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RESEARCH ARTICLE

Soil Minerals Serving as Source of Arsenic in Alluvial Aquifers of Holocene: A Case Study from Indus Delta, Sindh, Pakistan

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Abstract:

Groundwater arsenic contamination is recently reported in the alluvial aquifers of Indus deltaic plain. Since the source of arsenic is believed to be natural as widely reported in other deltaic aquifers of same age (Holocene), it is imperative to evaluate the soil characteristics for identifying the sources of arsenic and its mobilization mechanism. For this purpose, 49 soil samples were collected from near aquifer sites in all three talukas of Tando Muhammad Khan district. Visual analysis revealed that soil is light grey in color with fine texture ranging from silt to silty-clay. The X-ray diffraction study reveals the occurrence of quartz, mica and clay minerals in all collected soil samples. Plagioclase feldspar is second dominant mineral group in the order of albite (calcian) >albite>albite (disordered) = anorthite > anorthite (sodian) = anorthite (disordered). Calcite is major carbonate mineral which is detected in 40 out of total 49 soil samples. The occurrence of other occasional minerals includes amesite, nitro-calcite, rutile and zinnwaldite. The frequency of micaceous minerals in collected samples is in the order of clinochlore> polylithionite> Biotite > phlogopite> muscovite. Polylithionite is found in about half of the total soil samples, where most of the aquifers contain arsenic >20 μg/L (Khan, 2014). Phlogopite is observed in seven soil samples which are also associated with clinochlore. On the other hand, biotite is found in 14 sediment samples collected from Tando Muhammad Khan and Bhulri Shah Karim talukas and muscovite occurs in three soil samples of Tando Muhammad Khan taluka. It can be concluded from present study that fine-grained phyllosilicates have strong affinity for arsenic retention. These sediments are important source of arsenic Indus delta and other deltaic plains of the world.

Keywords: Arsenic, sediments, alluvial aquifers, Holocene, Indus delta, Pakistan.

1. Introduction

Arsenic is widespread contaminant in the environment and its adverse health effects are a global concer(WHO, 2010). There are two major sources of arsenic which includes weathering of minerals (Bhumbla and Keefer, 1994; Yan-Chu, 1994; Mandal and Suzuki, 2002; Foley and Ayuso, 2008; Mailloux *et al.*, 2009) and anthropogenic activities like mining activities, industrial wastes and agricultural in puts (Chilvers and Peterson, 1987). Chronic application of pesticides and herbicides also results in substantial accumulation in soils (Hiltbold, et al., 1974)Mineralogy is one of the important research approaches for disclosing the mechanism of environmental contamination (Akai *et al.*, 2004; Akai and Anawar, 2013). The geogenic As is of serious concern in countries like Bangladesh, India, and Vietnam. High concentration of As in soil and water has also been noted in developed countries, e.g., US (Peryea and Creger, 1994)and South Australia and Tasmania (Merry, et al., 1983) It is widely believed that high concentration of arsenic (As) is mainly confined to the sedimentary aquifers of Holocene age (Bhattacharya, et al., 1997; Ishiga, 2000; Anawar et al., 2002, 2003)High levels of arsenic in groundwater mainly result from natural contamination(Chowdhury, et al., 1999; Acharyya et al., 2000; Nicksonet al., 2000; McArthur and Ravenscroft, 2000; Anawar et al., 2002; Polizzotto and Harvey, 2005; Rabbani et al., 2017).Various theories have been put forward regarding the modes of arsenic release, ranging from oxidative or reductive degradation of arsenic-bearing solids to competitive ligand displacement by phosphate(Chakrapani et al., 1995; Bhattacharya, et al., 1997; Acharyya et al., 2000;

Nickson et al.,2000; McArthur and Ravenscroft, 2000).

Major As minerals occurring in nature are niccolite, realgar, orpiment, cobaltite, arsenopyrite, tennatite, enargite, arsenolite, claudetite, scorodite, annabergite, hoernesite, haematolite, conichalcite and pharmacosiderite (Smedley and Kinniburgh, 2002)These minerals originate in hydrothermal veins, hot springs, secondary minerals deposited oxidation products of associated As minerals. These mineral deposits are typically associated with orogeny where volcanic activity and metamorphism are quite common. Hence, the occurrence of As in Himalayan river basin is rational. All the rivers deposit fine to very fine textured sediments in deltaic region due to low energy and very high suspended load. These fine sediments are mainly comprised of minerals like quartz, feldspar and biotite which contains As concentration in the range of 0.4-1.3, 0.1-2.1 and 1.4 mg/kg respectively (Garlick and Wedepohl, 1969). On the other hand, calcite and dolomite contains Arsenic in the range of 1-8 and <3 mg/kg respectively.

Beside arsenic speciation and toxicity in the soil, several studies have documented relatively higher As concentration in the soil as compared to the aquifer materials (Onken and Hossner, 1995; Swartz et al., 2004; Polizzotto et al., 2006).It is due to the fact that arsenic compounds are absorbed strongly onto soil, and therefore transported only over short distances in surface and groundwater (Manning and Goldberg, 1997).Solid phase As and Fe becomes more reduced with depth (0.5-3.6 m) in the soil and released via redox cycling in surface soils/sediments into the sandy aquifer (Polizzotto et al., 2008).

Keeping in view these facts, it is likely that the constituent minerals in the alluvial deposits of Tando Muhammad Khan district (part of Indus deltaic flood plain)are probable source of As-enriched groundwater, similar to other highly As enriched groundwaters of (Anawar et al., 2003; Polizzotto et al., 2006) West Bengal (Nath et al., 2008; Hery et al., 2010; Nath et al., 2011)Vietnam(Berg et al., 2008) China (Xie et al., 2009) and Spain (Garcia-Sanchez et al., 2005).Substantial work has been carried out by various workers on the groundwater of Tando Muhammad Khan to explain the arsenic contamination(Husain et al., 2012; Khan et al., 2014, 2017) However, sediment characteristics have not yet been studied to explain the possible source/host of arsenic responsible for high arsenic groundwater in study area. Therefore, present study is aimed at characterizing the near aquifer site sediments in terms of mineral composition and chemical characteristics to link with the hydrogeochemical characters of the corresponding groundwater in order to complete the picture of arsenic release mechanism in study area.

2. Material and Methods

2.1. Study area

Indus Basin is topographically a plain area, characteristically devoid of any well-defined natural surface and subsurface drainage (Qureshi et al., 2008)It covers an area of 2600 sq. km covering the whole Hyderabad Division comprising of Tando Mohammad Khan, Tando Allayar and Matiari districts. Geology of Tando Muhammad Khan district is very simple where the Holocene fine sediments cover the surface and Indus River flows on the western margin of the basin (Fig.1). Surface soil comprises fine textured sediments dominated by silt and clay with subordinate sand (Kazmi, 1984). The entire study area is covered with marsh peat, micaceous silt and clay units similar to Bangladesh (Shamsudduha et al., 2008).

2.1.1. Quaternary Sediments

Quaternary sediments of Late Holocene have carpeted the surface geology of study area that are brought by the Indus River (Kazmi, 1984; Mehmood et al., 2009). Deposition of such young sediments is mainly controlled by orogenic movement of Himalayas which incepted in the Early Pleistocene time (Gill, 1952). This phase of orogeny was the strongest of all stages where major structural and tectonic events took place in terms of folding, faulting and uplift. This was the time when thick deposition of sediments in all parts of Himalayan basin occurred including deltaic part of Indus basin. (Acharyya, et al., 2000; Polizzotto et al., 2006; Alizai et al., 2012).

Interestingly, Holocene aquifers are the host of high arsenic groundwater worldwide.(Acharya, 2005). Similar is true about alluvial deposits of Tando Muhammad Khan district and adjoining areas where more than 600 ppb arsenic is reported in shallow alluvial aquifers (Husain et al., 2012). These flood plain deposits of study area have been classified in Table 1 out of which two are described below due to the fact that only these two comprises the surface geology of study district.
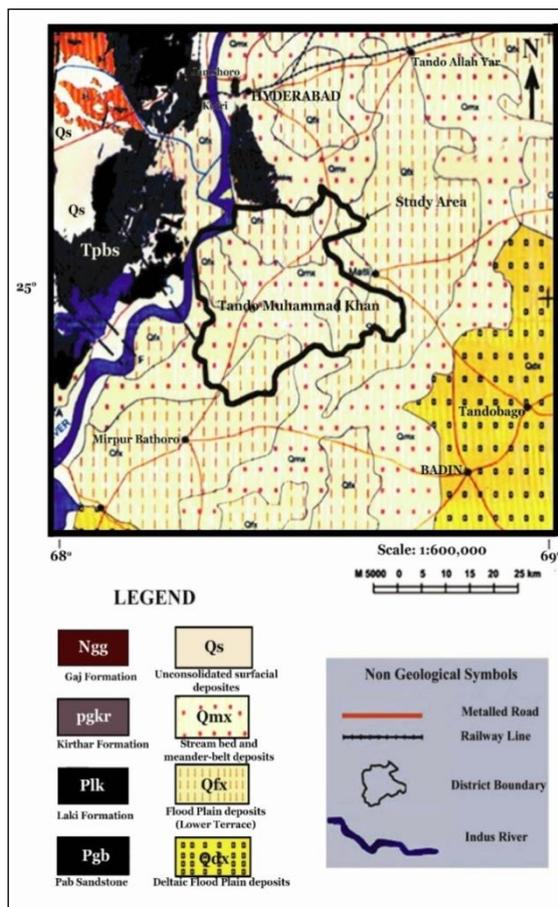

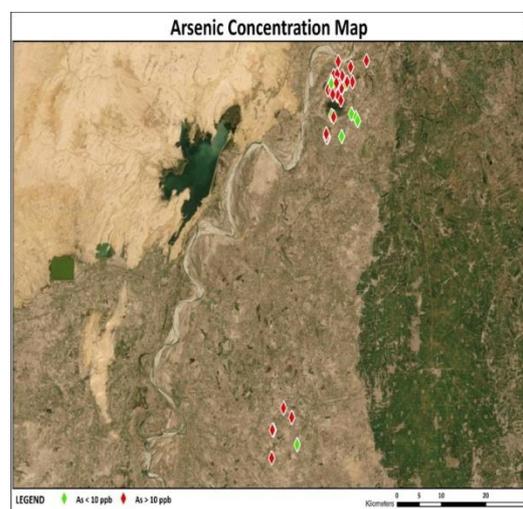Fig. 1 Geological map of Tando Muhammad Khan district and adjoining areas.

Fig. 2 Map showing the arsenic distribution in groundwater of study area.

2.1.2. Surficial Deposits of Alluvium

The surficial alluvial deposits in study and adjoining areas consists of fine sand, silt and clay transported and deposited by the streams resulting in the formation of cultivable land.

2.1.3. Extinct Streams Deposits

Extinct Streams Deposits carve the surface geology of Tando Muhammad Khan district (Table 1). These sediments form the flood plain deposits overlain by the river channel and meander belt deposits. The sediments of lower Indus flood plain comprise of greenish grey to grey clay and silt followed by fine sand. Sporadically these deposits are interlayered with some sticky, black and calcareous clay. These sediments can be characteristically seen in shallow depressions formed by the chocked estuaries and surrounded by salt at some places, interlayered with sticky black calcareous clay. These are characterized by long shallow depressions formed by choked estuaries and occupied by salt deposits.

The meander belt and stream bed deposits show imprints of older meander belts traces. These deposits are the admixture of poorly sorted sediments of fine sand with subordinate silty clay. These sediments are directly overlying the deltaic alluvium (Akhtar et al., 2012).

Table 1 Stratigraphic Units of Holocene In Tando Muhammad Khan District and Adjoining Areas (after (Akhtar et al., 2012).

Period	Epoch	Deposit / Formation	Sub Units	Lithological Description
Quartenary	Holocene	Stream bed deposits	Floodplain deposits	Low lying areas along river, frequently inundated during high floods. These are flat and relatively even surfaces
			Stream Bed and Meander belt deposits	Deposits characterized by river meanders, cut off, oxbow lakes, abandoned channels numerous point bars, swales, and sand ridges.
		Surficial alluvium deposits	Unconsolidated surficial deposits	Deposit consist of sand, silt and clayey material brought by streams
		Deposits of extinct streams	Stream bed and meander belt deposits	Poorly sorted fine to medium grained sand, silt, and least aboundant clay
			Floodplain deposits (lower Terraces)	Consist of greenish gray to gray silt and clay with subordinate fine sand, occasionally intercalated with sticky black clay

2.2. Soil Sampling for Mineralogical Analysis

Forty-nine representative soil samples (about 0.3 meters depth) near aquifer sites were taken from various parts of study area. Sample location was marked on the map using Global Positioning System. The soil samples were collected using hand shovel in the plastic bags. The physical properties (i.e. color, texture) of the collected samples were also documented in the field. The samples were air dried for about 2 days at room temperature and subsequently oven dried at 105°C. The dried sample was ground to very fine mesh and sieved through 2 mm screen to eliminate the coarse particles and other deleterious material.

Table 2. Minerals identified in the soil collected from various localities of Tando Muhammad Khan Taluka.

S.No.	Sample Code	Union Council	Coordinates Lat. ºN	Coordinates Long. ºE	Arsenic µg/L	Identified Minerals
1	TMK-1	UC-1	250753	683201	80	Quartz, Calcite (Magnician), Albite (Calcian), Clinochlore, Biotite
2	TMK-2	UC-2	250743	683209	400	Quartz, Albite (Calcian), Dolomite, Clinochlore, Muscovite
3	TMK-4	UC-3	250732	683150	30	Quartz, Calcite (Magnician), Albite (Calcian), Biotite, Rutile, Amesite
4	TMK-5	UC-2	250715	683145	40	Quartz, Calcite (Magnician), Clinochlore, Biotite
5	TMK-6	UC-1	250719	683234	5	Quartz, , Clinochlore, Albite (Calcian), Biotite
6	TMK-7	UC-1	250725	683212	20	Quartz, , Calcite, Clinochlore, Albite (Calcian), Biotite
7	TMK-13	TandoSaindad	250752	683240	30	Quartz, , Clinochlore, Albite (Calcian), Biotite
8	TMK-16	UC-1	250750	683316	400	Quartz, Albite (Calcian), Calcite (Magnician), Clinochlore, Biotite
9	TMK-18	UC-1	250740	683338	150	Quartz, Anorthite, Polylithionite, Clinochlore
10	TMK-19	TandoSaindad	250926	683433	150	Quartz, Albite, Calcite, Chlorite (Serpentinite), Muscovite
11	TMK-23	TandoSaindad	251138	683352	300	Quartz, Calcite (Magnician), Albite (Calcian), Biotite, Clinochlore
12	TMK-24	TandoSaindad	251152	683925	30	Quartz, Calcite (Magnician), Anorthite, Phlogopite, Clinochlore
13	TMK-26	TandoSaindad	250931	683256	10	Quartz, Calcite, Clinochlore, Albite, Phlogopite
14	TMK-41	TandoSaindad	250708	683402	80	Quartz, Albite (Calcian), Phlogopite, Clinochlore
15	TMK-42	TandoSaindad	250707	683410	500	Quartz, Calcite, Albite (Calcian), Phlogopite, Clinochlore
16	TMK-71	Lakhat	250018	683109	250	Quartz, Calcite, Albite, Dolomite, Clinochlore, Biotite
17	TMK-86	Lakhat	250018	683422	0	Quartz, Calcite, Albite (Calcian), Phlogopite, Clinochlore
18	TMK-87	UC-1	250743	683351	5	Quartz, Polylithionite, Calcite (magnician), Albite (calcian). Clinochlore
19	TMK-88	TandoSaindad	250737	683418	200	Quartz, Albite (calcian), Phlogopite, Nitro calcite, Clinochlore
20	TMK-89	TandoSaindad	250811	683341	80	Quartz, Polylithionite, Calcite (magnician), Clinochlore, Albite
21	TMK-90	TandoSaindad	250834	683326	20	Quartz, Polylithionite, Calcite, Anorthite (sodian)
22	TMK-91	TandoSaindad	250839	683343	10	Quartz, Polylithionite, Calcite (magnician), Albite (disordered), Clinochlore
23	TMK-92	TandoSaindad	250946	683331	60	Quartz, Polylithionite, Albite (calcian), Calcite, Clinochlore
24	TMK-93	TandoSaindad	250838	683220	60	Quartz, , Albite (calcian), Calcite, Polylithionite
25	TMK-95	UC-1	250806	683214	0	Quartz, Polylithionite, Albite (calcian)., Calcite, Clinochlore
26	TMK-97	UC-1	250721	683311	60	Quartz, Polylithionite, Albite (calcian). Clinochlore
27	TMK-98	UC-2	250636	683325	300	Quartz, Albite (calcian), Calcite, Clinochlore

28	TMK-99	UC-1	250627	683349	80	Quartz, Polylithionite, Calcite (magnician), Albite (calcian)
29	TMK-100	UC-2	250557	683405	100	Quartz, Calcite (magnician), Anorthite (disordered), biotite
30	TMK-108	TandoSaindad	250808	683503	0	Quartz, Calcite (magnician), Anorthite (sodian), muscovite
31	TMK-110	TandoSaindad	250835	683640	30	Quartz, Polylithionite, Anorthite (disordered), Clinochlore
32	TMK-112	Lakhat	250831	683534	100	Quartz, Calcite (magnician), Albite (disordered), zinnwaldite, Clinochlore
33	TMK- 127	Lakhat	250334	683219	5	Quartz, Polylithionite Calcite (magnician), Albite (disordered), zinnwaldite, Clinochlore
34	TMK- 129	Lakhat	250309	683259	30	Quartz, Calcite(magnician), Albite (calcian), Polylithionite, Clinochlore
35	TMK-135	Lakhat	250008	683134	60	Quartz, Calcite, Anorthite, Biotite, Clinochlore
36	TMK-136	Lakhat	250004	683117	80	Quartz, Polylithionite, Calcite(magnician), Albite (calcian), Clinochlore
37	TMK-138	Lakhat	250056	683111	40	Quartz, Polylithionite, Calcite(magnician), Albite (calcian), Clinochlore
38	TMK-141	UC-1	250815	683317	20	Quartz, Polylithionite, Calcite(magnician), Albite (calcian), Clinochlore
39	TMK-145	UC-2	250644	683244	80	Quartz, Polylithionite, Calcite(magnician), Albite (calcian)
40	TMK-153	TandoSaindad	251056	683603	60	Quartz, Albite (calcian), Calcite

Sample weighing 100 grams (n = 49) was sent to the laboratory for XRD analysis for mineral identification.

2.3. Sediment Analysis

Soil samples were analyzed by a widely used technique of X-ray diffraction (Bish and Post, 1989; Moore and Reynolds, 1997) to determine the crystalline phase of the same. All the samples were scanned through a range of 2θ angles. Variable orientation of the powdered soil provided all possible diffraction directions. The d-spacing of each peak was subsequently obtained by the conversion of diffraction peaks. The conversion of peaks into d-spacing indicated a specific mineral due to the fact that every mineral manifest a distinct set of differing d-spacing. At the end, the d-spacing was compared with standard reference pattern.

3. Results and Discussion

3.1. Mineralogical Characterization of near Aquifer Sediments

Forty-nine representative soil samples were collected from near well sites in three talukas of Tando Muhammad Khan district, where arsenic in groundwater occurs in the range of 10-500 µg/L (Fig. 2). In Tando Muhammad Khand taluka, arsenic varies between 10-500 µg/L in groundwater where about 80% of the wells have arsenic above WHO recommended value (10µg/L) for drinking purpose. On the other hand, 4 out of 6 wells in Bhulri Shah Karim taluka shows arsenic content in the range of 10-200 µg/L. Likewise, all 3 samples of water from Bhulri Shah Karim exceed the WHO guideline value (50-300 µg/L). Soil samples were collected from near these sites where groundwater exhibited the variable content of arsenic. Mineralogical study was carried out using XRD technique which revealed the occurrence of quartz, mica and clay minerals as major components in all collected samples (Table 1-3).

Table 3. Minerals identified in the soil collected from various localities of Bhulri Shah Karim Taluka.

| S. No. | Sample Code | Union Council | Coordinates | | Arsenic µg/L | Identified Minerals |
			Lat. ºN	Long. ºE		
41	TMK-39	Mullakatyar	250633	681808	0	Quartz, Calcite, Albite (Calcian), Phlogopite, Clinochlore
42	TMK-58	Bhulri Shah Karim	245204	682003	150	Quartz, Calcite (Magnician), Biotite, Clinochlore, Albite (Calcian)
43	TMK-66	Allayar Turk	245814	682410	200	Quartz, Calcite, Biotite, Clinochlore, Albite (Calcian)
44	TMK-118	Mullakatyar	245954	682244	10	Quartz, Albite (calcian), Polylithionite, Clinochlore
45	TMK-121	JhannanSoomro	245622	682036	60	Quartz, Calcite (Magnician), Albite (Calcian), Polylithionite
46	TMK-122	JhannanSoomro	245625	682017	80	Quartz, Calcite, Albite (Calcian), biotite

Table 4. Minerals identified in the soil collected from various localities of Taluka Tando Ghulam Hyder.

| S. No. | Sample No. | Union Council | Coordinates | | Arsenic µg/L | Identified Minerals |
			Lat. ºN	Long. ºE		
47	TMK-105	Nazarpur	250354	683622	300	Quartz, Calcite,polylithionite, Albite (calcian), clinochlore
48	TMK-106	Nazarpur	250302	683712	100	Quartz, Calcite (magnician), Albite (calcian), polylithionite, clinochlore
49	TMK-107	Nazarpur	250252	683745	50	Quartz, polylithionite, Calcite (magnician), Albite (calcian), clinochlore

Quartz occurred in all the collected samples while plagioclase feldspar is second frequent mineral group in the order of albite (calcian) >albite>albite (disordered) = anorthite>anorthite (sodian) = anorthite (disordered). Calcite is another dominate member among carbonate minerals which is detected in 40 out of total 49 soil samples. On the other hand, micaceous minerals span between frequency range of 3-38 samples in fine textured soil (silty-clay). These platy minerals varied in the order of clinochlore > polylithionite > biotite > phlogopite > muscovite in the study area. Other rare minerals include amesite, nitro-calcite, rutile and zinnwaldite.

These minerals occurring in the sediments of Tando Muhammad Khan district are mainly derived from western Himalayas during Holocene Period (Giosan et al., 2006). The source of these minerals is basic igneous and metamorphic rocks. Such micaceous minerals are possible source of Fe and arsenic in the sediments of study area. Interestingly, arsenic occurs in the range of 5-600 µg/L in groundwater samples collected from aquifers near to these micaceous sediments (Table 2-4). A study carried out by Seddique et al. (2008) in Bengal deltaic plain explained that arsenic is mainly fixed in silicate minerals as compared to Fe and Mn oxides which host only 5% As. It implies that the silicate minerals are main source of arsenic in the deltaic sediments.

3.1.2. Clinochlore

Clinochlore is a member of chlorite group and is one of the better-known members. A study carried out by Nath et al., (2009)has shown the occurrence of clinochlore in the aquifer

sediments of Bengal basin which is also drained by Ganges, Brahmaputra and Meghna rivers from Himalayas. Clinochlore seems to play a vital role in elevated concentration of arsenic and iron via desorption process in the groundwater of Tando Muhammad Khan district, where its occurrence is more prevalent than biotite and other phyllosilicates (Table 2-4). The occurrence of clinochlore in 36 soil samples from all three talukas of Tando Muhammad Khan district can have substitution of Fe in the cationic sites in the form of Fe^{+2} and /or Fe^{+3}, where a wide range of arsenic (5-500 μg/L) occurs in the groundwater(Mosaferi et al., 2014)

3.1.3. Polylithionite

About half of the collected samples contain polylithionite mineral where most of the aquifers contain arsenic > 20 μg/L (Table 3). Polylithionite is also reported in the sediments of Chandpur district, Bangladesh where almost all the shallow hand tube wells water is highly arsenic contaminated (Ahmed et al., 2008). This mineral is one of the lithium rich mica which is not a better-known mica mineral but its high occurrence in the sediments of Indus delta clued about its less chemical reactivity and abundance in the source area. The occurrence of objectionable arsenic concentration in the aquifers overlying the polylithionitic soil suggests a strong affinity with arsenic with this mineral.

3.1.4. Biotite-Phlogopite

Biotite occurred in the fourteen collected sediment samples from Tando Muhammad Khan and Bhulri Shah Karim talukas and muscovite occurs in three soil samples of Union Council-2 and Tando Saindad. The role of phyllosilicates to serve as As-fixing phase has been pointed out in previous studies (Foster et al., 2000; Breit et al., 2001; (Pal et al., 2002; Ahmed, 2004). Biotite shows more reactive site for arsenic adsorption as compared to muscovite. Likewise, silty mica as compared to sand size provide more effective site for arsenic adsorption. There is an effective role of pH on arsenic adsorption on micas. Studies carried out by Chakraborty *et* al., (2007) and Pal et al., (2002) revealed that silt-sized biotite retained 214 mg/kg of arsenate in circum neutral pH (6.5–7.5). conversely, silt sized.

It can be inferred from these studies that flood plain soil is more prone to retain arsenic as compared to aquifer sediments. Similar pattern is observed in the study area where surface sediments comprises micaceous minerals (muscovite biotite and phlogopite) which are thought to be the good absorbents of metals (Ansari, 1997; sing et al, 2005; Datta and Subramanian, 1997). These minerals absorb As into surface Fe(III) and As rich precipitates (Charlet et al, 2002).

Dissolution and alterations in biotite and muscovite within acidic to alkaline pH region have been investigated by various workers (Kalinowski and Sachweda, 1996; Malmstrom et al., 1996; Turpault and Trotignon, 1994; Samson et al, 2005). Interestingly, biotite provides more reactive surface as compared to muscovite (Farquhar et al, 1997). Moreover, edges of freshly cleaved muscovite surface are more reactive site than crystal face (Zhang and Bailey, 1998; Johnsson et al, 1992). However, the accumulation of arsenic both on edges and to lesser extent on the basal pinacoid of mica is reported by Charlet et al, (2005).

Beside iron sulfides and other primary Fe-bearing minerals, iron (hydro) oxides are pressured to be derived from weathering of micas(Polizzotto et al., 2006). It was observed by Chakraborty et al., (2007)in an experiment that biotite dissolution starts from the crystal's edges inward. Moreover, secondary minerals such as

Fe oxides are precipitated mostly at the edges relative to basal surfaces (Murakami et al., 2003). .Nath et al., (2008) shows that top soils are enriched in arsenic with low Fe-oxyhydroxides that can be compared with the findings of Métral et al. (2008). Chakraborty et al. (2007)explained that Fe(OH)₃ is presumed to be derived from the weathering of mica, iron sulfide and other primary Fe-bearing minerals in the Holocene aquifer sediments where highest arsenic concentrations are reported.

Phlogopite is fourth important micaceous mineral reported in the soil of study area where it is reported in seven soil samples. It is a yellow, greenish, or reddish-brown member of the mica family of phyllosilicates. Phlogopite is also known as magnesium mica which is the magnesium end member of the biotite solid solution series, with the chemical formula $KMg_3AlSi_3O_{10}(F, OH)_2$.

3.1.5.Chlorite

The chlorites are a group of phyllosilicate minerals. Chlorite is major detrital mineral transported through rivers which have been originated from Himalayas (Chakrapani et al., 1995)This mineral is the product of physical weathering which prevails in cold climate (Bockheim, 1982; Campbell and Claridge, 1982)Since the sediments have been sourced from Himalayan region (alpine glacier) and transported through Indus River to reach the deltaic setting, the occurrence of chlorite in high proportion is rational. Contrary to this, kaolinite (indicator of intense chemical weathering) was not detected in any soil sample (Table 2a-c). It implies that monsoon climate was weakened gradually since mid-Holocene and physical disintegration of rocks dominated over chemical weathering (Alizai et al., 2012)A study carried out by (Rasool et al., 2016) in upper reaches of Indus basin (Punjab plain) determined the occurrence of high arsenic groundwater in aerobic aquifers where sediments showed linear relationship to XRD intensity of chlorite. A study carried out in Bengal delta revealed that grey soft clay constitutes chlorite beside other minerals(Pal and Mukherjee, 2009)

3.1.6. Calcite

Calcite is reported to occur in 40 sediment samples (n =49) which is expected to be derived by the weathering of limestone beds of Eocene age which are cropping out in Ganja Hills located on the western bank of River Indus near study area. Moreover, calcite_magnesiun occurs more frequently as compared to calcite which is attributed to one of the important magnesium sources in the aquifers of Tando Muhammad Khan district. Nitro calcite is found in a sample collected from an irrigated well in agricultural land of Tando Saindad Union Council, where groundwater contained 200 μg/L arsenic. Although dolomite is reported only in two samples of UC-2 and Lakhat but a good correction has been observed with aqueous arsenic where groundwater contains 400 and 250 μg/L arsenic respectively.

Calcite is the major carbonate mineral in study area which suggests its proximal source due to the fact that carbonate minerals are less resistant against chemical weathering (Garrison, 1981)As a result, the transportation of calcite as residual grain from Himalayas to the Indus deltaic plain is not possible. Hence, the source of calcite is weathering of Laki limestone occurring in the proximity of Indus river in study area. The calcite contains 1-8 mg/kg of arsenic in it whereas dolomite host As < 3 mg/kg (Boyle and Jonasson, 1973). Likewise, limestone hosts about 2.6 mg/kg of arsenic (Baur and Onishi, 1969). Hence, these carbonate minerals are serving as potential minerals to adsorb As in calcareous soils,

where calcite plays a vital role in retention and solubility of arsenic (Mehmood et al., 2009).

4. Conclusion

Present study has revealed the occurrence of large number of Phyllosilicates which are also reported from Bengal delta plain in the fine fractions of the soil. These minerals included clinochlore, polylithionite, biotite and phlogopite as major platy minerals. These fine silicates are serving as main source of arsenic in the deltaic setting either by sorbing the arsenic or hosting this metalloid into their structure. Upon prevalence of anoxia caused by bacteria mediated organic matter decay, these minerals release their sorbed or structural arsenic into the water which reaches the aquifer depth upon infiltration. Calcite is major carbonate mineral which is serving as arsenic host. Further studies are required to assess the chemistry of soil and aquifer sediments to better explain the source and mechanism of arsenic mobilization in shallow alluvial aquifers of the deltaic system.

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6. References

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