

ARSENIC HAZARD IN GROUNDWATER WITH SPECIAL REFERENCE TO SOUTH WEST PARTS OF PUNJAB STATE, INDIA

K.P. Singh, Naval Kishore, Naresh Tuli, and R.S.Loyal

Centre of Advanced Study in Geology, P.U., Chandigarh-160014, India

Abstract: South West parts of Punjab State have been investigated for finding out arsenic hazard in groundwater in the top shallow aquifer (upto 50 m) system. The groundwater of the area has salinity as well as alkalinity hazards both in the upper unconfined aquifers (upto 30-50 m) as well as in the deeper aquifer system (more than 50 m), where, groundwater occurs under confined or semi confined conditions. The results of arsenic analysis of groundwater samples indicate that arsenic generally occurs in low concentration upto 5 µg/l which is well within the prescribed limits of 10µg/l by W.H.O. In order to confirm the findings, arsenic in groundwater was determined at the laboratory of Geology Department, University of Delhi as well as in the ICAP-AES laboratory of PAU, Ludhiana. Both the results indicate the large scale arsenic contamination in ground water is not prevalent as earlier reported by some workers. However, occurrence of arsenic in groundwater is controlled by mineralogical, hydrogeomorphological and hydrological regime. A few hot spots having arsenic concentration more than 10 µg/l do occur sparingly, especially, in areas where hydrological, mineralogical, geomorphological conditions are favorable.

1. Introduction:

Arsenic is a naturally occurring element found in soil, surface water and groundwater as a metalloid and in the form of organic and inorganic compounds [1]. Arsenic does not occur in the element state and is more common as sulphide and sulphate salts. It forms stable complexes with Fe (hydr-) oxides and aluminum [2, 3]. The most common source of arsenic is its presence in rock forming minerals including iron oxides and clays particularly concentrated in sulphide minerals from pyrite rich sedimentary aquifers. The second source of arsenic could be from industrial products such as insecticides, pesticides, wood preservatives and pharmaceuticals. The third source could be from the atmospheric pollution. Arsenic is released into the atmosphere from coal based power generation plants, burning vegetation and volcanic eruptions. The fourth source could be from the industrial effluents from dyeing industries and pesticides manufacturing industry, petroleum refineries, rare earth

industries and other organic and inorganic chemical industries.

Arsenic can occur in the environment in a number of oxidation states (- 3, - 1, 0, + 3 and + 5) but under natural conditions it is mostly found in inorganic form as trivalent **arsenite [As (III)]** or as oxyanions of pentavalent **arsenate [As (V)]**. Redox potential (Eh) and pH are the most important factors controlling speciation in aqueous system [4]. Arsenic (III) has been found to be more toxic in comparison to arsenic (V). Arsenic III is more common in groundwater whereas arsenic V is commonly found in surface waters. The current maximum contaminant level (MCL) for arsenic in drinking water as permitted by W.H.O standards is 10 µg/l [5]. The arsenic levels above the permissible limit of 10 µg/l in groundwater have been reported in many parts of the world [6].

In India, the effects of arsenic contamination in ground water were first noticed in July 1983 in

West Bengal, following reports of that many people were found to be suffering from arsenical skin diseases due to consumption of arsenic rich water. The total 8 million people from 61 blocks of West Bengal were found to be living at risk of arsenic poisoning. Later on, some more districts of Bihar, Chhattisgarh, Jharkhand, Assam, Manipur, Madhya Pradesh and U.P. states have been found to be affected by arsenic contamination of ground water.

Arsenic toxicity is a serious health hazard in countries like Bangladesh, inner Mongolia region of China, Taiwan, Japan, Thailand, Argentina, Ghana, Chile, Mexico, U.S.A, Hungary and Romania [7-11].

Recently in Punjab state, large scale arsenic contamination of groundwater has been reported [12], specially in southwest parts of Punjab. Sporadic occurrence of arsenic in groundwater (at 6 locations out of 105 locations) in Mansa district, SW Punjab has also been reported [13]. In the present paper an attempt has been made to examine the problem by analyzing the groundwater samples for arsenic and other trace elements especially in Talwandi Sabo block and Muktsar-Malout belt (Fig.1) representing southwest Punjab. To understand the regional occurrence and geomorphological controls of arsenic contamination, data of other organizations like CGWB and Punjab Water Supply and Sanitation Department for the Punjab State and also the adjoining Haryana state has also been examined in relation to hydro-geomorphological units identified on the basis of Indian Remote Sensing satellite and LANDSAT data which was not attempted earlier. The results of the study are presented in the present work.



Figure 1. Location map of study area (Muktsar- Malaut belt and Talwandi Sabo block, Punjab State).

2. Hydrogeology and groundwater conditions:

The area comprises of Indo-Gangetic alluvium of Quaternary age. Groundwater mainly occurs in alluvium comprising sand, silt, kankar (calcium carbonate concretions) and gravel beds. Clay beds occur at all levels making the aquifer system multiple as revealed by the study of borehole lithologs.

At shallow depths, groundwater occurs under unconfined conditions whereas deeper aquifers occurring at more than 50 m depth are under semi-confined /confined conditions. In order to understand the micro level variations in subsurface lithology, earth resistivity tomography (ERT) was carried out in village Jassiana lying in Muktsar block by the NGRI [14]. The results of the study indicate presence of thick saline /sediments upto 26 m depth with resistivity less than 10 Ohm-m followed by highly saline groundwater zones with resistivity less than 2 Ohm-m (Fig.2). These saline sediments have influenced the groundwater quality in the area.

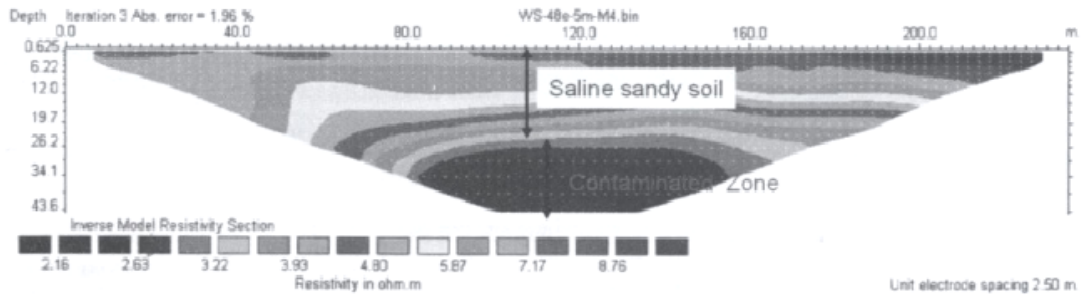


Figure 2. Vertical Cross section of ERT image in Jassiana village, Muktsar district, Punjab (Source: Surinaidu et al.,[14])

Average depth to groundwater ranges between 8-10 m below ground level in Talwandi Sabo block whereas in Muktsar-Malout belt, shallow depths upto 2 m are predominating making parts of the areas as water logged. Water-logging has led to the development of saline / alkaline soils in the area due to capillary rise of salts to the land surface (Fig. 3). The transmissibility values range from 500 to 700 m² / day and aquifers have low hydraulic conductivity (10-15 m/d). The groundwater flow is from NE to SW direction in general and average hydraulic gradient in about 0.32 m/km. Water levels in the area have been rising for the last more than 100 years (Fig.4). In some areas in Talwandi Sabo

block water level has stabilized now as revealed by the flattening of hydrograph curve (Fig.4). Groundwater is currently drawn out by number of handpumps having upto 15-30 m depth and shallow tubewells having upto 50 m depth inspite of the fact that chemical quality of groundwater is unfit or marginally fit for irrigation and drinking water purposes [15]. However, around canals, due to seepage of canal water, fresh water lenses have been formed having good quality of groundwater with electrical conductivity less than 2000 µmhos/cm at 25°C. Such fresh water lenses are more common in Muktsar – Malout belt especially around Rajasthan canal and Sirhind feeder.



Figure 3. Saline soils occurring in Muktsar Block

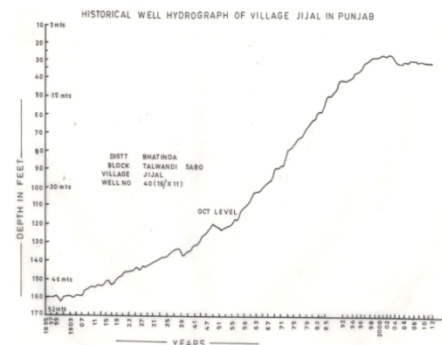


Figure 4. Showing rise in water levels in Talwandi Sabo area.

3. Material and Methods:

Groundwater samples were collected from hand pumps and tube wells in hard polythene bottles of one liter capacity. The GPS measurements were recorded in the field to mark the locations. The water bottles were washed and rinsed. Hand pumps and tube wells were pumped for 3-5 minutes to remove the stagnant water. The polythene bottles were sealed and brought to laboratory under refrigerating conditions for major element analysis i.e. Ca, Mg, Na, K, HCO₃, CO₃, SO₄, Cl, NO₃ and PO₄. For trace element analysis including arsenic, separate samples were collected in 250 ml bottles. The samples were filtered and acidified by nitric acid to bring down the pH and were kept under refrigerating conditions. The trace elements include arsenic were determined using ICAP-AES at the Soils department, Punjab Agriculture University, Ludhiana. Arsenic was also determined for some samples at the Geology Department, University of Delhi. Remote Sensing data available at Punjab Remote Sensing Centre, Ludhiana was used for identification of hydro-geomorphological units. Field interviews were conducted to know the cases of skin disorders, pigmentation changes (melanosis) and arsenicosis.

4. Results:

The results of major analysis of groundwater samples indicate that pH ranges from 8.21 to

9.14 indicating alkaline nature of water. Electrical conductivity values range from 440 to 10840 micromhos/cm at 25°C indicating that groundwater has medium to high mineralization. At places, close to hydrological boundaries i.e. canals; freshwater floats over native saline groundwater. Calcium ranges from 10.4 to 52.1 mg/l in Talwandi Sabo block and from 21.9 to 43.2 mg/l in Muktsar-Malout belt. Magnesium range from 10.2 to 167.1 mg/l in Talwandi Sabo and from 21.9 to 158.8 mg/l in Muktsar-Malout belt. Sodium ranges from 15.2 to 315.9 mg/l in Talwandi Sabo area and from 44 to 1205 mg/l in Muktsar-Malout belt. Potassium concentration is low and ranges from 9.5 to 310 mg/l in Talwandi Sabo area and from 44 to 112.5 mg/l in Muktsar-Malout belt. HCO₃ ranges from 125 to 515 mg/l in Talwandi Sabo area and from 230 to 425 mg/l in Muktsar-Malout belt. CO₃ was found to be absent. Sulphate ranges from 5.7 to 18.4 mg/l in Talwandi Sabo and from 8.9 to 28 mg/l in Muktsar-Malout belt. Nitrate ranges from 8.71 to 29.53 mg/l in Talwandi Sabo and from 4.63 to 29.89 mg/l in Muktsar-Malout belt. Phosphate ranges from 0.084 to 0.622 mg/l in Talwandi Sabo area from 0.12 to 0.340 mg/l in Muktsar-Malout belt. At places, fluoride has been found to be more than the permissible concentration of 1.00 mg/l prescribed for drinking water by W.H.O. [16]. Table I shows concentration range of various major ion parameters in the studied area.

Table I: Range of concentration of major parameters in Talwandi Sabo block and Muktsar-Malout belt in South West Punjab.

Parameter	Range in Talwandi Sabo area	Range in Muktsar-Malout belt
pH	8.7 – 9.14	8.21-9.12
Electrical conductivity (micromhos at 25°C.)	440-6860	560 -10840
Calcium	10.4 - 52.1 mg/l	21.9 – 43.2 mg/l
Magnesium	10.2 – 167.1 mg/l	21.9 – 158.8 mg/l
Sodium	15.2 – 315.9 mg/l	44 - 1205.4 mg/l
Potassium	10.4 – 310.5 mg/l	9.5 – 112.5 mg/l
Carbonate	Nil	Nil
Bicarbonate	125 – 515 mg/l	230 - 425 mg/l
Chloride	4.97 – 440.2 mg/l	106.5 – 1245.5 mg/l
Sulphate	5.7 – 18.4 mg/l	8.9 – 28.0 mg/l
Nitrate	8.71 – 29.53 mg/l	4.63 – 29.890 mg/l
Phosphate	0.084 – 0.622 mg/l	0.12 – 0.340 mg/l

4.1. Trace Element Geochemistry:

The results of trace element concentration of arsenic, chromium, cadmium, lead, nickel, copper, zinc are presented in Table II along with the GPS measurements taken at the sampling sites. The concentration range of these elements is shown in Table III. The results (Table II and III) indicate that the concentrations of most of the trace elements are within the permissible concentration prescribed by W.H.O. [16] for drinking water.

The results of arsenic analysis of some groundwater samples done at the geochemical

laboratory of Delhi University, Delhi using digital arsenator (Wagtech, U.K.) are shown in Table IV.

The results of arsenic analysis presented in Table II, III and IV indicate that concentration of arsenic is low and within the prescribed limit 10 µg/l of W.H.O. [16].

Table II. Results showing trace element concentration in mg/l in groundwater in Talwandi Sabo and Muksar- Malout belt.

Sample No	Location, Depth and Structure	GPS Location	Arsenic	Iron	Cadmi-um	Chromi-um	Lead	Zinc	Copper	Manganese	Nickel
1.	Jajjal (Gurdwara, HP, 50 ft)	29° 58' 8'' 75° 01' 48''	0.003	0.019	0.000	0.032	0.027	2.185	0.09	0.020	0.005
2.	Jajjal (Singh, HP, 65 ft)	29° 58' 02'' 75° 01' 42.3''	0.004	0.244	0.000	0.005	0.021	0.031	0.022	0.009	0.000
3.	Malbara (Roop , HP, 60 ft)	29° 56' 03.4'' 75° 02' 16.6''	0.004	0.056	0.001	0.038	0.026	0.236	0.185	0.028	0.007
4.	Gattewali (Sukhdev Singh, HP, 65ft)	29° 54' 06.2'' 75° 02' 27''	0.003	0.008	0.000	0.007	0.021	0.081	0.029	0.020	0.003
5.	Buttar Sarian Jagjit Singh, HP, 40ft)	30° 21' 23'' 74° 41' 02''	0.002	0.397	0.000	0.018	0.016	0.171	0.031	0.011	0.001

HP = Handpump

Table III: Results showing concentration range of trace element concentration in Talwandi Sabo and Muksar- Malout belt, Southwest Punjab.

Sample No.	Element	Concentration Range (µg/l)	W.H.O. (2004) Standards for drinking water (µg/l)
1	Arsenic	2-4	10
2	Cadmium	0-1	3*
3	Chromium	5-32	50
4	Copper	22-185	2000*
5	Lead	16-27	10
6	Zinc	31-2185	3000
7	Nickel	0-5	20
8	Iron	8-397	300
9	Manganese	9-28	100

*Provisional Guidelines

Table IV. Showing arsenic concentration in ground water in Talwandi Sabo block and Mukhtsar-Malout belt.

Sample No.	Location (Village)	GPS Location	Strucutre/ Owner	Depth (ft)	Arsenic Concentration in ppb (parts per billion)
S ₁	Jajjal	75° 11' 15.9" 29° 58' 36"	TW/Owner Gian Singh	100	Nd
S ₂	Jajjal	75° 01' 21" 29° 58' 35"	HP (Darshan Singh)	50	Nd
S ₃	Jajjal	75° 01' 47" 29° 57' 59"	HP (Dera Baba Gian Dass Ji)	60	Nd
S ₄	Jajjal	75° 01' 50" 29° 57' 51"	HP (Sarpanch)	60	Nd
S ₅	Maklana	75° 01' 47" 29° 57' 38"	TW (Jajjal-Malkana Road, Booba Singh)	80	Nd
S ₆	Maklana	75° 01' 59" 29° 56' 47"	HP (Near Brick Kiln, Surinder Kumar)	35	Nd
S ₇	Maklana	75° 01' 50" 29° 36' 10"	HP (Bus stop)	50	4 ppb
S ₈	Maklana	75° 01' 30" 29° 55' 14"	TW (Gujjar Singh)	70	Nd
S ₉	Gyana	75° 30' 37" 29° 53' 42"	HP (Amarjeet Singh)	45	1ppb
S ₁₀	Gyana	75° 10' 19" 29° 53' 25"	HP (Sukhdev Singh)	80	Nd
S ₁₁	Talwandi Sabo	75° 17' 08" 29° 46' 30"	HP (Gurudwara)	100	Nd
Muktsar-Malout Belt					
SM ₁	Husner		HP(Gurmail Singh)	40	Nd
SM ₂	Kotbhai		HP (Lackman Lal)	30	Nd
SM ₃	Chottian		HP (Sukhdev Singh)	30	Nd
SM ₄	Chakdohewala		HP	40	Nd
SM ₅	Karniwal		HP	35	Nd
SM ₆	Malout		HP	50	Nd

HP= Handpump
TW = Tubewell
Nd= Not detected

5. Geomorphological /Hydrological/ Mineralogical Controls:

In order to understand the relationship between occurrence of arsenic in groundwater and geomorphology, the results of 234 samples for arsenic concentration reported by C.G.W.B. [17] were examined along with their locations. The results indicate that arsenic hazard in groundwater does not occur on large scale. The areas of alluvial plains in general have negligible arsenic concentration ($<10 \mu\text{g/l}$). However, arsenic hotspots having arsenic concentration more than $10\mu\text{g/l}$ do occur around flood plains of major rivers (Fig.5). During post monsoon periods, arsenic concentration gets reduced due to dilution caused by recharge from rivers. Further, results of arsenic analysis of groundwater carried out by Punjab Water Supply and Sanitation Department were also

examined (Table V). The results indicate that arsenic hot spots are associated with newer alluvium (Pleistocene- Holocene) in flood plain zones. Areas around flood plain zones in Fategarh Churian and Dera Baba Nanak blocks have high arsenic in groundwater $63\text{-}85 \mu\text{g/l}$ (Table V). The location of occurrence of such hotspots is also shown in (Fig.5). Figure 6 shows false colour composite (FCC) of the area around Ravi river. Location of old river channels and occurrence of arsenic hotspots is also shown in this figure. Arsenic data of adjoining Haryana state reported by C.G.W.B. [17] also indicates occurrence of arsenic hot spots in groundwater around flood plains zones of Yamuna river (Fig.7).

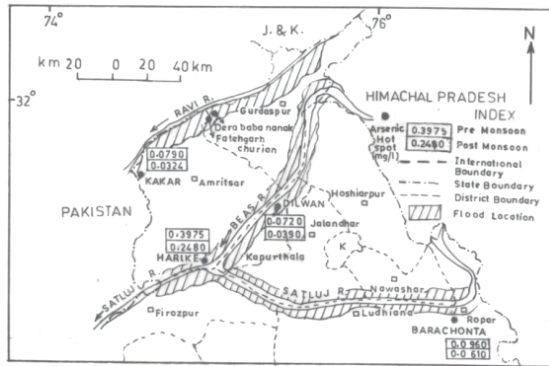


Figure 5. Flood plain zones showing occurrence of arsenic hotspots (arsenic concentration more than $10 \mu\text{g/l}$).

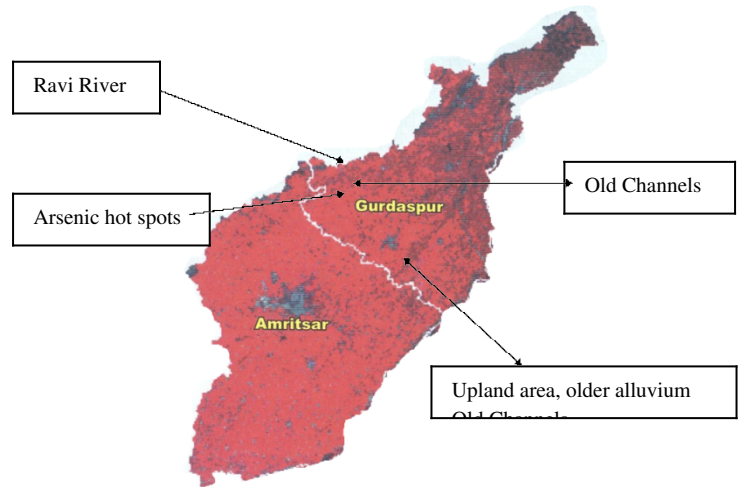


Figure 6. False Colour Composite of flood plains zones around Ravi River showing old river courses and upland area.

Table V: Showing arsenic concentration in groundwater in flood plains (Holocene) and Older alluvium (Pleistocene) in Gurdaspur District, Punjab.

Sample No.	Location/Village	District	Block	Geomorphological Unit	Nature of Structure	Depth (ft.)	Arsenic (mg/l)
1	Pabbarali	Gurdaspur	Fatehgarh Churain	Flood plains-Holocene	Deep Tubewell	450	0.085
2	Dogar	"	"	"	"	450	0.063
3	Dadujodh	"	"	"	"	450	0.077
4	Shahpur Jajjan	"	Derababa Nanak	"	"	450	0.074
5	Pahara Ghorai	"	Gurdaspur	Older Alluvium	"	450	Nd
6	Jiwanwal	"	"	Older Alluvium	"	450	Nd
7	Phara Ghorala	"	"	Older Alluvium	"	450	Nd

(Source Water supply and Sanitation Department Punjab)

Nd= Not Detected

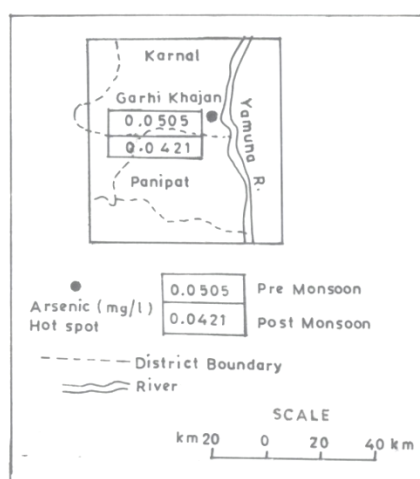


Figure7. Showing arsenic hotspots occurring around Yamuna River in Haryana.

The newer alluvium has been deposited by the rivers Ravi, Satluj and Beas which have drained the Himalayan metamorphic in their catchment area. The sediments have micaceous minerals both muscovite and biotite besides grains of feldspars and quartz. The mineralogical contributing factor here is biotite, weathering of which provides a potential source of iron oxides which get concentrated in finer sediments

belonging to newer younger alluvium. Arsenic probably is associated with iron oxides [18].

The above data clearly brings out the geomorphological/ hydrological/mineralogical relationship between occurrences of arsenic in groundwater with newer younger alluvium (Pleistocene- Holocene). The geomorphological/ hydrological/ mineralogical controls in Punjab state are similar to those observed in Ganga Flood plains in Uttar Pradesh [19] and elsewhere.

6. Mechanism of Arsenic mobilization:

The mechanism of arsenic mobilization is very complex. Several scientific institutions and exploratory agencies in India and research groups in other countries have tried to pool in their expertise to unravel this hydrological mystery specially in West Bengal and Bangladesh [20]. However, in the present study arsenic hotspots having arsenic concentration more than 10 µg/l are associated mainly with flood plains and adjoining areas. In villages located away from the flood plains of river Ravi

and lying over the older alluvium on upland surfaces in Gurdaspur district (eastern side of Ravi), there is virtually no arsenic in the groundwater and therefore, it was not detected (Table V). Similarly in Ropar area villages located on upland surfaces and away from flood plains, no arsenic has been found in groundwater contrast to a location at Bara chonta where arsenic hot spots do occur with arsenic concentration more than 10 µg/l.

Groundwater analyses indicate slightly alkaline ground water nature of water in flood plains with low concentration of HCO_3 at shallow depth (10-30 m) [21]. This is the most important anion species which competes with arsenic for adsorption sites at mineral surfaces, (clay minerals and weathered micas) and contribute arsenic to the ground water [19]. Raju [19] also observed similar association in Varanasi area and proposed the above mechanism. The elevated arsenic enrichment close to rivers is due to discrete phases of arsenic sorbed Fe-oxy hydroxide coated sediment grains preferentially entrapped in Holocene newer alluvium having also organic rich argillaceous sediments in entrenched channels and flood plains [19]. Presence of organic matter helps for reduction in iron oxide in releasing arsenic to groundwater close to hydrological boundaries in flood plains.

Further, low values of iron in groundwater which range from 0.008 to 0.397 mg/l in the study area in (Table III) compared to very high values in West Bengal (upto 39 mg/l) and Bangladesh (upto 30 mg/l) indicate that alluvial plain environment in Punjab state may not be of sufficiently reducing nature to mobilize iron and arsenic in groundwater on the large scale. This is further supported by the fact that the area has also low concentration of manganese and phosphate. However, wherever, localized not pose any health problems. In view of the present data, testing of arsenic in groundwater around flood plain zone is recommended so that

geochemical environment is favorable, arsenic can be mobilized even within the upland older alluvium causing arsenic hot spots to occur in a sporadic way.

7. Conclusions:

Arsenic hotspots i.e. areas having arsenic concentration more than 10µg/l occur in newer younger alluvium around flood plains or along paleo flood plains of major rivers. The relationship of occurrence of arsenic in groundwater in Punjab state follows similar relationship observed in Uttar Pradesh, Bangladesh and elsewhere where mobile arsenic is associated with younger Pleistocene – Holocene alluvial sediments which contain comparatively more organic matter and thus have a more reducing geochemical environment facilitating release of arsenic associated with iron oxides which are the weathered products of biotite present in fine grained sediments [19, 22, 23]. Localized arsenic hotspots can occur even in older alluvium wherever geochemical environment is favorable. Arsenic hazard in groundwater in Punjab is not as widespread as reported earlier [12]. This is supported by the fact that the studied area has low iron concentration which range from 0.0008 to 0.397 mg/l compared to very high values reported from West Bengal (upto 36 mg/l) and Bangladesh (upto 30 mg/l). In the study area, no case of arsenic skin lesions (arsenicosis) was noticed during field survey [24]. Other heavy metals like Cadmium, Chromium, Copper, Manganese, Nickel, Lead and Zinc have very low concentrations within the permissible limit of W.H.O. for drinking water [16] and do

remedial measures to provide safe drinking water using reverse osmosis technology could be taken by the state government in the effected areas.

8. Acknowledgements:

The authors thank Chairman, Department of Geology, Panjab University for providing facilities. KPS conveys his sincere thanks to UGC for awarding Emeritus Fellowship and sanctioning a major project. The authors also thankful to Jasbir Kaur Taak for her help.

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