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Arsenic content in ground and canal waters of Punjab, North-West India

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Abstract Groundwater is the primary source of drinking water for more than 95% of the population in Punjab. The world health organization and US Environment Protection Agency recently established a new maximum contaminant level of 10 ppb for arsenic in drinking water. The arsenic concentration of deep water tube wells located in Amritsar city used for domestic supply for urban population ranged from 3.8 to 19.1 ppb with mean value of 9.8 ppb. Arsenic content in hand pump water varied from 9 to 85 ppb with a mean value of 29.5 ppb. According to the safe limit of As, 54% and 97%, water samples collected from deep water tube wells and hand pumps, respectively, were not fit for human consumption. Arsenic content in canal water varied from 0.3 to 8.8 ppb with a mean value of 2.89 ppb. Canal water has got higher oxidation potential followed by deep tube well and hand pump water. The present study suggests the regular monitoring of arsenic content in deep tube well and shallow hand pump waters by water testing laboratories. The consumption of water having elevated concentration of As above the safe limit must be discouraged. In south-western districts of Punjab, it recommends the use of canal water for drinking purposes and domestic use by rural and urban populations than ground water sources.

Keywords Arsenic · Canal · Tube well · Hand pump · Ground water

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Introduction

Groundwater serves as the primary source of drinking water for more than 95% of the populations in Punjab, North-West India. In 1967, Punjab had around fifty five thousands tube wells only, whereas in 2008 this figure crosses one million mark. In the state, the extraction of groundwater has increased by 200 times during the last three decades. Arsenic in ground water is largely the result of minerals dissolving from weathered rocks and soils. The underground waters contain elevated arsenic concentration, which are usually above the WHO (1996) permissible safe limits of 10 ppb (Hundal et al. 2007). The problem is more severe at several sites in south-western districts of Punjab where the arsenic concentration exceeded more than 20 to 30 folds of the WHO safe limit. In this region, the department of sanitary and public health preferred to supply canal water to urban population due to brackish underground water, which is usually unfit for human consumption. In the northern and central parts of Punjab, deep tube wells are installed to supply underground water to urban populations. However, in rural areas the private owners of shallow tubewells and hand pumps are still using underground water for their daily use. Arsenic in drinking water can impact human health and is considered to be one of the prominent environmental causes of cancer mortality in the world (Smith et al. 1992, 2002). Arsenic has been known to cause a variety of adverse health effects, including skin and several internal cancers and cardiovascular and neurological effects (Murphy et al. 1981; Wu et al. 1989; Chiou et al. 1995; Mandal et al. 1996; Lynda et al. 2006). For the last one decade, cancer mortality is increasing with alarming proportion in many villages in south-western districts of Punjab (Singh 2005; Tandon 2007) due to elevated As content in drinking water. While providing access to safe drinking water remains an urgent problem, further long-term risks to human health and the environment may prove problematic. Until recently, arsenic concentration in drinking water was not routinely analyzed by state or national laboratories, and thus the information about the occurrence of arsenic in drinking water was not known as compared to the other drinking-water constituents. Therefore, the primary objective of this investigation is to determine arsenic content in deep tube wells, shallow hand pumps and canal waters in order to explore their suitability for human consumption and domestic use by the urban and rural population.

Materials and methods

Fieldwork was carried out during May and June of 2007 (Fig. 1). The soils of Punjab, northwest India are deep alluvium and illustrate varying degree of development due to different soil factors, such as climate and conditioned by topography over

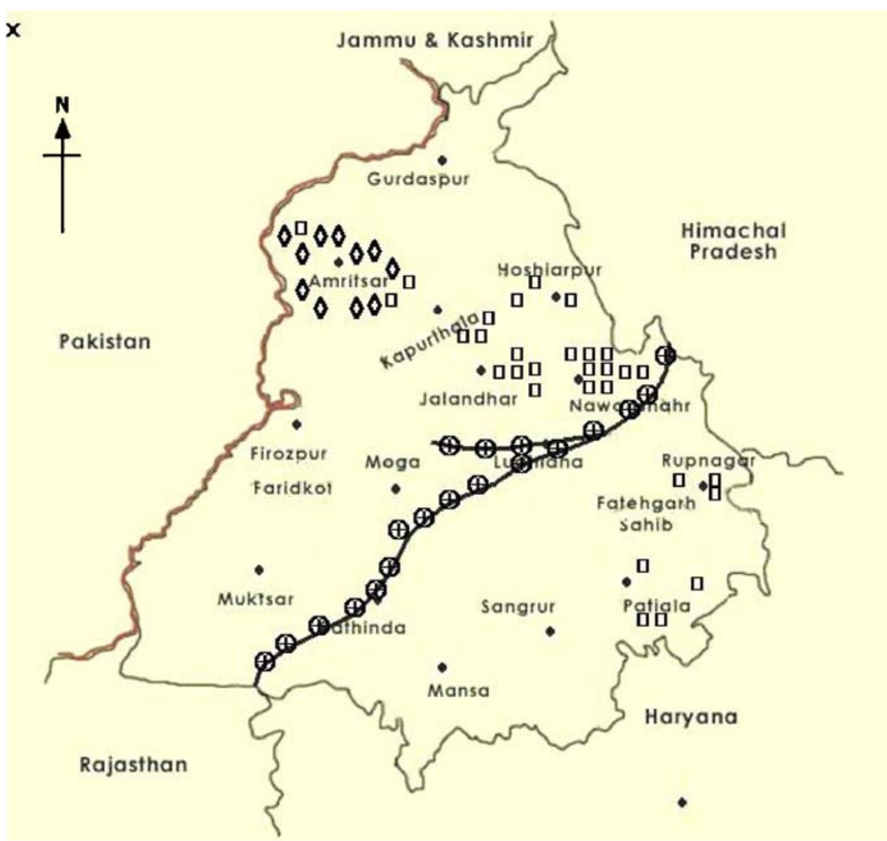

Fig. 1 Water sampling of ground water (*diamond*, deep tube wells; *square* hand pumps) and canal *circled plus symbol* from different locations of Punjab, Northwest India

a period of time (Sidhu et al. 1995). Geographically, the area of sampling lays between 73°53′ and 76°55′ E longitudes and between 29°33′ and 32°31′ N latitude and is 180–290 m above sea level.

Sample collection and pre-treatment of samples

Groundwater samplings were conducted from recently installed deep water tube wells located around the periphery of Amritsar city to be used for domestic supply.

Thirty water samples were also collected from shallow aquifers that reach a depth of approximately 15 m from where hand pumps were installed to extract ground water. Canal water samples were collected at 12 km intervals from main canal commenced from Ropar Headwork and flow towards Daki Sahib bridge. From Daki Sahib, main canal bifurcates into Bathinda branch and Sidhwan branch. The bifurcated canals were sampled at 12 km intervals up to Thermal Plant Bathinda and Punjab Agricultural University Ludhiana, respectively. Canal water sampling was repeated from the previous sites in the month of March, 2008. Polyethylene bottles of 50 ml volumes were used for collection of water samples. Bottles were fully filled with water and closed avoiding any air bubble. Field measurements of redox potential (Eh) were also made at the time of water sampling. Water samples collected from various locations were brought back to Laboratory at Punjab Agricultural University for further analyses. The samples were put in a cooled ice box during transportation and stored refrigerated until analysis (at 5°C). All samples were acidified with 69% HNO_3 prior to analysis.

Instrumentation

Inductively coupled argon plasma (ICAP-OES)

The acidified water samples were analyzed for arsenic on Thermo Electron Corporation's Emission Spectrometer, iCAP 6300 using on-line hydride generation kit. It is manufactured in United Kingdom and is world's most compact bench top ICP system with a Echelle spectrometer covering wavelength range of 166–847 nm. It has solid state RF generator working at a frequency 27.12 MHz and charge injection device (CID) detector. Plasma ignition and operation are fully automated and controlled from pc using iTEVA Software. The aqueous sample is introduced with inbuilt 3 channel peristaltic pump through glass concentric nebulizer and glass cyclonic type spray chamber to demountable quartz torch. iCAP 6300 Duo model allows for simultaneous analysis of all elements from sub ppb to % level. The detection limit for arsenic on the iCAP 6300 duo emission spectrometer is 1.43 ppb at a wavelength 189 nm.

Redox meter

Eutech make CyberScan pH 1100 Bench pH/mV RS232 meter, manufactured in Singapore, was used to measure the redox potential. In this instrument, measurement can be made using the millivolt (mV) mode of a pH meter. Its mV range is −1,850 to +1,850 mV and resolution and accuracy is 0.1 mV and ±0.2 mV. The potential of redox meter was adjusted to +226 mV at 25°C with Zobell's solution (Nordstrom 1977) and checked after every five observations, during the investigation period.

Validation of the method to check the accuracy

CertiPUR As (Arsenic) 1000 ppm standard solution (traceable to SRM from NIST H_3AsO_4 in HNO_3) LOT HC625147 purchased from Merck company was used to validate the analytical method. A blank and a standard 40 ppb As used for the calibration were tested after every 10 samples in order to validate our analytical work. Relative error between measured and Merck arsenic standard solutions were less than 5%.

Results and discussion

Arsenic content in deep tube wells water

The arsenic concentration of deep water tubewells located in Amritsar city used for domestic supply for urban population ranged from 3.8 to 19.1 ppb

Table 1 Arsenic content (ppb) in water samples collected from deep tube wells in Amritsar

Sr no.	Location	Depth (ft)	Arsenic Conc. (ppb)
1	Garden Enclave	300	3.8
2	Akash Avenue	515	15.5
3	Kot Baba Deep Singh	400	7.6
4	Chaatiwind Gate	400	10.1
5	Sakatri Bagh	550	19.1
6	Gur Ram Das Nagar	550	13.6
7	Hindustan Basti	650	5.8
8	Pink Plaza	550	4.6
9	Katra Baghian	500	11.1
10	1 km before Ram Tirath	500	6.2
11	BSF Ram Tirath	550	10.6

with mean value of 9.8 ppb As (Table 1). The median arsenic concentration of tubewells water samples is 9.9 ppb (Table 2). The 75th and 90th arsenic concentration percentiles are 12.35 and 15.50 ppb, respectively. This means that 75% samples contain arsenic concentration in tube well waters of Amritsar are below 12.35 ppb and 90% of the samples were below 15.50 ppb (Table 2). On the basis of safe Arsenic limit (10 ppb), water samples collected from Akash Avenue, Sakatri Bagh, Chhattiwing gate, Guru Ram Das Nagar, Katra Baghian and BSF camp at Ram Tirath are not fit for human consumption. Water samples taken from tubewells of Garden enclave, Kot Baba Deep Singh, Hindusthan Basti, Pink Plaza and Ram Tirath are fit for human consumption. According to the safe limit of As, 54% water samples collected from deep water tubewells were not fit for human consumption.

Arsenic content in hand pump water

Arsenic content in hand pump water varied from 9 to 85 ppb with a mean value of 29.50 ppb As (Table 3). The median arsenic concentration of hand pump water samples is 25 ppb (Table 2). The 75th and 90th arsenic concentration percentiles are 36 and 44.10 ppb, respectively. According to the safe limit (10 ppb As), 97% of the samples drawn from shallow water aquifers are unfit for drinking and cooking purposes. However, it is important to mention here that these water samples were taken from Zone I and II which fulfill all the parameters suitable for good quality of water set by public health department since the arsenic content is not included in their tests. Hundal et al. (2007) reported that the As concentration ranged from 11.4 to 688 ppb with average value of 76.8 ppb. In the aridic southwest, zone III, all

Table 2 Statistical parameters for arsenic content (ppb) and redox potential (mV) in deep tube well, hand pump and canal waters

Parameter	Tube well water		Hand pump water		Canal water	
	As content	Redox potential	As content	Redox potential	As content	Redox potential
Minimum	3.80	−19.0	9.00	−46.0	0.30	174.0
Maximum	19.10	170.0	85.00	56.0	8.80	229.0
Mean	9.80	81.3	29.50	21.6	2.89	190.8
Median	9.90	70.0	25.00	22.0	2.60	186.0
75th percentile	12.35	126.5	36.00	35.5	4.15	192.5
90th percentile	15.50	166.0	44.10	51.8	4.90	209.0

Table 3 Hand pump water samples were collected from zone I and II of Punjab, North-West India

Sr No.	Location	Arsenic conc. (ppb)
1	Suneta Banur – Kharar Road	24
2	Bhango Manra – Kharar	20
3	UCO Bank, Landran – Kharar	38
4	Auto centre, LC Road – Morinda	36
5	Railway station – Phagwara	16
6	Gurdwara Satnampura – Phagwara	20
7	Hadiabad – Phagwara	36
8	FCI Food Storage – Newan Shehar	36
9	Gurdwara-Manji Sahib – Newan Shehar	18
10	Judicial Court – Newan Shehar	13
11	New Bus stand – Hoshiarpur	33
12	Near Parbat Chowk – Hoshiarpur	31
13	Oriental Bank – Hoshiarpur	11
14	Bidipur Fatak – Jalandhar	18
15	Bus Stand-GT Road – Dayalpur	25
16	Sarawaan Village, Peerbaba-GT Road	20
17	Hotel Magholia, GT Road-Kartarpur	35
18	Mehmodpur- Balachaur	40
19	Bachori- Balachaur	20
20	SMIV Mandir, Garhi-Kangoan	24
21	Ladni (Mohatpur)-Balachaur	9
22	Vishkarma Colony- Balachaur	25
23	Gurbax Colony-Patiala	35
24	Rago Majra-Patiala	35
25	Guru Nagar-Patiala	38
26	Lakad Mandi-Patiala	22
27	Lakad Mandi, Near ChotiNadi-Patiala	33
28	Resort Ramtirath Road- Amritsar	45
29	BSF colony Ramtirathpur- Amritsar	43
30	Farm House, (Village) on Road-Amritsar	85

water samples contained As concentrations much greater than the safe limit and thus were not suitable for drinking purposes.

Arsenic content in canal water

Arsenic content in canal water sampled in June 2007 varied from 0.30 to 8.80 ppb with a mean value of 2.89 ppb (Table 4). According to Arsenic safe limit suggested by World Health Organization and US Environment Protection Agency (<10 ppb), all the water samples were found fit for drinking purpose with respect to their arsenic content. The median arsenic concentration of canal water is 2.6 ppb (Table 2). The 75th and 90th arsenic concentration percentiles are 4.15 and 4.90 ppb. This means that 75% samples contain arsenic concentration below 4.15 ppb and 90% of the samples were below 4.90 ppb. Repeat survey for arsenic content in canal water was conducted during the month of March 2008. The Arsenic content during this month varied from 3 to 8 ppb with a mean value of 5.37 ppb (Table 4). The arsenic content in canal water samples was comparatively high during the month of March 2008 than June 2007. Nevertheless, on the basis of safe limits (<10 ppb As), all the samples were suitable for human consumption. The median, 75th and 90th percentile concentrations of arsenic in canal water during the month of March 2008 were 5, 6 and 7 ppb, respectively (Table 2). Similarly, Geriesh et al. (2008) analyzed As content in the

Table 4 Water samples from Ropar headworks to sidhwan canal, Ludhiana and Bathinda branch to thermal plant Bathinda

Sr No.	Location	Distance (km)	Arsenic conc. (ppb)	
			June 2007	March 2008
1	Head Regulator Sirhind Canal	0	4.1	5.0
2	Budhkee Nadee da Pul	12	1.9	7.0
3	Chamkaur Sahib Bridge	24	4.8	5.0
4	Gurudwara Patshahi Daswaeen Bridge	36	1.9	6.0
5	Ghardi da Pul	48	4.2	5.0
6	Nellon Bridge	60	5.3	6.0
7	Daki Sahib Bridge	72	2.7	5.0
8	10 Km from Dhaki Sahib to Ludhiana	84	2.2	5.0
9	Jawadi Model Town Bridge	96	8.8	6.0
10	Rara Sahib Bridge	108	2.8	7.0
11	Jandli da Pul	120	4.2	5.0
12	Bridge Kalyan village	132	2.6	4.0
13	Mehal Kallan Bridge	144	2.5	5.0
14	Chananwal Dehlaan Bridge	156	0.7	8.0
15	Sehara village	168	1.7	5.0
16	Bridge Dopli	180	0.6	6.0
17	Maarhi village bridge	192	2.6	3.0
18	Bhai Kot Dua Bridge	204	0.3	5.0
19	Thermal Plant Bathinda Bridge	216	1	4.0

water samples collected during winter and summer seasons from Ismailia Canal representing the downstream of the main Nile river. There were slight variations and generally the concentrations of As in water samples were higher during winter (0.98–1.65 ppb) than summer (0–<1 ppb) seasons. However, the concentrations of As were very low with respect to WHO and USEPA safe limit of As (<10 ppb As) in the drinking water.

Redox potential of tube well, hand pumps and canal waters

The redox potential of deep tubewell water varied from −19.0 to +170 mV with a mean value of +81.3 mV (Table 2). The median redox potential of deep water tube well is +70 mV. The redox values for 75th and 90th percentiles are +126.5 and +166.0 mV for deepwater tubewells of Amritsar district. The redox potential of shallow water extracted by hand pump varied from −46.0 to +56.0 mV with a mean value of +21.6 mV (Table 2). The median redox potential of hand pump water samples is 22.0 mV. The 75th and 90th redox percentiles values are 35.5 and 51.8 mV. Field measured redox potential of canal water ranged from +174.0 to 229.0 mV with an average value of +190.8 mV (Table 2). The median redox potential of canal water is +186.0 mV. The 75th and 90th redox potential values are +192.5 and +209.0 mV. The results in the present investigation showed an inverse trend between arsenic content recorded in different sources of water and redox potentials. The canal water has higher magnitude of redox potential followed by deep tube water and hand pump, respectively. Thus, higher positive redox potential in canal water was elucidating the oxidized conditions which could also be the reason for low arsenic content in it. Similarly, the low redox potential values for hand pump waters extracted from shallow depth depict reduced conditions and eventually could be the cause of elevated arsenic content in the later case. Stollenwerk (2003) reported that geochemical processes are mainly responsible for the arsenic concentration in many groundwater systems. Clay minerals, Fe and Mn are commonly associated with aquifer solids and have been shown to be significant adsorbent of arsenic. The extent of adsorption or desorption of As is influenced by the chemistry of the aqueous phase (Smedley and Kinniburgh 2002) which includes pH, arsenic

Table 5 Statistical analysis using t test comparing arsenic concentration in canal, deep tube well and hand pump waters

Parameter	Canal waters at two different time intervals	Canal water and and deep tube well water	Deep tube well water and hand pump water	Canal water and hand pump water
Computed *t* value	4.625	5.528	4.409	7.973
Table *t* (0.05)	2.101	2.048	2.022	2.01
Degree of freedom	18	28	39	47

speciation, and the concentration of competing ions (Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}). In an oxidizing environment, native soluble iron and manganese get oxidized to solid iron and manganese oxy-hydroxides and served as the sorbing sites and eventually reduced the concentration of arsenic in natural water (Hundal et al. 2007). However, As adsorption decreases with the presence of phosphate, sulfate, carbonate, silica, and other anions, which have been shown to decrease adsorption of arsenic to varying degrees. Under moderately reducing conditions, trivalent arsenite is stable and its adsorption is lower as compared to arsenate. Under reduced environment, the solid Fe (III) and Mn (IV) oxides also dissolved to soluble Fe (II) and Mn (II) and thus releasing As from the sorption sites as well as fixed with precipitated oxy-hydroxides of iron and manganese compounds and thereby enhanced its concentration in ground waters.

Statistical analysis

A t-test was used to compare the canal waters with deep tube well and shallow hand pump waters (Table 5). The arsenic concentration in canal water determined in March, 2008 was significantly higher than arsenic concentration determined in June 2007. Arsenic content in canal waters analyzed during the two intervals was significantly lower than deep tube well and shallow hand pump water samples. Arsenic content in shallow hand pump water samples were significantly higher than deep tube well waters.

Conclusions and recommendations

It is conclusively evident from this investigation that water extracted by hand pumps from shallow aquifers of Punjab, northwest India usually has arsenic content above the safe limit and should not be used for drinking purposes. Arsenic content in water supplied from deep water tube wells to urban populations in Amritsar city by water works departments should be monitored on monthly basis in order to ensure the supply of drinking water containing arsenic below the safe limits. The canal water contain arsenic well below the safe limits and should be suitable alternative for human consumption than ground water. Water works departments, especially in south-western districts of Punjab, should supply canal water to urban and rural population. In future, the incidence of arsenic related health problems should also be monitored annually from the locations supplied with drinking water with arsenic content below and above the safe limits.

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