

MINERALOGICAL STUDY OF SEDIMENT SAMPLES OF KACHUA, CHANDPUR DISTRICT FOR INVESTIGATION OF ARSENIC BEARING MINERALS

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ABSTRACT

Sixteen sediment samples of different depth (up to 122 m) were studied by X-ray diffraction (XRD) method. The samples were collected from a test borehole, which was drilled by Bangladesh Water Development Board (BWDB) at Kachua, Chandpur district. All the samples were characterized and different minerals have been identified in the samples. Quartz is the major mineral and was found to be in the range of 54.97 - 97.88 %. Two arsenic bearing minerals namely, iron arsenate, $\text{Fe}_2\text{As}(\text{AsO}_4)_3$ and arsenic selenide telluride, $\text{AsSe}_{0.5}\text{Te}_2$ were found in the samples of depth 55.20 m and 100.60 m, respectively. Bangladesh Atomic Energy Commission (BAEC) in collaboration with the United States Geological Survey (USGS) conducted the groundwater sampling campaign for shallow and deep tubewells in Kachua upazila. From the hydro-chemical results, the concentrations of arsenic in shallow tubewells were found above the maximum permissible limit (50 ppb). Concomitantly, the mineralogical study of sediment samples in the same area reflects that the shallow aquifers of Kachua upazila are contaminated by arsenic due to the presence of arsenic bearing minerals.

INTRODUCTION

Clean drinking water supply is a basic requirement in primary health care in Bangladesh and groundwater is the dominant source of it. During the last 30 years about 4 million hand tubewells were installed in shallow aquifer to provide pathogen free drinking water.⁽¹⁾ Simultaneously, for self-sufficiency in food, the cultivation of high yielding variety of rice spread all over the country and large number of deep and shallow tube wells for irrigation were sunk. Most of shallow tubewells are reported contaminated with arsenic.^(1,2) Arsenic, in general, occurs widely in natural environments (air, soil, rock & minerals, and water). Scientists agree that in Bangladesh the cause of arsenic is natural (geogenic) and that it is not introduced by human activity such as mining. More than 100 arsenic bearing minerals are present and the most common are arsenopyrite (FeAsS), realgar (AsS) and orpiment (As_2S_3).⁽³⁾ Other minerals containing arsenic as accessory component are also well-known, such as pyrite and iron-hydroxides.

There are several fundamental factors in the processes of arsenic release into groundwater: one is the mineral, which bears arsenic. The second one is the environmental changes by which arsenic is released. The third one is groundwater chemistry and movements. The Japan International Cooperation Agency (JICA) team suggests that the disassociation of ferric oxy-hydroxide and release of iron and arsenic ion into groundwater occur under reduction condition.⁽⁴⁾ The dissolved arsenic migrates along with the movement of groundwater. The work done by the BWDB-GSB-USGS (BWDB interim report, 2003) suggests that high concentration of arsenic in the holocene sediments could be attributed to the dissolution of residual iron oxides.⁽⁵⁾ The low dissolved iron content is inconsistent with reductive dissolution. The arsenic enrichment of altered micas supports the association with phyllosilicates in reduced sediments.

In this context, a fundamental mineralogical study was envisaged to identify the arsenic bearing minerals in sediment. X-ray diffraction (XRD) is a versatile non-destructive analytical technique for qualitative identification and quantitative estimation of the various crystalline forms present in powdered or solid samples.⁽⁶⁾ In the present study XRD method was used to identify the arsenic bearing minerals in underground sediment of arsenic affected area of Kachua upazila under Chandpur district.

DESCRIPTION AREA

Kachua upazila under the Chandpur district is considered as highly arsenic affected area. Almost all the shallow hand tubewells water are highly arsenic contaminated. The test hole drilling site was selected at village Srirampur, Union-Karaia. Kachua Upazila

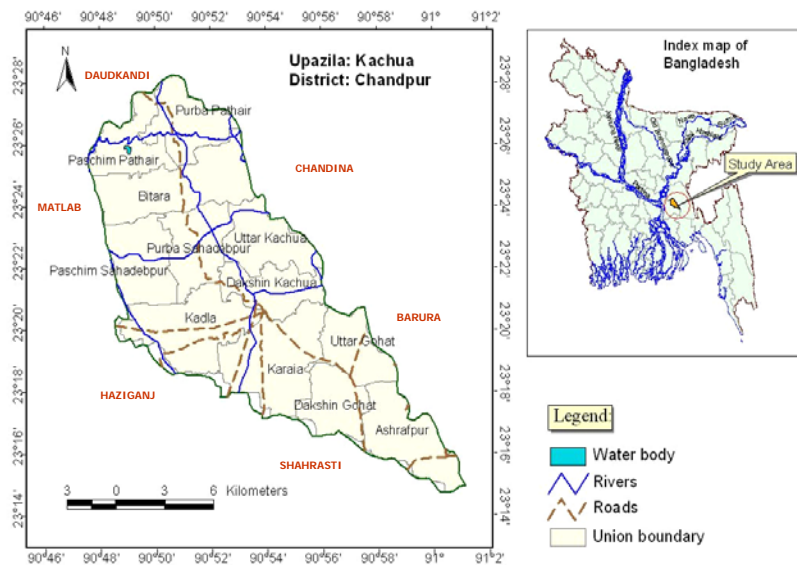


Fig. 1. Location Map of the study area.

area lies between 90°47'70" and 91°01'10" E longitude and 23°14'40" and 23°28'20" N latitude covering an area of about 160 km² with population of about 0.30 million. The

study area of Srirampur village is located at 23°33'49.9" N latitude and 90°89'36.3" E longitude. The location map of study area is shown in Fig. 1. The average annual rainfall in and around the study area is about 2000 mm in which about 97% is received between May and October. The temperature during pre-monsoon period is the highest and rise up to 33°C in April. Relative humidity is high throughout the year with average 95%. It is lowest in February (71%).

SAMPLE COLLECTION AND PREPARATION

A test hole was drilled by Groundwater Hydrology, Bangladesh Water Development Board (BWDB) down to 326 m to assess the sediment lithology, formation thickness and aquifer properties in the study area. EDECO strata Drill Rig was used to collect the sediment samples applying the direct hydraulic rotary method. A heavy duty mud pump, FJ casings of 152 mm dia, 76 mm dia NW drilling rod, 140 mm dia carbide and roller bits, split spoon and Denison samplers of 76 mm dia etc. were used during drilling process. A number of sediment samples were collected in PVC liner. A few samples were also collected in polythene bags, which were of wash boring.

For mineralogical study purposes, the sediment samples were collected at different depth down to 122 m. At first the collected samples were dried in an oven by fixing the temperature 65°C. After the samples become moisture free, about 5g sample was grinded to fine powder in an agate mortar and pestle to get an average particle size < 50 µm. An aluminum sample holder with a central groove of 15 × 10 × 1 mm³ dimension was used as a sample holder and the fine powdered sample (1g) placed into the groove. The surface of the sample was made sufficiently smooth using glass slide.

AQUIFER SYSTEM IN THE STUDY AREA

A lithological cross-section is drawn based on borelogs of BWDB and GSB and is presented in Fig. 2 to observe the formation thickness as well as aquifer system in the area. The aquifer system at the study site can be divided into three fairly distinct systems. The upper aquifer system or 1st aquifer is essentially the shallow aquifer, the middle or 2nd aquifer system has generally been called the deep aquifer and the deeper system or the 3rd aquifer is newly discovered at this site.

Aquiclude: The upper clay and silty clay layer, thickness varies from 5 to 7 m, is generally grey to light grey in colour and characterized by high porosity and low permeability.

First or shallow aquifer: The shallow aquifer extends down to a thickness that varies between 35 and 70 m. The aquifer sediments are composed of sand with lenses of clay. Water within this shallow aquifer is severely contaminated by arsenic.

Second or deep aquifer: The second aquifer system extends beneath an aquiclude underlying the shallow aquifer down to 290 to 300 m depth. This deep aquifer is hydraulically connected throughout the depth and is separated from the deeper or 3rd aquifer system by a confining layer of considerable thickness. The aquifer is composed

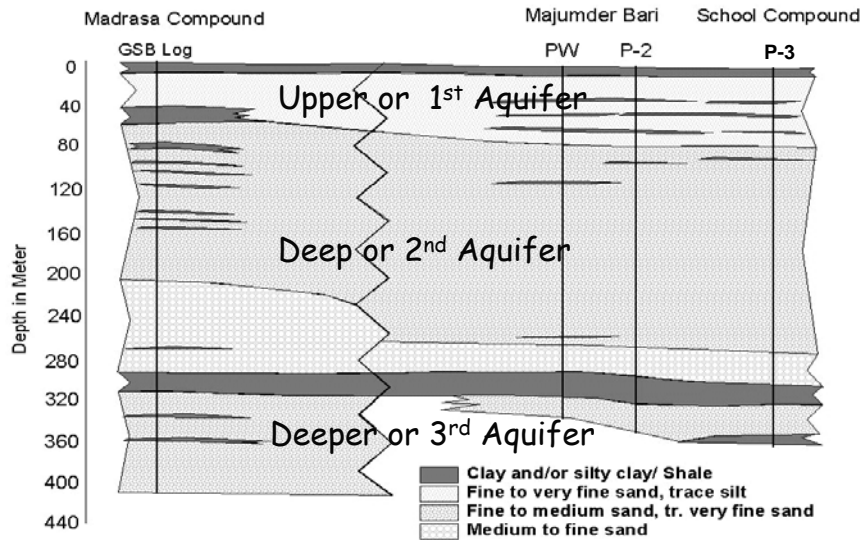


Fig. 2. Aquifer system in Srirampur area, union-Karaia, upazila-Kachua, Chandpur District (Source: BWDB).

mainly of fine to medium sand, gray to light brown in color, occasionally inter-bedded with clay bends. The thickness of this formation varies between 145 and 180 m. The lower part of the upper aquifer consists mainly of grey medium to fine sand and extends down to 285 to 295 m underlain by silty clay bed. The thickness of this part ranges between 40 and 85 m. Although the deep aquifer appears to be free of arsenic, in some areas and depths high concentrations of salt, iron, or manganese makes it unsuitable for drinking purposes.

Third or deeper aquifer: Below 10 to 15 m thick silty clay/shale bed the deeper (lower) or 3rd aquifer was encountered, composed mainly of grey to dark grey fine to medium sand in places alternated with thin sandy shale/clay lenses. This deeper aquifer below 285 to 295 m from surface is assumed to be sustainably safe and potential for good quality groundwater.

EXPERIMENTAL SYSTEM

A Philips X'Pert PRO X-ray diffractometer was used to get X-ray data for the samples at the Materials Science Division, Atomic Energy Centre, Dhaka, with a primary beam power of 40 kV and 30 mA for Cu radiation. A nickel filter was placed before the

sample to reduce CuK_β radiation and finally CuK_α radiation was only used as the primary beam. A θ - 2θ scan was taken from 10 to 100° to get possible fundamental peaks of the minerals present in the sample with the sampling pitch of 0.02° and time for each step data collection was 0.6 sec. Three different samples of each depth were irradiated to get sufficient data. The XRD machine was totally computer controlled and all the data were stored in the hard disk memory of the computer for further analysis.

All the X-ray data of the sediment samples were analysed using computer software X'Pert Highscore to get the interplanar spacing d value of the fundamental peaks and their integrated intensity. The interplanar spacing d was calculated using the formula $2d \sin\theta = \lambda$, where λ is the wavelength of the incident radiation and for $\text{Cu}(\text{K}_\alpha)$, $\lambda = 1.54178\text{\AA}$. All the minerals were identified correctly and their amounts were estimated within the error of maximum $\pm 1\%$ using XRD method. Concentration of each mineral has been calculated using the following standard method.⁽⁷⁾ The background of the system has been determined and subtracted from the total intensity data. The total detected minerals in a sample were considered 100 per cent. Only one peak for a single mineral was selected which has the maximum peak intensity (100% of I) among all the peaks for that particular mineral. Total integrated intensity for a particular peak was calculated using the following formula^(7, 8)

$$I_A = I_P \times \text{FWHM} \quad (1)$$

where I_A is the integrated intensity of a particular peak, I_P is the peak intensity of that particular peak and FWHM is the full width at half maximum of the peak. Again,

$$I_T = (I_1 + I_2 + I_3 + \dots + I_n) = \sum I_A \quad (2)$$

where I_T is the total integrated intensity of the detected minerals and $A = 1, 2, 3, \dots, n$. The concentration of a particular mineral is calculated by

$$C_A = (I_A/I_T) \times 100 \quad (3)$$

where C_A is the concentration of a particular mineral in the sample in weight percent.

RESULTS AND DISCUSSION

Fig. 3 shows an XRD pattern of sediment sample of IHD-12 with depth 55.2 m. In the figure, d -values were shown in the parenthesis and peaks of the minerals were identified as quartz (Q), albite (A) and iron arsenate (FeAs). The following minerals were found in the sediment samples namely, quartz, illite, albite, polyhalite, clinocllore, calcium aluminum silicate, polyolithionite-3T, sodium calcium aluminum silicate, iron arsenate and arsenic selenide telluride. The mineralogical summary of 16 sediment samples is given in Table 1. The weight percentage of quartz was found to be in the range of 54.97 - 97.88 % as the major mineral present in the sediment samples of the test borehole at Srirumpur, Kachua, Chandpur. The weight percentage of albite was present in the range of 1.49 - 29.36% as the second mineral in the samples. Two arsenic bearing minerals are found in two different depths. These two minerals, such as, iron arsenate, $\text{Fe}_2\text{As}(\text{AsO}_4)_3$ and arsenic selenide telluride, $\text{AsSe}_{0.5}\text{Te}_2$ were found in the depth of 55.20

and 100.60 m, respectively. As seen from the lithological description of test hole, these two sediment layers are composed of very fine sand to fine sand having trace of mica, silt and some dark minerals. The weight percentages of iron arsenate and arsenic selenide telluride were 1.60 and 2.12 %, respectively. Though their concentrations were observed in minor amount, but it shows the presence of arsenic bearing minerals in the sediment.

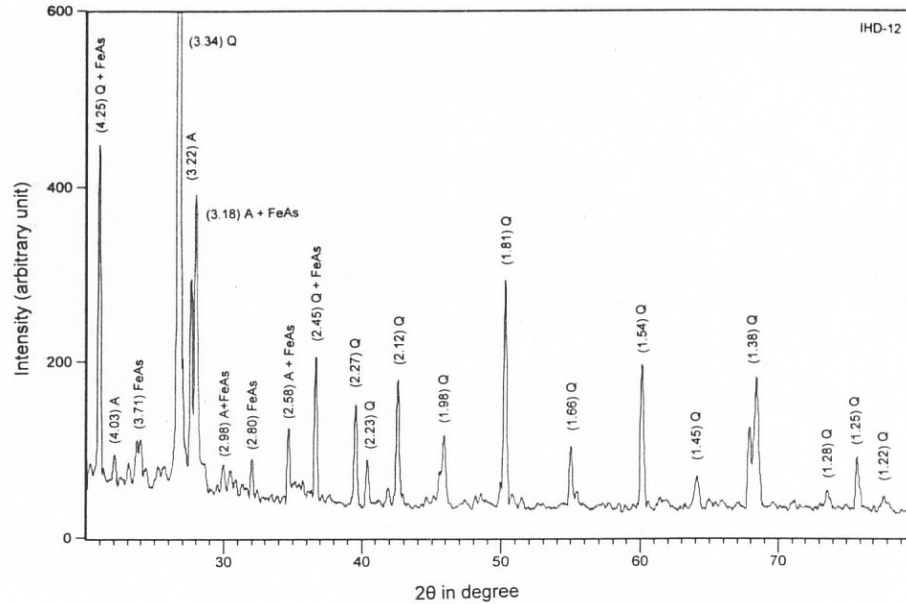


Fig. 3. XRD pattern of IHD-12 with depth 55.2 m. containing iron arsenate.

The two dominant minerals, such as, quartz and albite were plotted with respect to depth, as seen in Figs. 4 and 5. In the case of quartz, it shows the higher concentration (89 wt.%) near the surface and shows the decreasing trend (minimum concentration 55 wt.%) up to the depth 25.0 m. Below 25.0 m, it has an increasing tendency both in the shallow and deep aquifer zone and the quartz concentration increases in the range of about 77 - 98 wt.%. The maximum quartz value (97.88 wt.%) was found in 100.6 m depth i.e. in the deep aquifer zone. In this same depth the arsenic bearing mineral named arsenic selenide telluride is combined.

Though the albite concentration does not follow the regular trend with respect to the depth, but it shows some variation in concentration within the band of 4 - 19 wt.% in the same trend towards downward (Fig. 5). The maximum concentration of albite (29.36 wt.%) was observed in the depth 15.2 m and simultaneously the quartz concentration was found 64.97 wt.%.

Table 1
Mineralogical summary of sixteen sediment samples collected from a test borehole of
Srirampur, Kachua upazila

Sample ID	Depth (m)	Minerals	Chemical formula	Conc. (wt. %)	Conc. (gm/kg)
IHD-01	3.05 –3.66	(1) Quartz Low	SiO ₂	87.90	879.00
		(2) Illite	2K ₂ O.3MgO.Al ₂ O ₃ . 24SiO ₂ .12H ₂ O	4.54	45.40
		(3) Clinocllore	Al-Fe-SiO ₂ -OH	7.56	75.60
IHD-15	9.15	(1) Quartz	SiO ₂	89.76	897.60
		(2) Albite	NaCaAlSi ₂ O ₇	2.54	25.40
		(3) Orthoclase	K(Al,Fe)Si ₂ O ₈	7.70	77.00
IHD-02	15.25	(1) Quartz	SiO ₂	64.97	649.70
		(2) Calcium aluminum silicate	CaO.Al ₂ O ₃ .2SiO ₂	5.67	56.70
		(3) Albite	Na(AlSi ₃ O ₈)	29.36	293.60
IHD-14	24.4	(1) Quartz low	SiO ₂	54.97	549.70
		(2) Polyolithionite- 3T	K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂	22.08	220.80
		(3) Polyhalite	2CaSO ₄ .MgSO ₄ . K ₂ SO ₄ .2H ₂ O	22.95	229.50
IHD-03	30.5	(1) Quartz	SiO ₂	67.47	674.70
		(2) Sodium calcium aluminum silicate	NaCaAlSi ₂ O ₇	32.53	325.30
IHD-11	40	(1) Quartz	SiO ₂	84.64	846.40
		(2) Albite low	Na(AlSi ₃ O ₈)	15.36	153.60
IHD-04	49	(1) Quartz	SiO ₂	95.35	953.50
		(2) Albite	Na(AlSi ₃ O ₈)	4.65	46.50
IHD-12	55.2	(1) Quartz	SiO ₂	80.58	805.80
		(2) Albite low	Na(AlSi ₃ O ₈)	17.83	178.30
		(3) Iron arsenate	Fe ₂ As(AsO ₄) ₃	1.60	16.00
IHD-05	70.4	(1) Quartz	SiO ₂	89.29	892.90
		(2) Albite	Na(AlSi ₃ O ₈)	10.71	107.10
IHD-13	76.2	(1) Quartz low	SiO ₂	94.45	944.50
		(2) Albite high	Na(AlSi ₃ O ₈)	5.55	55.50
IHD-06	82.3	(1) Quartz low	SiO ₂	76.96	769.60
		(2) Illite	2K ₂ O.3MgO.Al ₂ O ₃ . 24SiO ₂ .12H ₂ O	6.99	69.90
		(3) Albite high	Na(AlSi ₃ O ₈)	16.06	160.60
IHD-07	91.5	(1) Quartz	SiO ₂	93.07	930.70
		(2) Albite high	Na(AlSi ₃ O ₈)	6.93	69.30
IHD-08	100.6	(1) Quartz low	SiO ₂	97.88	978.80
		(2) Arsenic selenide telluride	AsSe _{0.5} Te ₂	2.12	21.20
IHD-16	106.7	(1) Quartz	SiO ₂	88.87	888.70
		(2) Orthoclase	K(Al,Fe)Si ₂ O ₈	9.63	96.30
		(3) Albite high	Na(AlSi ₃ O ₈)	1.49	14.90
IHD-09	112.8	(1) Quartz low	SiO ₂	94.90	949.00
		(2) Proustite	Ag ₃ AsS ₃	0.49	4.90
		(3) Albite	Na(AlSi ₃ O ₈)	4.61	46.10
IHD-10	122.25	(1) Quartz low	SiO ₂	91.38	913.80
		(2) Albite high	Na(AlSi ₃ O ₈)	8.62	86.20

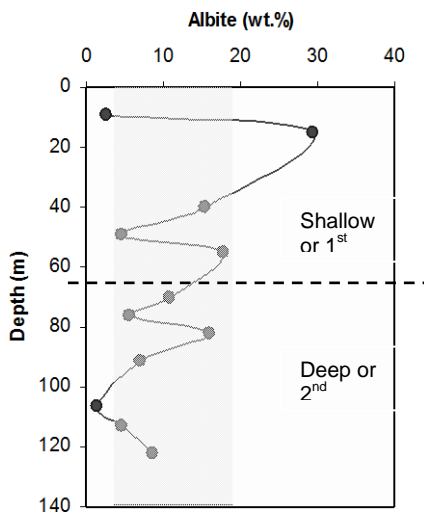


Fig. 5. Vertical distribution of albite (wt.%) in the sediment.

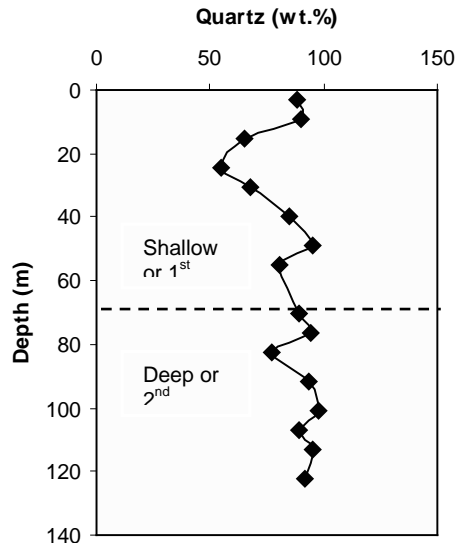


Fig. 4. Vertical distribution of quartz (wt.%) in the sediment.

The findings of the mineralogical compositions are contrasted with the arsenic concentrations of the water samples of the shallow and deep aquifers of the same Karaia union and the vicinity unions of Kachua upazila. These water samples were collected under the joint collaboration work of Bangladesh Atomic Energy Commission (BAEC) and United States Geological Survey (USGS). The vertical distribution of As in the shallow and deep aquifers has been plotted as shown in Fig. 6.

From Fig. 6 it is observed that the tubewells (depth range 18 - 56 m) in the shallow aquifer zone are highly arsenic contaminated. It is seen that most of the deep wells (depth range 125 - 280 m) are free from As contamination. Only three deep tubewells in the central part of Kachua upazila are found As concentration higher than the Bangladesh standard value 50 ppb. The high As contents in these three deep wells are, namely in Kachua south (As = 115 ppb and well depth, D = 137 m), in Kadla (As = 201 ppb and D = 128 m), and in Karaia (As = 364 ppb and D = 220 m).

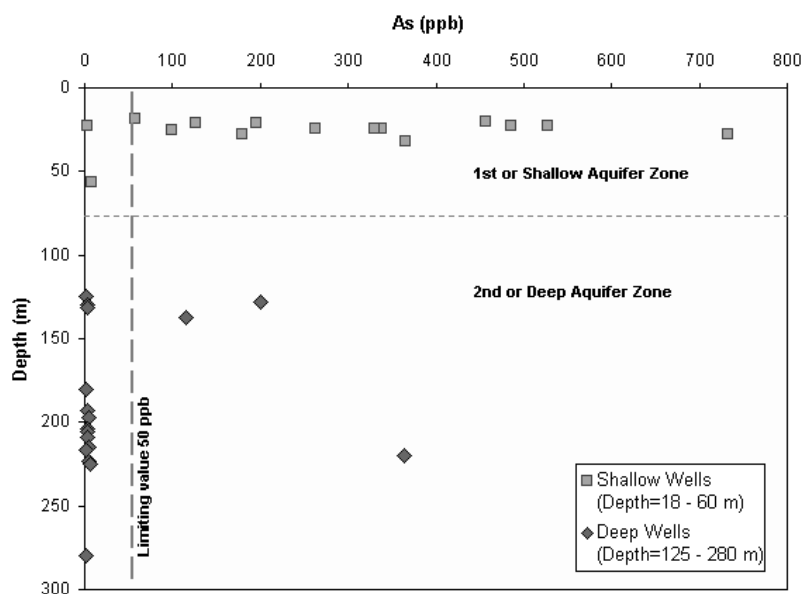


Fig. 6. Distribution of arsenic concentration in groundwater of shallow and deep aquifer zone.

To correlate the arsenic concentration of water with sediment samples, chemical analysis (XRF) has been performed on three different samples of IHD-12, IHD-08 and IHD-09 with depth of 55.2, 100.6 and 112.8 m, respectively and data are listed in Table 2 along with XRD data after calculation. In three different sediment samples, concentration of arsenic (in wt. %) in chemical method are in fairly good agreement with the XRD data. Fig. 7 shows XRD pattern of another arsenic bearing sediment sample of IHD-08 with depth 100.6 m, which contains arsenic selenide telluride.

Table 2
Chemical analysis (XRF) data of arsenic for three arsenic bearing sediment samples along with XRD data

Sample	Minerals	Chemical formula	Arsenic concentration in wt. %	
			Chemical data (XRF)	XRD data*
IHD-12	Iron arsenate	$\text{Fe}_2\text{As}_4\text{O}_{12}$	0.63	0.79
IHD-08	Arsenic selenide telluride	$\text{AsSe}_{0.5}\text{Te}_2$	0.38	0.43
IHD-09	Proustite	Ag_3AsS_3	0.05	0.07

* Wt. % of arsenic after calculation.

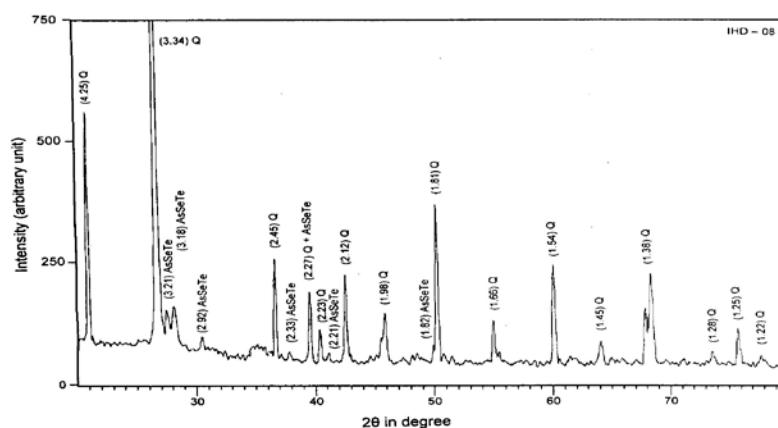


Fig. 7. XRD pattern of IHD-08 with depth 100.6 m. containing arsenic selenide telluride.

CONCLUSION

The clay mineral fraction (found in depth 3.2, 49.0, 60.0 and 82.0 m) is dominated by quartz and albite with minor illite and clinocllore. The sediment as a whole is dominated by quartz and albite. From the mineralogical study by XRD method of the sediment samples of Srirampur, Kachua, it is observed that the arsenic bearing minerals are found to be exist in the shallow and deep aquifer zone. As surveyed under the joint collaboration work of BAEC and USGS, the high arsenic contents are also identified in the groundwater of shallow tubewells and in a few deep wells in Kachua area.

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APPENDIX

Peak position (2θ), d value and intensity ratio of three arsenic bearing minerals, where $\lambda=1.54178 \text{ \AA}$.

Iron arsenate $\text{Fe}_2\text{As}_4\text{O}_{12}$			Arsenic selenide telluride $\text{AsSe}_{0.5}\text{Te}_2$			Proustite Ag_3AsS_3		
2θ in degree	d value in \AA	Intensity ratio in %	2θ in degree	d value in \AA	Intensity ratio in %	2θ in degree	d value in \AA	Intensity ratio in %
20.90	4.25	60	27.72	3.21	85	27.27	3.27	80
21.87	4.06	40	28.01	3.18	100	28.15	3.17	70
23.26	3.82	60	30.55	2.92	19	28.70	3.11	70
23.99	3.71	100	38.59	2.33	24	32.68	2.74	100
24.30	3.66	50	39.49	2.28	18	35.19	2.55	80
27.86	3.20	50	40.70	2.21	25	36.22	2.48	90
28.05	3.18	30	50.08	1.82	11	40.63	2.22	40
29.89	2.98	60				46.07	1.97	40
31.96	2.80	80				47.34	1.92	40
34.63	2.58	45				49.25	1.85	30
36.68	2.45	80				55.34	1.66	30
41.34	2.18	90				58.40	1.58	30

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