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Arsenic Contamination in Shallow Aquifers of Holocene: A Case Study from Three Union Councils of Tando Muhammad Khan District, Sindh, Pakistan

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Abstract: Groundwater samples (n = 72) were collected from shallow (depth < 30 meters) wells located in three union councils (Lakhat, Sheikh Bhirkyo, Tando Saindad) of Tando Muhammad Khan district. Data reveal that all three union councils are sewage impacted where severity increases in the order of Tando Saindad > Lakhat > Sheikh Bhirkyo. The same order of intensity is reported for As concentration i.e. Tando Saindad (n = 25; range: 10-600 μg/L) >Lakhat (n = 15; range: 20-250 μg/L) >Sheikh Bhirkyo (n = 6; range: 50-100 μg/L) suggesting the strong control of sewage mixing in arsenic release. Tando Saindad union council is worst arsenic affected which is located adjacent to Tando Muhammad Khan city suggesting the transport of anthropogenic contaminants to groundwater system through aquifer recharge. Principal component analysis (PCA) was applied on 15 variables with outcome of four significant factors (F) explaining the 79% of total variance. F1 suggested the intense water sediment interaction as indicated by strong loading (F1 > ± 0.6). F2 revealed the organic matter (natural and sewage derived) decomposition leading to arsenic and fluoride release from host sediments (mainly biotite). F3 strongly supports the prevalence of anoxia which is expressed by strong loading of pH and NO_3. Factor 4 is supporting the widely known mechanism of reductive dissolution of FeOOH which is mainly derived by organic matter respiration by bacteria in the host sediments of shallow aquifers.

Keywords: Holocene, shallow aquifers, anoxia, organic matter, sewage, arsenic.

Introduction

Toxicity of arsenic (As) to human health is well known since hundreds of years (Saha et al., 1999). The drinking of As contaminated groundwater tapped from young (Holocene) alluvial aquifers has caused many health related issues leading to cancer. Like other orogenic basins, the circum Himalayan countries including Bangladesh, west Bengal (India), China, Nepal, Cambodia, Vietnam and Pakistan have been reported for arsenic contaminated aquifers and associated arsenicosis (Ehrlich, 2002; Oremland and Stolz, 2003).

Arsenic is naturally occurring element available in soil and sediments (Korte, 1991; Schreiber et al, 2000, Smedley and Kinniburgh, 2002; Stollenwerk, 2003) ranging from 4.8-14 mg/kg (Kabata-Pendias and Pendias, 1992). Under acidic pH conditions ($pH< 3$) sorption of As onto organic matter may reduce the mobility of As in soil while its liberation may increase under alkaline conditions ($pH > 7$) (Wang and Mulligan, 2009 p.89). In fresh waters, common arsenic species are the trivalent arsenite (H3AsO3) and pentavalent arsenate (H3AsO4) where As+3 species are believed to be more mobile than As+5 due to strong affinity of latter with Fe-Mn-Al oxides (Karte and Fernando, 1991).

Chronic As diseases caused by drinking groundwater was first reported in West Bengal in 1982 (Saha, 1984) and since then, arsenic related health problems in Himalayan river basins (Indo-Gangetic plains) have been widely reported by various research groups (Guha Majumdar et al., 1988; Mandal et al., 1998; Chakraborty et al. 2001; Kapaj et al., 2006). However in Pakistan, only the upper reaches of Indus basin have been investigated for elevated arsenic contents in alluvial flood plain aquifers of Holocene age (e.g. Malana and Khosa, 2011) Farooqi et al., 2007; Ashraf et al., 1991; Rehman et al., 1997; Nickson et al., 2005) where the arsenic contamination seems to be the function of anthropogenic activities (Farooqi, 2007). On the other hand, a few studies have reported the high arsenic groundwater in lower reaches of Indus basin (Kazi et al., 2009; Arain et al., 2009; Husain 2009; Fatimi et al., 2014) where Tando Muhammad Khan district has been declared as “worst arsenic affected district” of Sindh (Husain, 2009). On the other hand, a couple of studies (Husain et al., 2012; Khan et al., 2014; Khan et al., 2017) have recently been carried out in deltaic flood plain of Tando Muhammad Khan district where As concentrations have been reported up to 300 µg/L. These studies have shown that arsenic source is natural sediments (silty-clay) which are releasing sorbed load into the aquifer water by anaerobic respiration of bacteria being fueled by organic matter decomposition.

However, the sources of arsenic and its mobilization mechanism in the shallow alluvial aquifers of Indus deltaic plain are still unclear due to limited data availability from study area. Therefore, present study is aimed at integrating the picture of arsenic source and its release in Indus delta by using hydro-geochemical signatures of groundwater in Tando Muhammad Khan district.

Material and Methods

Study area

Tando Muhammad Khan district is 35 km from Hyderabad with an area of 2600 sq. km. The climate of study 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 erratic with an average of about 130 mm. The monsoon dominates from July to September. About 70% of the district population is engaged in agriculture. Beside wheat and cotton, other main crops are sugarcane, rice, and banana which needs flood irrigation. Four big sugar mills of the country are located in Tando Muhammad Khan district. Phuleli, Pinyari and Akram canal are the main source of water-reservoir for irrigation in this district.

Tando Muhammad Khan district 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. 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). Tando Muhammad Khan district mostly occupies cultivable land constituting the huge quantity of detritus (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 rocks of Tertiary Period which are exposed on the western margin of study area (Fig. 1).

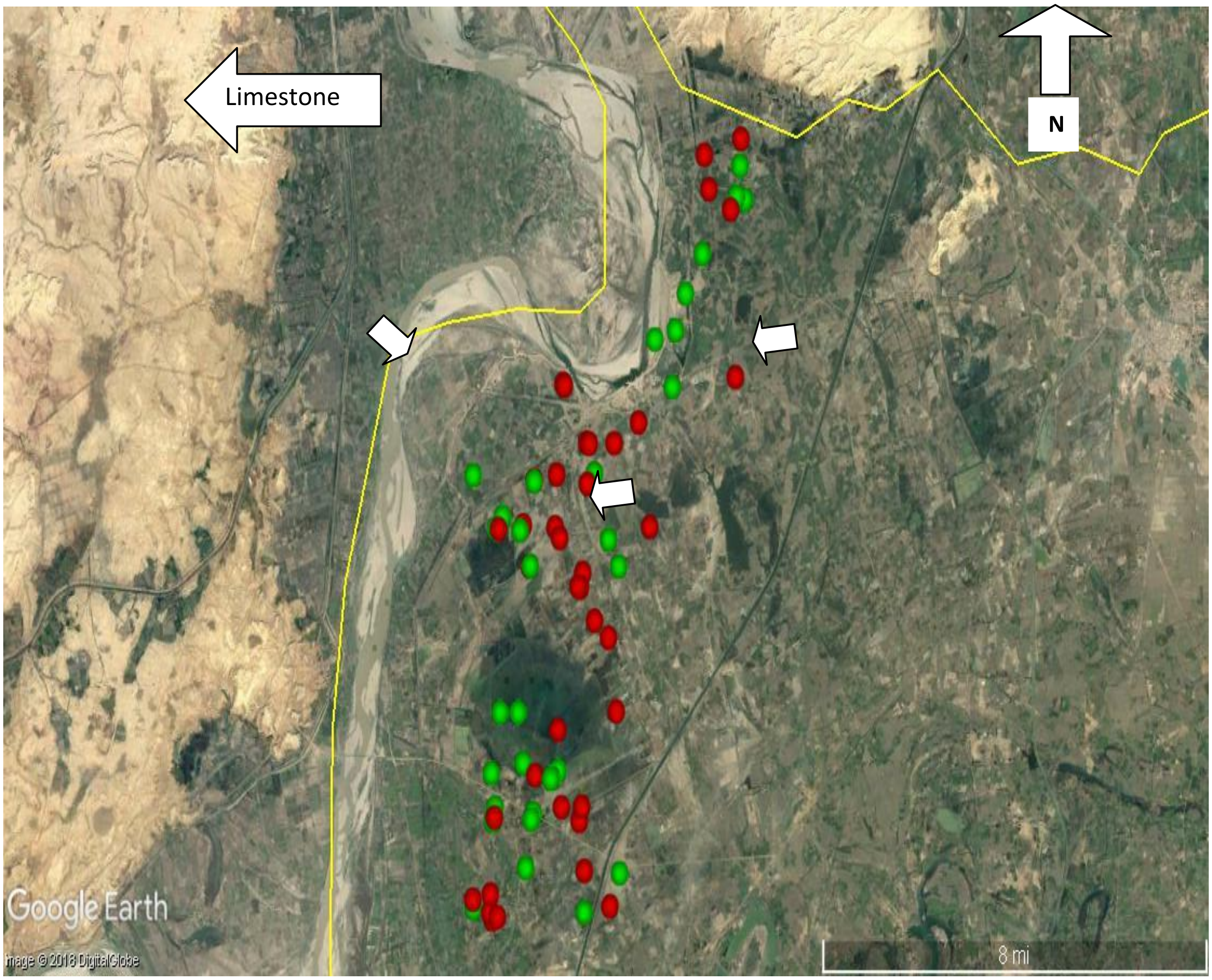

Fig. 1 Google Image showing the arsenic distribution in study area: small arrows show the oxbow lakes while big arrow is showing the limestone outcrop of Eocene time.

Sample collection

Seventy two groundwater samples were collected mostly from shallow wells (depth < 30 m)in sterile plastic bottles (0.5 and 1 liter) for the determination of physicochemical parameters including arsenic. For nitrate determination, groundwater samples were collected in100 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. Methods and equipments used to determine groundwater attributes have been summarized inTable 1.

Table 1 Equipment/methods used to analyze groundwater samples collected from three union councils of Tando Muhammad Khan district, Sindh.

S. No.	Parameters	Equipments
1.	Turbidity	Turbidity meter, Lamotte, model 2008, USA
2.	Electrical Conductivity/TDS	EC meter (Eutech Cyber Scan CON 11)
3.	pH	pH meter (JENCO 6230N)
4.	Alkalinity	2320 Standard Method (1992)
5.	Carbonate mg/L	Titration Method, (USSL, 1954)
6.	Bi-carbonate mg/L	Titration Method, (USSL, 1954)
7.	Calcium mg/L	EDTA Titration Method
8.	Chloride mg/L	Argentometric Titration Method
9.	Magnesium mg/L	Titration Method
10.	Potassium mg/L	Flame photometer (JENWAY PFP7)
11.	Sodium mg/L	Flame photometer (JENWAY PFP7)
12.	Sulphate mg/L	Spectrophotometer (DR 2800)
13.	Nitrate mg/L	Spectrophotometer, HACH-8171
14.	Hardness as $CaCo_3$	EDTA titration standard method (1992)
15.	iron	Spectrophotometer (Model: U-1100, HITACHI)
16.	Fluoride	Spectrophotometer, SPADNS (HACH).
17.	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 groundwater parameters of three union councils in Tando Muhammad Khan district. The output of PCA was used to explain the variation of major data set of interrelated variables with small set of independent variable and to trace the factors which affect each other. Components with Eigen values <1 were not taken into the account as these explain insignificant variations.

Results and Discussion

Major Chemistry

Groundwater samples were collected from three union councils Lakhat (LK), Sheikh Bhirkyo (SB) and Tando Saidad (TS) from shallow aquifers (mean depth: 62 ft). The data revealed that groundwater temperature is same (31±1 °C) in all three union councils which falls in the category of low temperature setting as classified by Scanlon et al., (2009). In low temperature natural environment arsenic can be transferred from enriched to non enriched ecosystem by anthropogenic activities (e.g. irrigational pumping). The groundwater pH is circum-neutral (6.8-7.3) which is within the permissible range of WHO (6.5-8.5) for drinking purpose.

Mean total dissolved solids (TDS) content is proximal in all three sites but a wide variation range of TDS occurs in the order of SB (469-3596 mg/L) > TS (372-2458 mg/L) > LK (490-3148 mg/L). This wide variation in the salinity of groundwater is mainly attributed to anthropogenic activities and geochemical processes (Jeevanandam et al., 2007) prevailing in the study area.

Table 2 Statistical descriptive of the quality parameters of groundwater samples from study area.

		Lakhat (*n* =30)				**Sheikh Bhirkyo** (*n* = 13)				**Tando Saindad** (*n* =29)			
S. No.	**Parameters**	**Min**	**Max**	**Mean**	**S.D**	**Min**	**Max**	**Mean**	**S.D**	**Min**	**Max**	**Mean**	**S.D**
1	pH	6.7	7.8	7.3	0.25	6.89	7.7	7.2	0.29	591	7.77	6.88	0.54
2	TDS	490	3148	1186	717	469	3596	1246.7	853.86	372	2458	1240.48	662.05
3	Temperature	24.2	31.4	30.27	2.27	24.4	31.5	28.63	3.33	24.7	31.7	30.88	1.722
4	Well Depth	16	90	46.16	17.64	40	200	95.38	58.75	80	30	49.72	5.06
5	Ca	40	384	113	77.27	52	332	108.92	73.23	28	344	107.58	58.56
6	Mg	15	122	53.4	27.13	32	126	60.53	28.86	17	119	59.03	28.77
7	Na	42	574	188	136.12	44	584	196	161.35	36	480	213.72	142.5
8	K	3.1	23.9	6.28	3.73	4.3	11.1	6.25	1.867	2	106	14.27	23.32
9	HCO_3	160	630	330	97.39	200	440	315.38	82.92	140	620	346.55	123.7
10	Cl-	74	1059	284	256.31	50	1383	319.3	361.58	42	887	313.17	231.27
11	SO_4	40	910	177	167.05	47	530	184	146.79	44	465	179.31	117.69
12	NO_3	0.4	2.87	1	0.53	0.38	4.64	1.12	1.159	0.37	9.87	1.51	2.13
13	PO_4	0.13	0.46	0.25	0.11	0.12	0.24	0.19	0.05	0.07	0.41	0.225	0.08
14	Fe	0.01	1.55	0.15	0.32	0.01	3.97	0.63	1.11	0.01	345	0.34	0.68
15	As	5	250	44	73.2	5	100	28.46	38.85	5	600	108.79	159.73
16	F-	0.04	1.88	0.64	0.31	0.13	0.87	0.49	0.26	0.14	0.84	0.43	0.18

Widespread water logging from Indus river irrigation system causes high saturation of salts in this semi-arid region which leads to concomitant arsenic enrichment in shallow aquifers (Baig et al., 2009). On the other hand Ca and Mg distribution pattern follows the order of LK > SB > TS (Table 2). Highly fluctuating concentration of Ca and Mg is reported from all three UCs which suggests the variable sources and ion exchange activities in the aquifers of study area. The Ca/Mg ratio of mean values ranges between 1.8-2.1 which suggest that the source is dolomite dissolution (Jeevanandam et al., 2007). It is consistent with the fact that left bank of River Indus is headed with the exposure of dolomitic Laki limestone. Other source of Ca is incongruent dissolution of plagioclase feldspars (Saether and Caritat, 2001). Likewise, K content is found to be more than double the concentration of LK (mean: 6.28 mg/L) and SB (6. 28 mg/L) in TS (14.27 mg/L). Relatively higher K content in the TS suggests more influence of agricultural activity and sewage discharge effects on groundwater (Malana and Khosa, 2011).

Bicarbonate content spans in the range of 200-440, 140-620 and 160-630 mg/L in Sheikh Bhirkyo, Tando Saindad and Lakhat respectively. Mean value of HCO_3 is relatively higher (346.55 mg/L) in TS as compared to other two UCs of Tando Muhammad Khan district (Table 2). Elevated bicarbonate content in the groundwater reflects carbonate mineral dissolution via active biodegradation of organic matter at shallow depths (Jeong, 2001; Shamsudduha et al, 2008; Lang et al., 2006; Arafin, 2003; Turner, 2006; Mukharjee et al., 2009). Chloride concentration revealed high deviation in Sheikh Bhirkyo (361.58) followed by Lakhat (256.31) and Tando Saindad (231.27). This wide variation in the chloride content of groundwater suggests local control of particular source or input from multiple sources in study area. Strong correlation of Cl with Na ($r^2 = 0.9$) followed by Ca ($r^2 = 0.87$) and Mg ($r^2 = 0.77$) suggests that evaporative concentration of major salts is increasing in the study area due to aridity and sewage infiltration.

Like other ions, a wide variation in the SO_4 content is reported where its highest mean value is reported in SB (range: 47-530; mean: 184 mg/L) followed by TS (range: 44-465; mean: 179 mg/L) and LK (range: 40-910; mean: 177 mg/L). The high sulphate content in the groundwater of study area suggests the gypsum dissolution, use of inorganic fertilizer and and recent recharge of saline water (Nguyen and Itoi, 2009; Anawar et al., 2013). A strong correlation between SO4 and Cl ($r^2 = 0.68$) support imprint of evaporation and agriculture activities (Nicollie et al., 2010). Contrary to this, very low nitrate is determined in all three union councils where the mean value is found to be 1± 0.5 mg/L. The high NO_3 occurs in the groundwater of shallow aquifers due to good permeable surface soil (Kim et al., 2009), flood irrigation and over fertilization (Voudouris et al., 2005). Generally nitrate moves in the soil with no transformation (Andrade and Stiger, 2009). In anaerobic condition, nitrate reducing bacteria use it to oxidize the organic matter resulting in high HCO_3 and low NO_3 content (REF). Similar is true about study area where bicarbonate up to 630 mg/L and nitrate less than 1 mg/L is reported. The low nitrate in collected groundwater samples is also due to the wet season as the nitrate concentration is high in the dry season which progressively starts decreasing at the onset of wet season (Voudouris et al., 2004b).

Minor/Trace Chemistry

Phosphate and iron

Very low phosphate ($PO_4 < 1$ mg/L) and iron concentrations (mean: 1± 0.5 mg/L) are determined in the groundwater of study area (Table). Relatively wide range of phosphate (0.07-0.41 mg/L) occurs in Tando Saindad as compared to other two UCs. Mean iron content is found to be 0.15 mg/L which is within WHO permissible range (0.3 mg/L) but same exceeded the guideline value in Sheikh Bhirkyo (mean: 0.3 mg/L) and Tando Saindad (mean: 0.34 mg/L) while within the reference range (0.15 mg/L) in Lakhat.

Arsenic and Fluoride Distribution

About 67% of collected samples (n=72) have been reported to contain arsenic in the range of 5-600 µg/L. 17 out of 30 collected samples in Lakhat showed the occurrence of arsenic (5-250 µg/L) where about 82% of arsenic rich wells exceeded the WHO limit of 10 µg/L for drinking water. On the other hand, about 83% of collected samples (n = 29) from Tando Saindad have been reported to contain arsenic in the range of 5-600 µg/L. likewise, about 50% of collected samples from Sheikh Bhirkyo have been found contaminated with As (5-100 µg/L). The data revealed that all three UCs are arsenic afflicted areas but the severity is highest in Tando Saindad where up to 600 μg/L As is reported in a sample tapped from a government primary school.

Fluoride content is found to be less than 1 mg/L in samples collected from all three UCs except one (1.8 mg/L) which was collected from Usman Laghari Goth in LK. Despite low fluoride concentrations, a strong positive correction ($r^2 = 0.52$) is found with As (Table 3). It suggests that both elements are genetically associated with each other. Khan (2014) has reported the occurrence of phylosilicates in the aquifer sediments of Tando Muhammad Khan district where a large part of these fine mica minerals is biotite. A study has shown that the chemical weathering of biotite under monsoon climatic conditions have resulted in the release of Arsenic followed by the Fluoride (Breit et al., 2004; Hasan et al., 2009). The other sources of these two elements are clay minerals which adsorb these elements on their surfaces due to electrically charged behavior.

Principle Component Analysis

Factor 1 of principle components explains the 45.48% of the total variance which shows climatic effects and intense water sediment interaction as indicated by strong loading of TDS (0.91) with major cations including Ca (0.92), Na (0.91) Mg (0.91) K (0.81) and anions SO_4 (0.95), Cl (0.92) NO_3 (0.64), HCO_3 (0.63). Since the study area has deltaic setting, the organic matter is prime driver of generating the organic acids which is significantly leaching the ions from soil and sediments as a result increased the specific conductance of water (Halim et al., 2010). On the other hand, semi-arid climate has also concentrated the salts in the groundwater due to intense evaporation (Farooqi et al., 2007; Panhwar, 1969).

Factor 2 showed 13.28% of total variance with strong positive loadings of temperature (0.65), PO_4 (0.76) and As (0.64). The PCA plot indicates that As is significantly correlated to the concentration of PO_4 suggesting that arsenic is being released from organic matter decomposition. Presence of organic matter in Bengal and Indus delta has been widely reported (e.g. Khan, 2014, Husain, 2012; Ahmed et al., 2004; McArthur et al., 2004; Ravenscroft et al., 2001). A study carried out by Hossain et al., (2013) concluded that organic matter not only serves as Redox driver but also as source of arsenic. The deltaic soil constitutes fine grained sediments, rich in organic matter containing high amount of arsenic, which is likely to be the part of aquifers by various geochemical processes (McArthur et al., 2001; Nickson et al., 2005). Bacteria mediated organic matter decomposition leads to release the sorbed As and the concomitant PO4 which upon irrigation practices infiltrates to aquifer depth.

However if only the organic matter would be source of arsenic the correlation between PO4 and As must be very strongly positive. However, moderate correlation (r2 = 0.47) is observed between two elements suggest that a part of arsenic is contributed from organic matter decomposition and fertilizer application. This could be attributed to the application of diammonium phosphate (DAP) is common to increase the yield of sugarcane which may contribute a part of arsenic from it. Since the paddy, sugarcane and banana crops are cultivated by flood irrigation practices, the prevalence of anoxia followed by bacteria mediated organic matter decomposition leads to release the sorbed load of fine sediments (clays) into the aquifer depth. On the other hand, anoxic water interacting with aquifer sediment leads to activate the fine sediments for releasing its sorbed or structural load of trace elements. Likewise, the strong loading of temperature in Factor1 clearly indicates the role of bacteria in arsenic liberation from organic matter. The role of temperature controlled microbial reduction of As(V) to As (III) is known (Mc Laren and Kim, 1995 p.167). Andrade and Stiger (2013) observed that most of the samples with As > 40 μg/L have high temperature (> 20 °C). The temperature range of 10-30°C occurs in the study area where it generally remains 25±3 °C in most part of the year. Similarly the temperature peaks to 31-38°C during June-July which is the most influential time of arsenic release into the aquifers of study area.

Table 4 Principle Component Matrix[a]

	Component			
	F1	F2	F3	F4
Temp	.153	**.654**	.132	**-.546**
pH	-.293	-.192	**.833**	.246
TDS	**.912**	.085	-.025	-.091
Ca	**.919**	-.146	-.093	-.146
Mg	**.914**	-.085	.112	.005
HCO_3	**.632**	.155	-.286	.312
Cl	**.922**	-.040	.086	-.207
SO_4	**.946**	.064	.177	-.013
PO_4	.012	**.768**	-.189	.238
NO_3	**.637**	.010	.139	**.451**
F	.300	.359	**.631**	**.443**
Na	**.911**	.135	.062	-.067
K	**.816**	-.312	-.035	-.104
Fe	.256	-.463	-.593	**.401**
As	-.025	**.642**	-.420	.235
Eigen Values	6.822	1.992	1.840	1.216
Variance %	45.482	13.280	12.263	8.107
Cumulative	45.482	58.763	71.026	79.133

Extraction Method: Principal Component Analysis.

a. 4 components extracted.

Factor 3 manifested the strong correlation between pH and the fluoride (Table 3) suggesting the release from reductive dissolution of Fe-(hydr)oxides. A study carried out by Kim et al., (2012) concluded that correlation between As and F is weak in reducing environment because arsenic released from the sediments can easily be removed from the water again when sulfate reduction occurs while fluoride is independent of such reaction therefore fluoride shows good correlation with pH than arsenic in the reducing aquifers.

Factor 4 explains the prevalence of anoxia as indicated by mildly strong positive loading of NO_3, F and Fe (Table 3). Bacterial respiration of organic matter through NO_3 is causing reductive dissolution of FeOOH associated with fine sediments which is releasing its sorbed load (including F) into the groundwater of Tando Muhammad Khan district. The co-occurrence of As and F in the groundwater is commonly reported from arid or semi-arid regions such as USA, Mexico, Argentina and China (Robertson, 1989; Levy et al., 1999; Wyatt et al., 1998; Mahlknecht et al., 2004; Smedley and Kinniburg, 2002; Bhattacharya et al., 2006; Gomez et al., 2009; Currell et al., 2011). It is believed that As and F will be increased by reductive dissolution of Fe-(hydr)oxides if it is the major host of As and F (Kim et al., 2012). As reported by Khan, (2014) the aquifer sediments in study area are rich in phylosilicates dominated by Fe-(hydr)oxides and biotite. Since factor 4 has explained the least variance (1.8%), it can be concluded that the Redox condition is in its early phase i.e. relatively less reduced as compared to Bengal delta.

Sewage and arsenic relationship

Out of total collected samples (n= 72) about 32% samples have been found sewage impacted. The sewage impacted samples which are also found arsenic contaminated varied in the order of TS (64%) > LK=SB (50%). Strong correlation of sewage impacted wells with As in TS is due to relatively denser population as compared to other two sites which is somehow linked with increased As toxicity (Nath et al., 2008). Previous studies have revealed that urban runoff transport the anthropogenic contaminants to groundwater system through aquifer recharge (Wilson, 1981; Foster and Chiltan, 2003; Lerner, 2004; Morris et al., 2005; Naik et al., 2008; Lohse et al., 2010). Thus, arsenic release into the groundwater may have been triggered by sewage contamination (Ravenscroft, et al., 2001;

Cole and Ryan, 2005;Nath et al., 2008) in Tando Muhammad Khan district (Husain, 2009; Mukherjee et al., 2010; Husain et al., 2012; Khan et al., 2017).

About half of sewage impacted wells have very high concentration (above WHO guideline values) of Na, K, Cl, and SO_4 in study area suggesting that unlined sanitation is responsible for high concentration of these ions (Cole et al., 2005; Husain, 2009; Husain et al., 2012). These shallow aquifers (depth < 30 meters) are contaminated with sewage due to lack of proper sanitation facilities, free roaming animals and open air excretion (Cole, 2005; Nath et al., 2008; Husain, 2009) which is common throughout the study area. It implies that unlined sanitation is significantly responsible for bacterial contamination and corresponding arsenic release in the groundwater of the study area. Interestingly, pathogen laden arsenic contaminated samples were mostly collected from very shallow depths (<15 meters) near canal or waste water ponds. These polluted (chemically and microbially) surface water bodies are hydraulically connected with shallow aquifers where reducing conditions are created due to bacteria mediated organic matter (natural and fecal) oxidation **(**Chkirbene et al., 2009; Petalas et al., 1996). Reducing condition is favorable for FeOOH reduction and release of concurrent arsenic from sediments to groundwater (Bhattacharya, 1997; Nickson et al., 1998; Zheng et al., 2004; Polizzotto et al., 2005; Halim et al., 2009; Ahmed et al., 2004).

Depth control of arsenic

A large section of groundwater samples with high arsenic concentrations is taken from wells at a depth of < 30 meters and the highest arsenic content of 600 μg/L was detected in a well installed at 20 meters depth in a government school in TS. The occurrence of high arsenic groundwater at optimum depth of around 30 meters (Frisbie et al., 1999; Karim et al., 1997; Roy Chowdhury et al., 1999; Acharyya et al., 1999; AAN, 1999) or in the range of 12-50 meters is widely reported (Wagener et al., 2005; Yu et al., 2003; Polizzotto et al, 2005, 2006; Bhattacharya et al., 2003; Bibi et al., 2006). Similarly, Bibi et al. (2006) reported high arsenic concentrations in shallow aquifers (24-35 meters depth) despite relatively low As concentration within aquifer sediments. It is in agreement with the depths occurring in the study area where As concentration peaks at the aquifer depth range of 10-30 meters.

It was observed by Farooqi et al. (2009) in the upper reaches of Indus basin that major cause of arsenic contamination in shallow groundwater was infiltration from the surface which is consistent with the case of study area. It may be due to As associated with FeOOH (Seddique et al., 2008; Reza et al., 2010; Wang et al., 2012) biotite (Ansari, 1997; Chakraborty et al., 2007; Nath et al., 2009; Hasan et al., 2009; Acharyya et al., 2005; Ravenscroft et al., 2005; Wagner et al., 2005;Chakraborty et al., 2011) and organic matter (Akai et al., 2004; McArthur et al., 2001; Bauer, 2008; Anawar et al., 2003, 2011, 2013) in the study area which is favored for deposition along with fined grained sediments (Padmalal et al., 1997) in deltaic setting (low energy environment).

Conclusion

Present study has revealed that groundwater in Tando Muhammad Khan District is highly saline. Shallow aquifers are mostly sewage impacted and arsenic contaminated in all three union council. Redox condition and geochemical signatures revealed that organic matter (natural and sewage derived) and aquifer sediments (FeOOH) are the main source/host of arsenic. However, by alkaline pH and relatively less reduced conditions it is concluded that arsenic is mainly sourced from organic matter than its common host (FeOOH) in other deltaic regions of the world. Anoxia is prevailing in study area by young and reactive organic matter available in the flood plain sediments and oxbow lakes followed by some input from sewage due to unlined sanitation.

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