater is influenced by a number of factors, such as temperature, pH, the presence or absence of complexing or precipitating ions and colloids, solubility of fluorine bearing minerals, anion exchange capacity of aquifer materials (i.e., OH− for F−), the size and type of geological formations traversed by water, and the contact time period during which water remains in contact with a particular formation (Apambire et al., 1997). Fluorite (CaF2) is the whole sole mineral of fluorine occurring in nature which is commonly found as an accessory in granitic gneiss (Ozsvath, 2006; Saxena & Ahmed, 2003). Similarly, fluorine is also abundant in other rock-forming minerals like apatite, micas, amphiboles, and clay minerals (Karro & Uppin, 2013; Narsimha & Sudarshan, 2013; Rafique et al., 2009; Naseem et al., 2010; Jha et al., 2010;

Carrillo-Rivera et al., 2002). The occurrence of mica minerals especially biotite in the sediments of study area (Khan, 2014) seems to be important source of fluoride beside the fertilizer and insecticides/pesticides used in the agricultural suburbs of Tando Muhammad Khan district.

On the other hand high values of K, PO_4 and NO_3 indicate fertilizer input. Although the study area is semi urban but surroundings are agricultural sites hence the nutrients leaching from fertilizer input in groundwater of study area is obvious. The strong loading of As and Fe is clear evidence of reductive dissolution of iron oxyhydroxide (FeOOH) which is widely believed mechanism of arsenic release in Holocene alluvial aquifers of the world (Smedley & Kinniburgh, 2002; Chatain et al., 2005; Pederson et al., 2006; Bennett & Dudas, 2003). Due to high affinity of As for iron oxides, arsenic concentrations in natural ferrihydrite samples have been documented with values up to 14 wt% As (Rancourt et al., 2001).

The third (F3) component of PCA revealed 9.4% of the total variations with positive loading K, Fe and F^- which clearly indicates the decomposition of biotite grains in the aquifer sediments. A study carried out by Khan (2014) has demonstrated the occurrence of biotite as an important mineral in the surface sediments of the study area. Muscovite and biotite dissolution and alterations have been investigated by many workers within acidic to alkaline pH region (Turpault & Trotignon, 1994; Samson et al., 2005). Anawar et al. (2009) discussed in detail about arsenic release from biotite into Holocene groundwater aquifers in Bangladesh. He pointed out that biotite accommodate more arsenic compared to muscovite. Seddique et al. (2008) in another study in Sonargaon, Bangladesh concluded that chemical weathering of biotite is the primary formation mechanism and prevailing reducing conditions contribute to the expansion of As-enriched groundwater in the study area.

Fe (iii) hydroxides are forced to be derived from weathering of micas, iron sulfides and other primary Fe-bearing minerals (Polizzotto et al., 2006). Chakraborty et al. (2007) in their experiment observed that the dissolution of biotite proceeds from the crystals edges inward and secondary minerals such as Fe oxide are precipitated mostly at the edges relative to basal surfaces (Murakami et al., 2003). Biotite provides greater reactive surface than muscovite (Farquhar et al., 1997). Moreover, arsenate retention on silt sized biotite in the ground water pH region (6.5-7.5) is higher than the sand sized biotite (Pal et al., 2003). It implies that flood plain soil has more potential for high arsenic retention compared to the sand of aquifer itself. The sediments in the study area consist of micaceous minerals (muscovite biotite and phlogopite) as described by Khan, 2014 which are good absorbents of metals (Ansari & Vink, 2007; Sing et al., 2005; Datta & Subramanian, 1997) and absorb As into surface Fe (III) and As rich precipitates (Charlet et al., 2006).

Factor 4 which is 8.2% of total variance showed very high loading of pH, temperature and NO_3. It indicates that bacterial reduction of nitrate is active in study area due to suitable temperature availability. It is consistent with the fact that the sampling was done in June which is very high temperature month in Pakistan. The decomposition of nitrate by bacteria turns it into NH_4 ion which causes change in the pH of groundwater. Direct application of nitrogen-based fertilizers to land is not the only source. Discharge from septic tank, leaking sewers, atmospheric deposition and the spreading of sewage sludge and manure to land can all contribute (Wakida & Lerner, 2005). Generally mineral constituents are not the major natural source of nitrate in the natural water bodies, fertilizer input and organic matter decomposition processes are the main factors causing nitrate generation and degradation in the study area.

The occurrence of oxbow lakes in study area itself is natural source of organic matter which upon degradation leads to produce nitrate. The organisms capable of denitrification tend to be ubiquitous in surface water, soil and groundwater (Beauchamp et al., 1989). They are found at great depths in aquifers: in clayey sands to 289 m (Francis et al., 1989); in limestone to 185 m (Morris et al., 1988); and in granite to 450 m depth (Nielsen et al., 2006). Denitrifiers are mostly facultative anaerobic heterotrophs and hence obtain both their energy and carbon from the oxidation of organic compounds. However, some denitrifying bacteria are autotrophs, obtaining their energy from the oxidation of inorganic species. In general, the absence of oxygen and the presence of organic carbon, reduced sulphur or iron facilitates occurrence of denitrification.

8. Conclusion

Present study revealed that groundwater quality is poor for drinking purpose in study area due to high salinity. Complex geochemical and microbiological processes (natural and anthropogenic) are operating in the study area. Arsenic contamination is reported in all three union councils but it is more prevalent in UC-2. Source of arsenic is both geogenic (minerals and natural organic matter) and fertilizer input. Anoxic environment due to bacteria mediated decomposition of organic matter is prevailing in the aquifers which are triggered by sewage mixing due to lack of sanitation facility in the study area. As a result, arsenic is released from host sediments (clays and biotite) and associated organic matter occurring in the aquifers. Sediment decomposition (biotite/muscovite) is releasing the sorbed load and structure bound elements including arsenic into the water leading to increase the groundwater solute.

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