Groundwater arsenic contamination – a multi directional emerging threat to water scarce areas of Pakistan

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Abstract Groundwater arsenic contamination has exponentially endangered the human life and complicated the efforts for obtaining and maintaining drinking water quality standards in Pakistan, particularly in the central and southern parts of the country. In the province of Sindh, groundwater arsenic concentration has reached up to 1100 µg/l against WHO limits of 10 µg/l. In the province of Punjab, over 20% and in the province of Sindh, around 36% of the population is exposed to arsenic contamination above WHO limits. Therefore, keeping in view the catastrophic situation, study on arsenic prevalence in the small village *Bhutewan* (which fulfils all the prerequisites for arsenic prevalence) district Rahim Yar Khan, Pakistan was carried out. During the year 2004, 13 water sources were tested having depth ranging from 14-50 m and the arsenic contamination between 150 µg/l to 400 µg/l was found in all the 13 water samples with minimum concentration of 50 µg/l at 45 m depth and maximum arsenic concentration of 400 µg/l at 13 ft. positive correlation between Fe concentration and arsenic concentration in samples indicated the reductive dissolution of arsenic bearing iron (hydro)oxides. In 2005, with the collaboration of UNICEF, 19307 water sources were tested in district Rahim Yar Khan and it was observed that out of 19307 samples, 9644 samples were within the safer limits <10 µg/l (49.95%) and the rest of 9663 samples (50.05%) were found with varying arsenic concentration from 20 µg/l to 500 µg/l. This paper is a part of the effort to evolve and develop a community based, sustainable arsenic mitigation system by establishing spatial and temporal prevalence of arsenic in the study area.

Key Words: Groundwater quality, arsenic contamination, soil strata, geochemical.

INTRODUCTION

Arsenic contamination has emerged as a serious public health concern in Pakistan. Occurrence of arsenic in natural water is dependent on the local geology, hydrogeology and geochemical characteristics of the aquifer, and climate changes as well as human activities. Natural sources of arsenic in water has been attributed to several natural geochemical processes, including oxidation of arsenic-bearing sulfides, de-sorption of arsenic from (hydro)oxides (e.g., iron, aluminum and manganese oxides), reductive dissolution of arsenic-bearing iron (hydro)oxides, release of arsenic from geothermal water, and evaporative concentration, as well as leaching of arsenic from sulfides by carbonates (Kim et al., 2000, Bennett and Dudas, 2003. Worldwide reported arsenic concentrations in natural water vary from 0.00002 mg/l to greater than 5 mg/l (Cullen and Reimer, 1989 and Smith et al., 2002).

Many countries in the world especially in Asia e.g., Bangladesh, India, Nepal, Vietnam, China and Myanmar are facing an arsenic problem and it has been recognized as a big threat and challenge to public health. Pakistan, following the arsenic crisis in Bangladesh and other neighbouring countries, has recognized the need of assessing drinking water quality for arsenic contamination. In this regard, the Government of Pakistan has undertaken many initiatives with the assistance from UNICEF since 1999. As a result of these initiatives, the presence of arsenic contamination has been recognized and consequently an arsenic mitigation programme, at national level has already been launched by the government of Pakistan with the assistance being provided by UNICEF. (Tameez et. al 2004). Alarming levels of ground water arsenic concentration has been observed during the course of water quality surveys conducted by PCRWR during 2001, 2003 and 2004 (PCRWR, 2004). District Rahim Yar Khan has been declared as worst hit arsenic contamination area. In this paper, conclusions of study on arsenic prevalence in the district of Rahim Yar Khan with the special focus on union council Rasul Pur (Punjab province, Pakistan) is shared on arsenic occurrence pattern in time and space dimensions.

Site Characteristics:

The union council Rasul Pur is situated near River Indus (4-6 km). This is an area where cotton, sugarcane are the main crops fruits like mango, orange are also cultivated. This indicates use of tremendous amount of fertilizers and pesticides. The location map is shown in Figure- 1.

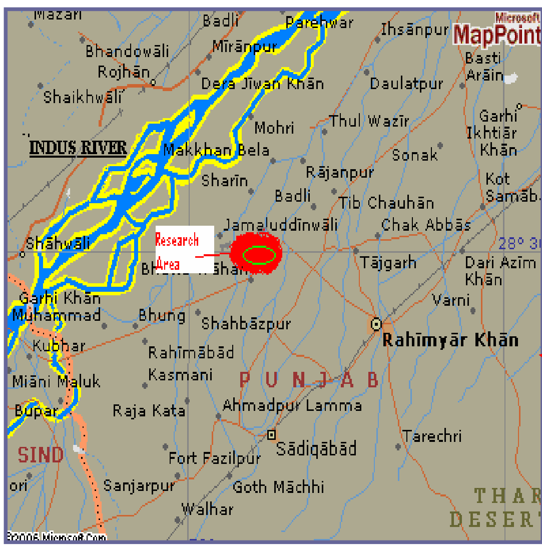


Figure 1 Location Map of research area (source: Microsoft power point website)

Union Council Rasul pur of district Rahim Yar Khan has been earmarked, where the arsenic contamination had been observed up to 500 µg/l, for carrying out subject research programme. Sampling points were selected on the basis of evidence regarding the presence of arsenic in specific areas. Uniform site selection criteria will be adopted and a grid size of 0.25 km^2 (0.5x0.5) was adopted. A distance of 0.5 or 1 km was maintained between the two monitoring points.

Arsenic concentrations were measured in the field using the Merck field-test kit. Arsenic concentrations in some of these samples were also analysed in lab by using hydride generation with Analyticjena Atomic Absorption Spectrophotometer (AAS). Some of samples were also analysed for Fe content by using same AAS.

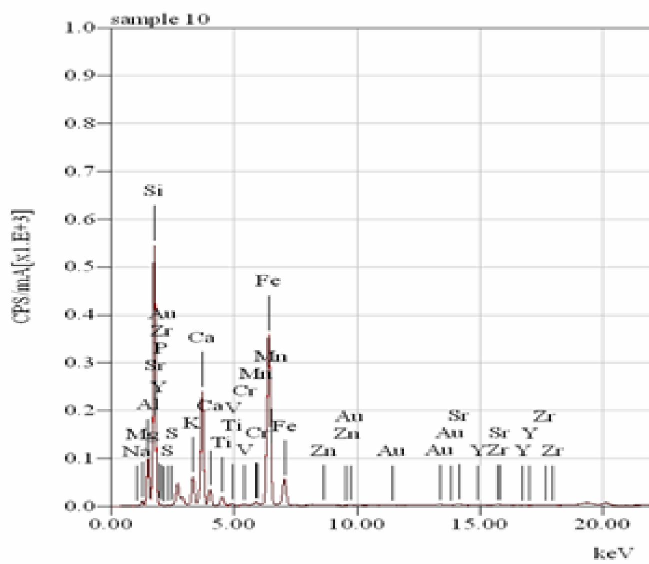
The first set of arsenic contamination testing was carried out from 13 water sources tube wells, hand pumps and shallow wells in research area, during the month of September, 2004.

Out of thirteen samples, two samples were tested with Atomic Absorption Spectrometer (highlighted with bold face). The test results are shown in Table-1 & Figure 2.

Table-1 Arsenic contamination testing results – September, 2004

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Depth(ft)	65	70	45	70	70	70	150	70	70	65	60	70	65
As Conc(µg/l)	200	300/**275**	400/**350**	200	150	200	50	200	200	200	180	180	200
Fe (mg/l)	1.39	0.32											

A bore hole was carried out for soil analysis by energy dispersive X-Ray florescence Spectrometer (XRF) Equipment. The elemental results are shown in Figure 2



Elm.	ms%	mol%	Sigma	Intensity	K.ratio
Na	1.2127	1.7015	5.8216	961	0.002494
Mg	3.6644	4.8618	0.6634	11943	0.011297
Al	13.7529	16.4415	0.0944	131001	0.056521
Si	43.0412	49.4327	0.1156	773412	0.177183
S	0.09	0.0905	0.036	2748	0.000406
K	5.1373	4.2379	0.09	95568	0.025441
Ca	17.8142	14.337	0.0722	432583	0.089799
Ti	1.2141	0.8176	0.0455	35567	0.00568
V	0.0252	0.0159	0.0389	858	0.000133
Cr	0.09	0.0558	0.0321	4131	0.000544
Mn	0.1585	0.0931	0.0298	7782	0.00101
Fe	13.5703	7.8381	0.0279	779509	0.091914
Zn	0.0214	0.0105	0.0275	1516	0.000174
Sr	0.0911	0.0335	0.0331	8303	0.00162
Y	0.0151	0.0055	0.0352	1338	0.000292
Zr	0.0542	0.0192	0.0386	5372	0.001141

Figure 2: The elemental constituents of soil sample at 50 feet depth of bore hole

There were total 10 samples which were investigated through XRF, the summary of results and soil profile showing concentration of various elements are shown in Figure 3.

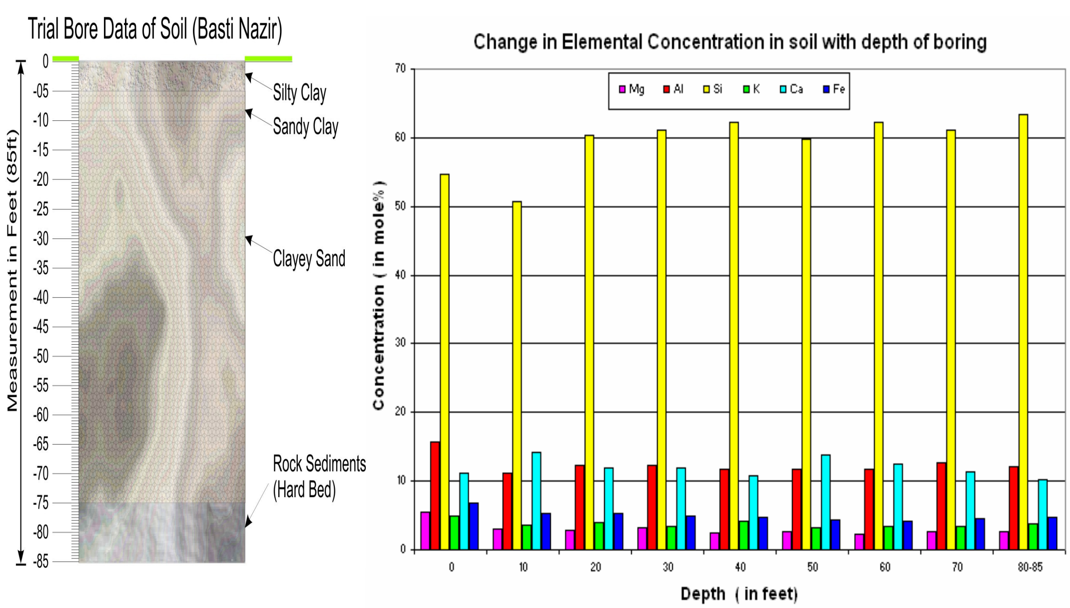


Figure 3 Soil strata profile and elemental constituents found during XRF analysis

The second set of testing was carried out in the month of May , 2005 (before the monsoon season). This time 46 water sources in the same area were tested with the additional information, as shown in the Table 2 and graphically depicted in Figure 4.

Table-2: Arsenic contamination survey results- May , 2005

Location	Distance from Ref points (km)	No samples	Source	Depth (ft)	Arsenic concentration (µg/l)
Basti Nazir	0	4	Rotor pump	65-70	100,80,100,100
Budu Wali	1	10	Rotor , HP	50- 80	2x10,80,50,5x100,80,10
Umer Kot	0.5	3	Rotor pump	60-80	50, 80, 100
Basti Madu	1	2	HP	50-55	40, 40
Basti Baloch	1	4	HP	55-70	100,100,100,100
Basti Korian	1	4	Rotor Pump	60 -200	60, 3x80
Basti Dudi	1.5	2	Rotor Pump	70	2x80
Basti Kalar	0.5	2	Rotor Pump	60-80	60, 100
Basti M. Bux	0.5	2	HP	60	40, 100

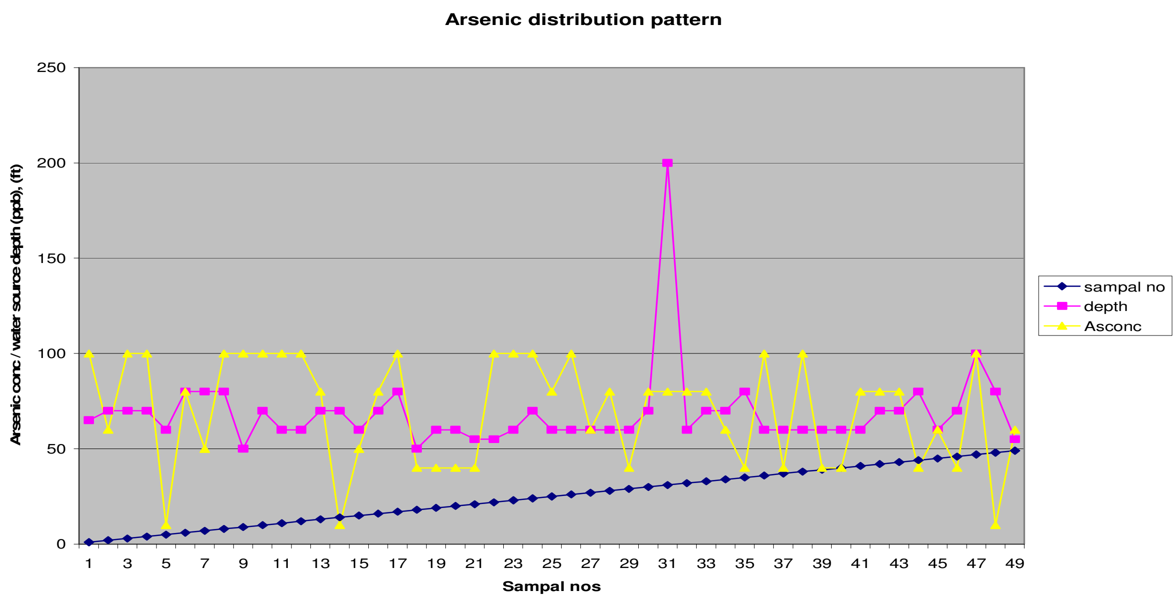


Figure-4 Graphical representation of 2nd set of test results-May 2005

On the basis of the results of Arsenic survey carried out in 2004 in the suspected villages of District Rahim Yar Khan, hence arsenic blanket testing survey was carried out in 2005 with help of UNICEF, Lahore office -Pakistan.

The arsenic testing results shown in table 3 indicates prevalence of arsenic in ground water in the entire district of Rahim Yar Khan. Out of 25000 water sources tested, 13440 water sources (53.76%) have been found contaminated with arsenic concentration > 20 ppb. This is a catastrophic situation which necessitates immediate arsenic mitigation measures in the form of short and long term strategies to address this problem. This arsenic contamination in the area may likely be got transferred into food chain due to use of arsenic contaminated ground water (only reliable source) for agriculture purposes and for live stock.

Table-3: Arsenic contamination survey results of District Rahim Yar Khan- UNICEF, 2005.

	Level of Arsenic contamination is as under:									
Tehsil	**<10**	**20-40**	**50**	**60-80**	**100**	**100-200**	**200-300**	**300-400**	**400-500**	**Total**
RYK	5306	2260	936	576	580	327	210	51	37	10283
KNP	5573	3119	2053	716	1281	520	149	28	4	13443
SDK	681	335	76	47	78	16	38	1	2	1274
Total	**11560**	**5714**	**3065**	**1339**	**1939**	**863**	**397**	**80**	**43**	**25000**
% age	46.24%	22.86%	12.26%	5.36%	7.76%	3.45%	1.59%	0.32%	0.17%	100

Thus on the bases of confirmation of prevalence of arsenic in the entire area, an other arsenic testing exercise was carried out in May and Nov 2006 with Merck field testing kit. Again in December 2006, the same water sources were tested with Atomic Absorption Spectrometer (AAS) to observe the accuracy of test results, carried out with field kits. The temporal distribution of arsenic contamination during 2006 also shows lesser arsenic contamination which is again due to heavy rains which has caused dilution to the arsenic concentration.

Two more parameters Electric Conductivity (EC) and Total Dissolve Solids (TDS). The pH values were also noted which were between 7.5 – 8.4. All the test results during 2006 are tabulated in table 4.

Table 4: Water quality survey-2006.

Sr.No.	Village / Location	Beneficiaries /installation Period	Source/Depth (ft)	Arsenic (µg/l) May 06 -with kit	Arsenic (µg/l) Nov 06 – with kit	Arsenic (µg/l)with AAS-Dec 06	E.C.	TDS
1	Nazir Ahmed	10/18 Months	Rotor Pump/65	100	100	120	1260	781
2	Nazir Ahmed	6/42 Months	Rotor Pump/70	60-80	50-100	99	1120	694
3	Nazir Ahmed	8/12 Months	Rotor Pump/70	> 100	50-100	46	840	462
4	Umar Kot	6/ 30 Months	Rotor Pump/80	100	50-100	108	1570	973
5	Hoth Baloch	4/18 Months	H.P/60	80-100	100	40	1320	818
6	Hoth Baloch	8/12 Months	Rotor Pump/70	80-100	100	87	1020	632
7	Hoth Baloch	5/42 Months	H.P/60	60-80	50-100	91	1250	775
8	Hoth Baloch	6/ 42 Months	H.P/60	100	100	90	900	495
9	Miran Bakash	54 Months	H.P/60	100	100	114	1170	725
10	Miran Bakash	35/42 Months	H.P/60	20-40	100	75	950	522
11	Jam Juhllan	7/18 Months	H.P/60	60-80	50-100	21	1020	632
12	Budu Wali	22/102 Months	Rotor Pump/80	60-80	100	98	830	456
13	Budu Wali	18/9 Months	H.P/60	100	100	128	1040	644
14	Budu Wali	4/42 Months	Rotor Pump/80	> 100	100	122	800	440
15	Budu Wali	Rafa/114 Months	H.P/50	80-100	50-100	109	970	533
16	Budu Wali	12/9 Months	H.P/70	60-80	50-100	72	990	544
17	Budu Wali	16/78 Months	H.P/60	100	100	124	960	528
18	Jalandhar	7/30 Months	Rotor Pump/80	80-100	50-100	84	860	473
19	Kallar wali	9/30 Months	Rotor Pump/60	80-100	50-100	76	1040	645
20	Korrian	11/30 Months	Rotor Pump/60	60-80	50-100	97	1290	780
21	Korrian	PublicPlace/54	Tube Well/70	60-80	50-100	92	1290	800
22	Korrian	15/10 Months	Rotor Pump/60	60-80	50-100	93	1530	979
23	Esa Dhudhi	20/9 Months	Rotor Pump/70	60-80	50-100	96	1060	657
25	Esa Dhudhi	15/18 Months	Rotor Pump/80	60-80	50-100	67	880	484
26	Esa Dhudhi	8/66 Months	H.P/60	20-40	100	72	1060	657
27	Dhudhi	5/30 Months	Rotor Pump/70	60-80	100	71	1050	651

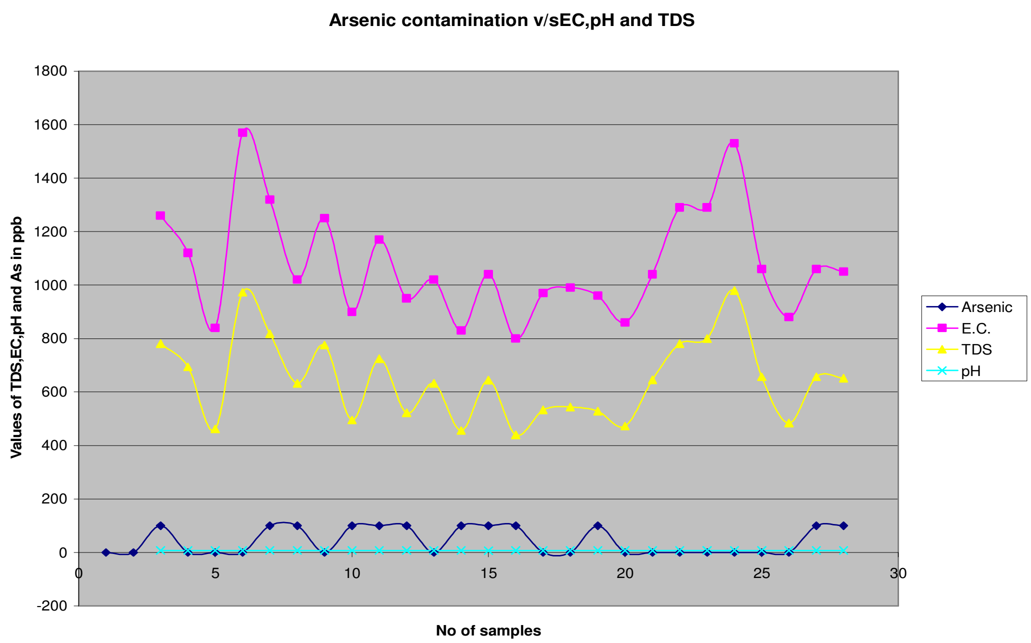


Figure 5: The graphical representation with constant pH (7.25)

From the water sample analysis, prevalence of arsenic in the area has been confirmed. It will be worth while to carry out the geo-chemical analysis of soil strata to know the mineralogy configuration and trends of arsenic concentration verses depth which will yield to interesting results. A test bore hole up to 100 feet carried out with following results;

For geo-chemical analysis, The same water sources were selected on 26 Sep,2007, as were tested on Sep, 2004. The arsenic and Iron contamination in six water sources was observed as shown in table: 5.

Table 5: Arsenic contamination with iron contents at and around Basti Nazeer

Sr. #	**Owner's Name**	**Basti**	**Source/Depth (ft)**	**As(µg/l) 2006**	**As(µg/l) 2007**	**Fe (ppm)**
1.	Nawab Ali Khan	Budhu Khan	Rotor Pump/65 ft	---	20	0.14
2.	M. Jameel	Faqeer Bux	Rotor Pump/65 ft	---	40	1.29
3.	Miran Bux	Dera Miran Bux	Hand Pump/60 ft	100	100	1.52
4.	Ali Hoth	Hoth Baloch	Rotor Pump/65 ft	---	40	0.85
5.	Nazir Ahmed	Nazir Ahmed	Rotor Pump/65 ft	100	100	2.72
6.	Nazir Ahmed	Nazir Ahmed	Trial Bore/85 ft	---	20	0.01

A trial bore was carried out to obtain soil samples at Nazir Ahmed, where arsenic and Iron contamination was 100 µg/l and 2.72 mg/l respectively. The soil profile along with arsenic, contamination, EC and pH at various depths are shown in table-6.2, below;

Table-6: Soil Profiling and As contamination up to the depth of 100 feet at research area

Sr. #	Sample Code	Sample Depth (ft)	Soil configuration	EC(m-S/cm	pH	As µg/l
1	Sample No.1	Top surface	Silty clay			
2	Sample No. 10	45	Sandy clay	1680	6.96	60
3	Sample No. 11	50	Sandy clay	1640	6.95	50
4	Sample No. 12	55	Sandy clay	1420	7.10	40
7.	Sample No. 13	60	Sandy clay	1220	7.12	40
8.	Sample No. 14	65	Sandy clay	1320	6.96	100
9.	Sample No. 15	70	Sandy clay	1350	7.08	20
10.	Sample No. 16	75	Sandy clay	1440	7.05	40
11.	Sample No. 17	80	Sandy clay	1470	7.04	20
12.	Sample No. 18	85	Gravel (Hard Bed)	1190	7.13	20

RESULTS & DISCUSSION

The test results in Table 1 indicate heavy iron and arsenic ground water contamination. Higher Fe concentration imparts colour to water and changes in water usage habits due to high Fe would indirectly lead to reduced exposure to As. This could also be viewed as beneficial as the storage with higher Fe concentrations would result in oxidation and removal of As and Fe and hence people were indirectly protected against As exposure. (Sharma, A.K., 2006) Storing groundwater for few hours with such a high Fe concentration can remove over 50% of As. (Khan, A.H., et al. 2000)

The release of As may be correlated to one of the three most established theories: 1) release of As due to P because of application phosphatic fertilizers; 2) desorption of As due to reductive dissolution of metal oxy-hydroxides; 3) oxidation of pyrite. XRF Elemental analyses of the soil strata at various depths showed no elemental arsenic implying the absence of arsenopyrite. Therefore oxidation theory of arsenopyrite may be ruled out. But this needs to be further validated by XRD analyses. However, positive correlation between arsenic and iron concentration supports the reductive dissolution theory.

In the research area, pesticides and fertilizers are being used on cotton and sugarcane crops. Phosphatic fertilizers are extensively used in the area. In many studies, elevated arsenic concentrations in groundwater have been found due to application of phosphatic fertilizers (Campos, V., 2002, Davenport,J.R. & Peryea,F.J. 1991). Water quality survey conducted by PCRWR in the study area revealed higher PO_4, concentration in the study area (water quality status in Pakistan, 2003). Hence preferential adsorption of phosphate on sediments can also be held responsible for the release of arsenic.

From temporal distribution of the arsenic, it can be inferred that monsoon season results in the attenuation of arsenic contamination because of high infiltration rate in the study area.

From table 6, it can be inferred that arsenic concentration decreases with increase in the depth. This is almost a general tendency found in many places of the world. Elevated As concentrations mainly occur at 10-150 m depths Very shallow wells (< 10 m depth), ponds and deep tube wells (> 150 m) are generally free from arsenic contamination. (Sharma, A.K., 2006). Hence, deep well boring can be a sustainable source of arsenic free water in the study area.

CONCLUSIONS:

Arsenic concentration was found alarmingly high in the study area. This was usually positively correlated with the concentration of iron suggesting reductive dissolution of oxyhydroxides of iron. Extensive application of phosphatic fertilizers in the area also triggered the arsenic release from sediments. Rainy season attenuated arsenic contamination in the area. Arsenic concentration decreased with increase in the depth of water sampling. Hence deep well pumping could be employed as a sustainable source of arsenic free water.

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